Supplementary Materials

Pore Engineering of Ultrathin Covalent Organic Framework Membranes for Organic Solvent Nanofiltration and Molecular Sieving

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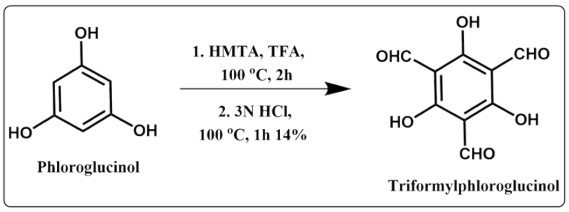
1. Materials

Phloroglucinol, hexamethylenetetramine (HMTA), trifluoroacetic acid (TFA), fluorene, *n*-butyl lithium (n-BuLi) (1.6 M, in n-hexane), 1-bromopropanre, 1-bromononane, tin (II) chloride dehydrate, toluene, hydrochloric acid (HCl), nitric acid (HNO_3), ammonium chloride, sodium bicarbonate, anhydrous sodium sulfate, tetrahydrofuran (THF), n-hexane, dichloromethane (DCM), and ethyl acetate (EtOAc), are all purchased from Sigma-Aldrich and used as received. The porous AAO support (anodisc^{TM}, diameter 25 mm, pore size 0.02 μm) was obtained from GE Healthcare Life Sciences, UK.

2. Precursor synthesis

2.1 Synthesis of 1,3,5-triformylphloroglucinol (TFP)



Scheme S1. The synthesis procedure of TFP

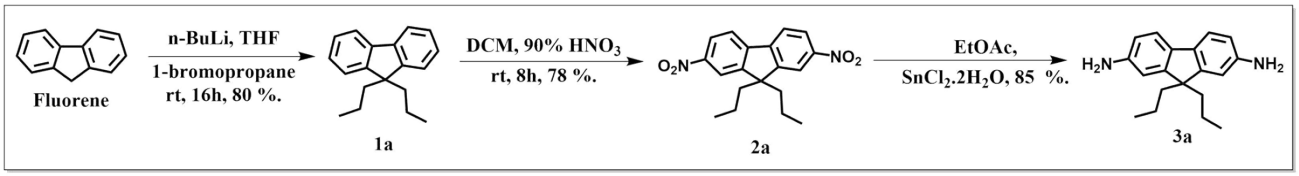
The synthesis procedure of TFP was adapted from a reported process that is illustrated in scheme S1.[1] First, phloroglucinol (6.75 g, 53.55 mmol) and HMTA (16.65 g, 118.2 mmol) were mixed in a 1000 mL two-neck round-bottom flask under argon atmosphere. TFA (105 mL) was added to the mixture at 0 °C and stirred for 20 min. The mixture was heated to 100 °C and kept for 2 h under argon atmosphere. Second, approximately 375 mL HCl solution (3 M) was added slowly at 100 °C and the reaction was continued for another 1 h. After that, the solution was cooled down to room temperature, and then filtered through a celite pad. The filtrate was extracted by dichloromethane twice (2 × 250 mL). The organic phase was separated and dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The obtained residue was washed with a copious amount of hot ethanol to obtain pure TFP (~1.78 g, 16% yield) as white solid.

1H NMR (400 MHz, $CDCl_3$) of TFP:

δ 14.08 (s, 3H), 10.15 (s, 3H).

2.2 Synthesis of 2,7-diamino-9,9-dipropylfluorene (DPF)

The synthesis of DPF is illustrated in Scheme S2, which contains three steps.



Scheme S2. The synthesis procedure of DPF

Step 1: Synthesis of compound 1a (9,9-Dipropylfluorene)

In a 500 mL single-neck round-bottom flask, fluorene (5.0 g, 30.08 mmol) was dissolved in dry THF (100 mL) under argon atmosphere. The *n*-BuLi (1.6 M, in hexane 22 mL, 35.2 mmol) solution was added dropwise over a 30-minute period at room temperature. The mixture was stirred for 30 min, then 1-bromopropane (4.83 g, 35.2 mmol) was added dropwise over a 20-minute period and stirred for 4h. The second portion of *n*-BuLi solution (1.6 M, in *n*-hexane, 22 mL, 35.2 mmol) and 1-bromopropane (4.83 g, 35.2 mmol) was added in the reaction mixtures following the same procedure. The reaction

was continued stirring for another 12 h. After that, the reaction mixture was neutralized by using a saturated aqueous solution of ammonium chloride (NH_4Cl). The obtained solution was extracted by dichloromethane twice (2×150 mL), dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated by rotary evaporator. The residue was purified by silica gel column chromatography using *n*-hexane as eluent to get pure compound **1a** (~6.025 g, 80 % yield) in yellow solid form.

^{1}H NMR (400 MHz, $CDCl_3$) of 9,9-dipropylfluorene:

δ 7.71 (2H, d, *J* = 8 Hz), 7.27-7.37 (6H, m, Ar-H), 1.95 (4H, m, CH_2), 0.60-0.71 (10 H, m, CH_2, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) of 9,9-dipropylfluorene:

δ 150.64, 141.05, 126.95, 126.67, 122.82, 119.59, 55.19, 42.75, 17.15, 14.44.

Step 2: Synthesis of compound 2a (2,7-Dinitro-9,9-diproylfluorene)

To a stirred solution of compound **1a** (4.0 g, 15.97 mmol) in dichloromethane (30 mL) was slowly added 90% HNO_3 (1.0 mL, 15.87 mmol) at 0 °C. After 15 min, to this stirred solution another portion of 90% HNO_3 (3.0 mL, 47.61 mmol) was added slowly and the temperature was allowed to rise to room temperature and stirring pursued for 8 h. After that, the reaction mixture was diluted by adding water. The solution was extracted by dichloromethane three times (3×50 mL), washed with a brine solution (10% sodium chloride, 50 mL), and then dried over anhydrous sodium sulfate (Na_2SO_4) and concentrated by rotary evaporator. The obtained residue was purified by silica gel column chromatography using 95:5 (v/v) *n*-hexane/ethyl acetate as eluent to get pure compound **2a** (~3.12 g, 78 % yield) in light reddish solid form.

