Supplementary Information

Conformation-driven exciton transfer in pyrene-sulfone covalent

organic frameworks for bifunctional photocatalysis

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Experimental details

Reagent

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetrabenzaldehyde (Py-CHO, C₄₄H₂₆O₄, A.R., 97%) was purchased from Shanghai Kylpharm Co., Ltd. 3,7-diaminodibenzo[b,d]thiophene 5,5-dioxide (Ts-NH₂, C₁₂H₁₀N₂O₂S, RG, 97%), p-toluenesulfonic acid monohydrate (PTSA, C7H8O3S·H2O, RG, 99%), trifluoromethanesulfonic acid (CHF₃O₃S, RG, 99%), trifluoroacetic acid (C₂HF₃O₂, HPLC, 99.5%), scandium(III) trifluoromethanesulfonate (Sc(SO₃CF₃)₃, RG, 99%), and mesitylene (mes, C₉H₁₂, RG, 99%) were purchased from Adamas. 1,2-dichlorobenzene (o-DCB, C₆H₄Cl₂, A.R., 98%) and 1-butanol (n-BuOH, C4H10O, A.R., 99.5%) were purchased from Macklin. glacial acetic acid (C₂H₄O₂, A.R., \geq 99.5%), 1,4-dioxane (dio, C₄H₈O₂, A.R., \geq 99.5%), N,N-dimethylformamide (DMF, C₃H₇NO, A.R., \geq 99.5%), tetrahydrofuran (THF, C₄H₈O, A.R., \geq 99.5%), acetone (C₃H₆O, A.R., \geq 99.5%), anhydrous ethanol (EtOH, C₂H₆O, A.R., \geq 99.7%), acetonitrile (MeCN, C₂H₃N, A.R., \geq 99.0%), and sodium sulfate (Na₂SO₄, A.R., \geq 99.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ascorbic acid (AA, A.R., \geq 99.0%) were obtained from Aladdin. Deionized water (18.25 MΩ) was produced from a water purifier. All chemicals were used as received without further purification.

Catalyst preparation

Twisted PyTs-COF

Py-CHO (11.60 mg), Ts-NH₂ (9.24 mg), o-DCB (0.5 ml), n-BuOH (0.5 ml) and PTSA solution (5 mM, 0.3 mL) were firstly added to a Pyrex tube. The mixture was then subjected to flash frozen at 77 K and degassed via a freeze-pump-thaw process for three times to remove the residual air. Subsequently, the tube was flame-sealed under evacuation followed by sonication for 10 min. The resulting homogeneous suspension was then heated in an oven at 150 °C for 72 h. After reaction, the product was collected by suction filtration and sequential washing with DMF, H₂O, THF and MeOH. Finally, yellow solids of twisted PyTs-COF were obtained after vacuum drying at 60 °C for 12 h. The products can also be obtained by replacing the PTSA solution with a Sc(OTf)₃ solution (0.05 mL, 5 mM). Here, a mixture of o-DCB and n-BuOH with a volume ratio of 1/1 was used as the solvent for the catalyst solution of PTSA or Sc(OTf)₃.

Planar PyTs-COF

The obtained twisted PyTs-COF was exposed to water vapor in a gas-tight bottle filled with water liquid. Upon contact with water, the color of the sample turned from yellow to red, suggesting the variation of the electronic structures. For complete color transformation, the sample was left undisturbed in the bottle for a certain period of time, finally giving rise to the red sample of planar PyTs-COF. For the structure evolution tests, the as-synthesized twisted PyTs-COF was exposed in the atmospheres of water vapor for different periods. Then, the water-saturated sample was taken out and left in air for natural volatilization. After evaporation for the designated time interval, the sample was ready for the corresponding measurement.

Material Characterization

Powder X-ray diffraction (PXRD) patterns were collected on a diffraction meter (Rigaku Smart Lab) at a scan rate of 10 ° min⁻¹ to determine the crystallinity of the catalysts. The microstructures and

