

η^5 -Cyclopentadienyl-Iron(II)-[14]Triphyrin(2.1.1) Sandwich Compounds: Synthesis, Characterization, and Stable Redox Interconversion

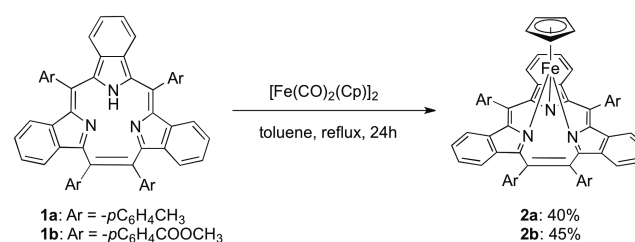
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((Dedication---optional))

Ferrocene, an iron(II) center sandwiched by a pair of aromatic cyclopentadienyl (Cp) ligands, is the first known and archetypal metallocene that was discovered in 1951.^[1] After that, research into ferrocene-containing compounds continues apace within diverse areas, such as redox mediator, catalyst, electron donor, rotational

hinge part, and so on.^[2] However the larger macrocyclic π -conjugated system with monovalent anionic character is scarcely reported so far, due to the weak coordination ability of π -extended Cp-type ligands. Especially, in porphyrin families there are a few reports in this context:^[3] (1) Cp–Sc^{III}–porphyrin,^[4a] Cp–Zr^{II}–porphyrin,^[4b] Cp*–Ru^{IV}–porphycene (Cp* = pentamethyl-cyclopentadienyl),^[4c] although porphyrin and porphycene are divalent ligands; (2) β,β' -fused monoruthenocenylporphyrins, bisferrocenoporphyryns,^[5a] metalloporphycenes^[5b] and cyclopentadienylruthenium π complexes of subphthalocyanines^[5c] where five-membered ring part (pyrrole or cyclohexadiene moiety) acted as ligands. Only recently double-decker iron(II) complexes of dithiaethyneporphyrin^[6] and N-fused porphyrin (NFP),^[7] where they behaved as macrocyclic tridentate ligands with a single negative charge, have been reported. During the synthesis of NFP complex, they detected the Cp–Fe^{II}–NFP compound by mass spectroscopy, which has yet to be isolated. To date, the synthesis of Cp–Fe^{II}–porphyrin sandwich compound remains a considerable challenge.

In 2008, we reported a facile protocol to synthesize [14]triphyrin(2.1.1) (TriP, **1**) as the first example of boron-free ring contracted porphyrins.^[8,9] In contrast to the reported dome-shaped boron subporphyrin complexes,^[10] these novel porphyrinoids opened up the way to a previously unexplored region of contracted porphyrinoid coordination chemistry as a mono-anionic cyclic tridentate ligand. Due to the flexibility of the macrocycle, TriP has realized octahedral rhenium(I), manganese(I), ruthenium(II), and platinum(IV) complexes and square-planar platinum(II) complexes.^[11] Now we report herein the synthesis, characterization and redox behavior of novel sandwich η^5 -cyclopentadienyl-iron(II) TriP complexes.



Scheme 1. Synthesis of Cp–Fe^{II}–TriP **2a** and **2b**.

The metalation procedure is shown in Scheme 1. A dry toluene solution of TriP **1** was treated with 5 equiv of $[Fe(CO)_2(Cp)]_2$ and refluxed for 24 h under argon. After an elimination of the solvent, the residue was dissolved in $CHCl_3$ and the solution was filtered to remove the precipitates. The solvent was again removed and the residue was purified by short silica gel column chromatography using $CHCl_3$ as an eluent. The first eluted purple fraction was evaporated to afford the crude product and then crystallization from

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toluene and pentane gave the pure target compound in 40% yield for **2a** (Ar = C₆H₄-*p*-CH₃) and 45% for **2b** (Ar = C₆H₄-*p*-COOCH₃). Sandwich TriP-Fe-TriP-type compounds were not obtained.

