Supporting Information

Charge-Transfer Complexes of Dinuclear Ruthenium Compounds/

Polyoxometalates for Multistate Electrochromism Covering Ultraviolet,

Visible, and Near-infrared Region

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Experimental Section

Materials.

cis-Ru(bpy)₂Cl₂·2H₂O was synthesized according to literature method.¹ Four types of POM structures different from the Keggin ones were prepared according to the literature method.²⁻⁴ *p*-Toluic acid, *p*-hydroxybenzoic acid, oxalyl chloride, methacryloyl chloride, ethyl benzoate, hydrazine hydrate, bromododecane, bromooctadecane, EDC·HCl, and DMAP were purchased from Alfa Aesar, Accela, Aladdin, Adamas-beta, J&K, InnoChem, or TCl Chemicals and used without further purification. Commercially available Keggin POMs (Sinopharm Chemical Reagent Co. Ltd), and tetra-*n*-butylammonium hexafluorophosphate (Bu₄NPF₆) (J&K Chemical) were used as received. Acetonitrile and dichloromethane were dried over CaH₂ or P₂O₅ and distilled. Dimethylformamide (DMF, Beijing Chemical Reagents Co., 99.5%) was purified by refluxing with CaH₂ under argon, followed by distillation under reduced pressure. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon or nitrogen.

Measurements.

¹H and ¹³C NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at ambient temperature with CDCl₃ or d_6 -DMSO as the solvent and tetramethylsilane (TMS) as an internal standard. Mass data were obtained with a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer. Elemental analyses were performed on an Elementar Vario EL instrument.

The UV-vis-NIR absorbance spectra were recorded on a Shimadzu UV 3600plus UVvis-NIR spectrophotometer. The solid diffuse reflectivity spectra were measured on UV 3600plus integrating-sphere accessory using $BaSO_4$ as a standard with 100% reflectance. An FLS920 Steady State Fluorescence Spectrometer (Edinburgh Instruments Ltd.) was used to measure the photoluminescence intensity. TEM images were obtained on a JEM-2100 (JEOL, Japan) transmission electron microscopy operated at 200 kV. The samples were prepared by drop-casting the sample solution onto a carbon-coated copper grid for a few minutes. Excess solution was blotted away with a strip of filter paper, and the sample grid was dried in air.

Infrared spectra of the samples in pressed KBr pellets were recorded on a Bruker Tensor27 spectrophotometer. Powder X-ray diffraction (XRD) experiments were carried out on a Philips X'Pert Pro instrument with a 3000 W ceramic tube as the X-ray source (Cu K α) and an X'celerator detector. The XPS studies were performed with an Axis Ultra (Kratos Analytical Ltd.) X-ray photoelectron spectrometer using monochromatic Al K α radiation (hv=1486.7 eV, 15 kV/40 mA). All XPS spectra were referred to the C 1s peak at 284.8 eV and spectral data were treated with the CasaXPS software after a Shirley background subtraction. For the analysis of work function and valence band of donor and acceptor molecules, ultraviolet photoelectron spectroscopy (UPS) measurements were performed using the He I (21.22 eV) excitation line.

Cyclic voltammetry measurements were collected on a CHI 840B electrochemical workstation (Shanghai Chenhua Instrument Corp., China), using glassy carbon electrode as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as reference electrode with nitrogen-purged 0.1 M Bu_4NPF_6 solution as a supporting electrolyte. All the electrochemical measurements were calibrated externally using a 5 mM solution of ferrocene (Fc/Fc⁺). The spectro-electrochemical experiments were measured on UV 3600plus UV-vis-NIR spectrophotometer and performed in an optical transparent thin layer (OTTLE) cell with platinum electrode against a silver pseudoreference electrode. The electrochemical spectra of sample solutions were measured with 0.1 M Bu_4NPF_6 in dry DMF as electrolytic solution, while that of the sample films prepared by casting sample solutions onto ITO substrates were measured with 0.1 mol/L LiCl in D₂O as electrolytic solution.

