Structural regulation of covalent organic frameworks via isomerism for enhanced photocatalytic hydrogen peroxide production

Guoye Yu[a], Ruoxuan Zhang[a], Xin Zhao[a], Jiaojiao Bi[b,*], Guangchao Han [c], Yingjie Zhao[a,*] & Yuancheng Wang[a,*]

[a] State Key Laboratory of Advanced Optical Polymer and Manufacturing Technology, College of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

[b] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

[c] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 10019, China

*Corresponding authors.

E-mail addresses: bijiaojiao0819@qust.edu.cn (J. Bi), yz@qust.edu.cn (Y. Zhao), wangyuancheng@qust.edu.cn (Y. Wang).

Supporting Information

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1. Supporting Methods

1.1 General materials and methods

Unless otherwise specified, all reactions were performed in dried glassware under ambient atmosphere. All other reagents were purchased commercially and used without further purification. Organic solvents including ethanol, dichloromethane (DCM), petroleum ether and tetrahydrofuran were purchased from Adamas; acetic acid and 1,4-dioxane were purchased from Alfa Aesar; dilute hydrochloric acid was purchased from Yantai Far East Fine Chemical Co., Ltd. All aqueous solutions were prepared with Milli-Q water.

^{1}H and ^{13}C NMR spectra were performed on 400 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. High-resolution solid-state NMR spectra were recorded on Agilent NMR Spectrometer (60054-ASC) using a standard CP pulse sequence probe with 4 mm (outside diameter) zirconia rotors.

Scanning electron microscope (SEM) images were collected using scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV. Transmission electron microscope (TEM) was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV.

TGA was carried out on an American TA-Q20 in nitrogen atmosphere using a 10 °C/min ramp without equilibration delay.

The Solid-state UV-Vis absorbance was measured by UV spectrophotometer (HITACHI, U-3900).

Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical Empyrean X-ray diffractometer with Cu Kα line focused radiation at 40 kV and 40 mA from $2\theta = 1.5°$ up to 40° with 0.02° increment by Bragg-Brentano. The powdered sample was added to the glass and compacted for measurement.

N_2 adsorption isotherms were measured up to 1 bar at 77 K using a Micrometrics ASAP 2460 surface area analyzer. Prior to measurements, samples (ca. 100 mg) were degassed for over 12 h at 120 °C. UHP grade N_2 and He were used throughout the adsorption experiments. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

1.1.1 Photocurrent measurements

Photocurrent measurements were performed on the CHI 760E electrochemical system (Shanghai, China), using indium fluorine doped oxide coated glass slides as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode in a three-electrode system. The mixed binder solution is made up of 75 microliters (polytetrafluoroethylene emulsion) and ethanol (675 microliters). The solution was mixed with the COF (5 mg), the COF sample was dispersed by ultrasound, and the solution (50 μl) was dropped onto the FTO glass working electrode (active area 1 cm^2). The samples were dried at 50 °C for 30 minutes. N_2 was used to purify the three electrode systems for 5 min before measurement. Measurements were performed in a 0.2 M Na_2SO_4 solution and the back of the FTO working electrode was illuminated with a solar simulator (1 Sun, ABA grade).

(1) Electrochemical Impedance Spectroscopy

The measurements were conducted at an applied bias of **-0.5 V (vs. Ag/AgCl)**. The AC perturbation amplitude was **5 mV**. The frequency range was set from **100 kHz to 0.1 Hz**. A quiet time of **2 s** was applied before each measurement.

The impedance data were collected in 0.2 M Na_2SO_4 aqueous electrolyte under dark conditions. The sensitivity scale was set to automatic. The **FT mode** was selected for frequencies above **100 Hz**. For each frequency decade, **12 data points** were recorded with **1 cycle** per frequency.

(2) Transient photocurrent

Transient photocurrent responses were recorded using an amperometric i-t technique on a CHI 760E electrochemical workstation with a three-electrode system. The applied bias was set at **0 V (vs. Ag/AgCl)**. The sampling interval was **0.1 s**, and the total measurement time was **400 s**. No quiet time was applied before measurement. The current sensitivity was set to **1×10^{-6} A V^{-1}**.

Measurements were carried out in 0.2 M Na_2SO_4 electrolyte under chopped light irradiation using a solar simulator (**1 Sun, ABA grade**). The illumination was periodically switched on and off to obtain transient photocurrent responses.

(3) Mott-Schottky

Mott-Schottky measurements were conducted on a CHI 760E electrochemical workstation using a three-electrode configuration. The COF-coated FTO glass was used as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode.

The applied potential was scanned from **+1.0 V to -1.0 V (vs. Ag/AgCl)** with a step potential of **0.01 V**. The AC perturbation amplitude was **5 mV**, and the measurement frequency was fixed at **500 Hz、600Hz and 800Hz**. For frequencies below 10 Hz, **5 cycles** were applied. A quiet time of **2 s** was set before each measurement. The sensitivity scale was set to automatic.

All measurements were performed in **0.2 M Na_2SO_4 aqueous solution** under dark conditions.

1.1.2 Photocatalytic hydrogen peroxide generation

5 mg COF sample was uniformly dispersed into a 25 mL aqueous solution (10 vol% ethanol or deionized water) with ultrasonication for 20 min. Then, O_2 was continually bubbled through the suspension and stirred in the dark for 30 min to achieve adsorption-desorption equilibrium before irradiation. Then, the suspension was irradiated with a 300 W xenon lamp (Perfect Light, Beijing) equipped with a 420 nm cutoff filter under stirring. During the photocatalytic experiment, the solution was sampled at 30-minute

time intervals using a 1 mL syringe, and the photocatalysts were removed using a 0.25 μm millipore filter. Then, the H_2O_2 concentration was quantified by Ti reagent solution using UV-visible spectroscopy.

