Supporting Information

PolyCOFs: A New Class of Freestanding Responsive Covalent Organic Framework Membranes with High Mechanical Performance

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General: All reagents were purchased from commercial sources and used without further treatments. PVDF membrane was prepared according to the literature. \(^1\) The solid phase \(^{13}\)C NMR spectra were obtained on a Varian 300 MHz Solid State Infinityplus 300 NMR spectrometer. \(^1\)H NMR and \(^{13}\)C NMR spectra was recorded on Bruker AV42 instruments at 400 MHz. Chemical shifts were reported in parts per million (ppm) down field from internal tetramethylsilane. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-K\(\alpha\) radiation by depositing powder on glass substrate, \(2\theta\) from 2° to 40° with 0.02° increment. The surface areas of tested materials were determined using a Micromeritics ASAP-2046. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the density functional theory (DFT) pore model for pillared clay with cylindrical pore geometry. Fourier transform infrared spectra (FT-IR) spectra were recorded on a Nicolet iS 50 ATR-FTIR instrument. Ultraviolet-visible absorption spectra of solution samples are collected using an Agilent Cary 100 UV/Vis spectrophotometer with background correction. Gel permeation chromatography (GPC) test was performed on Hitachi L-2490Hitachi. The stress and strain curves were measured using a Shimadzu AGS-X universal mechanical drawing machine. Scanning electron microscopy (SEM) images were taken with Hitachi JSM-7500F scanning electron microscopy. Transmission electron microscopy images were characterized on a Tecnai G2 F20 electron microscope. Atomic Force Microscopy (AFM) images were collected using Bruker Dimension Icon. Membranes were dried using a Tousimis Samdri-PVT-3D supercritical carbon dioxide dryer. The videos and photographs of the responsive behaviors of the poly\(_{26}\)COF-42 membrane were taken using an Honor 7 (mobile phone). If not specified, all tested polyCOF samples were prepared by combining 0.025 mmol TB with 0.0375 mmol (DTH+DTH-400). The membranes were washed with CH\(_3\)OH in a Soxhlet extractor for 24 h, and then dried by a supercritical carbon dioxide dryer. The percentage of polymers in polyCOFs were determined by tested the ratio of the unreacted DTH and DTH-400 in the reaction solution via \(^1\)H NMR spectra.

1. Experiment section

1.1 Synthesis of 2,5-diethoxy-terephthalohydrazide (DTH)

2,5-diethoxy-terephthalohydrazide (DTH) was prepared according to the literature.\(^2\) Diethyl
2,5-diethoxyterephthalate was dissolved in 90.0 mL of ethanol and 12.0 mL of hydrazine hydrate. The mixture was stirred and heated to 85 °C for 40 h, and then cooled to room temperature. The precipitate was produced, which were isolated by filtration and washed with cool water and ethanol. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.22 (s, 2H), 7.85 (s, 2H), 4.26 (q, $J = 7.0$ Hz, 4H), 4.19 (d, $J = 4.4$ Hz, 4H), 1.52 (t, $J = 7.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.37, 150.71, 123.11, 115.82, 65.50, 14.86.

1.2 Synthesis of DTH-400

![Scheme S1. Synthesis of DTH-400.](image)

