Supporting Information

A Photoactive Basket-like Metal-organic Tetragon Worked as an Enzymatic Molecular Flask for Light Driven H₂ Production

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1. Materials and Methods.

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. $^1$H NMR spectra were measured on a Varian INOVA 400 M spectrometer. Fourier–transform infrared (FT–IR) spectra were recorded as KBr pellets on a JASCO FT/IR–430 instrument. ESI mass spectra were carried out on a HPLC–Q–ToF MS spectrometer using methanol as mobile phase. Uv–vis spectra were measured on a HP 8453 spectrometer.

The solution fluorescent spectra were measured on JASCO FP–6500. Both excitation and emission slit widths were 2 nm. The solution of Ce–ZL was prepared in DMF, and the concentration was 1.0 mM. And stock solutions of model compound 1 and ATP (1.0 × 10$^{-3}$ M) were prepared in DMF and DMF/H$_2$O=1/1 solvents, respectively. Excitation at 335 nm.

All electrochemical measurements were carried under nitrogen at room temperature. Performed on a CHI 1130 (CH Instrument Co., Shanghai) electrochemical analyzer with a conventional three-electrode system with a homemade Ag/AgCl electrode as a reference electrode, a platinum silk with 0.5 mM diameter as a counter electrode, and glassy carbon electrode as a working electrode. All the results were choosing Fc/Fc$^+$ as standard. Cyclic voltamograms with the solution concentrations were ca. 1.0 mM for the Ce–ZL and 0.1 M for the supporting electrolyte, (n-Bu$_4$N)ClO$_4$. Electrodes were polished on a MD–Nap polishing pad.

**General Procedure for Hydrogen Production** For photoinduced hydrogen evolution, each sample was made in a 10 mL flask with a volume of 5 mL in MeCN/DMF/water (8:1:1 v/v). Typically, the sample contained 0.2 mM Ce–ZL, 0.4 mM model compound 1, and 2 mM NPr$_2$EtH·OAc as the sacrificial electron donor. The flask was sealed with a septum and protected from light, then degassed by bubbling nitrogen for 15 min under atmospheric pressure at room temperature. After that, the samples were irradiated by a 500 W Xenon lamp, the reaction temperature was 293 K by using a water filter to absorb heat. The generated photoproduct of H$_2$ was characterized by GC 7890T instrument analysis using a 5 Å molecular sieve column (0.6 m × 3 mm), thermal conductivity detector, and nitrogen used as carrier gas. The amount of hydrogen generated was determined by the external standard method. Hydrogen in the resulting solution was not measured and the slight effect of the hydrogen gas generated on the pressure of the flask was neglected for calculation of the volume of hydrogen gas. (*Dalton Trans.*, 2010, 39, 1204 – 1206; *J. Phys. Chem. C* 2011, 115, 15089 – 15096)
1.2 Preparation

9-Butylcarbazole\textsuperscript{S1}: Carbazole (6 g, 0.036 mol), benzyltriethylammonium chloride (BTEAC, 0.2 g), and 1-bromobutane were dissolved in benzene (20 mL), then NaOH aqueous (50%, 10 mL) was added, the obtained mixture was stirred and refluxed for 3 h. Then the solvent benzene was removed under the reduced pressure, and water (200 mL) was added to the flask and a white solid formed. The white solid was collected by filtration and washed with water. The solid was recrystallized from a mixture of ethanol and water and gave white needle crystals. Yield: 6.4 g, 80%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): 0.95 (t, 3H, CH\textsubscript{3}), 1.39 (m, 2H, CH\textsubscript{2}), 1.86 (m, 2H, CH\textsubscript{2}), 4.31 (t, 2H, NCH\textsubscript{2}), 7.19–7.48 (m, 6H, ArH), 8.00 (d, 2H, ArH).

