# **Electronic Supplementary Information**

Multi-component supramolecular gels induce protonation of porphyrin exciplex to achieve

improved collective optical properties for effective photocatalytic hydrogen generation

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## **1. Experimental Section**

## 1.1 Chemicals

Dihydrogen hexachloroplatinate (IV) hexahydrate ( $H_2PtCl_6$ , >99.9%) was purchased from Alfa Aesar and used as received without further treatments. All the other chemicals with analytical reagent grade were purchased from Sinopharm Chemical Reagent Company and used without further purification.

# 1.2 Synthesis

## Synthesis of 5,10,15,20-tetrakis(4-(hydroxyl)phenyl) porphyrin (THPP)

A solution of *p*-acetoxybenzaldehyde (2.26 g, 14 mmol) in propionic acid (50 mL) was brought to a flask, and pyrrole (0.95 mL, 14 mmol) was added. After reflux and stirring for 30 min, the reaction mixture was cooled to room temperature, and the product was collected by filtration. The purple precipitate was washed with propionic acid (25 mL) until the elution became colorless, and dried to give 0.56 g (19%) of H<sub>2</sub>(p-OCOMe)TPP:  $R_f = 0.63$  (2:1 toluene : ethyl acetate).

Porphyrin H<sub>2</sub>(*p*-OCOMe)TPP (0.50 g, 0.59 mmol) was combined with EtOH (1 mL), H<sub>2</sub>O (3 mL), and concentrated HCl (1 mL), and stirred under reflux for 1 h. After cooling to room temperature, the mixture was diluted with H<sub>2</sub>O (25 mL), neutralized with 5% NaOH until the color of the green solution changed into dark red with pH value becoming 7.5. The mixture was stirred vigorously for 1 h, ethyl acetate was added, and the mixture was further stirred for another 1 h. The organic layer was separated, washed twice with water, dried over anhydrous MgSO<sub>4</sub>, and concentrated to give 0.40 g (100%) of THPP:  $R_f = 0.31$  (2:1 toluene : ethyl acetate); <sup>1</sup>H NMR  $\delta$  - 2.89 (s, 2H), 7.20 (d, J = 8.4 Hz, 8H), 8.00 (d, J = 8.4 Hz, 8H), 8.86 (s, 8H), 9.96 (s, 4H); MALDI-TOF obsd 679.2388 (M + H)<sup>+</sup>, calcd 678.2267 (M = C<sub>44</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>).

## Synthesis of 5,10,15,20-tetrakis(4-(carboxyl)phenyl) porphyrin (TCPP)

In a 500 mL three necked flask, methyl *p*-formylbenzoate (6.9 g, 0.042 mol) was dissolved in propionic acid (100 mL). Pyrrole was then added dropwise (3.0 mL, 0.043 mol) and the solution was refluxed for 12 h. After the reaction, the mixture was cooled to room temperature, and the precipitates were collected by suction-filtration and washed with methanol, ethyl acetate and THF, respectively. After being dried in an oven for 12 h, 1.9 g purple solid (2.24 mmol, yield 21%) was obtained as pure product of 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl) porphyrin (TPPCOOMe). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.81 (s, 8H), 8.43 (d, 8H), 8.28 (d, 8H), 4.11 (s, 12H), 2.83 (s, 2H).

TPPCOOMe (0.75 g) was stirred in 50 mL mixture of THF and MeOH (v:v = 1:1), to which a solution of NaOH (2.40 g, 60.00 mmol) in H<sub>2</sub>O (25 mL) was introduced. This mixture was refluxed for 12 h. After cooling to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting aqueous phase and the mixture was heated until the solid was fully dissolved. Then the homogeneous solution was acidified with 1 M HCl until no further precipitate was detected. The precipitate was collected by filtration, washed with water and dried in vacuum oven for obtaining the product of **TCPP**. FT-IR (KBr, cm<sup>-1</sup>): v = 3444 (m), 3034 (w), 2634 (w), 1702 (s), 1614 (s), 1570 (m), 1404 (s), 1311 (m), 1277 (s), 1204 (m), 1180 (m), 1106 (m), 1004 (s), 862 (m), 799 (s), 770 (s), 721 (m). <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  8.86 (s, 8H), 8.38 (d, 8H), 8.34 (d, 8H).