**Synthesis of 3,6,9,12,15,18,21-heptaoxatricosane-1,23-diy l bis(4-methylbenzenesulfonate) (I).** PEG-400 (8.0 g, 20 mmol) and p-toluene sulfonyl chloride (9.8 g, 50 mmol) were suspended in 50.0 mL of THF. KOH (80 mmol) was dissolved in 10.0 mL of water and then slowly dropwise added to the PEG-400 mixture. The reaction was stirred for 24 h under room temperature. THF was removed by evaporation under vacuum, and the aqueous phase was extracted with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate, and concentrated under reduced pressure, which was purified by flash chromatographic column (petroleum ether/ethyl acetate:1/1) to afford I. $^1$H NMR (400 MHz, DMSO): $\delta$ 7.79 (d, $J = 7.9$ Hz, 4H), 7.48 (d, $J = 7.6$ Hz, 4H), 4.11 (s, 4H), 3.57 (s, 4H), 3.53-3.41 (m, 24H), 2.42 (s, 6H). $^{13}$C NMR (101 MHz, DMSO): $\delta$ 145.36, 132.84, 130.60, 128.10, 70.45, 70.23, 70.16, 70.11, 68.34, 21.55.
**Synthesis of DTH-400-ester.** Diethyl 2,5-dihydroxyterephthalate (1.02 g, 4 mmol), K2CO3 (2.25 g, 16 mmol) and compound (I) (2.9 g, 4 mmol) were charged into a two-neck round bottom flask. Subsequently, 32.0 mL of DMF was added under N2 atmosphere. The reaction mixture was heated at 80 °C for 24 h. After purified via a dialysis method (Molecular weight cut-off < 2000 g/mol) for a week, polymer DTH-400-ester was obtained after drying by a rotavap. 1H NMR (400 MHz, DMSO) δ 7.33 (s, 2H), 4.27 (s, 4H), 4.11 (s, 4H), 3.75 – 3.36 (m, 38H), 1.30 (s, 6H). 13C NMR (101 MHz, DMSO): δ 165.76, 151.10, 125.45, 116.56, 72.80, 70.49, 70.21, 69.90, 69.44, 61.45, 60.65, 14.45.

**Synthesis of DTH-400.** The product of DHT-400-ester was dissolved in 90.0 mL of ethanol and 12.0 mL of hydrazine hydrate. The mixture was stirred and heated to 85 °C for 40 h, and then cooled to room temperature. Ethanol was removed by evaporation under vacuum, and then the residue liquid was purified via a dialysis method (Molecular weight cut-off < 2000 g/mol) for a week. Polymer DTH-400 (brown viscous liquid) was obtained after drying by a rotavap. 1H NMR (400 MHz, DMSO) δ 9.38 (s, 2H), 7.54 (s, 2H), 4.65 (s, 4H), 4.23 (s, 4H), 3.95 – 3.23 (m, 38H). 13C NMR (101 MHz, DMSO): δ 163.55, 150.57, 125.25, 116.36, 72.80, 70.30, 70.21, 69.42, 68.94, 60.65, 56.50, 19.02.

**1.3 Synthesis of DTH-600**

![Scheme S2. Synthesis of DTH-600.](image)

**Synthesis of 3,6,9,12,15,18,21,24,27,30,33,36-dodecaoxaoctatriacontane-1,38-diylbis(4-methylbenzenesulfonate) (2).** PEG-600 (12.0 g, 20 mmol) and p-toluene sulfonyl chloride (9.8 g, 50 mmol) were suspended in 50.0 mL of THF. KOH (80 mmol) was dissolved in 10.0 mL
of water and then slowly dropwise added to the mixture. The reaction was stirred for 24 h under room temperature. THF was removed by evaporation under vacuum, and the aqueous phase was extracted with methylene chloride. The combined organic layer was dried over with anhydrous magnesium sulfate, and concentrated under reduced pressure, which was purified by flash chromatographic column (petroleum ether/ethyl acetate:1/1) to afford 2. $^1$H NMR (400 MHz, DMSO): $\delta$ 7.79 (d, $J = 7.6$ Hz, 4H), 7.49 (d, $J = 7.7$ Hz, 4H), 4.12 (s, 4H), 3.61 – 3.38 (m, 48H), 2.43 (s, 6H). $^{13}$C NMR (101 MHz, DMSO): $\delta$ 145.36, 132.84, 130.60, 128.10, 70.45, 70.23, 70.16, 70.11, 68.34, 21.55.

**Synthesis of DTH-600-ester.** Diethyl 2,5-dihydroxyterephthalate (1.02 g, 4 mmol), K$_2$CO$_3$ (2.25 g, 16 mmol) and 2 (3.5 g, 4 mmol) was charged into a 2-neck round bottom flask. Subsequently, 32.0 mL of DMF was added under N$_2$ atmosphere. The reaction mixture was heated at 80 ℃ for 24 h. After purified via a dialysis method (Molecular weight cut-off < 2000 g/mol) for a week, polymer DTH-600-ester was obtained after drying by a rotavap. $^1$H NMR (400 MHz, DMSO) $\delta$ 7.33 (s, 2H), 4.27 (q, $J = 7.0$ Hz, 4H), 4.11 (s, 4H), 3.71 (s, 4H), 3.51 (s, 50H), 1.29 (t, $J = 7.0$ Hz, 6H). $^{13}$C NMR (101 MHz, DMSO): $\delta$ 165.78, 151.10, 125.46, 116.55, 72.75, 70.49, 70.20, 69.92, 69.43, 61.48, 60.64, 14.43.

