

***Wege zur Multifunktionalität – TTF-basierte
Eisen(II)-Komplexe mit Spin-Crossover-
Eigenschaften***

Dissertation

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- Marie Curie -

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Abkürzungsverzeichnis

(in alphabetischer Reihenfolge)

A_2/A_1 (Mößbauer)	relative Intensitäten korrespondierender Linien eines gegebenen Dubletts
bispicen	<i>N,N'</i> -Bis(2-pyridylmethyl)-1,2-ethandiamin
bpee	<i>trans</i> -1,2-Bis(4-pyridyl)ethylen
bpp	2,6-Bis(pyrazol-1-yl)pyridin
bpy	2,2'-Bipyridin
bupy	4-tert-Butylpyridin
cat	Catechol
cf.	<i>confer/conferatur (lat.)</i> = vergleiche
CISSS	koordinationsbedingter Spinwechsel (<i>coordination induced spin state switch</i>)
CT	Charge-Transfer
CV	Cyclovoltammetrie
χ_M	molare magnetische Suszeptibilität
DCM	Dichlormethan
δ (Mößbauer)	Isomerieverschiebung
δ (NMR)	chemische Verschiebung
Δ_{SCoD}	Bindungslängenänderung während eines Spin-Crossover
ΔE (CV)	Peakabstand (<i>peak-to-peak separation</i>)
ΔE_{HL}^0	Unterschied in den Nullpunktenergien zwischen high-spin und low-spin Spezies
Δ_{SCoE}	Spin-Crossover-Energie
$\Delta\Delta_{\text{SCoE}}$	relative Unterschiede in den Spin-Crossover-Energien
ΔE_Q	Quadrupolaufspaltung
ΔG	Gibbs-Energie/freie Enthalpie
Δ_o	oktaedrische Ligandenfeldaufspaltung
Δq	Differenzielle Mulliken-Ladungen
diox	1,2-Benzochinon
DFT	Dichtefunktionaltheorie (<i>density functional theory</i>)
dmit	4,5-Dithiolato-1,3-dithiol-2-thion

Abkürzungsverzeichnis

DMF	Dimethylformamid
$E_{1/2}$	Halbstufenpotential
E_nT	Energietransfer
Et	Ethyl
EtOH	Ethanol
<i>et al.</i>	<i>et alii/aliae/alia (lat.)</i> = und Andere
eq	äquatorial (<i>equatorial</i>)
eq.	Äquivalent (<i>equivalent</i>)
ϵ_{\max}	maximaler Extinktionskoeffizient
$\Gamma/2$	halbe Halbwertsbreite der Lorentz-Linie
Γ_{FWHM}	volle Halbwertsbreite der Lorentz-Linie
γ_{HS}	high-spin-Anteil
H ₂ Bpz ₂	Dihydrobis(pyrazolyl)borat
HOMO	höchstes besetztes Molekülorbital (<i>highest occupied molecular orbital</i>)
HS	high-spin
ILCT	Intraligand-Charge-Transfer
IR	Infrarot
LUMO	niedrigstes besetztes Molekülorbital (<i>lowest occupied molecular orbital</i>)
LS	low-spin
λ	Wellenlänge
Me	Methyl
MeCN	Acetonitril
MO	Molekülorbital (<i>molecular orbital</i>)
MOF	metallorganische Gerüstverbindung (<i>metal organic framework</i>)
MS	Massenspektrometrie (<i>mass spectrometry</i>)
ND	Naphtyldiamin
NIR	naher Infrarot-Bereich
NMR	Kernspinresonanz (<i>nuclear magnetic resonance</i>)
OD	optische Dichte (<i>optical density</i>)
P	Spinpaarungsenergie
PA	Phenazin
PD	Phenylendiamin
PXRD	Pulverdiffraktometrie (<i>powder X-ray diffraction</i>)

Abkürzungsverzeichnis

py	Pyridin
qSalH	N-(8-Chinolyl)salicyldiamin
SalEn	N-(2-Ethylamino)ethylsalicyldiamin
S	Spinquantenzahl
SCE	gesättigte Kalomelelektrode
SCO	Spin Crossover
SQUID	supraleitende Quanteninterferenzvorrichtung (<i>superconducting quantum interference device</i>)
$T_{1/2}$	Spinübergangstemperatur
TCNQ	Tetracyanochinodimethan
TD-DFT	zeitabhängige Dichtefunktionaltheorie (<i>time dependent density functional theory</i>)
TGA	Thermogravimetrische Analyse
TMT-TTF	Tetrakis(methylthio)tetrathiafulvalen
tol	Toluol
TTF	Tetrathiafulvalen
TTF(py) ₂	4,4'-Di(pyridin-4-yl)-2,2'-bis(1,3-dithiolylyden)
UV-Vis	<i>ultraviolet-visible</i>
VT-UV-Vis	<i>variable temperature-ultraviolet-visible</i>
VT	valenztautomer/Valenztautomerie

1. Zusammenfassung

Das Ziel der vorliegenden Arbeit war die Synthese neuartiger Eisen(II)-Komplexe, welche neben Spin-Crossover-Eigenschaften auch redoxaktives Verhalten zeigen. Das Tetrathiafulvalen (TTF) ist für seine zwei reversiblen und leicht zugänglichen Oxidationsprozesse bekannt und sollte daher in die Ligandsphäre von SCO-Komplexen eingebracht werden.

Im ersten Teil der Arbeit wurde der axial verbrückende, zweizählige Ligand $\text{TTF}(\text{py})_2$ mit Schiff-Base-artigen Eisen(II)-Komplexen des Jäger-Typs $[\text{FeL}]$, welche eine $[\text{N}_2\text{O}_2]^{2-}$ Koordinationsumgebung besitzen, kombiniert. So konnten eindimensionale Koordinationspolymere mit zwei unterschiedlichen Äquatorialliganden – aus insgesamt drei verschiedenen Lösemitteln (Dimethylformamid, Acetonitril, Ethanol) – isoliert werden. Dabei wurde kristallographisch die Struktur des Komplexes $\{[\text{FeL}_2(\text{TTF}(\text{py})_2)] \cdot 2(\text{DMF})\}_n$ aufgeklärt. Dieser ist sowohl bei 273 K als auch bei 100 K im diamagnetischen LS-Zustand, was vor allem verschiedenen Wasserstoffbrückenbindungen zwischen Komplexmolekülen und co-kristallisiertem DMF zuzuschreiben ist. Mößbauerspektroskopie und magnetische Suszeptibilitätsmessungen bei Raumtemperatur identifizierten für alle pulverigen Proben den paramagnetischen HS-Zustand. Mit leichten Unterschieden zeigten alle Verbindungen unvollständiges SCO-Verhalten. Diese Unterschiede konnten durch Pulverdiffraktometrie und diffuse Reflexionsspektroskopie auf kleine Packungsunterschiede zurückgeführt werden. DFT-basierte Rechnungen an einem modellhaften Ausschnitt aus der Polymerkette $[(\text{py})\text{L}_1\text{Fe}(\text{TTF}(\text{py})_2)\text{FeL}_1(\text{py})]$ ergaben, dass ein Spinübergang mit einem enormen Spannungsaufbau innerhalb eines Polymerstrangs einhergeht. Dieser wurde als möglicher Grund für den unvollständigen Spinübergang identifiziert. Analysen der SCO-Energien deuteten auf eine vollständige Entkopplung der beiden Elektrophore TTF und Eisen(II) hin. Dies bestätigten cyclovoltammetrische Messungen, in denen alle Koordinationspolymere drei separate, reversible Oxidationsprozesse zeigten. Im Gegensatz zum Übergang $\text{Fe}^{2+}/\text{Fe}^{3+}$, welcher eine anodische Verschiebung um 100 mV aufwies, waren die Halbstufenpotentiale der beiden TTF-Oxidationen vergleichbar mit Literaturwerten.

Im zweiten Teil der Arbeit wurde der Schiff-Base-artige Äquatorialligand TTF^{LH_2} verwendet, bei dem die TTF-Einheit in das Ligand-Rückgrat integriert ist. Von diesem konnten kristallographische Daten erhalten werden, welche zeigten, dass die TTF-Einheit in ihrer neutralen und nicht oxidierten Form vorliegt. Es konnten zwei verschiedene Eisen(II)-Komplexe erhalten werden $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ und $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot 0,75(\text{tol})\}_n$. Aufgrund fehlender kristallographischer Daten erfolgte eine Strukturzuordnung durch quantenmechanische Modellierung mit dem Komplex $[\text{FeL}(\text{py})_2]$ als Referenzsystem. Eine Auswertung der UV-Vis-Spektren von $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ und $[\text{FeL}(\text{py})_2]$ ermöglichte

die Identifizierung charakteristischer TTF-Banden. Durch eine TD-DFT-Modellierung wurde anschließend sowohl für $[\text{FeL}(\text{py})_2]$ als auch für $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ der HS-Zustand als dominierende Spezies in Lösung bei Raumtemperatur (RT) identifiziert. Für das LS-Spektrum wurden bei $\lambda = 550$ nm charakteristische Banden in beiden Komplexen vorhergesagt, welche tatsächlich bei $\lambda = 530$ nm durch Abkühlen einer Lösung der Komplexe nachgewiesen werden konnten. Der Ligand zeigte in cyclovoltammetrischen Untersuchungen zwei Oxidationen, von denen jedoch nur die erste vollständig reversibel war. DFT-basierte Rechnungen zeigten, dass ein Teil des zweiten Redoxprozesses auf den Aminogruppen der Schiff-Base-Einheit lokalisiert und damit nur quasireversibel ist. Im Gegensatz dazu konnten in den Koordinationsverbindungen drei reversible Oxidationen identifiziert werden. Nach Auswertung der Ergebnisse von $[\text{FeL}(\text{py})_2]$ und $^{\text{TTF}}\text{LH}_2$ gelang eine erste Zuordnung der Elektrodenprozesse. Vergleichende spektroelektrochemische Untersuchungen von $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ und dem Liganden sollten diese Zuordnung bestätigen. Es konnten Ähnlichkeiten in den UV-Vis-Spektren der ersten Oxidation des Komplexes und der des Liganden festgestellt werden. Diese legen eine Ladungsverschiebung von der TTF-Einheit hin zum entstandenen Eisen(III)-Zentrum in Folge der ersten Oxidation von $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ nahe. Die magnetischen Suszeptibilitätsmessungen beider Komplexe zeigten SCO-Eigenschaften, wobei $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ mit einer Übergangstemperatur von $T_{1/2} = 146$ K mehrmaliges Heizen auf 400 K tolerierte. Das Koordinationspolymer hingegen verzeichnete beim stufenweisen Heizen auf 400 K einen Verlust von co-kristallisiertem Toluol und damit einhergehend veränderte SCO-Eigenschaften. Durch temperaturabhängige Mößbauerspektroskopie konnte der Spinübergang von $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot 0,75(\text{tol})\}_n$ nachvollzogen, jedoch kein eindeutiger Hinweis auf die Anwesenheit verschiedener Eisenplätze gefunden werden.

Das Einbringen von elektronenziehenden CF_3 -Gruppen führte im dritten Teil der Arbeit zu einer Modifikation des zuvor vorgestellten Liganden. Insgesamt konnten drei verschiedene Komplexe $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$, $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ und $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ erhalten werden. Von dem durch Pyridin axial koordinierten Komplex wurden kristallographische Daten erhalten. Diese zeigten, dass sich der Komplex bei 180 K im LS-Zustand befindet und neben Methanol auch co-kristallisiertes Pyridin enthält. Magnetische Suszeptibilitätsmessungen ergaben, dass $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ eher unvollständiges SCO-Verhalten zeigt und beim Heizen über 300 K hinaus Axialliganden verliert. Im Gegensatz dazu kann für $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ ein sehr gradueller, vollständiger und für $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ ein nahezu vollständiger Spinübergang mit $T_{1/2} = 187$ K beobachtet werden. Temperaturabhängige $^1\text{H-NMR}$ -Spektroskopie wurde an $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ und dem Referenzsystem $[\text{FeL}_{\text{CF}_3}(\text{py})_2]$ durchgeführt, um zu prüfen, ob Packungseffekte für den beobachteten unvollständigen SCO verantwortlich sind. Beide Substanzen zeigten charakteristische, für SCO typische Veränderungen des $^1\text{H-NMR}$ -Spektrums beim Kühlen. Cyclovoltammetrische Untersuchungen identifizierten für $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ und $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ drei reversible Redoxprozesse. Dabei war das Halbstufenpotential der Eisen(II)-

Oxidation, bedingt durch die elektronenziehenden CF_3 -Gruppen, stark anodisch verschoben, was auf eine Wechselwirkung zwischen den beiden Redoxzentren hindeutete. UV-Vis spektroelektrochemische Untersuchungen des freien Liganden $\text{TTF}_{\text{CF}_3}\text{H}_2$ und $[\text{Fe}^{\text{TTF}}_{\text{CF}_3}(\text{py})_2]$ bestätigten, dass die Redoxprozesse der ersten und zweiten Oxidation tatsächlich nicht isoliert betrachtet werden können. Vergleiche mit dem Referenzsystem und DFT-Rechnungen konnten das erste Redox-Ereignis bei Raumtemperatur als vorwiegend eisenzentriert identifizieren. Da in Lösung mittels $^1\text{H-NMR}$ -Spektroskopie Spinübergangsverhalten beobachtet werden konnte, erfolgten cyclovoltammetrische Messungen von $[\text{Fe}^{\text{TTF}}_{\text{CF}_3}(\text{py})_2]$ und $[\text{Fe}_{\text{CF}_3}(\text{py})_2]$ bei tiefen Temperaturen. Eine reversible Verschiebung des Eisen(II)-Elektrodenpotentials um ≈ 100 mV konnte in beiden Verbindungen beobachtet werden. Der TTF-basierte Komplex zeigte zusätzlich beim Kühlen eine reversible Aufspaltung des dritten elektrochemischen Oxidationssignals, was eine einzigartige Beobachtung ist.

2. Summary

The aim of this work was the synthesis of novel iron(II) complexes that exhibit redox-active behavior in addition to spin crossover properties. Tetrathiafulvalene is widely known for its two reversible and easily accessible redox processes. Thus, the intention was introducing it into the ligand sphere of SCO complexes.

In the first part of this thesis, the axial bridging bidentate ligand $\text{TTF}(\text{py})_2$ was combined with Schiffbase-like iron(II) complexes of the Jäger type $[\text{FeL}]$ that have an $[\text{N}_2\text{O}_2]^{2-}$ coordination sphere. One-dimensional coordination polymers with two different equatorial ligands, from a total of three different solvents (dimethylformamide, acetonitrile, ethanol), could be isolated this way. Thereby, the structure of the complex $\{[\text{FeL}_2(\text{TTF}(\text{py})_2)] \cdot 2(\text{DMF})\}_n$ was elucidated crystallographically. The complex is in the LS state at both 273 K and 100 K, which is mainly attributed to various hydrogen bonds between complex molecules and co-crystallized solvent molecules (DMF). Mössbauer spectroscopy and magnetic susceptibility measurements identify the paramagnetic HS state for all powdery samples at room temperature. With small differences, all complexes show incomplete SCO upon cooling. These differences were attributed to slight differences in crystal packing by X-ray powder diffraction and UV-Vis diffuse reflectance spectroscopy. DFT-based computation on a model fragment of the polymer chain $[(\text{py})\text{L}_1\text{Fe}(\text{TTF}(\text{py})_2)\text{FeL}_1(\text{py})]$ showed that SCO coincides with an enormous build-up of strain within a polymer chain. This was identified as a possible reason for the incomplete SCO in all complexes. Considerations of computed SCO energies indicated complete decoupling of the electrophores TTF and iron(II). Cyclovoltammetric measurements confirmed the electronic decoupling with the presence of three separate reversible oxidation processes in all coordination polymers. In contrast to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ transition, which was anodically shifted by 100 mV, the electrode potentials of both TTF oxidation agree with literature values.

In the second part of this thesis, the Schiff base-like ligand $^{\text{TTF}}\text{LH}_2$, where the TTF unit is incorporated in the ligand backbone, is used. Crystallographic data could be obtained from this novel ligand, which showed that the TTF unit is in its neutral and non-oxidized form. Two different coordination compounds $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ and $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot 0.75(\text{tol})\}_n$ were obtained. Due to the lack of crystallographic data structure assignment was performed by quantum chemical modelling with $[\text{FeL}(\text{py})_2]$ as a reference system. Evaluation of the UV-Vis spectra of $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ and $[\text{FeL}(\text{py})_2]$ allowed the identification of characteristic TTF absorption bands. TD-DFT modeling identified the HS state as dominant species at room temperature for both complexes. For the LS spectrum, characteristic absorption was predicted at $\lambda = 550$ nm, which was detected at $\lambda = 530$ nm by cooling a solution of the complexes. Cyclic voltammetry of the ligand showed two oxidation processes, from which only the first

one was fully reversible. DFT-based computation showed that part of the second redox process is localized on the amino groups of the Schiff base unit and is thus quasireversible. In contrast, three reversible oxidations were identified in the coordination compounds. By evaluating the results of $[\text{FeL}(\text{py})_2]$ and ${}^{\text{TTF}}\text{LH}_2$, an assignment of the electrode processes succeeded. Comparative spectroelectrochemical studies of $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ and the free ligand confirmed this assignment. Similarities were found in the UV-Vis spectra of the first oxidation of the complex and that of the ligand. These suggest a charge shift from the TTF unit to the formed iron(III) center after the first oxidation of $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$. Magnetic susceptibility measurements showed SCO properties in both complexes, with $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ tolerating multiple cycles of heating to 400 K with a transition temperature of $T_{1/2} = 146$ K. The coordination polymer, on the other hand, showed a loss of co-crystallized toluene upon stepwise heating up to 400 K, with a concomitant loss of SCO properties. Temperature-dependent Mössbauer spectroscopy traced the spin transition of $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot 0.75(\text{tol})\}_n$, but no clear indication of the presence of different iron centers was found.

The introduction of electron withdrawing CF_3 groups led to a modification of the previously presented ligand in the third part of the work. In total, three different complexes $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$, $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ and $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ were obtained. Crystallographic data were obtained from the complex axially coordinated by pyridine, showing that the complex is in the LS state at 180 K and contains co-crystallized pyridine in addition to methanol. Magnetic susceptibility measurements showed that $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ exhibits rather incomplete SCO behavior and loses axial ligands when heated over 300 K. In contrast, $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ showed a very gradual, complete spin transition and an almost complete spin transition can be observed for $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ with $T_{1/2} = 187$ K. Temperature-dependent ${}^1\text{H-NMR}$ spectroscopy was performed on $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ and the reference system $[\text{FeL}_{\text{CF}_3}(\text{py})_2]$ to test whether packing effects were responsible for the observed incomplete SCO. Both compounds showed characteristic changes in the ${}^1\text{H-NMR}$ spectrum upon cooling, typical of SCO. Cyclovoltammetric studies revealed three reversible redox processes for $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ and $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$. Here, the electrode potential of the iron(II) oxidation was strongly anodically shifted due to the electron withdrawing CF_3 groups, indicating an interaction between the two redox centers. UV-Vis spectroelectrochemical studies of the free ligand ${}^{\text{TTF}}\text{L}_{\text{CF}_3}\text{H}_2$ and $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ confirmed that the redox processes of the first and second oxidation indeed cannot be considered as isolated processes. Comparisons with the reference system and DFT computation identified the first redox event as predominantly iron-centered at room temperature. Since spin transition behavior could be observed in solution by ${}^1\text{H-NMR}$ spectroscopy, cyclic voltammetry of $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ and $[\text{FeL}_{\text{CF}_3}(\text{py})_2]$ was performed at low temperatures. A reversible shift of the iron(II) electrode potential by ≈ 100 mV was observed in both compounds. The TTF-based complex additionally showed reversible splitting of the third electrochemical oxidation wave upon cooling, which is an unique observation so far.

3. Einleitung

Die im Laufe der letzten Jahrzehnte stattgefundenene, rasante technologische Entwicklung hat die Art und Weise wie wir kommunizieren, wirtschaften und uns informieren grundlegend verändert.^[1] So hat auch der weltweite Ausbruch der Atemwegserkrankung COVID-19 und die damit einhergehende Pandemie einmal mehr verdeutlicht, wie wichtig und notwendig Digitalisierung in nahezu allen Bereichen des Lebens ist.^[2] Im Zuge dessen fallen immer größere Datenmengen an, welche gespeichert und verarbeitet werden müssen. Bereits 2018 ging man davon aus, dass die benötigte Datenmenge für die Vernetzung von physischen und virtuellen Gegenständen (Internet of Things) im Jahr 2020 auf 30 Billionen Einheiten anwachsen würde.^[3] In Anbetracht aller weltweiten Entwicklungen dürfte diese Zahl wohl sogar überschritten worden sein.

Damit verbunden entsteht eine immer größer werdende Lücke zwischen der Menge an produzierten digitalen Daten und der Größe der verfügbaren Speichermedien. Aktuell verwendete Speichertechnologien sind zunehmend herausgefordert, aufgrund ihrer begrenzten Speicherdichte und Schwächen im Hinblick auf Energieverbrauch, Kapazität und Lebensdauer.^[3]

Um im Vergleich zu etablierten Systemen eine noch höhere Datendichte zu erreichen, ist es erstrebenswert, einzelne Moleküle als Elementarspeicher zu verwenden. Bereits in den 90er Jahren wurde das Potential molekularer Materialien für die Datenspeicherung identifiziert. Unter molekularen Materialien sind in diesem Zusammenhang molekülbasierte Verbindungen zu verstehen, welche eine oder mehrere Eigenschaften zeigen, die sie zur Verwendung in einem Gerät befähigen.^[4] Eine grundlegende Anforderung an eine geeignete molekulare Speicherverbindung ist molekulare Bistabilität. Das molekulare System sollte demnach in der Lage sein in Abhängigkeit von äußeren Parametern, wie zum Beispiel Temperatur, Druck oder Lichteinstrahlung, in zwei verschiedenen elektronischen Zuständen zu existieren.^[4,5] Damit diese beiden Zustände auch in einem potentiellen Speichergerät ausgelesen werden können, sollte mit dem Wechsel zwischen den beiden Zuständen eine Antwort beispielsweise optischer oder magnetischer Natur einhergehen.^[5] Erste Erfolge auf dem Gebiet konnten beispielsweise durch Arbeiten von der Gruppe um J. Fraser Stoddart erzielt werden, der bereits 2007 über einen auf Rotaxan basierenden elektronischen Speicher berichtete, welcher 10^{11} Bits pro Quadratzentimeter aufweisen konnte.^[6] Andere geeignete Kandidaten für derartige Anwendungen könnten Koordinationsverbindungen sein, da deren magnetische Eigenschaften durch äußere Stimuli geschaltet werden können. Dieses bekannte Phänomen für molekulare Bistabilität wird als Spin Crossover (SCO) bezeichnet.

3.1 Grundlagen des Spin Crossover (SCO)

Die Entdeckung von markanten Unterschieden in den magnetischen Suszeptibilitäten bei verschiedenen substituierten Eisen(III)dithiocarbamaten durch Cambi und Szegő^[7] bereitete den Weg für nunmehr 90 Jahre Forschung auf dem Gebiet des Spin Crossovers. Nahezu zeitgleich wurden 1929 von Bethe die Grundlagen für die Ligandenfeldtheorie beschrieben, welche damals noch als Kristallfeldtheorie bezeichnet wurde. Einen weiteren, entscheidenden Beitrag leistete hierbei auch Van Vleck mit seinen Studien zum Thema Magnetismus.^[8] So konnten die Beobachtungen in den oktaedrisch koordinierten Eisen(III)-Komplexen durch ein temperaturabhängiges Gleichgewicht zwischen zwei möglichen Grundzuständen beschrieben werden.^[9] Möglich wird SCO in Koordinationsverbindungen, welche ein Zentralatom aus der ersten Reihe der Übergangsmetalle mit einer Elektronenkonfiguration d^4 – d^7 besitzen und bevorzugt oktaedrisch koordiniert sind. Die meisten Verbindungen, bei denen dieses Phänomen beobachtet werden kann, sind Verbindungen mit einem Fe^{2+} , Fe^{3+} oder Co^{2+} Zentralatom.^[10] Aber auch Komplexe mit einem Ni^{2+} , Co^{3+} , Mn^{3+} oder Cr^{2+} Metallzentrum können diese Art der Bistabilität zeigen.^[11] Die das Zentralatom umgebenden Liganden führen, abhängig von der Geometrie der umgebenden Liganden, zu einer partiellen Aufhebung der Entartung der d-Orbitale. In einem ideal oktaedrischen Ligandenfeld kommt es somit zu einer Aufspaltung der fünf d-Orbitale in die nichtbindenden t_{2g} Orbitale, bestehend aus d_{xy} , d_{yz} und d_{zx} und in die antibindenden e_g^* Orbitale $d_{x^2-y^2}$ und d_z^2 . Je nach Stärke der Ligandenfeldaufspaltung Δ_o (die durch den Parameter der Ligandenfeldstärke $10Dq$ dargestellt wird) relativ zur Spinpaarungsenergie P werden in einem System mit sechs d-Elektronen entweder Komplexe mit einem maximalen ($S = 2$, high-spin(HS)-Zustand) oder einem minimalem ($S = 0$, low-spin(LS)-Zustand) Gesamtspin gebildet. (Abbildung 1)

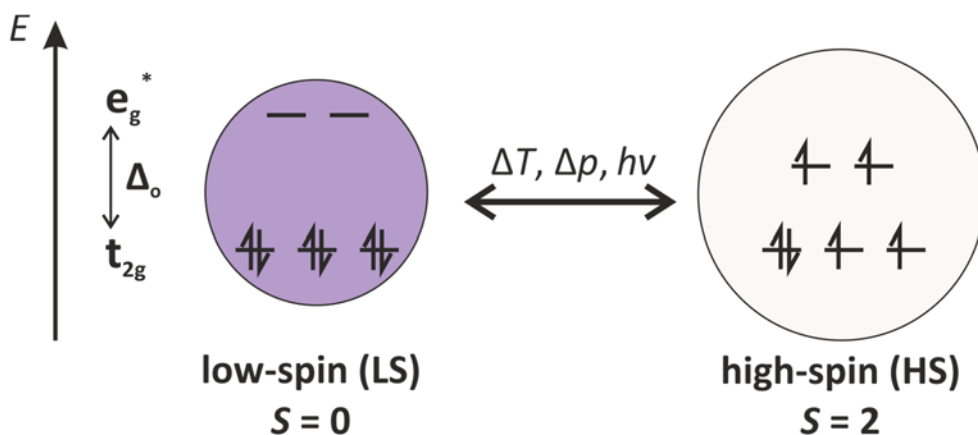


Abbildung 1 Schematische Darstellung des low-spin(LS)-Zustandes (links) und des high-spin(HS)-Zustandes (rechts) eines oktaedrisch koordinierten Systems mit sechs d-Elektronen.

Eine Verwendung von Liganden, die das Ligandenfeld stark aufspalten, sogenannte Starkfeldliganden (z. B. CN^-), führt dazu, dass Δ deutlich größer als P ist und der Komplex somit im LS-Zustand vorliegt. Das Gegenteil tritt bei der Verwendung von Schwachfeldliganden (z. B. Wasser) ein, wo Δ nun deutlich kleiner als die erforderliche Spinpaarungsenergie P ist. Das führt zu einer Orbitalbesetzung gemäß der Hund'schen Regel und somit zu einem Komplex im HS-Zustand. Bei einigen Koordinationsverbindungen haben Δ und P ähnliche Werte und somit liegt der Energieunterschied zwischen dem HS und dem LS-Zustand im Bereich der thermischen Energie ($k_B T$). In diesem Fall ist eine Besetzung und somit auch ein gezieltes Schalten, durch eine Änderung der Temperatur zwischen beiden Zuständen möglich (vgl. Abbildung 1).^[12] Auch durch das Anlegen eines Drucks, oder das Einstrahlen von Licht kann ein Schalten von einem in den anderen Zustand erfolgen. Da im paramagnetischen Eisen(II)-HS-Zustand die antibindenden e_g^* -Orbitale besetzt sind, ändert sich bei einem Spinübergang nicht nur der Magnetismus, sondern es tritt auch eine signifikante Änderung in der Metall-Ligand-Bindungslänge ein.^[13] Für Eisen(II)-Verbindungen beträgt die Änderung in der Bindungslänge während eines Spinüberganges häufig 0.2 Å. Typischerweise geht mit einem Spin Crossover auch ein Farbwechsel der Verbindung einher. Die dafür verantwortlichen d-d-Übergänge sind paritätsverboten aber spinerlaubt. Der Übergang von HS zu LS geht häufig mit einem intensiven Farbwechsel einher. Vor allem Eisen(II)-Komplexe mit Tetrazol- und Triazol-Liganden sind für derartige Änderungen in ihrer Farbe bekannt. Abbildung 2 zeigt die Verbindung $[\text{Fe}(\text{atrz})_3](\text{ClO}_4)_2$ (atrz = 4-Aminotriazol), welche bei Raumtemperatur farblos ist und im HS-Zustand vorliegt. Ein dazugehöriges UV-Vis-Spektrum zeigt eine schwache ${}^5T_2 \rightarrow {}^5E$ Bande im NIR.^[8,14] Nach Kühlen mit flüssigem Stickstoff befindet sich der Eisen(II)-Komplex im diamagnetischen LS-Zustand und ist nun intensiv rosa gefärbt. Das dazugehörige UV-Vis Spektrum zeigt nun die zwei erwarteten, spinerlaubten d-d-Banden, die den Übergängen ${}^1A_1 \rightarrow {}^1T_1$ und ${}^1A_1 \rightarrow {}^1T_2$ zugeordnet werden können.^[8,15] Häufig kommt es durch paritäts- und spinerlaubte Charge-Transfer-Übergänge zu einer Überlagerung dieser Banden und somit zu anderen Farbeindrücken. In Gegenwart von Akzeptor-Liganden ist nicht allein das Metallzentrum für die Farbigekeit verantwortlich. Dadurch bedingt sind in Folge von Charge-Transfer-Übergängen auch in vielen Fällen beide Spinzustände farbig.

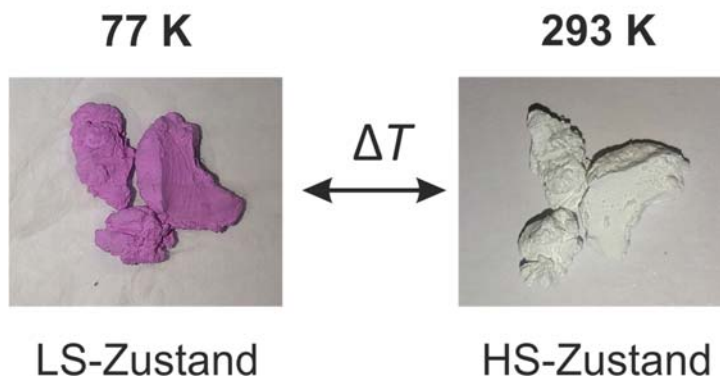


Abbildung 2 Farbwechsel der Eisen(II)-Koordinationsverbindung $[\text{Fe}(\text{atrz})_3](\text{ClO}_4)_2$ (atrz = 4-Aminotriazol) nach dem Kühlen mit flüssigem Stickstoff (links) und bei Raumtemperatur (rechts). Bei 293 K ist die Verbindung weiß und im HS-Zustand. Kühlen auf 77 K führt zu einem Spin Crossover und somit zum intensiv rosa gefärbten LS-Zustand.

Um zu verstehen, unter welchen Umständen die Energieunterschiede der beiden Zustände in einer thermisch zugänglichen Größenordnung ($k_B T$) liegen, kann deren potentielle Energie gegen den Bindungslängenabstand des Metallzentrums zum Donoratom aufgetragen werden (Abbildung 3).

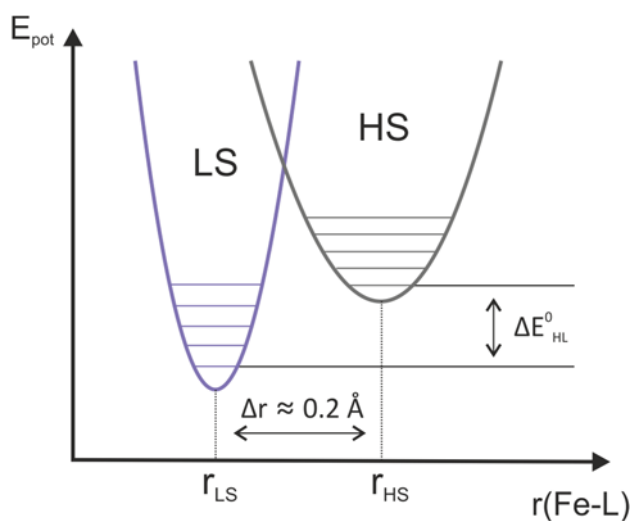


Abbildung 3 Adiabatische Potentiale des HS- und LS-Zustandes aufgetragen gegen die Metall-Ligand Bindungslänge $r(\text{Fe-L})$.

Die beiden daraus resultierenden Potentialtöpfe sind sowohl vertikal als auch horizontal gegeneinander verschoben. Entscheidend ist der Unterschied in den Nullpunktenergien der beiden Systeme, welcher dem Zusammenhang: $\Delta E^0_{\text{HL}} = E^0_{\text{HS}} - E^0_{\text{LS}}$ folgt.^[8] Demnach ist der LS-Zustand gegenüber dem HS-Zustand um ΔE^0_{HL} stabilisiert zu sein. Die vertikalen Linien im Diagramm repräsentieren Schwingungsniveaus und bei sehr niedrigen Temperaturen befindet sich das Metallzentrum in geeigneten Komplexen im LS-Zustand. Mit zunehmender Temperatur wird thermische Energie in Vibrationsenergie umgewandelt, was demzufolge zu einer Besetzung der

Schwingungsebenen bis hin zum Kreuzungspunkt der beiden adiabatischen Potentialkurven führt. An diesem kritischen Punkt ist die Geometrie zwischen HS und LS gleich und es erfolgt der Übergang zwischen dem LS- und HS-Zustand gemäß dem Prinzip von Franck-Condon.^[16] Die Differenz in den Enthalpien der beiden Zustände wird durch entropische Unterschiede zwischen HS- und LS-Zustand überwunden. An diesen Entropieunterschieden sind maßgeblich zwei Faktoren beteiligt. Zum einen der elektronische Beitrag, der sich aus der Spin- und Bahn-Entartung des HS-Zustandes ergibt und zum anderen der Vibrationsbeitrag. Dieser wird bedingt durch die generell niedrigeren Vibrationsfrequenzen und die höhere Dichte der Vibrationszustände im HS-Zustand. Daraus lässt sich ableiten, dass der LS-Zustand der quantenmechanische Grundzustand sein muss, jedoch bei höheren Temperaturen der HS bevorzugt wird und somit in diesem Fall der thermodynamisch stabile Zustand ist.^[8,16]

3.2 Kooperative Effekte in Spin-Crossover-Systemen

Wie aus den Erläuterungen des vorherigen Kapitels deutlich wird, ist das Spin-Crossover-Phänomen molekularer Natur. Jedoch werden bei der Synthese von Koordinationsverbindungen je nach Art der Herstellung oder des verwendeten Systems entweder feine Pulver oder eher kristalline Materialien erhalten. Die Eigenschaften dieser Substanzen im festen Zustand werden durch kooperative Wechselwirkung zwischen den Molekülen, aus denen der Stoff aufgebaut ist, beeinflusst. Die Auswirkungen solcher Interaktionen können mit Hilfe von magnetischen Suszeptibilitätsmessungen verfolgt werden. Hierbei wird entweder die HS-Fraktion (γ_{HS}) in Abhängigkeit von der Temperatur aufgetragen, alternativ erfolgt die Auftragung des Produktes aus molarer Suszeptibilität und der Temperatur ($\chi_M T$) gegen die gemessene Temperatur. In Abbildung 4 sind Beispiele typischer Kurvenverläufe dargestellt, in denen kooperative Effekte eine Rolle spielen. So können Spinübergänge zum einen sehr abrupt, teilweise mit Auftreten einer Hysterese, oder aber stufenweise verlaufen. In einigen Fällen ist auch ein eher gradueller Übergang über einen großen Temperaturbereich möglich. Auch unvollständige Übergänge, bei denen nur ein Teil der Moleküle den LS-Zustand erreicht, können beobachtet werden.^[17]

Einleitung

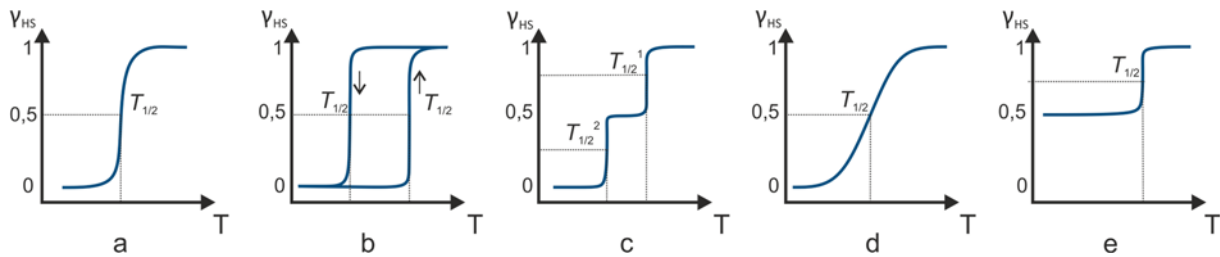


Abbildung 4 Modellhafte Darstellung verschiedener Spinübergangstypen: a) abrupt, b) abrupt mit Hysterese, c) stufenweise, d) graduell, e) unvollständig.

Welcher Kurvenverlauf im Rahmen eines SCO realisiert wird, hängt im hohen Maße davon ab, ob und wie die Strukturinformation eines Spinüberganges innerhalb des Kristallsystems von einem an weitere Moleküle weitergeleitet wird. Diese als kooperative Wechselwirkung bezeichnete Weiterleitung kann von verschiedenen Faktoren beeinflusst werden, wie zum Beispiel van-der-Waals-Wechselwirkungen, π - π -Wechselwirkungen oder Wasserstoffbrücken.^[13] Über diese Wechselwirkungen kann die Information der Verkürzung oder Verlängerung des Metall-Ligand-Abstandes eines Moleküls zu einem benachbarten weitergegeben werden. Diese Kooperativität ergibt sich aus der Volumenänderung eines SCO-Moleküls, welche zu weitreichenden Wechselwirkungen im Kristall führt und als innerer Druck des Systems verstanden wird. Bei diesem elastischen Ansatz der Kooperativität spielen Anzahl und Stärke der Wechselwirkungen, eine entscheidende Rolle.^[18] In einer jüngeren Betrachtung wird die Kooperativität mit der Änderung in der Ladungsverteilung entlang der Metall-Ligand-Bindung in Verbindung gebracht. Diese führt zu einem elektrostatischen Beitrag der Kooperativität, welcher dann von der Organisation des Metall-Ligand-Dipols in einer bestimmten Kristallpackung abhängt.^[19] In einer aktuellen Arbeit von M. G. Reeves *et. al.* werden Rechnungen zu Packungsenergien an mehreren ähnlichen Komplexen durchgeführt, um das Phänomen der Kooperativität besser zu verstehen.^[20] Bei der Betrachtung sind Energieunterschiede zwischen stabilisierenden bzw. destabilisierenden Wechselwirkungen von Bedeutung.^[20] Sind die Energieunterschiede klein und fehlen zusätzlich ausgleichende Energien, scheint das zu einer langsameren Ausbreitung des Spinübergangs im Kristallsystem zu führen und es liegt ein eher gradueller Spin Crossover vor (Abbildung 4d).^[20] Liegt im Gegensatz dazu ein hoher Grad an Kooperativität in einem Kristallsystem vor, so führt das zu großen Energieunterschieden und es findet ein abrupter Übergang statt (Abbildung 4a). Bei besonders hoher Kooperativität kann das System innerhalb eines Temperaturbereiches in einem metastabilen Zustand verbleiben, was zu unterschiedlichen Übergangstemperaturen beim Heizen und Kühlen führen kann (Abbildung 4b).^[13,21] Diese Verbindungen sind besonders interessant im Hinblick auf die Verwendung in molekularen Schaltern. Ein vielversprechender Ansatz für die gezielte Herstellung solcher Materialien ist die Vernetzung von Metallzentren mit verbrückenden zweizähligen Liganden. In solchen Koordinationspolymeren besteht durch die verbrückt vorliegenden Metallzentren eine erhöhte Chance auf das Auftreten von kooperativen Effekten. Je nach Packungsart können auch

stufenweise Übergänge (Abbildung 4c) stattfinden, bei denen beispielsweise zwei verschiedene Metallzentren innerhalb eines Kristalls vorliegen. In so einem Fall haben die verschiedenen Metallzentren unterschiedliche Spinübergangstemperaturen $T_{1/2}$ ^[12]. Es ist auch möglich, dass nur ein bestimmter Anteil der Metallzentren in der Lage ist, einen SCO zu vollziehen. So können beispielsweise co-kristallisiertes Lösemittel oder starke intermolekulare Wechselwirkungen die notwendige Änderung des Metall-Ligand-Abstandes und somit auch einen Spinübergang, zumindest teilweise, verhindern (Abbildung 4e).^[17,20] Je nach System und Art der Wechselwirkung kann demnach ein Spinübergang entweder begünstigt, oder auch behindert werden.

3.3 Multifunktionale Spin-Crossover-Systeme

Verbindungen mit Spin-Crossover-Eigenschaften werden vor allem im Hinblick auf die Entwicklung von molekülbasierten elektronischen Geräten untersucht. Auch im Bereich der Spintronik, bei der versucht wird Informationen mit Hilfe des magnetischen Moments eines Elektrons darzustellen, spielen SCO-Verbindungen eine wichtige Rolle. Um den komplexen Anforderungen heutiger Technologien gerecht zu werden, ist es notwendig, das Phänomen des Spin Crossovers mit weiteren Schlüsseleigenschaften zu kombinieren.^[16] In solchen dabei entstehenden multifunktionalen Materialien können beispielsweise magnetische mit entweder elektrisch leitenden oder speziellen optischen Eigenschaften kombiniert sein. Auch Materialien, welche neben magnetischen Eigenschaften besonderes dielektrisches Verhalten zeigen, sind für den Einsatz in technischen Anwendungen interessant.^[22] Eine gängige Strategie beim Design von molekülbasierten Geräten besteht daher in der Verknüpfung von SCO-Molekülen mit einer der genannten Eigenschaften. Dabei ist es wichtig, dass durch einen zugeführten Stimulus (z. B. Temperaturänderung, Lichteinstrahlung, Anlegen eines Druckes) sich mindestens eine Eigenschaft der Substanz ändert. Diese Eigenschaftsänderung sollte durch einfache Messmethoden ausgelesen werden können.

3.3.1 Spin Crossover und elektrische Leitfähigkeit

Da die Verkleinerung von Silicium-basierten elektronischen Bauteilen physikalisch limitiert ist, wächst das Interesse am Gebrauch von einzelnen Molekülen als Transistoren.^[23] Aus diesem Grund soll auch laut der *International Roadmap for Devices and Systems* (IRDS) ein industrieller Wechsel hin zu organischen und hybriden organisch-anorganischen Materialien erfolgen.^[24] Koordinationsverbindungen sind in diesem Kontext von großem Interesse, da durch die Wahl verschiedener Liganden deren Eigenschaften gezielt beeinflusst werden können. Insbesondere elektrisch leitende SCO-Materialien sind aufgrund ihrer hervorragenden Signalübertragung Gegenstand aktueller Forschung.^[24] Prinzipiell gibt es verschiedene Möglichkeiten zur Herstellung von SCO-Materialien mit elektrisch leitenden Eigenschaften. In vielen Fällen erfolgt die Kombination von Kationen oder Anionen, die SCO-Eigenschaften zeigen, mit molekülbasierten Kationen oder Anionen, welche selbst elektrisch leitend sind.^[22] Am häufigsten wird dies durch Co-Kristallisation der entsprechenden Einheiten erreicht. Als leitender Baustein werden häufig redoxaktive, organische Moleküle mit planarer Struktur verwendet. Diese können wie beispielsweise das einfach oxidierte Tetrathiafulvalen (TTF⁺) kationischer, oder wie das Tetracyanochinodimethan (TCNQ^{-/2-}) anionischer Natur sein. Jedoch sind die meisten SCO-Einheiten Kationen und dementsprechend bestehen die bisher untersuchten Co-Kristalle aus einer kationischen SCO-Einheit und einem Anion mit leitenden Eigenschaften.^[25] Moleküle wie beispielsweise das Tetrathiafulvalen (TTF) werden eher durch kovalente Bindungen an die entsprechende SCO-Einheit gebunden.^[26] Um Materialien mit besonders guten elektrisch leitenden Eigenschaften zu erhalten, ist es vorteilhaft, wenn die leitenden Moleküle innerhalb des Kristalls getrennte Schichten formen. Somit kommt es im Kristallverband zu der Ausbildung von leitenden Ebenen, vergleichbar mit dem aus dem Bändermodell bekannten Leitungsband.^[27] Da bei einem Spinübergang zwischen HS und LS aufgrund der bereits diskutierten Bindungslängenunterschiede eine Volumenänderung stattfindet, entsteht innerhalb des Kristalls ein chemischer Druck. Dadurch wird der Ladungstransfer zwischen den leitenden Molekülen beeinflusst, was wiederum zu einer veränderten Leitfähigkeit in solchen Materialien führt.^[28] Realisiert wurden solche Systeme von Takahashi oder auch Faulmann und Mitarbeitenden^[29,30], indem der für seine elektrische Leitfähigkeit bekannte Baustein [Ni(dmit)₂]⁻ (dmit = 4,5-Dithiolato-1,3-dithiol-2-thion) mit SCO-Kationen der Form [Fe^{III}(L)_x]⁺ (L = Schiff-Base-artiger Ligand) kombiniert wurde (siehe Abbildung 5).

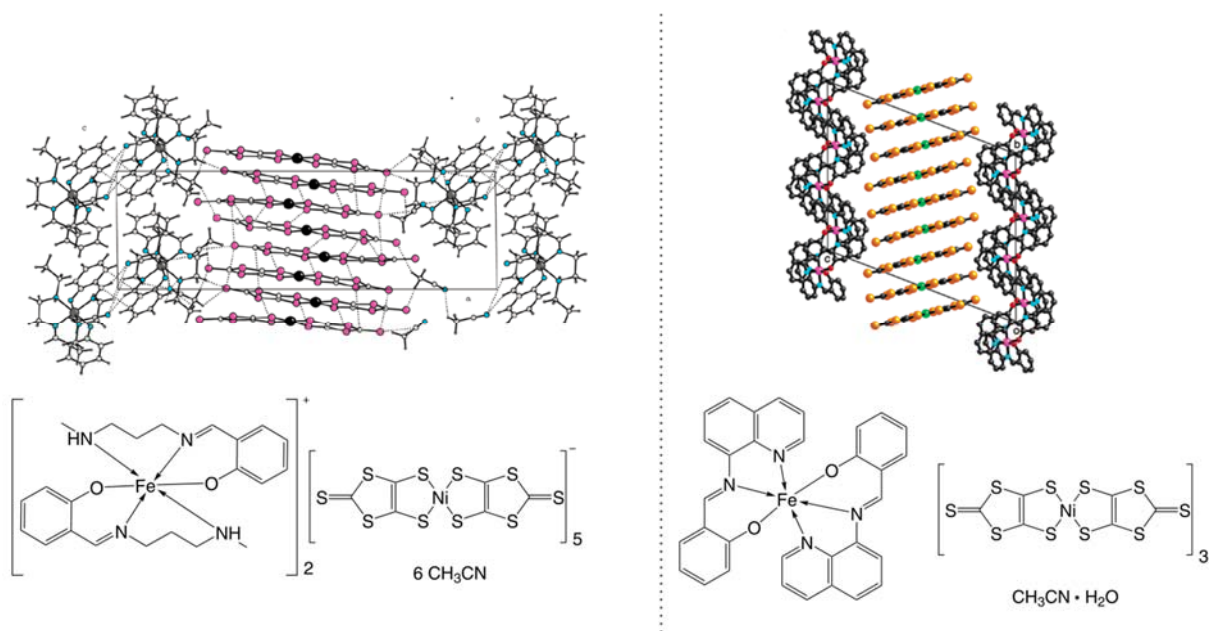


Abbildung 5 (links) Kristallstruktur mit zugehöriger molekularer Strukturformel des Komplexes $[\text{Ni}(\text{dmit})_2]_5[\text{Fe}(\text{salEen})_2]_2 \cdot 6 \text{CH}_3\text{CN}$ ($\text{salEen} = N$ -(2-ethylamino)-ethyl)-salicyldiamin)^[30] (rechts) Kristallstruktur mit dazugehöriger Strukturformel von $[\text{Fe}(\text{qsal})_2][\text{Ni}(\text{dmit})_2]_3 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ ($\text{qsalH} = N$ -(8-quinoly)-salicyldiamin)^[26].

So konnte in diesen Beispielen, neben einigen anderen^[31], ein eindeutiger Synergismus zwischen elektrischer Leitfähigkeit und Spin-Crossover-Verhalten beobachtet werden. Neben dmit wird häufig auch TCNQ⁻ als leitendes, oft radikalisches Anion verwendet.^[32] Bei genauerer Betrachtung fällt jedoch auf, dass die erhaltenen Substanzen zwar durch ihre leitenden Eigenschaften im Bereich der Koordinationsverbindungen hervorstechen, jedoch im Vergleich mit anderen Materialien eher geringe Leitfähigkeiten im Halbleiterbereich aufweisen. So besitzt beispielsweise Kupfer eine hohe elektrische Leitfähigkeit von $6 \cdot 10^5 \text{ S/cm}$ und Silicium zeigt je nach Grad der Dotierung elektrische Leitfähigkeiten im Bereich von 10^{-2} bis 10^4 S/cm .^[33] In der Komplexchemie haben vielversprechende Vertreter elektrische Leitfähigkeiten von 0,2 bis 2 S/cm .^[34] Dies liegt unter anderem an der vergleichsweise großen Bandlücke, die in derartigen Komplexen vorliegt. Ein Ansatz, um dieses Problem zu umgehen, ist die Verankerung von SCO-Komplexen mit leitenden Polymeren. So kann beispielsweise insitu aus dem für seine einzigartigen SCO-Eigenschaften bekannten Koordinationspolymer $[\text{Fe}(\text{trz})(\text{Htrz})_2][\text{BF}_4]$ ($\text{Htrz} = 1,2,4\text{-}4\text{H-Triazol}$ und $\text{trz} = \text{deprotonierter Triazolato-Ligand}$) und dem Monomer für Polypyrrol ein Kompositmaterial erhalten werden, welches als dünner Film ausgebracht werden kann.^[35] Die erhaltenen Filme zeigen einerseits die vom Komplex bekannten SCO-Eigenschaften und andererseits ändert sich auch die elektrische Leitfähigkeit dieses Materials in Abhängigkeit vom magnetischen Zustand. Ein Durchbruch auf dem Gebiet der leitenden SCO-Hybridmaterialien wurde 2021 durch die Einbettung des SCO-Komplexes $[\text{Fe}(\text{H}_2\text{Bpz}_2)_2(\text{L})]$ ($\text{H}_2\text{Bpz}_2 = \text{Dihydrobis}(\text{pyrazolyl})\text{borat}$, $\text{L} = 1,10\text{-Phenanthrolin}$ oder $2,2'\text{-Bipyridin}$) in leitende, einwandige Kohlenstoff-Nanoröhren erzielt.^[23] Dadurch

wird ermöglicht, dass SCO-Moleküle zukünftig in Nanobauteilen positioniert und durch das leitende Rückgrat elektrisch ausgelesen werden können.

3.3.2 Spin Crossover und Lumineszenz

Lumineszente Materialien werden unter anderem im Hinblick auf ihre unterschiedlichen Anwendungsmöglichkeiten erforscht. So werden sie bereits in Lasern, Lampen, biologischen Markern, Sicherheitstinte, Computerdisplays oder Leuchtstickern verwendet.^[36] Charakteristisch für Vertreter dieser Stoffklasse ist, dass sie einen Teil der elektromagnetischen Strahlung absorbieren und dann mit neuer Wellenlänge emittieren. Diese Eigenschaft macht sie interessant für die Entwicklung neuartiger Leuchtstoffe.^[37,38] So ist eine Anwendung vor allem im Bereich der Photovoltaik, der medizinischen Bildgebung oder aber der Festkörper-basierten Beleuchtung denkbar.^[38] Systeme, deren optische Eigenschaften sich bei einem thermisch induzierten Spinübergang ändern, sind für die Entwicklung von magnetooptischen Schaltern von besonderer Bedeutung.^[37] So kann die Modulation des Lumineszenzsignals als Folge eines Spin Crossovers eine Auslesemöglichkeit für den Spinzustand des untersuchten Systems sein. Damit hätte man eine kontaktlose Signaldetektion mit hoher zeitlicher und räumlicher Auflösung geschaffen.^[36] Für den SCO interessante Metallzentren ($\text{Fe}^{2+/3+}$, Co^{2+} , Ni^{2+}) sorgen häufig in resultierenden Komplexen für eine Löschung der Lumineszenz. Um das zu verstehen, müssen häufig vorkommende angeregte Zustände von Metallkomplexen betrachtet werden. Es handelt sich dabei oftmals um metallzentrierte d-d-Zustände, bei denen ein Elektron von einem besetzten d-Orbital des Metallzentrums in ein unbesetztes Orbital angeregt wurde. Alternativ resultieren π - π^* -Zustände aus einer Anregung von einem besetzten Ligand- π -Orbital in ein unbesetztes π^* -Orbital des Liganden. Derartige π - π^* - und d-d-Zustände zeigen in ihrer Wellenfunktion große Überschneidungen mit der des Grundzustandes und führen daher zu einer sehr schnellen Relaxation des angeregten Zustandes.^[39] Dennoch wird intensiv an der Kombination aus SCO und Lumineszenz in einem Material geforscht. In solchen Systemen sollen die drastischen elektronischen und strukturellen Änderungen während eines SCO die Umgebung des Luminophores so beeinflussen, dass eine lumineszente Antwort als Folge möglich wird.^[36] Für eine derartige Kombination eignen sich Zwei-Komponenten-Systeme, bestehend aus einem SCO aktiven Baustein und einer Signaleinheit, deren Emission durch den Spinzustand beeinflusst wird. In diesen einfachen Donor-Akzeptor- (D-A) oder verbrückten Donor-Brücke-Akzeptor-Dyaden (D-B-A) fungiert das Luminophor als Energie-Donor und beispielsweise ein im Komplex befindliches Eisen(II)-SCO-Zentrum als Energie-Akzeptor. In Abbildung 6 ist die mögliche Funktionsweise einer solchen Dyade schematisch dargestellt.

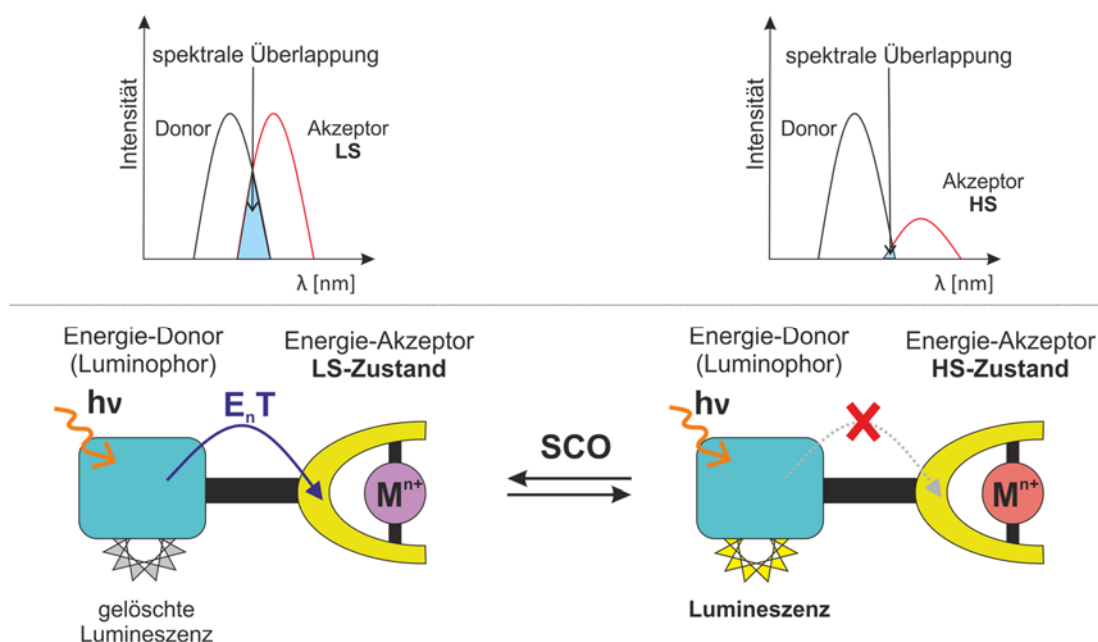


Abbildung 6 (oben) Darstellung der spektralen Überlappung für ein Donor-Akzeptor System im LS- oder HS-Zustand. (unten) Mögliche Änderung der lumineszenten Eigenschaften eines Metallkomplexes (M^{n+} = Metallzentrum), hervorgerufen durch einen Spin Crossover. Im HS-Zustand ist durch die geringe spektrale Überlappung kein Energietransfer (E_nT) möglich und die Lumineszenz des Donors bleibt bestehen.^[37]

In diesen Systemen kann idealerweise die Absorptionsänderung, die während eines $HS \rightarrow LS$ -Überganges stattfindet, ausgenutzt werden. Da der LS-Zustand einen relativ hohen Absorptionskoeffizienten im sichtbaren Bereich des elektronischen Spektrums besitzt und zusätzlich energetische Nähe zu den gängigen, im ultravioletten (UV) und sichtbaren Bereich emittierenden Luminophoren hat, ist er ein besserer Energie-Akzeptor.^[37] Durch die daraus resultierende Überlappung zwischen Emission des Donors (Luminophor) und Absorption des Akzeptors (LS-Zustand) kommt es zwangsläufig zu einer Löschung der Lumineszenz. Im Gegensatz dazu zeigt der HS-Zustand nur eine sehr geringe Absorption im nahen Infrarotbereich, was zu deutlich geringerer spektraler Überlagerung führt. Diese Änderung könnte ausreichen, um die Lumineszenz der Donor-Einheit aufrechtzuerhalten.^[37] Bis heute existieren nur wenige Koordinationsverbindungen, in denen tatsächlich ein Zusammenhang zwischen Spinzustand und Lumineszenz besteht. In einem zweikernigen Eisenkomplex der Form $[Fe_2(L1)_5(NCS)_4] \cdot 4(MeOH)$ ($L1 = N$ -Salicyliden-4-amino-1,2,4-triazol), welcher von der Gruppe um Garcia beschrieben wurde, konnte ein Zusammenhang zwischen den auftretenden lumineszenten Eigenschaften und dem stattfindenden SCO festgestellt werden.^[40] Ein weiteres Beispiel liefert ein Eisen(II)-Koordinationspolymer mit einem Phenazin-basierten Schiff-Base-Liganden, welcher von Lochenie erstmals charakterisiert wurde.^[41] Auch etablierte Komplexe mit bpp-Liganden ($bpp = 2,6$ -Bis(pyrazol-1-yl)pyridin) zeigen vielversprechende Ergebnisse hinsichtlich der Kombination von Lumineszenz und Spin Crossover.^[42] Oftmals beruht die beobachtete Synergie jedoch nur auf der mit dem SCO einhergehenden Volumenänderung des untersuchten Systems, weil die lumineszente Einheit lediglich mit der an das Metallzentrum koordinierenden verknüpft ist.^[37]

3.4 Valenztautomerie

3.4.1 Theoretischer Hintergrund

Von valenztautomeren (VT) Übergängen wird gesprochen, wenn in einem Molekül ein Elektronenübergang zwischen einem redoxaktiven Metallzentrum und einem redoxaktiven Liganden, oder einem zweiten Metallzentrum angeregt wird. Derartige Übergänge können sowohl im Festkörper als auch in Lösung beobachtet werden und treten vor allem bei Koordinationsverbindungen mit Übergangsmetallzentren (z. B. Mn, Fe, Co, Ni, Cu, Rh, Ir) kombiniert mit verschiedenen redoxaktiven Liganden auf.^[43] Generell handelt es sich bei solchen Liganden um organische Moleküle, welche definierte Redoxprozesse zeigen. Solche organischen Moleküle, die in Kombination mit einem Metallzentrum mit diesem in starken Austausch treten, werden als redoxaktive oder nicht-unschuldige Liganden bezeichnet.^[44] Valenztautomere existieren in zwei elektronischen Zuständen, welche in ihren Energien ähnlich sind, sich jedoch in der Ladungsverteilung innerhalb der Moleküle deutlich unterscheiden. Aufgrund ihrer ähnlichen Energien reagieren beide Zustände sehr sensibel auf äußere Einflüsse, wie zum Beispiel Temperatur, Druck oder Lichteinstrahlung.^[43,45] Somit kann, ähnlich wie bei einem Spin Crossover, zwischen beiden Tautomeren durch Variation äußerer Stimuli geschaltet werden.^[46] Damit ein System Valenztautomerie zeigt, müssen zwei grundlegende Voraussetzungen erfüllt sein. Der Kovalenzgrad der Interaktion zwischen dem Metall-Ion und dem redoxaktiven Liganden muss klein sein. Zusätzlich müssen die Grenzorbitale des Metallzentrums und die des Liganden ähnliche Energien haben, da sich so die π^* -Orbitale des Liganden mit den $d\pi$ -Orbitalen des Metallzentrums mischen können.^[47] Sind nun die elektronischen Beiträge beider Partner über das Molekül delokalisiert, können Grenzstrukturen formuliert werden und je nach äußeren Bedingungen tritt eine Struktur bevorzugt auf.^[43]

Forschungen auf dem Gebiet starteten bereits in den 60er Jahren, als begonnen wurde das schon lange bekannte Berliner Blau, oder das vor mehr als hundert Jahren zuerst beschriebene Cs_2SbCl_6 , spektroskopisch zu untersuchen.^[48,49] Durch die Analyse der Kristallstrukturen von vollständig oxidierten und reduzierten bzw. gemischtvalenten Komplexionen konnten die beobachteten spektroskopischen Eigenschaften durch phononengekoppelte Übergänge zwischen zwei Metallzentren erklärt werden.^[49] Simultan wurde erkannt, dass anhand der Unterschiede in den Kristallstrukturen eine Einteilung in verschiedene Klassen vorgenommen werden kann.^[49–51] Je nach Grad der elektronischen Delokalisierung wird nach Robin und Day zwischen drei Klassen

unterschieden. Abbildung 7 zeigt eine schematische Darstellung der Energiediagramme, aufgetragen gegen die Reaktionskoordinaten für die drei verschiedenen Klassen.