$Ti(SO_4)_2$ solution as an indicator was prepared to interact with H_2O_2. In detail, 10 g $Ti(SO_4)_2$ was blended in 50 mL concentrated H_2SO_4 solution (98%) and the deionized water was added until the total volume reaches 500 mL. The Ti^{4+} solution will become a yellow complex when it interacts with H_2O_2 as shown in Equation S1.

$$Ti(SO_4)_2 + H_2O_2 \rightarrow H_2[Ti_2(SO_4)_2] \qquad \text{Equation (S1)}$$

Calibrations for the measurements of the H_2O_2 solution. H_2O_2 solution with the specific concentration were prepared. The as-prepared solution (2 mL) was added into the $Ti(SO_4)_2$ solution and monitored by UV-Vis spectrophotometer. The absorbance of these solutions and the corresponding calibration curve are presented:

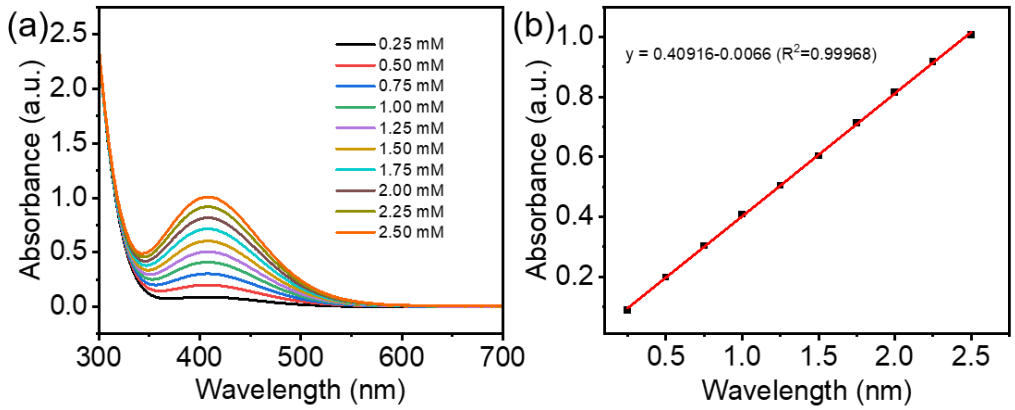
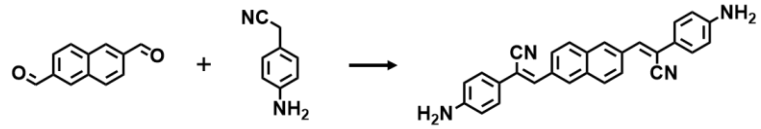


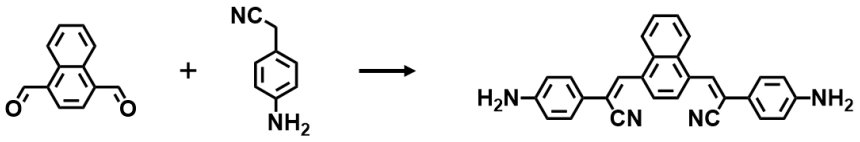
Fig. S1. a) UV-Visible spectra of $Ti(SO_4)_2$ solution with the addition of H_2O_2 solution with different concentration; b) The linear calibration curve between absorbance and H_2O_2 concentration.

1.2 Synthesis procedure



NDA-26

A mixture of 2,6-naphthalenedicarboxaldehyde (0.5 g, 2.71 mmol), 4-aminophenylacetonitrile (1.076g, 8.14 mmol), and sodium hydroxide (2.5 g, 62.5 mmol) was dissolved in a mixed solvent of water (50 mL) and anhydrous ethanol (50 mL). The reaction mixture was heated to 85 °C and stirred for 24 h. After cooling to room temperature, the precipitated solid was collected by filtration, washed sequentially with water, ethanol, and ethyl acetate, and dried under vacuum to afford the product as an orange solid powder (0.96 g, 60.9%). ^{1}H NMR (400 MHz, DMSO-d$_6$, δ): 8.35 (s, 1H), 8.10 (d, J = 8.7 Hz, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.87 (s, 1H), 7.51 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.7 Hz, 2H), 5.68 (s, 2H).



NDA-14

Synthesis of the NDA-14

A mixture of 1,4-naphthalenedicarboxaldehyde, 4-aminophenylacetonitrile, and sodium hydroxide was dissolved in a mixed solvent of water and anhydrous ethanol. The reaction mixture was heated to 85 °C and stirred for 24 h. After cooling to room temperature, the precipitated solid was collected by filtration, washed sequentially with water, ethanol, and ethyl acetate, and dried under vacuum to afford the product as an orange solid powder. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ): 8.37 (s, 1H), 8.23 (s, 1H), 8.00 (s, 1H), 7.74 (s, 1H), 7.61 (s, 2H), 6.77 (s, 2H), 5.73 (s, 2H).

Synthesis of the Trans-COF

A 10 ml Pyrex glass tube was charged with (2Z,2'Z)-3,3'-(naphthalene-2,6-diyl)bis(2-(4-aminophenyl)acrylonitrile) (29.4 mg, 0.0714 mmol), 2,4,6-Trimethoxy-1,3,5-benzenetricarboxaldehyde (12 mg, 0.0476 mmol), o-dichlorobenzene (1.4 mL), benzyl alcohol (0.6 mL) and 6 M aqueous acetic acid (0.2 mL). After being degassed by freeze-pump-thaw technique for three times and sealed under vacuum, the tube was placed in an oven at 120 ℃ for 7 d. The resulting precipitate was filtered by tetrahydrofuran and ethanol, and dried at 120 ℃ under vacuum for 12 h. The Trans-COF was isolated as a red powder.