#### Synthesis of N,N'-bis(octadecyl)-L-Boc-glutamic diamide (LBG)

LBG was synthesized by following the procedure of literature.<sup>11a</sup> Boc-glutamic acid (2.47 g, 0.01 mol) and octadecylamine (5.39, 0.02 mol) were mixed in a 250 mL flask and dichloromethane (200 mL) was added. Then 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC·HCl) (4.02 g, 0.022 mol) and 1-hydroxybenzotrizole (HOBt, 2.97 g, 0.022 mol) were added to the mixture, which was stirred at room temperature for 72 hours. The obtained white solid was isolated by filtration and washed three times with dichloromethane. The crude product was dissolved in THF and precipitated by water. A fine white solid was obtained as LBG (6.5 g, 87% yield).

### **1.3 Apparatus and Measurements**

Transmission electron microscopy (TEM) studies were conducted on a TECNAI-G20 electron microscope operating at an accelerating voltage of 200 kV. SEM images were obtained by Hitachi SU8010 scanning electron microscope. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX 400 spectrometer. MALDI-TOF mass spectra were measured on a Bruker Microflex<sup>TM</sup> LRF spectrometer with dithranol as the matrix. XPS was performed on a Thermo ESCALAB 250X Photoelectron Spectrometer. X-ray diffraction (XRD) patterns of the samples were obtained with a Philips diffactometer using Ni-filtered Cu Ka radiation. FT-IR spectra were recorded on a Bruker Tensor 37 spectrometer. UV-vis absorption spectra of the samples were recorded on a TU1810 SPC spectrophotometer. The CD spectra were recorded using JASCO-1500 spectropolarimeter. Fluorescence spectra were recorded using a FL-2500 fluorospectrophotometer with the excitation wavelength of 420nm. The measurement of photoelectrical response was performed with a CHI660B potentiostat/galvanostat electrochemical analyzer. The fluorescence lifetime was recorded on a timeresolved FL spectrometer (FLS980, Edinburgh instruments, UK). The slit width was 2 nm for excitation and emission. A 405 nm laser (EPL) was used as exciting source to measure the fluorescence lifetime. Electrochemical measurements were carried out on a CHI 760E electrochemical workstation (CH Instruments, Inc.).

## **1.4 Procedures**

## Preparation of multi-component supramolecular gels

Experimentally, porphyrins, LBG and solvents were mixed in a capped test tube (for LBG/TCPP/THPP DMF gels, 2mg porphyrins and 10 mg LBG are in 1mL DMF), and the mixture was heated until the solid was dissolved completely. The solution was subsequently cooled to room

temperature. Gelation was determined by the absence of flow of the solvent when the tube was inverted. And the corresponding xerogels were prepared upon vacuum drying.

## Electrochemistry studies and photoelectrical response of porphyrin/LBG assemblies

The working electrode was prepared by covering indium tin oxide (ITO) electrode with porphyrin/LBG assemblies. The LSV (linear sweep voltammetry) curve of LBG/TCPP/THPP assemblies were measured in  $0.1 \text{ M Na}_2\text{SO}_4$  aqueous solution at a scan rate of 0.1 V/s. For measuring LSV of LBH/TCPP/THPP assemblies, the counter electrode is the platinum net, while the reference electrode is saturated calomel electrode (SCE).

The photoelectrical response measurements were performed by using platinum wire as the counter electrode, and Ag/AgCl electrode as the reference electrode. The surface of the working electrode exposed to the electrolyte is a square film with the surface areas of 1 cm<sup>2</sup>. The supporting electrolyte is ascorbic acid (AA) mixed with 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous. The working electrode was irradiated with a GY-10 xenon lamp (150 W) during the measurement.