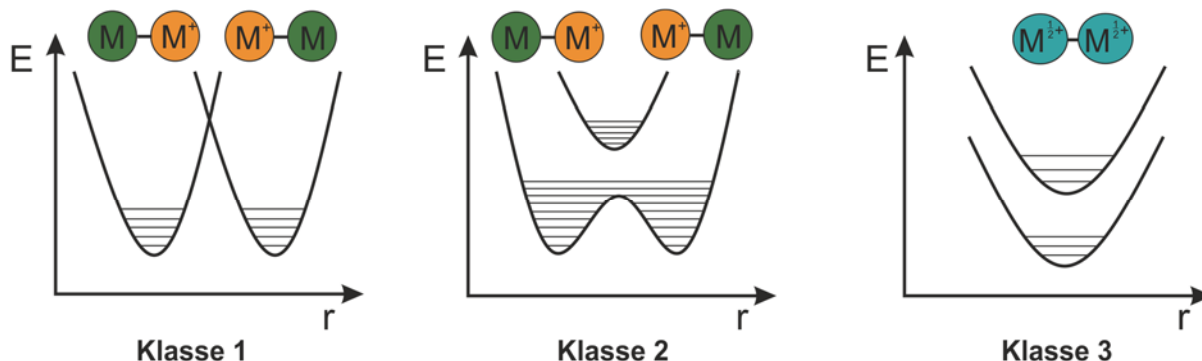


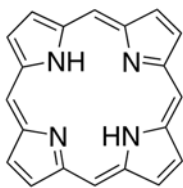
Abbildung 7 Schematische Darstellung der Energiediagramme, aufgetragen gegen die Reaktionskoordinaten für die drei verschiedenen Klassen von gemischtvalenten Systemen.

Findet zwischen den beiden Redoxzentren wenig bis keine Wechselwirkung statt, so sind die Elektronen in ihren jeweiligen Zuständen lokalisiert und die Verbindung gehört der Klasse 1 an. Ist im Gegensatz dazu die Interaktion zwischen beiden Zentren so intensiv, dass das Elektron über das gesamte System delokalisiert ist und somit nur ein Zustand existiert, so liegt eine Verbindung der Klasse 3 vor. Zwischen diesen beiden Extremen liegen Verbindungen der Klasse 2, bei denen eine moderate Interaktion zwischen den Redoxzentren vorherrscht. Das bedeutet, dass das Elektron auf einem der Redoxzentren, getrennt durch eine Energiebarriere (ΔG), lokalisiert ist. Diese Barriere kann wiederum durch einen externen Stimulus überwunden werden und auf diese Weise ist es möglich gezielt zwischen zwei elektronischen Zuständen zu schalten.^[46,49,51] Ursprünglich bezogen sich die Betrachtungen auf Verbindungen mit zwei identischen Metallionen in verschiedenen Oxidationsstufen. Generell kann die Klassifizierung jedoch auf alle Systeme übertragen werden, in denen mindestens zwei Zentren existieren, die in unterschiedlichen Oxidationsstufen stabil sind.^[46,49,52] Die Untersuchung derartiger Systeme ist weiterhin aus verschiedenen Gründen wichtig. Einerseits kann anhand solcher Modellsysteme der Elektronentransfer zwischen Liganden und Metallzentren nachvollzogen und studiert werden. Andererseits kann durch die Betrachtung dieser Systeme ein tieferes Verständnis über die Zusammenhänge zwischen Elektronentransfer und Spinübergang erhalten werden.^[44]

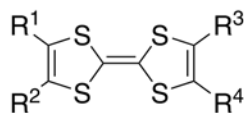
3.4.2 Valenztautomerie in Koordinationsverbindungen

Die 1972 von Creutz und Taube beschriebenen zweikernigen Rutheniumkomplexe der Form $[(\text{NH}_3)_5\text{Ru}-\text{Brücke}-\text{Ru}(\text{NH}_3)_5]^{5+}$ bilden die Grundlage für die Erforschung von Koordinationsverbindungen, die der Klasse 2 nach Robin und Day angehören.^[52,53] Vor allem in hetero- oder homonuklearen, mehrkernigen Metallkomplexen konnten intramolekulare Elektronenübergänge nachgewiesen werden. Seltener sind Verbindungen, in denen neben dem Metall eine rein organische Einheit das Redoxzentrum bildet. Bekannte Beispiele solcher Liganden und Verbindungen sind unter anderem Tetraphenylporphyrine, Tetrathiafulvalene, Ferrocene, Polychlorotriphenylmethylradikale (PTM), Chinone und Kronether (siehe Abbildung 8).^[44,54] Aber auch der aus vielen biologischen Prozessen bekannte Nitrosyl-Ligand (NO) ist ein klassischer redoxaktiver Ligand, der reversibel Elektronen aufnehmen und abgeben kann.^[55] Auch Vorgänge, bei denen die Koordination von Sauerstoff an Metallzentren eine Rolle spielt, sind Gegenstand aktueller Forschungen.^[56]

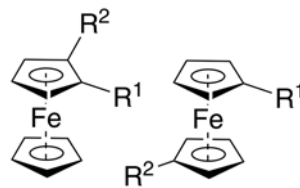
1) Tetraphenylporphyrine



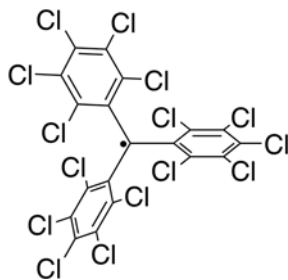
2) Tetrathiafulvalene



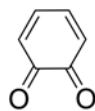
3) Ferrocene



4) PTM



5) Chinone



6) Kronether

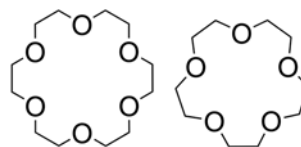


Abbildung 8 Schematische Darstellung von verschiedenen redoxaktiven Liganden.

Die populärsten Vertreter aus der Gruppe der valenztautomerer Koordinationsverbindungen sind oktaedrisch koordinierte Cobaltkomplexe mit 1,2-Benzochinon-Liganden der Form $[\text{Co}(\text{N}_2\text{L})(\text{diox})_2]$ oder $[\text{Co}(\text{N}_4\text{L})(\text{diox})]^+$ ($\text{N}_2\text{L}/\text{N}_4\text{L}$ = zwei- oder vierzählige Chelatliganden, diox = 1,2-Benzochinon in der Catechol (cat) oder Semichinon-Form (sq)). In diesen Komplexen geht häufig mit einem Elektronenübergang auch ein Spinübergang am Metallzentrum einher. Abbildung 9 zeigt schematisch den intramolekularen Elektronenübergang, der zwischen dem Metallion und den π^* -Orbitalen des 1,2-Benzochinon-Liganden stattfindet. Demnach überträgt das diamagnetische Catechol (cat) ein Elektron auf das $\text{LS-Co}^{\text{III}}$ -Zentrum, was gleichzeitig zu einem metallbasierten Spinübergang führt. Durch

die Besetzung der antibindenden e_g^* -Orbitale im daraus resultierenden $HS-Co^{II}$ -Zentrum verlängert sich auch die $Co-O/N$ -Bindung.^[44,47,54]

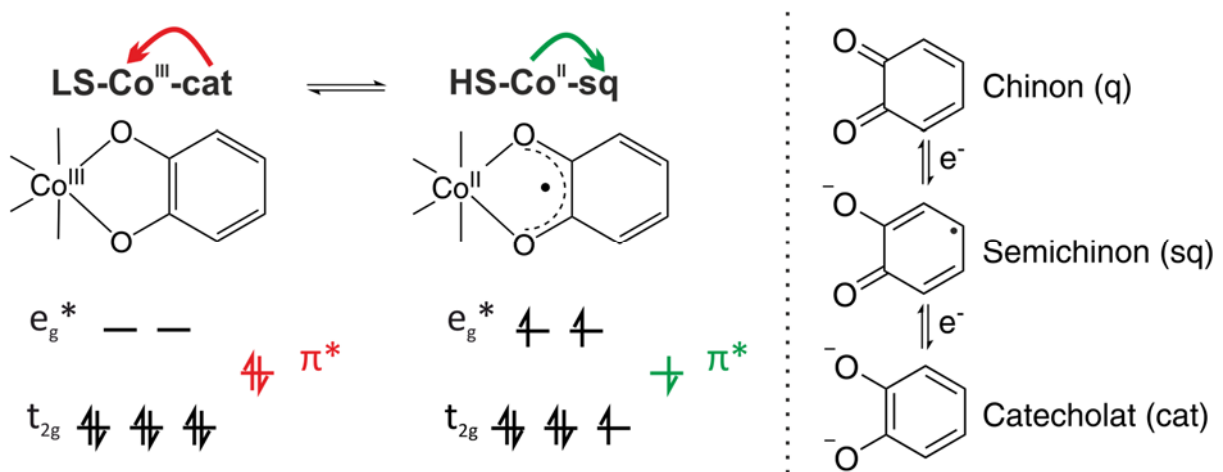


Abbildung 9 (links) Schematische Darstellung der durch Valenztautomerie bedingten elektronischen Zustände eines oktaedrisch koordinierten Cobaltkomplexes mit einem 1,2-Benzochinonligand (cat = Catechol-Ligand, sq = Semichinon-Ligand). (rechts) Stufenweise Reduktion des Chinons zum Catechol.

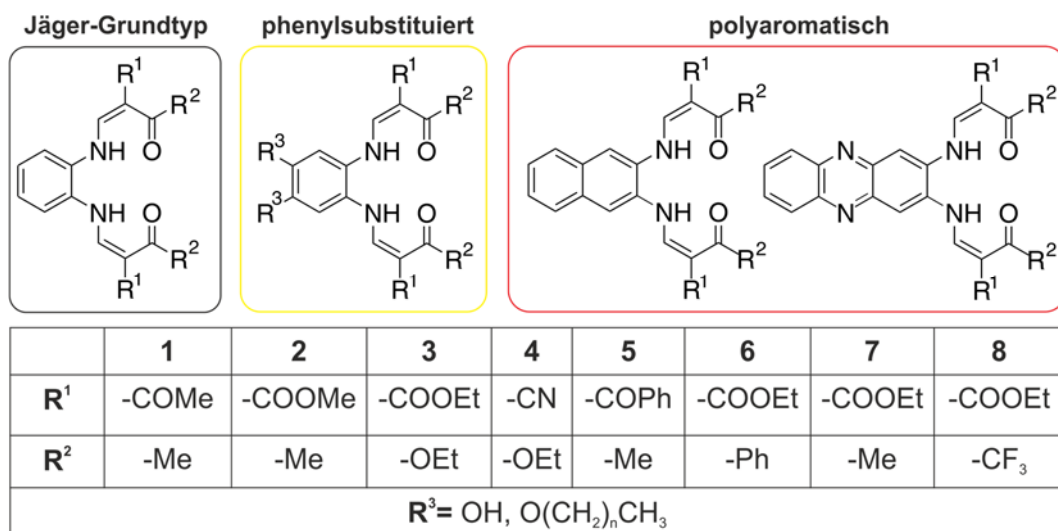
Erste Berichte über derartige valenztautomere Verbindungen gehen auf das Jahr 1980 zurück, in dem Buchanan *et al.* über einen thermisch induzierten Elektronentransfer in einem Cobaltkomplex der Form $[Co^{II}(3,5-DBsq)_2(bpy)]$ bzw. $[Co^{III}(3,5-DBcat)(3,5-DBSQ)(bpy)]$ (3,5-DBsq = 3,5-Di-tert-butyl-1,2-benzosemichinon; 3,5-DBcat = 3,5-Di-tert-butyl-catechol, bpy = 2,2'-Bipyridin) berichten.^[57] An das im LS-Zustand vorliegende Cobalt(III)-Tautomer koordiniert zum Einen der monoanionische Semichinon-Ligand und zusätzlich der dianionische Catechol-Ligand. Der Catechol-Ligand ist in der Lage, bei Änderung der äußeren Bedingungen (Temperaturänderung) ein Elektron auf das Zentralatom zu übertragen, was mit einem Übergang von LS-Co^{III} zu HS-Co^{II} einhergeht.^[57] Zahlreiche auf diesem System basierende Verbindungen wurden hinsichtlich ihrer magnetischen, optischen und elektrochemischen Eigenschaften, sowohl im Festkörper als auch in Lösung intensiv untersucht.^[44,47,52,54] Neben Cobalt rückten auch andere Metallzentren, wie zum Beispiel Kupfer, Nickel, Eisen, Mangan in das Interesse der Forschung zu Valenztautomeren. Tatsächlich konnten auch für andere Metallzentren Valenztautomere mit entsprechenden Catechol-Liganden gefunden werden. So zeigt beispielsweise der Komplex $[Mn(bupy)_2(3,6-DBQ)_2]$ (bupy = 4-tert-Butylpyridin, 3,6-DBQ = 3,6-Di-tert-butyl-1,2-benzochinon) in Abhängigkeit von der Temperatur charakteristische Banden in den elektronischen Spektren, welche auf ein Mn^{4+}/Mn^{3+} Gleichgewicht zurückzuführen sind.^[58] Auch für Kupfer und Nickel können Gleichgewichte zwischen entsprechenden Tautomeren identifiziert werden.^[59,60] Für Eisen hingegen ging man lange davon aus, dass valenztautomere Übergänge in Eisenkomplexen mit Catechol-Liganden nicht möglich sind.^[61,62] Es wurde vermutet, dass die im Vergleich zu Cobaltkomplexen geringere Änderung der Bindungslänge beim Übergang von Fe^{2+} zu Fe^{3+} nicht ausreicht, um einen Elektronentransfer entropisch zu begünstigen.^[62] In den letzten Jahren

konnten jedoch auch für Eisenkomplexe valenztautomere Gleichgewichte beschrieben werden. Beispielsweise kann in der Verbindung $[\text{Fe}^{\text{III}}(\text{bispicen})(\text{Cl}_4\text{cat})(\text{Cl}_4\text{sq})]$ (bispicen = *N,N'*-Bis(2-pyridylmethyl)-1,2-ethandiamin) ein thermisch induzierter Elektronenübergang auf das Eisenzentrum spektroskopisch nachgewiesen werden.^[60,61] Auch in von der Natur inspirierten Modellsystemen, wie zum Beispiel einem synthetischen Modell des Cytochrom P450, kann Valenztautomerie in Eisenkomplexen beobachtet werden.^[63] Die Familie der P450-Cytochrome spielt eine entscheidende Rolle bei der oxidativen Umwandlung von exogenen und endogenen Molekülen in allen Lebensformen. Die Zahl an beschriebenen, unterschiedlichen Vertretern dieser Gruppe nimmt stetig zu und daher ist die Erforschung solcher Systeme auch weiterhin von großem Interesse.^[64] Gerade bei der Entwicklung neuer Katalysatoren für die Energieumwandlung und Speicherung (künstliche Photosynthese), oder die Umwandlung organischer Moleküle sind Abkömmlinge aus der Familie P450-Cytochrome ein wichtiger Ansatzpunkt um neue Modellsysteme zu etablieren.^[65]

3.5 Das Ligandsystem

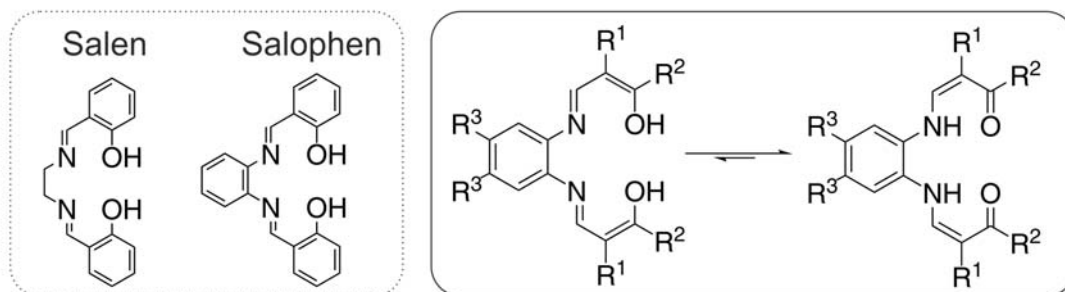
3.5.1 Die äquatoriale Koordinationsumgebung: N_2O_2 -Chelatliganden vom Typ Jäger

Da die Chelatkomplexe des Eisens in biologischen Stoff- und Energiewandlungen eine wichtige Stellung einnehmen, etablierte E.-G. Jäger 1966 ein vierzähniges, Schiff-Base-artiges Ligandsystem.^[66] Eisenkomplexe mit diesen Liganden sollten als Modellsystem in Anlehnung an Komplexe vom Häm-Typ fungieren und ein besseres Verständnis über die Wirkung der Ligandenumgebung auf die Redoxpotentiale $\text{Fe}^{2+}/\text{Fe}^{3+}$ und die Bindung kleinerer Moleküle (z. B. O_2 , CO_2 , NO) liefern.^[66,67] Alle aus dieser Gruppe stammenden Liganden bieten eine quadratisch-planare Koordinationsumgebung und die Möglichkeit der Feinjustierung der Ligandenfeldstärke durch die Variation der verschiedenen Substituenten (Schema 1).



Schema 1 Allgemeine Struktur des Schiff-Base-artigen N₂O₂-Ligandensystems mit einigen Substitutionsmöglichkeiten.

Im Gegensatz zu anderen, ähnlichen Ligandtypen (Salen oder Salophen) liegt das Tautomerengleichgewicht in diesen Liganden nahezu vollständig auf der Seite des Keto-Enamins und nicht auf der Enol-Imin-Seite (Schema 2). Durch Deprotonierung des Liganden wird ein zweifach negativer Ligand erhalten, welcher durch Koordination mit zweiwertigen Metallionen (M²⁺) neutrale Komplexe bildet.^[68]



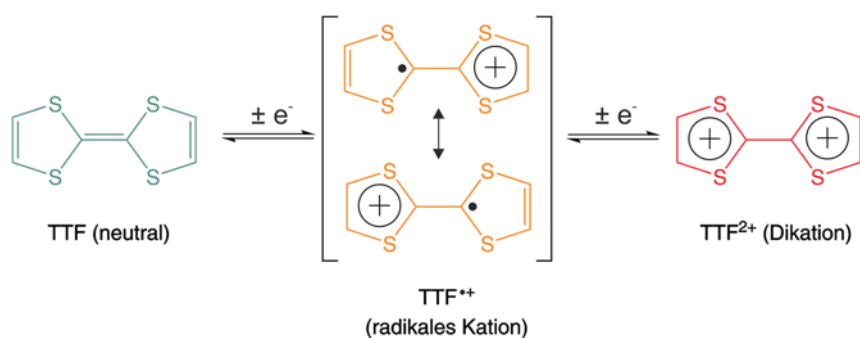
Schema 2 (gestricheltes Rechteck) Struktur der verwandten Salen und Salophen Liganden. Gleichgewicht zwischen (links) der Enol-Imin-Form und (rechts) der Keto-Enamin-Form.

Aber nicht nur die Eisenkomplexe dieser Verbindungsklasse sind interessant. Den Startpunkt der Forschung bildeten Komplexe mit Ni²⁺ als Metallzentrum und bis heute sind außerdem Koordinationsverbindungen mit Fe^{2+/3+}, Cu²⁺, Co²⁺, Zn²⁺ und Mn²⁺ bekannt.^[66,67,69,70] Vor allem Fe²⁺ bevorzugt eine oktaedrische Koordinationsumgebung und ist somit zusätzlich axial koordiniert entweder von einzähnigen Liganden wie z. B. Methanol oder Pyridin, oder zweizähnigen, verbrückenden Liganden, wie 4,4'-Bipyridin oder *trans*-1,2-Bis(4-pyridyl)ethylen. Durch die Modifikation der axialen Liganden kann eine zusätzliche Variation der Ligandenfeldstärke und der Eigenschaften der Koordinationsverbindungen erreicht werden. Durch variable Substitution kann nicht nur die Ligandenfeldstärke beeinflusst werden. Hydroxidgruppen am Phenylring erlauben den Zugang

zu Eisen(II)-Koordinationsverbindungen mit einem ausgeprägten Netzwerk an Wasserstoffbrücken.^[71-73] Die Fähigkeit zur Ausbildung von Wasserstoffbrücken führt jedoch häufig zur Co-Kristallisation von Lösemittel, was wiederum vielfältige Auswirkungen auf das temperaturabhängige magnetische Verhalten haben kann.^[72,73] Das Einbringen von langen Alkylketten (12–22 Kohlenstoffatome) liefert bei der Herstellung von Koordinationspolymeren Verbindungen mit abruptem Spinübergang, welche zusätzlich zur Ausbildung von Filmen geeignet sind.^[74] Andere Derivate dieser Koordinationsverbindungen mit kürzeren Alkylketten zeigen besondere kinetische Effekte, welche auf Packungseffekte, bedingt durch die eingebrachten Alkylketten, zurückzuführen sind.^[75] Die Erweiterung des Phenylrückgrates durch weitere aromatische Bausteine führt zu polyaromatischen Liganden, die entweder durch das Auftreten von Hysteresen oder sogar lumineszente Eigenschaften hervorstechen. So zeigen die Eisenkomplexe des Naphthalenderivats – axial mit 4-Phenylpyridin koordiniert– Spinübergänge mit Hystereseverhalten, welche auf intermolekulare Wechselwirkungen in der Kristallpackung zurückgeführt werden.^[76] Das Phenazinanalogon liefert Koordinationsverbindungen mit interessanten fluoreszenten Eigenschaften. So konnte beispielsweise eine der ersten fluoreszierenden Eisen(II)-Spin-Crossover-Verbindungen synthetisiert werden.^[41] Erst kürzlich gelang mit diesem Derivat die Synthese eines fluoreszierenden Nickelkomplexes, welcher bis heute einzigartig ist. Zusätzlich reagiert die Fluoreszenz dieses Komplexes deutlich empfindlicher auf einen koordinationsbedingten Spinübergang (CISSS = *coordination induced spin state switch*) als dessen Absorption.^[70] Die genannten Beispiele stellen nur einen kleinen Ausschnitt aus der Vielfalt an Koordinationsverbindungen, welche sich vom Jäger System ableiten, dar. Auch die Herstellung von zweikernigen, makrozyklischen, oder schwefelhaltigen Koordinationsverbindungen ist durch geschickte Modifikation möglich.^[77] Dieses Schiff-Base-artige System bietet somit eine optimale Grundlage für die gezielte Synthese von Koordinationsverbindungen, welche neben SCO-Eigenschaften auch interessante Elektronentransfereigenschaften aufweisen.

3.5.2 Die redoxaktive Einheit: Tetrathiafulvalen (TTF)

Im Jahr 1970 berichteten die Arbeitsgruppen um Wudl und Coffen als Erste über die Synthese von Tetrathiafulvalen (TTF) und legten damit den Grundstein für die vielfältige Forschung auf diesem Gebiet.^[78,79] Bei der redoxaktiven TTF-Einheit handelt es sich um ein nichtaromatisches π -Elektronen-System, welches zweimal reversibel oxidiert werden kann (Schema 3). Dabei erfolgt die Oxidation zum radikalischen Kation und zum Dikation nacheinander, reversibel und bei relativ niedrigen Elektrodenpotentialen ($E_{1/2}^1 = 0,37 \text{ V}$, $E_{1/2}^2 = 0,67 \text{ V}$ in DCM gegen gesättigte Kalomelektrode (SCE)).^[80,81]



Schema 3 Ablauf der beiden Ein-Elektronen-Oxidationen des Tetrathiafulvalen (TTF) mit den dazugehörigen gebildeten Spezies.^[82]

Schon 1973 wurde ein weiterer Meilenstein erreicht, indem in einem rein organischen, aus TTF und Tetracyanoquinodimethan (TCNQ) bestehenden Charge-Transfer(CT)-Komplex elektrische Leitfähigkeit beobachtet wurde, die der eines Metalls gleicht.^[83] Ab diesem Zeitpunkt wurde viel Arbeit in die Verbesserung der Donoreigenschaften von TTF-Analogen gesteckt, um die Leitfähigkeiten von entsprechenden Salzen und CT-Komplexen zu erhöhen.^[81] Die Stabilität der beiden oxidierten Spezies lässt sich über eine Aromatisierung im Sinne von Hückel erklären. Nach der ersten Oxidation wird einer der beiden 5-Ringe des TTF zu einem aromatischen 6π -Elektronen-System. Diese Stufe wird außerdem durch die mögliche Bildung einer resonanzstabilisierten Grenzstruktur stabilisiert. Nach der zweiten Oxidation liegt dann ein aromatisches 1,3-Ditholium-Kation vor, bei dem nun auch der zweite Ring ein 6π -Elektronen-System bildet.^[82]

Im neutralen Zustand ist die TTF-Einheit ein starker π -Donor und wird häufig in makrozyklischen Donor-Akzeptor-Komplexen mit π -Elektronenmangel verwendet. Werden durch die einfache Oxidation die π -Donoreigenschaften erheblich abgeschwächt, so kann das TTF²⁺-Kation als elektronenarm bezeichnet werden.^[78,80] Eine Eigenschaft, die TTF als Baustein außerdem interessant für die Verwendung macht, ist die relative einfache Auslesemöglichkeit des Oxidationszustandes anhand von unterschiedlichen optischen Eigenschaften.^[82,84,85] So zeigt beispielsweise das Tetrakismethylthio-Derivat des TTF im

neutralen Zustand bei 350 nm eine schwache Absorption. Durch Oxidation zum Radikalkation treten zwei charakteristische intensive Banden bei 450 nm und 800 nm auf. Das Dikation ist durch eine starke Bande bei 700 nm charakterisiert (Abbildung 10).^[80,84] Bei der Interpretation von UV-Vis-Spektren muss beachtet werden, dass einige TTF-Radikale in der Lage sind, in Lösungen gemischtvalente Dimere auszubilden, welche spektroskopisch durch eine Blauverschiebung der entsprechenden Absorptionsbanden zu identifizieren sind.^[84]

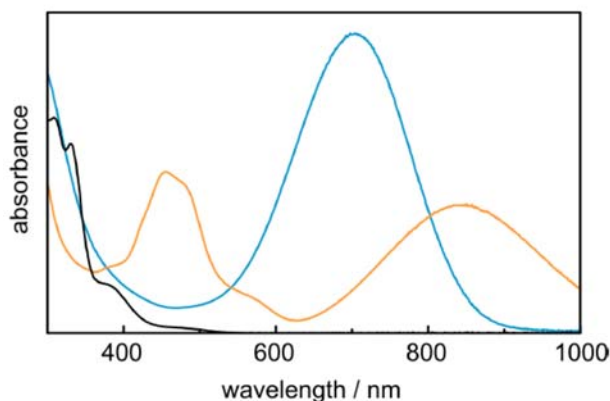
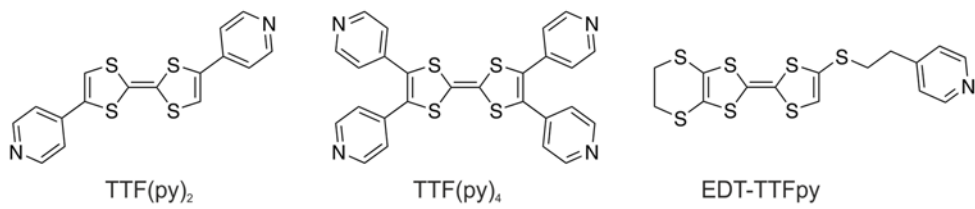


Abbildung 10 UV-Vis-Spektrum des Tetrakismethylthio-Derivats des TTF in der neutralen (schwarz), einfach (orange) und zweifach (blau) oxidierten Form.^[82]

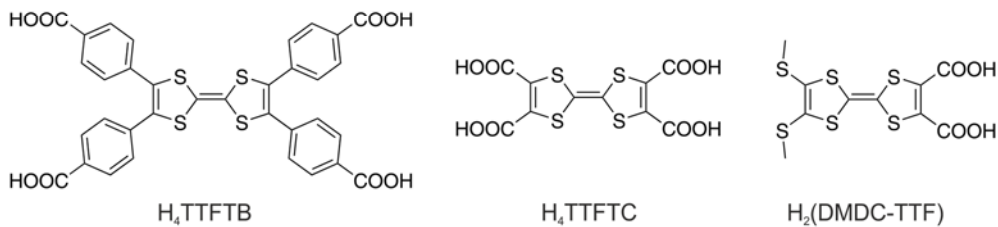
Wie zu Beginn schon erwähnt, hat in den letzten Jahrzehnten das Interesse an multifunktionalen Materialien stark zugenommen, welche beispielsweise elektrisch leitende, oder supraleitende Eigenschaften mit anderen nützlichen Funktionen wie zum Beispiel Lumineszenz, magnetischer oder elektrischer Bistabilität vereinen. Ein Vorteil solcher Materialien ist die große strukturelle Flexibilität, welche aus der Kombination von Metallionen und organischen Liganden mit speziellen Eigenschaften resultiert.^[86] Im Kristallsystem zeigen TTF-Einheiten oftmals kurze S...S-Wechselwirkungen, oder bilden $\pi \cdots \pi$ -Stapel. Damit einhergehend tritt häufig erhöhte elektrische Leitfähigkeit auf.^[87] Es gibt mehrere Möglichkeiten einen TTF-Baustein in ein Koordinationspolymer einzubringen. In den meisten Fällen wird auf TTF-haltige, möglichst starre Brückenliganden mit günstig orientierten Bindungsstellen zurückgegriffen. Abbildung 11 zeigt eine kleine Auswahl an möglichen, verbrückenden Liganden mit verschiedenen Donoratomen. Erst 2017 gelang es der Arbeitsgruppe um Wang mit dem Liganden TTF(py)₄ aus der Gruppe der N-Donor-Liganden eine metallorganische Gerüstverbindung (engl. *metal organic framework* = MOF) der Form $\{[\text{Fe}(\text{dca})_2][\text{TTF}(\text{py})_4]_{0,5} \cdot 0,5\text{CH}_2\text{Cl}\}_n$ herzustellen. Diese Eisen(II)-Gerüstverbindung zeigt neben redoxaktiven Eigenschaften auch einen stufenweisen Spinübergang. Durch eine Dotierung mit Iod kann durch die gezielte Oxidation der TTF-Einheit eine Steigerung in der Leitfähigkeit der Substanz beobachtet werden.^[88] Auch mit dem auf Carboxylat basierendem Liganden H₄TTFTB lassen sich metallorganische Gerüstverbindungen der Form $[\text{M}_2(\text{TTFTB})]$ (M = Mn²⁺, Co²⁺, Zn²⁺, Cd²⁺) herstellen. In diesen Verbindungen konnte durch den Gebrauch unterschiedlich großer Kationen

ein eindeutiger Zusammenhang zwischen der Größe des S...S-Abstandes und der elektrischen Leitfähigkeit beobachtet werden. Eine Vergrößerung des Kations führt oftmals zu einer internen Kontraktion der zentralen TTF-Bindung $((SR)_2C=C(SR)_2)$.^[89] Dementsprechend hat die Verbindung $[Cd_2(TTFTB)]$ mit dem kürzesten S...S-Abstand auch die höchste elektrische Leitfähigkeit $\sigma = 2.86 \cdot 10^{-4}$ S/cm.^[89] Des Weiteren gibt es auch TTF-Derivate, bei denen Schwefelatome als Koordinationspartner fungieren. So konnten beispielsweise verschiedene Kupferkomplexe mit dem TMT-TTF-(Tetrakis(methylthio)tetrathiafulvalen)-Liganden hergestellt werden. Auch hier ist die Länge der S...S-Abstände von großem Interesse. Im Komplex $[(Cu_2(\mu-Br)_2(\mu-TMT-TTF))]_n$ nimmt das zweidimensionale Koordinationspolymer durch kurze S...S-Kontakte eine dreidimensionale Struktur an. Im Gegensatz dazu bilden sich im Bromidderivat $[(Cu_2(\mu-Br)_2(\mu-TMT-TTF))]_n$ helikale Strukturen aus. In beiden Komplexen liegt die TTF-Einheit im nicht-oxidierten Neutralzustand vor und die Verbindungen haben isolierende Eigenschaften. Durch eine Dotierung mit Iod kann auch hier eine gezielte Oxidation der TTF-Einheit herbeigeführt werden, was wiederum zu einer Steigerung der elektrischen Leitfähigkeit bis in den Bereich der Halbleiter führt.^[90] In der Literatur finden sich zahlreiche weitere Beispiele, von deren kompletter Auflistung im Rahmen dieser Einleitung abgesehen wird.^[86]

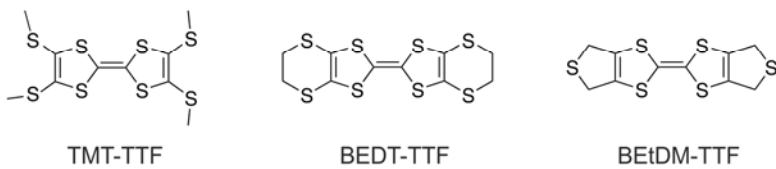
N-Donor-Liganden



Carboxylat-Liganden



S-Donor-Liganden



CN-Donor-Liganden

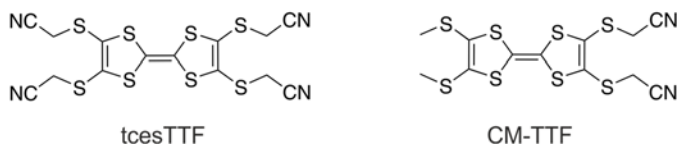


Abbildung 11 Strukturformeln (mit in der Literatur verwendeten Abkürzungen) für eine Auswahl an Brückenliganden mit TTF-Einheit.^[86]

Neben solchen verbrückenden Liganden gibt es eine Vielzahl an Liganden, welche nur an ein Metallzentrum koordinieren. Der Struktur und Form scheinen dabei nahezu keine Grenzen gesetzt zu sein.^[81,91] Generell können alle Liganden nach der Art der Metallbindungsfunktion, die sie aufweisen, eingeteilt werden. Wie schon durch Abbildung 11 angedeutet, lassen sich dadurch verschiedene Gruppen von Liganden bilden. Dazu gehören zum Beispiel Dithiol-, Tetrathiol-, Pyridin-basierte, Phosphin-basierte, Carboxylat-basierte, Schiff-Base-artige Liganden und β -Diketone.^[91] Abbildung 12 zeigt drei Beispiele für Schiff-Base-artige TTF-Liganden und daran angelehnte Derivate, welche für diese Arbeit besonders interessant sind, da sie in der Form ihrer Koordinationstasche stark dem Schiff-Base-artigen System von Jäger ähneln.

Schiff-Base-artige TTF-Liganden und Derivate

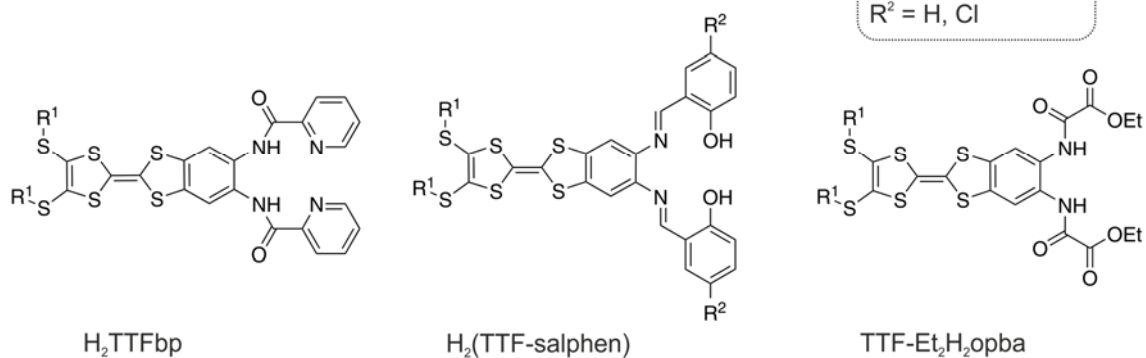


Abbildung 12 Strukturformeln mit in der Literatur verwendeten Abkürzungen für Schiff-Base-artige TTF-basierte Liganden und mit diesen verwandte Derivate.^[86,92–94]

Eine Analyse literaturbekannter Beispiele zeigt neben dem Variationsreichtum der gewählten Liganden auch die Vielfältigkeit der verwendeten Metallionen. So finden sich neben einigen Metallen der ersten und zweiten Übergangsreihe (Mn, Co, Ni, Cu, Zn, Ag) auch mehrere Vertreter der Hauptgruppenmetalle (Rb, Ca, Mg, Ba, Pb).^[86] Des Weiteren wurden auch Koordinationsverbindungen von Lanthanoiden mit TTF-basierten Linkern untersucht.^[94,95] Jedoch ist die Anzahl an Beispielen mit dem für seine magnetische Bistabilität bekanntem Eisen(II) sehr überschaubar.^[88,96] Auch für Eisen(III)-Komplexe finden sich nur wenige Beispiele.^[93,97] Aus diesem Grund soll im Rahmen dieser Arbeit die Synthese und Charakterisierung von Eisen(II)-Koordinationsverbindungen erfolgen, welche die TTF-Einheit als zentrales Strukturmotiv aufweisen. Durch die Kombination dieser redoxaktiven Einheit mit einem System, welches für seine SCO-Eigenschaften bekannt ist, sollen multifunktionale Verbindungen mit einzigartigen Eigenschaften erhalten werden. In diesen kann möglicherweise eine Kommunikation zwischen den beiden Redoxzentren Eisen(II) und TTF stattfinden. Welche Auswirkungen eine derartige elektronische Kommunikation auf die optischen und magnetischen Eigenschaften dieser Koordinationsverbindungen hat, ist auch im Hinblick auf die potenzielle Anwendbarkeit solcher Verbindungen von Interesse. Damit soll diese Arbeit einen Beitrag zum besseren Verständnis von TTF-basierten Eisen(II)-Komplexen mit Spin-Crossover-Eigenschaften leisten.

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4. Synopsis

Die vorliegende Arbeit besteht aus drei Manuskripten, von denen zwei bereits in Fachjournalen veröffentlicht sind (Kapitel 6 und 7). Die dritte Arbeit liegt im einreichbaren Zustand vor und stellt das Kapitel 8 dar. Die einzelnen Beiträge, welche von mir und den Co-Autoren zu den gemeinsamen Publikationen geleistet wurden, sind im Kapitel 5 zusammengefasst. Das hier beschriebene Forschungsvorhaben beruht auf der Idee, Eisen(II)-Spin-Crossover-Komplexe mit redoxaktiven Eigenschaften herzustellen. So sollen multifunktionale Verbindungen synthetisiert und charakterisiert werden, welche nicht nur durch magnetische, sondern auch eine elektrische Bistabilität gekennzeichnet sind. Darauf aufbauend soll außerdem ein tieferes Verständnis hinsichtlich der Kommunikation zwischen der redoxaktiven Einheit und dem Eisen(II)-Metallzentrum erlangt werden. Gerade Tetrathiafulvalene (TTF) sind dahingehend interessante Kandidaten. Zum einen können sie zweimal reversibel oxidiert werden, zum anderen sind sie strukturell sehr vielfältig und können so mit weiteren funktionalen Gruppen und Bausteinen kombiniert werden. Im Rahmen dieser Arbeit wurden zwei verschiedene Strategien zur Herstellung der entsprechenden Koordinationsverbindungen mit den gewünschten Eigenschaften verfolgt. Ein Ansatz besteht in der Kombination des von Jäger *et al.* entwickelten Ligandsystems mit einem TTF-haltigen, zweizähligen Linker, um so Koordinationspolymere zu erhalten, welche die SCO-Eigenschaften des Eisen(II)-Zentrums mit denen der axialen TTF-Einheit kombinieren. Eine andere Möglichkeit bietet die Variation des Schiff-Base-artigen Liganden, indem die Baueinheit TTF äquatorial in dessen Rückgrat integriert wird (Abbildung 13).

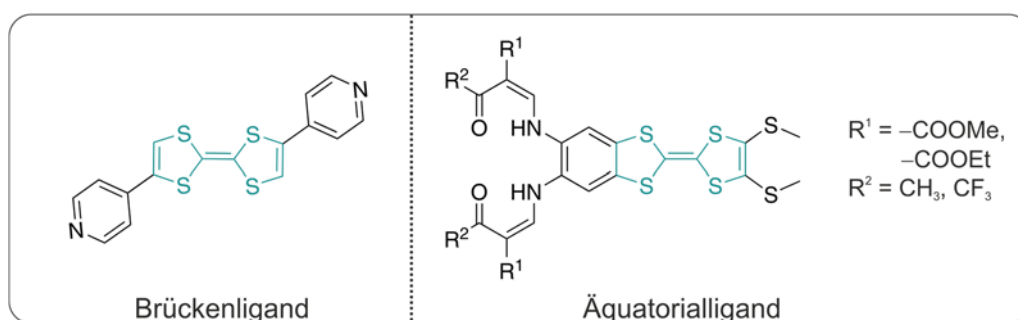
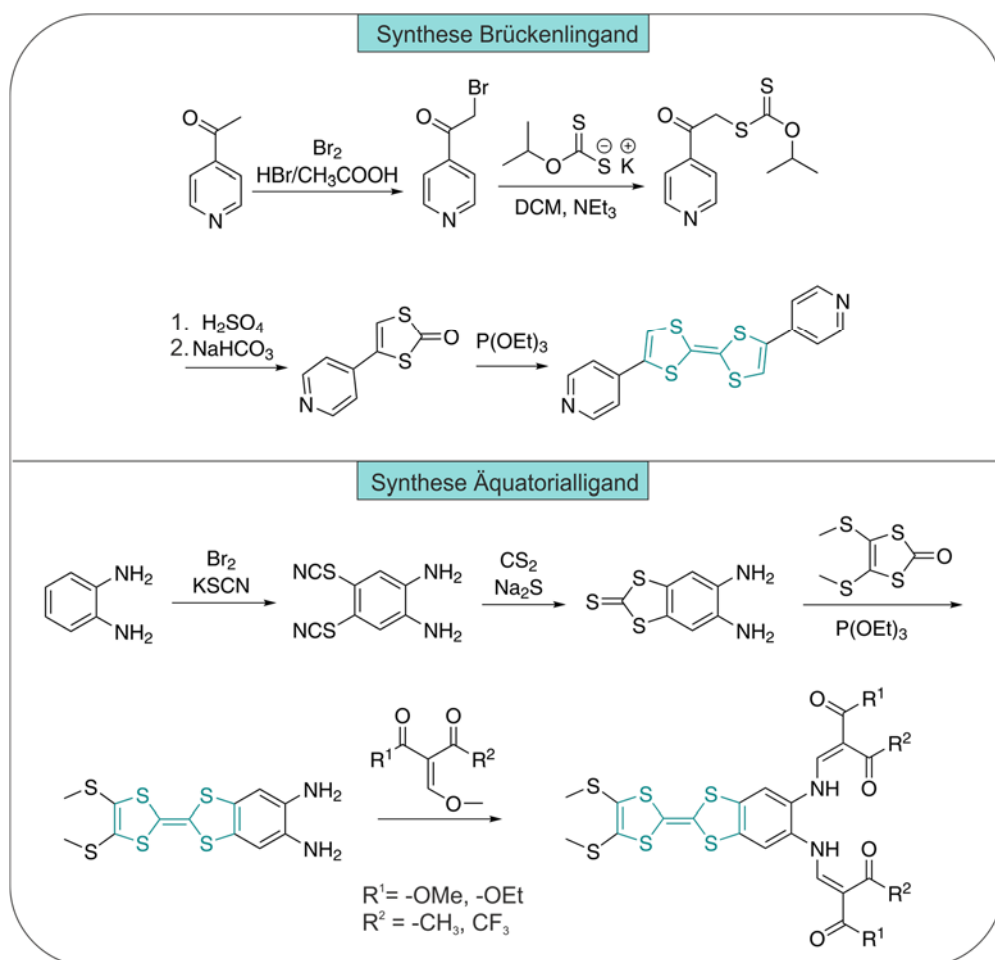


Abbildung 13 Strukturformeln des verwendeten Brücken- und Äquatorialliganden.

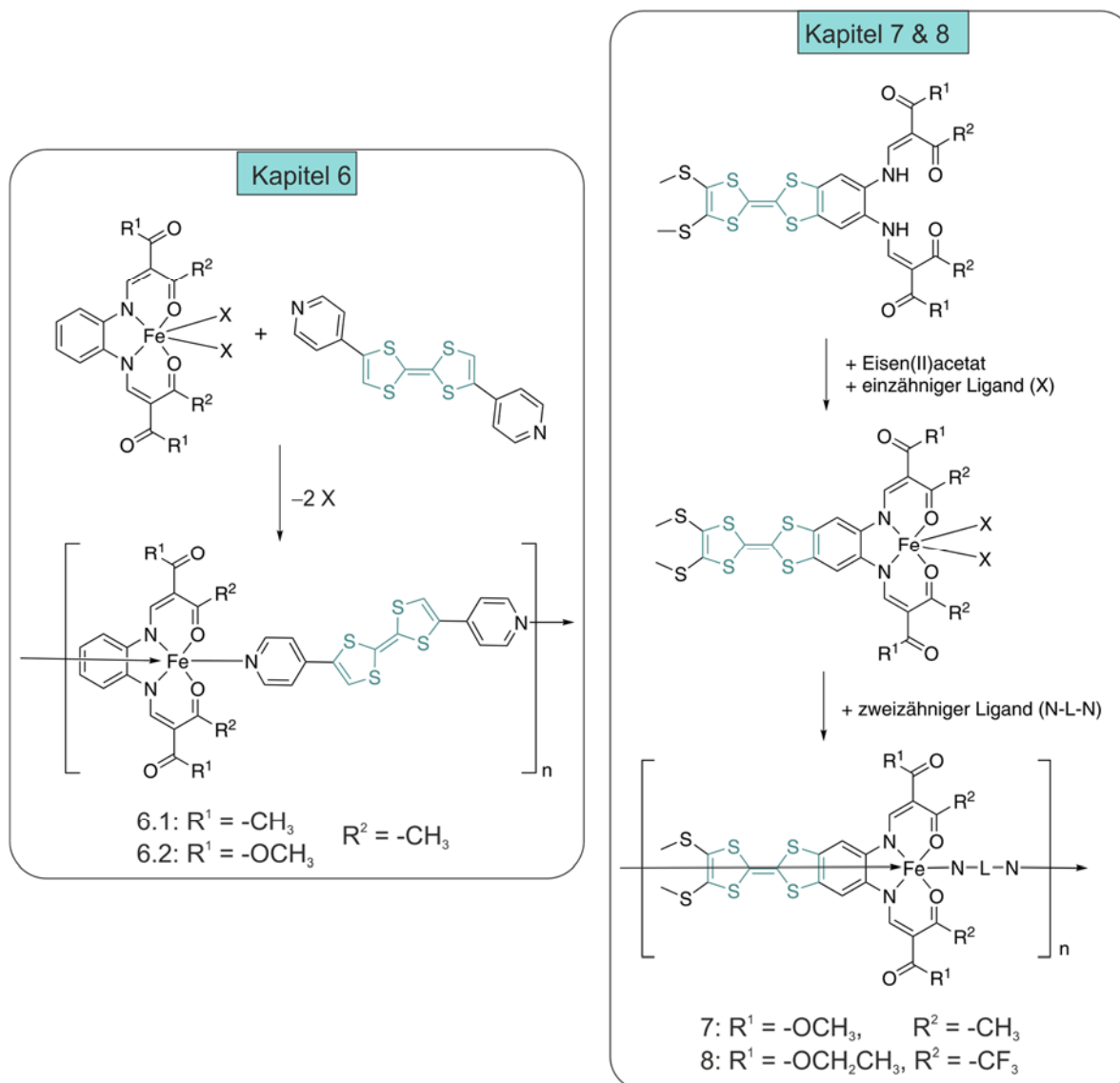
Das aus der Literatur bekannte Bispyridylderivat $\text{TTF}(\text{py})_2$ ($\text{TTF}(\text{py})_2 = 4,4'$ -Di(pyridin-4-yl)-2,2'-bi(1,3-dithiolylden)) ist ein geeigneter zweizähliger Linker, welcher zur Herstellung von Koordinationspolymeren verwendet werden kann. Sowohl der Brückenligand als auch der Äquatorialligand können mit Hilfe einer phosphitvermittelten Kreuzkupplung von 1,3-Dithiol-2-thionen oder 1,3-Dithiol-2-ketonen hergestellt werden. Das im Fall des Äquatorialliganden erhaltene

Diamin kann in einem weiteren Syntheseschritt mit einem entsprechenden Keto-Enol-Ether zum gewünschten Liganden mit unterschiedlichen Substituenten umgesetzt werden. Die generelle Syntheseroute für die zentralen, in dieser Arbeit verwendeten Liganden ist in Schema 4 gegeben.



Schema 4 Allgemeiner Syntheseweg für die Herstellung des in Kapitel 6 verwendeten Brückenliganden und des in Kapitel 7 und 8 verwendeten Äquatorialliganden.

Der Brückenligand $\text{TTF}(\text{py})_2$ kann in einem weiteren Schritt über eine klassische Ligandenaustauschreaktion mit einem durch Methanol koordinierten Komplex des Jäger-Typs umgesetzt werden, um Koordinationspolymere der gewünschten Form zu erhalten. Im Gegensatz dazu werden die verschiedenen Koordinationsverbindungen des TTF-basierten Äquatorialliganden durch Umsetzung des Liganden mit Eisen(II)-acetat in einem geeigneten Lösemittel, unter Zugabe von einfach koordinierenden Liganden (z. B. Pyridin), erhalten. Auch diese Koordinationsverbindungen können in einem weiteren Schritt unter Austausch des einzähnigen Liganden mit verbrückenden, zweizähnigen Liganden unter Bildung von Koordinationspolymeren umgesetzt werden. Schema 5 gibt einen Überblick über die in den Kapiteln 6–8 durchgeführten Reaktionen.



Schema 5 Allgemeiner Syntheseweg für die Herstellung der in Kapitel 6 diskutierten Koordinationspolymere und der in Kapitel 7 und 8 synthetisierten Koordinationsverbindungen.

In Kapitel 6 wird die Synthese von Koordinationspolymeren der Form $\{[\text{FeLx}(\text{TTF}(\text{py})_2)]_n\}$ mit zwei verschiedenen Äquatorialliganden (L1: R¹ = -CH₃, R² = -CH₃; L2: R¹ = -OCH₃, R² = -CH₃) präsentiert. Beide Derivate wurden jeweils aus drei unterschiedlichen Lösemitteln (DMF, MeCN und EtOH) hergestellt. Elementaranalytische Untersuchungen ergaben, dass in allen Fällen Polymere der gewünschten Zusammensetzung erhalten werden konnten. Eine Ausnahme bildet das aus DMF erhaltene $\{[\text{FeL1}(\text{TTF}(\text{py})_2)]_n\}$. Die Werte der Elementaranalyse zeigen eine signifikante Abweichung, die auf die Anwesenheit von etwa 0,7 Molekülen DMF pro monomerer Wiederholeinheit hindeutet. Diese Vermutung wurde durch thermogravimetrische Analysen bestätigt, in denen ein dazu passender Massenverlust identifiziert werden konnte. Es gab für alle anderen Verbindungen keine Hinweise auf co-kristallisiertes Lösemittel. Für die Verbindungen $\{[\text{FeL2}(\text{TTF}(\text{py})_2)]_n\}$ konnten aus dem Lösemittel DMF Kristalle erhalten werden, welche geeignet für die Einkristallstrukturanalyse waren. (siehe

Abbildung 14, links). In dieser Struktur sind, im Gegensatz zu den erhaltenen pulvrigen Materialien, zwei Moleküle DMF pro monomerer Wiederholeinheit co-kristallisiert. Interessanterweise ist außerdem der LS-Zustand des Eisen(II)-Zentrums weitgehend konserviert, da die bei 100 K und die bei 273 K gemessenen Kristallstrukturen nur geringfügige Unterschiede aufweisen. Die Bindungslängen der inneren Koordinationssphäre sind typisch für Eisen(II) im LS-Zustand. Die Bindungslänge der zentralen (SR)₂C=C(SR)₂-Bindung in der TTF-Einheit deutet mit 1,34 Å auf einen nicht oxidierten, neutralen Zustand hin. Offenbar spielen die co-kristallisierten DMF-Moleküle eine entscheidende Rolle, da von ihnen ausgehend fünf Wasserstoffbrückenbindungen zur TTF-Einheit und den koordinierenden Pyridylringen identifiziert werden können. In dieser intermolekularen Wechselwirkung findet sich ein Grund für den konservierten Spinzustand.

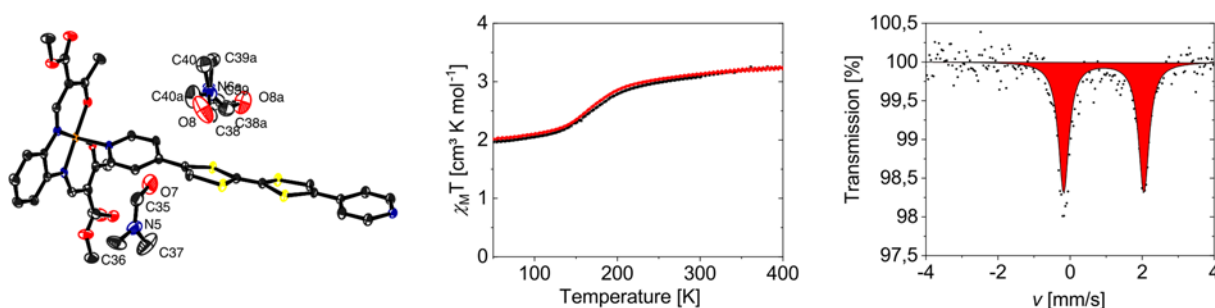


Abbildung 14 (links) ORTEP Zeichnung der asymmetrischen Einheit der Verbindung $\{[\text{FeL}_2(\text{TTF}(\text{py})_2)] \cdot 2(\text{DMF})\}_n$ aus DMF bei 100 K. (mitte) Grafische Darstellung des $\chi_M T$ Produkts in Abhängigkeit von der Temperatur von $\{[\text{FeL}_2(\text{TTF}(\text{py})_2)]_n$ (aus DMF). (rechts) Mößbauer Spektrum der Verbindung $\{[\text{FeL}_2(\text{TTF}(\text{py})_2)]_n$ (aus DMF) bei Raumtemperatur.

Im Gegensatz dazu kann durch Mößbauerspektroskopie und magnetische Suszeptibilitätsmessungen bei Raumtemperatur der HS-Zustand für alle sechs Koordinationspolymere identifiziert werden (siehe Abbildung 14, mitte/rechts exemplarisch für $\{[\text{FeL}_2(\text{TTF}(\text{py})_2)]_n$ in DMF synthetisiert). Beim Kühlen zeigen alle Verbindungen eine Abnahme im $\chi_M T$ -Produkt. Jedoch erreicht keine Substanz den diamagnetischen LS-Zustand im untersuchten Temperaturbereich. Es können kleine Unterschiede zwischen Polymeren mit unterschiedlichen Substituenten am Äquatorialliganden festgestellt werden. Zusätzlich dazu zeigen auch die aus unterschiedlichen Lösemitteln erhaltenen Polymere desselben Äquatorialliganden kleinere Abweichungen in ihrem magnetischen Verhalten. Ein Vergleich der Pulverdiffraktogramme aller Verbindungen zeigt, dass die aus unterschiedlichen Lösemitteln erhaltenen Verbindungen desselben Ligandtyps offenbar trotz gleicher Stöchiometrie Packungsunterschiede aufweisen. Besonders auffällig ist der Vergleich zwischen dem aus der erhaltenen Kristallstruktur errechneten und dem experimentell erhaltenen Pulverdiffraktogramm der aus DMF gewonnenen Verbindung $\{[\text{FeL}_2(\text{TTF}(\text{py})_2)]_n$. Wie zu erwarten, unterscheiden sich die beiden Spektren stark, da die im Pulver vorliegende Substanz bei Raumtemperatur im HS-Zustand vorliegt und

laut Elementaranalyse kein co-kristallisiertes Lösemittel enthält. Demgegenüber enthält der Einkristall zwei Moleküle co-kristallisiertes DMF und liegt im LS-Zustand vor. Begründen lassen sich die Unterschiede durch die verschiedenen Herstellungsmethoden der Substanzen. Mit Hilfe von diffuser Reflexionsspektroskopie an mit BaSO₄ verdünnten Proben kann bestätigt werden, dass grundlegend unabhängig vom verwendeten Lösemittel das gleiche Koordinationspolymer erhalten wird. In allen Fällen dominieren Banden, die der Absorption der TTF-Einheit zugeordnet werden können. Unterschiede sind nur in unverdünnten Proben sichtbar, im Bereich des nahen Infrarotbereichs. Dort können kleinere Unterschiede zwischen den Chargen, die aus DMF und denen, die aus MeCN und EtOH gewonnen wurden, beobachtet werden. Untersuchungen der Substanzen in Lösung zeigen, dass offenbar nicht das Molekül selbst, sondern die Packung im Kristall für das Unvermögen, einen vollständigen SCO zu vollziehen, verantwortlich ist. So zeigen alle Filtrate beim Kühlen mit flüssigem Stickstoff eine charakteristische Farbänderung von rotbraun nach lila, was typisch für einen Spinübergang in Lösung ist.