element distributions were investigated using field-emission scanning electron microscopy (FE-SEM, SU8010, Hitachi) and high-resolution transmission electron microscopy (HR-TEM, Talos-F200X) equipped with energy dispersive X-ray spectroscopy (EDS). The element contents of C, H, N, S were determined by element analysis (EA) on an elemental analyzer (Vario EL Cube, Elementar). The Brunauer-Emmett-Teller (BET) surface area and porosity were measured on a specific surface area and pore size analyzer (BSD-PS1, BeiShiDe Instrument) at 77 K. Prior to the test of N₂ adsorption and desorption, the catalyst was activated by solvent exchange through sequential immersion in MeOH, acetone, and CH₂Cl₂ (24 h for each solvent), followed by vacuum drying at 60 °C for 6 h. Fourier transform infrared (FTIR) spectra were recorded on a Fourier transform infrared spectrometer (VERTEX70, Bruker Optics) to examine the chemical structures and functional groups of the catalysts. Ultraviolet-visible (UV-vis) diffuse reflectance spectra (UV-DRS) were taken on a UV-vis near-infrared spectrophotometer (Lambda950, PE) equipped with an integrating sphere using BaSO₄ as the background. UV-vis absorption spectra were measured on an ultraviolet-visible spectrophotometer (UV-2600, SHIMADZU). Steady-state photoluminescence (PL) and temperature-dependent photoluminescence (TD-PL) spectra were recorded on F-4600 (Hitachi) and FLS980 (Edinburgh Instruments) fluorescence spectrophotometers, respectively, at an excitation light wavelength of 400 nm. The exciton binding energy (E_b) for the twisted and planar PyTs-COF can be obtained from the temperature-dependent photoluminescence (PL) spectra and the Arrhenius equation (I = $I_0 / (1 + Aexp(-Eb/kBT))$, where I is the integrated PL intensity, I_0 is the intensity at 0 K, A is a constant, T is the temperature and k is the Boltzmann constant). Femtosecond transient absorption (fs-TA) spectra were afforded on a visible femtosecond transient absorption spectrometer (HELIOS, Ultrafast Systems) at a pump light wavelength of 400 nm to reveal the behavior of the excited states and the charge transfer kinetics. Electron paramagnetic resonance (EPR) spectra were taken on the electron spin resonance spectrometer (E500 10/12, Bruker Biospin GMBH) in the dark or under irradiation with a 420 nm cut-off filter. Surface chemical states and the valence band minimum (VBM) of the catalysts were analyzed using core-level X-ray photoelectron spectra (XPS) and ultraviolet photoelectron spectra (UPS) measured on an ESCALAB 250Xi instrument (ThermoFisher) with Al K α radiation and He I (21.22 eV) as the excitation light source, respectively. The hydrophilicity of the catalyst was assessed using a static contact angle meter (Theta Lite, Biolin). The water uptake capability was further evaluated according to the water adsorption curve taken on an intelligent gravimetric analyzer (Belsorp-max, MicrotracBEL).

Photoelectrochemical measurement

Photoelectrochemical tests were conducted on an electrochemical workstation (CHI660, CHENHUA) in a three-electrode system. Firstly, a catalyst ink was prepared by mixing 2 mg of catalyst, 0.9 mL of EtOH and 0.1 mL of Nafion solution (5 wt%). The mixture was sonicated for 0.5 h to obtain a homogeneous suspension. The working electrode was fabricated by drop-casting the catalyst ink onto a clean ITO glass slide. A piece of Pt foil and Ag/AgCl electrode were employed as the counter and reference electrodes, respectively. 0.5 M NaSO₄ aqueous solution was used as the electrolyte.

Photocatalytic reaction

Photocatalytic hydrogen evolution reaction (PHER)

In a typical run, 5 mg of catalyst (PyTs-COF) were dispersed in 100 mL of AA aqueous solution

(0.1 M) with the addition of certain amount of H₂PtCl₆ aqueous solution under ultrasonication. The homogeneous suspension was then poured into a gas-tight top-irradiation reactor, which was connected to a photocatalytic device equipped with a cyclic cooling water apparatus (Labsolar-6A, PerfectLight, Beijing). The system was then evacuated thoroughly to remove the residual air and back-filled with high-purity Ar gas for three times. Then, the reaction was commenced with light irradiation (300 W Xe lamp) with a 420 nm cutoff filter. Pt was loaded on the catalyst via in-situ photo-deposition. The evolved gas products were quantified by an online gas chromatography (Fuli 7820A) equipped with a thermal conductivity detector. The cycling stability of the photocatalytic activity was assessed by evacuating the system every 4 h following by re-initiation of the reaction. Apparent quantum yield (AQY) was acquired in a similar way under irradiation with monochromic bandpass (650, 600, 550, 520, 450 and 420 nm). The specific value was determined according to the following equation,

 $AQY = \frac{\text{The number of electrons participating in the reaction}}{\text{The total number of the photons of the incident light}} = \frac{2 \times \text{the number of evolved H}_2 \text{ molecules}}{E\lambda/hc}$

where E is the total energy of the incident light (J), λ is the wavelength of the irradiation light (nm), h is the Planck constant (6.626 × 10⁻³⁴ J s⁻¹), c is the speed of light (3 × 10⁸ m s⁻¹).

Photocatalytic oxygen evolution reaction (POER)

In a typical procedure, CoO_x (3 wt%) was firstly loaded onto 10 mg of catalyst (PyTs-COF) by a photodeposition process. The mixture was then dispersed in an aqueous solution of AgNO₃ (0.1 M) with La₂O₃ (0.1 g) as a pH buffer. The resulting suspension was then transferred to a gas-tight topirradiation reactor, which was connected to a photocatalytic device equipped with a cyclic cooling water apparatus (Labsolar-6A, PerfectLight, Beijing). Subsequently, the system was thoroughly evacuated to remove the residual air and backfilled with high-purity Ar gas for three times. Finally, the reaction was initiated by light irradiation (300 W Xe lamp). The evolved gas products were quantified by an on-line gas chromatography (Fuli 7820A) equipped with a thermal conductivity detector.

Computational methods

Crystal structure determination

The structural models of planar and twisted PyTs-COF were created, optimized and refined using a Materials Studio software (Material Studio ver. 2019, Accelrys Software Inc.). Geometry optimizations were performed using the universal force field in the Forcite module. The unit cell parameters were optimized until an energy convergence criterion of 2.0×10-5 kcal mol-1 was met. The optimized structures were then subjected to Pawley refinement in combination with the experimental XRD patterns using the Powder Refinement option in the Reflex module. Finally, the refinement was successfully completed with a fitting convergence at small residuals and the calculated XRD patterns showed good agreement with the experimental ones. In this way, the crystal structure of the COFs can be determined.

