Supporting Information

A (001) Dominated Conjugated Polymer with High-performance of Hydrogen Evolution under Solar Light Irradiation

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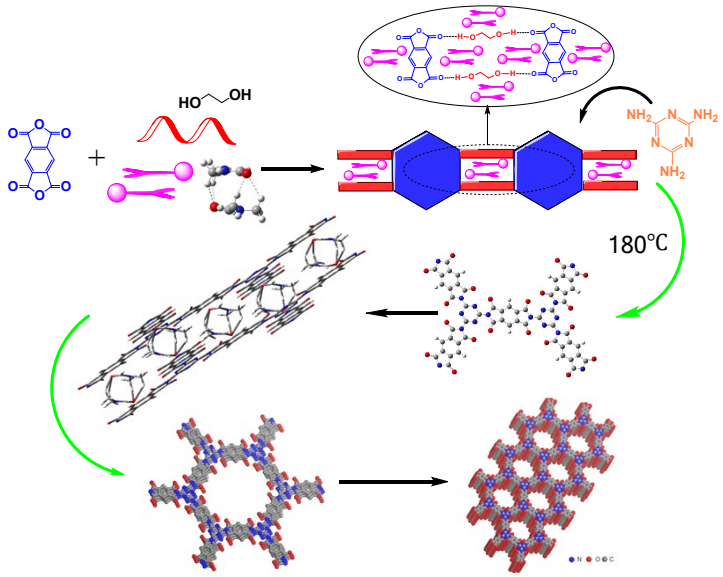
Synthesis of PI-SM

PI-SM was synthesized in an autoclave with Teflon lining. As typically shown in scheme S1: 3.27g (3.0eq, 15mmol) pyromellitic dianhydride (PMDA) was firstly dissolved into a mixture of N, N-Dimethylformamide (DMF) and ethanediol (10 mL with a ratio v/v of 1:1) under stirring, and then 1.26 g (2.0eq, 10 mmol) melamine (MA) was slowly added into the transparent solution. This solution had been stirring until gel-like precursor formed, and afterward the mixture was heated at 180 Celsius degree for 3 days in preheated oven. The resultant precipitate was collected by filtration followed by washed with acetone and water (at 90 Celsius degree), and finally the product was dried at 100 ℃ under vacuum.



Scheme S1. Proposed synthesis mechanism for (001) dominated PI-SM.

Synthesis of PI-TC and g-C_3N_4

PI-TC sample was synthesized by direct thermal polymerization of PMDA and MA at 325 Celsius degree for 4h according to literature [S1] for comparison, while g-C_3N_4 was prepared by heating dicyandiamide at 823K for 4h as previously reported. [S2]

Characterization:

FTIR spectra of samples were recorded on a Nicolet NEXUS870 spectrometer. XRD tests were performed on a Bruker D8 Advance X-ray diffractometer equipped with a θ/2θ Bragg–Brentano geometry and nickel-filtered Cu Kαradiation (Kα1 = 1.5406 Å, Kα2 = 1.5444 Å, Kα1/Kα2 = 0.5), with the tube voltage and current were 40 kV and 40 mA, respectively. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker EMX-10/12 instrument with equal amount samples (50 mg). The transmission electron microscopy (TEM) image was recorded on a JEM-2100 electron microscope operating at 200 kV. SEM images were acquired on a Hitachi S4800 FE-SEM microscope at 20 kV, 10 μA. The UV-Vis spectra of samples were collected with Shimadzu UV-2550 spectrometer. Photoluminescence spectra were recorded on a Varian Cary Eclipse spectrophotometer. Small-angle X-ray scattering (SAXS) experiments were performed at beamline BL19U2 of the National Center for ProteinScience Shanghai (NCPSS) at Shanghai Synchrotron Radiation Facility (SSRF).

Photocatalytic tests:

Photocatalytic reactions were carried out in a closed gas-circulation system, for which a 300W Xenon lamp was used as the light source, and 50 mg catalyst was dispersed in an aqueous solution (400 mL) containing methanol (10 vol%) as the sacrificial electron donor and 3 wt% Pt as the cocatalyst. Pt was photo-deposited on the catalyst by using H_2PtCl_6 dissolved in the reactant solution, and the evolved H_2 was analyzed by an online gas chromatography (GC-2014, Shimadzu, TCD, Argon carrier) during the reaction. For long-time hydrogen evolution test with three runs of cycle, the amount of catalyst was increased to 200 mg while the Pt loading were 1 wt% and 3wt% respecively. The quantum efficiency was measured generally using the

equation: Φ (%) = (2 × H/I) × 100, where H and I represent the numbers of evolved H_2 molecules and incident photons, respectively. The number of incident photons was measured to be 1.5×10^{21} photons·h^{-1} at 365±10 nm using Newport handheld power meters.

