Spatial Regulation of Acceptor Units in Olefin-Linked COFs toward Highly Efficient Photocatalytic H₂ Evolution

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Supporting Information

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Section 1. Experimental details.

General. All materials were commercially available and used without further purification. All solvents were of analytical grade and used without further purification. 2,4,6-trimethyl-1,3,5-triazine (TA-CH₃), [2,2′-bipyridine]-5,5′-dicarbaldehyde (Bpy-CHO) and benzoic anhydride were purchased from Energy Chemical (97%), HEOWNS (98%) and Aladdin (98%), respectively.

Characterization. ¹H and ¹³C nuclear magnetic resonance (NMR) was recorded on Bruker 400 M NMR spectrometer. Magic angle spinning (MAS) solid-state Nuclear magnetic resonance (ssNMR) spectra were recorded using a Bruker Avance III WB 400 spectrometer. PXRD patterns of all the materials were collected at ambient temperature on Rigaku Dmax 2500 diffractometer using Cu Kα (λ=1.5418 Å) radiation, with a scan speed of 5 sec/step, a step size of 0.01° in 2θ, and a 2θ range of 1.5° to 30°. Fourier transform infrared spectra (FT-IR) were recorded on Nicolet IS10. X-ray photoelectron spectroscopy (XPS) measurements were performed on an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB Xi+). Low pressure gas adsorption measurements were measured with BELSORP MaxII for surface area and pore size analysis. A liquid nitrogen bath was used for the N₂ measurements at 77 K and CO₂ sorption isotherms were measured at 298 K. UV-vis diffused reflectance spectra were measured on a UV spectrophotometer (UV-2700, Shimadzu). Steady-state photoluminescence (PL) and excited-state decay spectra were measured on FLS1000-Edinburgh Instruments. Photoelectrochemical characterization was carried out on a CHI600E workstation. Hydrophobic angle of the COFs were tested on a SINDIN SDC-200. The transmission electron microscopy (TEM, JEOL-JEM 2100 F) was used to analyze the morphologies of NKCOFs. Hall effect was performed by Ecopia HMS-7000 at 300 K.

Photocatalytic H₂ evolution
A flask was charged with a given mass of the COFs powder, 10 mL Triethanolamine (TEOA), 90 mL water solution, and a certain proportion hexachloroplatinic acid (50mM aqueous solution) as a Pt precursor. Then the resulting suspension was transferred into a Pyrex top-irradiation reaction vessel connected to a closed gas system. The resulting suspension was ultrasonicated for 20 min before degassing. The reaction mixture was evacuated several times to ensure complete removal of air and then was illuminated with a 300 W Xe light source ($\lambda > 420$ nm) with appropriate filters for the period specified. The temperature of the reaction solution was maintained at room temperature by the flow of cooling water. The evolved gases were analyzed by gas chromatography with argon as the carrier gas. Hydrogen was detected with a thermal conductivity detector (TCD) referencing standard gas with a known concentration of hydrogen. After the photocatalysis experiment, the COFs were recovered by washing with methanol before drying at 120 °C.

Photocatalytic oxygen evolution

50 mg of Pt@COFs was well dispersed by ultrasonication in an aqueous solution (100 mL) containing, Ce(NH$_4$)$_2$(NO$_3$)$_6$ (0.1 mol L$^{-1}$) as electron acceptor and La$_2$O$_3$ (0.2 g) as pH buffer. The suspension was poured into a Pyrex top-irradiation reaction vessel connected to a closed gas system. Then it was evacuated several times to completely remove air prior to irradiation under a 300 W Xe lamp ($\lambda > 420$ nm). The temperature of the reaction solution was maintained at room temperature by the flow of cooling water. The evolved gases were analyzed by gas chromatography with argon as the carrier gas. Oxygen was detected with a thermal conductivity detector (TCD) referencing against standard gas with a known concentration of oxygen.

Photocatalytic overall water splitting

50 mg of Pt@COFs was well dispersed by ultrasonication in 100 mL of deionized water.
The suspension was poured into the Pyrex top-irradiation reaction vessel connected to a closed gas system. Then it was evacuated several times to completely remove air prior to irradiation under a 300 W Xe lamp ($\lambda > 420$ nm). The temperature of the reaction solution was maintained at room temperature by the flow of cooling water. The evolved gases were analyzed by gas chromatography with argon as the carrier gas.