Um diese Beobachtung besser zu verstehen, wird an einem zweikernigen Modellausschnitt **[(py)L1Fe(TTF(py)₂)FeL1(py)]** aus der Polymerkette eine DFT-basierte Modellierung durchgeführt. Die Ergebnisse der optimierten Strukturen stimmen trotz der Vereinfachungen mit den Parametern der experimentell erhaltenen Kristallstrukturen gut überein. Eine interessante Beobachtung ist die erhebliche Expansion des Fe...Fe-Abstandes entlang der z-Achse beim Übergang vom LS- zum HS-Zustand. Es ist vorstellbar, dass diese Abstandsänderung zu einem enormen Spannungsaufbau innerhalb einer Polymerkette führt und dies einen weiteren Grund für das unvollständige Spinübergangsverhalten der Verbindungen in Kapitel 6 liefert.

Im Rahmen der DFT-basierten Untersuchungen konnten auch SCO-Energien für die Modellsysteme **[(py)L1Fe(TTF(py)₂)FeL1(py)]** und **[FeL1(py)₂]** erhalten werden. Diese deuten stark darauf hin, dass der SCO mithin indifferent gegenüber der axialen Variation bleibt. Eine Betrachtung der Molekülorbitale (Abbildung 15, links) zeigt, dass weder Pyridin, noch TTF(py)₂ als Axialligand etwas an dem metallischen d-Charakter der am höchsten besetzten Molekülorbitale (HOMO) ändert. Dementsprechend sollte die erste Oxidation des Systems metallzentriert sein. Tatsächlich führt eine Koordination von TTF(py)₂ jedoch zu einer Stabilisierung aller Orbitale mit d-Charakter. Das trifft vor allem auf das nichtbindende, redoxaktive β-HOMO (d_{xz}) zu, was bedeutet, dass der zweikernige Modellkomplex gegenüber dem einkernigen **[FeL1(py)₂]** schwerer zu oxidieren ist.

Dies kann durch cyclovoltammetrische Messungen bestätigt werden. Für alle Verbindungen können drei reversible Elektronendurchtrittsreaktionen, bei denen jeweils ein Elektron übertragen wird, identifiziert werden. Diese sind der Oxidation des Eisen(II)-Zentrums und den beiden Oxidationen der TTF-Einheit zum radikalischen Kation und Dikation zuzuordnen (Abbildung 15, rechts).

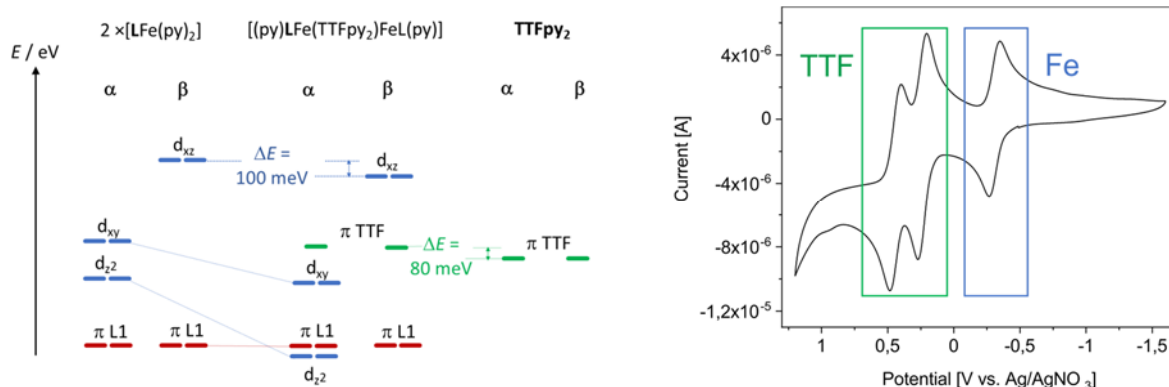


Abbildung 15 (links) Charakter und energetische Abfolge der höchstbesetzten Molekülorbitale für die Modellverbindungen $[(py)L1Fe(TTF(py)_2)FeL1(py)]$, $[FeL1(py)_2]$ und den Brückenliganden $TTF(py)_2$. (rechts) Cyclovoltammogramm für die Verbindung $\{[FeL1(TTF(py)_2)]\}_n$ hergestellt in DMF mit Tetrabutylammoniumhexafluorophosphat (NBu_4PF_6 , 0,1 M) als Leitsalz, vermessen an einer Platin Arbeits- und Gegenelektrode mit einer Vorschubgeschwindigkeit von $50 \text{ mV} \cdot \text{s}^{-1}$ mit einer nichtwässrigen $Ag/AgNO_3$ Referenzelektrode.

In Kapitel 7 wird zunächst die Synthese des neuen Schiff-Base-artigen Äquatorialliganden TTF^LH_2 , dessen π -System um die TTF-Einheit erweitert ist, vorgestellt und die erhaltene Kristallstruktur diskutiert. Sowohl 1H -NMR-Spektroskopie als auch die Daten der Kristallstrukturanalyse zeigen, dass das Molekül vorwiegend in der Keto-Enamin-Form vorliegt. Die zentrale $(SR)_2C=C(SR)_2$ -Bindung zwischen den beiden TTF-Heterozyklen hat mit einer Länge von $1,34 \text{ \AA}$ eindeutig Doppelbindungscharakter. Das Molekül liegt somit in der neutralen, nicht oxidierten Form vor. In der Kristallpackung können kurze $S \cdots S$ -Abstände ($3,7 \text{ \AA}$) zwischen benachbarten, in einer Ebene liegenden TTF-Einheiten identifiziert werden. Zusätzlich treten starke π - π -Interaktionen zwischen den Phenylringen übereinanderliegender Moleküle auf. Dadurch ordnen sich Liganden benachbarter Ebenen um ca. 130° gedreht zueinander an und zeigen wiederum keine $S \cdots S$ -Interaktionen.

Um einen genaueren Einblick in die elektronische Struktur des neuen Liganden zu bekommen, erfolgt eine DFT-Analyse der Grenzorbitale des Liganden TTF^LH_2 und anderer π -verwandter Derivate (Phenazin, Phenyl- und Naphthyl-Abkömmlinge). Der Phenazin- und der TTF-basierte Ligand zeigen starke Ligand basierte Absorptionen und haben dementsprechend auch eine intensive Farbe (rot/ orange). Die schwach gelben Phenyl- und Naphthyl-Derivate zeigen dieses Verhalten nicht, da sie ein weniger ausgedehntes π -System haben. Generell werden die HOMO- und LUMO-Energien durch die Variation des π -Systems kaum verändert. Aber im Fall des TTF (Elektronendonator) und des Phenazin (Elektronenakzeptor) treten in der Grenzorbitallandschaft zusätzliche Donor- bzw. Akzeptor-Niveaus auf, welche für eine Verkleinerung der HOMO-LUMO-Lücke sorgen (siehe Abbildung 16) und somit unter anderem die unterschiedlichen optischen Eigenschaften erklären.

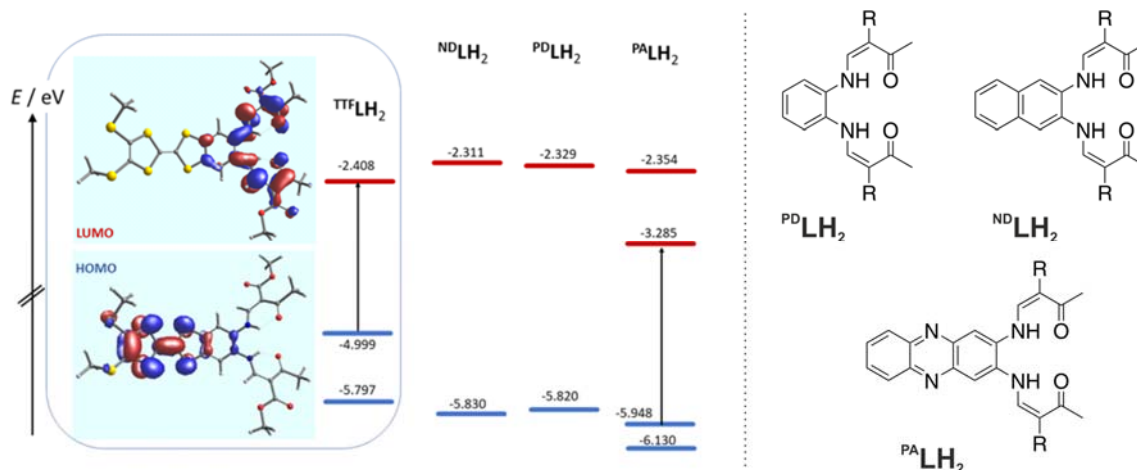


Abbildung 16 (links) Grenzorbitallandschaft des Schiff-Base-artigen TTF-basierten Äquatorialliganden ${}^{\text{TTF}}\text{LH}_2$ und seiner π -verwandten Derivate (ND = Naphthyldiamin, PD = Phenyldiamin, PA = Phenazin). (rechts) Strukturformeln der π -verwandten Derivate von ${}^{\text{TTF}}\text{LH}_2$.

Im weiteren Verlauf des Kapitels erfolgt eine Beschreibung der Synthese zweier verschiedener Eisen(II)-Komplexe mit dem neuen Äquatorialliganden. Es wird zunächst der axial durch Pyridin koordinierte Komplex $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ erhalten, welcher dann in einem zweiten Schritt durch eine Ligandenaustauschreaktion mit *trans*-1,2-Bis(4-pyridyl)ethen (bpee) zum Koordinationspolymer $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})]\}_n$ umgesetzt wird. Elementaranalytische Untersuchungen bestätigen den Erhalt beider Verbindungen, wenn auch im Fall des Koordinationspolymers etwa 0,75 Äquivalente Toluol cokrystallisiert sind, was zu einer Formulierung der Form $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})]\cdot 0,75(\text{tol})\}_n$ (tol = Toluol) führt.

Da in beiden Fällen keine kristallographischen Daten erhalten werden konnten, wurde eine Strukturzuordnung mittels quantenmechanischer Modellierung durchgeführt. Zum Erhalt von Vergleichswerten wird das Phenylderivat als Referenzsystem gewählt. Die mit quantenmechanischen Methoden erhaltenen Werte stimmen gut mit bereits veröffentlichten Kristallstrukturen überein und gewähren somit Aussagekraft für die Daten, welche für das TTF-basierte System erhalten werden.

Demnach bleibt durch eine Koordination des Liganden an ein Eisen(II)-Zentrum die TTF-Einheit unverändert. Auch in diesem Komplex ist mit der charakteristischen Änderung der Bindungslänge der inneren Koordinationsumgebung um ca. 0,2 Å bei einem Übergang von HS zu LS zu rechnen.

Viele Vertreter der Schiff-Base-basierten Ligandfamilie zeigen SCO-Eigenschaften, welche jedoch häufig von Packungseffekten dominiert sind. Aus diesem Grund erfolgt eine Ermittlung der SCO-Energien $\Delta_{\text{SCO}}E$ mittels DFT-Methoden relativ zur bekannten Referenzverbindung ($[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$). Um die Aussagekraft zu erhöhen, werden die Komplexe der zuvor erwähnten Vertreter ${}^{\text{PA}}\text{LH}_2$ und ${}^{\text{ND}}\text{LH}_2$ auch miteinbezogen. Für alle Vertreter können demnach einheitliche SCO-Energien erwartet werden, was die Zuordnung zu einer Ligandfamilie rechtfertigt.

Experimentell wird dies mittels temperaturabhängiger UV-Vis-Messungen bestätigt. Zunächst wird durch vergleichende Messungen von $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ und $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ in Pyridin der Grad an elektronischer Kopplung zwischen TTF-Einheit und Eisen(II)-Zentrum bestimmt. Dabei können zwei vom TTF stammende, charakteristische Banden identifiziert werden, welche in $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ fehlen. Um die Banden genauer zuordnen zu können, wird eine TD-DFT Modellierung der optischen Spektren durchgeführt. Die für die HS-Form erhaltenen Spektren stimmen sehr gut mit den experimentell erhaltenen überein. Dabei wird auch die Ähnlichkeit zwischen $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ und $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ deutlich. Im TTF-Komplex sind die vom TTF stammenden Banden identifizierbar, das darunterliegende Subspektrum ist jedoch eindeutig vergleichbar mit dem von $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$. Im Vergleich zum HS-Spektrum sollte das LS-Spektrum bei $\lambda = 550 \text{ nm}$ charakteristische Banden aufweisen. Da bei RT die HS-Spezies dominierend ist, wurde die Pyridinlösung auf 235 K gekühlt. Tatsächlich kann in den UV-Vis-Spektren eine Intensivierung der Absorption bei 530 nm beobachtet werden, was sich auch in einer Verfärbung der Lösung von Rot nach Lila beim Kühlen widerspiegelt. Somit kann in beiden Fällen der LS-Zustand in Lösung identifiziert werden.

Da sich im Komplex $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ zwei potente RedoxEinheiten befinden, welche Elektronen spenden können, stellt sich die Frage, in welcher Reihenfolge die Oxidationen im Molekül stattfinden. Mittels cyclovoltammetrischer Messungen kann in $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ mit Literaturwerten übereinstimmend der $\text{Fe}^{2+}/\text{Fe}^{3+}$ -Übergang bei einem Elektrodenpotential von $E_{1/2} = -0,395 \text{ V}$ (gegen Ag/AgNO_3) identifiziert werden (siehe Abbildung 17, links).

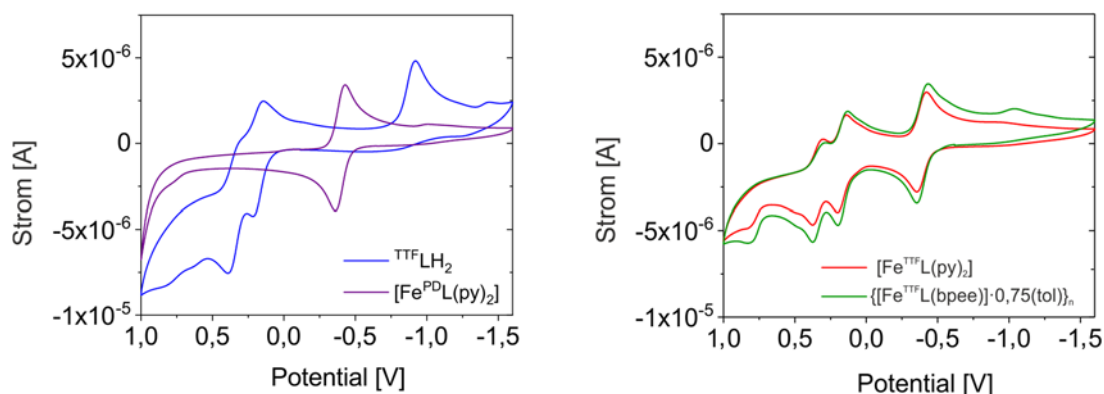


Abbildung 17 (links) Cyclovoltammogramm von TTF-LH_2 und $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ (rechts) Cyclovoltammogramm von $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ und $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot 0,75(\text{tol})\}_n$ in DMF ($c = 1 \text{ mM}$) mit Tetrabutylammoniumhexafluorophosphat (NBu_4PF_6 ; $0,1 \text{ M}$) als Leitsalz an einer Platin Arbeits- und Gegenelektrode mit einer Vorschubgeschwindigkeit von $50 \text{ mV} \cdot \text{s}^{-1}$, mit einer nicht-wässrigen Ag/AgNO_3 Referenzelektrode.

Der reine Ligand TTF-LH_2 zeigt statt der erwarteten zwei reversiblen Oxidationen nur eine vollständig reversibel erfolgende bei $E_{1/2} = 0,181 \text{ V}$ (gegen Ag/AgNO_3), nämlich die der Oxidation der TTF-Einheit zum kationischen Radikal TTF^+ . Aufgrund der ungleichen kathodischen und anodischen Ströme kann im Fall der zweiten Oxidation nur von einem quasireversiblen Prozess ausgegangen werden. Zudem ist

das Halbstufenpotential dieser Oxidation auch weniger anodisch als man von Seiten der Literaturwerte her erwartet hätte. Auch in diesem Fall gewährt die DFT einen Einblick in die Gründe für dieses Verhalten. So scheint ein Teil des zweiten Redoxprozess partiell delokalisiert zu sein und liegt teilweise auf den freien Aminogruppen der Schiff-Base-Einheit. Die Anwesenheit des Metallzentrums im Komplex stellt die Reversibilität der TTF-Oxidationsprozesse wieder her. Beide Komplexe zeigen drei reversible Oxidationen mit jeweils einem Elektron. Ähnlich wie in $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ kann bei $E_{1/2} = -0,386 \text{ V}$ der Übergang von $\text{Fe}^{2+}/\text{Fe}^{3+}$ identifiziert werden. In Übereinstimmung mit Literaturwerten finden die Oxidationsschritte des TTF bei $E_{1/2} = 0,170 \text{ V}$ und $0,340 \text{ V}$ statt (Abbildung 17, rechts). Hierbei scheint die Koordination an das Metallzentrum die Oxidationsprozesse nicht zu beeinflussen. Wie schon die DFT-basierte Analyse der optischen Spektren vermuten ließ, liegen im Fall der neuen Verbindungen vollständig entkoppelte Elektrophore vor.

Um die Zuordnung der Redoxprozesse zu bestätigen, erfolgten spektroelektrochemische Untersuchungen des Liganden und des Komplexes $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$. Überraschenderweise zeigen die Spektren nach der ersten Oxidationswelle des Liganden und nach der ersten Oxidation des Eisenkomplexes Ähnlichkeiten. Besonders interessant sind die im nahen Infrarotbereich herauswachsenden Banden, die in Molekülen mit oxidierten TTF-Einheiten häufig auftreten. Sie lassen vermuten, dass im Fall der ersten Oxidation des Eisenkomplexes, welche laut DFT metallzentriert ist, eine Ladungsverschiebung vom TTF zum entstandenen Eisen(III) stattfindet und somit eine Formulierung der Form $\text{Fe}^{\text{III}}\text{L}^+$ zulässt.

Um nach den Studien in Lösung auch die Festkörpereigenschaften zu untersuchen, wurden magnetische Suszeptibilitätsmessungen an beiden Komplexen durchgeführt. Beide Koordinationsverbindungen zeigen beim Kühlen nahezu vollständiges Spinübergangsverhalten und befinden sich bei Raumtemperatur im paramagnetischen HS-Zustand. Überraschenderweise toleriert $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$, welches eine Übergangstemperatur von $T_{1/2} = 146 \text{ K}$ besitzt, mehrmaliges Aufheizen auf 400 K , ohne drastische Veränderungen im Kurvenverlauf zu zeigen. Andere strukturverwandte Vertreter sind dafür bekannt, beim Heizen axiale Pyridin-Liganden und somit auch ihre SCO-Eigenschaften zu verlieren. Eine thermogravimetrische Analyse (TGA) bestätigt die außergewöhnliche Stabilität des Komplexes bis zu einer Temperatur von 150°C (423 K). Das Koordinationspolymer $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot 0,75(\text{tol})\}_n$ zeigt einen stufenweisen Spinübergang mit einem schwach definierten Plateau bei 154 K . Dieses Verhalten ist jedoch nur im Bereich zwischen 300 und 50 K stabil reproduzierbar. Heizen über 300 K geht mit einem Verlust von co-kristallisiertem Toluol und auch mit einem veränderten Spinübergangsverhalten einher. Dies kann auch durch thermogravimetrische Analyse des Komplexes bestätigt werden. Durch temperaturabhängige Mößbauerspektroskopie sollte herausgefunden werden, ob die Anwesenheit von zwei verschiedenen Eisenzentren den stufenweisen

Übergang hervorruft. Durch die Messung kann der SCO zwar eindeutig nochmals nachvollzogen werden, es ist jedoch nicht möglich eine eindeutige Aussage bezüglich der Anwesenheit zweier verschiedener Eisenplätze im Gitter zu treffen.

Das 8. Kapitel dieser Arbeit befasst sich mit der Modifikation des in Kapitel 7 vorgestellten Liganden durch das Einbringen elektronenziehender CF_3 -Gruppen in der Äquatorialebene. Durch diese Gruppen soll eine Annäherung der Redoxpotentiale des Eisen(II)-Zentrums und der TTF-Einheit erfolgen. Genau wie in Kapitel 7 kann auch mit dem neuen Liganden durch Umsetzung mit Eisen(II)-acetat in Pyridin und Methanol ein axial durch Pyridin koordinierter Eisen(II)-Komplex $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ erhalten werden. Im Rahmen einer Ligandenaustauschreaktion mit dem verbrückenden zweizähnigen Liganden **bpee** kann das Koordinationspolymer $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ erhalten werden. Zusätzlich erfolgt die Synthese und Charakterisierung des mit 4-Dimethylaminopyridin (DMAP) variierten Komplexes $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$. Von dem Komplex $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ konnten Einkristalle für die Kristallstrukturanalyse erhalten werden. Die Kristallstruktur zeigte, dass gemeinsam mit dem Komplexmolekül Methanol und Pyridin co-kristallisieren. Aus dem Bindungsabstand der in der TTF-Einheit liegenden, zentralen $(\text{SR})_2\text{C}=\text{C}(\text{SR})_2$ -Bindung kann abgelesen werden, dass diese im neutralen und nicht-oxidierten Zustand vorliegt. Eine Analyse der Bindungslängen und Winkel in der inneren Koordinationsumgebung offenbart, dass das Eisen(II)-Zentrum bei 180 K im diamagnetischen LS-Zustand vorliegt. Die Kristallpackung zeigt einige Besonderheiten. So liegen die zwei zentralen TTF-Einheiten gestapelt und um 180° zueinander verdreht vor (Abbildung 18, links). Darunter und darüber ordnen sich weitere Komplexmoleküle um 90° gedreht zu diesen an. Diese wechselwirken wiederum mit Molekülen aus benachbarten Elementarzellen, was zu einer knotenartigen Anordnung der TTF-Gruppen bei Betrachtung entlang der a -Achse führt (Abbildung 18, rechts). In den dadurch entstehenden Hohlräumen befindet sich das co-kristallisierte Pyridin.

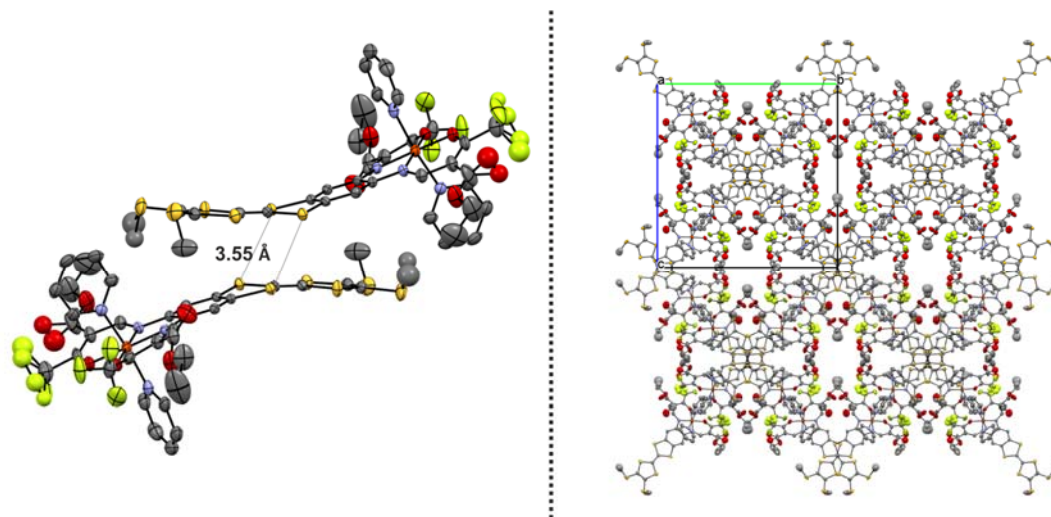


Abbildung 18 (links) Stapelung der zwei zentral gelegenen Komplexmoleküle in der Elementarzelle. (rechts) Molekülpackung des Komplexes $\{[\text{Fe}^{\text{Tf}}\text{L}_{\text{CF}_3}(\text{py})_2] \cdot (\text{MeOH})(\text{py})\}$ mit Blick entlang der a -Achse. Wasserstoffatome und Pyridinmoleküle wurden aus Gründen der Übersichtlichkeit weggelassen.

Magnetische Suszeptibilitätsmessungen zeigten, dass Pulverproben von $[\text{Fe}^{\text{Tf}}\text{L}_{\text{CF}_3}(\text{py})_2]$ im Gegensatz zum untersuchten Einkristall bei Raumtemperatur im HS-Zustand vorliegen. Auch beim Kühlen auf 50 K kann nur ein teilweiser Übergang in den LS-Zustand beobachtet werden; mehr als 80 % der Moleküle bleiben im paramagnetischen HS-Zustand. Im Gegensatz dazu zeigt der nur leicht veränderte, mit DMAP koordinierte Komplex $[\text{Fe}^{\text{Tf}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ einen nahezu vollständigen, graduellen Spinübergang beim Kühlen auf 50 K. Auch das Koordinationspolymer $\{[\text{Fe}^{\text{Tf}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ vollzieht einen fast vollständigen Übergang vom paramagnetischen HS zum diamagnetischen LS-Zustand bei einer Übergangstemperatur von $T_{1/2} = 187$ K. Durch temperaturabhängige ^1H -NMR-Spektroskopie in einer 1:1 Mischung aus Toluol und Pyridin wurde überprüft, ob der Komplex $[\text{Fe}^{\text{Tf}}\text{L}_{\text{CF}_3}(\text{py})_2]$ in Lösung SCO-Eigenschaften zeigt (Abbildung 19). Zum eindeutigen Vergleich wurde zusätzlich ein geeignetes Referenzsystem $[\text{Fe}^{\text{Pd}}\text{L}_{\text{CF}_3}(\text{py})_2]$ auf die gleiche Weise untersucht, welches im Festkörper einen abrupten SCO zeigt.

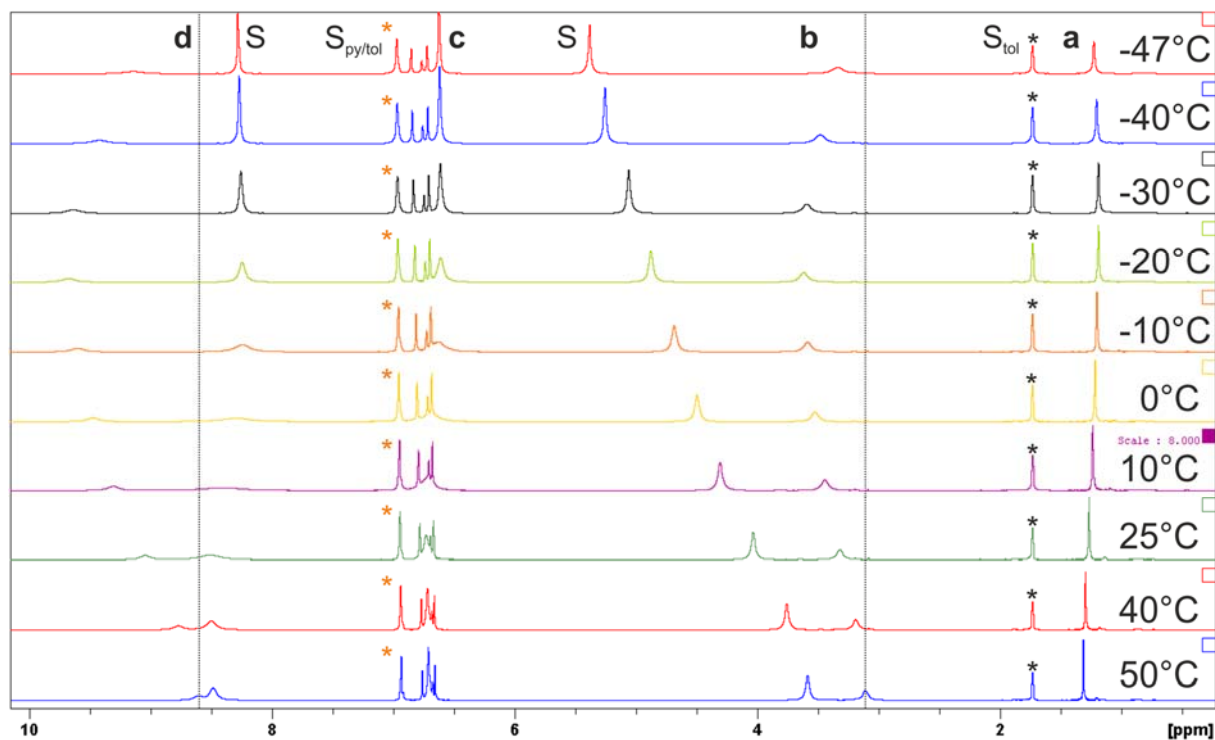


Abbildung 19 Temperaturabhängige $^1\text{H-NMR}$ -Spektren des Komplexes $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ gelöst in einer Mischung aus Pyridin- d^5 und Toluol- d^8 . Die Spektren wurden jeweils bei den angegebenen Temperaturen aufgenommen.

Unter Berücksichtigung der paramagnetischen Verschiebung der dem Eisenzentrum naheliegenden Protonen kann eine eindeutige Zuordnung aller Signale erfolgen. Beim Kühlen der Lösungen fällt auf, dass besonders die dem Eisen(II)-Zentrum naheliegenden Protonen eine erhebliche *Tieffeld*verschiebung bis -20°C erfahren. Ein weiteres Abkühlen der beiden Lösungen führt dann aber zu einer charakteristischen *Hochfeld*verschiebung. Diese gegenläufige Verschiebung und eine damit einhergehende Verbreiterung der Linien der Signale sind Ausdruck einer zunehmenden Menge an diamagnetischem LS-Eisen(II). Dadurch kann gezeigt werden, dass das Packungsverhalten in $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ vermutlich einen vollständigen SCO verhindert.

Zur Untersuchung der Redox Eigenschaften wurden alle Substanzen mittels cyclovoltammetrischer Messungen untersucht. Eine Analyse des Liganden zeigt, dass das Einbringen von elektronenziehenden CF_3 -Gruppen keinen großen Einfluss auf die Potentiallage der TTF-Oxidationsswellen hat. Wie erhofft liegt das Halbstufenpotential der Referenzverbindung $[\text{Fe}^{\text{PD}}\text{L}_{\text{CF}_3}(\text{py})_2]$ nahe dem der Redoxprozesse des TTF-Liganden und zeigt somit im Vergleich zu ähnlichen Verbindungen ohne CF_3 -Gruppen ein um etwa 400 mV anodisch verschobenes Halbstufenpotential. In der Koordinationsverbindung $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ liegen die Potentiale der ersten beiden Elektronenübergänge so nah beieinander, dass sie nicht eindeutig einem konkreten Prozess zugeordnet werden können. Die Ergebnisse des Koordinationspolymers decken sich weitgehend mit diesen Ergebnissen und variieren nur in Intensität und Ausprägtheit der einzelnen Übergänge, was der Polymerstruktur zuzuschreiben ist. Im Gegensatz dazu zeigt das Cyclovoltammogramm der Verbindung $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ ein grundlegend

anderes Redoxverhalten. So können zwar die charakteristischen Peaks für die Oxidation des Eisens und der TTF-Einheit auch in dieser Verbindung wiedergefunden werden, es existieren jedoch noch zwei zusätzliche Übergänge. Das abweichende Verhalten kann im Rahmen dieser Arbeit nicht vollständig aufgeklärt werden.

Da die ersten beiden Redoxprozesse in den cyclovoltammetrischen Untersuchungen stark überlappen, wurde $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ mittels UV-Vis-Spektroelektrochemie untersucht. Hierbei zeigt sich, dass sowohl der Ligand als auch der Komplex beim Adressieren des ersten Redoxpotentials sehr ähnliche Änderungen in der Bandenstruktur zeigen. In Kapitel 7 konnten Übereinstimmungen in UV-Vis-Spektren nach einmaliger Oxidation zwischen dem Liganden und dem Komplex festgestellt werden. Auch das mit CF_3 -Gruppen modifizierte System zeigt ähnliche Übereinstimmungen. Demnach ist der erste elektronische Übergang zwar vorwiegend auf dem Eisenzentrum zentriert, zeigt aber auch deutlichen TTF-Charakter. Eine genaue Zuordnung der einzelnen Redoxereignisse ist bei Raumtemperatur daher nicht möglich.

Da sowohl der Komplex $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ als auch das dazugehörige Referenzsystem $[\text{Fe}^{\text{PD}}\text{L}_{\text{CF}_3}(\text{py})_2]$ SCO-Verhalten in Lösung zeigen, wurden beide Verbindungen bei tiefen Temperaturen (-76°C) cyclovoltammetrisch untersucht. Hierbei wird für $[\text{Fe}^{\text{PD}}\text{L}_{\text{CF}_3}(\text{py})_2]$ eine kathodische Verschiebung des Eisen(II)-Redoxpotentials um 100 mV beobachtet. Dieses Verhalten kann eindeutig einer Zunahme an LS-Spezies während der Kühlung zugeschrieben werden. Genau diese 100 mV große Verschiebung konnte auch im ersten Halbstufenpotential von $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ wiedergefunden werden. Dadurch wird die Annahme bestätigt, dass der erste Übergang bei Raumtemperatur eher der Oxidation des Eisen(II)-Zentrums zuzuschreiben ist. Entgegen der Erwartung zeigt die untersuchte TTF-Verbindung bei tiefen Temperaturen vier statt nur drei vollständig reversible Elektronenübergänge. Ein erneutes Aufwärmen der Lösung stellt das ursprüngliche Spektrum vollständig wieder her. Genauere Betrachtung zeigt, dass die zweite Oxidationswelle der TTF-Einheit in zwei separate aufgeteilt ist. Der Mittelwert aus beiden Halbstufenpotentialen entspricht dabei dem Wert bei Raumtemperatur. Ein Erklärungsansatz für dieses einzigartige Verhalten ist die in der Literatur umfangreich beschriebene Ausbildung von TTF-Dimeren in Lösung. Im Gegensatz zu den in der Literatur beschriebenen Verbindungen zeigt $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ jedoch eine Aufspaltung der zweiten TTF-Oxidation.

5. Einzelne Beiträge zu gemeinsamen Publikationen

Die in dieser Arbeit präsentierten Ergebnisse sind durch Kooperation mit anderen Wissenschaftlern und Wissenschaftlerinnen entstanden und wurden entweder bereits von einem Journal akzeptiert und publiziert, oder sollen in der beschriebenen Form eingereicht werden. In diesem Kapitel sind die Einzelbeiträge aller Co-Autoren und Co-Autorinnen genauer erklärt. Das Sternchen markiert die korrespondierende Co-Autorin.

Kapitel 6

Diese Arbeit wurde publiziert in der Zeitschrift für anorganische und allgemeine Chemie (*Z. Anorg. Allg. Chem.* **2021**,647, 295–305) mit dem Titel:

„Spin States of 1D Iron(II) Coordination Polymers with Redox Active TTF(py)₂ as Bridging Ligand“

Sophie Schönfeld, Gerald Hörner, Frank W. Heinemann, Anja Hofmann, Roland Marschall and Birgit Weber*

Im Rahmen dieser Arbeit habe ich alle Liganden und Koordinationsverbindungen hergestellt und charakterisiert. Des Weiteren habe ich alle magnetischen Suszeptibilitäts- und Mößbauermessungen und alle cyclovoltammetrischen Messungen durchgeführt und ausgewertet. Zusätzlich wurden bis auf den Teil „DFT Structure Modelling“, welcher von Gerald Hörner verfasst wurde, alle Kapitel von mir verfasst. Die Kristallstruktur wurde von Frank W. Heinemann gemessen und gelöst. Die dazugehörige Interpretation der erhaltenen Daten, sowie die Erstellung von Abbildungen wurden von mir vorgenommen. Die Pulverdiffraktogramme wurden durch den technischen Assistenten Florian Puchtler aufgenommen und von mir ausgewertet. Die thermogravimetrischen Analysen wurden durch Marco Schwarzmann durchgeführt und von mir inhaltlich und grafisch aufbereitet. Unter Anleitung von Anja Hofmann habe ich die diffusen Reflexionsspektren aufgenommen und mit ihrer Hilfe ausgewertet. Gerald Hörner hat alle DFT-basierten Modellierungen durchgeführt und alle damit verbundenen Abbildungen erstellt. Er war außerdem an der Korrektur des Manuskripts beteiligt. Birgit Weber begleitete die Arbeit und war in wissenschaftliche Diskussionen und die Korrektur des Manuskripts involviert.

Kapitel 7

Diese Arbeit wurde publiziert in der Fachzeitschrift *Inorganic Chemistry* (*Inorg. Chem.* **2020**, *59*, 8320–8333) mit dem Titel:

„Iron(II) Spin Crossover Complexes Based on a Redox Active Equatorial Schiff-Base-Like Ligand“

Sophie Schönfeld, Katja Dankhoff, Dirk Baabe, Marc-Kevin Zaretzke, Martin Bröring, Konstantin Schötz, Anna Köhler, Gerald Hörner and Birgit Weber*

Alle in dieser Arbeit diskutierten Liganden und Komplexe wurden von mir synthetisiert und charakterisiert. Ich habe alle cyclovoltammetrischen und magnetischen Suszeptibilitätsmessungen, sowie die UV-Vis-Messungen bei Raumtemperatur durchgeführt und interpretiert. Die Kristallstruktur des Liganden wurde von Katja Dankhoff vermessen, gelöst und ausgewertet. Von mir wurden die dazugehörigen Abbildungen erstellt. Gerald Hörner hat alle DFT-basierten Modellierungen und Rechnungen durchgeführt und dazugehörige Abbildungen erstellt. Des Weiteren hat er die zu den Daten gehörenden Textbausteine verfasst und war an der Korrektur des Manuskripts beteiligt. Dirk Baabe hat das temperaturabhängige Mößbauerspektrum des Koordinationspolymer aufgenommen und die Daten entsprechend ausgewertet. Die Interpretation der Daten erfolgte in Absprache mit ihm. Marc-Kevin Zaretzke hat die spektroelektrochemischen Messungen durchgeführt und die Abbildungen erstellt. Die Interpretation und Auswertung wurden von mir vorgenommen. Konstantin Schötz hat die temperaturabhängigen UV-Vis-Spektren aufgenommen und die dazugehörigen Abbildungen erstellt. Die Interpretation und Auswertung der Daten wurden von mir vorgenommen. Birgit Weber begleitete die Arbeit durch wissenschaftliche Diskussionen und die Korrektur des Manuskripts.

Kapitel 8

Diese Arbeit soll in einem Fachjournal eingereicht werden mit dem Titel:

„Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff-Base-Like Equatorial Ligand“

Sophie Schönfeld, Gerald Hörner, Harald Maid, Marc-Kevin Zaretzke, Martin Bröring, Birgit Weber*

Alle Liganden und Koordinationsverbindungen, die in diesem Kapitel diskutiert sind, wurden von mir synthetisiert und charakterisiert. Ich habe die von Gerald Hörner gemessene Kristallstruktur gelöst, die erhaltenen Ergebnisse ausgewertet, interpretiert und alle Abbildungen erstellt. Des Weiteren habe ich alle magnetischen Suszeptibilitätsmessungen durchgeführt und ausgewertet. Zusätzlich habe ich alle cyclovoltammetrischen Messungen durchgeführt und den Aufbau für die cyclovoltammetrische Tieftemperaturmessung entworfen. Harald Maid führte die temperaturabhängigen NMR-Messungen durch, welche von mir unter Erstellung aller Abbildungen ausgewertet und interpretiert wurden. Marc-Kevin Zaretzke führte die spektroelektrochemischen Messungen durch und erstellte die dazugehörigen Abbildungen. Die Interpretation der Daten erfolgte durch mich. Gerald Hörner führte alle DFT-basierten Modellierungen und Rechnungen durch, erstellte entsprechende Abbildungen und formulierte dazugehörige Textbausteine, welche in das von mir formulierte Manuskript eingearbeitet wurden. Birgit Weber begleitete die Arbeit durch wissenschaftliche Diskussionen und die Korrektur des Manuskripts.

6. Spin States of 1D Iron(II) Coordination Polymers with Redox Active TTF(py)₂ as Bridging Ligand

Sophie Schönfeld,^[a] Gerald Hörner,^[a] Frank W. Heinemann,^[b] Anja Hofmann,^[c] Roland Marschall,^[c] Birgit Weber*^[a]

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Dedicated to Prof. Thomas Klapötke on the occasion of his 60th birthday

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Abstract In this manuscript, we report the solvent-dependent synthesis of 1D coordination polymers derived from two planar N₂O₂-coordinate iron(II) complexes FeL1 and FeL2 which incorporate TTF(py)₂ as a bridging bis-monodentate ligand. The obtained 1D polymers have been characterized through elemental analysis, Mössbauer spectroscopy, single crystal structure analysis for 2a · (DMF)₂, magnetic susceptibility measurements, X-ray powder diffraction, cyclic voltammetry, and diffuse reflectance spectroscopy; supplemented by DFT computation. The results revealed additive electronic properties of the sub-units FeL and TTF(py)₂ with only minor mutual influence. Intriguingly however, the solvent-of-synthesis is found to be a steering factor of the magnetic spin crossover properties of the resulting materials, yielding divergent behavior if obtained from DMF, MeCN or EtOH. This becomes strikingly evident for the magnetic properties of the DMF-derived polymer which is found trapped in the low-spin state in the single crystal (2a · (DMF)₂) but shows a gradual spin crossover if all solvent is removed.

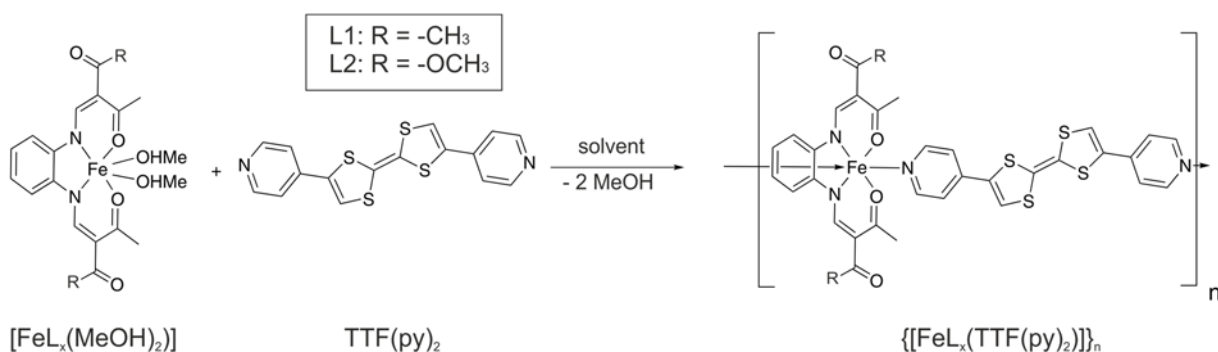
6.1 Introduction

In recent years, the research of molecular magnetic materials has increased in interest due to the application potential in spintronics, memory devices or molecular actuators.^[1,2] Switchable coordination compounds are extensively studied as building blocks of such functional molecular materials, often relying on spin crossover (SCO) between energetically close lying spin states. It is, by now, well established that octahedral complexes with an iron(II) metal center can be switched between the paramagnetic high spin ($S = 2$) and diamagnetic low spin ($S = 0$) state by external stimuli such as temperature, pressure or light, provided suitable ligands were selected.^[3,4,5] To address the multifaceted challenges of today's life, it is desirable to design materials that offer multifunctionality by integrating several properties. The combination of spin crossover with several additional effects realizes molecular sensors and actuators which can be controlled in a targeted manner.^[2,5,6] First important steps towards multifunctional materials have been made through the investigation of additional properties such as magnetic exchange interactions^[7], photoluminescence^[8] or lipid layer like packing through long alkyl chains leading to phase transitions.^[9] More recent studies have focused on the integration of SCO in redox-active materials.^[10,11] Especially for a possible application in data storage devices, electrical conductivity is an interesting feature of the material.^[12] A promising candidate to realize a linkage between conductivity, redox activity and spin crossover is tetrathiafulvalene (TTF) that is known for its excellent electron-donating properties.^[10,13–15] The diverse chemistry of TTF began 1973 by discovering the first organic metal TTF-TCNQ (TCNQ = tetracyanoquinodimethane),^[16] making use of the reversible oxidation of TTF to the stable radical cation (TTF^{•+}) and the dication (TTF²⁺).^[17] While mononuclear complexes incorporating TTF moieties have been known for a while, it was only very recently that incorporation into iron(II)-based coordination polymers with ligand-appended TTF was reported.^[13,14] In both studies the Schiff base-like equatorial ligand system established by Weber and Jäger *et al.* is used, known for its variety of spin transitions.^[3,18,19,20] As a large number of interesting iron(II) coordination polymers with descendants of bidentate pyridine-containing ligands is known,^[3,18,21] the ligand 2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene (TTF(py)₂) reported 2007 by Han *et al.*, is an interesting aspirant for the synthesis of coordination polymers combining SCO behavior and redox active properties.^[22,23] The combination of these two systems in a 1D coordination polymer, has recently been communicated to be successful^[24] and will be further deepened in the course of this work. Here we investigate the impact of solvents used during the synthesis of two different coordination polymers on their magnetic properties.

6.2 Results and Discussion

6.2.1 Synthesis of Coordination Polymers {[FeL_x(TTF(py)₂)]_n}

The redox active ligand TTF(py)₂ was synthesized as described in the literature.^[22,25,26] Coordination polymers were formed in a one-pot reaction from equimolar mixtures of the mononuclear iron(II) complexes [FeL_x(MeOH)₂] and the bridging ligand TTF(py)₂. The iron(II) precursors were obtained as oxygen-sensitive fine crystalline powders as previously described.^[27] L1/L2 denotes the remote substitution pattern with R = -CH₃ and -OCH₃ for L1 and L2, respectively (Scheme 1). The polymer synthesis was carried out in three different solvents, *N,N*-dimethylformamide (DMF), ethanol (EtOH) and acetonitrile (MeCN) at elevated temperature (Table 1). Whereas the iron(II) precursor is well soluble in all three solvents, the bridging ligand is reasonably soluble only in DMF and EtOH, but shows a rather low solubility in MeCN. In the latter medium, the solid product **1b/2b** is therefore obtained in a reprecipitation reaction from solid TTF(py)₂; complete turnover in this case is assigned visually with respect to the markedly different color of reactant and product. In Scheme 1, the general synthesis of the complexes is displayed. The desired products could be obtained from all three solvents used giving satisfying elemental analysis in solvent-free formulations for **1b**, **c** and **2a–c**. Reproduction of the compounds in the respective medium always provided the same elemental analysis results. The synthesis, single crystal X-ray structure and solid-state redox properties of **1c** have been recently communicated,^[24] but will be covered in more detail with regard to the properties in solution herein.



Scheme 1. General synthesis of the iron(II) coordination polymer {[FeL_x(TTF(py)₂)]_n} and used abbreviations.

It was only for **1a** obtained from DMF, where we observed a significant deviation from a solvent-free 1:1 stoichiometry of FeL_{1/2} and TTF(py)₂, pointing to the presence of additional DMF molecules in the fine crystalline product. Thermogravimetric analysis (see Supporting Information, Figure S1) indeed revealed significant thermal weight losses of ca. 6.5 % between 80°C < ϑ < 120°C for **1a**; that corresponds to 0.7 molecules DMF per formula unit. Intriguingly, this behavior is not observed in powder samples of **2a**, which differs from **1a** only in substitution of a side group. Nevertheless, single crystalline material obtained from **2a** likewise proves the presence of uncoordinated DMF molecules

in the solid state (see below). As DMF clearly is the most potent donor among the solvents used,^[28] coordination towards the metal center, if in part, cannot be ruled out for the powder sample.^[28,29]

Table 1. Overview of the solvents used during synthesis and corresponding results of the elemental analysis. The calculated values correspond to the solvent-free formulation.

results elemental analysis (1)		solvent	results elemental analysis (2)	
C₃₄H₂₈FeN₄O₄S₄			C₃₄H₂₈FeN₄O₆S₄	
1a^{a)}	C: 53.86 H: 4.29	DMF	2a	C: 52.16 H: 3.88
	N: 8.69 S: 17.11			N: 7.88 S: 16.19
1b	C: 55.18 H: 3.76	MeCN	2b	C: 52.22 H: 3.71
	N: 7.48 S: 16.96			N: 7.06 S: 16.55
1c	C: 54.70 H: 3.98	EtOH	2c	C: 52.57 H: 3.95
	N: 7.69 S: 17.41			N: 7.17 S: 16.03
C: 55.13 H: 3.81		expected	C: 52.85 H: 3.65	
N: 7.56 S: 17.32			N: 7.25 S: 16.60	

a) Formulation indicated by elemental analysis: C₃₄H₂₈FeN₄O₄S₄ · 0.7 C₃H₇NO

6.2.2 Single Crystal X-ray Structure Analysis

Crystals suitable for X-ray structure analysis of **2a** were obtained directly from the DMF synthesis solution; it is hereinafter referred to as **C2a**. The crystallographic data were obtained at 100 K and 273 K and are summarized in Table S1. The coordination polymer **C2a** crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The ORTEP drawing together with the used atom numbering scheme is displayed in Figure 1. Within each monomeric repeat unit, two molecules of DMF are detected. The oxygen atom O3 of the free ester group is disordered at 100 K. The co-crystallized DMF molecules are also disordered at both temperatures. The C=C bond length of the TTF unit of the axial ligand is a good indicator for the oxidation state of the ligand. With a bond length of 1.34 Å at 100 K and 273 K, the TTF(py)₂ ligand is at both temperatures in the non-oxidized, neutral state.^[30]

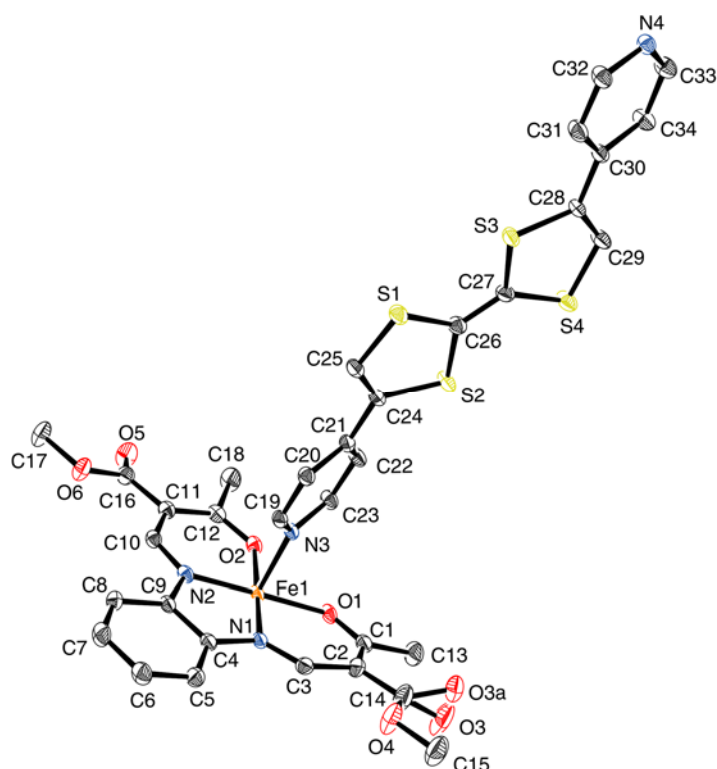


Figure 1. ORTEP drawing of the asymmetric unit of **C2a** (100 K) with the atom numbering scheme used in the text, co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids presented at 50% level. Hydrogen atoms are omitted for clarity (for ORTEP drawing of the asymmetric unit of **C2a** (100 K) with co-crystallized solvent see Figure S2, Supporting Information).

The octahedral N₄O₂ coordination sphere of the iron(II) center consists of the Schiff base-like equatorial ligand and the axially bridging ligand TTF(py)₂ that is bound through the terminal pyridyl groups. Selected bond lengths and angles within the inner coordination sphere are summarized in Table 2. **C2a** is clearly in the LS state at 100 K, considering the average Fe–N bond lengths of 1.90 Å and an O_{eq}–Fe–O_{eq} angle of 87.8°. [3,18] Heating to 273 K only leads to minor changes in bond lengths and angles around the central metal; thus the spin state is conserved. (see Figure S3). Strikingly, the previously published crystals of **1c** conserve the HS state down to 100 K. [24]

The crystal packing of **C2a** at 100 K is displayed in Figure 2a/b; as temperature variation has only minor effects the discussion is focused on the low-temperature data. In the rich literature on solid-state structures of TTF derivatives, stacking of adjacent TTF units is a recurrent motif which often dominates among the non-covalent interactions and serves to define the packing. [14,31,32] For instance, the single crystals of the recently reported iron(II) coordination polymer **1c**, [24] feature extensive stacking of adjacent TTF units. By contrast, TTF does not stack among themselves in **C2a**. Several short intermolecular contacts are observed as summarized in Table S2. A closer look at the packing pattern of **C2a** reveals that the polymer strands are arranged in opposite directions (Figure 2c). Following the Miller direction (*h k l*), one polymer strand is oriented in direction (0 1 –1) and the other in direction (0 –1 1). The Schiff base-like equatorial unit is organized in a slightly staggered fashion while the

phenylene backbones of two polymer strands point in opposite directions. The co-crystallized solvent DMF seems to play a decisive role for the packing. A total of five hydrogen bonds can be identified in which one of the DMF molecules is involved. Predominantly contacts to the axial TTF(py)₂ ligands occur. This involves both the TFF unit (C36-H36B...S4/C25-H25...O7) and the coordinating pyridyl rings (C31-H31... O8/C34-H34...O8A^b).

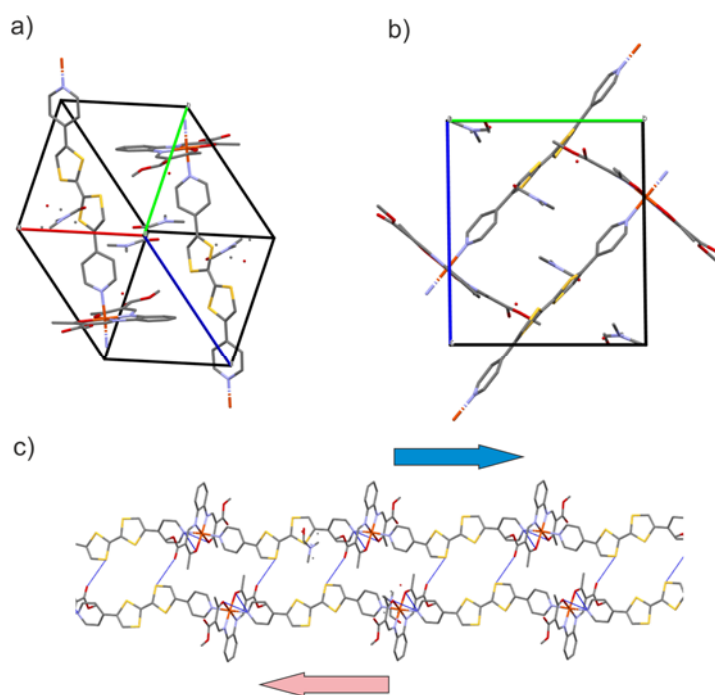


Figure 2. Molecular packing of compound **C2a** in the crystal at 100 K. (a) view along unit cell direction [1 1 1] and (b) view along unit cell direction [1 0 0] (c) Excerpt of two polymer strands with the interchain contacts given as dashed line. Hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) within the inner coordination sphere of the iron(II) complex **C2a** at 100 K and 273 K.

T /K	Fe–N _{eq}	Fe–O _{eq}	Fe–N _{ax}	O _{eq} –Fe–O _{eq}	N _{ax} –Fe–N _{ax}
100	1.900(2)	1.936(18)	1.984(2)	87.79(8)	175.34(9)
	1.905(2)	1.937(18)	1.991(2)		
273	1.903(3)	1.940(2)	1.994(3)	88.29(10)	175.35(11)
	1.905(3)	1.943(2)	2.004(3)		

6.2.3 Mössbauer Spectroscopy

⁵⁷Fe Mössbauer spectra were collected from the polymers **1a–c** and **2a–c** to validate the purity of the samples and to specify the spin state of the powdered samples at room temperature. As a representative example the spectrum of **2c** is displayed in Figure 3, the spectra of the other complexes are given in the Supporting Information, Figure S4. All spectra show one doublet with a quadrupole splitting $\Delta E_Q \approx 2.2 \text{ mm s}^{-1}$ and an isomer shift $\delta \approx 0.9 \text{ mm s}^{-1}$. These values are in the range typical of high-spin iron(II) complexes of this ligand type.^[3] The presence of μ -oxido impurities as a notorious thermodynamic sink in the presence of dioxygen can be safely ruled out through the absence of signals at $\Delta E_Q = 0.80$ and $\delta \approx 0.30 \text{ mm s}^{-1}$ and the rather symmetric doublets. The Mössbauer parameters are summarized in Table 3. The complete HS configuration is at odds with the results from the single-crystal structure of **C2a**, which is clearly low-spin at 273 K. Slightly changed synthesis conditions under which **C2a** was obtained compared to **2a** (see experimental section) and differences in the elemental composition could be an explanation for the different magnetic properties. Unfortunately, it was not possible to record a Mössbauer spectrum of **C2a** or to perform a magnetic susceptibility measurement, because only a few small crystals were obtained.

Table 3. Parameters of the hyperfine interactions of $\{[\text{FeL1}/2(\text{TTF}(\text{py})_2)]\}_n$ obtained from either DMF (a), MeCN (b) or EtOH (c). The spectra were recorded at room temperature.