Electrostatic potential distribution and dipole moment

DFT calculations of the electrostatic potential and electron density distributions and the dipole moments of the twisted and planar PyTs-COF were performed using the DMol3 module with

generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange correlation as the functional and DNP+ as the basis set. The fragments shown in the Figure S11 were used to represent the two conformations of PyTs-COF.

TD-DFT calculations

Time-dependent density-functional theory (TD-DFT) calculations were performed at the B3LYP/6-31G(d) level with an implicit solvent model (SMD) (Gaussian 09 software). The number of excited states calculated was set to 20. Molecular fragments taken from the optimized ground state structures were used to represent the structures of twisted and planar PyTs-COF, which consist of a Py-CHO moiety and a Ts-NH₂ moiety linked by an imine bond and are terminated with hydrogen atoms (Figure S19). DMF and H₂O were used as the solvents for twisted and planar PyTs-COF, respectively. Electron and hole distributions and the transition dipole moments were visualized and analyzed using the Multiwfn and VMD software.

Supplementary figures



Scheme S1. Schematic illustration of the synthetic process of PyTs-COF. Our initial attempts using acetic acid as the catalyst were failed with varying reaction temperatures, time, and solvents. The starting materials hardly reacted, and only transparent liquids or amorphous solids could be obtained. This may be due to the strong electron withdrawing ability of sulfone groups in the amine monomer, which makes the nitrogen atoms electron-deficient and less prone to donate electrons, and hinders the nucleophilic attack of the nitrogen atoms on the carbon atoms of the aldehyde. Thus, it's difficult for the condensation reaction to occur under conventional reaction conditions.



Figure S1. FTIR spectra of the twisted and planar PyTs-COF and the monomers of Py-CHO and Ts-NH₂.



Figure S2. UV-DRS of PyTs-COF in contact with solvents with different polarities.



Figure S3. UV-vis absorption (a) and fluorescence emission (b) spectra of PyTs-COF in solvents of different polarities.

Figure S2 show the UV-vis absorption and fluorescence emission spectra of PyTs-COF in solvents of different polarities, including H₂O, DMF, MeCN, EtOH and THF with dielectric constants of 78.36, 37.78, 35.69, 24.85 and 1.89. The absorption maximum in water shows a redshift compared with those in solvents with lower polarity, indicating a solvent polarity-induced change of the electronic structures of PyTs-COF. Meanwhile, the fluorescence emission spectra exhibit a wavelength dependence on the solvent polarity, demonstrating the dipolar interactions between PyTs-COF and the surrounding environment (*Phys. Rev. B, 2010, 81, 205421*). It's noticeable that for the protonic solvents, the fluorescence emission shows an obvious redshift and a considerable quenching, suggesting that hydrogen bonding between COF and solvent is also at play. In all, these experimental results provide more direct evidence for the solvatochromism and dipolar interactions between the PyTs-COF and the polar media.



Figure S4. XRD patterns of the twisted PyTs-COF, the planar PyTs-COF (water-adsorbed) and the monomers of Py-CHO and Ts-NH₂.



Figure S5. Molecular fragments of the twisted (a) and planar PyTs-COF (b) viewed along different directions, which were generated from the corresponding optimized structures and terminated with hydrogen atoms at the 4-positions of the eight outer benzene ring moieties.



Figure S6. Simulated crystal structures (a, b) and XRD patterns (c) of twisted PyTs-COF with the AB stacking. The experimental XRD patterns of twisted PyTs-COF are also shown in c.



Figure S7. SEM (a-b), TEM (c), STEM (d) and elemental mapping images (e) of PyTs-COF.



Figure S8. C 1s (a), N 1s (b), O 1s (c) and S 2p (d) XPS of PyTs-COF.

The C 1s XPS can be deconvoluted into three components, namely, C-C/C=C (284.0 eV), C-N/C=N (285.1 eV) and $\pi - \pi *$ (289.1 eV). The N 1s spectrum can be divided into two major components and one minor component, which correspond to C-N (398.7 eV), C=N (399.2 eV) and C=NH+ (402.1 eV), respectively. The C=NH+ peak could be caused by water adsorbed on the surface. Both the O 1s and S 2p XPS are composed of two peaks. For the O 1s spectrum, the peak with a higher binding energy (533.0 eV) can be attributed to the S=O groups, while the other one (532.0 eV) can be ascribed to the hydroxyl (OH) group derived from surface adsorbed water. As expected, C-S (168.1 eV) and S=O (169.3 eV) bonds are observed in the S 2p XPS. These results demonstrate not only the presence of the elements of C, O, N and S, but also the presence of imine bonds and sulfone groups in the PyTs-COF.