Synthesis of the Cis-COF

A 10 ml Pyrex glass tube was charged with (2Z,2'Z)-3,3'-(naphthalene-1,4-diyl)bis(2-(4-aminophenyl)acrylonitrile) (29.4 mg, 0.0714 mmol), 2,4,6-Trimethoxy-1,3,5-benzenetricarboxaldehyde (12 mg, 0.0476 mmol), o-dichlorobenzene (1.4 mL), benzyl alcohol (0.6 mL) and 6 M aqueous acetic acid (0.2 mL). After being degassed by freeze-pump-thaw technique for three times and sealed under vacuum, the tube was placed in an oven at 120 ℃ for 7 d. The resulting precipitate was filtered by tetrahydrofuran and ethanol, and dried at 120 ℃ under vacuum for 12 h. The Cis-COF was isolated as a dark red powder.

2. Fig.s and Legends

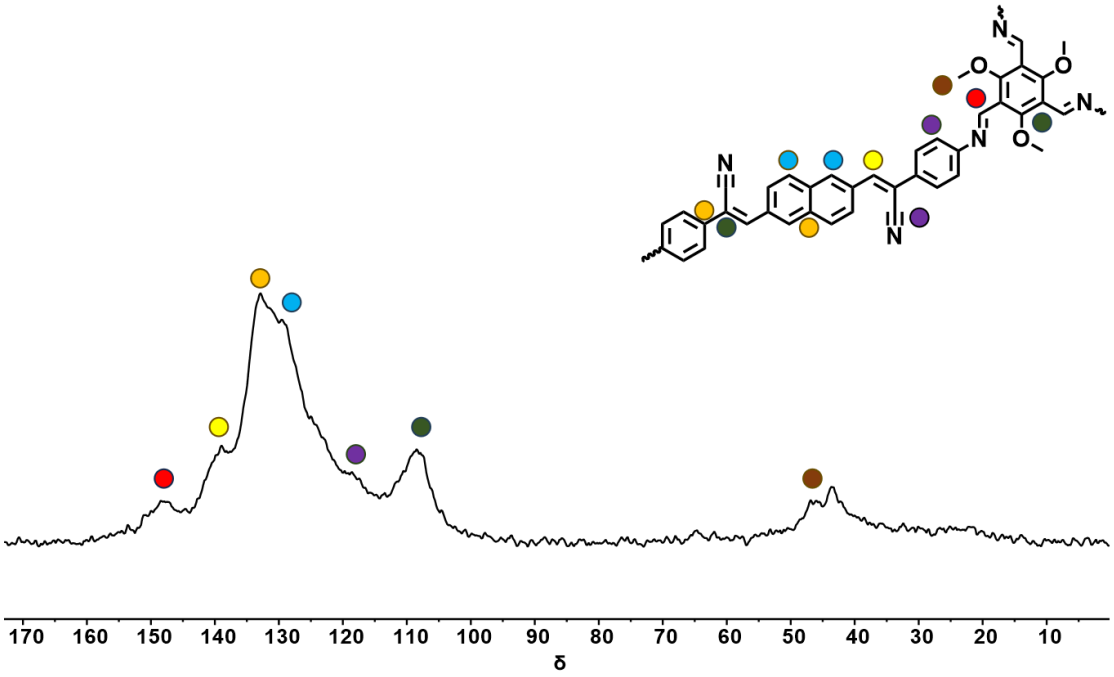


Fig. S2. Solid-state ^{13}C CP/MAS NMR spectra of Trans-COF.

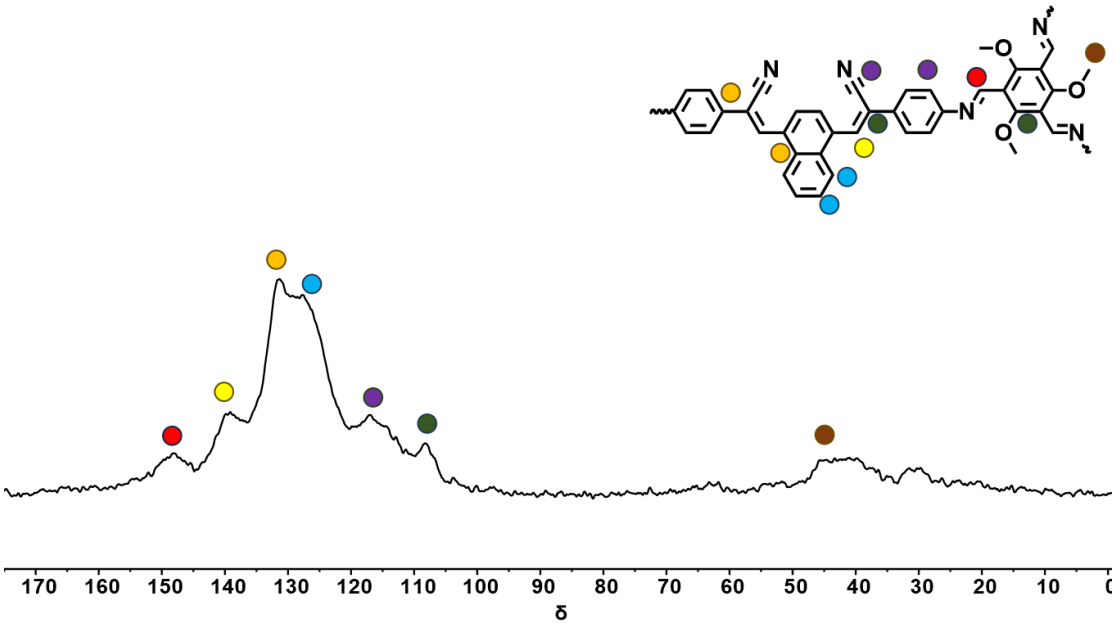


Fig. S3. Solid-state ^{13}C CP/MAS NMR spectra of Cis-COF.

