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A Brønsted ligand molecular switch with five accessible states

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Abstract: A mononuclear Fe(II) complex, prepared with a Brønsted diacid ligand, H₂L (H₂L = 2-[5-phenyl-1*H*-pyrazole-3-yl] 6-benzimidazole pyridine), shows switchable physical properties and was isolated in five different electronic states. The spin crossover (SCO) complex, [Fe^{II}(H₂L)₂](BF₄)₂ (**1A**), exhibits abrupt spin transition at $T_{1/2} = 258$ K, and treatment with base yields a deprotonated analogue [Fe^{II}(HL)₂] (**1B**), which shows gradual SCO above 350 K. A range of ferric analogues were also characterized. [Fe^{III}(HL)(H₂L)](BF₄)Cl (**1C**) has an $S = 5/2$ spin state, while the deprotonated complexes [Fe^{III}(L)(HL)], (**1D**), and (TEA)[Fe^{III}(L)₂], (**1E**) exist in the low-spin $S = 1/2$ state. The electronic properties of the five complexes were fully characterized and we demonstrate *in situ* switching between multiple states in both solution and the solid-state. The versatility of this simple mononuclear system illustrates how proton donor/acceptor ligands can vastly increase the range of accessible states in switchable molecular devices.

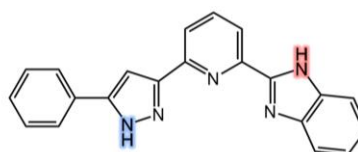
Next-generation intelligent molecular devices will rely on simple, nanoscale species possessing multiple distinct interchangeable electronic states.^[1] Amongst the most promising candidates capable of fulfilling these criteria are coordination complexes based on cheap, readily-available 1st row transition metals.^[2] These can exhibit switchable magnetic, electronic and optical properties in response to temperature, light, pressure or guest absorption/desorption.^[3] The key advantage of such species is their amenability to novel molecular design approaches, allowing control over both structure and composition, and accordingly, their electronic properties, which can be tuned by modification of both the inner- (via ligand design),^[4] and outer- (via hydrogen-bonding, anion or solvent interactions) coordination spheres.^[5]

For instance, modification of capping ligands affects their binding strength and facilitates fine-tuning of high-spin (HS) to

low-spin (LS) state interconversion in Fe^{II} or Fe^{III} spin cross-over (SCO) complexes under thermal- or photo-excitation.^[4a, 6] Likewise, valence conversion – where an external stimulus is used to trigger an electron-transfer-coupled spin transition (ETCST) – can be achieved in poly-nuclear systems where strong electronic interactions between neighbouring metal centres are engineered by careful (or serendipitous) ligand selection/design.^[7]

Outer-sphere coordination effects rely on weak interactions and can be used to modify spin states upon exposure to chemical stimuli. For example, the interaction of guest molecules with coordination systems can be used to achieve spin state switching.^[8] More recently, the development of pH-responsive systems using multi-dentate ligands which retain an acidic proton has allowed the design of a new class of switchable complexes.^[9] These “Brønsted ligands”, which act as both Brønsted acids and bases, couple the properties of the complex to its environment, where protonation/deprotonation of the ligand dramatically modifies the ligand field around coordinated metal cation(s), and as a result, the redox properties of the system. Brønsted ligand complexes typically form hydrogen-bonded networks through -N-H...N- donor-acceptor interactions,^[10] and can interact with further proton donors/acceptors, leading to the enhancement of spin transition phenomena through cooperative interactions.^[11]

To date, very few examples of protonation-controlled state-switching in molecular species are known. Most recently, Lehn and co-workers showed that the SCO behaviour of a polynuclear {Fe₄} grid-type complex can be modified in response to pH by using protic ditopic ligands.^[12] And while mononuclear Fe^{II}-complexes which reversibly respond to protonation/deprotonation are known, these systems can be switched between just two discrete states.^[4b, 9b, 13] Here, we describe a novel ligand design strategy employing an asymmetric Brønsted ligand (Scheme 1) that can be used to isolate a mononuclear Fe-complex with five independently accessible physical states. This species, [Fe^{II}(H₂L)₂](BF₄)₂ (**1A**) (where H₂L = 2-[5-phenyl-1*H*-pyrazole-3-yl]6-benzimidazole pyridine), permits step-wise deprotonation of the non-equivalent imidazole and pyrazole sites (e.g. imidazole $pK_a = 19.8$, pyrazole $pK_a = 16.4$),^[14] allowing the complex to be protonated/deprotonated sequentially under thermodynamic control. The ligand field strength is widely tuned by protonation and allows access to five different species: [Fe^{II}(H₂L)₂](BF₄)₂ (**1A**), [Fe^{II}(HL)₂] (**1B**), [Fe^{III}(HL)(H₂L)](BF₄)Cl (**1C**), [Fe^{III}(L)(HL)] (**1D**), and (TEA)[Fe^{III}(L)₂] (**1E**) (Figure 1).