**The apparent quantum yield (AQY) measurements**

The apparent quantum yield (AQY) for H$_2$ evolution was measured using 300 W Xe lamp with band pass filter of 420 ± 10 nm, 450 ± 10 nm, 475 ± 10 nm, 500 ± 10 nm, 550 ± 10 nm and 600 ± 10 nm the intensities were 4.8, 6.2, 6.4, 5.4, 5.7 and 4.8 mW cm$^{-2}$, respectively. The irradiation area was controlled as 3.14 × 2.6$^2$ cm$^2$. The AQY was calculated according to the follow Eq.:

$$\eta_{AQY} = \frac{N_e}{N_p} \times 100\% = \frac{2^\times M \times N_A \times h \times c}{S \times \lambda} \times 100\%.$$

Where, $N_e$ is the amount of generated electrons for H$_2$, $N_p$ is the amount of incident photons, $M$ is the amount of H$_2$ molecules (mol) during 0.5 hour, $N_A$ is Avogadro constant (6.022 × 10$^{23}$ mol$^{-1}$), $h$ is the Planck constant (6.626 × 10$^{-34}$ J·s), $c$ is the speed of light (3 × 10$^8$ m/s), $S$ is the irradiation area (m$^2$), $P$ is the intensity of irradiation light (W /m$^2$), $t$ is the photoreaction time (t=1800 s), $\lambda$ is the wavelength of the monochromatic light (m).

**The Solar-to-hydrogen (STH) measurements**

The STH energy conversion efficiency ($\eta$) was calculated according to the following Eq.:

$$\eta_{STH} = \frac{R_H \times \Delta G^0}{P \times S} \times 100\%;$$

where $R_H$, $\Delta G^0$, $P$, and $S$ denote the rate of H$_2$ evolution (mol s$^{-1}$) in photocatalytic water splitting, standard Gibbs energy of water (237.13 × 10$^3$ J mol$^{-1}$), intensity of simulated sunlight (0.1 W cm$^{-2}$), and irradiation area (21.2 cm$^2$), respectively.
Structure simulations. Structural modeling of all the COFs was generated using the Accelrys Materials Studio software package. The lattice model was geometry optimized using the Forcite module. Pawley refinement was applied to define the lattice parameters.

Computation methods

The calculations were carried out using the Vienna Ab Initio Simulation Package (VASP)\cite{1} with the frozen-core projector-augmented wave (PAW) method\cite{2}. The generalized gradient approximation in the Perdew-Burke-Ernzerhof (GGA-PBE)\cite{3} function was employed for the exchange-correlation energy. A cutoff energy of 400 eV was selected for the plane-wave expansion. The convergence criteria for the force and electronic self-consistent iteration were set to 0.03 eV/Å and $10^{-4}$ eV, respectively. The Gamma k-point was used to sample the Brillion zone.

Adsorption energies were calculated according to $E_{ads} = E_{x/slab} - [E_{slab} + E_{x}]$, where $E_{x/slab}$ is the total energy of the slab with adsorbents in its equilibrium geometry, $E_{slab}$ is the total energy of the bare slab, and $E_{x}$ is the total energy of the free adsorbents in the gas phase. Therefore, the more negative the $E_{ads}$, the stronger the adsorption.

COFs Activation:

The as-synthesized olefin-linked COFs were Soxhlet extracted with tetrahydrofuran and methanol for 48 h. And then these materials were activated by supercritical CO$_2$ for 3 h.

Electrochemical measurements

Cyclic voltammetry measurements were performed in a typical three electrode cell system with a scan rate of 0.05 V/s. The cleaned ITO glass was coated with NKCOFs suspension solutions (1 mg/mL in EtOH and H$_2$O (V : V=1 : 1) with a few droplets of 5 wt% Nafion) and then dried in air as the working electrode. The Pt flake and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. For photocurrent intensity response and flat band potential ($E_{fb}$) measurements, the electrolyte was changed to 0.1 M Na$_2$SO$_4$
aqueous solution, the reference electrode was altered to Ag/AgCl electrode and the light source was provided by a 300 W Xe-lamp with an ultraviolet cut-off filter (λ > 420 nm).

**Synthesis of 2,4,6-Tris(4-formylphenyl)-1,3,5-triazine (TA-1Ph-CHO)**

2,4,6-Tris(4-formylphenyl)-1,3,5-triazine was synthesized according to the reported literature. 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (1.48 g, 2.71 mmol) dissolved in dry THF (200 mL) under a Ar atmosphere. To the stirred solution, n-BuLi was added dropwise (2.5 M in n-hexane, 11 mL, 27.5 mmol) at −78 °C. The temperature was allowed to rise to −60 °C and stirred for 3 h. The obtained solution was treated with anhydrous N, N-dimethylformamide (DMF) (4.19 mL, 54.2 mmol) at −78 °C. The mixture was stirred overnight, while the temperature was allowed to rise to 25 °C. The mixture was acidified with aqueous 3 M HCl (46 mL). The organic volatiles were partially removed by evaporation under reduced pressure, and the product was extracted with CH₂Cl₂ and further purified by silica gel column using CH₂Cl₂ as eluent to afford colorless crystals (600 mg, 55% yield). ¹H NMR (400 MHz, Chloroform-d) δ = 10.20 (s, 3H), 8.96 (d, 6H), 8.13 (d, 6H).

