Supplementary Information

A Mononuclear Nonheme Iron(III)-Peroxo Complex Binding Redox-Inactive Metal Ions†

Yong-Min Lee,^{‡a} Suhee Bang,^{‡a} Yun Mi Kim,^{‡a} Jaeheung Cho,^{ab} Seungwoo Hong,^a

Takashi Nomura,^c Takashi Ogura,^c Oliver Troeppner,^d Ivana Ivanović-Burmazović,^d Ritimukta Sarangi,^{*e} Shunichi Fukuzumi,^{*af} and Wonwoo Nam^{*a}

^a Department of Bioinspired Science, Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea

^b Department of Emerging Materials Science, DGIST, Daegu 711-873, Korea

^c Picobiology Institute, Graduate School of Life Science, University of Hyogo, Hyogo 678-1297, Japan

^d Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, 91058 Erlangen, Germany

^e Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

^f Department of Material and Life Science, Graduate School of Engineering, Osaka University, and ALCA, Japan Science Technology Agency (JST), Suita, Osaka 565-0871, Japan

*To whom correspondence should be addressed.

E-mail: wwnam@ewha.ac.kr, fukuzumi@chem.eng.osaka-u.ac.jp, ritis@slac.stanford.edu

[‡]These authors contributed equally to this work.

Experimental Section

Materials. All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use^[1]. H₂¹⁸O₂ (90% ¹⁸O-enriched, 2% H₂¹⁸O₂ in water) was purchased from ICON Services Inc. (Summit, NJ, USA). [(TMC)Fe^{II}(CF₃SO₃)₂], [(TMC)Fe^{III}(O₂)]⁺ (1), and [(TMC)Fe^{IV}(O)(CH₃CN)]²⁺ (4) were prepared according to the literature methods^[2-4]. 1 was generated in the reaction of [(TMC)Fe^{II}(CF₃SO₃)₂] (69.3 mg, 0.10 mmol) with 5 equiv. H₂O₂ (51 μ L, 30% in water, 0.50 mmol) in the presence of 2 equiv. triethylamine (TEA; 28 μ L, 0.20 mmol) in CF₃CH₂OH (2 mL) at -40 °C. Then, Et₂O (40 mL) was added to the solution of 1 to yield a purple precipitate at -40 °C. This purple precipitate was washed with Et₂O and dried under Ar atmosphere. [(TMC)Fe^{III}(¹⁸O₂)]⁺ (1-¹⁸O₂) was also prepared by adding 5 equiv. H₂¹⁸O₂ (8 μ L, 90% ¹⁸O-enriched, 2% H₂¹⁸O₂ in water) to a solution containing [(TMC)Fe^{III})²⁺ (1 mM) and 2 equiv. TEA in CF₃CH₂OH (2 mL) at -40 °C.

Instrumentations. UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments for low-temperature experiments or with a circulating water bath. Fast reactions were monitored using a Hi-Tech Scientific SF-61 DX2 cryogenic stopped-flow spectrometer equipped with a Xe arc lamp and a KinetaScan diode array rapid scanning unit. Electrospray ionization mass spectra (ESI MS) were collected on a UHR-TOF Bruker Daltonik (Bremen, Germany) maXis, an ESI-ToF MS capable of resolution of at least 40,000 FWHM. Detection was in positive-ion mode with source voltage 4.5 kV and flow rates 300 µL/hour. The drying gas (N₂), was held at -35 °C and the spray gas was held at -40 °C. The machine

was calibrated prior to every measurement via direct infusion of the Agilent ESI-TOF low concentration tuning mixture, which provided an m/z range of singly charged peaks up to 2700 Da. Resonance Raman spectra were obtained using a liquid nitrogen cooled CCD detector (CCD-1024×256-OPEN-1LS, HORIBA Jobin Yvon) attached to a 1-m single polychromator (MC-100DG, Ritsu Oyo Kogaku) with a 1200 groovs/mm holographic grating. An excitation wavelength of 515-nm was provided by an Ar ion laser (NEC, GLG3200) with 15 mW power at the sample point. All measurements were carried out with a spinning cell (1000 rpm) at -20 °C. Raman shifts were calibrated with indene, and the accuracy of the peak positions of the Raman bands was ± 1 cm⁻¹. X-band EPR spectra were recorded at 5 K using X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperature was achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR measurement were as follows: Microwave frequency = 9.647 GHz, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 1.0×10^4 , modulation frequency = 100 kHz, time constant = 40.96 ms, and conversion time = 81.00 ms.