^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-dinitro-9,9-diproylfluorene:

δ 8.33 (2H, d, *J* = 8 Hz, Ar-H), 8.29-8.26 (2H, m, Ar-H), 7.92 (2H, dd, *J* = 8 and 2 Hz, Ar-H), 2.12-2.06 (4H, m, CH_2), 0.74-0.66 (6H, m, CH_3), 0.65-0.55 (4H, m, CH_2)

^{13}C NMR (100 MHz, $CDCl_3$) of 2,7-dinitro-9,9-diproylfluorene:

δ 153.47, 148.41, 144.64, 123.53, 121.49, 118.52, 56.57, 41.99, 17.17, 14.15.

Step 3: Synthesis of compound 3a (DPF)

To a stirred solution of compound **2a** (3.0 g, 8.81 mmol) in ethyl acetate (100 mL) was added tin (II) chloride dihydrate (11.95 g 52.96 mmol) at room temperature. The resultant mixture was heated to reflux for 12 h on an oil bath at 90 °C. After that, the solution was allowed to cool down to room temperature. The reaction mixture was cooled to 0 °C and then neutralized by using a saturated aqueous solution of $NaHCO_3$. The resultant solution was filtered through a filter paper (Whatman®). The filtrate was extracted by ethyl acetate twice (2×150 mL), dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated by rotary evaporator. The obtained residue was purified by neutral silica gel column chromatography using 90:10 (v/v) hexane/ethyl acetate as eluent to get pure DPF (~2.11 g, 85% yield) in solid form.

^{1}H NMR (400 MHz, $CDCl_3$) of DPF:

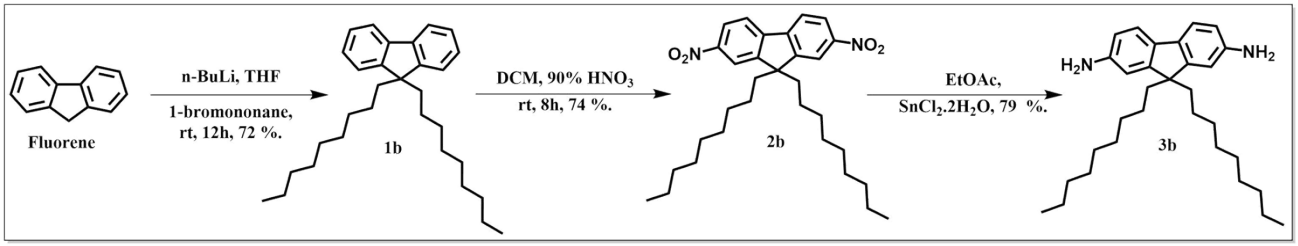
δ 7.32 (2H, d, J = 8 Hz, Ar-H), 6.62 (2H, s, Ar-H), 6.60 (2H, d, J = 8 Hz, Ar-H), 3.65 (s, 4H, NH_2), 1.82-1.79 (4H, m, CH_2), 0.71-0.59(4H, s, CH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) of DPF:

δ 151.59, 144.50, 133.07, 119.01, 113.82, 110.02, 54.83, 43.20, 17.09, 14.46.

2.3 Synthesis of 2,7-diamino-9,9-dinonylfluorene (DNF)

The synthesis of DNF is similar to that of DPF, which is illustrated in Scheme S3.



Scheme S3: Synthesis procedure of DNF

Step 1: Synthesis of compound 1b (9,9-dinonylfluorene)

In a 500 mL single-neck round-bottom flask, fluorene (5.0 g, 30.08 mmol) was dissolved in dry THF (100 mL) under argon atmosphere. The *n*-BuLi (1.6 M in hexane, 22 mL, 35.2 mmol) was added dropwise over a 30-minute period at room temperature and stirred for 30 min. After that, 1-bromononane (7.29 g, 35.2 mmol) was added dropwise over a 20-minute period. After that, the same procedure was followed as that of compound 1b to get the pure compound 2b (~9.06 g, 72 % yield) in yellow solid form.

^{1}H NMR (400 MHz, $CDCl_3$) of 9,9-Dinonylfluorene:

δ 7.70 (2H, d, J = 8 Hz), 7.35-7.28 (6H, m, Ar-H), 1.97-1.92 (4H, m, CH_2), 1.31-1.12 (14H, m, CH_2), 1.08-0.97 (12H, m, CH_2), 0.84 (6H, t, J = 8 Hz, CH_3), 0.65-0.57 (4H, m, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) of 9,9-Dinonylfluorene:

δ 150.89, 141.45, 127.28, 127.01, 123.03, 119.92, 55.26, 40.67, 32.48, 30.52, 30.02, 29.87, 29.52, 24.20, 22.96, 14.37

Step 2: Synthesis of compound 2b (2,7-Dinitro-9,9-dinonylfluorene)

To a stirred solution of compound **1b** (8.5 g, 20.30 mmol) in dichloromethane (40 mL) was slowly added 90% HNO_3 (1.0 mL, 15.87 mmol) at 0 °C. After 15 min, to this stirred solution another portion of 90% HNO_3 (3.0 mL, 47.61 mmol) was added slowly. Then, the same procedure was followed as that of compound **2a** to yield pure compound 2**b** (~7.64 g, 74 % yield) in light reddish solid form.

