

Supporting Information

Highly Efficient Photocatalytic Hydrogen Production from Pure Water via Photoactive Metal-organic Framework and Its PDMS@MOFs

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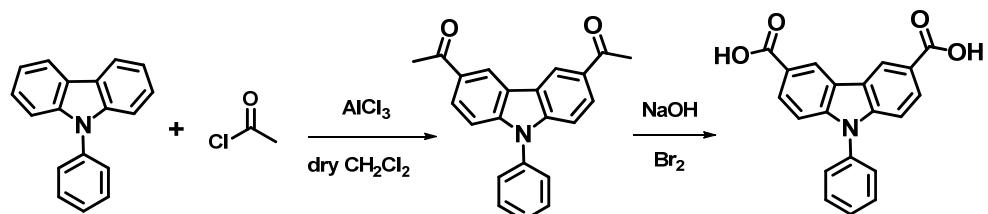
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1. Materials and Methods.

Reagents and chemicals: All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Tris(bipyridine)Cobalt was synthesized according to the published procedure.^{S1} 9-Phenylcarbazole was purchased from Qingdao Frontierchem Co., Ltd..

Instruments and spectroscopic measurements: The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. ¹H NMR spectra were measured on a Bruker-400 spectrometer with Me₄Si as an internal standard. X-Ray powder diffraction (XRD) patterns of the Zn-PDA2 was recorded on a Rigaku D/max-2400 X-ray powder diffractometer (Japan) using Cu-K α ($\lambda = 1.5405 \text{ \AA}$) radiation. Thermogravimetric analysis (TGA) was carried out at a ramp rate of 5 °C/min in a nitrogen flow with a Mettler-Toledo TGA/SDTA851 instrument. FT-IR spectra were recorded as KBr pellets on Bruker Optics TENSOR 27 FT-IR spectrophotometer. The Zn²⁺ content before and after catalytic were measured by Inductively Coupled Plasma Spectrometer (Perkin Elmer). Solid Uv-vis spectra were recorded on a HP 8453 spectrometer. The solution fluorescent spectra were measured on Hitachi F-4600. Both excitation and emission slit widths were 2.5 nm, and fluorescence measurements were carried out in a 1 cm quartzcuvette with stirring the suspension of Zn-PDA2. Solid-state voltammograms were measured by using a carbon-paste working electrode, a well-ground mixture of each bulk sample and carbon paste (graphite and mineral oil) was set in the channel of a glass tube and connected to a copper wire. A platinum-wire with 0.5 mm diameter counter electrode and Ag/AgCl reference electrode were used. Measurements were performed by using a three-electrode system in phosphate-buffered saline [PBS] at a scan rate of 50 mV s⁻¹, in the range 0.8–1.4 V.

Synthesis of the H₂PDA ligand.



(a) Synthesis of 3,6-diacetyl 9-phenylcarbazole.

To the solution of 9-phenylcarbazole (2.0 g, 8.2 mmol) and 2.4 g (18.0 mmol) AlCl₃ in 100 mL dry CH₂Cl₂, 2.7 mL (28.28 mmol) acetyl chloride in 30 mL dry CH₂Cl₂ was added dropwisely. Then the reaction was carried out at room temperature for 12 hours and 100 mL water was added. The aqueous layer was further extracted with CH₂Cl₂ (3 × 150 mL); the combined organic layers were dried by Na₂SO₄. The solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (1: 10 hexanes–CH₂Cl₂) to afford a yellow solid (1.46 g, 54.3%). ¹H NMR (CDCl₃, ppm): δ 9.16 (s, 2H_{Ar}), 8.08 (d, J = 8.0 Hz, 2H_{Ar}), 7.73 (d, J = 8.0 Hz, 2H_{Ar}), 7.67-7.61 (m, 3H_{Ar}), 7.42 (d, J = 8.0 Hz, 2H_{Ar}), 2.72 (s, 6H_{COCH₃}).