Generation of $[(TMC)Fe^{III}(O_2)]^+$ -Sc³⁺ (2-Sc) and $[(TMC)Fe^{III}(O_2)]^+$ -Y³⁺ (2-Y). 2-Sc and 2-Y were generated by adding 3 equiv. of scandium triflate $[Sc(CF_3SO_3)_3]$ and 5 equiv. of yttrium triflate $[Y(CF_3SO_3)_3]$ to the solution of isolated 1 in acetone/CF₃CH₂OH (v/v = 3:1) at -40 °C, respectively. ¹⁸O-incorporated 2-Sc and 2-Y were generated using isolated $[(TMC)Fe^{III}(^{18}O_2)]^+$ (1-¹⁸O₂) under the identical reaction conditions. When the reactions were carried out in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C, addition of one equiv. of Sc³⁺ and Y³⁺ was sufficient to fully convert 1 to 2-Sc and 2-Y, respectively.

Kinetic Measurements. The kinetic measurements of electron transfer from Fc derivatives to 2-Sc and 2-Y were performed in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C. Rates of electron transfer from electron donors (e.g., Fc and Fc derivatives) to 2-Sc and 2-Y were monitored by the decay of absorption bands corresponding to 2-Sc at 535 nm and 2-Y at 570 nm or the formation of the absorption bands corresponding to $[(TMC)Fe^{IV}(O)]^{2+}$ (4) at 820 nm and ferrocenium cation (Fc⁺) at 620 nm. All kinetic measurements, except for the reactions of Me₂Fc with 2-Sc and Me₈Fc with 2-Y, were carried out under pseudo-first-order conditions, where the concentrations of Fc derivatives were maintained to be more than 10-folds excess of those of 2-Sc and 2-Y. Kinetic measurements for the reactions of Me₂Fc with 2-Sc and Me₈Fc with 2-Y. Kinetic measurements of Me₂Fc with 2-Sc and Me₈Fc with 2-Y. Kinetic measurements for the reactions of Me₂Fc with 2-Sc and Me₈Fc with 2-Y. Kinetic measurements for the reactions of Me₂Fc with 2-Sc and Me₈Fc with 2-Y. Kinetic measurements for the reactions with the concentration of 0.25 mM for both electron donor and 2-M, since electron transfer rates were too fast to follow in these reactions under pseudo-first-order conditions even with the use of a stopped-flow spectrometer.

X-ray Absorption Spectroscopy The Fe K-edge X-ray absorption spectra of 2-Sc and 2-Y were measured at the Stanford Synchrotron Radiation Laboratory (SSRL) on the unfocussed 20-pole 2 T wiggler side-station beam line 7-3 under standard ring conditions of 3 GeV and ~350 mA. A Si(220) double crystal monochromator was used for energy selection. A Rh-coated harmonic rejection mirror was used on beam line 7-3 to reject components of higher harmonics. The solution samples for 2-Sc and 2-Y (~120 μ L) were transferred into 2 mm delrin XAS cells with 70 μ m Kapton tape windows under synthesis conditions. The solution samples were immediately frozen after preparation and stored under liquid N₂. During data collection, the samples were maintained at a constant temperature of ~10 – 15 K using an Oxford Instruments CF 1208 liquid helium cryostat.