Figure S9. (a) IR spectra for the monomers of Py-CHO and Ts-NH₂ with and without water. (b) Partially enlarged IR spectra for Ts-NH₂ with and without water

To investigate the influence of water on the monomers, both Py-CHO and Ts-NH₂ were exposed to water vapor for 2 h prior to the IR spectrum measurements. As expected, an extra broad peak centered around 3400 cm⁻¹ is observed in both samples compared to the control samples without water treatment, which is typical of hydrogen-bonded -OH and can be attributed to the surface adsorbed water molecules. Furthermore, the slightly blue-shifted peaks of sulfone groups (~1300 and 1150 cm⁻¹) indicate the presence of hydrogen bonds between water and sulfone groups (Figure 3b), which is consistent with the case of the planar PyTs-COF. It's noteworthy that the change is not as significant as for the planar COF. This may be due to the lack of ordered pores in the Ts-NH₂ monomer, which makes it unable to confine the water molecules in the periodic pores and enhance the intermolecular interaction, *i.e.*, hydrogen bonding, unlike the porous PyTs-COF. Taken together, this additional experimental result further supports our conclusion that hydrogen bonding exists between water and the sulfone groups of PyTs-COF and contributes to the conformational transition of PyTs-COF in water.



Figure S10. (a) Electron density and electrostatic potential distributions for twisted and planar PyTs-COF (isovalue = 0.017). (b) Schematic illustration showing the hydrogen bonding and dipolar interaction between the polar water molecule and the polar PyTs-COF with a D-A structure.

The electrostatic potential distributions of twisted and planar PyTs-COF were calculated using the representative fragments. For both cases, the negative charges are mainly located at the sulfone groups and the imine bonds, while the positive charges are dominated at the pyrene moieties. In the meantime, distinctions could be seen in the dipole moment (4.79 *vs* 4.15 Debye) and in the spatial distribution of electron density. Thus, we can tentatively deduce that hydrogen bonding and dipolar interactions between water and PyTs-COF might be responsible for the solvatochromism and planarization process, which are likely to rotate the single C-C bonds connecting the building blocks, leading to structural transformation from the C2 to the P2M space group with enhanced coplanarity, conjugation degree and delocalization. These are promising to improve the charge transfer kinetics, making PyTs-COF inherently advantageous for catalyzing reactions taking place in water.



Figure S11. Comparison of transient absorption mapping spectra of twisted PyTs-COF (a, b) and the monomers of Py-CHO (c, d) and Ts-NH₂ (e, f) probed in the visible (a, c, e) and near infrared (b, d, f) region. Pump light: 400 nm, 1.34 mW.



Figure S12. Transient absorption spectra of twisted PyTs-COF probed in the visible region (a-c) and absorption kinetics (d-f) probed at 500 nm (d), 660 nm (e) and 780 nm (f). Pump light: 400 nm, 1.34 mW.



Figure S13. Transient absorption spectra of planar (a, b) PyTs-COF probed in the visible region and absorption kinetics (c, d) probed at 565 nm (c) and 780 nm (d). Pump light: 400 nm, 1.34 mW.



Figure S14. Transient absorption spectra of twisted (a, b) and planar (d, e) PyTs-COF probed in the near infrared region (a, b, d, e) and absorption kinetics (c, f) probed at 900 nm (c) and 1000 nm (f). Pump light: 400 nm, 1.34 mW.



Figure S15. Transient absorption spectra of the monomers of Py-CHO (a, b) and Ts- NH_2 (d, e) probed at the visible region and absorption kinetics (c, f) probed at different wavelengths. Pump light: 400 nm, 1.34 mW.



Figure S16. Transient absorption spectra of the monomers of Py-CHO (a, b) and Ts-NH₂ (d, e) probed in the near infrared region and absorption kinetics (c, f) probed at different wavelengths. Pump light: 400 nm, 1.34 mW.



Figure S17. Comparison of transient absorption kinetics of twisted (top panel) and planar (bottom panel) PyTs-COF probed at different wavelengths. Pump light: 400 nm, 1.34 mW.



Figure S18. Steady-state UV-vis absorption (a, b) and photoluminescence (PL) (c-f) spectra of PyTs-COF and the monomers of Py-CHO and Ts-NH₂ in DMF and H₂O. All the PL spectra were excited at 400 nm.

In DMF, PyTs-COF shows two broad peaks around 425 and 520 nm in the UV-vis absorption spectrum and three relatively narrow peaks at 430, 460 and 515 nm in the PL spectra. In water, broad absorption features ranging from 500 to 800 nm were observed for PyTs-COF, with centers positioned around 600 nm and 750 nm. In contrast, a much narrower peak at about 590 nm was detected in the PL spectra. Obviously, the UV-vis absorption and the PL spectra for PyTs-COF overlapped in a wide range from 400 to 600 nm, regardless of the solvent in which it was dispersed. Noticeably, the absorption peaks in water were red-shifted compared to those in DMF. This was also the case for the PL spectra. Meanwhile, the peak intensity in the PL spectra was significantly decreased, indicating the PL quenching and suppressed carrier recombination in water.

In DMF, Py-CHO showed an absorption in the wavelength range from 350 to 450 nm, while Ts- NH_2 showed a relatively red-shifted absorption from 370 to 470 nm. In water, Py-CHO showed a broad absorption from 400 to 550 nm, red-shifted compared to the case in DMF. In contrast, Ts- NH_2 had only marginal absorption at wavelengths longer than 400 nm. When the solvent was changed from DMF to H_2O , the PL peak for Py-CHO shifted from 475 to 575 nm, while that for Ts- NH_2 shifted from 500 nm to 550 nm. In addition to the red shit of the peak position, the peak intensity was significantly decreased for both Py-CHO and Ts- NH_2 .