(b) Synthesis of 9-phenylcarbazole-3,6-dicarboxylic acid.^{S2}

3 mL Br₂ were added dropwisely to the solution of NaOH (7 g, 0.18 mol) in 30 mL water on ice-bath, and further stirred for 20 min. The solution were dumpage to a isobarically funnel and were added dropwisely to a solution of 3,6-diacetyl 9-phenylcarbazole (1.2 g, 3.6 mmol) in 30 mL 1,4-Dioxane on 45 °C during 5 h. Then the mixture was put on ice-bath, saturated hydroxylamine HCl was added to deoxidize excessive sub-bromo-sodium. The solution was acidified by muriatic acid and the solid product was filtered and dried under vacuum. The crude was recrystallized from acetic acid to afford pure products as a white solid. (1.0 g, 84.5 %). ¹H NMR (DMSO-*d*₆, ppm): δ 12.84 (s, 2H_{COOH}), 9.0 (s, 2H_{Ar}), 8.10 (d, J = 8.0 Hz, 2H_{Ar}), 7.76-7.63 (m, 5H_{Ar}), 7.44 (d, J = 8.0 Hz, 2H_{Ar}). ¹³C NMR (DMSO-*d*₆, ppm): δ 167.7 (C_{COOH}), 143.5 (C_{Ar}), 135.9 (C_{Ar}), 130.5 (C_{Ar}), 128.7 (C_{Ar}), 128.3 (C_{Ar}), 127.1 (C_{Ar}), 123.6 (C_{Ar}), 123.0 (C_{Ar}), 122.5 (C_{Ar}), 109.9 (C_{Ar}). Anal calc. for C₂₀H₁₃NO₄: C 72.50, H 3.95, N 4.23%; Found: C 72.52, H 3.94, N 4.22%. TOF MS calcd for C₂₀H₁₃NO₄ 331.32, found 331.41.

Synthesis of Zn-PDA2: A mixture of 9-phenylcarbazole-3,6-dicarboxylic acid (H₂PDA) (17 mg, 27 mM), Zn(NO₃)₂·6H₂O (75 mg, 125 mM) and 15 μL TEA were dissolved in dimethylacetamide/water (9/1, 5 mL) in a screw capped vial. The resulting mixture was placed in an oven at 120 °C for 3 days. Colorless

crystals with block-shape were obtained after filtration. Yield: 80%. Anal calc. for C₇₂H₆₀N₆O₂₀Zn₄: C 54.36, H 3.80, N 5.28%; Found: C 54.25, H 3.86, N 5.24%.

Polydimethylsiloxane (PDMS) coating of Zn-PDA2: The PDMS coating of the Zn-PDA2 was carried out by a simple vapor deposition technique.^{S3} Typically, a certain amount of Zn-PDA2 powder (spreading to layer as thin as possible) was flat on glass dish, which was placed in a sealed glass container with some fresh PDMS stamp. The glass container was maintained at 235 °C for 6 h in a oven and then allowed to cool to room temperature naturally to give PDMS-coated Zn-PDA2.

Photo-induced Hydrogen Production: For photo induced hydrogen evolution, each sample was made in a 10 mL flask with a volume of 5 mL in water. Typically, the sample contained 0.34 μM Zn-PDA2, 0.34 mM [Co(bpy)₃]Cl₂, and 5% (v/v) TEA as the sacrificial electron donor. The flask was sealed with a septum and protected from light, then degassed by bubbling nitrogen for 25 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 H₂ 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.^{S4,S5}

2. X-ray Crystallography (Single-crystal diffraction) and Characterizations of Zn-PDA2.

2.1 Crystal data of Zn-PDA2:

$C_{72}H_{60}N_6O_{20}Zn_4$, Mr = 1590.74, Monoclinic, space group $P2(1)/n$, $a = 14.7811(5)$, $b = 38.2896(13)$, $c = 16.6609(6)$ Å, $\alpha = 90.00$, $\beta = 94.001(2)$, $\gamma = 90.00$, $V = 9406.5(6)$ Å³, $Z = 4$, $D_c = 1.066$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.123$ mm⁻¹, $T = 296(2)$ K. 16565 unique reflections [$R_{\text{int}} = 0.0967$]. Final R_I [with $I > 2\sigma(I)$] = 0.0733, wR_2 (all data) = 0.2288, GOOF = 0.963. CCDC number: 1527602.

2.2 Crystallography:

Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphitemonochromated Mo-K α ($\lambda = 0.71073$ Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms.

