Electronic Supplementary Information (ESI) for ***Journal of Materials Chemistry A***
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# Exfoliated conjugated porous polymers nanosheets for highly efficient photocatalytic hydrogen evolution

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Solid state magic angle spinning $^{13}C$ CP/MAS NMR measurement was carried out on a Bruker Avance 400 model 400 MHz NMR spectrometer at a MAS rate of 10 kHz. FT-IR spectrum was measured on a FT-IR spectrometer (Bruker, ALPHA) in transmission mode at room temperature. Morphology of CPPs was obtained by a field emission scanning electron microscope (SEM, MLA650F, American). The samples were dispersed in MeOH and NMP by ultrasonic for 30 min and then deposited on the copper network. After vacuum drying, its morphology was characterized by transmission electron microscopy (TEM, Tecnai G2-20, American). The ultrathin sheets of **B-B**, **B-T**, **Py-B**, **Py-T, Py-Tt** and **Py-Ttt** obtained by ultrasonication in NMP deposited on the mica sheets, and thickness of the solvent-exfoliated CPPs were characterized by a Bruker Multimode 8 atomic force microscope (AFM) under Scan Asyst mode (Bruker, USA). Specific surface areas were determined by a Tristar II 3020 (Micromeritics, Norcross, Georgia) with nitrogen as analytical gas. Samples were degassed under vacuum at ambient temperature for 24 h. The volume of nitrogen adsorption was recorded over a relative pressure range between 0.05 and 0.995. 28 points in the relative pressure range of 0.05–0.995 were used for the calculation of the surface area according to the Brunauer-Emmet-Teller (BET) theory.

UV-vis diffuse reflectance spectra were carried out on UV-2600 scanning UV-vis spectrophotometer. Time-resolved fluorescence spectroscopy and photoluminescence (PL) spectra were obtained on HORIBA Instruments FL-1000 fluorescence spectrometer. Cyclic voltammetry (CV) measurement was carried out on a CHI660E (Chenhua, Shanghai) electrochemical workstation in a three electrode-cell system: $Ag/Ag^+$ work as the reference electrodes, glassy carbon electrodes as the working electrode, t platinum wire work as the counter electrode. The tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$, 1.5 g) dissolved in 5 mL acetonitrile was used as the electrolyte solution. The electrochemical workstation was taken with a s can rate of 100 mV $s^{-1}$ in the range of –2.5 V to 2.5 V and two times. Before the electrochemical test, CPP (2 mg) was dispersed in ethanol and then pipet 5 μL of the mixed solution onto the working electrode. After the ethanol was air-dried, 5 μL of chitosan was added to deposit the sample on the electrode.

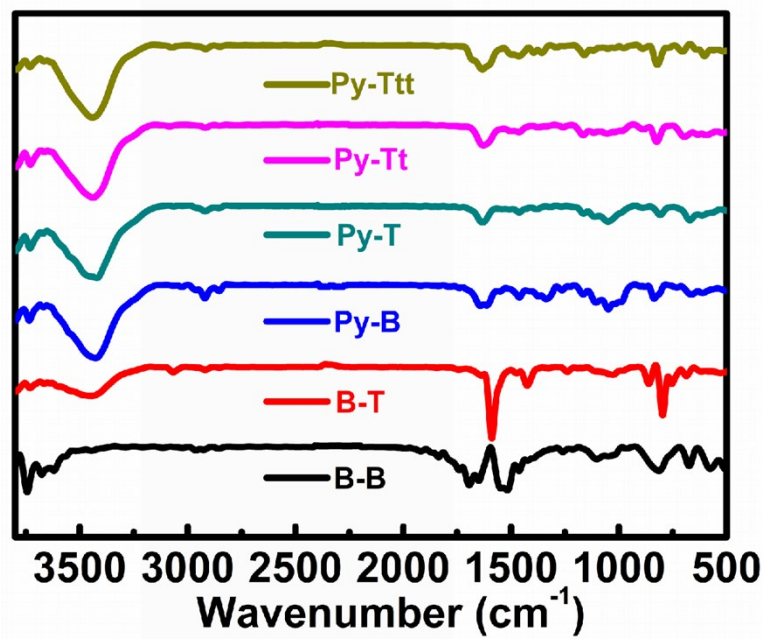


Fig. S1 FT-IR spectra of as-prepared **B-B**, **B-T, Py-B, Py-T**, **Py-Tt** and **Py-Ttt**.

