Supporting information

Quinacridone-pyridine dicarboxylic acid based donor-acceptor supramolecular nanobelts for significantly enhanced photocatalytic hydrogen production

Mengyu Xu^a, Kangyi Kong^a, Haoran Ding^a, Yanmeng Chu^b, Shicong Zhang^a, Fengtao Yu^a, Haonan Ye^a, Yue Hu^b and Jianli Hua^{*a}

^a Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China ^bMichael Grätzel Center for Mesoscopic Solar Cells, Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, Hubei, PR China.

* Corresponding author. Tel.: +86 21 64250940; fax.: +86 21 64252758.E-mail address: jlhua@ecust.edu.cn (J. Hua)

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1. Experimental Section

1.1 Preparation of QAP-C4 and QAP-C8 molecule

Synthesis of compound QAP-C4 and QAP-C8



Scheme S1. Synthetic route of QAP-C4 and QAP-C8.

Synthesis of compound 1

4-chloro-pyridine-2, 6-dicarboxylic (2 g, 10 mmol), isopropanol 100 mL were added into a two-necked flask and stirred in an ice bath for 10 min, then the SOCl₂(1.78g, 15mmol) was added into the two-necked flask. After that, the mixture was heated to reflux temperature for 5h. After cooling to room temperature, remove the solvent, extract with H₂O, DCM, then purify by column chromatography to get the white solid 1 (dichloromethane). Yield: 2.4 g (85%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 2H), 5.32 (m, 2H), 1.43 (d, *J* = 6.3 Hz, 12H). ¹³C NMR (101 MHz, Chloroform-d) δ 163.03, 150.19, 127.80, 77.33, 70.63, 21.78 . *m/z* HRMS (ESI) calculated for [M+Na]⁺: 308.0666; found 308.0645.

Synthesis of compound 2

1 (2.4 g, 8.5 mmol) was dissolved in acetonitrile, NaI (7.65 g, 51 mmol) was added with stirring, and then acetyl chloride (80 mL) was added, and the mixture was heated under reflux for 8 h. After the reaction mixture was cooled to room temperature, the mixture was filtered under reduced pressure, and the filtrate was washed with ethyl acetate. The filtrate was collected, and the aqueous K_2CO_3 and Na_2SO_4 solution was dropped to the filtrate to be clarified, and extracted with H_2O and EA. The crude product was purified by column chromatography (dichloromethane) to yield white solid. Yield: 2.54 g (80%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 2H), 5.31 (m, 2H), 1.43 (d, *J* = 6.3 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 162.81, 149.11, 136.63, 127.83, 106.71, 70.63, 29.70, 21.79. *m/z* HRMS (ESI) calculated for [M+H]⁺: 400.0022; found 400.0035.

Synthesis of compound 3a

Quinacridone (1.56 g, 5 mmol), sodium hydroxide (4 g, 0.1mol) and tetrabutylammonium bromide (0.33 g, 1mmol) were dissolved in DMSO (30 mL) and stirred at room temperature for 2 h, 1-iodobutane (5.5 g, 30 mmol) was added under nitrogen atmosphere. The resulting mixture was reacted at 80 °C for 6 h. After cooling to room temperature, it was poured into 200 mL of water and filtered under reduced pressure. And then put it in a vacuum oven for drying. The crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane=1/1) to get the orange solid 3. Yield:1.50 g (75%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.78 (s, 2H),

8.57 (dd, J = 8.0, 1.6 Hz, 2H), 7.76 (ddd, J = 8.7, 6.9, 1.7 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 7.4 Hz, 2H), 4.56 – 4.50 (m, 4H), 2.01 (m, 4H), 1.71 – 1.63 (m, 4H), 1.12 (t, J = 7.4 Hz, 6 H). ¹³C NMR (101 MHz, CDCl₃) δ 178.08, 142.18, 135.62, 134.55, 128.00, 126.18, 120.78, 114.58, 113.43, 46.10, 29.11, 20.27, 13.93. m/z HRMS (ESI) calculated for [M+H]⁺: 425.2229; found 425.2233.¹

Synthesis of compound 3b

The synthetic method resembled that of compound 3a, and the compound was purified by column chromatography on silica gel (petroleum ether / dichloromethane = 3/1) to give an orange solid (1.9 g, yield 70%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 2H), 8.60 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.78 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 4.57 – 4.49 (m, 4H), 2.01 (q, *J* = 8.6 Hz, 4H), 1.63 (dd, *J* = 10.6, 4.8 Hz, 4H), 1.52 – 1.41 (m, 4H), 1.36 – 1.29 (m, 12H), 0.92 – 0.88 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 178.03, 142.13, 135.56, 134.50, 127.97, 126.15, 120.99, 120.74, 114.57, 113.40, 77.35, 77.24, 77.03, 76.72, 46.35, 31.81, 29.44, 29.34, 27.13, 27.05, 22.67, 14.12. *m/z* HRMS (ESI) calculated for [M+H]⁺: 537.3481; found 537.3480.