^{1}H NMR (400 MHz, $CDCl_3$) of 2,7-Dinitro-9,9-dinonylfluorene:

δ 8.33 (2H, dd, J = 8 and 2 Hz, Ar-H), 8.26 (2H, d, J = 8, Ar-H), 7.92 (2H, d, J = 8 Ar-H), 2.04-2.12 (4H, m, CH_2), 1.28-1.11 (12H, m, CH_2), 1.08-0.99 (12H, m, CH_2), 0.84 (6H, t, J = 8 Hz, CH_3), 0.61-0.46 (4H, m, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) of 2,7-Dinitro-9,9-dinonylfluorene:

δ 153.62, 148.45, 145.12, 124.08, 122.02, 118.91, 56.82, 40.31, 32.19, 30.12, 29.98, 29.12, 24.21, 23.03, 14.35

Step 3: Synthesis of compound 3b (DNF)

To a stirred solution of compound **2b** (7.0 g, 13.76 mmol) in ethyl acetate (150 mL) was added tin (II) chloride dihydrate (18.5 g 81.99 mmol) at room temperature. The reaction mixture was warmed up to 80 °C and refluxed for 12 h. After that, the same procedure was followed as that of compound **3a** to obtain pure DNF (~4.87 g, 79% yield) in viscous form.

^{1}H NMR (400 MHz, $CDCl_3$) of DNF:

δ 7.36 (2H, d, *J* = 8 Hz, Ar-H), 6.63 (2H, s, Ar-H), 6.61 (2H, d, *J* = 8 Hz, Ar-H), 3.58 (s, 4H, NH_2), 1.84-1.79 (4H, m, CH_2), 1.28-1.14 (12H, m, CH_2), 1.10-1.01 (12H, m, CH_2), 0.84 (6H, t, *J* = 7 Hz, CH_3), 0.70-0.59 (4H, s, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) of DNF:

δ 151.92, 144.67, 133.46, 119.33, 114.17, 110.38, 77.00, 54.90, 41.20, 32.13, 30.52, 29.94, 29.68, 29.55, 24.05, 22.95, 14.40.

2.4 Synthesis of TFP-DPF and TFP- DNF powder by a solvothermal process

TFP-DPF COF: To a Pyrex tube (o.d.×i.d. = 22×12 mm and length 20 cm) was charged with TFP (63.0 mg, 0.30 mmol), DPF (153.17 mg, 0.45 mmol), 6.0 mL mesitylene, 2.0 mL 1,4-dioxane, and 0.5 mL of 6.0 M aqueous trifluoroacetic acid (TFA) solution, subsequently. After that, the mixture was sonicated for 12 min to get a homogenous dispersion. Then, the reaction tube was frozen at 77 K by immersing in a liquid N_2 bath and then degassed by a freeze-pump-thaw cycle 3 times to ensure the removal of dissolved gases. After that, the glass tube was sealed off and heated to 120 °C for 72 h. The red precipitate was collected by either centrifugation or filtration, and then gently washed with mesitylene, copious amount of water and acetone. The powder collected was further solvent exchanged

with acetone for 3-4 times and then dried at 120 °C under vacuum for 24 h. The final product, TFP-DPF COF, was obtained as a red colored powder with around 70% yield.

IR: υ_{max} 2962, 2926, 2868, 1597, 1572, 1537, 1456, 1439, 1352, 1281, 1251, 1164, 1124, 1089, 1032, 989, 863, 810 and 731 cm^{-1}

^{13}CSS NMR (100 MHz): 184.24, 152.77, 148.23, 137.79, 128.89, 120.77, 114.10, 107.53, 101.12, 55.57, 42.37, 17.43, and 14.43.

Elemental analysis: Theoretical: C, 77.58; H, 6.76; N, 7.92; Experimental: C, 72.43; H, 6.34; N, 6.87.

TFP-DNF COF: To a Pyrex tube (o.d.×i.d. = 22×12 mm and length 20 cm) was charged with TFP (63.0 mg, 0.30 mmol), DNF (201.93), 10.0 mL mesitylene, 2.0 mL 1,4-dioxane, and 0.5 mL of 6.0 M aqueous trifluoroacetic acid (TFA) solution, subsequently. After that, the same procedure was followed as that of TFP-DPF COF to get TFP-DNF COF. The yield of TFP-DNF was around 68% in dark red powder.

IR: υ_{max} 2955, 2923, 2857, 1599, 1575, 1553, 1468, 1440, 1415, 1351, 1250, 1222, 1091, 998, 870, 806 and 726 cm^{-1}.

^{13}CSS NMR (100 MHz): 184.21, 151.31, 146.50, 137.14, 129.34, 120.64, 112.69, 106.82, 101.91, 54.44, 40.37, 30.11, 22.62 and 13.59.

Elemental analysis: Theoretical: C, 79.55; H, 9.56; N, 5.50; Experimental: C, 75.38; H, 8.78; N, 5.94.

3. Membrane characterization

The prepared membranes were characterized by optical microscope (Olympus BX61), SEM (Magellan XHR SEM), AFM (Agilent 5400 Scanning Probe Microscope), XRD (Bruker D8-advance

diffractometer using Ni-filtered Cu Kα radiation at 40 kV and 40 mA), FT-IR (Nicolet iS10 FT-IR spectrometer in the range from 4000 to 525 cm^{-1}), confocal Raman spectroscopy (Horiba Aramis with a Laser of 673 nm), XPS (Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) and a hemispherical analyzer with a resolution from 0 to 0.5 eV), NMR (Bruker 500 MHz), TGA in N_2 atmosphere at a heating rate of 5 °C/min (TG50 analyzer, Mettler Toledo), and nitrogen physisorption (ASAP2020, Micromeritics instrument).

4. Membrane transfer to a substrate surface by the Langmuir-Schaefer method

A substrate was held horizontally and lowered down at a speed of 3.0 mm min^{-1} until it touched the membrane surface. After a few seconds, the substrate was lifted with the same speed of 3.0 mm min^{-1} until the film was detached completely from the surface. The obtained membranes were kept at room temperature until it got completely dry. Multilayer coatings were achieved by repeating the transfer process.