**Synthesis of 4',4'''',4''''''-(1,3,5-triazine-2,4,6-triyl)tris((1,1'-biphenyl)-4-carbaldehyde) (TA-2Ph-CHO)**

1,3,5-tribromobenzene (2.73 g, 5.0 mmol), 4-formylphenylboronic acid (2.40 g, 16.0 mmol), Pd(PPh₃)₄ (0.58 g, 0.5 mmol) and K₂CO₃ (5.53 g, 40 mmol) dissolved in mixed solvent (water : 1,4-dioxane = 1:4, v:v) (200 mL) under a Ar atmosphere. The resulting suspension was heated at 100 °C and reflux for three days. After being cooled to room temperature, a large amount of water was poured into the solution. The precipitate was filtered and washed with acetone, water and methanol. The resulting solid was recrystallized in 1,4-dioxane, the desired product as off-white solid. (1.5 g, 47 %). ¹H NMR (400 MHz, Chloroform-d) δ = 10.04 (s, 3H), 8.86 (d, 6H), 7.97 (d, 6H), 7.82 (d,12H).
Synthesis of 5,5′-bis(cyanomethyl)-2,2′-bipyridine (BPy-CN)

5,5′-bis(cyanomethyl)-2,2′-bipyridine (BCBPy) was synthesized according to the reported literature.[4] A 100 mL round-bottom flask was charged with NiCl₂·6H₂O (0.12 g, 0.5 mmol) and DMF (20 mL). The resulting solution was stirred and heated to 40 °C, and then 2-(6-chloropyridin-3-yl) acetonitrile (10 mmol), anhydrous LiCl (0.43 g, 10 mmol), and zinc dust (0.78 g, 12 mmol) were added. When the temperature rose to 50 °C, a grain of iodine crystal and two drops of acetic acid were added to the mixture. The mixture was stirred at 55-60 °C for 2-3 h until complete conversion of 2-(6-chloropyridin-3-yl) acetonitrile. The cooled reaction mixture was added to 1 N HCl aqueous solution (15 mL) to consume the remaining zinc dust. The resulting mixture was made alkaline with aqueous ammonia (25%) and taken up with CH₂Cl₂. The organic layers were collected, dried over anhydrous Na₂CO₃, and concentrated. The crude material was purified by flash chromatography to give the desired colorless crystals (500 mg, 84% yield).¹H NMR (400 MHz, Chloroform-d) δ = 8.65 (d, 1H), 8.46 (d, 1H), 7.86 (dd, 2.4, 1H), 3.85 (s, 2H).

Synthesis of NKCOF-112-M.

A 10 mL pyrex tube was charged with 2,4,6-trimethyl-1,3,5-triazine (TA-CH₃) (12.3 mg, 0.1 mmol), [2,2′-bipyridine]-5,5′-dicarbaldehyde (Bpy-CHO) (31.8 mg, 0.15 mmol) and benzoic anhydride (45 mg, 0.2 mmol). This mixture was degassed through three freeze-pump-thaw cycles, sealed under vacuum. Then the tube was transferred into an oven to heat at 200 °C for 3 days yielding a yellow solid that was washed with tetrahydrofuran and methanol in a Soxhlet extractor for 48 h (yield ~90%). NKCOF-112-M was then activated by drying under vacuum at 80 °C for 12 h.

Synthesis of NKCOF-113-M.
A 10 mL pyrex tube was charged with 2,4,6-Tris(4-formylphenyl)-1,3,5-triazine (TA-1Ph-CHO) (12.6 mg, 0.032 mmol), 5,5'-bis(cyanomethyl)-2,2'-bipyridine (BPy-CN) (11.3 mg, 0.048 mmol) and benzoic anhydride (22.5 mg, 0.1 mmol). This mixture was degassed through three freeze-pump-thaw cycles, sealed under vacuum. Then the tube was transferred into an oven to heat at 200 °C for 3 days yielding a yellow solid that was washed with tetrahydrofuran and methanol in a Soxhlet extractor for 48 h (yield ~95%). NKCOF-113-M was then activated by drying under vacuum at 80 °C for 12 h.

**Synthesis of NKCOF-114-M.**

A 10 mL pyrex tube was charged with 4',4'''',(1,3,5-triazine-2,4,6-triyl)tris(([1,1'-biphenyl]-4-carbaldehyde)) (TA-2Ph-CHO) (19.9 mg, 0.032 mmol), 5,5'-bis(cyanomethyl)-2,2'-bipyridine (BPy-CN) (11.3 mg, 0.048 mmol) and benzoic anhydride (22.5 mg, 0.1 mmol). This mixture was degassed through three freeze-pump-thaw cycles, sealed under vacuum. Then the tube was transferred into an oven to heat at 200 °C for 3 days yielding a yellow solid that was washed with tetrahydrofuran and methanol in a Soxhlet extractor for 48 h (yield ~95%). **NKCOF-114-M** was then activated by drying under vacuum at 80 °C for 12 h.