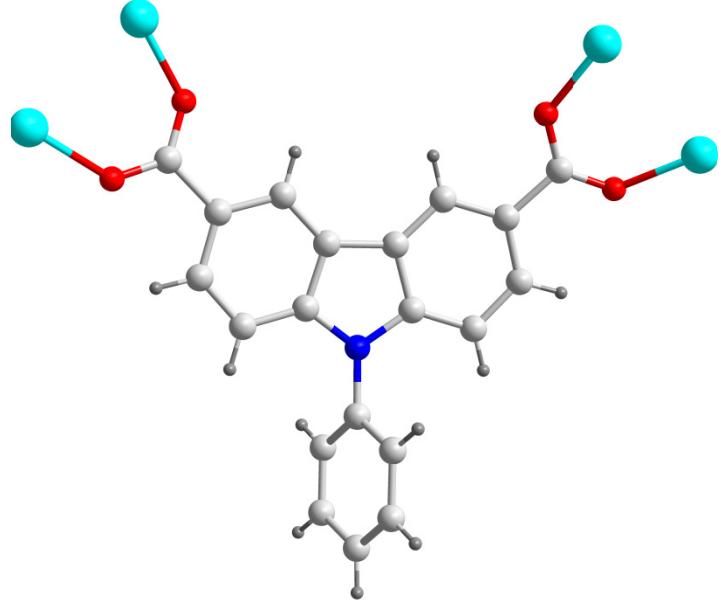
2.3 Table S1 Selective bond distance (Å) and angle (°) in Zn-PDA2.

Zn(1)–O(20)	1.926(3)	Zn(1)–O(12A)	1.935(3)
Zn(1)–O(6B)	1.968(3)	Zn(1)–O(8)	1.981(3)
Zn(2)–O(20)	2.021(3)	Zn(2)–O(2W)	2.072(5)
Zn(2)–O(11A)	2.088(4)	Zn(2)–O(3)	2.116(3)
Zn(2)–O(9)	2.174(4)	Zn(2)–O(100)	2.193(3)
Zn(3)–O(10)	1.922(3)	Zn(3)–O(20)	1.927(3)
Zn(3)–O(5B)	1.958(3)	Zn(3)–O(1B)	1.990(3)
Zn(4)–O(20)	1.925(3)	Zn(4)–O(4)	1.934(3)

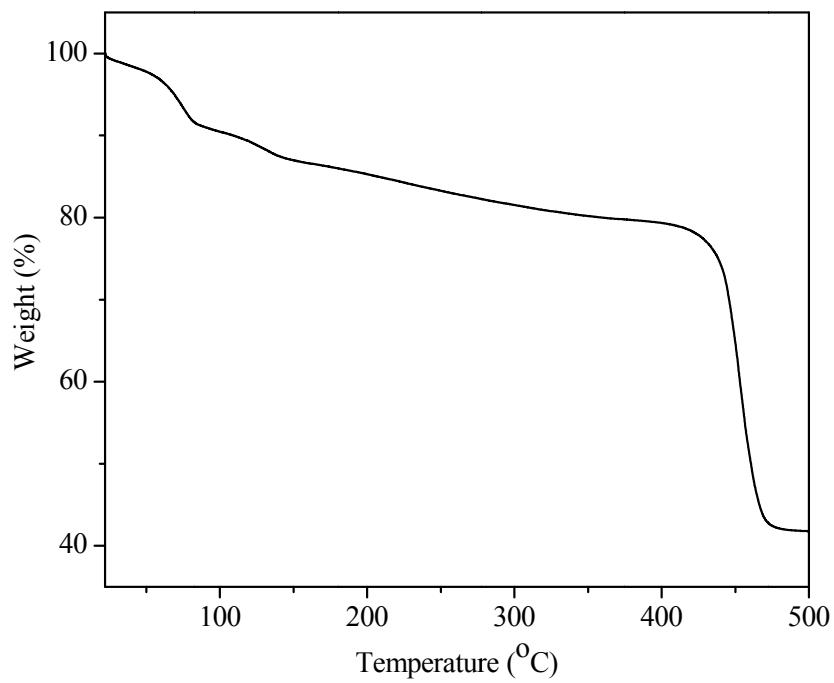
Zn(4)–O(2B)	1.960(3)	Zn(4)–O(7)	1.994(3)
O(20)–Zn(1)–O(12A)	116.29(15)	O(20)–Zn(1)–O(6B)	111.97(14)
O(12A)–Zn(1)–O(6B)	114.06(16)	O(20)–Zn(1)–O(8)	111.18(14)
O(12A)–Zn(1)–O(8)	102.96(15)	O(6B)–Zn(1)–O(8)	98.45(16)
O(20)–Zn(2)–O(2W)	174.79(17)	O(20A)–Zn(2)–O(11)	95.56(14)
O(2WA)–Zn(2)–O(11)	88.47(18)	O(20)–Zn(2)–O(3)	95.49(13)
O(2W)–Zn(2)–O(3)	87.58(17)	O(11A)–Zn(2)–O(3)	92.97(15)
O(20)–Zn(2)–O(9)	92.40(13)	O(2W)–Zn(2)–O(9)	84.50(17)
O(11A)–Zn(2)–O(9)	87.09(14)	O(3)–Zn(2)–O(9)	172.07(15)
O(20)–Zn(2)–O(100)	84.48(15)	O(2W)–Zn(2)–O(100)	91.17(19)
O(11A)–Zn(2)–O(100)	174.24(15)	O(3)–Zn(2)–O(100)	92.75(15)
O(9)–Zn(2)–O(100)	87.16(15)	O(10)–Zn(3)–O(20)	123.27(14)
O(10B)–Zn(3)–O(5)	106.48(16)	O(10B)–Zn(3)–O(1)	111.61(14)
O(10B)–Zn(3)–O(1)	104.52(16)	O(20B)–Zn(3)–O(1)	108.59(13)
O(5B)–Zn(3)–O(1B)	99.63(15)	O(20)–Zn(4)–O(4)	115.36(14)
O(20B)–Zn(4)–O(2)	115.82(13)	O(4B)–Zn(4)–O(2)	109.95(15)
O(20)–Zn(4)–O(7)	112.31(14)	O(4)–Zn(4)–O(7)	99.59(16)
O(2B)–Zn(4)–O(7)	101.80(15)		

