

## **Supplementary Information**

### **Multielectron-Transfer Reactions at Single Cu(II) Centers Embedded in Polyoxotungstates Driven by Photo-Induced Metal-to-Metal Charge Transfer from Anchored Ce(III) to Framework W(VI)**

Toshihiro Takashima,<sup>a</sup> Akira Yamaguchi,<sup>a</sup> Kazuhito Hashimoto,<sup>\*a,b</sup> and Ryuhei Nakamura<sup>\*a</sup>

<sup>a</sup> *Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo,  
Bunkyo-ku, Tokyo 113-8656, Japan*

<sup>b</sup> *ERATO/JST, HASHIMOTO Light Energy Conversion Project*

E-mail: nakamura@light.t.u-tokyo.ac.jp; hashimoto@light.t.u-tokyo.ac.jp

#### **Table of Contents**

1. Experimental
2. UV-vis absorption spectrum of Ce/PW<sub>12</sub>O<sub>40</sub>-MCM-41 (Fig. S1)
3. Change in UV-vis absorption spectrum of Ce/CuPW<sub>11</sub>O<sub>39</sub>-MCM-41 (Fig. S2)

## 1. Experimental

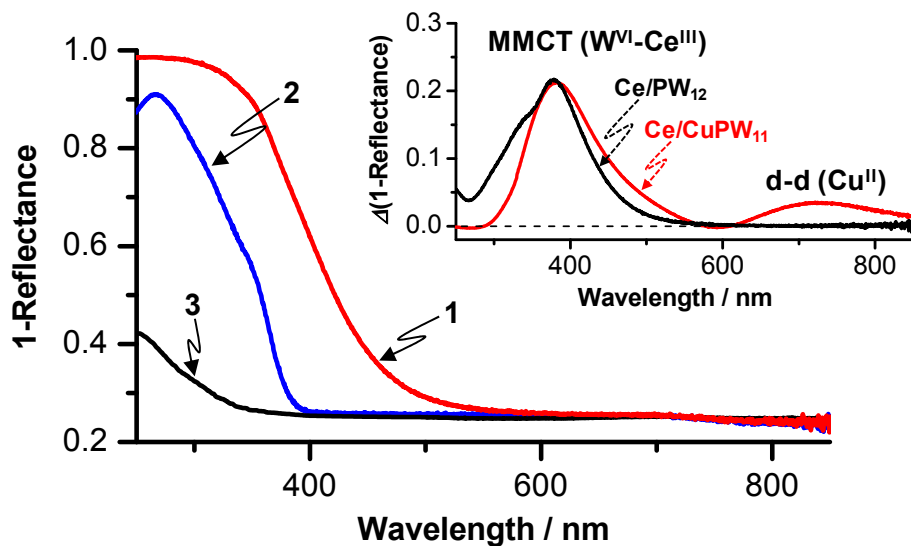
**Synthesis of MCM-41:** Siliceous MCM-41 sieve was prepared using the following hydrothermal method. Cetyltrimethylammonium bromide (2.2 g, CTABr, Wako) template was dissolved in 52 mL of water at 40 °C, followed by the dropwise addition of 26 mL of ammonium hydroxide (Aldrich, 30%) and 10 mL of TEOS (tetraethylorthosilicate, Aldrich). The reaction continued under stirring at room temperature for 4 h. The resultant cloudy solution was incubated at 110 °C inside a Teflon-lined steel autoclave for 3 days without stirring. The sample was recovered by filtration, washed, and dried at room temperature overnight. After calcination at 550 °C for 8 h in air, a white powder was obtained.

**Synthesis of  $K_5CuPW_{11}O_{39}$ :** Dodecatungstophosphoric acid ( $H_3PW_{12}O_{40}$ ) was purchased from Wako Pure Chemical Industries Ltd. and purified by recrystallization. A monovacant derivative,  $K_7PW_{11}O_{39}$ , was synthesized from  $H_3PW_{12}O_{40}$  using methods described in literature and purified by recrystallization using hot water.  $K_7PW_{11}O_{39}$  (7.35 g) was dissolved in 15 mL of water (pH 4.3) at 60 °C, followed by the dropwise addition of a 2.7 mM  $CuSO_4 \cdot 5H_2O$  (Wako) aqueous solution (3 mL). The reaction continued under stirring at 60 °C for 15 min. After filtering, the supernatant was subjected to slow evaporation giving pale blue block single crystals.