**Synthesis of DTH-600.** The product of DTH-600-ester was dissolved in 90.0 mL of ethanol and 12.0 mL of hydrazine hydrate. The mixture was stirred and heated to 85 ℃ for 40 h, and then cooled to room temperature. Ethanol was removed by evaporation under vacuum, and then the residue liquid was purified via a dialysis method (Molecular weight cut-off < 2000 g/mol) for a week. Polymer DTH-600 (brown viscous liquid) was obtained after drying by a rotavap.$^1$H NMR (400 MHz, DMSO): $\delta$ 9.39 (s, 2H), 7.55 (s, 2H), 4.67 (s, 4H), 4.24 (s, 3H), 3.79 (s, 4H), 3.55 (d, $J = 49.4$ Hz, 50H). $^{13}$C NMR (101 MHz, DMSO): $\delta$ 163.54, 150.58, 125.28, 116.38, 72.80, 70.31, 70.22, 69.43, 68.94, 60.64, 14.43.

**1.4 Synthesis of PIM-1 membrane.**

To form a membrane, PIM-1 (50.0 mg) was dissolved in CHCl$_3$ (3 mL). The polymer solution was poured into a flat-bottomed glass petri dish (6 cm) and the solvent allowed to evaporate in air for 12 h, giving a yellow membrane of thickness 22 μm.

**1.5 General procedure for syntheses of polyxCOF-42 membranes.**
The synthesis of the poly_COF-42 membranes were provided in Experimental Section. Notably, all reactions possessed >80% yields, which are comparable to the reported yield of COF-42 (78%) under solvothermal conditions at 120 °C for 72 h. In addition, we also tried to make mixed matrix membrane with COF-42 powder and DTH-400 (brown viscous liquid). We can’t obtain freestanding membrane for that DTH-400 was brown viscous liquid and fail to form membrane. This result further indicated that polyCOF membranes were not formed by mixed matrix membrane approach, but with covalently bonding.

1.6 Control of membrane thickness.

The thickness of the polyCOF membranes was tuned by just varying the precursor concentrations. Glass beakers of 25 mL were used as reactors, and the content of precursor was varied under identical conditions. DTH (0.00025 mmol) and DTH-400 (0.000125 mmol) was dissolved in the mixture solvent of 1.0 mL H2O and 1.0 mL dioxane as a bottom layer in the beaker. TB (0.00025 mmol) and 525 μL CH3COOH were dissolved in 3.0 mL mesitylene as an upper layer. The reaction was kept at room temperature without disturbance for 48 h. A thin film with thickness of ~40 nm was formed on the interface. FT-IR spectra of the film showed the presence of the -C=N- bonds, which can match well with the corresponding values of crystalline poly26/COF-42. In order to obtain thinner films, we decreased the concentration of precursor to TB (0.0001 mmol), DTH (0.0001 mmol) and DTH-400 (0.00005 mmol). We have successfully fabricated a film as thin as 4.5 ± 0.3 nm. The atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of this thin film were exhibited in Fig. 4e and S13. Unfortunately, the products are too few to further characterization tests.

1.7 Testing solvent permeation of membranes.

Solvent permeability of the membranes was evaluated via passing 20.0 mL solvent through the membranes (inner diameter: 12.0 mm) under 1 bar pressure. Four consecutive readings were collected and the corresponding fluxes were calculated by $P=V/(A\cdot t\cdot p)$ [unit: liters per square meter hour bar (L m⁻² h⁻¹ bar⁻¹)], where V is the volume of permeate (unit: L), A is the effective membranes filtration area (unit: m²) and t is the filtration time (unit: h).

1.8 Rejection analysis of dyes using membranes. Rejection analysis of poly26/COF-42 membrane was measured by nanofiltration process using a home-made cross-flow filtration
device (filter housing 12.0 mm). The membrane was equipped into filter housing. Subsequently, 10 μM aqueous solutions of organic dyes were driven through membrane. The permeate was collected at 0.5 bar upstream pressure. The permeance ($P$, L m$^{-2}$ h$^{-1}$ bar$^{-1}$) was determined by normalizing the volume of permeate collected during the $t$ time. The concentration of dyes in the feed ($C_i$) and permeate ($C_p$) was determined by a UV/Vis spectroscopy. The rejection (R, %) of the dyes was calculated based on $R=(1-C_p/C_i)*100\%$.