Symmetry code A: - x , 1- y , 1- z ; B: -0.5+ x , 0.5- y , -0.5+ z .

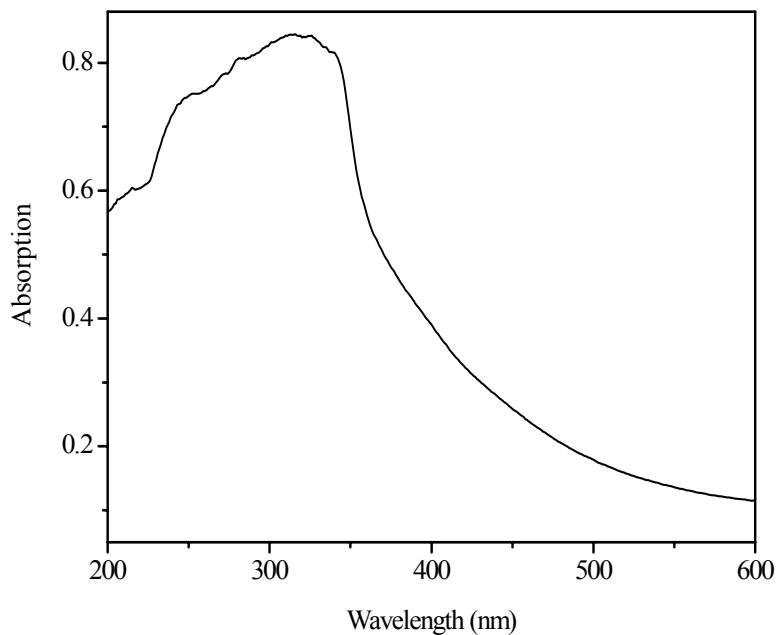
2.4 Figure S1 The coordination mode of PDA^{2-} ligands in Zn-PDA2.



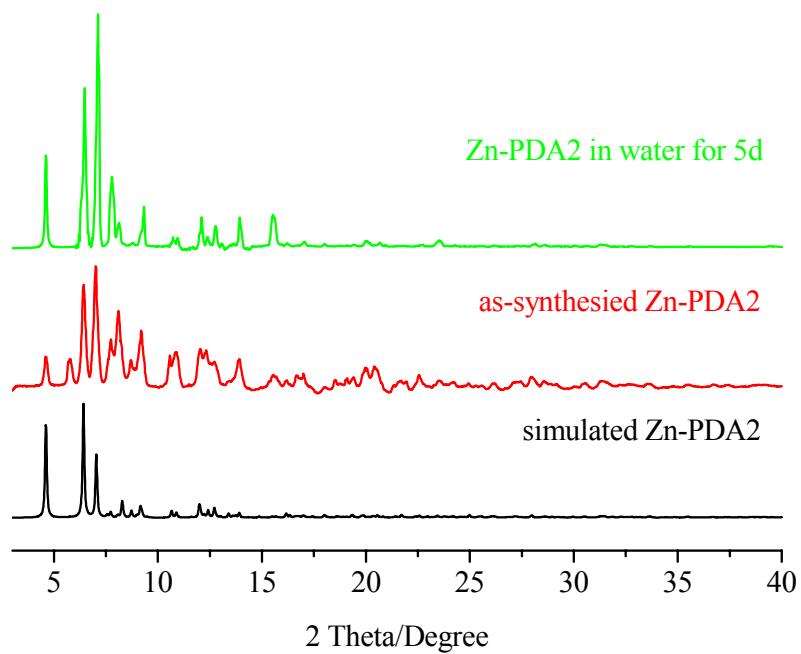
2.5 Figure S2 TGA traces of Zn-PDA2 ranging from room temperature to 500 °C.