5. Structure determination by PXRD

The cell parameter of TFP-DPF and TFP-DNF was first determined by peak indexing. Based on that, the most common three types of stacking models, eclipsed (AA), inclined (AA) and staggered (AB), were simulated by self-consistent charge density-functional tight-binding (SCC-DFTB) technique with the method of 3ob.[2, 3] The relative position of the substituted propyl and nonyl groups were optimized by energy minimization. It was found that the inclined AA stacking model gave the best fitting to the experimental PXRDs in both cases. The cell parameter was then refined by the Pawley refinement method using the space group P1.

6. Further explanation of the chemical structure analysis by XPS and Raman

The high-resolution C 1s XPS spectra of TFP-DPF (Fig. S8b, ESI) consisted of five components with the most intense peak at 284.41 eV for C=C, 284.81 eV for C–C, and small intense peaks at 286.36 eV for C–O or C–N, 287.91 eV for C=O and 291.36 eV for π-excitation, the peaks at 286.36 eV which

was corresponds to aliphatic alkyl chain in the diamine monomer which was not involved in the reaction. The components at 284.81 and 287.91 eV were related to the bond of *β*-ketoenamine linkage formation in between the two monomers. Similarly, the same peaks were observed in TFP-DNF at 284.43 eV for C=C, 284.83 eV for C–C, 286.34 eV for C–O or C–N, 287.94 eV for C=O and 291.33 eV for π-excitation (Fig. S8f, ESI). The high-resolution O1s spectra for TFP-DPF (Fig. S8c, ESI) and TFP-DNF (Fig. S8g) showed signals at ~531.28 eV and 531.28 eV for C=O; 533.22 eV and 533.22 eV for C-OH, respectively. The high-resolution N1s spectra for TFP-DPF (Fig. S8d) and TFP-DNF (Fig. S8h) showed signals at ~400.29 eV and 400.2 eV, where were associated to the enamine nitrogen (-C=C–NH–).

In the confocal Raman spectroscopy (Fig. S9, ESI), the vibrational band of -C=O- in TFP appeared at 1692 cm^{-1} and the primary -NH_2 group in DPF or DNF appeared at 1358 cm^{-1}. All these bands were absent in the COF structure. While new vibrational bands at ~1610 and ~1586 cm^{-1} appeared in both COF membranes that were associated with the -C=O and -C=C bonds, respectively. In conclusion, all the chemical analysis results strongly suggested the complete reaction of TFA with DNF or DPF, and the formation of the *β*-ketoenamine linkage in the COF framework.[3-6]

7. Supplementary figures

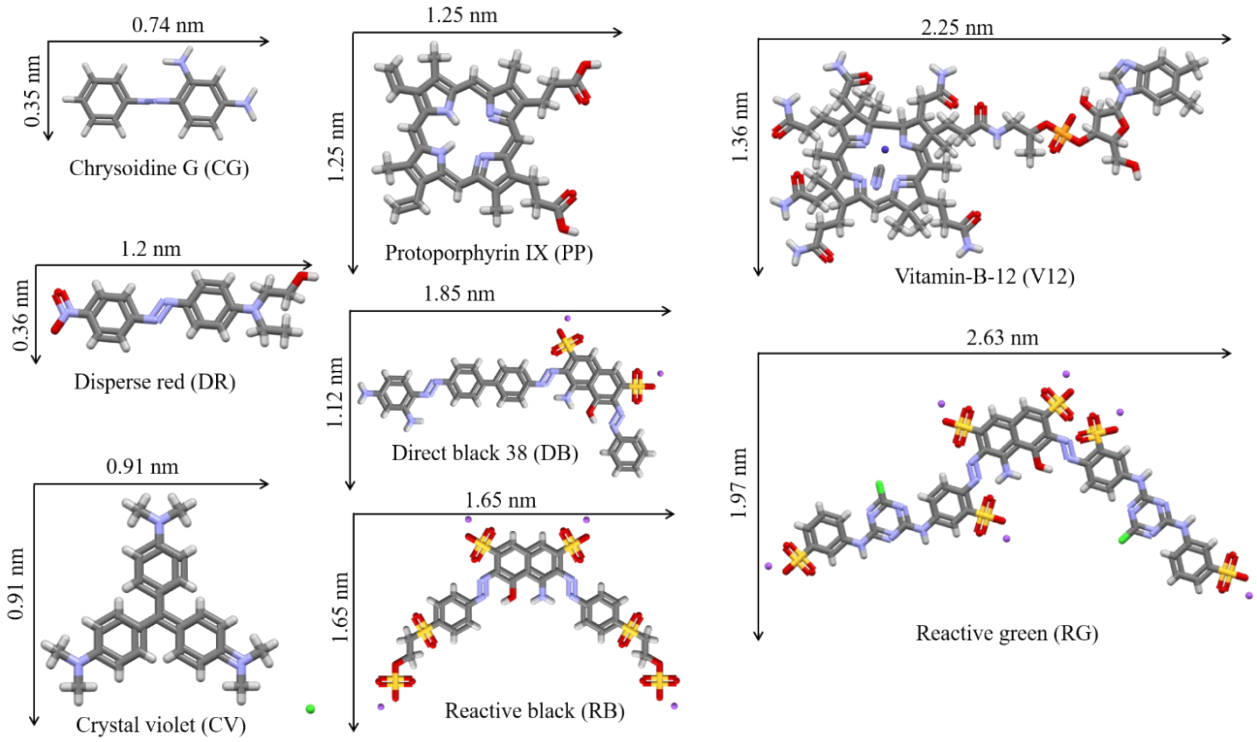


Figure S1. Molecular structure and dimensions of dyes.