Electrical conductivity experiments were performed by DC two probe measurement using sample films spin-coated on SiO₂/Si substrates. Gold paste was utilized for electrodes and electrode distance was about 40 μ m. The current was monitored with an Agilent 4155C semiconductor characterization system and a Karl Suss (PM5) manual probe station, with a constant bias voltage ranging between -1 V and +1 V for 10 cycles.

1. Synthesis procedures

(1a) Synthesis of methyl ligand (MCH)



Benzoyl hydrazine (1.80 g, 13.2 mmol) and pyridine (1.2 mL, 14.5 mmol) was

dissolved in 20 mL anhydrous CH_2Cl_2 . Methacryloyl chloride (1.86 g, 12.0 mmol) in anhydrous CH_2Cl_2 was added dropwise to the flask at 0 °C under nitrogen atmosphere and stirred overnight at room temperature. After termination of the reaction with water, the mixture were washed successively with 0.2 M HCl, 0.2 M NaHCO₃, and brine. The white solid product (3.89 g, 78%) was afforded with silica gel using dichloromethane/ethyl acetate (15/1, V/V) as eluent.

¹H NMR (400 MHz, DMSO-*d₆*): δ 10.46 (d, 2H, NH-NH), 7.99-7.89 (m, 2H, ph-H), 7.84 (d, 2H, ph-H), 7.67-7.48 (m, 4H, ph-H), 7.34 (d, 2H, ph-H), 2.39 (s, 3H,-CH₃). ¹³C NMR (100 Hz, DMSO-*d₆*): δ 166.25, 142.32, 133.08, 132.31, 130.24, 129.51, 128.99, 127.93, 40.61, 40.40, 40.19, 39.98, 39.78, 39.36, 21.51. EI-HRMS calcd for C₁₅H₁₄N₂O₂: 255.11 for [M+H]⁺ Element analysis: Calcd: C,70.85;H,5.55;N,11.02; Found: C,70.69;H,5.48;N,10.95

(1b) Synthesis of dinuclear ruthenium donor with methyl ligand (MCH-Ru)



A solution of MCH (0.016 g, 0.064 mmol), *cis*-Ru(bpy)₂Cl₂·2H₂O (0.067 g, 0.13 mmol), and sodium carbonate(0.019 g, 0.18 mmol) in DMF (15 mL) was heated to reflux for 48h under argon. After cooling to room temperature, a solution of ammonium hexafluorophophate (1.0 g in 35 mL of water) was added. The red dark precipitate was filtered off and redissolved in acetone (20 mL). The ruthenium complex was then precipitated out with ether and dried under vacuum at room temperature (70% yield).

EI-HRMS (m/z) calcd for C₅₅H₄₄N₁₀O₂ Ru₂P₂F₁₂: 540.10 for [M-2PF₆]²⁺ Element analysis: Calcd: C, 48.25; H, 3.24; N, 10.23; Found: C, 47.99; H, 3.32; N, 9.96

(2a) Synthesis of dodecyl ligand (C₁₂DCH)



To a 250 mL round bottom flask containing above-prepared acid (4.65 mmol, 1.42 g), benzoyl hydrazine (5.58 mmol, 0.76 g) and $CH_2Cl_2(80 \text{ mL})$, DMAP (0.70 mmol, 0.85 g) and EDC-HCl (7.0 mmol,1.34 g) were added. The reaction mixture were stirred overnight at room temperature. The crude product was filtered off and washed with CH_2Cl_2 then purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/4, V/V) to yield 1.28 g of white solids (65% yield).

¹H NMR (400 MHz, DMSO-*d*₆): δ 10.39 (d, 2H,NH-NH), 7.91 (m, 4H, ph-H), 7.60 (t, H, ph-H), 7.52 (t, 2H, ph-H), 7.04 (d, 2H, ph-H), 4.04(t,2H,-OCH₂-), 1.73 (m, 2H,-CH₂-), 1.50-1.16 (m, 18H,-CH₂-), 0.86 (t, 3H,-CH₃).