The structures of **2a** and **2b** were characterized by high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectra and ¹H, ¹³C, and H-H COSY NMR spectra. HR-ESI-TOF mass spectra of **2a** and **2b** displayed the parent ion peaks at *m/z* 875.2934 (calcd. for C₆₁H₄₅N₃Fe: 875.2945 [*M*]⁺) and 1051.2512 (calcd. for C₆₅H₄₅N₃O₈Fe: 1051.2557 [*M*]⁺), respectively (Figures S1 and S2). ¹H NMR spectra of **1a** and **2a** are shown in Figure 1 and Figures S3-S8. The sharp peaks observed for **2a** suggested that the Fe ion is low spin and divalent, not trivalent. For **2a**, the NH proton of **1a** at 8.25 ppm disappeared and proton peaks of Cp rings at 2.84 ppm resonated in remarkably higher field due to the strong ring current effect of the TriP. This phenomenon has been reported previously for the Cp-Sc^{III}-porphyrin.^[4a] The similar trend was observed for **1b** and **2b**, as shown in Figure S9.

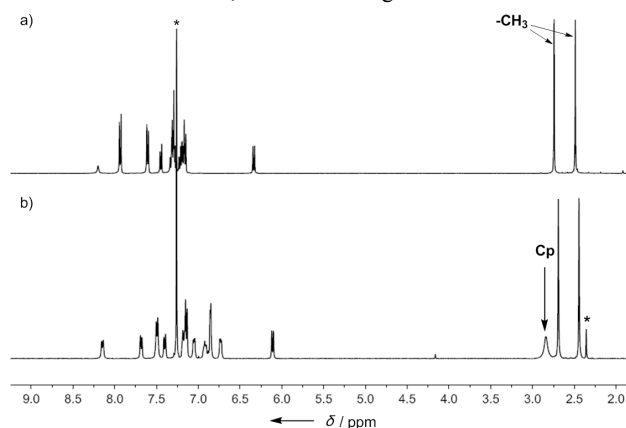


Figure 1. ¹H NMR spectra of a) **1a** and b) **2a** in CDCl₃. *: solvents.

The structures of complexes **2a** and **2b** are unambiguously determined by single crystal X-ray diffraction analysis.^[12] The crystal structures of **2a** and **2b** are summarized in Figures 2, S10 and Table S1. The crystal of **2a** includes four independent molecules in a unit cell. It is clear that in both **2a** and **2b**, iron(II) center is sandwiched between one Cp ring and one TriP macrocyclic ligand. The Cp ring is coordinated to Fe^{II} ion through the five carbon atoms, with the distances of 1.694 (± 0.012) Å for **2a** and 1.694 Å for **2b**, which are almost the same with the distance between Fe^{II} ion and Cp in ferrocene. The average Fe–C bond length is 2.06–2.08 Å for **2a** and 2.073 Å for **2b**, respectively. Moreover, the Fe^{II} ion is sitting on the top of the NNN plane of TriP ligand. The distances between Fe^{II} ion and the four *meso*-carbon plane of complexes **2a** and **2b** are 1.483 (± 0.013) and 1.422 Å, which are much more shorter than those of the reported metalotriphyrin complexes; 1.825 Å for [Re^I(TriP)(CO)₃]; 1.678 Å for [Ru^{II}(TriP)(CO)₂Cl] and 1.631 Å for [Pt^{IV}(TriP)Cl₃]. The average Fe–N bond lengths are 1.894–1.897 Å for **2a** and 1.895 Å for **2b**, respectively, which are similar to [Fe^{II}(NFP)₂].^[7]

The absorption spectra of **2a** and **2b** have essentially similar shapes as well as positions of the main absorptions at 374, 538 and 596 nm for **2a** and 370, 545 and 592 nm for **2b** (Figure S11), which are similar to the spectrum of [Re^ITriP(CO)₃] complex.^[8b] The spectra of **2a** and **2b** are considerably blue-shifted and broadened as compared with those of free-base TriPs, indicating strong electronic interaction between triphyrin ligand and the metal d orbital. The peaks at 370 nm are assigned to B bands, in analogy with [Re^ITriP(CO)₃] complex. The intense absorption peaks from 530 nm

