

A convenient procedure for the synthesis of fluoro-iron(III) complexes of common synthetic porphyrinates

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ABSTRACT: We report here an improved method for the preparation of fluoro-iron(III) porphyrinate complexes. Treatment of $[Fe_2(P)_2(\mu-O)]$ (P = tetraphenylporphyrinate {TPP}, tetra-*p*-tolylporphyrinate {TTP}, or octaethylporphyrinate {OEP}) or $[Fe(OH)(OH_2)(TMP)]$ (TMP = tetramesitylporphyrinate) with the commercially available fluorinating agent, Et₃N·3HF, in dichloromethane affords the desired [FeF(P)] complexes in a straightforward fashion and in good yield while avoiding the use of aqueous hydrofluoric acid. All fluoro-iron(III) complexes have been completely characterized by a series of different spectroscopic techniques including cyclic voltammetry. Reaction of a representative complex, [FeF(OEP)], with various chloride reagents demonstrates that halide exchange with chloride is facile, but only proceeds at an appreciable rate in the presence of proton sources. Unexpectedly, treatment of [FeF(OEP)] with NOBF₄ did not to lead formation of an oxidized species, but rather to formation of the {Fe–NO}⁶ complex, [Fe(NO)(OEP)](BF₄).

KEYWORDS: iron(III) porphyrinates, fluoride complexes, synthetic procedures.

INTRODUCTION

Examples of transition metal complexes containing fluoride ligands remain relatively scarce in comparison to those containing the heavier halogens [1-5]. Despite a recent surge in interest due to their ability to effect catalytic C-F bond forming reactions [6], metal fluoride complexes are often neglected in studies of metal halide compounds because of their difficulty of preparation. In contrast to binary metal chlorides, bromides, and iodides, binary metal fluorides (MF_x) are often unavailable, especially if lower metal oxidation states are desired [7]. Introduction of fluoride ligands is therefore usually accomplished at a later stage in the metal complex synthesis by halogen exchange. Halogen exchange is not always straightforward, however, typically requiring large excesses of fluoride salts such as NaF or KF, or hydrofluoric acid.

In the area of porphyrin chemistry, examples of terminal fluoride and difluoride complexes have been reported for several transition metals [8-21]. Recently, a high-valent Mn porphyrin fluoride complex was demonstrated to carry out catalytic fluorination with excellent efficiency [22, 23]. Among transition metal porphyrinates, however, the most well-studied fluoride complexes are those of iron(III). Fluoro-iron(III) porphyrinates have been structurally characterized for a series of different porphyrin ligands and various aspects of their spectroscopy have been examined in detail [24–32]. Particular attention has been paid to the effects of fluoride ligation in modulating the reactivity of high valent oxo-iron porphyrinates and in determining the electronic structure of porphyrin π -cation radicals [33–44]. In addition, fluoro-iron(III) porphyrinates are also of interest as models for fluoride interaction with heme proteins [45-48].

During the course of recent investigations into the chemistry of iron(III) porphyrinates containing silanethiolate ligands, we discovered that treatment of oxygenligated iron(III) porphyrinates with the easy to use,

⁶SPP full member in good standing

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commercially available HF source, $Et_3N\cdot 3HF$, resulted in near quantitative formation of fluoro-iron(III) porphyrinates [49]. We have now optimized this protocol and found it to be general for a variety of synthetic porphyrin ligands. We report here this new fluorination procedure along with detailed characterization of the fluoride complexes.

