

Electronic Supplementary Information for

Water-soluble fulleranol-mediated electron transfer in

molecular systems toward enhanced solar hydrogen

production

Tongliang Liu,^{a,b,c} Fang Wang,^{a,b,c} Zhengguo Zhang,^{a,b,c} and Shixiong Min^{*a,b,c}

^a School of Chemistry and Chemical Engineering, North Minzu University, Yinchuan, 750021, P. R. China.

^b Ningxia Key Laboratory of Solar Chemical Conversion Technology, North Minzu University, Yinchuan 750021, P. R. China.

^c Key Laboratory of Chemical Engineering and Technology, State Ethnic Affairs Commission, North Minzu University, Yinchuan, 750021, P. R. China

*Corresponding authors: sxmin@nun.edu.cn

1. Experimental

1.1 Chemicals and materials

All chemicals were of analytical grade and used as received without further purification. C₆₀ (99.9%) was purchased from Shanghai Aladding Blochemical Technology Co., Ltd. Triethanolamine (TEOA, >99.8%) was purchased from Xilong Scientific. Erythrosin B (ErB, >97%) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Eosin Y (EY, >80%) was purchased from Tianjin Dingsheng Xin Chemical Co., Ltd. Pt(NO₃)₂ (98%), Co(NO₃)₂·6H₂O (99%), and Ni(NO₃)₂·6H₂O (98%) were purchased from Shanghai Titan Scientific Co., Ltd. NaOH was purchase by Tianjin Beilian Fine Chemicals Development Co., Ltd. H₂O₂ was purchase by Shanghai Guangnuo Chemical Technology Co., Ltd. Tetrabutylammonium hydroxide solution (TBAH) was purchase by Tianjin Kemio Chemical Reagent Co., Ltd. Methanol was purchased from Tianjin Dingshengxin Chemical Co., Ltd. Benzene was purchased from Yantai Shuangshuang Chemical Co., Ltd. Commercial Pt/C (20 wt.% Pt, average size of Pt: 3~5 nm) catalyst was purchased from Alfa Aesar (Shanghai, China). All solutions were prepared with ultrapure water (18.2 MΩ cm).

1.2 Preparation of C₆₀(OH)₂₄

C₆₀(OH)₂₄ was prepared from C₆₀ by oxidation with H₂O₂ in the presence of tetrabutylammonium hydroxide (TBAH) as the phase transfer catalyst according to the reported procedures.¹ Briefly, 50 mg of C₆₀ was first dissolved in 50 mL of benzene and stirred for 12 h. Then, 2 mL of 2 M NaOH solution and 2 mL of 40% tetrabutylammonium hydroxide (TBAH) solution were successively added to the above C₆₀ benzene solution followed by the addition of 0.5 mL of 30% H₂O₂ under various stirring. After a 24 h reaction, the formed two phases were separated. The organic phase was washed twice with 2-3 mL of water and combined with the aqueous phase. The

aqueous phase was filtered to obtain a homogenous $C_{60}(OH)_{24}$ solution. Finally, 20 mL of methanol was added to the above $C_{60}(OH)_{24}$ solution and the precipitated $C_{60}(OH)_{24}$ were separated by high-speed centrifugation and freeze-dried.

1.3 Characterizations

X-ray diffraction (XRD) measurements were performed on a Rigaku Smartlab diffractometer using a nickel filtrated Cu $K\alpha$ radiation source at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using a monochromatic Al $K\alpha$ X-ray source (1486.6 eV). The binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp^2 hybridized (C=C) carbon from the sample. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a FEI Talos F200x field emission transmission electron microscope. Photoluminescence (PL) spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. Fourier transform infrared spectroscopy (FTIR) spectra of the samples were collected by using a Thermo Nicolet Avatar 380 FT-IR spectrometer. UV-vis absorption spectra were taken with a Thermo Scientific Evolution 220 spectrophotometer.

1.4 Photocatalytic H_2 evolution experiments

Photocatalytic H_2 evolution experiments were performed in a sealed Pyrex reactor (315 mL) with a top flat quartz window (38.47 cm^2) for light irradiation and a silicone rubber septum was fixed on its side for sampling the produced H_2 . In a typical procedure, ErB, $C_{60}(OH)_{24}$, and a certain amount of aqueous solution containing metal salts ($Pt(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, or $Ni(NO_3)_2 \cdot 6H_2O$) were added to the reaction cell containing 100 mL of 10 vol.% TEOA (pH 8) under vigorous stirring (600 rpm). Upon mixing $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ with TEOA solution, the Co-, or Ni-TEOA

complexes ($[M(\text{TEOA})_2]^{2+}$, $M=\text{Co}$ and Ni) can be assembled *in situ* and serve as the H_2 evolution catalysts.²⁻⁶ Then, the reaction solution was thoroughly degassed by repeated evacuation- N_2 filling, and finally refilled with N_2 to reach ambient pressure. After that, the reaction solution was irradiated by a 30-W white LED lamp equipped with a 420 nm cut-off filter. During the reaction, the mixture solution was continuously stirred (300 rpm). The amount of H_2 produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column, and with N_2 as carrying gas.