**Synthesis of  $Ce/CuPW_{11}O_{39}$ -MCM-41:**  $K_5CuPW_{11}O_{39}$  was immobilized on the pores of MCM-41 by mixing 280 mg of  $K_5CuPW_{11}O_{39}$  and 300 mg of MCM-41 in an aqueous solution (10 mL) at pH 1.0. After stirring for 3 h at room temperature, the suspension was dried at 60 °C and washed by dehydrated acetonitrile (Wako). Thus,  $CuPW_{11}O_{39}$ -MCM-41 was obtained. Subsequently, a trivalent cerium ion was anchored on the grafted  $CuPW_{11}O_{39}^{5-}$  center by a reaction with  $Ce(NO_3)_3 \cdot 6H_2O$  (Wako) in an anhydrous acetonitrile solution at 60 °C ( $Ce : CuPW_{11}O_{39} = 2 : 1$ ) for 12 h. The color of silica powder changed from pale blue to pale green. The resultant pale green suspension was filtered, washed, and dried under dynamic vacuum at room temperature for 12 h.,

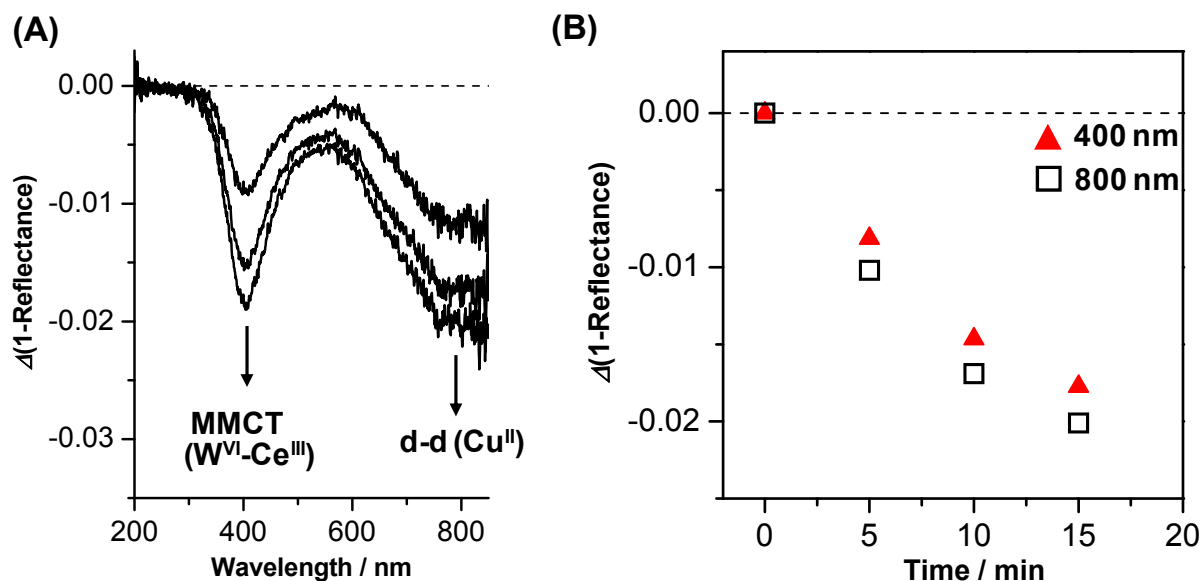
**Photochemical reaction:** The photochemical reaction was conducted at room temperature, using a 300-W Xe lamp (Asahi SPECTRA, MAX-301), equipped with an interference filter. Monochromatic light at 450 nm with a band width of 10 nm was used to irradiate the samples, where the light intensity was adjusted to  $1 \text{ mWcm}^{-2}$  with neutral density filters.  $Ce/CuPW_{11}O_{39}$ -MCM-41 powder (2 mg) was pressed into a self-supporting wafer (13 mm in diameter). The wafer was then mounted in a transmission infrared vacuum cell equipped with  $CaF_2$  windows. The IR intensity versus wavenumber was obtained by averaging 200 scans at a resolution of  $1 \text{ cm}^{-1}$  using an FTIR spectrometer (Vertex 70, Bruker).

## 2. UV-vis absorption spectrum of Ce/PW<sub>12</sub>O<sub>40</sub>-MCM-41



**Fig. S1** DR UV-vis spectra of pressed wafers of (1) Ce/PW<sub>12</sub>O<sub>40</sub>-MCM-41, (2) H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-MCM-41, (3) Ce-MCM-41. The difference spectra between (1) and (2) (black line), and between Ce/CuPW<sub>11</sub>O<sub>39</sub>-MCM-41 and CuPW<sub>11</sub>O<sub>39</sub>-MCM-41 (red line) are shown in the inset.

### 3. Change in UV-vis absorption spectrum of Ce/CuPW<sub>11</sub>O<sub>39</sub>-MCM-41



**Fig. S2** (A) Time course of the difference DR UV-vis spectrum for a pressed wafer of Ce/CuPW<sub>11</sub>O<sub>39</sub>-MCM-41 after monochromatic-light irradiation at 450 nm in the presence of CO (40 Torr) and N<sub>2</sub> (720 Torr). Spectra were recorded 5, 10, and 15 min after light irradiation. (B) Decrease in absorption intensities at 400 (▲) and 800 (□) nm, corresponding to MMCT (Ce<sup>III</sup> → W<sup>VI</sup>) transition and d-d (Cu<sup>II</sup>) transition, respectively, as a function of light irradiation time.