**Synthesis of polymeric carbon nitride (PCN).** Urea powder of 10.0 g was put into an alumina crucible with a cover and then heated to 550 °C in a muffle furnace for 3 h. PCN was obtained after cooling down to room temperature.
Section 2. Supporting Figures and tables.

**Figure S1.** PXRD patterns of the olefin-linked COFs: experimentally observed (Black), simulated using eclipsed AA-stacking (Red) and staggered AB stacking (Blue) models: (a) NKCOF-112-M, (b) NKCOF-113-M, (c) NKCOF-114-M; The eclipsed AA stacking models of (a-1) NKCOF-112-M, (b-1) NKCOF-113-M, (c-1) NKCOF-114-M; The staggered AB stacking models of (a-2) NKCOF-112-M, (b-2) NKCOF-113-M, (c-2) NKCOF-114-M.
Figure S2. PXRD patterns of the olefin-linked COFs after various treatments: (a) NKCOF-112-M, (b) NKCOF-113-M, (c) NKCOF-114-M; (d) PXRD pattern of the olefin-linked COFs treated by 12 M HCl aqueous solution. The crystallinity of the COFs was influenced by concentrated HCl due to the protonation of the framework. 12M HCl-1M NaOH means after treating with 12 M HCl, 1M NaOH was used to treat the sample. The results showed the crystallinity for all COFs could be recovered due to the deprotonation.

Figure S3. The FT-IR spectra of the olefin linked COFs after various treatments: (a) NKCOF-112-M; (b) NKCOF-113-M; (c) NKCOF-114-M.
Figure S4. Ultraviolet photo-electron spectroscopy (UPS) of (a) NKCOF-112-M, (b) NKCOF-113-M, (c) NKCOF-114-M.
Figure S5. The Mott-Schottky plots for (a) NKCOF-112-M, (b) NKCOF-113-M and (c) NKCOF-114-M at different frequencies.
Figure S6. Electronic properties of (a) NKCOF-112-M and (b) NKCOF-114-M using DFT calculations and corresponding density of states (DOS); (c) The calculated energy levels of the COFs.
Figure S7. DFT optimized molecular orbital plots (HOMO and LUMO) of NKCOF-112-M and NKCOF-114-M.

Figure S8. Hydrophobic angle measurement of (a) NKCOF-112-M; (b) NKCOF-113-M; (c) NKCOF-114-M. (NKCOF-112-M absorbed water drops in 2 s.)
Figure S9. The standard curves of (a) $H_2$ and (b) $O_2$.

Figure S10. Time course $H_2$ evolution under visible light ($\lambda > 420$ nm) irradiation using 10 mg of NKCOF-113-M with different Pt loading (wt%).

Figure S11. Time course $H_2$ evolution of Pt@NKCOF-113-M under visible light ($\lambda > 420$ nm) irradiation using different sacrificial agents (AA: ascorbic acid; TEOA: Triethanolamine). Conditions: 50 mg of NKCOF-113-M with 5 wt% Pt loading at room temperature.
Figure S12. (a) PXRD, (b) TEM, (c) FT-IR and (d) AQY values of PCN. (The conditions of photocatalytic H₂ evolution are same as the NKCOF-113-M.)

Figure S13. Time course O₂ evolution under visible light (λ > 420 nm) irradiation using 50 mg samples.
Figure S14. (a) Full scan XPS spectra and high-resolution (b) N 1s and C1s spectra of the as-synthesized COFs.
Figure S15. DFT calculated energy profiles of the Pt\(^0\) (the white ball) adsorption at the N sites. site 1: TA; site 2: Bpy; site 3 Cyano.

Figure S16. The TEM images of (a) Pt@NKCOF-112-M, (b) Pt@NKCOF-114-M, The Pt nanoparticle size distribution on the surface of (c) NKCOF-112-M, (d) NKCOF-114-M; Statistical distances between centers of neighboring Pt nanoparticles on the surface of (e) NKCOF-112-M, (f) NKCOF-114-M.
Figure S17. The HRTEM image of NKCOF-113-M.

Figure S18. The TEM image of the (a) Pt@NKCOF-113-M and (b) Pt@NKCOF-114-M.
Figure S19. (a) The frontier orbital distribution of the model molecules and the possible energy/electron transfer between the model molecules according to their energy levels in the COF skeleton: (b) NKCOF-112-M, (b) NKCOF-113-M, (c) NKCOF-114-M.