The monochromatic apparent quantum efficiencies (AQEs) of the H_2 evolution were measured under conditions similar to those in the above photocatalytic reaction except that the light source was equipped with various band-pass filters (450, 475, 500, 520 and 550 nm). The photon flux of incident light was determined using a ray virtual radiation actinometer (Apogee MQ-500, a silicon ray detector, light spectrum, 389-692 nm; measurement range, 0-4000 $\mu\text{mol m}^{-2} \text{s}^{-1}$). The AQE was calculated from the ratio of the number of reacted electrons during H_2 evolution to the number of incident photons according to Equation (1) as follows:

$$\text{AQE (\%)} = \frac{2 \times \text{number of evolved } \text{H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100\% \quad (1)$$

1.5 UPS analysis

Ultraviolet photoelectron spectrum (UPS) of $\text{C}_{60}(\text{OH})_{24}$ was measured by Termo Scientific Escalab-250xi X-ray photoelectron spectrometer with Photon Energy of 21.2 eV (He I radiation). We estimated a work function (W) in the unit of eV (vs. vacuum) using Equation (2):

$$W = -h\nu + E_{\text{cutoff, high}} - E_F \quad (2)$$

where $h\nu$ is the energy of incident light (21.2 eV), $E_{\text{cutoff,high}}$ is the high-binding-energy cutoff, and E_F is the fermi level, which is set to be zero binding energy. A HOMO level was calculated according to Equation (3):

$$E_{HOMO} = W - (E_{\text{cutoff, low}} - E_F) \quad (3)$$

where $E_{\text{cutoff,low}}$ is the low-binding-energy cutoff. The unit conversion from eV (vs. vacuum) to V_{NHE} is in accordance with Equation (4):

$$E_{eV} = (-e) \times (E_{\text{NHE}} + 4.5 \text{ V}) \quad (4)$$

2. Additional data

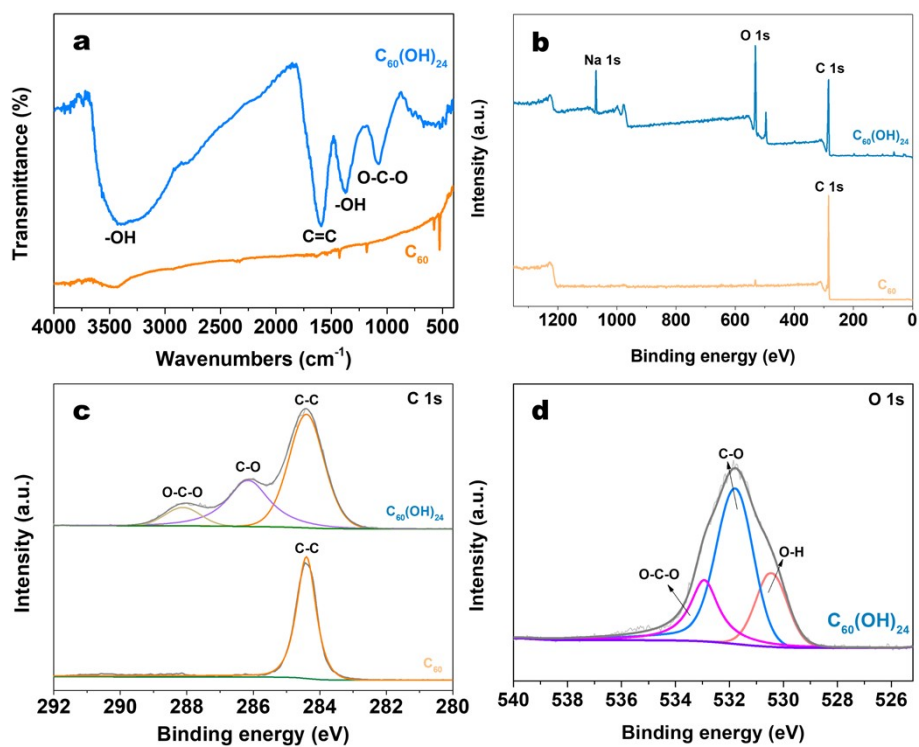


Fig. S1 (a) FTIR, (b) XPS survey, and (c) C 1s spectra of C_{60} and $C_{60}(OH)_{24}$. (d) O 1s

XPS spectrum of $C_{60}(OH)_{24}$.



