

## Supporting Information

# Redox-active Copper Triangle Worked as an Enzymatic Molecular Flask for Light-driven Hydrogen Production

Liang Zhao, Jianwei Wei, Feili Zhang, Cheng He, Sijia Zheng and Chunying Duan\*

### Contents

1. Experimental Section.
2. Preparation and Characterizations.
3. Single Crystal X-ray Crystallography.
4. Data for Spectral Titrations.
5. Isothermal Titration Calorimetry (ITC) Titrations.
6. Data Relative to Hydrogen Production.
7. References.

## 1. Experimental Section

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.  $^1\text{H}$ NMR spectra were measured on a Varian INOVA 400 M spectrometer. 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 elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. The solution fluorescent spectra were measured on Edinburgh FS-920. Both excitation and emission slit widths were 2 nm. The solution of Cu–**OBP**, Cu–**OMP** and Cu–**WBP** were prepared in  $\text{CH}_2\text{Cl}_2$ , and the concentration was 1.0 mM. The solution of fluorescein (1.0 mM) was prepared in EtOH/ $\text{H}_2\text{O}$ =1/1 solvents, respectively. The high concentration of the stock solutions of ATP (10.0 mM) were prepared directly in 1:1 EtOH/ $\text{H}_2\text{O}$  (v:v).

All electrochemical measurements were carried out under argon gas at room temperature. Performed on a ZAHNER ENNIUM electrochemical workstation 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.

### General Procedure for Hydrogen Production

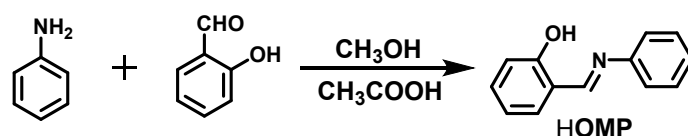
For photoinduced hydrogen evolution, each sample was made in a 25 mL flask. Varying amounts of the catalyst, FI and TEA in 1:1 EtOH/ $\text{H}_2\text{O}$  were added to obtain a total volume of 5.0 mL. Typically, the sample contained 0.01 mM catalyst, 4 mM FI as photosensitizer, and 15% (v/v)  $\text{Et}_3\text{N}$  as the sacrificial electron donor. The flask was sealed with a septum and protected from air, then degassed by bubbling argon gas for 20 min under atmospheric pressure at room temperature. The pH of this solution was adjusted to a specific pH by adding HCl or NaOH and measured with a pH meter. 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  $\text{H}_2$  was characterized by GC 7890T instrument analysis using a 5 Å molecular sieve column (0.6 m  $\times$  3 mm), thermal conductivity detector, and argon 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.<sup>S1</sup>

### **General Procedure for carbon dioxide reduction**

Photoinduced carbon dioxide reduction were carried out in a 25 mL flask. The sample contained 0.01 mM catalyst, 4.0 mM **FI** as photosensitizer, and 15% (v/v) Et<sub>3</sub>N as the sacrificial electron donor. The flask was sealed with a septum and degassed by bubbling argon for 30 min and carbon dioxide for 5 min under atmospheric pressure at room temperature. The pH of this solution was adjusted to a specific pH by adding hydrochloric acid and measured with a pH meter. After that, the samples were irradiated by using a 500 W xenon lamp, and the reaction temperature was maintained at 293K by using a super constant temperature circulating water tank. The generated HCOOH was characterized on a DIONEX ICS-5000 instrument using a guard column IonPac AG11-HC and the column temperature was maintained at 30 °C.

## 2. Preparation and Characterizations.

**Scheme S1** The synthetic route of ligand **HOMP**.



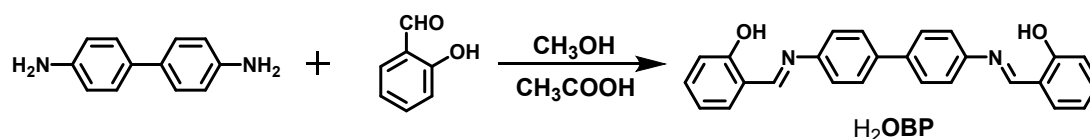
### Prepare of ligand **HOMP**:

Aniline (0.5mL, 6.0mmol) and salicylaldehyde (0.6mL, 6.0mmol) were mixed in methanol (30 mL) and refluxed for 5 h. The solution was then evaporated to 5 mL, and the yellow product was filtered out and dried under vacuum. Yield: 0.90 g, 80%.  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz, ppm):  $\delta$  13.12 (s, 1H, OH), 8.95 (s, 1H, N=CH), 7.66 (d,  $J = 8.0$  Hz, 1H, ArH), 7.48-7.39 (m, 5H, ArH), 7.31 (t, 1H, ArH), 7.00-6.96 (m, 2H, ArH). Anal calc. for  $\text{C}_{13}\text{H}_{11}\text{NO}$ : H 5.62, C 79.17, N 7.10 %. Found: H 5.07, C 79.57, N 7.07 %.

### Prepare of **Cu–OMP**:

A mixture solution of  $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$  (0.19 g, 0.75 mmol), **HOMP** (0.30 g, 1.50 mmol) and NaOH (0.06 g, 1.5 mmol) in  $\text{CH}_3\text{OH}$  was stirred for 1 h. X-ray quality black block crystals were obtained after the solution left for two weeks at room temperature and dried in vacuum. Yield: 77 %. Anal calc. for  $\text{Cu}(\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2)$ : H 4.92, C 68.48, N 6.14 %. Found: H 4.43, C 65.67, N 5.70 %. ESI-MS:  $m/z=478.11$   $[\text{NaCu}(\text{OMP})_2]^+$ , 935.22  $\{\text{Na}[\text{Cu}(\text{OMP})_2]_2\}^+$ .

**Scheme S2** The synthetic route of ligand **H<sub>2</sub>OBP**.



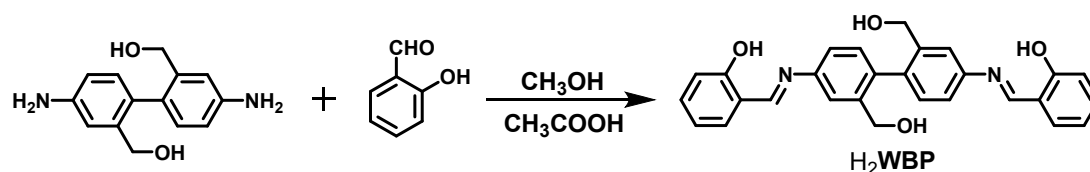
### Prepare of ligand **H<sub>2</sub>OBP**:

The ligand **H<sub>2</sub>OBP** was synthesized according to the literature methods.<sup>S2</sup> Benzidine (0.55 g, 3.0 mmol) and salicylaldehyde (0.73 g, 6.0 mmol) were mixed in methanol (30 mL) and refluxed for 2 h. The solution was then evaporated to 5 mL, and the yellow product was filtered out, washed with methanol and dried under vacuum. Yield: 1.10 g, 90%.

### Prepare of Cu–OBP:

A methanol solution (10 mL) of  $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$  (0.36 g, 1.5 mmol) was added with stirring to a methanol solution (20 mL) of  $\text{H}_2\text{OBP}$  (0.59 g, 1.5 mmol) and NaOH (0.12 g, 3.0 mmol). A brown precipitate developed immediately and was filtered out. Then the solid was extracted by chloroform and the resulting solution was allowed to evaporate slowly in air. Dark brown crystals of Cu–OBP suitable for single crystal X-ray diffraction were isolated directly from solution after one week. yield: 65%.