Table S1. Apparent quantum Yield (AQY) of the COF photocatalysts for H₂ evolution.

| COFs              | HER (mmol h⁻¹ g⁻¹) | AQY            | Conditions       | Reference                      |
|------------------|--------------------|----------------|------------------|-------------------------------|
| NKCOF-113-M      | 13.1               | 56.2% (475 nm) | TEOA λ > 420 nm  | This work                     |
| CYANO-CON        | 134.2              | 82.6% (450 nm) | AA λ > 420 nm    | Nat Commun., 2022, 13 (1): 2357 |
| CN-COF           | 10.1               | 20.7% (425 nm) | TEOA λ > 420 nm  | Chem. Commun., 2019, 55 (41): 5829-5832 |
| TpPa-Cl₂         | --                 | 17% (400 nm)   | SA λ > 420 nm    | Chem. Eng. J., 2021, 419      |
| WO₃@TpPa-1-COF/rGO (30%) | 16.65               | 12.08% (450 nm) | SA λ > 420 nm    | Chem. Eng. J., 2022, 431      |
| Material       | Refractive Index | Tareo | Source                           |
|---------------|----------------|-------|----------------------------------|
| r-CTF         | 10.25          | 11.3% (420 nm) | TEOA, λ > 420 nm, Angew. Chem. Int.Ed. 2021, 60, 25381–25390 |
| PEG@BT-COF    | 11.4           | 11.2% (420 nm) | AA, λ > 420 nm, Nat. Commun., 2021, 12 (1): 3934. |
| ATNT-4        | 14.2           | 9.75% (500 nm) | AA, λ > 420 nm, J. Am. Chem. Soc., 2020, 142 (10): 4862-4871 |
| Py-CITP-BT-COF| 8.9            | 8.45% (420 nm) | AA, λ > 420 nm, Angew. Chem. Int. Ed., 2020, 59, 2. |
| Pt-PY-DHBD-COF| 71.16          | 8.4% (420 nm)  | AA, λ > 420 nm, Nat. Commun, 2022, 13 (1): 1355. |
| TiO2-TpPa-1-COF| 11.19         | 7.6% (420 nm)  | SA, λ > 420 nm, Appl. Catal. B: Environ., 2020, 266: 118586 |
| CTF-HUST-A1   | 9.2            | 7.4% (420 nm)  | TEOA, λ > 420 nm, Angew. Chem. Int. Ed., 2020, 59, 6007. |
| Pd0.033/TPTTA/SiO2 | 150          | 7.3% (420 nm)  | AA, λ > 420 nm, ACS Appl. Mater. Interfaces 2022, 14, 6885–6893 |
| COF-alkene    | 2.33           | 6.7% (420 nm)  | TEOA, λ > 420 nm, Adv. Sci., 2020, 7 (12): 1902988 |
| RC-COF-1      | ~28            | 6.39% (420 nm) | AA, λ > 420 nm, Nature, 2022, 604 (7904): 72-79. |
| g-C40N3-COF   | 4.12           | 4.84% (420 nm) | TEOA, λ > 420 nm, Nat. Commun., 2019, 10:2467 |
| sonoCOF-3     | 16.6           | 3.71% (420 nm) | AA, λ > 420 nm, Nat. Synth., 2022, 1 (1): 87-95 |
| FS-COF        | 10.1           | 3.2% (420 nm)  | AA, λ > 420 nm, Nat. Chem., 2018, 10, 1180 |
| NKCOF-108     | 11.6           | 2.96% (520 nm) | AA, λ > 420 nm, ACS Catal., 2021, 11 (4): 2098-2107 |
| P-CTF         | 6.59           | 2.11% TEOA    | Chem. Mater., |


|           | (420 nm) | λ > 420 nm | 2022, 34 (4): 1481-1490 |
|-----------|----------|------------|--------------------------|
| COF-BPDA  | 3.23     | 2.1%       | AA λ > 400 nm            |
|           | (435 nm) | AA λ > 420 nm | J Am Chem Soc, 2022, 144 (8): 3653-3659 |
| BTH-1     | 10.5     | 1.569%     | AA λ > 420 nm            |
|           | (420 nm) | AA λ > 420 nm | Nat. Commun., 2022, 13 (1): 100 |
| TZ-COF-4  | 4.3      | 1.3%       | AA λ > 420 nm            |
|           | (420 nm) | AA λ > 420 nm | J. Am. Chem. Soc. 2020, 142, 11131 |
| ODA-COF   | 2.6      | 0.42%      | TEOA λ > 420 nm          |
|           | (420)    |             | Angew. Chem. Int. Ed., 2022, 61 (10): e202115655 |

AA: Ascorbic acid; TEOA: Triethanolamine; SA: Sodium ascorbate

Table S2. Fractional atomic coordinates of the NKCOF-112-M unit cell.

