

All-organic mixed-matrix membranes with single-crystal covalent organic frameworks for carbon capture

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1. Supplementary methods

Materials

COF synthesis

1,3,5-trimethyl-2,4,6-tris(4-aminophenyl)benzene (TTAB, 99%), 1,3,5-trimethyl-2,4,6-tris(4-formylphenyl)benzene (TTFB, 99%), 1,3,5-tris-(4-aminophenyl)benzene (TAPB, 97%), 2,5-dimethoxyterephthalaldehyde (DMPDA, 99%), 1,4-Phthalaldehyde (PA, 99%), Tetrakis(4-aminophenyl)methane (TAM, 99%), adamantane-1,3,5,7-tetracarbaldehyde (ADA-CHO, 80%), tetrakis(4-aminophenyl)ethylene (TPE-NH₂, 99%), 5'-(4-aminophenyl)-2',4',6'-trifluoro-[1,1':3',1"-terphenyl]-4,4"-diamine (97%), 4,4"-diamino-5'-(4-aminophenyl)-[1,1':3',1"-terphenyl]-2'-ol (98%), 1,3,5-Triformylphloroglucinol (Tp, 98%), and pyrene-1,6-diamino (PyDA, 98%) were purchased from Jilin Chinese Academy of Sciences—Yanshen Technology Co., Ltd. (Changchun, China). Aniline (99%), benzaldehyde (99%), trifluoroacetic acid (TFA, 99%), dioxane (99.5%), 1,2-dichlorobenzene (99%), and tetrahydrofuran (THF, 99%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Benzoic acid (99%), benzonitrile (99%), acetic acid (99.5%), and dimethyl sulfoxide (DMSO, 99%) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China).

6FDA-DAM synthesis

4,4'-(hexafluoroisopropylidene) dipthalic anhydride (6FDA, 99%) and 2,4,6-trimethyl-m-phenylenediamine (DAM, 99%) were purchased from Sigma-Aldrich and were purified by vacuum sublimation before polymerization. Acetic anhydride (C₄H₆O₃, 99.5%), triethylamine ((C₂H₅)₃N, 99.5%), and N-Methylpyrrolidone (NMP, 99%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China).

PIM-1 synthesis

2,3,5,6-tetra-fluoroterephthalonitrile (TFTPN, 99%) was obtained from Sigma-Aldrich (Shanghai) Trading Co., Ltd. 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, 97%) was purchased from Alfa Aesar (China) Chemical Co., Ltd. Dichloromethane (DCM, 99%), *N,N*-dimethylformamide (DMF, 99%) and anhydrous potassium carbonate (K₂CO₃, 99.95%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Anhydrous methanol (99%) was purchased from Tianjin Guangfu Technology Development Co., Ltd. (Tianjin, China). Hydrochloric acid (HCl, 36.0-38.0%) was purchased from Rianlon Corporation (Tianjin, China).

MOFs and zeolite synthesis

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), 2-methylimidazole (2-mIm, 98%), Zirconium (IV) chloride (ZrCl₄, 99%), 2-aminoterephthalic acid (99%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Silicalite-1 zeolite particles were kindly provided by Nanjing Tech University, China.

Methods

Models and computational details

Interaction energy calculation

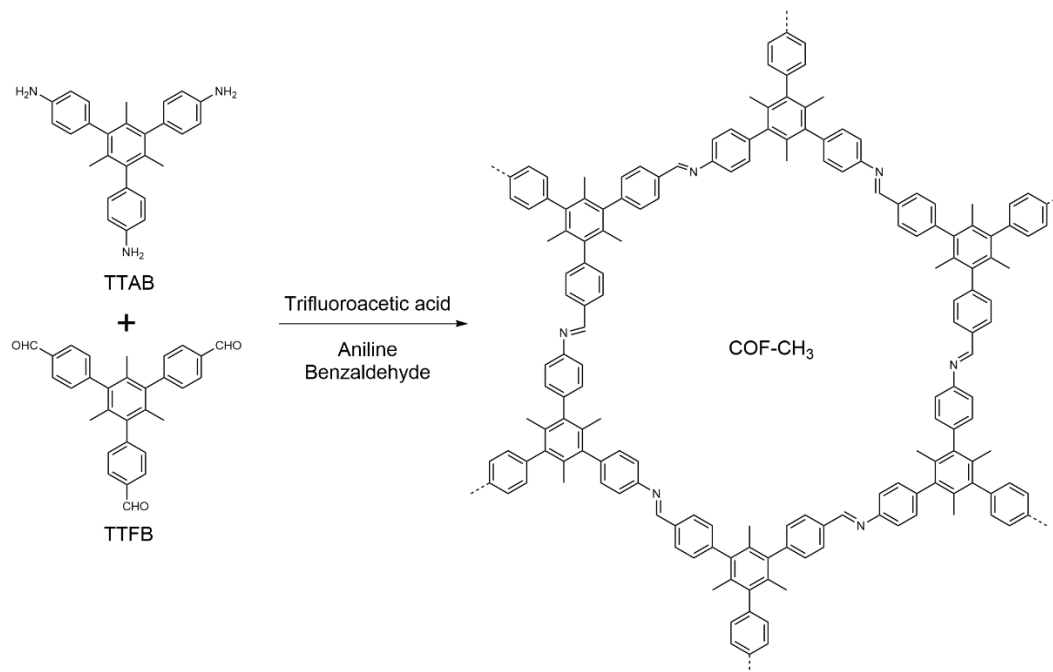
The interaction energy between the 6FDA-DAM polymer with COF systems was investigated by classic molecular dynamics (MD) simulations. Here, the polymer systems are composed of 10 polymer chains, each of which contains 20 monomers. The surface-dependent non-bonded interaction energies were examined by contacting the polymer systems with the hexagonal (001) surfaces and lateral (100)/(010) surfaces of COF crystals. The resulting interaction energy was calculated based on the surface area proportion of each plane. In addition, the COF sheets were chemically functionalized with -H, -CH₃, -F, and -OH groups to reveal the effect of functional groups on the interaction energies. Periodic boundary conditions (PBCs) were applied in the two orthogonal directions (x and y) along the COF surface to simulate an infinitely large-area COF substrate, while a wall-boundary condition was applied in the normal direction of the COF surface to avoid the PBC image. To describe the atomic interactions in COF-based systems, the Polymer Consistent Force Field (PCFF)¹ was utilized. To describe the non-bonded interactions, the van der Waals (vdW) interactions were considered by the Lennard-Jones 9-6 potential with a cut-off distance of 10 Å, while the long-range electrostatic interactions are described by the standard Coulomb potential using the particle-particle-particle-mesh (PPPM) algorithm. Before MD simulations, as-investigated systems were geometrically minimized to a local configuration with energy and force tolerances of 1.0×10^{-4} Kcal/mol and 1.0×10^{-4} Kcal/(mol·Å), respectively. MD simulations with 1,000,000 timesteps were then performed at a temperature of 300 K under NVT ensemble (constant number of particles, constant volume, and constant temperature) to investigate the interaction energies and the diffusion of 6FDA-DAM polymer in COF systems. During the MD simulations, the temperature was controlled by the Nose-Hoover thermostat technique, and the coordinates of the COF crystals were fixed. The dynamics of atoms in the systems were described by the classical Newton's motion equation, which is solved by the velocity-Verlet algorithm with a timestep of 1.0 fs. All the MD simulations were implemented using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package².

The interaction energy between the COF crystals was investigated through similar procedures. Here, three-layered COFs were placed in the bottom region, while identical three-layered COF sheets were placed in the top region. PBCs were applied in the three orthogonal directions to simulate infinitely large-area COF layers. To describe the atomic interactions in COF systems, the PCFF¹ was utilized. To describe the non-bonded interactions, the van der Waals (vdW) interactions were considered by the Lennard-Jones 9-6 potential with a cut-off distance of 10 Å, while the long-range electrostatic interactions were described by the standard Coulomb potential using the PPPM algorithm. Before MD simulations, as-investigated systems were geometrically minimized to a local configuration with energy and force tolerances of 1.0×10^{-4} Kcal/mol and 1.0×10^{-4} Kcal/(mol·Å), respectively. MD simulations with 500,000 timesteps were then performed at a temperature of 300 K and 1 bar in the z-direction under NPT ensemble (constant number of particles, constant pressure, and constant temperature) to investigate the interaction energies between COF crystals. Following the MD simulations, the top and bottom three-layered COFs adsorbed onto each other, forming a stacked structure. Finally, production MD simulations with 500,000 timesteps were performed to obtain the interaction energies between COF crystals. During the MD simulations, the temperature and pressure were controlled by Nose-Hoover thermostat and barostat techniques, respectively. The dynamics of atoms in the systems are described by the classical Newton's motion equation that is solved by the velocity-Verlet algorithm with a timestep of 1.0 fs. All the MD simulations are implemented using the LAMMPS package².

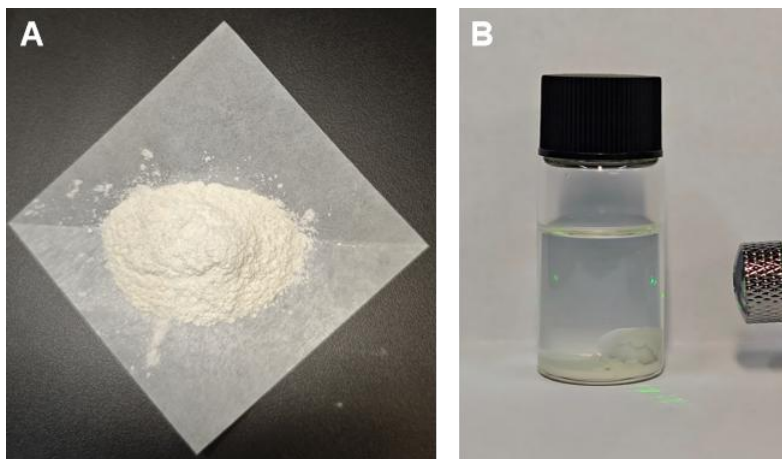
Polymer chain packing simulation

Molecular dynamics (MD) simulations were performed using the LAMMPS software package to investigate pore distribution in hybrid systems comprising COF materials and 6FDA-DAM polymer. Three types of finite-sized lamellar COF-R particles with H, CH₃, and F functional groups were constructed, with aldehyde groups and hydrogen atoms as terminating structures. Fifteen 6FDA-DAM polymer chains (degree of polymerization: 17) were co-packaged with the COF structures using the PACKMOL software. The General Amber Force Field (GAFF), combined with Restrained Electrostatic Potential (RESP) charges fitted using the Multiwfn program, was applied to the system, with a cutoff radius of 1.2 nm and a timestep of 1 fs. During dynamics, the COF was initially treated as rigid. Multiple high-temperature NPT annealing and relaxation cycles were conducted to ensure thorough mixing, allowing the 6FDA-DAM polymer to fully entangle. The COF rigidity constraint was subsequently removed, and the system was relaxed under ambient NPT conditions to achieve volume stabilization. The final COF crystal volume fraction was approximately 50-60%, with the average interlayer spacing and lamellar structure largely preserved. Following relaxation, pore analysis was conducted using the zeo++ software, generating pore size distribution histograms and 3D pore distribution maps for a 1.55 Å probe radius, rendered with the VMD software. Connectivity maps for probes of 1.55 Å and 0.85 Å were generated for each system.

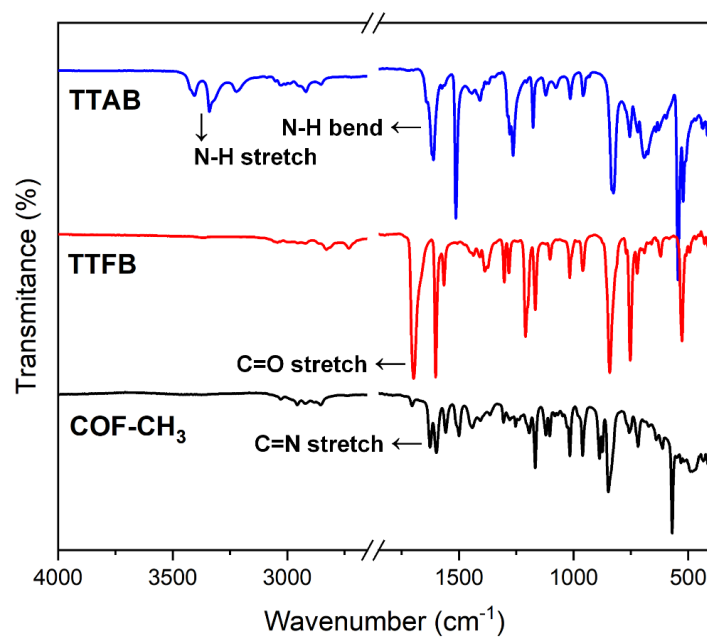
2. Supplementary figures



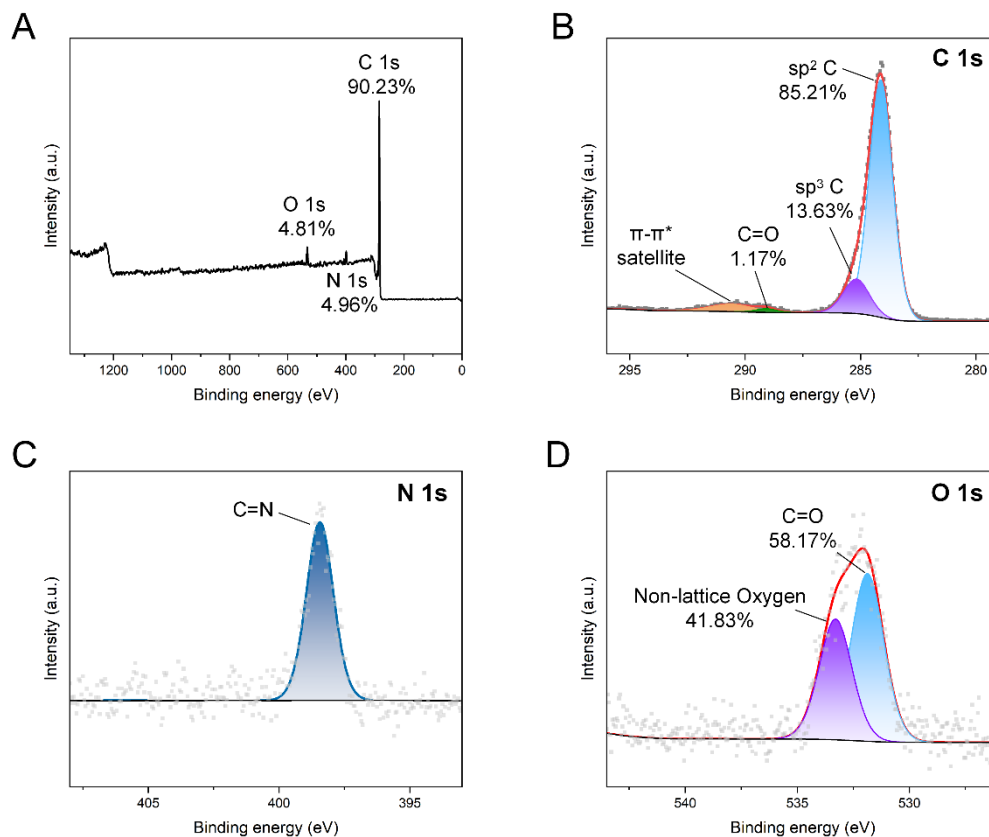
Supplementary Fig.1. Synthesis and chemical structure of COF-CH₃.



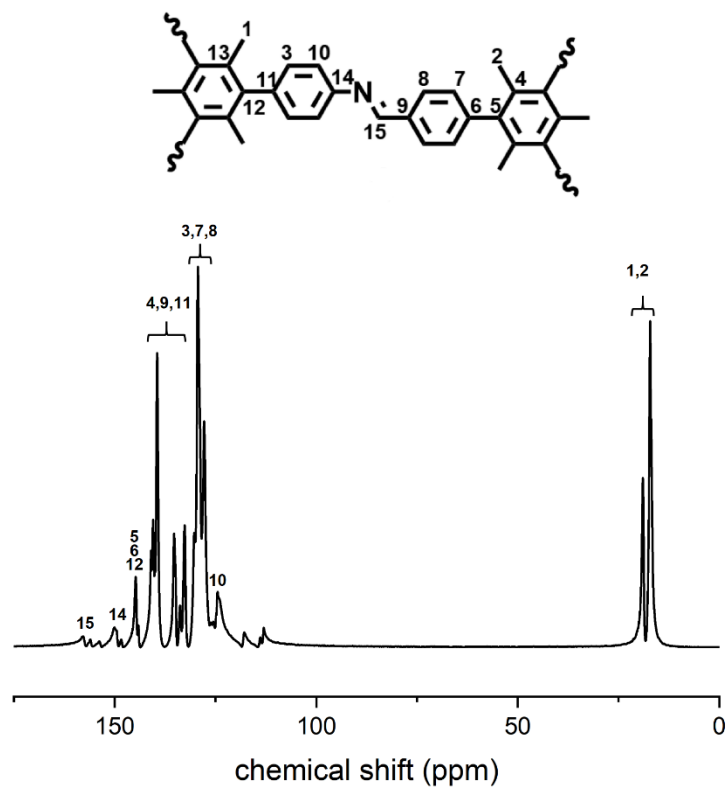
Supplementary Fig.2. (A) Optical image of COF-CH₃ powder; (B) THF dispersion of COF-CH₃. COF crystals were dispersed in THF under 24 h of stirring and 0.5 h of sonication (the same procedure as used for membrane fabrication). After standing for three days, no obvious Tyndall effect was observed in the supernatant, indicating that no significant exfoliation of COF nanosheets occurred under these conditions.



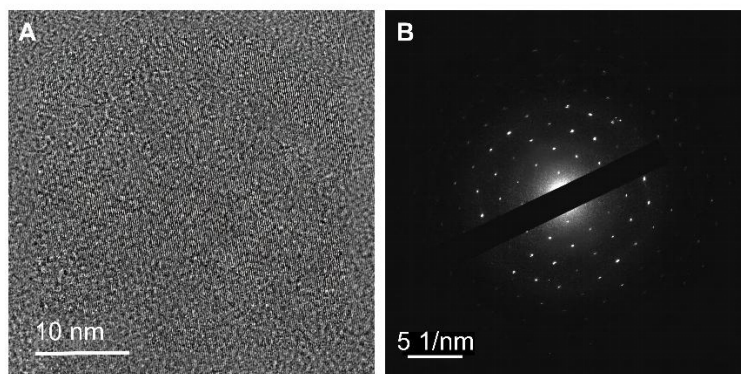
Supplementary Fig.3. FT-IR spectra of COF-CH₃ crystals and the monomers. The emergence of C=N stretching vibrations at 1626 cm⁻¹, and the disappearance of N-H stretching vibrations (3450-3150 cm⁻¹) and N-H bending (1610 cm⁻¹) confirm the effective Schiff-base condensation and the successful synthesis of COF-CH₃.



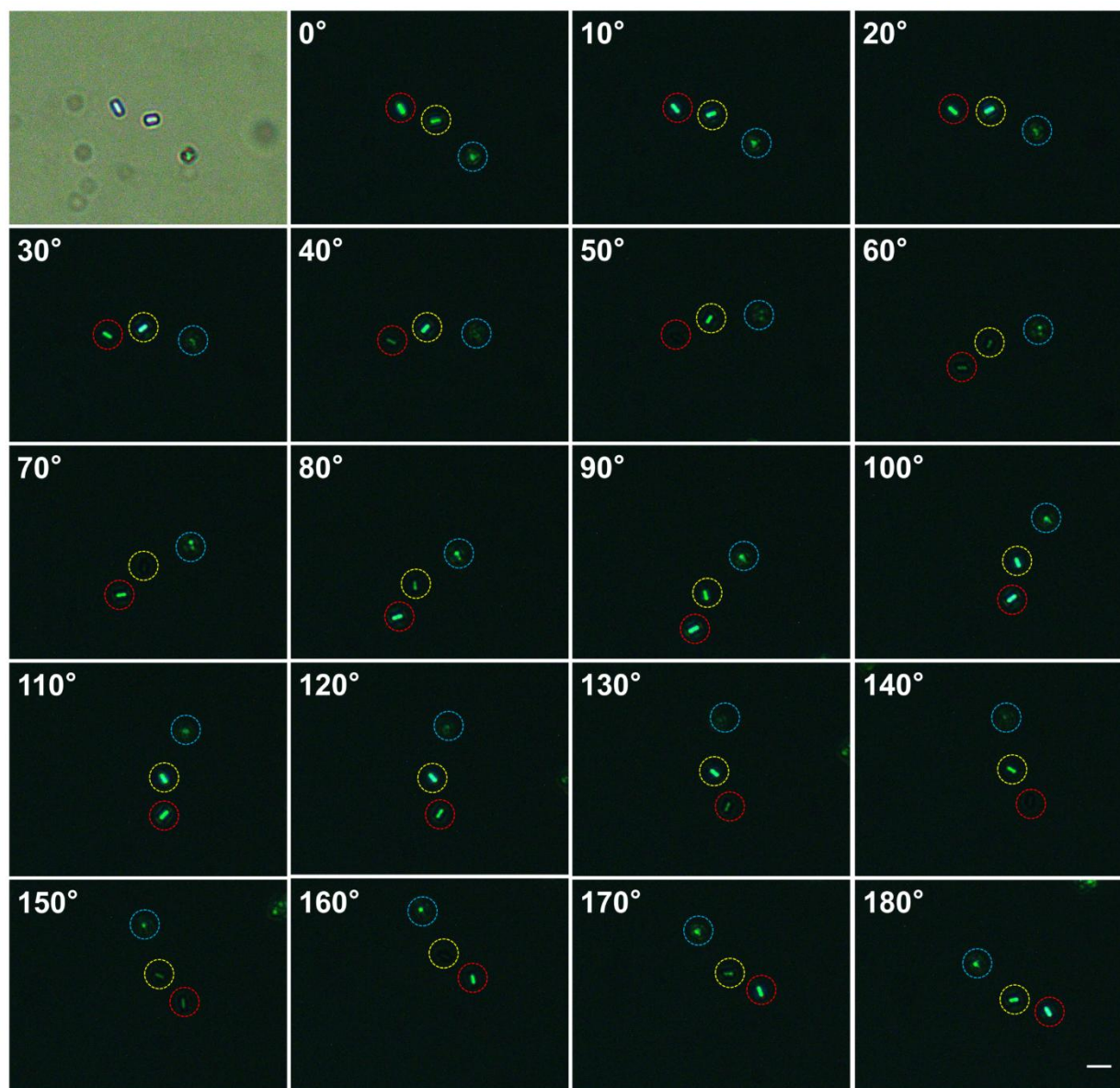
Supplementary Fig.4. XPS spectra of COF-CH₃. C 1s peaks at 284.2, 285.2, 289.0, and 290.7 eV are assigned to sp² carbon, sp³ carbon, C=O bond, and π-π* satellite. N 1s peak at 398.5 eV is assigned to the C=N bond. O 1s peak is divided into two peaks of 532.0 and 533.4 eV, which belong to the C=O bond and adsorbed non-lattice oxygen species.