9-Butyl-3,6-diformylcarbazole: A solution of N,N-dimethylformamide (12.5 g, 0.17 mol) in 1,2-dichloroethane (10 mL) was added dropwise to phosphoryl chloride (21.9 g, 0.145 mol) at 0 °C. Then the reaction mixture was heated to 35 °C, and 9-butylcarbazole (2.23 g, 0.01 mol) was added. After being stirred for 48 h at 90 °C, the mixture was poured into water (200 mL), extracted with chloroform, and the organic layer was washed with water, dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane, 1:3 as an eluent). Yield: 0.98 g, 35%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): 0.96 (t, 3H, CH\textsubscript{3}), 1.39–1.92 (m, 4H, CH\textsubscript{2}), 1.86 (m, 2H, CH\textsubscript{2}), 4.31 (t, 2H, NCH\textsubscript{2}), 7.55 (d, 2H, ArH), 8.08 (d, 2H, ArH), 8.67 (s, 2H, ArH), 10.13 (s, 2H, CHO).

9-Butyl-3,6-dicarboxycarbazole: A solution of KMnO\textsubscript{4} (4.0 g, 25 mmol) in water (30 mL) was added dropwise to the 9-Butyl-3,6-diformylcarbazole (2.8 g, 10 mmol) in acetone (30 mL). The reaction mixture was stirred over 12 h at room temperature. Then the solid was collected by filtration and washed with water. Yield: 2.65 g, 85%. \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz, ppm): 0.88 (t,
3H, CH₃), 1.28 – 1.80 (m, 4H, CH₂), 4.49 (t, 2H, NCH₂), 7.76 (d, 2H, ArH), 8.11 (d, 2H, ArH), 8.88 (s, 2H, ArH), 12.73 (s, 2H, COOH).

**9-Butyl-3,6-dimethoxycarbonylcarbazole:** 9-butyl-3,6-dicarboxycarbazole (3.1 g, 10 mmol) was refluxed for 4 h in methanol (20 mL) in the presence of a catalytic amount of concentrated H₂SO₄. Solvent was evaporated, and the residue was dissolved in water, neutralized with a saturated solution of sodium bicarbonate, and then extracted with ethyl acetate to the desired compound as the solid. Yield: 3.15 g, 93%. ¹H NMR (CDCl₃, 400 MHz, ppm): 0.96 (t, 3H, CH₃), 1.37–1.89 (m, 4H, CH₂), 3.99 (s, 6H, COOCH₃), 4.34 (t, 2H, NCH₂), 7.43 (d, 2H, ArH), 8.21 (d, 2H, ArH), 8.86 (s, 2H, ArH).

**9-Butyl-3,6-dicarbohydrazidecarbazole:** A mixture solution of 80% hydrazine hydrate (2.5 g, 40 mmol) and 9-Butyl-3,6-dimethoxycarbonylcarbazole (3.4 g, 10 mmol) in methanol (30 mL) was stirred over 12 h at 85°C. The precipitate was collected by filtration, washed with methanol and dried in vacuum. Yield: 2.2 g, 65%. ¹H NMR (DMSO-d₆, 400 MHz, ppm): 0.87 (t, 3H, CH₃), 1.26–1.78 (m, 4H, CH₂), 4.45 (t, 2H, NCH₂), 4.60 (s, 4H, NH₂), 7.70 (d, 2H, ArH), 8.00 (d, 2H, ArH), 8.72 (s, 2H, ArH), 9.75 (s, 2H, CONH).

**H₄ZL:** 9-Butyl-3,6-dicarbohydrazidecarbazole (1 mmol, 0.34 g) was added to a methanol solution (50 mL) containing salicylaldehyde (2.2 mmol, 0.27 g). After 5 drops of acetic acid was added, the mixture was refluxed for 24 h. The white solid was collected by filtration, washed by methanol and dried on vacuum. Yield: 0.45 g, 83%. Anal calc. for C₃₂H₂₉N₅O₄: C 67.19, H 4.56, N 11.19%. Found: C 67.01, H 4.67, N 10.89%. ¹H NMR (DMSO-d₆, ppm): 0.90 (t, 3H, H₁₂), 1.30–1.83 (m, 4H, H₁₀,₁₁), 4.54 (t, 2H, H₉), 6.95(m, 4H, H₂₃), 7.32(t; 2H, H₁), 7.58(d, 2H, H₄), 7.85(d, 2H, H₇), 8.16(d, 2H, H₈), 8.70(s, 2H, H₆), 8.92(s, 2H, H₅), 11.41(s, 2H, ArOH), 12.19(s, 2H, CONH).

