Ru-Fe Bimetallic Supramolecular Cage with D_4 Symmetry from Tetrapyridyl Iron(I) Metalloligand

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1. Synthesis

General Considerations Triethylamine was distilled from sodium hydroxide, and tetrahydrofuran (THF) was distilled from K(s)/benzophenone. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). All other reagents were purchased (Aldrich or Acros) and used without further purification. Diruthenium complex **2** was analogously synthesized according to the reported procedures.[1] NMR spectra were recorded on a Varian Unity instrument (300 MHz). The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Element analysis was performed in Atlantic Microlab (Norcross, GA). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system.

Preparation of Iron(I) Compound 1

4,4'-Dipyridylacetylene (200 mg, 1.1 mmol), Cp*Fe(CO)$_2$ (139.8 mg, 0.28 mmol), and xylene (20 mL) were charged to a 250 mL round bottom flask and heated under reflux for 48 h under an N_2 atmosphere. After the reaction, the solvent was evaporated. The solid was chromatographed on silica gel (eluent: CHCl$_3$/EtOH, 10:1). Then crude product was re-chromatographed on silica gel (CHCl$_3$/EtOH, 20:1) to give pure product. The product was recrystallized from chloroform and hexane. (yield = 23%) ESI-MS: m/z calcd for $C_{34}H_{31}FeN_4$ [M]$^+$: 551.19, found 551.20. IR (KBr-disk, cm^{-1}): 1588(s), 1413(w), 830(w). Anal. Calcd for $C_{34}H_{31}FeN_4 \cdot 1/3CHCl_3$): C, 69.74; H, 5.58; N, 9.37. Found: C, 69.74; H, 5.34; N, 9.48.

Preparation of Tetragonal Prism 3. Diruthenium complex **2** (4.1 mg, 7.26 μmmol), silver triflate (3.7 mg, 14.5 μmol), and iron compound **1** (2.0 mg, 3.65 μmol) were placed in a 5 mL vial, and a 0.4 mL acetonitrile-d_3 was added. The reaction mixture was stirred for 12 h in the dark at room temperature. Then, the mixture was filtered by membrane filter. Slow diffusion of diethyl ether into the solution at –20 °C produced cube-type orange crystals. (Yield = 95%). IR (KBr-disk, cm^{-1}) : 1635(s), 1588(m),

1260(s) ESI-MS: 2118.0 (calcd for $(M-2OTf)^{2+}$ 2115.9) 1361.6(calcd for $(-3OTf)^{3+}$ 1360.9). Anal. Calcd for $C_{178}H_{203}Fe_2N_{11}O_{42}Ru_8S_8(8\cdot3CH_3CN,2C_4H_{10}O)$: C, 44.33; H, 4.57; N, 3.12. Found: C, 44.53; H, 4.26; N, 3.21.

2. Cyclic Voltammetry

Cyclic voltammetry measurements were carried out for **1** (5×10^{-4} M in DMF) with a three-electrode cell configuration consisting of platinum working and counter electrodes and a $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode at room temperature. Tetra-*n*-butylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The redox potentials were recorded at a scan rate of 200 mV/s and are reported with reference to the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. The measurements were performed using an AUTOLAB/PGSTAT101 system.

3. X-ray Structure Determination

Reflection data for **1** and **3** were collected on a Bruker APEX-II CCD-based diffractometer with graphite-monochromated MoKα radiation (λ = 0.7107 Å). The hemisphere of reflection data were collected as ω scan frames with 0.5°/frame and an exposure time of 10 s/frame. Cell parameters were determined and refined by the SMART program.[2] Data reduction was performed using SAINT software.[3] The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.[4] The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms.[5] The crystals of **3** were diffracted very weakly due to the large amount of disordered solvents and anions. Geometrical restraints, i.e. DFIX, SADI, SIMU, and AFIX 66 on part of the hexagonal aromatic rings, were used in the refinements.

Note: Some A- and B-level alerts were found through the IUCR's CheckCIF routine for complex **3**, all of which originated from the limited diffraction ability of this kind of supramolecular compound in the crystal state.

4. References

1. Yan, H.; Su¨ss-Fink, G.; Neels A. and Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1997**, 4345.

2. SMART, version 5.0, Data collection software, Bruker AXS, Inc., Madison, WI, 1998.

3. SAINT, version 5.0, Data integration software, Bruker AXS Inc., Madison, WI, 1998.

4. Sheldrick, G. M. SADABS, Program for absorption correction with the Bruker SMART system, Universitat Gottingen, Germany, 1996.