	Spin State	$\delta / \text{mm s}^{-1}$	$\Delta E_Q / \text{mm s}^{-1}$	$\Gamma/2 / \text{mm s}^{-1}$
1a	HS	0.936(12)	2.19(2)	0.221(19)
1b	HS	0.903(17)	2.15(3)	0.27(3)
1c	HS	0.95(3)	2.22(6)	0.19(4)
2a	HS	0.94(4)	2.23(8)	0.18(3)
2b	HS	0.935(12)	2.20(2)	0.217(18)
2c	HS	0.940(10)	2.21(2)	0.189(16)

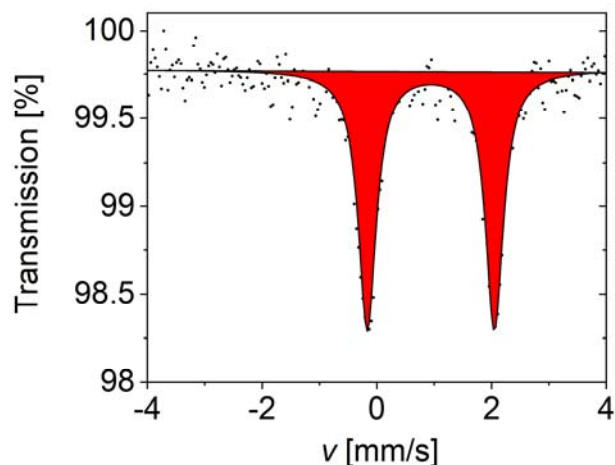


Figure 3. Exemplary Mössbauer spectrum of **2c**. The relative transmission is plotted against the speed of the source.

6.2.4 Magnetic Susceptibility Measurements and X-ray Powder Diffraction

Magnetic susceptibility measurements in the temperature range from 400 K to 50 K allow a more detailed investigation of the magnetic properties of the compounds **1a–c** and **2a–c** to address the different spin states obtained from SC-XRD and Mössbauer spectroscopy. Heating-cooling sequences in the order 300 K → 50 K → 400 K → 50 K → 300 K were used for all samples. The results of these measurements reveal similar, however slightly different behavior, illustrated in Figure 4. In fact, SCO occurs in all powdered materials but remains incomplete.

Table 4. $\chi_M T$ product for $\{[\text{FeL1}/2(\text{TTF}(\text{py})_2)]\}_n$ obtained from either DMF (a), MeCN (b) or EtOH (c). Values are given for different temperatures (300, 50, 400 K) and at 50 K after one heating cycle to 400 K.

	$\chi_M T$ product 300 K	$\chi_M T$ product 50 K	$\chi_M T$ product 400 K	$\chi_M T$ product 50 K after heating
1a	3.15	2.96	3.27	2.48
1b	3.43	2.63	3.57	2.78
1c	3.35	2.39	3.52	2.39
2a	3.07	1.96	3.24	2.01
2b	3.55	1.84	3.85	1.91
2c	3.04	1.67	3.17	1.66

Upon cooling, in all cases a decrease in the $\chi_M T$ values is detectable. Characteristic individual values are listed in Table 4. At room temperature, all compounds exhibit $\chi_M T$ products around $3.15 \pm 0.15 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. The magnetic moment is in a range typical for a high spin iron(II) coordination compound with an octahedral environment.^[3]

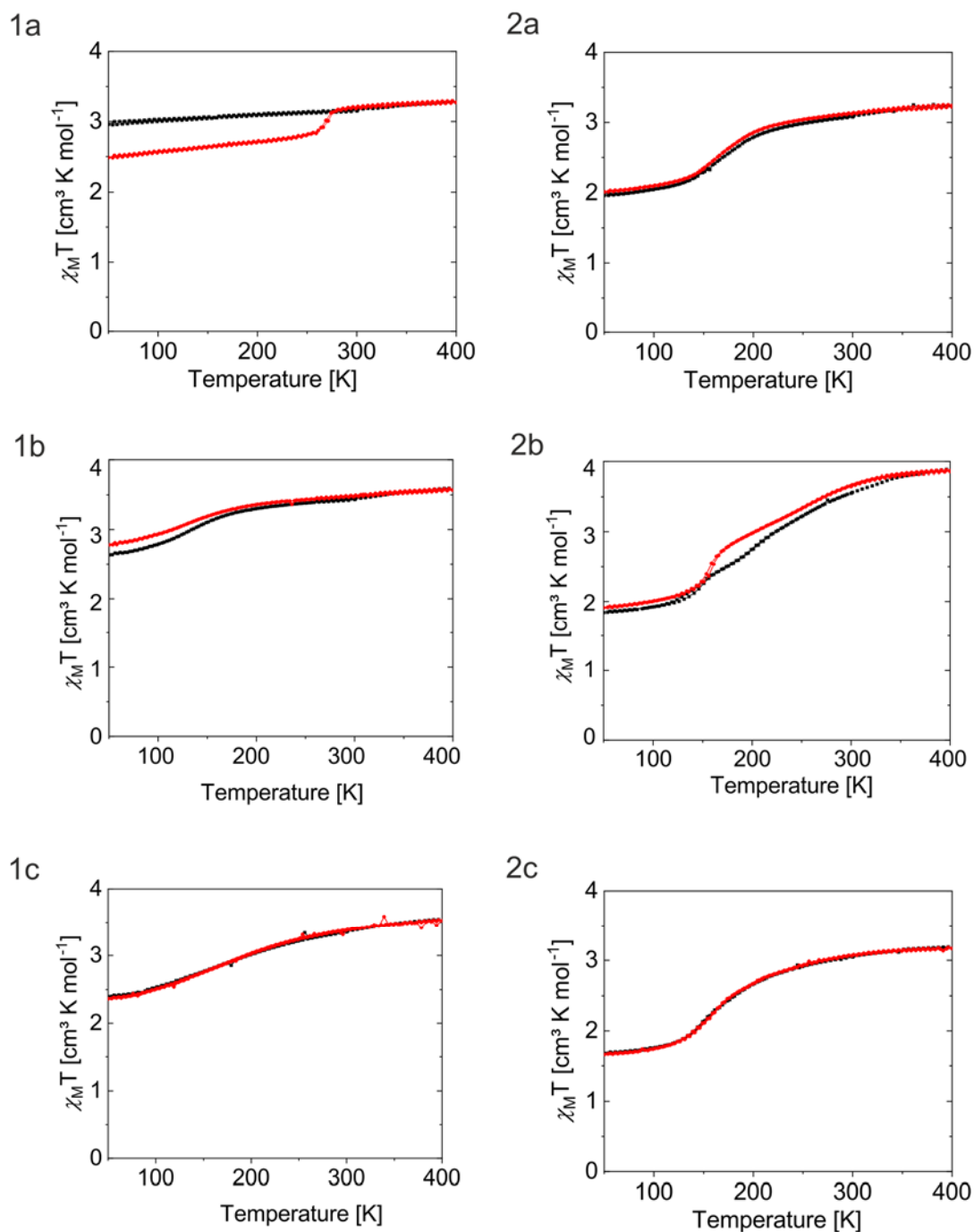


Figure 4. Plot of the $\chi_M T$ product vs. Temperature in the range 400–50 K with a cooling rate of $5 \text{ K} \cdot \text{min}^{-1}$. Black curve: cooling and heating between 300 K and 50 K, and red curve: cooling and heating between 400 K and 50 K.

The small differences in the SCO behavior between **2b** ($\chi_{HS}(50\text{ K}) = 0.50$ (red) 0.48 (black)) and the relatively similar **2c** ($\chi_{HS}(50\text{ K}) = 0.53$) on the one hand and **2a** ($\chi_{HS}(50\text{ K}) = 0.61$) on the other is reflected by small differences in crystal packing as becomes evident from the powder XRD patterns given in Figure 5. Firstly, co-crystallization of free TTF(py)₂ can be safely ruled out, based on the absence of prominent reflections of the axial ligand (e.g. at 8.6°). Secondly the reflexes recorded of **2b** and **2c** are highly similar, pointing to a conserved packing of the polymers if derived from MeCN and EtOH. By contrast the pattern of **2a** differs significantly due to the presence of DMF in the lattice. It is furthermore noted that the PXRD pattern of powdered **2a** likewise differs significantly from the implications of the crystal structure of **C2a** (black and red curves in Figure 5). The PXRD patterns of **1a–c** are given in Figure S5. In line with the results of the magnetic measurements, the differences in these measurements are reflected by differences in the PXRD patterns. It is important to note that the axial ligand used can be in the cis as well as in the trans configuration. Accordingly, there is the possibility that both isomers are involved in polymer formation in different proportions. The preference for one of the two isomers under the given reaction conditions, such as the boiling point of the solvent used, could also lead to small differences in magnetic behavior.

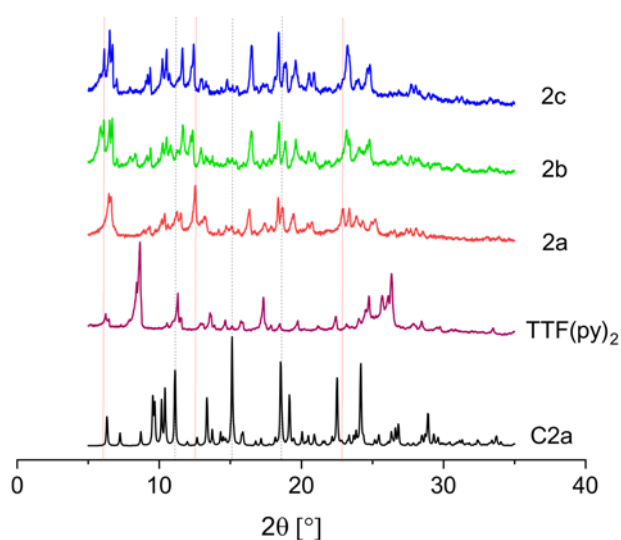


Figure 5. PXRD pattern of the coordination polymers, **2a–c** and the axial ligand TTF(py)₂ in the angular range of $2\theta = 5\text{--}30^\circ$ at room temperature; for comparison a computed PXRD pattern derived from single-crystalline **C2a** at 100 K is shown.

6.2.5 UV-Vis Diffuse Reflectance Spectra

The optical properties of the samples were addressed with UV-Vis diffuse reflectance spectroscopy in order to resolve possible differences among the different batches. The red-brown color of the powder samples along series 2 translates into reflectivity spectra analogous to the one shown for **2a** in Figure 6, blue line. In a broad spectral range from 1200–600 nm the reflectivity continuously decreases, indicating significant light absorption across a wide range of the visible spectrum. Further analysis of the spectrum was conducted using Kubelka-Munk theory (Equation 1)^[33] to process the reflectivity data into the $F(R)$ parameter which is proportional to the optical absorption coefficient (Equation 1; $R = k/s$; k and s : absorption and scattering coefficient; red in Figure 6). Significant bands at 675, 539 and 492 nm which dominate the visible color impression can be identified in all materials (for **2b/c** see SI, Figure S6).

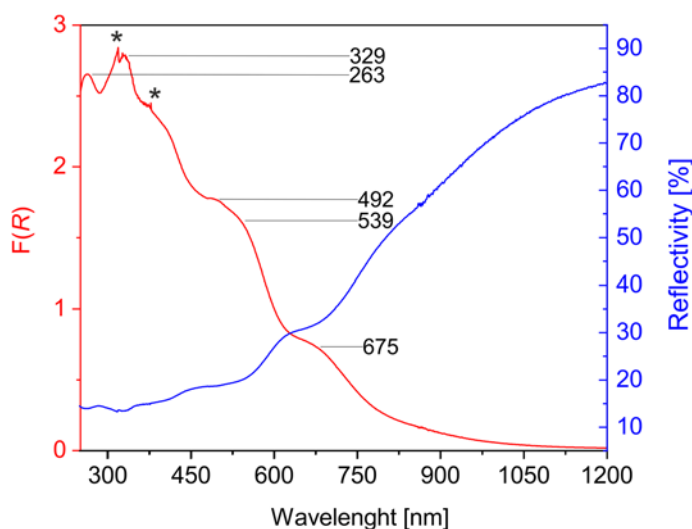


Figure 6. Reflectivity of **2a** which was optically diluted 1:4 with BaSO₄ (blue line). Kubelka-Munk converted diffuse reflectance spectrum according to equation (1) (red line). Asterisks denote small discontinuities due to lamp and filter change of the spectrometer.

The absorption in this area is mainly attributed to the TTF contained in the complex matrix. Since this is identical for all materials regardless of the solvent used, it can be assumed that essentially the same coordination polymer is formed in all three cases.

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

However, the small differences between the individual materials become clear again when the diffuse reflection spectrum of the near-infrared range of the undiluted samples is considered (Figure S7). The band structure here is basically similar in all three samples examined. However, an additional band at

1861 nm can be identified in **2a**, which cannot be found in **2b/c**. Thus, once again the presence of DMF in the powder of **2a** is a differentiating factor.

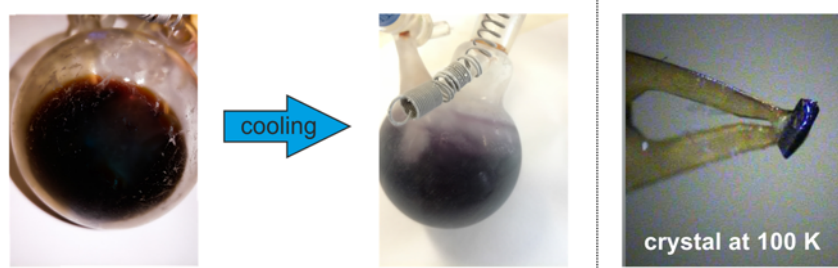


Figure 7. Color change of the filtrate of **2c** upon cooling with liquid nitrogen. As a comparison, the single crystal **C2a** at 100 K is shown.

Unfortunately, it was not possible for us to trace the color changes using UV-Vis spectroscopy by cooling a solution as the axial ligand dissociates at the required concentrations. For this reason, we decided to use DFT-based structural modelling to better understand the behavior of the complex. Finally, we note that the failure of **1** and **2** to undergo complete SCO in the powder is not due to a molecule-borne limitation. As is shown exemplarily for **2c**, the systems are generally able to perform a complete spin crossover in solution. Upon cooling to liquid nitrogen temperature, all filtrates from the polymer syntheses show characteristic color changes from red brown to intense purple as shown in Figure 7. The room temperature color and the impression at low temperature are consistent with SCO as they closely match results reported and analyzed recently for a related system.^[13] At 100 K the single crystal **C2a** has the same color as the cooled filtrate as can be seen in Figure 7.

6.2.6 DFT Structure Modelling

To analyze the steric requirements of SCO along a polymer strand in more detail, we performed a DFT-inquiry in the molecular structures and spin-state dependent energies of truncated bimolecular model compounds. To this end, we introduce a binuclear iron(II) complex $[(\text{py})\text{L1Fe}(\text{TTF}(\text{py})_2)\text{FeL1}(\text{py})]$, which conserves the experimental setting with respect to equatorial ligand L1 and bridging ligand TTF(py)₂ (L1 was used herein instead of L2 to avoid complications due to notorious rotation of the flexible –C(O)OMe group). At the terminal axial positions of Fe(a) and Fe(b) we placed pyridine molecules as a close mimic of the ligand properties of TTF(py)₂. This approach complements a recent theoretical study wherein we approximated the electronic properties of polymer **1** as the mononuclear complex $[\text{FeL1}(\text{pyTTF})_2]$, carrying two axially coordinated TTF units.^[24] The metrics were optimized with the BP86 functional and large TZVP basis sets. This setting has been found suitable to match the metrics of iron(II) complexes in a number of previous cases.^[13] The optimized structure of $[(\text{py})\text{L1Fe}(\text{TTF}(\text{py})_2)\text{FeL1}(\text{py})]$ in the all-low spin electron configuration corresponding to singlet multiplicity with $S = 0$ closely matches the experimental metrics of **C2a** (Table 5). Similarly, the all-high spin structure of $[(\text{py})\text{L1Fe}(\text{TTF}(\text{py})_2)\text{FeL1}(\text{py})]$ fully matches the implications of **C1c** (Figure 8; structure plot of $S = 2$ is given in the SI, Figure S8). Importantly, the intra-chain distance Fe...Fe of 18.7 Å in the crystal is very well matched by the binuclear model if treated in the all-low spin state $S = 0$.

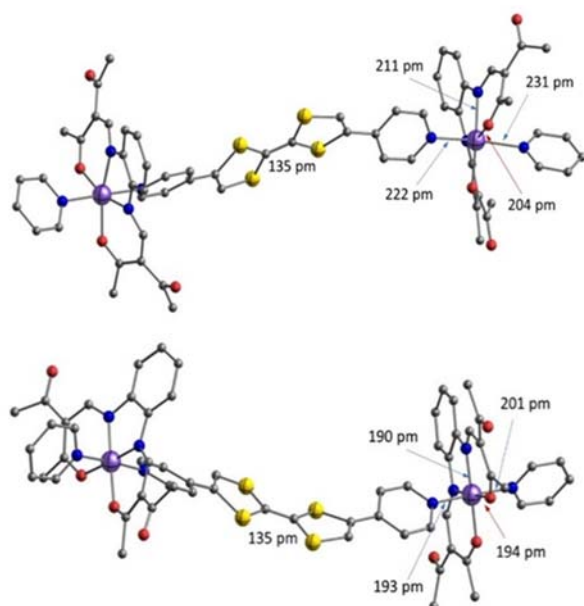


Figure 8. DFT-optimized structure of the binuclear model $[(\text{py})\text{L1Fe}(\text{TTF}(\text{py})_2)\text{FeL1}(\text{py})]$ in the all-high spin state, $S = 8/2$ (top) and in the all-low spin state, $S = 0$ (bottom).

Table 5. Metrics of the inner coordination sphere in the crystal structure of **[FeL1(TTF(py)₂)_n]** and DFT-optimized metrics in the binuclear model complex **[(py)L1Fe(TTF(py)₂)FeL1(py)]** in three global spin states $S = 0, 2$ and 4 ^{a), c)}.

	Exp. C2a (100K/273K)	Exp. C1c ^{b)} (100 K)	Singlet		Quintet		Nonet ^{b)}	
			Fe(a)	Fe(b)	Fe(a)	Fe(b)	Fe(a)	Fe(b)
Fe-N _{eq}	1.90/ 1.91	2.127	1.90	1.90	1.91	2.11	2.11(1)	2.10(5)
Fe-O _{eq}	1.94/ 1.94	2.051	1.95	1.95	1.95	2.04	2.04	2.03
Fe-N _{ax}	1.99/ 2.00	2.279	2.00	2.00(1)	2.00	2.25(5)	2.26(5)	2.27(4)
Fe...Fe	18.7/ 18.7	–	18.5		18.9		19.1	
>C=C<	1.34/ 1.34	1.345(3)	1.35		1.35		1.35	
<i>cis</i> O _{eq} -Fe-O _{eq}	87.8/ 88.3	112.7/115.1	90.4	89.3	90.0	114.8	116.0	112.3
<i>trans</i> N _{ax} -Fe-N _{ax}	175.3/ 175.3	–	176.9	176.5	174.5	170.0	170.3	177.0
<i>trans</i> N _{eq} -Fe-O _{eq}	178.5/ 178.4 177.9/ 178.0	–	177.3(2)	178.0(1)	177.5	161.2(1)	160.9(4)	162.8(1)

a) optimized with **BP86-D3/TZVP/COSMO**; b) from solid state structure of **[FeL2(TTFpy₂)_n]** in **Ref.**^[24]

c) A rotation by 90° of neighbored [FeN₂O₂]-units corresponds to the situation in **C1c**; it is noted that the energy difference between rotated and eclipsed constellations is not significant

Selected metrical data obtained for all spin states are compared with experimental data in Table 5. It is noted that an increase of overall spin in the models from $S = 0$ to $S = 2$ indicates localized structural response; that is, Fe(a) and Fe(b) become dissymmetric with local configurations of $S = 0$ and $S = 2$, respectively. The finding of electronic asymmetry is significant and reliable and rules out the possible formation of intermediate-spin centers with $S = 1$ both on Fe(a) and Fe(b); the inherently asymmetric electronic structure of **[(py)L1Fe(TTF(py)₂)FeL1(py)]** therefore overrides the well-known tendency of the BP86 functional towards symmetric formulations.^[34] Structural changes due to SCO largely reflect isotropic breathing of the iron-donor bonds by up to $\Delta d \approx 0.2$ Å as is typically observed for iron(II) complexes in general^[3,6,10] and specifically for the Schiff base-like N₄O₂ environment.^[3,18,20] Breathing along the intra-chain z-axis leads to expansion/contraction of the Fe...Fe distance in the binuclear model by ≈ 0.6 Å, similar values prevail when **C1c** (HS) and **C2a** (LS) are compared. That means that complete SCO of all iron(II) centers along a given chain in the crystal must lead to massive strain build-up.

6.2.7 Electronic Structure: Theory and Experiment

The conserved SCO energy computed in this work for **[FeL1(py)₂]** and **[(py)L1Fe(TTF(py)₂)FeL1(py)]** suggests the presence of decoupled electrochromes, TTF and iron(II). In fact, recent work had shown that a TTF unit remains electronically unaffected by an iron(II) center if incorporated in the equatorial ligand L₁,^[14] conserved electrochemical potentials had reflected an additive frontier orbital pattern of undisturbed metal-borne and TTF-borne contributions. Intriguingly, closer inspection of the binuclear model compound **[(py)L1Fe(TTF(py)₂)FeL1(py)]** reveals that axially appended TTF units significantly affect the orbital energies. Figure 9 highlights the highest occupied MOs of the py-terminated mononuclear complex (left), of the bridging TTF ligand (right) and of the binuclear complex with an embedded TTF bridge. Referring to the experimental findings for powdered samples the complexes are in $S = 2$ (mononuclear) and $S = 4$ states (binuclear), respectively (a corresponding diagram for the $S = 0$ case is given in the SI, Figure S9). Color in the plot denotes the predominant character of the MO. Firstly, the metal- d -character of the highest occupied MO remains unaffected by the presence of either axial pyridine or TTF(py)₂. (Electro-)chemical oxidation therefore must be expected to be metal borne.

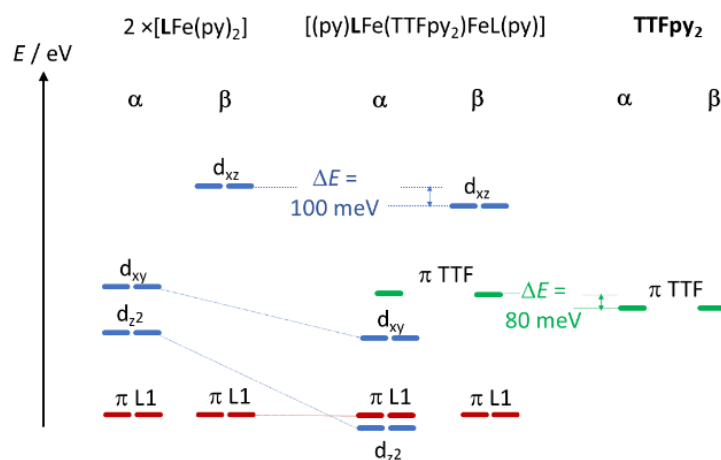


Figure 9. Character and energetic order of the highest occupied MOs; blue: metal-centered; red: centered on the equatorial ligand L₁; green: TTF centered.

Interestingly however, the coordination of TTF(py)₂ acts as to significantly stabilize all orbitals with significant d -character by up to 400 meV; in particular stabilization of the largely non-bonding redox-active β -HOMO (d_{xz}) amounts to approximately 100 meV. In zero order (neglecting charge redistribution and/or SCO after oxidation), this shift suggests oxidation of the binuclear complex (and of the coordination polymer **1**) to be significantly disfavored with respect to mononuclear **[L1Fe(py)₂]**. Indeed cyclovoltammetric studies, given in Figure 10, reveal an anodic shift of the iron(II/III) couple by

approximately 100 mV if axially decorated with TTF(py)₂ across the entire series **1** and **2**; the iron(II/III) couple in [L₂Fe(py)₂] resides at $E_{1/2} = -0.395$ V^[13], whereas the values of **1** and **2** crowd at $E_{1/2} \approx -0.28$ V.

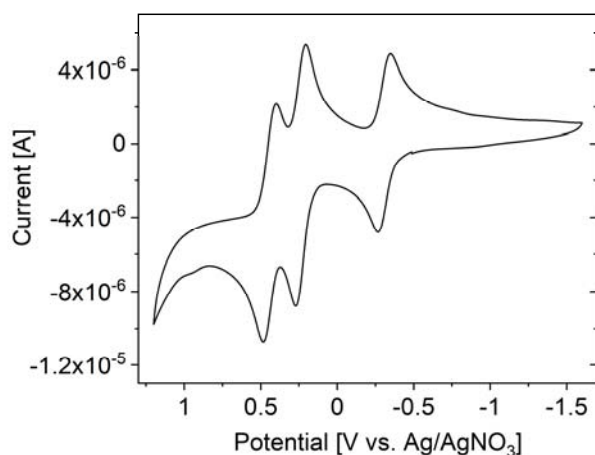


Figure 10. Cyclic voltammogram of **1a** in DMF with tetrabutylammonium hexafluorophosphate (NBu₄PF₆) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at 50 mV s⁻¹ with a nonaqueous Ag/AgNO₃ reference electrode.

Electrochemical characteristics of all complexes were investigated by cyclic voltammetry (CV) at room temperature with dimethyl formamide (DMF) as solvent. For all measurements, a non-aqueous Ag/AgNO₃ ($c_{\text{Ag}^+} = 10$ mM) reference electrode was used. Figure 10 exemplarily shows the curve recorded for **2a**. The cyclic voltammograms of all the other compounds investigated, look similar and are given in the SI, Figure S10. Since the concentration of the examined solution in cyclovoltammetric measurements is many times higher than in UV-Vis measurements, a dissociation of the axial ligand is unlikely, and an intact polymer can be expected. Each complex exhibits three one-electron redox couples. Half wave potentials and peak-to-peak separations are listed in Table 6.

Table 6. Half-wave potentials and peak-to-peak separations for complex **1a–c**, **2a–c** and TTF(py)₂. The peak-to-peak separation in the table refers to a scan rate of 50 mV·s⁻¹.

	$E_{1/2}^1$ /mV	$E_{1/2}^2$ /mV	$E_{1/2}^3$ /mV	ΔE_1 /mV	ΔE_2 /mV	ΔE_3 /mV
1a	-308	238	441	81	66	84
1b	-282	267	469	99	63	90
1c	-284	265	463	84	59	79
2a	-302	238	437	66	55	67
2b	-265	267	468	96	59	73
2c	-294	266	464	96	60	82
TTF(py) ₂	-	138	339	-	63	75
[FeL ₂ (MeOH) ₂]	-388	-	-	68	-	-

The first half-wave potential of the six different complexes $E_{1/2}^1$ can be assigned to the redox process $\text{Fe}^{2+}/\text{Fe}^{3+}$. For all compounds these values are in agreement with investigations of similar systems by Jäger *et al.*^[35] Both more anodic redox couples correspond to the oxidation of the TTF(py)₂ ligand to the radical-cation (TTF(py)₂^{•+}) $E_{1/2}^2$ and in a second step to the dication (TTF(py)₂²⁺) $E_{1/2}^3$ (Table 6). The potentials of the first oxidation of coordinate TTF(py)₂ match the free ligand for all iron(II) coordination compounds.^[25] The peak-to-peak separations (Table 6) are in a range typical for either a reversible or a quasi-reversible redox process.^[35,36] All half wave potentials are stable over numerous measuring cycles (see Figure S11), for this reason follow-up chemistry of the oxidized species can be ruled out. It cannot be completely excluded that even at higher concentrations of the coordination polymer, a ligand exchange with the solvent used does not occur. It can be assumed that this only has a negligible effect, if at all, on the measurements carried out, since the half-wave potentials differ characteristically from the educts used and the products obtained. However, for further studies it would be interesting to perform electrochemical and conductive measurements of the compounds in the solid state.

6.2.8 Discussion

There are already several examples demonstrating that the choice of solvent is not trivial for the synthesis of coordination polymers of the general type $[\text{Fe}(\text{LN}_2\text{O}_{2\text{eq}})(\text{L}_{\text{ax}})]_n$, as co-crystallized solvent molecules can have a significant impact on the magnetic properties.^[20] In keeping with this, it became evident in elemental analysis and was also proven by thermogravimetric investigations that solvent inclusion is relevant for the coordination polymers discussed here. These differences go beyond the effect of remote ligand substitution but rather reflect major effects of the solvent selection on the crystal packing. The finding of a conserved low-spin state of **C2a** at both 100 K and 273 K was a surprise for two reasons: First, magnetic properties of powdered samples of **2a–c** indicated pure high-spin character at room temperature and only partial crossover to the low-spin state at $T = 50$ K. Second, a previously reported single-crystal **C1c** · (EtOH)_x obtained from EtOH is entirely high-spin at 100 K and 250 K.^[24] It is well known that in order to perform spin crossover, a system must have enough flexibility to be able to make the necessary changes to the bond lengths.^[3] The DMF molecules crystallized in the case of **C2a** are involved in crucial intra- and intermolecular contacts. These interactions may be one of the reasons for the sideways offset arrangement of the polymer strands and, accordingly, the TTF units. As a result, no stacking of TTF units, as described before in literature^[23,32,37], can be observed. The strong interaction with the DMF molecules may also well be responsible for the different magnetic behavior of the single crystal material **C2a** and the solvent-free powdered product **2a**.

For all samples it can be noted that upon cooling the magnetic moment decreases to an extent which clearly depends both on the substitution pattern (series **1** versus **2**) and the solvent of synthesis (**a**, **b**, **c**). In general, samples derived from ligand series L2 host more complete SCO, although it must be noted that in none of the materials the low-spin fraction at $T = 50$ K goes below $\gamma_{LS} > 0.50$. As computation of the singlet-quintet splitting of the model complexes [FeL1(py)₂] and [FeL2(py)₂] with the TPSSh functional indicates, an only very mild influence of ligand substitution on the ligand-field strength is expected (difference in SCO energy: $\Delta\Delta_{SCO}E = 0.1$ kJ mol⁻¹). We ascribe this differential effect on SCO of lateral -C(O)Me and -C(O)OMe substitution between series 1 and 2 largely to different packing effects.

Using DFT, we examined the changes in the intra-chain distance Fe...Fe distance during spin transition. The studies indicated that a spin transition is accompanied by a massive build-up of tension within the polymer strains. We think that packing-frustrated contraction/expansion may contribute to the observed hindrance of SCO in the bulk $\{[FeL1(TTF(py)_2)]\}_n$ which is seen in SQUID magnetometry. The bridging TTF(py)₂ ligand is not in plane but shows a slight curvature. A spin-state dependent change of an axial bond length within the coordination center therefore requires an additional reorientation of the bonds within the axial ligand. Thus, in the polymer chain, the bond contraction due to SCO might be hindered. In a follow-up work we will investigate, if through the synthesis of nanoparticles those strain effects can be reduced.^[38]

After fine differences in the materials from different solvents had been identified by diffuse reflection spectroscopy and powder diffraction, differences in the electrochemical behavior also became apparent. While the overall pattern is similar for all polymers, the ones obtained from DMF, **1a** and **2a**, consistently show lower half-wave potentials for all three redox events. This might be read to be caused by variable average chain lengths of the polymers under the action of the varying donor numbers of the used solvents.^[28,29] In this sense, it is clearly more likely in DMF than in the weaker donors EtOH and MeCN that the terminal iron(II) centers are coordinated by DMF rather than a TTF(py)₂ molecule; this would indeed rationalize shorter chains in **1a** and **2a**, a notion which is corroborated by the deviating PXRD pattern of **2a**.

6.3 Conclusion

In this work the synthesis of new 1D coordination polymers is described that integrate the spin-state variability of iron(II) in the field of a Schiff base-like N₂O₂ ligand and the redox activity of a bis-monodentate bridging ligand. The ligand TTF(py)₂ with its interesting electrochemical behavior was used with the aim to synthesize iron(II) SCO complexes combined with redox active properties. Due to the poor solubility of the axial ligand TTF(py)₂ the synthesis was carried out in a selection of solvents with different reaction conditions. Electrochemical studies by cyclic voltammetry reveal three (quasi-)reversible one-electron events involving the iron center and the tetrathiafulvalene unit and demonstrate the successful combination of an electronically switchable bridge with an iron(II) center. Intriguingly, small but significant differences in the magnetic and electrochemical behavior of the derived polymers could be observed despite the conserved bulk chemical composition. Crystal structure analysis, X-ray powder diffraction and diffuse reflection spectroscopy aided in a preliminary rationalization and pointed to a high susceptibility of the polymer properties towards the presence and the relative number of solvent molecules in the lattice. In single crystalline material **C2a**, the presence of two DMF molecules in the unit cell acts to trap the LS state up to $T = 273$ K. By contrast, as-synthesized powders of **2a** with a residual lattice solvation of 0.7 DMF molecules per unit is likewise trapped, but in the high spin state. If the synthesis is performed in MeCN or EtOH, no co-crystallized solvent can be identified, resulting in high spin formulations. Divergent X-ray powder diffraction pattern suggest that it is indeed the divergent packing in the solid, which translates into solvent-of-synthesis dependent properties.

6.4 Experimental Section

If not stated otherwise all reactions were carried out using Schlenk technique with fresh degassed or distilled solvents. The axial ligand TTF(py)₂ was prepared according to literature procedures.^[21] Chemicals used for synthesis were commercially available and used as received. **Elemental analysis** has been conducted with a Unicube from Elementar with sulfanilamide as standard. The samples were placed in a small tin boat. Mass spectra were recorded with a Finnigan MAT 8500 with a data system MASPEC II. Magnetic measurements were done on a MPMS-XL SQUID magnetometer from Quantum Design. The samples were put in a gelatin capsule and placed in a straw.

⁵⁷Fe Mössbauer Spectroscopy: The spectra were recorded in transmission geometry at constant acceleration using a conventional Mössbauer spectrometer with a 50 mCi ⁵⁷Co(Rh) source. The samples were prepared under argon atmosphere. Isomer shift values were reported with respect to α -Fe as a reference at room temperature.

Diffuse Reflection Measurements: Data were recorded on a PerkinElmer Lambda 750 UV/VIS/NIR spectrometer. A Praying-Mantis unit from Harrick was used for the measurements. The undiluted samples were calibrated with a Spektralon tablet and the diluted samples with BaSO₄ from Alfa Aesar. At 379.2 nm a filter change from filter BG38 to filter UG11 takes place and at 319.2 nm a lamp and filter change occur from filter UG11 at $T = 100\%$. At 860.8 nm there is a detector switch for the NIR region.

X-ray crystal structure analysis: A suitable single crystal was embedded in protective perfluoropolyalkylether oil and transferred to the cold nitrogen gas stream of the diffractometer. Intensity data of **C2a** were collected at 100 K and 273 K using MoK α irradiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Kappa PHOTON 2 μ S Duo diffractometer equipped with QUAZAR focusing Montel optics. Data were corrected for Lorentz and polarization effects; semi-empirical absorption corrections were performed on the basis of multiple scans using SADABS.^[15] The structures were solved by direct methods (SHELX XT 2014/5)^[39a] and refined by full-matrix least-squares procedures on F^2 using SHELXL 2018/3.^[39b] Material for publication was prepared using OLEX2.^[40] All non-hydrogen atoms were refined with anisotropic displacement parameters. In the crystal structure of **C2a** at 100 K the oxygen (O3) of one keto group was disordered. Two alternative orientations were refined and resulted in site occupancies of 54(2) and 46(2) % for O3 and O3A, respectively. The compound crystallized with two molecules of DMF (dimethyl formamide), one of which was disordered. Two alternative orientations were refined and resulted in site occupancies of 49.7(6) and 50.3(6) % for the atoms O8, N6, C38–C40 and O8A, N6A, C38A–C40A, respectively. Similarity restraints were applied to the anisotropic displacement parameters of the disordered atoms. In the crystal structure of **C2a** at 273 K the disorder of oxygen O3 was no longer observed. Instead, both of the co-crystallized DMF solvent molecules were disordered. Two alternative orientations each were refined and resulted in site occupancies of 40.5(8) and 59.5(8) % for the atoms O7, N5, C35–C37 and O7A, N5A, C35A–C37A, and of 46.3(13) and 53.7(13) % for the atoms O8, N6, C38–C40 and O8A, N6A, C38A–C40A respectively. Similarity restraints were applied to the anisotropic displacement parameters of the disordered atoms. Additional pseudo-isotropic restraints were applied to the anisotropic displacement parameters of the disordered atoms of DMF O8–C40 and O8A–C4A, respectively. All hydrogen atoms were placed in positions of optimized geometry; their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2017572 (for **C2a** at 273 K) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Cyclic Voltammetry: Cyclic voltammetry measurements were performed with an Electrochemical Analyzer CHI610E from CH Instruments in a three-electrode setup with a platinum working and counter electrode and a Ag/AgNO₃ non-aqueous reference electrode filled with the solvent used and tetrabutylammonium hexafluorophosphate as conducting salt.

{[FeL1(TTF(py)₂)]_n}

Synthesis in DMF (1a): A solution of [FeL1(MeOH)₂] (0.2 g, 0.45 mmol) and TTF(py)₂ (0.17 g, 0.48 mmol) in DMF (15 mL) was heated to reflux for 2 h. After cooling and leaving to stand at 8°C for 48 h a dark red solid precipitated. The dark reddish powder was filtered off, washed with methanol two times (2 mL) and dried in vacuo to give {[FeL1(TTF(py)₂)]·(0.7 DMF)}_n (yield 0.13 g, 41.3 %) Elemental analysis calcd (%) for C₃₅H₃₀FeN₄O₄S₄·0.7C₃H₇NO (791.88 g mol⁻¹) C 54.76, H 4.19, N 8.31, S 16.19; found: C 53.86, H 4.29, N 8.69, S 17.11. MS (DEI(+), 70 eV): m/z (%): 358 (100) [TTF(py)₂], 382 (31) [[FeL1]], 179 (69) [C₈H₅NS₂²⁻], 103 (97) [C₃H₃S₂⁻], 76 (21) [C₆H₄²⁺].

Synthesis in acetonitrile (1b): A suspension of [FeL1(MeOH)₂] (0.21 g, 0.47 mmol) and TTF(py)₂ (0.18 g, 0.50 mmol) in acetonitrile (20 mL) was heated to reflux for 3 h. After cooling and leaving to stand to room temperature for 2 d, the red powder was filtered off. The precipitate was washed with acetonitrile three times (3 mL) and dried in vacuo to give {[FeL1(TTF(py)₂)]_n} (yield 0.19 g, 52.58 %) Elemental analysis calcd (%) for C₃₅H₃₀FeN₄O₄S₄ (754.05 g mol⁻¹) C 55.70, H 4.01, N 7.42, S 16.99; found: C 55.18, H 3.76, N 7.48, S 16.96. MS (DEI(+), 70 eV): m/z (%): 358 (100) [TTF(py)₂], 382 (56) [[FeL1]], 179 (57) [C₈H₅NS₂²⁻], 103 (97) [C₃H₃S₂⁻].

Synthesis in ethanol (1c): A solution of [FeL1(MeOH)₂] (0.14 g, 0.31 mmol) and TTF(py)₂ (0.12 g, 0.33 mmol) in ethanol (30 mL) was heated to reflux for 4 h. After cooling and leaving to stand at 8°C for 24 h a dark red solid precipitated. The dark reddish powder was filtered off, washed with methanol two times (2 mL) and dried in vacuo to give {[FeL1(TTF(py)₂)]_n} (yield 0.09 g, 41.3 %) Elemental analysis calcd (%) for C₃₅H₃₀FeN₄O₄S₄ (754.05 g mol⁻¹) C 55.70, H 4.01, N 7.42, S 16.99; found: C 54.70, H 3.98, N 7.69, S 17.41. MS (DEI(+), 70 eV): m/z (%): 358 (100) [TTF(py)₂], 382 (25) [[FeL1]], 179 (58) [C₈H₅NS₂²⁻], 103 (97) [C₃H₃S₂⁻].

{{[FeL2(TTF(py)₂)]_n}

Synthesis in DMF (2a): A solution of [FeL2(MeOH)₂] (0.28 g, 0.58 mmol) and TTF(py)₂ (0.22 g, 0.62 mmol) in DMF (20 mL) was heated to reflux for 2.5 h. After cooling and leaving to stand at room temperature for 3 d, a dark reddish powder was filtered off, washed with methanol three times (2 mL) and dried in vacuo to give {{[FeL1(TTF(py)₂)]_n} (yield 0.25 g, 58.2 %) Elemental analysis calcd (%) for C₃₄H₂₈FeN₄O₆S₄ (772.02 g mol⁻¹) C 52.85, H 3.65, N 7.25, S 16.60; found: C 52.16, H 3.88, N 7.88, S 16.19. MS (DEI-(+), 70 eV): m/z (%): 415 (98) [FeL2], 359 (100) [TTFpy₂], 179 (33) [C₈H₅NS₂²⁻], 103 (75) [C₃H₃S₂].

Preparation of C2a: A solution of [FeL2(MeOH)₂] (0.20 g, 0.42 mmol) and TTF(py)₂ (0.16 g, 0.44 mmol) in DMF (20 mL) was heated to reflux for 3 h. After cooling and leaving to stand at room temperature for 3 d some fine black crystals precipitated. An attempt to filter them failed due to insufficient amounts of solid particles present. The reagent solution was mixed with 2 mL methanol and stored at -38°C. After 6 days crystals were obtained which are suitable for single crystal structure analysis. **C2a**

Synthesis in acetonitrile (2b): A suspension of [FeL2(MeOH)₂] (0.20 g, 0.41 mmol) and TTF(py)₂ (0.16 g, 0.44 mmol) in acetonitrile (25 mL) was heated to reflux for 3 h and 15 min. After cooling and leaving to stand at room temperature for 2 d, a red powder was filtered off. The precipitate was washed with acetonitrile three times (3 mL) and dried in vacuo to give {{[FeL2(TTF(py)₂)]_n} (yield 0.21 g, 66.28 %) Elemental analysis calcd (%) for C₃₄H₂₈FeN₄O₆S₄ (772.02 g mol⁻¹) C 52.85, H 3.65, N 7.25, S 16.60; found: C 52.2, H 3.71, N 7.06, S 16.55. MS (DEI-(+), 70 eV): m/z (%): 358 (100) [TTF(py)₂], 414 (31) [[FeL2]], 179 (67) [C₈H₅NS₂²⁻], 103 (97) [C₃H₃S₂], 76 (23) [C₆H₄²⁻]

Synthesis in ethanol (2c): A solution of [FeL2(MeOH)₂] (0.2 g, 0.41 mmol) and TTF(py)₂ (0.16 g, 0.44 mmol) in ethanol (30 mL) was heated to reflux for 4 h. Upon heating, a dark red powder precipitated. After cooling and leaving to stand at room temperature for 1 d, a dark reddish powder was filtered off, washed with methanol three times (2 mL) and dried in vacuo to give {{[FeL1(TTF(py)₂)]_n} (yield 0.23 g, 72.7 %) Elemental analysis calcd (%) for C₃₄H₂₈FeN₄O₆S₄ (772.02 g mol⁻¹) C 52.85, H 3.65, N 7.25, S 16.60; found: C 52.57, H 3.95, N 7.17, S 16.03. . MS (DEI-(+), 70 eV): m/z (%): 358 (100) [TTF(py)₂], 414 (31) [[FeL2]], 179 (67) [C₈H₅NS₂²⁻], 103 (97) [C₃H₃S₂], 76 (23) [C₆H₄²⁻]

Supporting Information (see footnote on the first page of this article): Thermogravimetric Analysis of **1a-c** and **2a-c**, Crystallographic data of **C2a** at 100 K and 273 K, Mössbauer spectra of **1a-c** and **2a-b**, PXRD pattern of **1a-c**, Diffuse reflection spectrum of **2b** and **2c**, Diffuse reflection spectrum of pure **2a-c** in NIR range, DFT-optimized structure of binuclear model [(py)L1Fe(TTF(py)₂)FeL1(py)] in the low spin/high spin state, S = 2, Character and energetic order of the highest occupied molecular orbitals, Cyclic voltammogram of **1a-c** and **2a-c**.

Acknowledgements

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Keywords: Tetrathiafulvalene; Iron(II) complex; Iron; Spin crossover; Redox active

6.5 References

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6.6 Supporting Information

Thermogravimetric Analysis: Thermogravimetric analysis was done with a Netzsch TG 209 F1 Libra under nitrogen atmosphere using 4 mg–10 mg of the sample with a heating rate of 10 K min⁻¹.

Complex **1a** shows no appreciable loss of mass up to 70°C (343 K). An abrupt loss of 6.4 % in mass occurs from this point on. This can be attributed to a loss of about 0.7 DMF. Above 245°C (518 K), the compound decomposes continuously.

The complexes **1b** and **1c** show no appreciable loss of mass up to 245°C (518 K). From this point on a continuous loss of mass indicates the decomposition of both compounds.

Examining the thermogravimetric analysis of the compounds **2a–c**, it is noticeable that complex **2a** does not differ as sharply from **2b** and **c** in its mass loss as **1a** to **1b** and **c**. Here, compound **2a** clearly shows the most weight loss starting at 100°C (373 K). The loss of mass occurs continuously up to a temperature of 233°C (506 K). From this point on, the compound decomposes continuously. **2b** does not lose significant amounts of mass up to a temperature of 225 K and starts to decompose constantly from there. **2c** exhibits a small loss of mass from a temperature of 133°C (406 K) onwards, with a total loss of 2.3% up to a temperature of 233°C (506 K).

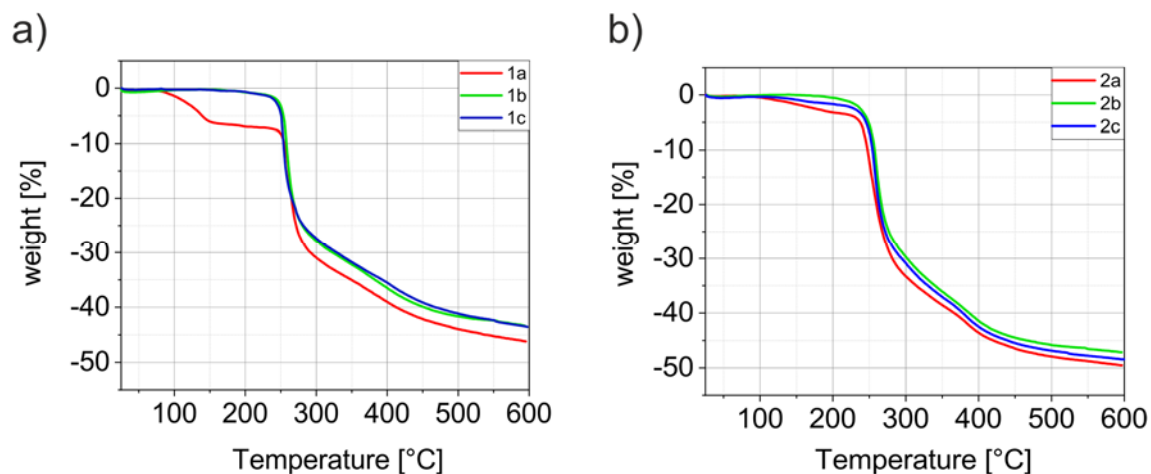


Figure S1. Thermogravimetric analysis of complexes **1a–c** and **2a–c** in a temperature range of 26–600°C.

Table S1. Crystallographic data of {[FeL2a(TTF(py)₂)]·(2DMF)}_n

Compound	{[FeL2a(TTF(py) ₂)]·(2DMF)} _n	
	100 K CCDC-2017572	273 K CCDC-2017571
Formula	C ₃₄ H ₂₈ FeN ₄ O ₆ S ₄ ·2(C ₃ H ₇ NO)	C ₃₄ H ₂₈ FeN ₄ O ₆ S ₄ ·2(C ₃ H ₇ NO)
CCDC	2017572	2017571
<i>Mr</i> / g mol ⁻¹	918.88	918.88
Crystal size / mm	0.28 x 0.18 x 0.10	0.28 x 0.18 x 0.10
λ / Å	0.71073	0.71073
<i>T</i> / K	100	273
Crystal system	triclinic	triclinic
Space group	P $\bar{1}$	P $\bar{1}$
<i>a</i> / Å	12.3417(12)	12.4599 (13)
<i>b</i> / Å	12.8369(12)	12.4656 (13)
<i>c</i> / Å	14.0138(14)	14.5967 (15)
α / °	87.947(3)	86.113 (4)
β / °	85.779(3)	87.007 (4)
γ / °	71.985(3)	72.577 (4)
<i>V</i> / Å ³	2105.4(4)	2157.0 (4)
<i>Z</i>	2	2
<i>d</i> _{calcd} / Mg cm ⁻³	1.449	1.415
μ / mm ⁻¹	0.616	0.60
Θ range / °	2.2–27.9	1.7–27.1
Reflections collected	62431	71604
Indep. reflections	10033	9472
Obsvd. reflections (<i>F</i> _o > 2 <i>s</i> (<i>F</i>))	8643	7802
<i>R</i> _{int}	0.048	0.054
<i>R</i> (<i>F</i>), (<i>F</i> _o > 2 <i>s</i> (<i>F</i>))	0.0500	0.0591
w <i>R</i> ₂ (<i>F</i> ²), all data	0.1192	0.1621
Goof	1.084	1.073

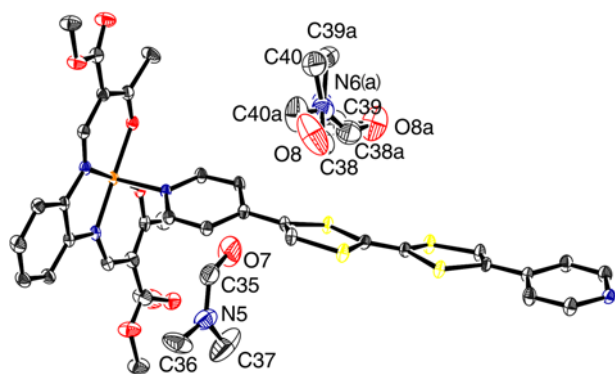
Figure S2. ORTEP drawing of the asymmetric unit of **C2a** (100 K) with the atom numbering scheme of the DMF molecules used in the text. Thermal ellipsoids presented at 50% level. Hydrogen atoms are omitted for clarity.

Table S2 Selected distances [Å] and angles [°] of the hydrogen bonds in the crystal packing of $\{[\text{FeL2a}(\text{TTF}(\text{py})_2)] \cdot (2\text{DMF})\}_n$ at 100 K. The co-crystallized DMF molecules are involved in orange marked hydrogen bonds.

D–H...A	D–H	H...A	A...D	D–H...A
C15–H15A...S3 ^[a]	0.980	2.943	3.495	116.72
C17–H17A...S1 ^[b]	0.980	2.996	3.468	110.84
C18–H18B...O5	0.980	2.221	2.739	111.65
C19–H19...O6 ^[c]	0.950	2.430	3.141	131.48
C25–H25...O7 ^a	0.950	2.135	3.052	161.75
C29–H29...O3 ^a ^[d]	0.950	2.317	2.999	128.21
C31–H31... O8 ^a ^[e]	0.950	2.368	3.259	156.09
C34–H34...O8A ^b ^[f]	0.950	2.485	3.241	136.57
C36–H36B...S4 ^[g]	0.980	2.964	3.550	119.40
C36–H36C...O5 ^[h]	0.980	2.619	3.333	129.86

^[a] [x, y, z+1], ^[b] [x, y-1, z], ^[c] [-x+1, -y, -z+1], ^[d] [-x+2, -y+1, -z+1],
^[e] [-x+1, -y+1, -z], ^[f] [-x+2, -y+1, -z], ^[g] [x-1, y, z], ^[h] [-x+1, -y, -z+1]

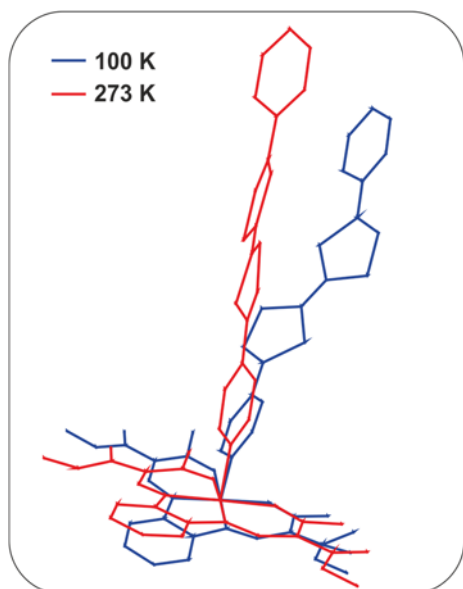


Figure S3. Structural changes upon heating from 100 K to 273 K.

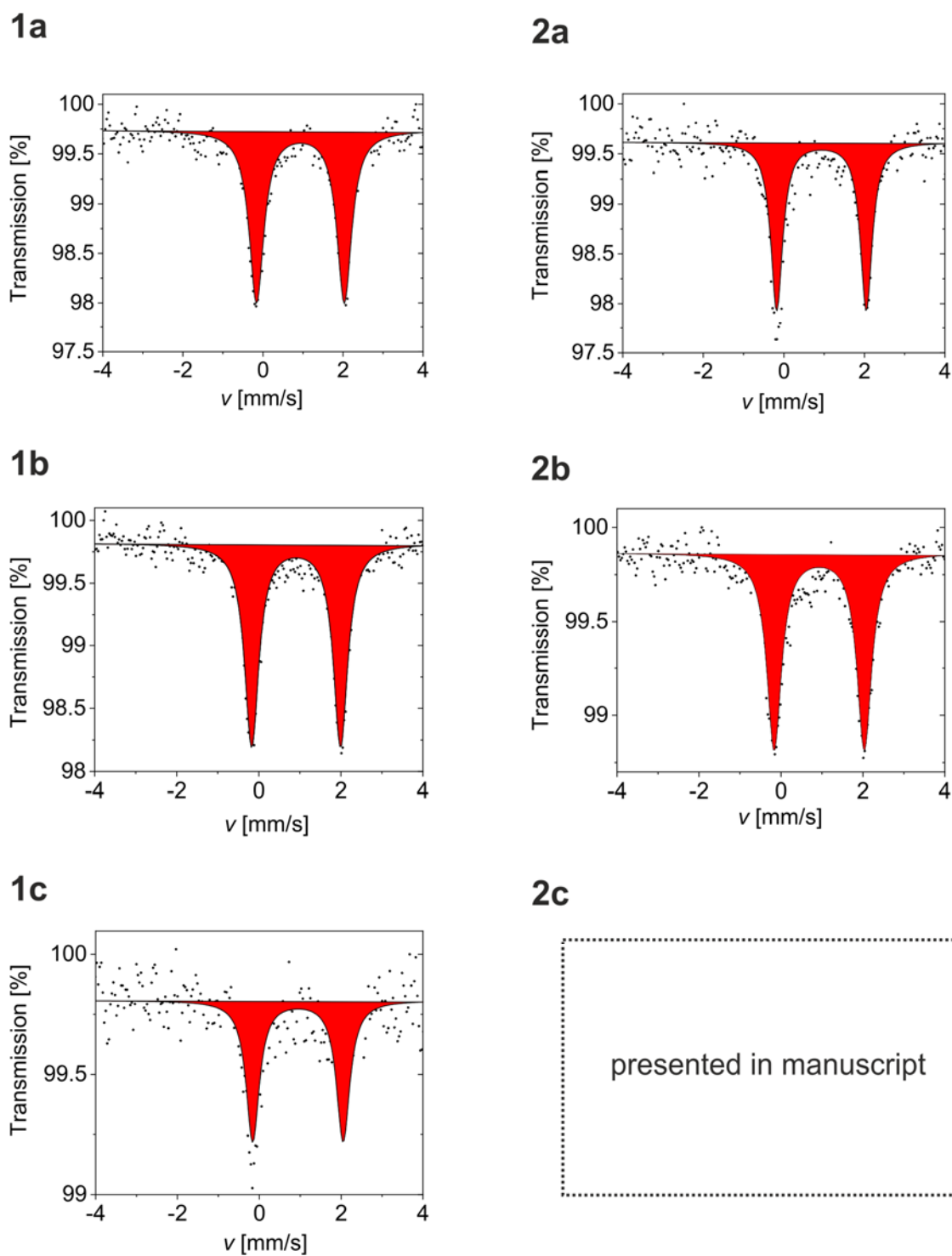


Figure S4. Mössbauer spectra of **1a–c** and **2a/b**. The relative transmission is plotted against the speed of the source.

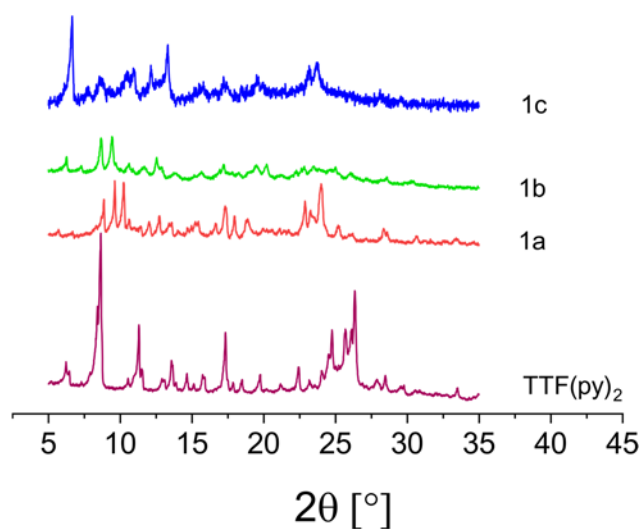


Figure S5. PXRD pattern of 1a–c and the axial ligand TTF(py)₂ in the range of 5–30° 2θ at room temperature.

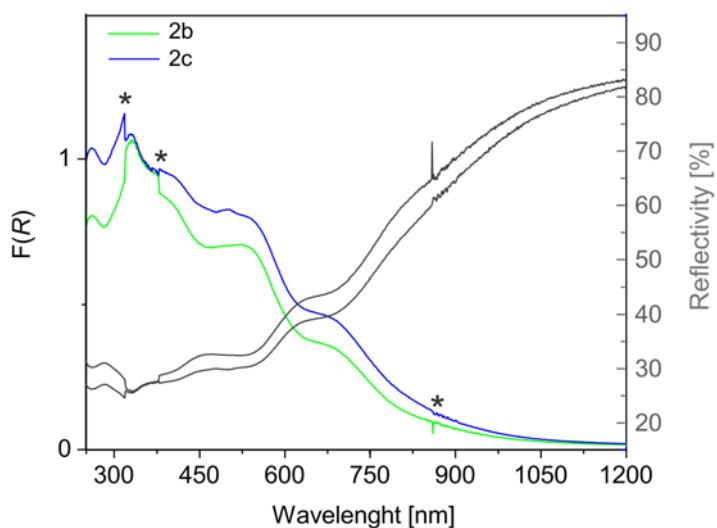


Figure S6. Diffuse reflection spectrum of **2b** and **2c** which were optically diluted with four times the amount of BaSO₄ (grey lines). Kubelka-Munk function according to equation (1) (green and blue line). The spikes marked with * are caused by lamp, filter and detector change, respectively.

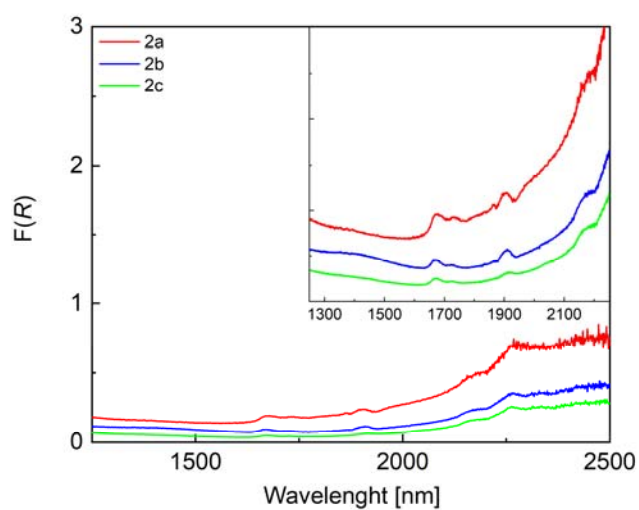


Figure S7. Diffuse reflection spectrum of pure **2a–2c** in the NIR-range.

