Supporting Information for

Interior Aliphatic C-H Bond Activation on Iron(II) N-Confused Porphyrin Through Synergistic Nitric Oxide Binding and Iron Oxidation

Wei-Min Ching[a,b] and Chen-Hsiung Hung*[a]

[a]*Institute of Chemistry, Academia Sinica, Nankang, Taipei 115, Taiwan. Fax: 886-2-27831237; Tel: 886-2-27898570; E-mail: chhung@chem.sinica.edu.tw*
[b]*Department of Chemistry, National Taiwan Normal University, Taipei Taiwan*

Contents

General Information. Dichloromethane, toluene, *n*-hexane and THF were degassed and dried under N_2 using PS-400 solvent purification system (Innovative Technology) equipped with activated alumina stainless steel columns. Each freshly distilled solvent was stored in a round-bottom flask with J-Young tap, sent into an inert atmosphere dry box, and bubbled with nitrogen for at least 30 min to remove any residual oxygen. The starting compound [CTPP*CH₃*]H_2, was prepared following previously reported procedures.[1,2] The iron metalltion of [CTPP*CH₃*]H_2 is modified from the literature method and the spectroscopic data is consistent with the literature report.[3] Other starting materials were commercially obtained and used without further purification. UV-vis spectra were recorded with an Agilent 8453 spectrophotometer. FT-IR measurements were carried out by a Perkin Elmer Paragon 1000 spectrophotometer. Elemental analyses were carried out with a PerkinElmer CHN Analyzer (Model 2400). The ESI mass spectrum was recorded on a QSTAR™ Hybrid LC/MS/MS system. ^1H NMR spectra were recorded on a Bruker Spectrospin 400 Ultra Shield™ and a Bruker Spectrospin 500 Ultra Shield™ spectrometer. EPR spectra were recorded on a Bruker E580 FT/CW EPR spectrometer.

Synthesis of [Fe(CTPP*CH₃*)NO] (3). In a N_2-filled dry box, [Fe^{II}(*H*CTPP*CH₃*)Br] (19.6 mg, 0.0257 mmol) dissolved in 6 mL of anhydrous THF was added into 2.1 equiv of NaOMe (5.46×10^{-2} M in MeOH, 1.0 mL), and the mixture was stirred at ambient temperature for 0.5 h. A completion of reaction was obtained when the *Soret* band was shifted from 466 nm, for starting [Fe^{II}(*H*CTPP*CH₃*)Br], to 470 nm. The solvent was removed under reduced pressure, and the solid was redissolved in small amount of CH_2Cl_2. The solution was filtered through a No. 2 paper filter to remove excess NaOMe and NaBr. The solvent was removed under reduced pressure again.

The solid was redissolved in 10 mL of THF then send out of the dry-box. The solution was bubbled with 1% NO gas under N_2-filled atmosphere. After 20 minutes, the color of solution was changed from light green to dark green. The solvent was removed by reduced pressure and the solid was stored in a N_2-filled dry-box. Recrystallization in dry-box using vapor diffusion of *n*-hexane into CH_2Cl_2 solution of crude Fe(*H*CTPP*CH₃*)NO afforded pure product (11.8 mg, 91.5% yield). The crystals obtained from recrystallization can be used directly for X-ray crystallographic analysis.

^{1}H NMR (500 MHz, chloroform-*d*, 298 K): δ = 17.01 (s, 1H), 16.23 (s, 1H), 13.90 (s, 1H), 13.24 (s, 1H), 10.39 (s, 2H), 7.4–9.0 (m, 21H). UV-VIS (CH_2Cl_2) [λ_{max}, nm (log ε, $M^{-1}cm^{-1}$)]: 321 (4.47), 440 (4.80). HSMS (ESI-MS): Calcd. for $C_{45}H_{31}N_5FeO$ $\{M + H\}^+$, 713.1878; Found: 713.1876. FT-IR (KBr, cm^{-1}): 1659 ν(NO).

Synthesis of [Fe(CTPP*CH₃*)(^{15}NO)]. Following the same synthetic procedures for the preparation of [Fe(CTPP*CH₃*)NO] starting with [Fe^{II}(*H*CTPP*CH₃*)Br] (20.9 mg, 0.0274 mmol) and 2.7 equiv of NaOMe (1.88 × 10^{-2} M in MeOH, 1.0 mL) in 9 mL mixed solvent of THF/MeOH (8:1, *v*/*v*). FT-IR (KBr, cm^{-1}): 1630 *v*(^{15}NO). Other spectroscopic data is identical to **3**.