Scheme 1. Structure of ligand H₂L, highlighting the two acidic protons which permit sequential protonation/deprotonation in response to external stimuli.

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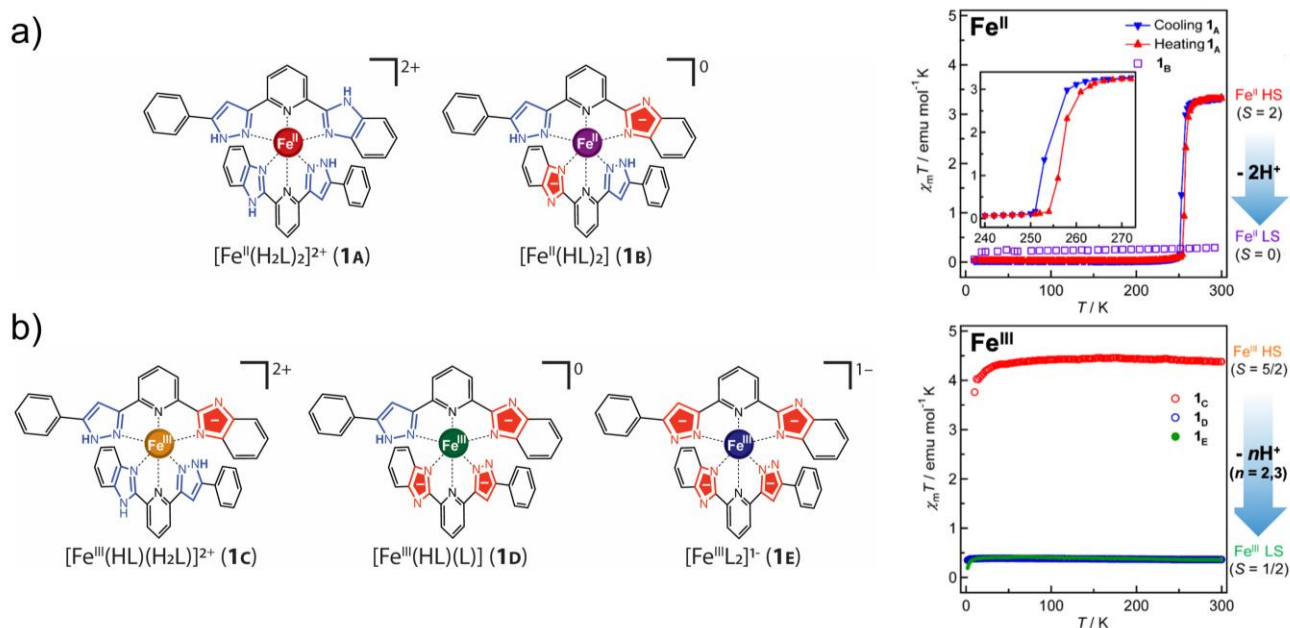


Figure 1. Structures of complexes **1A–E**, showing each of the five electronic states accessed through deprotonation of the acidic benzimidazole and imidazole moieties. Ferrous species are shown top (**a**) and ferric species bottom (**b**), where the colour of the Fe ion in each complex corresponds to the colour of the isolated crystals. Temperature dependent magnetic susceptibility data for complexes **1A–1E** are shown (right), highlighting how deprotonation of the ligand in both cases results in a HS \rightarrow LS transition at room temperature. Magnetic hysteresis in **1A** on cooling (blue) and subsequent heating (red) cycles is shown inset.

One-pot methods were used to prepare the complexes from the free ligand. The fully protonated complex, **1A**, was obtained as red block crystals (monoclinic, space group $C2/c$ (Figure S1)) by slow evaporation of a butyronitrile solution of H_2L and $Fe(BF_4)_2 \cdot 6H_2O$. The central Fe(II) ion exists in an octahedral environment, coordinated by six N atoms from the two H_2L ligands. At 100 K, the average Fe–N distance is 1.96 Å, and the Σ value (the sum of the deviation of each of the 12 *cis* N–Fe–N angles from 90°) = 96.40° , indicative of a slightly distorted LS Fe(II) ion. A supramolecular one-dimensional chain is formed *via* π – π stacking interactions between the phenyl and pyridine groups of neighbouring molecules and interactions between BF_4^- anions and ligand N–H moieties (Figure S1b).

