The title page of a research paper discussing the synthesis and characterization of novel metalloporphyrinoids, specifically focusing on 

**η⁵-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 metalloccene that was discovered in 1951. 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. 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: (1) Cp-Se³-porphyrin, Cp-Zr³⁺-porphyrin, Cp*–Ru¹°–porphyrine (Cp* = pentamethylcyclopentadienyl), although porphyrin and porphycene are divalent ligands; (2) β,β'-fused monoruthenocenylporphyrins, biferrrocenoporphyrins, and cyclopentadienylniobium π complexes of subphthalocyanines where five-membered ring part (pyrrole or cyclohexadiene moiety) act as ligands. Only recently, double-decker iron(II) complexes of dithiaethyneporphyrin and N-fused porphyrin (NFP) 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⁺–NFP compound by mass spectrometry, which has yet to be isolated. To date, the synthesis of Cp–Fe⁺–porphyrin sandwich compound remains a considerable challenge.

In 2008, we reported a facile protocol to synthesize [14]triphyrin(2.1.1) (TriP, I) as the first example of boron-free ring contracted porphyrins. In contrast to the reported dome-shaped boron subporphyrin complexes, 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(II), ruthenium(II), and platinum(IV) complexes and square-planar platinum(II) complexes. Now we report herein the synthesis, characterization and redox behavior of novel sandwich η⁵-cyclopentadienyl-iron(II) TriP complexes.

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**Scheme 1. Synthesis of Cp–Fe⁺–TriP 2a and 2b.**

The metalation procedure is shown in Scheme 1. A dry toluene solution of TriP I was treated with 5 equiv of [Fe(CO)₃Cp]₂ and refluxed for 24 h under argon. After an elimination of the solvent, the residue was dissolved in CHCl₃ 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 CHCl₃ 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 = \(\text{C}_2\text{H}_5-p\)-CH\(_3\)) and 45% for 2b (Ar = \(\text{C}_2\text{H}_5-p\)-COOCH\(_3\)). 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 \(^1\)H, \(^{13}\)C, 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 \(\text{C}_{43}\text{H}_{37}\text{N}_{10}\text{Fe}: 875.2945 \text{ [M]}\)) and 1051.2512 (calcd. for \(\text{C}_{43}\text{H}_{37}\text{N}_{10}\text{O}_2\text{Fe}: 1051.2557 \text{ [M]}\)), respectively (Figures S1 and S2). \(^1\)H 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 dative, 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.\(^{[4d]}\) The similar trend was observed for 1b and 2b, as shown in Figure S9.

**Figure 1.** \(^1\)H NMR spectra of a) 1a and b) 2a in CDCl\(_3\). *: 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 metalloc triglyptipyrin complexes; 1.825 Å for [Re\(^4\)(TriP)Cl\(_2\)CO\(_3\)]\(2+\); 1.678 Å for [Ru\(^3\)(TriP)Cl\(_2\)CO\(_3\)] and 1.631 Å for [Pt\(^4\)(TriP)Cl\(_2\)]\(2+\). 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\(^2\)(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\(^3\)TriP(CO)]\(2+\) complex.\(^{[10c]}\) 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 tripyrerin ligand and the metal d orbital. The peaks at 370 nm are assigned to B bands, in analogy with [Re\(^3\)TriP(CO)]\(2+\) 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-n conjugated orbitals. But the HOMO is composed of the top Cp ring \(\pi\) orbitals while LUMO is only composed of TriP \(\pi\)-orbitals. This situation is totally different as compared to the parent [Fe\(^{II}\)Cp\(_2\)]. 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 an 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 CH\(_2\)Cl\(_2\) containing 0.1 M TBAPF\(_6\) scan rate 0.1Vs\(^{-1}\).

The electrochemical properties of 2a and 2b were examined by cyclic voltammetry (CV) (Figure 3 and Table S2) in CH\(_2\)Cl\(_2\) containing 0.1 M TBAPF\(_6\) 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 [Fe$^{II}$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 tripheyrin 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). 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. Fe/Fe$^+$), the peaks at 374, 540, and 589 nm decreased and at the same time 392 and 489, 575 nm increased, which corresponds to the Fe$^{III}$ complex in agreement with the spectrum in the presence of Ag$^+$ ion. The spectrum change was reversed to the original spectrum by keeping the applied potential at –1.0 V (vs. Fe/Fe$^+$) (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 EPR 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 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 Cp–Fe$^{III}$–TriP. Fortunately, the crystallization of the oxidized 2a with excess amount of CF$_3$SO$_2$Ag gave tiny crystals, from which we could perform the X-ray diffraction analysis (Figure 5 and Table S1). The structure determined contained [CF$_3$SO$_2$]$_2$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]

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

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Figure 4. Spectrophotometric titration of 2a with TFA (a) and then with DBU (b) in CH$_2$Cl$_2$ at 298 K.

Figure 5. X-ray crystal structure of [Cp–Fe$^{II}$–TriP][[CF$_3$SO$_2$]$_2$Ag]$.\) Solvent molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are scaled to 20% probability.
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M. J. Frisch, et al. Gaussian 09, R. C., Gaussian, Inc., Wallingford CT, 2004. The full list of authors is given in Supporting Information.


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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 $^1$H NMR spectra, and electrochemical measurements.