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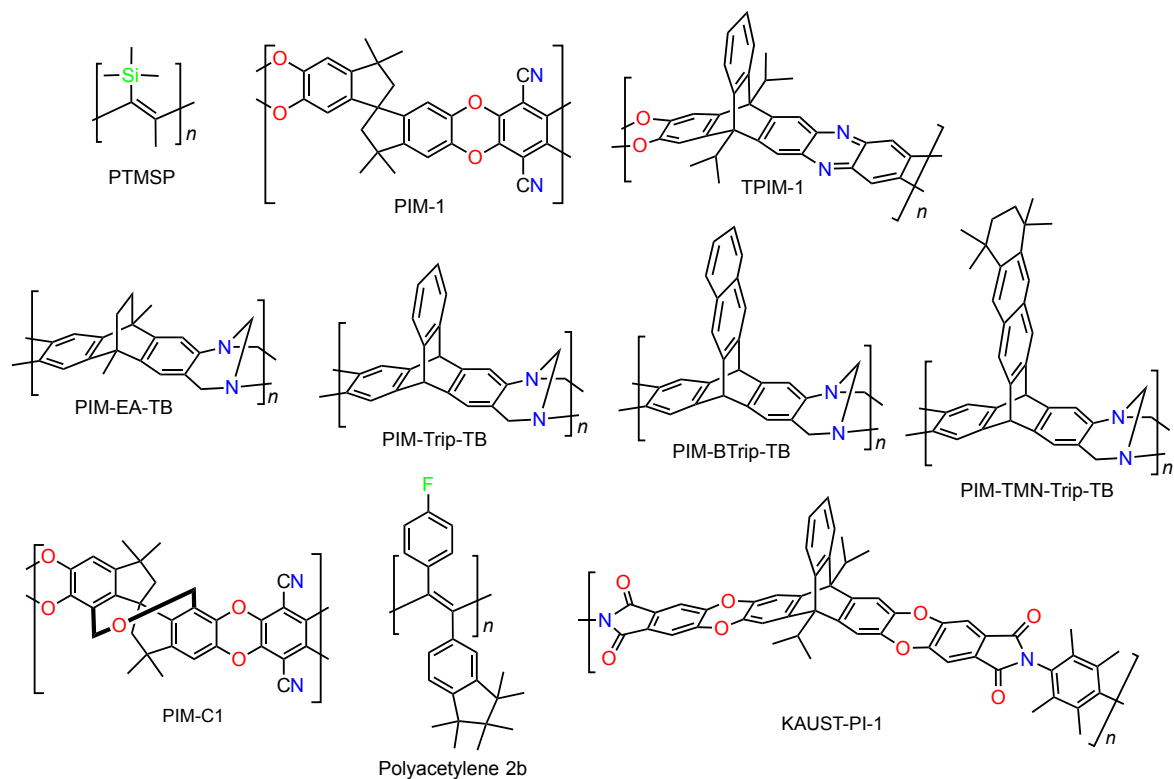
Polymer Ultrapermiability from the Inefficient Packing of 2D Chains

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Supplementary Figure 1. Structure of polymers for which data is given in Supplementary Table 1.

Supplementary Table 1. The gas permeability data for the polymers shown in Supplementary Figure 1.

Polymer	¹ Film history	P_{He} (P_{He}/P_{N_2})	P_{H_2} (P_{H_2}/P_{N_2})	P_{O_2} (P_{O_2}/P_{N_2})	P_{CO_2} (P_{CO_2}/P_{N_2})	P_{N_2}	P_{CH_4} (P_{CH_4}/P_{N_2})	Ref.
PTMSP	1	5250 (0.95)	13900 (2.5)	7850 (1.4)	28100 (5.1)	5510 (-)	14500 (2.6)	¹
	1	-	15000 (3.1)	9000 (1.4)	27000 (4.1)	6600 (-)	15000 (2.3)	²
	1	5080 (1.0)	13200 (2.7)	7730 (1.6)	28000 (5.6)	4970 (-)	13000 (2.6)	³
	1/3	9700 (0.8)	25000 (2.1)	14800 (1.3)	47000 (4.0)	11700 (-)	30000 (2.6)	⁴
	3	-	23200 (2.5)	12900 (1.4)	43800 (4.7)	9350 (-)	23300 (2.5)	⁵
	4(1460 days)	-	500 (8.3)	150 (2.5)	1200 (20)	60 (-)	130 (2.1)	⁶
Polyacetylene 2b	1/3	15800 (1.0)	33300 (2.1)	17900 (1.1)	47000 (3.0)	15600 (-)	34300 (2.2)	⁴
PIM-1	1	1950 (2.4)	5010 (6.1)	2270 (2.8)	13600 (16.5)	823 (-)	1360 (1.7)	⁷
	1	1320 (2.2)	3300 (5.4)	1530 (2.5)	11260 (18.5)	610 (-)	1160 (1.9)	⁸
	2	1368 (1.9)	3580 (4.9)	1790 (2.5)	8310 (11.4)	727 (-)	- (-)	⁹
	4(1348 days)		1544 (24.0)	317 (5.0)		64 (-)		¹⁰
TPIM	2	-	2666 (49)	368 (6.8)	1549 (28.7)	54 (-)	50 (1.1)	¹¹
	4(15 days)		3304 (37)	525 (5.9)		60 (-)		¹⁰
KAUST-PI-1	2	1771 (16.6)	3983 (37.2)	627 (5.9)	2389 (22.3)	107 (-)	105 (1.0)	¹²
PIM-EA-TB	1	2685 (4.6)	8114 (14.0)	2294 (3.9)	7696 (13.3)	580 (-)	774 (1.3)	¹³
	3	-	-	-	15000	(-)	-	¹⁴
	4(470 days)	1630	4442	933	2644	188	219	¹⁵

	days)	(8.6)	(23.7)	(4.9)	(14.0)	(-)	(1.2)	
PIM-Trip-TB	1	2500 (4.0)	8039 (12.8)	2718 (4.3)	9709 (15.4)	629 (-)	905 (1.4)	¹⁵
	4(100 days)	1585 (8.4)	4740 (25.1)	1073 (5.6)	3951 (18.1)	189 (-)	218 (1.2)	¹⁵
PIM-BTrip-TB	1	2932 (3.2)	9980 (10.8)	3290 (3.6)	13200 (14.2)	926 (-)	1440 (1.6)	¹⁶
	4(166 days)	1470 (6.8)	4280 (19.8)	1170 (5.4)	4150 (19.2)	216 (-)	283 (1.3)	¹⁶
PIM-TMN-Trip-TB	1	2300 (5.80)	6100 (15.4)	2030 (5.13)	6068 (16.0)	396	710 (1.9)	-
PIM-C1	1	3880 (3.9)	9870 (10.1)	3410 (3.5)	18900 (19.3)	980 (-)	1310 (1.3)	¹⁷

