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Supplementary Information

Hydroxyl-functionalized Covalent Organic Framework Membranes: Fast Organic Solvent Nanofiltration

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1. Materials

All chemicals, commercial solvents and reagents were purchased from Sigma-Aldrich, Fisher Scientific, Acros Organic, and TCI Chemicals, and used as received without any purification, unless otherwise stated. The porous AAO support (anodiscTM, diameter 25 mm, pore size 20 nm) was purchased from GE Healthcare Life Sciences, UK.

2. Precursor synthesis

2.1 Synthesis of 9-methyl-9H-fluorene

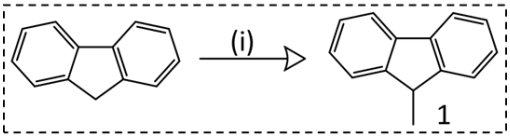

Fig. S1. The synthesis of 9-methyl-9H-fluorene (1) amd reagenrs (i) n-butyllithium (1.6 M, in n-hexane), tetrahydrofuran (THF), iodomethane (MeI), 0 °C to room temperature, 14h.

The starting material fluorene (7.0 g, 42.11 mmol) was dissolved in dry tetrahydrofuran (200 mL) under argon atmosphere at 0 °C in a single-neck round-bottom flask (500 mL) equipped with a magnetic stirrer. To this solution was added the n-BuLi solution (1.6 M, in hexane 26.32 mL, 35.2 mmol) over a period of 30 minutes at 0 °C. The resulting mixture was stirred for a further 30 minutes, then iodomethane (MeI) (7.17 g, 50.53 mmol) was added dropwise over a period of 15-20 minutes and stirred for 2 hours. The reaction mixture was then slowly warmed to room temperature and stirred for a further 12 hours. After completion of the reaction, the reaction mixture was neutralized with a saturated aqueous solution of ammonium chloride (NH_4Cl). The obtained solution was extracted three times with dichloromethane (3×120 mL), dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, pure hexane) to afford pure compound 1a (~5.46 g, 72% yield) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$):
δ 7.80-7.76 (2H, m), 7.55-7.51 (3H, d, J = 7.0 Hz), 7.41-7.32 (4H, m), 3.97 (1H, q), and 1.55 (3, d).
^{13}C NMR (100 MHz, $CDCl_3$):
δ 149.02, 140.55, 126.96, 126.94, 124.04, 119.88, 42.48 and 18.23

2.1 Synthesis of Synthesis of compound 3-(2,7-diamino-9-methyl-9H-fluoren-9-yl)propan-1-ol ($MP_{OH}F$)

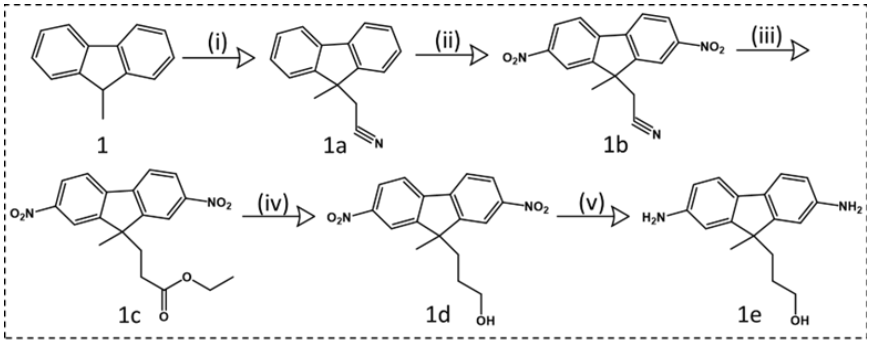

Fig. S2. The synthetic route for $MP_{OH}F$. Reagents and chemicals: (i) 1,4-dioxane, 40% aqueous solution of Triton B, acrylonitrile, 40 °C, 12h; (ii) dichloromethane, 90% HNO_3, 0 °C to room temperature for 8 h.; (iii) concentrated H_2SO_4, ethanol, reflux at 150 °C, 24 h, (iv) $CaCl_2$, $NaBH_4$, 0 °C, 24 h, (c) 10% Pd/C, ethyl acetate, 80 °C, 16 h.

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Step 1: Synthesis of compound 2-(9-methyl-9H-fluoren-9-yl)acetonitrile (1a)

A 100 mL two-neck round-bottom flask equipped with a magnetic stirrer and reflux condenser was charged with 9-methylfluorene (5.0 g, 27.76 mmol) in dry 1,4-dioxane (30 mL). The 40% aqueous solution of Triton B (2.32 g, 5.512 mmol) was then added dropwise at room temperature under argon atmosphere. Then the reaction mixture was heated to 40 °C and distilled acrylonitrile (2.95 g, 55.52 mmol) was slowly added dropwise into the reaction mixture (The reaction is exothermic, keep the temperature inbetween 30 to 40 °C). After completion of the addition, the reaction mixture was stirred at 40 °C for 12 hours. After completion of the reaction, the yellow reaction solution was neutralized with 10% HCl (hydrochloric acid). The product was then precipitated by adding deionized water (35 mL). The crude product was separated by filtration and the residue obtained was recrystallized with 95% ethanol to afford white crystals as pure compound (5.35 g, 88%).

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

δ 7.74-7.71 (2H, m), 7.41-7.33 (6H, dd, *J* = 7.2, 1.6 Hz), 2.44-2.40 (2H, m), 1.53 (3H, s), and 1.52-1.48 (2H, m).