Synthesis of {[Fe(*H*CTPP*CH₃*)]₂O}(BF₄)₂ (4). In a N_2-filled dry box, [Fe^{II}(*H*CTPP*CH₃*)Br] (23.3 mg, 0.0305 mmol) and $AgBF_4$ (13.0 mg, 0.0668 mmol) were dissolved in 10 mL of anhydrous THF, and the reaction was refluxed for 1 h. The solvent was removed by reduced pressure and the solid was redissolved in small amount of CH_2Cl_2. The solution was filtered through a No. 2 paper filter to remove excess $AgBF_4$ and AgBr. The solvent was removed under reduced pressure again. The solid was redissolved in 10 mL of dry THF, sent out from the drybox, and stirred under air for 1.5 hours. The shift of *Soret* band from 420 to 407 nm was observed; the solvent was removed by reduced pressure and the solid was stored in a N_2-filled dry-box. Recrystallization in dry-box using vapor diffusion of *n*-hexane into THF solution of crude {Fe(*H*CTPP*CH₃*)]₂O}(BF₄)₂ afforded pure product (15.9 mg, 66.9%

yield).

^{1}H NMR (500 MHz, chloroform-*d*, 298 K): δ = 21.69 (b, 3H), 16.0–14.0 (m, 4H), 11.32 (s, 1H), 10.06 (s, 1H), 7.0–6.0 (m, 21H), 4.33(b, 1H). UV-VIS (CH_2Cl_2) [λ_{max}, nm (log ε, $M^{-1}cm^{-1}$)]: 314 (4.82), 342 (4.83), 407 (4.92), 445 (4.87), 580 (4.10), 758 (4.12). HSMS (ESI-MS) : Calcd. for $C_{90}H_{61}N_8Fe_2O$ {M–2(HBF_4)+H}$^+$, 1381.3667; Found: 1381.3680.

Synthesis of [Fe(*H*CTPP*CH₂*)NO][BF₄] (5). Method (a) In a N_2-filled dry box, [Fe(CTPP*CH₃*)NO] (11.5 mg, 0.01614 mmol) and $AgBF_4$ (7.2 mg, 0.0370 mmol) were dissolved in 5 mL of anhydrous THF, and the reaction was stirred at ambient temperature for 15 minutes. The shift of *Soret* band from 440 to 474 nm was observed; the solvent was removed under reduced pressure and the solid was redissolved in small amount of CH_2Cl_2. The solution was filtered through a No. 2 paper filter to remove excess $AgBF_4$ and AgBr. The solvent was removed under reduced pressure again. Recrystallization in dry-box using vapor diffusion of *n*-hexane into CH_2Cl_2 solution of crude [Fe(*H*CTPP*CH₂*)NO][BF_4] afforded pure product (11.8 mg, 91.5% yield).

Method (b) In a N_2-filled dry box, [Fe^{II}(*H*CTPP*CH₃*)Br] (20.9 mg, 0.0274 mmol) and $AgBF_4$ (11.9 mg, 0.0611 mmol) were dissolved in 15 mL of anhydrous THF, and the reaction was refluxed for 1.5 hour. The solvent was removed by reduced pressure and the solid was redissolved in small amount of CH_2Cl_2. The solution was filtered through a No. 2 paper filter to remove excess $AgBF_4$ and AgBr. Extra 25 mL DCM added into the solution then send out of the dry-box. The solution reacted with 1% NO gas in the N_2-filled atmosphere. After 30 minutes, the color of reaction was changed from green to brown. The ^{1}H NMR, Uv-vis and IR spectra of the final product were identical to the product from the method (a).

^{1}H NMR (400 MHz, chloroform-*d*, 298 K): δ = 14.17 (s, 1H), 9.79 (d, *J* = 3.5 Hz, 1H), 8.67 (d, *J* = 5.0 Hz, 1H), 8.62 (d, *J* = 5.0 Hz, 1H), 8.48 (d, *J* = 5.0 Hz, 1H), 8.40 (d, *J* = 5.1 Hz, 1H), 8.36 (d, *J* = 5.1 Hz, 1H), 8.28 (d, *J* = 5.0 Hz, 1H), 8.2-8.1 (m, 2H), 8.06 (d, *J* = 6.7 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.9–7.6 (m, 13H), -1.28 (d, *J* = 1.3 Hz, 1H), -1.51 (d, *J* = 1.3 Hz, 1H). UV-VIS (CH_2Cl_2) [λ_{max}, nm (log ε, $M^{-1}cm^{-1}$)]: 336 (4.50), 375 (4.45), 474 (4.67). HSMS (ESI-MS): Calcd. for $C_{45}H_{30}N_5OFe$ {M – BF_4}$^+$, 712.1800; Found, 712.1799. FT-IR (KBr, cm^{-1}): 1706 ν(NO).