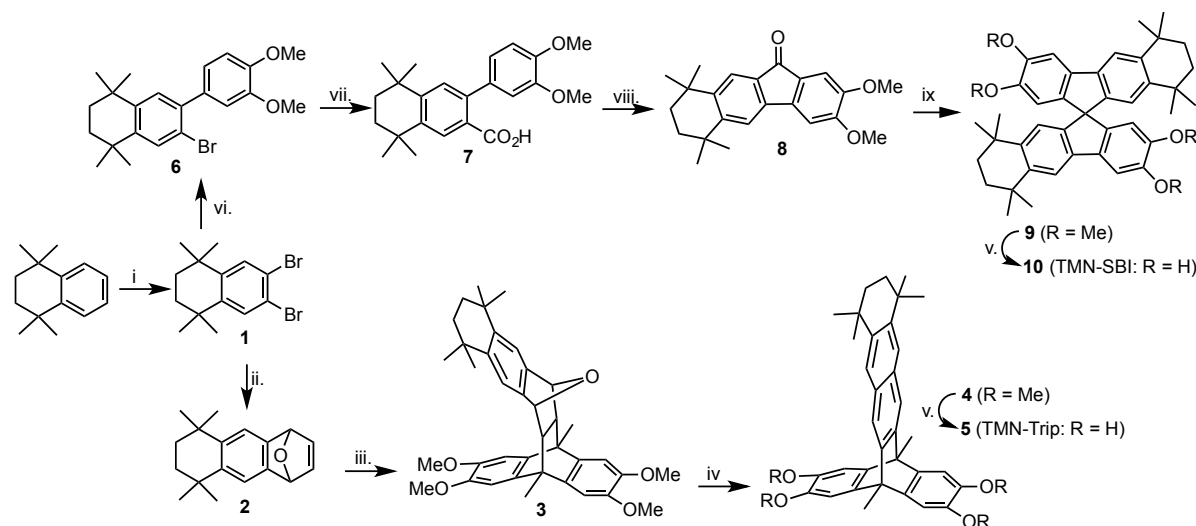
Gas permeability values (P_x , Barrers) and selectivities (P_x/P_{N_2}) for polymers shown in Fig. 1 from films with different processing histories.

¹Film Histories. 1. Methanol treated film measured 24 h after treatment and with exposure to high vacuum; 2. Methanol treated film heated at 140 °C for 24 h then aged for 14 days; 3. Methanol treated film measured immediately after treatment without exposure to high vacuum; 4. Film aged over specified time.

Note. It would appear that wide variation of gas permeability values reported for PTMSP and other polymers is due to the difference in film treatment between its removal from methanol and measurement.^{5,18} The anomalously high values reported for PTMSP are probably derived from films measured immediately after removal from methanol. Similar have also been observed from a PIM (PIM-EA-TB) that had not been dried under vacuum following methanol treatment.¹⁴

S1. Polymer synthesis

S1.1 Summary of key monomer synthesis.



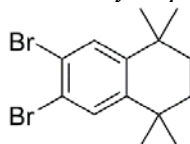
Supplementary Scheme 1. Synthesis of monomers TMN-Trip and TMN-SBI. *Reagents and conditions:* i. Br₂, Fe, DCM, rt, 3 h; ii. *n*-BuLi, furan, THF, -78 °C, 1.5 h; iii. 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene, DMF, 250 °C, 7 bar, 2 h, microwave irradiation; iv. trifluoroacetic acid, rt, 24 h.; v. BBr₃, DCM; vi. 3,4-dimethoxyphenylboronic acid, Pd(PPh₃)₄, PPh₃, K₂CO₃, THF, H₂O, 80 °C 36 h; vii. *n*-BuLi, CO₂, hexane, -78 °C, 2 h, acid work-up; viii. MeSO₃H, rt, 3 h. ix. Compound 6, *n*-BuLi, THF, -78 °C, 12 h then HCl/AcOH, reflux, 3 h.

S1.2 General methods and equipment. Commercially available reagents were used without further purification. Anhydrous dichloromethane was obtained by distillation over calcium hydride under nitrogen atmosphere. Anhydrous *N,N*-dimethylformamide was bought from Aldrich. All reactions using air/moisture sensitive reagents were performed in oven-dried or flame-dried apparatus, under a nitrogen atmosphere. TLC analysis refers to analytical thin layer chromatography, using aluminium-backed plates coated with Merck Kieselgel 60 GF₂₅₄. Product spots were viewed either by the quenching of UV fluorescence, or by staining with a solution of cerium sulfate in aqueous H₂SO₄. Flash chromatography was performed on silica gel 60A (35-70 micron) chromatography grade (Fisher Scientific). Microwave irradiation synthesis was performed with a Biotage Initiator microwave reactor. Melting points were recorded using a Gallenkamp Melting Point Apparatus and are uncorrected. ¹H NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 (400 MHz) or DPX 500 (500 MHz) instruments, with ¹³C NMR spectra recorded at 100 MHz or 125 MHz respectively. Low-resolution mass spectrometric data were determined using a Fisons VG Platform II quadrupole instrument using electron impact ionization (EI) unless otherwise stated. High-resolution mass spectrometric data were obtained in electron impact ionization (EI) mode unless otherwise reported, on a Waters Q-TOF micromass spectrometer. The TGA was performed using the device Thermal Analysis SDT Q600 at a heating rate of 10 °C/min from room temperature to 1000 °C. Gel Permeation Chromatography was carried out using a Viscotek GPC Max1000 system which includes a refractive index detector and two columns (Malvern, LT5000L). The analysis used dilute solution of polymer in chloroform (1 mL min⁻¹). Crystallographic data (See

Fig. S2 and S4) were collected at 120.0 K on a Rigaku Oxford Diffraction SuperNova diffractometer. Suitable single crystals were selected and mounted on a MITIGEN holder in Paratone oil. Using **Olex2**¹⁹, the structure was solved with the **ShelXT**²⁰ structure solution program, using the Direct Methods solution method. The model was refined with version of **ShelXL**²¹ using Least Squares minimization.