1.9 Procedure for reusing polyCOF membranes for filtration.

PolyCOF membrane can be easily regenerated after filtration experiment. In order to remove adsorbed dye, the filtration device was immersed in methanol. The dye molecules can be easily removed from the filtration device. In this process, we need to replace the methanol was changed for three times. Subsequently, the filtration device was washed with water (5.0 mL). The filtration device can be directly used as separation in the next runs. (Figure S20-23)

2.0 Solvent vapor stimulus actuations.

Organic solvents were placed in a glass breaker about 20 °C. Then the membrane (2mm×13mm×11μm) was placed above the liquid phase of the solvent and the response was recorded. The membrane was triggered to fast bending motion, and then pulled back into air to accomplish the shape recovery. The response process was recorded using an Honor 7 for further analysis. The curvature (mm$^{-1}$) was calculated by equation below.$^9$

\[ r = \frac{180L}{\theta \pi}; \text{Curvature } = \frac{1}{r}. \]

$L$ is the length of the actuator (unit : mm); $\theta$ the central angle and $r$ is radius of the bended arch.
Figure S1. Representative structure of COF-42 and ideal sizes of PEG-400 and PEG-600 with straight chains.

| Name         | $M_n$ | $M_w$ | PDI |
|--------------|-------|-------|-----|
| DTH-400-ester| 8343  | 12578 | 1.51|

Figure S2. GPC traces of DTH-400-ester obtained using a refractive index (RI) detector. Peaks centered around 32 min are ascribed to the eluent. DTH-400 was not selected to test GPC because the GPC column can bond with the -NH$_2$ groups in DTH-400 which will damage the GPC column.
Figure S3. The photographs of COF-42 and various poly$_x$COF-42 membranes with different polymer contents ($x = 1/6, 2/6, 3/6, 4/6, 5/6, 1$). COF-42 can form continuous membrane in solution. However, COF-42 membrane became fracture after drying. All poly$_x$COF-42 membranes can form continuous membranes in solution or after drying in air.
Figure S4. N$_2$ adsorption isotherms (a) and PXRD pattern (b) of poly$_{26}$COF-42 membrane after mechanical treatments.

Figure S5. Cartoon representation of the possible location of PEG chains in COF channels. Beside of the ideal intralayer linking modes, it should be noted that the cross-linking of linear polymer may widely exist among interlayers.
Figure S6. PXRD patterns of polyPEG-400.

Figure S7. FT-IR spectra of poly₂₆COF-42 membrane and its reactants. Representative peaks for the -C=O (1672 cm⁻¹) and the stretching modes at 1617 cm⁻¹ and 1220 cm⁻¹ were associated with the formation of the -C=N- bonds. These band assignments were confirmed by the observation of similar peaks in the FT-IR spectrum of COF-42. Notably, the peak at 2867 cm⁻¹ in the poly₂₆COF-42 spectrum attributed to polymer building block (DTH-400) indicated the existence of polymer building blocks in poly₂₆COF-42.
Figure S8. FT-IR spectra of COF-42 and polyₓCOF-42 with different polymer contents (x = 1/6, 2/6, 3/6, 4/6, 5/6, 1). It is notable that the peaks of ethyl groups from PEG groups gradually enhanced with increasing content (x) of DTH-400, indicating the existence of polymer building blocks in polyₓCOF-42.