The partially deprotonated neutral complex **1B** was obtained as purple columnar crystals (monoclinic space group $P2_1/n$, (Figure S2)) by the diffusion of ammonia vapour into a solution of **1A**. The structure is almost identical to that of **1A**, but the average Fe–N bond length of 1.95 Å and Σ value of 89.10° are typical of a LS Fe(II) ion. π – π -stacking interactions and N–H...N hydrogen bonds between the protonated pyrazole and deprotonated benzimidazole moieties of neighbouring $[Fe^{II}(HL)_2]$ units form a one dimensional chain-like array of complexes (Figure S2b).

Ligand deprotonation significantly affects the electronic properties of complexes **1A** and **1B**. In addition to the colour change from red to purple (see Figure S3–S5), the magnetic response can also be switched by ligand deprotonation. Temperature dependent magnetic susceptibility data for **1A** and **1B**, in the form of $\chi_m T$ versus T plots, are shown in Figure 1. **1A** displays rapid spin conversion with 2.8 K hysteresis at $T_{1/2\downarrow} = 257.7$, $T_{1/2\uparrow} = 260.5$ K. Between 300 K and 260 K, the $\chi_m T$ value of **1A** was constant at $3.33 \text{ emu mol}^{-1} \text{ K}$, which is close to the spin only value expected for four unpaired electrons ($S = 2$, $3.0 \text{ emu mol}^{-1} \text{ K}$). Mössbauer spectroscopy and high temperature

single-crystal X-ray structural analysis of **1A** support this assignment (described fully in the SI). At 300 K, a quadrupole doublet with an isomer shift, δ , of 0.966 mm s^{-1} and quadrupole splitting, ΔE_Q , of 2.103 mm s^{-1} is observed, typical of HS Fe(II). On cooling to 100 K, values of $\delta = 0.415 \text{ mm s}^{-1}$ and $\Delta E_Q = 0.646 \text{ mm s}^{-1}$ correspond well with LS Fe(II) ions. Whilst **1A** is diamagnetic at low temperatures, conversion to the HS state occurs through light-induced excited spin state trapping (LIESST) upon irradiation with both green and red laser light (see Figure S6).^[3a] **1B**, on the other hand, appeared to be in the LS Fe(II) state below 300 K ($\delta = 0.366 \text{ mm s}^{-1}$, $\Delta E_Q = 0.469$ at 20 K), albeit with a small residual paramagnetic impurity attributed to partial oxidation of Fe^{II} to Fe^{III} upon destabilisation of the Fe^{II} state after deprotonation (discussed further below). The $\chi_m T$ value gradually increased at higher temperatures, which is consistent with a partial LS–HS SCO transition (Figure S7).

We note that the abrupt change in $\chi_m T$ values in **1A** suggests the existence of significant cooperativity effects. The structure of **1A** is mediated by intermolecular π – π stacking and extensive hydrogen bonding interactions (Figure S1), ensuring that the magnetic switching of the molecular species propagates in three dimensions. In **1B**, the molecular species pack into isolated 1-D chains due to the modified H-bonding interactions in the partially deprotonated HL groups (Figure S2), leading to diminished cooperativity between neighbouring complexes and more gradual SCO transition. Together, these results neatly illustrate how asymmetric Brønsted ligands are uniquely able to modulate magnetic properties by simultaneously tuning both the ligand field strength and H-bonding dynamics.

We anticipated that the optical and electrochemical behaviour of the complexes should be tuneable in response to ligand

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deprotonation. *In situ* switching of the electronic properties in the solution-state was explored using cyclic voltammetry (CV) on an

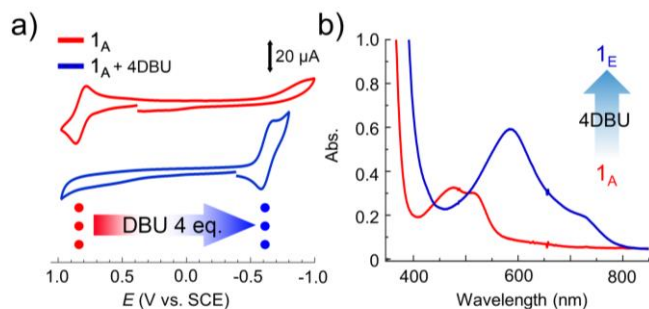


Figure 2. Solution-state switching experiments, showing: **a)** cyclic voltammograms of **1_A** (red) and **1_A** following titration with 4 equivalents of base (blue). This agrees well with the corresponding CV of pure **1_E** (Fig. S9). **b)** UV-vis titration data showing the solution phase conversion of **1_A** to **1_E** upon addition of 4 equivalents of base. Note that the UV-vis profile of **1_E**, as formed *in situ*, corresponds closely to the matching spectra of the as-synthesised product (Fig. S4).