Fig. S2 Photographs of as-prepared $C_{60}(OH)_{24}$ powder and its solution in water (0.5 $mg\ mL^{-1}$) showing no obvious Tyndall effect.

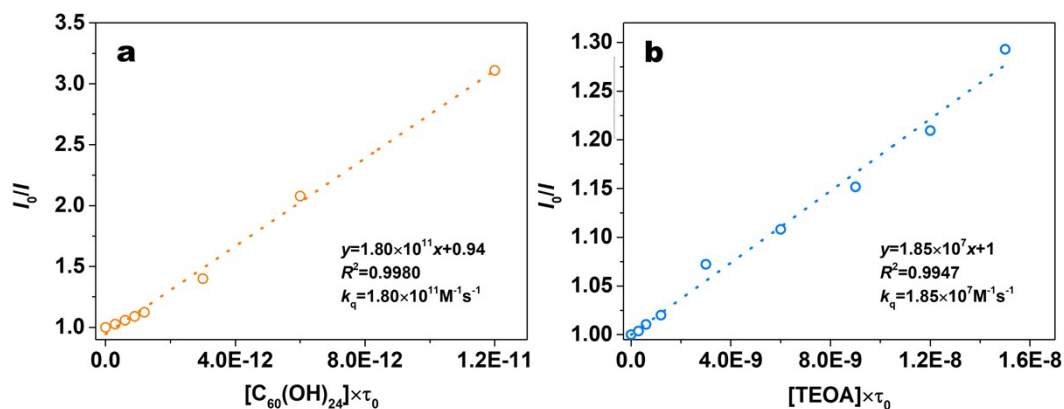


Fig. S3 Stern-Volmer plots for PL mission quenching of ErB solution (10 mM) with (a) $C_{60}(OH)_{24}$ and (b) TEOA ($\tau_{ErB}=0.15$ ns).

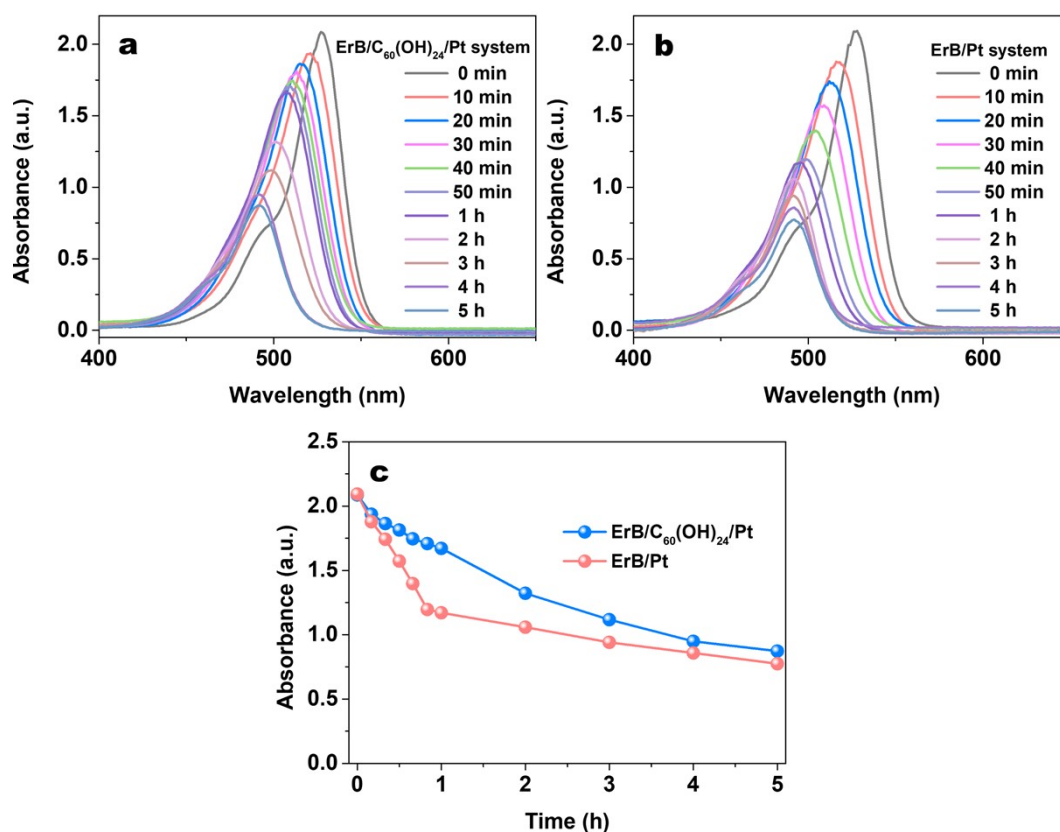


Fig. S4 UV-vis absorption spectra of (a) ErB/ $C_{60}(OH)_{24}$ /Pt and (b) ErB/Pt systems as a function of irradiation time. (c) The variation of the maximum absorbance of ErB in the ErB/ $C_{60}(OH)_{24}$ /Pt and ErB/Pt reaction systems with the time. Prior to measurements, the reaction solution was diluted by 10 times.