Figure S9. Solid-phase ¹³C NMR spectra of COF-42, poly₂₆COF-42, poly₄₆COF-42 and polyPEG-400. The characteristic peak at 150 ppm in all test materials can be attributed to the formation of -C=N- bonds. We observed that with increasing contents (x) of DTH-400, the peaks of ethyl groups from DTH at 13 and 65 ppm gradually disappeared and a new peak (71 ppm) ascribed to the carbons in PEG groups appeared, indicating the existence of polymer building blocks in polyₓCOF-42.
Figure S10. PXRD patterns of poly$_{26}$COF-42 treated with various solvents (THF, boiling H$_2$O, CH$_3$COCH$_3$, CH$_3$OH, CH$_2$Cl$_2$, DMF, DMSO), acid (6M HCl) and base (1M NaOH) for 5 days.
**Figure S11.** SEM images for pristine COF-42 and poly₅₉COF-42 membranes. (Left) Top view SEM images of the freestanding COF-42 and poly₅₉COF-42 membranes with different amounts of polymers \((x = 1/6, 2/6, 3/6, 4/6, 5/6, 1)\) (the upper layer of polyCOF membranes close to mesitylene solution); (Right) Cross-section SEM images of corresponding membranes. poly₅₉COF-42 membranes were prepared via reaction of 0.025 mmol TB with 0.0375 mmol DTH + DTH-400.
**Figure S12.** TEM images for various membranes. (a) The pristine COF-42 membrane; (b) poly_{2\%}COF-42 membrane; (c) poly_{4\%}COF-42 membrane; (d) polyPEG-400 membrane; (e) HR-TEM image of poly_{2\%}COF-42 membrane. poly_{x\%}COF-42 membranes were prepared via reaction of 0.025 mmol TB with 0.0375 mmol DTH + DTH-400. The tested samples were prepared via sonication treatment to obtain uniformly dispersed particles.

**Figure S13.** TEM image of poly_{2\%}COF-42 thin film. The thin film was fabricated with a reduced amount of TB (0.0001 mmol), DTH (0.0001 mmol) and DTH-400 (0.00005 mmol). The obtained film was directly transferred onto microsyn.
Figure S14. Pore size distribution of COF-42 (a), poly\textsubscript{1/6}COF-42 (b), poly\textsubscript{2/6}COF-42 (c) and poly\textsubscript{3/6}COF-42 (d) calculated from the N\textsubscript{2} sorption data using the DFT method.

Table S1. Water flux water and Coomassie brilliant blue R-250 dye rejection in water against different nanofiltration membrane.

| Membrane Materials | Water flux value L m\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-1} | % Rejection |
|--------------------|---------------------------------|-------------|
| COF-42             | 1125.8                          | 65%         |
| poly\textsubscript{1/6}COF-42 | 168.2                            | 98%         |
| poly\textsubscript{3/6}COF-42 | 137.6                            | 99%         |
| poly\textsubscript{3/6}COF-42 | 25.5                             | 97%         |
| poly\textsubscript{4/6}COF-42 | 45.9                             | 93%         |
| poly\textsubscript{5/6}COF-42 | 31.8                             | 98%         |
| polyPEG-400        | 40.2                            | 93%         |
| poly\textsubscript{2/8}COF-42* | 127.4                           | 95%         |
Table S2. Pure solvent permeation through poly26COF-42 (11μm thickness) membranes.

| Name                    | Solvent Permeance (L m⁻² h⁻¹ bar⁻¹) |
|-------------------------|-------------------------------------|
| Water                   | 137.6 ± 10.4                        |
| Methanol                | 229.3 ± 20.1                        |
| Ethanol                 | 122.3 ± 15.4                        |
| Acetone                 | 428.1 ± 40.2                        |
| Acetonitrile            | 275.2 ± 20.8                        |
| Tetrahydrofuran         | 168.2 ± 8.2                         |
| Dichloromethane         | 152.9 ± 15.1                        |

Table S3. Current State of Art: Water flux value against different NF membrane.

| Membrane type          | Value (L m⁻² h⁻¹ bar⁻¹) | References   |
|------------------------|-------------------------|--------------|
| M-TpTD                 | 118                     | Ref. S3      |
| M-TpBD                 | 92                      | Ref. S3      |
| PBI                    | 4                       | Ref. S4      |
| PMMA                   | 45                      | Ref. S5      |
| Graphene               | 51                      | Ref. S6      |
| DBX cross-linked       | 12                      | Ref. S7      |
| Tp-Bpy thin film       | 211.5                   | Ref. S8      |
| Tp-Azo thin film       | 45.9                    | Ref. S8      |
| **Poly26COF-42**       | **137**                 | **This work** |
Figure S15. UV-Vis spectra of Coomassie brilliant blue R-250 aqueous solution Feed and Permeate by poly$_{x}$COF-42 membrane. (a) COF-42, (b) poly$_{1/6}$COF-42, (c) poly$_{2/6}$COF-42, (d) poly$_{3/6}$COF-42, (e) poly$_{4/6}$COF-42, (f) poly$_{5/6}$COF-42, (g) polyPEG-400 and (h) poly$_{2/6}$COF-42*