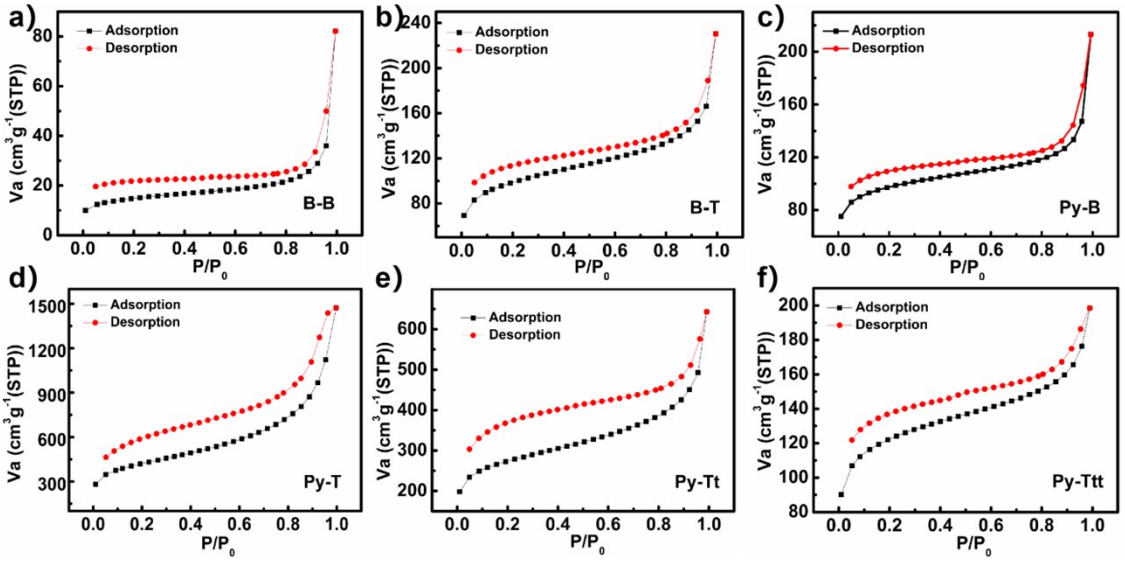


Fig. S2 $N_2$ adsorption-desorption isotherms of **B-B**, **B-T, Py-B**, **Py-T**, **Py-Tt** and **Py-Ttt**.

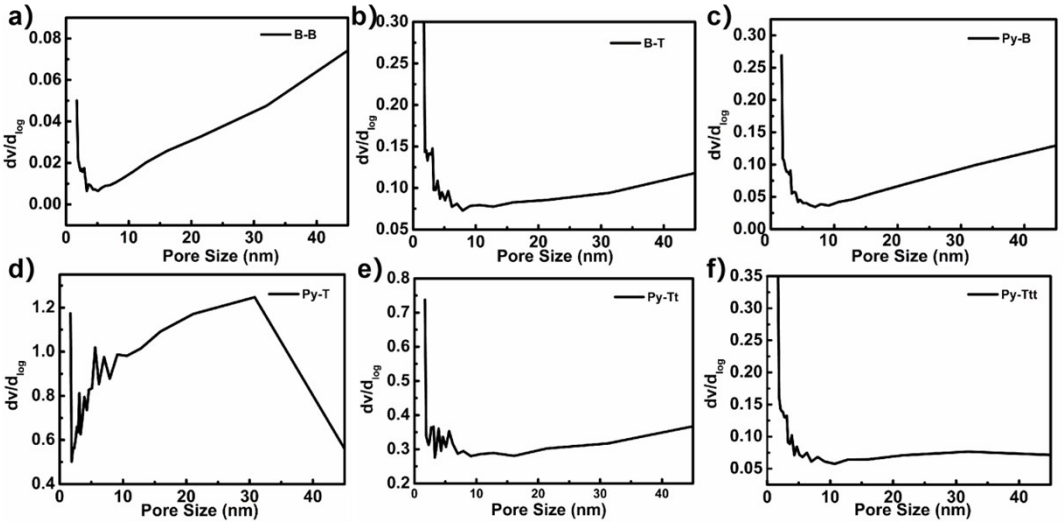


Fig. S3 Pore size distributions of **B-B**, **B-T**, **Py-B**, **Py-T**, **Py-Tt** and **Py-Ttt**.