Figure S19. UV-vis absorption and photoluminescence (PL) emission spectra of pure DMF. The PL spectrum is excited at 400 nm. It's clear that pure DMF shows negligible absorption but emits fluorescent light around 430 nm and 460 nm. Therefore, the observed PL peaks at 430 nm and 460 nm for PyTs-COF dispersed in DMF are attributed to the fluorescent emission of DMF, rather than that of the twisted PyTs-COF.



Figure S20. Temperature-dependent photoluminescence (TD-PL) spectra of the twisted (a) and planar (b) PyTs-COF.



Figure S21. Transient photocurrent response of PyTs-COF under chopped light irradiation.



Figure S22. Nyquist plots of PyTs-COF under irradiation and in dark.



Figure S23. Structures of molecular fragments for the twisted (a) and planar (b) PyTs-COF for TD-DFT calculations, which are taken from the corresponding ground-state crystal structures after geometric optimization and terminated with hydrogen atoms.



Figure S24. Hole and electron distributions, charge density difference (CDD, green and purple regions represent hole and electron, respectively) and overlapping of electron and hole distribution (Sr, yellow) for the first (S1), second (S2) and third (S3) excitations of the twisted PyTs-COF.

At S1, the electrons and holes have a high degree of overlapping for both conformations, indicating the presence of larger amounts of Frenkel excitons. With higher excitation energy, the electrons and holes become more separated, suggesting the increased percentage of the CT excitons. Overall, the separation of electron and hole distributions in the planar PyTs-COF is more significant compared to that in the twisted conformation.



Figure S25. Hole and electron distribution, charge density difference (CDD, green and purple regions represent hole and electron, respectively) and overlapping of electron and hole distribution (Sr, yellow) for the first (S1), second (S2) and third (S3) excitations of the planar PyTs-COF.



Figure S26. Influence of the crystallinity of PyTs-COF on the PHER performance.



Figure S27. Influences of Pt loading amount (a) and AA concentration (b) on the PHER performance of PyTs-COF.



Figure S28. XRD patterns of PyTs-COF after PHER test.



Figure S29. HRTEM (a), high-magnification HRTEM (b, indicated by the white square in a), STEM (c) and the elemental mapping images (d) of PyTs-COF after PHER test. The clear lattice fringes indicate the maintenance of the high crystallinity and stability of PyTs-COF after PHER test. The white spots in (c) indicate the small size of Pt nanoparticles loaded on PyTs-COF and their dense and homogenous distribution.

Supplementary tables

Entry	Solvent	Solvent Catalyst		Time	Result
	(mL/mL)		(°C)	(h)	
1	o-dcb/n-BuOH (0.5/0.5)	9 M AcOH (0.1 mL)	120	72	unreacted
2	dio/mes ^a (0.5/0.5)	9 M AcOH (0.1 mL)	120	72	unreacted
3	o-dcb/n-BuOH (0.5/0.5)	9 M AcOH (0.2 mL)	150	72	unreacted
4	o-dcb/n-BuOH (0.5/0.5)	9 M AcOH (0.3 mL)	150	72	unreacted
5	o-dcb/n-BuOH (0.5/0.5)	5 mM CF ₃ SO ₃ H (0.1 mL)	150	72	black solid
6	o-dcb/n-BuOH (0.5/0.5)	5 mM CF ₃ COOH (0.1mL)	150	72	black solid
7	dio/mes ^a (0.5/0.5)	5 mM Sc(OTf) ₃ (0.1 mL)	150	72	unreacted
8	o-dcb/n-BuOH (0.5/0.5)	5 mM Sc(OTf) ₃ (0.1 mL)	150	72	poorly crystalline
9	o-dcb/n-BuOH (0.5/0.5)	5 mM Sc(OTf) ₃ (0.1 mL)	150	72	poorly crystalline
10	o-dcb/n-BuOH (0.5/0.5)	5 mM Sc(OTf) ₃ (0.1 mL)	100	72	moderatelycrystalline
11	o-dcb/n-BuOH (0.5/0.5)	5 mM Sc(OTf) ₃ (0.05 mL)	150	72	highly crystalline
12	o-dcb/n-BuOH (0.5/0.5)	10 mM PTSA (0.3 mL)	150	72	amorphous
13	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.1 mL)	150	72	lowly crystalline
14	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.2 mL)	150	72	moderately crystalline
15	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.4 mL)	150	72	poorly crystalline
16	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.5 mL)	150	72	poorly crystalline
17	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.3 mL)	150	48	poorly crystalline
18	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.3 mL)	150	120	poorly crystalline
19	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.3 mL)	120	72	amorphous
20	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.3 mL)	180	72	amorphous
21	o-dcb/n-BuOH (0.5/0.5)	5 mM PTSA (0.3 mL)	150	72	highly crystalline

Table S1. Optimization of the synthetic conditions for PyTs-COF

Note: ^a dio/mes is short for dioxane/mesitylene.