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

δ 148.92, 140.13, 127.84, 127.76, 122.56, 120.24, 119.62, 49.91, 36.06, 26.35 and 12.38

Step 2: Synthesis of compound 3-(9-methyl-2,7-dinitro-9H-fluoren-9-yl)propanenitrile (1b)

A solution of compound 1a (5.00 g, 22.82 mmol) was dissolved in 35 mL of dichloromethane, cooled to 0 °C, and treated with 90% HNO_3 (0.47 mL, 11.41 mmol) and stirred for 15 min. Again, another portion of 90% HNO_3 (3.23 mL, 79.87 mmol) was slowly added dropwise to the reaction solution and stirred for another 30 minutes at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 8 hours. After completion of the reaction, the reaction mixture was diluted with deionized water. The obtained solution was extracted three times with dichloromethane (3×50 mL) and also washed with a salt solution (10% sodium chloride, 50 mL). Then the organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The crude product obtained was purified by silica gel column chromatography using n-hexane/ethyl acetate as eluent to afford pure compound 1b (~5.17 g, 70% yield) in solid form.

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

δ 8.41-8.37 (2H, m), 8.36-8.34 (2H, m), 7.99 (2H, d), 2.62-2.52 (2H, m), 1.68 (3H, s), and 1.67-1.64 (2H, m).

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

δ 151.71, 148.64, 143.74, 124.59, 122.25, 118.71, 117.94, 51.06, 34.97, 26.67 and 12.66

Step 3: Synthesis of compound ethyl 3-(9-methyl-2,7-dinitro-9H-fluoren-9-yl)propanoate (1c)

A 1000 mL two-neck round-bottom flask equipped with a magnetic stirrer and reflux condenser was charged with 3-(9-methyl-2,7-dinitro-9H-fluoren-9-yl)propanenitrile (1b) (5.0 g, 15.47) in 95% ethanol (300 mL). Concentrated sulfuric acid (H_2SO_4) (80 mL) was added slowly to the solution at room temperature. Then the reaction mixture was heated to reflux at 150 °C for 24 hours. After completion of the reaction, the resulting solution was cooled to room temperature. Then the obtained precipitate was filtered off and washed with deionized water to remove the traces of sulfuric acid. The collected compound was recrystallized with 95% ethanol to give yellow crystals as pure product ethyl 3-(9-methyl-2,7-dinitro-9H-fluoren-9-yl)propanoate1c (3.55 g, 62%).

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

δ 8.37-8.32 (4H, m), 7.95 (2H, d), 3.92 (2H, q), 2.55-2.49 (2H, m), 1.63 (3H, s), 1.61-1.56 (2H, m) and 1.12 (3H, t).

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

δ 172.14, 153.26, 148.52, 143.75, 124.03, 121.87, 118.73, 60.51, 51.25, 34.41, 29.38, 26.05 and 14.01

Step 4: Synthesis of compound ethyl 3-(9-methyl-2,7-dinitro-9H-fluoren-9-yl)propanoate (1d)

A solution of compound 1c (3.20 g, 8.65 mmol) was dissolved in 35 mL of tetrahydrofuran and cooled to 0 °C and treated with calcium chloride ($CaCl_2$) (1.15 g, 10.38 mmol) and sodium borohydride ($NaBH_4$) (1.47 g, 38.75 mmol) and stirred at 0 °C for 15 minutes. Then the reaction mixture was warmed to room temperature and stirred further for 24 hrs. After completion of the reaction, the green reaction mixture was cooled to 0 °C. Then the reaction mixture was diluted with deionized water and then neutralized with 25% hydrochloric acid. The tetrahydrofuran solvent was evaporated under reduced pressure and the obtained aqueous layer was extracted three times with chloroform (3×100 mL). The obtained organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using n-hexane/ethyl acetate as eluent to afford the pure compound 1d (1.85 g, 65% yield) in solid form.

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

δ 8.35-8.31 (4H, m), 7.94 (2H, dd), 3.44 (2H, t), 2.24-2.20 (2H, m), 1.63 (3H, s) and 0.94-0.87 (2H, m)

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

δ 154.30, 148.51, 143.76, 123.78, 121.75,118.60, 62.32, 51.05, 36.23, 27.43 and 26.03

Step 5: Synthesis of compound 3-(2,7-diamino-9-methyl-9H-fluoren-9-yl)propan-1-ol (1e) ($MP_{OH}F$)

The high-pressure autoclave reactor with Teflon-coated stir bar was charged with 3-(9-methyl-2,7-dinitro-9H-fluoren-9-yl)propan-1-ol (1.65 g, 5.03 mmol) and Pd/C (10 wt% palladium on activated carbon) in ethyl acetate (25.0 mL) in the glovebox. The autoclave reactor was then removed from the glovebox. It was then purged three times with hydrogen gas and then pressurized with hydrogen gas (35 bar). The autoclave reactor was heated to 80 °C for 16 hours with stirring. After completion of the reaction, the autoclave reactor was cooled to room temperature and the excess amount of hydrogen gas was slowly discharged. Then the reaction solution was filtered off through a celite pad. The filtrate was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The crude compound obtained was purified by flash silica gel column chromatography using n-hexane/dichloromethane/triethyamine as eluent to afford pure compound 1e (~1.01 g, 75% yield) in solid form.