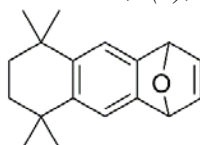
S1.3 Synthesis of PIM-TMN-Trip

6,7-Dibromo-1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene (**1**)



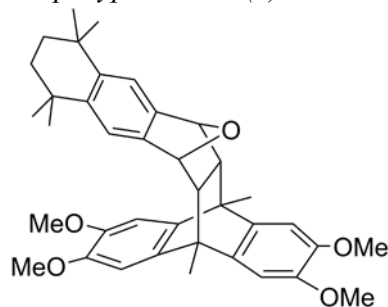
1,1,4,4-Tetramethyl-1,2,3,4-tetrahydronaphthalene (23.80 g, 126 mmol), prepared according to the procedure reported by H. Toyama,²² was dissolved in anhydrous DCM (200 mL) and Fe powder (catalytic amount) was added. To this solution, bromine (60.60 g, 379 mmol) was added drop-wise over 1 h and the mixture was left at RT for 3 h. The mixture was then poured into water, the organic layer separated and washed with sodium carbonate solution (3 x 100 mL). The organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane) to yield **1** (33.0 g, 75 %) as a white crystalline solid; mp: 111-112 °C; $\nu_{\max}$ (cm⁻¹): 2953, 2936, 2922, 2862, 1460, 1387, 1362, 1348, 1296, 1261, 1211, 1190, 1132, 1105, 1070, 1047, 1020, 887, 860, 839, 756, 685; ¹H NMR (500 MHz, CDCl₃) δ 7.50 (s, 2H), 1.66 (s, 4H), 1.25 (s, 12H); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 146.4, 131.8, 121.4, 34.7, 34.3, 31.6; HRMS (EI, *m/z*): [M⁺] calcd. for C₁₄H₁₈Br₂, 345.9749 found: 345.9751.

5,5,8,8-Tetramethyl-15-oxatetracyclo pentadeca-2,4(9),10,13-tetraene (**2**)



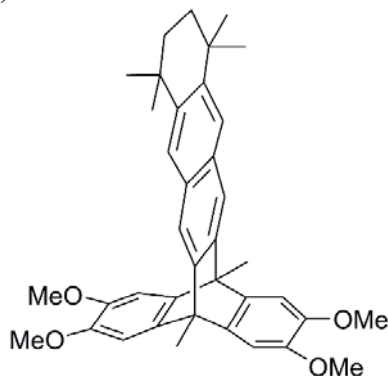
Following the general procedure reported by Luo *et al.*²³, compound **1** (13.21 g, 38 mmol) and anhydrous furan (24.98 mL, 344 mmol) were dissolved in anhydrous THF (30.0 mL) and cooled to -78 °C. To this solution *n*-BuLi (2.5 M in hexanes, Sigma-Aldrich, 19.84 mL, 50 mmol) in anhydrous THF (10.0 mL) was added drop-wise over 0.5 h and the reaction left to stir at -78 °C for 1.5 h. The resulting solution was allowed to warm to room temperature and water added (100 mL). The organic layer was extracted with DCM and dried over MgSO₄. The solvent was removed under reduced pressure. The resulting solid was washed with a small amount of hexane, filtered off and dried to give the desired product (7.62 g, 79 %) as a white powder; mp: 124-126 °C; $\nu_{\max}$ (cm⁻¹): 2961, 2920, 2857, 1464, 1360, 1283, 1161, 1001, 968, 868, 853, 833, 694, 660; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.20 (s, 2H), 6.98 (t, 2H, *J* = 1.1 Hz), 5.65 (t, 2H, *J* = 1.1 Hz), 1.64 (s, 4H), 1.24 (s, 12H); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 145.3, 142.6, 140.9, 118.6, 82.3, 35.2, 34.4, 31.8, 31.7; HRMS (EI, *m/z*): [M⁺] calcd. for C₁₈H₂₂O, 254.1665; found, 254.1677.

(5*s*,14*s*)-2,3,18,19-tetramethoxy-5,8,8,11,11,14-hexamethyl-5,5*a*,6,8,9,10,11,13,13*a*,14-decahydro-5,14-[1,2]benzeno-6,13-epoxypentacene (**3**)



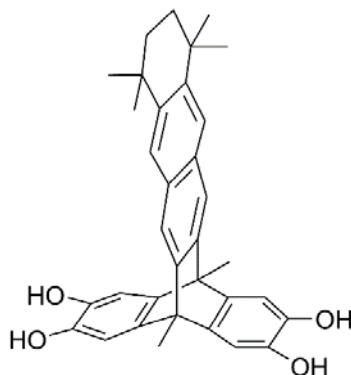
Following the general procedure reported by Swager *et al.*²⁴, 2,3,6,7-tetramethoxy-9,10-dimethylantracene (2.00 g, 6.0 mmol), prepared according to the method reported by McKeown *et al.*²⁵, and compound **2** (1.56 g, 6.00 mmol) were dissolved in DMF (15 mL) and heated in microwave reactor at 250 °C for 2 h at a pressure of 7 bar. The resulting solution was poured into water and the precipitate collected by filtration and washed with water. The crude product was purified by column chromatography DCM/ethyl acetate (9:1, v/v) to yield adduct **3** (2.69 g, 77 %) as a light brown crystalline solid; mp: 288-290 °C; $\nu_{\max}$ (cm⁻¹): 2934, 1506, 1489, 1437, 1404, 1279, 1242, 1227, 1196, 1163, 1049, 1032, 854, 835, 822, 785, 748; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.03 (s, 2H), 6.87 (s, 2H), 6.84 (s, 2H), 4.92 (s, 2H), 3.89 (s, 6H), 3.83 (s, 6H), 2.07 (s, 6H), 1.99 (s, 2H), 1.60 (s, 4H), 1.19 (s, 12H); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 146.8, 146.4, 144.1, 142.5, 140.5, 136.8, 116.4, 106.7, 106.0, 79.6, 56.8, 56.4, 56.4, 43.1, 35.2, 34.4, 32.1, 31.9, 17.1 HRMS (EI, m/z): [M⁺] calcd. for C₃₈H₄₄O₅, 580.3183; found, 580.3180.