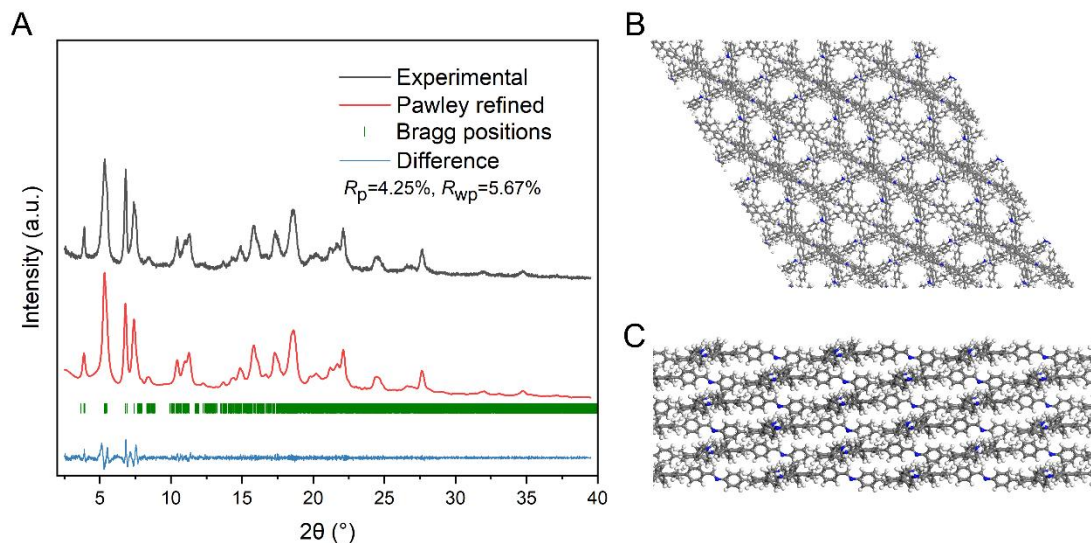
Supplementary Fig.5. NMR spectra of COF-CH₃ crystals. Characteristic peaks at ~154 ppm represent the formation of the C=N groups.



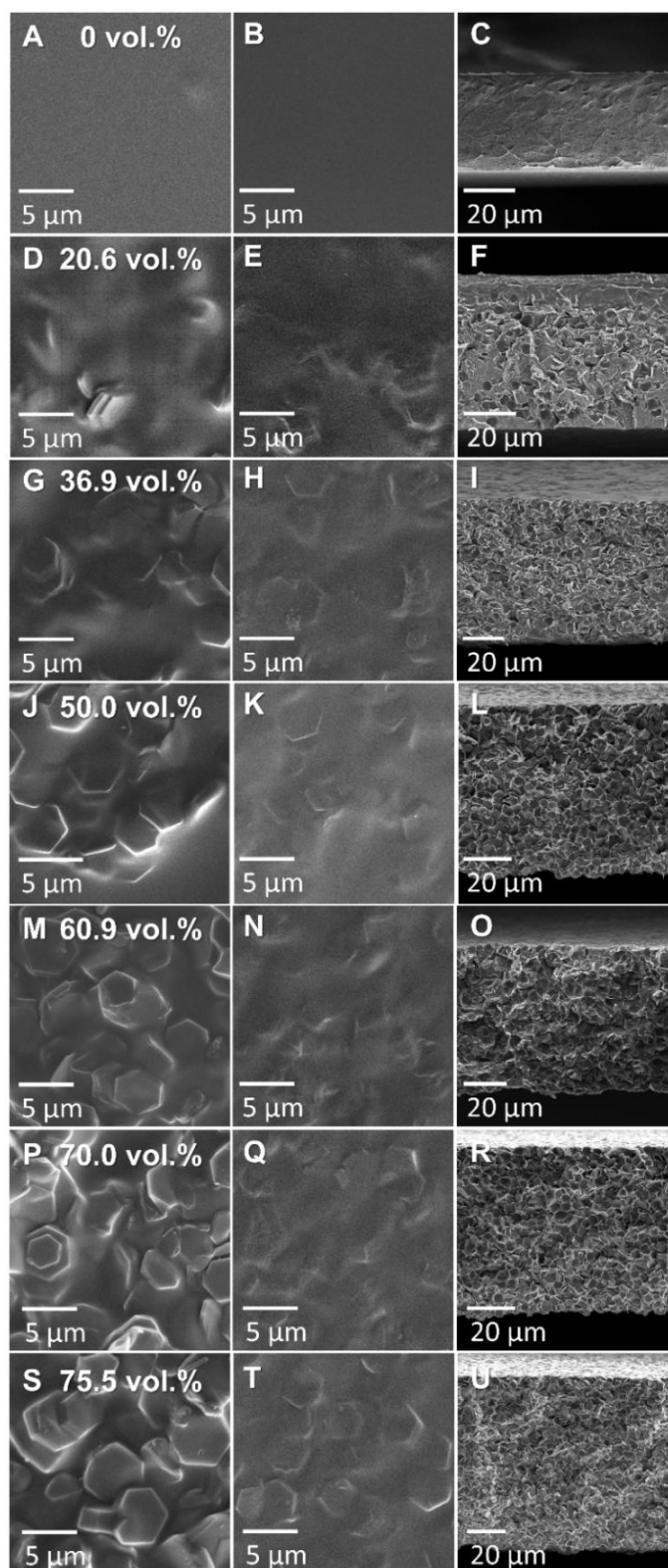
Supplementary Fig.6. High-resolution transmission electron microscopy (HRTEM) image **(A)** and selected-area electron diffraction (SAED) pattern **(B)** of COF-CH₃ crystals.



Supplementary Fig.7. Optical microscope and cross-polarized microscope images of COF-CH₃ single-crystal particles. Scale bar: 10 μ m. The crystals shown here were characterized directly after synthesis, while those shown in Fig. 2a underwent under the same ultrasonication treatment used for membrane fabrication prior to characterization.

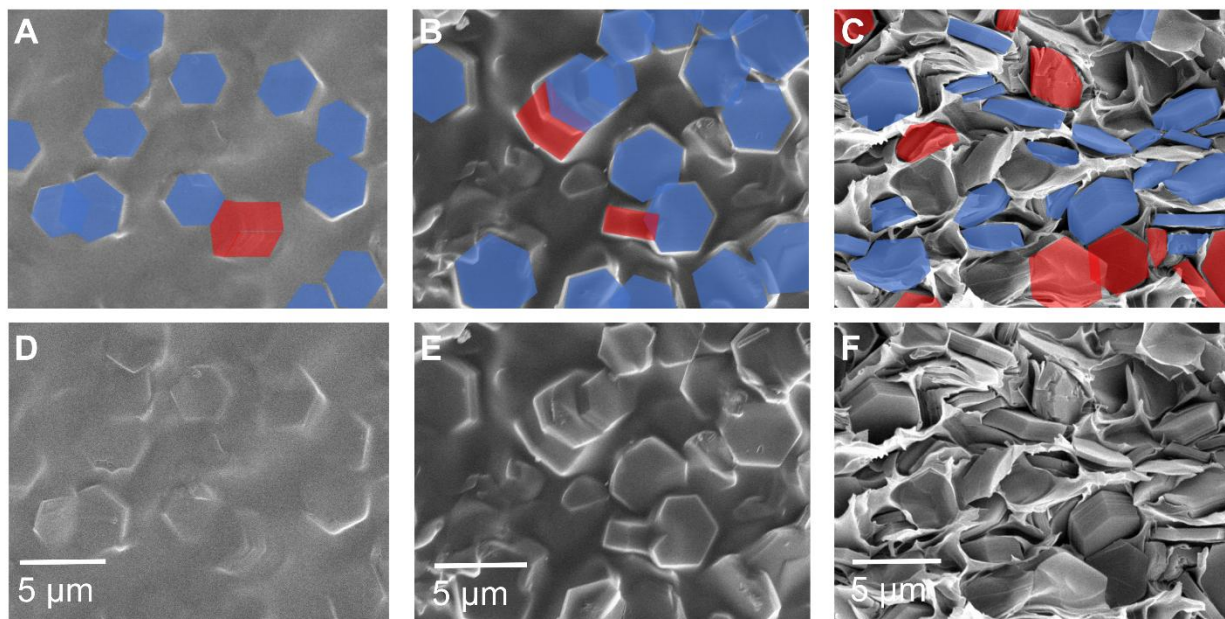


Supplementary Fig.8. Structure of COF-CH₃ single crystals with an interlayer shift of 11 Å along the AB direction. (A) Refined XRD pattern; (B) top view and (C) side view of the crystal structure. The XRD pattern shows well-defined diffraction peaks, including those for high-index lattice planes, which exhibit an excellent fit with the refined pattern derived from single-crystal data. Furthermore, SEM imaging reveals highly regular structures with specific geometric shapes and smooth crystal faces. TEM results display clear lattice fringes and clear SAED patterns. The combination of these structural and morphological characterizations collectively demonstrates the single-crystalline nature of the COF material, in agreement with the literature³.

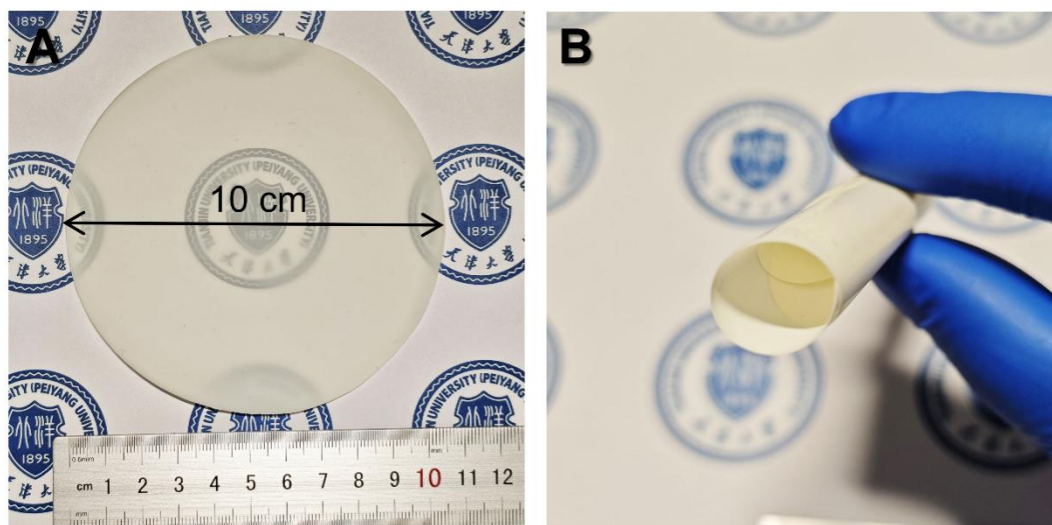


Supplementary Fig.9. SEM images of top surface (left), bottom surface (middle), and cross-sectional views (right) of COF-CH₃/6FDA-DAM MMMs with different filler packing densities. The surface and bottom morphologies of the membranes also display the polymer-COF

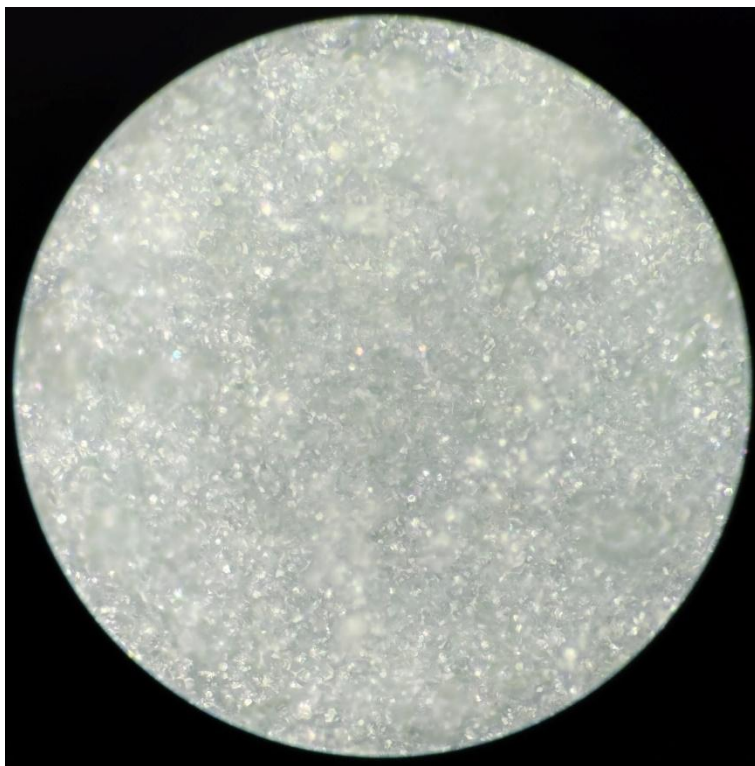
interfacial structures (seamless fusion), in agreement with the FIB-SEM image (Fig. 3a in the manuscript), which indicates favorable interfacial compatibility between the polymer matrix and the COF fillers.



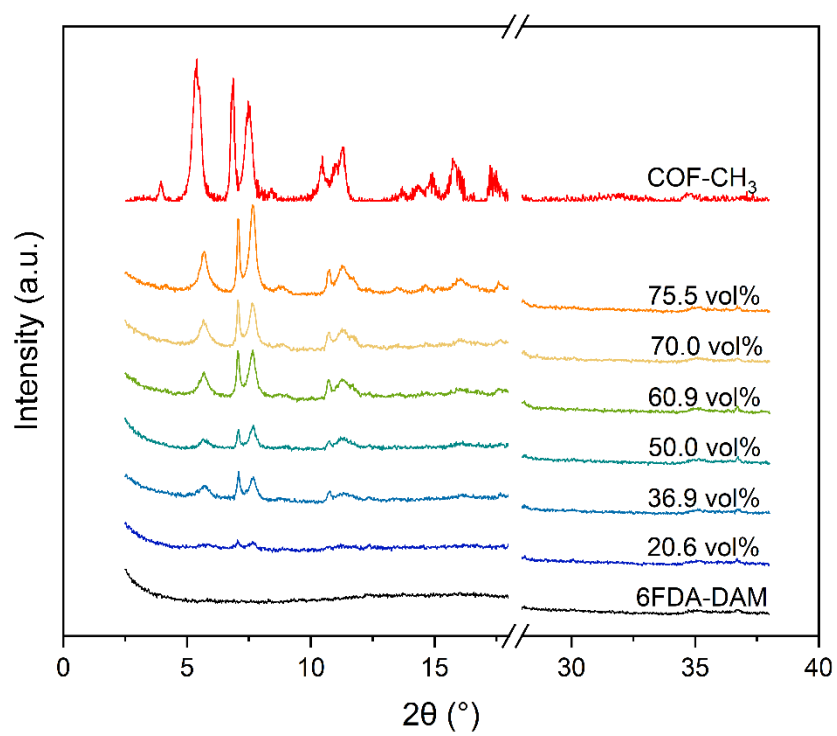
Supplementary Fig.10. Annotation of the crystal orientation in the COF-CH₃/6FDA-DAM MMMs. (A-C) Top, bottom and cross-section surface with markings of crystal orientation. (D-F) Unmarked original images corresponding to (A-C). Crystals that visible are marked with different colors: blue indicates crystals whose pore align well with the diffusion flow, and red indicates crystals whose pore orientation deviates significantly from the diffusion flow. It can be observed that the majority of crystals exhibit pores that are well aligned with the diffusion flow. It should be noted that the gaps between crystals and polymer observed in C) and F) result from mechanical stress applied during the preparation of cross-section samples.



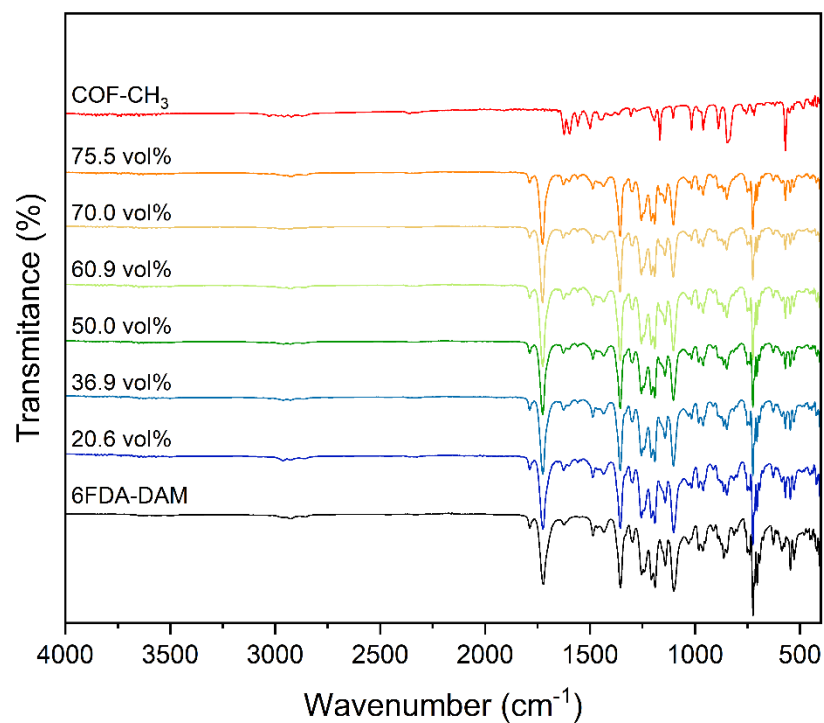
Supplementary Fig.11. Optical images of the COF-CH₃/6FDA-DAM MMMs with 75.5 vol% of filler (A) and the bent morphology (B). Note that most reported mixed matrix membranes (MMMs) with high filler packing density display a non-transparent structure. The semi-transparent feature of our membrane suggests the crystal-like structure.



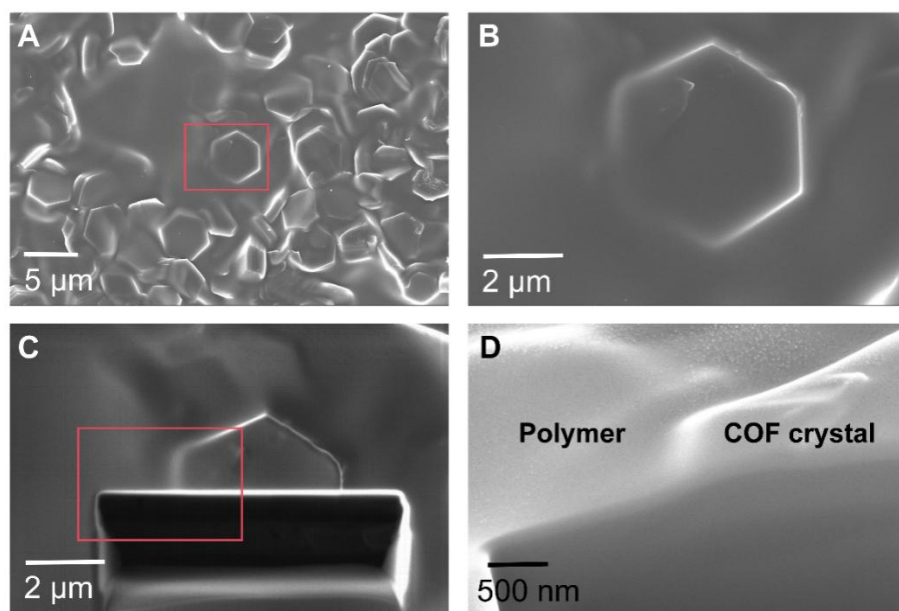
Supplementary Fig.12. Optical microscopy images of the COF-CH₃/6FDA-DAM MMMs with 75.5 vol% of filler.



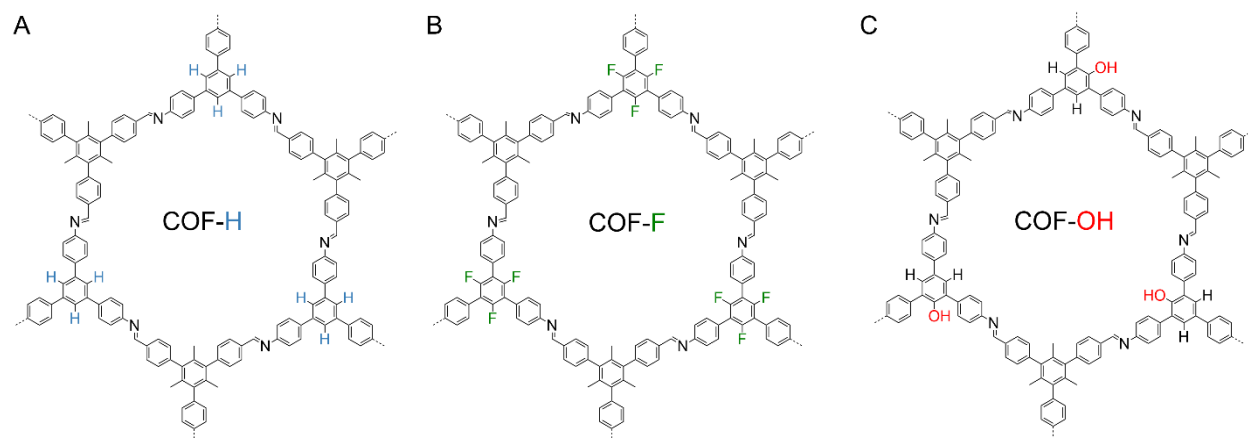
Supplementary Fig.13. XRD pattern of COF-CH₃/6FDA-DAM MMMs with different packing densities.