Synthesis of compound 4a

3a (424 mg, 1mmol), N-bromosuccinimide (NBS) (1.1g, 6mmol) were placed in a 25 mL Schlenk tube and 10 mL DMF was added under nitrogen. The resulting mixture was heated to 60 °C and reacted in a dark environment for 8 h. After cooling to room temperature, the solvent was removed and the crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane=2/1) to get the orange solid 4a.^{1, 2}Yield: 407 mg (70%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 2H), 8.59 (d, *J* = 2.5 Hz, 2H), 7.79 (dd, *J* = 9.2, 2.6 Hz, 2H), 7.38 (d, *J* = 9.3 Hz, 2H), 4.51 – 4.44

(m, 4H), 1.99 – 1.91 (m, 4H), 1.68 – 1.61 (m, 4H), 1.11 (t, J = 7.4 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 177.27, 140.82, 137.35, 135.45, 130.20, 126.03, 122.02, 116.73, 113.74, 29.58, 20.21, 13.90. *m/z* HRMS (ESI) calculated for [M+H]⁺: 581.0439; found 581.0435.

Synthesis of compound 4b

The synthetic method resembled that of compound 4a, and the compound was purified by column chromatography on silica gel (petroleum ether /

dichloromethane=4/1) to give an orange solid (520 mg, yield 77%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 2H), 8.44 (d, *J* = 2.5 Hz, 2H), 7.71 (dd, *J* = 9.2, 2.5 Hz, 2H), 7.28 (d, *J* = 2.1 Hz, 2H), 4.43 – 4.34 (m, 4H), 1.89 (m, 4H), 1.60 (m, 4H), 1.48 – 1.41 (m, 4H),

1.39 – 1.31 (m, 12H), 0.94 – 0.90 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 176.33, 140.48,

137.14, 135.03, 129.95, 125.61, 121.62, 116.68, 114.02, 113.49, 31.79, 29.29, 26.98, 22.66, 14.12. *m/z* HRMS (ESI) calculated for [M+H]⁺: 693.1691; found 693.1685.

Synthesis of compound 5a

4a (582 mg, 1mmol), bis (pinacolato)diboron (1.27 g, 5 mmol), potassium acetate (600 mg, 6 mmol), [1,1'-bis (dihenylphosphino) ferrocene] palladium(II) chloride (280 mg, 0.4 mmol) were dissolved in 1,4-Dioxane (15 mL) in a 50 mL Schlenk tube under the nitrogen environment. The mixture was heated to 100 °C for 8 h. After cooling to room temperature, the solvent was removed and the crude product was extracted with water and dichloromethane. And it was purified by silica gel column chromatography (petroleum ether/dichloromethane=1/1) to get the light orange solid 5a.³ Yield:486 mg (72%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.07 (d, *J* = 1.6 Hz, 2H), 8.81 (s, 2H), 8.13 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 4.58 – 4.52 (m, 4H), 2.01 (d, *J* = 6.5 Hz, 4H), 1.69 – 1.64 (m, 4H), 1.38 (s, 24H), 1.11 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 177.96, 143.83, 139.91, 135.61, 126.48, 120.36, 113.74, 83.91, 29.06, 24.95, 20.19, 13.91. *m/z* HRMS (ESI) calculated for [M+H]⁺: 677.3933; found 677.3940.