| Space group | P-6 |
|-------------|-----|
| Calculated unit cell | a = 30.1062, b = 30.1062, c =3.4475 |
|               | α=β= 90°, γ=120° |
| Atom | x | y | z |
| C1 | 0.13631 | 0.59063 | 0.5 |
| C2 | 0.10773 | 0.61577 | 0.5 |
| C3 | 0.05424 | 0.58793 | 0.5 |
| C4 | 0.02869 | 0.53402 | 0.5 |
| N5 | 0.05723 | 0.51042 | 0.5 |
| C6 | 0.10933 | 0.53667 | 0.5 |
| C7 | -0.02811 | 0.5013 | 0.5 |
| N8 | -0.04857 | 0.44947 | 0.5 |
| C9 | -0.09992 | 0.41624 | 0.5 |
| C10 | -0.13462 | 0.43444 | 0.5 |
| C11 | -0.1145 | 0.48786 | 0.5 |
| C12 | -0.06156 | 0.52122 | 0.5 |
| C13 | 0.19321 | 0.62225 | 0.5 |
| C14 | 0.22516 | 0.6033 | 0.5 |
| C15 | 0.28134 | 0.63659 | 0.5 |
| C16 | -0.19043 | 0.39647 | 0.5 |
| C17 | -0.22774 | 0.40849 | 0.5 |
| C18 | -0.28252 | 0.36911 | 0.5 |
| N19 | 0.30344 | 0.68852 | 0.5 |
| N20 | -0.31833 | 0.38392 | 0.5 |
| H21 | 0.12689 | 0.65727 | 0.5 |
| H22 | 0.03404 | 0.60907 | 0.5 |
| H23 | 0.12877 | 0.51479 | 0.5 |
| H24 | -0.1136 | 0.37545 | 0.5 |
Table S3. Fractional atomic coordinates of the NKCOF-113-M unit cell.

| Atom | x    | y    | z    |
|------|------|------|------|
| C1   | 0.09031 | 0.57463 | 0.5       |
| C2   | 0.06795 | 0.58782 | 0.5       |
| C3   | 0.03275 | 0.56648 | 0.5       |
| C4   | 0.01898 | 0.53111 | 0.5       |
| C5   | 0.04064 | 0.51862 | 0.5       |
| C6   | 0.07502 | 0.53876 | 0.5       |
| C7   | 0.98181 | 0.50646 | 0.5       |
| N8   | 0.97144 | 0.47273 | 0.5       |
| C9   | 0.93817 | 0.44811 | 0.5       |
| C10  | 0.91205 | 0.45646 | 0.5       |
| C11  | 0.92258 | 0.49153 | 0.5       |
| C12  | 0.957   | 0.51625 | 0.5       |
| C13  | 0.12848 | 0.59855 | 0.5       |
| C14  | 0.15092 | 0.58696 | 0.5       |
| C15  | 0.18919 | 0.60589 | 0.5       |
| C16  | 0.87506 | 0.42851 | 0.5       |
| C17  | 0.84913 | 0.4354  | 0.5       |
| C18  | 0.81121 | 0.41198 | 0.5       |
| C19  | 0.20503 | 0.58594 | 0.5       |
| C20  | 0.24038 | 0.60079 | 0.5       |
| C21  | 0.26125 | 0.63625 | 0.5       |
| C22  | 0.24587 | 0.65644 | 0.5       |
| C23  | 0.21047 | 0.64159 | 0.5       |
| C24  | 0.791   | 0.42754 | 0.5       |
| C25  | 0.75554 | 0.40831 | 0.5       |
| C26  | 0.73894 | 0.37268 | 0.5       |
| C27  | 0.7587  | 0.35684 | 0.5       |
| C28  | 0.79422 | 0.37608 | 0.5       |
| H29  | 0.07735 | 0.6149  | 0.5       |
| H30  | 0.01706 | 0.57812 | 0.5       |
| H31  | 0.08946 | 0.52588 | 0.5       |
| H32  | 0.93251 | 0.42199 | 0.5       |
| H33  | 0.90504 | 0.50094 | 0.5       |
| H34  | 0.9635  | 0.54258 | 0.5       |
| C35  | 0.13999 | 0.63453 | 0.5       |
| H36  | 0.14069 | 0.55993 | 0.5       |

Space group: \( P-6 \)

Calculated unit cell: \( a = 45.3935, \ b = 45.3935, \ c = 3.4485 \)

\( \alpha = \beta = 90^\circ, \ \gamma = 120^\circ \)
Table S4. Fractional atomic coordinates of the NKCOF-114-M unit cell.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C1   | 0.06762 | 0.56129 | 0.5   |
| C2   | 0.05076 | 0.57105 | 0.5   |
| C3   | 0.02441 | 0.55495 | 0.5   |
| C4   | 0.01421 | 0.52847 | 0.5   |
| N5   | 0.03054 | 0.51923 | 0.5   |
| C6   | 0.05629 | 0.53442 | 0.5   |
| C7   | -0.01361 | 0.50989 | 0.5   |
| N8   | -0.02125 | 0.48465 | 0.5   |
| C9   | -0.04615 | 0.46612 | 0.5   |
| C10  | -0.06581 | 0.47224 | 0.5   |
| C11  | -0.05804 | 0.49848 | 0.5   |
| C12  | -0.03229 | 0.5171  | 0.5   |
| C13  | 0.09619  | 0.57932 | 0.5   |
| C14  | 0.11311  | 0.57076 | 0.5   |
| C15  | 0.14179  | 0.58507 | 0.5   |
| C16  | -0.09348 | 0.45121 | 0.5   |
| C17  | -0.11299 | 0.45624 | 0.5   |
| C18  | -0.14139 | 0.43858 | 0.5   |
| C19  | 0.15379  | 0.57034 | 0.5   |
| C20  | 0.18028  | 0.58155 | 0.5   |
| C21  | 0.19631  | 0.60829 | 0.5   |
| C22  | 0.18415  | 0.62302 | 0.5   |
| C23  | 0.1576   | 0.61173 | 0.5   |
| C24  | -0.15663 | 0.45002 | 0.5   |
| C25  | -0.18319 | 0.43554 | 0.5   |
| C26  | -0.19602 | 0.40863 | 0.5   |