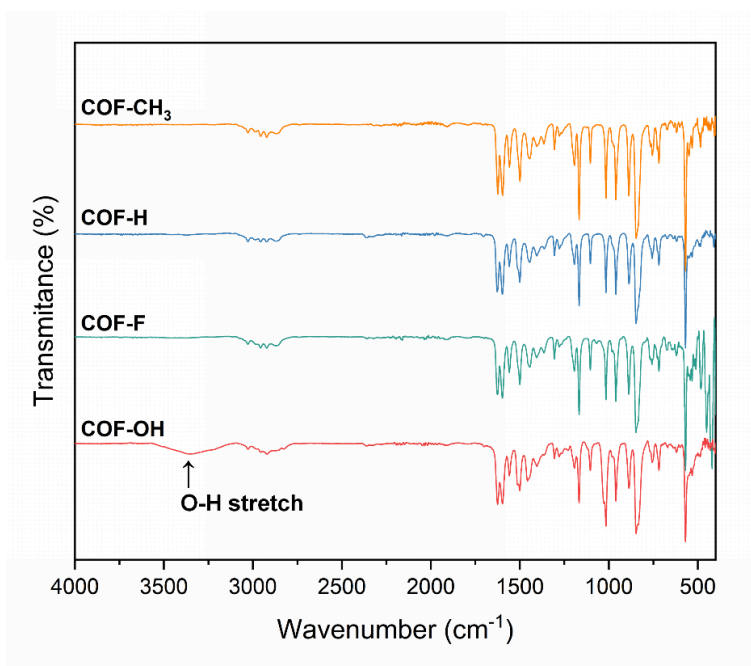
Supplementary Fig.14. FT-IR spectra of COF-CH₃/6FDA-DAM MMMs with different filler packing densities. FT-IR spectra confirm the retention of the chemical structures of COF crystals within the membranes.



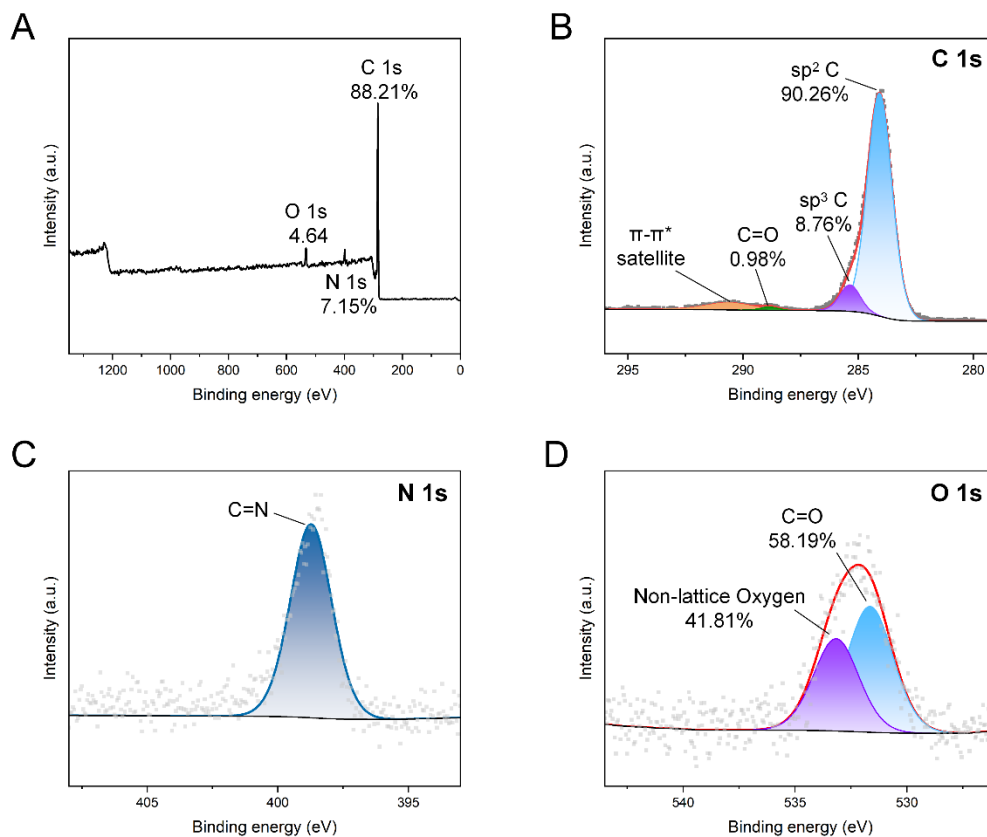
Supplementary Fig.15. Focused ion beam (FIB)-SEM image of the COF-CH₃/6FDA-DAM MMMs with 60.9 vol% of filler.



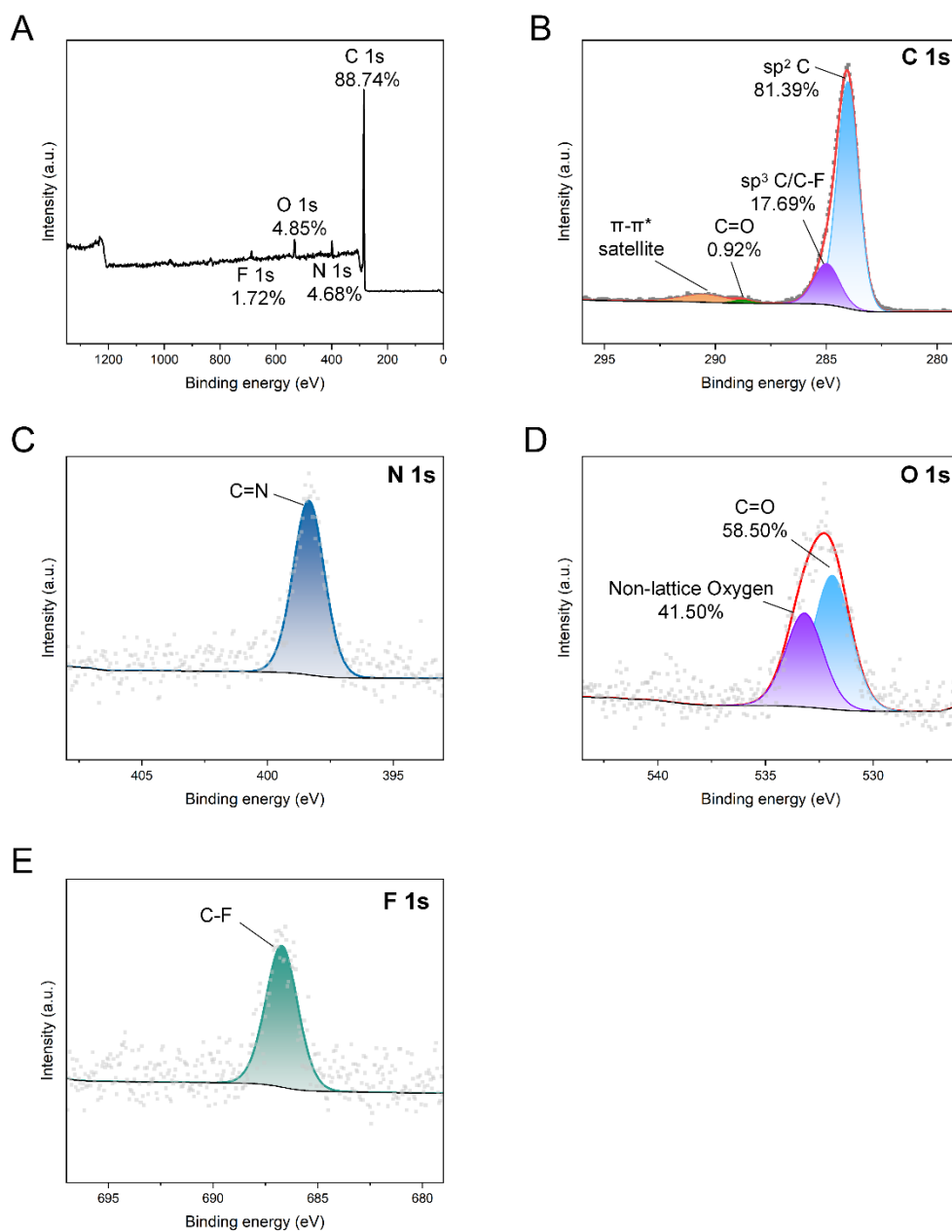
Supplementary Fig.16. Chemical structure of COF-H (**A**), COF-F (**B**), and COF-OH (**C**).



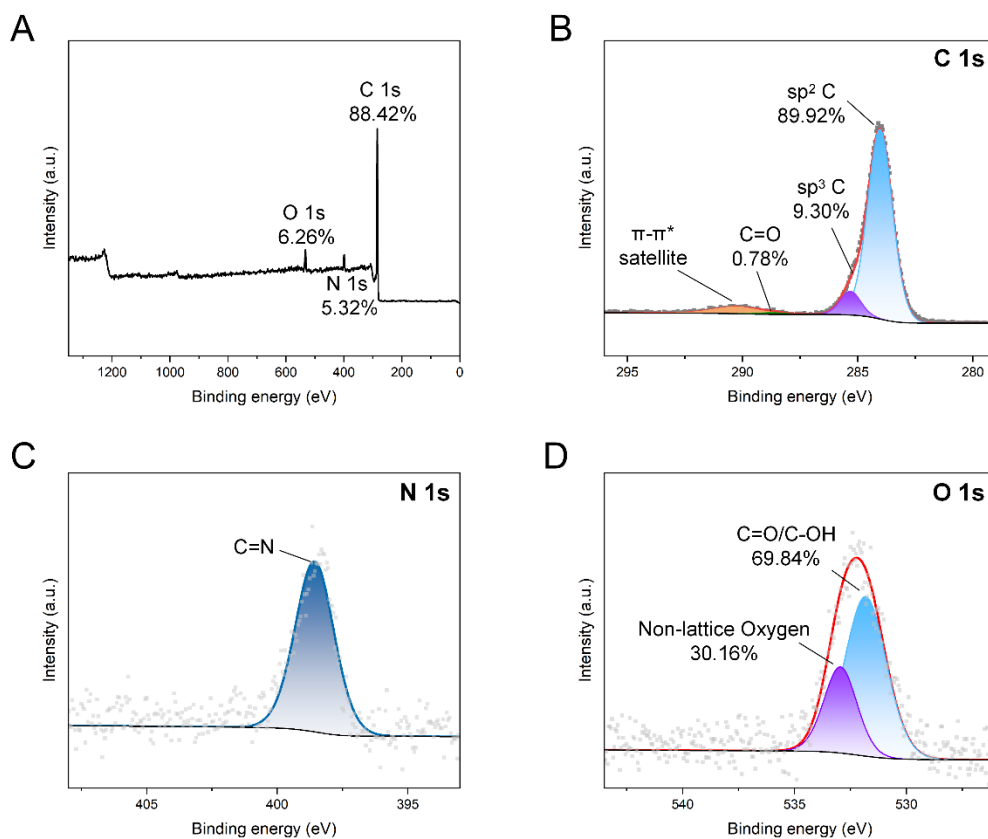
Supplementary Fig.17. FT-IR spectra of COF-R Crystal. For COF-OH, the broad peak at 3350 cm⁻¹ could be assigned to O-H stretching, confirming the introduction of phenolic hydroxyl groups. For COF-H and COF-F, there is no apparent difference from that of COF-CH₃ in FT-IR spectra since the linker exchange only takes place at the surface of the crystals, and the slight signal variations are undetectable.



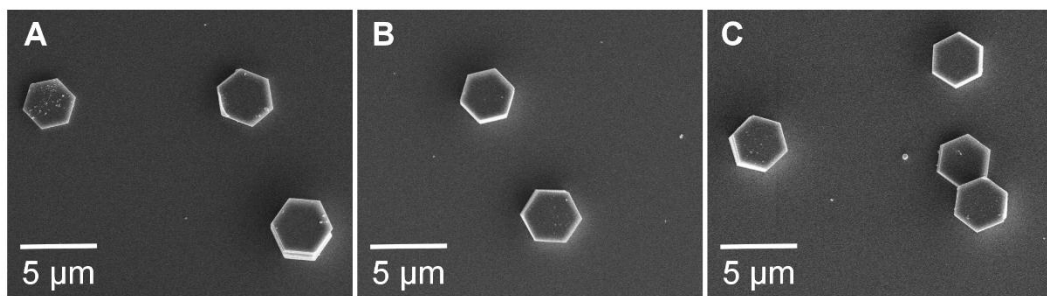
Supplementary Fig.18. XPS spectra of COF-H crystals. Compared with COF-CH₃ crystals (Supplementary Fig. 4), the decrease of carbon content (from 90.23% to 88.21%) and sp^3 C peak at 285.2 eV (from 13.63% to 8.76%) confirms the replacement of methyl groups by hydrogen.



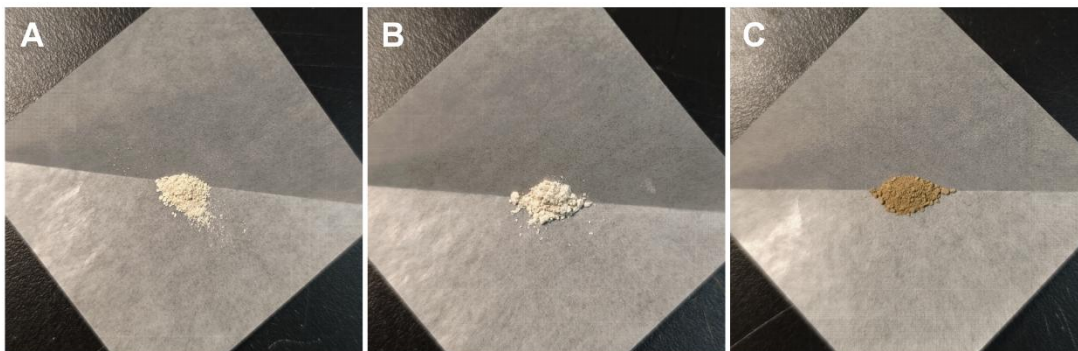
Supplementary Fig.19. XPS spectra of COF-F crystals. The occurrence of the F 1s peak at 686.7 eV confirms the replacement of methyl groups by fluorine atoms.



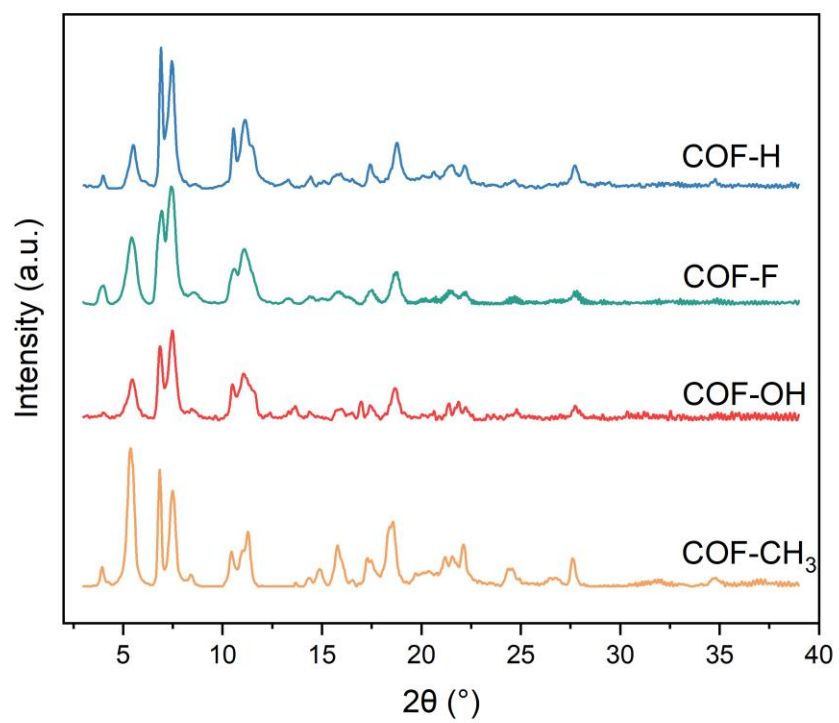
Supplementary Fig.20. XPS spectra of COF-OH crystals. Compared with COF-CH₃ crystals (Supplementary Fig. 4), the increase of oxygen content (from 4.81% to 6.26%) and O 1s peak at 532.0 eV (from 58.17% to 69.84%) confirms the replacement of methyl groups by hydroxyl groups.



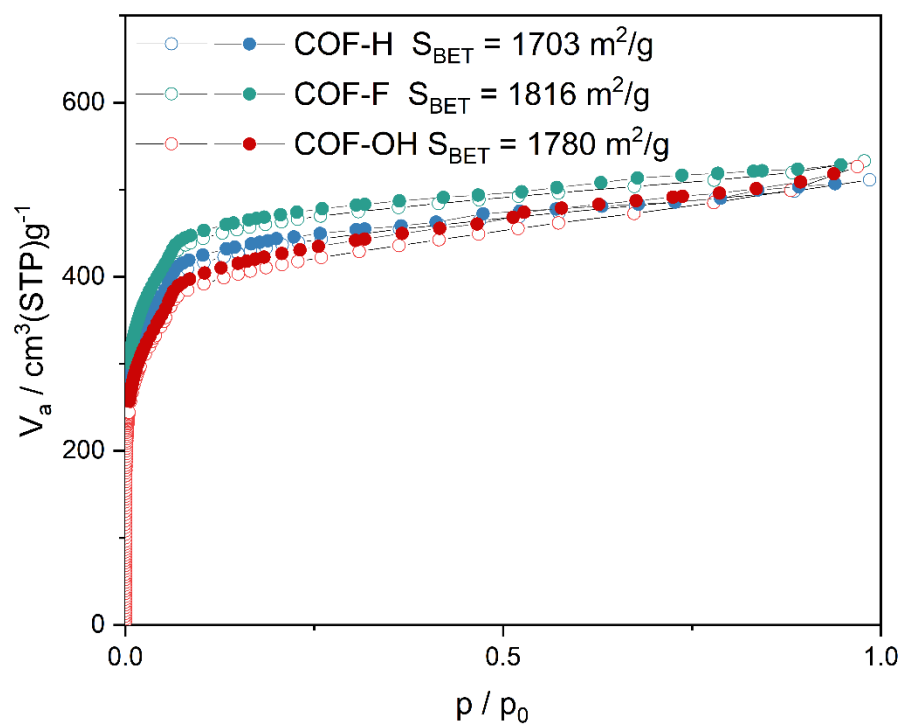
Supplementary Fig.21. SEM images of COF-R crystals. (A) COF-H, (B) COF-F, (C) COF-OH. The crystals preserved the original hexagonal prism morphology after linker exchange.



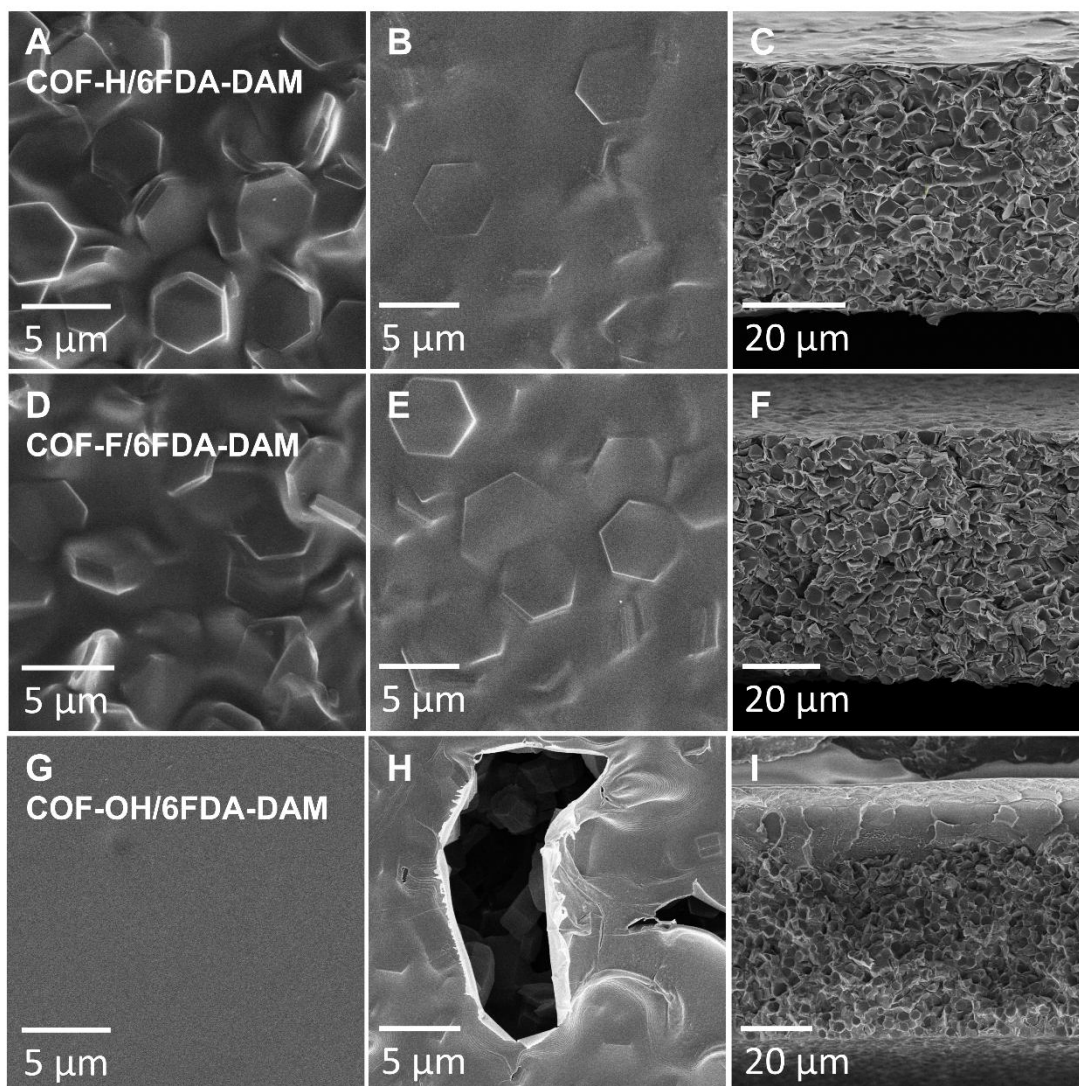
Supplementary Fig.22. Optical image of COF-R powder. (A) COF-H, (B) COF-F, (C) COF-OH.



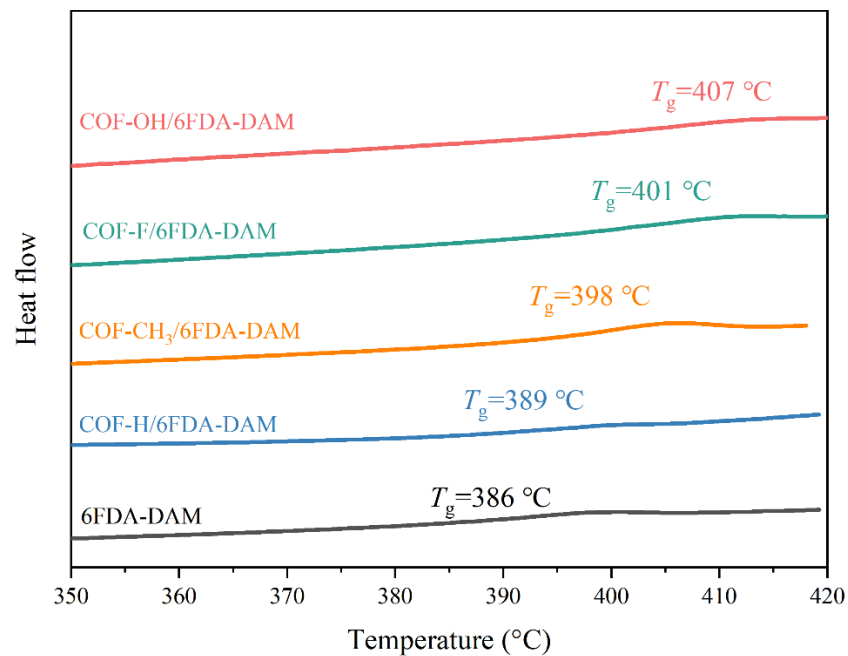
Supplementary Fig.23. XRD pattern of COF-R crystals.



