Communications

Metalloporphyrinoids

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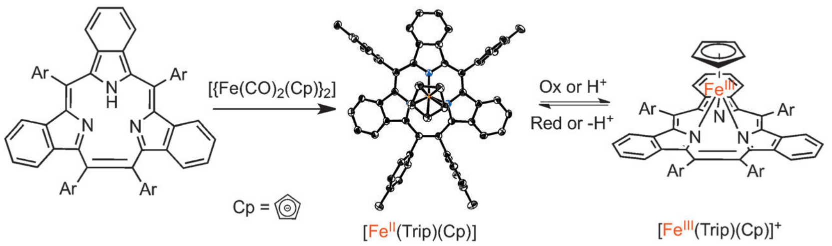
η^5-Cyclopentadienyliron(II)–[14]Triphyrin(2.1.1) Sandwich Compounds: Synthesis, Characterization, and Stable Redox Interconversion



A semiferrocene complex with a [14]triphyrin(2.1.1) (TriP) ligand has been synthesized. The structure and properties are characterized by X-ray crystallographic analysis, UV/Vis spectroscopy, and variable-temperature ^{1}H NMR spectroscopy. The Fe^{II} and Fe^{III} complexes are electrochemically reversible.

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DOI: 10.1002/anie.201302815

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

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Ferrocene, an iron(II) center sandwiched by a pair of aromatic cyclopentadienyl (Cp) ligands, is the first known and archetypal metallocene; it was discovered in 1951.[1] Thereafter, research into ferrocene-containing compounds has continued apace within diverse areas, such as a redox mediator, catalyst, electron donor, rotational hinge part, and so on.[2] However larger macrocyclic π-conjugated systems with monovalent anionic character has been scarcely reported to date, which is due to the weak coordination ability of π-extended Cp-type ligands. Especially in porprhyin families, there are a few reports in this context:[3] 1) Cp-Sc^{III}-porphyrin,[4a] Cp-Zr^{II}-porphyrin,[4b] and Cp*-Ru^{IV}-porphycene (Cp* = pentamethylcyclopentadienyl),[4c] although porphyrin and porphycene are divalent ligands; and 2) β,β′-fused monoruthenocenylporphyrins, bisferrocenoporphyrins,[5a] metaloporphyrcenes,[5b] and cyclopentadienylruthenium π complexes of subphthalocyanines,[5c] where that five-membered ring moiety (pyrrole or cyclohexadiene moiety) acted as ligands. Only recently, double-decker iron(II) complexes of dithiaethyne-porphyrin[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, the Cp-Fe^{II}-NFP compound was detected by mass spectroscopy; this compound has yet to be isolated. To date, the synthesis of Cp-Fe^{II}-porphyrin sandwich compounds remains a considerable challenge.

In 2008, we reported a facile procedure 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 monoanionic cyclic tridentate ligand. Owing 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 η^5-cyclopentadienyliron(II) TriP sandwich complexes.

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 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; crystallization from toluene and pentane then gave the pure target compound in 40 % yield for **2a** ($Ar = C_6H_4$-*p*-CH_3) and 45 % for **2b** ($Ar = C_6H_4$-*p*-$COOCH_3$). Sandwich TriP-Fe-TriP-type compounds were not obtained.

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[**] We are grateful to Prof. Haruyuki Nakano, Kyusyu University (Japan) for his fruitful discussions on DFT calculations. This work was supported by JSPS Postdoctoral Fellowship for Foreign Researchers (to Z.-L.X.) and partly supported by Grants-in-Aid (No. 24655034 to H.Y. and D.K., No. 20108010 to S.F. and No. 23750014 to K.O.), and the Green Photonics Project in NAIST sponsored by the MEXT (Japan) and NRF/MEST of Korea through the WCU (R31-2008-000-10010-0) and GRL (2010-00353) Programs.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302815.