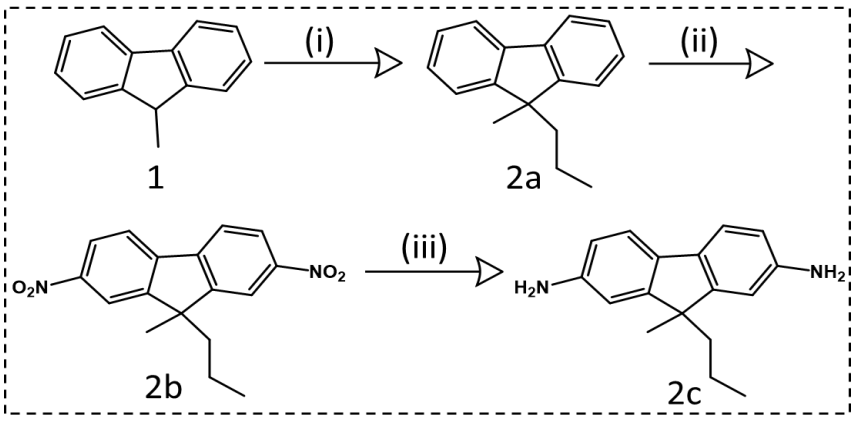
^{1}H NMR (400 MHz, DMSO-d_6):

δ 7.19 (2H, d), 6.56 (2H, d), 6.45 (2H, dd), 4.92 (4H, bs), 3.15 (2H, t), 1.79-1.71 (2H, m), 1.27 (3H, s) and 0.82-0.71 (2H, m)

^{13}C NMR (100 MHz, DMSO-d_6):

δ 151.80, 146.63, 129.46, 118.50, 112.58, 108.56, 61.19, 49.20, 37.07, 27.95 and 27.33

2.3: The synthesis of 9-methyl-9-propyl-9H-fluorene-2,7-diamine (MPF)



Scheme S3: The synthetic procedure for MPF. Reagents and chemicals: (ii) tetrahydrofuran, n-butyllithium (1.6 M, in n-hexane), 1-bromopropane, room temperature, 12 h; (iii) dichloromethane, 90 % HNO_3, 0°C to room temperature, 8h.; (iv) ethyl acetate, tin (II) chloride dihydrate, reflux, 16 h.

Step 1: Synthesis of compound 59-methyl-9-propyl-9H-fluorene (1a)

A solution of n-BuLi (1.6 M, in hexane 21.65 mL, 34.64 mmol) was added dropwise to a stirred solution of 9-methyl-9H-fluorene (1) (5.2 g, 28.87 mmol) in dry THF (100 mL) under an argon atmosphere at room temperature. The resulting mixture was stirred for an additional 30 minutes. Then 1-bromopropane (4.26 g, 34.64 mmol) was added dropwise to the stirred solution and stirred for 12 hours. After completion of the reaction, the reaction mixture was neutralized with a saturated aqueous solution of ammonium chloride (NH_4Cl) at 0 °C. The obtained solution was extracted twice with dichloromethane (2×100 mL). The obtained organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford pure compound 1a (~6.04 g, 94% yield) as a yellow solid.

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

δ 7.76-7.73 (2H, m), 7.44-7.41 (2H, m), 7.39-7.31 (4H, m), 1.99 (ddd, 2H), 1.50 (3H, s), and 0.74-0.68 (5H, m).

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

δ 152.10, 140.09, 127.06, 126.79, 50.78, 43.11, 26.61, 17.68 and 14.40

Step 2: Synthesis of compound 9-methyl-2,7-dinitro-9-propyl-9H-fluorene

A solution of compound 1b (5.75 g, 25.88 mmol) in dichloromethane (35 mL) was cooled to 0 °C and treated with 90% HNO3 (0.54 mL, 12.94 mmol) and stirred for 15 minutes. Then another portion of 90% HNO3 (3.78 mL, 90.58 mmol) was added dropwise to the stirred solution and the reaction mixture was stirred at 0 °C for another 30 min. The reaction mixture was then warmed to room temperature and stirred for 8 hours. After completion of the reaction, the reaction mixture was diluted with deionized water. The obtained solution was extracted three times with dichloromethane (3×50 mL) and also washed with a salt solution (10% sodium chloride, 50 mL). Then the organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The crude product obtained was purified by silica gel column chromatography using n-hexane/ethyl acetate as eluent to afford pure compound 2a (~5.98 g, 74% yield) in solid form.

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

δ 8.36-8.31 (4H, m), 7.97 (2H, d), 2.14-2.09 (2H, m), and 0.77-0.67 (5H, m).

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

δ 154.71, 148.37, 143.74, 123.57, 121.64, 118.53, 52.03, 42.32, 25.92, 17.65 and 14.08

Step 3: Synthesis of compound synthesis of 9-methyl-9-propyl-9H-fluorene-2,7-diamine (MPF):

A round bottom flask (1 L) equipped with a reflux condenser and magnetic stir bar was charged with 9-methyl-2,7-dinitro-9-propyl-9H-fluorene (5.5 g, 17.62 mmol) in ethyl acetate (150 mL) and tin(II)chloride dihydrate (23.86 g, 105.72 mmol) was added at room temperature. The reaction mixture was heated to reflux for 16 hours. After completion of the reaction, the mixture was cooled down to room temperature. Then the reaction solution was neutralized with a saturated aqueous solution of sodium bicarbonate at 0 °C and the obtained solution was filtered through Whatman® filter paper. The obtained filtrate was extracted with ethyl acetate (3 ×125 mL) and the organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$). The solution was concentrated under reduced pressure. The crude product obtained was purified by silica gel column chromatography using n-hexane/ethyl acetate/trimethylamine as eluent to afford pure compound 1c (~3.10 g, 72% yield) in solid form.

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

δ 7.36 (2H, d), 6.69 (2H, d), 6.64 (dd, 2H), 3.60 (3H, s), 1.89-1.83 (2H, m), 1.39 (s, 3H), and 0.81-.064 (5H, m).