Parameter	twisted PyTs-COF	planar PyTs-COF
Cell formula	C136H76N8O8S4	C136H76N8O8S4
Space group	<i>C</i> 2	<i>P2M</i>
a	32.3625	42.3198
b	37.1802	39.8444
c	4.47701	5.0134
α	90.0000	90.0000
β	85.3274	90.0000
γ	90.0000	87.8884
Cell volume	5369.03	8446.80

 Table S2. Crystal structure information of the twisted and planar PyTs-COF.

Table S3. Contents of C, N, S and H in PyTs-COF determined by elemental analysis (EA) and	
derived from theoretical calculations.	

Sampe		C (wt%)		N (wt%)		S (wt%)		H (wt%)	
	_	exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.
PyTs-CC)F	72.38	78.59	4.92	5.39	6.48	6.17	4.28	3.69

Sample	UV-vis Abs. (nm)		PL (PL (nm)		A (nm)
	DMF H ₂ O		DMF	H_2O	DMF	H ₂ O
Py-CHO	350-450	400-550	475	575	-	-
Ts-NH ₂	370-470	marginal ^a	500	550	-	-
PyTs-COF	425	600	440	580	B1: 495	B1: 565
	520	750	460		A1: 660	A2: 780
			520		A2: 780	A3:1000
					A3: 900	

Table S4. Peak information from steady-state UV-vis absorption and photoluminescence (PL) spectra and femtosecond transient absorption (TA) spectra of Py-CHO, Ts-NH₂ and PyTs-COF in DMF and H₂O.

^a Ts-NH₂ showed only marginal absorption at wavelengths longer than 400 nm.

Table S5. Detailed information on the calculated excited states for the twisted PyTs-COF, including the excitation energies (in eV) and wavelength (in nm), oscillator strengths (f) and the molecular orbital transition contributions (in %) to each excited state, and the spin multiplicity. Only the transition contributions greater than 5% are given here.

#1 2.4476 eV 506.55 nm f=0.73620 Spin multiplicity= 1: H -> L 97.9% 2.8529 eV 434.59 nm f= 0.57540 Spin multiplicity= 1: #2 H -> L+1 97.4% #3 3.0863 eV 401.72 nm f= 0.14390 Spin multiplicity= 1: H -> L+2 95.4% #4 3.2997 eV 375.74 nm f= 0.89470 Spin multiplicity= 1: H-1 -> L 86.3% 3.4261 eV 361.88 nm f= 0.03120 Spin multiplicity= 1: #5 H -> L+4 30.8%, H-2 -> L 28.5%, H -> L+3 15.5%, H-2 -> L+1 10.0%, H-1 -> L+1 7.9% 3.6279 eV 341.75 nm f=0.00470Spin multiplicity= 1: #6 H-1 -> L+1 50.8%, H-1 -> L+2 20.1% 3.7302 eV f= 0.37560 Spin multiplicity= 1: #7 332.38 nm H-2 -> L 24.9%, H -> L+4 17.4%, H-4 -> L 10.0%, H-1 -> L+1 7.8%, H-9 -> L 7.4%, H-1 -> L 6.6% #8 3.7614 eV 329.62 nm f= 0.01650 Spin multiplicity= 1: H -> L+3 34.7%, H -> L+6 31.2%, H -> L+4 8.0%, H-2 -> L 6.1%, H -> L+5 6.0% #9 3.8080 eV 325.59 nm f= 0.00340 Spin multiplicity= 1: H-2 -> L 25.2%, H -> L+6 13.4%, H-1 -> L+1 12.7%, H-1 -> L+2 8.7%, H-9 -> L 7.7%, H-4 -> L 7.1% #10 3.8789 eV 319.64 nm f= 0.00910 Spin multiplicity= 1: H -> L+3 30.3%, H -> L+6 17.8%, H-3 -> L 17.6%, H -> L+4 10.2%, H-3 -> L+1 5.2% #11 3.9356 eV 315.03 nm f= 0.08110 Spin multiplicity= 1: H-3 -> L 36.3%, H-1 -> L+2 13.7%, H-4 -> L 8.8%, H -> L+3 7.1%, H -> L+6 6.9%, H-3 -> L+1 5.8%, H-1 -> L+1 5.1% Spin multiplicity= 1: #12 3.9686 eV 312.41 nm f= 0.12600 H-1 -> L+2 31.0%, H-3 -> L 20.4%, H-4 -> L 8.1%, H -> L+4 7.3%, H -> L+6 7.1%, H-1 -> L+1 6.9% 4.0363 eV #13 307.17 nm f= 0.28270 Spin multiplicity= 1: H-2 -> L+1 35.0%, H-9 -> L 12.6%, H-4 -> L 11.0%, H -> L+4 6.5%, H-1 -> L+2 5.6% 4.0959 eV 302.70 nm f= 0.22590 Spin multiplicity= 1: #14 H-2 -> L+1 30.7%, H-4 -> L 14.7%, H -> L+7 10.1%, H -> L+4 6.8% 300.92 nm f=0.00580Spin multiplicity= 1: #15 4.1202 eV H-8 -> L 31.5%, H-5 -> L 15.0%, H -> L+8 7.6%, H -> L+7 7.0%, H-9 -> L 6.7%, H-12 -> L 5.9% #16 4.1627 eV 297.85 nm f= 0.00370 Spin multiplicity= 1: H-5 -> L 16.8%, H-11 -> L 16.5%, H-12 -> L 10.5%, H -> L+8 10.2%, H-4 -> L 10.0%, H-9 -> L 8.5%