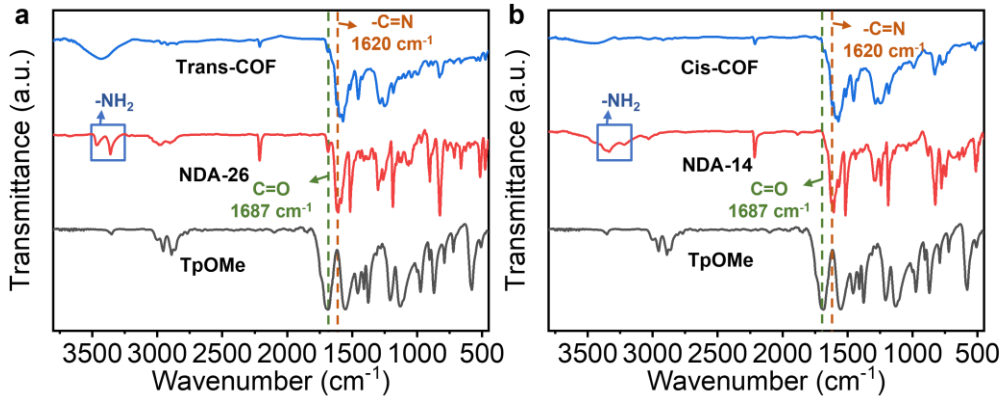


Fig. S4. (a) FTIR spectra of Trans-COF and monomers; (b) FTIR spectra of Cis-COF and monomers.

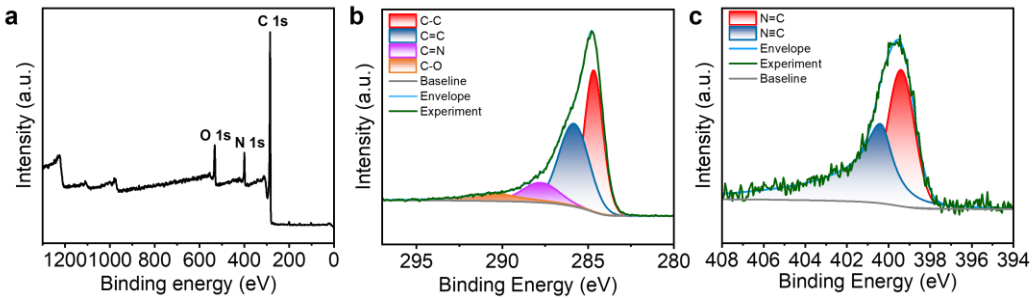


Fig. S5. (a) XPS spectra of Trans-COF; (b) C 1s XPS spectra of Trans-COF; (c) N 1s XPS spectra of Trans-COF.

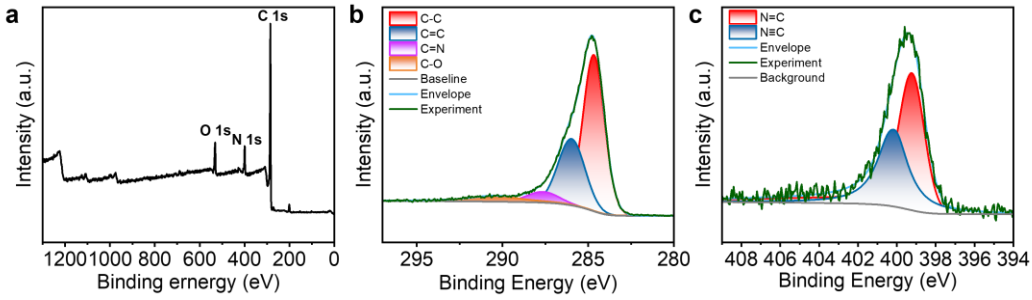


Fig. S6. (a) XPS spectra of Cis-COF; (b) C 1s XPS spectra of Cis-COF; (c) N 1s XPS spectra of Cis-COF.

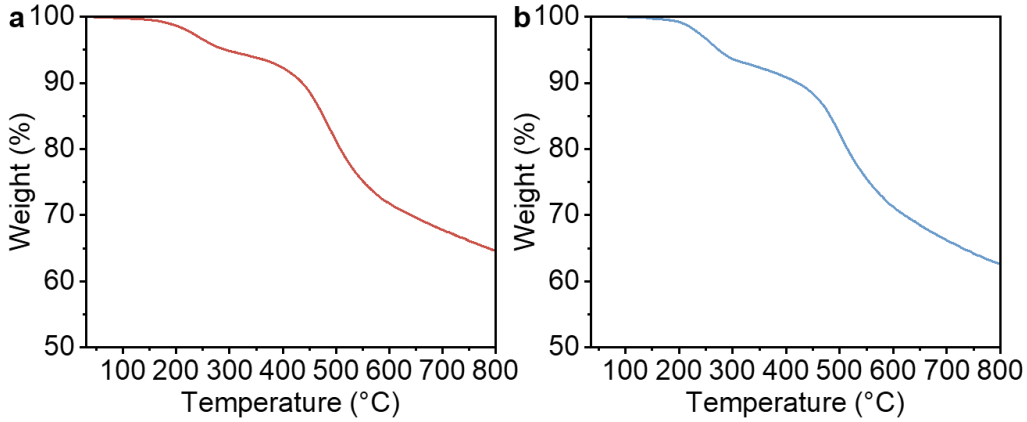


Fig. S7. TGA profiles of Trans-COF (a) and Cis-COF (b).