2.6 Figure S3 The UV-vis absorption spectra for solid Zn-PDA2.

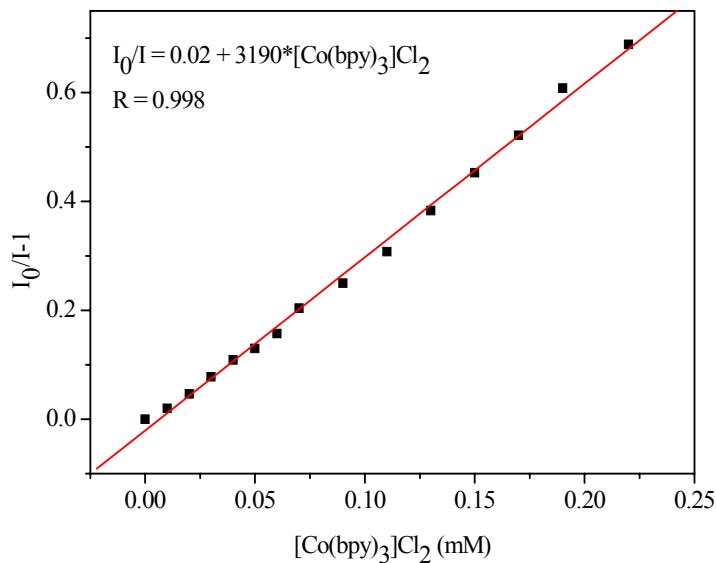


2.7 Figure S4 Powder XRD patterns of Zn-PDA2 simulated from single-crystal X-ray diffraction results, the as-synthesized Zn-PDA2 and Zn-PDA2 treated with water.