**Ce-ZL:** A solution of Ce(NO₃)₃·6H₂O (17.4 mg, 0.04 mmol), H₄ZL (21.9 mg, 0.03 mmol) and KOH (3.4 mg, 0.06 mmol) in CH₃OH/DMF (v:v = 1:7, 8 mL) was stirred for 2 h. X-ray quality black block crystals were obtained after the solution left for two weeks at room temperature and dried in vacuum. Anal calc. For Ce₄(C₁₉₂H₁₆₀N₃₀O₂₄)(NO₃)₂: H 4.08, C 58.29, N 11.33%. Found: H 4.46, C 57.64, N 11.88%. Yield: 52%.
2. Crystallography:

Intensities of the complexes were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares methods with SHELXTL version 5.1.

Crystal data of Ce-ZL: C_{222}H_{238}Ce_{4}N_{42}O_{44}, M = 4759.02, Monoclinic, space group C2/c, black block, a = 37.452(7) Å, b = 21.717(4) Å, c = 35.226(7) Å, β = 105.94(1)°, V = 27549(9) Å³, Z = 4, $D_c = 1.147$ g cm$^{-3}$, μ(Mo-Kα) = 0.717 mm$^{-1}$, $T = 293(2)$ K. 24206 unique reflections [$R_{int} = 0.0932$]. Final $R_I$ [with $I > 2σ(I)$] = 0.0838, $wR_2$ (all data) = 0.2211 for $2θ = 50°$.

In the structural refinement of Ce–ZL, except the solvent water molecules, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms, whereas no hydrogen atoms corresponding to the solvent molecules were added and refined. The carbazole moiety in one ligand were disordered into two parts with the s.o.f of each part being fixed at 0.5, respectively. SQUEEZE was used with the number being 2. To assist the stability of refinements, several restraints were applied: (1) For several benzene rings in the ligands and several solvent DMF molecules, the geometrical constraints of idealized regular polygons were used; (2) For several benzene rings and butyl moieties in the ligands, as well as the solvent DMF molecules, thermal parameters on adjacent atoms in the solvent molecules were restrained to be similar.
3. **Figure S1** XPS spectrum of Ce 3d from surface and near surface region of Ce–ZL.
4. Figure S2 Normalized absorption (red line) and emission spectrum (black line) of Ce–ZL, excitation at 335 nm.
5. **Figure S3.1** ESI-MS spectra of Ce–ZL (30 μM) in DMF/CH₃OH solution in present of KOH (0.1 mM), the peak 1914.78 and 1934.25 are assigned to the species [Ce₄(HZL₃)(H₂ZL)₃]²⁻ and [Ce₄(HZL₄)(H₂ZL)₂K]²⁻.

**Figure S3.2** ESI-MS spectra of Ce–ZL upon the addition of 2 equiv of model compound 1 in DMF/CH₃OH in present of KOH (0.1 mM).
6. Figure S4 Comparison of the ν(CO) IR spectra of model compound 1 in the absence (bottom) and presence (top) of 0.5 equivalents of Ce–ZL.
7. **Figure S5** Luminescence responses of Ce–ZI (30 μM) upon addition of ATP (0.40 mM) interested. Excitation at 335 nm.
8. **Figure S6** DPV plots of 1.0 mM Ce–ZL in DMF solution containing n-Bu₄NClO₄ (0.1 mol L⁻¹) with the scan rate of 100 mVs⁻¹.
9. **Figure S7** Control photochemical reduction of protons catalyzed experimental for ATP inhibiting system by model compound 1 (14 μM) and [Ru(bpy)_3]Cl_2 (bpy=bipyridine) (140 μM) serves as a photosensitizer and ascorbic acid (100 mM) serves as a proton and sacrificial electron donor for homogeneous photochemical proton reduction in 1:1 H_2O/DMF at pH = 5.5. (*Chem. Eur. J.* 2010, **16**, 60-63)