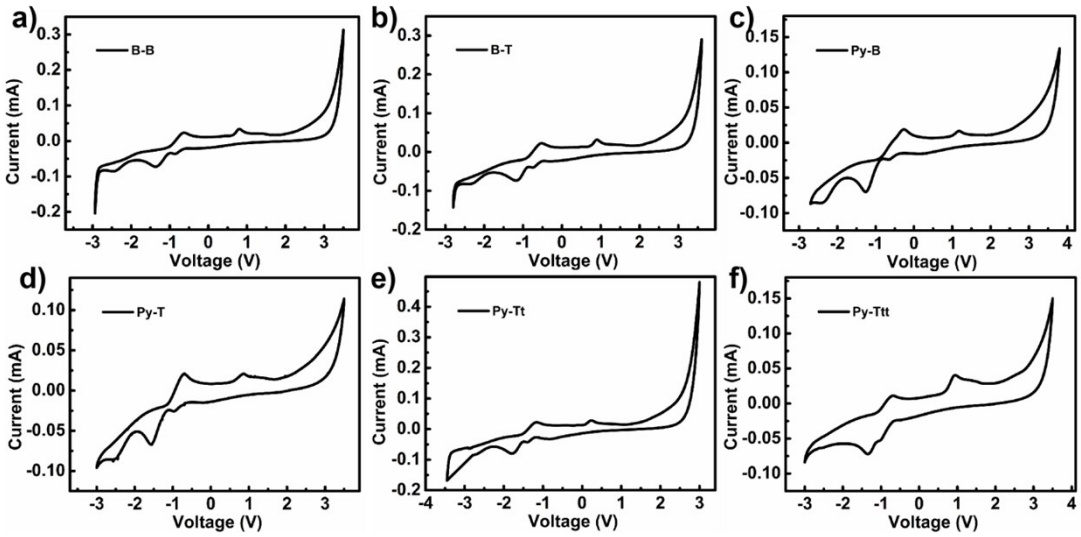


Fig. S4 CV curves of **B-B**, **B-T**, **Py-B**, **Py-T**, **Py-Tt** and **Py-Ttt**.

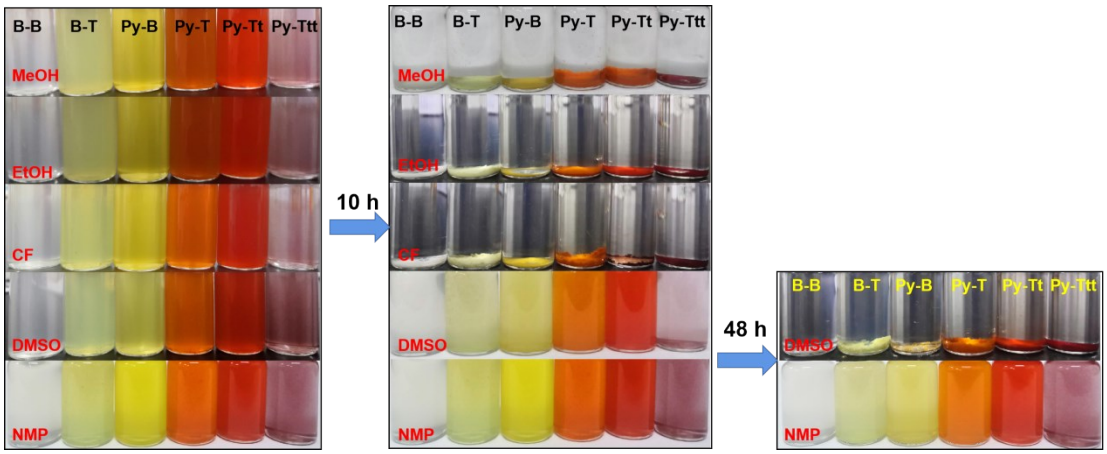


Fig. S5 **B-B**, **B-T**, **Py-B**, **Py-T**, **Py-Tt** and **Py-Ttt** ultrasonically dispersed for 60 min in varied solvents, and standing for 0 h, 10 h and 48 h (from left to right), respectively.