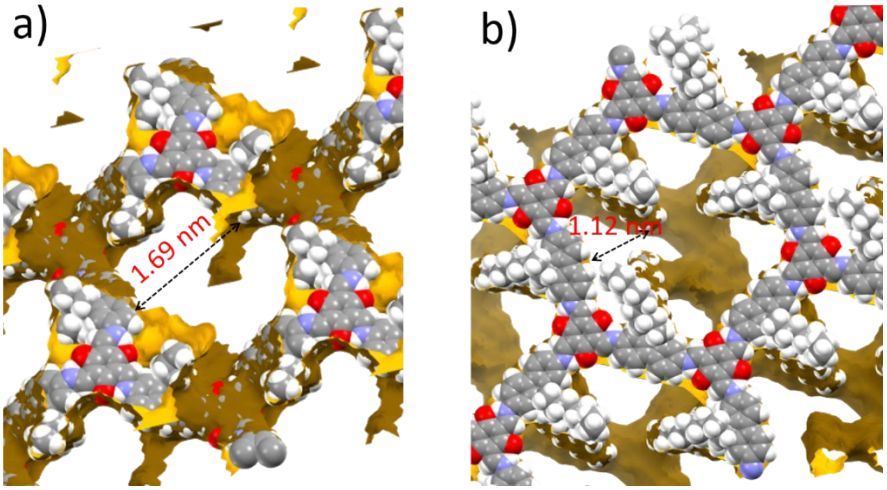


Figure S2. Pore size estimation from the simulated (a) TFP-DPF and (b) TFP-DNF structure.

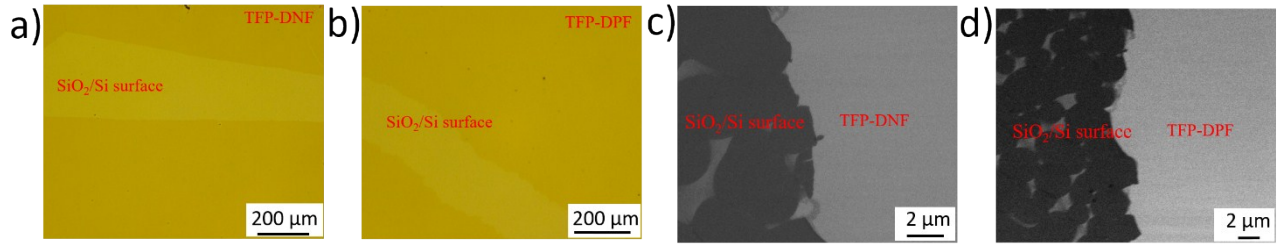


Figure S3. (a and b) Optical images of TFP-DNF and TFP-DPF, respectively; (c and d) surface SEM image of TFP-DPF and TFP-DNF, respectively film deposit on SiO_2/Si surface.

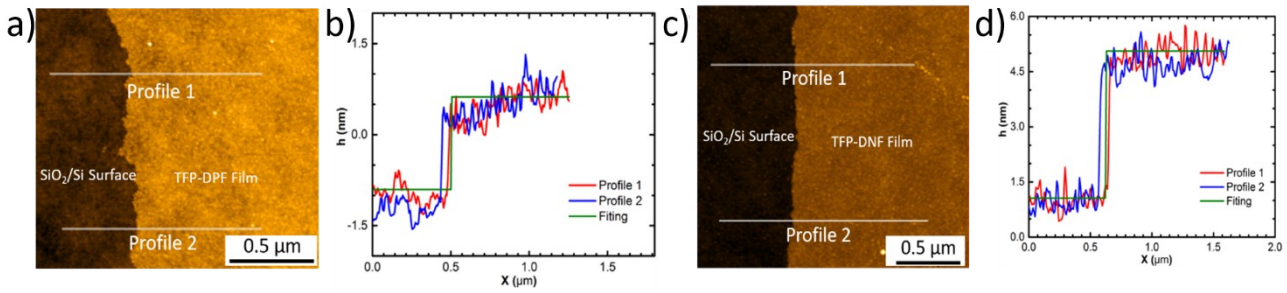


Figure S4. The Surface and thickness profiles measured by AFM from different samples of TFP-DPF and TFP-DNF.

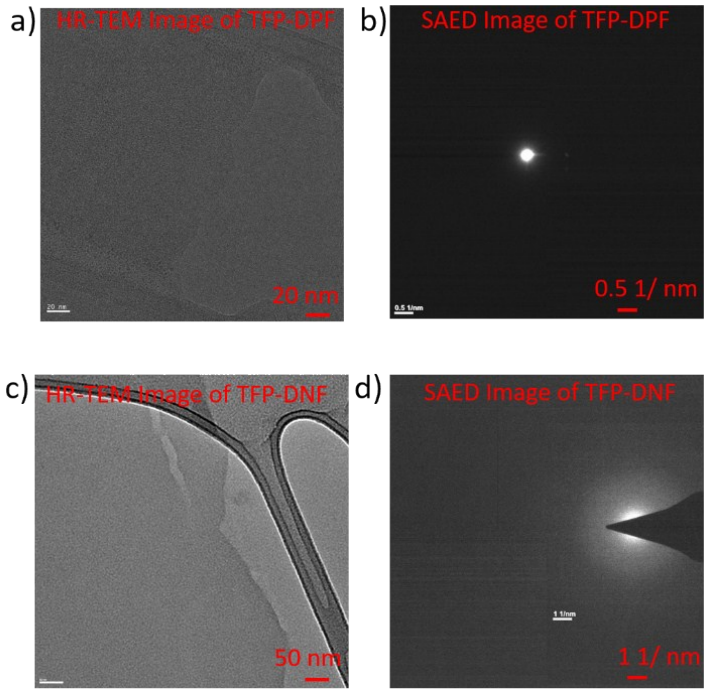


Figure S5: High resolution TEM (a) and Selected area electron diffraction (SAED) (b) images of the TFP-DPF membrane and high resolution TEM (c) and SAED (d) images of the TFP-DNF membrane.