EXPERIMENTAL

General comments

Unless noted, manipulations were performed under ambient atmosphere. Tetrahydrofuran, diethyl ether, methylene chloride, pentane, and toluene were purified by sparging with argon and passage through two columns packed with 4 Å molecular sieves. Benzene, benzene- d_6 , and 2-methyltetrahydrofuan were dried over sodium then vacuum-distilled. ¹H NMR spectra were recorded in benzene- d_6 on a Varian INOVA spectrometer operating at 500 MHz and referenced to the residual C₆D₅H peak of the solvent (δ 7.16 ppm vs. TMS). UV-vis spectra were recorded at ambient temperature in toluene on a Cary-60 spectrophotometer in Teflon-capped quartz cells. Cyclic voltammetry measurements were performed in dichloromethane in a single compartment cell under a nitrogen atmosphere (in the glovebox) at 25 °C using a CH Instruments 620D electrochemical workstation. A 3-electrode set-up was employed comprising a 1 mm diameter Pt disk working electrode, platinum wire auxiliary electrode, and Ag quasi-reference electrode. Triply recrystallized Bu₄NPF₆ or Bu₄NBF₄ was used as the supporting electrolyte. All electrochemical data were referenced to the ferrocene/ferrocenium couple at 0.00 V. EPR measurements were recorded in 4 mm quartz tubes on a Bruker E500 EPR spectrometer operating at the X-band (9.33 GHz) at a modulation frequency of 100 kHz and modulation amplitude of 10G. Low temperature measurements were made in frozen 2-MeTHF glasses at 80 K with temperature control maintained by a nitrogen (77 K) flow cryostat (ESR900, Oxford Instruments, Inc.). Elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, GA.

Materials

Metalloporphyrinates, $[Fe_2(TPP)_2(\mu-O)]$, $[Fe_2(TTP)_2(\mu-O)]$, $[Fe_2(OEP)_2(\mu-O)]$, and $[Fe(OH)(H_2O)(TMP)]$, were prepared by literature procedures [50–52]. Et₃N·3HF and NOBF₄ were purchased from commercial suppliers (Aldrich and Strem, respectively) and used as received. Et₃NHCl was prepared by treatment of Et₃N with HCl·dioxane (4.0 M) in diethyl ether.

Synthesis

General procedure for preparation of [FeF(P)]. A 50 mL round bottom flask is charged with 100 mg

(116–167 µmol Fe) of the desired oxo-bridged iron(III) porphyrinate, $[Fe_2(P)_2(\mu-O)]$, or hydroxide complex, [Fe(OH)(H₂O)(TMP)]. The solid is dissolved completely in 25 mL of CH2Cl2 and 40.0 µL (245 µmol) of Et3N·3HF is added. The resulting mixture is allowed to stir for 18 h at ambient temperature (20-23 °C). The solvent is removed in vacuo and the resulting purple microcrystalline solid is washed with cold acetone yielding the desired fluoride complex. Yields and characterization data for specific porphyrinate ligands appear below. Spectroscopic data (UV-vis, IR, and EPR) matched those available in the literature [24, 25, 28, 38, 53, 54]. All fluoro complexes were found to retain variable amounts of water, which could be observed as a broad singlet near 0 ppm in the ¹H NMR spectrum. In the case of the TPP and TTP complexes, insufficient solubility in benzene- d_6 precluded definitive assignment of the ortho-aryl protons by ¹H NMR.

[FeF(TPP)]. 87% yield. ¹H NMR: $\delta_{\rm H}$, ppm 81.2 (v br s, 8 pyr-CH), 11.0 (br s, 4 *m*-ArH), 10.2 (br s, 4 *m*-ArH), 6.67 (s, 4 *p*-ArH). UV-vis (toluene): $\lambda_{\rm max}$, nm (ε, M⁻¹.cm⁻¹) 328 (34,000), 415 (140,000), 534 (sh), 594 (6700), 634 (sh). IR (KBr): v, cm⁻¹ 3054 (w), 1597 (m), 1485 (m), 1440 (m), 1340 (m), 1202 (m), 1175 (m), 1071 (m), 1004 (vs), 996 (s), 804 (s), 750 (m), 720 (s), 702 (m), 660 (m), 611 (m, v_{Fe-F}). EPR: g_{\perp} = 5.77, g_{\parallel} = 1.98. Anal. calcd. for C₄₄H₂₈FFeN₄·1.5H₂O: C, 73.95; H, 4.37; N, 7.84. Found C, 73.85; H, 3.94; N, 7.92.