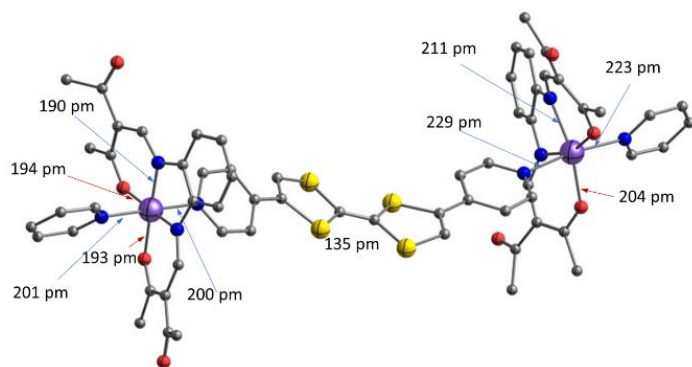


Figure S8. DFT-optimized structure of the binuclear model $[(py)L1Fe(TTFpy_2)FeL1(py)]$ in the low spin/high spin state, $S = 2$.

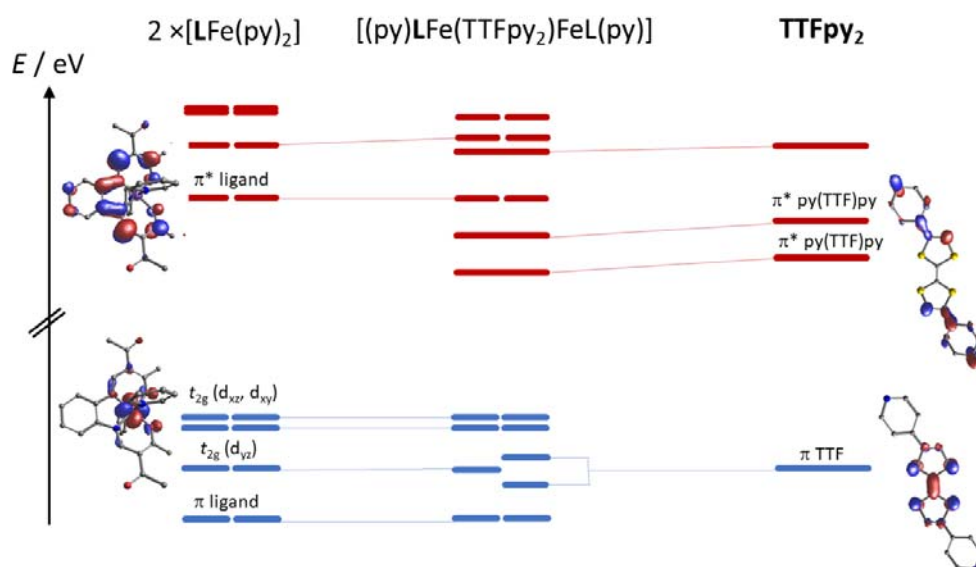


Figure S9. Character and energetic order of the highest occupied MOs ($S = 0$); blue: metal-centered; red: centered on the equatorial ligand L1.

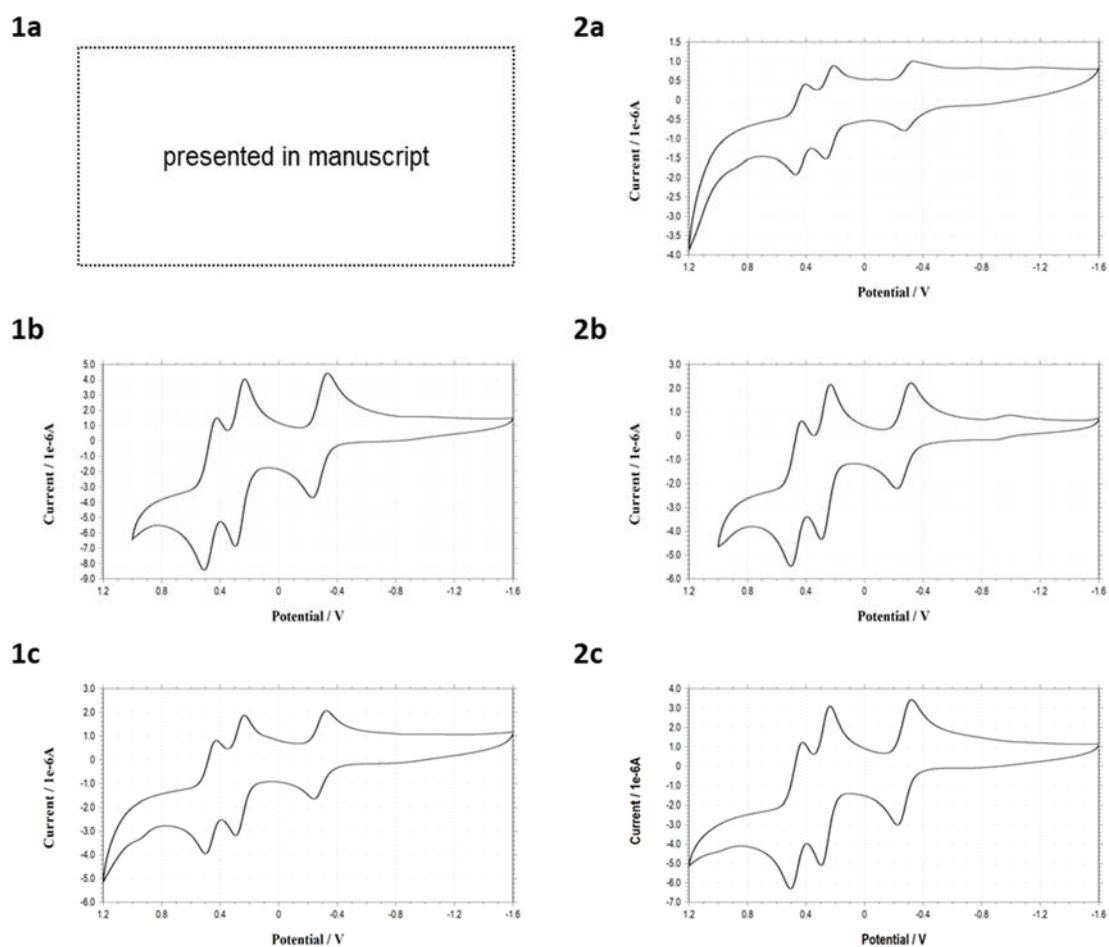


Figure S10. Cyclic voltammogram of **1b/c** and **2a–c** in DMF with tetrabutylammonium hexafluorophosphate (NBu₄PF₆) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at 50 mV s⁻¹ with a nonaqueous Ag/AgNO₃ reference electrode.

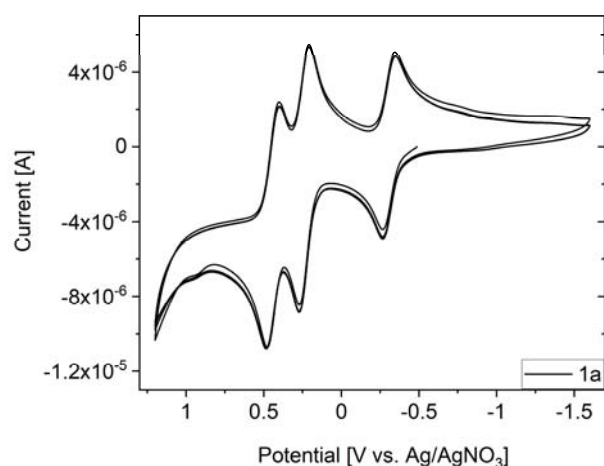


Figure S11. Cyclic voltammogram with 7 sweep segments of **1a** in DMF with tetrabutylammonium hexafluorophosphate (NBu₄PF₆) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at 50 mV s⁻¹ with a nonaqueous Ag/AgNO₃ reference electrode.

7. Iron(II) Spin Crossover Complexes Based on a Redox Active Equatorial Schiff Base-Like Ligand

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ABSTRACT

In this work two iron(II) coordination compounds with an N₂O₂ coordinating Schiff base-like ligand bearing a redox active tetrathiafulvalene (TTF) unit and pyridine or *trans*-1,2-bis(4-pyridylethylene) as axial ligand are synthesized. Crystals suitable for single X-ray structure analysis were obtained for the new ligand. The complexes were characterized by magnetic susceptibility measurements, *T*-dependent UV-Vis spectroscopy and cyclic voltammetry. Both complexes display spin transition behavior below room temperature with *T*_{1/2} values of 146 K and 156 K. The mononuclear iron(II) complex [Fe^{TTF}L(py)₂] is relatively stable up to 400 K compared to similar complexes, showing no loss of axial ligands upon heating. Temperature dependent Mössbauer spectroscopy was conducted for the coordination polymer {[Fe^{TTF}L(bpee)]_n to get more information regarding the origin of the stepwise spin crossover (SCO) behavior observed in the magnetic measurements. The change of the spin state is accompanied by a change of the optical properties, which can be monitored by VT-UV-Vis spectroscopy for the mononuclear complex and has been analyzed by theoretical studies. The redox behavior of the iron(II)

complexes reveals three reversible redox steps which are centered at the iron center and at the TTF unit of the ligand. Oxidation of the TTF unit induces characteristic changes in the UV-Vis spectrum that can be followed by spectroelectrochemical UV-Vis spectroscopy. Addressing the potential of the iron-centered redox process results in similar changes in the UV-Vis spectrum, which indicates an electronic coupling of the redox active unit with the metal center under certain circumstances.

7.1 Introduction

One of the current challenges in the field of coordination chemistry is the synthesis and investigation of compounds that show synergetic effects between multiple physical properties.^[1–5]

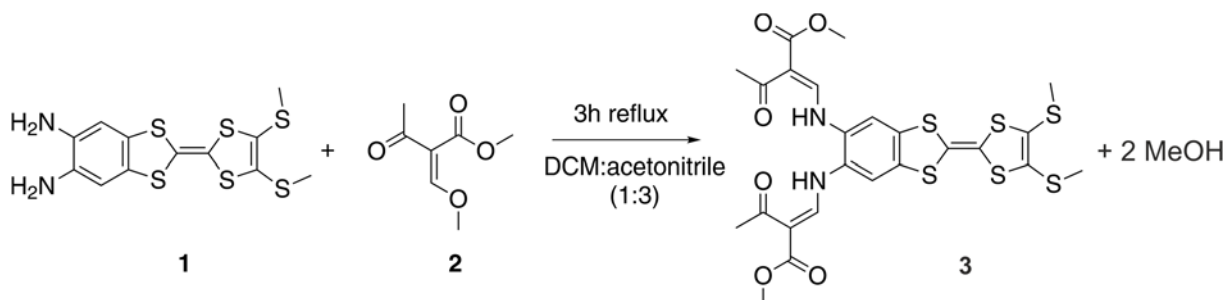
Particularly complexes of iron(II) ions which undergo spin crossover (SCO) between diamagnetic singlet and paramagnetic quintet electronic d states provide a promising platform for multifunctional materials. Iron(II) complexes are very actively investigated because of their possible magnetic switchability.^[6–14] Such a switch between spin states can be caused by external stimuli such as temperature change, light irradiation or change of pressure. Caused by the spin transition not only the magnetic properties change; in most cases there is also a massive variation of structural, vibrational and electronic properties.^[15] Recent examples to reach multifunctionality have focused, for example, on the implementation of ligand-borne fluorescence in iron(II) SCO complexes.^[16–19] Another promising approach is the implementation of redox active ligands and/or substituents.^[20–23] In particular, the presence of a second electron donor site besides the iron(II) center renders the site of oxidation variable; that is, ligand-centered $\text{Fe}^{\text{II}}\text{L}^+$ versus metal-centered $\text{Fe}^{\text{III}}\text{L}$. Different optical and magnetic properties can be expected if selective access to both valence tautomeric forms is possible.^[24–26] In this work we combined the redox active tetrathiafulvalene (TTF) unit with coordinated iron(II) ions that are known for their variable optical or magnetic properties, in order to create materials which are addressable optically, thermally and electrochemically. Because of their variety of electronic phases tetrathiafulvalene(TTF)-based organic charge-transfer complexes gained interest in different fields of research.^[27, 28] The intense studies of TTF began as early as 1973 by discovering the first organic metal TTF-TCNQ (TCNQ = tetracyanoquinodimethane).^[29] The TTF molecule itself is unique because it can be reversibly oxidized to the stable radical cation ($\text{TTF}^{\cdot+}$) and the dication (TTF^{2+}).^[30] During the last decade, many TTF-containing materials, functional coordination polymers and metal complexes with usage in electro catalysis or as photoconductive switches have been reported.^[31–33] Also a combination with sensing properties for applications as optical sensors is possible.^[34] During the last years especially neutral metal complexes with sulfur rich ligands have attracted more attention.^[35] Tanaka *et al.* showed that transition metal complexes are suitable candidates to observe the described properties

in a single-component system.^[36] In this work, we report the synthesis of a new Schiff base-like equatorial N₂O₂ tetra-dentate ligand ^{TTF}LH₂ bearing a TTF unit as an in-plane extension of the equatorial π-ligand backbone. Ligands of the open chain N₂O₂-type have been first reported by Jäger *et al.*^[37] and are known for their broad variability in their properties, covering different aspects such as catalysis, model complexes for biological systems, or molecular magnetism.^[38]

7.2 Results and Discussion

7.2.1 Synthesis and Geometric and Electronic Structure of a TTF-Containing N₂O₂ Ligand

The synthesis of the ligand precursor 5,6-diamino-2-(4,5-bis(methylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole (**1**) was carried out following literature procedures.^[39–41] The ligand ^{TTF}LH₂ (**3**) was obtained via modified Claisen condensation analogous to the procedures described by Bauer *et al.*^[42] Heating **1** with the methoxymethylene derivative (*E*)-methyl-2-(methoxymethylidene)-3-oxobutanoate (**2**) in a 1:3 mixture of dichloromethane (DCM) and acetonitrile as a solvent resulted in the new Schiff base-like ligand ^{TTF}LH₂ (**3**) as orange participate in good yields (Scheme 1).



Scheme 1. Synthesis of the redox active Schiff base-like ligand ^{TTF}LH₂ (**3**).

The ¹H-NMR spectrum of the ligand and the signal assignment is displayed in Figure S1. Assignment is based on resolved spin-spin couplings and comparison with literature data. Strong vicinal H-H coupling with ³*J* = 12.0 Hz between the *ene*-proton **e** and the NH proton **f** suggests that most of the ligand is in its keto-enamine form.^[42]

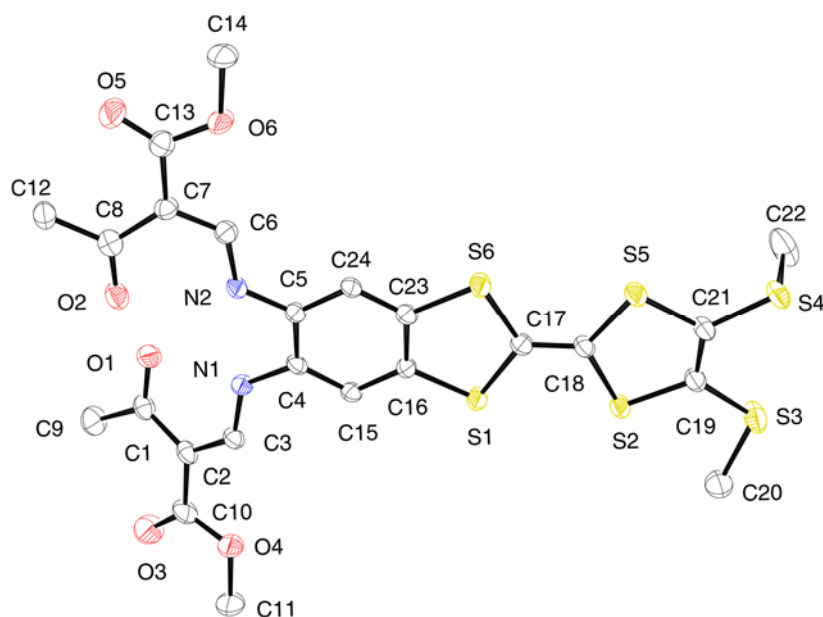


Figure 1. ORTEP drawing of the asymmetric unit of ligand **3** with the atom numbering scheme used in the text. Hydrogen atoms are omitted for clarity. Thermal ellipsoids presented at 50% level.

Crystals of the free ligand **3** suitable for X-ray analysis were obtained from hot dimethylformamide (DMF) by slow cooling of the solution to room temperature. The crystallographic data were obtained at 133 K and are summarized in Table S1. The asymmetric unit of the monoclinic cell ($C2/c$) consists of one ligand molecule and is shown in Figure 1, selected bond lengths are summarized in Table S2. Two tautomers can be expected for compounds of this type: the keto-enamine or imino-enol form.^[43] Ligand **3** crystallizes in the keto-enamine form. The C2–C3/C6–C7 bond lengths of approximately 1.38 Å approach the range of a formal double bond whereas the terminal C1–C2/C7–C8 bonds are significantly longer ($d(\text{C-C}) = 1.46 \text{ \AA}$) in line with a single bond character. This finding supports the results from ^1H NMR spectroscopy and agrees with previously reported structures of this Schiff base-like ligand type.^[44–46] The C17–C18 bridge between the sulfur heterocycles carries significant double-bond character (1.35 Å), rendering the $\text{S}_2\text{C}=\text{CS}_2$ unit planar and attesting the neutral charge state of **3**. The bonds C16–C23 (1.40 Å) and C19–C21 (1.34 Å) also show double bond character and thus support the assumption that ligand **3** is neutrally charged.^[47] Planarity prevails for the TTF unit in **3** as a whole, as has been previously found in several TTF derivatives in the solid state.^[48–50]

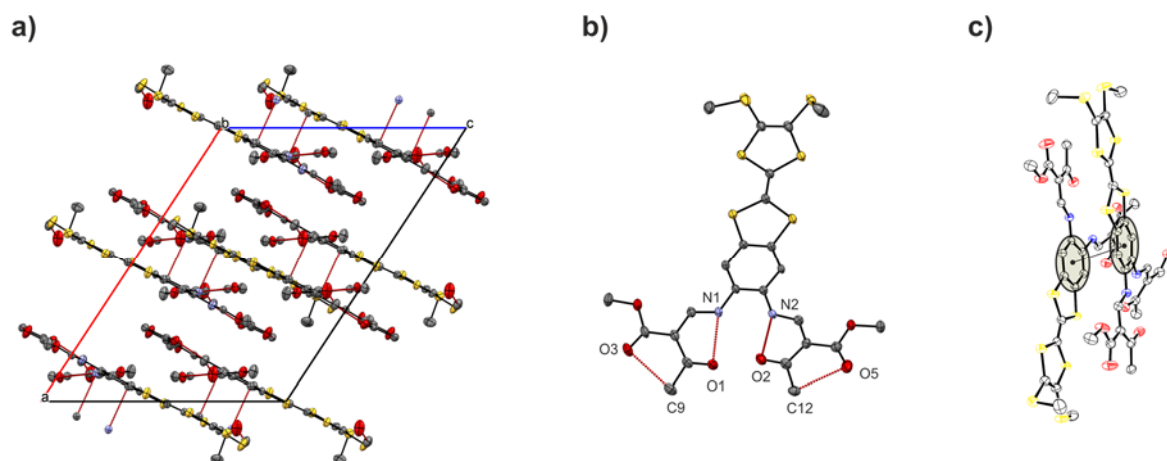


Figure 2. Molecular packing of **3** in the crystal at 133 K. (a) view along *b* axis and (b) asymmetric unit with hydrogen bonds represented as red dashed lines. (c) detail of the stacking of two molecules within the crystal structure, grey rings focus on the stacking phenyl rings.

Different from previous members of this ligand family, ligand **3** integrates a TTF unit with highly polarizable sulfur atoms, rendering the ligand backbone predisposed to intermolecular interactions. Several solid-state reports in TTF derivatives have identified such supramolecular packing motifs.^[51–53] Figure 2 displays the packing of ligand **3**. The details on metrics and nature of several short contacts are summarized in Tables S3–5. A relatively short S···S distance (3.7 Å) between two neighboring TTF units within one layer can be observed. The packing enforces strong π ··· π interactions between the phenyl rings of adjacent ligand molecules, yielding parallel, π -planes at a distance of 3.466(3) Å (Figure 2, c). This causes pairs of neighboring ligands to be turned by approximately 130° resulting in an absence of interlayered stacking of TTF units. The protic groups of the ligand are engaged intramolecularly in classical hydrogen bonds between the enamines and the keto oxygen rendering them unavailable for intermolecular H-bonding (Figure 2, b). The proximity of the ligands supports the formation of additional contacts such as C–H··· π interactions between a methyl group of one ligand and the phenyl ring of C–O··· π interactions between a keto group of a side chain of **3** and the TTF unit, interactions between methyl groups and the keto oxygen of a neighbor and supramolecular contacts of aromatic C–H group and a sulfur atom (Figure 2, a).

Besides steric effects of the bulky units on the molecular packing, the electronic structure of the ligand can be affected through integration of potent donor or acceptor groups in the ligand backbone. This combination renders the resulting complexes multi-functional. Installation of an electron-accepting phenazine unit in $^{\text{PA}}\text{LH}_2$, for instance, yielded luminescent iron(II) SCO complexes with strong ligand-borne absorption bands in the visible.^[17] Similarly, TTF-appended **3** is deeply orange and generally echoes the optical properties of the phenazine system. As a matter of fact, the optical spectra of the derived iron(II) complexes are dominated by TTF-borne transitions, as discussed later. By contrast, such

ligand-based optical transitions are largely absent in the faint yellow ligands deriving from phenylene diamine ($^{\text{PD}}\text{LH}_2$) and naphthyl diamine ($^{\text{ND}}\text{LH}_2$) because of less extended π -systems. This divergence in spectroscopic behavior can be readily traced to the altered frontier orbital landscape of the respective ligands (Figure 3, structures of the free ligands can be found in Scheme 2). Linear extension of the π -system from $^{\text{PD}}\text{LH}_2$ to $^{\text{ND}}\text{LH}_2$ does not significantly affect HOMO and LUMO energies. The presence of potent acceptors or donors in $^{\text{PA}}\text{LH}_2$ and $^{\text{TTF}}\text{LH}_2$ similarly leaves the overall pattern unaffected, but adds acceptor and donor levels, which significantly narrow the HOMO-LUMO gap in both cases. In particular, the highly destabilized TTF-borne HOMO of $^{\text{TTF}}\text{LH}_2$ is expected to compete with metal-borne orbitals in the resulting iron(II) complexes.

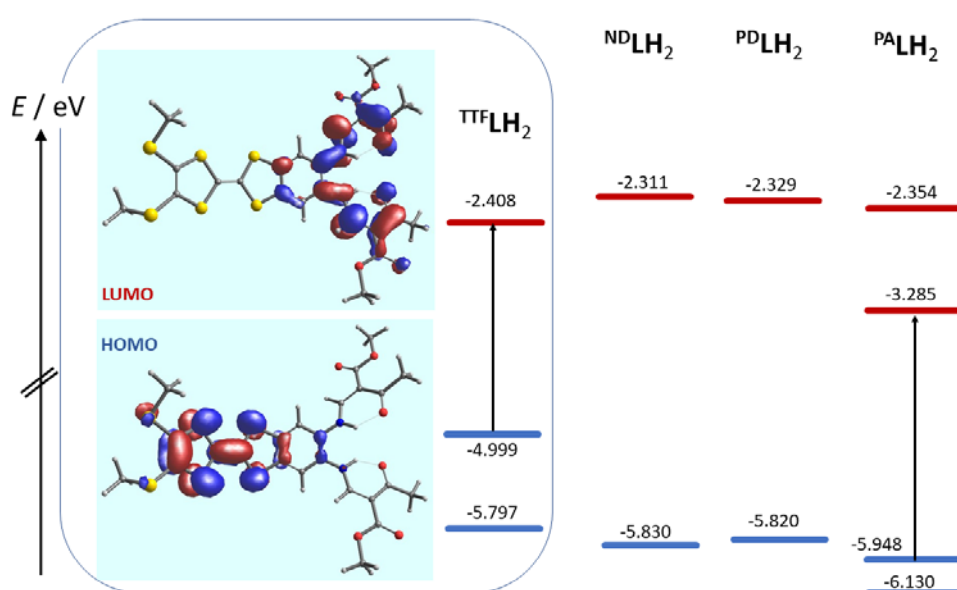
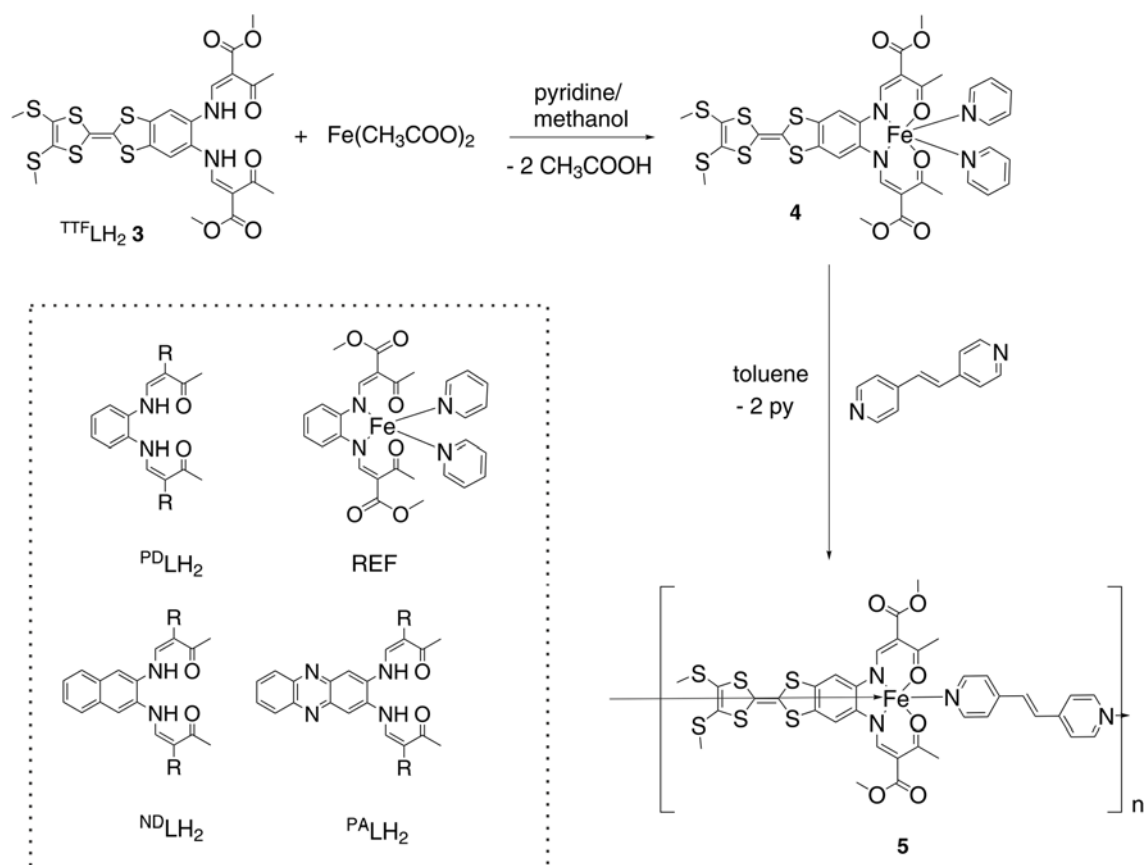


Figure 3. Frontier orbital landscape of **3** and π -varied congeners (TPSSh-D3/TZVP/COSMO(MeCN)).

7.2.2 Synthesis of Iron(II) Complexes of $^{\text{TTF}}\text{LH}_2$ and Structure Modelling

The synthesis of the octahedral iron(II) complex $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ (**4**) is accomplished in a one-pot reaction of ligand **3** and a slight stoichiometric excess of anhydrous iron(II) acetate in a 1:1 mixture of pyridine and methanol, heated under reflux. The resulting black fine-crystalline powder which separates from the mixture upon cooling is analytically pure **4**. For the formation of the coordination polymer $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})]\}_n$ (**5**) the pyridine complex **4** serves as precursor. The polymer was obtained by ligand substitution through heating **4** in toluene in presence of a tenfold excess of bpee (bpee = *trans*-1,2-bis(4-pyridyl)ethene) yielding a green powder. Scheme 2 displays the synthetic procedure for the complex formation. Elemental analysis indicates that there is additional toluene (tol) included in the filtered and dried product resulting in a formulation as $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})]\cdot(0.75\text{tol})\}_n$. Co-crystallized toluene is a recurrent motif for this kind of coordination polymers.^[54]



Scheme 2. Synthesis of the monomeric iron(II) coordination compound **4** and its 1D coordination polymer **5**. Dashed rectangle gives an overview of the free ligands used for theoretical studies and the structure of the reference system [Fe^{PD}L(py)₂] (**REF**).

Akin to other N₂O₂ ligands of this type, the deprotonated form of **3** presumably acts as an equatorial ligand whereas pyridine molecules occupy the axial positions of an axially slightly extended octahedron. As neither **4** nor **5** gave crystals suitable for XRD analysis, the above structure assignment was corroborated by quantum chemical modelling of **4** in its high-spin and low-spin form with the GGA functional BP86. Calibration of the structure prediction was established through comparison of theoretical and experimental metrics^[37] in a closely related reference system, **REF**, which features the phenylene diamine backbone ligand ^{PD}LH₂. Very good agreement between measured and computed structure details of **REF** prevails throughout. Pertinent metrical data of **4** and **REF** are summarized in Table 1. First, it is noticed that coordination of the ligand to iron(II) does not affect the metrics of the TTF unit. Double-bond character of the inner-TTF C–C bond is conserved as are the C–S bond lengths, indicating minor electronic communication among the potential redox centers. As has been previously found in related systems, the complex metrics are not significantly affected by the nature of the equatorial Schiff-base like ligand, neither in the HS nor in the LS form. The singlet-quintet transition is predicted also in **4** to cause substantial radial breathing of the N₄O₂ coordination sphere.

As a common feature of this ligand family, breathing is not isotropic yielding $\Delta_{\text{SCO}}d > 0.2 \text{ \AA}$ for the Fe–N bonds but only $\Delta_{\text{SCO}}d < 0.1 \text{ \AA}$ for the Fe–O bonds. All other structural features are unexceptional and well match the established implications of this family of ligands.

Table 1. Selected Bond Metrics [\AA] in Optimized **4** and **REF**;^a Data in Italics from an X-ray Structure Elucidation of **REF**^b

	hs-4	ls-4	hs-REF	ls-REF
Fe–N_{eq}	2.081(1)	1.893(1)	2.090(1) / <i>2.062/2.053</i>	1.899(1) / <i>1.923/1.918</i>
Fe–N_{ax}	2.178/2.250	1.965(2)	2.161/2.228 / <i>2.195/2.256</i>	1.965(2) / <i>2.025/2.023</i>
Fe–O_{eq}	2.011(3)	1.936(1)	2.016(1) / <i>2.017/1.990</i>	1.943(1) / <i>1.962/1.955</i>
N_{ax}–Fe–N_{ax}	178.5	178.3	178.6	178.1
N_{eq}–Fe–O_{eq}	163.7(1)	179.2(1)	164.0(1)	178.9(1)
O_{eq}–Fe–O_{eq}	110.6	87.0	109.9/ <i>106.3</i>	87.3/ <i>92.4</i>

^a BP86-D3/TZVP/COSMO(MeCN); ^b reported in Ref. [37].

Complexes of NDLH₂, ^{PD}LH₂ and of ^{PA}LH₂ have been studied previously.^[17,42,56] They all undergo SCO in the bulk material, with the characteristic parameters presumably being strongly biased by packing effects. For instance, [Fe^{PD}L(py)₂] undergoes gradual SCO at $T_{1/2} = 220 \text{ K}$ ^[15], whereas [FeNDL(py)₂] shows a stepwise spin transition behavior with $T_{1/2}^1 = 150 \text{ K}$ and $T_{1/2}^2 = 80 \text{ K}$.^[56] For [Fe^{PA}L(bipy)]_n an unique, abrupt SCO with a wide hysteresis is observable.^[17] **REF**, which derives from ^{PD}LH₂, has been studied in solution also. It was found by ¹H NMR studies to undergo gradual SCO, centered at $T_{1/2} = 220\text{--}230 \text{ K}$ in toluene/pyridine mixtures.^[57] DFT modeling of the SCO energetics corroborates this view. Following the routines put forward by Jakubikova *et al.*,^[58] which were successfully applied by us in studies on N₆–N₈ auto adaptive SCO at iron(II)^[59], we studied the SCO energies $\Delta_{\text{SCO}}E$, in an *exact-exchange scan* relative to the known compound **REF**.^[15] In order to address the effect of altered π -systems on the SCO energies more comprehensively, we included in this in-silico study also the iron(II) complexes of ^{PD}LH₂, NDLH₂ and ^{PD}LH₂. The resulting plots are summarized in Figure S2. Narrowly clustering slopes of the plots ($\Delta\Delta_{\text{SCO}}E/\delta a_0 = (625 \pm 5) \text{ kJ}\cdot\text{mol}^{-1}$) justify a unified treatment within a complex family. Accordingly, the relative offsets of the plots translate to the relative differences in SCO energies, that is, $\Delta\Delta_{\text{SCO}}E$. Evidently, the variation in the offsets is very small, $\Delta\Delta_{\text{SCO}}E < 7 \text{ kJ mol}^{-1}$. Reasonably assuming a constant SCO entropy for all members of the family, $T_{1/2}$ is expected to vary by no more than 100 K in solution. The validity of this hypothesis was studied through VT-UV-Vis spectroscopy of **4** and **REF**.

7.2.3 Spin State Variation of REF and **4** in Solution

UV-Vis spectroscopy was first used to characterize the degree of electronic coupling between the iron(II) center and the remote TTF unit. In order to spectrally isolate the influence of the TTF unit $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ (formed in-situ from $[\text{Fe}^{\text{PD}}\text{L}(\text{MeOH})_2]$) with the phenylene diamine derived ligand $^{\text{PD}}\text{LH}_2$ was taken as reference. All absorption spectra were recorded at room temperature in pyridine as solvent (Figure 4). The polymer **5** dissociates under these conditions, giving independent equivalents of $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ and free bpee. Accordingly, the Vis regions of spectra **4** and **5** in pyridine coincide. Both show a strong absorption peak at $\lambda = 418 \text{ nm}$ ($\epsilon_{\text{max}} = 3 \cdot 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) with a less-intense tailing throughout the entire visible range (a finite offset throughout the visible is evident for **REF** also; $\epsilon_{\text{max}} = 1 \cdot 10^3 \text{ cm}^{-1} \text{ M}^{-1}$). The strong band at the Vis/UV border appears in the spectra of **3** (if shifted slightly to the blue, $\lambda = 394 \text{ nm}$), but is missing in the spectra of **REF**. Comparison with similar systems containing the TTF motif yields absorption bands in the same region,^[34,54] safely associating this strong absorption with the TTF unit. Coordination of **3** goes along with a red-shift of the TTF-borne bands by ca. 1500 cm^{-1} . While the exchange $2 \times \text{H}^+ \rightarrow \text{Fe}^{2+}$ conserves the charge, incorporation of iron(II) aligns the two NO ligand subunits and enforces (approximately) co-planarity of the coordination site and the TTF-electrophore. A second significant difference between **4** and **REF** is a peak around 340 nm ($\epsilon_{\text{max}} = 7 \cdot 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) which is dominating the near UV regime of the ligand and **4**, but is missing in **REF**. It can be assigned to a local transition within the TTF moiety.^[60,61]

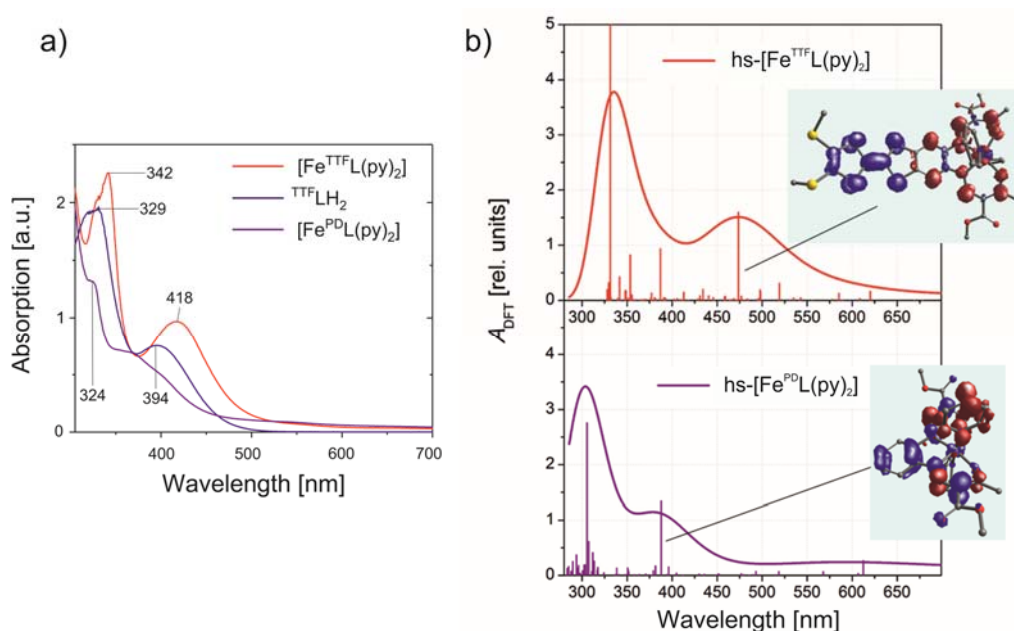


Figure 4. (a) UV-Vis absorption spectra of $^{\text{TTF}}\text{LH}_2$ (**3**), $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ (**4**) and $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ (**REF**) in pyridine as solvent; (b) TD-DFT derived optical spectra of **4** (red) and **REF** (purple); vertical bars: differential transitions; full lines: broadened convolution of the bar spectra; orbital plots denote difference densities of diagnostic transitions (blue: source; red: sink).

In order to validate the assignment of the optical transitions and unravel the spectral effects of the TTF unit in **4**, TD-DFT modeling of the optical spectra has been performed. To this end, 80–110 low-lying transitions have been computed for **4** and **REF** in the singlet and quintet spin states. Solvent polarity has been accounted for in a dielectric continuum model, parameterized for pyridine. The resulting broadened spectra obtained for the high-spin states of **4** and **REF** match the experimental data both qualitatively and quantitatively (Figure 4b); plots of the difference densities of diagnostic transitions are given as insets). In fact, the presence of TTF in **4** mainly acts to add TTF-borne transitions to the spectra at $\lambda = 330$ and 470 nm, whereas the underlying sub-spectrum of the coordinated iron(II) center remains largely unaffected. For instance, the transition diagnostic of **REF** at $\lambda = 385$ nm is present in **4** as well, fully conserved with respect to energy and intensity. While this transition implies some charge shift from the phenylene π -system to the coordinating N_2O_2 ligand, it is dominated by π - π^* -character. The additivity of the sub-spectra is reflected by the frontier orbital pattern of **REF** which cleanly integrates the donor levels of **3** to give high-spin **4** (Figure S3). The diagnostic vis transition of **4** relies on charge transfer from TTF to the coordination site, showing only minor contributions from the metal. Without affecting much the absolute orbital energies, the donor levels of TTF in **4** intercalate the block of largely metal-borne occupied MOs which characterize **REF**. Similar observations have been recently made in a N_6 coordinate cobalt(II) triarylamine diade, where the electrophores were found electronically uncoupled.^[62] With respect to redox of **4** it is important to note that it is clearly a metal-localized orbital which features at highest energy. This fact once more points out the similarity among **4** and **REF** and therefore suggests metal centered oxidation. TTF-borne donor states which reside approximately 1 eV lower in energy in the neutral form of **4** will become accessible to redox chemistry in $[4]^+$, that is only after initial oxidation of the iron center.

The match of theoretical and experimental spectra identifies the high-spin states of **4** and **REF** to be the dominating species in solution at RT. In particular, the measured spectra fully lack of additional strong absorption bands centered at $\lambda = 550$ nm which are predicted for the respective low-spin species. In keeping with $T_{1/2} = 220$ – 230 K measured by NMR for **REF** and the small differences in the SCO energies predicted by DFT, significant amounts of the low-spin species should be found at lower temperature.

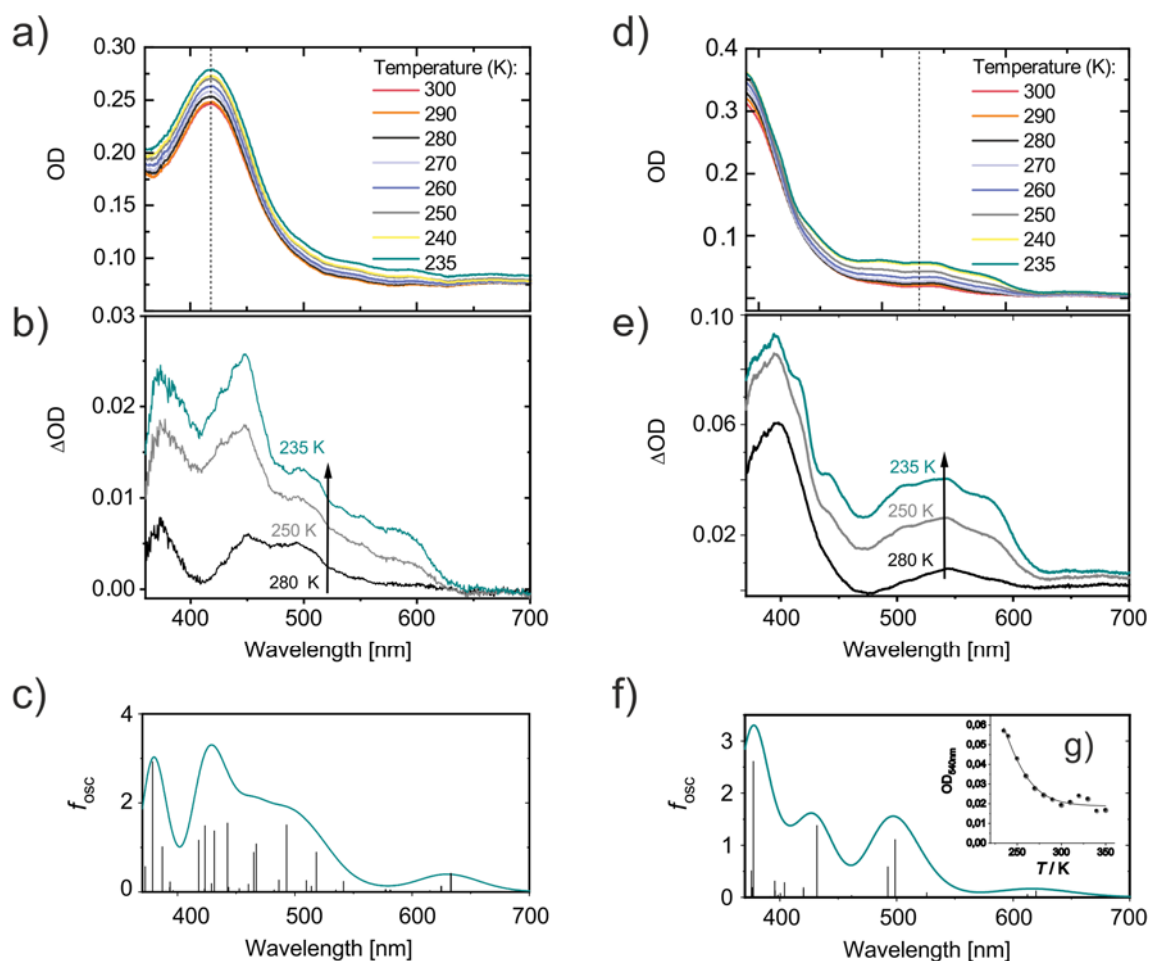


Figure 5. VT-UV-Vis absorption spectroscopy of (left) $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ (**4**) and (right) $[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$ (**REF**) in pyridine as solvent. Solutions were cooled to 235 K and incrementally heated in 5 or 10 K steps. (a, d) Absorption spectra between 235 K < T < 300 K (for $T > 300$ K, see Figure S4); (b, e) Selected difference spectra relative to the spectrum recorded at $T = 340$ K; (c, f) TD-DFT derived spectra (black bars: transitions; line: broadened line spectrum); (g) Temperature dependence of the optical density (OD) at 540 nm for **REF** fitted to a sigmoidal function (see text).

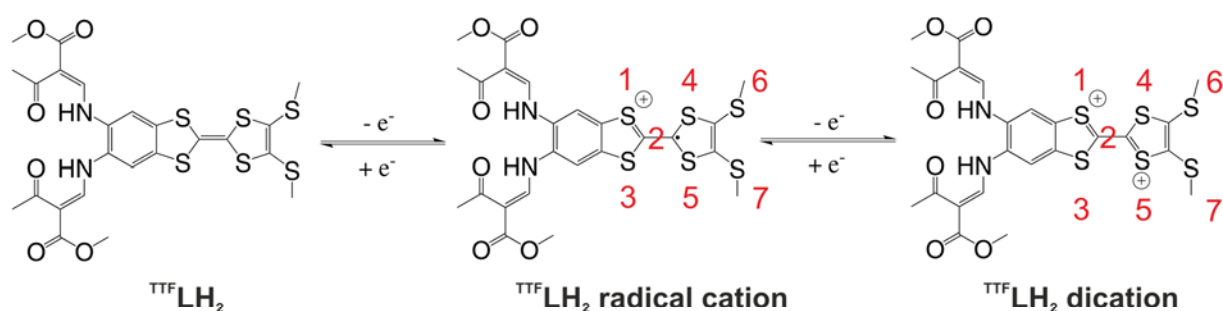
In fact, VT-UV-Vis experiments with solutions of **4** and **REF** in neat pyridine ($T < 300$ K in Figure 5; data for $T > 300$ K, see Figure S4) reveal an intensification of broad absorption bands around 530 nm upon cooling for **REF** (Figure 5b). Consistent with TD-DFT modeling which predicts several intense transitions in the vis regime, this increase is also observable for **4** but is less pronounced. A small part of the increase in absorption is certainly due to temperature-dependent volume contraction. But in fact, a change in color of a solution of **4** during cooling with liquid nitrogen can also be observed with the naked eye. (Figure S4c) The blue to violet color impression obtained fits perfectly to the intensification of the band around 530 nm. The spectral dynamics during the temperature scan become most obvious from difference spectra, $\Delta OD(\lambda) = OD(\lambda; T) - OD(\lambda; 340 \text{ K})$ shown in Figure 5b, e. We selected the spectrum recorded at $T = 340$ K as the high-temperature standard representative of the pure high-spin forms of **4** and **REF**. The latter assignment is justified with a view to the very minor evolution of the spectra at $T > 300$ K (see Figures S4). Clearly the isolated sub-spectra of the low-temperature forms coincide with TD-DFT derived optical data of **4** and **REF** (Figure 5c, f). That is, the increase of the optical density (OD) around 540 nm is diagnostic of an increase in the LS fraction. Shown in Figure 5g is a fit of

the measured optical densities to a Boltzmann model, which adequately captures the dynamics with $T_{1/2} = 223 \pm 2$ K (the low-temperature limit of $OD_{540\text{nm}}$ was fixed at 0.12). While this cannot be fully conclusive, owing to the limited temperature window of pyridine, the data well matches $T_{1/2} = 220$ – 230 K for **REF**^[56] which was found in NMR studies. The weaker spectral dynamics of **4** do not allow a corresponding analysis. Suffice to say here that a lower $T_{1/2} < 200$ K is to be expected based on the spectral data, which would be well in agreement with the implications of the exact-exchange plot of $\Delta_{\text{SCO}}E$ (see Figure S2).

7.2.4 Electrochemical Investigations in Solution

The presence of two potent electron donor sites, TTF and iron(II), in one molecule raises the question on the relative order of the redox events. In order to discern the electrochemical properties of the ligand ^{TTF}LH₂, reference complex **REF** and the TTF-containing complexes **4** and **5** were investigated by cyclic voltammetry (CV) at room temperature with dimethyl formamide (DMF) as solvent. For all measurements, a non-aqueous Ag/AgNO₃ ($c_{\text{Ag}^+} = 10$ mM) reference electrode, with DMF as solvent was used. **REF** served as a single-redox site reference compound.

Figure 6 displays the voltammograms of the free ligand ^{TTF}LH₂ and of the single-site reference compound **REF**. In agreement with previous electrochemical measurements on related systems^[59], a single reversible redox event is expected for **REF** at a halfwave potential of $E_{1/2}^1 = -0.390$ V (vs. Fc⁺/Fc).^[60,63] Indeed a single redox event has been detected at $E_{1/2}^1 = -0.395$ V (vs. Ag/AgNO₃). This event is readily attributable to the Fe^{2+/3+} couple. The irreversible reduction process of ^{TTF}LH₂ at $E_{\text{p}}^{\text{Red4}} = -0.921$ V has been observed before in ligands of a similar type and does not relate to the TTF moiety.^[64–66] Instead TTF containing compounds are well known to undergo two separated, reversible redox events under anodic conditions ($E > 0.3$ V, vs. Fc⁺/Fc), corresponding to the step wise aromatization of both TTF sub-units. Scheme 3 adopts this view for the redox process of ^{TTF}LH₂. According to Hückel's rule the TTF unit itself is nonaromatic because the 14 π -electrons lack conjugation.^[67] Both the cation and the dication are aromatic in Hückel sense, however, as a result of six π -electron heteroaromaticity. As a matter of fact, this scheme seems to oversimplify the electrochemical reality in the present case.



position	TTF-LH_2 radical cation	TTF-LH_2 dication
1	0.12	0.25
2	0.05	0.08
3	0.13	0.26
4	0.13	0.23
5	0.18	0.31
6	0.04	0.09
7	0.09	0.16

Scheme 3. Reversible oxidation of TTF-LH_2 resulting in two stable cationic species (top). Differential Mulliken charges Δq relative to TTF-LH_2 (TPSSh-D3/TZVP/COSMO(MeCN)) (bottom).

Other than expected there is only one reversible redox couple detectable for TTF-LH_2 . The half wave potential $E_{1/2}^2 = 0.181$ V is unexceptional for TTF compounds^[1,64] and can be assigned to the first oxidation of the TTF unit to the radical cation $\text{TTF}^{\cdot+}$.^[1,39,68] The second oxidation takes place at an electrode potential $E_p^{\text{Ox}3} = 0.391$ V and is not fully reversible as can be read from divergence of anodic and cathodic peak currents. Additionally the oxidation event takes place at an electrode potential which is less anodic than reported in the literature.^[1,39,47,64] Scan rate variation to higher or lower values does not establish reversibility (values Table S8). With a view to the redox-related charge redistribution in the molecule (Mulliken charges in Scheme 3), the lack of reversibility may be traced to the partial non-locality particularly of the second redox event. As much as a fraction of ca. 0.5e is predicted by DFT to localize on the Schiff base-like moiety, what may cause irreversible follow-up chemistry.^[67–69] The reduction process at $E_p^{\text{Red}4} = -0.921$ V was observed before in ligands of a similar type.^[64–66] and probably indicates redox vulnerability of the free amino group.

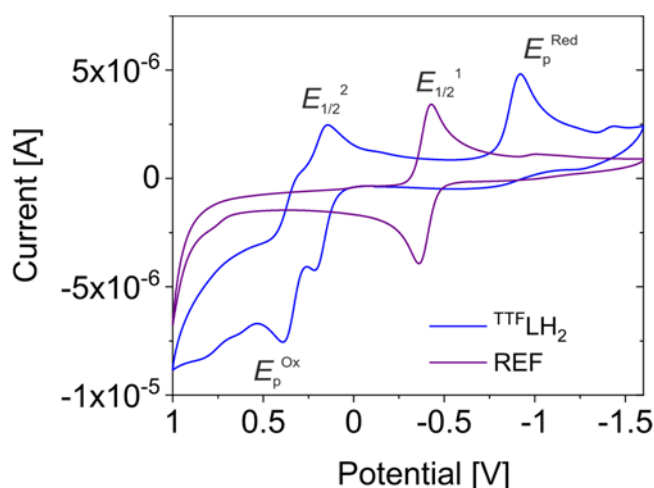


Figure 6. Cyclic voltammograms of TTF LH_2 and **REF** in DMF ($c = 1 \text{ mM}$) with tetrabutylammonium hexafluorophosphate (NBu_4PF_6) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at 50 mV s^{-1} with a nonaqueous Ag/AgNO_3 reference electrode.

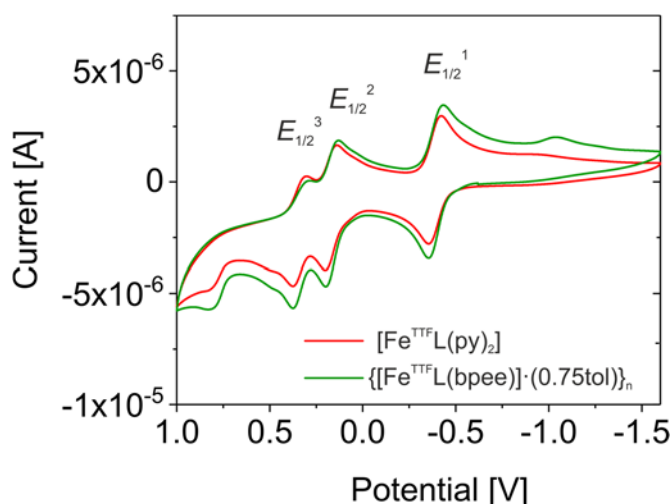


Figure 7. Cyclic voltammograms of $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ (**4**) and $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})]\cdot(0.75\text{tol})\}_n$ (**5**) in DMF ($c = 1 \text{ mM}$) with tetrabutylammonium hexafluorophosphate (NBu_4PF_6) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at 50 mV s^{-1} with a nonaqueous Ag/AgNO_3 reference electrode.

In contrast to the free ligand, the presence of the metal center in the complexes **4** and **5** re-establishes electrochemical reversibility on the TTF redox events. The peak-to-peak separations vary from $\Delta E = 63\text{--}90 \text{ mV}$ and are therefore in a range typical for either a reversible or a quasireversible redox process.^[70,71] Scan rate variation $25 \text{ mV s}^{-1} < \nu < 100 \text{ mV s}^{-1}$ does not significantly affect the peak-to-peak separation. The results are summarized in Table S8. For $\nu > 100 \text{ mV s}^{-1}$ the peak-to-peak separation increases, indicating that the redox processes are comparably slow. As expected upon coordination the irreversible reduction peak of the free ligand is absent in both iron(II) complexes (Figure 7). The close similarity of mononuclear **4** and formally polymeric **5** indicates dissociation of the latter under the experimental conditions. Both complexes exhibit three one-electron redox couples, which largely appear as a superposition of the CVs of the two constituents (Figure 7 and Table 2).

Table 2. Electrochemical parameters^a of the investigated compounds in DMF ($c = 1$ mM) with supporting electrolyte tetrabutylammonium hexafluorophosphate (NBu₄PF₆) (0.1 M) at a 50 mV s⁻¹ scan rate and the corresponding peak-to-peak separations.

	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^3$	ΔE_1	ΔE_2	ΔE_3
3	/	0.181	(0,396) ^b	/	0.075	0.09
REF	-0.395	/	/	0.069	/	/
4	-0.386	0.170	0.340	0.068	0.063	0.072
5	-0.394	0.166	0.330	0.08	0.066	0.089
Fc^{0/+}	0.028	/	/	0.123	/	/

^a Potentials are recorded against Ag/AgNO₃; ^b process is not fully reversible, anodic peak potential is given

In particular, the potential of $E_{1/2}^1 = -0.386$ V recorded for the Fe^{2+/3+} redox wave in **4** and **5** echoes the observations made with **REF** and is in agreement with investigations of similar systems by Jäger *et al.*^[60] The two other redox couples show up in the potential range^[39] typical of step wise TTF oxidation to the radical-cation TTF^{•+} ($E_{1/2}^2$) and to the dication TTF²⁺ ($E_{1/2}^3$).^[40] As a matter of fact, the coordination of an iron(II) center has no significant influence on the redox potentials of the TTF unit and vice versa. The additional positive charge present in the [**4**]⁺²⁺ couple does not affect the second TTF oxidation. The electrophores in **4** are largely decoupled. A complementary conclusion on decoupled chromophores had been drawn from the DFT-based analysis of the optical spectra of neutral **4** and **REF**.

To spectroscopically confirm the assignment of the oxidized species spectroelectrochemical measurements of **3** and **4** were performed in DMF (Figure 8). The compounds were kept at suitable constant potentials corresponding to either the redox process of the iron center or the first oxidation process of the TTF unit over $\Delta t = 10$ min. The reversibility of the process was tested through addressing the redox events with sufficiently cathodic potentials. Despite the different potentials both spectra show some similarities. The free ligand **3** shows transition at $\lambda = 325$ nm and 394 nm which are assignable to an intraligand charge-transfer (ILCT) between the TTF unit and the phenyl moiety of the ligand with the Schiff base-like coordination sphere.^[72,73] The metal complex features similar absorption slightly shifted to higher wavelengths $\lambda = 336$ nm and 408 nm. A Fe^{II} → ligand MLCT is additionally involved in the much more intense band at 408 nm.^[25] During oxidation of the ligand **3** at 0.155 V (vs. Fc^{0/+}) in a DMF solution the two characteristic bands vanish and the appearance of three new absorption maxima is observable ($\lambda = 267$ nm, 492 nm, and 840 nm). (Figure 8a) These bands, especially the broad absorption around 800 nm, are characteristic for molecules associated with the radical cation TTF^{•+}.^[74,75] Oxidation of the iron(II) complex **4** at 0.065 V (vs. Fc^{0/+}) in DMF solution also causes the loss of intensity of the characteristic TTF linked bands and the outgrowth of distinctive radical cation absorption maxima ($\lambda = 295$ nm, 488 nm and 870 nm) (Figure 8c).