- #17 4.1989 eV 295.28 nm f= 0.01680 Spin multiplicity= 1:
- H -> L+7 39.7%, H-3 -> L+1 11.1%, H-3 -> L 9.4%, H-6 -> L 6.5%, H-4 -> L 5.1%
- #18 4.2114 eV 294.40 nm f= 0.00260 Spin multiplicity= 1: H-6 -> L 74.4%, H-6 -> L+1 11.5%
- #19 4.2201 eV 293.79 nm f= 0.02650 Spin multiplicity= 1:
- H-11 -> L 35.7%, H -> L+5 16.3%, H-12 -> L 15.6%, H-13 -> L 7.3%, H-11 -> L+1 5.8%
- #20 4.2278 eV 293.26 nm f= 0.00340 Spin multiplicity= 1: H-5 -> L 26.7%, H-8 -> L 25.2%, H-7 -> L 18.4%, H-8 -> L+1 7.2%

Table S6. Detailed information on the calculated excited states for the planar PyTs-COF, including the excitation energies (in eV) and wavelength (in nm), oscillator strengths (f) and the molecular orbital transition contributions (in %) to each excited state, and the spin multiplicity. Only the transition contributions greater than 5% are given here.

Spin multiplicity= 1: #1 2.2836 eV 542.93 nm f=1.33620 H -> L 97.8% 2.6732 eV 463.80 nm f = 0.24050Spin multiplicity= 1: #2 H -> L+1 96.8% #3 2.9544 eV 419.66 nm f = 0.04700Spin multiplicity= 1: H -> L+2 90.6% #4 3.0867 eV 401.67 nm f= 0.53600 Spin multiplicity= 1: H-1 -> L 74.3%, H -> L+3 8.1%, H -> L+2 6.7% 3.3283 eV 372.52 nm f= 0.28710 #5 Spin multiplicity= 1: H-2 -> L 67.1%, H-3 -> L 8.8%, H-1 -> L 5.1% 3.4304 eV 361.43 nm f= 0.42090 Spin multiplicity= 1: #6 H-3 -> L 57.1%, H -> L+3 11.2%, H -> L+5 8.3%, H-1 -> L 6.8%, H-1 -> L+1 6.4% 3.5690 eV 347.39 nm Spin multiplicity= 1: #7 f=0.11370 H-1 -> L+1 44.3%, H-2 -> L 15.0%, H-3 -> L 13.8%, H -> L+3 10.3%, H-2 -> L+1 5.7% 3.6228 eV 342.23 nm f=0.00020 Spin multiplicity= 1: #8 H-10 -> L 59.9%, H-10 -> L+1 21.6%, H-10 -> L+2 15.4% #9 3.6418 eV 340.45 nm f= 0.23020 Spin multiplicity= 1: H -> L+3 30.2%, H-1 -> L+1 15.0%, H -> L+4 11.5%, H-2 -> L+1 11.2%, H-1 -> L+2 6.0%, H-2 -> L 5.8%, H-1 -> L 5.2% #10 3.7062 eV 334.53 nm Spin multiplicity= 1: f= 0.00220 H -> L+4 34.5%, H -> L+5 26.4%, H -> L+3 12.2%, H-6 -> L 7.9% Spin multiplicity= 1: #11 3.7263 eV 332.73 nm f= 0.00180 H-6 -> L 22.4%, H-4 -> L 21.7%, H -> L+4 12.1%, H-5 -> L 11.2%, H-9 -> L 10.5%, H-2 -> L 5.9% #12 3.7882 eV 327.29 nm f = 0.04280Spin multiplicity= 1: H-1 -> L+2 14.0%, H-2 -> L+1 13.9%, H-1 -> L+1 13.1%, H-4 -> L 12.8%, H -> L+5 12.8%, H-5 -> L 9.5%, H-3 -> L+1 6.8%, H -> L+3 5.5% #13 3.8124 eV 325.21 nm f= 0.04360 Spin multiplicity= 1: H-4 -> L 54.8%, H-6 -> L 23.5% Spin multiplicity= 1: #14 3.8592 eV 321.27 nm f= 0.00020 H-8 -> L 50.0%, H-9 -> L 11.2%, H-5 -> L 6.8%, H-7 -> L 6.5%, H-6 -> L 6.1% 3.8998 eV #15 317.92 nm f= 0.03850 Spin multiplicity= 1: H -> L+5 18.4%, H-7 -> L 15.2%, H -> L+4 10.7%, H-5 -> L 8.5%, H-2 -> L+1 7.9%, H-3 -> L 7.8%, H-1 -> L+2 6.6% #16 3.9059 eV 317.43 nm f = 0.00420Spin multiplicity= 1: H-5 -> L 23.3%, H-7 -> L 16.1%, H -> L+4 11.0%, H-6 -> L 10.6%, H -> L+5 9.8%, H-9 -> L 8.5%, H-8 -> L 5.6% #17 3.9258 eV 315.82 nm f= 0.00630 Spin multiplicity= 1:

H-7 -> L 49.5%, H-8 -> L 29.0%, H-6 -> L 10.2%

- #18 3.9327 eV 315.26 nm f= 0.41650 Spin multiplicity= 1: H-2 -> L+1 44.0%, H-1 -> L+2 36.8%, H-2 -> L+2 9.7%
- #19 3.9810 eV 311.44 nm f= 0.01110 Spin multiplicity= 1: H-9 -> L 47.2%, H-5 -> L 17.6%, H -> L+7 6.6%, H-7 -> L 5.9%
- #20 4.0153 eV 308.78 nm f= 0.00920 Spin multiplicity= 1: H-3 -> L+1 72.2%, H -> L+5 5.4%

Sample	Excited	D-index	$\Delta \mu$	Ec	Sr index	t index	Δσ	H index	HDI	EDI
	state	(Å)	(Debye)	(eV)	(a.u.)	(Å)	(Å)	(Å)		
planar	S 1	3.69	17.78	2.80	0.78	-0.72	1.81	5.46	4.95	4.18
PyTs-COF	S2	8.62	41.48	2.07	0.59	3.66	3.05	5.98	5.02	4.38
	S3	10.17	48.93	1.85	0.50	5.63	1.58	5.41	4.85	5.23
twisted	S1	7.40	35.53	2.40	0.56	3.10	1.48	4.95	5.33	5.19
PyTs-COF	S2	5.73	27.50	2.50	0.73	0.50	3.56	5.96	5.26	4.27
	S3	8.65	41.52	2.17	0.56	3.92	2.24	5.39	5.28	4.91

Table S7. Summary of parameters associated with the excited states and analysis of electron and hole distributions and exciton transfer.

Note:

1) D index represents the distance between the centroids of hole and electron distributions.

2) $\Delta\mu$ represents the ground to excited state transition electric dipole moments.

3) Ec is the coulomb barrier or the coulomb attractive energy between the holes and electrons.

4) Sr index represents the overlapping degree of the hole and electron.

5) t index is a measure of the charge transfer character. When it is negative, it means the charge transfer is not sufficient. When it turns positive, it means the charge transfer excitation dominates.

6) $\Delta \sigma$ is a measure of the difference between the root mean square deviation (RMSD) of the overall spatial distribution of electrons and holes and is positively correlated with the charge transfer excitation.

7) H index is also positively correlated with the charge transfer excitation.

8) HDI and EDI are hole delocalization index and electron delocalization index, respectively.

Photocatalyst	Cocatalyst	Sacrificial agent	Light source	AQY (%)	H_2 (mmol g ⁻¹ h ⁻¹)	Ref.
PyTs-COF	5% Pt	0.1 M AA	>420 nm	4.89 ^a	21.554	This work
SP ² C-OF _{ERDN}	3% Pt	10 vol% TEOA	>420 nm	0.46 ^a	2.120	1
A-TEBPY- COF	2.2% Pt	10 vol% TEOA pH = 7	AM 1.5G		0.098	2
Py-HTP-BT- COF	5% Pt	0.1 M AA	>420 nm		1.078	3
Py-FTP-BT- COF	5% Pt	0.1 M AA	>420 nm		2.875	3
Py-ClTP-BT- COF	5% Pt	0.1 M AA	>420 nm	8.45 ª	8.880	3
Ni-Py-COF	Pt	0.017 M AA	>420 nm	4.28 ^a	13.231	4
PyTA-BC- COF	Pt	0.1 M AA	>420 nm	1.46 ^a	5.030	5
PyTA-BC- Ph-COF	Pt	0.1 M AA	>420 nm	1.83 a	2.760	5
PyTz-COF	3% Pt	0.1 M AA	AM 1.5G		2.072	6
Py-MPA- COF	7% Pt	0.1 M AA	>420 nm		5.166	7
Py-PDCA- COF	7% Pt	0.1 M AA	>420 nm		15.450	7
Py-DHBD- COF	0.5% Pt	0.01 M AA	>420 nm		16.980	8
Benzd-COF	3% Pt	0.1 M AA	350-780 nm	6.3 ^b	2.027	9
Azod-COF	3% Pt	0.1 M AA	350-780 nm	4.2 ^b	0.537	9
TZ-COF-4	8% Pt	0.1 M AA	>420 nm		4.296	10
IL-COF-2	8% Pt	0.1 M AA	>420 nm		1.644	10
S-COF	8% Pt	0.1 M AA	>420 nm		4.440	11
FS-COF	8% Pt	0.1 M AA	>420 nm		10.000	11
P7-CMP	Pt	TEOA/MeOH	>420 nm	2.25 ^a	4.644	12
P10		H ₂ O/TEOA/MeOH (1/1/1)	>420 nm		2.825	13
FS4		H ₂ O/TEOA/MeOH (1/1/1)	>420 nm	1.09 ª	0.238	14
FS5		H ₂ O/TEOA/MeOH (1/1/1)	>420 nm	2.07 ª	1.370	14
P62		H ₂ O/TEOA/MeOH	AM 1.5G		5.203	15
P64		H ₂ O/TEOA/MeOH	AM 1.5G		6.039	15

Table S8. PHER performances of reported pyrene- or sulfone-based polymers and COFs.

^a The AQY was measured under irradiation with a monochromic bandpass of 420 nm.

^b The AQY was measured under irradiation with a monochromic bandpass of 365 nm.

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