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

δ 153.48, 144.29, 132.05, 119.24, 113.98, 110.01, 50.40, 43.40, 27.01, 17.60 and 14.38

3. Membrane characterization

The prepared membranes were analyzed using an optical microscope (Olympus BX61), SEM (Magellan XHR SEM), XRD (Bruker D8-Advance diffractometer with Ni-filtered Cu Kα radiation at 40 kV and 40 mA), FT-IR (Nicolet iS10 FT-IR spectrometer ranging from 4000 to 525 cm^{-1}), 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 of 0 to 0.5 eV), NMR (Bruker 500 MHz), TGA in N2 atmosphere at a heating rate of 5 °C/min (TG50 analyzer, Mettler Toledo), and nitrogen physisorption (ASAP2020, Micromeritics Instrument).

3.1 Structure determination by PXRD

First, the unit cell parameters of TFP-$MP_{OH}F$ and TFP-MPF are obtained by peak indexing. Based on the obtained cell parameters, the possible stacking structures, such as eclipsed (AA), inclined (AA), and staggered (AB), are simulated using the self-consistent charge density functional tight-binding (SCC-DFTB) technique with the 3ob.[1,2] The simulated structure fitted with the experimental PXRD. It is observed that the inclined AA stacking model for TFP-$MP_{OH}F$ and TFP-MPF was best fitted. Finally, the unit cell parameters are refined using the Pawley refinement method in the P1 space group.

4. Supplementary Figures

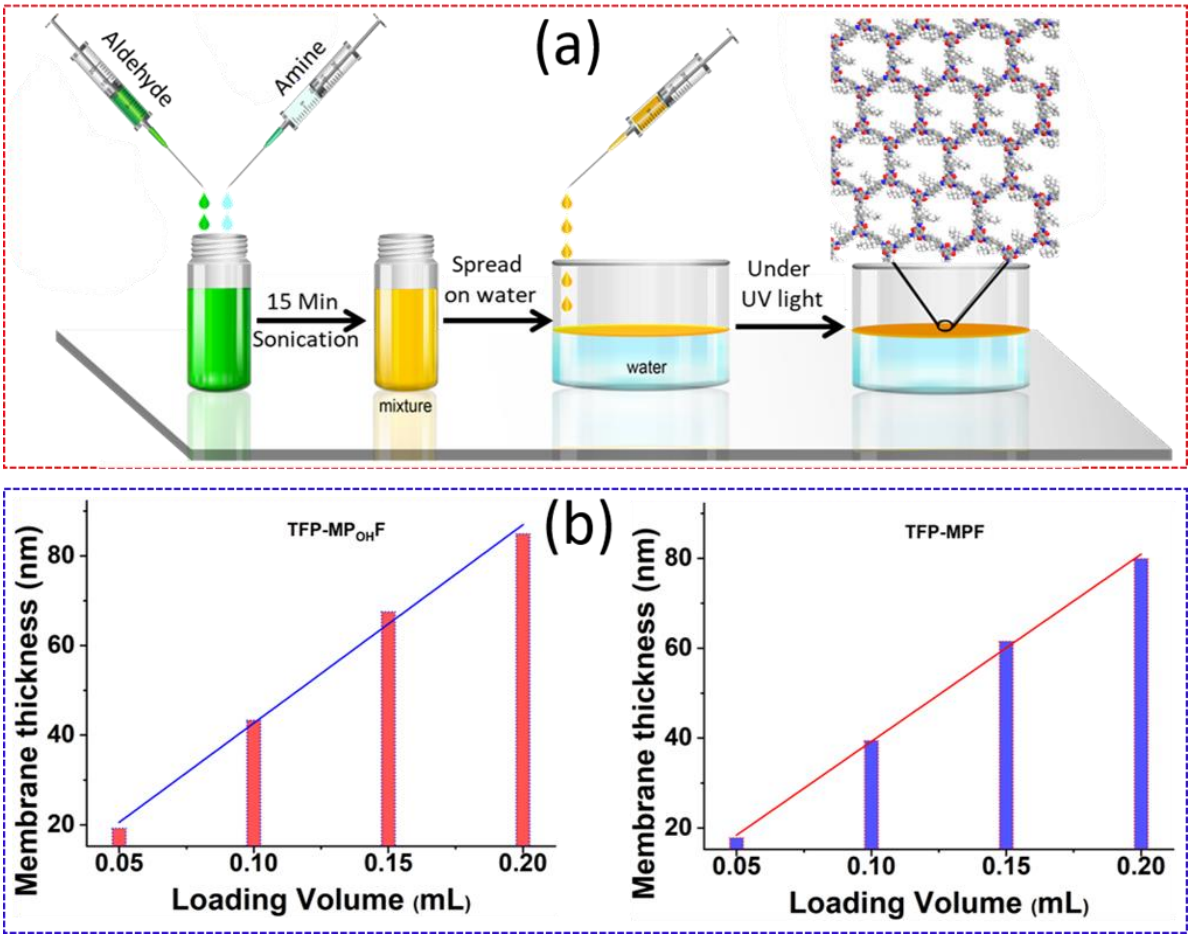


Figure S1. Systematic illustration of the fluorene based COF membrane preapartion (a), and the relationship between the membrane thickness and the loading volume of mixed TFP and $MP_{OH}F$/MPF.