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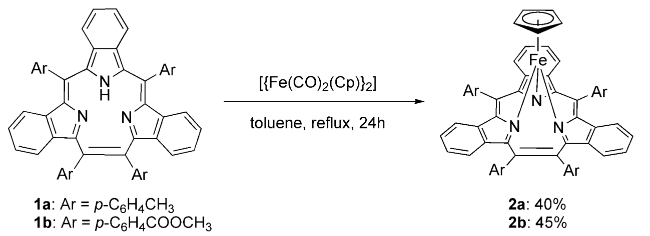

Scheme 1. Synthesis of Cp-$\mathrm{Fe^{II}}$-TriP complexes **2a** and **2b**.

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** showed the parent ion peaks at m/z 875.2934 (calcd for $\mathrm{C_{61}H_{45}N_3Fe}$: 875.2945 $[\mathrm{M}]^{+}$) and 1051.2512 (calcd for $\mathrm{C_{65}H_{45}N_3O_8Fe}$: 1051.2557 $[\mathrm{M}]^{+}$), respectively (Supporting Information, Figure S1 and S2). ^{1}H NMR spectra of **1a** and **2a** are shown in Figure 1 and the Supporting Information, Figures S3–S5. The sharp peaks observed for **2a** suggest 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 were observed at remarkably higher field owing to the strong ring-current effect of the TriP ligand. This phenomenon has been reported previously for the Cp-$\mathrm{Sc^{III}}$-porphyrin.[4a] The similar trend was observed for **1b** and **2b**, as shown in the Supporting Information, Figure S6–S9.

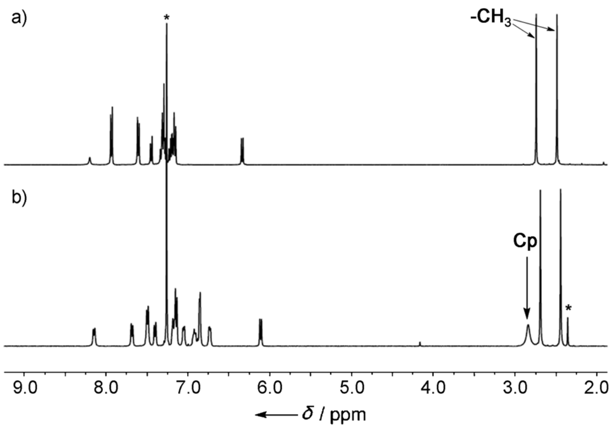

Figure 1. ^{1}H NMR spectra of a) **1a** and b) **2a** in $\mathrm{CDCl_3}$. ⋆ indicates solvents.

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 Figure 2 and the Supporting Information, Figure 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 $\mathrm{Fe^{II}}$ 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 as the distance between $\mathrm{Fe^{II}}$ 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 $\mathrm{Fe^{II}}$ ion is found on the top of the NNN plane of TriP ligand. The distances between $\mathrm{Fe^{II}}$ 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 previously reported metallotriphyrin complexes: 1.825 Å for $[\mathrm{Re^{I}(TriP)(CO)_3}]$, 1.678 Å for $[\mathrm{Ru^{II}(TriP)(CO)_2Cl}]$, and 1.631 Å for $[\mathrm{Pt^{IV}(TriP)Cl_3}]$. 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 $[\mathrm{Fe^{II}(NFP)_2}]$.[7]

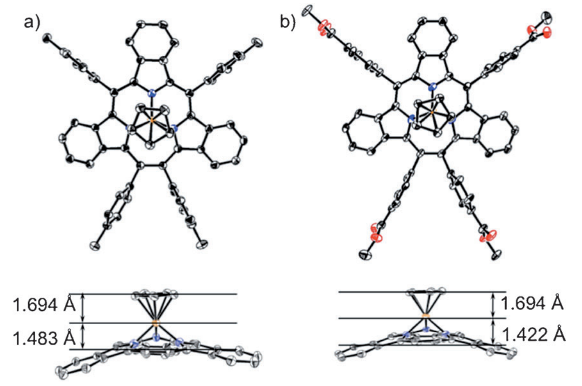

Figure 2. Crystal structures of a) **2a** and b) **2b**; top view (top) and side view (bottom) with phenyl groups omitted. Solvent molecules and hydrogen atoms are also omitted for clarity. Ellipsoids are set at 50% probability. One of the four crystallographically independent molecules in a unit cell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

