Metallocenes

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Double-Decker Ferrocene-Type Complex of N-Fused Porphyrin: A Model of π-Extended Ferrocene?**

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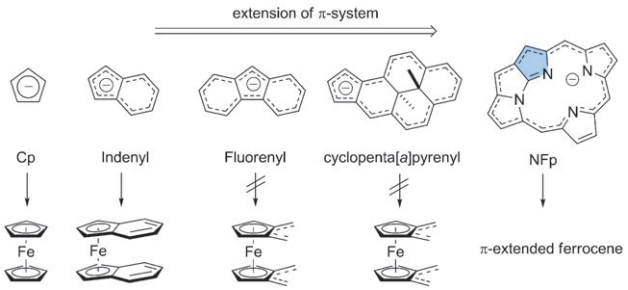
Since the discovery of ferrocene in 1951,[1] this molecule has continued to play important roles in diverse areas. In ferrocene, a d^6 iron(II) center is sandwiched between a pair of 6-π-electron aromatic cyclopentadienyl (Cp) ligands. As a method to modify the electronic properties of ferrocene, extension of the conjugated π system of the Cp ligands has gathered considerable attention. In spite of extensive investigation, a limited number of examples has been reported of isolation and unequivocal characterization of ferrocene-type complexes possessing π-extended Cp-type ligands. Although a bis(indenyl) iron(II) complex was successfully characterized,[2] larger analogues such as bis(fluorenyl) and bis(cyclopenta[*a*]pyrenyl) iron(II) complexes could not be identified, possibly owing to the weak coordination of π-extended Cp-type ligands leading to ring-slippage or metal shifting (Scheme 1).[3] Exceptionally, notable success was gained by

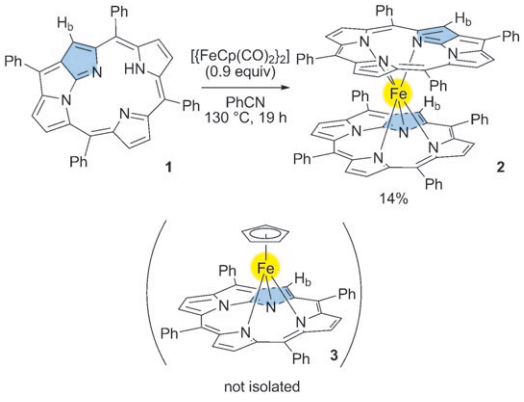


Scheme 1. Extension of the π system in ferrocene.

the aid of nonplanar ligands such as C_{70} derivatives and helicene-like ligands.[4] The key point in this success would be localization of negative charge on the Cp moiety. Nevertheless, development of a new strategy to prepare ferrocene-type complexes bearing π-extended ligands is still an important subject to be addressed.[5]

As a remedy for the weak coordination ability of π-extended Cp-type ligands, we had the idea to use a nitrogen-containing aromatic molecule that is isoelectronic to Cp ligands. Tridentate nitrogen ligands with a single negative charge, represented by tris(pyrazolyl)borate (Tp) and related scorpionate ligands, commonly show good coordination abilities.[6] Thus, an N-fused porphyrinato ligand (NFp), which is isoelectronic to Cp and Tp, was anticipated to form a π-extended ferrocene-type complex.[7] Although the negative charge of NFp would be delocalized over its large π-conjugated system, it still maintains sufficient coordination ability to metal centers because of the presence of three appropriately arranged nitrogen atoms.[8] We examined the preparation of π-extended ferrocene-type complexes with an NFp ligand and found the formation of the double-decker complex $[Fe^{II}(NFp)_2]$ in a one-pot synthesis. Herein, synthesis, structure, and fundamental properties of the double-decker ferrocene-type complex with NFp ligands are reported. Furthermore, the electronic state of $[Fe^{II}(NFp)_2]$ is compared with those of hypothetical π-extended ferrocene derivatives to evaluate their similarity.