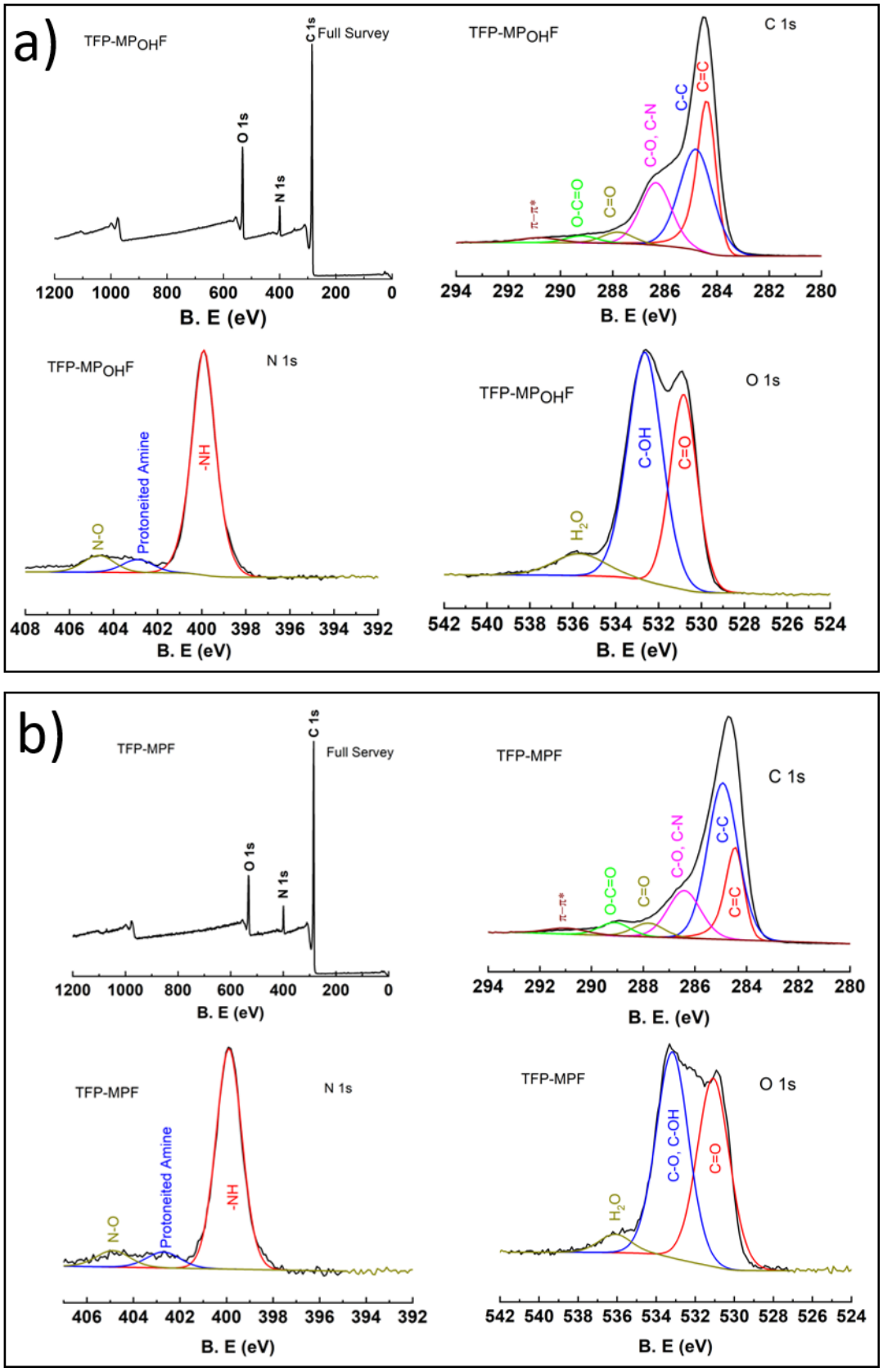


Figure S2. XPS spectra of (a) TFP-MP$_{OH}$F and (b) TFP-MPF.

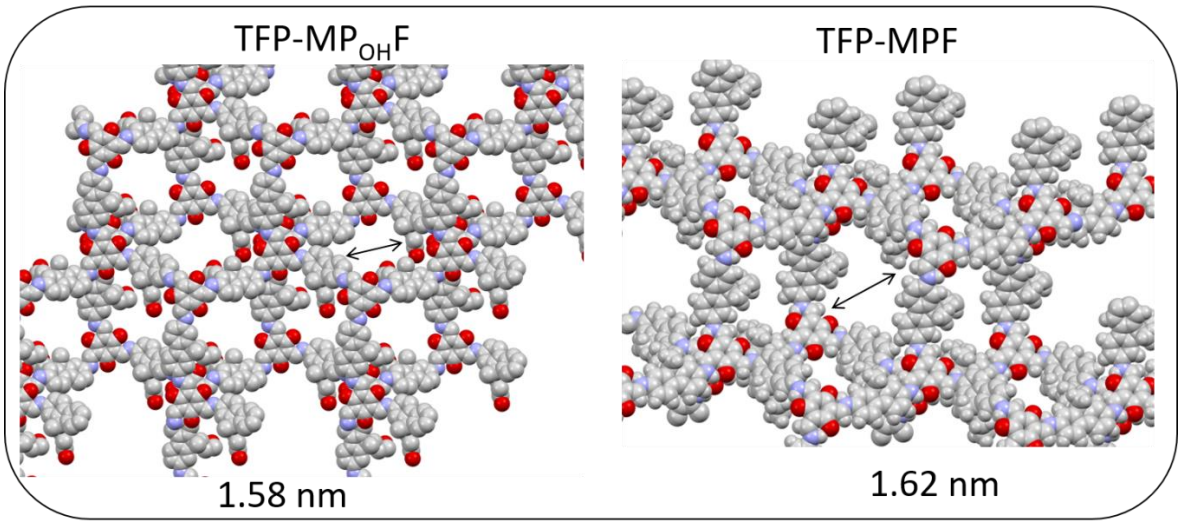


Figure S3. Pore size calculated from the simulated crystal structures of TFP-MP$_{OH}$F, and TFP-MPF.