Synthesis of compound 5b

The synthetic method resembled that of compound 5a, and the compound was purified by column chromatography on silica gel (petroleum ether / dichloromethane=2/1) to give an orange solid (512 mg, yield 65%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.05 (d, *J* = 1.6 Hz, 2H), 8.78 (s, 2H), 8.12 (dd, *J* = 8.7, 1.6 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 4.56 – 4.50 (m, 4H), 2.03 – 1.95 (m, 4H), 1.65 – 1.60 (m, 4H), 1.50 – 1.44 (m, 4H), 1.39 (s, 24H), 1.34 – 1.25 (m, 12H), 0.92 – 0.88 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 177.99, 143.90, 139.95, 136.01, 135.69, 126.59, 120.44, 113.76, 83.91, 31.80, 29.40, 29.28, 27.09, 26.97, 24.94, 22.65, 14.12. *m/z* HRMS (ESI) calculated for [M+H]⁺: 789.5195; found 789.5185.

Synthesis of compound 6a

5a (676 mg, 1 mmol), 2 (935 mg, 2.5 mmol), [1,1'-bis (dihenylphosphino) ferrocene] palladium(II) chloride (150 mg, 0.2 mmol) were added into THF (40 mL) and heated to 50 °C, then added potassium phosphate aqueous solution (1 g potassium phosphate dissolved in 5 mL water). After stirred for 5 minutes, it was heated to 70 °C for 4 h. After cooling to room temperature, the solvent was removed and the crude product was extracted with water and dichloromethane. And it was purified by silica gel column chromatography (dichloromethane/ ethyl acetate = 40/1) to get the light purple solid 6a. Yield:553 mg (60%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 2.4 Hz, 2H), 8.89 (s, 2H), 8.59 (s, 4H), 8.21 (dd, *J* = 9.1, 2.4 Hz, 2H), 7.75 (d, *J* = 9.2 Hz, 2H), 5.43 – 5.36 (m, 4H), 4.68 – 4.60 (m, 4H), 2.13 – 2.04 (m, 4H), 1.77 – 1.70 (m, 4H), 1.49 (d, *J* = 6.3 Hz, 24H), 1.17 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 177.96, 143.83, 139.91, 135.61, 126.48, 120.36, 113.74, 83.91, 29.06, 24.95, 20.19, 13.91. *m/z* HRMS (ESI) calculated for [M+H]⁺: 945.4051; found 945.4055.

Synthesis of compound 6b

The synthetic method resembled that of compound 6a, and the compound was purified by column chromatography on silica gel (dichloromethane/ ethyl acetate =50/1) to give an orange solid (692 mg, yield 67%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 2.4 Hz, 2H), 8.87 (s, 2H), 8.59 (s, 4H), 8.20 (dd, *J* = 9.1, 2.4 Hz, 2H), 7.74 (d, *J* = 9.2 Hz, 2H), 5.45 – 5.35 (m, 4H), 4.67 – 4.57 (m, 4H), 2.12 – 2.03 (m, 4H), 1.73 – 1.65 (m, 8H), 1.49 (d, *J* = 6.3 Hz, 24H), 1.38 – 1.29 (m, 12H), 0.91 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 177.85, 164.24, 149.79, 149.10, 142.97, 135.92, 128.80, 126.92, 126.61, 124.64, 121.35, 116.13, 114.16, 70.36, 31.79, 29.31, 27.05, 22.66, 21.89, 14.12. *m/z* HRMS (ESI) calculated for [M+H]⁺: 1057.5303; found 1057.5305.

Synthesis of compound QAP-C4

6a (530 mg, 0.57mmol), 5 mL aqueous solution of sodium hydroxide (456 mg, 11.4 mmol) were added into ethanol (30 mL). The mixture was heated to 100 °C for 20 h. After cooling to the room temperature, the solvent was removed. Then added 2 mL

dilute hydrochloric acid aqueous solution dropwise to adjust to pH=2~3. The mixture was centrifuged and dried in a vacuum oven at 50 °C to get the purple solid QAP-C4. Yield: 380 mg (90%).

The synthetic route of **QAP-C8** is the same as that of **QAP-C4**. Yield: 796 mg (92%).

Self-assembled supramolecule QAP-C4 and QAP-C8

Self-assembled supramolecule QAP-C4 and QAP-C8 were prepared through an acidbase neutralization reaction. Firstly, above product was dispersed in 300 mL deionized water, and it would dissolve in water by dropping 1M TEOA solution (0.5 mL) until the pH = 8. After the solid was dissolved, the filtrate was precipitated by adding 2M HCl solution (1 mL) until pH = 5 then self-assembled QAP-C4 (SQAP-C4) was formed. After that the purple solid can get by centrifugation to remove the salt dissolved in the acid water. The collected solid was dried in oven at 50 °C overnight for further application.