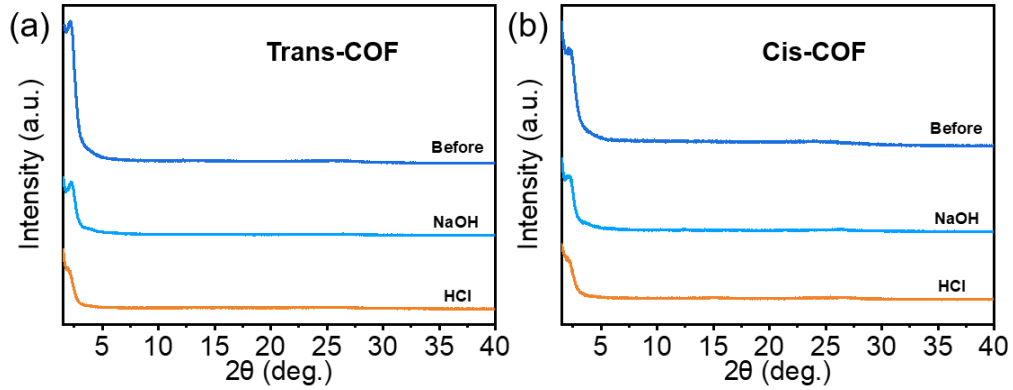


Fig. S8. The chemical stability of the Trans-COF and Cis-COF.

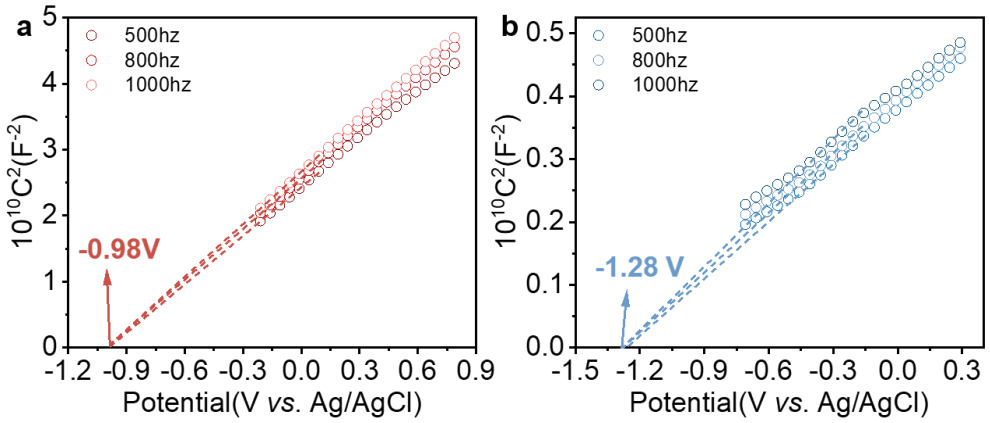


Fig. S9. Mott-Schottky plots of Trans-COF (a) and Cis-COF(b).

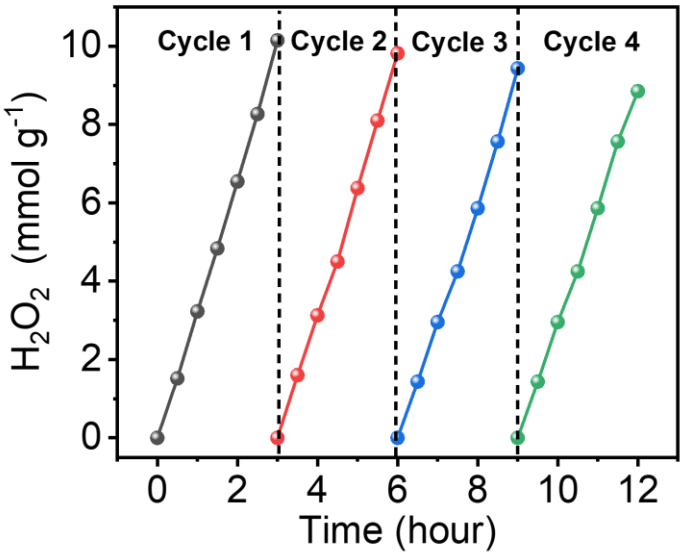


Fig. S10. Photocatalytic H_2O_2 evolution for Trans-COF in a water/benzyl alcohol mixture (9:1, v/v) over three hours for different cycles.

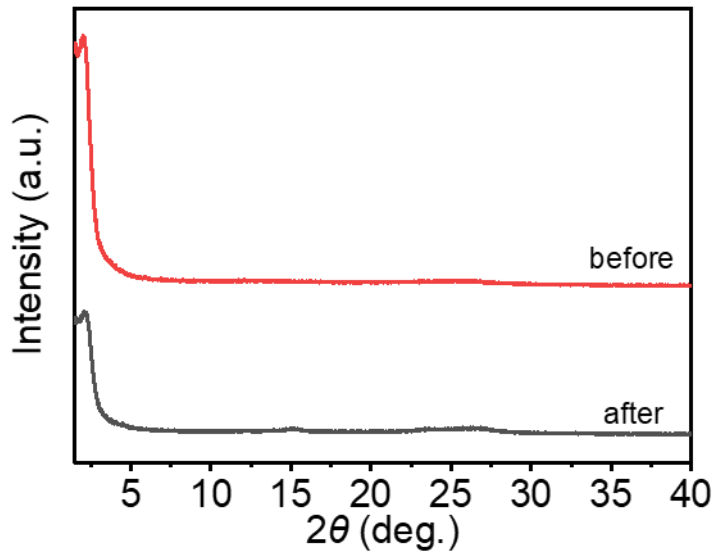


Fig. S11. PXRD patterns of Tran-COF after photocatalytic H_2O_2 evolution.