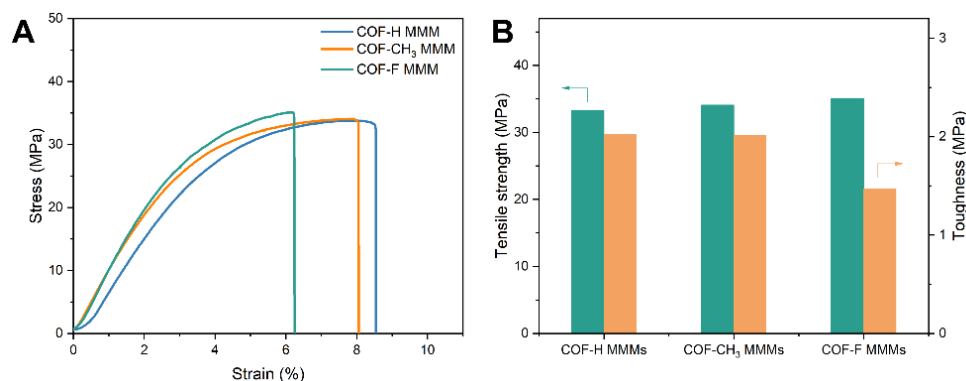
Supplementary Fig.24. Nitrogen adsorption-desorption isotherms and BET surface area of COF-H, COF-F, and COF-OH crystals.



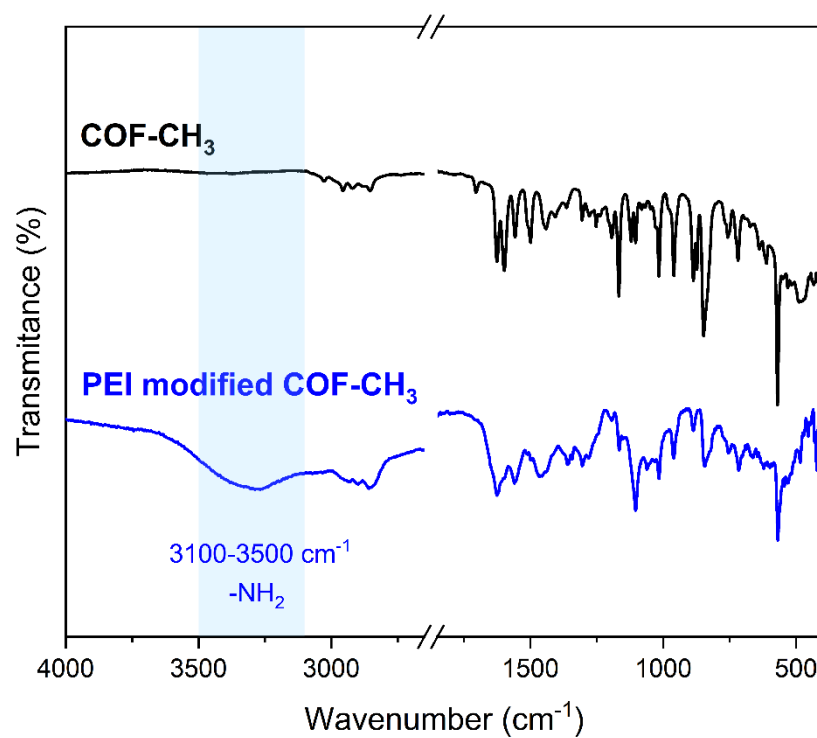
Supplementary Fig.25. SEM images of top, bottom views, and cross-sections of MMMs filled with different COF-R crystals with a packing density of 60.9 vol%.



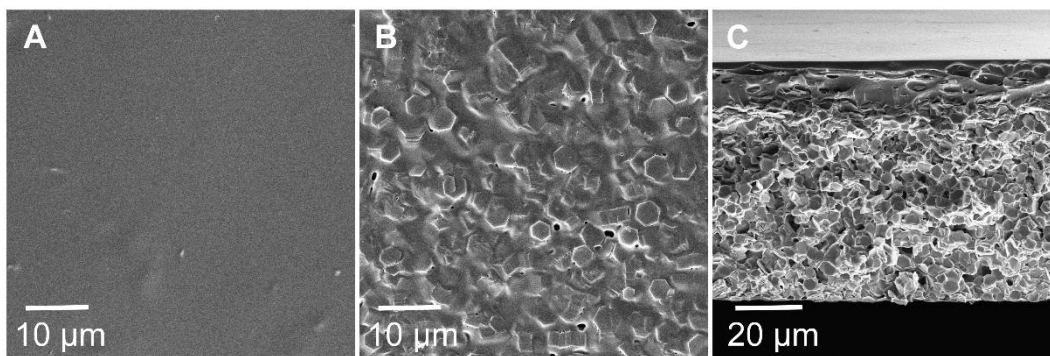
Supplementary Fig.26. Differential scanning calorimetry (DSC) curves of 6FDA-DAM and MMMs with different COF-R fillers. When increasing the interfacial interaction energy, the glass transition temperature (T_g) of the membranes increases, indicating that higher interfacial interactions bring more stressed interfacial structure.



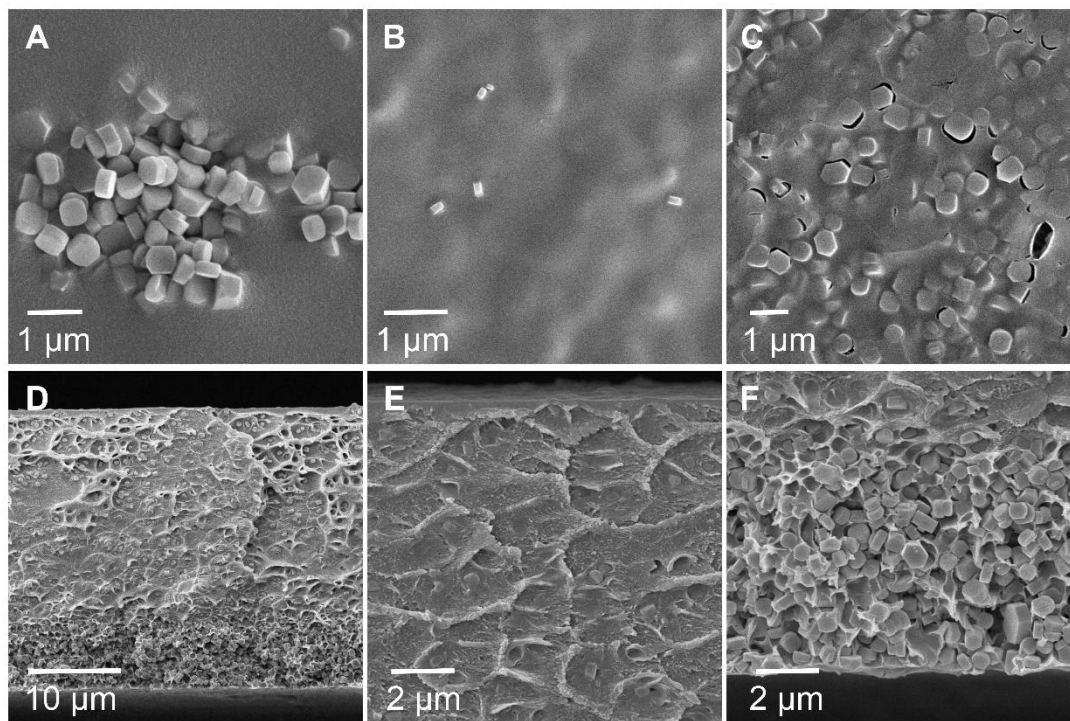
Supplementary Fig.27. The results of the mechanical tensile test of 6FDA-DAM and MMMs with different COF-R fillers. (A) Engineering stress-strain curves; (B) Comparison of tensile strength and toughness. The COF-F MMM exhibits higher tensile strength (35.1 MPa) due to stronger interfacial interactions. However, its toughness decreases to 1.47 MPa because the stronger interfacial bonding restricts interfacial sliding and polymer-chain rearrangement during deformation, thereby reducing the ability of the membrane to dissipate mechanical energy. In contrast, MMMs with weaker interfacial interactions exhibit lower tensile strength but improved toughness (33.3 MPa and 2.02 MPa for COF-H MMM; 34.1 MPa and 2.01 MPa for COF-CH₃ MMM). As for the COF-OH MMM, filler sedimentation leads to a highly inhomogeneous membrane structure consisting of a polymer-rich layer and a filler-rich layer with markedly different properties; therefore, the macroscopic mechanical test is not meaningful and the test is not performed.



Supplementary Fig.28. FT-IR spectra of COF-CH₃ and PEI modified COF-CH₃ crystals. The broad peak of -NH₂ at 3100-3500 cm^{-1} confirms the successful PEI modification of COF-CH₃ fillers.

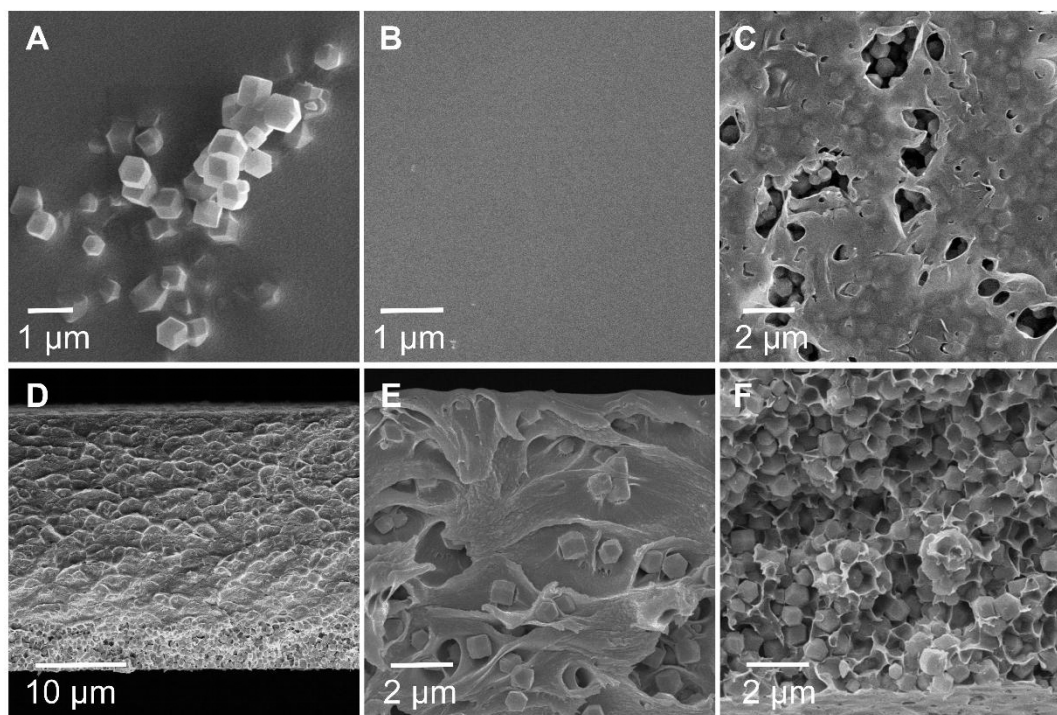


Supplementary Fig.29. SEM images of PEI-modified COF-CH₃/6FDA-DAM MMMs with 60.9 vol% of filler. (A) Top view; (B) Bottom view; (C) Cross-sectional view. Hydrogen bond networks formed between PEI-modified fillers induced severe filler agglomeration and sedimentation. As a result, distinct defects were observed from both the bottom and cross-sectional views of the SEM images

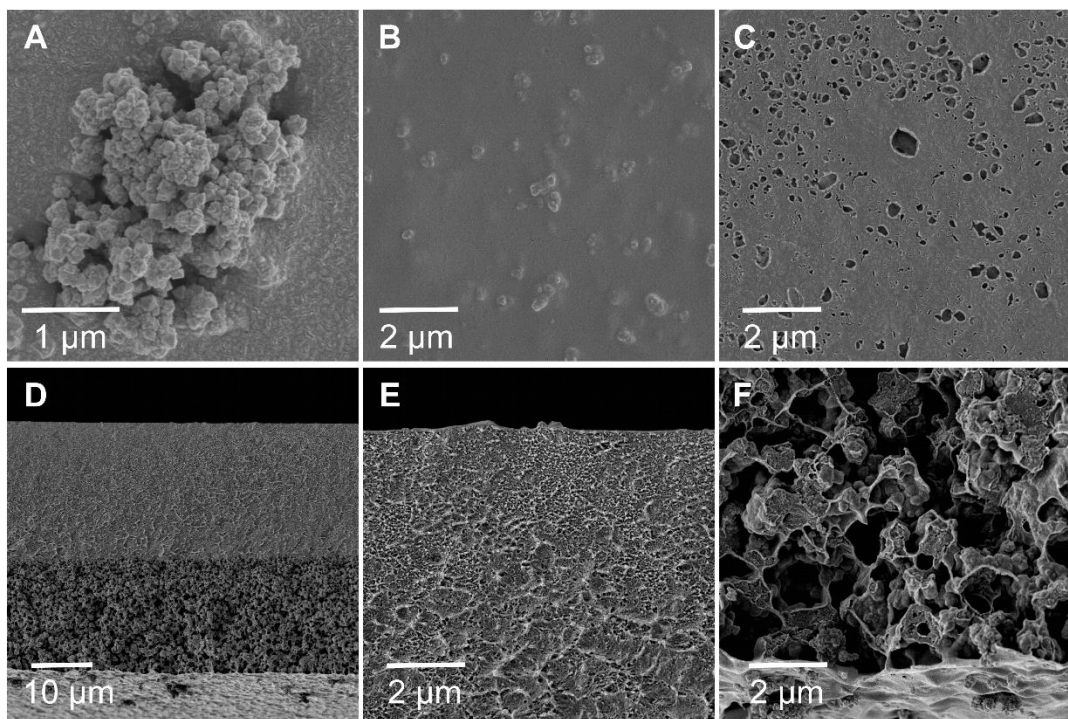


Supplementary Fig.30. SEM images of Silicalite-1/6FDA-DAM MMMs with 29.7 vol% of filler. (A) Silicalite-1 crystals; (B) Top view, (C) Bottom view, and (D-F) Cross-sectional views of the MMMs. (E) and (F) show the cross-sectional morphologies of the top and bottom parts of the membrane, respectively.

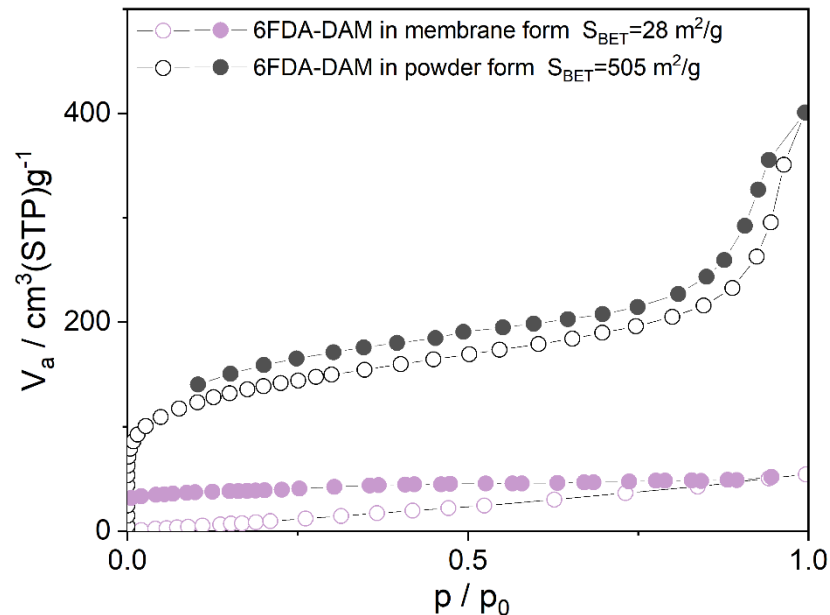
To compare the structures of organic- and inorganic-filler-based MMMs, three representative inorganic filler-based MMMs were fabricated with zeolite (silicalite-1) and MOF (ZIF-8 and UiO-66-NH₂) as fillers (Supplementary Fig. 30-32). All these membranes, with 29.7 vol% silicalite-1, 28.7 vol% ZIF-8, and 33.9 vol% UiO-66-NH₂ as fillers, exhibit obvious non-ideal structures including severe filler aggregation and sedimentation, and numerous defects despite their packing density being much lower than single-crystal COF MMMs. These behaviors are most probably attributed to the inferior compatibility and unmatched density between the polymer and inorganic fillers. In particular, UiO-66-NH₂ fillers, with a smaller size and stronger filler-polymer interactions, are considered capable of achieving a uniform and defectless membrane structure from previous viewpoints. However, the membrane exhibits obvious voids and defects induced by severe filler aggregation, indicating that modifying fillers with highly polar groups may not be a rational solution to compatibility issues.



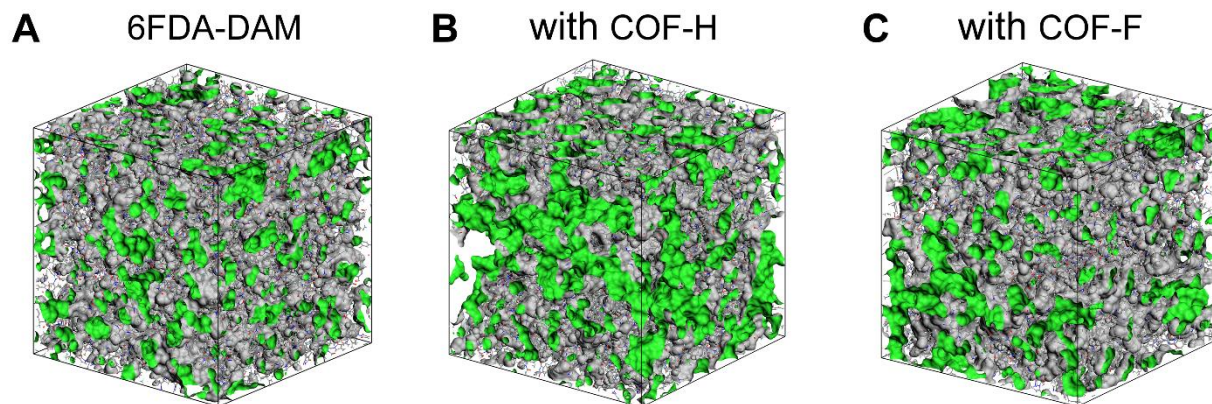
Supplementary Fig.31. SEM images of ZIF-8/6FDA-DAM MMMs with 28.7 vol% of filler. (A) ZIF-8 crystals; (B) Top view, (C) Bottom view, and (D-F) Cross-sectional views of the MMMs. (E) and (F) show the cross-sectional morphologies of the top and bottom parts of the membrane, respectively.



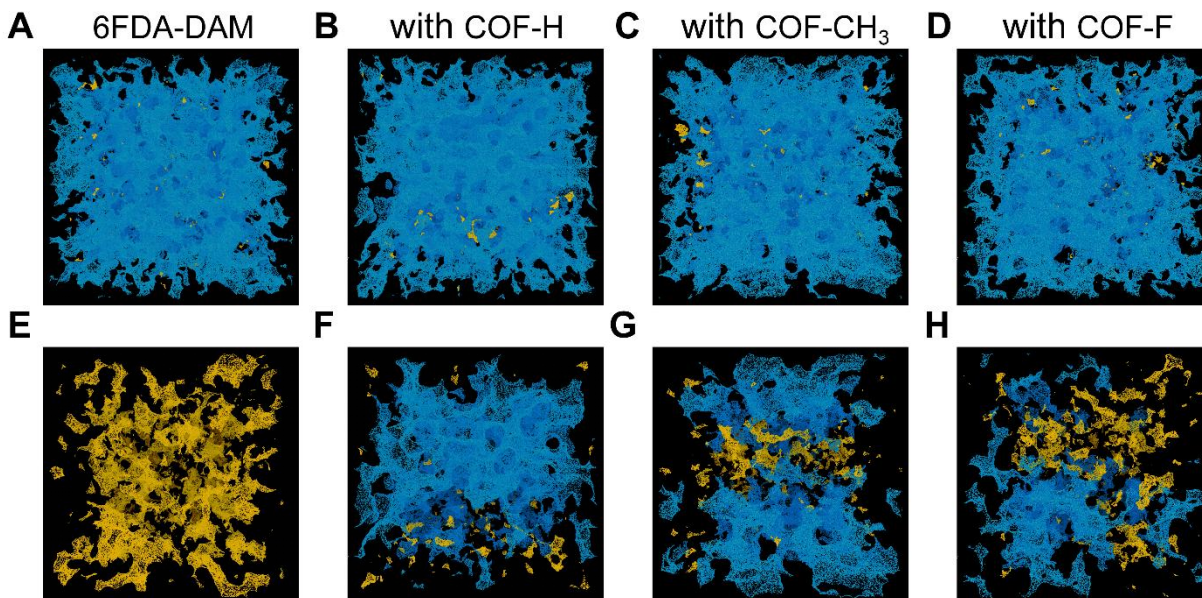
Supplementary Fig.32. SEM images of UiO-66-NH₂/6FDA-DAM MMMs with 33.9 vol% of filler. (A) UiO-66-NH₂ crystals; (B) Top view, (C) Bottom view, and (D-F) Cross-sectional views of the MMMs. (E) and (F) show the cross-sectional morphologies of the top and bottom parts of the membrane, respectively.