Density Functional Calculations. The structures of the models [Fe(NCP*CH₃*)(NO)] (**3a**)/[Fe(*H*NCP*CH₂*)(NO)] (**3b**) for $\{Fe(NO)\}^7$ and $[Fe(NCP\mathit{CH_3})(NO)]^+$ (**5a**)/$[Fe(\mathit{H}NCP\mathit{CH_2})(NO)]^+$ (**5b**) for $\{Fe(NO)\}^6$ have been fully optimized using BP86/TZVP. For all of the calculations, the four phenyl rings on the N-confused porphyrin core have been replaced by hydrogen to simplify the calculations. The starting coordinates of 3a and 5b were adopted directly from the crystal structures of 3 and 5 while the removal of an electron and addition of an electron from 3a and 5b resulted initial setup of 5a and 3b for optimization. Vibrational frequencies have been calculated showing no imaginary frequencies. All these methods were used as implemented in the Gaussian 03 package.

Crystal Structure Determinations for $[Fe(\mathit{H}CTPP\mathit{CH_3})Br]$ (2), $[Fe(CTPP\mathit{CH_3})NO]$ (3), $\{[Fe(\mathit{H}CTPP\mathit{CH_3})]_2O\}(BF_4)_2$ (4), and $[Fe(\mathit{H}CTPP\mathit{CH_2})NO][BF_4]$ (5)

Diffraction measurements were carried out at 150(2) K on a Bruker SMART Apex CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined using full-matrix least-squares methods against F^2 values using the SHELXTL[4, 5] program packages. Most of the protons can be observed from the residual electron density maps but further refinements didn’t provide good model. Therefore, the positions of the hydrogen atoms were geometrically generated with a fixed distance and were assigned isotropic thermal parameters by the SHELXTL idealization methods. Refinement was carried out using anisotropic thermal parameters for all the non-hydrogen atoms. The absorption correction program SADABS[6] was used for these three structures. Summary and experimental details for X-ray data collections are provided in Table S1.

Table S1. Structural Parameters for [Fe(*H*CTPP*CH*$_3$)Br] (**2**), [Fe(CTPP*CH*$_3$)NO] (**3**), {[Fe(*H*CTPP*CH*$_3$)]$_2$O}(BF$_4$)$_2$ (**4**), and [Fe(*H*CTPP*CH*$_2$)NO][BF$_4$] (**5**)

	2	**3**	**4**	**5**
code	i12300mp	i11526p2	i10995mp	i11970mc
formula	$C_{49}H_{39}BrFeN_4O$	$C_{46}H_{32}Cl_2FeN_5O$	$C_{93}H_{68}B_2Cl_6F_8Fe_2N_8O$	$C_{46.5}H_{33}BCl_3F_4FeN_5O$
formula weight	835.60	797.50	1811.57	926.79
crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	*P-1*	$P2_1/n$	$C2/c$
a, Å	12.4227(9)	11.7119(11)	18.0177(11)	35.1501(17)
b, Å	25.958(2)	12.9672(10)	16.7896(10)	13.7918(6)
c, Å	13.1178(12)	14.6335(11)	28.1291(17)	19.1196(9)
α, deg	90	64.680(5)	90	90
β, deg	114.087(5)	86.090(6)	106.170(3)	119.319(3)
γ, deg	90	65.569(5)	90	90
V, Å^3	3861.8(6)	1813.0(3)	8172.7(9)	8081.6(6)
Z value	4	2	4	8
ρ_{calc}, g/cm^3	1.437	1.461	1.472	1.523
μ, mm^{-1}	1.470	0.610	0.625	0.636
F_{000}	1720	822	3704	3784
T, K	150	150	150	150
hkl ranges	$-14 \leqq h \leqq 14$	$-14 \leqq h \leqq 13$	$-19 \leqq h \leqq 21$	$-41 \leqq h \leqq 41$
	$-29 \leqq k \leqq 31$	$-13 \leqq k \leqq 15$	$-20 \leqq k \leqq 19$	$-16 \leqq k \leqq 15$
	$-15 \leqq l \leqq 15$	$-17 \leqq l \leqq 17$	$-32 \leqq l \leqq 33$	$-22 \leqq l \leqq 22$
GOF	1.034	0.934	1.071	1.064
R_1, wR_2 (I>2σ(I))	0.0568, 0.1341	0.0744, 0.1605	0.0834, 0.2009	0.0454, 0.1320
Largest diff. peak and hole (e.Å^{-3})	1.263 and -0.610	0.673 and -0.613	0.881 and -0.816	1.226 and -0.690

$R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(| F_o |)$

References

1. I. Schmidt and P. J. Chmielewski, *Inorg. Chem.*, 2003, **42**, 5579-5593.
2. P. J. Chmielewski, L. Latos-Grazynski and T. Glowiak, *J. Am. Chem. Soc.*, 1996, **118**, 5690-5701.
3. K. Rachlewicz, D. Gorzelanczyk and L. Latos-Grazynski, *Inorg. Chem.*, 2006, **45**, 9742-9747.
4. Sheldrick, G. M. *SHELXS-97—Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.
5. Sheldrick, G. M. *SHELXL-97—Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
6. Sheldrick, G. M. *SADABS*, *Siemens Area Detector Absorption Correction Program*; University of Göttingen: Germany, 1996.