to 700 nm for **2a** and **2b** can be assigned to metal-to-ligand charge transfer (MLCT) bands on the basis of density functional theory (DFT) calculations, in combination with weak Q-bands (Figure S12).^[13] The energy level of the highest occupied molecular orbital (HOMO) is significantly destabilized while the lowest unoccupied molecular orbital (LUMO) remains the same level compared to the free-base TriP. In-depth analyses on the MOs, both the HOMO and LUMO are composed of d-π conjugated orbitals. But the HOMO is composed of the top Cp ring π orbitals while LUMO is only composed of TriP π-orbitals. This situation is totally different as compared to the parent [Fe^{II}Cp₂]. The absorption spectra of **2a** and **2b** were nearly independent of solvent (Figure S13), which implied that intramolecular charge transfer would not be important in the photoexcitation of such kind of sandwich compound.

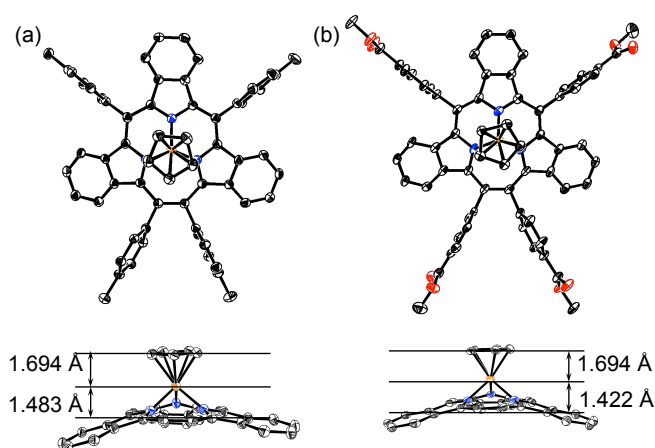


Figure 2. Crystal structures of a) **2a** and b) **2b**; top view (top) and side view (bottom) with phenyl groups omitted. Solvent molecules and hydrogen atoms are also omitted for clarity. Thermal ellipsoids are scaled to 50% probability. One of the four crystallographically independent molecules in a unit cell is shown for **2a**. The distances for **2a** are average value of four molecules.

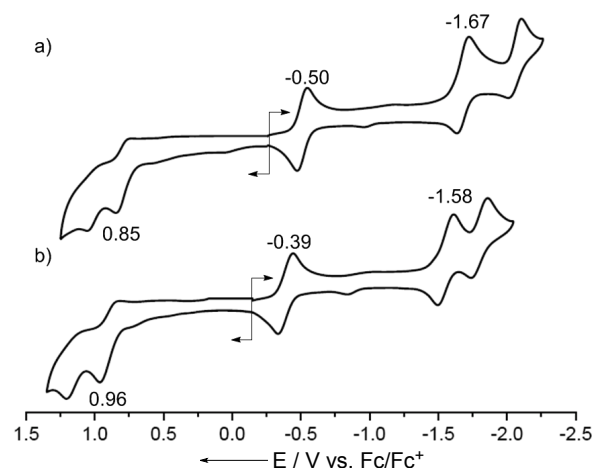


Figure 3. Cyclic voltammograms of a) **2a** and b) **2b** in CH₂Cl₂ containing 0.1 M TBAPF₆, scan rate 0.1 Vs⁻¹.

The electrochemical properties of **2a** and **2b** were examined by cyclic voltammetry (CV) (Figure 3 and Table S2) in CH₂Cl₂ containing 0.1 M TBAPF₆ at room temperature. Apparently,

oxidation potentials of the Fe^{II} ion of **2a** and **2b** are by -0.50 and -0.39 V lower than that of ferrocene. These data were comparable to $[\text{Fe}^{\text{II}}\text{TPP}]$ (TPP = tetraphenylporphyrin)^[14] and agreed with the results of DFT calculations (Figure S12). The second and third oxidation peaks together with the first and second reduction peaks were assigned to the triphyrin macrocycle. As compared to free-base TriP, the reduction potentials showed almost no change while the oxidation potentials became much 0.2-0.3 V higher than free-base TriP (Table 3).