[FeF(TTP)]. 89% yield. ¹H NMR: $\delta_{\rm H}$, ppm 81.0 (v br s, 8 pyr-*CH*), 10.95 (s, 4 *m*-Ar*H*), 10.17 (s, 4 *m*-Ar*H*), 6.68 (s, 12 *p*-Ar*CH*₃). UV-vis (toluene): $\lambda_{\rm max}$, nm (ϵ , M⁻¹. cm⁻¹) 329 (28,000), 415 (120,000), 590 (5200), 635 (sh). IR (KBr): v, cm⁻¹ 3023 (w), 1596 (m), 1485 (m), 1440 (m), 1334 (m), 1201 (m), 1174 (m), 1070 (m), 1003 (vs), 995 (s), 805 (s), 749 (s), 721 (m), 702 (s), 660 (m), 612 (m, $v_{\rm Fe-F}$). EPR: g_{\perp} = 5.77, g_{\parallel} = 1.98. Anal. calcd. for C₄₈H₃₈FFeN₄·0.5H₂O: C, 76.60; H, 4.95; N, 7.44. Found C, 76.38; H, 4.93; N, 7.47.

[FeF(OEP)]. 85% yield. ¹H NMR: δ_{H} , ppm 34.9 (br s, 8 Et-*CH*₂), 34.2 (br s, 8 Et-*CH*₂), 5.10 (s, 24 Et-*CH*₃), -34.0 (v br s, 4 *meso*-*CH*). UV-vis (toluene): λ_{max} , nm (ε, M⁻¹.cm⁻¹) 347 (47,000), 394 (130,000), 478 (12,000), 506 (sh), 591 (11,000). IR (KBr): v, cm⁻¹ 2964 (vs), 2930 (s), 2868 (s), 1466 (m), 1445 (m), 137 (m), 1315 (m), 1267 (m), 1214 (m), 1146 (s), 1111 (m), 1055 (s), 1014 (s), 981 (m), 957 (s), 915 (m), 843 (m), 747 (m), 734 (m), 719 (m), 703 (m), 600 (m, v_{Fe-F}). EPR: g_{\perp} = 5.83, g_{\parallel} = 1.99. Anal. calcd. for C₃₆H₄₄FFeN₄·H₂O: C, 69.11; H, 7.41; N, 8.93. Found C, 69.32; H, 7.18; N, 8.98.

[FeF(TMP)]. 81% yield. ¹H NMR: $\delta_{\rm H}$, ppm 80.1 (v br s, 8 pyr-CH), 12.35 (s, 4 *m*-ArH), 11.49 (s, 4 *m*-ArH), 4.5 (v br s, 12 *o*-ArCH₃), 3.32 (s, 12 *p*-ArCH₃), 2.9 (v br s, 12 *o*-ArCH₃). UV-vis (toluene): $\lambda_{\rm max}$, nm (ϵ , M⁻¹.cm⁻¹) 323 (36,000), 416 (130,000), 593 (5900), 636 (sh). IR (KBr): v, cm⁻¹ 3020 (m), 2917 (m), 2870 (m), 1610 (m), 1478 (m), 1440 (m), 1387 (m), 1328 (m), 1202 (m), 1063 (m), 1000 (vs), 868 (m), 852 (m), 832 (s), 804 (s), 725 (m),

614 (m, $v_{\text{Fe-F}}$). EPR: $g_{\perp} = 5.79$, $g_{\parallel} = 1.98$. Anal. calcd. for $C_{56}H_{52}FFeN_4 \cdot 0.5H_2O$: C, 77.77; H, 6.18; N, 6.46. Found C, 77.41; H, 6.15; N, 6.49.

Preparation of [Fe(NO)(OEP)](BF₄) from [FeF-(OEP)]. A vial was charged with 30.1 mg (43.8 μmol) of [FeF(OEP)] and 7.4 mg (63 μmol) of NOBF₄. The solids were suspended in 4 mL of CH₂Cl₂ and allowed to stir for 18 h at ambient temperature in the glovebox under an atmosphere of nitrogen. All volatiles were removed *in vacuo* and the resulting purple solid was triturated with pentane and collected by filtration. Mass: 20.0 mg (58% yield). Spectroscopic features were found to match those of [Fe(NO)(OEP)]⁺ in the literature [55]. ¹H NMR (CD₂Cl₂): δ_H, ppm 7.96 (br s, 4 *meso-CH*), 3.14 (br s, 16 Et-CH₂), 1.41 (br s, 24 Et-CH₃). UV-vis (CH₂Cl₂): λ_{max}, nm 361, 383 (sh), 555. IR (KBr): v, cm⁻¹ 1838 (v_{NO}).