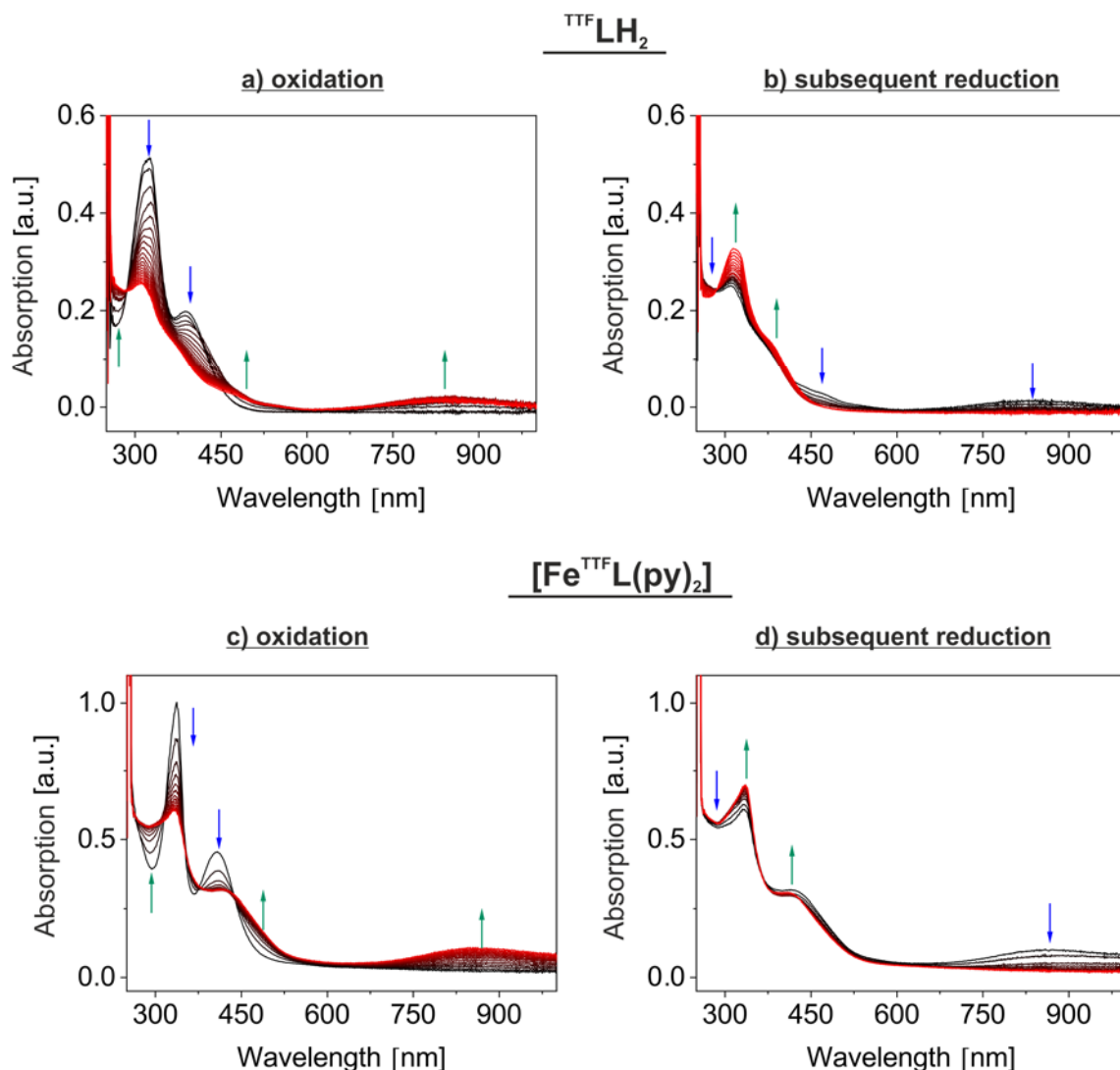


Figure 8. UV/Vis-spectroelectrochemical investigation of top: TTF^{LH_2} ($0.2 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$, obtained at a constant potential of (a) 0.155 V (vs. $\text{Fc}^{0/+}$) (b) -0.785 V (vs. $\text{Fc}^{0/+}$) and bottom: $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ ($0.2 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$, obtained at a constant potential of (c) 0.065 V (vs. $\text{Fc}^{0/+}$) (d) -0.785 V (vs. $\text{Fc}^{0/+}$). Black lines represent measurements at $t = 0 \text{ min}$, red lines after $t = 10 \text{ min}$ at the corresponding electrode potential. Green arrows denote outgrowing bands and blue arrows bleaching.

The major spectroscopic difference between $\mathbf{3}^+$ and $\mathbf{4}$ is the bleach at 400 nm , which is accompanied by the buildup of a broad, red-shifted absorption band ($\lambda = 450 \text{ nm}$) of approximately conserved intensity with significant tailing towards lower energy. While residual absorbance prevails across the visible region also for ligand $\mathbf{3}$, there is no buildup of a defined absorption band in this region. Most intriguingly, however, both the oxidation of $\mathbf{3}$ and $\mathbf{4}$ yield similar NIR bands, located at ca. 840 nm and 870 nm for $\mathbf{3}^+$ and $\mathbf{4}^+$, respectively. Consequently, it is tempting to conclude that what we observe after oxidation is a TTF^+ chromophore in both cases, strikingly indicating a formulation of $\mathbf{4}^+$ as $\text{Fe}^{\text{II}}\text{L}^+$. Subsequent to iron-centered oxidation a charge-shift from the TTF moiety to the iron center in complex $\mathbf{4}^+$ may rationalize the similarity of the spectra of oxidized ligand and complex. The resulting valence tautomeric behavior of $\mathbf{4}^+$ therefore seems to negate the presence of electronically decoupled

electrophores, which was concluded from the additivity in the optical behavior of **4**. Further work is certainly required to unravel the origin of these intriguing observations. Suffice here to note that a possible reason for the seemingly contradictory conclusions may be the altered nature of the axial donors. These are pyridine ligands in native **4** but, very probably, DMF ligands in the electrochemical experiments. While the ligand exchange certainly weakens the overall ligand-field strength, far-reaching consequences on additional electronic properties are highly probable. Subsequent electrochemical reduction does not fully restore the original spectrum of neither the ligand nor the complex (Figure 8b, d), indicating that the process is not reversible on the timescale of the UV-Vis experiments, whereas it was (quasi-)reversible in the CV.

7.2.5 Magnetic Properties of **4** and **5** in the Solid

Magnetic susceptibility measurements in a temperature range from 400 K to 50 K were performed for both samples. The resulting $\chi_M T$ vs. T plots in Figure 9 reveal nearly complete spin crossover in both cases. At room temperature $\chi_M T$ product equals to $3.35 \text{ cm}^3 \text{ K mol}^{-1}$ (**4**) and $3.14 \text{ cm}^3 \text{ K mol}^{-1}$ (**5**). These values are typical for iron(II) in the paramagnetic high-spin state^[37] Upon cooling to 50 K $\chi_M T$ sharply decreases to $0.11 \text{ cm}^3 \text{ K mol}^{-1}$ (**4**) and $0.49 \text{ cm}^3 \text{ K mol}^{-1}$ (**5**), where most of the iron centers are in the diamagnetic low-spin state.^[15] The mononuclear pyridine complex $[\text{Fe}^{\text{TFL}}(\text{py})_2]$ undergoes a rather steep and complete SCO below 200 K. The critical temperature, where 50% of the iron(II) centers have reached the LS state, of this transition is $T_{1/2} = 146 \text{ K}$. Similar behavior was observed in tetrathiafulvalene-fused dipyridophenazine and 2,6-di(pyrazol-1-yl)pyridine iron(II) complexes before.^[47,75] Surprisingly, the $\chi_M T$ plot is largely conserved upon iterated cycles between $400 \text{ K} > T > 50 \text{ K}$, indicating an unforeseen stability against heating. Several heating cycles up to 400 K are tolerated with only small but ever-growing background $\chi_M T$ -values at 50 K, which indicate a minor lack of reversibility, presumably through thermal losses of axial ligand. Usually, similar complexes with monodentate ligands like pyridine lose those ligands almost entirely upon heating above 350 K, resulting in a disappearance of the SCO properties.^[56] A thermogravimetric analysis was carried out to provide a more profound understanding of the stability of the compound (see Figure S7). In accordance with the results of the magnetic measurement, the complex remains stable in its composition up to 75°C (348 K) against loss of mass. The observable change of the magnetic behavior during heating is accompanied by a continuous loss of mass, which can be attributed to the loss of toluene. (see supporting information)

The presence of bpee as bridging ligand in the coordination polymer **5** gives rise to subtle effects in the $\chi_{\text{M}}T$ vs. T plots. The compound remains in the HS state until 229 K. Below this temperature a stepwise SCO takes place, which is more gradual than in **4** (Figure 9). A poorly defined plateau at $\chi_{\text{M}}T = 1.8 \text{ cm}^3 \text{ K mol}^{-1}$, hardly visible due to the small size, is reached at 154 K. At this point, about 50% of all iron sites implemented a spin transition. Upon further cooling, the second step of the SCO takes place immediately. The observed spin transition behavior is stable in the temperature range between 300 and 50 K and does not show any dependence on the cooling rate used. Additionally, the stability of the spin transfer behavior at higher temperatures was investigated. For this the compound was gradually heated to 400 K in 25 K steps and cooled down to 50 K after each heating step. After heating to 325 K no change in the $\chi_{\text{M}}T$ plot over the whole temperature range can be observed. After heating the compound to 350 K, a slightly increased magnetic moment appears over the whole temperature range, but the stepwise course of the spin transition is maintained ($\chi_{\text{M}}T(50 \text{ K}) = 0.76 \text{ cm}^3 \text{ K mol}^{-1}$). A further heating of **5** to 375 K almost leads to a disappearance of the plateau at 154 K. The occurrence of a small 6 K wide hysteresis in the range between 84 and 90 K is new for this progression of the curve. At 50 K the magnetic moment only reaches a value of $1.7 \text{ cm}^3 \text{ K mol}^{-1}$. Further heating up to 400 K again results in a generally higher magnetic moment on cooling ($\chi_{\text{M}}T(50 \text{ K}) = 2.54 \text{ cm}^3 \text{ K mol}^{-1}$). The small hysteresis is maintained and widens by 1 K. Since elemental analysis indicates that toluene is present in **5**, the modified spin transition behavior can be explained by a loss of this co-crystallized solvent. To support this theory a thermogravimetric analysis of **5** has been performed (see Figure S7 with corresponding discussion).

A possible reason for the stepwise spin transition that occurs between 300 and 50 K is the presence of two slightly different iron centers with slightly different chemical surrounding.^[77] This idea is supported by the changed magnetic behavior when heating **5** and has been observed before.^[55] Alternatively, for similar coordination polymers the formation of inequivalent iron centers upon spin crossover is observed leading to alternating HS-LS centers within the chain in the region of the plateau. Restraining interactions between the polymer chains that prevent a uniform change of the metal-ligand bond lengths are made responsible in those cases.^[15,78–80] Another possibility for such behavior might be a phase transition around 150 K that proceed with a change of the space group, resulting in slightly different metal ions in the asymmetric unit.^[81]

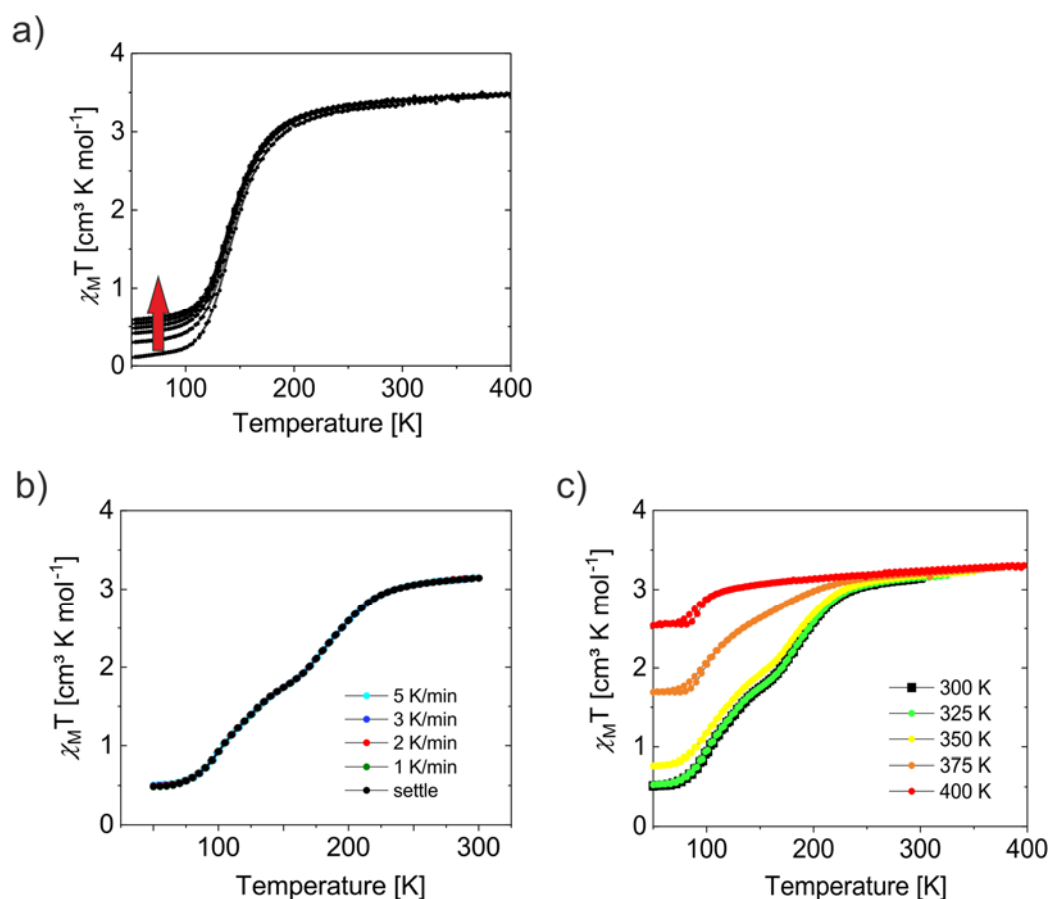


Figure 9. (a) Plot of the $\chi_M T$ product vs. T over the range 400–50 K with 5 K min⁻¹ rates of cooling for $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ (**4**) over six cycles of heating and cooling between 400–50 K. (b) Plot of the $\chi_M T$ product vs. T over five cycles of heating and cooling between 300–50 K with various rates of cooling and heating of $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot (0.75\text{tol})\}_n$ (**5**) (c) Plot of the $\chi_M T$ product vs. T of $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot (0.75\text{tol})\}_n$ (**5**) with different initial temperatures.

Mössbauer spectroscopy is a valuable tool to detect inequivalent iron centers and by this to analyze potential reasons for the occurrence of steps in the transition curve of **5**. Temperature dependent zero-field ⁵⁷Fe-Mössbauer measurements were conducted upon cooling at five different temperatures between $T = 300$ and 50 K following the spin transition process. All spectra can satisfactorily be analyzed with a simple two-component model that assumes the presence of only two doublets of Lorentzian lines, representing the iron(II) HS and iron(II) LS sites in the spin crossover complex **5** (Figure 10). In agreement with magnetic susceptibility measurements, at room temperature a doublet with quadrupole splitting $\Delta E_Q = 2.203(2)$ mm s⁻¹ and an isomer shift $\delta = 0.918$ mm s⁻¹ – indicative for HS iron(II) – is observed. Cooling results in the outgrowth of a second doublet with both a smaller quadrupole splitting $\Delta E_Q = 1.230(1)$ mm s⁻¹ and isomer shift $\delta = 0.466(1)$ mm s⁻¹ (at $T = 50$ K) indicating iron(II) in the LS state (see Table S7 for details).

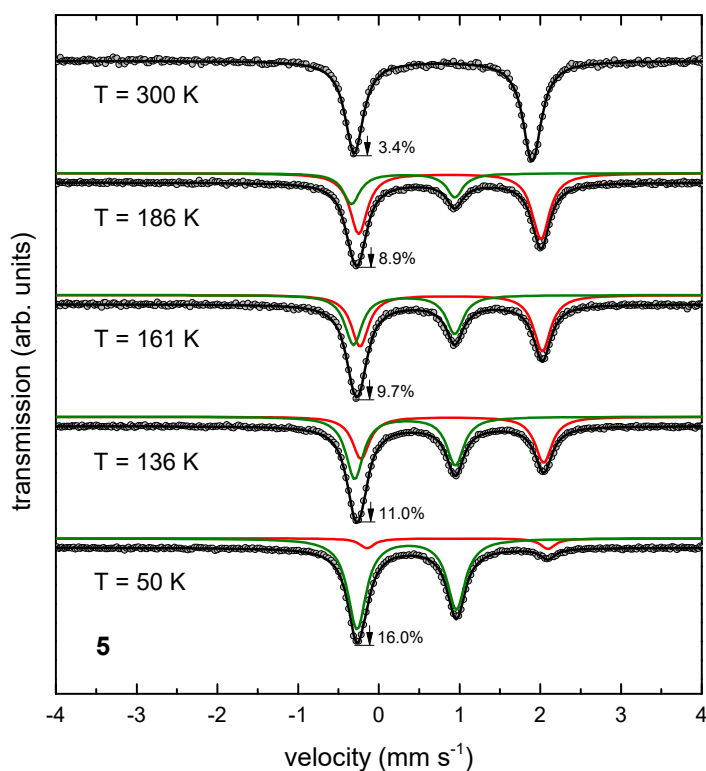


Figure 10. Zero-field ^{57}Fe Mössbauer spectra of **5**, recorded at temperatures between $T = 300$ and 50 K. The measurements were carried out upon zero-field cooling. Symbols: Experimental data. Lines: Fit with doublets of Lorentzian lines. The colored lines illustrate the corresponding sub-spectra of the fit, which are attributed to the Fe(II) low-spin (green) and Fe(II) high-spin sites (red), respectively. The parameters of the fit are summarized in Table S6.

We also observed relatively large intensities of the Mössbauer absorption lines at low temperature (of ca. 16% at $T = 50$ K). To confirm the validity of the thin absorber approximation we reproduced the low-temperature measurements with a sample with reduced weight and obtained virtually the same values for the isomer shift, quadrupole splitting and line width (cf., Table S7 in the supporting information). In Table 3 the molar fraction of high-spin molecules (ν_{HS}) determined by both Mössbauer spectroscopy and magnetic susceptibility measurements is compared. The values obtained from this match well and thus allow the data from both experiments to be compared.

Table 3. Comparison of the molar fraction of high-spin molecules (γ_{HS}) determined by Mössbauer spectroscopy and magnetic susceptibility measurements.

T (K)	γ_{HS} ^[a]	γ_{HS} ^[b]	γ_{HS} ^[c]
300	1.00	-	1.00
186	0.71	-	0.74
161	0.55	0.53	0.60
136	0.44	0.45	0.51
50	0.09	0.08	0.16

[a] sample weight of ca 80 mg and [b] sample weight of ca. 40 mg: Values determined by Mössbauer spectroscopy (cf., Table S7). [c] Values determined by our magnetic susceptibility measurements (cf., Figure 9b), assuming that the value of $\chi_M T = 3.14 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ measured at $T = 300 \text{ K}$ corresponds to $\gamma_{HS} = 1.00$.

The overall determined line widths range between $\Gamma_{FWHM} = 0.22$ and 0.27 mm s^{-1} and are close to the experimental line widths of our spectrometer (i.e., $< 0.24 \text{ mm s}^{-1}$), confirming the good quality of the sample used in these measurements and suggesting the presence of only equivalent iron sites. However, as clearly observed in the spectrum obtained at $T = 300 \text{ K}$, the relative intensities (A_2/A_1) of the two corresponding lines of a given doublet are different, which we attributed to the presence of texture effects due to partial orientations of crystallites on compacting the powder in the sample containment. Alternatively, deviations from the expected value of $A_2/A_1 = 1$ in case of absent texture can also be caused by presence of two slightly different iron sites. This, and the observation of a stepwise SCO in the magnetic susceptibility measurements gave reason to analyze the spectrum at $T = 300 \text{ K}$ also with two non-equivalent iron sites (cf., Figure S5).

Interestingly, a site population ratio of 3:1 for both iron(II) HS sites are determined in good agreement with elemental analysis, that suggest the presence of 0.75 eq. co-crystallized solvent. However, it should be noted here, that this value of the site population ratio is strongly dependent on the starting values used in the fit and, hence, this result is not significant enough to safely rule out the presence of only equivalent iron sites in **5**. Furthermore, within this model, it is expected that due to different critical temperatures of the spin crossover, associated with the anticipated slightly different iron sites, the site population ratio should also be dependent on the temperature. Unfortunately, due to the very similar Mössbauer values for the isomer shift and quadrupole splitting for these two iron sites, a reliable determination of the site population ratio cannot be achieved. Certainly, at low temperatures when the SCO is completed, this model predicts a site population ratio of again 3:1 for the two non-equivalent (LS) iron sites A fit of the spectrum recorded at $T = 50 \text{ K}$ based on these assumptions revealed again a good agreement with the experimental data (cf., Figure S6 in the Supporting Information). In summary, considering co-crystallized toluene suggested by elemental analysis the existence of two iron sites with a slightly different chemical surrounding seems possible. But the 3:1

ratio does not support the occurrence of the plateau at a 1:1 HS:LS ratio and the data obtained from Mössbauer spectroscopy also support the presence of only equivalent iron sites.

7.3 Conclusion

In this study, the synthesis of a new equatorial Schiff base-like ligand bearing a redox active unit based on tetrathiafulvalene (TTF) is described. DFT modeling of the electronic structure of TTF-LH_2 and a series of π -varied congeners confirms the incorporation of potent TTF-borne donor levels. The ligand TTF-LH_2 was used in an attempt to combine spin crossover and redox active behavior in iron(II) coordination compounds. Indeed, the synthesis of two novel iron(II) complexes with the monodentate ligand pyridine (**4**) and the bridging bidentate ligand *trans*-1,2-bis(4-pyridylethylene) (bpee) (**5**) was successful presenting the first iron(II) complexes of that ligand type. Extended DFT-based modeling indicates very mild influence of the equatorial ligand scaffold on the spin crossover energies, indicating conserved ligand-field strength throughout the entire ligand family. In fact, UV-Vis and VT-UV-Vis experiments of **5**, **4** and **REF** ($[\text{Fe}^{\text{PD}}\text{L}(\text{py})_2]$) with PD = phenyldiamine) support this theory. The main species in pyridine solution at room temperature are the HS complexes, whereas in VT-UV-Vis experiments we successfully identified the in-growing of the associated LS species. Magnetic susceptibility measurements and Mössbauer spectroscopy in the solid state also showed that both compounds have interesting SCO behavior. While complex **4** repeatedly and reversibly passes through $T_{1/2} = 146$ K, despite intervening heating to 400 K, complex **5** exhibits a step wise transition with a small plateau at 154 K whose characteristics depends on the amount of co-crystallized toluene. Gradual heating of the compound results in a change of the stepwise spin transition behavior. The comparison with a suitable reference compound revealed additivity among TTF-related chromophores and metal-borne motifs of **REF** in the spectra of **4**, what suggests broadly uncoupled chromophores. This notion is corroborated by cyclovoltammograms of **4** which cleanly integrate the CVs of **3** and **REF** without affecting the potentials. However, the half wave potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox process seems to be unaffected by the presence of the TTF unit in the equatorial ligand as the values for **REF**, **4** and **5** are almost identical and in a typical range for this ligand type.^[60] Spectroelectrochemical investigation showed strong similarities between the oxidation of the free ligand **3** and the oxidation of the iron center in complex **4**. This led to the conclusion that in the oxidized iron(III) state, communication between the metal center and the redox-active unit takes place, which leads to subsequent oxidation of the ligand under these conditions.

7.4 Experimental Section

Computational Details. DFT calculations were performed using ORCA2.9.1.^[82] Large TZVP basis sets^[83] were used throughout. The structures of the ligands and of the iron(II) and iron(III) complexes were optimized with the GGA functional BP86.^[84] Complexes were optimized both in their LS and HS states. Cartesian coordinates of all optimized structures are compiled in the file SI-xyz. In order to assess the SCO energies, we used five derivatives of the well-established hybrid functional B3LYP^[85–87] in single-point calculations. In these derivative functionals the amount of exact exchange a_0 has been varied stepwise from 0.20 (native B3LYP) to 0.00. Optical spectra were derived from TD-DFT routines implemented in ORCA; 80-110 low-lying transitions were computed in each case. Dispersion contributions were approximated using Grimme's DFT-D3 atom pairwise dispersion corrections of the parent B3LYP functional.^[88] Solvent effects were accounted for in a dielectric continuum approach (COSMO),^[89] parameterized for MeCN, DMF or pyridine.

If not stated otherwise all reactions were carried out using Schlenk technique with fresh degassed or distilled solvents. The precursor **1** was prepared according to literature procedures.^[40,69] Chemicals used for synthesis were commercially available and used as received. ¹H NMR spectra were recorded at room temperature with a Varian INOVA 300. Elemental analysis was measured with a Unicube from Elementar with sulfanilamide as standard. The samples were placed in a small tin boat. Mass spectra were recorded with a Finnigan MAT 8500 with a data system MASPEC II. Magnetic measurements were done on a MPMS-XL SQUID magnetometer from Quantum Design. The samples were put in a gelatin capsule and placed in a straw. Cyclic voltammetry measurements were performed with an Electrochemical Analyzer CHI610E from CH Instruments in a three-electrode setup with a platinum working and counter electrode and a Ag/AgNO₃ non-aqueous reference electrode filled with the solvent used and tetrabutylammonium hexafluorophosphate as conducting salt.

Zero-field ⁵⁷Fe Mössbauer measurements on polycrystalline powders of **5** (ca. 80 mg) were performed on a commercial transmission spectrometer with sinusoidal velocity sweep. The temperature-dependent measurements at temperatures between $T = 50$ and 300 K were conducted on a CryoVac continuous-flow cryostat. After positioning the sample container, the sample chamber was evacuated, flushed five times with helium gas, and kept at ca. 50–100 mbar during the measurement. The temperature was measured with a calibrated silicon diode located close to the sample container, providing a temperature stability of better than 0.1 K. The nominal activity of the ⁵⁷Fe Mössbauer source used was 50 mCi of ⁵⁷Co in a rhodium matrix, stored at ambient temperatures during the measurement. Velocity calibration was done with an α -iron foil at ambient temperature; the minimum experimental line width (FWHM) was $< 0.24 \text{ mm s}^{-1}$. Isomer shifts (δ) were specified relative to metallic

iron at room temperature but were not corrected in terms of the second-order Doppler shift. The spectra were analyzed by least-square fits using doublets of Lorentzian lines utilizing the software package NORMOS.^[90]

$\text{Fe}^{\text{II}}\text{LH}_2$ (3). In a mixture of DCM and acetonitrile (1:3) 5,6-diamino-2-(4,5-bis(methylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole (**1**) (0.5 g, 1.33 mmol, 1 eq.) and (*E*)-Methyl-2-(methoxymethylidene)-3-oxobutanoate (**2**) (0.63 g, 3.98 mmol, 3 eq) were suspended. The mixture was heated to reflux for 4 h. An orange precipitate already formed in the boiling heat. The mixture is allowed to cool to room temperature. The orange solid is filtered off three times washed with methanol and dried in air. Yield: 0.59 g (628.82 g mol⁻¹, 71 %). Elemental analysis (C₂₄H₂₄N₂O₆S₆, %) calcd. C 45.84, H 3.85, N 4.45, S 30.59; found C 45.45, H 3.83, N 4.83, S 30.89. ¹H NMR (298 K, dms_o-d₆, 300 MHz): δ = 2.42 (s, 6H, COMe), 2.46 (s, 6H, SMe), 3.69 (s, 6H, CO₂Me), 7.79 (s, 2H, CH_{arom}), 8.22 (d, ³J = 12.7 Hz, 2H, CH), 12.44 (d, ³J = 12.8 Hz, 2H, NH). – MS ((+)-DEI), 70 eV): *m/z* (%) = 628 (3) [M]⁺, 480 (32) [C₁₈H₁₂N₂O₆S₄], 43 (100) [C₂H₃O⁺].

[Fe^{II}L(py)₂] (4). In pyridine (16 mL) the ligand H₂L (**3**) (0.5 g, 7.95 mmol, 1 eq.) and iron(II) acetate (0.22 g, 12.72 mmol, 1.6 eq) were dissolved. After addition of methanol (16 mL), the mixture was heated under reflux for 3 h. After cooling to room temperature, a black fine-crystalline solid precipitated. The mixture was left to stand at 8°C for 12 h. The solid was filtered off, washed with 3 mL methanol three times, and dried under vacuo. Yield: 0.455 g (840.86 g mol⁻¹, 68 %) Elemental analysis (C₃₄H₃₂FeN₄O₆S₆, %) calcd. C 48.57; H 3.84; N 6.66; S 22.88 found C 48.65; H 3.87; N 6.99; S 22.23 – MS ((+)-DEI), 70 eV): *m/z* (%) = 682 (5) [FeL]⁺, 624 (3) [L]⁺, 79 (100) [py]⁺.

{[Fe^{II}L(bpee)]·0.75(tol)}_n (5). In toluene (24 mL) [FeL(py)₂] (**4**) (0.2 g, 2.37 mmol, 1 eq.) and *trans*-1,2-bis(4-pyridyl)ethylene (bpee) (0.43 g, 23,70 mmol, 10 eq.) were dissolved. The mixture was heated under reflux for 2 h. Already in the boiling heat a green powder precipitated. After cooling down to room temperature the powder was filtered, washed three times with 3 mL of methanol and dried in vacuo. Yield: 0.156 g (864.88 g mol⁻¹, 76 %) Elemental analysis (C_{41.25}H₃₈FeN₄O₆S₆, %) calcd. C 53.05; H 4.10; N 6.00; S 20.60 found C 53.37; H 4.18; N 6.17; S 20.11 – MS ((+)-DEI), 70 eV): *m/z* (%) = 682 (8) [FeL]⁺, 182 (100) [C₁₂H₁₀N₂].

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Supporting Information

For this paper supporting information is available: NMR spectrum of **3**, crystallographic data, bond lengths and angles, metrics of intra- and intermolecular H-bonding, supplementary information of the DFT-derived (B3LYP-D3/TZVP) SCO energies with fitting results of the linear regression, frontier molecular orbital landscape of ligand **3**, reference compound **REF** and TTF-containing **4**, VT-UV-Vis absorption spectroscopy at high temperature, detailed data on the Mössbauer parameter, alternative fitting, all oxidation and reduction values for compound **REF**, **3**, **4** and **5** at different scan rates

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7.6 Supporting Information

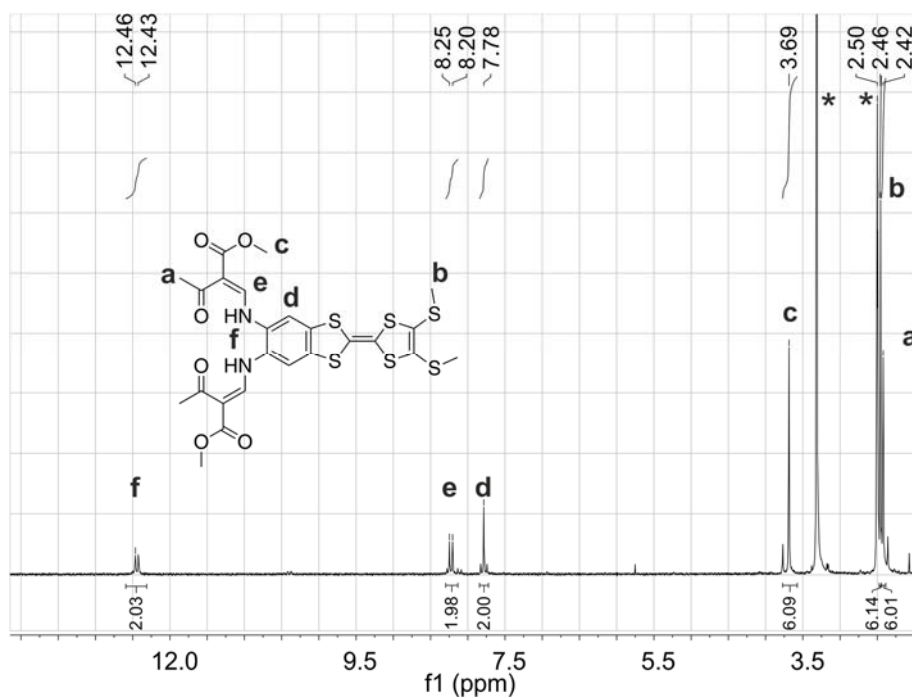


Figure S1. ¹H NMR spectrum of **3** in dmsO-d₆ (300 MHz) with signal assignment. Signals of solvent marked with *.

Table S1. Crystallographic data of the ligand ^{TT}F₂LH₂.

Compound	^{TT} F ₂ LH ₂
Formula	C ₂₄ H ₂₄ N ₂ O ₆ S ₆
CCDC	1981418
<i>Mr</i> / g mol ⁻¹	628.81
λ / Å	0.71073
<i>T</i> / K	133
Crystal system	monoclinic
Space group	C2/c
<i>a</i> / Å	21.0453(8)
<i>b</i> / Å	19.6783(9)
<i>c</i> / Å	15.7622(6)
α / °	90
β / °	123.387(3)
γ / °	90
<i>V</i> / Å ³	5450.4(4)
<i>Z</i>	8
<i>d</i> _{calcd} / mg cm ⁻³	1.533
μ / mm ⁻¹	0.546
Θ range / °	2.3–28.5
Reflections collected	17040
Indep. reflections	6447
<i>R</i> _{int}	0.112
<i>R</i> (F)	0.0628
w <i>R</i> ₂ (F ₂)	0.1717
Goof	0.93

Iron(II) Spin Crossover Complexes Based on a Redox Active Equatorial Schiff Base-Like Ligand

Table S2. Selected bond lengths/ Å of **3**, data in italics from DFT optimization (TPSSh-D3/TZVP/COSMO(MeCN)).

N1–C3	1.3424(4) / 1.332	N2–C6	1.341(5) / 1.331
C2–C3	1.389(5) / 1.391	C6–C7	1.377(6) / 1.389
C1–C2	1.468(6) / 1.456	C7–C8	1.464(5) / 1.458
C1–O1	1.235(5) / 1.251	C8–O2	1.242(5) / 1.251
C17–C18	1.353(6) / 1.342		
C17–S1	1.755(4) / 1.769	C18–S2	1.762(4) / 1.768(1)
C17–S6	1.763(4) / 1.769	C18–S5	1.744(4) / 1.768(1)
C21–S5	1.772(4) / 1.777	C19–S2	1.749(4) / 1.780
C16–S1	1.752(3) / 1.775	C23–S6	1.755(4) / 1.771
C(16)–C(23)	1.399(5) / 1.399	C(19)–C(21)	1.341(5) / 1.348

Table S3. Summary of the C–H... π / X–Y... π interactions of **3**.

	C_g	H... C_g [Å] Y... C_g [Å]	X–H... C_g [°] X–Y... C_g [°]	X... C_g [Å]
C12–H12C	C4–C5–C24–C23–C16–C15 ^a	2.78	120	3.376(5)
C13–O5	S2–C18–S5–C21–C29 ^b	3.581(5)	89.3(3)	3.764(5)

a: 3/2–x, 1/2–y, 2–z; b: 1–x, y, 3/2–z.

Table S4. Selected distances [Å] and angles [°] of the π – π interaction in **3**. $C_g(I)$ is the centroid of the ring with number I, α is the dihedral angle between the rings, β is the angle between the vector $C_g(I) \rightarrow C_g(J)$ and the normal ring I, γ is the angle between the vector $C_g(I) \rightarrow C_g(J)$ and the ring J.

$C_g(I)$	$C_g(J)$	C_g – C_g	α	β	γ
C4–C5–C24–C23–C16–C15	C4–C5–C24–C23–C16–C15 ^a	3.466(3)	6.2(2)	14.7	14.7

a: 1–x, y, 3/2–z.

Table S5. Metrics of intramolecular and intermolecular H-bonding in **3**, data in italics from DFT optimization (TPSSh-D3/TZVP/COSMO(MeCN)).

Donor	Acceptor	H...A [Å]	D...A [Å]	D–H...A [°]
N1–H1	O1	1.95 / 1.723	2.581(4) / 2.565	127 / 135
N1–H1	N2	2.43 / 2.613	2.752(4) / 2.754	102 / 87
N2–H2	O2	1.89 / 1.722	2.574(4) / 2.567	133 / 136
N2–H2	N1	2.38 / 2.504	2.752(4) / 2.754	106 / 93
C11–H11B	O1 ^a	2.53	3.458(5)	158
C14–H14C	O4 ^b	2.55	3.501(7)	164
C24–H24	S4 ^c	2.84	3.759(3)	164

a: x, –y, –1/2+z; b: 3/2–x, 1/2–y, 2–z; c: 1–x, 1–y, 1–z.

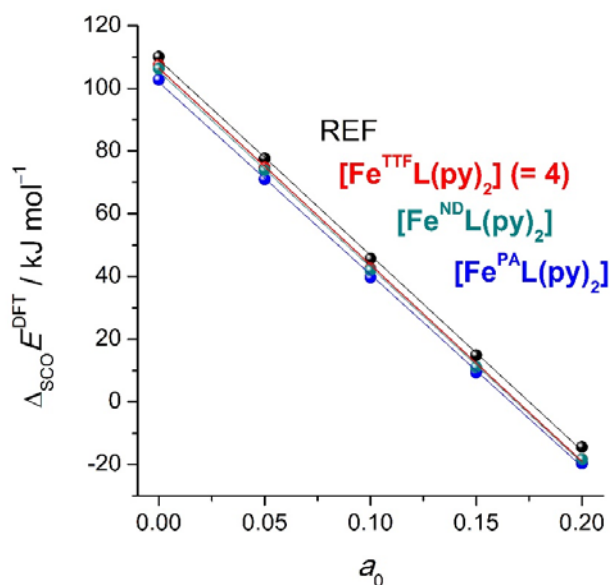


Figure S2. DFT-derived (B3LYP-D3/TZVP) apparent SCO energies of iron(II) complexes as a function of the amount of exact exchange α_0 .

Table S6. Fitting results of the linear regressions in Figure S2; $\Delta_{\text{SCO}}E = \Delta_{\text{SCO}}E^0 - \alpha_0 \times \delta_{\text{SCO}}E$.

	$\Delta_{\text{SCO}}E^0$ [kJ mol ⁻¹]	$\delta_{\text{SCO}}E$ [kJ mol ⁻¹]
REF	109.1 ± 0.9	623 ± 7
4	106.5 ± 1.0	627 ± 8
[Fe ND L(py) ₂]	105.4 ± 0.8	624 ± 7
[Fe ^{PA} L(py) ₂]	102.0 ± 0.8	613 ± 6

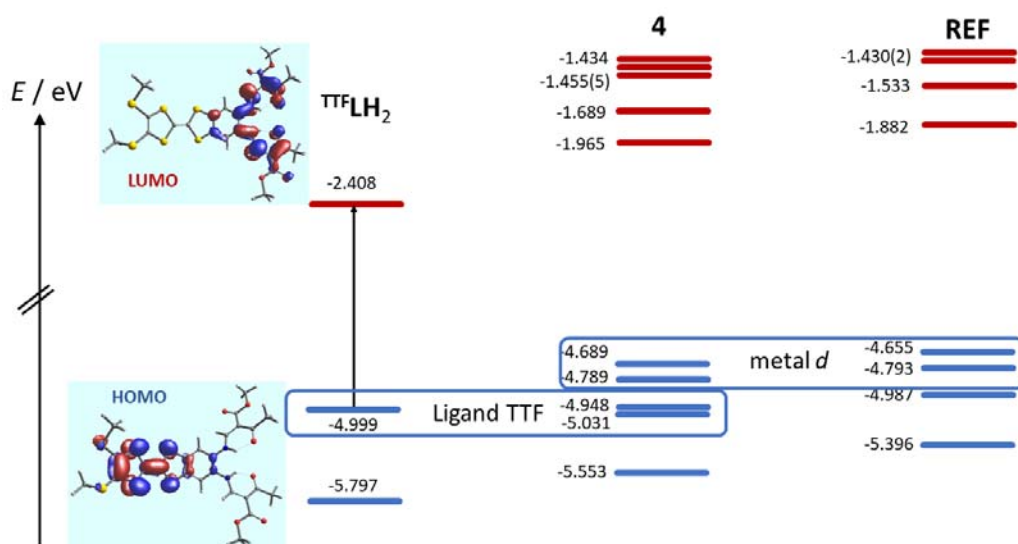


Figure S3. Frontier molecular orbital landscape of ligand **3**, reference compound **REF** and TTF-containing **4** (complexes in their singlet state).

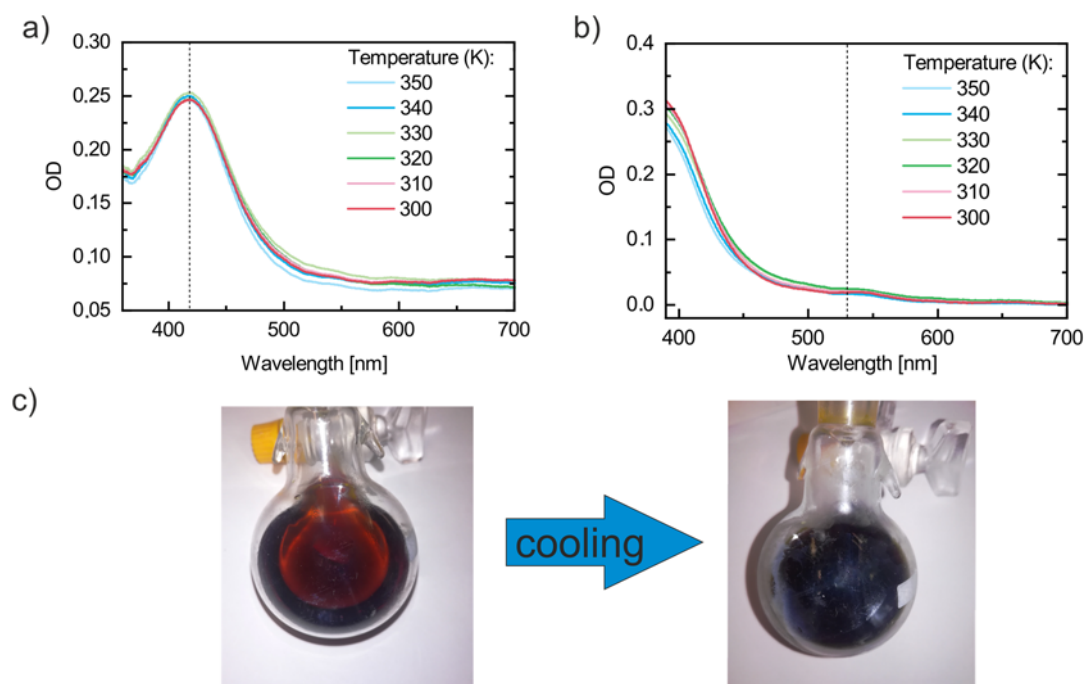


Figure S4. VT-UV-Vis absorption spectroscopy of (a) $[\text{Fe}^{\text{TFFL}}(\text{py})_2]$ (**4**) and (b) $[\text{Fe}^{\text{PDL}}(\text{py})_2]$ (**REF**) in pyridine as solvent. Solutions were cooled to 235 K and incrementally heated in 5 or 10 K steps. Presented for $T > 300$ K. (c) Change in color visible to the naked eye when cooling a 10 mM concentrated pyridine:DCM solution (1:1) of $[\text{Fe}^{\text{TFFL}}(\text{py})_2]$ with liquid nitrogen.

Table S7. Summary of Mössbauer parameters determined for **5** by a fit with doublets of Lorentzian lines, with isomer shift δ , quadrupole splitting ΔE_Q and Lorentzian line width Γ_{FWHM} (full width at half maximum). A_2/A_1 describes the relative intensities of the two corresponding lines of a given doublet, while AREA quotes the relative (integral) intensities of the individual doublet. The measurements were carried out upon zero-field cooling.

ca. 80 mg sample weight (**5**)

T (K)	δ [a] (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	Γ_{FWHM} (mm s ⁻¹)	A_2/A_1 [b]	AREA (%)
300 ^[c]	0.865(23)	2.194(7)	0.214(45)	1.09(1)**	25.2
	0.940(13)	2.207(3)	0.265(5)	1.09(1)**	74.8
300	0.918(1)	2.203(2)	0.273(2)	1.09(1)	100
186	1.000(1)	2.256(3)	0.263(2)	1.09*	70.9
	0.423(2)	1.277(3)	0.249(7)	0.78*	29.1
161	1.016(2)	2.257(3)	0.258(4)	1.09*	55.3
	0.435(2)	1.254(4)	0.254(6)	0.78*	44.7
136	1.031(1)	2.262(2)	0.256(3)	1.09*	44.2
	0.445(1)	1.246(2)	0.258(2)	0.78*	55.8
50	1.096(4)	2.241(8)	0.222(11)	1.09*	9.3
	0.466(1)	1.230(1)	0.273(2)	0.78(1)	90.7

ca. 40 mg sample weight (5')

T (K)	δ ^[a] (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	Γ_{FWHM} (mm s ⁻¹)	A_2/A_1 ^[b]	AREA (%)
161	1.013(1)	2.260(4)	0.261(4)	1.09*	52.9
	0.438(2)	1.239(4)	0.267(6)	0.85*	47.1
136	1.026(3)	2.38(7)	0.250(7)	1.09*	44.7
	0.443(1)	1.234(3)	0.246(4)	0.85*	55.3
50	1.110(6)	2.300(23)	0.235(23)	1.09*	8.1
	0.473(1)	1.243(2)	0.272(3)	0.85(1)	91.9
50 ^[d]	1.126(9)	2.239(15)	0.244(23)	1.09*	8.3
	0.495(2)	1.250(3)	0.249(4)	0.85(1)**	68.8**
	0.402(5)	1.212(6)	0.229(9)	0.85(1)**	22.9**

Values marked with an asterisk (*) were fixed in the fit. [a]: The isomer shifts were specified relative to metallic iron at room temperature but were not corrected in terms of the second-order Doppler shift. [b]: In case of polycrystalline powders with random orientations of the crystallites, the expectation value of this parameter is $A_2/A_1 = 1$.^[98] Deviations from this value, which are clearly observed at $T = 300$ K, are attributed to the presence of texture effects due to partial orientations of crystallites on compacting the powder in the sample containment. [c] and [d]: An alternative fit was also performed with [c] two Fe(II) high-spin sites or [d] one Fe(II) high-spin and two Fe(II) low-spin sites; to reduce the (large) number of free fit parameters in these models, we used the same parameter A_2/A_1 and a fixed site population ratio of 3:1 for both corresponding Fe(II) sites (these values were marked with (**)).

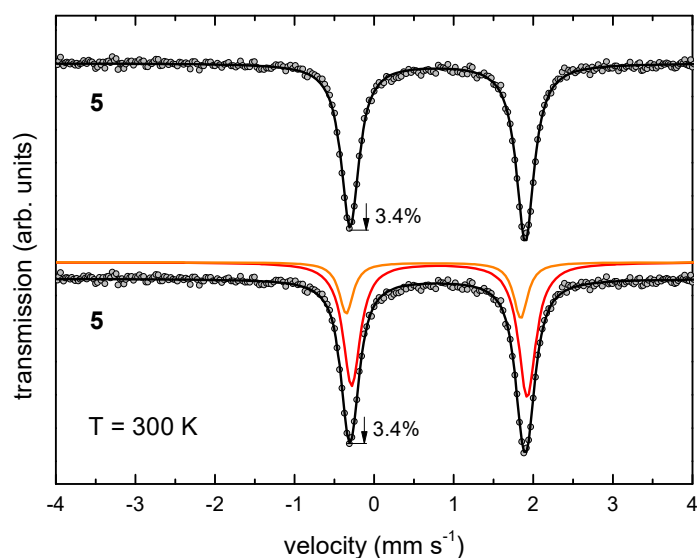


Figure S5. Zero-field ⁵⁷Fe Mössbauer spectrum of **5**, recorded at $T = 300$ K. Symbols: Experimental data. Lines: Alternative fits with one or two doublets of Lorentzian lines, respectively (see main text). The colored lines illustrate the corresponding sub-spectra of the fit, which are attributed here to two slightly different Fe(II) high-spin sites (red and orange). The parameters of the fit are summarized in Table S3.

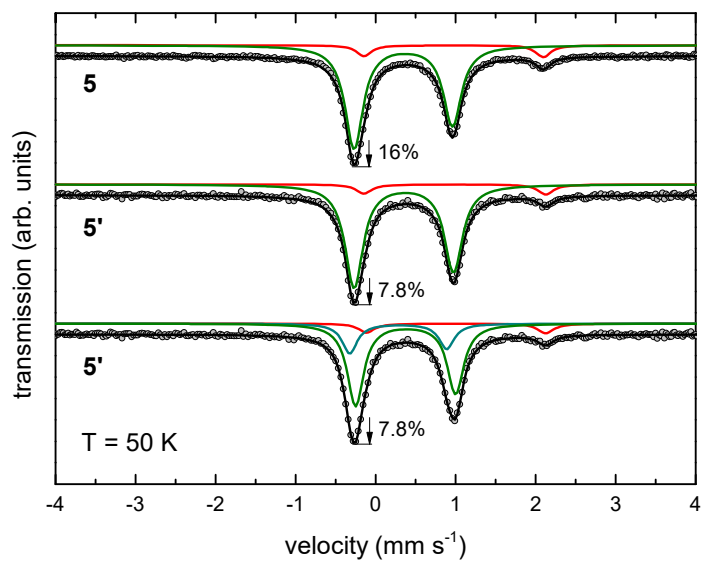


Figure S6. Zero-field ^{57}Fe Mössbauer spectra of two samples of **5** with different sample weight of ca. 80 (**5**) and ca. 40 mg (**5'**), respectively, recorded at $T = 50$ K to confirm the validity of the thin absorber approximation. Symbols: Experimental data. Lines: Alternative fits with two or three doublets of Lorentzian lines, respectively (see main text). The colored lines illustrate the corresponding sub-spectra of the fit, which are attributed to the Fe(II) high-spin (red) and Fe(II) low-spin sites (green and/or turquoise). The parameters of the fit are summarized in Table S3.

Table S8. Oxidation and reduction values for compound **REF**, **3**, **4** and **5** at different scan rates.

	scan rate [mV]	E_p^{Ox1} [V]	E_p^{Ox2} [V]	E_p^{Ox3} [V]	E_p^{Ox4} [V]	E_p^{Ox5} [V]	E_p^{Red1} [V]	E_p^{Red2} [V]	E_p^{Red3} [V]	E_p^{Red4} [V]
3	25	/	0.215	0.396	/	/	0.140	0.285	/	-0.943
	50	/	0.218	0.391	/	/	0.143	0.301	/	-0.921
	100	/	0.218	0.338	/	/	0.146	0.305	/	-0.94
REF	25	-0.362	/	/	/	/	-0.428	/	/	/
	50	-0.360	/	/	/	/	-0.429	/	/	/
	100	-0.360	/	/	/	/	-0.431	/	/	/
4	25	-0.353	0.201	0.383	/	/	-0.417	0.138	0.304	/
	50	-0.354	0.201	0.376	/	/	-0.422	0.138	0.304	/
	100	-0.339	0.207	0.408	/	/	-0.433	0.121	0.301	/
5	25	-0.353	0.196	0.375	0.495	0.833	-0.422	0.135	0.298	/
	50	-0.354	0.199	0.374	/	0.831	-0.434	0.133	0.285	/
	100	-0.351	0.203	0.379	/	0.833	-0.428	0.137	0.295	/
Fc^{0/+}	25	0.079	/	/	/	/	-0.025	/	/	/
	50	0.089	/	/	/	/	-0.034	/	/	/
	100	0.99	/	/	/	/	-0.047	/	/	/

TGA measurements

Thermogravimetric Analysis: Thermogravimetric analysis was done with a Netzsch TG 209 F1 Libra under nitrogen atmosphere using 4 mg–10 mg of the sample with a heating rate of 10 K min⁻¹.

Complex **4** shows no appreciable loss of mass up to 150°C (423 K). An abrupt loss of 11% in mass occurs from this point on. This can be attributed to a loss of about 1.17 pyridine. Above 200°C (473 K), the compound decomposes continuously.

Complex **5** shows no appreciable loss of mass up to 75°C (348 K). From this point on a continuous loss of mass totaling 6.4% to 170°C (443 K) is observed. This corresponds roughly to the 0.75 toluene (one would expect a loss of 7.4% in this case) which, according to elemental analysis, is co-crystallized in complex **5**. From this point a plateau forms up to 200°C. A further loss of mass of about 8.4% occurs up to a temperature of 256°C. Starting at 288°C the sample is continuously decomposed.

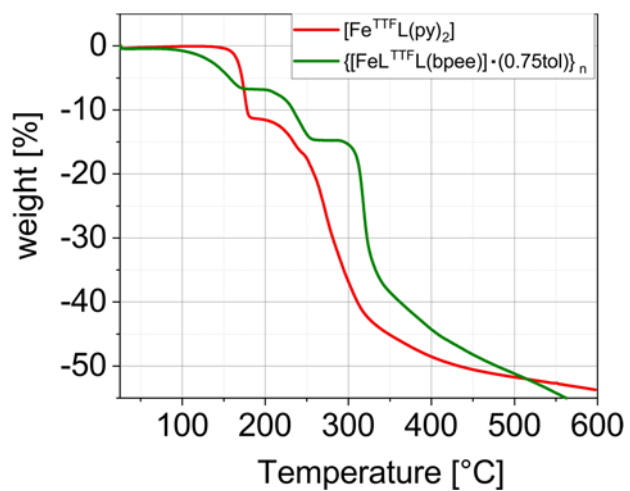


Figure S7. TGA measurement of $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ (4) and $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})] \cdot (0.75\text{tol})\}_n$ (5).

8. Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

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Abstract

Three novel iron(II) complexes based on an equatorial N₂O₂ coordinating Schiff base-like ligand bearing CF₃-groups and the redox active tetrathiafulvalene (TTF) unit are investigated. Two of the complexes are axially decorated with either pyridine (py) or 4-(dimethylamino)-pyridine (DMAP) as monodentate ligands. Additionally, a coordination polymer was formed with *trans*-1,2-bis(4-pyridyl) ethene (bpee) as bridging bidentate ligand. Crystals suitable for single X-ray structure analysis were obtained for the pyridine complex [Fe^{TTF}L_{CF₃}(py)₂]. The complexes were characterized by magnetic susceptibility measurements, *T*-dependent ¹H NMR spectroscopy and cyclic voltammetry. All three compounds show spin transition behavior. The coordination polymer {[Fe^{TTF}L_{CF₃}(bpee)]_n and the complex with DMAP as ligand [Fe^{TTF}L_{CF₃}(DMAP)₂], in particular, show almost complete spin crossover with *T*_{1/2} = 187 K for {[Fe^{TTF}L_{CF₃}(bpee)]_n and a very gradual transition for [Fe^{TTF}L_{CF₃}(DMAP)₂]. [Fe^{TTF}L_{CF₃}(py)₂] shows incomplete spin crossover (SCO) behavior and loss of axial ligands upon heating. Temperature dependent ¹H NMR spectroscopy was conducted for [Fe^{TTF}L_{CF₃}(py)₂] and reference system [FeL_{CF₃}(py)₂] (REF) to clarify if the incomplete SCO behavior is caused by packing effects. Indeed, the NMR spectra of both compounds show characteristic changes upon cooling which point to a SCO in solution. Additional theoretical studies are in line with those findings and support a packing borne prevention of spin transition in solid [Fe^{TTF}L_{CF₃}(py)₂]. The redox behavior of the iron(II) complexes reveals in case of the coordination polymer and the pyridine complex three reversible redox steps involving the iron center and the TTF unit. As a result of the electron-withdrawing CF₃ groups, the potential of the iron(II) oxidation is very close to the potential of the first TTF oxidation. Therefore, no clear assignment of the

redox processes in the cyclic voltammogram can be made. Spectroelectrochemical UV-Vis spectroscopy gives an insight into the nature of the first two oxidations reflecting their mixed character. Since SCO behavior was observed in ^1H NMR spectroscopy low temperature cyclic voltammetry was performed for the pyridine complex and REF. In REF the spin transition results in a cathodic shift of the electrode potential by ≈ 100 mV. The TTF-containing complex shows the same shift of the iron(II) oxidation and as a unique characteristic, a splitting of the third oxidation wave can be observed. Such behavior has to the best of our knowledge never been monitored before.

8.1 Introduction

Over the past 90 years, the scientific community has been preoccupied with the phenomenon of spin crossover (SCO), from its basic understanding to its possible applications.^[1] The switching among two electronic states of metal centers has been demonstrated for electron configurations d^4 to d^7 , with a clear predominance of d^6 configured iron(II) compounds, often associated with nitrogen or oxygen containing chelating ligands. These coordination compounds can be switched between the paramagnetic high-spin (HS, $S = 2$) and the diamagnetic low-spin (LS, $S = 0$) state by external stimuli like temperature, pressure or light irradiation.^[2,3,4] This ability makes them suitable candidates for potential molecular switches especially in the area of magneto-optical devices^[5], high density information storage^[5], light-responsive switches^[6] or spintronics^[7]. The focus of current research is on combining the SCO phenomenon with other physical or chemical effects in order to gain access to multifunctional materials for future applications.^[8] Particularly appealing is the combination with redox active ligands, since the spin-state dependence of electrical transport is a central requirement of molecular spintronics.^[9]

Valence tautomerism is a related phenomenon, which combines the spin-state change with an intra molecular redox reaction either between two metal ions or a metal ion and a coordinated redox-active ligand.^[10] Through the reversible change in the electronic structure, a potential molecular-sized application in the field of data storage is within reach.^[11] Excellent candidates for this field of research are homo- and heterometallic mixed-valence complexes due to their frequently occurring electron transfer properties.^[12] In these compounds two metal atoms are connected by an organic bridging ligand providing excellent conditions for electron transfer. Systems that have been extensively studied in this respect are predominantly cobalt complexes with the redox-active 1,2-dioxolene ligands (semiquinone, catecholate, quinone series), which are widely known for their ability to exhibit valence tautomeric behavior.^[10,13,14] Besides those cases, only a handful of electroactive organic ligands

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have been at the center of attention. However, molecules containing a unit of 2,2'-bi-1,3-dithiolydene better known as tetrathiafulvalene (TTF) are particularly suitable candidates for the synthesis of redox active coordination compounds and have been used in this manner before.^[15] TTF is a conjugated, non-aromatic 14- π -electron system that becomes aromatic in accordance with the Hückel rule during oxidation.^[16] Additionally, the two fully reversible oxidation processes are addressable at relatively low potentials ($E_{1/2}^1 = 0.37$ V and $E_{1/2}^2 = 0.67$ V vs. saturated calomel electrode (SCE) in dichloromethane (DCM)^[16] making the TTF an excellent electron donor. Coordination compounds with iron, especially iron(II), have been studied very little, if at all, with respect to valence tautomerism.^[14,17] They are of more interest because of their electrically conductive or optical properties, which in combination with SCO properties provide interesting multifunctional materials.^[17,18,19] However, if we consider the typical range of electrode potentials of the iron(II/III) couples, it is noticeable that they are often not far from those of TTF.^[3,20,21] It has been shown before that the implementation of a second donor site besides the iron(II) center enables these to communicate with each other to some point.^[14,21,22] Ideally, the strength of the interaction between these redox centers is similar to a Robin and Day classification in category II. If so, the electron would be vibrationally localized in one of the redox centers due to the presence of an activation barrier but it can be overcome by an external stimulus to trigger an intramolecular electron transfer.^[11]

Therefore, in recent work on a TTF-containing iron(II) complex **[Fe^{TTF}L(py)₂]**, we have synthetically assessed the potential of compounds with multiple redox sites. Within this study we had to notice that the metal-borne and TTF-borne electrochromes can be addressed rather independent of each other. The lack of intramolecular electronic communication was referred to the mismatch of the site-specific redox potentials. As a reaction to missing electronic communication in **[Fe^{TTF}L(py)₂]** we have reconsidered the coordination environment. In this work we present a study of a modified Schiff base-like tetradentate ligand with electron withdrawing CF₃-groups, appended close to the iron(II) coordination site. In the following we report on the structural aspects of the CH₃/CF₃ ligand modification and their reflection in electronic properties. Through these electron-withdrawing groups, a convergence of the iron-borne and TTF-localized redox potentials is indeed achieved which finally allows for electronic communication between these two redox centers. Thus, the ligand system first reported by Jäger *et al.* is to be extended, paving the way to new multifunctional materials.