**Scheme S3** The synthetic route of ligand  $\text{H}_2\text{WBP}$ .



### Prepare of ligand $\text{H}_2\text{WBP}$ :

2,2'-bis(hydroxymethyl) benzidine<sup>S3</sup> (0.73 g, 3.0 mmol) and salicylaldehyde (0.73 g, 6.0 mmol) were mixed in methanol (30 mL) and refluxed for 2 h. The solution was then evaporated to 5 mL, and the yellow product was filtered out, washed with ethyl ester and dried under vacuum. Yield: 1.15 g, 84%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, ppm):  $\delta$  12.46(s, 2H, OH), 8.98 (s, 2H, N=CH), 7.83 (d, *J* = 8.0 Hz, 4H, ArH), 7.50 (d, *J* = 8.0 Hz, 4H, ArH), 7.27 (d, 2H, *J* = 3.2 Hz, ArH), 7.06 (dd, 2H, *J* = 12.0 Hz, ArH), 6.90 (d, 2H, *J* = 9.2 Hz, ArH), 4.06 (t, 4H, *J* = 9.6 Hz, CH<sub>2</sub>), 3.65 (d, 4H, *J* = 9.6 Hz, CH<sub>2</sub>), 3.31 (s, 6H, CH<sub>3</sub>).

### Prepare of Cu–WBP:

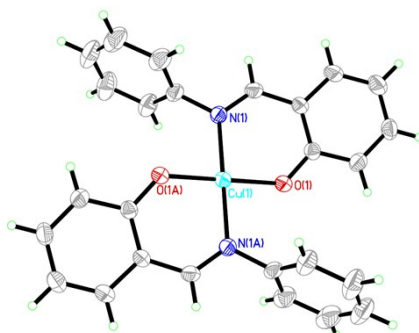
A methanol solution (10 mL) of  $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$  (0.36 g, 1.5 mmol) was added with stirring to a methanol solution (20 mL) of  $\text{H}_2\text{WBP}$  (0.68 g, 1.5 mmol) and NaOH (0.12 g, 3.0 mmol). A brown precipitate developed immediately and was filtered out. Then the solid was extracted by chloroform and the resulting solution was allowed to evaporate slowly in air. Dark brown crystals of Cu–OBP suitable for single crystal X-ray diffraction were isolated directly from solution after one week. yield: 57%. Anal calc. for  $\text{Cu}_3(\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4)_3$ : H 4.31, C 65.42, N 5.45 %. Found: H 4.43, C 65.67, N 5.70 %. ESI-MS: *m/z* = 771.65 [ $\text{H}_2\text{Cu}_3(\text{WBP})_3$ ]<sup>2+</sup>, 782.64 [ $\text{HNaCu}_3(\text{WBP})_3$ ]<sup>2+</sup>, 793.62 [ $\text{Na}_2\text{Cu}_3(\text{WBP})_3$ ]<sup>2+</sup>.

### 3. Single Crystal X-ray Crystallography.

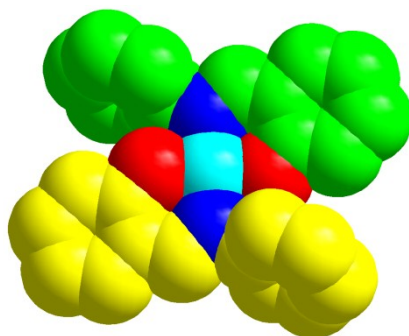
Intensities of the Cu–OMP was collected at 200(2) K on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) using the SMART and SAINT programs.<sup>S4,S5</sup> The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods with SHELXTL version 5.1. In the structural refinement of Cu–OMP, the skeleton non-hydrogen atoms were refined anisotropically. The hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms.

Crystal data: Cu–OMP: Cu(C<sub>13</sub>H<sub>10</sub>NO)<sub>2</sub>,  $M = 455.98$ , monoclinic, space group  $P2_1/n$ , black block,  $a = 11.9298(4) \text{ \AA}$ ,  $b = 7.9557(3) \text{ \AA}$ ,  $c = 12.2145(4) \text{ \AA}$ ,  $\beta = 112.172(2)^\circ$ ,  $V = 1073.55(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.411 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 1.042 \text{ mm}^{-1}$ ,  $T = 200(2) \text{ K}$ . 1897 unique reflections [ $R_{\text{int}} = 0.0507$ ]. Final  $R_1$  [with  $I > 2\sigma(I)$ ] = 0.0391,  $wR_2$  (all data) = 0.1122. CCDC number 1483351.

**Figure S1** An ORTEP plot of the molecular tetrahedron Cu–OMP, showing 30% probability displacement ellipsoids of non-hydrogen atoms. Symmetry code A:  $2-x, -y, 1-z$ .



**Figure S2.** Space-filling structure of Cu–OMP.



**Table S1** All bond distance (Å) in Cu–OMP.

bond distance (Å)		bond distance (Å)	
Cu(1)-O(1)	1.878(2)	C(4)-C(5)	1.364(4)
Cu(1)-N(1)	1.997(2)	C(5)-C(6)	1.413(4)
O(1)-C(1)	1.307(3)	C(6)-C(7)	1.435(4)
N(1)-C(7)	1.294(4)	C(8)-C(13)	1.370(5)
N(1)-C(8)	1.442(4)	C(8)-C(9)	1.361(5)
C(1)-C(2)	1.404(4)	C(9)-C(10)	1.402(5)
C(1)-C(6)	1.407(4)	C(10)-C(11)	1.348(7)
C(2)-C(3)	1.382(5)	C(11)-C(12)	1.355(7)
C(3)-C(4)	1.371(5)	C(12)-C(13)	1.389(5)

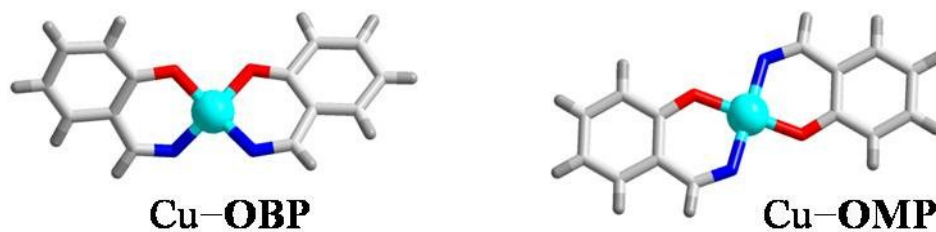
Symmetry code A: 2-x, -y, 1-z

**Table S2** All bond angle (°) in Cu–OMP.

bond angle (°)		bond angle (°)	
O(1)-Cu(1)-O(1A)	180.0	C(5)-C(4)-C(3)	118.7(3)
O(1)-Cu(1)-N(1A)	88.41(9)	C(4)-C(5)-C(6)	121.8(3)
O(1A)-Cu(1)-N(1A)	91.59(9)	C(1)-C(6)-C(5)	119.2(3)
O(1)-Cu(1)-N(1)	91.59(9)	C(1)-C(6)-C(7)	122.6(3)
O(1A)-Cu(1)-N(1)	88.41(9)	C(5)-C(6)-C(7)	118.2(3)
N(1A)-Cu(1)-N(1)	180.0	N(1)-C(7)-C(6)	126.5(3)
C(1)-O(1)-Cu(1)	128.2(2)	C(13)-C(8)-C(9)	120.5(3)
C(7)-N(1)-C(8)	116.7(2)	C(13)-C(8)-N(1)	119.1(3)
C(7)N(1)-Cu(1)	122.9(2)	C(9)-C(8)-N(1)	120.4(3)
C(8)-N(1)-Cu(1)	120.17(19)	C(8)-C(9)-C(10)	118.8(4)
O(1)-C(1)-C(2)	118.8(3)	C(11)-C(10)-C(9)	120.4(4)
O(1)-C(1)-C(6)	123.4(3)	C(10)-C(11)-C(12)	120.8(4)
C(2)-C(1)-C(6)	117.9(3)	C(11)-C(12)-C(13)	119.7(5)
C(3)-C(2)-C(1)	120.8(3)	C(8)-C(13)-C(12)	119.8(4)
C(2)-C(3)-C(4)	121.6(3)		

Symmetry code A: 2-x, -y, 1-z

**Figure S3.** Structures of the complexes Cu–OBP and Cu–OMP showing the coordination geometry of copper ions. Copper, oxygen, nitrogen and carbon atoms are drawn in green, red, blue and gray, respectively.