X-ray crystallography

A crystal of [FeF(TTP)]·2CH₂Cl₂ suitable for X-ray diffraction was mounted in Paratone oil onto a glass fiber and frozen under a nitrogen cold stream maintained by an X-Stream low-temperature apparatus. The data were collected at 98(2) K using a Rigaku AFC12/Saturn 724 CCD fitted with Mo K α radiation ($\lambda = 0.71073$ Å). Data collection and unit cell refinement were performed using Crystal Clear software [56]. The total number of data were measured in the range $3.1 < \theta < 27.6^{\circ}$ using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with Crystal Clear and ABSCOR [57], respectively. The structure was solved by direct methods and refined on F^2 using full-matrix, least-squares techniques with SHELXL-97 [58, 59]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model.

The crystal of $[FeF(TTP)] \cdot 2CH_2Cl_2$ was found to be twinned, displaying a two-fold axis. The TWIN command was used to account for this condition during refinement. Due to the severe disorder in the co-crystallized CH_2Cl_2 molecules, the PLATON SQUEEZE command was used to remove one of the two molecules, resulting in a 132 Å³ void. The structure also exhibits pseudo-symmetry. The correct space group should be $P2_1/c$, however, Pc gave a better description of the structure. The fact that the structure shows almost but not quite a twofold screw axis along *b* explains the partially fulfilled systematic absences. Inspection of the systematic absence statistics clearly indicated the presence of a glide plane along *c*. However, the twofold screw axis was unclear, with 65% of the 32 reflections that should be absent for the monoclinic 2_1 axis being observed but at significantly weaker intensity (by a factor of 3) than the rest of the data.

RESULTS AND DISCUSSION

The standard procedure for synthesis of fluoro-iron(III) porphyrinates makes use of aqueous hydrofluoric acid as a fluorinating agent [28, 29]. In this procedure, the oxo-bridged iron(III) porphyrinate, $[Fe_2(P)_2(\mu-O)]$, is treated with HF (aq) to afford the desired fluoro-iron(III) complex, [FeF(P)]. Low yields, the need to avoid glass reaction vessels, and the danger associated with handling HF (aq) render this procedure un-ideal as a practical means of preparing the fluoride complexes of iron(III) porphyrinates. Other procedures have also been reported, including direct metallation of the porphyrin ligand with FeF₃, although the generality of such procedures has not been established [27]. We therefore sought to examine the utility of a new fluorination protocol involving treatment of oxygen-ligated iron(III) porphyrinates with Et₃N·3HF. We had identified this reaction previously during studies of iron(III) porphyrinates containing silanethiolate ligands [49]. At that time, we observed that the hydroxo-iron(III) complex, [Fe(OH)(H₂O)(TMP)], reacted readily with Et₃N·3HF to afford the fluoroiron(III) porphyrinate, [FeF(TMP)] (Equation 1). We reasoned that related oxo-bridged iron(III) porphyrinates containing ligands other than TMP might react in similar fashion with Et₃N·3HF thereby providing a convenient synthesis for a series of different fluoro-iron(III) species [53]. Et₃N·3HF is a commercially available fluorinating agent that can be handled in straightforward fashion with standard laboratory protocol thereby obviating the need for plastic reaction vessels. Previous work has also demonstrated the utility of this reagent in converting oxygen bound ligands to fluorides with other transition metal platforms [60].

Reactions of a series of oxo-bridged iron(III) complexes containing porphyrin ligands featuring *meso* and pyrrolic substitution with $Et_3N\cdot 3HF$ in dichloromethane were found to afford the desired fluoride complexes in excellent yield (Scheme 1). Confirmation of the presence of the fluoride ligand was provided by IR spectroscopy (v_{Fe-F})





Scheme 1. Synthesis of fluoro-iron(III) porphyrinates

and by comparison of the UV-vis spectra to previous work (see Experimental section). A moderate excess of $Et_3N\cdot 3HF$ was found to be optimal, as prolonged exposure to CH_2Cl_2 in the presence of proton sources was found to lead to formation of chloro-iron(III) complexes (*vide infra*). Washing the isolated fluoride complexes with cold acetone was found to remove excess $Et_3N\cdot 3HF$ affording pure material. All attempted purification of the complexes by alumina chromatography, however, resulted in recovery of a mixture of $[Fe_2(P)_2]-\mu$ -O and [FeCl(P)].