Space group: P-6

Calculated unit cell:

- \(a = 60.5891\), \(b = 60.5891\), \(c = 3.4482\)
- \(\alpha = \beta = 90^\circ\), \(\gamma = 120^\circ\)
|     |  x  |  y  |  z  |  s  |
|-----|-----|-----|-----|-----|
| C27 | -0.18061 | 0.39721 | 0.5 |   |
| C28 | -0.15401 | 0.41178 | 0.5 |   |
| H29 | 0.05771 | 0.59132 | 0.5 |   |
| H30 | 0.01257 | 0.56358 | 0.5 |   |
| H31 | 0.0672 | 0.52486 | 0.5 |   |
| H32 | -0.05029 | 0.44658 | 0.5 |   |
| H33 | -0.07126 | 0.50545 | 0.5 |   |
| H34 | -0.02752 | 0.5368 | 0.5 |   |
| C35 | 0.10469 | 0.60625 | 0.5 |   |
| H36 | 0.10554 | 0.55053 | 0.5 |   |
| C37 | -0.0982 | 0.42536 | 0.5 |   |
| H38 | -0.10816 | 0.47586 | 0.5 |   |
| H39 | 0.18753 | 0.56857 | 0.5 |   |
| H40 | 0.1946 | 0.64351 | 0.5 |   |
| H41 | -0.19307 | 0.44616 | 0.5 |   |
| H42 | -0.18848 | 0.37689 | 0.5 |   |
| C43 | 0.22512 | 0.62057 | 0.5 |   |
| C44 | -0.22489 | 0.3928 | 0.5 |   |
| C45 | 0.24116 | 0.64738 | 0.5 |   |
| C46 | 0.26768 | 0.65864 | 0.5 |   |
| C47 | 0.2793 | 0.64365 | 0.5 |   |
| C48 | 0.26377 | 0.61709 | 0.5 |   |
| C49 | 0.23725 | 0.60575 | 0.5 |   |
| C50 | -0.23773 | 0.36582 | 0.5 |   |
| C51 | -0.26431 | 0.35128 | 0.5 |   |
| C52 | -0.27919 | 0.36302 | 0.5 |   |
| C53 | -0.26686 | 0.38968 | 0.5 |   |
| C54 | -0.24029 | 0.40429 | 0.5 |   |
| H55 | 0.14256 | 0.54972 | 0.5 |   |
| H56 | 0.15043 | 0.62464 | 0.5 |   |
| H57 | -0.14795 | 0.47059 | 0.5 |   |
| H58 | -0.14422 | 0.40121 | 0.5 |   |
| C59 | 0.30744 | 0.65564 | 0.5 |   |
| C60 | -0.30739 | 0.34756 | 0.5 |   |
| N61 | 0.31859 | 0.64098 | 0.5 |   |
| N62 | -0.32171 | 0.35908 | 0.5 |   |
| H63 | 0.2339 | 0.66035 | 0.5 |   |
| H64 | 0.27908 | 0.67924 | 0.5 |   |
| H65 | 0.27209 | 0.60489 | 0.5 |   |
| H66 | 0.22683 | 0.58526 | 0.5 |   |
| H67 | -0.22784 | 0.35521 | 0.5 |   |
| H68 | -0.27317 | 1.33071 | 0.5 |   |
| H69 | -0.27775 | 0.39942 | 0.5 |   |
| H70 | -0.23246 | 0.42461 | 0.5 |   |
| N71 | 0.11091 | 0.6277 | 0.5 |   |
| N72 | -0.10139 | 0.40485 | 0.5 |   |