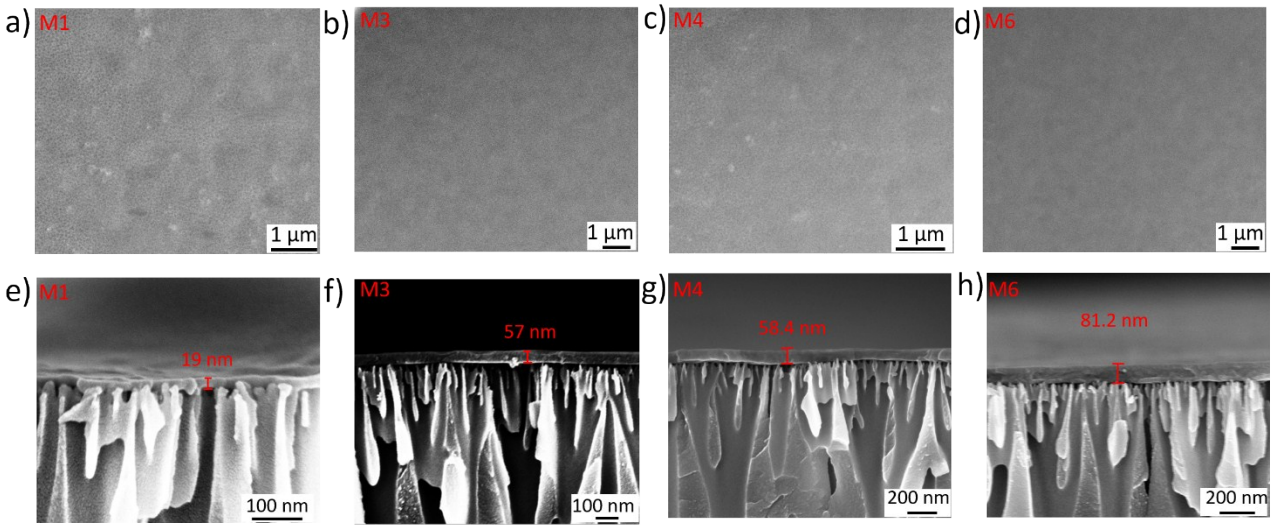


Figure S6. Top Surface SEM images (a) 10 layers (M1), (b) 30 layers (M3) of TFP-DPF membranes (c) 5 layers (M4), (d) 15 layers (M6) of TFPDNF membranes at different numbers of coatings; Cross-section SEM images (e) 10 layers (M1), (f) 30 layers (M3) of TFP-DPF membranes (g) 5 layers (M4), (h) 15 layers (M6) of TFPDNF membranes at different numbers of coatings.

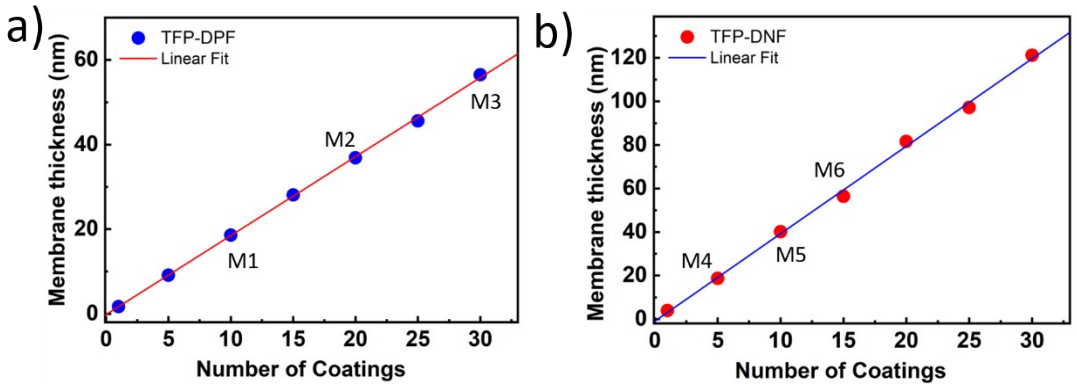


Figure S7. (a) The number of coating of (a) TFP-DPF and (b) TFP-DNF.

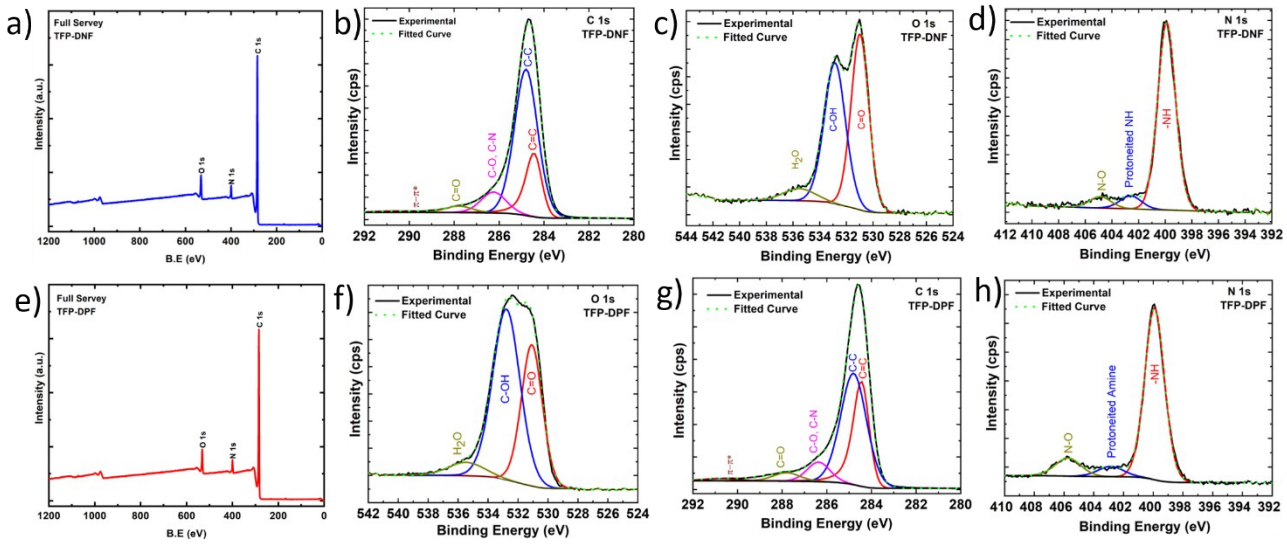


Figure S8. (a) The full XPS survey of TFP-DPF, (b) high-resolution C 1s, (C) N 1s, and (d) O 1s, XPS spectra of the TFP-DPF; (e) The full XPS survey of TFP-DNF, (f) the high-resolution C 1s, (g) N 1s, and (h) O 1s, XPS spectra of the TFP-DNF.