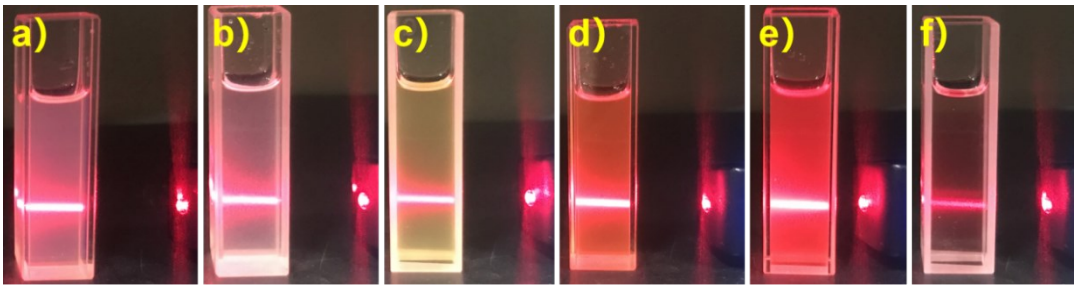


Fig. S6 Light beams pass through the stored dispersions of **B-B** (a), **B-T** (b), **Py-B** (c), **Py-T** (d), **Py-Tt** (e)and **Py-Ttt** (f) in NMP, respectively.

**Table S1 Density, dispersion forces and surface tension coefficient of solvents and CPPs.**

| Solvents | Densities ($g\ cm^{-3}$) | Dispersion forces ($cal^{1/2}cm^{3/2}$) |
|---|---|---|
| MeOH | 0.79 | 14.50 |
| EtOH | 0.79 | 12.70 |
| $CHCl_3$ | 1.50 | 9.30 |
| DMSO | 1.10 | 13.40 |
| NMP | 1.03 | 11.18 |
| **B-B** | 1.21 | 10.63 |
| **B-T** | 1.29 | 10.58 |
| **Py-B** | 1.28 | 11.24 |
| **Py-T** | 1.38 | 11.44 |
| **Py-Tt** | 1.40 | 11.24 |
| **Py-Ttt** | 1.35 | 10.65 |

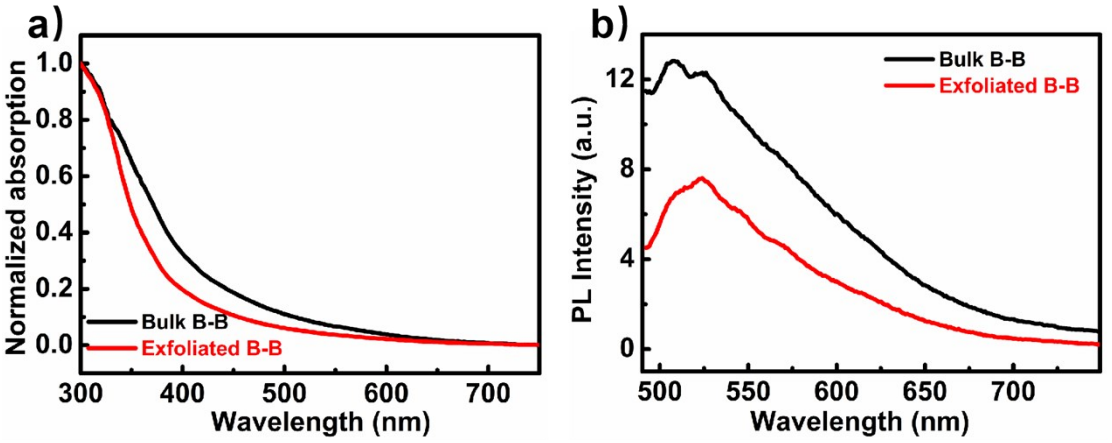


Fig. S7 (a) UV-vis absorption and (b) PL spectra of exfoliated and as-prepared bulk **B-B** dispersed in NMP, respectively, with and without ultrasonication.