acetonitrile solution of **1_A** before and after addition of 4 equivalents of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) under air. Addition of fewer than four equivalents of base produced poor/uninterpretable data due to the insolubility of the partially deprotonated homologues (*c.f.* the neutral complex **1_B**), whereas complete deprotonation of the complex should form an anionic species. Figure 2a shows the voltammogram of **1_A** in which a quasi-reversible Fe^{III/II} redox couple appears, centred at +0.84 V vs. SCE. Addition of 4 equivalents of DBU causes the Fe-centred redox process to shift to -0.68 V vs. SCE, suggesting that the Fe(II) ion has been destabilised by ligand deprotonation and spontaneously oxidised to Fe(III). This process was also followed *via* UV-vis spectrometry, where titration with 4 equivalents of DBU led to a clear red shift in the observed absorption maxima from 475 nm to 585 nm, which tends towards saturation after addition of more than *ca.* 3.5 equivalents of base (Figure 2b), consistent with the formation of a new stable complex. The lack of a clear isosbestic point however, indicates that the switching process is not straightforward, which can be attributed to both the formation of less-soluble intermediates (such as **1_B**) and the spontaneous oxidation of the complex in response to base.

To confirm these assignments, a fully deprotonated complex was prepared in an analogous manner to **1_A**, but in the presence of additional base and charge compensating tetraethylammonium (TEA) ions. The resultant product, (TEA)[Fe^{III}(L)₂] (**1_E**), was isolated as blue-plate crystals and electrochemical analysis (Figure S10 and S12) of the as-synthesised complex found an $E_{1/2}$ value of -0.68 V vs. SCE, exactly matching that of the deprotonated species formed *in-situ* during DBU titration. Similarly, UV-vis spectroscopy of the product **1_E** was found to exactly match that of the signal observed at 585 nm on the titration of **1_A** with 4 equivalents of DBU. For comparison, two partially deprotonated ferric homologues, [Fe^{III}(HL)(H₂L)](BF₄)Cl (**1_C**) and [Fe^{III}(L)(HL)] (**1_D**), were then prepared (single crystal X-ray structural analysis for the three oxidised analogues **1_{C-E}** is presented in detail in the SI). While the neutral complex **1_D** was not suitable for comparative voltammetric analysis due to its insolubility, CV analysis of **1_C** in methanol ($\epsilon_{\text{MeOH}} = 32.7$, $\epsilon_{\text{MeCN}} =$

37.5) showed an $E_{1/2}$ value of +0.44 V vs. SCE for the Fe^{III/II} redox couple (Figure S11). This is intermediate between that of **1_A** and

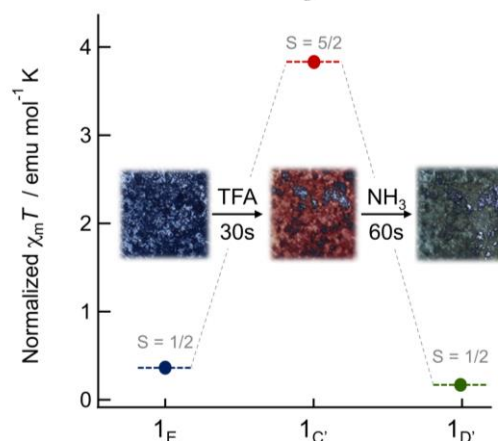


Figure 3. Solid-state switching experiments showing the change in both colour and molar susceptibility (at 300 K) between the ferric complexes **1_{C-E}** in response to treatment with acidic or basic vapours. Susceptibility is normalised to the expected $\chi_m T$ value for **1_E**, where differences between the expected and observed values for **1_C** and **1_D** are accounted for by incomplete conversion and inclusion of diamagnetic salts resulting from the vapour treatment.

1_E, as might be expected by partial deprotonation. We also note that while reversibly switching between **1_E** and **1_A** under acid/base control was not possible due to the need for additional reductant, addition of trifluoroacetic acid (TFA) into a solution of **1_E** was shown to yield the protonated ferric complex **1_C** (Fig. S13).