1.2 Pt loaded 100 mg of the photocatalyst was dispersed in a mixed solution of 100 mL of water and 25 mL of methanol, and then a calculated amount of H_2PtCl_6 was added. Then the mixture was irradiated by a 300W xenon lamp (CEL-HXF300F3, Beijing ceaulight, China) for 5h.

2. Testing section

2.1 Instruments

A Brücker AM 400 spectrometer was employed to obtain ¹H NMR spectra with TMS as the internal standard. The crystal structure of the prepared photocatalysts were characterized by using a powder X-ray diffraction (XRD) system (D/max2550VB/PC, Cu Kα radiation). DRS UV–vis absorption spectra were recorded at room temperature on a Varian Cary 500 spectrophotometer. The FTIR spectra were recorded on NICOLET 380 spectrometer using a standard KBr pellet technique in the frequency range of 4000–400 cm⁻¹. The morphology of the photocatalysts was characterized with a scanning electron microscope (SEM, FE-SEM, GeminiSEM 500). TEM and HRTEM images were taken on a transmission electron microscope (TEM, JEM-2100). AFM images were taken on an atomic force microscope (AFM, Veeco/DI). Raman spectra were measured on the microscopic confocal Raman spectrometer (invia reflex) with an excitation of 514 nm laser light. The Photoluminescence (PL) spectrums were obtained on a Hitachi F-4500 fluorescence spectrophotometer at room temperature with an excitation wavelength of 550 nm.

2.2 Photoelectrochemical Measurement

Cyclic voltammetry (CV) curves were measured by a CHI650E electrochemical workstation in a normal three-electrode cell which using films electrodes as the working electrode, Pt plate as counter electrode and Ag/AgCl electrode as the reference electrode. The experiments were carried out in THF solutions with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 0.05V s⁻¹. The ferrocenium/ferrocene (Fc/Fc+) redox couple was used as an external potential reference (20 mg ferrocene was dissolved in 100 mL of electrolyte). The transient photocurrent responses (I–t) and electrochemical impedance spectra (EIS) of composite photocatalyst samples were investigated on a CHI650E electrochemical workstation with a three-electrode (films electrodes, Pt plate, and Ag/AgCl as working, counter, and reference electrode, respectively) system. A THF solution of 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) was used as the supporting electrolyte and a 300 W Xe-lamp served as the light source. The films electrodes were prepared as follows:

30 mg SQAP-C4/SQAP-C8 was uniformly ground, 20 μ L of Nafon (5%) and 50 u L of ethanol were added, and the milling was continued to form a slurry, and the slurry was uniformly spread onto ITO glass electrodes with an active area of 0.25 cm². and these electrolytes were dried at 120 °C for 1 h to evaporate the solvent in muffle furnace. The photocurrent intensity of as-prepared electrodes was measured at 0.3 V versus Ag/AgCl with the light on and off. EIS was determined over the frequency range of 10^2 – 10^6 Hz with an ac amplitude of 10 mV at the open circuit voltage under room-light illumination.

2.3 Hydrogen Production Test

The photocatalytic H₂ production reaction was carried out on the CEL-SPH2N. Usually, 30mg photocatalyst powders were dispersed in the in 50 mL (containing 3 g ascorbic acid (AA)) aqueous. The light source was a 300W xenon lamp (CEL-HXF 300). Then sealed with rubber diaphragm air. Before light irradiation, the dissolved air must be thoroughly removed by vacuum pump. And then the aqueous suspension was irradiated from the top using a 300 W xenon lamp jointing a cutoff filter to obtain visible-light irradiation (400 nm < λ < 780 nm). The reaction mixture was kept under constant stirring using a magnetic stirring bar during irradiation and the amount of H₂ gas was detected with the gas phase were determined by an online gas chromatograph (GC 2060, TCD detector, and Ar carrier).



3. Atomic force micrograph (AFM) of supramoleculars

Fig. S1 Atomic force micrograph (AFM) of SQAP-C4.



Fig. S2 Atomic force micrograph (AFM) of SQAP-C8.

Table S1. Vert distance of **SQAP-C4** and **SQAP-C8**

Vert distance	(a)	(b)	(c)	(d)	
SQAP-C4	36.8 nm	32.0 nm	37.5 nm	36.7 nm	
SQAP-C8	54.2 nm	56.5 nm	57.3 nm	58.5 nm	

4. The UV-vis absorption spectroscopy of compound 3a and QAP-C4



Fig. S3 UV-vis absorption spectroscopy of compound 3a in DMSO and QAP-C4 in DMSO and DMSO/water mixtures with different water fractions (f_w (vol%)).