Figure S16. Coomassie brilliant blue R-250 aqueous solution feed and permeate by COF-42 membrane. UV-Vis spectra of Coomassie brilliant blue R-250 aqueous solution feed and permeate.
Figure S17. Separation of Coomassie brilliant Blue R-250 by filtration with a poly26COF-42 membrane. UV-Vis spectra of Coomassie brilliant blue R-250 aqueous solution feed and permeate.

Figure S18. Separation of Coomassie brilliant Blue R-250 and methyl orange dye solution by filtration with a poly26COF-42 membrane.
**Figure S19.** Separation of Coomassie brilliant Blue R-250 and methyl orange dye solution by filtration with a COF-42 membrane.

**Figure S20.** Recyclability of poly26COF-42 membrane for rejection Coomassie brilliant blue R-250 for 5 cycles.
Figure S21. PXRD pattern after five recycle test of poly2/6COF-42 membrane. The poly2/6COF-42 membrane would adsorb disordered dye molecules in the process of rejection testing, which could disturb the π−π stacking interactions among the layers to result to the decrease of crystallinity.

Figure S22. FT-IR spectra after five recycling tests of poly2/6COF-42 membrane.

Figure S23. N₂ sorption isotherm and BET plot of recycled poly2/6COF-42 membrane.
Figure S24. GPC traces of DTH-600-ester obtained using a refractive index (RI) detector. Peaks centered around 32 min are ascribed to the eluent. DTH-600 was not selected to test GPC because the GPC column can bond with the -NH₂ groups in DTH-600 which will damage the GPC column.

| Name       | $M_a$ | $M_w$ | PDI |
|------------|-------|-------|-----|
| DTH-600-ester | 10904 | 17794 | 1.63 |

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Figure S25. The photographs of COF-42, poly_{2/6}COF-42*, poly_{4/6}COF-42* and polyPEG-600 membranes.

Figure S26. PXRD patterns of poly_{x}COF-42* membranes with different polymer contents (x = 0, 2/6, 4/6, 1). Red (COF-42), Black (poly_{2/6}COF-42*), Blue (poly_{4/6}COF-42*), Green (polyPEG-600).
Figure S27. Solid-phase $^{13}$C NMR spectra of COF-42, poly$_{2/6}$COF-42*, poly$_{4/6}$COF-42* and polyPEG-600. The characteristic peak at 150 ppm in all test materials can be attributed to the formation of -C=N- bonds. We observed that with increasing contents (x) of DTH-600, the peaks of ethyl groups from DTH at 13 and 65 ppm gradually disappeared and a new peak (71 ppm) ascribed to the carbons in PEG groups appeared, indicating the existence of polymer building blocks in poly$_x$COF-42.

Figure S28. FT-IR spectra of poly$_{2/6}$COF-42* membrane and its reactants. The poly$_{2/6}$COF-42* membranes showed characteristic stretching at 1617 cm$^{-1}$ and 1220 cm$^{-1}$ associated with the formation of the -C=N- bonds which agreed well with pure COF-42.
Figure S29. FT-IR spectra of COF-42, poly$_{2/6}$COF-42*, poly$_{4/6}$COF-42* and polyPEG-600 membranes.

Figure S30. N$_2$ adsorption isotherms for COF-42, poly$_{2/6}$COF-42*, poly$_{4/6}$COF-42* and polyPEG-600 membranes.
**Figure S31.** Pore size distribution of poly\(_{2/6}\)COF-42* membranes.