In an early stage of this study, reactions of N-fused tetraphenylporphyrin (NFTPpH, **1**) with $[Fe^{II}Cp(CO)_2I]$ under basic conditions were attempted to prepare $[Fe^{II}$-(NFTPp)Cp] (**3**). The reactions did not proceed, or nucleophilic ring opening of **1** gave N-confused porphyrin derivatives.[9] Then, metal complexation under neutral conditions was examined. Fortunately, when **1** was heated with $[\{Fe^{I}Cp(CO)_2\}_2]$ in PhCN at 130 °C for 19 h under Ar, $[Fe^{II}(NFTPp)_2]$ (**2**) was obtained in 14% yield as a single isomer (Scheme 2). Formation of **3** was suggested by the mass analysis of the crude product (*m*/*z* 732 for $[M]^+$), however, isolation has been unsuccessful to date. Complex **2** was stable enough to be purified with standard silica gel column chromatography and to be recrystallized in air. In the mass analysis of **2**, only one set of peaks was observed around *m*/*z*



Scheme 2. Thermal reaction of NFTPpH (**1**) with $[\{FeCp(CO)_2\}_2]$.

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1278 ($[M]^+$), and this set was nearly identical to the simulated mass pattern. In the ^{1}H NMR spectra, the β proton on the N-confused pyrrole moiety (H_β) was observed as a singlet signal at $\delta = 8.05$ ppm in $CDCl_3$, which supported that **2** would be C_2-symmetric and that the compound was isolated as a single isomer.

The structure of **2** was unambiguously determined by X-ray crystallographic analysis (Figure 1).[10] In the crystal, two independent molecules are observed, which differ in the

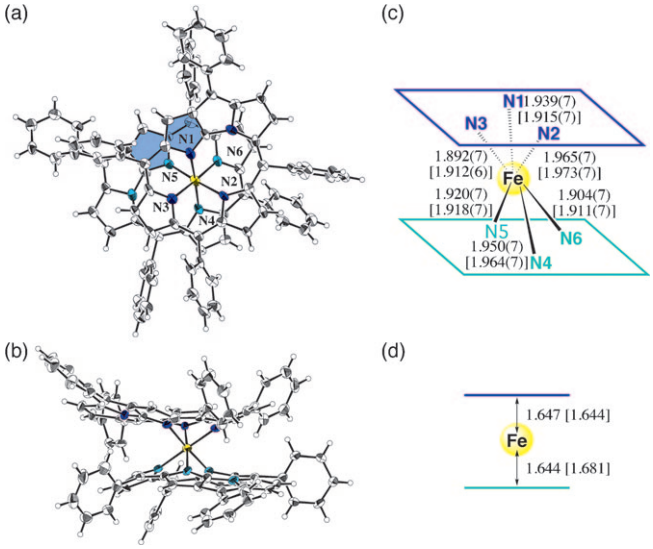

Figure 1. X-ray structure of **2**: a) top view, b) side view, c) bond lengths (Å) around the iron atom, d) distances (Å) between the iron atom and the NFp mean planes. One of the two independent molecules is shown in (a) and (b). The values in the square brackets are data of another molecule in the same crystal. The thermal ellipsoids are shown at the 30% probability level. Fe yellow, N light and dark blue, C gray, H white.

dihedral angles between the NFp plane and the *meso*-phenyl groups. The iron center is sandwiched between the two rigid NFTPp ligands, and the distances between the iron atom and the two NFTPp mean planes composed of 24 heavy atoms each are 1.644–1.681 Å, which are comparable to the distances between the iron atom and the Cp planes of $[Fe^{II}Cp_2]$ (1.643 Å) and $[Fe^{II}Cp^*_2]$ (1.657 Å, $Cp^* = C_5Me_5$).[11] From the structural parameters, considerable π–π interaction between the NFTPp ligands would be expected.

The absorption spectra of **1** and **2** in CH_2Cl_2 are shown in Figure 2. The spectral profile of **2** is totally different from that of **1**, indicating strong electronic interactions between two NFTPp ligands through the metal d orbital or through space. It should be noted that all absorption spectra of reported NFTPp metal complexes are similar to that of **1**.[8] The absorption spectra of **2** were nearly independent of solvent (Figure S6 in the Supporting Information), which implied that intramolecular charge transfer would not be important in the photoexcitation of **2**. Obviously, $[Fe^{II}Cp_2]$ did not show any solvent effects either.