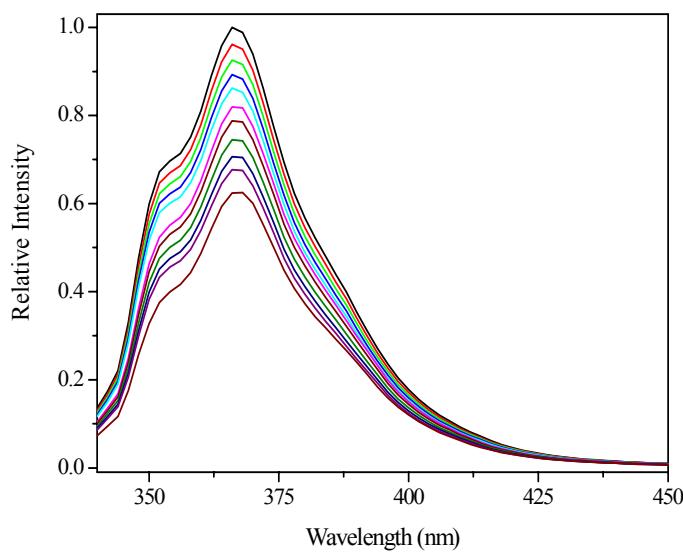


3. Host-guest properties between Zn-PDA2 and $[\text{Co}(\text{bpy})_3]\text{Cl}_2$.

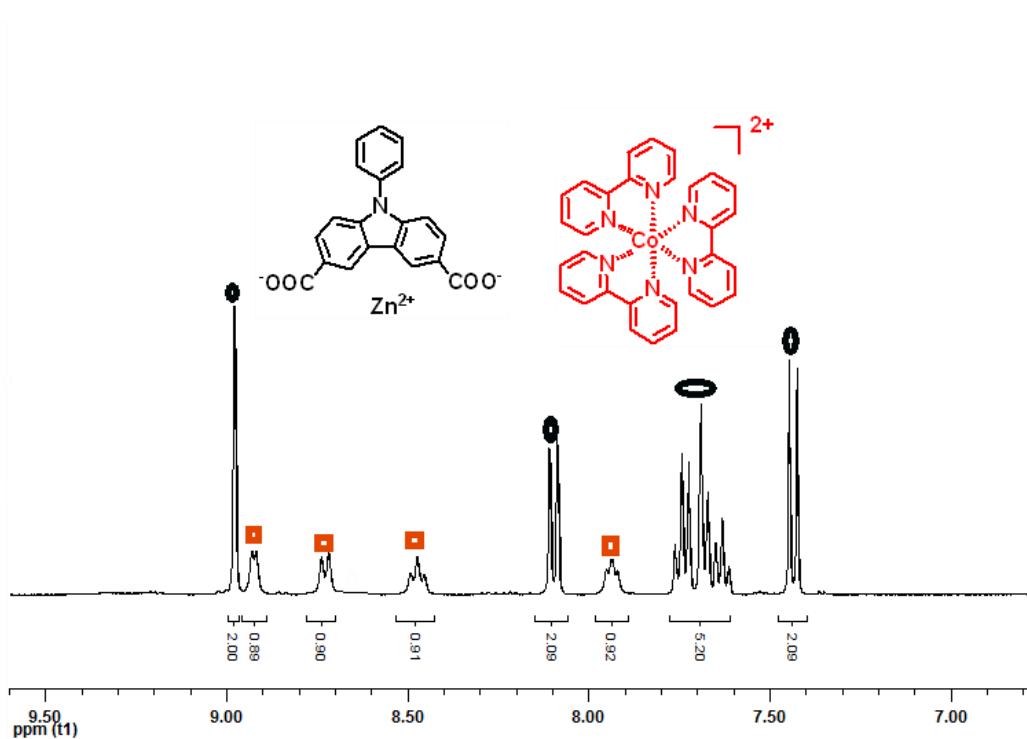
3.1 Figure S5 The Stern–Volmer plot of Zn–PDA2 quenched by $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ in 5 % TEA aqueous solution, where I_0 and I are the fluorescence intensity ratio before and after $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ incorporation, respectively.



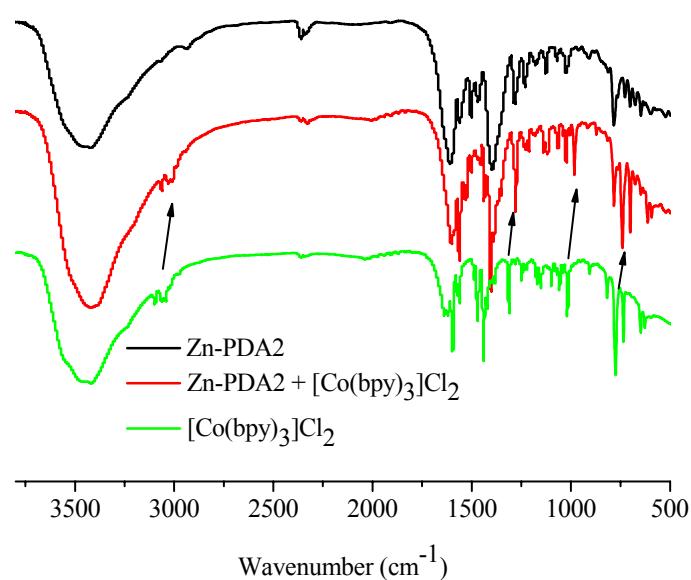
3.2 Figure S6 Family of emission spectra of Zn–PDA2 suspension (0.1 mM) upon addition of compound $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ in aqueous solution up to 0.22 mM.



3.3 Figure S7 The ^1H -NMR spectra after $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ adsorption in the Zn-PDA2 (decomposed by DCl).