In all cases, the fluoride complexes were found to retain several equivalents of water, which could be observed in the ¹H NMR spectrum as a broad singlet near 0 ppm and accounted for during combustion analysis. We believe the presence of water results from the desire of the fluoride ligand to retain hydrogen-bond donors in the secondary coordination sphere [40, 61]. This proposal is corroborated by the fact that all known crystal structures of fluoro-iron(III) porphyrinates feature co-crystallized CHCl₃ molecules engaging in a hydrogen-bonding interaction with the fluorine atom [24, 26, 28]. Attempts to grow crystals of the fluoro-iron(III) porphyrinates in the present study in order to observe hydrogen-bonding with water molecules were unsuccessful. However, the crystal structure of [FeF(TTP)]·2CH₂Cl₂ was obtained by slow evaporation of a solution of $[FeF(TTP)] \cdot xH_2O$ in CH_2Cl_2 (Fig. 1). This complex is the only member of the series of fluoride complexes described here not disclosed previously. Similar to reported fluoro-iron(III) porphyrinate structures, the solid-state structure of [FeF(TTP)] displays a short Fe–F bond distance of 1.805(4) Å [28, 62]. The complex features two molecules of CH_2Cl_2 in the asymmetric unit. Unfortunately, a crystallographic disorder prevented satisfactory refinement of both solvent

molecules (see Experimental section and Supporting information). Nonetheless, the positions of the CH_2Cl_2 molecules suggest a hydrogen bonding interaction with the fluoride ligand is present in the solid state.

Previous studies on fluoro-iron(III) porphyrinates have examined many of their spectroscopic features [40, 63–68], including their electrochemical behavior [53, 54, 69]. For completeness, we have examined the electrochemistry of each of the fluoride complexes described above in dichloromethane. All species show three reversible or quasi-reversible electrochemical events by cyclic voltammetry in dichloromethane (Fig. 2, Table 1, and see Supporting information). Interestingly, reduction to iron(II) is nearly reversible in all cases, whereas the analogous reduction event is completely irreversible in the chloro-iron(III) complexes (see Supporting information). In contrast to the first reduction event, the first and second oxidation events for both chloro and fluoro complexes are nearly identical, consistent with these events corresponding to ligand-based processes [36, 42, 46, 69-72].

The reversibility of the first oxidation wave in [FeF(OEP)] prompted us to consider its chemical oxidation in order to determine whether a fluoroiron porphyrin π -cation radical complex could



Fig. 1. Thermal ellipsoid (50%) rendering of the solid-state structure of $[FeF(TTP)] \cdot 2CH_2Cl_2$. Hydrogen atoms, minor components of the disorder and co-crystallized CH₂Cl₂ molecules omitted for clarity. Selected bond distances (Å): Fe(1)-F(1) = 1.805(4); Fe(1)-N(1) = 2.052(4); Fe(1)-N(2) = 2.022(4); Fe(1)-N(3) = 2.076(4); Fe(1)-N(4) = 2.090(4); displacement of Fe(1) from N₄ plane = 0.437 Å



Fig. 2. Electrochemical events observed for [FeF(OEP)] in dichloromethane at a platinum electrode. Top trace is the DPV and the bottom trace is the CV (50 mV/s scan rate). The supporting electrolyte is $0.1 \text{ M Bu}_4\text{NPF}_6$

Table 1. Electrochemical data for [FeF(P)] complexes prepared in this study $\!\!\!^{\ddagger}$

Compound	[FeF(P)] ^{0/-}	[FeF(P)] ^{0/+}	[FeF(P)]+/2+
[FeF(TPP)]	-1.03	+0.63	+1.13
[FeF(TTP)]	-1.01	+0.66	+1.13
[FeF(OEP)]	-1.12	+0.53	+1.11
[FeF(TMP)]	-1.21	+0.62	+1.10

^{*}Potentials represent $E_{\nu_{2}}$ values determined by cyclic voltammetry in CH₂Cl₂ at a platinum electrode. All potentials reported *vs*. Fc/Fc⁺.

be isolated. The analogous complex containing a chloride ligand bound to iron has been described for a series of different porphyrin ligands [73–75]. As a chemical oxidant we examined NOBF₄ reasoning that it would be sufficiently oxidizing while minimizing

the likelihood for fluoride abstraction. Surprisingly, treatment of [FeF(OEP)] with NOBF₄ did not lead to formation of $[FeF(OEP)](BF_4)$, but rather to the oxidized nitrosyl complex, $[Fe(NO)(OEP)](BF_4)$, as judged by NMR, IR, and UV-vis spectroscopy (Equation 2). At this time we have no data to suggest a possible stoichiometry for this reaction or the fate of the fluoride ligand. However, the procedure proved reliable on multiple attempts with isolated yields approaching 60%.