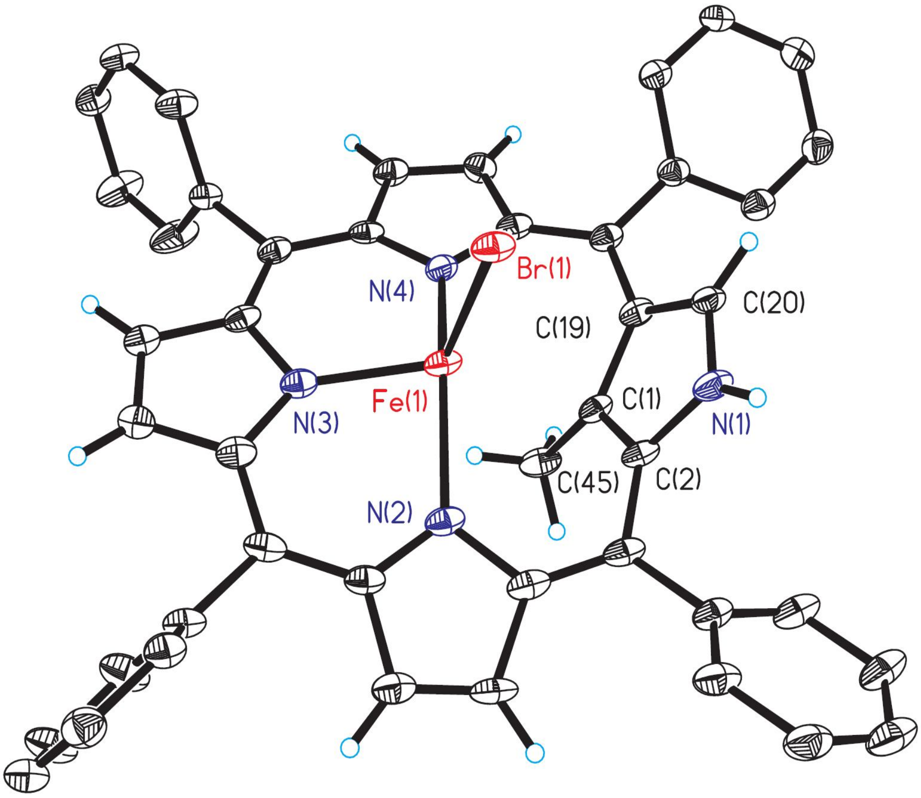

Figure S1. The crystal structure of [Fe^{II}(*H*CTPP*CH$_3$)*Br] **(2)**. Selected Distances:

Fe(1)-N(3), 2.055(5); Fe(1)-N(4), 2.139(4); Fe(1)-N(2), 2.145(4); Fe(1)-Br(1), 2.4220(9); Fe(1)-C(1), 2.466(6); N(1)-C(20), 1.341(6); N(1)-C(2), 1.393(7); N(1)-H(1), 0.8800.

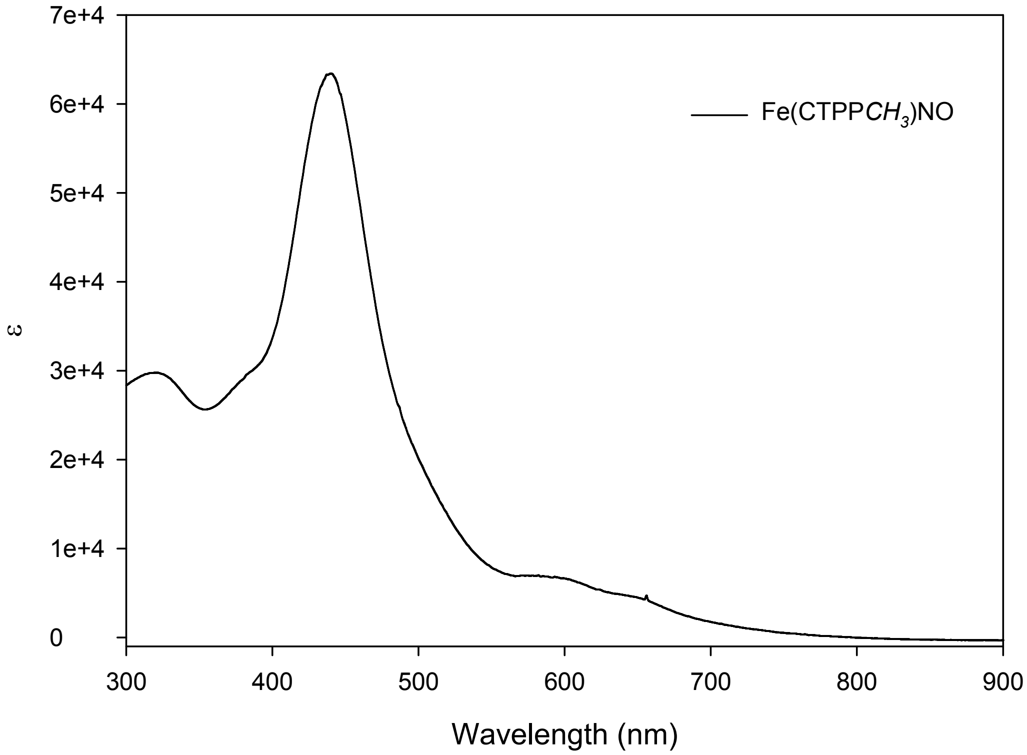

Figure S2. The Uv-vis spectrum of [Fe(CTPPCH_3)NO] (**3**)