**Table S3.** Selection bond distances (Å) of the two complexes.

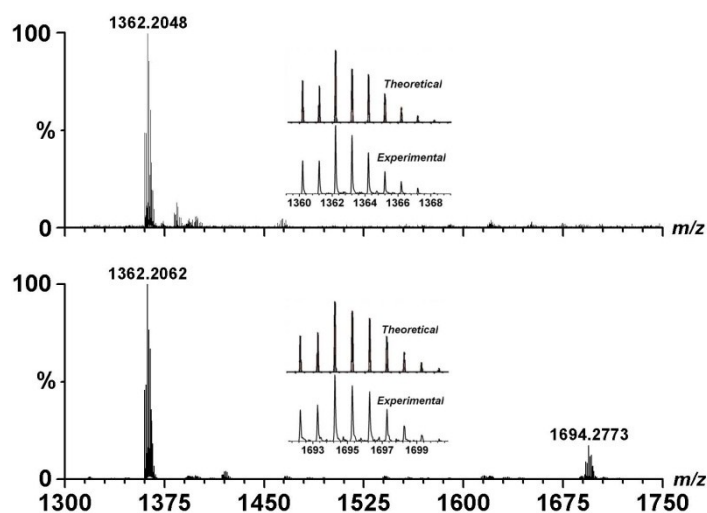
	Cu–OBP	Cu–OMP
Cu–O in an average	1.874(6)	1.878(2)
Cu–N in an average	1.951(5)	1.997(2)
C–O in an average	1.303(8)	1.307(2)
C=N in an average	1.300(6)	1.294(4)
C <sub>Ar</sub> –N in an average	1.419(6)	1.442(4)



## 4. Data for Spectral Titrations.

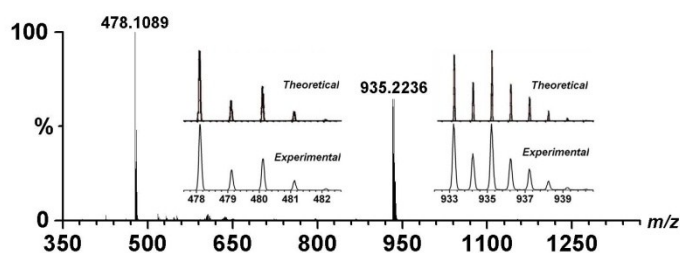
### 4.1 ESI-MS Spectra

**Figure S4.** ESI-MS spectra of Cu-OBP (0.10 mM) in EtOH solution (top) and of fluorescein in the aforementioned solution (bottom). The inserts show the measured and simulated isotopic patterns at  $m/z = 1362.20$  (top) and 1694.28 (bottom), respectively.



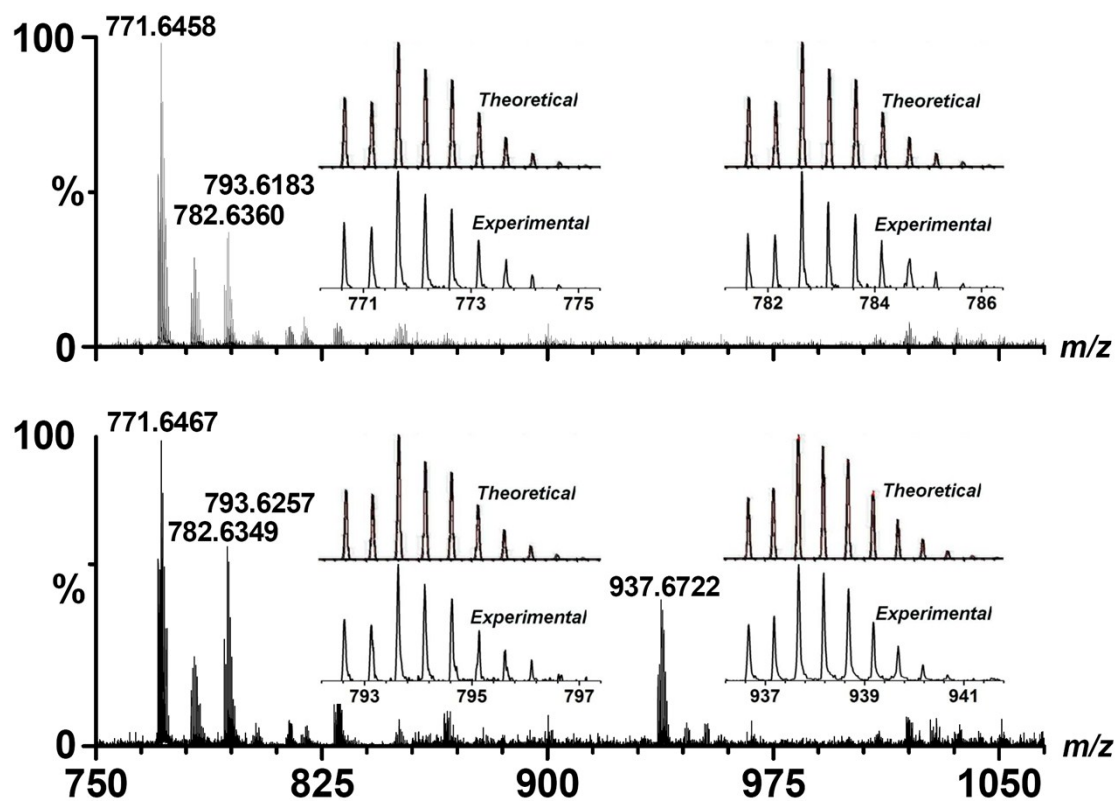
Peak	Value of $m/z$	Specie assigned
1	1362.2048	$[\text{HCu}_3(\text{OBP})_3]^+$
2	1694.2773	$[\text{HCu}_3(\text{OBP})_3 \supset \text{Fl}]^+$

**Figure S5.** ESI-MS spectra of Cu-OMP (0.30 mM) in EtOH solution. The inserts show the measured and simulated isotopic patterns at  $m/z = 478.11$  and 935.22, respectively.



Peak	Value of $m/z$	Specie assigned
1	478.1089	$[\text{NaCu}(\text{OMP})_2]^+$
2	935.2236	$\{\text{Na}[\text{Cu}(\text{OMP})_2]_2\}^+$

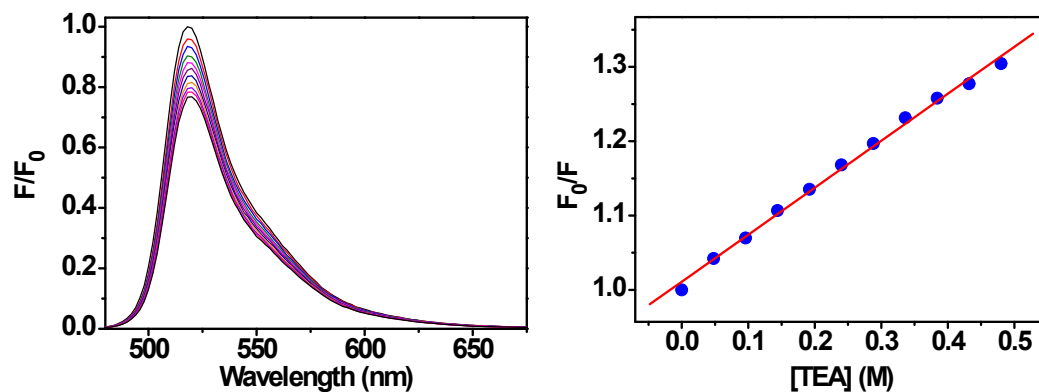
**Figure S6.** ESI-MS spectra of Cu–WBP (0.10 mM) in EtOH solution. The inserts show the measured and simulated isotopic patterns at  $m/z = 771.64$ , 782.63, 793.62 and 937.67, respectively.