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** (Supporting Information, Figure S11), which are similar to the values found in the spectrum of the $[\mathrm{Re^{I}TriP(CO)_3}]$ complex.[8b] The spectra of **2a** and **2b** are considerably blue-shifted and broadened 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 $[\mathrm{Re^{I}Trip(CO)_3}]$ 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 (Supporting Information, 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 show that 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 the LUMO is only composed of TriP π orbitals. This situation is totally different as compared to the parent $[\mathrm{Fe^{II}Cp_2}]$. The absorption spectra of **2a** and **2b** were nearly independent of solvent (Supporting Information, Figure S13), which implied that intramolecular charge transfer would not be important in the photoexcitation of such kind of sandwich compound.

The electrochemical properties of **2a** and **2b** were examined by cyclic voltammetry (CV; Figure 3; Supporting

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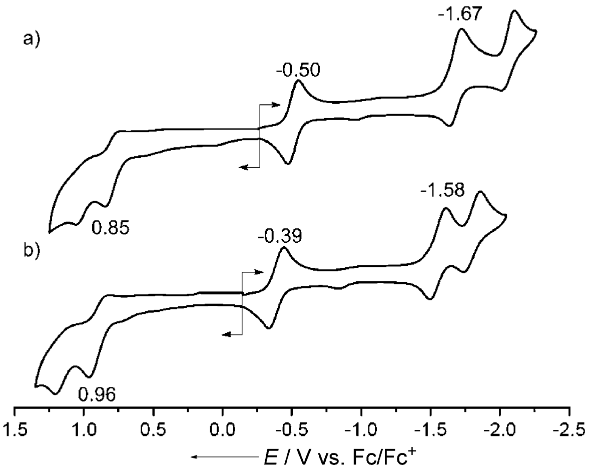

Figure 3. Cyclic voltammograms of a) **2a** and b) **2b** in CH_2Cl_2 containing 0.1 M nBu$_4$NPF$_6$, scan rate 0.1 V s^{-1}.

Information, Table S2) in CH_2Cl_2 containing 0.1 M nBu$_4$NPF$_6$ at room temperature. Apparently, oxidation potentials of the Fe^{II} ion of **2a** and **2b** are −0.50 and −0.39 V lower than that of ferrocene. These data are comparable to [Fe^{II}TPP] (TPP = tetraphenylporphyrin)[14] and agree with the results of DFT calculations (Supporting Information, 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 0.2–0.3 V higher than free-base Trip (Supporting Information, Table S2).