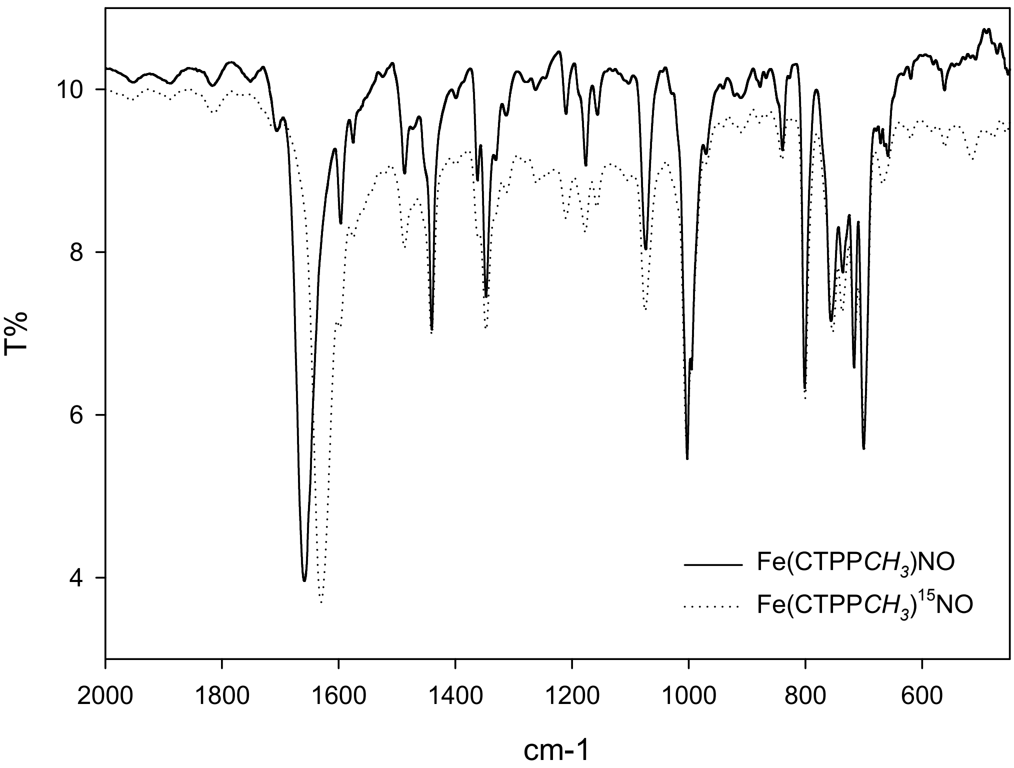

Figure S3. The IR spectrum of $\{Fe(NO)\}^7$ [Fe(CTPP*CH*$_3$)NO] (**3**) and [Fe(CTPP*CH*$_3$)^{15}NO].