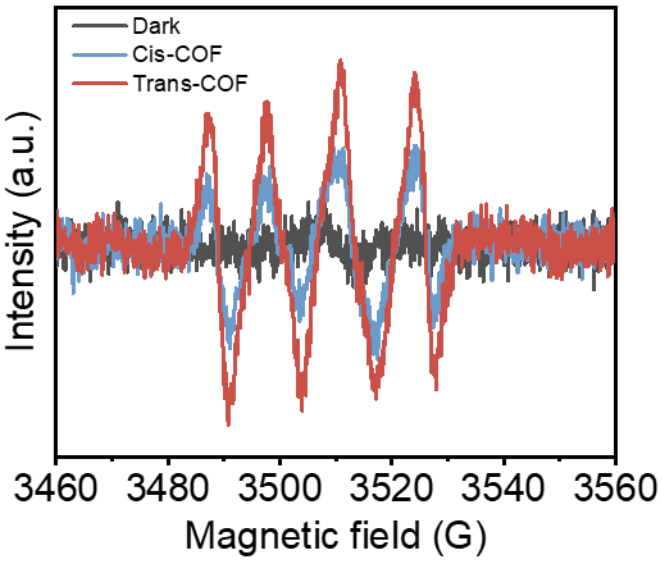


Fig. S12. EPR signals of a dispersion of Trans-COF and Cis-COF in water in the dark and under light illumination in the presence of DMPO as a spin trap.

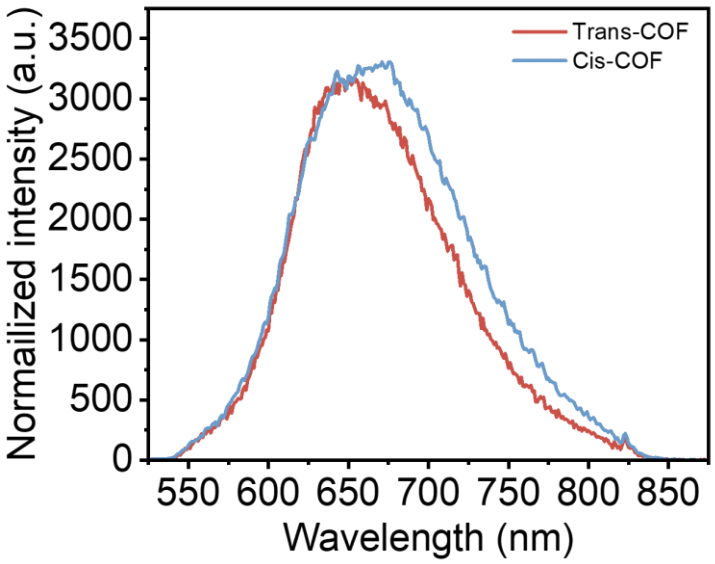


Fig. S13. Solid-state fluorescence spectroscopy of Trans-COF (red curve) and Cis-COF (blue curve).

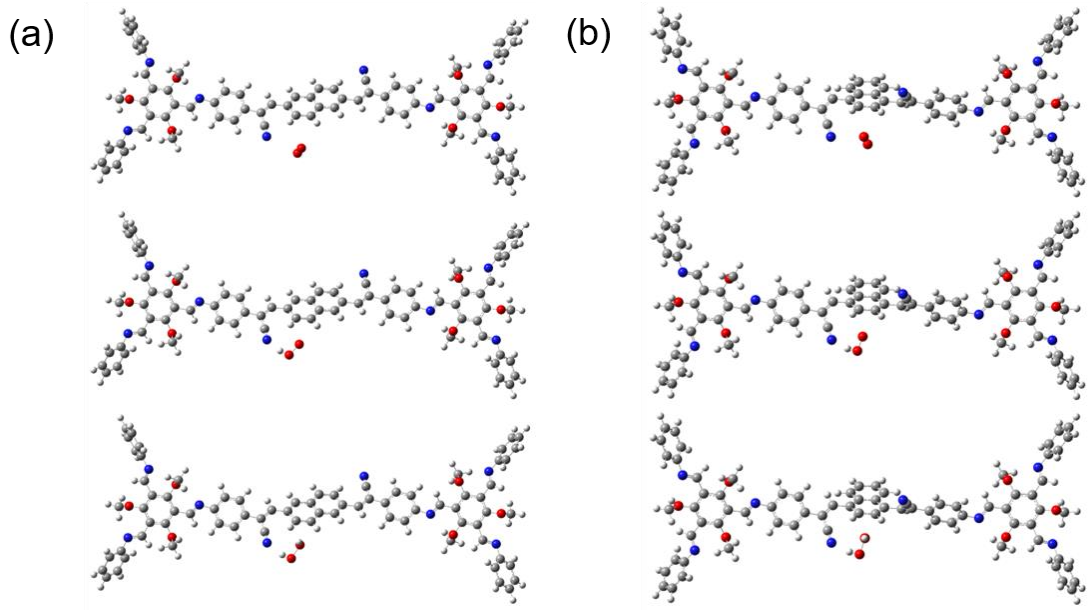


Fig. S14. Optimized adsorption configurations of O_2 and intermediates on possible active sites of Tans-COF (a) and Cis-COF (b).