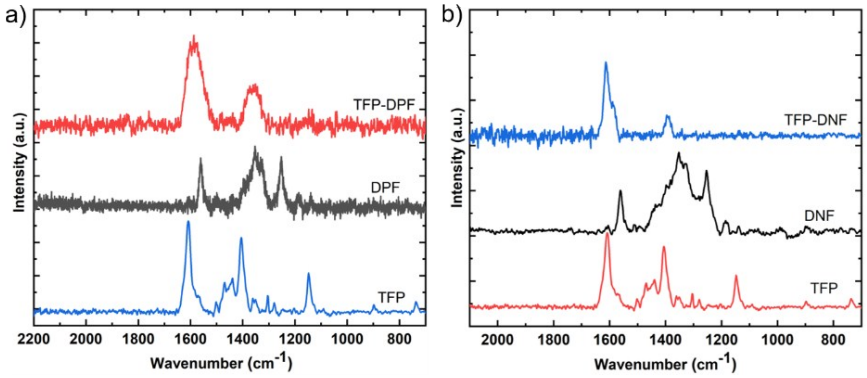


Figure S9: (a) Raman spectra of TFP-DPF (red), DPF (black) and TFP (blue) and (b) Raman spectra of TFP-DNF (blue), DNF (black) and TFP (red).

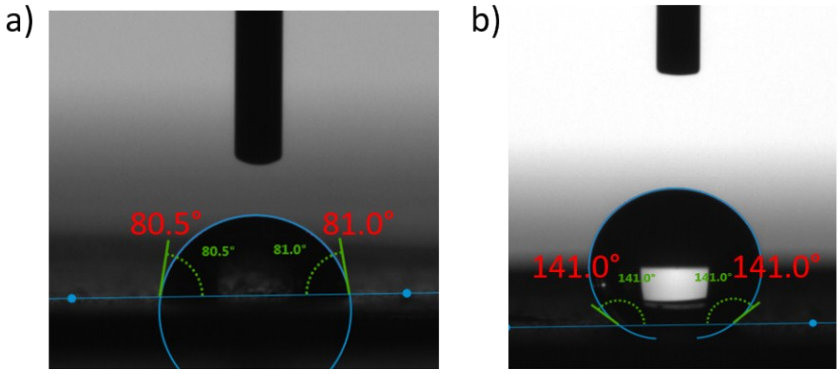


Figure S10. The water contact angle of (a) TFP-DPF membrane and (b) TFP-DNF membrane coated on AAO support.

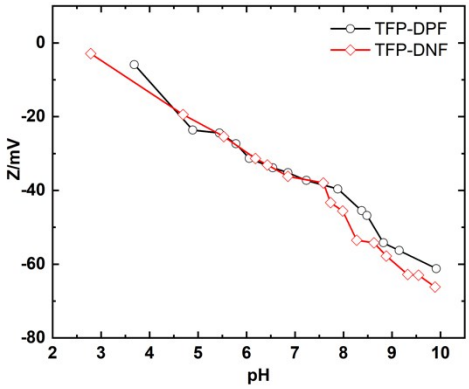


Figure S11: Surface zeta potential of TFP-DPF and TFP-DNF membranes in aqueous solutions at different pH.

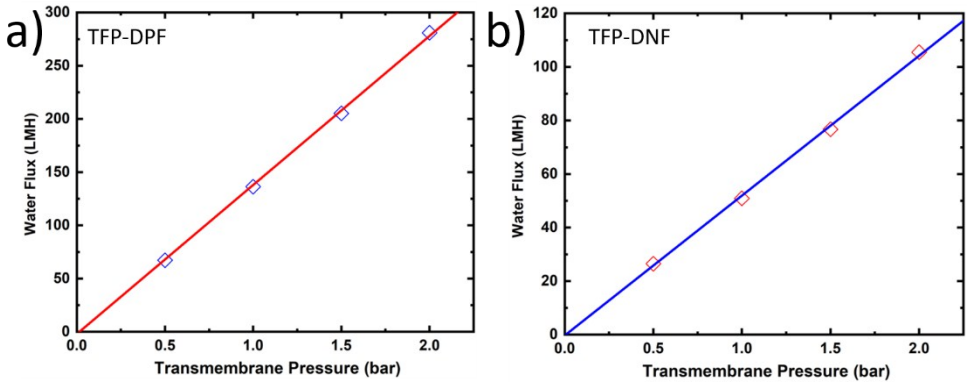


Figure S12. (a and b) The water permeance of TFP-DPF and TFP-DNF membranes respectively.

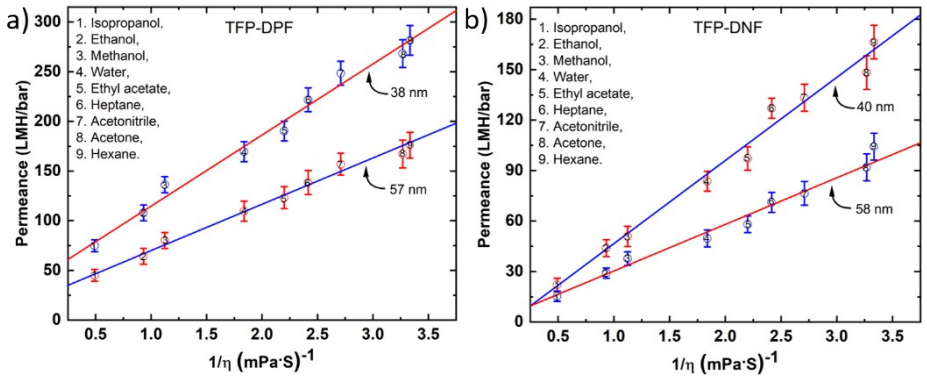


Figure S13. The permeances of solvents through the TFP-DPF (a) and TFP-DNF (b) membranes with different thicknesses are plotted with the inverse of their viscosities.