Data were measured to $k = 15 \text{ Å}^{-1}$ (fluorescence mode) by using a Canberra Ge 30-element array detector. Internal energy calibration was accomplished by simultaneous measurement of the absorption of an Fe-foil placed between two ionization chambers situated after the sample. The first inflection point of the foil spectrum was fixed at 7111.2 eV. Data presented here are 34-scan (2-Sc) and 47-scan (2-Y) average spectra. The large number of scans was required to obtain high signal/noise ratio data at high k, where heavy atom scattering contribution is prominent. Data were processed by fitting a second-order polynomial to the pre-edge region and subtracting this from the entire spectrum as background. A five-region spline of orders 2, 3, 3, 3 and 3 was used to model the smoothly decaying post-edge region. The data were normalized by subtracting the cubic spline and assigning the edge jump to 1.0 at 7130 eV using the Pyspline program^[5]. Data were then renormalized in Kaleidagraph for comparison and quantitation purposes. Theoretical EXAFS signals $\chi(k)$ were calculated by using FEFF (macintosh version 8.4)^[6–8]. Structural models for 2-Sc and 2-Y were generated by one of two methods: a) modifying the crystal structure of [(TMC)Fe-O-Sc(OTf)₃(OH)] in Avogadro^[9] and b) choosing DFT optimized structures of 2-Sc and 2-Y. The theoretical models were fit to the data using EXAFSPAK^[10]. The structural parameters varied during the fitting process were the bond distance (R) and the bond variance σ^2 , which is related to the Debye-Waller factor resulting from thermal motion, and static disorder of the absorbing and scattering atoms. The nonstructural parameter E_0 (the energy at which k = 0) was also allowed to vary but was restricted to a common value for every component in a given fit. Coordination numbers was systematically varied in the course of the fit but were fixed within a given fit.

Density Functional Theory Gradient-corrected, (GGA) spin-unrestricted, broken-

symmetry, density functional calculations were carried out using the ORCA package^[11,12] on a 12-cpu linux cluster. The Becke88^[13,14] exchange and Perdew86^[15,16] correlation nonlocal functional (BP86) was employed to study the geometric structures of **2**-Sc and **2**-Y. The BP86 functional was chosen for **2**-Sc and **2**-Y for comparison with [Fe(14-TMC)O₂]⁺ (**1**), for which a hybrid functional such as B3LYP^[13,14,17] resulted in an incorrect ground state (the calculated O-O distance in **1** using the B3LYP functional was 1.35 Å, indicating superoxide like character). The coordinates obtained from the crystal structure of [(TMC)Fe-O-Sc(OTf)₃(OH)] were modified to generate both end-on and side-on bound [(TMC)Fe-O₂-Sc(OTf)₃]⁺ and [(TMC)Fe-O₂-Y(OTf)₃]⁺ models, which were used as the starting input structure for **2**-Sc and **2**-Y, respectively. The Ahlrichs' all electron triple- ξ TZVP^[18-20] basis set was used on all other atoms. Populations were obtained using a Mulliken Analysis (MPA)^[21]. Compositions of molecular orbitals and overlap populations between molecular fragments were calculated using the QMForge^[22]. Numerical frequency calculations were visualized using the numfreq keyword in ORCA. The calculated vibrational modes were visualized using gopenmol^[23,24].

References

- W. L. F. Armarego and Chai, C. L. L. *Purification of Laboratory Chemicals*, 6th ed.;
 Pergamon Press: Oxford, 2009.
- [2] J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E.
 Münck, W. Nam and L. Que, Jr., *Science*, 2003, 299, 1037-1039.
- [3] J. Annaraj, Y. Suh, M. S. Seo, S. O. Kim and W. Nam, *Chem. Commun.*, 2005, 4529-4531.

- [4] J. Cho, S. Jeon, S. A. Wilson, L. V. Liu, E. A. Kang, J. J. Braymer, M. H. Lim, B. Hedman, K. O. Hodgson, J. S. Valentine, E. I. Solomon and W. Nam, *Nature*, 2011, 478, 502-505.
- [5] A. Tenderholt, B. Hedman and K. O. Hodgson, *AIP Conference Proceedings*, 2007, 882, 105-107.
- [6] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers and M. J. Eller, *Phys. Rev. B: Condens. Matter*, 1995, **52**, 2995-3009.
- [7] J. J. Rehr, J. Mustre de Leon, S. I. Zabinsky and R. C. Albers, J. Am. Chem. Soc., 1991, 113, 5135-5140.
- [8] J. Mustre de Leon, J. J. Rehr, S. I. Zabinsky and R. C. Albers, *Phys. Rev. B: Condens. Matter*, 1991, 44, 4146-4156.
- [9] Avogadro: an open-source molecular builder and visualization tool. Version 1.XX. http://avogadro.openmolecules.net/.
- [10] G. N. George, EXAFSPAK and EDGE-FIT. Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford, CA, 2000.
- [11] F. Neese and G. Olbrich, *Chem. Phys. Lett.*, 2002, **362**, 170-178.
- [12] Neese, F. ORCA: An ab initio, DFT and semiempirical SCF-MO package, Version 2.8.20, 2010.
- [13] A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- [14] A. D. Becke, *Phys. Rev. A.*, 1998, **38**, 3098-3100.
- [15] J. P. Perdew, K. Burke and Y. Wang, Phys. Rev. B: Condens. Matter, 1998, 57, 14999.
- [16] J. P. Perdew, K. Burke and Y. Wang, Phys. Rev. B: Condens. Matter, 1996, 54, 16533-16539.