2,3,6,7-Tetramethoxy-9,10-dimethyl-[12,13]-(5',5',8',8'-tetramethyl-5',6',7',8',-tetrahydronaphthyl)triptycene (**4**)

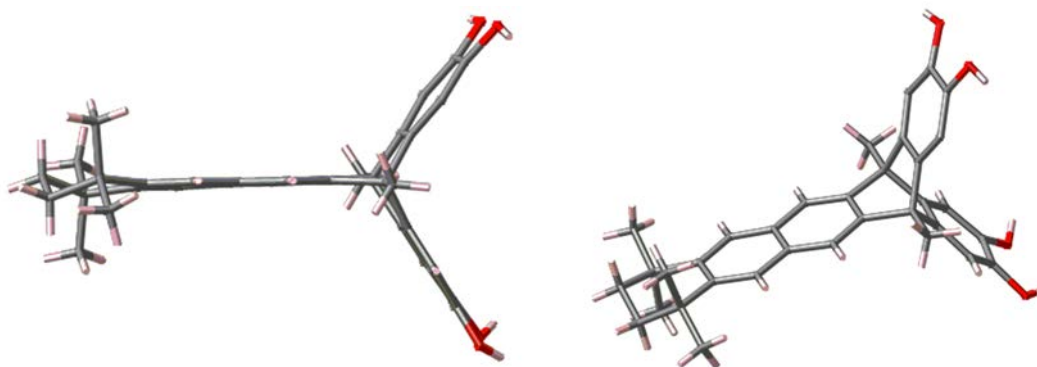


Adduct **3** (2.00 g, 3.4 mmol) was dissolved in TFA (40.0 mL) and left at room temperature for 24 h. The reaction mixture was poured into water and filtered off. The precipitate was washed with water. The crude product was purified by column chromatography (CHCl₃) to yield compound **4** (1.20 g, 62 %) as a white powder; mp: > 300 °C; $\nu_{\max}$ (cm⁻¹): 2955, 2928, 2859, 1601, 1489, 1462, 1439, 1404, 1285, 1250, 1165, 1146, 1042, 903, 868, 856, 764, 752, 633, 621, 536; ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.64 (s, 2H), 7.56 (s, 2H), 6.96 (s, 4H), 3.84 (s, 12H), 2.47 (s, 6H), 1.71 (s, 4H), 1.31 (s, 12H); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 146.1, 145.0, 143.9, 140.8, 129.5, 124.5, 117.4, 106.0, 56.4, 47.4, 35.1, 34.4, 32.5, 14.2; HRMS (EI, m/z): [M⁺] calcd. for C₃₈H₄₂O₄, 562.3077; found, 562.3068.

2,3,6,7-Tetrahydroxy-9,10-dimethyl-[12,13]-(5',5',8',8'-tetramethyl-5',6',7',8',-tetrahydronaphthyl)tritycene (Monomer TMN-Trip) (**5**)

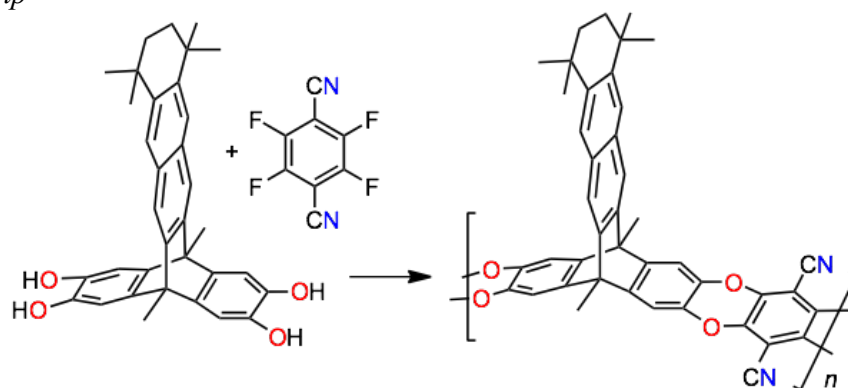


Compound **4** (1.18 g, 2.09 mmol) was dissolved in anhydrous DCM (40 mL) and cooled to 0 °C. BBr_3 (1.57 g, 6.3 mmol) was added drop-wise and the solution left at 0 °C for 0.5 h, then allowed to warm to rt for 2.5 h. The reaction mixture was poured into ice-water and the DCM allowed to evaporate. The solid was collected by filtration, washed with water and dried under N_2 to yield the desired product **5** (0.98 g, 92 %) as a white powder. mp: > 300 °C; ν_{max} (cm^{-1}): 3121, 2951, 2228, 1592, 1491, 1442, 1376, 1299, 1265, 1163, 969, 865, 763, 680; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 7.72 (s, 2H), 7.56 (s, 2H), 7.44 (s, 4H), 6.88 (s, 4H), 2.32 (s, 6H), 1.72 (s, 4H), 1.33 (s, 12H); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{CO}$) δ (ppm) 147.0, 144.1, 141.1, 130.7, 125.4, 117.8, 109.8, 47.5, 35.9, 35.0, 32.8, 14.6; HRMS (EI, m/z): $[\text{M}^+]$ calcd. for $\text{C}_{34}\text{H}_{34}\text{O}_4$, 506.2451; found, 506.2455 $[\text{M}^+]$. Crystal Data. $\text{C}_{37}\text{H}_{40}\text{O}_6$, $M_r = 580.69$, orthorhombic, $Pbca$ (No. 61), $a = 9.95710(10)$ Å, $b = 14.6854(2)$ Å, $c = 41.7722(7)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 6108.10(15)$ Å³, $T = 120.0$ K, $Z = 8$, $Z' = 1$, $\mu(\text{CuK}\alpha) = 0.678$, 114700 reflections measured, 6395 unique ($R_{\text{int}} = 0.0915$) which were used in all calculations. The final wR_2 was 0.3451 (all data) and R_1 was 0.1367 ($I > 2(I)$). The data can be obtained free of charge from the from the Cambridge Crystallographic database (CCDC) under deposition number CCDC 1495014.