The oxidized **2a** (2a^+) was identified by NMR, HR-ESI-MS, and EPR measurement. When **2a** was oxidized by AgPF_6 , the NMR peaks were broadened in the range of 0 to 28 ppm (Figure S14). The EPR spectrum of 2a^+ oxidized with *p*-chloranil was measured at 77 K. The largely anisotropic EPR signal was observed at $g = 4.13$, 2.41 and 2.04, which is identified as an Fe^{III} complex with the $S = 5/2$, $3/2$ intermediate spin state (Figure S15).^[15] DFT calculation also suggested that the spin density was localized on the Fe^{III} ion (Figure S16). The change in the absorption spectra with the oxidation of **2a** was also monitored (Figure S17a). When the applied potential of the oxidation of **2a** was kept at -0.34 V (vs. Fc/Fc^+), the peaks at 374, 540, and 589 nm decreased and at the same time 392 and 489, 575 nm increased, which corresponded to the Fe^{III} complex in agreement with the spectrum in the presence of Ag^{I} ion. The spectrum change was reversed to the original spectrum by keeping the applied potential at -1.0 V (vs. Fc/Fc^+) (Figure S17b). The oxidation and reduction of the Fe ion of **2a** and **2b** were stable during the 20-cycle repeats (Figure S18). Interestingly, the TFA titration of **2a** showed similar UV-vis change with electrochemical oxidation. By addition of TFA the color of solution changed from purple to brown and UV-vis of **2a** changed to the similar spectrum with 2a^+ , which went back

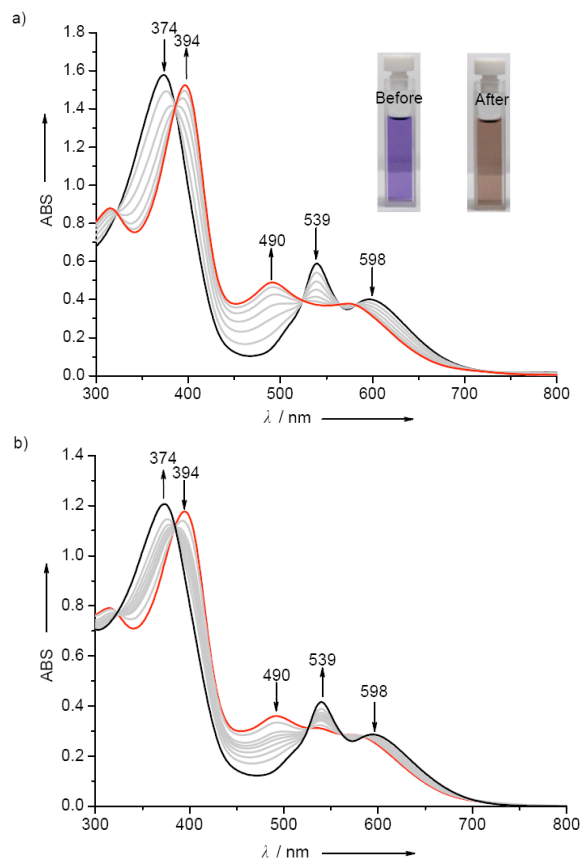


Figure 4. Spectrophotometric titration of **2a** with TFA (a) and then with DBU (b) in CH_2Cl_2 at 298 K.

to the spectrum of **2a** by addition of DBU (Figure 4). The NMR and HR-ESI-MS spectra of **2a** in the presence of TFA showed the same spectrum with that of 2a^+ (Figure S14 and S19). These results indicated **2a** was easily oxidized to 2a^+ by oxygen in the presence of TFA and 2a^+ is remarkably stable even under the acidic conditions.^[16]

This stability allowed us to make single crystals of the oxidative state of **2a**, namely $\text{Cp-Fe}^{\text{III}}\text{-TriP}$. Fortunately, the crystallization of the oxidized **2a** with excess amount of $\text{CF}_3\text{SO}_3\text{Ag}$ gave tiny crystals, from which we could perform the X-ray diffraction analysis (Figure 5 and Table S1). The structure determined contained $[\text{CF}_3\text{SO}_3]_2\text{Ag}^-$ as a counter anion. The Cp ring is coordinated to Fe^{III} ion through the five carbon atoms, with the distance of 1.723 Å, which is longer than that of **2a**, suggesting that the additional positive charge in 2a^+ is mostly localized on the formal Fe^{III} atom.^[17]