The iron complex **2** is a multifaceted compound and belongs in many categories. Herein, three important categories are selected to discuss the properties of **2**: 1) an analogue of $[Fe^{II}Tp_2]$, 2) a double-decker porphyrin metal complex, and 3) a model of π-extended ferrocene derivatives.

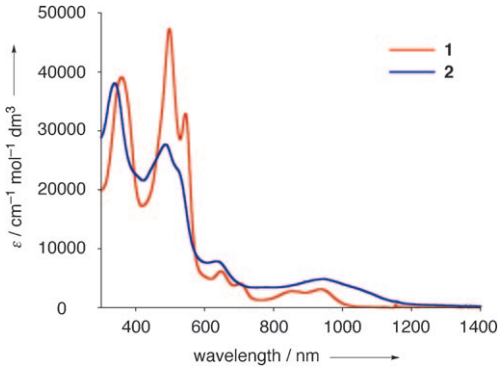

Figure 2. Absorption spectra of **1** and **2** in CH_2Cl_2.

The first topic is the analogy to $[Fe^{II}Tp_2]$. In $[Fe^{II}Tp_2]$, an iron center is coordinated by the six nitrogen atoms, which are arranged in a pseudo-tetragonal-bipyramidal manner similar to **2**.[12] Depending on temperature and the substituents on the pyrazole ring, $[Fe^{II}Tp_2]$ derivatives often exhibit spin crossover.[13] Generally, low-spin states ($S = 0$) were observed with small substituents at lower temperature (roughly 90–150 K), where Fe–N bond lengths are around 1.98 Å. Meanwhile, high-spin states ($S = 2$) were observed with large substituents at higher temperature (roughly 150–294 K), where Fe–N bond lengths are around 2.19 Å. X-ray analysis at 173 K indicated that the averaged Fe–N bond lengths of **2** are 1.930 Å, which suggests a low-spin state. As expected, **2** was ESR-silent at room temperature and kept silent until at least 100 °C. Furthermore, in ^{1}H NMR spectral analyses of **2**, all the signals appeared in the region of $\delta = 6.6$–8.4 ppm up to 100 °C, suggesting the diamagnetic character ($S = 0$) of **2**. A sign of spin-crossover phenomena has not yet been observed in **2**.

The second topic is that **2** is a double-decker porphyrin metal complex. In double-decker complexes, the porphyrin macrocycles are rotatable when the distance between two porphyrin planes is long.[14] The average distance between the two NFp planes in **2** is 3.308 Å, which is relatively short among double-decker porphyrin metal complexes (3.2–3.6 Å).[15] In the variable-temperature ^{1}H NMR spectra of **2**, only slight shifts were detected for the pyrrolic proton signals (Figure S3 in the Supporting Information), which indicated that the mutual rotation of NFTPp ligands would not occur on the time scale of NMR spectroscopy up to 100 °C. Meanwhile, a significant broadening of the signal arising from the phenyl protons was detected, which might mean that the phenyl rings rotate only at elevated temperature. Similar phenomena were also observed in the double-decker porphyrin zirconium complexes.[16]

Since the NFp ligand has an unsymmetrical structure and would not rotate up to 100 °C, six isomers of $[Fe^{II}(NFp)_2]$ could exist. A set of rotamers (**A**–**C**) is incompatible with another set of rotamers (**D**–**F**) without ligand dissociation (Figure 3). Theoretical estimation of the relative energies in **2** suggests that two (**C** and **F**) or more isomers could be formed, because their energy differences are small.[17] Nevertheless,