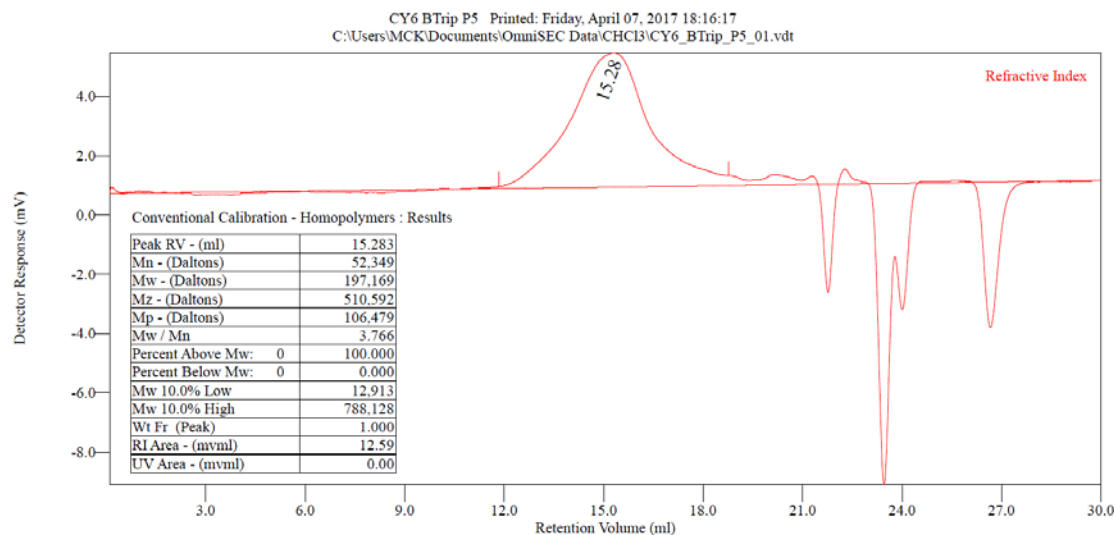


Supplementary Figure 2. Single crystal XRD structure of monomer **TMN-Trip** (**5**). Solvent has been removed for clarity.

PIM-TMN-Trip

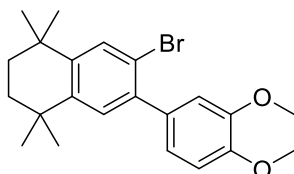


Monomer TMN-Trip **5** (2.34 g, 4.61 mmol) and tetrafluoroterephthalonitrile (0.92 g, 4.61 mmol) were dissolved in anhydrous DMF (40.0 mL). To this, anhydrous K_2CO_3 (5.09 g, 36.9 mmol) was added and the mixture heated to 65 °C for 96 h. The reaction mixture was poured into water, neutralised with dilute HCl solution and the solid collected by filtration then washed with water, acetone and methanol. The polymer was purified by repeated precipitation from $CHCl_3$ solution by dropping into a mixture of methanol: acetone (2:1). The purified polymer was collected by filtration and dried under vacuum at 100 °C to yield a yellow powder (1.95 g, 67 % based on the molecular weight of the repeated unit); ν_{max} (cm^{-1}): 2924, 2239, 1740, 1607, 1435, 1385, 1269, 1155, 1005, 905, 883, 750, 669, 538; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.66 (bs, 2H), 7.56 (bs, 2H), 6.96 (bs, 4H), 2.37 (bs, 6H), 1.82–1.10 (m, 16H); ^{13}C NMR (101 MHz, *solid state*) δ (ppm) 143.9, 138.7, 130.5, 124.7, 117.8, 109.1, 94.5, 47.6, 34.3, 12.9; BET surface area = 1034 $m^2 g^{-1}$; total pore volume = 0.87 $cm^3 g^{-1}$ at $P/P_o = 0.98$ from N_2 adsorption at 77 K; GPC ($CHCl_3$): $M_n = 52,300 g mol^{-1}$, $M_w = 197,000 g mol^{-1}$; TGA analysis (nitrogen): Initial weight loss due to thermal degradation commences at ~474 °C

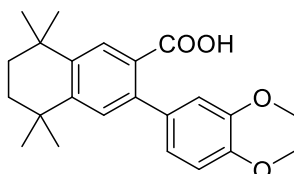


Supplementary Figure 3. GPC trace for PIM-TMN-Trip.

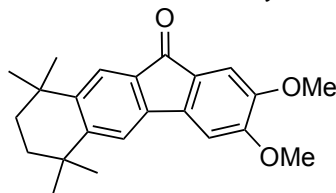
S1.4 Synthesis of PIM-TMN-SBF

6-Bromo-7-(3,4-dimethoxyphenyl)-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene (**6**)

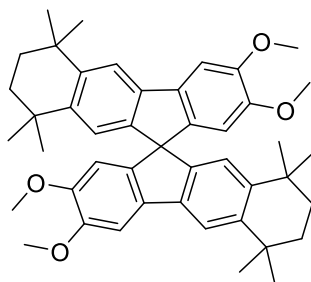
3,4-dimethoxyphenylboronic acid (4.75 g, 13.72 mmol), 6,7-dibromo-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene (2.50 g, 13.72 mmol), K_2CO_3 (5.68 g, 41.16 mmol), triphenylphosphine (0.110 g, 0.41 mmol), and $Pd(PPh_3)_4$ (0.238 g, 0.205 mmol) were added to a degassed solution of H_2O (50 ml) and THF (30 ml). The solution was heated to 80 °C and. After 36 h, the reaction mixture was allowed to reach r.t., the THF was removed under *vacuum* and the product extracted with dichloromethane (DCM). The solution was dried over anhydrous $MgSO_4$ and filtered then the solvent was evaporated under reduced pressure. The resulting solid was purified by column chromatography on silica, eluting with hexane/ethyl acetate (9/1). Further purification by recrystallization by slow evaporation of methanol afforded **6** as colourless crystals. (2.50 g, 45%); mp: 100-102 °C; ν_{max} (cm^{-1}): 2953, 1580, 1518, 1483, 1449, 1366, 1315, 1244, 1171, 1140, 1070, 1022, 854, 764; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.55 (s, 1H), 7.26 (s, 1H), 6.93 (m, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 1.70 (s, 4H), 1.32 (s, 6H), 1.29 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 148.4, 148.2, 146.1, 144.5, 139.3, 134.1, 131.0, 129.6, 121.7, 119.8, 113.2, 110.6, 56.0, 55.9, 34.9, 34.8, 34.2, 34.2, 31.8, 31.7; HRMS (EI, m/z): $[M^+]$ calcd. for $C_{22}H_{27}^{79}BrO_2$, 403.1267; found, 403.1271.