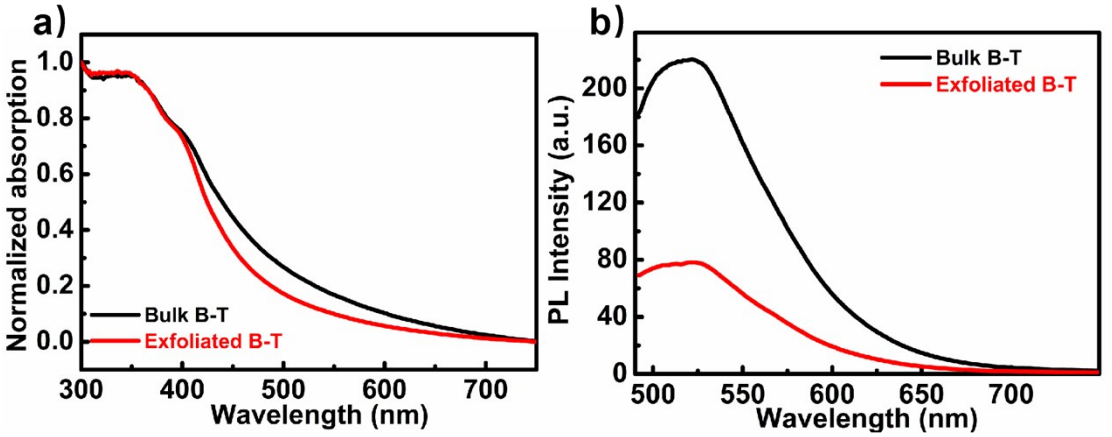


Fig. S8 (a) UV-vis absorption and (b) PL spectra of exfoliated and as-prepared bulk **B-T** dispersed in NMP, respectively, with and without ultrasonication.

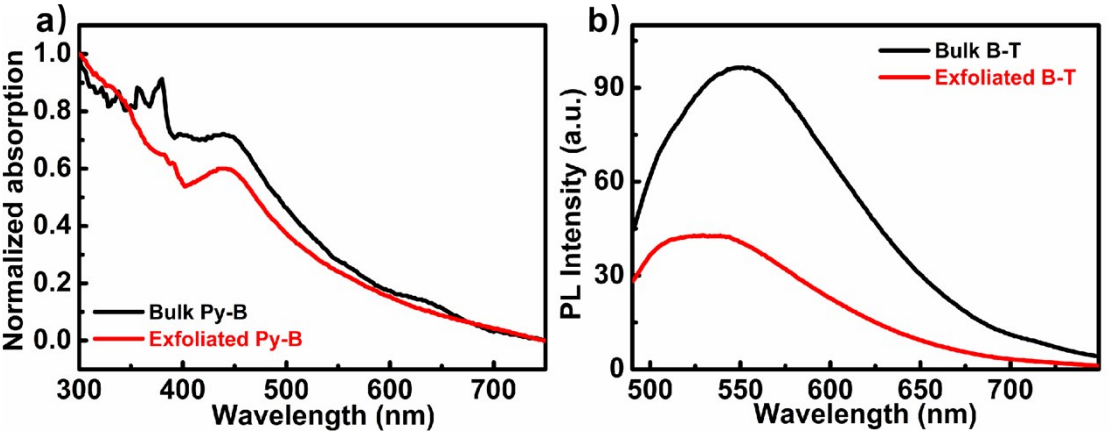


Fig. S9 (a) UV-vis absorption and (b) PL spectra of exfoliated and as-prepared bulk **Py-B** dispersed in NMP, respectively, with and without ultrasonication.

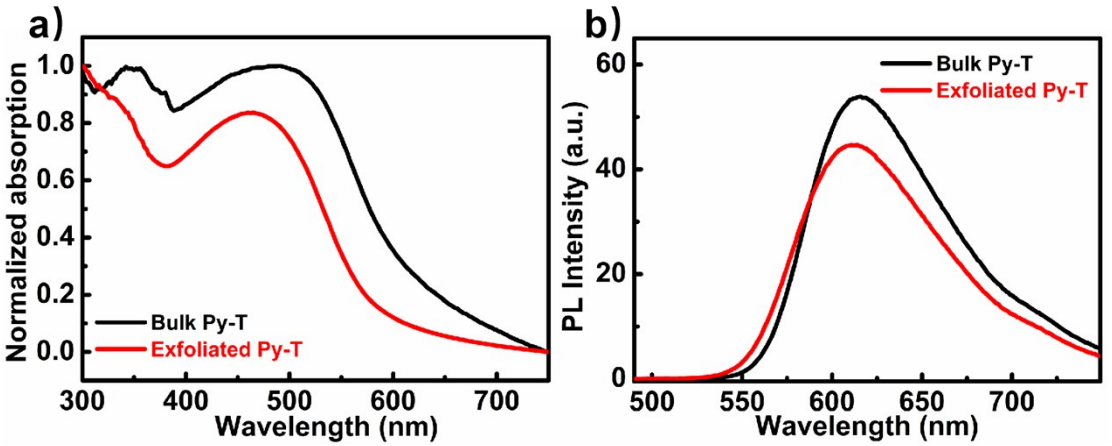


Fig. S10 (a) UV-vis absorption and (b) PL spectra of exfoliated and as-prepared bulk **Py-T** dispersed in NMP, respectively, with and without ultrasonication.