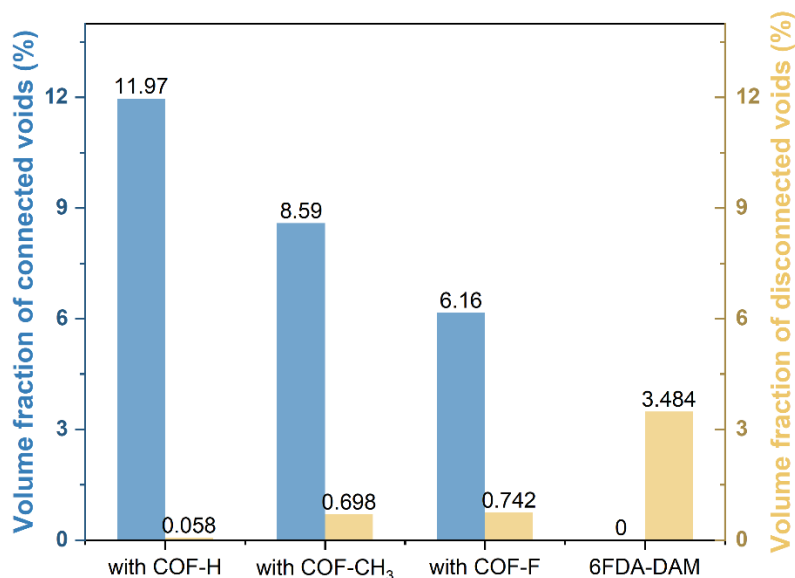
Supplementary Fig.33. N_2 adsorption-desorption isotherms at 77 K and the BET surface area of 6FDA-DAM in membrane form and powder form. Using 6FDA-DAM in powder form is essential for obtaining reliable data. This is because, for 6FDA-DAM in membrane form, the slow diffusion rate of gas molecules within the material, combined with the relatively thick membrane thickness, prevents adsorption equilibrium from being reached within the measurement time. Consequently, the true adsorption capacity and specific surface area cannot be accurately reflected. In contrast, for MMMs containing single-crystal COF fillers, the test results show no difference between the membrane form and powder form. This consistency arises because the introduction of single-crystal COF fillers enhances the gas diffusion rate within the membrane, allowing gas molecules to rapidly penetrate into the interior and reach adsorption equilibrium within the time window allowed by the adsorption instrument.



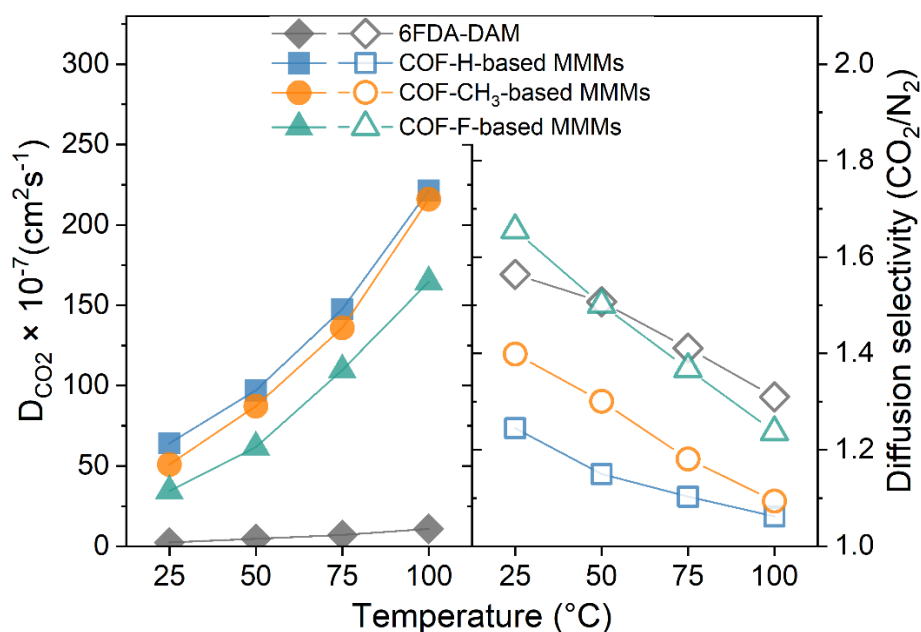
Supplementary Fig. 34. Computational model of polymer chain packing in 6FDA-DAM membrane (A), COF-H/6FDA-DAM MMM (B), and COF-F/6FDA-DAM MMM (C). The green regions represent the accessible free volume, whereas the grey regions denote the polymer/COF-occupied space.



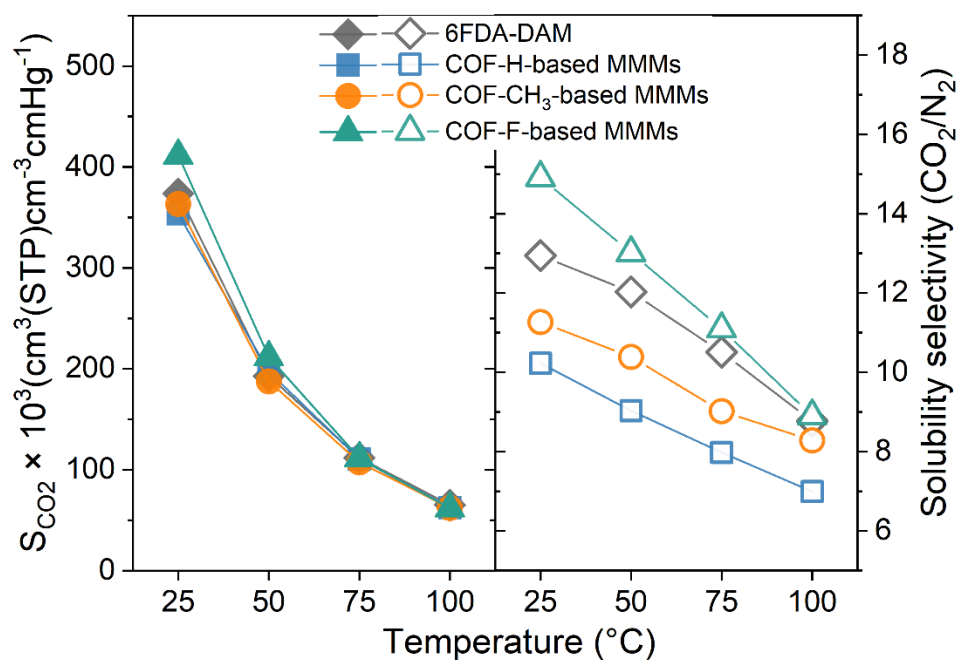
Supplementary Fig.35. Interconnected (blue) and disconnected (yellow) free volume voids in pure 6FDA-DAM membranes and membranes with different COF-R fillers with respect to a probe 0.85 Å in radius (**A-D**) and a probe 1.55 Å in radius (**E-H**), respectively. All membranes exhibit high-density transport channels with high connectivity when using a 0.85 Å probe (**A-D**). As for the case of using a 1.55 Å probe, almost all the free volume voids seem disconnected from each other in the 6FDA-DAM membrane due to the dense membrane structure (**E**). When incorporating COF-R fillers, the connectivity of free volume is significantly enhanced. The COF-H membranes show better connectivity, while the COF-F membranes show more disconnected free volume, as elucidated quantitatively in Supplementary Fig. 36. The results show a negative correlation between the interfacial interaction energy and transport channel connectivity.



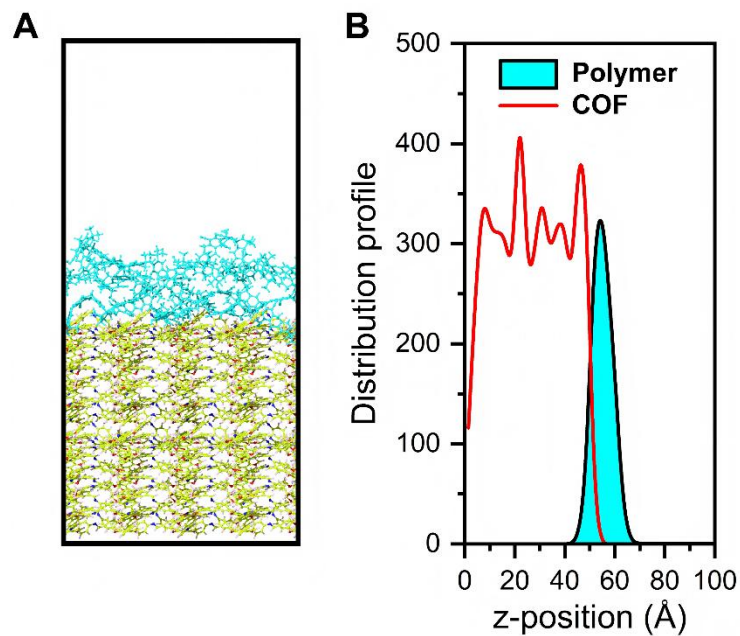
Supplementary Fig.36. Volume fraction of connected and disconnected voids in pure 6FDA-DAM membranes and membranes with different COF-R fillers. COF-H-based MMMs show a higher volume fraction of connected voids (11.97%) compared with that of COF-CH₃ and COF-F-based MMMs (8.59% and 6.16%, respectively) with larger probes. For the disconnected volume, a contrary trend was observed where COF-F and COF-CH₃-based MMMs exhibited higher volume fraction (0.742% and 0.698%, respectively) compared with COF-H-based MMMs (0.058%) due to the polymer free volume shrinkage caused by strengthened interfacial interactions. The varying free volume connectivity shows a negative correlation with their interfacial interaction energy, which would influence gas transport behavior significantly.



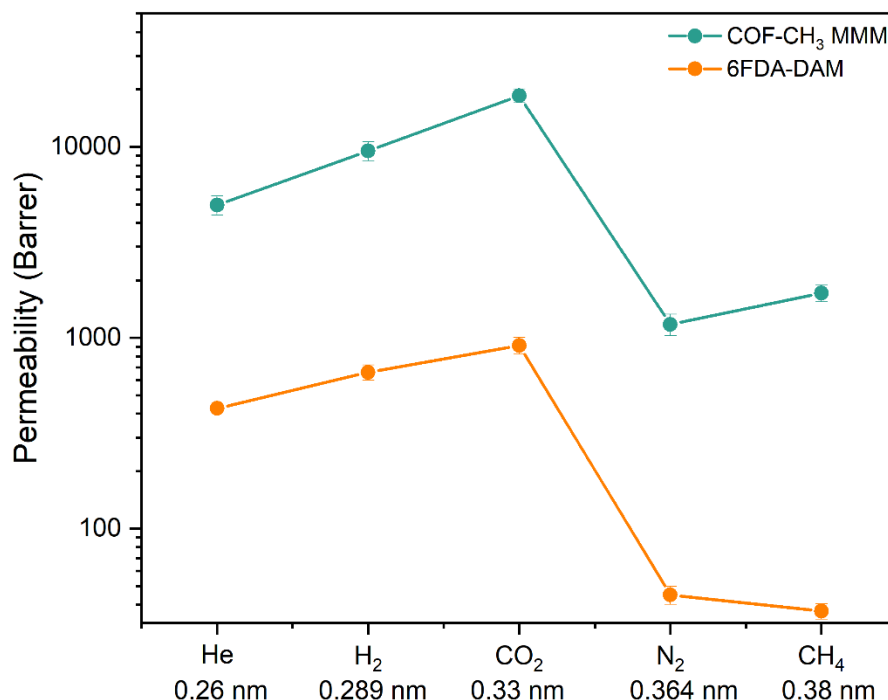
Supplementary Fig.37. Diffusion coefficients and selectivity of COF-R/6FDA-DAM MMMs with 60.9 vol% of COF and pure 6FDA-DAM membranes. COF-H-based MMMs with unstressed interfaces afford low-resistance molecular transport, yielding high CO₂ and N₂ diffusivity ($6.41 \times 10^{-6} \text{ cm}^2/\text{s}$ and $5.15 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively) but low CO₂/N₂ diffusivity selectivity (1.24). Shrunk interfacial micropores of COF-F-based MMMs impose stronger hindrance on N₂ than CO₂, inducing decreased diffusivity by increasing diffusivity selectivity to 1.66. COF-CH₃-based MMMs obtain moderate diffusivity ($3.64 \times 10^{-6} \text{ cm}^2/\text{s}$ for CO₂) and moderate selectivity (1.40). All membranes significantly surpass pure polymer in diffusivity ($2.4 \times 10^{-7} \text{ cm}^2/\text{s}$ and $1.6 \times 10^{-7} \text{ cm}^2/\text{s}$ for CO₂ and N₂, respectively), confirming the dominance of COF nanochannels on the transport properties. Rising temperature accelerates gas mobility and chain dynamics, synchronously enhancing both CO₂ and N₂ diffusivity, but reduces the diffusivity selectivity.



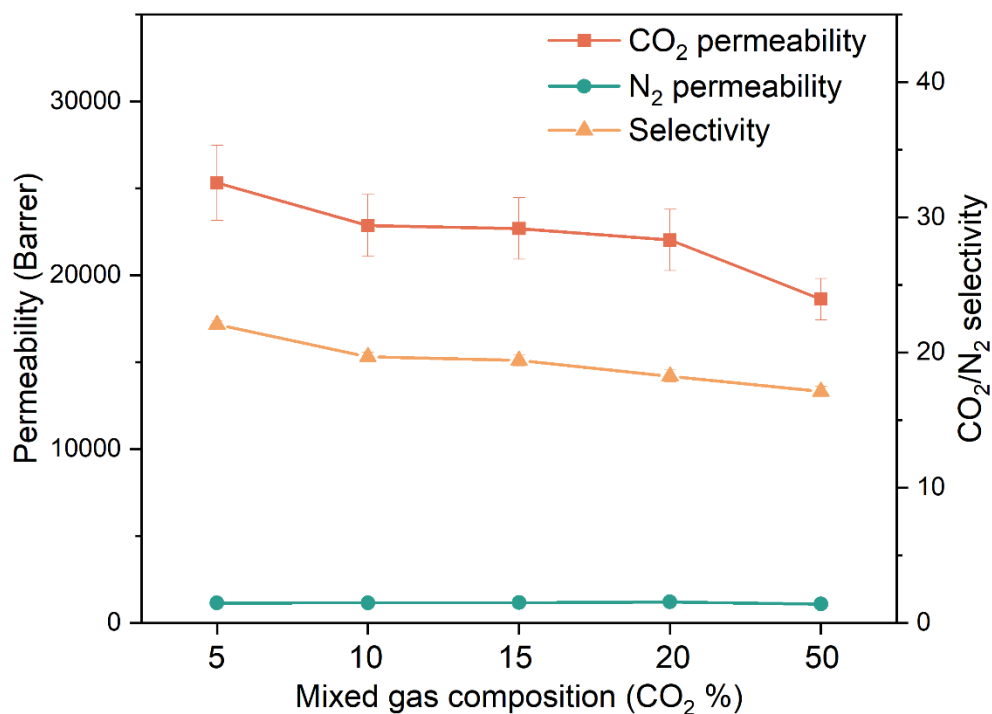
Supplementary Fig.38. Solubility coefficients and selectivity of COF-R/6FDA-DAM MMMs with 60.9 vol% of COF and pure 6FDA-DAM membranes. MMMs with COF-CH₃ and COF-H crystals show comparable solubility selectivity (CO₂/N₂ solubility selectivity = 11.27 and 10.23, respectively) due to the similar properties in CO₂ adsorption. In contrast, the fluorine-rich structure of COF-F amplifies CO₂-philic adsorption via dipole-quadrupole interactions, leading to higher solubility selectivity (CO₂/N₂ solubility selectivity = 14.91).



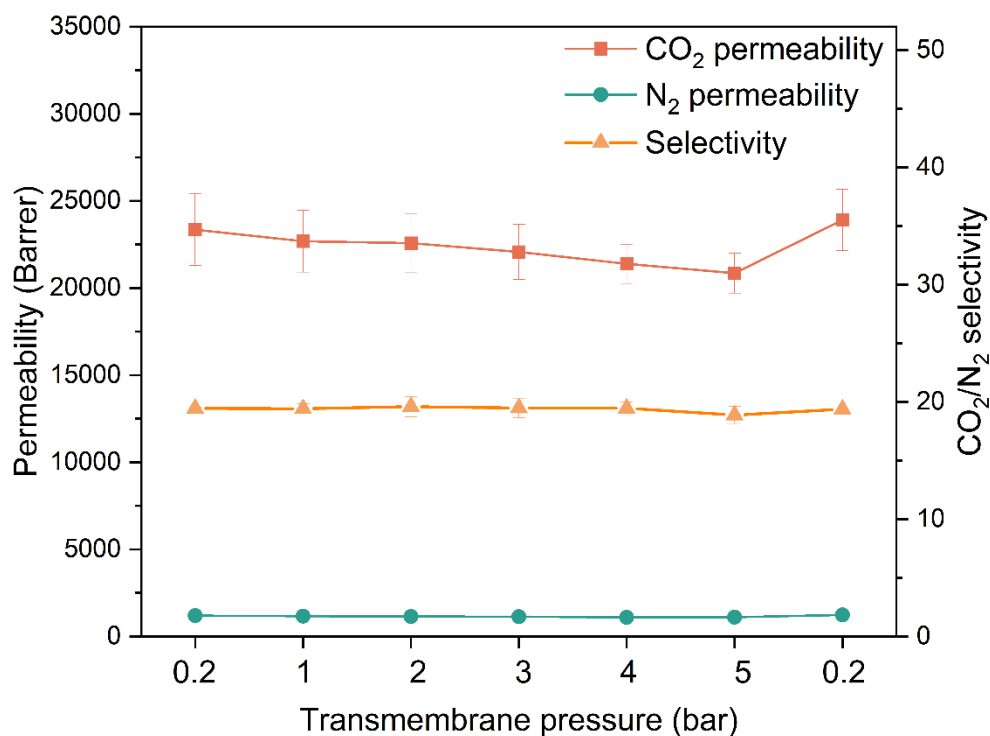
Supplementary Fig.39. (A) Schematic representation of the COF-CH₃/6FDA-DAM composite; (B) Distribution profile of COF-CH₃ and 6FDA-DAM composite along the direction perpendicular to the (001) surface of COF-CH₃.



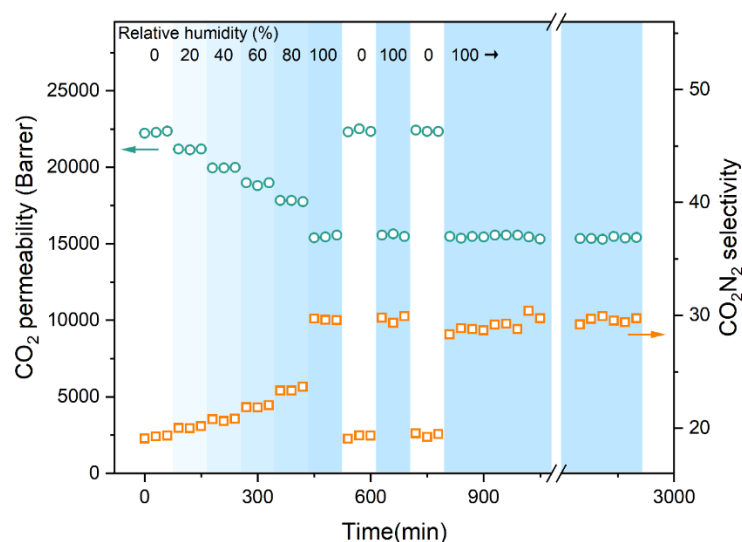
Supplementary Fig.40. Pure gas permeation performance of COF-CH₃/6FDA-DAM MMMs with 60.9 vol% of filler and pure 6FDA-DAM membranes. Comparing the results between the pure-gas test and the mixed-gas test, we observed slightly enhanced CO₂ permeability and CO₂/N₂ selectivity under mixed-gas feeds (15:85). The improved performance arises from two aspects: (1) the competitive adsorption between CO₂ and N₂. The membranes exhibit preferential adsorption of CO₂. In mixed-gas measurements, once the adsorbed CO₂ occupies the transport channels, the permeation of N₂ is hindered, resulting in a decrease in N₂ permeability and an enhancement in CO₂/N₂ selectivity. (2) the low CO₂ partial pressure in mixed-gas tests. Under low CO₂ partial pressure, the CO₂-affinitive sites in the membranes are not saturated, allowing most CO₂ molecules to be rapidly and selectively captured by these adsorption sites, which enhances the CO₂ permeability. Considering both competitive adsorption and the low CO₂ partial pressure in the feed gas, the mixed-gas test exhibits significant performance enhancement. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



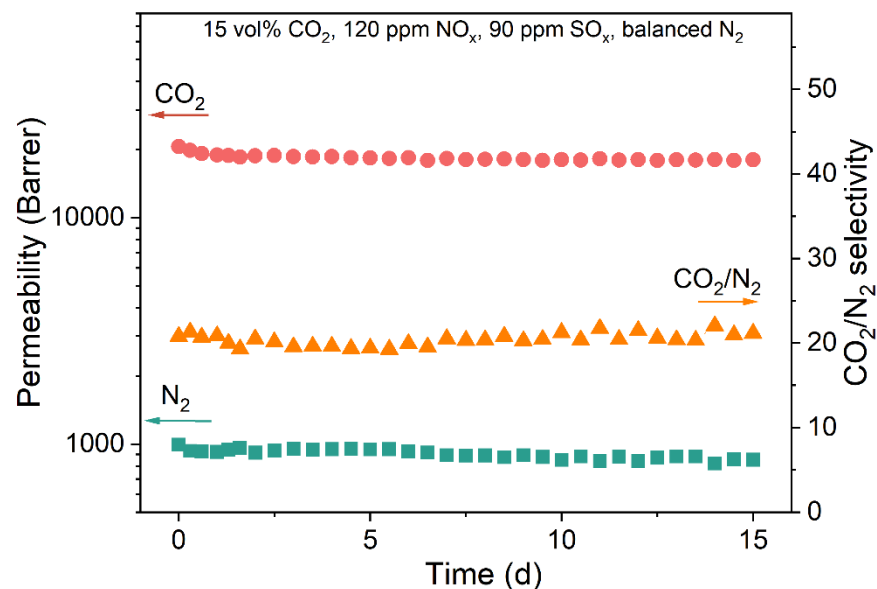
Supplementary Fig.41. Variation of CO₂/N₂ separation performance of COF-CH₃/6FDA-DAM MMMs with 60.9 vol% of filler, with feed CO₂ concentration varying from 5% to 50%. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