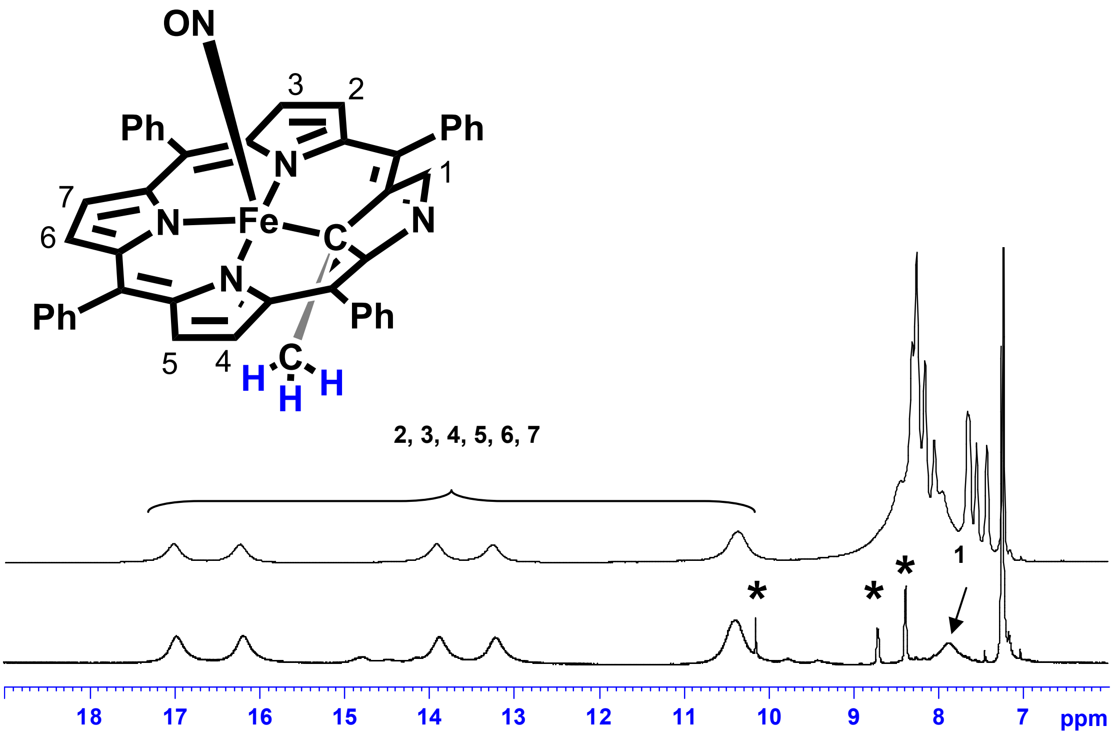

Figure S4. The NMR spectra of [Fe(CTPPCH_3)NO] (**3**) and [Fe(d_{20}-CTPPCH_3)NO].

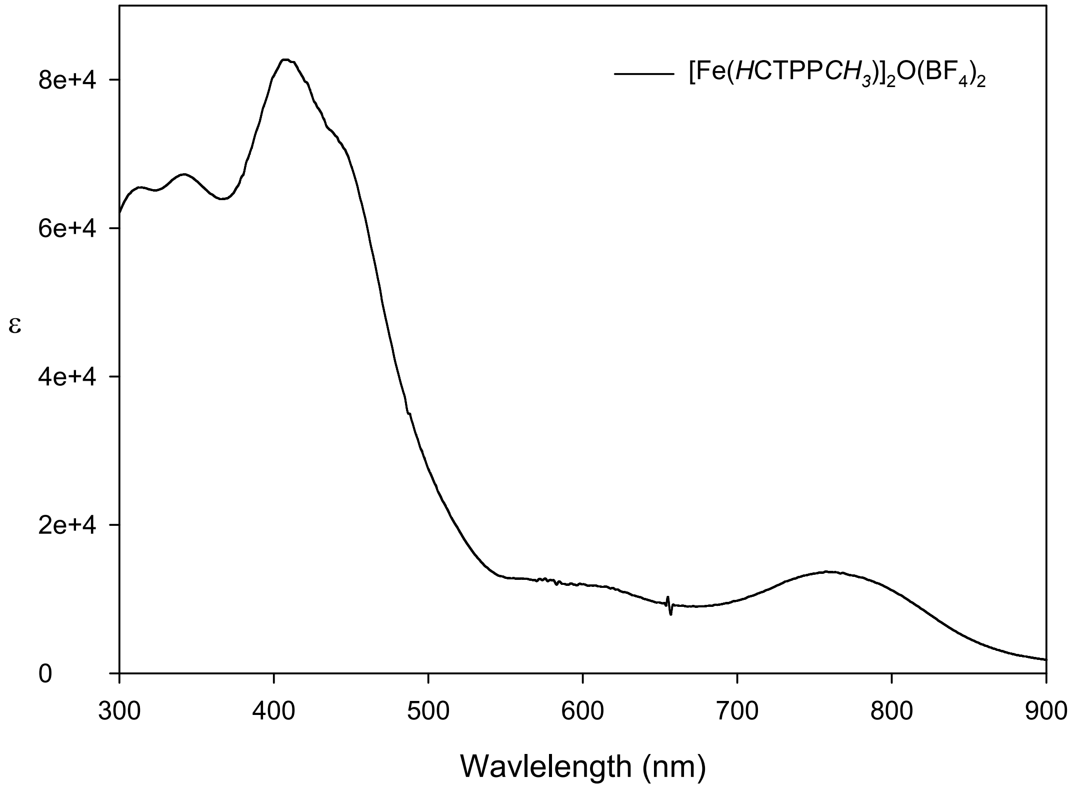

Figure S5. The Uv-vis spectrum of $\{[Fe(HCTPPCH_3)]_2O\}(BF_4)_2$ (**4**).