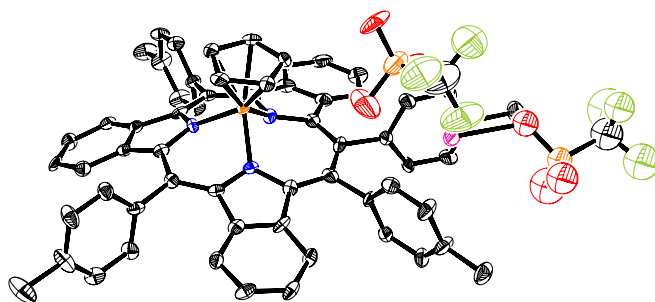


Figure 5. X-ray crystal structure of $[\text{Cp-Fe}^{\text{III}}\text{-TriP}]^+[(\text{CF}_3\text{SO}_3)_2\text{Ag}]^-$. Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are scaled to 20% probability.

In summary, we have successfully synthesized and characterized the unique sandwich iron(II) compounds **2a** and **2b** prepared from the corresponding free-base [14]triphyrin(2.1.1) **1a** and **1b** with $[\text{Fe}(\text{CO})_2(\text{Cp})]_2$. From the single crystal X-ray structure analysis, the central iron(II) ion is sandwiched by one Cp ring and one triphyrin ligand. The oxidation potential of Fe^{II} complex was lower than that of Fc and reversible. Protonation of Fe^{II} complex with TFA gave Fe^{III} complex, which was reduced to Fe^{II} complex with DBU reversibly.

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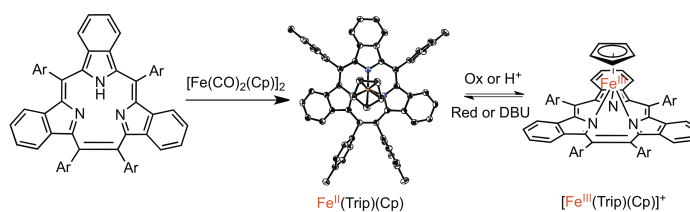
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- [1] a) T. J. Kealy, P. L. Pauson, *Nature* **1951**, 168, 1039; b) *Ferrocenes: Ligands, Materials and Biomolecules* (Ed.: P. Stepnicka), Wiley, Chichester, **2008**.
- [2] C. Bucher, C. H. Devillers, J. -C. Moutet, G. Royal, E. Saint-Aman, *Coord. Chem. Rev.* **2009**, 253, 21.
- [3] L. Cuesta, J. L. Sessler, *Chem. Soc. Rev.* **2009**, 38, 2716 and references cited therein.
- [4] a) J. Arnold, C. G. Hoffman, *J. Am. Chem. Soc.* **1990**, 112, 8620; b) H. -J. Kim, S. Jung, Y.-M. Jeon, D. Whang, K. Kim; *Chem. Commun.* **1997**, 2201; c) L. Cuesta, E. Karnas, V. M. Lynch, P. Chen, J. Shen, K. M. Kadish, K. Ohkubo, S. Fukuzumi, J. L. Sessler, *J. Am. Chem. Soc.* **2009**, 131, 13538.
- [5] a) H. J. H. Wang, L. Jaquinod, M. M. Olmstead, M. G. H. Vicente, K. M. Kadish, Z. Ou, K. M. Smith, *Inorg. Chem.* **2007**, 46, 2898; b) G. I. Vargas-Zúñiga, V. V. Roznyatovskiy, A. Nepomnyaschii, V. M.