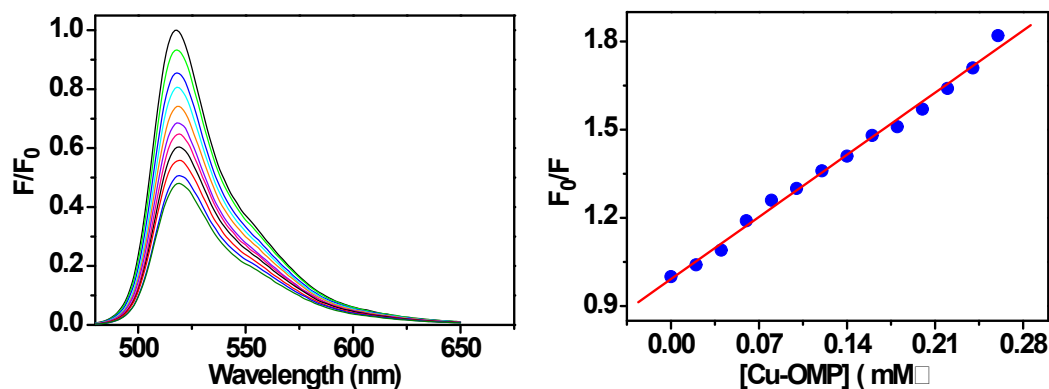
Peak	Value of $m/z$	Specie assigned
1	771.6458	$[\text{H}_2\text{Cu}_3(\text{WBP})_3]^{2+}$
2	782.6360	$[\text{HNaCu}_3(\text{WBP})_3]^{2+}$
3	793.6183	$[\text{Na}_2\text{Cu}_3(\text{WBP})_3]^{2+}$
4	937.6722	$[\text{H}_2\text{Cu}_3(\text{WBP})_3 \supset \text{Fl}]^{2+}$

## 4.2 Luminescent Titrations

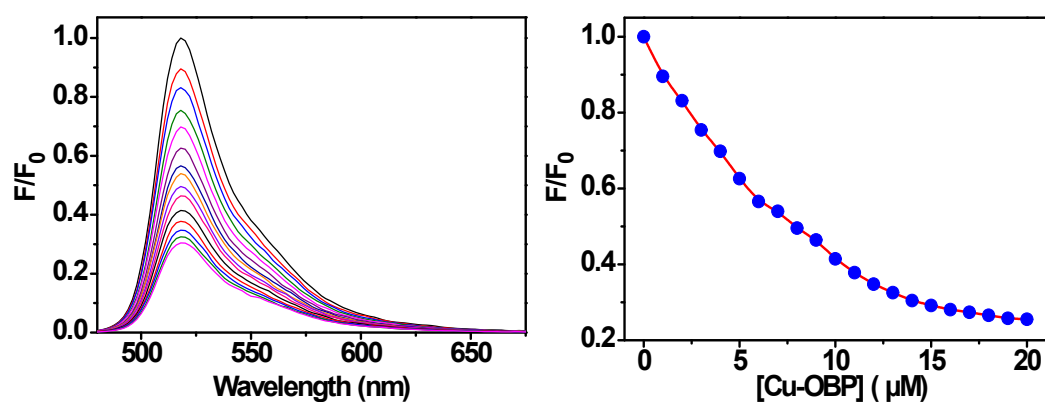
**Figure S7.** (Left) Family of luminescence spectra of fluorescein (10  $\mu\text{M}$ ) in EtOH/H<sub>2</sub>O = 1:1 solution at pH= 12.50 upon the addition of TEA. (Right) The Stern-Volmer Fitting of the titration curve. Fluorescence intensity were recorded at 518 nm, excited at 470 nm.



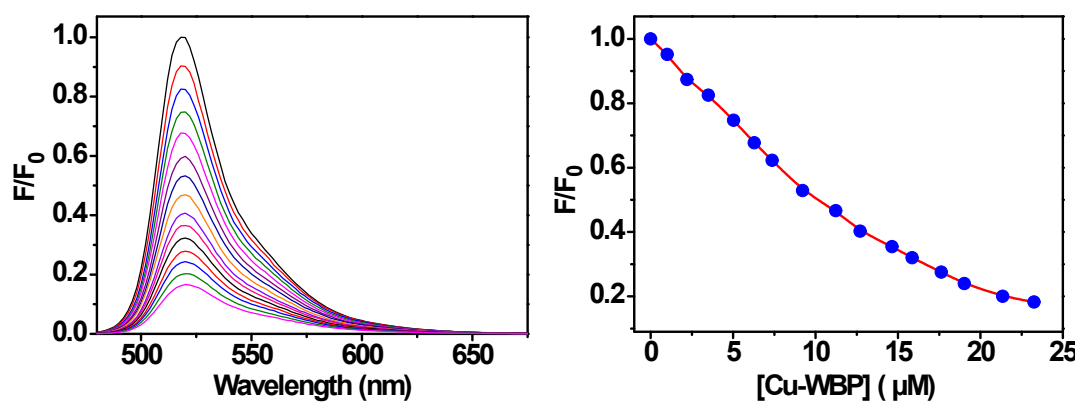
**Figure S8.** (Left) Family of luminescence spectra of fluorescein (10  $\mu\text{M}$ ) in EtOH/H<sub>2</sub>O = 1:1 solution at pH= 12.50 upon the addition of Cu-OMP. (Right) The Stern-Volmer Fitting of the titration curve. Fluorescence intensity were recorded at 518 nm, excited at 470 nm.



**Figure S9.** (Left) Family of luminescence spectra of fluorescein ( $10\ \mu\text{M}$ ) in EtOH/H<sub>2</sub>O = 1:1 solution at pH= 12.50 upon the addition of Cu-OBP. (Right) The picture show the normalized luminescence vs. [Cu-OBP].

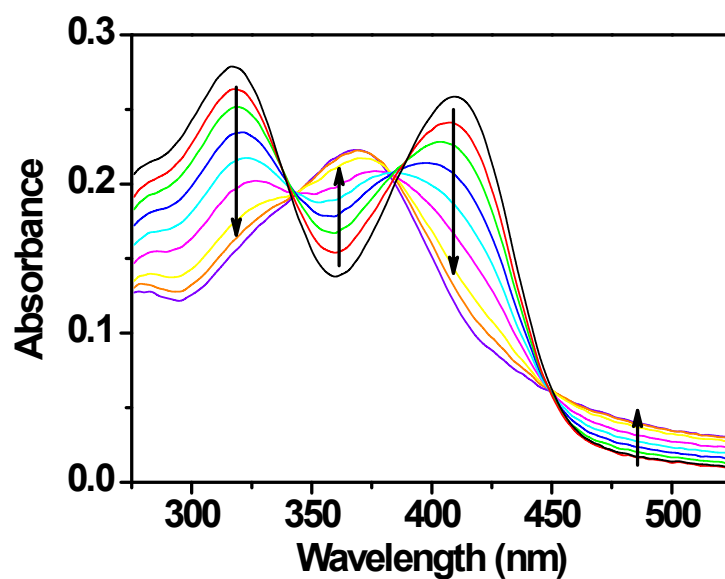


**Figure S10.** (Left) Family of luminescence spectra of fluorescein ( $10\ \mu\text{M}$ ) in EtOH/H<sub>2</sub>O = 1:1 solution at pH= 12.50 upon the addition of Cu-WBP. (Right) The picture show the normalized luminescence vs. [Cu-WBP].