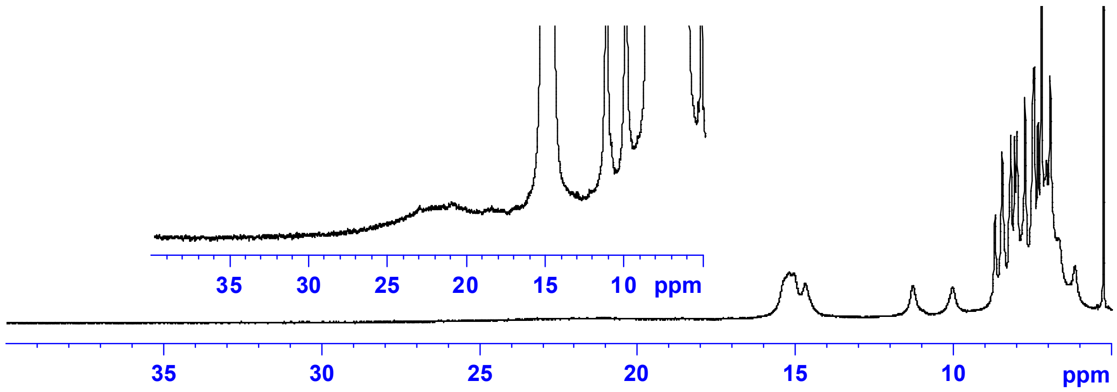

Figure S6. The NMR spectrum of $\{[\mathrm{Fe}(\mathit{H}\mathrm{CTPP}\mathit{CH_3})]_2\mathrm{O}\}(\mathrm{BF_4})_2$ (**4**).

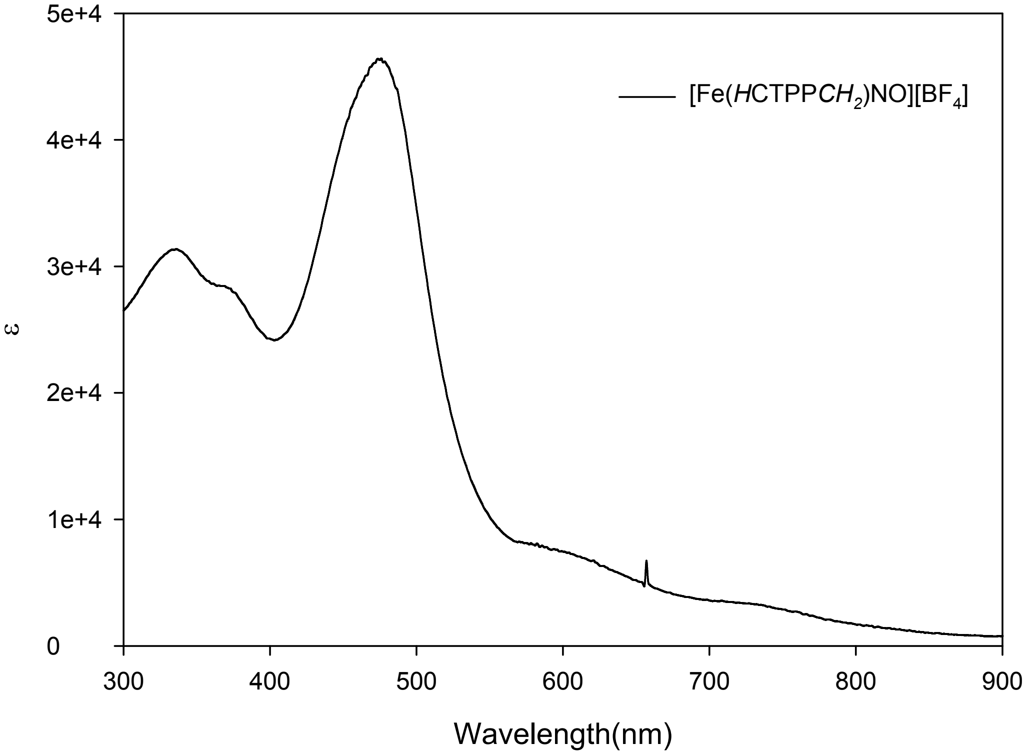

Figure S7. The Uv-vis spectrum of [Fe(*H*CTPP*CH*$_2$)NO][BF$_4$] (**5**)