Given the facile nature of axial ligand exchange in iron(III) porphyrinates, we next examined the stability of the [FeF(P)] complexes in the presence of various chloride sources. Prolonged exposure (days) of the fluoroiron(III) complexes to dichloromethane or chloroform was found to result in conversion to the chloro-iron(III) complexes as judged by NMR spectroscopy. In solutions of chloroform-d that had not been treated to remove traces of HCl, this conversion was found to take place within a matter of minutes. Conversely, reaction of a representative complex, [FeF(OEP)], with Bu₄NCl was found to result in little to no conversion to the chloroiron complex as judged by UV-vis spectroscopy. This result suggests that halide exchange at the iron(III) porphyrinate is facilitated by proton sources, a conclusion consistent with the observed instability of the fluoro-iron complexes towards alumina chromatography. To test this hypothesis more concretely, we examined the reaction of [FeF(OEP)] with Et₃NHCl. Addition of a dichloromethane solution of Et₃NHCl to [FeF(OEP)] lead to immediate conversion to the corresponding chloro-iron complex (Equation 3). Conducting the same reaction in pure toluene where Et₃NHCl is sparingly soluble provided the opportunity to monitor this conversion by UV-vis. Figure 3 displays the spectral changes associated with the reaction of [FeF(OEP)] with Et₃NHCl. As is evident from the spectrum, conversion of [FeF(OEP)] to [FeCl(OEP)] is clean displaying several well defined isosbestic points. Thus, halide exchange reactions of the fluoro-iron(III) porphyrinate appear to require a proton source. To further confirm this conclusion, we revisited the reaction of [FeF(OEP)] with Bu₄NCl in the presence of a proton source. Accordingly,





Fig. 3. Electronic absorption spectra of the reaction of [FeF(OEP)] (---) with excess Et₃NHCl in toluene showing conversion to [FeCl(OEP)] (---)



Fig. 4. Electronic absorption spectra of [FeF(OEP)] and 1 equiv. Bu₄NCl in toluene/THF before (---) and after addition of p-TsOH (— 1 equiv., grey; — 2 equiv., black). Initial spectrum is identical to that of [FeF(OEP)] and the final spectrum is identical to that of [FeCl(OEP)]

addition of *p*-toluenesulfonic acid (*p*-TsOH) to a mixture of [FeF(OEP)] and Bu_4NC1 led to immediate conversion to [FeCl(OEP)] as judged by UV-vis spectroscopy (Fig. 4). These results coupled with the apparent desire of the fluoro-iron(III) porphyrinates to associate with hydrogen-bond donors (*vide supra*) strongly points to an important role for hydrogen-bonding in mediating halide exchange [25, 26].

CONCLUSION

In this contribution we have described a facile new procedure for the preparation of a series of fluoroiron(III) porphyrinates. This new method utilizes the commercially available fluorinating agent, $Et_3N\cdot 3HF$, and avoids the difficulties associated with handling aqueous hydrofluoric acid. Purification of the complexes is facile and isolated yields are greater than 80%. Studies with the fluoro-iron complexes demonstrate the sensitivity of the compounds towards halide exchange with chloride in the presence of proton sources. Thus, an effort to minimize prolonged exposure to chlorinated solvents should be made when handling fluoro-iron(III) porphyrinates.

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Supporting information

Additional spectra and the cif file for [FeF(TTP)]-2CH₂Cl₂ (Figs S1–S13 and Table S1) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/ jpp/jpp.shtml.

Coordinates for [FeF(TTP)]·2CH₂Cl₂ have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-990086. Copies can be obtained on request, free of charge, *via* www. ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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