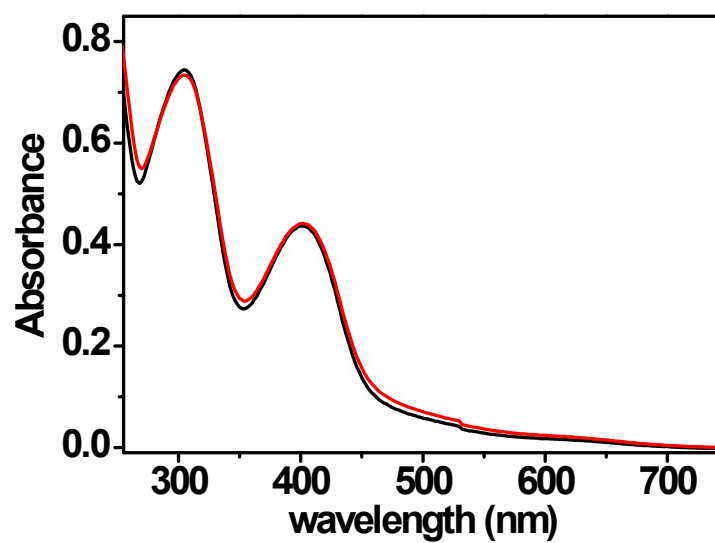


### 4.3 UV-vis Titrations

**Figure S11.** The family of UV-vis absorption spectra of Cu-OBP (2.0  $\mu\text{M}$ ) in 1:1 EtOH/H<sub>2</sub>O solution upon the addition of ATP.



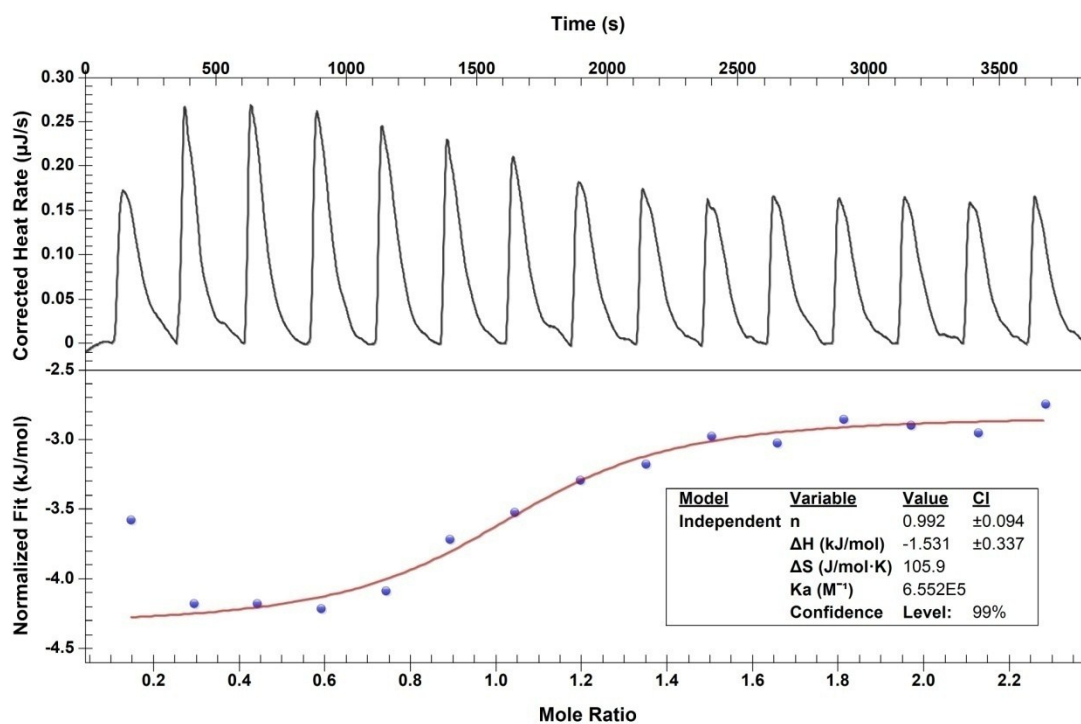
**Figure S12.** UV-vis absorption spectra of Cu-WBP (10.0  $\mu\text{M}$ ) in 2:8 EtOH/H<sub>2</sub>O solution (blank line) and incubating for 24 h (red line).



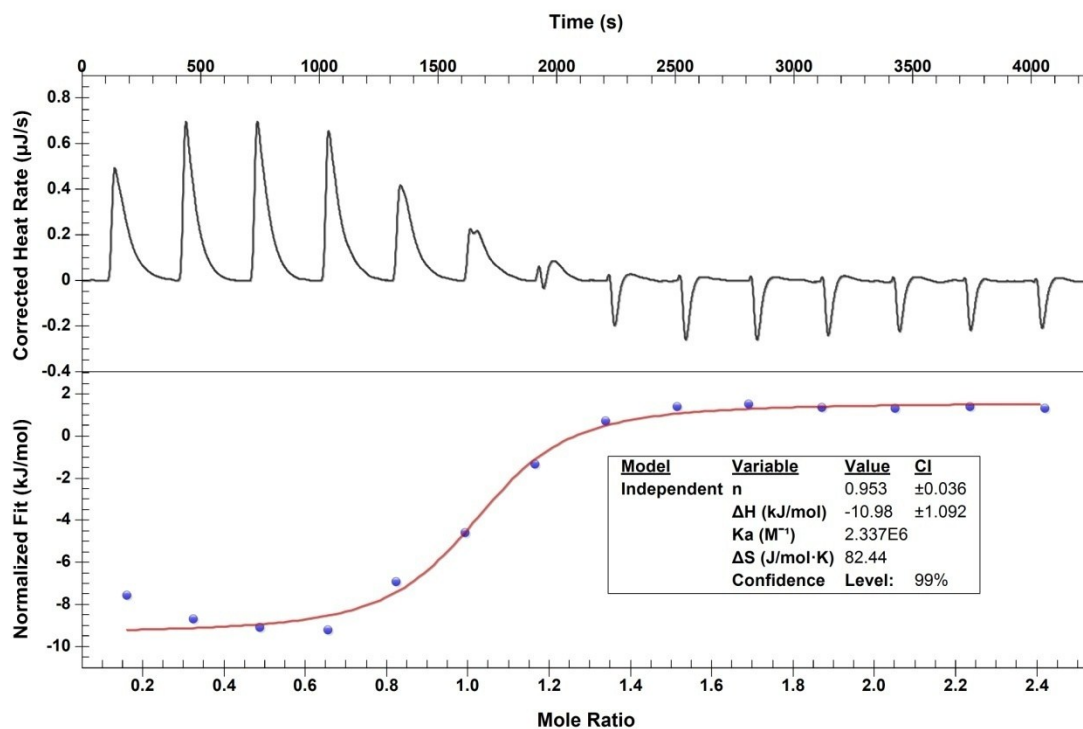
## 5. Isothermal Titration Calorimetry

The ITC experiments were performed by an isothermal titration microcalorimeter at atmospheric pressure and at 25.00 °C, giving the association constants (K) and the thermodynamic parameters. A solution of guest in a 0.250 mL syringe was sequentially injected with stirring at 250 rpm into a solution of host in the sample cell (1.30 mL volume). All the thermodynamic parameters reported in this work were obtained by using the ‘independent’ model.

**Figure S13.** Microcalorimetric titration of Cu–OBP with FI in EtOH solution at 298.15K. (a) Raw data for sequential 15 injections (5.0  $\mu\text{L}$  per injection) of FI solution (1.0 mM) injecting into Cu–OBP solution (35.0  $\mu\text{M}$ ). (b) Apparent reaction heat obtained from the integration of calorimetric traces.