5. The UV-vis absorption spectroscopy of compound 3b and QAP-C8

Fig. S4 UV-vis absorption spectroscopy of compound 3b in DMSO and QAP-C8 in DMSO and DMSO/water mixtures with different water fractions (f_w (vol%)).



6. Fourier transform infrared spectra of supramolecular

Fig. S5 Fourier transform infrared (FT-IR) spectra of 6a, QAP-C4 and SQAP-C4.



Fig. S6 Fourier transform infrared (FT-IR) spectra of 6b, QAP-C8 and SQAP-C8.

Table S2. IR peaks in the 6a, QAP-C4 , SQAP-C4, 6b, QAP-C8, SQAP-C8					
	C-H stretch	C=O stretch	C=N stretch	C-N stretch	
6а	2927cm ⁻¹	1710cm ⁻¹ ,1743cm ⁻¹	1633cm ⁻¹	1270cm ⁻¹	
QAP-C4	2919cm ⁻¹	1724cm ⁻¹	1625cm ⁻¹	1288cm ⁻¹	
SQAP-C4	2931cm ⁻¹	1725cm ⁻¹	1630cm ⁻¹	1292cm ⁻¹	
6b	2925cm ⁻¹	1710cm ⁻¹ ,1743cm ⁻¹	1633cm ⁻¹	1274cm ⁻¹	
QAP-C8	2921cm ⁻¹	1720cm ⁻¹	1627cm ⁻¹	1284cm ⁻¹	
SQAP-C8	2923cm ⁻¹	1726cm ⁻¹	1631cm ⁻¹	1288cm ⁻¹	



7. The X-ray diffraction (XRD) of supramoleculars and precursors

Fig. S7 X-ray diffraction (XRD) spectra of QAP-C4 and SQAP-C4.



Fig. S8 X-ray diffraction (XRD) spectra of QAP-C8 and SQAP-C8.

8. Cyclic voltammograms curves of supramolecular and ferrocene/ferrocenium

(Fc/Fc+) redox couple



Fig. S9 Cyclic voltammograms curves of SQAP-C4 and SQAP-C8.



Fig. S10 Cyclic voltammograms curves of ferrocene/ferrocenium (Fc/Fc+) redox couple. The energy levels of the highest occupied molecular orbital (HOMO) of the selfassembled supramolecular were determined by oxidative half cyclic voltammetry in THF (Fig. S5). Ferrocene/ferrocenium (Fc/Fc⁺) wasused as an internal reference and 0.1 M tetra-nbutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte (Fig. S6). The HOMO levels of SQAP-C4 and SQAP-C8 were located at 1.13 V and 1.27 V vs NHE, respectively, upon the basis of the following relationship

$$E_V vs.vacuum = -(E^{onset} - E_V vs.Fc/_{Fc}^{+} + 4.8 eV)$$

9. Diagram of molecular dipoles and electrons distribution





10. Photocurrent-time curves on supramolecular membrane electodes



Fig. S11 Photocurrent-time (I-t) curves on SQAP-C4 and SQAP-C8 membrane electrodes (0.3 bias).

11. EIS Nyquist plots of supramolecular



Fig. S12 EIS Nyquist plots of SQAP-C4 and SQAP-C8 at open circuit voltage.

12. Photoluminescence spectra of supramolecular



Fig. S13 Photoluminescence (PL) spectra of the SQAP-C4 and SQAP-C8.

13. TEM images of SQAP-C4/Pt



Fig. S14 TEM images of SQAP-C4/Pt.



14. Time-dependent photocatalytic hydrogen evolution over QAP-C4 and QAP-C8.

2 Time (h) Fig. S15 Time-dependent photocatalytic hydrogen evolution over QAP-C4 and QAP-C8.

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15. The X-ray diffraction (XRD) of supramoleculars and recycled catalyst.

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Fig. S16 XRD patterns of SQP-C4 and RSQAP-C4 (a); SQAP-C8 and RSQAP-C8 (b).

16. Fourier transform infrared spectra of supramoleculars and recycled catalyst



Fig. S17 Fourier transform infrared (FT-IR) spectra of SQAP-C4 and RSQAP-C4 (a); SQAP-C8 and RSQAP-C8.