3-(3,4-Dimethoxyphenyl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (**7**)

Compound **6** (2.75 g, 6.81 mmol) was dissolved in anhydrous THF (60 mL) under inert atmosphere. A solution of butyl lithium (3.40 mL, 2.5 M in hexane, 8.52 mmol) was added at -78 °C and left under stirring for 1 hour. Dry gaseous CO_2 was bubbled through the solution for 2 hours. The reaction was quenched with ice water (50 mL) and the THF evaporated under *vacuum*. To the resulting product was added water (100 mL) and the solution carefully acidified until pH 5 and the resulting white precipitate collected under suction to afford **7** as white solid (2.05 g, 82%); mp: 228-230 °C; ν_{max} (cm^{-1}): 2959, 2924, 1692, 1670, 1514, 1493, 1441, 1263, 1246, 1175, 1136, 1030, 856, 806, 764; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 7.66 (s, 1H), 7.30 (m, 2H), 7.26 (m, 1H), 4.32 (s, 3H), 4.26 (s, 3H), 2.12 (s, 4H), 1.74 (s, 6H), 1.70 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 172.4, 149.8, 148.6, 148.5, 144.3, 140.0, 134.3, 129.7, 129.6, 126.5, 121.0, 112.5, 111.0, 56.1, 56.0, 35.00, 34.8, 34.3, 31.9, 31.8; HRMS (EI, m/z): $[M^+]$ calcd. for $C_{23}H_{29}O_4$, 369.2060; found, 369.2073.

1,2-Dimethoxy-6,6,9,9-tetramethyl-6H,7H,8H,9H,11H-cyclohexa[b]fluoren-11-one (8)

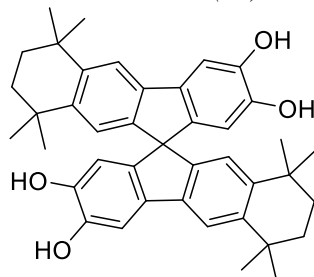
Compound **7** (2.00 g, 5.48 mmol) was dissolved into methanesulfonic acid (MeSO_3H , 20 g) and left under stirring for 3 hours. The reaction was quenched with iced water and the resulting precipitate collected under suction and recrystallized from methanol affording **8** as a yellow/orange solid. (1.77 g, 92%); mp 197–199 °C; ν_{max} (cm^{-1}): 2960, 1699, 1593, 1497, 1462, 1416, 1400, 1366, 1292, 1261, 1248, 1217, 1150, 1107, 1045, 866, 783; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.55 (s, 1H), 7.28 (s, 1H), 7.18 (s, 1H), 7.00 (s, 1H), 4.03 (s, 3H), 3.92 (s, 3H), 1.69 (s, 4H), 1.34 (s, 6H), 1.29 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 193.7, 154.7, 151.9, 149.6, 145.4, 140.9, 140.1, 132.8, 127.7, 122.9, 117.6, 107.4, 103.4, 56.5, 56.4, 35.3, 35.0, 35.0, 34.9, 31.6; HRMS (EI, m/z): $[\text{M}^+]$ calcd. for $\text{C}_{23}\text{H}_{27}\text{O}_3$, 351.1954; found, 351.1970.

2,2',3,3'-Tetramethoxy-6,6,6',6',9,9,9',9'-octamethyl-6,6',7,7',8,8',9,9'-octahydro-11,11'-spirobi[cyclohexa[b]fluorene] (9)

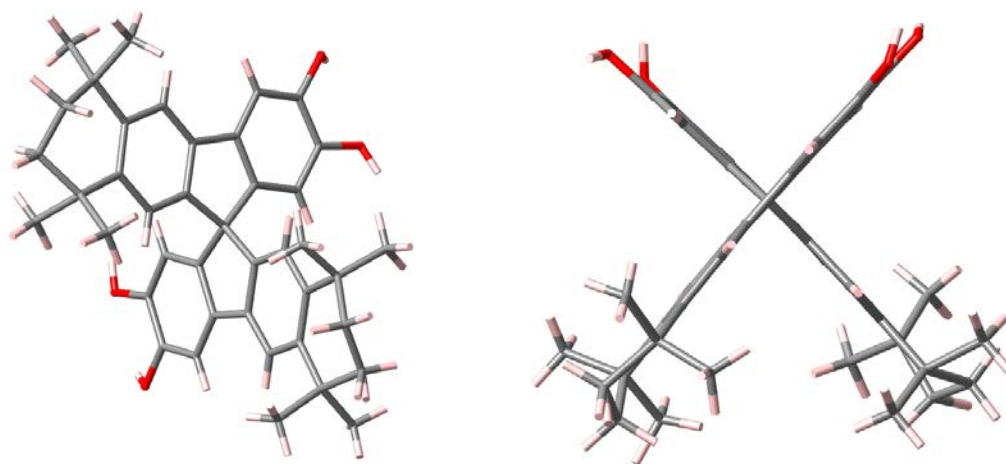
n-Butyl lithium solution in hexane (2.10 mL, 2.5 M, 5.20 g) was added drop-wise to a solution of **6** (1.94 g, 4.80 mmol) in anhydrous THF (40 mL) at -78 °C. After 1.5 hour, **8** (1.40 g, 4.00 mmol) was added to the reaction mixture, which was allowed to slowly reach r.t. and stirred for 12 hours then quenched with water. The THF was evaporated under *vacuum*, and the aqueous layer extracted with DCM. The organic extracts were washed with water, dried with anhydrous MgSO_4 , filtered and the solvent evaporated under reduced pressure. The crude pale yellow carbinol precursor was triturated in methanol then filtered to afford a white solid. The obtained solid was dissolved in cold glacial acetic acid and conc. hydrochloric acid was added drop-wise to the solution, which was then refluxed for 3h. After cooling the mixture was poured into water and the precipitate was filtered off then triturated in methanol to afford the pure product as white solid (2.15 g, 82%); mp 242–244 °C; ν_{max} (cm^{-1}): 2947, 2860, 1607, 1483, 1495, 1400, 1170, 1204, 1184, 1132, 1058, 1020, 853, 775; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.60 (s, 2H), 7.30 (s, 2H), 6.54 (s, 2H), 6.18 (s, 2H), 4.04 (s, 6H), 3.63 (s, 6H), 1.68 (m, 4H), 1.60 (m, 4H), 1.42 (s, 6H), 1.41 (s, 6H), 1.03 (s, 6H), 0.98 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 149.1, 149.0, 147.1, 143.9, 143.7, 142.3, 139.4, 134.6, 121.9, 116.3, 107.4, 102.6, 65.6, 56.3,