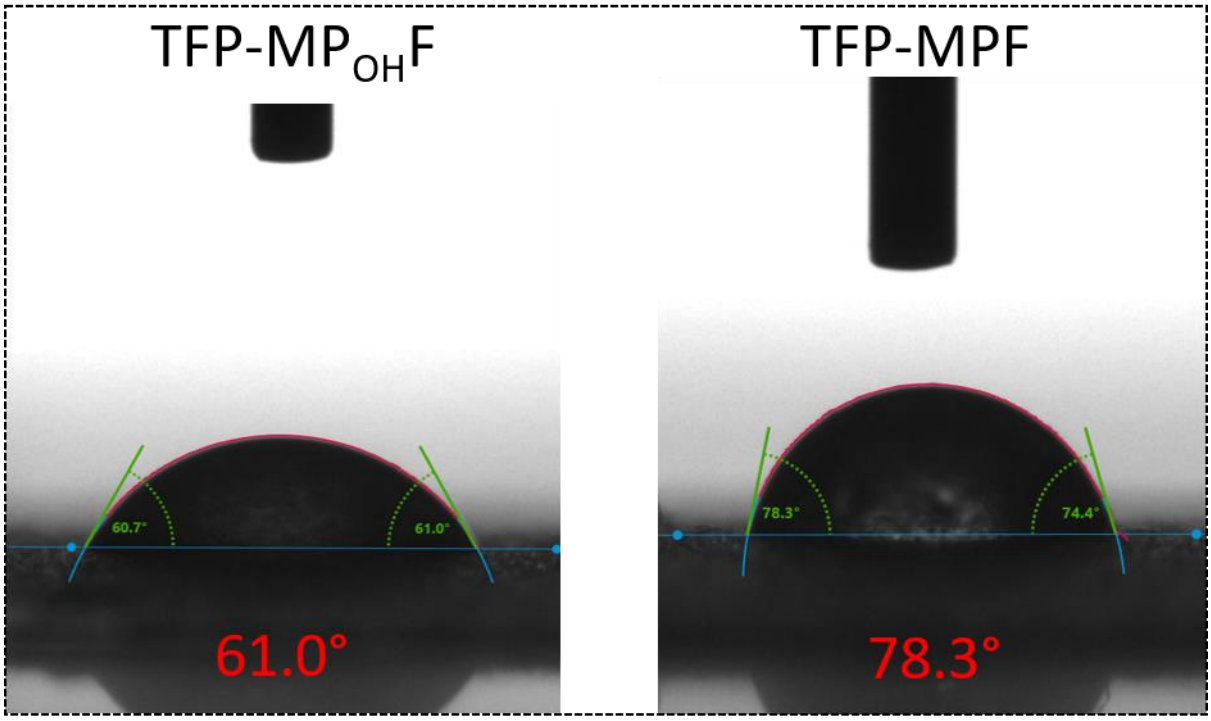


Figure S4: The water contact angle of TFP-MP$_{OH}$F and TFP-MPF membranes.