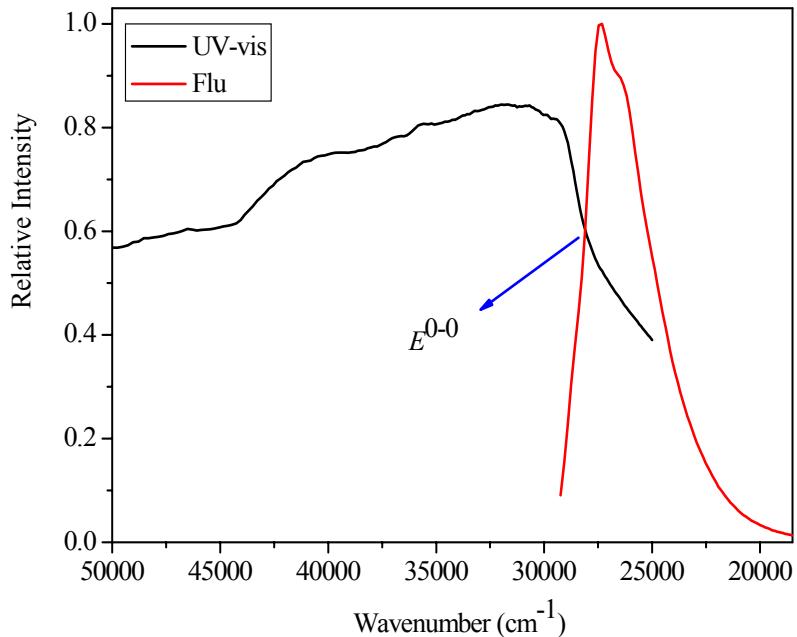


3.4 Figure S8 FT-IR spectra of Zn-PDA2 (top), Zn-PDA2 obtained after the absorption of $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ (middle) and $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ itself (bottom).

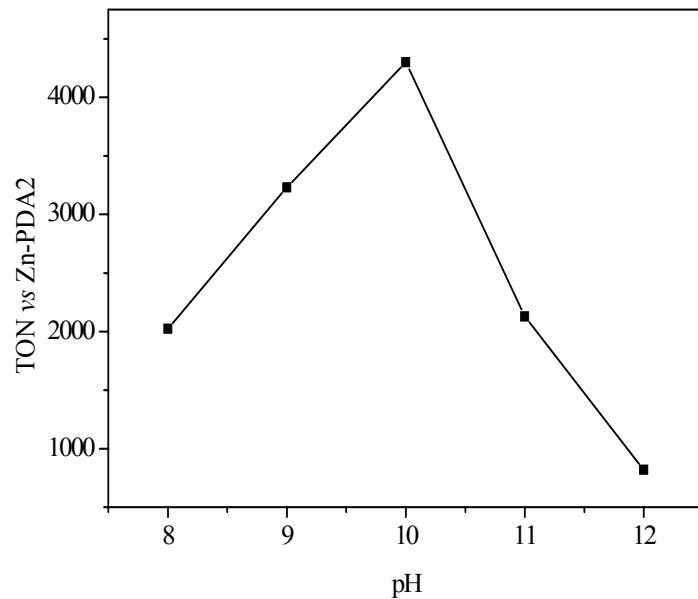


4. Studies on the hydrogen evolution based on Zn-PDA2.

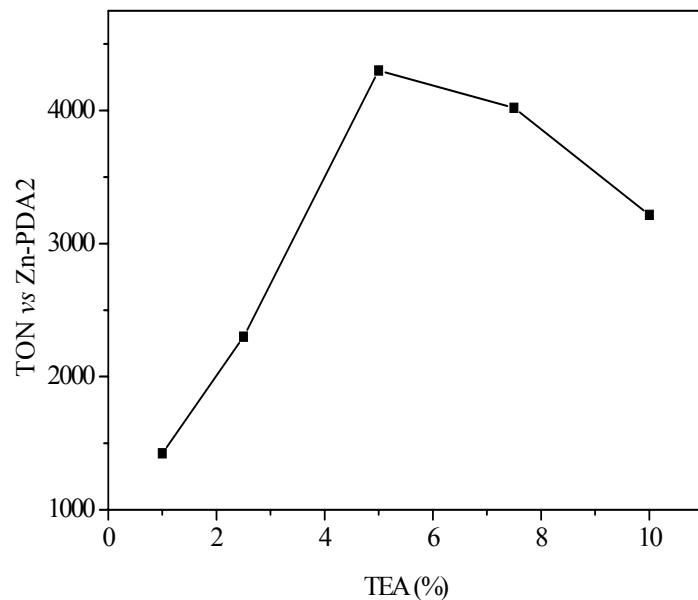
4.1 **Figure S9** Normalized absorption (black line) and emission spectrum (red line) of Zn-PDA2, excitation at 326 nm.



4.2 **Figure S10** Influence of the pH on photoinduced hydrogen production from the system comprising $0.34 \mu\text{M}$ Zn-PDA2 and $[\text{Co}(\text{bpy})_3]^{2+}$ (0.34 mM) in a 5% TEA water solution after 9 h of irradiation.