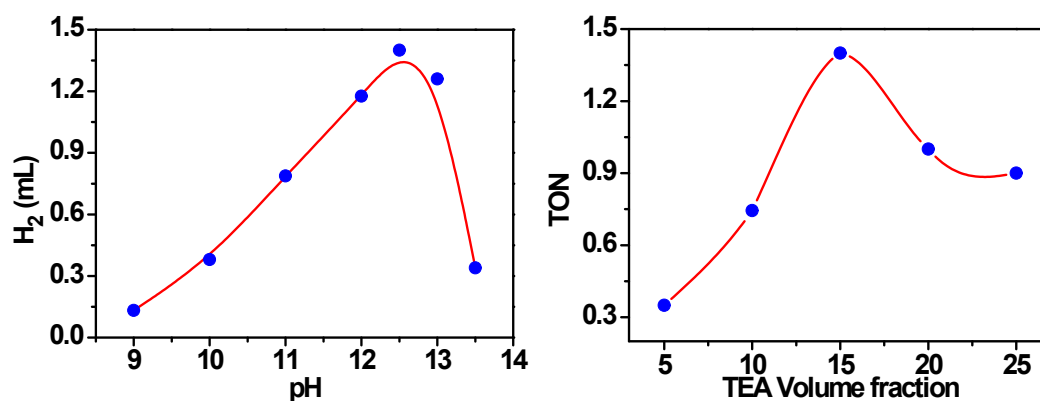


**Figure S14.** Microcalorimetric titration of Cu-OBP with ATP in CH<sub>3</sub>CN solution at 298.15K. (a) Raw data for sequential 10 injections (10  $\mu$ L per injection) of ATP solution (0.50 mM) injecting into Cu-OBP solution (35.0  $\mu$ M). (b) Apparent reaction heat obtained from the integration of calorimetric traces.

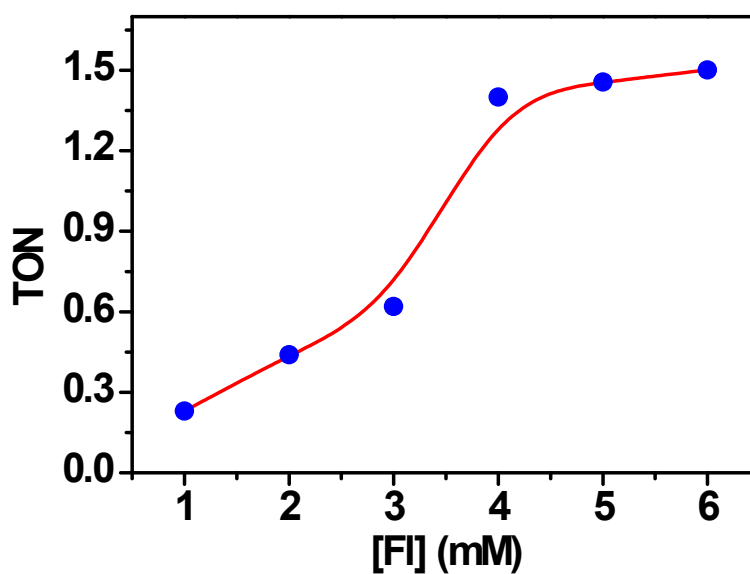


## 6. Data Relative to Hydrogen Production.

**Figure S15.** Left picture: Photocatalytic hydrogen evolution in 1:1 EtOH/H<sub>2</sub>O of the systems containing Cu-OBP (10.0 μM), FI (4.0 mM) and TEA (15% v/v) at different pH values, and Right one: Photocatalytic hydrogen evolution in 1:1 EtOH/H<sub>2</sub>O of the systems containing Cu-OBP (10.0 μM), and FI (4.0 mM) at pH= 12.5 with various TEA concentration.

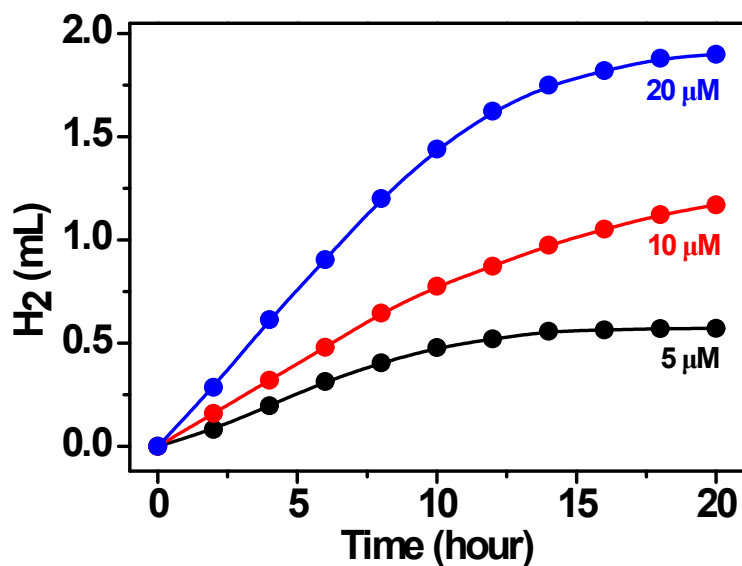


**Figure S16.** Photocatalytic hydrogen evolution in 1:1 EtOH/H<sub>2</sub>O of the systems containing Cu-OBP (10.0 μM), and TEA (15% v/v) at pH= 12.5 with various FI concentration.