- [17] C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785-789.
- [18] F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297-3305.
- [19] A. Schaefer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829-5835.
- [20] A. Schaefer, H. Horn and R. Ahlrichs, J. Chem. Phys., 1992, 97, 2571-2577.
- [21] R. S. Mulliken, J. Chem. Phys., 1955, 23, 1833-1840.
- [22] A. Tenderholt, *QMForge* 2007.
- [23] L. Laaksonen, J. Mol. Graph., 1992, 10, 33-34.
- [24] D. L. Bergman, L. Laaksonen and A. Laaksonen, J. Mol. Graph. Model., 1997, 15, 301-306.

Complex	Coordination/Path	$R(\text{\AA})^a$	$\sigma^2(\text{\AA}^2)^b$	$E_0 (eV)$	F^{c}
2 -Sc	2 Fe-O	1.98	570		
	4 Fe-N	2.17	448		
	4 Fe-C	2.95	224		
	6 Fe-C	6 Fe-C 3.10 424			
	16 Fe-C-N	3.38	939	-6.17	0.26
	4 Fe-C-N	3.53	443		
	1 $\operatorname{Fe-Sc}^d$	3.80	389		
	4 Fe-O-Sc ^{d}	3.84	/389		
	4 Fe-C-N	4.78	390		
2- Y	2 Fe-O	1.97	750		
	4 Fe-N	2.19	581		
	4 Fe-C	2.98	336		
	6 Fe-C	3.11	562		
	16 Fe-C-N	3.39	344	-6.97	0.28
	4 Fe-C-N	3.56	886		
	1 Fe- \mathbf{Y}^d	4.00	404		
	4 Fe-O- \mathbf{Y}^d	4.10	/404		
	4 Fe-C-N	4.83	427		

 Table S1. EXAFS Least Squares Fitting Results

^{*a*}The estimated standard deviations for the distances are in the order of ± 0.02 Å. ^{*b*}The σ^2 values are multiplied by 10⁵. ^{*c*}Error is given by $\Sigma[(\chi_{obsd} - \chi_{calcd})^2 k^6] / \Sigma[(\chi_{obsd})^2 k^6]$. ^{*d*}/ indicates the σ^2 value for the path is linked to the preceding path. The S_0^2 factor was set at 0.95.

Complex	Mulliken Charge			Mayer Bond Order			
	Fe	O ₂	N^{a}	Sc/Y	Fe-O ^a	Fe-N ^a	0-0
1	0.67	-0.42	-0.26	-	0.95	0.32	0.84
2 -Sc	0.77	-0.63	-0.27	1.60	0.72	0.42	0.68
2- Y	0.74	-0.50	-0.27	1.25	0.75	0.43	0.70
Complex	Mulliken Population Fe(O ₂)						
	d _{xy} +O ₂		d _{yz}	d_z^2	d_x^2	2 y	$d_{xz}\!\!+\!\!O_2\pi^*_{\sigma}$
1	47.2(50.3)	^b 89.	1(6.0)	81.4(5.6)	80.2(0.8)	57.9(35.5)
2 -Sc	78.2(16.6)	^c 82.2	$(10.4)^{c}$	83.2(5.1)	67.1(0.6)	64.2(17.8)
2- Y	72.2(24.1)	^b 86.	7(4.9)	83.2(5.1)	68.2(0.6)	64.9(19.6)

Table S2. Selected DFT Parameters

^{*a*}Average O and N charges and bond orders. ^{*b*}A δ -bond between Fe(d_{xy}) and O₂. ^{*c*}The δ -bond is split into two π -type interaction between Fe and O₂ involving Fe(d_{xy})-O1 and Fe(d_{yz})-O2.