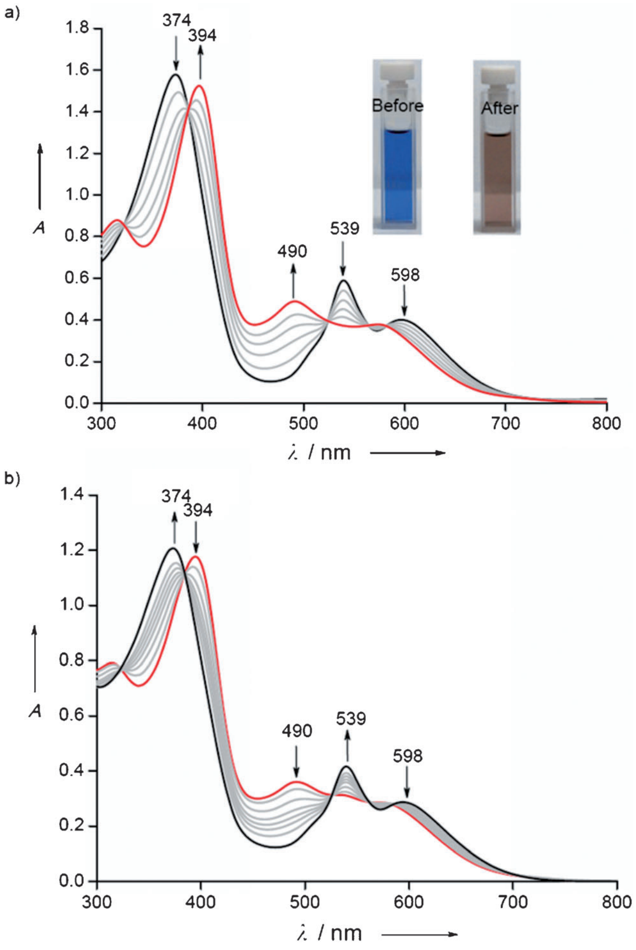

Figure 4. Spectrophotometric titration of **2a** with trifluoroacetic acid (TFA) (a) and then with DBU (b) in CH_2Cl_2 at 298 K.

The oxidized **2a** (**2a**$^+$) was identified by NMR, HR-ESI-MS, and EPR measurements. When **2a** was oxidized by AgPF$_6$, the NMR peaks were broadened in the range of 0 to 28 ppm (Supporting Information, 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 (Supporting Information, Figure S15).[15] DFT calculations also suggested that the spin density was localized on the Fe^{III} ion (Supporting Information, Figure S16). The change in the absorption spectra with the oxidation of **2a** was also monitored (Supporting Information, 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$^+$ (Supporting Information, Figure S17b). The oxidation and reduction of the Fe ion of **2a** and **2b** were stable during the 20-cycle repeats (Supporting Information, Figure S18). Interestingly, the TFA titration of **2a** showed a similar UV/Vis spectral 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 to that of **2a**$^+$ (Supporting Information, Figures S14 and S19). These results indicated that **2a** is 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 oxidized state of **2a**, namely Cp-Fe^{III}-TriP. Fortunately, the crystallization of the oxidized species **2a** with excess CF_3SO_3Ag gave tiny crystals, from which we could perform

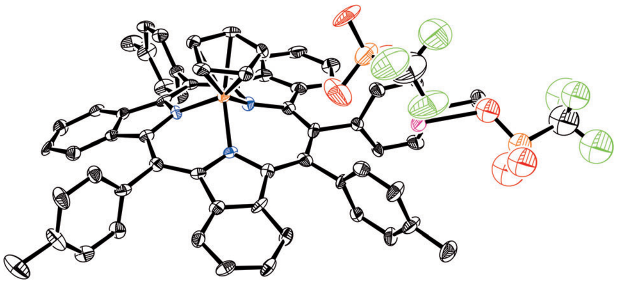

Figure 5. X-ray crystal structure of [Cp-Fe^{III}-TriP]$^+$[(CF_3SO_3)$_2$Ag]$^-$. Solvent molecules and hydrogen atoms are omitted for clarity. Ellipsoids are set at 20% probability.

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the X-ray diffraction analysis (Figure 5; Supporting Information, Table S1). The structure determined contained $[CF_3SO_3]_2Ag]^-$ as a counteranion. 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 $\mathbf{2a}^+$ 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]triphyrin(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 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.

Received: April 5, 2013
Published online: ■■ ■■, ■■■■

Keywords: ferrocene · metalloporphyrinoids · redox activity · sandwich complexes · triphyrin

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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 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 ($\mathbf{2a}^+$) 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 O_2 is a well-known phenomenon to produce Fe^{II} complexes and H_2O_2; 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 H_2O_2 to oxidize the Fe^{II} complexes back to the Fe^{III} complexes, whereby deprotonated H_2O_2 is oxidized to O_2.
[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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