## Measurements of photocatalytic performances

The photocatalytic reaction was carried out in a 100 mL quartz flask equipped with a flat optical entry window. In a typical photocatalytic experiment, 20 mL of aqueous solution of ascorbic acid (AA, 0.15 M) containing 20  $\mu$ L of H<sub>2</sub>PtCl<sub>6</sub> solution (38.6 mM) and 7.7 or 8.7 mg of dried porphyrin/LBG assemblies (with Mass Ratio equal to THPP/TCPP/LBG=1/1/10) were added into the quartz flask. Before irradiation, the dispersion mixture solution was sonicated about 20 min to obtain a homogeneous suspension. The system was vacuumed for 20 min, then irradiated for 1 h to achieve reduction of platinum. The system was further vacuumed for another 10 min. Next, the solution was

irradiated by a Xenon lamp with UV-vis 420 cut (output 440-780nm, 19.63 mw•cm<sup>-2</sup>) under continuous stirring. The distance between the liquid level and the lamp was maintained at 15 cm. The hydrogen evolution was detected using an online gas chromatograph (GC1650) equipped with a thermal conductivity detector (TCD), where nitrogen was used as a carrier gas. The concentration of  $H_2$  was counted by standard curve of  $H_2$ . The yield of hydrogen was defined as the moles of  $H_2$  (n) evolved over per milligram of used porphyrin catalyst (m) in a certain reaction time (t).

$$yield(H_2) = \frac{n_{H2}}{m_{catalyst}}$$

# Calculation of theoretical solar spectrum efficiency

The theoretical spectral efficiency of LBG/TCPP/THPP DMF gels was calculated by comparing the wavelength range of the the UV-vis spectra of LBG/TCPP/THPP DMF gels with that of solar spectrum.<sup>6e</sup>

 $The rotical \ spectrum \ efficiency = \frac{Absorption \ range}{Measured \ solar \ spectrum \ range} = \frac{750 - 300 \ nm}{1200 - 300 \ nm} = 50\%$ 



Fig. S1. Photographs of THPP/LBG gels and TCPP/LBG gels formed in DMF or ethanol.



Fig. S2. UV-Vis spectra of LBG/TCPP/THPP DMF gels with high concentration of porphyrins.



Fig. S3. UV-Vis spectra of LBG/TCPP/THPP DMF gels with varied ratios of TCPP and THPP.



**Fig. S4.** UV-Vis spectra of TCPP and THPP in DMF solution (a), LBG/TCPP and LBG/THPP DMF gels (b).



**Fig. S5.** a) UV-Vis spectra of LBG/TCPP DMF gels and LBG/TCPP DMF gels (10mg LBG and 2mg porphyrin in 1ml DMF) upon treated with 0.1mol/L TFA (trifluoroacetic acid). b, c) UV-Vis spectra of LBG/TCPP DMF gels containing TFA with different concentrations.



Fig. S6. O 1s region XPS of xerogels from LBG/TCPP/THPP DMF gels.



**Fig. S7.** a) TEM images of pure LBG gels formed in DMF. b, c) SEM (b) and TEM (c) images of TCPP/LBG gels formed in DMF. d, e) SEM (d) and TEM (e) images of THPP/LBG gels formed in DMF.



Fig. S8. SEM images of LBG/TCPP/THPP DMF gels with varied the ratios of TCPP and THPP.



**Fig. S9.** UV-Vis spectra of TCPP and THPP in ethanol solution (a), LBG/TCPP and LBG/THPP ethanol gels (b).



**Fig. S10**. a) SEM image of pure LBG/TCPP/THPP ethanol gels. b, c) SEM (b) and TEM (c) images of TCPP/LBG gels formed in ethanol. d, e) SEM (d) and TEM (e) images of THPP/LBG gels formed in ethanol.



**Fig. S11.** FT-IR spectra of LBG (black), TCPP (red), deprotonated TCPP (TCPP treated by triethylamine (TEA), yellow) THPP (blue), xerogel of LBG/TCPP/THPP DMF gels (pink), xerogel of LBG/TCPP/THPP DMF gels with high concentrations of porphyrin (green).



Fig. S12. a) XRD pattern of different multi-component supramolecular gels. b) Possible staking model of LBG.



Fig. S13. CD spectra of different multi-component supramolecular gels formed in DMF (a) and ethanol (b).



Fig. S14. Fluorescence spectra of TCPP, THPP and TCPP/THPP mixture in ethanol solution.



**Fig. S15.** Linear sweep voltammetry of LBG/TCPP/THPP assemblies, which were prepared in DMF(a) or ethanol(b). Measured in 0.1 M  $Na_2SO_4$  aqueous at a scan rate of 0.1V/s, with platinum net working as the counter electrode, and saturated calomel electrode (SCE) working as the reference electrode.