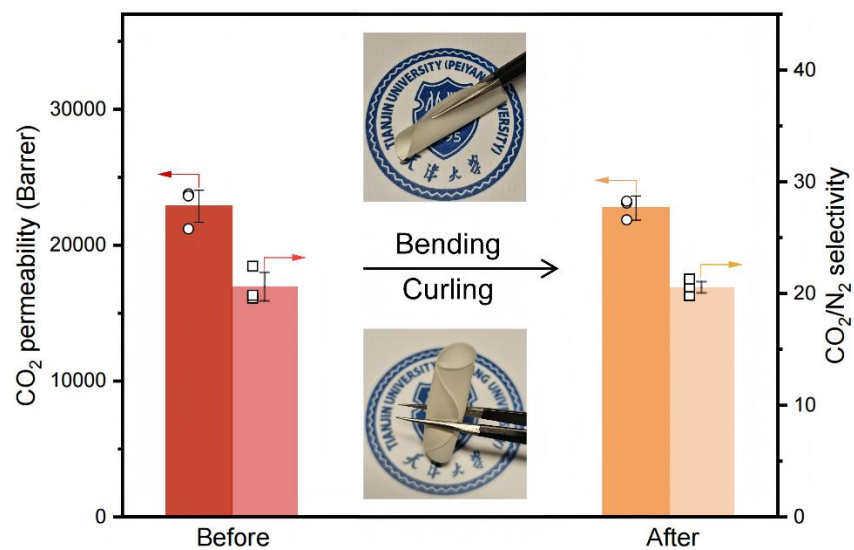
Supplementary Fig.42. Variation of CO₂/N₂ separation performance of COF-CH₃/6FDA-DAM MMMs with 60.9 vol% of filler under feed pressure varying from 0.2 to 5 bar. The separation performance exhibits a slight decrease as the feed pressure increases, with nearly full performance recovery upon pressure release, underscoring the excellent pressure resistance. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



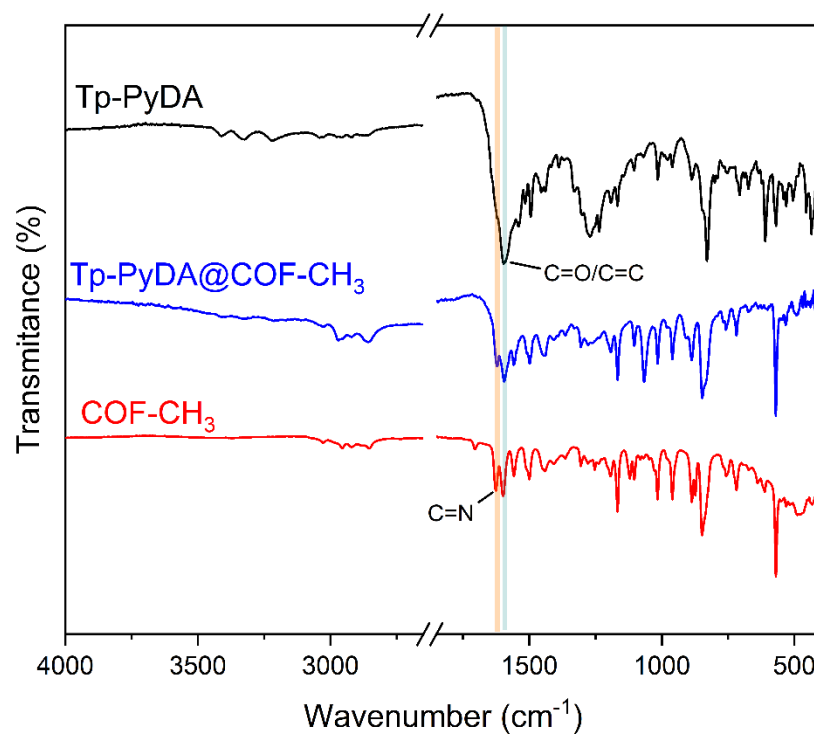
Supplementary Fig.43. The humidity stability test of COF-CH₃/6FDA-DAM MMMs with 60.9 vol% of filler. During the variable relative humidity tests, the CO₂ permeability of the membrane decreased while the CO₂/N₂ selectivity increased with the increasing relative humidity in the feed gas. When the relative humidity was raised to 100%, the membrane still maintained a relatively high CO₂ permeability of ~15400 Barrer, while the CO₂/N₂ selectivity increased to 29.6. Moreover, the membrane exhibited excellent stability in both cyclic and long-term tests, demonstrating its potential for application under complex humidity conditions.



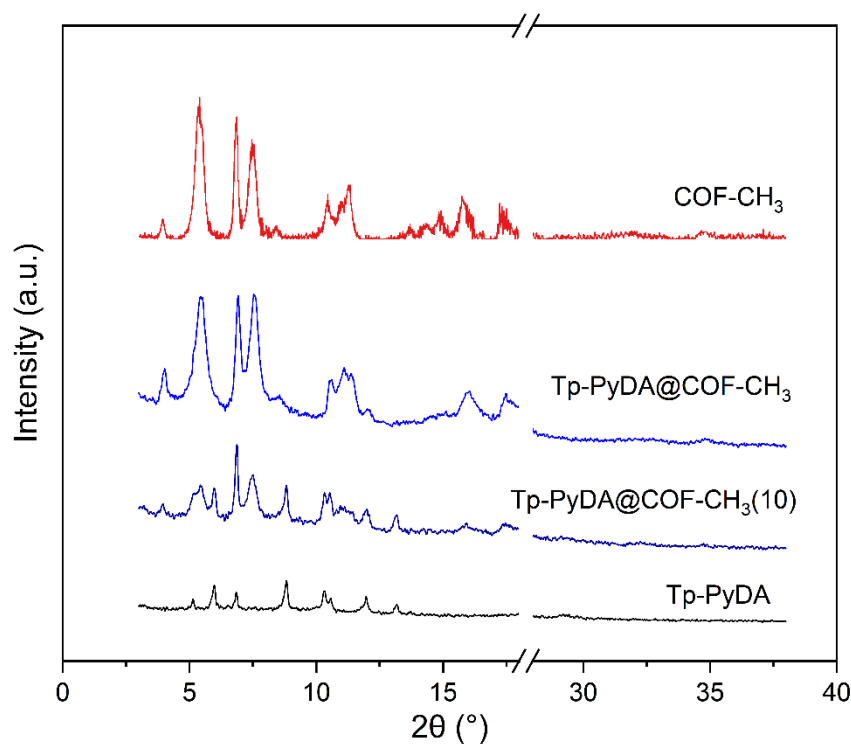
Supplementary Fig.44. The NO_x/SO_x stability test of COF-CH₃/6FDA-DAM MMMs with 60.9 vol% of filler. A comparison of the simulated flue gas composition used in this work with the literature is provided in Supplementary Table 4. The membrane exhibits good tolerance to NO_x and SO_x. Although the CO₂ permeability decreases slightly at the beginning, the membrane performance reaches a steady state after 3 days of testing and maintains a high level of performance (CO₂ permeability of ~18000 Barrer and CO₂/N₂ selectivity of ~20).



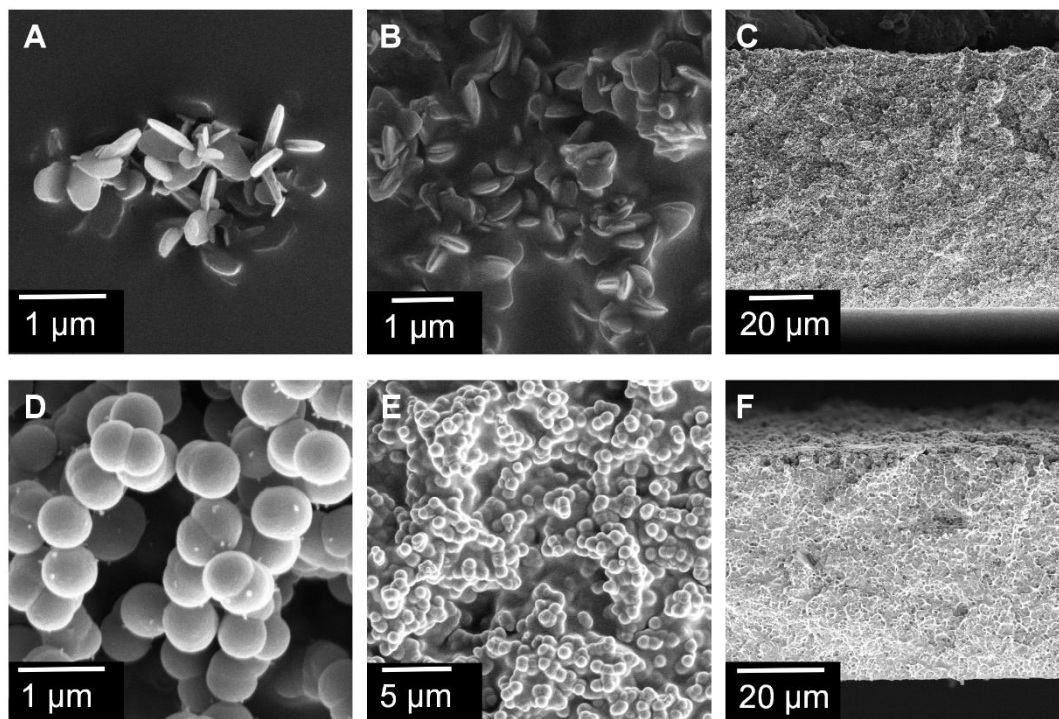
Supplementary Fig.45. Separation performance of MMMs with 60.9 vol% COF-CH₃ before and after bending/curling. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



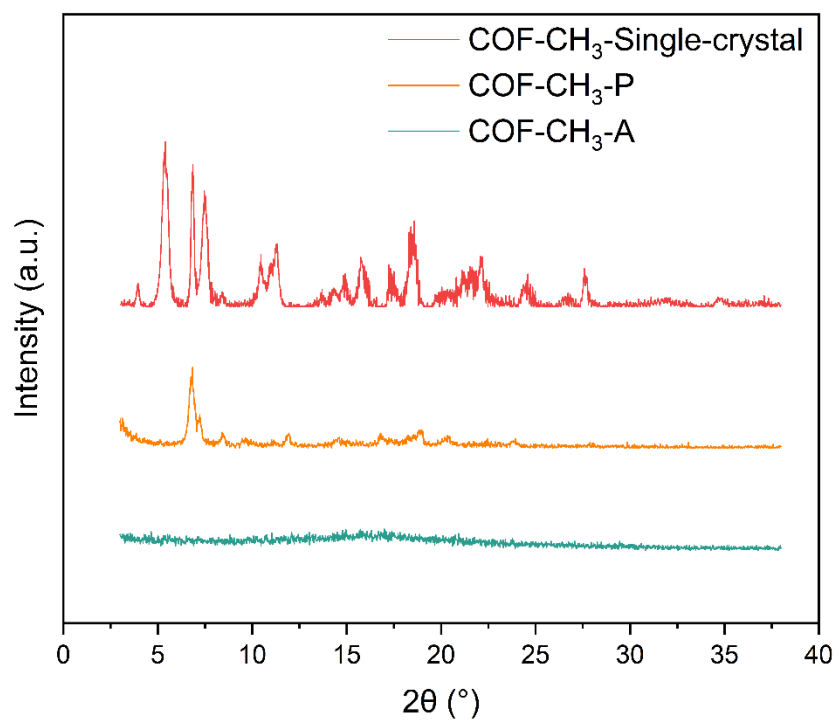
Supplementary Fig.46. FT-IR spectra of Tp-PyDA, COF-CH₃, and Tp-PyDA@COF-CH₃ crystals. The C=N stretch peak and C=O/C=C stretch peak are observed simultaneously in the spectra of Tp-PyDA@COF-CH₃ crystals.



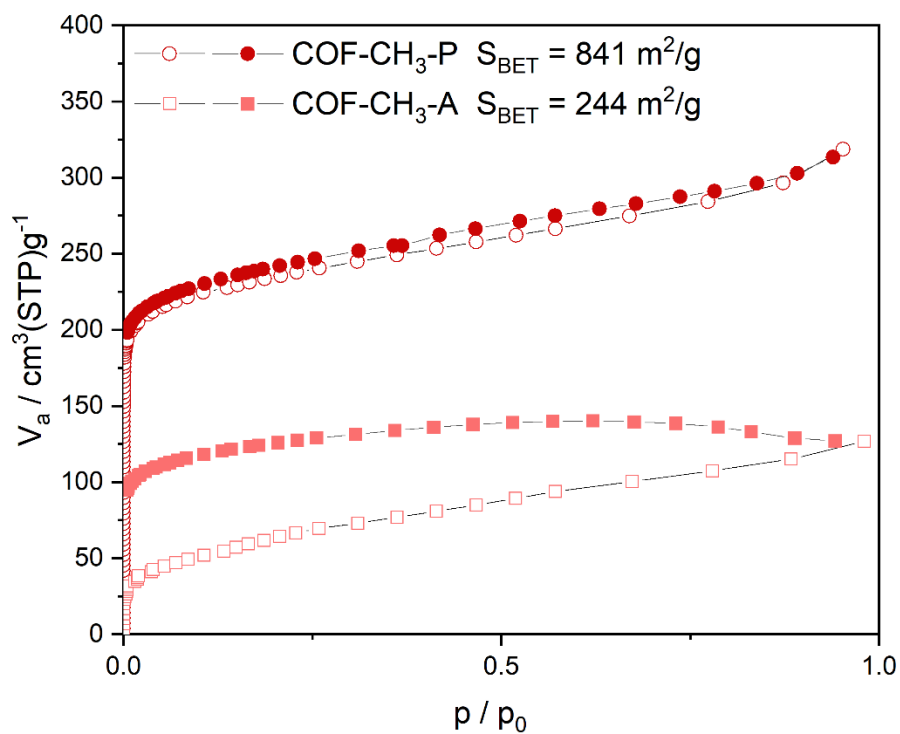
Supplementary Fig.47. XRD pattern of Tp-PyDA, COF-CH₃, and Tp-PyDA@COF-CH₃ crystals. The Tp-PyDA@COF-CH₃ crystals possess a very similar XRD pattern compared with that of COF-CH₃, since the thickness of the Tp-PyDA layer is too small to be detected via XRD. Thus, we synthesized another Tp-PyDA@COF-CH₃ crystal, but with ten times the amount of Tp and PyDA monomers, named Tp-PyDA@COF-CH₃(10). Both the characteristic peaks of Tp-PyDA and COF-CH₃ could be observed in the XRD pattern of the Tp-PyDA@COF-CH₃(10) crystal.



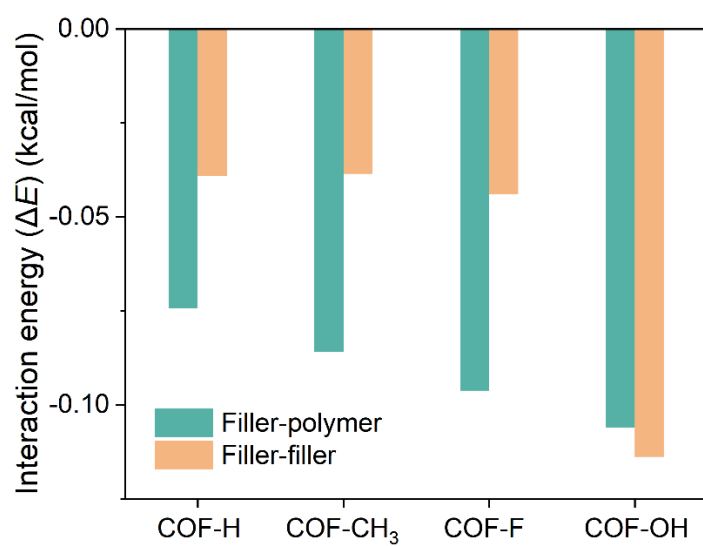
Supplementary Fig.48. SEM images of COF-CH₃-P, COF-CH₃-A crystals, and corresponding MMMs with 60.9 vol% of filler. (A) COF-CH₃-P crystals; (B) Surface morphology of COF-CH₃-P membranes; (C) Cross-section morphology of COF-CH₃-P membranes; (D) COF-CH₃-A crystals; (E) Surface morphology of COF-CH₃-A membranes; (F) Cross-section morphology of COF-CH₃-A membranes.



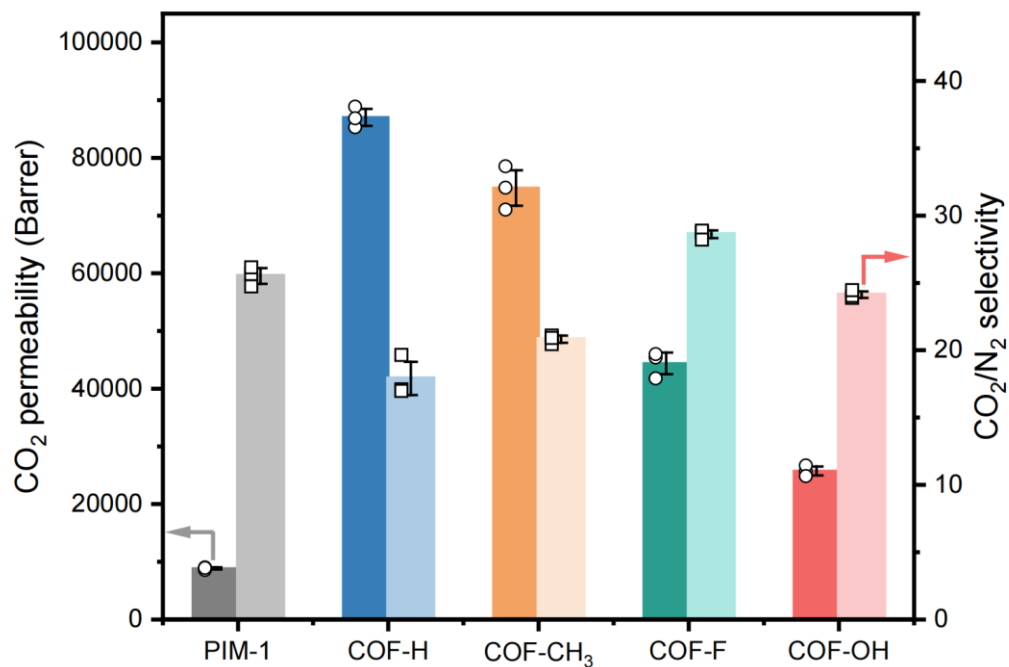
Supplementary Fig.49. XRD pattern of COF-CH₃ single crystals, COF-CH₃-P, and COF-CH₃-A crystals.



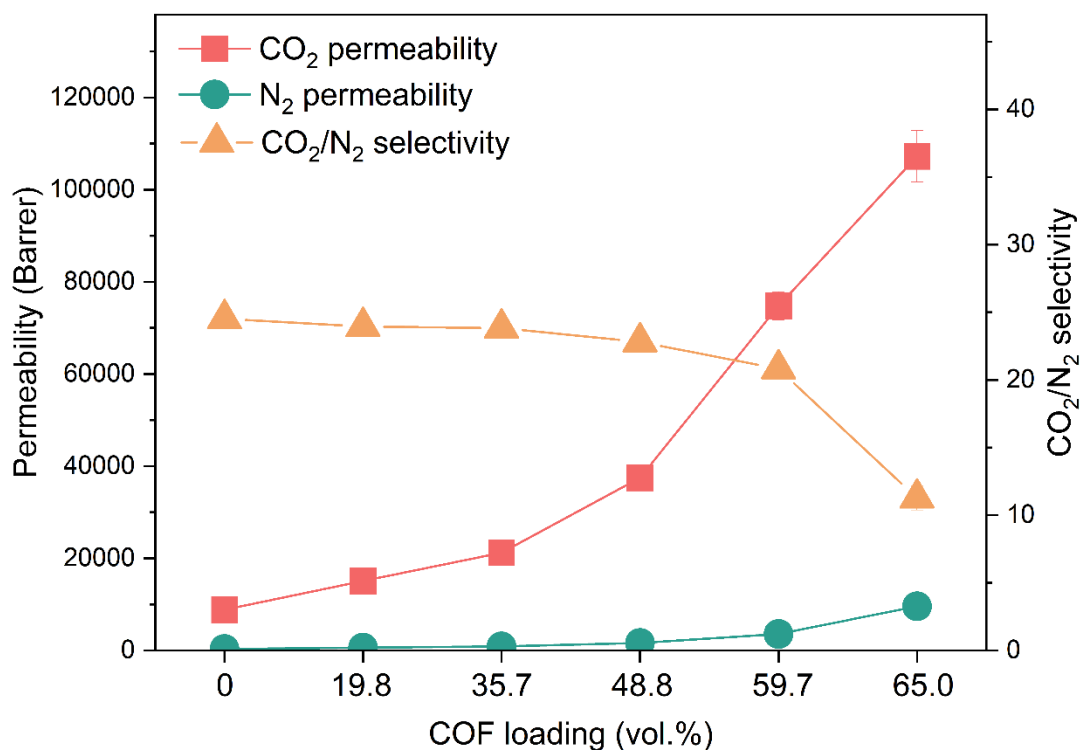
Supplementary Fig.50. Adsorption isotherms of COF-CH₃-P and COF-CH₃-A crystals. COF-CH₃-A displays significantly reduced porosity ($S_{\text{BET}} < 200 \text{ m}^2/\text{g}$), leading to insufficient contribution to permeability enhancement.



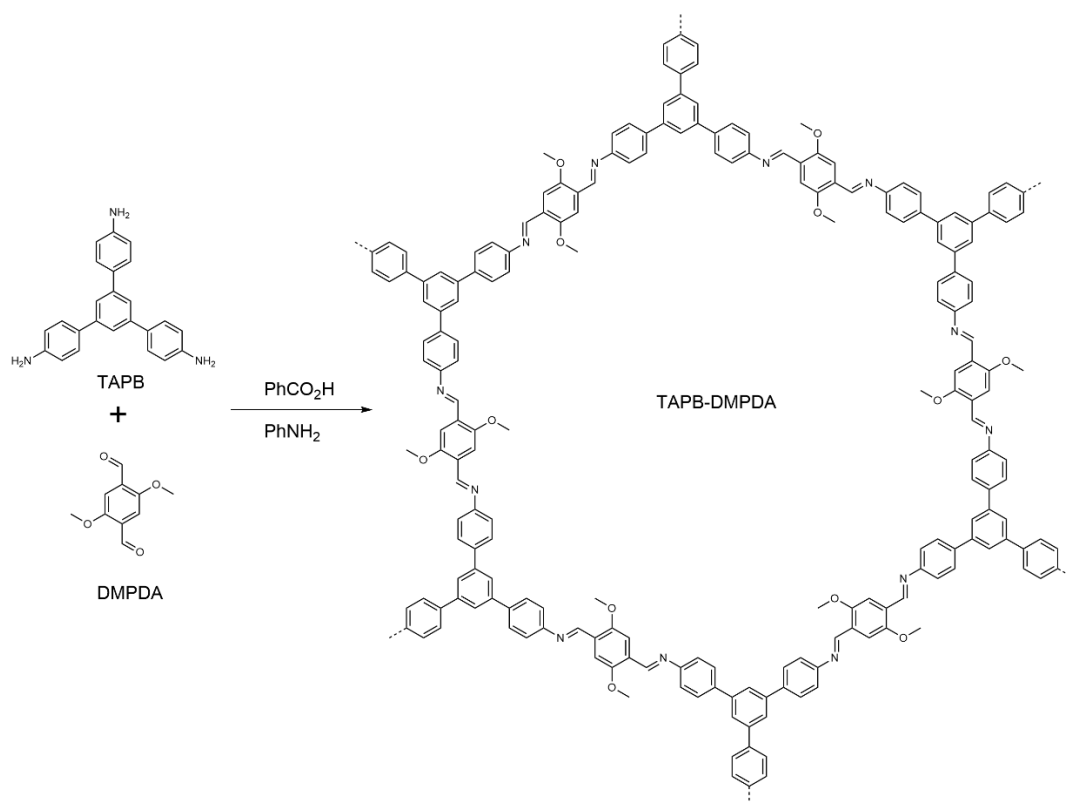
Supplementary Fig.51. Calculated interaction energy between filler-polymer and filler-filler in PIM-1-based MMMs.



