Supporting Information for:

Redox-induced switch between luminescent and magnetic properties in a trinuclear cyanide-bridged compound

Xiao-Quan Zhu, Shao-Dong Su, Yue-Hong Wen, Lin-Tao Zhang, Yu-Ying Yang, Xin-Tao Wu and Tian-Lu Sheng* Preparation of compounds and Physical Measurements All synthesizing manipulations are performed under a nitrogen atmosphere with the use of standard Schlenk techniques unless otherwise stated. The compounds *trans*-Ru(DMAP)₄(CN)₂, $trans-Ru(DMAP)_4(CN)_2(PF_6)^1$ (DMAP = 4-dimethylaminopyridine) and ligand PY5Me₂² (2.6-bis(1.1-bis(2-pyridyl)ethyl)pyridine) were prepared according to literature procedures. All other reagents were available commercially and used without further purification. Elemental analyses (C, H, N) was carried out on Vario MICRO elemental analyzer. Electrochemical measurements were performed using V3-Studio in CH₂Cl₂ solutions containing 0.1 M (Bu₄N)(PF₆) as a supporting electrolyte at a scan rate of 100 mV/s. Glassy graphite and platinum were used as working and counter electrodes, respectively, and the potentials were measured against a saturated Ag/AgCl reference electrode. Infrared (IR) spectra were recorded on a Vertex 70 FT-IR spectrophotometer with KBr pellet. UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer. Fluorescence spectra were measured on solid samples with a FLS920 spectrofluorimeter at room temperature. Magnetic susceptibilities on solid samples were measured with a Quantum Design MPMS-XL SQUID suscepto-meter under an applied magnetic field of 1 kOe in the 2-300 K range. Diamagnetic corrections were made using Pascal's constants.³ AC magnetic susceptibility measurements were performed on a Physical Property Measurement System (PPMS) PPMS-9 T with a 3 Oe AC oscillating field under zero DC field. The single crystal data for compounds 1-**R**, **1-O** and **2** were collected on a Saturn724 + CCD diffractometer equipped with

graphitemonochromatic Mo K α (λ = 0.71073 Å) radiation by using an ω -scan

model technique at 123 K. All the structures were solved using SHELXL-2014 and refined by the full-matrix least-squares techniques on F^2 with SHELXL-2014.⁴

Synthesis of *trans*-Ru(DMAP)₄(CN)₂[(PY5Me₂)Mn]₂[PF₆]₄ (1-R).

Mn(CF₃SO₃)₂ (353 mg, 1.0 mmol) was dissolved in 20 mL methanol, and ligand PY5Me₂ (443 mg, 1.0 mmol) was added. The solution was refluxed for 5 hours and then *trans*-Ru(DMAP)₄(CN)₂ (320.5 mg, 0.50 mmol) was added. After further refluxing for 12 hours, excess NH₄PF₆ and 5 mL water were added. After filtration, the yellow precipitate was dissolved in 15 mL acetonitrile. The solution was layered with diethyl ether and yellow-green crystals $1-R\cdot5CH_3CN\cdot2H_2O$ were obtained after one week. The pure crystals were collected after washed with methanol and diethyl ether (yield: 620.7 mg, 56%). Anal. Calc for RuMn₂C₈₈N₂₀H₉₀P₄F₂₄: C 47.64, H 4.09, N 12.63 %. Found: C 47.94, H 4.37, N 12.52 %. IR (v_{CN}, KBr pellet, cm⁻¹): 2014 (s).

Synthesis of *trans*-Ru(DMAP)₄(CN)₂[(PY5Me₂)Mn]₂[PF₆]₅ (1-O).

Compound *trans*-Ru(DMAP)₄(CN)₂[(PY5Me₂)Mn]₂[PF₆]₄ (**1-R**) (221.6 mg, 0.10 mmol) was dissolved in 5 mL CH₃CN and then Cp₂Fe(PF₆) (36.4 mg, 0.110 mmol) was added to the solution. The resulting blue solution was stirred for 30 min and then 60 mL diethyl ether was added. After precipitating out completely, the blue precipitate was filtered out and washed with diethyl ether. The solution of precipitate dissolved in CH₃CN was layered with diethyl ether and dark blue single crystals **1-O** for X-ray diffraction were formed after several days. Anal. Calc for RuMn₂C₉₀N₂₁H₉₉P₅F₃₀O₃: C 43.97, H 4.06, N 11.96 %. Found: C 43.38, H 4.05, N 11.98 %. IR (ν_{CN} , KBr pellet, cm⁻¹): 2100 (w), 2030(w).