35.5, 35.4, 34.7, 32.4, 32.3, 32.1, 31.9; HRMS (EI, m/z): $[M]^+$ calcd. for $C_{45}H_{52}O_4$, 656.3860; found, 656.3853.

2,2',3,3'-Tetrahydroxy-6,6,6',6',9,9,9',9'-octamethyl-6,6',7,7',8,8',9,9'-octahydro-11,11'-spiro-bi[cyclohexa[b]fluorene, monomer TMN-SBF (10)

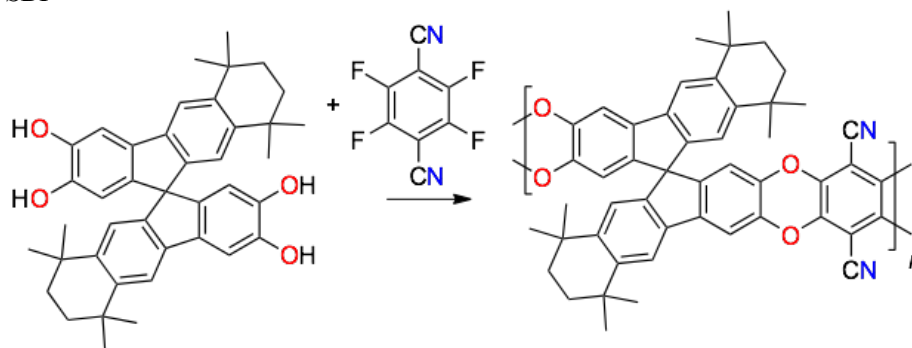


BBr_3 (2.29 mL, 9.14 mmol) and 2,2',3,3'-tetramethoxy-6,6,6',6',9,9,9',9'-octamethyl-6,6',7,7',8,8',9,9'-octahydro-11,11'-spirobi[cyclohexa[b]fluorene] (2.00 g, 3.04 mmol) in anhydrous DCM (40 mL) were reacted for 3 h at 0 °C, under N_2 atmosphere, then poured into water (50 mL). The DCM was allowed to evaporate and the white solid formed was filtered and washed with water. The isolated product was then dried under high *vacuum* to give monomer **10** as a white powder (1.74 g, 95%); mp. decomposes before melting; ν_{max} (cm^{-1}): 3547, 3373, 2961, 2922, 1603, 1483, 1402, 1325, 1292, 1269, 1152, 1099, 1047, 880, 783; ^1H NMR (500 MHz, MeOD) δ (ppm) 7.61 (s, 2H), 7.23 (s, 2H), 6.58 (s, 2H), 6.04 (s, 2H), 1.73 (m, 4H), 1.54 (m, 4H), 1.43 (s, 6H), 1.40 (s, 6H), 1.06 (s, 6H), 1.02 (s, 6H). ^{13}C (126 MHz, MeOD) δ (ppm) 148.6, 146.2, 146.2, 144.9, 144.1, 143.5, 141.2, 134.9, 122.5, 117.2, 111.6, 107.2, 66.1, 36.4, 35.5, 35.4, 32.8, 32.5, 32.4, 32.2; HRMS (EI, m/z): $[M]^+$ calcd. for $C_{41}H_{44}O_4$, 600.3234; found 600.3235. **Crystal Data.** $C_{104.015}H_{143.04}O_{13.505}$, $M_r = 1609.48$, triclinic, $P-1$ (No. 2), $a = 15.6611(4)$ Å, $b = 20.5710(5)$ Å, $c = 20.8916(5)$ Å, $\alpha = 64.217(2)^\circ$, $\beta = 68.464(2)^\circ$, $\gamma = 77.459(2)^\circ$, $V = 5624.1(3)$ Å³, $T = 120.0$ K, $Z = 2$, $Z' = 1$, $\mu(CuK\alpha) = 0.482$, 38790 reflections measured, 38790 unique ($R_{int} = 0.0$) which were used in all calculations. The final wR_2 was 0.4608 (all data) and R_1 was 0.1499 ($I > 2(I)$). The data can be obtained free of charge from the Cambridge Crystallographic database (CCDC) under deposition number CCDC 1495015.