Fig. S16. Transient fluorescence lifetime of TCPP and THPP in different solutions and gels.



**Fig. S17.** SEM images of LBG/TCPP/THPP assemblies formed in DMF containing Pt nanoparticles before photocatalytic experiments.



**Fig. S18.** Hydrogen evolution photocatalyzed by LBG/TCPP DMF gels and LBG/TCPP/THPP DMF gels. The sacrificial reagents for LBG/TCPP/THPP DMF gels systems can be TEOA (triethanolamine) or ascorbic acid.



**Fig. S19.** SEM images of LBG/TCPP/THPP assemblies containing Pt nanoparticles after photocatalytic experiments. a) TCPP/THPP/LBG/Pt formed in DMF; b) TCPP/THPP/LBG/Pt formed in ethanol.

Sample	$ au_1$	$\tau_2$	$B_1$	B <sub>2</sub>	$\frac{-}{\tau}$	$\chi^2$	
TCPP/THPP							
/Pt(in LBG	1.82		1		1.82	1.140	
DMF Gel)							
TCPP/THPP							
/Pt(in LBG	1.02	10.80	0.0816	0.9184	10.003	1.118	
Ethanol Gel)							
TCPP(in DMF	0.67		1		0.67	1 272	
Sol)	9.07		1		9.07	1.272	
TCPP(in	2 00		1		2.00	1 20/	
Ethanol Sol)	2.99	I		2.33		1.504	
TCPP(in LBG	11.26		1		11.26	1.050	
DMF Gel)	11.20		1		11.20	1.039	
TCPP(in LBG	10.47		1		10.47	1 106	
Ethanol Gel)	10.47		1		10.47	1.100	
THPP(in DMF	0.21		1		0.21	0.020	
Sol)	9.31		I		9.51	0.929	
THPP(in	8 74		1		Q 71	1 261	
Ethanol Sol)	8./4		1		0.77	1.201	
THPP(in LBG	9 10		1		9 10	0 006	
DMF Gel)	7.17	1			2.12	0.900	
THPP(in LBG	8.82		1		8.82	1.087	

Table S1. The FL lifetime of different assemblies.

Ethanol Gel)				
TCPP/THPP(in	8 <u>7</u> 2	1	8 <u>7</u> 2	1.052
DMF Sol)	8.23	1	6.25	1.032
TCPP/THPP(in	o <b>วว</b>	1	° 22	1 221
Ethanol Sol)	0.22	1	0.22	1.231
TCPP/THPP(in				
LBG DMF	10.44	1	10.44	1.020
Gel)				
TCPP/THPP(in				
LBG Ethanol	10.72	1	10.72	1.097
Gel)				

The data was fitted with using multiple exponential formulas (1). And the average decay time  $\tau$  was calculated by the formula (2).

 $R(t) = B_1 e^{\frac{-t}{\tau_1}} + B_2 e^{\frac{-t}{\tau_2}} + B_3 e^{\frac{-t}{\tau_3}} \cdots \cdots (1)$  $\bar{\tau} = \frac{B_1 \times \tau_1^2 + B_2 \times \tau_2^2 + B_3 \times \tau_3^2}{B_1 \times \tau_1 + B_2 \times \tau_2 + B_3 \times \tau_3} \cdots \cdots (2)$ 

Resources	Catalysts	H <sub>2</sub> evolved (mmol h <sup>-1</sup> g <sup>-1</sup> )	Sacrificial agents	Light source
Ref. 1	TPPH-RGO/Pt	1.06	TEOA	Xe lamp
Ref. 2	GO-Sm-DPDPP	0.55	TEOA	Xe lamp
Ref. 3	TiO <sub>2</sub> MS-Cu-TCPP	1.33	TEOA	Xe lamp
Ref. 4	HNTM-Ir/Pt	0.20	TEOA	Xe lamp
				(λ>400 nm)
Ref. 5	THPP NR/Pt	14.6	AA	Xe lamp
				(λ>420 nm)
Our result	LBG/TCPP/THPP/Pt	1.3	AA	Xe lamp
				(λ>420 nm)

 Table S2. Comparison of photocatalytic hydrogen generation with different porphyrin-based

 systems.

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