5. Sheldrick, G. M. SHELXL-93: Program for the refinement of crystal structures; Universitat Gottingen: Germany, 1993.

Table S1. Crystallographic data and parameters for **1** and **3**

	1	3
formula	$C_{36}H_{33}Cl_6N_4Fe$	$C_{124}F_{24}Fe_2N_8O_{40}Ru_8S_8$
formula weight	790.21	3874.06
crystal system	Triclinic	Monoclinic
space group	P-1	$P2_1/c$
a (Å)	11.8102(4)	25.1459(6)
b (Å)	13.0820(4)	25.1199(6)
c (Å)	13.9126(4)	30.3639(8)
α (°)	95.332(2)	90
β (°)	95.332(2)	90.075(2)
γ (°)	103.045(2)	90
V (Å^3)	1865.31(10)	19179.7(8)
Z	2	4
ρ_{calc} (g cm^{-3})	1.407	1.342
μ (mm^{-1})	0.865	1.075
$F(000)$	810	7472
T (K)	100(2)	100(2)
scan mode	ω and ϕ	ω and ϕ
hkl range	-14<=h<=14, -16<=k<=16, -17<=l<=17	-19<=h<=19, -19<=k<=19, -23<=l<=22
measd reflns	30147	99662
unique reflns [R_{int}]	7568[0.315]	9249
reflns used for refinement	7568	9249
refined parameters	485	660
$R_1{}^a$ (I > 2σ(I))	0.0607	0.2263
$wR_2{}^b$ all data	0.1012	0.5499
GOF on F^2	1.002	2.217
ρ_{fin} (max/min) (e Å^{-3})	0.519 / -0.386	1.858 / -1.095

[a] R1 = $\Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] wR2 = $\{[\Sigma w(Fo^2 - Fc^2)^2]/[\Sigma w(Fo^2)^2]\}^{1/2}$.

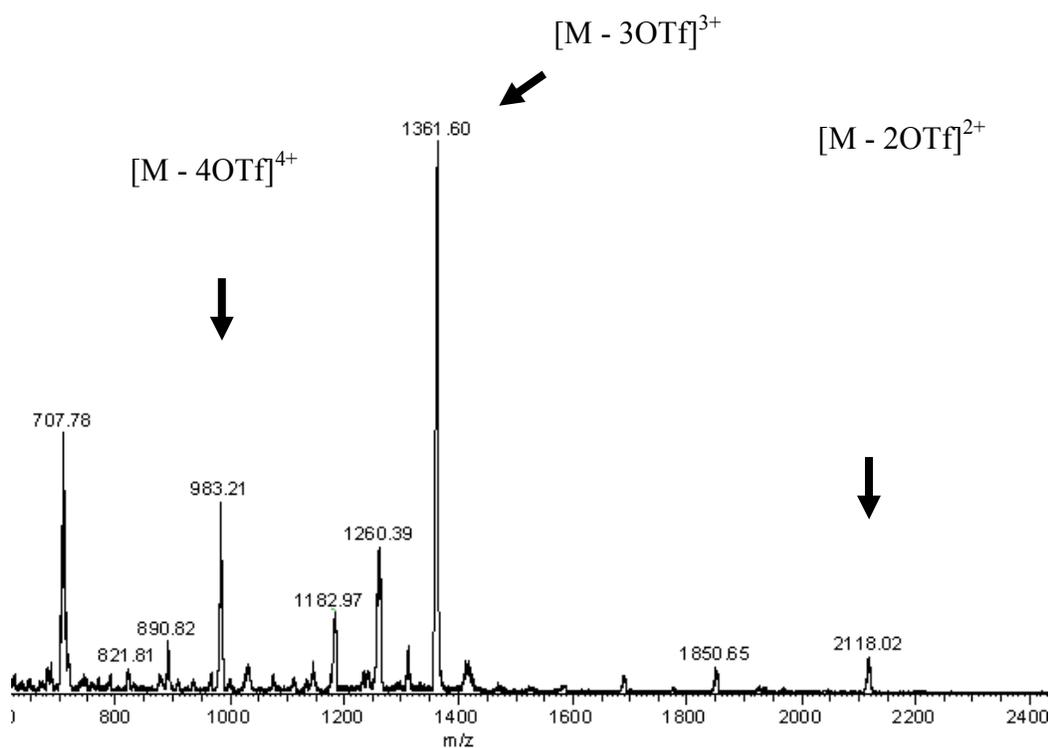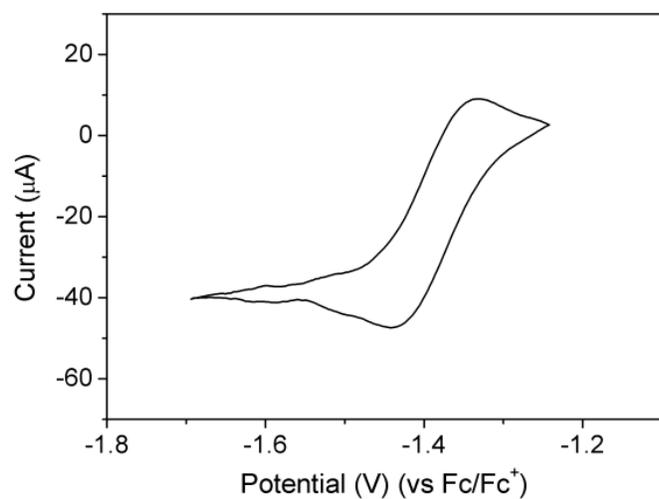**Fig. S1.** ESI mass spectrum of **3**.

Fig. S2. Cyclic voltammogram of **1** (in DMF, scan rate = 200 mV/s).