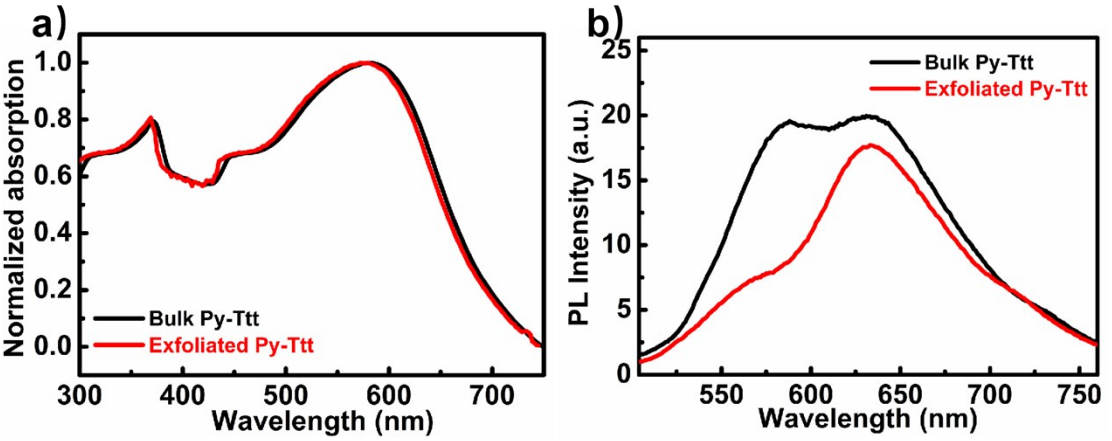


Fig. S11 (a) UV-vis absorption and (b) PL spectra of exfoliated and as-prepared bulk **Py-Ttt** dispersed in NMP, respectively, with and without ultrasonication.

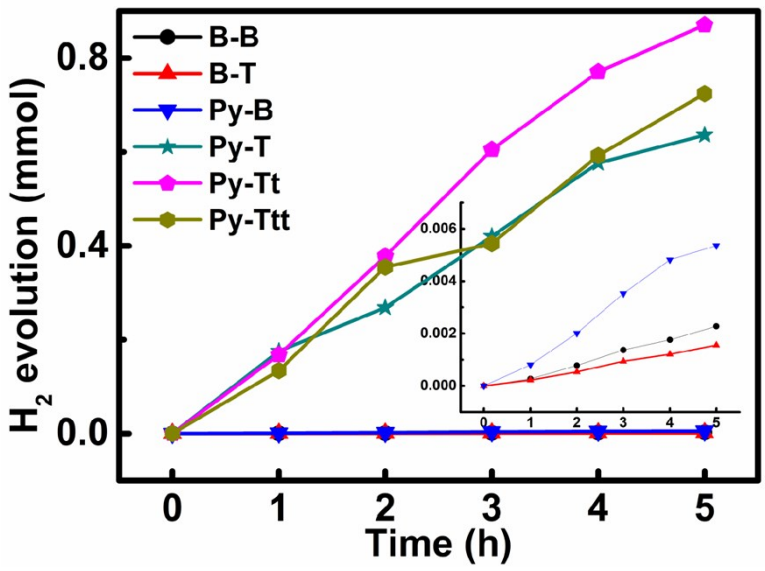


Fig. S12 $H_2$ evolutions of 6 mg catalysts dispersed in AA/$H_2O$/MeOH. (B-B, B-T were tested in full-arc irradiation, **Py-B**, **Py-T**, **Py-Tt** and **Py-Ttt** were under visible light irradiation).