**Figure S32.** (a-d) Top view SEM images and (e-h) cross-section of the COF-42, poly\(_{2/6}\)COF-42*, poly\(_{4/6}\)COF-42* and polyPEG-600 membranes (the upper layer of polyCOF membranes close to mesitylene solution). Both of the top and cross-section views of SEM images demonstrated the dense and cohesive packing nature of polyPEG-600 membrane. poly\(_{x}\)COF-42* membranes were prepared by combining 0.025 mmol TB with 0.0375 mmol DTH + DTH-600.
Table S4. Comparison of the mechanical properties of polyCOF-42 vs. reported COFs membranes.

| Sample               | Ultimate Stress (MPa) | Reference                                      |
|----------------------|-----------------------|------------------------------------------------|
| COF-42               | 0.27                  | This work                                      |
| poly_{1/6}COF-42     | 7                     | Angew. Chem. Int. Ed. 2018, 57, 10894–10898    |
| poly_{2/6}COF-42     | 32                    |                                               |
| poly_{3/6}COF-42     | 42                    |                                               |
| poly_{4/6}COF-42     | 33                    |                                               |
| poly_{5/6}COF-42     | 24                    |                                               |
| polyPEG-400          | 19                    |                                               |
| PTSA@TpAzoCOFM       | 17                    |                                               |
| Tp-Bpy               | No detectable         |                                               |
| DaTp                 | 12                    | ACS Appl. Mater. Interfaces 2018, 10, 28139–28146 |
| Dq_{1}Da_{1}Tp       | 7                     |                                               |
| Dq_{1}Da_{2}Tp       | 6                     |                                               |
| DqTp                 | 2                     |                                               |
| TAPB-PDA COF         | No detectable         |                                               |
Figure S33. Stress-strain curves for poly$_{3/6}$COF-42 vs. PVDF and PIM-1 membranes.

|                      | poly$_{3/6}$COF-42 | PVDF | PIM-1 |
|----------------------|--------------------|------|-------|
| Young's modulus (MPa)| 914                | 1024 | 930   |
| Ultimate Stress (MPa)| 42.1               | 38.6 | 25.2  |

Figure S34. Vapor-responsive behaviors of COF-42 and poly$_{x}$COF-42 ($x = 1/6, 2/6, 3/6, 4/6, 5/6, 1$) membrane placed in ethanol vapor (5.8 kPa, 20°C). Ethanol was placed in the bottom of the baker.
| Solvent               | Vapor pressure (kPa) | Response Time (s) |
|-----------------------|----------------------|-------------------|
| dichloromethane       | 47.4                 | 0.5               |
| acetone               | 24.7                 | 0.8               |
| tetrahydrofuran       | 19.3                 | 1.6               |
| methanol              | 12.8                 | 3.1               |
| ethanol               | 5.8                  | 4.0               |
| N,N-dimethylformamide | 0.3                  | 20                |

**Figure S35.** Curvature of poly26COF-42 membrane (2 mm × 13 mm × 11 μm) actuator in vapors of different solvents (20 °C).

**Figure S36.** (a) Top view SEM images and (b) cross-section of the PEG-20000 membrane.
Figure S37. Comparison of the vapor-responsive behaviors of poly$_{20}$COF-42 and PEG-20000 membrane (2 mm × 13 mm × 11μm) placed in ethanol vapor (5.8 kPa, 20 °C) for 4 s.
Figure S38. BET plot from N$_2$ adsorption data at 77 K. (a) COF-42, (b) poly$_{1/6}$COF-42, (c) poly$_{2/6}$COF-42, (d) poly$_{3/6}$COF-42, (e) poly$_{4/6}$COF-42, (f) poly$_{5/6}$COF-42.
**Figure S39.** BET plot from N\textsubscript{2} adsorption data at 77 K for poly\textsubscript{2\&6}COF-42\textsuperscript{*}.

**Figure S40.** Control experiment of reaction of linear DTH-400 polymer with terephthalaldehyde under identical conditions of poly\textsubscript{3}COF membranes. First, DTH-400 (0.0375 mmol, 22.5mg) was dissolved in the mixture solvent of 1.0 mL H\textsubscript{2}O and 1.0 mL dioxane as a bottom layer in the beaker. Terephthalaldehyde (0.05 mmol, 5.0 mg) and 525 \textmu L CH\textsubscript{3}COOH were dissolved in 3.0 mL mesitylene. This mixture was added into the beaker on top of the hydrazine layer. The reaction was kept at room temperature without disturbance for 48 h. Finally, gel was obtained instead of membrane.
**Figure S41.** FT-IR spectra of formed gel in Figure S40 and its reactants. Characteristic stretching at 1617 cm\(^{-1}\) and 1220 cm\(^{-1}\) associated with the formation of the -C=N- bonds were observed, indicated the condensation of the DTH-400 and terephthalaldehyde.

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