17. Raman spectra of supramoleculars and recycled catalyst



Fig. S18 Raman spectra of SQAP-C4, SQAP-C8, RSQAP-C4 and RSQAP-C8 powder.

18. The reported work previously

Photocatalyst	Light Iradiation	Hydrogen Evolution Reaction (HER)	Sacrificial agents	Cocatalyst	Ref.
PTCDI/Pt/TiO ₂	λ ≥ 420 nm	0.075 μmol g ⁻¹ h ⁻¹	TEOA	H2PtCl6 0.5wt%	4
PTCDI-1/Pt/g- C3N4	λ ≥ 420 nm	0.375 μmol g ⁻¹ h ⁻¹	TEOA	H2PtCl6 0.5wt%	5
PBI-F/PVP-Pt	λ ≥ 300 nm	0.815 μmol g ⁻¹ h ⁻¹	Methanol	H2PtCl6	6
SA-TCPP	λ ≥ 420 nm	40.8 µmol g ⁻¹ h ⁻¹	TEOA	-	7
SA-TCPP	λ ≥ 420 nm	70.5 μmol g ⁻¹ h ⁻¹	TEOA	H2PtCl6 5wt%	7
PorFN-Pt	λ ≥ 420 nm	200 μmol g ⁻¹ h ⁻¹	ΤΕΟΑ	H2PtCl6 3wt%	8
ANP	λ ≥ 420 nm	2 μmol g ⁻¹ h ⁻¹	DA	-	9
NSs	λ ≥ 420 nm	352 μmol g ⁻¹ h ⁻¹	OA	H2PtCl6 1wt%	10
P-CMPDI	λ ≥ 400 nm	0.83 mmol g ⁻¹ h ⁻¹	AA	H2PtCl6 3wt%	11
P-PMPDI	λ ≥ 400 nm	11.7 mmol g ⁻¹ h ⁻¹	AA	H2PtCl6 3wt%	11
SQAP-C4	λ ≥ 400 nm	656 μmol g ⁻¹ h ⁻¹	AA	-	This work

Table S4. Comparison of the photocatalytic activity among supramolecular systems.

SQAP-C4	λ ≥ 400 nm	1.93 mmol g ⁻¹ h ⁻¹	AA	H ₂ PtCl ₆	This work
				1wt%	

19. Reference

- 1. M. Akita, I. Osaka and K. Takimiya, *Materials* 2013, **6**, 1061[1071.
- H.-J. Song, D.-H. Kim, E.-J. Lee, S.-W. Heo, J.-Y. Lee and D.-K. Moon, *Macromolecules*, 2012, 45, 781507822.
- 3. J. Jia, T. Li, Y. Cui, Y. Li, W. Wang, L. Han, Y. Li and J. Gao, *Dyes Pigment*, 2019, **162**, 26^[]35.
- 4. S. Chen, Y. Li and C. Wang, *RSC Adv.*, 2015, **5**, 15880 15885.
- 5. S. Chen, C. Wang, B. R. Bunes, Y. Li, C. Wang and L. Zang, *Appl. Catal. A-Gen.*, 2015, **498**, 63¹68.
- M. C. Nolan, J. J. Walsh, L. L. E. Mears, E. R. Draper, M. Wallace, M. Barrow, B. Dietrich, S. M. King, A. J. Cowan and D. J. Adams, *J. Mater. Chem.*, 2017, 5, 755507563.
- 7. Z. Zhang, Y. Zhu, X. Chen, H. Zhang and J. Wang, *Adv. Mater.*, 2019, **31**, e1806626.
- X. Yang, Z. Hu, Q. Yin, C. Shu, X. F. Jiang, J. Zhang, X. Wang, J. X. Jiang, F. Huang and Y. Cao, *Adv. Funct. Mater.*, 2019, 29, 1808156.
- K. Nath, M. Chandra, D. Pradhan and K. Biradha, ACS Appl. Mater. Interfaces, 2018, 10, 29417
 29424.
- 10. G.-Q. Zhang, W. Ou and Y.-S. Xu, *Sci. China-Mater.*, 2018, **61**, 1001 1006.
- 11. K. Kong, S. Zhang, Y. Chu, Y. Hu, F. and J. Hua, *Chem. Comm.*, 2019, **55**, 8090[[8093.