- Lynch, J. L. Sessler, *J. Porphyrins Phthalocyanines*, **2012**, *16*, 479; c) E. Caballero, J. Fernández-Ariza, V. M. Lynch, C. Romero-Nieto, M. S. Rodríguez-Morgade, J. L. Sessler, D. M. Guldi, T. Torres, *Angew. Chem.* **2012**, *124*, 11499; *Angew. Chem. Int. Ed.* **2012**, *51*, 11337.
- [6] A. Berlicka, L. Latos-Grażyński, *Inorg. Chem.* **2009**, *48*, 7922.
- [7] M. Toganoh, A. Sato, H. Furuta, *Angew. Chem.* **2011**, *123*, 2804; *Angew. Chem., Int. Ed.* **2011**, *50*, 2752.
- [8] a) Z. L. Xue, Z. Shen, J. Mack, D. Kuzuhara, H. Yamada, T. Okujima, N. Ono, X. Z. You, N. Kobayashi, *J. Am. Chem. Soc.* **2008**, *130*, 16478. b) Z. L. Xue, J. Mack, H. Lu, L. Zhang, X. Z. You, D. Kuzuhara, M. Stillman, H. Yamada, S. Yamaguchi, N. Kobayashi, Z. Shen, *Chem. Eur. J.* **2011**, *17*, 4396.
- [9] D. Kuzuhara, H. Yamada, Z. L. Xue, T. Okujima, S. Mori, Z. Shen, H. Uno, *Chem. Commun.* **2011**, *47*, 722.
- [10] a) Y. Inokuma, J. H. Kwon, T. K. Ahn, M. -C. Yoo, D. Kim, A. Osuka, *Angew. Chem.* **2006**, *118*, 975; *Angew. Chem. Int. Ed.* **2006**, *45*, 961; b) N. Kobayashi, Y. Takeuchi, A. Matsuda, *Angew. Chem.* **2007**, *119*, 772; *Angew. Chem., Int. Ed.* **2007**, *46*, 758; c) Y. Inokuma, Z. S. Yoon, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 4747; d) Y. Takeuchi, A. Matsuda, N. Kobayashi, *J. Am. Chem. Soc.* **2007**, *129*, 8271; e) Y. Inokuma, A. Osuka, *Dalton Trans.* **2008**, 2517; f) S. Saito, K. S. Kim, Z. S. Yoon, D. Kim, A. Osuka, *Angew. Chem.* **2007**, *119*, 5687; *Angew. Chem., Int. Ed.* **2007**, *46*, 5591; g) Y. Inokuma, A. Osuka, *Chem. Commun.* **2007**, 2938.
- [11] Z. L. Xue, D. Kuzuhara, S. Ikeda, T. Okujima, S. Mori, H. Uno, H. Yamada, *Inorg. Chem.* **2013**, *52*, 1688.
- [12] CCDC-871230 (**2a**), 871231 (**2b**), and 929554 (**2a**⁺) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [13] M. J. Frisch, et al. Gaussian 09, R. C., Gaussian, Inc., Wallingford CT, **2004**. The full list of authors is given in Supporting Information.
- [14] L. A. Constant, D. G. Davis, *Anal. Chem.* **1975**, *47*, 2253.
- [15] a) S. P. Bew, M. R. Cheesman, S. V. Sharma, *Chem. Commun.*, **2008**, 5731; b) D. V. Behere, H. M. Goff, *J. Am. Chem. Soc.*, **1984**, *106*, 4945.
- [16] The proton coupled electron transfer (PCET) reduction of Fe(III) complexes by O₂ is well known phenomenon to produce Fe(II) complexes and H₂O₂ (see: a) S. Fukuzumi, *Chem. Lett.* **2008**, *37*, 808-813; b) S. Fukuzumi, *Prog. Inorg. Chem.* **2009**, *56*, 49). The reverse process may occur in the presence of DBU, which deprotonates H₂O₂ to oxidize the Fe(II) complexes back to the Fe(III) complexes, when deprotonated H₂O₂ is oxidized to O₂.
- [17] Y. Miyake, S. Watanabe, S. Aono, T. Nishinaga, A. Miyazaki, T. Enoki, H. Miyasaka, H. Otani M. Iyoda, *Chem. Commun.*, **2008**, 6167.
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Metalloporphyrinoids

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[14]Triphyrin(2.1.1) Sandwich

Compounds: Synthesis,

Characterization, and Stable Redox

Interconversion

A new kind of semi-ferrocene complex with [14]triphyrin(2.1.1) ligand is synthesized. The structure and properties are characterized with X-ray crystallographic analysis, UV-vis spectra, variable-temperature ^1H NMR spectra, and electrochemical measurements.