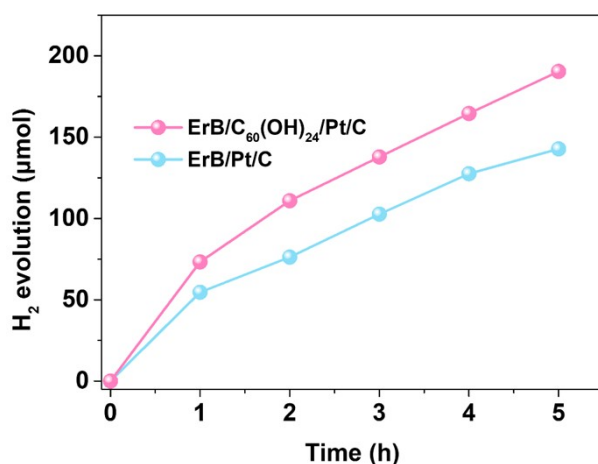


Fig. S5 Photocatalytic H₂ evolution from the ErB/C₆₀(OH)₂₄/Pt/C and ErB/Pt/C systems. Light source: 30-W white LED lamp, $\lambda \geq 420$ nm; TEOA: 10 vol%, 100 mL, pH 8; C₆₀(OH)₂₄: 5 mg; Pt/C: 0.1 mg.

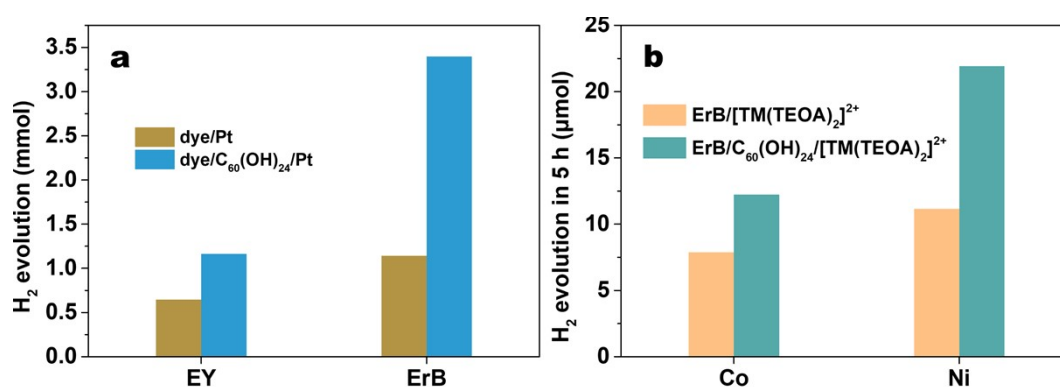


Fig. S6 (a) Photocatalytic H₂ evolution from the systems sensitized with different xanthene dyes (dye: 0.5 mM; Pt: 8 μM). (b) Photocatalytic H₂ evolution from the systems with different [TM(TEOA)₂]²⁺ complexes (ErB: 0.5 mM; TM: 8 μM). Light source: 30-W white LED lamp, $\lambda \geq 420$ nm; TEOA: 10 vol%, 100 mL, pH 8; C₆₀(OH)₂₄: 5 mg.

Supplementary references

1. T. Li, K. Huang, X. Li, H. Jiang, J. Li, X. Yan, J. Li and S. Zhao, *Chem. J. Chinese U.*, 1998, **19**, 858-860.
2. M. N. Hughes and K. J. Rutt, *J. Chem. Soc. A*, 1968, 2788-2790.
3. B. Sen and R. L. Dotson, *J. Inorg. Nucl. Chem.*, 1970, **19** **32**, 2707-2716.

4. J. Dong, M. Wang, X. Li, L. Chen, Y. He and L. Sun, *ChemSusChem* 2012, **5**, 2133-2138.
5. F. Niu, S. Shen and L. Guo, *J. Catal.*, 2016, **344**, 141-147.
6. A. Lê, D. Floner, T. Roisnel, O. Cador, L. Chancelier and F. Geneste, *Electrochim. Acta*, 2019, **301**, 472-477.