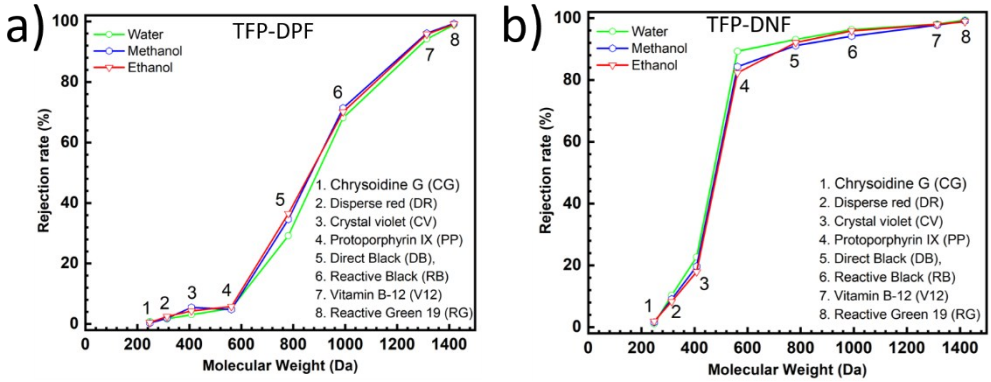


Figure S14. The various dyes rejection rates through the TFP-DPF (a) and TFP-DNF membrane. (The Protoporphyrin IX (PP) was dissolved in the 9:2 in water: methanol mixture and 9:2 Ethanol: Methanol mixture).

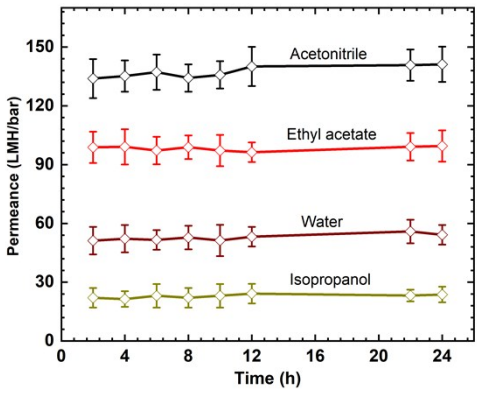


Figure S15. The durability test of solvent permeance of various organic solvents (acetonitrile, ethyl acetate, isopropanol) and water over a long period of test on TFP-DNF.

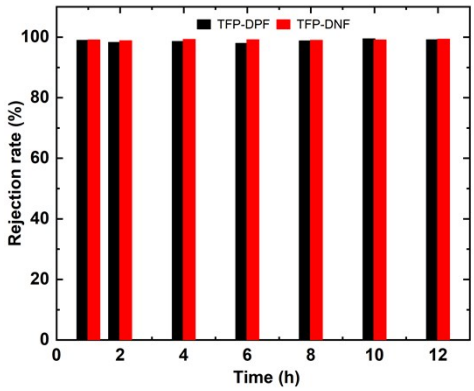


Figure S16. Long-term stability of dye rejection of reactive green (RG) in water.

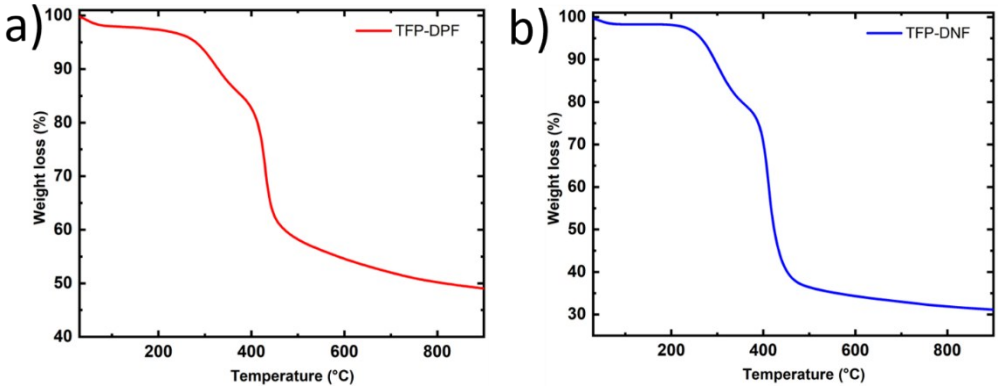


Figure S17. (a) TGA analysis of TFP-DPF and (b) TGA analysis of TFP-DNF under N_2 atmosphere

Reference

1. J. H. Chong, M. Sauer, B. O. Patrick and M. J. MacLachlan, *Org. Lett.*, 2003, **5**, 3823-3826.
2. S. Chandra, T. Kundu, K. Dey, M. Addicoat, T. Heine and R. Banerjee, *Chem. Mater.*, 2016, **28**, 1489-1494.
3. D. B. Shinde, G. Sheng, X. Li, M. Ostwal, A.-H. Emwas, K.-W. Huang and Z. Lai, *J. Am. Chem. Soc.*, 2018, **140**, 14342-14349.
4. Y. Li, M. Zhang, X. Guo, R. Wen, X. Li, X. Li, S. Li and L. Ma, *Nanoscale Horiz.*, 2018, **3**, 205-212.
5. A. C. Ferrari and J. Robertson, *Phys. Rev. B*, 2000, **61**, 14095-14107.
6. A. P. Dementjev, A. de Graaf, M. C. M. van de Sanden, K. I. Maslakov, A. V. Naumkin and A. A. Serov, *Diamond Relat. Mater.*, 2000, **9**, 1904-1907.