Reduction of 1-O to 1-R

Compound *trans*-Ru(DMAP)₄(CN)₂[(PY5Me₂)Mn]₂[PF₆]₅ (**1-O**) (118.1 mg, 0.050 mmol) was dissolved in 5 mL CH₃CN and then Cp₂Co (10.4 mg, 0.055 mmol) was added to the solution. The resulting solution was kept warm at 60 °C, and the blue solution turn to green slowly. After about 20 min, the undissolved substance was filtered out, and diethyl ether was added to filtrate. After precipitating out completely, the yellow-green precipitate was filtered out and washed with diethyl ether. IR (v_{CN}, KBr pellet, cm⁻¹): 2015 (s).

	1-R·5CH ₃ CN·2H ₂ O	1-O·7CH ₃ CN
Empirical formula	$C_{98}H_{105}F_{24}Mn_2N_{25}O_2P_4Ru$	$C_{102}H_{111}F_{30}Mn_2N_{27}P_5$ Ru
Color and Habit	green Prism	blue Prism
Crystal Size (mm)	0.451×0.372×0.336	0.254×0.196×0.163
Temperature(K)	123(2)	123(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (A)	12.2621(8)	12.359(2)
b (A)	15.9092(16)	15.942(2)
c (A)	16.0561(14)	16.259(2)
alpha (deg.)	114.126(4)	65.653(3)
beta (deg.)	90.781(3)	88.991(5)
gamma (deg.)	93.483(4)	86.804(5)
Volume(A^3)	2850.8(4)	2913.8(8)
Ζ	1	1
Formula weight	2455.89	2650.98
Density(cal.)(Mg/m^3)	1.431	1.511
μ (MoK _{α} , mm ⁻¹)	0.502	0.516
F(000)	1254	1351
Theta range (deg.)	2.78 to 27.48	2.19 to 25.00
Reflections measured	29112	24723
	-15<=h<=15,	-14<=h<=14,
Index ranges	-20<=k<=20,	-18<=k<=18,
	-20<=1<=19	-19<=1<=19
Independent reflections	12882 ($R_{int} = 0.0479$)	10191 ($R_{int} = 0.0256$)
Relative Transmission Factor	0.7648 - 1.0000	0.9171 - 1.0000
Parameter/Restraints/Data(obs.)	727 / 33 / 7807	775 / 3 / 8830
Final R indices (obs.)	$R_1 = 0.0806,$	$R_1 = 0.0412,$
	$wR_2 = 0.2403$	$wR_2 = 0.1027$
R indices (all)	$R_1 = 0.1012,$	$R_1 = 0.0486,$
	$WR_2 = 0.2528$	$wR_2 = 0.1088$
Goodness-of-fit	1.005	1.040

Table S1. Crystallographic data for compounds 1-R and 1-O

 $R_1 = \Sigma(||F_0| - |F_c||) / \Sigma |F_0|;$

 $\mathbf{wR}_2 = [\mathbf{\Sigma}\mathbf{w}(|F_0^2| - |F_c^2|)^2 / \mathbf{\Sigma}\mathbf{w}|F_0^2|^2]^{1/2}$

	2		
Empirical formula	$C_{30}H_{40}F_6N_{10}PRu$		
Color and Habit	blue Prism		
Crystal Size (mm)	0.188×0.145×0.120		
Temperature(K)	123(2)		
Crystal system	Triclinic		
Space group	P^{1}		
a (A)	8.535(8)		
b (A)	9.567(9)		
c (A)	10.751(10)		
alpha (deg.)	91.663(19)		
beta (deg.)	90.941(14)		
gamma (deg.)	98.96(2)		
Volume(A^3)	866.5(14)		
Z	1		
Formula weight	786.76		
Density(cal.)(Mg/m^3)	1.508		
μ (MoK _{α} , mm ⁻¹)	0.568		
F(000)	F(000) 403		
Theta range (deg.)	2.16 to 27.36		
Reflections measured	12672		
Index ranges of measured data	-10<=h<=10, -12<=k<=12, -13<=l<=13		
Independent reflections	$3873 (R_{int} = 0.0789)$		
Relative Transmission Factor	0.8248 - 1.0000		
Parameter/Restraints/Data(obs.)	220 / 0 / 2715		
Final R indices (obs.)	$R_1 = 0.0510, wR_2 = 0.1151$		
R indices (all)	$R_1 = 0.0735, wR_2 = 0.1234$		
Goodness-of-fit	1.001		