These results show that a range of electronic states can be accessed, *in situ*, simply by controlling the degree of ligand protonation. They do, however, also highlight the technical challenges which must be addressed to realise the potential of this system – chiefly issues with the insolubility of neutral charge states. To mitigate this, we also explored the solid-state properties of complexes **1_{A-E}**. The magnetic properties of the Fe(III) complexes were studied in response to deprotonation of the ligand groups (Figure 1b). At 300 K, the $\chi_m T$ value of **1_C** is 4.38 emu mol⁻¹ K, consistent with the expected value for a high-spin Fe(III) ion (Mössbauer parameters: $\delta = 0.483$ mm s⁻¹, $\Delta E_Q = 0.501$ at 20 K), whilst **1_D** and **1_E** exhibit $\chi_m T$ values of 0.407 and 0.365 emu mol⁻¹ K respectively ($\delta = 0.097, 0.099$ mm s⁻¹, $\Delta E_Q = 3.004, 2.931$ at 100 K), consistent with low-spin Fe(III) ions. In the case of complexes **1_C** and **1_E**, a decrease in the $\chi_m T$ value is observed at low temperature which we attribute to intermolecular interactions (Curie-Weiss plots for **1_{C-E}** are provided in the SI). As before, switching of the spin states of **1_C** (HS, $S = 5/2$) and **1_D** and **1_E** (LS, $S = 1/2$) arises from the increased ligand basicity upon deprotonation.

In situ solid-state switching properties of complexes **1_{A-E}** were explored via a combination of colorimetric and magnetic measurements. A ground sample of compound **1_A** immobilized on filter paper was exposed to NH₃ vapour, yielding a clear colour change from red to purple, indicating deprotonation and the formation of **1_B**. Subsequent exposure to TFA vapour however did not lead to reversible conversion to **1_A**, instead forming a mixed red-orange phase which we attribute to partial, uncontrolled oxidation to Fe(III). In contrast, exposure of **1_E** to TFA vapour was found to yield an orange product, **1_C**, which could

further be converted to a green phase, **1D'**, on treatment with NH₃ (Figure 3). Magnetic susceptibility measurements normalised to the initial $S = 1/2$ spin state of **1E** support these assignments, showing a LS→HS→LS transition, in line with that expected due to protonation and subsequent deprotonation of the Fe(III) complex. Cycling experiments between **1ED'** and **1c** show promise (Fig S15), however, accumulation of ammonium trifluoroacetate salt impedes the cyclability in this proof of concept system.

In conclusion, we have demonstrated that a novel ligand design strategy employing an asymmetric, tridentate, Brønsted ligand permits multi-state switching behaviour in a simple mononuclear coordination complex. Unlike the handful of previous examples of protonation-triggered switching in mononuclear metal complexes, which show exclusively binary switching responses, we have demonstrated that five distinct electronic states can be accessed, all of which show differing colorimetric, electrochemical and/or magnetic properties. This unique multi-step switching response is due to the asymmetric design of the Brønsted ligand groups, allowing the ligand field of the central Fe ion to be carefully tuned in the solution and solid-states by sequential deprotonation steps. The acid/base vapour-driven solid-state interconversion between magnetic states is a significant milestone in the development of functional molecular materials, and emphasises the potential for asymmetric Brønsted ligands as components in novel molecular switches, supramolecular assemblies or sensors based on molecular recognition *via* dynamic H-bonding interactions. We propose that multi-responsive, proton-coupled systems based on this strategy will represent an important next-step in the development of smart molecular devices with switchable physical and electronic states.

Acknowledgements

This work was supported by a Grant-in-Aid for Challenging Exploratory Research (no. 18K19088), Grant-in-Aid for Scientific Research (C) (no. 17K05800) and Grant-in-Aid for Scientific Research on Innovative Areas 'Coordination Asymmetry' (no. JP16H06523) from the Japan Society for the Promotion of Science (JSPS). This work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2018G102). We thank the University of Nottingham Propulsion Futures Beacon and the Leverhulme Trust (RPG-2016-442) for funding towards this research.

Keywords: iron • magnetism • redox • spin crossover • Brønsted acid/base

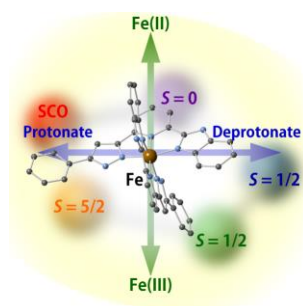
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Entry for the Table of Contents

Layout 1:

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A mononuclear Fe(II) complex prepared with an asymmetric Brønsted ligand exhibited multi-state switchable properties and was isolated in five distinct electronic states. By modifying the degree of protonation, both spin- and redox-interconversion was observed, resulting in a range of tuneable magnetic, electrochemical and optical properties.



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