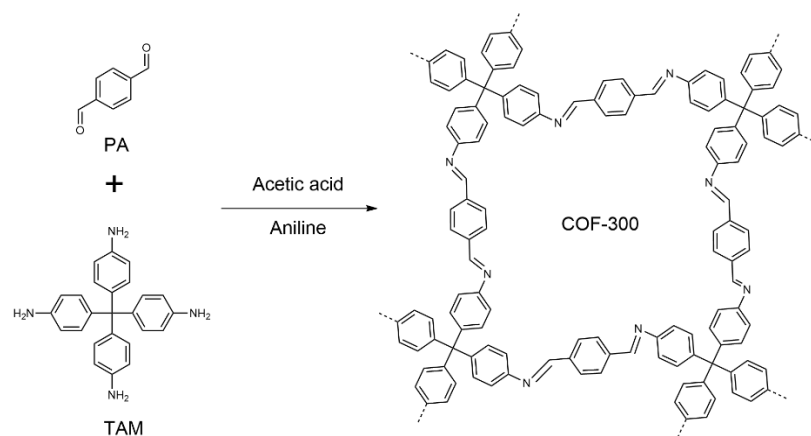
Supplementary Fig.52. CO₂ permeability and CO₂/N₂ selectivity of 59.7 vol% MMMs with PIM-1 matrix and different COF fillers at 25 °C and 2 bar. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



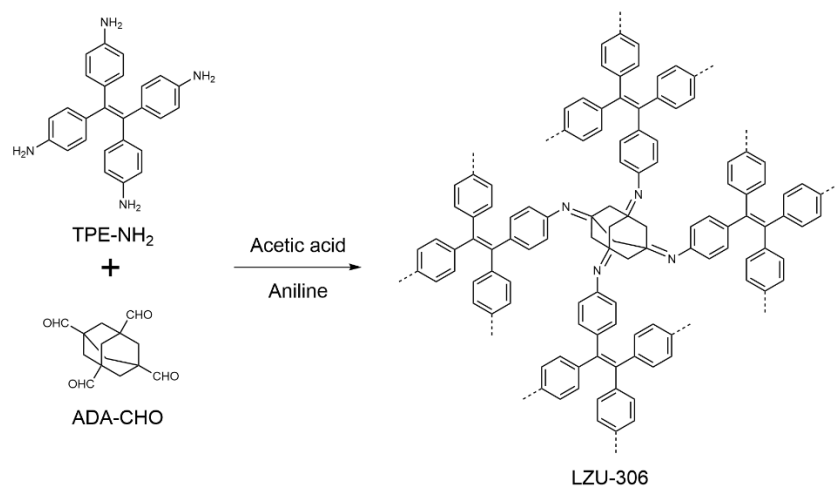
Supplementary Fig.53. CO₂/N₂ separation performance of COF-CH₃/PIM-1 MMMs at different filler packing densities from 0 vol% to 65.0 vol%. Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.



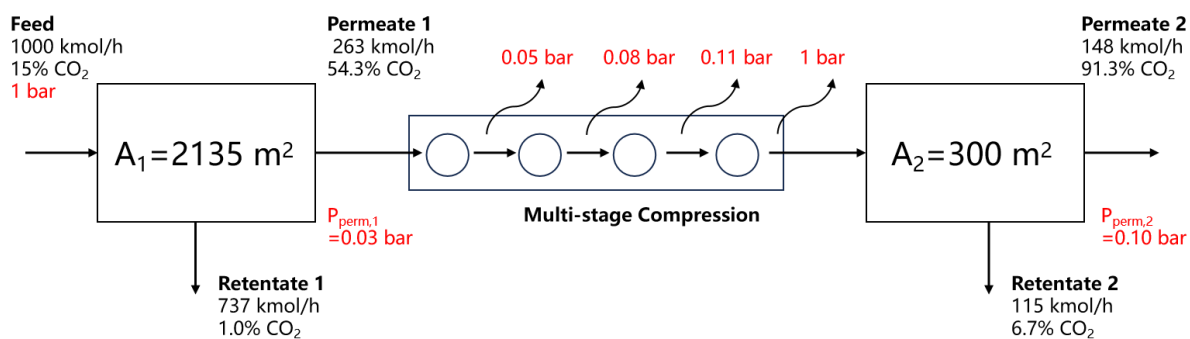
Supplementary Fig.54. Synthesis and chemical structure of TAPB-DMPDA.



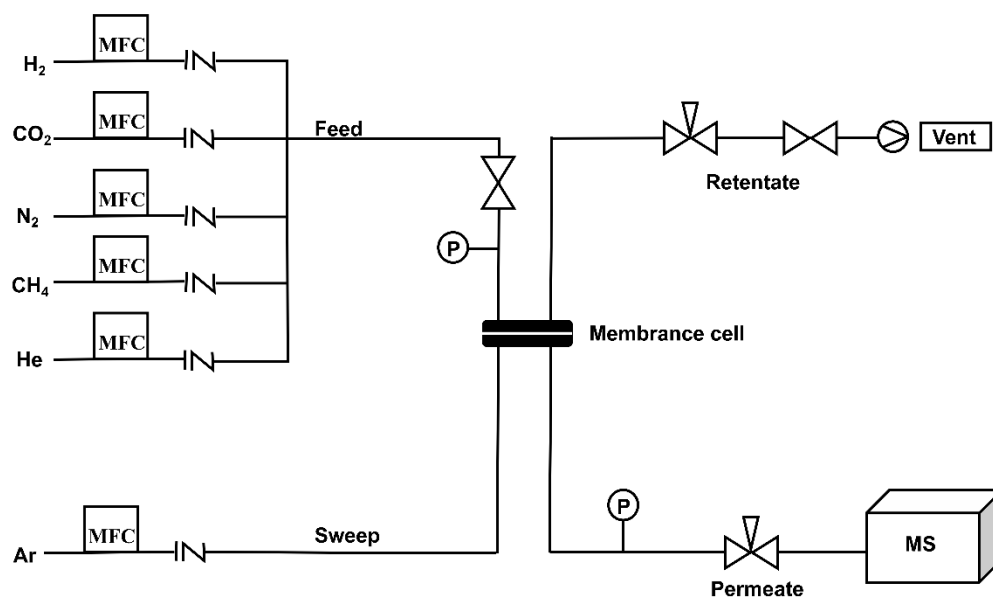
Supplementary Fig.55. Synthesis and chemical structure of COF-300.



Supplementary Fig.56. Synthesis and chemical structure of LZU-306.



Supplementary Fig.57. The layout of the double-stage membrane separation process for CO₂ capture. The system can achieve a recovery of 90.0% and a purity of 91.3% while processing a dry gas mixture (1000 kmol/h, 15% CO₂, 85% N₂)



Supplementary Fig.58. Schematic diagram of gas permeation apparatus.

3. Supplementary Note

Supplementary Note 1

The synthesis optimization of single-crystal COF fillers

Rapid synthesis of single-crystal COF with high yield, moderate size, and regular morphology is crucial yet challenging for preparing composite membranes. High-yield synthesis within a short reaction time is the prerequisite for practical feasibility. Moderate crystal size could preserve the long-range mass transfer channels while maintaining favorable dispersion without sedimentation. Regular morphology facilitates the even dispersion of the fillers, thereby effectively avoiding the severe agglomeration typically associated with particles that show an irregular morphology and are highly entangled.

However, achieving these objectives simultaneously presents significant challenges, requiring collaborative optimization of crystal nucleation, growth, and crystallization behavior. The rapid growth process often conflicts with high crystallinity requirements. As nucleation constitutes the rate-limiting step in crystal synthesis, decoupling nucleation from growth emerges as the key to resolving this contradiction. Our approach implements an ultrasonication step before growth initiation to achieve high-density nucleation, followed by controlled crystal growth under mild conditions. This methodology enables rapid synthesis of single-crystal COF with high yield (81.5 wt%), superior to the protocol for the COF-CH₃ synthesis in literature (15 days with a yield less than 5 wt%). Synchronized nucleation timing ensures uniform crystal size by providing similar growth durations. Moreover, the high nucleation density effectively controls crystal size, preventing monomer concentration on limited nuclei that would form oversized crystals. Although Ostwald ripening would theoretically compromise crystal size uniformity, we didn't observe this phenomenon within our synthesis timeframe.

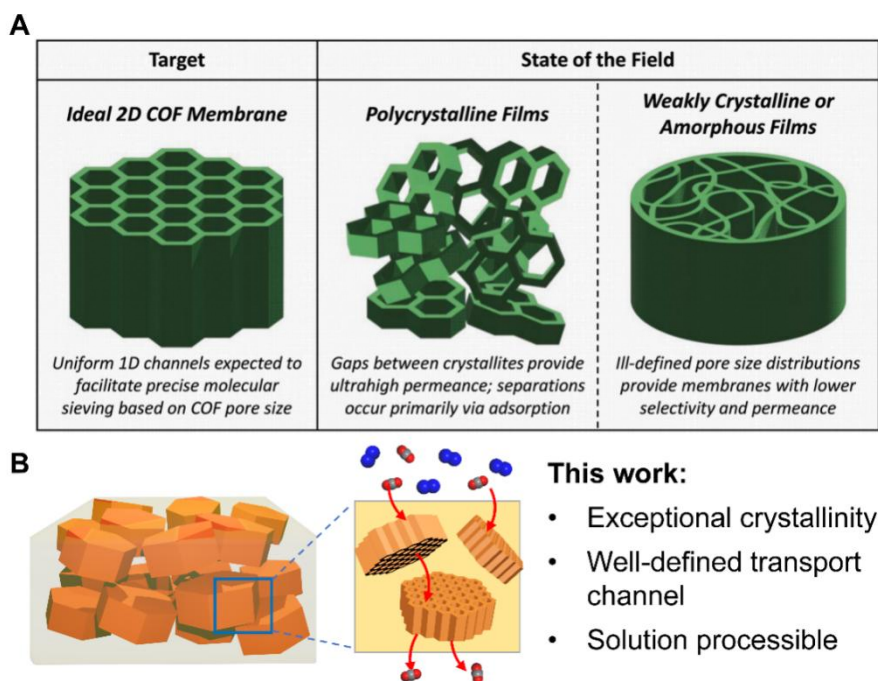
For the 2D COF, the crystal growth process involves both in-plane covalent reactions and out-of-plane nucleation. Surface nucleation exhibits significantly lower energy barriers than bulk nucleation, yet displays kinetic disparities with in-plane growth. Temperature modulation is the key to balancing the kinetics between in-plane growth and out-of-plane nucleation. Higher temperatures facilitate the lateral growth across the surface. Consequently, any nucleation event on the COF surface is quickly extended into a new, well-ordered layer, resulting in a regular hexagonal prismatic structure. In contrast, decreased temperature suppresses the in-plane growth, producing more spherical morphologies. Furthermore, appropriate increases in catalyst concentration and reaction temperature can further reduce synthesis time, albeit with a sacrifice in crystal quality.

Supplementary Note 2

The target COF membranes and the characteristics of our membrane.

Target COF membranes should possess uniformly sized, high-density, and highly tunable pores, making them well-suited for high-end separation processes unavailable to conventional polymer membranes. However, currently fabricated COF membranes are usually polycrystalline or weak crystalline films, as illustrated in Supplementary Fig. 59A. The insufficient crystallinity is reflected by the XRD patterns, which usually only show a single, broadened, and low-intensity weak peak, with no discernible peaks for higher-index crystal planes⁴⁻¹². As a result, the well-defined nanochannels intrinsic to COF remain underutilized, leading to suboptimal separation performance.

All-organic MMMs incorporating single-crystal COF address the above bottleneck issue in the field (Supplementary Fig. 59B). The high crystallinity of these COFs facilitates the formation of well-defined, high-density, and highly continuous transport channels. The inherent compatibility between the COF and the polymer matrix, combined with rationally designed interfacial interactions, ensures that the distinctive properties of the COF are faithfully translated into the membranes. As a result, the membranes not only exhibit a crystal-like structure (Fig. 2b in the manuscript) and facilitate rapid mass transport but also leverage the polymer's processability. This enables a simple solution-processible approach for fabricating membranes from the high-crystallinity COF, significantly enhancing their potential for practical application.



Supplementary Fig.59. (A) A comparison between target COF membranes and the existing ones, reported by Livingston, Dichtel *et al.*¹³; (B) Schematic illustration and characteristics of our membranes.

Supplementary Note 3

The origin of interfacial compatibility in single-crystal COF MMMs

The superior interfacial compatibility in single-crystal COF MMMs originates from molecular orbital homology and can be rationalized through the lens of the hard-soft acid-base (HSAB) theory. In this context, organic polymers and fillers are both categorized as “soft” phases, characterized by their polarizable nature, ensuring large orbital overlap. Their frontier molecular orbitals (FMOs), particularly the HOMO and LUMO, exhibit closely aligned energy levels and compatible symmetry. This alignment enables a large orbital overlap integral, facilitating extensive delocalization and coupling of their diffuse electron clouds. Although the individual interaction energy is weaker than that of a covalent, coordination, or hydrogen bond, the abundant, uniformly distributed weak interactions (e.g., van der Waals force and dipole-dipole interactions) collectively enhance the interfacial interaction energy, giving rise to macroscopic compatibility. This is a manifestation of the HSAB principle that “soft prefers soft”.

Benefiting from the above mechanism, low-surface-energy COF fillers used in this work can provide sufficient polymer/COF interfacial adhesion energy while delivering lower filler-filler interaction energy that resists self-aggregation (Fig. 3f). The abundance of weak interactions ensures excellent polymer-filler adhesion, while the low surface energy simultaneously weakens the filler-filler attraction, thereby suppressing filler aggregation and enabling uniform dispersion even at high packing density.

In contrast, typical organic-inorganic MMMs represent a typical “soft-hard” combination. The organic polymer (soft base) and the inorganic filler (hard acid or base) interact through sparse, localized, and strong Lewis acid-base interactions. More fundamentally, the large disparity in electron cloud polarizability leads to a pronounced mismatch in orbital energy levels and symmetry, resulting in a negligible orbital overlap integral. This electronic incompatibility prevents effective orbital hybridization and delocalization, yielding low interfacial interaction energy. To minimize the total free energy, the system reduces the unfavorable “soft-hard” contact area, inevitably leading to filler agglomeration and macroscopic phase separation.

Supplementary Note 4

Current efforts for the compatibility enhancement of MMMs with inorganic fillers

The poor compatibility between inorganic fillers and organic polymers leads to high interfacial energy. At the same time, the high mass density of inorganic fillers makes it difficult to maintain suspension in the casting solution. Due to these two reasons, the use of inorganic fillers often requires the design of strong interfacial interactions to achieve uniform filler distribution.

Some inorganic fillers inherently possess highly polar surface functional groups without the need for further modification, such as imidazole groups on ZIF-8¹⁴, and amino groups on UiO-66-NH₂¹⁵ and ZIF-8-NH₂¹⁶. In addition, several studies have explored post-synthetic modification strategies to enhance interactions with polymers by introducing adhesive layers onto the filler surface, including amino-ionic liquid¹⁷, PEI¹⁸, and polyphenol¹⁹. Interfacial crosslinking via covalent bonds has also proven effective in compatibility improvement^{20,21}.

These strategies usually lead to agglomeration and sedimentation when the filler packing density is high because of the simultaneous enhancement of filler-filler interaction among the “sticky” fillers. Moreover, excessively strong interfacial interactions may lead to deterioration of separation performance due to the chain rigidification or pore blockage.

Supplementary Note 5

The rationale of using single-crystal COFs as fillers

To date, several efforts have been made to develop COF-based composite membranes, yet these studies have been constrained by low filler packing density (<30 vol%) and marginal performance improvements (Supplementary Tables 7 and 9). The primary fundamental obstacle stems from the poor processability of COFs, which hinders the preparation of monodisperse crystals with controlled morphology and crystallinity. The highly crystalline structure is essential to prevent the formation of “dead zones” with low mass transfer capabilities, which is a common phenomenon in the reported COF fillers. These “dead zones” arise from the non-ideal structures (amorphous phase or lattice-mismatched crystal boundaries) that lead to discontinuous and ineffective pathways, thereby hindering the translation of the superior transport properties of COF fillers into membrane performance. As demonstrated by the morphology and separation performance of the COF-CH₃-P-based MMMs in our study, although the filler exhibits relatively strong XRD peaks indicating good crystallinity (Supplementary Fig. 49), the presence of non-ideal mass transfer pathways results in a much lower performance enhancement compared to single-crystal fillers. Moreover, low crystallinity is often accompanied by agglomerated, entangled morphology, hindering the even dispersion of the COFs. **In conclusion, achieving high-crystallinity COF fillers with minimized “dead zones” and well-controlled morphology is essential to fully leverage the structural and performance advantages of COF materials.**

Supplementary Note 6

Maxwell modeling calculations

To predict the gas separation performance of pure COF fillers, we applied the Maxwell model, which was originally developed for the estimation of dielectric properties of composite materials²². The COF crystals are uniformly dispersed and don't have a significant influence on the polymer phase due to the weak interfacial interaction, meeting the requirement for applying the Maxwell model. This model is given as Equation (1):

$$P_{MMM} = P_c \frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \quad (1)$$

where P_{MMM} refers to the gas permeability of the mixed matrix membrane; P_c and P_d refer to the gas permeability of the continuous polymer matrix phase and the dispersed filler phase, respectively; ϕ_d refers to the volume percentage of the dispersed filler phase in the membranes. The density of PIM-1 is measured as 1.20 g cm⁻³; the density of COF-CH₃ is calculated as 0.539 g cm⁻³. The volume percentage ϕ_d of fillers in MMMs is defined as Equation (2)

$$\phi_d = \frac{m_d/\rho_d}{m_d/\rho_d + m_c/\rho_c} \quad (2)$$

where m and ρ refer to the mass and density of the polymer and fillers, respectively, denoted by subscripts “c” and “d”. To ensure the validity of the prediction, we applied the calculation on a low-filling COF-CH₃/PIM-1 MMMs (5 wt%, 11.8 vol%). Detailed experimental and predicted results are listed in Supplementary Table 6. Notably, the COF-CH₃ filler shows a moderate CO₂/N₂ selectivity (20.2), which appears incompatible with its pore size (>1 nm). We propose that the fillers in this system consist of COF crystals coupled with thin polymer layers around the crystals, thus the calculated filler performance exhibits both high permeability and selectivity.

Supplementary Note 7

Techno-economic analysis of single-crystal COF MMMs-based carbon capture

In the case of the membrane separation process, a mathematical model of the membrane was established using Aspen Custom Modeler V12 software (ACM), which utilized an equation-oriented programming language. The separation performance of membranes was derived from our mixture gas permeation test results, which evaluated a 15% CO₂/85% N₂ mixture at ambient temperature. The Redlich–Kwong–Soave property method was selected from the Aspen properties database. The membrane model was divided into 100 units, configured for counter-flow to accurately simulate the process conditions. The equations are detailed below:

For each unit within the module, the area was calculated as follows:

$$A_u = \frac{A}{N_{unit}} \quad (3)$$

where A means total membrane area.

For each unit, the mass balance equation was calculated by:

$$F_R^{n-1} = F_R^n + F_P^n \quad (4)$$

where F is the flow rate, which is indicated in the subscript as P (permeate side) or R (retentate side), and the superscript represents the number of units, the same as below.

For each component in the feed stream, the mass balance equation was calculated by:

$$F_R^{n-1} Z_{R,i}^{n-1} = F_R^n Z_{R,i}^n + F_P^n Z_{P,i}^n \quad (5)$$

$$\sum_{i=1}^N Z_{R,i}^n = 1 \quad (6)$$

$$\sum_{i=1}^N Z_{P,i}^n = 1 \quad (7)$$

where Z is the mole fraction of component i.

The equation of mass permeation through each membrane unit (J) was calculated by:

$$J_i^n = F_R^{n-1} Z_{R,i}^{n-1} - F_R^n Z_{R,i}^n = A_u L_i^n (P_R^n Z_{R,i}^n - P_P^n Z_{P,i}^n) \quad (8)$$

An economic analysis of the process was conducted using the Aspen Process Economic Analyzer (APEA) with a little modification²³. The calculation included the labour, maintenance, utilities, and capital expenditure (CAPEX), which were estimated utilizing standardized values provided by the US system database in Aspen Plus. For the purification cost calculations, the annual plant costs can be estimated by a straight-line depreciation method as detailed in equation (9). These calculations considered a plant lifetime of 20 years. For the membrane cost, we estimate the synthesis cost based on the actual reagent prices from our chemical suppliers. As for a 2 μm thick membrane, the total raw material cost for the single-crystal COF MMMs is estimated to be \$26.69/m² (Supplementary Table 11). Considering the price of polymer substrate (\$82.92/m², Shandong Megavision Membrane Technology Co., Ltd), as well as the costs associated with labor, maintenance, and utilities, the total membrane cost was estimated to be less than \$150/m², assuming a 5-year lifespan as the base scenario. All associated replacement, disposal, and construction costs for the membrane were factored into the final membrane cost. The total annual plant cost was then apportioned based on the total CO₂ production to ascertain the carbon capture costs.

$$Annualcost_{Membrane} = labor + maintenance + utilities + \frac{Membrane}{5} \quad (9)$$

Supplementary Note 8

The scaling considerations of COF-CH₃ single crystals

The COF-CH₃ single crystals used in this work were synthesized via a mild solvothermal method that proceeds at a low temperature (60 °C or even room temperature) and does not require water-free or oxygen-free conditions, significantly reducing the complexity of scale-up. Besides, a yield of 81.5 wt% over 3 days is advantageous compared to many existing reports on single-crystal COF synthesis. Nevertheless, for carbon capture at the scale of multiple gigatons per year, the space-time yield remains a major hurdle.