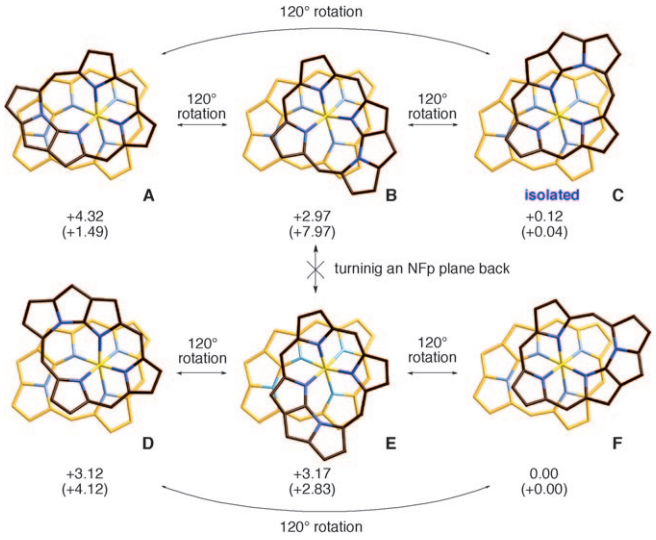

Figure 3. Relative energies (kcal mol^{-1}) of six isomers of [Fe^{II}(NFp)$_2$] and [Fe^{II}(NFTPp)$_2$] calculated at the B3LYP/631T level. The values of the latter are shown in the parentheses. The *meso*-phenyl groups and hydrogen atoms are omitted for clarity.

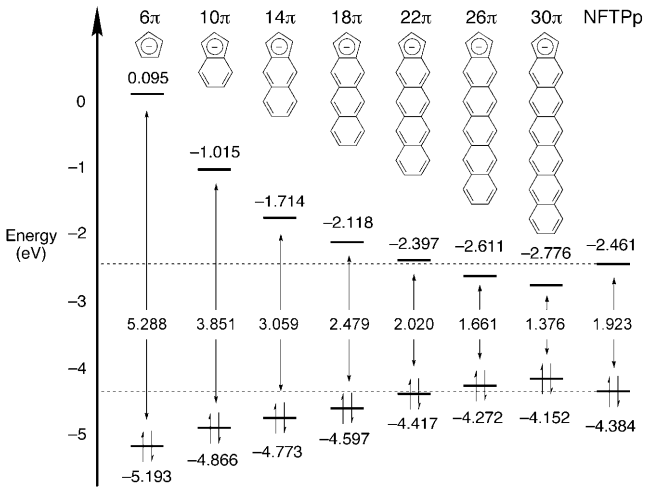

Figure 4. HOMO–LUMO levels and their gap energies of **2** and π-extended ferrocene derivatives. Structures of the corresponding π ligands are shown.

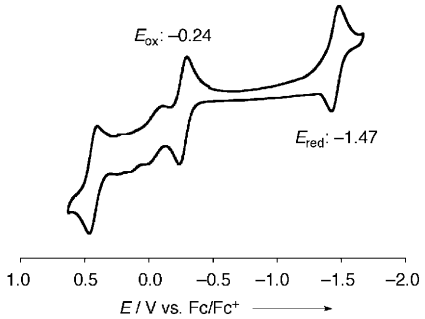

Figure 5. Cyclic voltammogram of **2** in CH_2Cl_2 with 0.1 M Bu_4NPF_6 (Pt electrode, scan rate 100 mV s^{-1}). Fc = ferrocene, Fc^+ = ferrocenium.

only a single isomer (**C**) was isolated in the reaction of **1** with [{FeCp(CO)$_2$}$_2$] for an as yet unknown reason. When the reaction of *meso*-4-*tert*-butylphenyl NFp with [{FeCp(CO)$_2$}$_2$] was examined, a 10:3 mixture of two isomers was obtained. Besides, the reaction of **1** with $FeBr_2$ in the presence of 2,6-lutidine afforded a mixture of three isomers in a ratio of 50:38:12, in which **2** is the major product. Unfortunately, separation of these isomers was difficult, and thus detailed analysis of the isomers of [Fe(NFp)$_2$] will require further investigation.

The third topic is the model of π-extended ferrocenes. Since poor experimental data are available, electronic states of the π-extended ferrocenes are estimated theoretically. While the theoretical study of ferrocene is conventionally problematic, the reliability of density functional theory (DFT) calculations was recently verified.[18] Thus, DFT calculations were carried out on a series of π-extended ferrocenes and also on **2**. A series of linear polyacene-fused Cp ligands was used for calculations.[17] The energy levels of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the π-extended ferrocenes are summarized in Figure 4. The HOMO–LUMO gap energies become smaller with an increasing number of π electrons. While the LUMO energy level is significantly stabilized, the HOMO energy level rises in small steps through extension of the π system. In this diagram, NFTPp corresponds to a 22-π-electron ligand. The narrow HOMO–LUMO band gap of **2** in spite of its [18]annulenic substructure could be explained by the unique electronic properties of NFTPpH.[19]