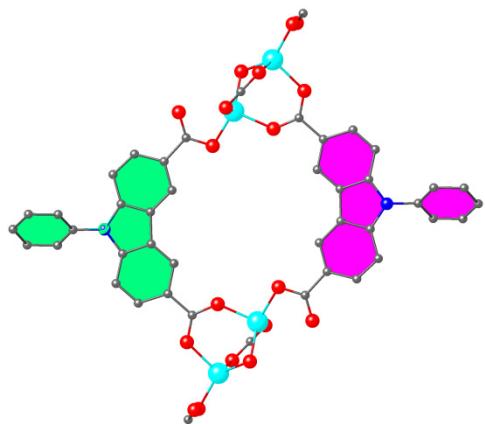


4.3 Figure S11 Influence of the TEA content on photoinduced hydrogen production from the system comprising $0.34 \mu\text{M}$ Zn-PDA2 and $[\text{Co}(\text{bpy})_3]^{2+}$ (0.34 mM) in a $\text{pH} = 10$ water solution after 9 h of irradiation.

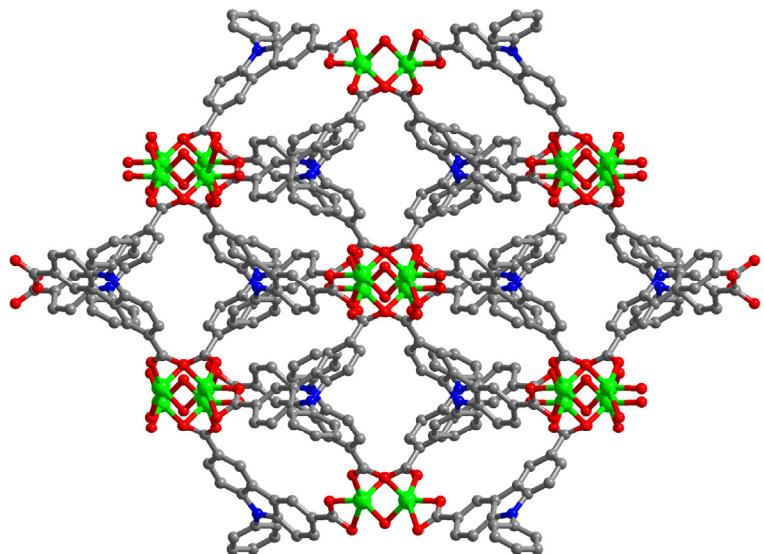


5. Crystal structure of Zn-PDA1 and fluorescent titration of $[\text{Co}(\text{bpy})_3]\text{Cl}_2$.

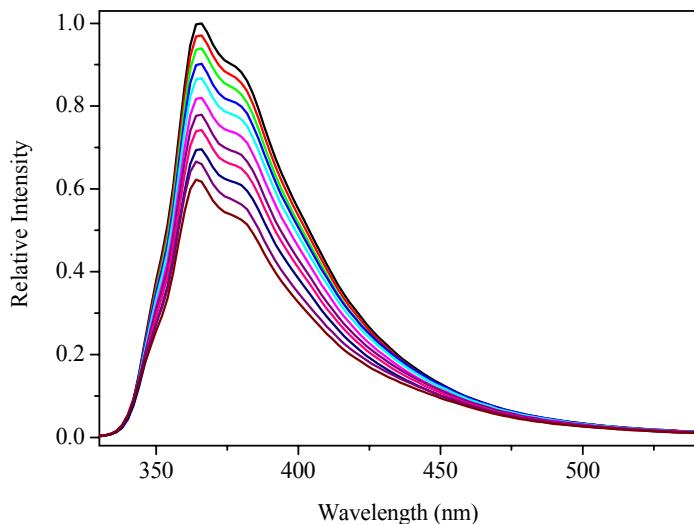
5.1 **Figure S12** View of the rhombus channels composed of PDA²⁻ and Zn²⁺ in Zn-PDA1.



5.2 **Figure S13** View of Zn-PDA1 crystal packing along *c* direction showing the rhombus channels.



5.3 Figure S14 Family of emission spectra of Zn–PDA1 suspension (0.1 mM) upon addition of compound $[\text{Co}(\text{bpy})_3]\text{Cl}_2$ in 5% TEA aqueous solution up to 0.22 mM (pH = 10.0).



6. Reference.

- S1. (a) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 7238; (b) Goldsmith, J. I.; Hudson, W. R.; Lowry, M. S.; Anderson, T. H.; Bernhard, S. *J. Am. Chem. Soc.* **2005**, *127*, 7502.
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- S5. Zhang, P.; Wang, M.; Na, Y.; Li, X.; Jiang, Y.; Sun, L. *Dalton Trans.* **2010**, *39*, 1204.