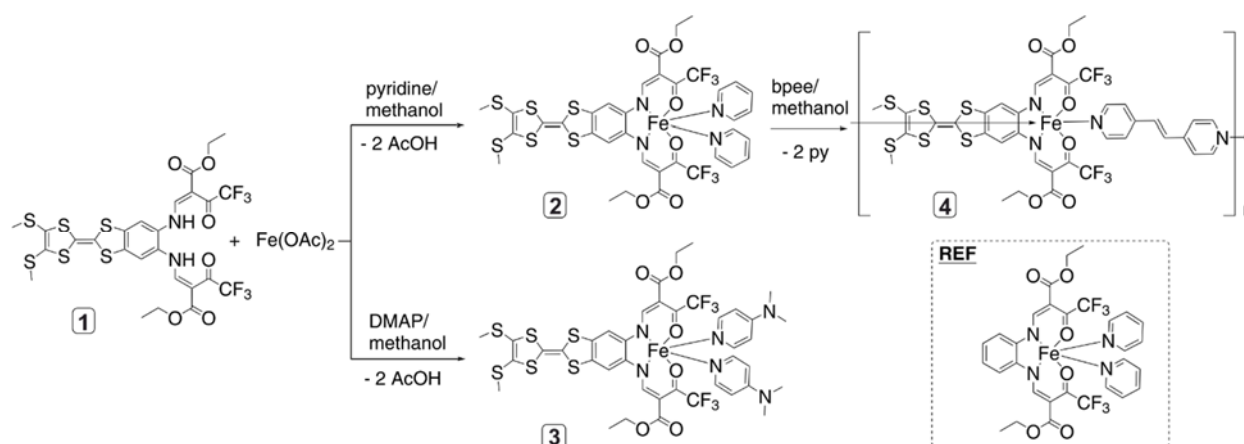
8.2 Results and Discussion

8.2.1 Synthetic Procedures

Adopting established procedures^[21,23], the Ligand $\text{TTF}_{\text{L}_{\text{CF}_3}\text{H}_2}$ (**1**) was synthesized in a thermal condensation of precursor 5,6-diamino-2-(4,5-bis(methylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole and ethyl-2-(ethoxymethylen)-4,4,4-trifluoro-3-oxobutyrate in hot DMF. The product was obtained as a red powder in good yield (92%, Scheme 1). In Figure S1 the ^1H NMR spectrum of the ligand and the signal assignment are displayed. Based on well-known similar systems, a signal assignment based on spin–spin couplings could be made.^[21,23] The presence of a doubled single set of some proton sites with 1.3:0.7 intensity reflects the presence of two tautomers due to *cis-trans* isomerism of the double bond (see supporting information). This observation clearly reflects the presence of the strongly withdrawing CF_3 groups in **1** as its CH_3 -congener TTF_{LH_2} does not show extensive signal doubling.^[21] Interestingly the amino function of the new ligand is shifted to high field compared with the CH_3 containing sibling TTF_{LH_2} . Apart from these distinctive features, the spectra of both compounds are highly similar with respect to the peak positions. In both derivatives the chemical shift of the protons of the phenyl ring, the thiomethyl-groups and the one next to the amino group are almost identical. Accordingly, there no long-range inductive effect of the CF_3 groups can be identified.

A one-pot reaction of ligand **1** with a slight excess of anhydrous iron(II) acetate in a 1:3 mixture of pyridine and methanol, heated to reflux, yielded a 1:1 adduct of ligand and metal, compatible with the formulation $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ (**2**). Black needles could be separated from the mixture after storage at -22°C for several days. DMAP (4-(dimethylamino)-pyridine) serves as an alternative axial ligand in $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ (**3**). The coordination polymer $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ (**4**) was obtained as a brown powder by ligand metathesis through heating **2** in methanol with a tenfold excess of *trans*-1,2-bis(4-pyridyl)ethene (**bpee**) yielding a brown powder. By using DMAP instead of pyridine as axial ligand, the subtly different complex $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ (**3**) can be obtained. Scheme 1 gives an overview of the synthetic procedures.

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Scheme 1 Synthesis of the mononuclear iron(II) complexes [Fe^{TTF}L_{CF₃}(py)₂] (**2**), [Fe^{TTF}L_{CF₃}(DMAP)₂] (**3**) and 1D coordination polymer {[Fe^{TTF}L_{CF₃}(bpee)]_n} (**4**).

8.2.2 Single Crystal X-ray Structure Analysis

Crystals suitable for X-ray structure analysis of **2** were obtained directly from the synthesis solution of **2** after storage at -22°C for 5 days. The crystallographic data were obtained at 180 K, crystallographic details are summarized in Table S1 (Supporting Information, Table S1). The material crystallizes in the orthorhombic space group *Pbcn* with eight formula units in the unit cell. The ORTEP drawing of one formula unit together with the used atom numbering scheme is displayed in Figure 1. In the crystal, **2** features as a fairly undisturbed octahedral iron(II) complex, together with co-crystallized methanol and pyridine, to obey the analytical formula **2** · (MeOH)(py). Due to strong disorder co-crystallized pyridine molecules had to be removed from the final model using the Squeeze routine within Platon. Additional disorder is located in the non-coordinated carbonyls and the CF₃ groups (C16, C26 O3, F1, and F3).

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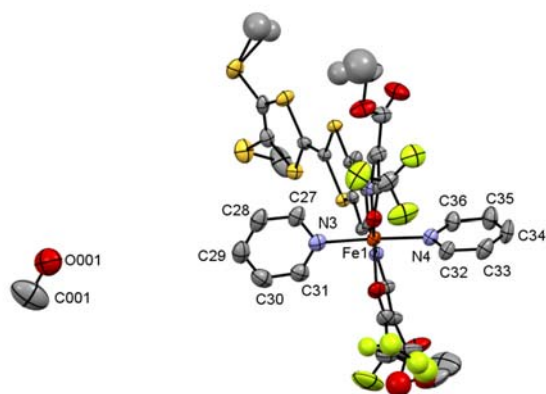
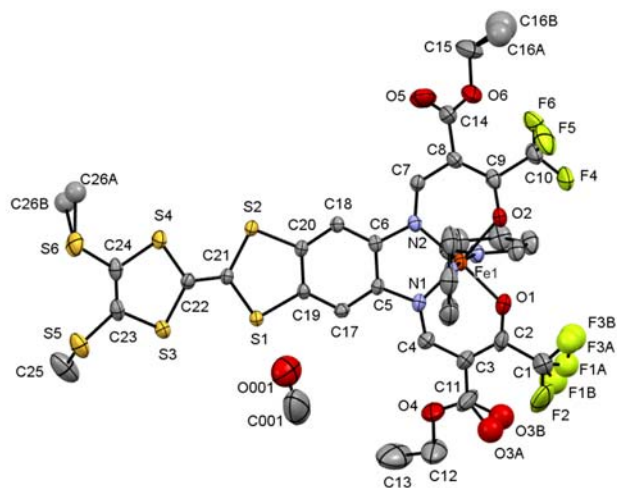


Figure 1 ORTEP drawing of the asymmetric unit of complex **2** with the atom numbering scheme (top: equatorial ligand bottom: axial ligands) used in the text. Hydrogen atoms are omitted for clarity. Thermal ellipsoids presented at 50% level.

The iron(II) center in **2** resides in an octahedral N_4O_2 coordination sphere which subsumes the planar environment of the redox active equatorial Schiff base-like ligand and two axial pyridine ligands. Selected bond lengths and angles within the inner coordination sphere are summarized in Table 1. Bond length and angle consideration aids in an assignment of the spin state of the iron(II) center. At 180 K complex **2** is clearly in the electronic low-spin state, as can be read from the short equatorial Fe–O and Fe–N bond lengths and the small equatorial opening angle, $O_{eq}\text{–Fe–}O_{eq}$ of only 93° that serve as diagnostic spin-state marker.^[2] Furthermore, the internal C=C bond of the TTF moiety is a good indicator of the oxidation state of the equatorial ligand. In **2** the bond length equals 1.34 Å, indicating an unoxidized, neutral state of the tetrathiafulvalene (TTF) unit.^[2,19,24]

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Table 1 Selected bond lengths /Å and angles /° within the inner coordination sphere of the iron(II) complex $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ at 180 K.

Fe–N _{eq}	Fe–O _{eq}	Fe–N _{ax}	O _{eq} –Fe–O _{eq}	N _{ax} –Fe–N _{ax}
1.926(3)	1.944(3)	2.035(3)	92.86(12)	173.79(13)
1.935(3)	1.958(3)	2.038(3)		

Decisively responsible for packing within the crystal is the contact between the sulfur atoms S1 and S2 of one complex molecule with S1 and S2 of a neighboring one (see Figure 2). This leads to a head-to-tail arrangement of two complex molecules rotated by 180° to each other. Due to the small distance of only 3.5 Å between the two sulfur atoms S1 and S2, dispersion forces among these are conceivable. This dispersion dimer is located in the center of the unit cell. Both above and below, two additional molecules are arranged at a rotation angle of 90° with respect to the stacking pair. These are again rotated by 180° relative to each other, giving a node of rotated TTF-units along the axis *a* in the center of the unit cell. This rotated arrangement creates voids filled by pyridine. In Figure 3 a more extended view of the crystal packing in solid **2** is displayed. Some intra- and intermolecular short contacts (details see Table 2) can be identified. The co-crystallized methanol molecule is involved in the two intermolecular contacts where one molecule is in contact with two different complex molecules, either S5 from the TTF backbone or O5 from the equatorial plane. Thereby, electrically conductive properties of the material could be favored.^[15,17]

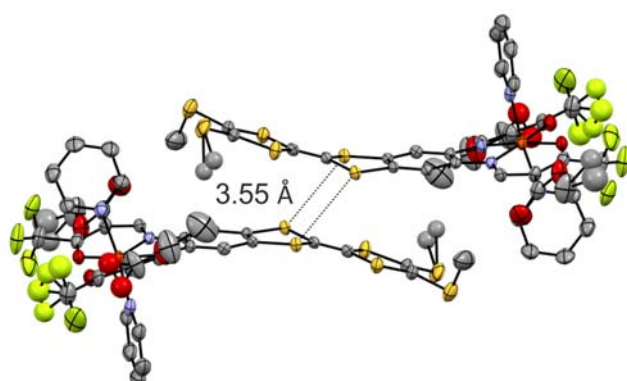


Figure 2 Head-to-tail stacking of two formula units of **2**, forming dispersion dimers within the unit cell of **2** · (MeOH)(py); hydrogen atoms are omitted for visual clarity.

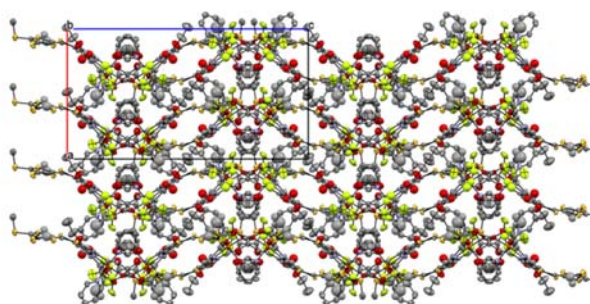
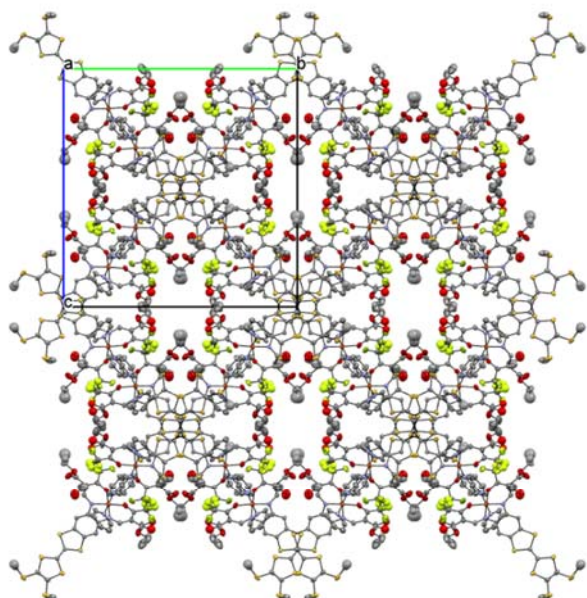


Figure 3 Molecular packing of **2 · (MeOH)(py)** in the crystal at 180 K. Top: view along the axis *a*. Bottom: view along axis *b*; hydrogen atoms and pyridine molecules are omitted for clarity.

Table 2 Selected distances /Å and angles /° of short contacts observed in the crystal structure.

D–H···A	D–H	H···A	A···D	D–H···A
O001–H001···O5 ^[a]	0.84	2.57	3.051(6)	117
O001–H001···S5 ^[a]	0.84	2.61	3.352(5)	147
C4–H4···O4	0.95	2.24	2.628(5)	103
C32–H32···O1	0.95	2.58	2.964(5)	105
C32–H32···O2	0.95	2.59	2.916(5)	101

^[a][1/2+x,1-y,z]

8.2.3 Magnetic Susceptibility Measurements

Magnetic susceptibility measurements in a temperature range from either 375 K or 400 K to 50 K were performed for $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ (**2**) and $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ (**4**). Unlike the previously reported, very similar coordination polymer $\{[\text{Fe}^{\text{TTF}}\text{L}(\text{bpee})]\}_n$, no loss of solvent upon heating to 400 K is observed in thermogravimetry of the coordination polymer **4**. The latter shows high stability up to 485 K. For this reason, **4** could be heated up to 400 K during magnetic susceptibility measurements with conserved $\chi_{\text{M}}T$ plots after iterative heating cycles. The resulting $\chi_{\text{M}}T$ vs. T plot in Figure 4a reveals almost complete spin crossover from the typical HS-iron(II) value of $3.3 \text{ cm}^3 \text{ K mol}^{-1}$ at RT,^[2,25] down to $0.73 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 K where a fraction of approximately 80 % of the iron centers is in the LS state. The curve progression is rather gradual with a critical temperature of $T_{1/2} = 187 \text{ K}$ where 50 % of the iron(II) centers are in the diamagnetic LS state.

By contrast, thermogravimetric analyses reveal (see supporting information) the mononuclear pyridine complex **2** to be stable only up to 373 K. Therefore **2** was only heated up to this temperature. The thermal robustness was addressed in heating-cooling cycles with T_{max} increased stepwise from 300 K to 375 K (Figure 4b). As a result of the continuous increasing T_{max} , SCO becomes more and more incomplete for the mononuclear pyridine complex **2**, whereas the high-temperature value of $\chi_{\text{M}}T$ varies only slightly with T_{max} ($3.19 - 3.41 \text{ cm}^3 \text{ K mol}^{-1}$). This finding is in agreement with previous results on similar systems that are known to lose axial pyridine ligands upon heating.^[26] Upon cooling to 50 K during the first cycle $\chi_{\text{M}}T$ gradually decreases to $2.09 \text{ cm}^3 \text{ K mol}^{-1}$. This value is neither characteristic for the HS, nor for the LS state of iron(II). Among the several reasons for the incompleteness of the spin transition, complex-intrinsic restrictions in the packing^[27] can be safely discarded as the diamagnetic LS state can be reached in the single crystal **2** · (MeOH)(py) already at 180 K. As complete SCO is impossible in the powdered product **2**, the incorporation of large amounts of solvent and the associated impact on the coordination environment seem to play a decisive role. This finding clearly deviates from the previously reported CH_3 congener **2**^{CH₃} where almost complete SCO upon cooling and a high thermal stability were identified.

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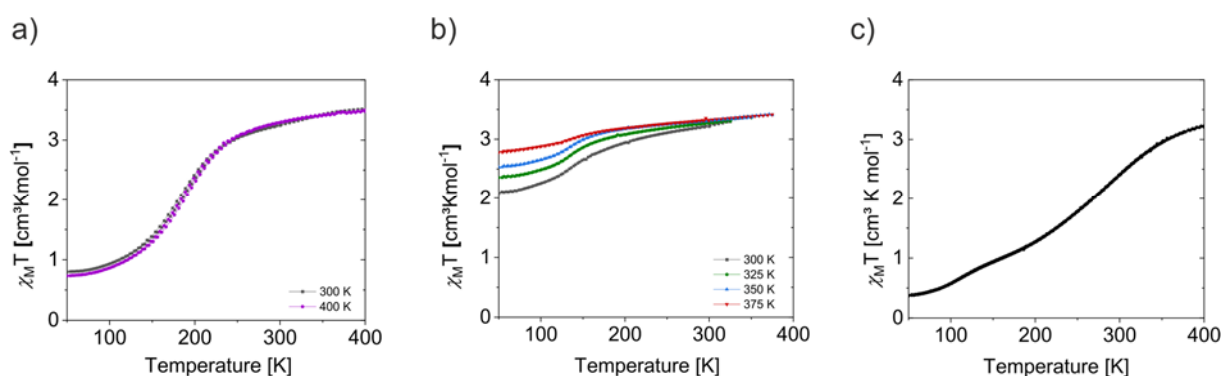


Figure 4 (a) Plot of the $\chi_M T$ product vs. T over two cycles of cooling and heating with different initial temperatures within the range 400–50 K with 5 K min⁻¹ rates of cooling for $\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ (**4**) (b) Plot of the $\chi_M T$ product vs. T over five cycles of cooling and heating with different initial temperatures within the range 375–50 K with 5 K min⁻¹ rates of cooling for $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ (**2**) (c) Plot of the $\chi_M T$ product vs. T over 5 cycles of step-wise heating starting at 300 K (in 25 K steps) and cooling to 50 K with a scan rate of 5 K min⁻¹ for $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{DMAP})_2]$ (**3**).

In contrast to **2**, almost all iron centers in solid **3** can reach the diamagnetic LS state at low temperature (Figure 4c). This is a result of the slightly modified axial ligand and supports the suggestion that packing and solvent effects in **2** prevent a large fraction of iron centers from performing a SCO. The presence of DMAP instead of pyridine should not have a major influence regarding SCO energies, but will certainly affect packing in the crystal due to the bulky dimethylamino group. Different from **2**, the spin transition in **3** is close-to-complete but exceedingly broad, yielding the $\chi_M T$ limiting values 0.38 and 3.22 cm³ K mol⁻¹ at 50 K and 400 K, respectively. The latter value once more is typical for iron(II) in the HS state.^[2] The compound tolerates multiple heating cycles up to 400 K with unambiguously reproducible curves.

8.2.4 Temperature Dependent NMR Measurements

8.2.4.1 Spin State in Solution: ^1H NMR Spectra of **2** at +50°C

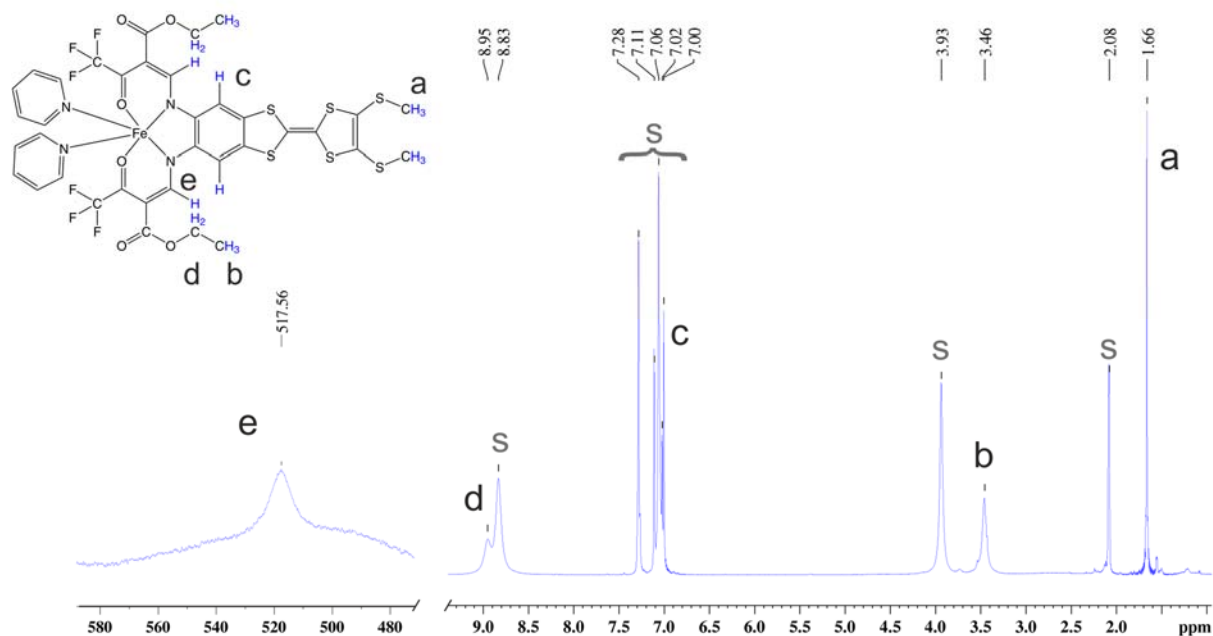


Figure 5 ^1H NMR spectrum of $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ (**2**) in a pyridine:toluene (1:1) mixture at 50°C (500 MHz). The signal assignment is given at the left. S denotes residual solvent peaks.

In the solid state the spin-state dynamics of **2** heavily depend on the degree and nature of lattice solvation (Figure 4). In solution the intrinsic properties of isolated **2** can be studied. Figure 5 displays the ^1H NMR spectrum of **2** in a pyridine:toluene (1:1) at +50°C. For the signal assignment literature values of similar complexes and the shifts of the free ligand were considered.^[28,29] Compared to the free ligand, the CH_2 protons of the ethoxycarbonyl group experience a clear paramagnetic shift and can therefore be assigned to signal **d**. Most strongly influenced by the paramagnetic iron(II) is the Schiff base proton site **e** due to the small distance to this metal center. This highly unshielded proton gives a signal with an extraordinary linewidth of 15000 Hz, which again reflects the impact of the HS-iron center. These findings are in good agreement with former signal assignment of similar systems.^[28,29] Diagnostic signals of HS-**2** are recorded at $\delta = 8.9$ ppm and, at extremely low field, at $\delta = 517$ ppm for sites **d** and **e**, respectively. Comparison with **REF** (Figure S 5) reveals large similarities with respect to the protons that are expected to have similar shifts. Only signals due to proton site **a** are missing in **REF**, as expected.

8.2.4.2 Temperature Dependence of the Isotropic Shifts of **2**

According to the susceptibility measurement in the solid state, **2** remains predominantly in the HS state over the whole temperature range investigated. However, in solution there is a characteristic color change from red brown to deep green when cooling the solution with liquid nitrogen (Figure S 15a). This variation in color caused by a temperature change reflects a shift in the thermal equilibrium between LS and HS state. Very similar switching has been recently observed in the same temperature range with reference compounds **REF**^[29] and **REF**^{CH₃}.^[21] This phenomenological coincidence points to rather conserved SCO energetics throughout the series of compounds, irrespective of the presence of π -donating or σ -accepting substituents. Indeed, results of an experimental inquiry via VT-NMR is in line with the analysis with DFT methods (see Figure S 6, ESI), which both support narrowly clustering of the SCO energies. Computed apparent SCO energies point to a slight preference for the LS state of **REF**. In Figure 6a we summarize the results of a VT-NMR study of **2** in pyridine/toluene mixtures; the VT ¹H NMR spectra with different targeted temperatures are displayed.

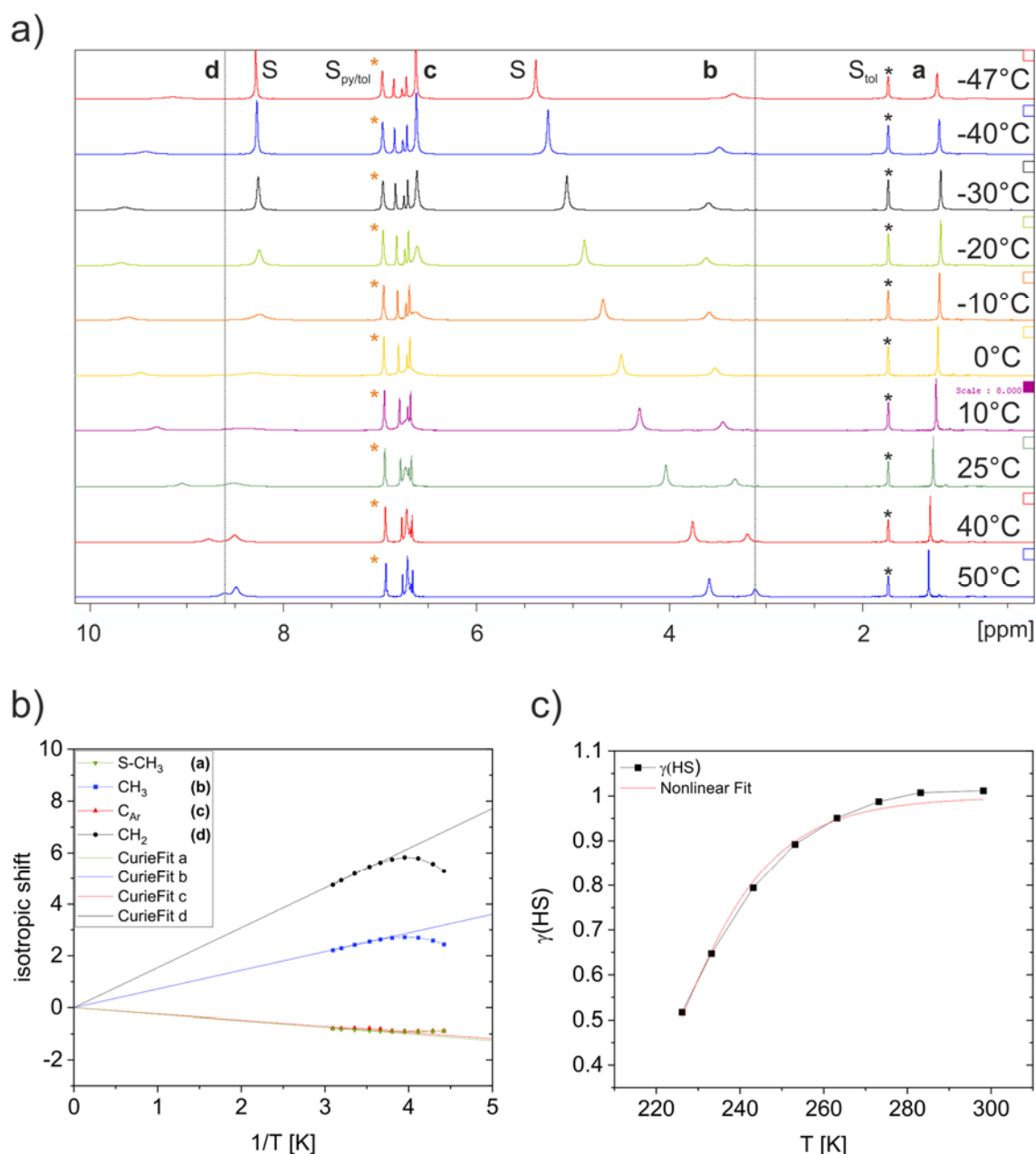


Figure 6 (a) VT ¹H NMR spectra of complex **2** in a solution of a 1:1 mixture of toluene-*d*₈ and pyridine-*d*₅. The given temperatures are target temperatures of the probe. (b) Isotropic shifts of **2** plotted versus 1/*T* (dots). The solid lines represent the calculated shifts of the pure HS complex using extended Curie law. (c) Averaged HS mole fraction (γ_{HS}) of **2** fitted with equation 3.

At room temperature, protons which are close to the paramagnetic metal center (**b**, **d**) experience a strong isotropic shift, whereas the more remote sites **a** and **c** are left rather undisturbed. Accordingly, variation of temperature will predominantly affect the sites **b** and **d**, resulting from two competing effects of opposite sign. First a further, continuous down-field shift must be expected, if the HS-character is conserved, according to Curies law. By contrast, signals will be high-field shifted, if LS-character becomes sizeable. Furthermore, the line width of all diagnostic NMR signals of an SCO system is required to vary in a specific way, typically running through a sharp maximum with decreasing temperature.^[25,28,30] Similar observations hold for ¹H NMR studies of **REF** that undergoes SCO in the

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bulk,^[29] results are summarized in the supporting information (Figure S 5 and S 7). Most importantly, the isotropic shifts respond to temperature variation in a discontinuous way, supporting the presence of two effects of opposite sign (Figure 6a, b). Specifically, the chemical shifts pass through a maximum upon cooling, indicating the presence of two contrary effects. This becomes most evident as a deviation from linearity in the Curie plots for the proton sites **b** and **d**, as expected (less obvious effects prevail for sites **a** and **c**).^[28] The temperature dependence of the chemical shift for the HS state ($\delta_{HS}(T)$) thus was determined from the linear branch of the plot and extrapolated to $T < 283$ K. With the values for $\delta_{HS}(T)$ at hands, the mole fraction of the spin isomers of **2** was determined as a function of temperature (eq 1).

$$\gamma_{LS} = \frac{\delta_{obs} - \delta_{HS}(T)}{\delta_{LS} - \delta_{HS}(T)} \quad \text{with } \gamma_{HS} = 1 - \gamma_{LS} \quad (1)$$

The results of this examination are illustrated in Figure S 4. As already suspected from the observable color change in solution at low temperature, the HS state is significantly depleted with $T_{1/2} \approx 220$ K. A very similar value of $T_{1/2} \approx 200$ K is recorded for reference compound **REF** which lacks the TTF unit indicating very similar SCO thermodynamics of **2** and **REF**. A plot of $\gamma(HS)$ derived from the diagnostic NMR shifts of proton sites **b** and **d** served to evaluate $\Delta_{SCO}H$ and $\Delta_{SCO}S$ according to equation 2 (see Figure 6c).

$$\gamma_{HS} = \frac{1}{1 + e^{\left(\frac{\Delta H}{k_B T} - \frac{\Delta S}{k_B}\right)}} \quad (2)$$

While the extracted values of SCO enthalpy ($\Delta_{SCO}H = 38.5 \pm 5.5$ kJ·mol⁻¹) and entropy ($\Delta_{SCO}S = 168 \pm 24$ J·K⁻¹·mol⁻¹) are in the typical range of iron(II) spin crossover compounds, their significance is limited by both, the significant statistic error of the non-linear fit and the incomplete coverage of the SCO profile. In conclusion, **2** and **REF** undergo SCO in solution, which remains incomplete within the liquid temperature range. Nevertheless, the nature of the reduced species in the following electrochemical oxidation experiments must be expected to reflect the temperature dependence of the SCO equilibrium. We therefore anticipated a large effect of temperature on the electrochemical parameters in **2**, both qualitatively and quantitatively.

8.2.5 Electrochemical Investigations

8.2.5.1 Cyclic Voltammetry at Ambient Temperature

In recent work, the electrochemical response of the CH₃-substituted congeners **TTF^{CF3}LH₂**, **REF^{CH3}** and **2^{CH3}** was interpreted in terms of additive electrochromes with minor communication between the redox-sites, iron(II/III) and TTF(0/+2).^[21] At room temperature, the first redox event in **REF^{CH3}** and **2^{CH3}** at $E_{1/2} = -390$ mV was clearly assigned to the iron(II/III) couple, both located distinctly cathodic of the first TTF-borne potential by $\Delta E_{1/2} > 450$ mV. While the nature of the reduced species at room temperature was identified by optical spectroscopy as the HS iron(II) state, it was not possible to determine the spin state of the oxidized complexes in SQUID magnetometry and Mössbauer spectroscopy. In the present study, exchange of CF₃ for CH₃ substituents in the equatorial ligand were supposed to anodically shift the iron-borne redox events. As described in the section above, the HS-state preference of the reduced form is conserved despite the exchange of substituents when going from **2^{CH3}** to **2** (and **REF^{CH3}** to **REF**). Effects of the spin state on the nature and potential of the redox events, if present, therefore, are likely similar across the entire series. Shown in Figure 8 are the cyclic voltammograms recorded of the free ligand **1** (Figure 7a) and the single-site reference compound **REF** (Figure 7b) in dichloromethane (DCM) solution at $T = 295 \pm 1$ K. For the ligand (Figure 7a) the CV recorded of the CH₃ congener **1^{CH3}** is overlaid for comparison.

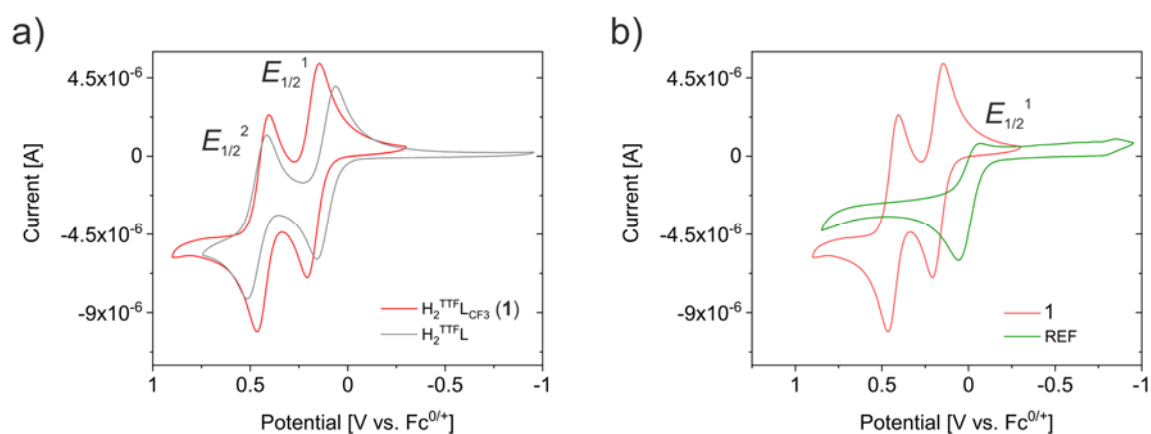


Figure 7 Cyclic voltammograms of (a) ligands **1** and **TTF^{CF3}LH₂** and (b) of the single-redox components **REF** compared with **1** in DCM ($c = 1$ mM) with tetrabutylammonium hexafluorophosphate (NBu₄PF₆; 0.1 M) as a supporting electrolyte on a platinum working and counter electrode at 50 mV s^{-1} with a saturated calomel reference electrode.

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For the ligand **1** two reversible redox events can be observed at $E_{1/2}^1 = 0.173$ and $E_{1/2}^2 = 0.431$ V (vs. $\text{Fc}^{0/+}$). Both events are ascribable to the established TTF-borne redox couples.^[21,31] It is noted that the second potential of **1** well matches the value recorded of **1**^{CH₃} whereas the first oxidation is shifted anodically by ca. 50 mV. This minor effect points to a range-limited impact of the CH_3/CF_3 substituents on the electronic properties of the ligand. Clearly **REF** is much more affected by the presence of CF_3 groups, adjacent to the coordination site. For **REF** a single redox event is observed at a half wave potential of $E_{1/2} = -0,005$ V (vs. $\text{Fc}^{0/+}$), which is attributed to the to the $\text{Fe}^{2+/3+}$ couple.^[3,32] Compared with **REF**^{CH₃} and **2**^{CH₃} the metal-centered event is anodically shifted by almost 400 mV. Large peak-to-peak separation ($\Delta E = 125$ mV) and $I_{\text{pa}} \gg I_{\text{pc}}$ render this redox process quasireversible.^[33] As a major result of the CF_3/CH_3 exchange, the metal-borne redox event in **REF** now overlaps with the first TTF-borne oxidation wave in ligand **1**.

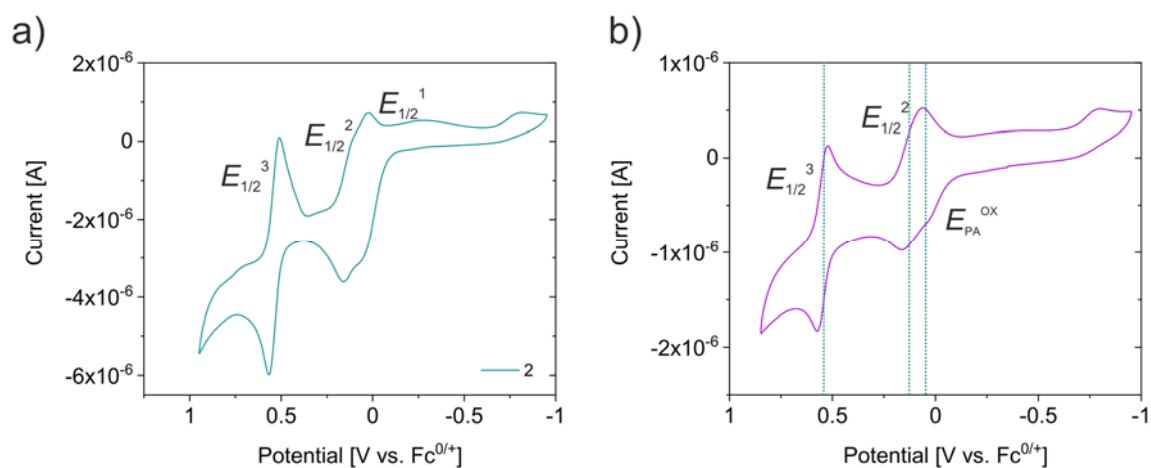


Figure 8 Cyclic voltammograms of (a) complex **2** and (b) **3** in DCM ($c = 1$ mM) with tetrabutylammonium hexafluorophosphate (NBu_4PF_6 ; 0.1 M) as a supporting electrolyte on a platinum working and counter electrode at 50 mV s^{-1} with a saturated calomel reference electrode. Dashed green lines represent the half wave potentials of **2**.

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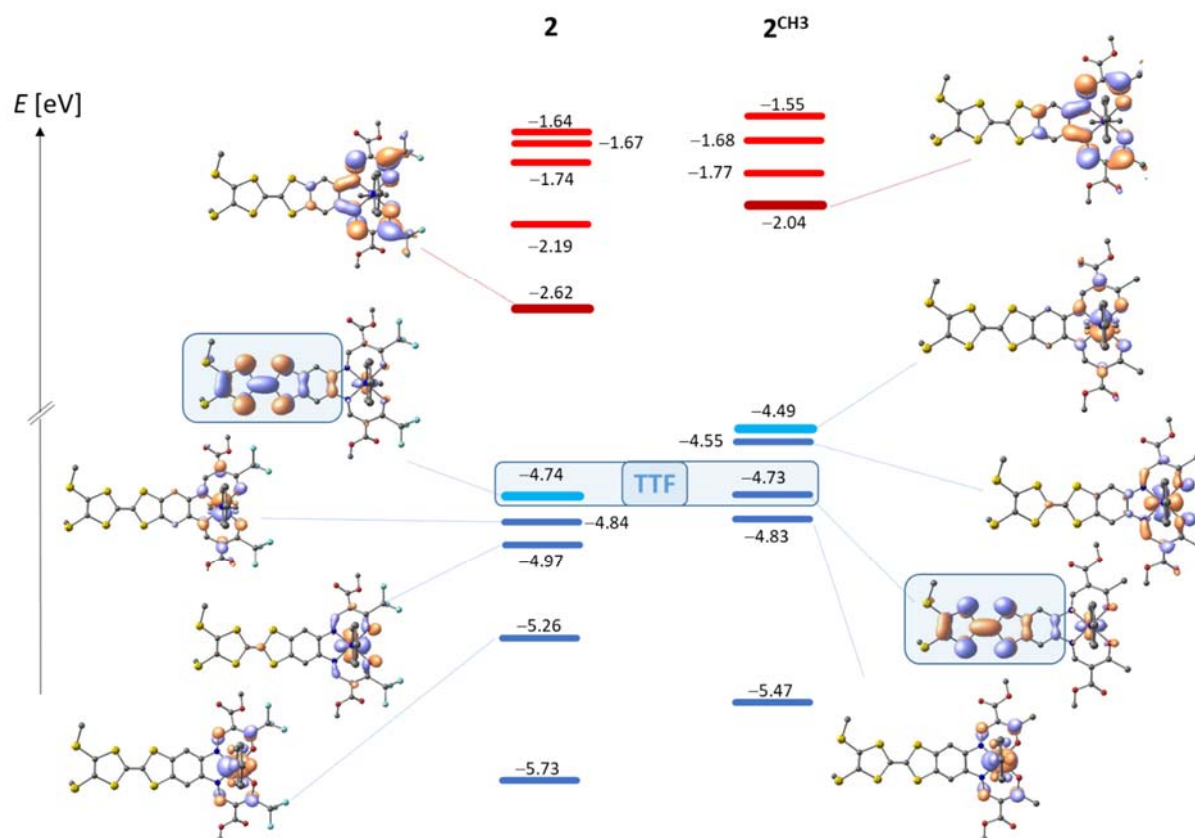


Figure 9 DFT calculated energies of occupied molecular orbitals (MOs) (blue) and unoccupied MOs (red) for TTF-appended $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ (left), and its CH_3 -substituted congener $[\text{Fe}^{\text{TTF}}\text{L}(\text{py})_2]$ (right), varying nature of the HOMO (highest occupied molecular orbital) is highlighted.

As seen previously in $\mathbf{2}^{\text{CH}_3}$,^[21] the redox properties of the isolated electrophores are largely additive also in $\mathbf{2}$ and the coordination polymer $\mathbf{3}$ (Figure 8). While additivity in $\mathbf{2}^{\text{CH}_3}$ yielded a well-defined and readily assignable order of separate redox events, the situation gains complexity in complex $\mathbf{2}$. In fact, an assignment in $\mathbf{2}$ has to cope with narrowly spaced and strongly overlapping waves ($E_{1/2}^1 = 0.049$ V and $E_{1/2}^2 = 0.127$ V). Comparison of $\mathbf{2}$ with the mono-electrophore **REF** may suggest an assignment of the first observed process in $\mathbf{2}$ as iron-centered; $E_{1/2}^1 = 0.049$ V in $\mathbf{2}$ rather matches $E_{1/2}^1 = -0.005$ V in **REF** than $E_{1/2}^1 = 0.178$ V in $\mathbf{1}$. This tempting assignment of $E_{1/2}^1$ and $E_{1/2}^2$ as metal-centered and TTF-borne, respectively is not supported by the DFT calculated energies of occupied and unoccupied molecular orbitals of complex $\mathbf{2}$. While the highest occupied orbital in the system without CF_3 groups is clearly iron-centered, it apparently originates from the TTF in the case of $\mathbf{2}$ (Figure 9). Comparison of the DFT calculated energies of $\mathbf{2}$ with those of the free ligand and **REF** supports the assertion that the HOMO in $\mathbf{2}$ originates from TTF (Figure S 8). However, computation of the frontier orbitals also shows the small energetic difference between the iron-centered and the TTF-centered orbitals. The order may well be affected by the choice of DFT settings, what demonstrates how energetically close the two states are. This is reflected by cyclic voltammetry where the first two oxidation processes are not only very close to each other, but even overlap. A comparison of the energies of the complex with

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those of the free ligand and the reference system also shows how close the two oxidation processes are (Figure S 8). Finally, the third redox process is in a range typical for the second oxidation of the TTF unit to the dication (TTF^{2+}). Compared to the corresponding second oxidation in the free ligand, the half wave potential in **2** is anodically shifted by 110 mV. This shift is clearly a consequence of a third positive charge which is introduced in the event $\mathbf{2}^{2+} \rightarrow \mathbf{2}^{3+}$.

Akin to the previously reported CH_3 -substituted system, the redox potentials in the coordination polymer **3** do not significantly differ from the mononuclear complex. A peak-by-peak comparison with **2** reveals that both $E_{1/2}^2$ and $E_{1/2}^3$ match quantitatively, whereas the first event lacks full reversibility, as far as can be deduced from the highly convoluted events. A distinctive characteristic that can be observed, nevertheless, is the much smaller current corresponding to the reactions on the electrodes. The smaller currents may be referred to the presence of a polymer chain resulting in poorer solubility of the material. Surprisingly the cyclic voltammogram of **3** shows substantial differences compared to that of **2** (Figure S 10). Comparison reveals that the characteristic peaks of the pyridine complex with very similar potentials can be found in this compound. However, there are two additional events. Within the scope of this study, it cannot be satisfactorily clarified where the two additional peaks at $E_{1/2}^1 = -0.259 \text{ V}$ and $E_{1/2}^4 = 0.401 \text{ V}$ originate from. It appears reasonable to assign the cathodic event with an iron-borne process, indicative of additional species in solution. The anodic wave in turn indicates that the oxidation events of the TTF unit are further split. While such behavior may be ascribable to the formation of dimers in solution that occasionally lead to a splitting of redox events, [34–37] it has been, to the best of our knowledge, never observed in TTF containing metal complexes.

8.2.5.2 UV-Vis Spectroelectrochemistry

As the first two redox events in **2** overlap in the CV experiment, additional insights into the nature of these processes were expected from a spectroelectrochemical study. The redox-dependent optical spectra of **2** were recorded in DCM solution at room temperature; for sake of comparison the free ligand **1** was studied under the same conditions. The compounds were kept at suitable constant potentials to either address the first, second or third redox process over a period of 10 min. The reversibility of each process was verified by addressing sufficiently cathodic potentials subsequently (see Figure S 11–S 13 in the SI). In Figure 10 the spectra recorded during the first and second oxidation of the ligand **1** and the three oxidation steps of complex **2** are displayed.

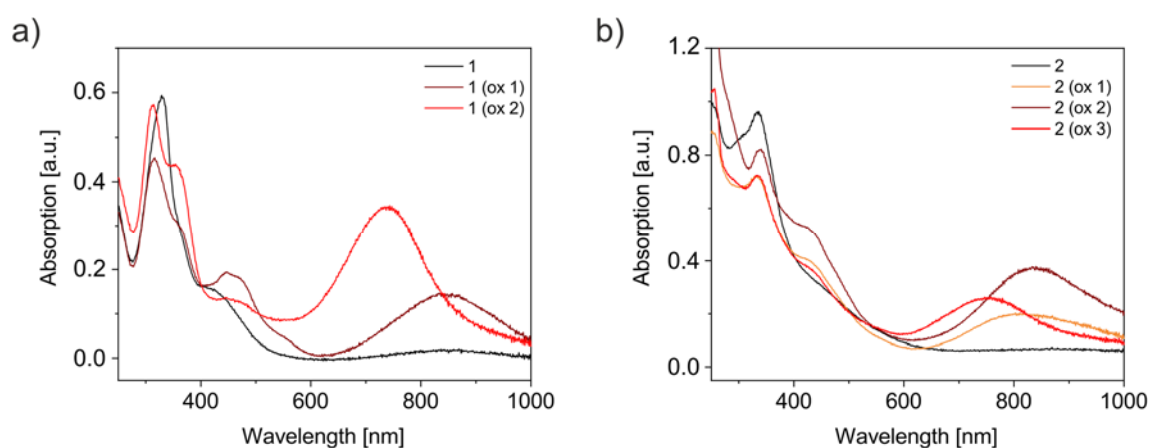


Figure 10 (a) UV-Vis spectra recorded of **1** in DCM ($0.2 \text{ mol}\cdot\text{L}^{-1} \text{NBu}_4\text{PF}_6$), during electrochemical oxidation at a constant potential corresponding to the potential of the first and second oxidation. (b) UV-Vis spectroelectrochemical investigation of **2** ($0.2 \text{ mol}\cdot\text{L}^{-1} \text{NBu}_4\text{PF}_6$, obtained at a constant potential corresponding to the potential of the three redox events).

Upon initial oxidation of the free ligand **1**, the characteristic absorption bands of the neutral form at $\lambda = 327$ and $\lambda = 420 \text{ nm}$ (ILCT, TTF \rightarrow ligand core)^[21,38,39] are replaced by intense transitions in the visible at 450 nm and, most diagnostically, by a broad NIR band centered at 850 nm. It is noted that a similar NIR band was observed in oxidized **1**^{CH3}, with significantly smaller intensity, however.^[21] The transition at 850 nm is usually interpreted in terms of the formation of the so-called π -dimer of the TTF^{•+} cation (TTF^{•+})₂. Formation of π -dimers has been described multiple times in different TTF containing systems.^[34,40,41] This assignment is apparently corroborated by the absence of the characteristic absorption of the monomeric radical cation around 650 nm. However, room temperature CV of **1** gave no sign of signal splitting due to dimer formation of the monocation. We therefore embarked on TD-DFT modelling of the optical spectra of the entire redox series **1**^{0/•+/2+} in order to validate the suggested speciation. As a matter of fact, the spectra predicted for monomeric **1**^{•+} and **1**²⁺ fairly well match the experimentally observed NIR response in Figure 10a (see Figure S 9). Formation of the dication is

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accompanied by an intense absorption band growing in at 737 nm at the expense of the π -dimer band. Akin to the observations made in **1**, oxidation of complex **2** features in the UV-Vis-NIR spectra most diagnostically in the NIR regime (Figure 10b). Upon the first oxidation the intense intraligand absorption band at $\lambda = 330$ nm is replaced by two characteristic bands centered at $\lambda = 430$ nm and $\lambda = 810$ nm. Accordingly, the first oxidation event must be considered to be a mixture of iron- and TTF-centered at room temperature. This assignment is in agreement with the previous assignment which was based on analogies of **REF** and **2** in the CV potentials. It is further supported by additional low-temperature CV experiments (see below). Addressing of the second oxidation event causes no qualitative changes but rather serves to intensify the ingrowing bands (430 nm & 810 nm) combined with a distinct red shift of the latter. The final oxidation event serves to fully bleach the strong NIR band at 820 nm, which is replaced by a significantly weaker band centered at 750 nm. The spectral evolution during the third oxidation thus greatly echoes features characteristic of the TTF dication.^[39,42]

8.2.5.3 Cyclic Voltammetry at Low Temperature

It was shown in a previous section that solution NMR spectra of **2** in mixed toluene/pyridine media evolve with decreasing temperature to reflect a ratio $[\text{HS-2}]/[\text{LS-2}] \approx 1:1$ at the lowest accessible temperatures (see Figure 6). Thus, electrochemical studies at low temperature must be expected to reflect the sharply varied speciation. An investigation of the electrochemical properties of **2** and **REF** at $T = 197 \pm 2$ K indeed showed that the iron-borne events exhibit a substantial cathodic shift by $\Delta E > 100$ mV. Measurements were performed in DCM with a modified setup developed by Nishida *et al.* (details in the Experimental Section, Figure S 15 & S 17).

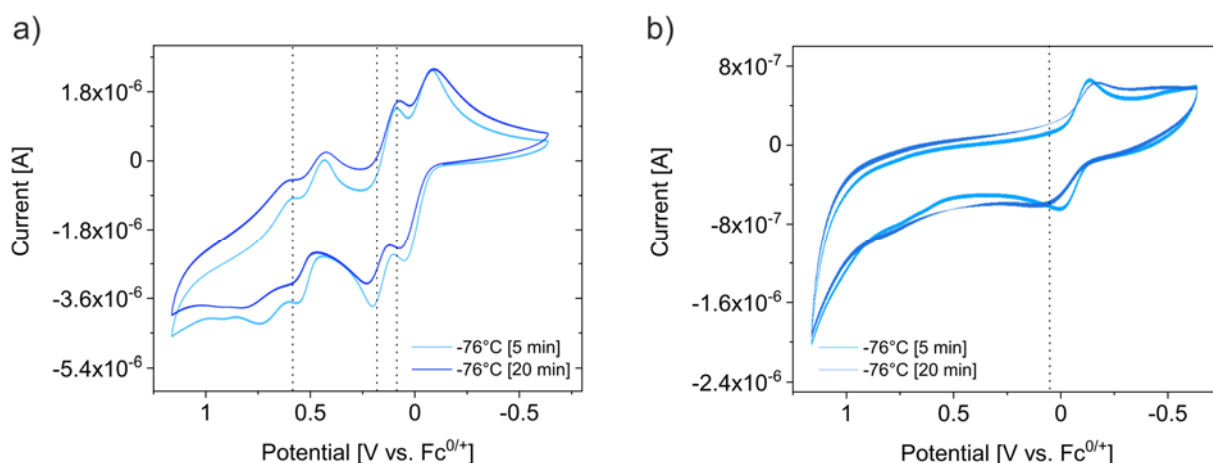


Figure 11 Cyclic voltammogram of (a) **2** and (b) **REF** in DCM with tetrabutylammonium hexafluorophosphate ($0.1 \text{ mol}\cdot\text{L}^{-1}$ NBu_4PF_6) as supporting electrolyte on a platinum working and counter electrode at $100 \text{ mV}\cdot\text{s}^{-1}$ with an Ag/Ag^+ reference electrode. Dashed lines mark the half wave potentials at room temperature.

Shown in Figure 11 are the results of the low temperature CV measurements of **2** and **REF** in DCM (potentials vs. Fc/Fc^+); the derived electrochemical parameters are listed in Table 3. It is important to note that TTF-borne events in ligand **1** shift cathodically by only -20 mV at 196 ± 2 K (VT-CV data of ligand **1** in the SI). An overall decline in currents at lower temperatures reflects increased solvent resistivity and decreasing diffusion coefficients.^[43] Comparison with the room-temperature potentials highlights the direction and magnitude of temperature-dependent effects. Different from the TTF-events in **1**, the iron-borne event in **REF** is markedly shifted to more negative potentials upon cooling, with $\Delta E > 100$ mV. This cathodic shift reflects significant destabilization of the ferrous state at low temperature, which is accompanied by the aforementioned shift in the SCO equilibrium. Accordingly, we associate the cathodic shift of $E_{1/2}$ with the continuous increase of the LS-population at low temperature.

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As the single-redox site complex **REF** reasonably serves to calibrate the CV measurements of multi-site complex **2**, a similar cathodic shift of the iron-centered redox events must be expected in **2**, whereas TTF-borne processes should be largely invariant with temperature. Indeed, the potential of $E_{1/2}^1$ shifts cathodically upon cooling by approximately 100 mV and is therefore most likely iron borne. At low temperatures **2** deviates from known oxidation behavior by splitting of the second TTF oxidation wave in $E_{1/2}^{3.1}$ and $E_{1/2}^{3.2}$. An overlay of the voltammograms of **1** and **2** recorded at 196 ± 2 K (Figure 12) shows that $E_{1/2}^2$ and $E_{1/2}^{3.1}$ are TTF borne since they clearly overlap. A closer examination of the second TTF oxidation at low temperature indicates invariant TTF-events. $E_{1/2}^3 = 0.543$ V at 196 K (average value of the split waves $E_{1/2}^{3.1}$ and $E_{1/2}^{3.2}$) versus $E_{1/2}^3 = 0.541$ V at 295 K. However, what was a single-wave event at RT, is split at 196 K into two reversible redox steps of equal weight. It is noted that wave splitting reversibly disappears in **2** upon heating (Figure S 16), whereas it is entirely absent in ligand **1** (Figure S 14). CV wave splitting is a recurrent observation in TTF redox chemistry, which is usually associated with the formation of dimers after or during the first redox event ($2 \text{ TTF}^+ \rightarrow \{(\text{TTF})_2\}^{2+}$).^[34-37,40,44] Different from the reported cases, complex **2** supports splitting of the second TTF oxidation event.

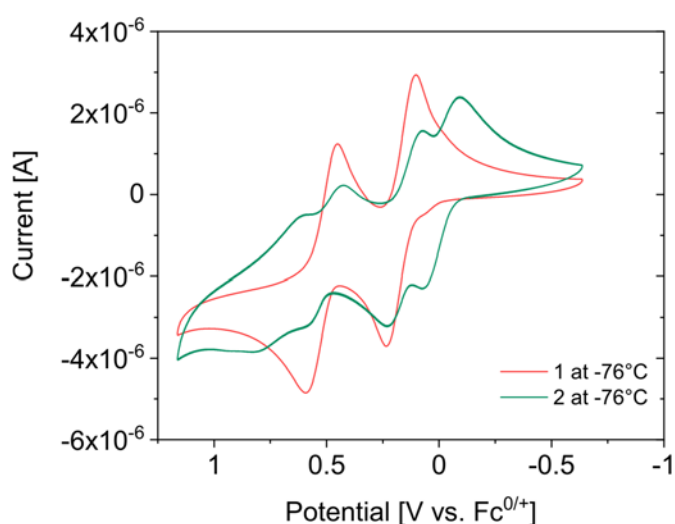


Figure 12 Combination of the spectra of the ligand **1** and complex **2** in DCM with tetrabutylammonium hexafluorophosphate (NBu_4PF_6) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at $100 \text{ mV}\cdot\text{s}^{-1}$ with a Ag/Ag^+ reference electrode after 20 min of cooling with an isopropanol dry ice bath.

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Table 3 Electrochemical parameters of **2** in DCM ($c = 1 \text{ mM}$) with supporting electrolyte tetrabutylammonium hexafluorophosphate (NBu_4PF_6 ; 0.1 M) at a scan rate of 100 mV s^{-1} included with corresponding peak-to-peak separations at different temperatures. For the measurement, an Ag/Ag^+ reference electrode and a platinum working, and counter electrode was used.

	$E_{1/2}^1$ [V]	$E_{1/2}^2$ [V]	$E_{1/2}^{3.1}$ [V]	$E_{1/2}^{3.2}$ [V]	ΔE_1 [V]	ΔE_2 [V]	$\Delta E_{3.1}$ [V]	$\Delta E_{3.2}$ [V]
20°C start	0.087	0.185	0.586	–	0.059	0.062	0.075	–
–76°C [5 min]	–0.032	0.121	0.460	0.626	0.105	0.103	0.105	0.141
–76°C [30 min]	–0.029	0.128	0.464	0.630	0.091	0.097	0.105	0.123
20°C after warming [5 min]	0.034	0.172	0.567	–	0.059	0.072	0.092	–
20°C after warming [20 min]	0.044	0.138	0.528	–	0.064	0.072	0.089	–

8.3 Conclusion

In this manuscript, the effect of the simultaneous presence of strongly electron-releasing and electron-withdrawing groups on the iron(II/III) coordination chemistry of Schiff base-like equatorial ligands is studied. To this end, the TTF-appended ligand backbone was modified by the introduction of electron-withdrawing CF_3 groups at the Schiff base-like side chain. On the one hand, the resulting ligand $\text{TTF}^{\text{L}}\text{CF}_3\text{H}_2$ was used to combine spin crossover and redox active behavior. On the other hand, fine-tuning of the electrophores served to match the iron-borne redox potentials with the first TTF oxidation event to allow communication between the two redox centers. In the crystal structure of **2** · (MeOH)(py) at 180 K with the octahedral environment of iron(II) saturated by axial pyridine donors, the TTF unit is in the non-oxidized neutral state and the iron(II) center is in the low spin state. This is in contrast to magnetic susceptibility measurements which show only incomplete SCO for this complex resulting in a residual HS fraction of more than 80% at 180 K. Packing effects and, most importantly, co-crystallized solvents in the single crystal are held responsible for these differences. In contrast, nearly complete spin transition behavior can be observed in both the closely related complex **3** with axial DMAP ligands and the coordination polymer **4**, deriving from bpee bridges. Temperature-dependent ^1H NMR spectra of **2** and the suitable reference compound **REF** in solution (pyridine:toluene = 1:1) reveal characteristic isotropic shifts of the signals, most significant of the sites close to the paramagnetic iron(II) center. This behavior is typical for an increasing amount of diamagnetic iron(II) species in solution due to a SCO.