Electrochemical measurements on **2** are consistent with the theoretical evaluation (Figure 5). In the cyclic voltammogram of **2**, the first reversible oxidation wave was detected at $E_{ox} = -0.24$ V (vs. Fc/Fc$^+$), and the first reversible reduction wave was detected at $E_{red} = -1.47$ V. Apparently, **2** is more easily oxidized than [Fe^{II}Cp$_2$]. Meanwhile, observation of the reversible reduction wave is exceptional among ferrocene-type complexes, which is in line with the highly stabilized LUMO energy level compared to the parent [Fe^{II}Cp$_2$].

Orbital analyses give further insight into the electronic structure of **2** (Figure 6). The HOMO of [Fe^{II}Cp$_2$] (6 π electrons) is essentially composed of a metal d orbital, and the LUMO is composed of d–π conjugated orbitals. When the number of π electron increases, the LUMOs maintain the d–π conjugated character, while contribution of π orbitals becomes increasingly significant in the HOMOs in addition to the metal d orbital. In accordance with this tendency, both the HOMO and LUMO of **2** are composed of d–π conjugated orbitals to construct a unique 3D-structured electronic system.

When attention is drawn to the metal d orbitals, the obtained result is very fascinating. Normally, contribution of a metal d orbital and a ligand π orbital would be observed independently when the energy levels differ significantly. Indeed, contribution of metal d orbitals is weak or negligible in the HOMO and LUMO of reported NFp metal complexes.[8] Meanwhile, contribution of the metal d orbital as well as the ligand π orbital is clearly observed in the LUMO of **2**, even though the LUMO energy levels are significantly

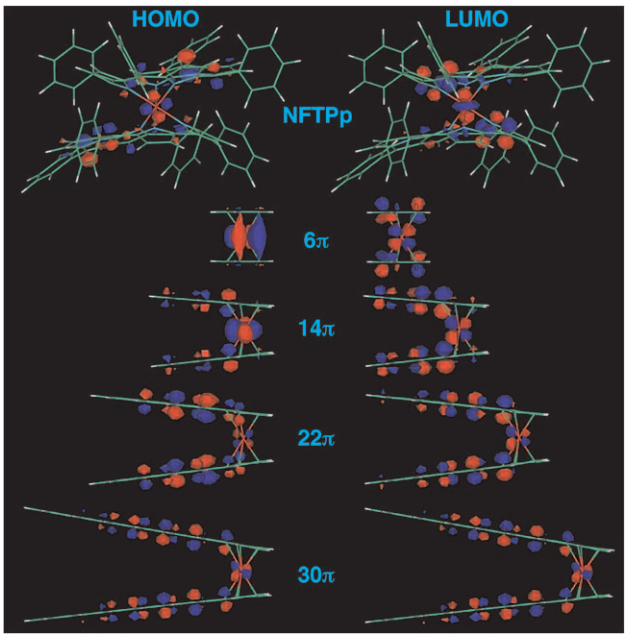

Figure 6. HOMO and LUMO of **2** and π-extended ferrocene derivatives.

stabilized compared to $[Fe^{II}Cp_2]$. In other words, the energy level of the metal d orbital is strongly affected by the NFTPp ligands. Although clear evidence has not been obtained, the sandwich structure might play an important role in this unusual observation. Incidentally, ferrocenes and ruthenocenes embedded in or conjugated with porphyrinoids have been reported increasingly in recent years, and hence rapid expansion in this field would help us to understand this issue.[5,20]

In summary, we have synthesized the double-decker ferrocene-type NFTPp complex **2** in a one-pot manner, and its crystal structure was determined. The properties of **2** are discussed from three viewpoints. As an analogue of $[Fe^{II}Tp_2]$, **2** adopts a low-spin state, and no spin crossover is observed up to 100 °C. As a double-decker porphyrin complex, no mutual rotation of NFTPp ligands is observed. Finally, as a model of π-extended ferrocenes, **2** shows similar electronic structures to the ferrocene derivative possessing 22-π-electron ligands, where unusual perturbation from the NFTPp ligands to the iron center is observed. Further investigation on the d–π conjugated system of **2** and synthesis of related metal complexes will be reported in the near future.

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