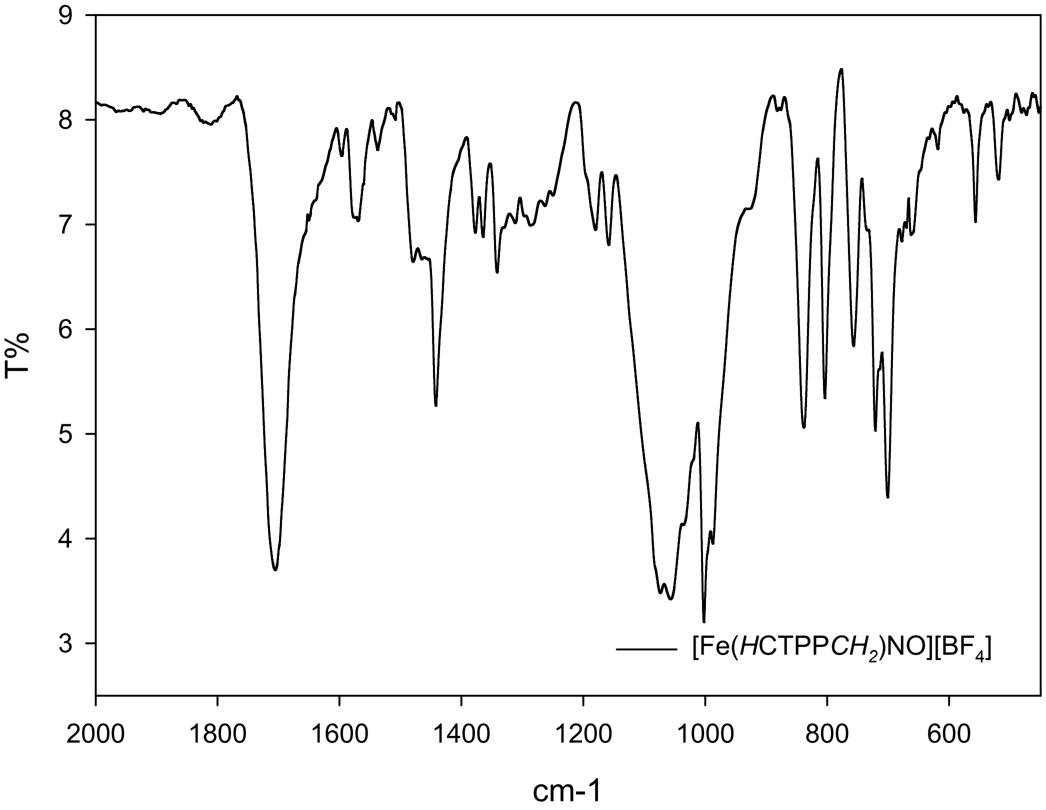

Figure S8. The IR spectrum of {Fe(NO)}^{6} [Fe(*H*CTPP*CH*$_2$)NO][BF$_4$] (**5**).

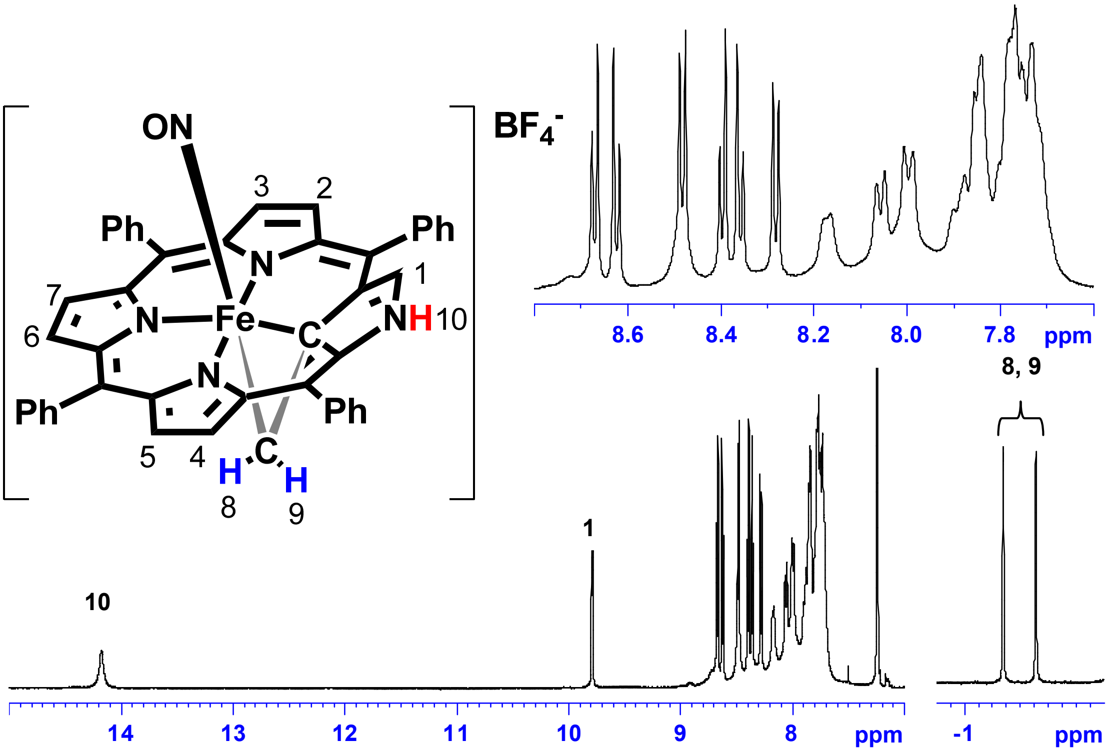

Figure S9. The NMR spectrum of $[\mathrm{Fe}(\mathit{H}\mathrm{CTPP}\mathit{CH_2})\mathrm{NO}][\mathrm{BF_4}]$ (**5**).