**Table S5.** The pore structure of the reported olefin-linked COFs
| COFs           | Shape of the pore | Pore size (nm) | References                          |
|---------------|-------------------|---------------|-------------------------------------|
| NKCOF-112-M   | Hexagonal         | 2.2           | *This work*                         |
| NKCOF-113-M   | Hexagonal         | 3.8           |                                     |
| NKCOF-114-M   | Hexagonal         | 5.6           |                                     |
| Sp²-COF       | Quadrilateral     | 1.9           | Science, 2017, 357, 673             |
| Sp²-COF-2     | Quadrilateral     | 2.4           | Nat. Commun., 2018, 9:4143          |
| Sp²-COF-3     | Quadrilateral     | 2.7           |                                     |
| Sp²-COF-4     | Hexagonal         | 3.2           | Angew. Chem. Int. Ed. 2020, 59, 12162 |
| Sp²-COF-5     | Hexagonal and Triangle | 3.6 and 1.4   |                                     |
| Sp²-COF-6     | Hexagonal         | 1.9           | Angew. Chem. Int. Ed. 2022, 61, e2021150 |
| Sp²-COF-7     | Hexagonal         | 1.7           |                                     |
| Sp²-COF-8     | Hexagonal         | 1.7           |                                     |
| Sp²-COF-9     | Hexagonal         | 1.8           |                                     |
| Sp²-COF-10    | Hexagonal         | 1.7           |                                     |
| Sp²-COF-11    | Hexagonal         | 2.5           |                                     |
| Sp²-COF-12    | Hexagonal         | 2.5           |                                     |
| Sp²-COF-13    | Hexagonal         | 2.0           |                                     |
| Sp²-COF-14    | Quadrilateral     | 2.0           |                                     |
| 2DPPV         | Hexagonal         | 1.6           | Polym. Chem., 2016, 7, 4176         |
| g-C₆₀N₃-COF   | Hexagonal         | 3.2           | Nat. Commun., 2019, 10:2467         |
| g-C₃₁N₃-COF   | Hexagonal         | 2.4           |                                     |
| g-C₃₇N₃-COF   | Hexagonal         | 1.6           |                                     |
| g-C₃₄N₆-COF   | Hexagonal         | 1.6           | Angew. Chem. Int. Ed. 2019, 58,12065 |
| COF-p-3Ph,    | Hexagonal         | 3.0           | J. Am. Chem. Soc. 2020, 142, 11893  |
| COF-p-2Ph     | Hexagonal         | 2.2           |                                     |
| COF-m-3Ph     | Hexagonal         | 1.7           |                                     |
| COF-DFB       | Quadrilateral     | 1.4           | J. Am. Chem. Soc. 2022, 144, 3653   |
| COF-BPDA      | Quadrilateral     | 1.7           |                                     |
| Por-sp2c-COF  | Quadrilateral     | 1.8           | Angew. Chem. Int. Ed. 2019, 131, 6496 |
| COF1          | Hexagonal         | 1.1           | Angew. Chem. Int. Ed. 2019, 58,13753 |
| COF2          | Hexagonal         | 1.1           |                                     |
| COF3          | Hexagonal         | 1.1           |                                     |
| V-COF-1       | Hexagonal         | 1.7           | Angew. Chem. Int. Ed. 2019, 58,14865 |
| V-COF-2       | Hexagonal         | 0.8           |                                     |
| P2PV          | Hexagonal         | 1.1           | J. Am. Chem. Soc. 2020, 142, 8862   |
| P3PcB         | Hexagonal         | 1.1           |                                     |
| P2NV          | Hexagonal         | 1.1           |                                     |
| P3NcB         | Hexagonal         | 1.1           |                                     |
| DBOV-COF      | Hexagonal         | 1.9           | Angew. Chem. Int. Ed. 2022, 61, e2021140 |
| V-2D-COF-1    | Hexagonal         | 2.3~3.2       | Angew. Chem. Int. Ed. 2022, 61, e202202492 |
| V-2D-COF-2    | Hexagonal         | 2.3~3.2       |                                     |
| V-2D-COF-3    | Hexagonal         | 3.2~4.2       |                                     |
| V-2D-COF-4    | Triangle          | 1.3 and 1.8   |                                     |
| Bpy-sp²c-COF  | Quadrilateral     | 2.4           | Chem. Sci. 2020, 11, 543            |
| TP-COF        | Hexagonal         | 2.2           | Angew. Chem. Int. Ed. 2019,         |
Table S6. The PL decay lifetime of the COFs.

| Sample       | τ_1  | τ_2  | τ_3  | τ_Ave |
|--------------|------|------|------|-------|
| NKCOF-112-M  | 1.02 | 2.71 | 9.23 | 2.5   |
| NKCOF-113-M  | 0.83 | 3.03 | 8.87 | 2.8   |
| NKCOF-114-M  | 0.66 | 2.43 | 9.12 | 2.2   |

Table S7. The measurements of the Hall effect for the COFs

| Sample       | T (K) | σ     | μ     | n   | R_H  | f-factor |
|--------------|-------|-------|-------|-----|------|----------|
| NKCOF-112-M  | 300   | 4.21·10^3 | 0.12 | 1.24·10^{16} | -0.504 | 0.687 |
| NKCOF-113-M  | 300   | 3.19·10^3 | 0.13 | 1.27·10^{16} | -0.496 | 0.691 |
| NKCOF-114-M  | 300   | 2.16·10^3 | 0.137| 1.30·10^{16} | -0.309 | 0.670 |

T: Temperature; σ: Resistivity; μ: Charge Mobility; n: Carrier concentration; R_H: Hall coefficient

Supplementary References

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