electron donor ^a	$\frac{E_{\text{ox}}}{(vs. \text{ SCE, V})^b}$ —	2 -Sc		2 -Y	
		$k_{\rm et},{\rm M}^{-1}{\rm s}^{-1}$	$\Delta G_{\rm et}$ [‡] , eV	$k_{\rm et},{\rm M}^{-1}{\rm s}^{-1}$	$\Delta G_{\rm et}^{\ \ddagger}$, eV
Me ₈ Fc	-0.04	С	С	$1.1(1) \times 10^{6}$	0.23
Me ₂ Fc	0.26	$2.5(2) \times 10^5$	0.26	$8.2(3) \times 10^2$	0.37
Fc	0.37	$1.6(1) \times 10^4$	0.31	5.8(3) × 10	0.43
BrFc	0.54	$4.0(3) \times 10^2$	0.39	$2.0(1) \times 10^{-1}$	0.54
AcFc	0.62	$2.0(2) \times 10$	0.45	d	d
Br ₂ Fc	0.71	1.2(1)	0.50	d	d

Table S3. Second-Order Rate Constants (k_{et}) and Activation Free Energies (ΔG_{et}^{\ddagger}) Determined in the Reactions of [(TMC)Fe^{III}(O₂)]–M³⁺, where M³⁺ = Sc³⁺ (**2**-Sc) and Y³⁺ (**2**-Y), and One-Electron Donors in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C

^{*a*}Abbreviations: Me₈Fc = octamethylferrocene, Me₂Fc = dimethylferrocene, Fc = ferrocene, BrFc = bromoferrocene, AcFc = acetylferrocene, and Br₂Fc = dibromoferrocene. ^{*b*}Taken from ref.: Park, J. *et al. J. Am. Chem. Soc.* **135**, 5052 (2013). ^{*c*}Too fast. ^{*d*}Too slow.



Figure S1. UV-vis spectral changes showing the formation of $[(TMC)Fe^{III}(O_2)]-Sc^{3+}$ (2-Sc) (**a**, blue) at 535 nm and $[(TMC)Fe^{III}(O_2)]-Y^{3+}$ (2-Y) (**b**, red) at 570 nm and the disappearance of $[(TMC)Fe^{III}(O_2)]^+$ (1) (black) at 850 nm by addition of Sc^{3+} (**a**) and Y^{3+} (**b**), respectively, to the solution of **1** (0.50 mM) in increments of 0.2 equiv. in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -20 °C (left panels). Right panels show the plots of absorbance versus equiv. of metal ions (i.e., Sc^{3+} (**a**, blue) and (Y^{3+} , (**b**, red)) added to the solution of **1** (black) in increments of 0.2 equiv.



Figure S2. X-band EPR spectra of 2-Sc and 2-Y in acetone/CF₃CH₂OH (v/v = 3:1) at 5 K. Spectral conditions: microwave power = 1.0 mW, frequency = 9.647 GHz, receive gain = 1.0×10^4 , modulation amplitude = 10 G, and modulation frequency = 100 kHz.



Figure S3. High resolution ESI MS spectrum of **2**-Sc obtained in the reaction of **1** (0.50 mM) with Sc³⁺ (1.5 mM) in acetone/CF₃CH₂OH (v/v = 3:1) at a spray gas temperature of – 40 °C and a dry gas temperature of –35 °C. Peak at m/z = 835.9966 corresponds to [Fe^{III}(TMC)(O₂)Sc^{III}(CF₃SO₃)₃]⁺ (calculated m/z = 835.9989). Inset shows the observed isotope distribution patterns for [Fe^{III}(TMC)(O₂)Sc^{III}(CF₃SO₃)₃]⁺.



Figure S4. High resolution ESI MS spectrum of **2**-Y obtained in the reaction of **1** (0.50 mM) with Y^{3+} (1.5 mM) in acetone/CF₃CH₂OH (v/v = 3:1) at a spray gas temperature of – 40 °C and a dry gas temperature of –35 °C. Peak at m/z = 879.9496 corresponds to $[Fe^{III}(TMC)(O_2)Y^{III}(CF_3SO_3)_3]^+$ (calculated m/z = 879.9489). Inset shows the observed isotope distribution patterns for $[Fe^{III}(TMC)(O_2)Y^{III}(CF_3SO_3)_3]^+$.