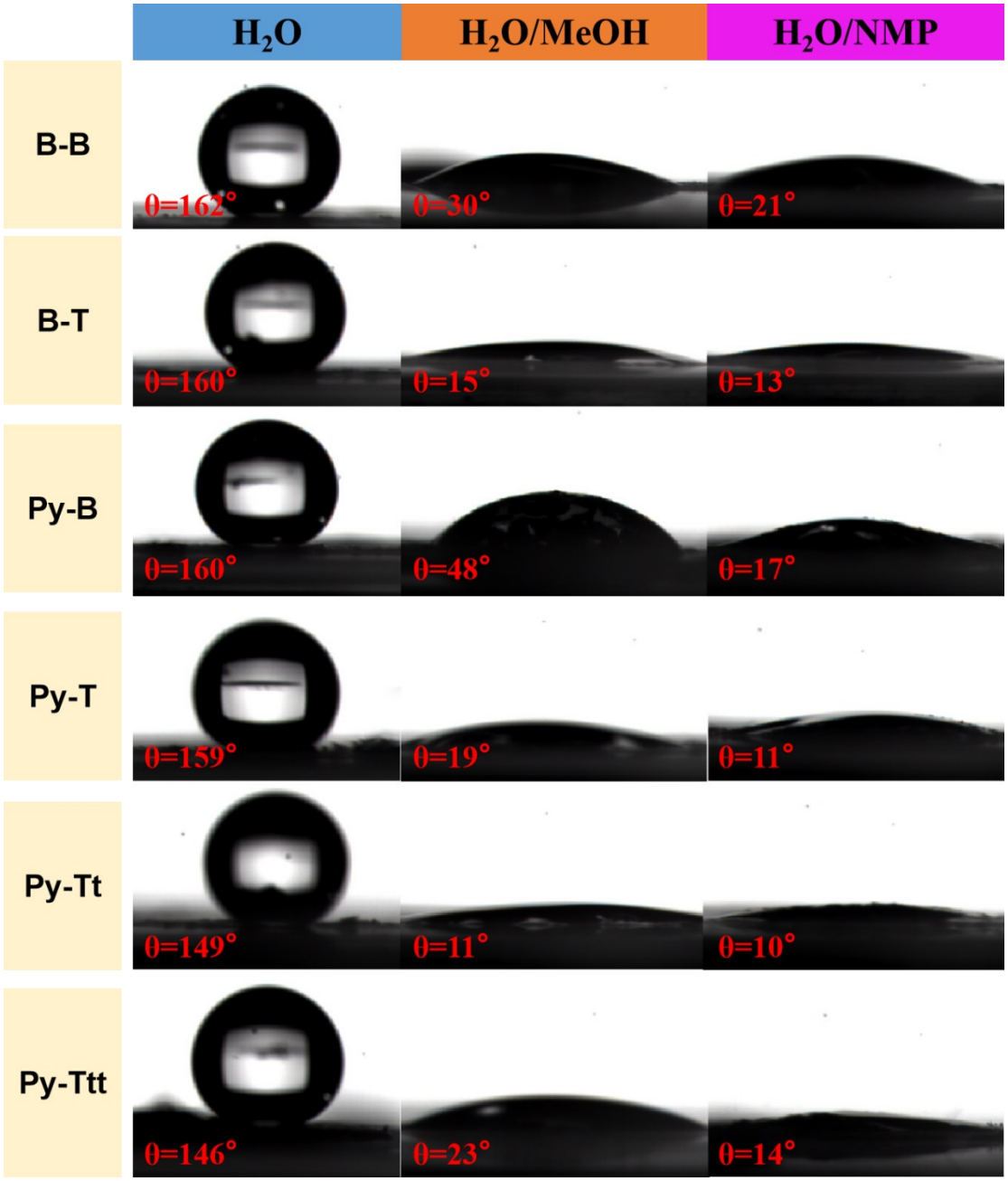


Fig. S13 Images of $H_2O$, $H_2O$/MeOH (5/1, v/v) and $H_2O$/NMP (5/1, v/v) droplets used for contact angles measurements on cast films of B-B, B-T, Py-B, Py-T, Py-Tt and Py-Ttt.