 Table S2. Crystallographic data for compound 2

 $R_1 = \Sigma(||F_0| - |F_c||) / \Sigma |F_0|;$

 $\mathbf{wR}_2 = [\mathbf{\Sigma}\mathbf{w}(|F_0^2| - |F_c^2|)^2 / \mathbf{\Sigma}\mathbf{w}|F_0^2|^2]^{1/2}$

	1-R	1-0
Ru(1)-C(1)	2.024(6)	2.048(3)
Ru(1)-N(2)	2.110(5)	2.095(2)
Ru(1)-N(4)	2.123(4)	2.094(2)
Mn(1)-N(1)	2.136(4)	2.157(2)
Mn(1)-N(6)	2.220(5)	2.243(2)
Mn(1)-N(8)	2.222(5)	2.233(2)
Mn(1)-N(7)	2.227(5)	2.216(2)
Mn(1)-N(9)	2.231(5)	2.231(2)
Mn(1)-N(10)	2.275(4)	2.251(2)
N(1)-C(1)	1.167(7)	1.154(4)
C(1)-Ru(1)-C(1) ^{#1}	180.0(5)	180.0(3)
C(1)-N(1)-Mn(1)	164.5(4)	168.3(2)
N(1)-C(1)-Ru(1)	178.1(5)	178.7(2)

Table S3. Bond lengths (Å) and angles (deg.) for compounds 1-R and 1-O



Figure S1. Cyclic voltammogram of **1-R** in the CH_2Cl_2 solution of 0.1 M (Bu₄N)(PF₆) using a glassy carbon working electrode, 100 mV/s scan rate.



Figure S2. IR spectroscopic data of **1-R** (green), **1-O** (blue) and reduced product of **1-O** (orange). The strong absorption peak at 2014 cm⁻¹ of **1-R** is attributed to the stretching vibration of $C \equiv N$ bonding with Ru^{II}, and the weak absorption peak at 2030 and 2100 cm⁻¹ of **1-O** is attributed to the stretching vibration of $C \equiv N$ bonding with Ru^{III}.¹



Figure S3. Variable-temperature DC magnetic susceptibility data for compound trans-Ru^{III}(DMAP)₄(CN)₂(PF₆) (2).



Figure S4. Curie-Weiss fit of 1-O in 2-60 K range and its fitting parameters (top) and the curve of M vs. H for 1-O at 2 K (bottom).



Figure S5. Out-of-phase AC magnetic susceptibility vs. frequency for **1-O** under zero DC field from 2 to 5 K.



Figure S6. Fluorescence spectrum of ligand PY5Me₂ in solid state (left) and CH₂Cl₂ solution $(1 \times 10^{-5} \text{ mol/L})$ (right) at room temperature excited at 275 nm.



Figure S7. Fluorescence spectrum of solid sample *trans*-Ru(DMAP)₄(CN)₂ at room temperature excited at 275 nm.



Figure S8. Fluorescence spectrum of solid sample $(PY5Me_2)Mn(CH_3CN)(PF_6)_2$ at room temperature excited at 275 nm.

Peak Index	Energy (nm)	Osc. Strength	Major contribs	CI coef (>0.2)
3 822.35	822.35	0.1146	389β →395β	0.25099
			$393\beta \rightarrow 395\beta$	0.86386
			$394\beta \rightarrow 395\beta$	0.42086
4	782.96	0.0466	389β →395β	0.58924
			$393\beta \rightarrow 395\beta$	0.48165
			$394\beta \rightarrow 395\beta$	0.63623
5	777.64	0.2298	390β →395β	0.20960
			392β →395β	0.97111

Table S4. Composition of calculated transitions of $1-O^{5+}$ ion.



Figure S9. Molecular orbital diagrams of 1-O⁵⁺ ion

Peak Index	Energy (nm)	Osc. Strength	Major contribs
4	665.76	0.2064	$151\beta \rightarrow 153\beta$
5	649.85	0.2403	$149\beta \rightarrow 153\beta$

Table S5. Composition of calculated transitions of 2^+ ion.



Figure S10. Molecular orbital diagrams of 2⁺ ion



Figure S11. Structure of reference compound 2 (H-atoms, counterions and crystallization solvent omitted for clarity).



Figure S12. Absorption of 1-O (red) and emission spectra of 1-R (green) with the spectral overlap indicated in grey at room temperature. Due to the existence of strong double frequency peak of excitation light at about 550 nm, the emission spectra can only be shown below 540 nm.

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