Figure S5. UV-vis spectral changes showing the disappearance of **2**-Y at 570 nm and the formation of $[(TMC)Fe^{IV}(O)]^{2+}$ (**4**) at 820 nm and Fc⁺ ion at 620 nm by addition of Fc (0.0 – 1.0 mM) into a solution of **2**-Y (0.50 mM) in increments of 0.2 equiv. in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C. Inset shows the spectroscopic titration at 820 nm for the formation of **4** as a function of the equiv. of Fc added to the solution of **2**-Y (0.50 mM) in increments of 0.2 equiv.



Figure S6. Plots of pseudo-first-order rate constants (k_{obs}) versus concentration of Fc derivatives to determine the second-order rate constants of electron transfer from Fc derivatives [Fc (**a**), BrFc (**b**), AcFc (**c**), and Br₂Fc (**d**)] to **2**-Sc (0.10 mM) in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C.



Figure S7. Plots of pseudo-first-order rate constant (k_{obs}) versus concentration of Fc derivatives to determine the second-order rate constants of electron transfer from Fc derivatives [Me₂Fc (**a**), Fc (**b**), and Br₂Fc (**c**)] to **2**-Y (0.10 mM) in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C. (**d**) Second-order plot of 1/[Me₈Fc] versus time for electron transfer from Me₈Fc (0.25 mM) to **2**-Y (0.25 mM).



Figure S8. Plot of pseudo-first-order rate constants (k_{obs}) versus concentration of Fc to determine the second-order rate constant of electron transfer from Fc (0 – 20 mM) to 4 (0.50 mM) in the presence of Sc³⁺ (0.50 mM) in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C.

Discussion on the comparison of 2-Sc and 2-Y with 4 in electron-transfer reactions. Although the $E_{\rm red}$ value of $[(\rm TMC)\rm Fe^{\rm IV}(O)]^{2+}$ (4) (0.39 V vs. SCE)^{*a*} is similar to that of 2-Sc (0.40 V vs. SCE) and much greater than that of 2-Y (0.16 V vs. SCE), the larger λ value of the electron-transfer reduction of $[(\rm TMC)\rm Fe^{\rm IV}(O)]^{2+}$ (2.37 eV)^{*a*} than those of 2-Sc and 2-Y (1.29 eV) resulted in no further reduction of $[(\rm TMC)\rm Fe^{\rm IV}(O)]^{2+}$ by Fc (0.37 V vs. SCE) in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C. In addition, the $k_{\rm et}$ value of $[(\rm TMC)\rm Fe^{\rm IV}(O)]^{2+}$ (4) (4.4 × 10⁻² M⁻¹ s⁻¹ at -40 °C, Fig. S9) is 3.6 × 10⁵ and 1.3 × 10³ times smaller than those of 2-Sc (1.6 × 10⁴ M⁻¹ s⁻¹ at -40 °C, Fig. S7a) and 2-Y (5.8 × 10 M⁻¹ s⁻¹ at -40 °C, Fig. S8b) in the reactions of Fc, respectively (^{*a*}see references: ref 45 in Text and Hong, S. *et al. Dalton Trans.* 42, 7842-7845 (2013)).



Figure S9. ESI MS spectrum of the reaction solution of **2**-Sc (0.50 mM) and Fc (0.50 mM) in CH₃CN/CF₃CH₂OH (v/v = 1:1) at -40 °C. The peak at m/z = 477.1 is assigned to [Fe^{IV}(O)(TMC)(CF₃SO₃)]⁺ (calculated m/z = 477.1). Peaks at m/z = 424.9, 465.9, 652.9, and 666.9 are assigned to [Sc^{III}(O)(CF₃CH₂OH)₂(CH₃CN)₄]⁺ (calculated m/z = 425.1), [Sc^{III}(O)(CF₃CH₂OH)₂(CH₃CN)₅]⁺ (calculated m/z = 466.1), [(Sc^{III}(O))₂(CF₃SO₃)-(CF₃CH₂OH)₃(CH₃CN)₂]⁺ (calculated m/z = 653.0), and [(Sc^{III}(O))₂(CF₃CH₂O)-(CF₃CH₂OH)₂(CH₃CN)₆]⁺ (calculated m/z = 667.1), respectively.