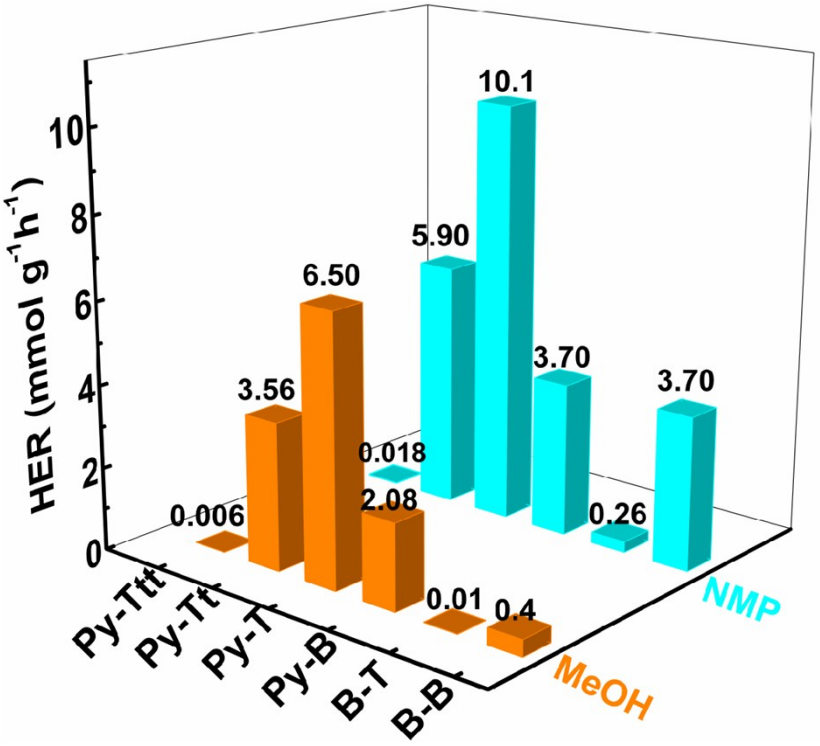


Fig. S14 The HER of catalysts dispersed in TEOA/$H_2O$/MeOH, TEOA/$H_2O$/NMP. (**B-B**, **B-T** were tested in full-arc irradiation, **Py-B**, **Py-T**, **Py-Tt** and **Py-Ttt** were tested under visible light irradiation).

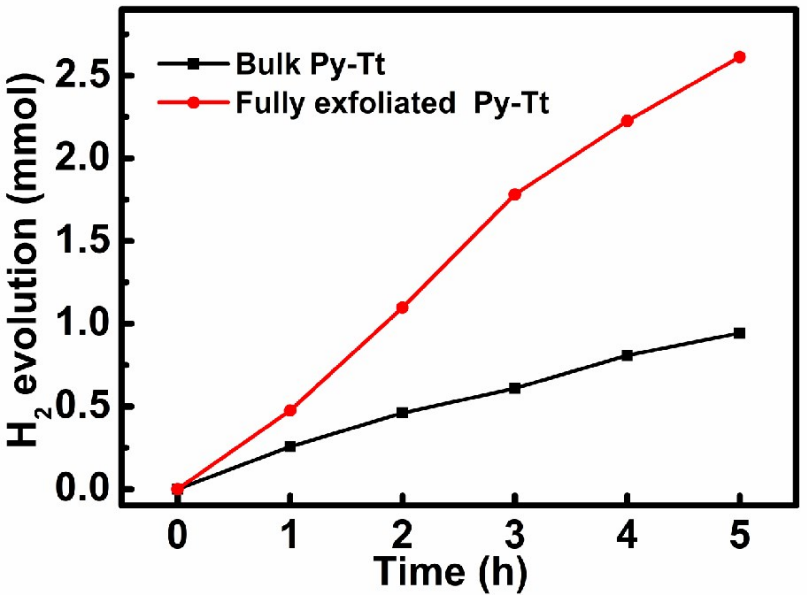


Fig. S15 $H_2$ evolutions of bulk and fully exfoliated **Py-Tt** in AA/$H_2O$/NMP mixed solution under visible light.

**Table S2 Optical properties of the bulk and colloidal CPPs in NMP.**

| CPPs | $\lambda_{max}$(nm)[a] | | PL intensity (a.u.)[b] | |
|---|---|---|---|---|
| | Bulk CPPs | Colloidal CPPs | Bulk CPPs | Colloidal CPPs |
| B-B | < 300 | < 300 | 12.8 | 7.6 |
| B-T | 332 | 318 | 220.5 | 78.4 |
| Py-B | 438 | 436 | 96.6 | 42.8 |
| Py-T | 490 | 460 | 53.9 | 44.7 |
| Py-Tt | 510 | 504 | 67.9 | 32.6 |
| Py-Ttt | 578 | 573 | 20.0 | 17.8 |

[a] Uv-vis maximum absorption wavelength. [b] PL relative intensity (Colloidal CPPs were obtained by centrifugating treatment (2000 rpm) on its ultrasonication-derived dispersion in NMP, and filtered the sediments. Bulk CPP dispersions were obtained by simply redistributing the filtered sediments into the NMP without ultrasonication).

**Table S3 Molar attraction constants (F) of groups.**

| Groups | F ($cal^{1/2}cm^{3/2}mol^{-1}$) |
|---|---|
|  | 117.1 |
|  | 98.1 |
|  | 209.4 |