References

[S1] S. Chu, Y. Wang, Y. Guo, P. Zhou, H. Yu, L. L. Luo, F. Kong, Z. G. Zou, *J. Mater. Chem.* **2012**, *22*, 15519.

[S2] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76.

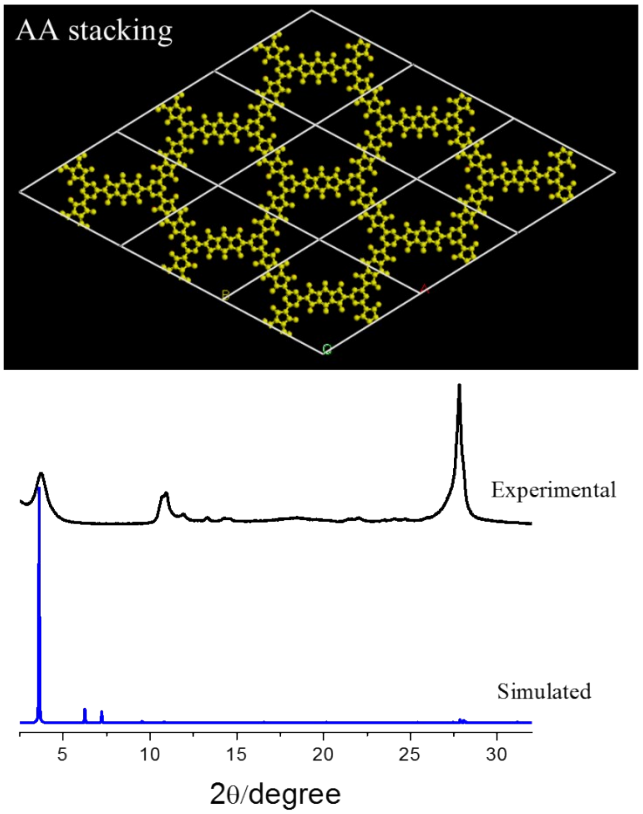


Figure S1. Simulated PXRD pattern of PI-COF with AA stacking

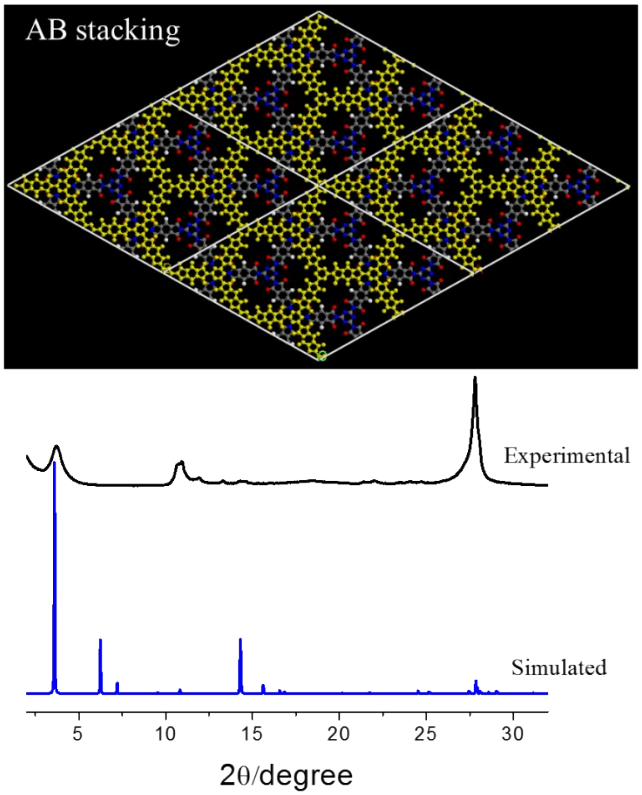


Figure S2. Simulated PXRD pattern of PI-COF with AB stacking