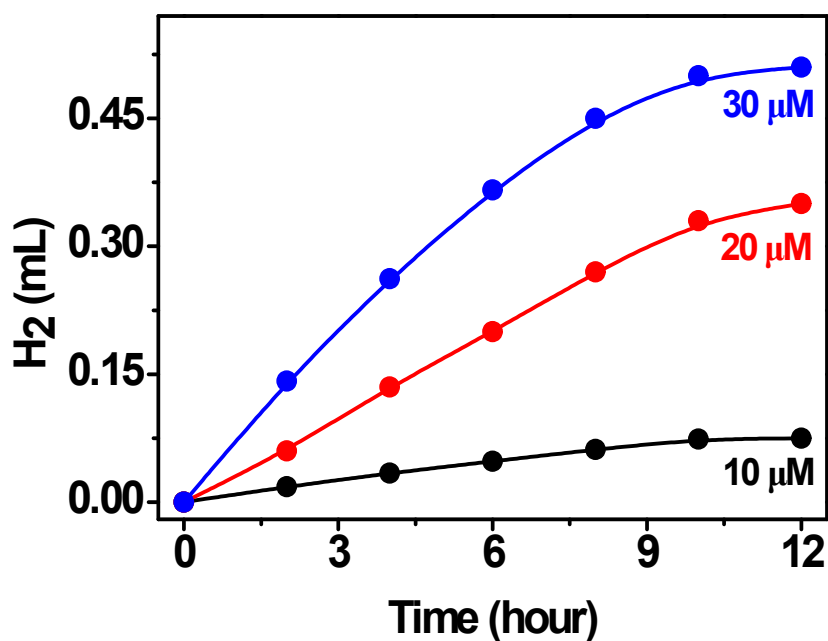




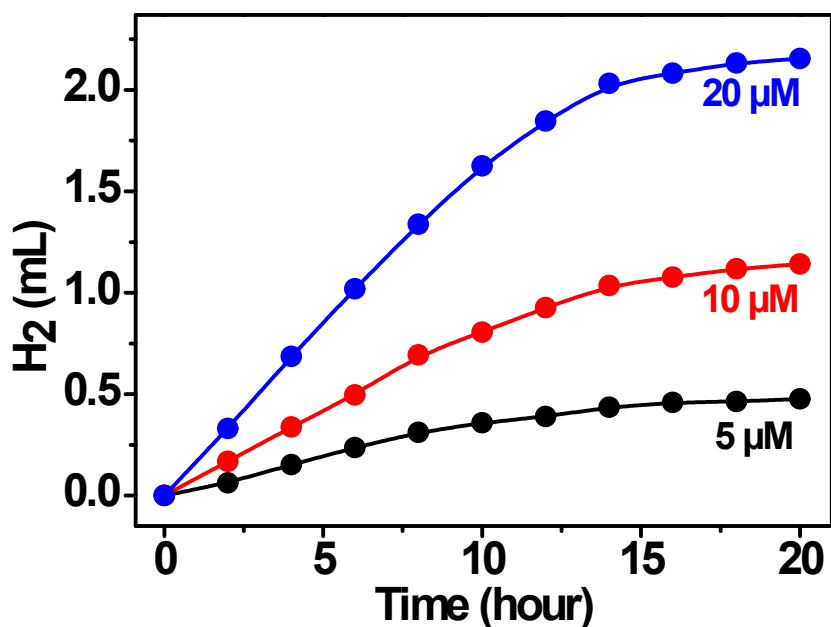
**Figure S17.** Light-driven hydrogen evolution of the systems containing **FI** (4.0 mM),  $\text{NEt}_3$  (15% v/v), and **Cu-OBP** in an EtOH/ $\text{H}_2\text{O}$  solution (1:1, pH = 12.5) with the concentration of **Cu-OBP** fixed at 5.0  $\mu\text{M}$  (black), 10.0  $\mu\text{M}$  (red line), and 20.0  $\mu\text{M}$  (blue line).



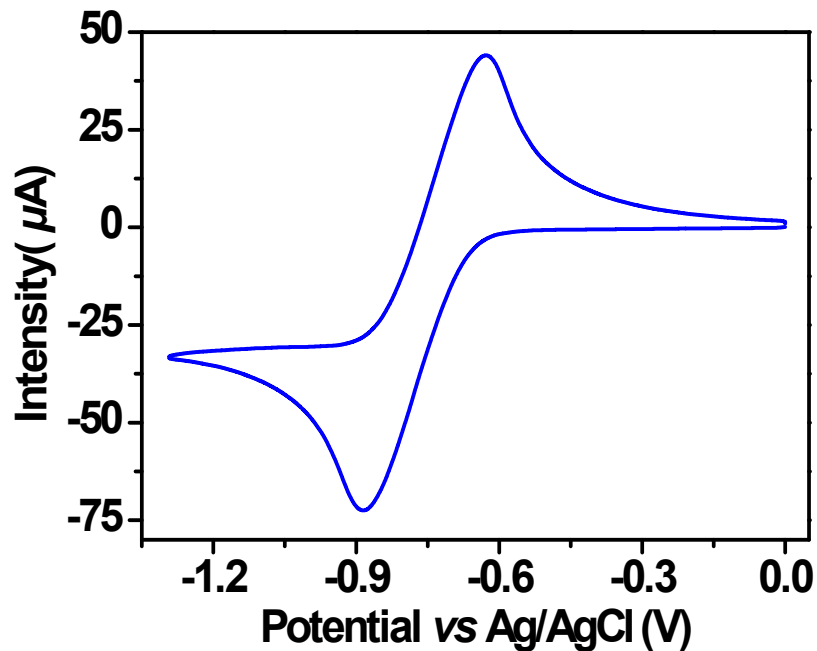
**Figure S18.** Light-driven hydrogen evolution of the systems containing **FI** (4.0 mM),  $\text{NEt}_3$  (15% v/v), and **Cu-OMP** in an EtOH/ $\text{H}_2\text{O}$  solution (1:1, pH = 12.5) with the concentration of **Cu-OMP** fixed at 10.0  $\mu\text{M}$  (black), 20.0  $\mu\text{M}$  (red line), and 30.0  $\mu\text{M}$  (blue line).



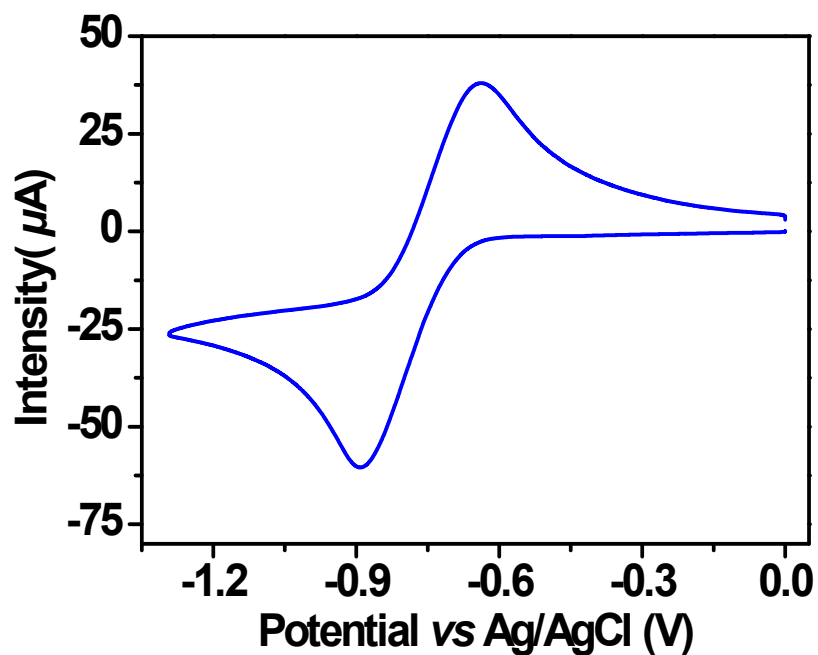
**Figure S19.** Light-driven hydrogen evolution of the systems containing **FI** (4.0 mM),  $\text{NEt}_3$  (15% v/v), and **Cu-WBP** in an EtOH/ $\text{H}_2\text{O}$  solution (1:1, pH = 12.5) with the concentration of **Cu-WBP** fixed at 5.0  $\mu\text{M}$  (black), and 10.0  $\mu\text{M}$  (red line).



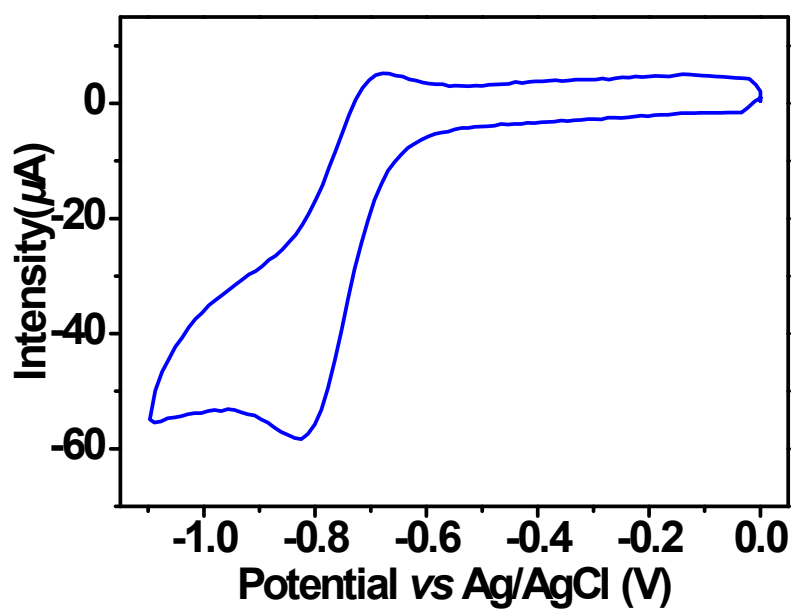
**Figure S20.** Cyclic voltammogram of 0.30 mM **Cu-OMP** in  $\text{CH}_2\text{Cl}_2$  containing 0.10 M  $\text{TBAPF}_6$ . Scan Rate: 100 mV/s.