¹³C NMR (100 Hz, DMSO-*d*₆): δ 166.36, 165.80, 161.96, 133.20, 132.31, 129.82, 128.96, 127.91, 125.00, 114.66, 68.19, 31.69, 29.52, 29.50, 29.48, 29.24, 29.19, 29.05, 25.95, 22.51, 14.43.

EI-HRMS calcd for $C_{26}H_{36}N_2O_3$: 425.28 for [M+H]⁺

Element analysis: Calcd: C, 73.55; H, 8.55; N, 6.60; Found: C, 73.44; H, 8.62; N, 6.56

(2b) Synthesis of dinuclear ruthenium donor with single dodecyl chains (C_{12} DCH-Ru). (Similar synthesis procedures with 1b)



EI-HRMS (m/z) calcd for $C_{66}H_{66}N_{10}O_3Ru_2P_2F_{12}$: 624.69 for $[M-2PF_6]^{2+}$, 837.34 for $[M-Ru(bpy)_2(PF_6)_2+H]^+$

Element analysis: Calcd: C, 51.50; H, 4.32; N, 9.10; Found: C, 51.54; H, 4.54; N, 8.96

(3a) Synthesis of octadecyl ligand (C₁₈DCH)

(Similar synthesis procedures with 2a)

$$OH \longrightarrow OH + Br \longrightarrow H^{17} \xrightarrow{KOH} C_{18}H_{37}O \longrightarrow OH$$

 $C_{18}H_{37}O \longrightarrow O H \xrightarrow{1. H_2SO4, ethanol} C_{18}H_{37}O \longrightarrow HN-NH_2$

$$C_{18}H_{37}O \longrightarrow O^{-} + O^{-}OC_{18}H_{37} \xrightarrow{EDC \cdot HCI} C_{18}H_{37}O \longrightarrow O^{-}OC_{18}H_{37}O \xrightarrow{EDC \cdot HCI} C_{18}H_{37}O \xrightarrow{HN-NH} O^{-}OC_{18}H_{37}O \xrightarrow{HN-NH} O^{-}OC_{18}O \xrightarrow{HN-NH} O^{-}OC_{18}O \xrightarrow{HN-NH} O^{-}OC_{18}O$$

¹H NMR (400 MHz, DMSO-*d*₆): δ 9.97 (s, 2H, NH-NH), 7.86 (d, 4H, ph-H), 6.99 (m, 4H, ph-H), 4.05(t, 4H,-OCH₂-), 1.73 (m, 4H,-CH₂-), 1.47-1.05 (m, 60H,-CH₂-), 0.86 (t, 6H,-CH₃).

¹³C NMR (100 Hz, DMSO-*d*₆): δ 161.26, 159.33, 128.83, 124.72, 113.70, 67.56, 30.66, 28.36, 28.32, 28.11, 28.00, 21.36, 13.07.

EI-HRMS (m/z) calcd for C₅₀H₈₄N₂O₄: 777.65 for [M+H]⁺, 799.63 for [M+Na]⁺ Element analysis: Calcd: C, 77.27; H, 10.89; N, 3.60; Found: C, 76.12; H, 10.78; N, 3.73

(3b) Synthesis of dinuclear ruthenium donor with symmetrical octadecyl chains (C₁₈DCH-Ru) (Similar synthesis procedures with 1b)



EI-HRMS (m/z) calcd for $C_{90}H_{114}N_{10}O_4Ru_2P_2F_{12}$: 801.36 for $[M-2PF_6]^{2+}$, 1189.67 for $[M-Ru(bpy)_2(PF_6)_2+H]^+$

Element analysis: Calcd: C, 57.13; H, 6.07; N, 7.40; Found: C, 57.10; H, 6.09; N, 7.37

(4) Synthesis of charge-transfer complexes

The charge-transfer complexes were prepared by a co-solvent method in acetonitrile. PMo_{12} (denotes $H_3PMo_{12}O_{40}$) solution was added dropwise to MCH-Ru acetonitrile solutions with vigorous stirring overnight. The initial molar ratios of MCH-

Ru against PMo_{12} were controlled at 3:2 for the complete replacement of the counterion H⁺. The mixture became turbid at the end of the reaction, which caused the obvious color change from purple to light brown. The brown solid product was separated by filtration, washed with acetonitrile and deionized water, and then dried in vacuum oven overnight at 40°C. Similar experiment operations for other POM-based charge-transfer complexes according to the charge stoichiometric ratio f=0.5.