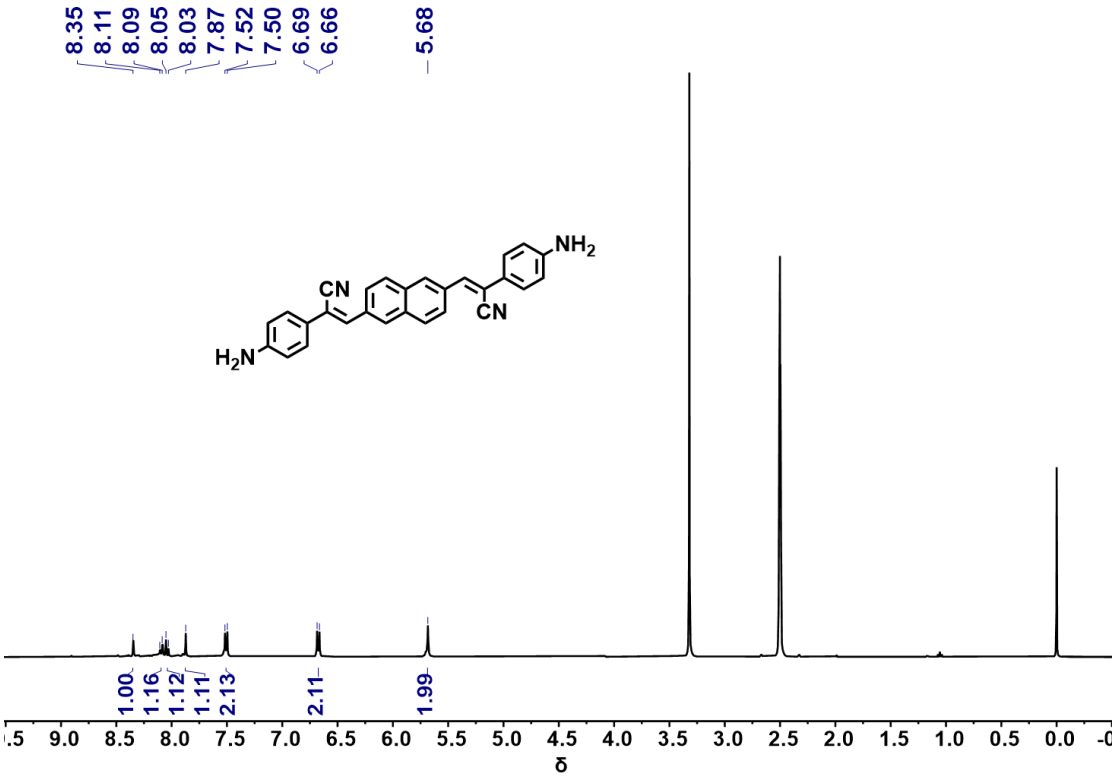


Fig. S15. ^{1}H NMR spectra of NDA-26.

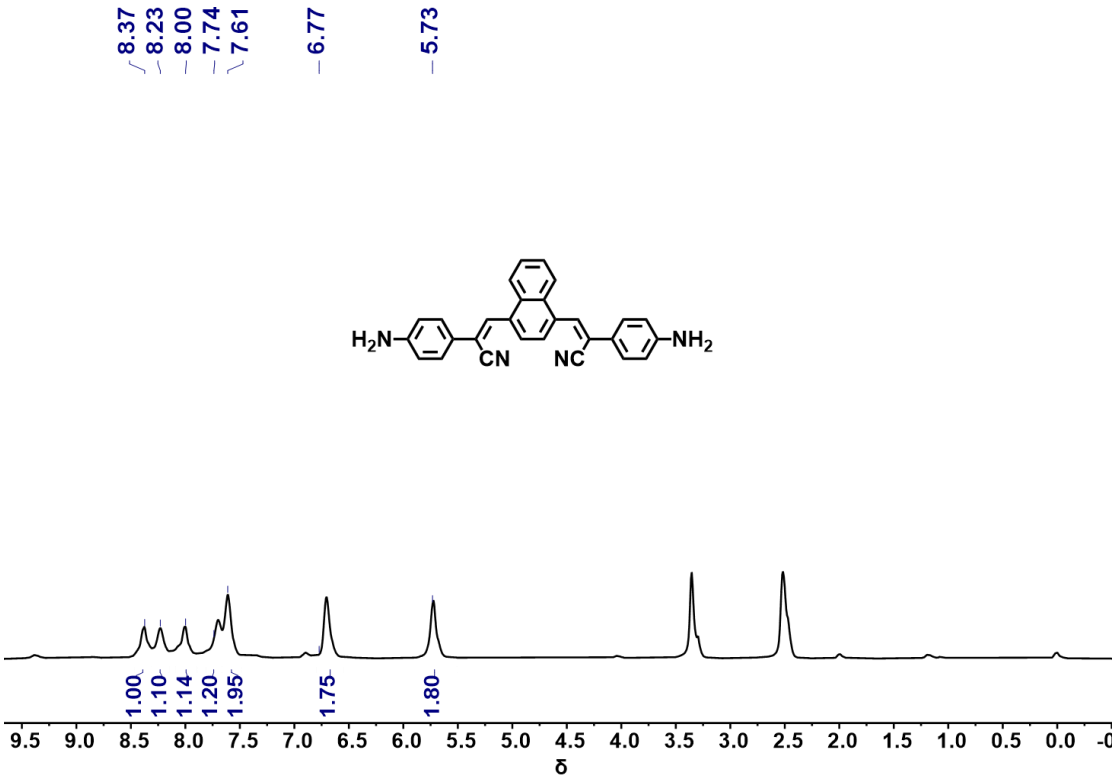


Fig. S16. ^{1}H NMR spectra of NDA-14.