Currently, the field of COF synthesis is advancing rapidly. Fast, high-yield, and even solvent-free methods for producing high-quality COFs are constantly being developed^{24,25}, with synthesis costs potentially reaching as low as \$50/kg, and ton-scale production already demonstrated. For single-crystal COFs specifically, yields and synthesis speeds are steadily improving^{26,27}, and the fastest syntheses have been shortened to within 5 mins. Although the solvothermal method remains necessary for obtaining the high-quality COF-CH₃ single crystals in this fundamental study, future scale-up can draw on these emerging strategies. Additionally, the very thin separation layer of a membrane requires only a very small amount of material. Therefore, further improvements in production efficiency hold great promise for meeting the demands of carbon capture membranes.

Supplementary Note 9

The comparison between CALF-20 and single-crystal COF MMMs

CALF-20, an efficient CO₂ adsorbent, was first reported in 2021 by Svante Technologies Inc. with collaborators²⁸. As one of the few MOFs that have reached commercial pilot scales, CALF-20 exhibits outstanding adsorption capacity, fast adsorption-desorption kinetics, and excellent stability, which can contribute to improved process productivity and potentially lower operating costs. In adsorption-based processes using CALF-20, the overall energy penalty consists mainly of the heat for sorbent regeneration. CALF-20 is considered a low-regeneration-energy material due to its modest heat of adsorption, which gives it a potential advantage over amine-based sorbents. Advanced rapid-cycle technologies can shorten the cycle time of CALF-20-based adsorption processes to as low as 64-107 seconds²⁹, enabling higher throughput and lower capital costs. According to the data from Svante's pilot-scale demonstration project^{30,31}, when processing flue gas with a CO₂ concentration of 19-20%, CALF-20 achieved a product purity of 94-95% and a CO₂ recovery of 85-90%, with an energy penalty of 2.5-3.9 GJ/tCO₂ and a capture cost of \$38-43/tCO₂.

In contrast, membrane separation operates continuously at steady state and therefore does not require adsorption-desorption cycles or sorbent regeneration. The primary driving force is the CO₂ partial-pressure difference, mainly provided by compression on the feed side and vacuum generation on the permeate side, which constitutes the major energy consumption. Based on the separation performance reported in this work, a two stage membrane carbon capture process simulation was carried out (Supplementary Fig. 57). In this process, we achieved a CO₂ recovery of 90.0% and a purity of 91.3%, with a relatively lower energy penalty (1.52 GJ/tCO₂) and a capture cost of \$38/tCO₂.

Undeniably, CALF-20, as one of the few MOF materials that have reached commercial pilot scales, holds significant advantages in large-scale production and system integration. Nevertheless, adsorption and membrane separation process different strengths and are increasingly viewed as

complementary rather than directly competing technologies. Adsorption technology is well-suited for scenarios involving high product purity requirements. In contrast, membrane separation is more suitable for continuous operation and low requirements for CO₂ purity. In fact, hybrid systems (e.g., membrane separation as a preconcentration unit followed by a solid sorbent for deep purification) are increasingly regarded as a promising pathway toward achieving low-energy, high-recovery carbon capture.

Supplementary Note 10

Design considerations for all-organic MMMs

Herein, we propose three design considerations for the development of high-performance all-organic MMMs for broad applications:

(i) Utilize highly crystalline and readily dispersible COF fillers. Highly crystalline COF fillers possess abundant, interconnected nanochannels that facilitate molecular transport, thereby significantly enhancing the permeability. The use of single-crystal fillers is highly advantageous as they provide well-defined structure-property relationships and unimpeded diffusion pathways. Equally critical is excellent filler dispersibility in casting solvents, which inhibits aggregation and sedimentation. This requires the synthesis of organic fillers with well-defined and tailored morphology.

(ii) Employ weak interactions to modulate interfacial compatibility. In high-filler-loading casting solutions, filler aggregation due to frequent filler collision can be suppressed through strategic surface functionalization with low-surface-energy groups (-CH₃, -H, -F). These groups reduce interparticle adhesion, minimize aggregation, and prevent sedimentation. The low-surface-energy fillers can also form a defect-free interface with the polymer phase because the chemical homology renders favorable compatibility. In contrast, the frequently used highly polar groups that promote filler-filler adhesion, such as -OH and -NH₂, can trigger serious aggregation and sedimentation, deteriorating the separation performance.

(iii) Select rigidity-matching polymers to suppress COF pore blockage. The large intrinsic pore channels of COF bring pore penetration when flexible polymers are used, leading to reduced permeability. Glassy polymers with high chain rigidity effectively restrict excessive polymer penetration into COF pores, thereby preserving high permeability.

4. Supplementary Table

Supplementary Table 1

Calculated interfacial interaction energy between COF crystals and polymer matrix.

Interface type		Interaction energy (ΔE)		
Part A	Part B	(kcal/mol)		
		Total	vdW	Columbic
COF-H	6FDA-DAM	-0.07423	-0.07135	-0.00288
COF-CH ₃		-0.08595	-0.08272	-0.00323
COF-F		-0.09621	-0.09211	-0.00409
COF-OH		-0.10610	-0.10137	-0.00473
COF-H	PIM-1	-0.06103	-0.05936	-0.00167
COF-CH ₃		-0.06885	-0.06819	-0.00066
COF-F		-0.07420	-0.07297	-0.00123
COF-OH		-0.08918	-0.08754	-0.00164
COF-H	COF-H	-0.03899	-0.03782	-0.00116
COF-CH ₃	COF-CH ₃	-0.03850	-0.03835	-0.00015
COF-F	COF-F	-0.04387	-0.04343	-0.00044
COF-OH	COF-OH	-0.11380	-0.11054	-0.00326

Supplementary Table 2

Solubility and diffusivity of CO₂ and N₂, and CO₂/N₂ solubility selectivity and diffusion selectivity in single-crystal COF MMMs at different temperatures.

Temperature (°C)		Uptake (cm ³ (STP) /cm ³)	Permeability (Barrer)	Solubility (10 ⁻³ cm ³ (STP) cm ⁻³ cmHg ⁻¹)	Diffusivity (10 ⁻⁷ cm ² s ⁻¹)	Solubility Selectivity	Diffusivity selectivity
COF-H/6FDA-DAM MMMs							
25	CO ₂	26.88	22675.7	353.66	64.12	10.23	1.24
	N ₂	2.63	1780.3	34.56	51.50		
50	CO ₂	14.99	19155.5	197.30	97.09	9.03	1.15
	N ₂	1.66	1845.2	21.85	84.44		
75	CO ₂	8.41	16339.9	110.69	147.62	7.98	1.10
	N ₂	1.05	1856.6	13.88	133.79		
100	CO ₂	4.76	13856.0	62.58	221.39	6.99	1.06
	N ₂	0.68	1866.5	8.95	208.45		
COF-CH ₃ /6FDA-DAM MMMs							
25	CO ₂	27.61	18511.0	363.35	50.94	11.27	1.40
	N ₂	2.45	1174.5	32.25	36.42		
50	CO ₂	14.25	16361.8	187.52	87.25	10.39	1.30
	N ₂	1.37	1210.8	18.05	67.08		
75	CO ₂	8.15	14575.4	107.21	135.95	9.02	1.18
	N ₂	0.90	1368.2	11.89	115.10		
100	CO ₂	4.72	13428.2	62.15	216.07	8.28	1.09
	N ₂	0.57	1483.3	7.51	197.59		
COF-F/6FDA-DAM MMMs							
25	CO ₂	31.25	13765.0	411.25	33.47	14.91	1.66
	N ₂	2.10	557.4	27.57	20.21		
50	CO ₂	16.09	12364.8	211.71	58.40	13.02	1.50
	N ₂	1.24	633.0	16.27	38.91		
75	CO ₂	8.47	10795.4	111.45	96.86	11.09	1.37
	N ₂	0.76	711.2	10.05	70.79		

100	CO ₂	4.69	8857.9	61.76	143.42	8.90	1.24
	N ₂	0.53	804.4	6.94	115.90		
6FDA-DAM							
25	CO ₂	28.40	912.9	373.70	2.44	12.94	1.56
	N ₂	2.19	45.1	28.87	1.56		
50	CO ₂	14.65	888.9	192.83	4.61	12.03	1.51
	N ₂	1.22	49.0	16.03	3.06		
75	CO ₂	8.49	786.9	111.72	7.04	10.51	1.41
	N ₂	0.81	53.1	10.63	4.99		
100	CO ₂	4.95	704.6	65.15	10.82	8.77	1.30
	N ₂	0.56	61.3	7.43	8.25		

Supplementary Table 3

The performance of COF-CH₃/6FDA-DAM MMMs for CO₂/N₂ separation after long-term storage (vacuum at room temperature). Data are presented as mean values $\pm$ SD. n=3 different membrane samples are measured independently for each data point.

Filler	Polymer	Packing density (vol%)	CO ₂ permeability (Barrer)	CO ₂ /N ₂ selectivity
Day-1				
COF-CH ₃	6FDA-DAM	60.9	22864.3 $\pm$ 1180.2	20.6 $\pm$ 1.3
COF-CH ₃	6FDA-DAM	70.0	28832.6 $\pm$ 622.2	16.8 $\pm$ 0.3
Day-180				
COF-CH ₃	6FDA-DAM	60.9	19263.4 $\pm$ 406.1	23.6 $\pm$ 0.4
COF-CH ₃	6FDA-DAM	70.0	25462.8 $\pm$ 363.9	20.8 $\pm$ 0.2

Supplementary Table 4

The composition of simulated and realistic flue gas reported in literature and in this work.

No.	Type	Flue gas composition			Ref.
		CO ₂	NO _x	SO _x	
1	Absorption	14%	120-200 ppm	93 ppm	32
2	Absorption	14%	90 ppm	250 ppm	33
3	Absorption	13-14.5%	< 100 ppm	< 5 ppm	34
4	Absorption	17.8%	180-250 mg/Nm ³	< 130 mg/Nm ³	35
5	Absorption	14%	80-90 ppm	170-250 ppm	36
6	Absorption	12%	< 65 ppm	< 10 ppm	37
7	Absorption	13-15%	60 ppm	5 ppm	38
8	Adsorption	8.6%	91.4 ppm	-	28
9	Adsorption	17%	72 ppm	-	28
10	Membrane	16%	2-3 ppm	< 1 ppm	39
11	Membrane	12% ($\pm 1\%$)	1.5-4 ppm	0.5-5 ppm	40
12	Membrane	10.5-12%	100-120 ppm	0-3 ppm	41
13	Membrane	14.5%	76-91 ppm	50-100 ppm	42
14	Membrane	15%	120 ppm	90 ppm	This work

Supplementary Table 5

The performance of MMMs based on different COF crystals and polymer matrices at optimized packing density for CO₂/N₂ separation.

No.	Filler	Polymer	Packing density (vol%)	CO ₂ permeability (Barrer)	CO ₂ /N ₂ selectivity
1	-		0	968.8 ± 6.2	25.9 ± 0.1
2	COF-H	6FDA-DAM	60.9	26601.0 ± 609.0	16.7 ± 0.5
3	COF-CH ₃		60.9	22864.3 ± 1180.2	20.6 ± 1.3
4	COF-F		60.9	16031.9 ± 148.6	27.2 ± 0.7
5	COF-OH		60.9	3897.6 ± 112.6	28.3 ± 0.2
6	-		0	8852.2 ± 234.6	24.5 ± 0.7
7	COF-H	PIM-1	59.7	87022.0 ± 1458.7	17.9 ± 1.2
8	COF-CH ₃		59.7	74797.9 ± 5583.4	20.8 ± 0.3
9	COF-F		59.7	44396.1 ± 1868.9	28.6 ± 0.3
10	COF-OH		59.7	25741.1 ± 763.9	24.1 ± 0.2
11	-	Pebax® MH 1657	0	89.1 ± 10.9	37.7 ± 2.5
12	COF-CH ₃		58.5	478.6 ± 22.8	32.3 ± 2.8
13	-	Matrimid® 5218	0	9.7 ± 0.3	41.1 ± 0.1
14	COF-CH ₃		54.9	216.3 ± 12.7	24.8 ± 0.9
15	TAPB-DMPDA		73.1	10155.4 ± 905.7	34.3 ± 0.7
16	COF-300	6FDA-DAM	60.4	26906.9 ± 1603.4	14.4 ± 0.9
17	LZU-306		66.4	16622.7 ± 384.3	22.5 ± 1.0

Supplementary Table 6

Experimental and predicted CO₂/N₂ separation performance (pure gas) of COF-CH₃/PIM-1 MMMs by the Maxwell model.

Membranes	Packing density (vol%)	CO ₂ permeability (Barrer)	N ₂ permeability (Barrer)	CO ₂ /N ₂ selectivity
COF-CH ₃ /PIM- 1 MMMs	11.8	9834.1	436.8	22.5
PIM-1	0	7450.8	329.0	22.6
COF-CH ₃ (predicted)	100	106916.3	5299.6	20.2

Supplementary Table 7

The performance of COF-filled MMMs from the literature for CO₂/N₂ separation.

No.	Polymer	COF	Loading (wt%)	CO ₂ permeability (Barrer)	CO ₂ /N ₂ selectivity	Ref.
1	Pebax 2533	COF-300	15	740.9	33.2	43
2	Pebax 2533	COF-300-Amide	15	697.3	51.7	43
3	PIM-1	TpPa-1	7	6336	20.1	44
4	PIM-1	TpPa-1	10	6440	17.7	44
5	Pebax 1657	COF-316	0.5	330	73.4	45
6	Pebax 1657	COF-316	1	240	57.14	45
7	PIM-1	TAPB-DMTP	3	8977.6	19.5	46
8	PIM-1	TAPB-DMTP	5	7579.1	17.8	46
9	PIM-1	TD-COF	3	8427.1	16.9	5
10	PIM-1	PDA@TD-COF	3	9750.6	26.4	5
11	PIM-1	TpTta-COF	6	9672	26.3	47
12	PIM-1	TpTta-COF	8	7039	20.0	47
13	PEO	TAPB-BDB	1.23	803.9	61.4	48
14	Pebax 1657	COF-5	0.4	493	49.3	49
15	6FDA-DAM	COF-300	7	1205	32.6	50
16	6FDA-DAM	PEI@COF-300	7	1154	48.7	50
17	Pebax 1657	COF-300	10	125	56.6	50
18	Pebax 1657	PEI@COF-300	10	126	84.2	50
19	Matrimid 5218	ACOF-1	16	17.7	34.7	51
20	6FDA-DAM	ACOF-1	24	1282.7	20.9	51
21	PIM-1	SNW-1	10	7552	20.7	52
22	PSF	SNW-1	12	22.4	40	53

Supplementary Table 8

The performance of pure COF membranes from the literature for CO₂/N₂ separation.

No.	COF	CO ₂ permeance (GPU)	Thickness (μm)	CO ₂ permeability (Barrer)	CO ₂ /N ₂ selectivity	Ref.
1	TpPa-1-CF ₃	-	-	6661.2	19.1	6
3	r-PATA	1060	0.92	975.2	30.6	54
4	r-PATA	2491.7	0.42	1046.51	28.7	54
5	TpBD-(COOH) ₂	1004	0.058	58.23	33.7	11
6	COF-316-COOH	400	0.083	33.2	30	7
7	COF-316-AO	500	0.073	36.5	45	7
8	TpPa-SO ₃ H@PEI	1371	0.008	10.97	33	9
9	NCOFN	1068	0.057	60.88	35	8
10	TAPB-BTCA	-	-	346	21.4	55
11	PPDA-BTCA	-	-	553	15.5	55

Supplementary Table 9

The comparison of packing density and CO₂ permeability between MMMs from the literature for CO₂/N₂ separation.

No.	Polymer	Filler	Loading (wt%)	Packing density (vol%)	CO ₂ permeability (Barrer)	Ref.
Zeolite						
1	Pebax 1074	SAPO-34	20	15.35	175	56
2	Matrimid 5218	ZSM-5	30	22.8	14.6	57
3	Matrimid 5218	ZSM-5	20	14.7	19.2	58
4	Matrimid 5218	Na-SSZ-39	55	50.6	8300	59
5	Pebax 1657	SAPO-34	50	43.6	338	60
MOF						
6	6FDA-DAM	HKUST-1	30	37.8	2500	61
7	6FDA-DAM	AlFFIVE-1-Ni	59.6	55.7	1200	62
8	Pebax 1657	CuBDC	2.5	2.1	123	63
9	PIM-1	UiO-66-NH ₂	20	19.1	12498	21
10	Pebax 1657	MIL-53(Al)	10	7.4	129	64
11	PIM-1	ZIF-8	50	56.5	8262	19
12	PIM-1	UiO-66-NH ₂	40	36.8	1727	65
13	6FDA-Durene	UiO-66-NH ₂	40	41.1	1610	66
14	Matrimid 5218	UiO-66-NH ₂	40	39.0	30	67
15	Pebax 2533	UiO-66-NH ₂	40	34.4	425	68
16	PEO	ZIF-8	-	51.8	2490	69
17	6FDA-DAM	MIL-53(Al) -NH ₂	20	13.5	737	70
18	Pebax 1657	ZIF-7	8	6.7	145	71
19	Pebax 1657	UiO-66-NH ₂	10	9.1	130	72
20	PMPS	ZIF-8	8.3	8.8	827	73
21	PIM-1	KAUST-7	30	22.2	5928	74
22	PUI- PEDEGA	ZIF-8	-	40	112	75
23	PIM-1	ZIF-HNPs	-	28	7128	76

24	6FDA-DAM	UiO-66-NH ₂	16	15.9	1912	77
COF						
25	6FDA-DAM	COF-300	-	26.2	5133	50
26	Pebax 1657	COF-300	-	23.3	359	50
27	Pebax 1657	COF-5	0.4	0.8	493	49
28	Pebax 1657	COF-316	0.5	1.07	330	45
29	PIM-1	TpPa-1	10	15.9	6440	44
30	Pebax 2533	COF-300	15	19.49	740.9	43
31	Pebax 1657	COF-300	7	10.53	1280	78
this work						
32	PIM-1	COF-CH ₃	39.8	59.7	74797.9	this
33	6FDA-DAM	COF-CH ₃	56.8	75.5	40001.2	work

Supplementary Table 10

The performance of MOF-based and zeolite-based membranes with high permeability (>1,000 Barrer) from the literature for CO₂/N₂ separation.

No.	Polymer	Filler	Loading (wt%)	CO ₂ permeability (Barrer)	CO ₂ /N ₂ selectivity	Ref.
Zeolite						
1	Matrimid 5218	Na-SSZ-39	50	8300	60	⁵⁹
2	Matrimid 5218	Na-CHA-10	60	7080.6	48.7	⁷⁹
3	ODPA-TMPDA	PS-MFI	30	2397	28.8	⁸⁰
4	ODPA-TMPDA	ETS-10	20	1225	36.6	⁸⁰
5	ODPA-TMPDA	SAPO-34	30	2615	31.7	⁸⁰
6	PTMSP	Zeolite A	20	8800	11	⁸¹
7	6FDA-DAM	Mg-MCM-41	8	1214	24.4	⁸²
		Pure ZSM-58	-	1367	28.62	⁸³
		Silicalite-1/SSZ-13	-	20710	22	⁸⁴
		Pure SSZ-13	-	7276	44	⁸⁵
		Pure SSZ-13	-	4438	12	⁸⁶
		Pure CHA zeolite	-	1746	16	⁸⁷
		Pure CHA zeolite	-	2692	31	⁸⁸
		SAPO-17	-	28402	14	⁸⁹
		AlPO-18	-	13979	45	⁹⁰
MOF						
8	PIM-1	Bi-HHTP	50	4021	42.1	⁹¹
9	PIM-1/PIM-1	F-UiO	25	9234	32.97	⁹²
10	PIM-1	ZIF-94-umIm	5	8900	20.2	⁹³
11	PIM-1	AFIL@ZIF-8	10	7864	29.66	¹⁷
12	PIM-1	HUiO	20	17712	12.4	⁹⁴
13	PIM-1	IL@HUiO	10	11758	21.5	⁹⁴
14	PIM-1	ZIF-8-umIm	10	16667	15.4	⁹⁵
15	PIM-1	Mof-808 (Ce)	2	6854	23.2	⁹⁶
16	PIM-1	CALF-20	5	8003	17.5	⁹⁷
17	PIM-1	UiO-66	15	7211.7	26.0	⁹⁸

18	PIM-1	polyMOF	20	9659	21.5	99
19	PIM-1	Ag ⁺ @UiO-66-NH ₂	30	15000	30	100
20	PIM-1	HZIF-8	16.7	8268	25.1	19
21	PIM-1	HZIF-8	50	11057	19.5	19
22	PIM-1	BCoC-ZIF	10	7326	32.5	101
23	PIM-1	NUS-8-NH ₂	10	14638	29	102
24	PIM-1	NUS-8-COOH	2	10400	31	103
25	PIM-1	ZIF-8	24.14	6338	24.4	104
26	PIM-1	UiO-66-FA	20	16591	23.1	105
27	PDMS	UiO-66-MS	40	2586	18	106
28	PIM-1	IL@MOF-808	5	9420	29	107
29	PIM-1	IL@ZIF-67	10	12848.5	13.7	108
30	PIM-1	MUF-15	15	23380	15.68	109
31	sPIM-1	UiO-66-CN	20	12063.3	53.5	110
32	6FDA-DAM	HKUST-1	30	2480	16.3	61
33	PIM-1	NUS-8	2	6725	26.8	103
34	PIM-1	UiO-66	20	12498	54.2	21
35	PTMSP	ZIF-L	5	25191.4	6.6	111
36	PIM-1	UiO-66-NH ₂	10	2641	28.3	65
37	6FDA-Durene	IL@HKUST-1	10	1106.6	27.1	112
		Pure CAU-1	-	9916	22.8	113
		Pure ZIF-62 glass	-	2486	34	114
		Pure UiO-66	-	2012	27.5	115
		Pure CAU-1	-	6570	14.8	116
		Pure ZIF-69	-	9270	6.3	117
		Pure ZIF-8	-	2299	10.8	118
this work						
54	6FDA-DAM	TpPyDA@COF-CH ₃	75.5 (vol%)	31328.9	29.4	
55	PIM-1	COF-H	59.7 (vol%)	87022.0	17.9	This
56	PIM-1	COF-CH ₃	59.7 (vol%)	74797.9	20.8	work
57	PIM-1	COF-F	59.7 (vol%)	44396.1	28.6	

Supplementary Table 11

Material cost of fabricating the single-crystal COF MMMs.

Raw materials	Cost (\$/m ²)
TTAB	7.58
TTFB	6.64
TP	0.83
PyDA	5.65
CF ₃ COOH	0.030
Aniline	0.0026
Benzaldehyde	0.0026
1,4-dioxane	0.59
1,2-dichlorobenzene	2.36
6FDA-DAM	3.00
Total for single-crystal COF	26.69
MMMs	
PAN support	82.92
Total	109.61

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