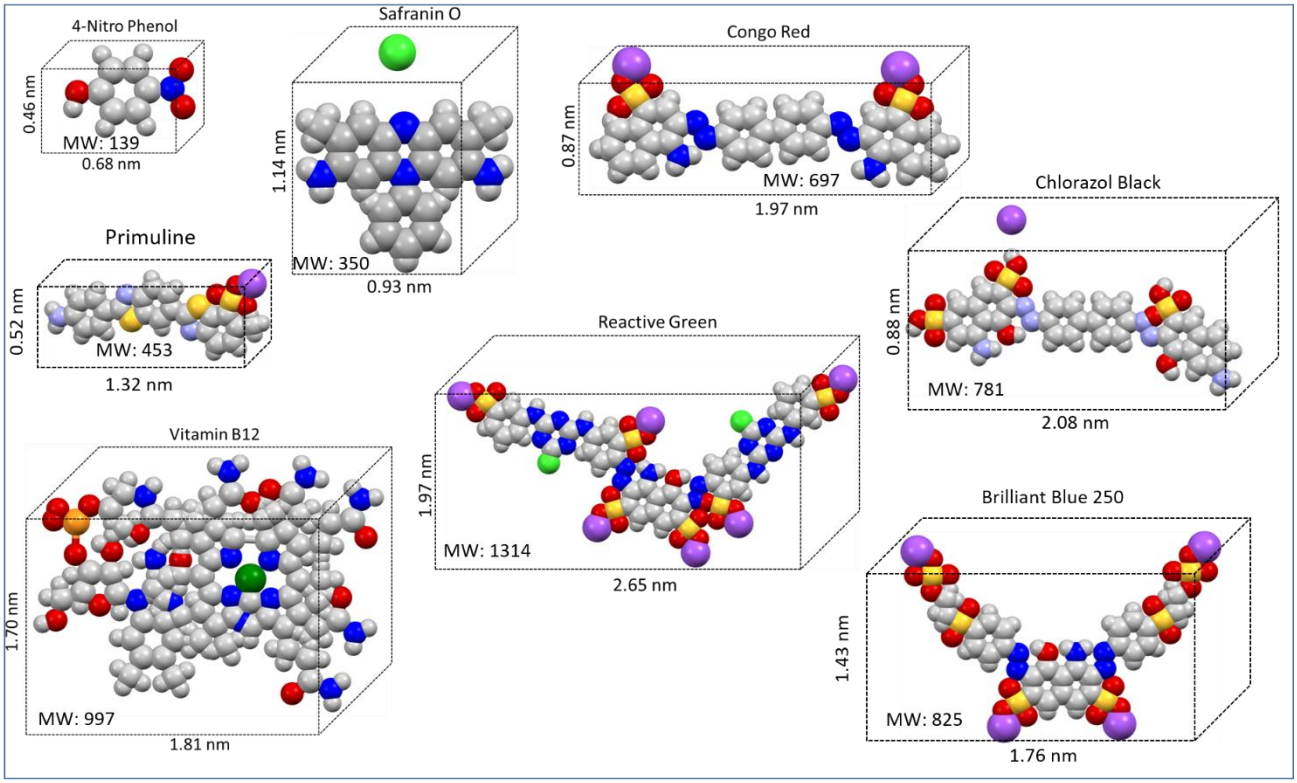


Figure S5. Chemical strctures with molecular dimensions of various types dyes used in this study.

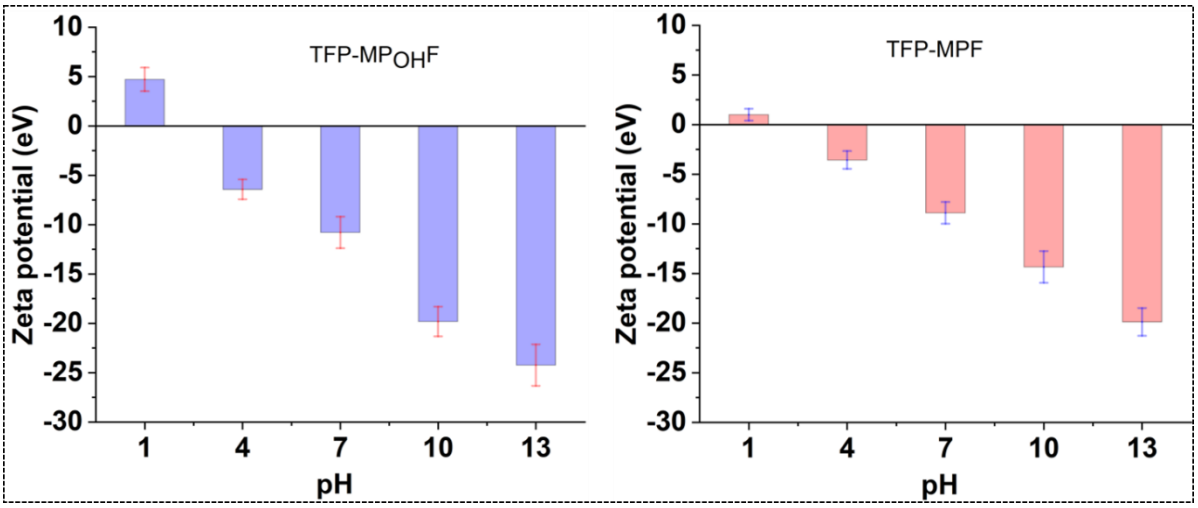


Figure S6. Zeta potential of the TFP-MP$_{OH}$F and TFP-MPF membranes at different Ph values.