Table S1. Atomic coordinates of the AA-stacking model of Cis-COF using DFTB method.

Space group: P31M a = 44.8735 Å, b = 44.8735 Å, c =4.0126 α = β = 90°, γ = 120°			
	X	Y	Z
N1	0.60939	0.37107	0.14437
C2	0.41652	0.39862	-0.6268
C3	0.41279	0.44876	-0.476
C4	0.44533	0.46368	-0.3203
C5	0.46002	0.49642	-0.1658
C6	0.49228	0.51012	-0.0127
C7	0.51474	0.44041	-0.1269
C8	0.45315	0.54849	-0.1871
C9	0.43234	0.56484	-0.1103
C10	0.44767	0.59708	0.04755
C11	0.42805	0.61213	0.13433
C12	0.39267	0.59537	0.05891
C13	0.37748	0.56336	-0.1004
C14	0.39706	0.54824	-0.1859
C15	0.48729	0.56973	-0.323
N16	0.51461	0.58684	-0.4311
C17	0.36806	0.68847	0.31654
C18	0.34438	0.70052	0.30274
C19	0.38119	0.64069	0.23904
O20	0.30924	0.59366	0.30028
C21	0.28329	0.70731	0.57609
H22	0.40551	0.37375	-0.7471
H23	0.3982	0.46196	-0.4864
H24	0.50319	0.5342	0.12174
H25	0.49966	0.41444	-0.0318
H26	0.47472	0.61024	0.11207
H27	0.4407	0.63633	0.26637
H28	0.35032	0.5501	-0.1595
H29	0.38467	0.52367	-0.3132
H30	0.40824	0.65914	0.24167
H31	0.28324	0.73052	0.48156
H32	0.30559	0.71579	0.74496
H33	0.25908	0.69157	0.71607

Table S2. Atomic coordinates of the AA-stacking model of Trans-COF using DFTB method.

Space group: P3 a = 48.3139 Å, b = 48.3139 Å, c = 3.7543 α = 90°, β = 90°, γ = 120°			
	X	Y	Z
C1	-6.65021	-4.2994	-0.49624
C2	-6.6842	-4.31698	-0.49766
C3	-6.59732	-4.2971	-0.52104
O4	-6.63312	-4.36712	-0.55407
N5	-6.58132	-4.26983	-0.35562
C6	-6.60813	-4.36241	-0.31303
C7	-6.89147	-4.70477	0.1938
C8	-6.87737	-4.72415	0.16221
C9	-6.84442	-4.70958	0.08965
C10	-6.82603	-4.67639	0.03462
C11	-6.84078	-4.65743	0.04784
C12	-6.87348	-4.67181	0.12992
C13	-6.79299	-4.66173	-0.02561
C14	-6.77469	-4.62858	-0.07395
C15	-6.78929	-4.60948	-0.0788
C16	-6.82245	-4.62432	-0.01299
C17	-6.77141	-4.57389	-0.12179
C18	-6.8954	-4.75926	0.22728
C19	-6.7425	-4.55514	-0.27595
C20	-6.9259	-4.77977	0.12658
C21	-6.72914	-4.51994	-0.29471
C22	-6.94051	-4.81471	0.19628
C23	-6.69678	-4.49898	-0.21076
C24	-6.68395	-4.46582	-0.23177
C25	-6.70295	-4.45295	-0.34164
C26	-6.73548	-4.47386	-0.42309
C27	-6.74836	-4.50703	-0.401
C28	-6.97281	-4.83286	0.30136
C29	-6.98678	-4.86574	0.3655
C30	-6.96891	-4.88115	0.32516
C31	-6.93666	-4.86322	0.2166
C32	-6.92267	-4.83035	0.15178
C33	-6.94522	-4.76892	-0.05616
C34	-6.72365	-4.56759	-0.43552
N35	-6.96085	-4.76038	-0.20135
N36	-6.7082	-4.57717	-0.56392
N37	-6.93068	-4.0157	0.39027

C38	-6.96615	-3.98084	0.45043
C39	-6.98539	-3.96624	0.4407
C40	-6.96171	-4.03055	0.38166
O41	-6.93255	-3.96266	0.41246
C42	-7.0638	-3.97871	0.64901
H43	-6.58496	-4.30671	-0.67119
H44	-6.58588	-4.35531	-0.46733
H45	-6.61508	-4.38535	-0.17457
H46	-6.60306	-4.34381	-0.11025
H47	-6.91615	-4.71473	0.27587
H48	-6.8331	-4.72416	0.07645
H49	-6.885	-4.65748	0.15179
H50	-6.78112	-4.67581	-0.02659
H51	-6.74916	-4.61845	-0.09414
H52	-6.83401	-4.60994	-0.00487
H53	-6.78365	-4.5619	-0.01657
H54	-6.88195	-4.76896	0.35699
H55	-6.68152	-4.50827	-0.12474
H56	-6.65902	-4.45003	-0.16322
H57	-6.75122	-4.46494	-0.49961
H58	-6.77329	-4.52261	-0.47088
H59	-6.98718	-4.82154	0.33766
H60	-7.01164	-4.87928	0.44801
H61	-6.92238	-4.8746	0.17797
H62	-6.89805	-4.81732	0.06043
H63	-7.08619	-3.98833	0.48991
H64	-7.06018	-3.957	0.79296
H65	-7.00311	-4.06975	0.84951