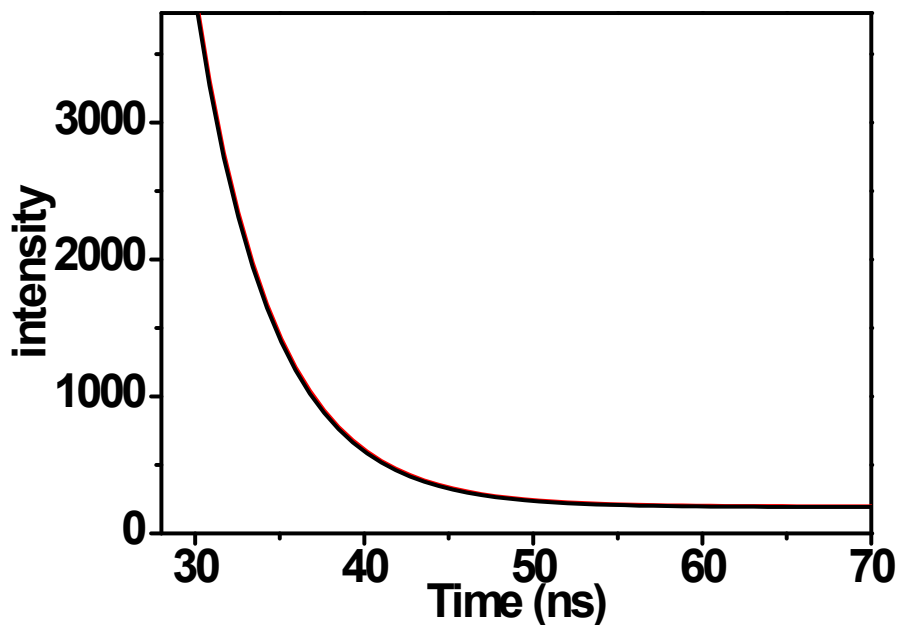
**Figure S21.** Cyclic voltammogram of 0.10 mM Cu-OBP in CH<sub>2</sub>Cl<sub>2</sub> containing 0.10 M TBAPF<sub>6</sub>. Scan Rate: 100 mV/s.



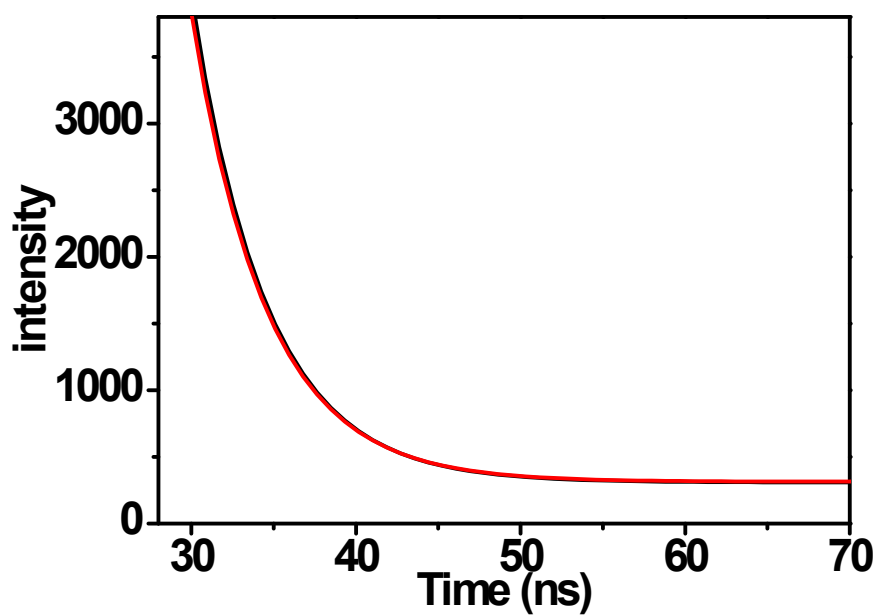
**Figure S22.** Cyclic voltammogram of 0.10 mM Cu-WBP in CH<sub>2</sub>Cl<sub>2</sub> containing 0.10 M TBAPF<sub>6</sub>. Scan Rate: 100 mV/s.



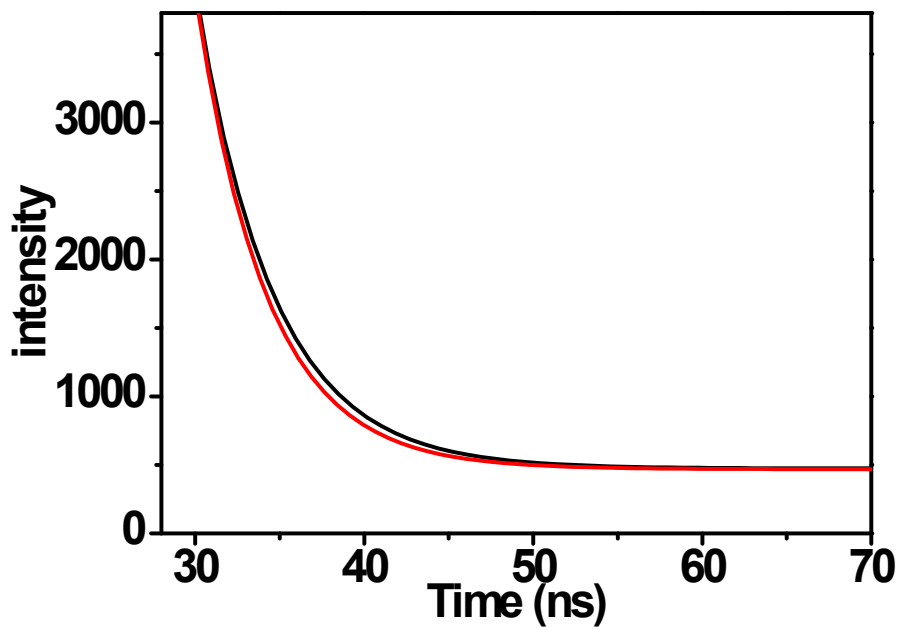
**Figure S23.** Luminescence decay of FI (10.0  $\mu\text{M}$ , black line,  $t=4.53\text{ns}$ ) in EtOH/ H<sub>2</sub>O (1:1, pH = 12.5) and of the aforementioned solution upon addition of Cu-OBP (30.0  $\mu\text{M}$ , red line,  $t = 4.53 \text{ ns}$  ). The intensity was recorded at 520 nm; the excitation wavelength was 472.6 nm.



**Figure S24.** Luminescence decay of FI (10.0  $\mu\text{M}$ , black line,  $t=4.53\text{ns}$ ) in EtOH/ H<sub>2</sub>O (1:1, pH = 12.5) and of the aforementioned solution upon addition of Cu-WBP (30.0  $\mu\text{M}$ , red line,  $t = 4.54 \text{ ns}$  ). The intensity was recorded at 520 nm; the excitation wavelength was 472.6 nm.



**Figure S25.** Luminescence decay of **FI** (10.0  $\mu\text{M}$ , black line,  $t=4.53\text{ns}$ ) in EtOH/  $\text{H}_2\text{O}$  (1:1,  $\text{pH} = 12.5$ ) and of the aforementioned solution upon addition of **Cu-OMP** (90.0  $\mu\text{M}$ , red line,  $t= 4.19 \text{ ns}$  ). The intensity was recorded at 520 nm; the excitation wavelength was 472.6 nm.



## 7. References:

- S1: J. Dong, M. Wang, P. Zhang, S. Yang, J. Liu, X. Li and L. C. Sun, *J. Phys. Chem. C*, 2011, **115**, 15089.
- S2: D. Guo, C. Q. Qian, C. Y. Duan, K. L. Pang and Q. J. Meng, *Inorg. Chem.*, 2003, **42**, 2024.
- S3: S. Zarra, J. K. Clegg, and J. R. Nitschke, *Angew. Chem. Int. Ed.* **2013**, 52, 4837.
- S4: SMART, Data collection software (version 5.629) (Bruker AXS Inc.; Madison, WI, 2003).
- S5: SAINT, Data reduction software (version 6.45) (Bruker AXS Inc.; Madison, WI, 2003).