2. Characterization data



Figure S1. Emission spectra of hybrid complex under excitation of 520 nm light at room temperature in different mixed-valence state.



Figure S2. Cyclic voltammograms of (a) C_{18} DCH-Ru and (c) PMo₁₂ in DMF at a scan rate of 50, 100, 200, 300, 400, 500 mV/s (with 0.1 M Bu₄NPF₆); absorption spectra of (b) C_{18} DCH-Ru in oxidation states and (d) PMo₁₂ in reduction states obtained in DMF using the OTTLE cell (with 0.1 M Bu₄NPF₆). Inset: photographs of C_{18} DCH-Ru or PMo₁₂ in different electrochromic state.



Figure S3. The XPS full spectra of MCH-Ru-PMO₁₂ complex deposited on Si substrates.



Figure S4. Ru 3d and Mo 3d/W 4f core levels of the XPS spectra of different chargetransfer complexes deposited on Si substrates. (a) MCH-Ru/PMo₁₂, (B) MCH-Ru/SiMo₁₂, (c) MCH-Ru/PW₁₂, (d) MCH-Ru/SiW₁₂, (e) C₁₂DCH-Ru/PMo₁₂, (f) C₁₈DCH-Ru/PMo₁₂.

Table S1. Comparison of molar contents of the mixed-valence species estimated from the XPS spectra of different charge-transfer complexes (M=Mo, W).

Donor	Acceptor	Ru ^{III} /(Ru ^{II} +Ru ^{III})	M [∨] /(M ^{∨I} +M [∨])	Possible structures
C ₁₈ DCH-Ru	PMo ₁₂	17.4%	5.5%	lamellar
C ₁₂ DCH-Ru	PMo ₁₂	9.8%	2.9%	cubic
MCH-Ru	PMo ₁₂	16.2%	4.8%	disordered
MCH-Ru	SiMo ₁₂	12.9%	4.4%	disordered
MCH-Ru	PW_{12}	9.3%	2.4%	disordered



Figure S5. UPS photoemission spectra of films consisting of (a) MCH-Ru, (b) PMo_{12} , (c) SiMo₁₂, (d) PW_{12} , (e) SiW₁₂, (f) Mo₆O₁₉, (g) P_2W_{18} , (h) P_5W_{30} , (i) P_8W_{48} spin-coated on Ag substrates.



Figure S6. Tauc's plot of the absorption spectra of (a) MCH-Ru, (b) PMo_{12} , (c) $SiMo_{12}$, (d) PW_{12} , (e) SiW_{12} , (f) Mo_6O_{19} , (g) P_2W_{18} , (h) P_5W_{30} , (i) P_8W_{48} for the determination of their optical bandgap (E_g) according to the Tauc's relation⁵: $ahv = B(hv - E_g)^n$, we adopt n=2 because of direct bandgap materials without the conservation of wavevectors.⁶



Figure S7. The possible layered structure model of interdigitated configuration proposed based XRD results.



Figure S8. I-V characteristics between -1 V and +1 V for 10 cycles at room temperature.



Figure S9. Multistate UV-vis-NIR electrochromism of the charge-transfer complex C_{18} DCH-Ru-PMo₁₂ with 0.1 M Bu₄NPF₆ in DMF at different oxidation-reduction states (0.6 V, 1600 nm; 1.2 V, 660 nm; -0.8 V, 920 nm) for repeated tests of the same sample.



Figure S10. Multistate UV-vis-NIR electrochromism of the charge-transfer complex C_{18} DCH-Ru-PMo₁₂ film with 0.1 M LiCl in D₂O at different oxidation-reduction states: (a) 0.6 V at Ru^{II}/Ru^{III} state; (b) 1.2 V at Ru^{III}/Ru^{III} state; (c) -0.8 V at Mo^{VI}/Mo^V state.

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