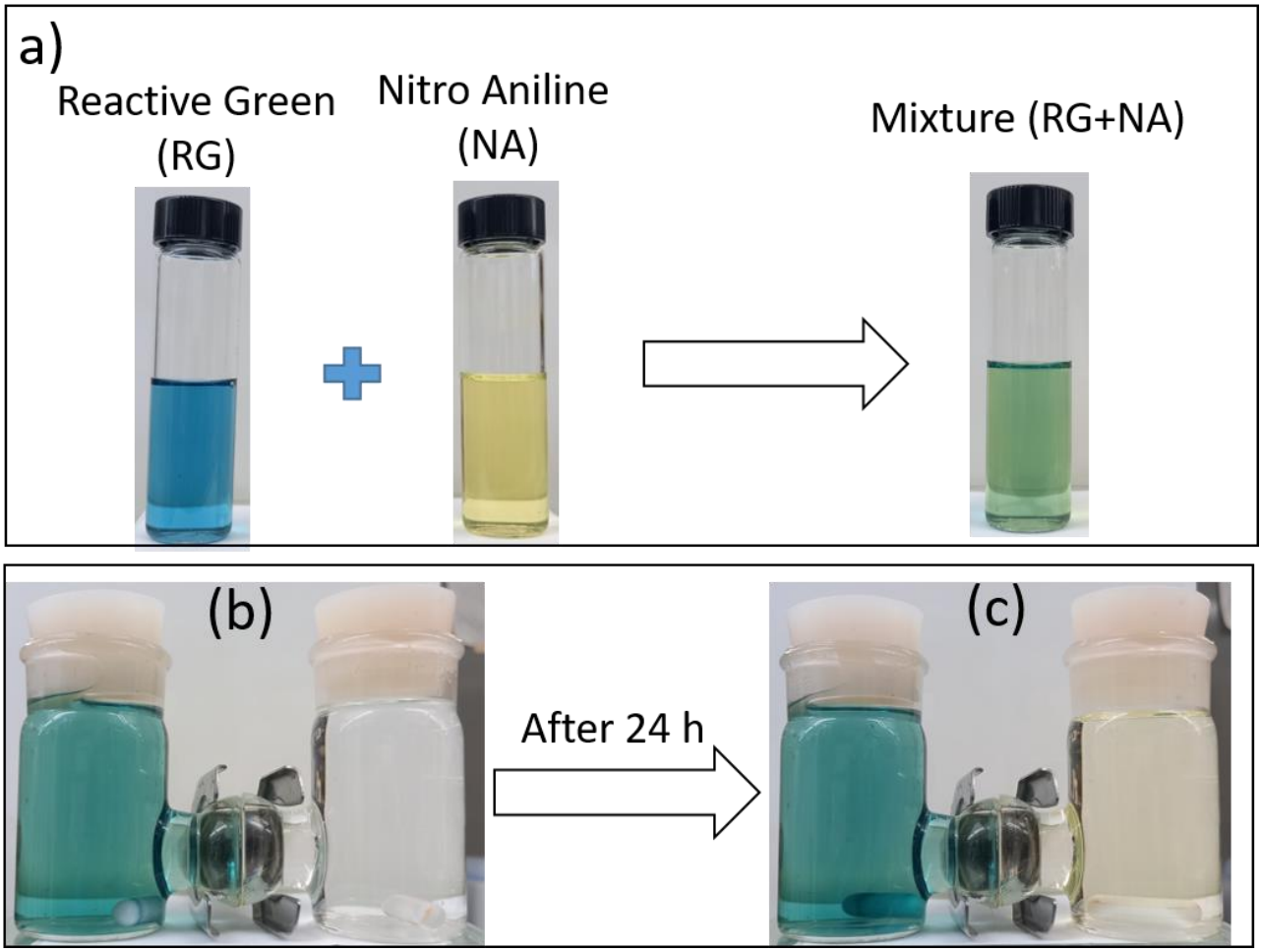


Figure S7. (a) Dyes solution and their mixture; Dye separation cell set up separated by prepared TFP-$MP_{OH}F$ membrane: b) Left chamber is filled with fresh methanol and right chamber is filled with a mixture of NP and RG dyes. b) After 24 h the as-synthesized membrane allowed NP to pass through while rejecting RG which is affirmed by the appearance of yellow color in the left chamber.

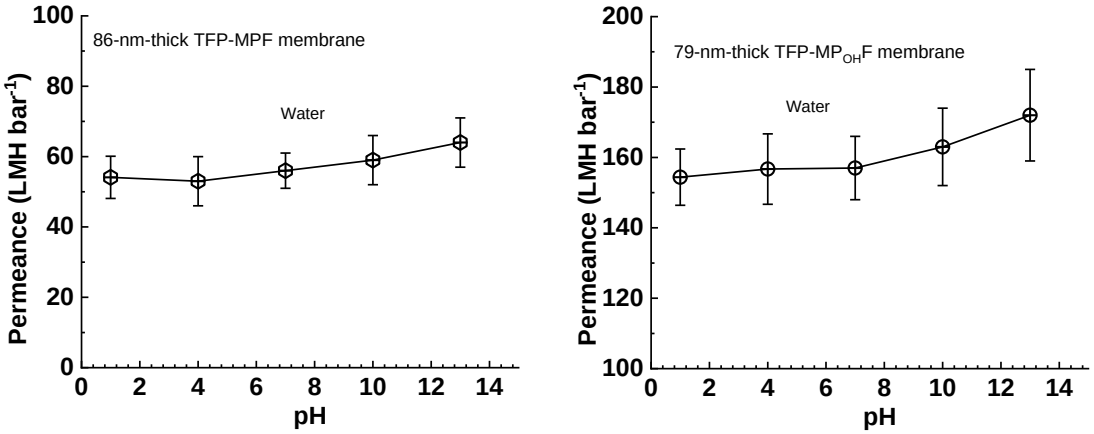


Figure S8. The water permeance at different pH TFP-TFP-$MP_{OH}F$ and TFP-MPF membrane.

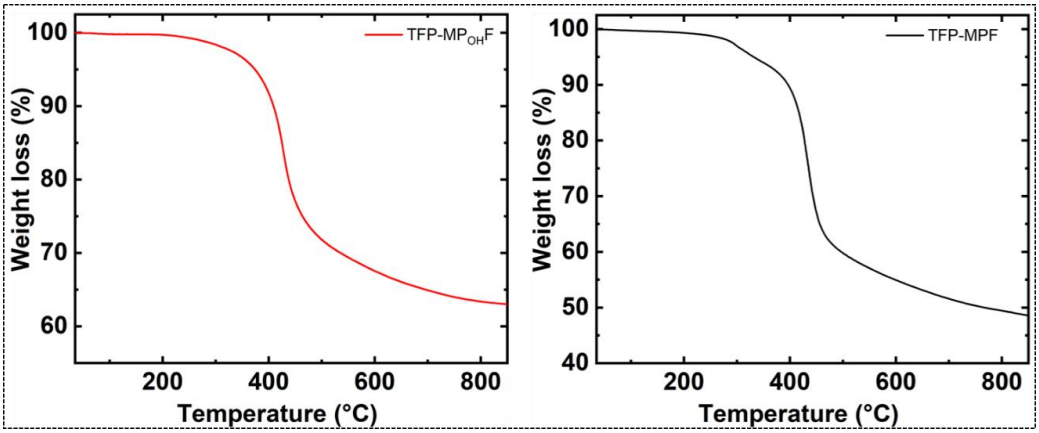


Figure S9. TGA analysis of TFP-MP$_{OH}$F and TFP-MPF membranes

Table S1 Compared solvent permeance data

Membranes	Solvent	Permeance (LMH/bar)	References
Polyamide	Methanol	52.2	[1]
PBI	Water	12	[2]
Polyamide	Water	20.8	[3]
COF-TpBpy	Methanol	108	[4]
COF-TpBpy	Water	211	
TFP-DHF	Methanol	110	[5]
TFP-MP$_{OH}$F	Methanol	327	This work
TFP-MP$_{OH}$F	Water	215	

Reference

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