Cyclic voltammetry of the ligand and the derived complexes revealed an only mild impact of the electron-withdrawing CF_3 groups on the TTF-borne redox processes. In contrast the iron(II/III) couple suffered a massive cathodic shift by almost 400 mV. Both complex **2** and polymer **3** exhibit three reversible redox processes with almost identical half wave potentials. The derivative **3** exhibits two additional processes where either the basicity of the ligand or eventual splitting of the redox events of the TTF unit play a crucial role. Signal assignment of the first two redox processes in **2** and **3** to a defined redox process appears to be challenging since they are very close to each other. Spectroelectrochemical UV-Vis spectroscopy of **2** and the free ligand gave insight into the nature of the events. Since both the spectra of the first oxidation of the ligand and also the complex reveal shows strong similarity, communication between the two redox centers appears to be possible. Although the first redox event is predominantly iron centered, it also has a clear TTF character according to the UV-Vis spectra and an exact assignment at room temperature is difficult. Since SCO in solution was observed for **2** and **REF** the redox behavior of both complexes was also studied at low temperature. Thereby, a cathodic shift of the iron(II) redox potential by about 100 mV was monitored in **REF** that is clearly attributed to the growth of LS species. A shift of 100 mV can be found in the first redox event

of **2** as well, which confirms the previous assumption that this event is rather ferrous. Instead of three upon cooling complex **2** shows four reversible redox events. Interestingly, appearance and disappearance of the fourth peak is depending on temperature and reversible.

8.4 Experimental Section

If not stated otherwise all reactions were carried out using Schlenk technique with fresh distilled solvents. All solvents were purified as described in literature and distilled under argon. The synthesis of iron(II) acetate was conducted as described in literature.^[45] The ligand **1** was synthesized in a slightly modified way based on already published procedures. Chemicals used for synthesis were commercially available and used as received.

¹H NMR spectra were recorded at room temperature with a Varian INOVA 300. **JMOD ¹³C NMR:** The *J*-modulated (JMOD) pulse sequence was employed for recording the ¹³C spectrum of the ligand ^{TTF}L_{CF3}H₂. In the JMOD ¹³C NMR spectra the methine and methyl signals (down) have opposite phase to those of quaternary and methylene (up) resonances. All peaks in the spectrum are doubled because of the *cis-trans* isomerism of the double bond of the equatorial ligand. In the experimental section the prominent peak (*cis* isomer) is given.

T-dependent NMR Spectroscopy Pyridine-*d*5 (D, 99.5%) and toluene-*d*8 (D, 99.6%) were purchased from Euriso-top. The solvents were degassed with argon using Schlenck techniques. The NMR samples were prepared in a glove box under nitrogen atmosphere in a 5 mm NMR tube with PTFE valve from Deutero. Saturated solutions of the iron(II) complexes were prepared in pyridine-*d*5 : toluene-*d*8 (50 : 50 v : v) mixtures VT NMR spectra were recorded on a Ascend 500 magnet with a AVANCE NEO console operating at 500.34 MHz equipped with a PATBO500S1BB-H/F-D-05ZFB sample head and a variable temperature unit over a temperature range of -47 to + 50°C (226–323 K).

Elemental analysis was measured with a Unicube from Elementar with sulfanilamide as standard. The samples were placed in a small tin boat.

Magnetic susceptibility measurements on bulk materials were performed using a MPMS-XL5 SQUID magnetometer from Quantum Design with an applied field of 5000 Oe in the temperature range from 50 to 400 K in the sweep mode with 5 K·min⁻¹. The samples were put in a gelatin capsule and placed in a straw. The raw data were corrected for the diamagnetic part of the sample holder and the diamagnetism of the organic ligand using tabulated Pascal's constants.

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Cyclic voltammetry measurements were performed with an Electrochemical Analyzer CHI610E from CH Instruments in a three-electrode setup with a platinum working and counter electrode and a saturated calomel reference electrode CHI150 from CH Instruments.

Cyclic Voltammetry at low temperatures were performed using a modified setup developed by Nishida *et al.* with a platinum working and counter electrode and an Ag/Ag⁺ reference electrode that was brought to -76°C with an isopropanol dry ice bath.^[46]

X-ray Structure Analysis The intensity data of **2** were collected with a Stoe StadiVari diffractometer using graphite-monochromated Mo- K_{α} radiation at 180 K. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR-2019) and refined by full-matrix least-square techniques against $F_o^2 - F_c^2$ (SHELXL-2018). All hydrogen atoms were calculated in idealized positions with fixed displacement parameters. Mercury2020.1 was used for structure and molecule packing representation. Due to a strong disorder the included solvent (pyridine) could not be solved and was squeezed with PLATON.^[55]

Computational Details

DFT calculations were performed using ORCA2.9.1.^[47] Large TZVP basis sets were used throughout.^[48] The structures of the iron(II) complexes were optimized with the GGA functional BP86.^[49] Molecular orbitals and electronic properties were extracted from single-point calculations in the optimized positions with the global hybrid functional TPSSH.^[50] These settings provide reliable optical transition energies as shown recently for planar nickel(II)^[51] and octahedral iron(II) complexes.^[21] In order to assess the SCO energies, we used five derivatives of the well-established hybrid functional B3LYP^[52] in single-point calculations. In these derivative functionals the amount of exact exchange a_0 has been varied stepwise from 0.20 (native B3LYP) to 0.00. Dispersion contributions were approximated using Grimme's DFT-D3 atom pairwise dispersion corrections of the parent B3LYP functional.^[53] Solvent effects were accounted for in a dielectric continuum approach (COSMO),^[54] parametrized for MeCN.

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$\text{TTF}_{\text{L}_{\text{CF}_3}\text{H}_2}$ (1). 5,6-diamino-2-(4,5-bis(methylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole (0.5 g, 1.33 mmol, 1 eq.) was dissolved in 10 mL dimethylformamide (DMF) and Ethyl-2-(ethoxymethylen)-4,4,4-trifluor-3-oxobutyrate (0.95 g, 4 mmol, 0.8 mL, 3 eq.) was slowly added with a syringe. The reaction mixture was heated to 70°C for 4 h with an oil bath. After cooling to room temperature 10 mL of water are added. A red solid immediately precipitates, which is filtered off. The air-dried raw product was recrystallized from ethanol, filtered off and again dried in air. Yield: 0.53 g (764.82 g·mol⁻¹, 53%). Elemental analysis (C₂₆H₂₂F₆N₂O₆S₆, %) calcd.: C 40.83 H 2.90 N 3.66 S 25.15; found: C 40.96 H 2.88 N 3.96 S 24.91. ¹H NMR (298 K, DMSO-*d*⁶, 300 MHz): δ 1.24 (t, ³J = 7.11 Hz, 6H, CH₃), 2.44 (s, 6H, -S-CH₃), 4.18 (q, ³J = 7.29 Hz, 4H, -CH₂(trans)), 4.24 (q, ³J = 7.29 Hz, 4H, -CH₂(cis)), 7.85 (s, 2H, C_{ar}), 8.14 (d, ³J = 13.53 Hz, 2H, CH (cis)), 8.26 (d, ³J = 13.98 Hz, 2H, CH (trans)), 11.07 (d, ³J = 13.29 Hz, 2H, -NH(cis)), 11.88 (d, ³J = 14.13 Hz, 2H, -NH(trans)). ¹³C{¹H} JMOD NMR (298 K, DMSO-*d*⁶, 300 MHz): δ 13.91↓, 18.48↓, 60.34↑, 99.22↑, 110.19↑, 114.72↑, 117.25↓, 118.54↑, 122.34↑, 126.37↑, 132.34↑, 135.90↑, 159.32↓, 164.29.

[Fe^{TTF}L_{CF₃}(py)₂] (2). In freshly distilled methanol (10 mL), the ligand $\text{TTF}_{\text{L}_{\text{CF}_3}\text{H}_2}$ (1) (0.7 g, 0.92 mmol, 1 eq.) and iron(II) acetate (0.25 g, 1.5 mmol, 1.6 eq.) were dissolved. After the addition of pyridine (5.2 mL), the reaction mixture was heated to reflux for 2 h 15 min. After cooling to room temperature and storage at -22°C for 13 d a black fine-crystalline solid precipitated. The solid was filtered off, washed with 1.5 mL of methanol two times, and dried in vacuo. Yield: 0.26 g (976.85 g·mol⁻¹, 30%). Elemental analysis (C₃₆H₃₀F₆FeN₄O₆S₆, %) calcd.: C 44.26 H 3.10 N 5.74 S 19.69; found: C 44.48 H 3.15 N 5.75 S 19.63.

[Fe^{TTF}L_{CF₃}(DMAP)₂] (3). In freshly distilled methanol (20 mL), the ligand $\text{TTF}_{\text{L}_{\text{CF}_3}\text{H}_2}$ (1) (0.145 g, 0.19 mmol, 1 eq.), iron(II) acetate (0.053 g, 0.3 mmol, 1.6 eq.) and 4-(dimethylamino)pyridine (1.15 g, 9 mmol, 50 eq.) were dissolved. The reaction mixture was heated to reflux for 3 h. After cooling to room temperature and storage at 8°C for 24 h a black crystalline solid precipitated. The solid was filtered off, washed with 2 mL methanol two times, and dried in vacuo. Yield: 0.15 g (1062.99 g·mol⁻¹, 74%) Elemental analysis (C₄₀H₄₀F₆FeN₆O₆S₆, %) calcd.: C 45.20 H 3.79 N 7.91 S 18.10; found: C 45.46 H 3.88 N 8.04 S 18.49.

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$\{[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{bpee})]\}_n$ (**4**). The coordination compound **2** (0.098 g, 0.1 mmol, 1 eq.) and *trans*-1,2-bis(4-pyridyl)ethene (0.188 g, 1 mmol, 10 eq.) were dissolved in 8 mL of freshly distilled methanol. The reaction mixture was heated to reflux for 1.5 h. Already in the boiling heat a light brown powder is formed. After cooling to room temperature, the brown powder was filtered and washed with 2 mL of methanol and dried in vacuo. Yield: 0.083 g (972.82 g·mol⁻¹, 82%) Elemental analysis (C₃₈H₂₆F₆FeN₄O₆S₆, %) calcd.: C 45.60 H 3.02 N 5.60 S 19.22; found: C 45.62 H 2.94 N 5.91 S 18.90.

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8.6 Supporting Information

Table S 1: Crystallographic data of $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$

Formula	$\text{C}_{36}\text{H}_{24}\text{F}_6\text{FeN}_4\text{O}_6\text{S}_6 \cdot \text{CH}_4\text{O}$
CCDC	2070878
$M_r / \text{g mol}^{-1}$	1002.84
Crystal size / mm	0.164 x 0.731 x 0.144
$\lambda / \text{\AA}$	0.71073
T / K	180
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
$a / \text{\AA}$	14.1755(2)
$b / \text{\AA}$	25.7398(5)
$c / \text{\AA}$	26.2383(4)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	9573.7(3)
Z	8
$d_{\text{calcd}} / \text{Mg cm}^{-3}$	1.391
μ / mm^{-1}	0.647
θ range/ $^\circ$	1.6–28.5
Reflections collected	68155
Indep. reflections	11705
Obsvd. reflections ($F_o > 2s(F)$)	6843
R_{int}	0.072
$R(F), (F_o > 2s(F))$	0.0627
$wR_2(F^2), \text{all data}$	0.1835
Goof	1.04

Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

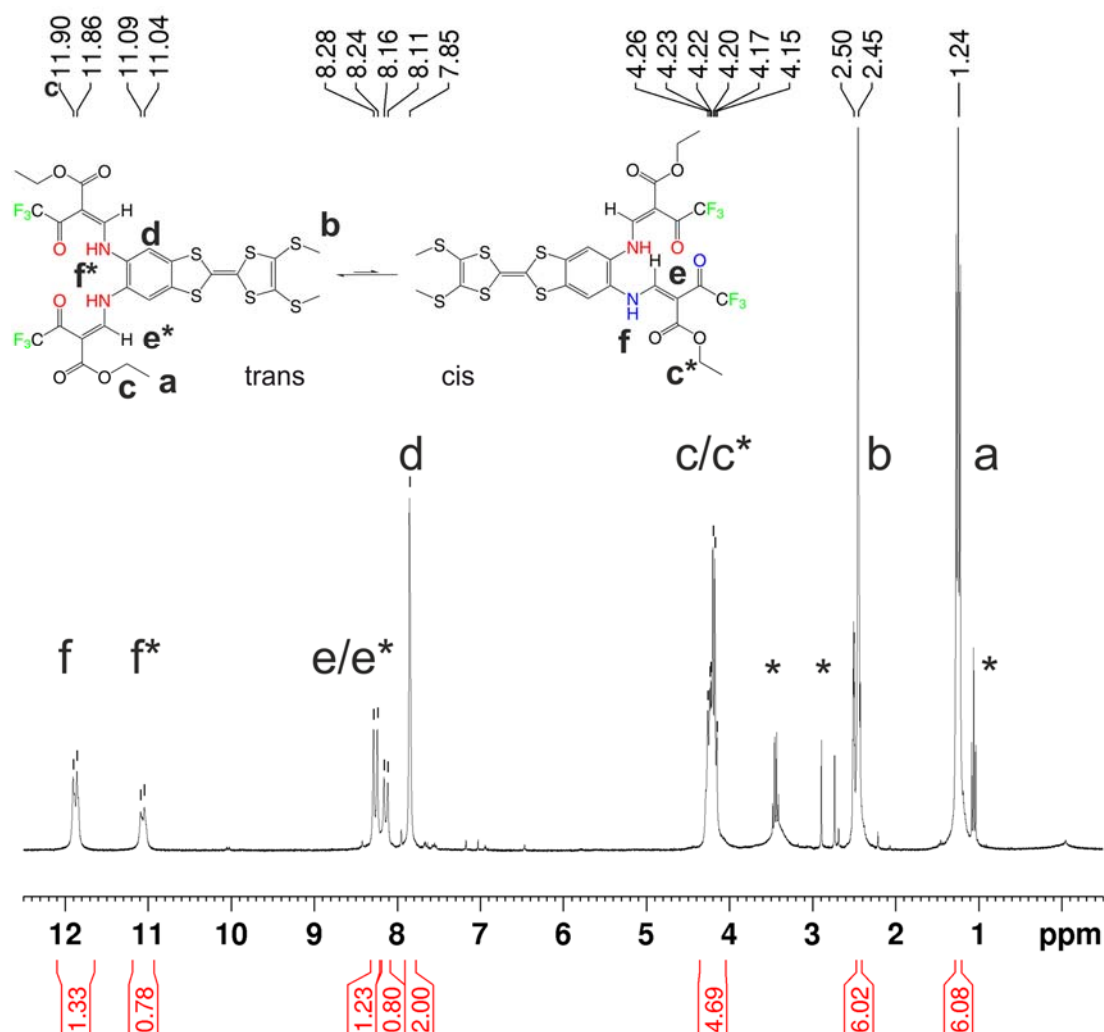


Figure S1 ^1H NMR spectrum of $\text{TTF}_{\text{LCF}_3\text{H}_2}$ (**1**) in dimethyl sulfoxide (DMSO) at 300 MHz with the signal assignment given within the spectrum.

The ^1H NMR spectrum of the ligand $\text{H}_2\text{TTF}_{\text{LCF}_3}$ (**1**) shows the expected signals^[1] of the Schiff base-like unit and the TTF unit. Signals **c**, **e** and **f** are duplicated in the spectrum. As shown in the signal assignment there is a *cis-trans* isomerism of the double bond that leads to shifted signals for the isomer. As can be seen from the intensity of the signals the *cis* isomer seems to be the dominant species in solution.

The associated ^{13}C NMR spectrum in Figure S2 reveals that there are 14 prominent signals. Signal assignment was performed on the symmetric *cis* molecule and is given within the figure. A closer inspection of the spectrum reveals that almost all peaks (except 2, 3 and 9) are duplicated. Compared with the ^1H NMR spectrum the intensity ratio of the prominent peak and its doubled sibling are similar. If again the *cis-trans* isomerism is considered in this molecule all peaks in the ^{13}C NMR spectrum have to be doubled. Apparently, the carbon atoms of the S–Me, the S–C_{quar} and the CH₂ group are not affected by this.

Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

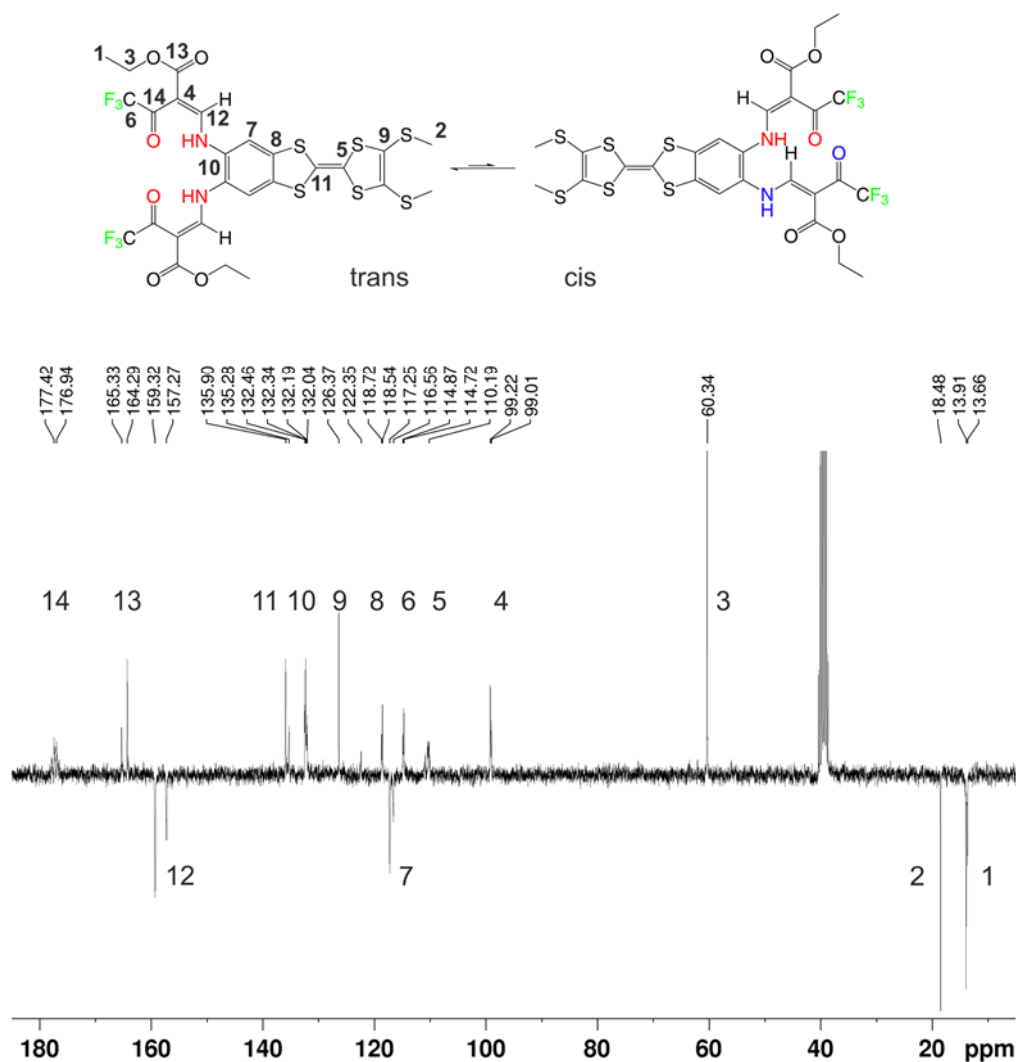


Figure S2 ^{13}C NMR spectrum of $\text{H}_2^{\text{TTF}}\text{LCF}_3$ (**1**) in dimethyl sulfoxide (DMSO) at 300 MHz in the *J*-modulated (JMOD) pulse sequence. Methine and methyl signals (down) have opposite phase to quaternary and methylene (up) signals. Signal assignment is given above the spectrum.

8.6.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted with a Netzsch TG 209 F1 Libra under nitrogen atmosphere using 4–19 mg of the sample with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$.

Complex **2** shows no significant mass loss up to 80°C (353 K) although even at 30°C app. 0.4% of loss can be recorded. Starting at 80°C a rather abrupt weight loss is detectable where up to a temperature of 160°C a total of 5.9% mass loss is recorded. This corresponds approximately to the loss of 0.7 molecules of pyridine. From that point on, a rather constant loss occurs up to a temperature of 245°C (518 K). With a loss of 8.7%, the loss of an entire pyridine molecule can be assumed from this point on. Further heating leads to an abrupt continuous decomposition of the complex **2**.

Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

The examination of the thermogravimetric analysis of the coordination polymer **4** shows that the product is stable up to quite high temperatures. Up until 212°C (485 K) no significant mass loss is detected. Further heating results in an abrupt loss of 8% corresponding to 0.4 molecules of bpee. The polymer **4** probably starts to degrade at this point. Further heating above 300°C (573 K) leads to a constant decomposition of complex **4**.

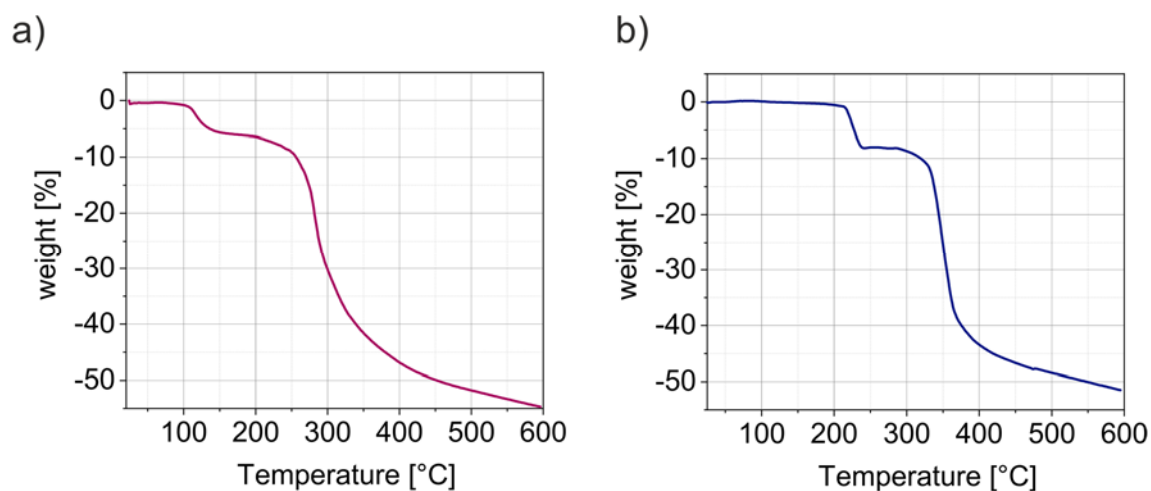


Figure S3 Thermogravimetric analysis of complex (a) [Fe^{TTF}L_{CF3}(py)₂] (**2**) and (b) {[Fe^{TTF}L_{CF3}(bpee)]}_n (**4**) in a temperature range of 23–600°C.

8.6.2 Temperature Dependent NMR Measurements

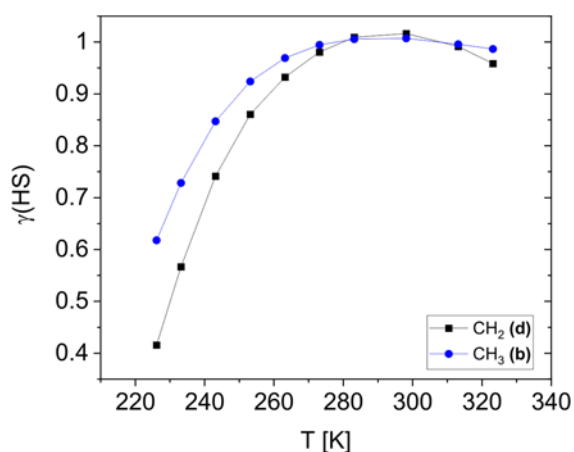


Figure S4 HS mole fraction (γ_{HS}) of **2** obtained by interpretation of the isotropic shift assuming ideal Curie behavior.

8.6.3 Signal Assignment of the ^1H NMR Spectra of REF

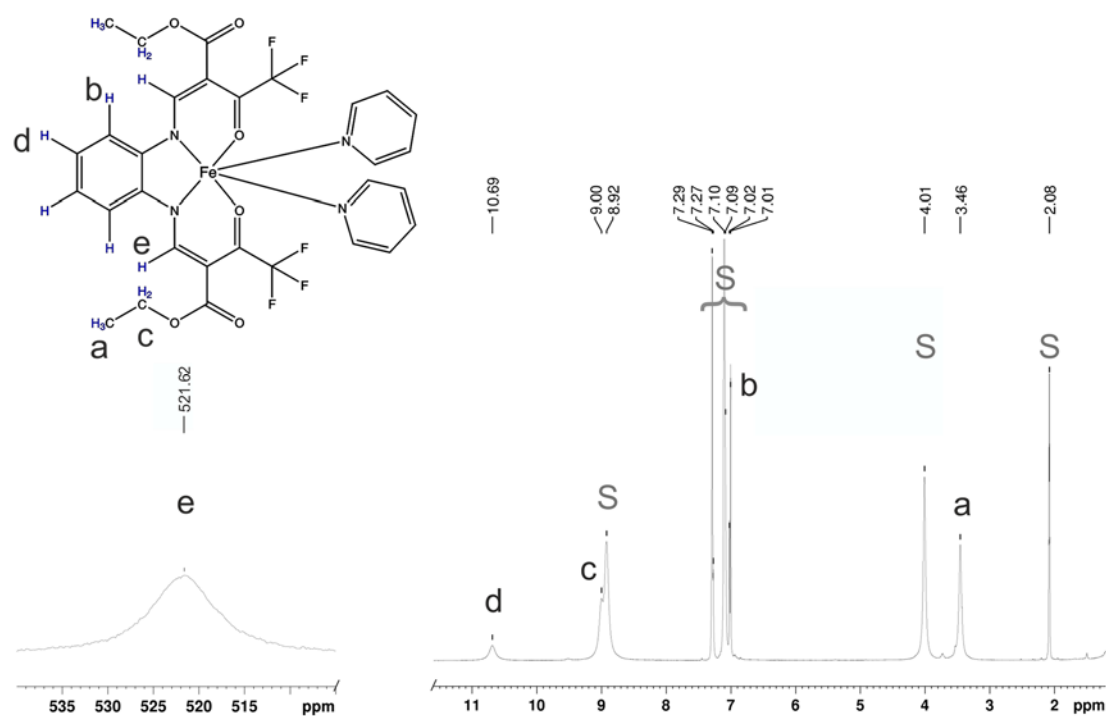


Figure S5 ^1H NMR spectrum of REF in a pyridine:toluene (1:1) mixture at $+50^\circ\text{C}$. The signal assignment is given at the left. S denotes the characteristic solvent peaks.

For the signal assignment literature values of similar complexes and the shifts of the free ligand were considered.^[2,3] Compared with similar complexes all signals are in the expected range and compared with **2** the signals **a**, **b**, **c** and **e** have almost identical shifts. The additional signal **d** in REF is missing in **2** but is in a range expected in comparison with literature values.^[2,4]

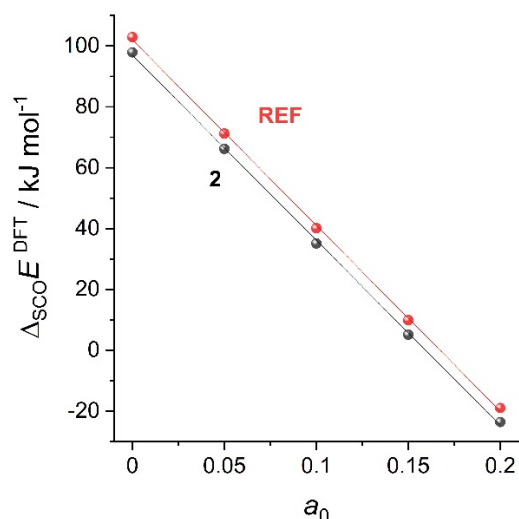


Figure S6 DFT-derived (B3LYP-D/TZVP) apparent SCO energies of iron(II) complexes **2** and REF as a function of the amount of exact Fock-exchange a_0 .

8.6.4 Temperature Dependence of the Isotropic Shifts of REF

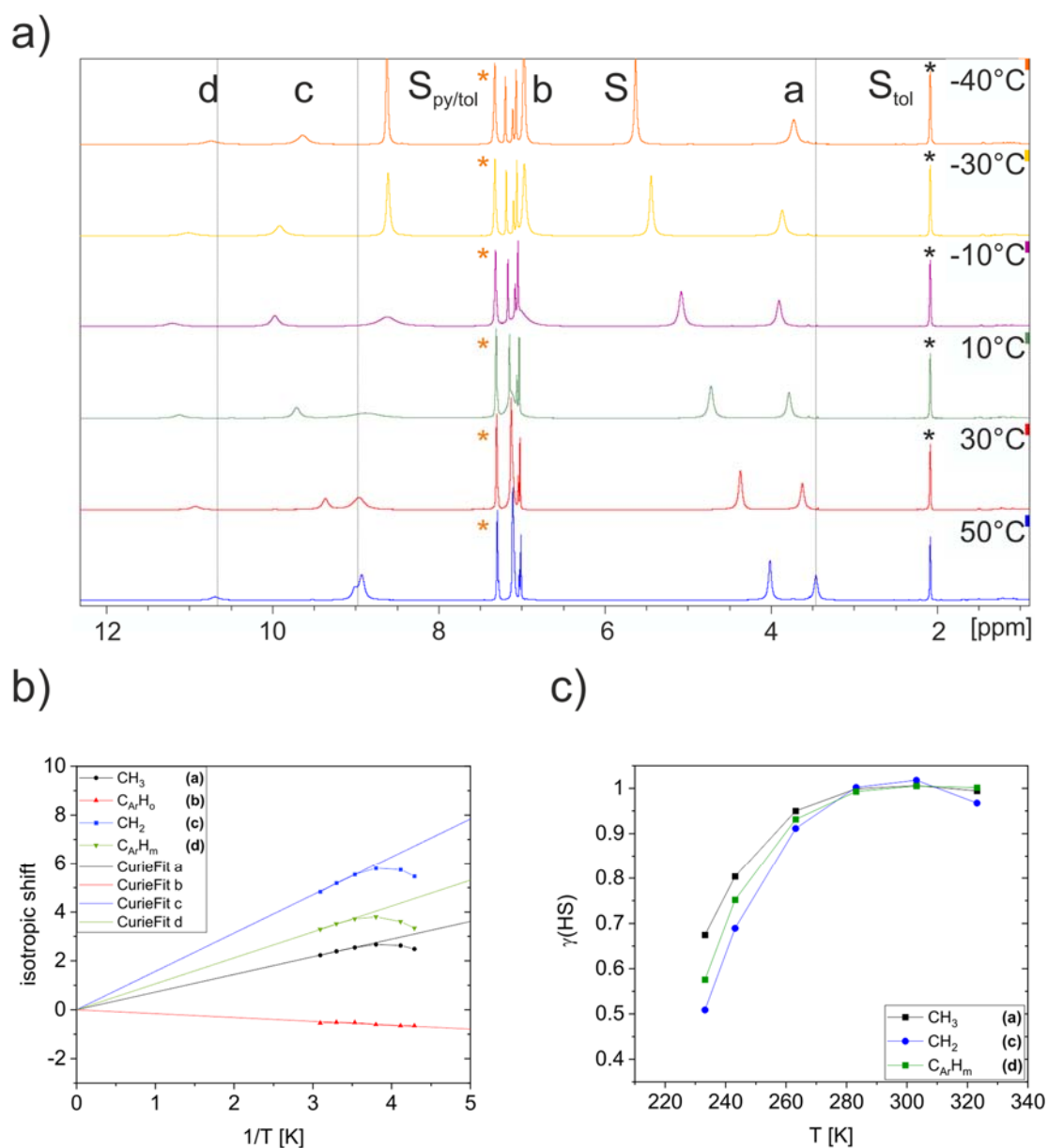


Figure S7 (a) VT ^1H NMR spectra of REF in a solution of a 1:1 mixture of toluene- d_8 and pyridine- d_5 . The given temperatures are target temperatures of the probe. (b) Isotropic shifts of REF plotted versus $1/T$ (dots). The solid lines represent the calculated shifts of the pure HS complex using extended Curie law. (c) HS mole fraction (γ_{HS}) of REF obtained by interpretation of the isotropic shift assuming ideal Curie behaviour.

8.6.5 Electrochemical Investigations

8.6.5.1 Cyclic Voltammetry at Ambient Temperature

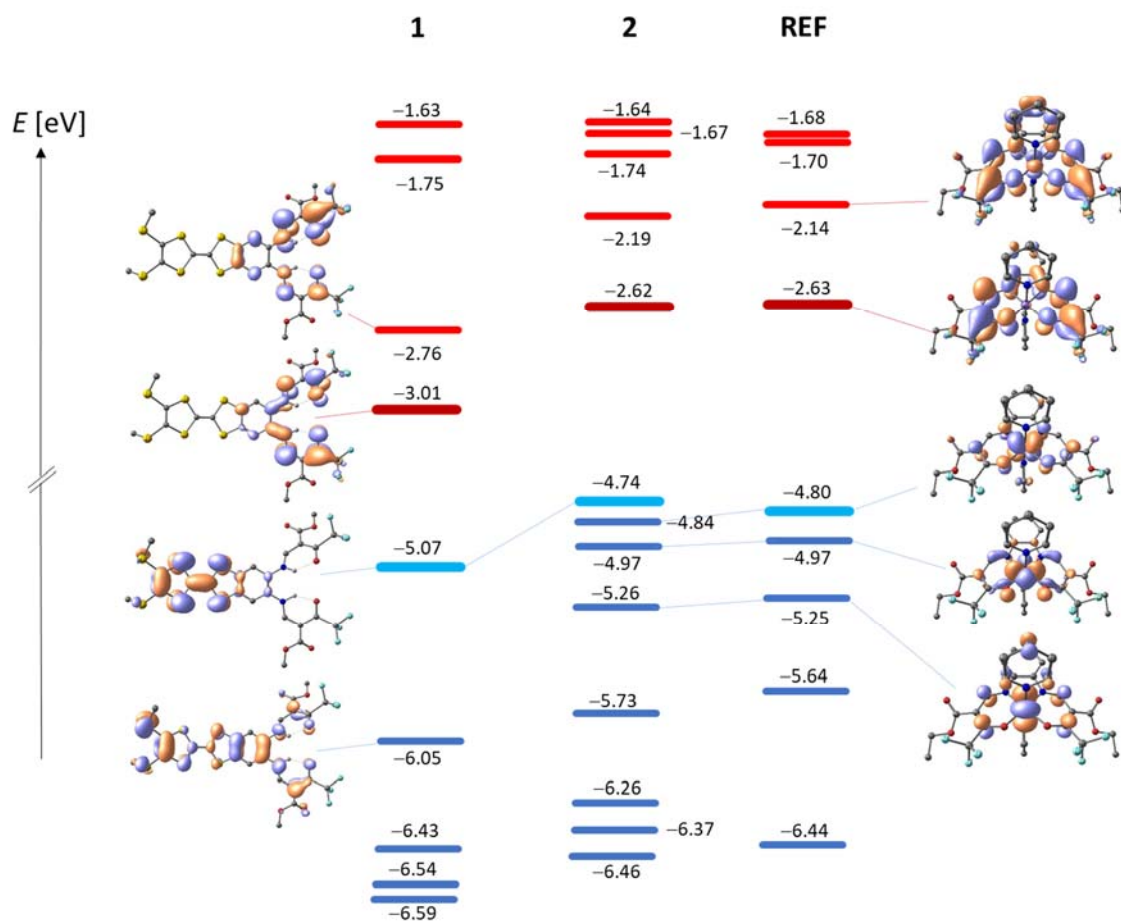


Figure S8 DFT calculated energies of occupied MOs (blue) and unoccupied MOs (red) for TTF-appended $[\text{Fe}^{\text{TTF}}\text{L}_{\text{CF}_3}(\text{py})_2]$ (middle), the reference complex REF (right), and ligand $\text{TTF}_{\text{L}_{\text{CF}_3}\text{H}_2}$ (left); frontier MOs are given for the single-site compounds.

Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

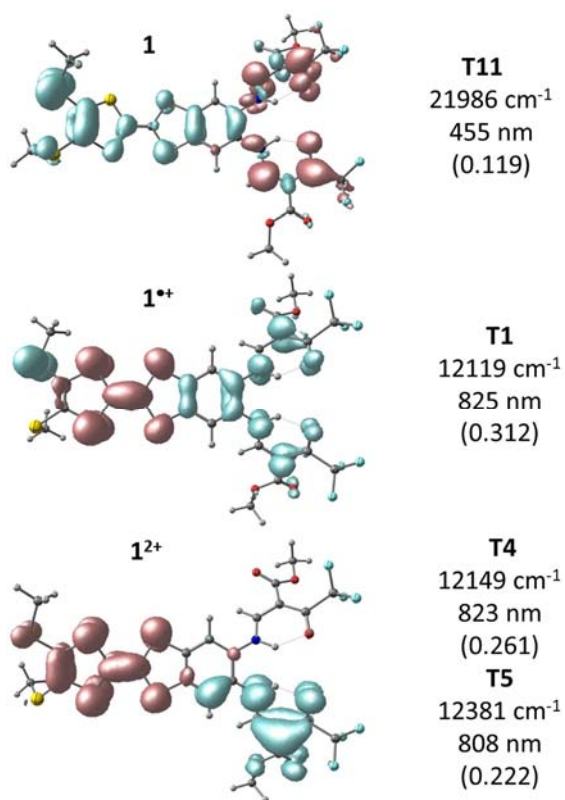


Figure S9 TD-DFT derived orbital plots of the free ligand **1** in the neutral state and after first and second oxidation **1⁺** and **1²⁺** with expected diagnostic transitions. Different colors denote differences in densities with blue as source and red as sink.

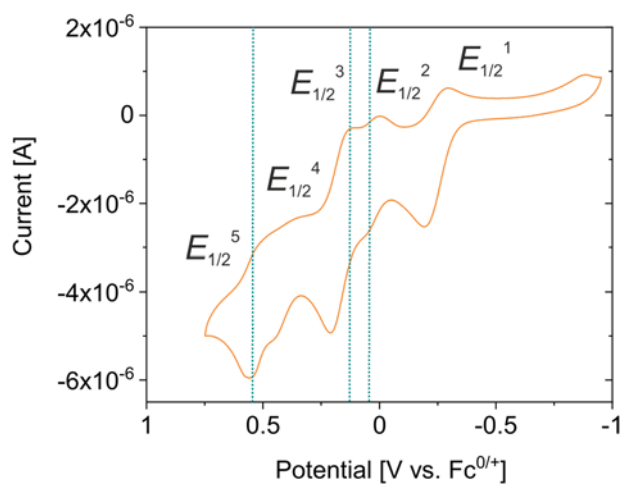


Figure S10 Cyclic voltammograms of complex **3** in DCM ($c = 1$ mM) with tetrabutylammonium hexafluorophosphate (NBu_4PF_6 ; 0.1 M) as a supporting electrolyte on a platinum working and counter electrode at 50 mV s^{-1} with a saturated calomel reference electrode. Dashed green lines represent the half wave potentials of **2**.

8.6.5.2 UV-Vis Spectroelectrochemistry

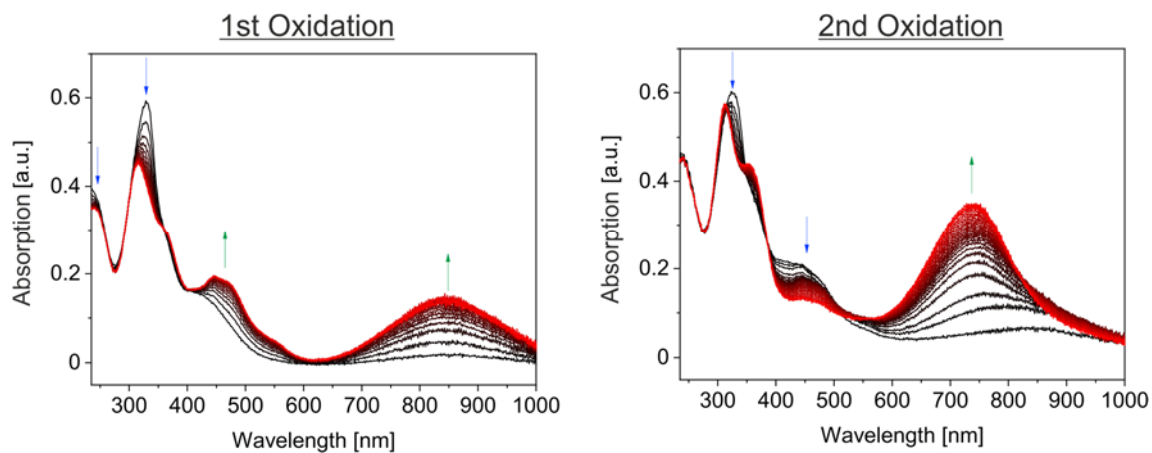


Figure S11 UV-Vis spectra recorded of **1** in DCM ($0.2 \text{ mol}\cdot\text{L}^{-1} \text{ NBu}_4\text{PF}_6$), during electrochemical oxidation at a constant potential of 0.46 V (1st oxidation) and 0.80 V (2nd oxidation) recorded against ferrocene with a platinum working and counter electrode and a silver wire as reference electrode. Black lines represent measurements at $t = 0 \text{ min}$, red lines after $t = 10 \text{ min}$ at the corresponding electrode potential. Green arrows denote outgrowing bands and blue arrows bleaching.

Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

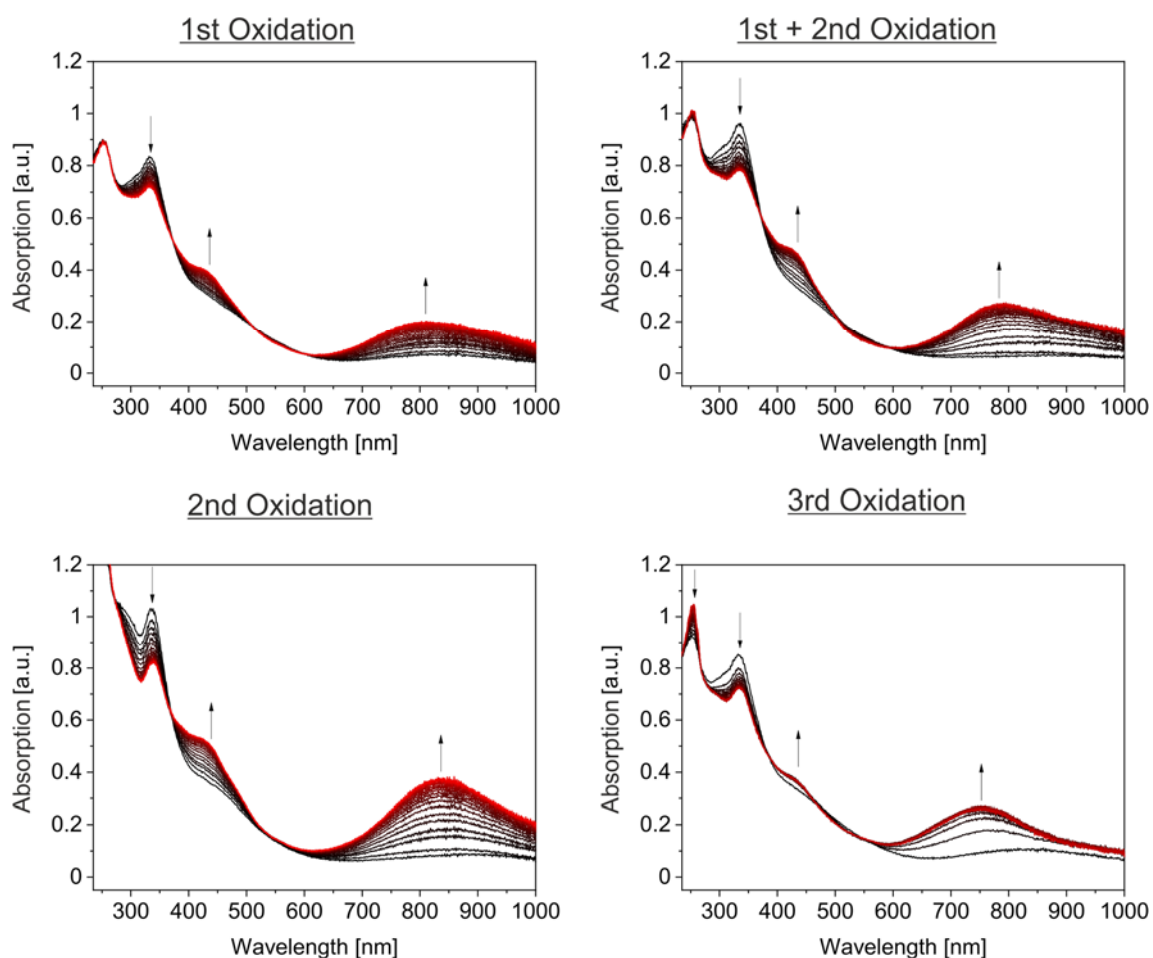


Figure S12 UV-Vis spectroelectrochemical investigation of **2** ($0.2 \text{ mol}\cdot\text{L}^{-1} \text{NBu}_4\text{PF}_6$, obtained at a constant potential of 0.23 V (1st oxidation), 0.37 V (1st and 2nd oxidation), 0.51 V (2nd oxidation) and 0.85 V (3rd oxidation) recorded against ferrocene with a platinum working and counter electrode and a silver wire as reference electrode. Black lines represent measurements at $t = 0$ min, red lines after $t = 10$ min at the corresponding electrode potential. Green arrows denote outgrowing bands and blue arrows bleaching.

Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

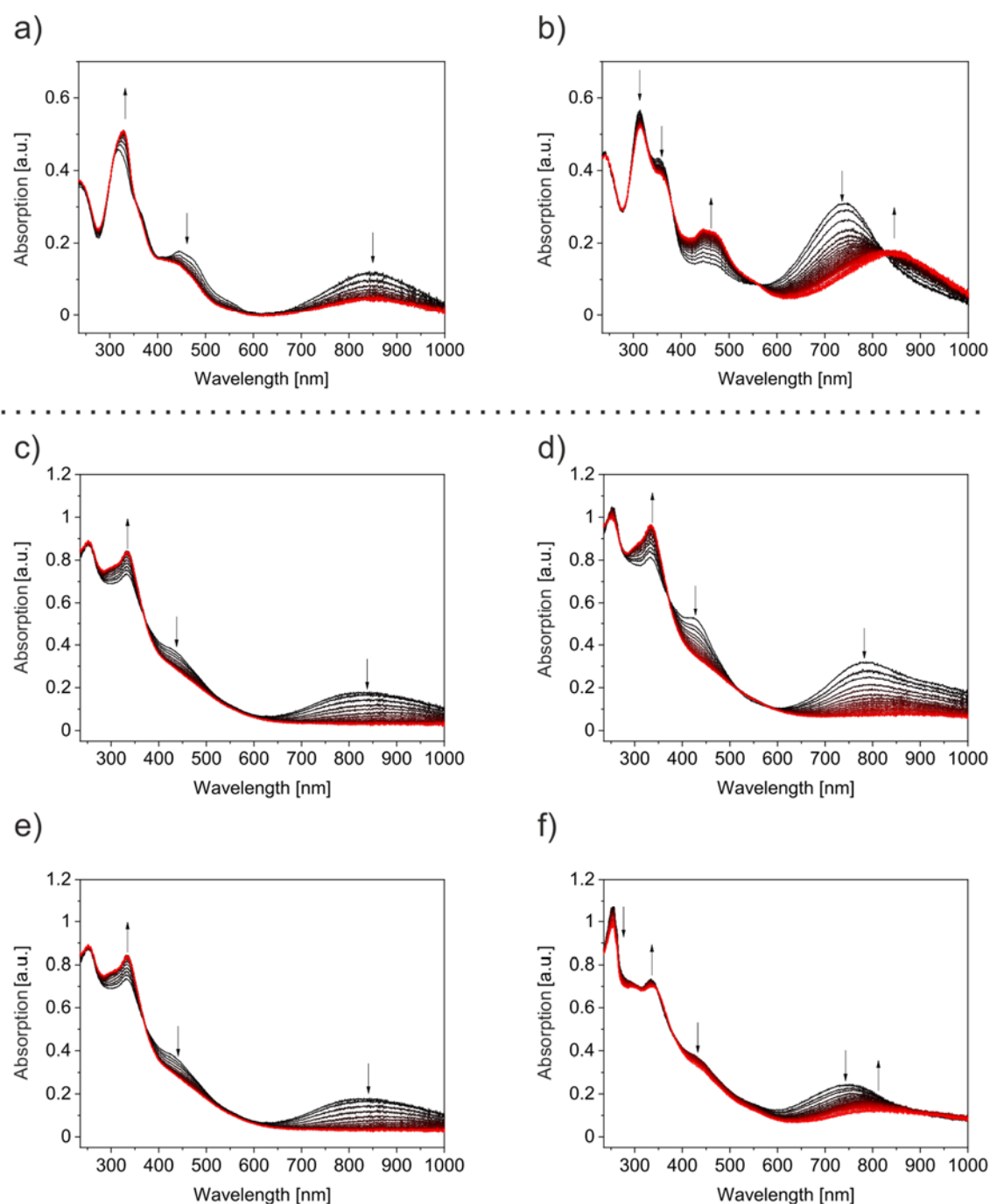


Figure S13 UV-Vis spectroelectrochemical investigation of the subsequent reduction of **1** ($0.2 \text{ mol}\cdot\text{L}^{-1} \text{NBu}_4\text{PF}_6$, obtained at a constant potential of (a) 0.10 V (1st reduction) and (b) 0.52 V (2nd reduction). UV-Vis spectroelectrochemical investigation the subsequent reduction of **2** ($0.2 \text{ mol}\cdot\text{L}^{-1} \text{NBu}_4\text{PF}_6$, obtained at a constant potential of (c) -0.05 V (1st reduction) (d) 0.05 V (1st and 2nd reduction) (e) 0.15 V (2nd reduction) and (f) 0.54 V (3rd reduction) recorded against ferrocene with a platinum working and counter electrode and a silver wire as reference electrode. Black lines represent measurements at $t = 0 \text{ min}$, red lines after $t = 10 \text{ min}$ at the corresponding electrode potential. Green arrows denote outgrowing bands and blue arrows bleaching.

8.6.5.3 VT Cyclic Voltammetry

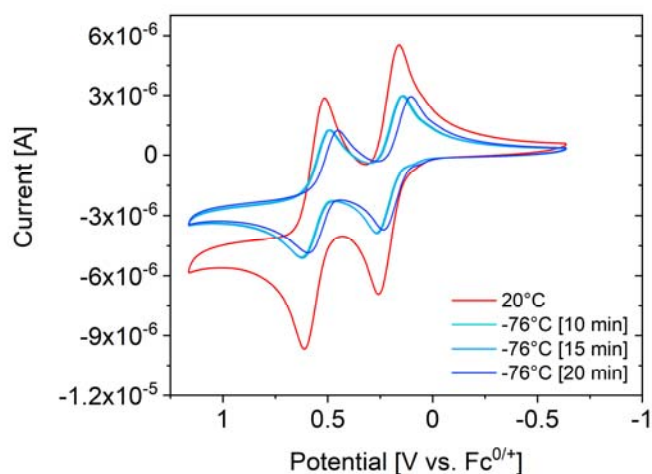


Figure S14 Cyclic voltammogram of $\text{H}_2^{\text{TTF}}\text{LCF}_3$ (**1**) in DCM with tetrabutylammonium hexafluorophosphate (NBu_4PF_6) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at $100 \text{ mV}\cdot\text{s}^{-1}$ with an Ag/Ag^+ reference electrode.

Ligand **1** shows a small shift of the electrode potential and a loss in intensity expected by increased solvent resistivity and decreasing diffusion coefficients.^[5] A maximum shift of 21 mV without any splitting of peaks is observed.

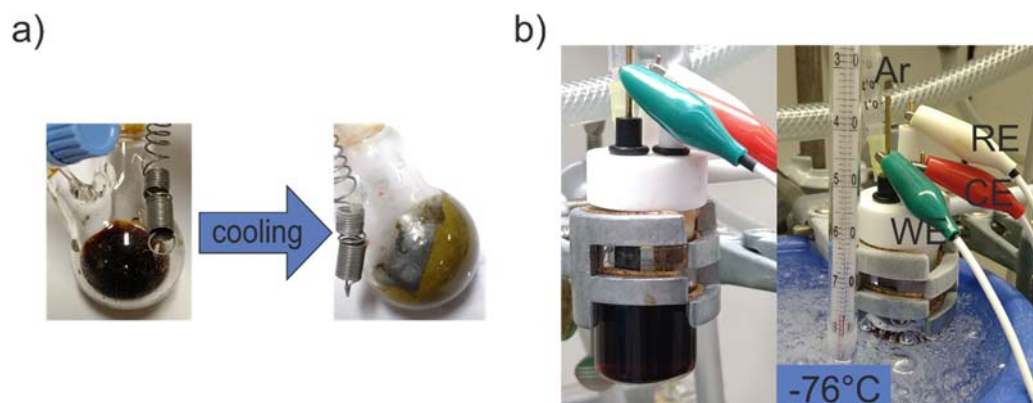


Figure S15 (a) color change of a solution of **2** in DCM upon cooling with liquid nitrogen (b) electrochemical cell used for the measurement at room temperature and at -76°C (cooled with a dry ice in isopropanol bath), WE = working electrode, CE = counter electrode, RE = reference electrode, Ar = persistent argon flow.

Redox Amphoterism and Spin Crossover in TTF-Based Iron(II) Complexes with a Redox Active Schiff Base-Like Equatorial Ligand

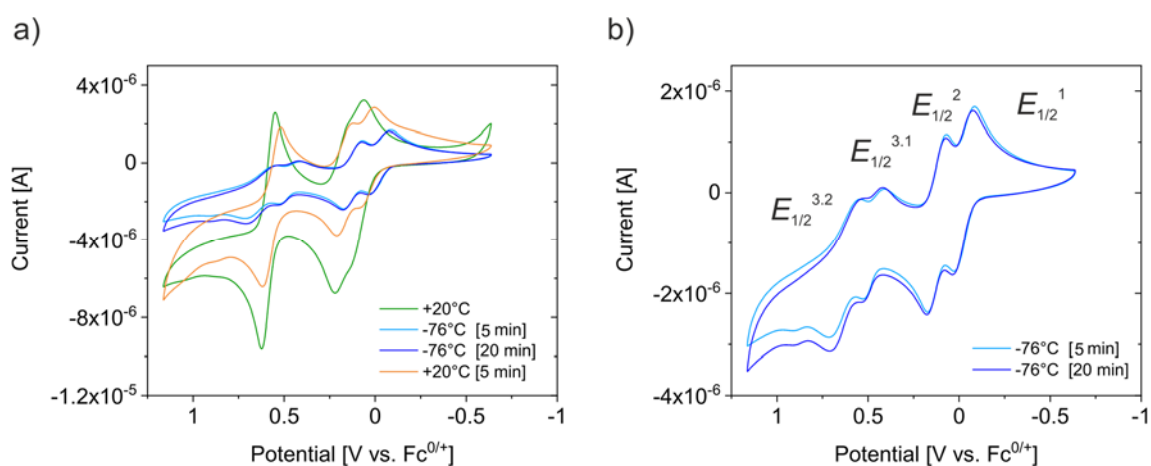


Figure S16 Cyclic voltammogram of **2** in DCM with tetrabutylammonium hexafluorophosphate (NBu₄PF₆) (0.1 M) as supporting electrolyte on a platinum working and counter electrode at 100 mV·s⁻¹ with an Ag/Ag⁺ reference electrode. (a) combined cooling and warming process (b) spectrum of only the cooled species.

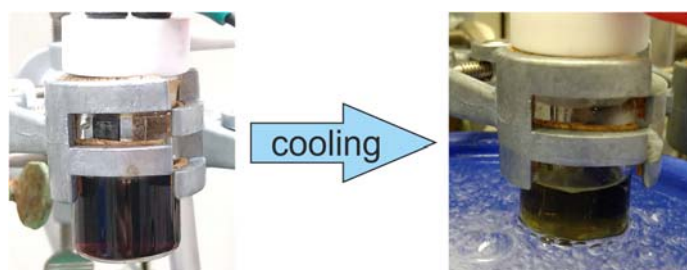


Figure S17 Color change of the examined solution of **REF** upon cooling with an isopropanol dry ice bath.

Figure S 17 reveals that upon cooling **REF** undergoes a SCO in solution that is accompanied by a color change from brown to green. Associated with this is an observable shift of 120 mV. Considering the Nernst equation, a shift is expected upon temperature change. As can be seen from the equations below the potentials should be shifted by at least 9 mV. Of course, one has to keep in mind that also diffusion of the oxidized and reduced species plays a crucial role.

$$\text{Nernst equation}^{[5]}: \quad E = E^0 + \frac{RT}{z_e F} \cdot \ln \frac{a_{ox}}{a_{Red}}$$

$$20^\circ\text{C} \quad E = E^0 + \frac{0.0252 \text{ V}}{z_e} \cdot \ln \frac{a_{ox}}{a_{Red}}$$

$$-76^\circ\text{C} \quad E = E^0 + \frac{0.0169 \text{ V}}{z_e} \cdot \ln \frac{a_{ox}}{a_{Red}}$$

8.6.6 References

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9. Publikationsliste

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A. Anas, S. S. Mondal, A. Wruck, A. Kelling, U. Schilde, P. Brandt, C. Janiak, S. Schönfeld, B. Weber, L. Rybakowski, C. Herrmann, K. Brennstuhl, S. Eidner, M. Kumke, K. Behrens, C. Günter, H. Müller, H.-J. Holdt: "Hydrogen-bonded supramolecular metal-imidazolate frameworks: gas sorption, magnetic and UV/Vis spectroscopic properties", *J. Inclusion Phenom. Macrocyclic Chem.* **2019**, *94*, 155–165.

L. Zappe, S. Schönfeld, G. Hörner, K. A. Zenere, C. F. Leong, C. Kepert, D. M. D'Alessandro, B. Weber, S. M. Neville: "Spin crossover modulation in a coordination polymer with redox-active bis-pyridyltetrathiafulvalene (py₂TTF) ligand", *Chem. Commun.* **2020**, *56*, 10469–10472.

S. Schönfeld, K. Dankhoff, D. Baabe, M.-K. Zaretzke, M. Bröring, K. Schötz, A. Köhler, G. Hörner, B. Weber: "Iron(II) Spin Crossover Complexes Based on a Redox Active Equatorial Schiff-Base-Like Ligand", *Inorg. Chem.* **2020**, *59*, 8320–8333.

S. Schönfeld, W. Bauer, S. Thallmair, G. Hörner, B. Weber: "Running in the Family: Molecular Factors controlling Spin Crossover of Iron(II) Complexes with Schiff-base like Ligand", *Z. Anorg. Allg. Chem.* **2021**, *647*, 905–914.

S. Schönfeld, G. Hörner, F. W. Heinemann, A. Hofmann, R. Marschall, B. Weber: "Spin States of 1D Iron(II) Coordination Polymers with Redox Active TTF(py)₂ as Bridging Ligand", *Z. Anorg. Allg. Chem.* **2021**, *647*, 295–305.

S. Schönfeld, F. Baier, J. Jungklaus, G. Hörner, S. Winterstein, A. Enders, J. Senker, B. Weber: "Iron(II) spin crossover complexes with a sulfur rich ligand backbone", *J. Appl. Phys.* **2021**, *129*, 083901-1–083901-10.

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Hiermit erkläre ich, dass ich die Dissertation nicht bereits zur Erlangung eines akademischen Grades eingereicht habe und dass ich nicht bereits diese oder eine gleichartige Doktorprüfung endgültig nicht bestanden habe.

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