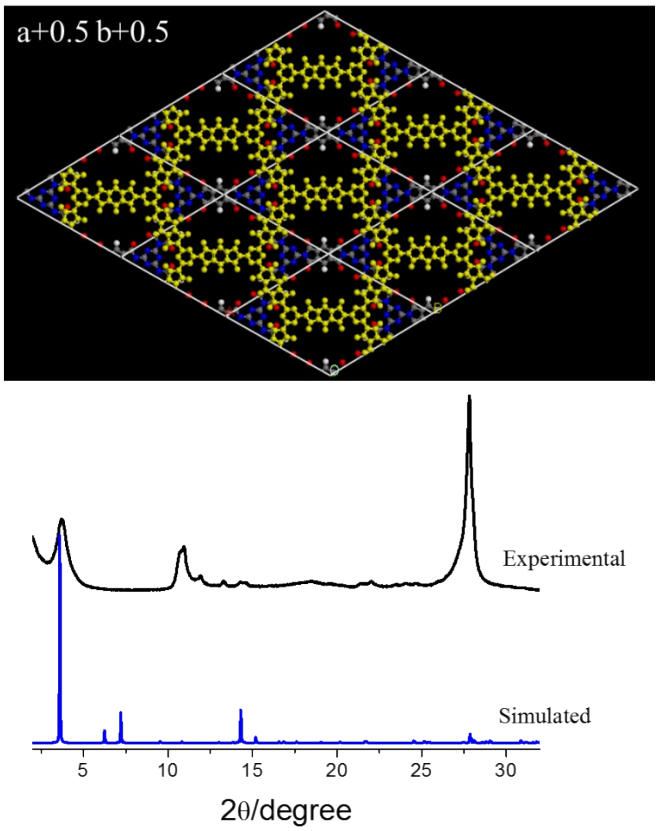


Figure S3. Simulated PXRD pattern of PI-COF with slipped distance of 1/2 unit cell along a and b axis

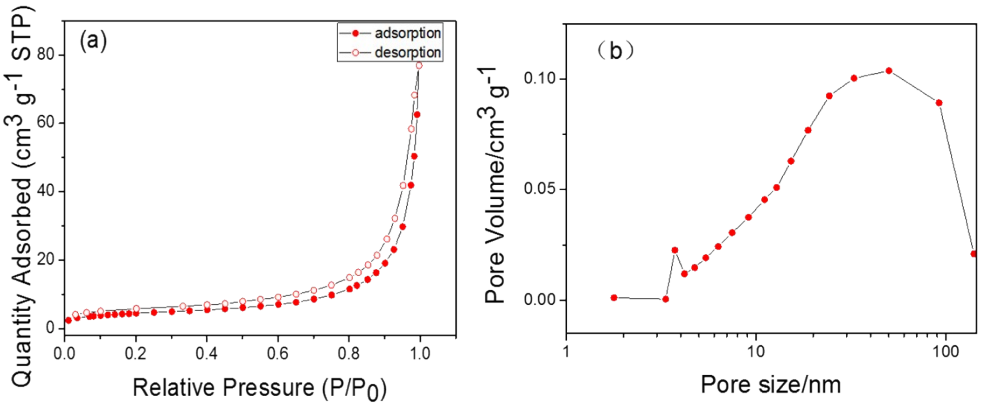


Figure S4. N_2 adsorption isotherm (a) and Pore size distribution (b) of PI-COF

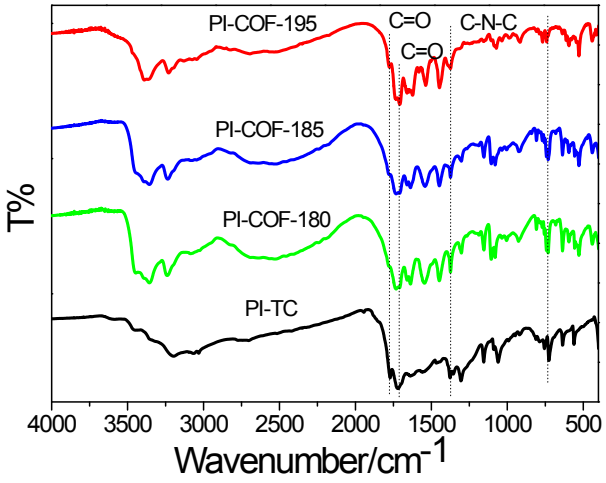


Figure S5. FTIR spectrum of PI-COF and PI-TC.