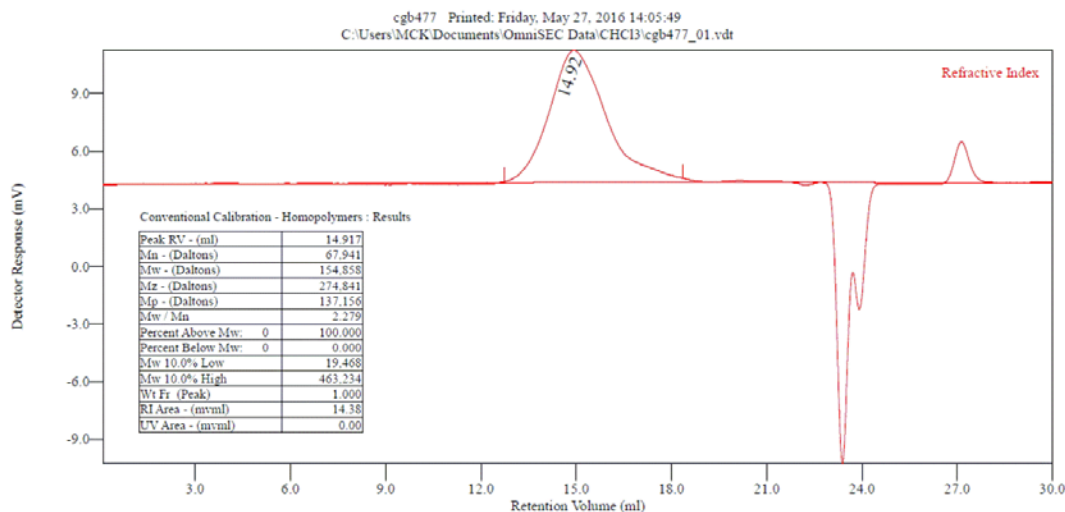


Supplementary Figure 4. Single crystal XRD structure of monomer **TMN-SBF (10)**. Solvent has been removed for clarity.

PIM-TMN-SBF

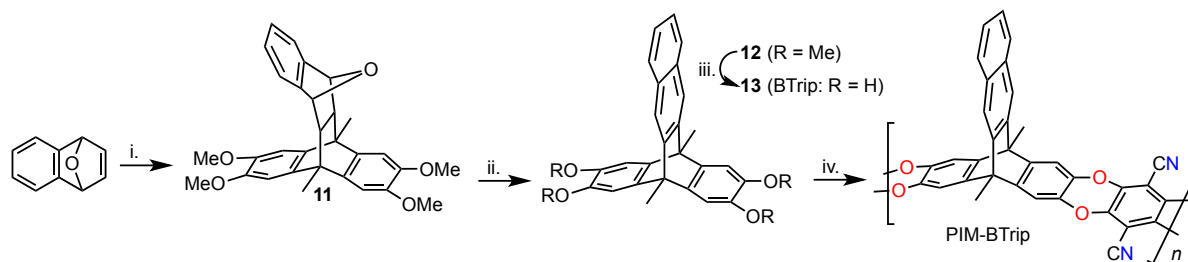


A mixture of monomer TMN-SBF **10** (1.286 g, 2.1410 mmol) and 2,3,5,6-tetrafluoroterephthalonitrile (428 mg, 2.1410 mmol) in anhydrous DMF (25 mL) was stirred under a dry nitrogen atmosphere. The mixture was heated to 30 °C and anhydrous K₂CO₃ (2.36 g, 17.13 mmol) was added. The temperature was then raised to 65 °C and the mixture stirred for 92 h. After cooling, the reaction was poured into water (150 mL), the precipitate filtered off and washed repeatedly with water and acetone and dried in a vacuum oven. The solid was purified by reprecipitation from CHCl₃ solution (60 mL), which was filtered through cotton wool then poured into a flask containing a mixture of acetone/methanol (2/1, 180 mL). The product was collected by filtration and dried under high vacuum overnight to give the final product as yellow solid (1.320 g, 85% based on the molecular weight of the repeated unit); $\nu_{\max}$ (cm⁻¹): 2959, 1445, 1400, 1364, 1263, 1171, 1144, 1010, 874, 748; ¹H NMR (500 MHz, CDCl₃) (ppm) 7.66 (br s, 1H), 7.43 (br s, 1H), 6.67 (br s, 1H), 6.32 (br m, 1H), 1.69 (br s, 4H), 1.42 (s, 6H), 1.07 (br m, 6H); ¹³C NMR (101 MHz, *solid state*) δ (ppm) 145.5, 139.4, 117.5, 108.2, 95.5, 66.0, 34.6, 31.5; BET surface area = 1013 m² g⁻¹; total pore volume = 0.93 cm³ g⁻¹ at $P/P_0 = 0.98$, from N₂ adsorption at 77 K; GPC (CHCl₃); $M_n = 68,000$ g mol⁻¹, $M_w = 154,000$ g mol⁻¹; TGA analysis (nitrogen): 1.0 % loss of weight occurred below 300 °C. Initial weight loss due to thermal degradation commences at ~465 °C.



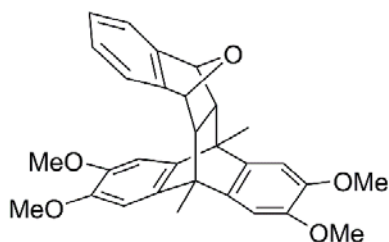
Supplementary Figure 5. GPC trace for PIM-TMN-SBF.

S1.5 Synthesis of PIM-BTrip

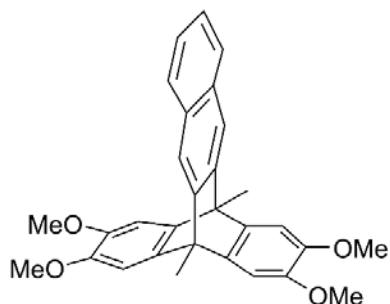


Supplementary Scheme 2. Synthesis of PIM-BTrip. *Reagents and conditions:* i. 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene, DMF, 250 °C, 7 bar, 2 h, microwave irradiation, ii. trifluoroacetic acid, rt, 24 h.; iii. BBr₃, DCM, rt, 3 h; 2,3,5,6-tetrafluorophthalonitrile, K₂CO₃, DMF, 65 °C for 96 h.

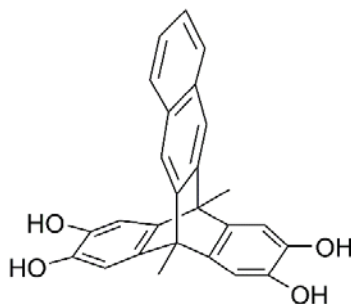
(5*s*,12*s*)-2,3,16,17-Tetramethoxy-5,12-dimethyl-5,5*a*,6,11,11*a*,12-hexahydro-5,12-[1,2]benzeno-6,11-epoxytetracene (**11**)



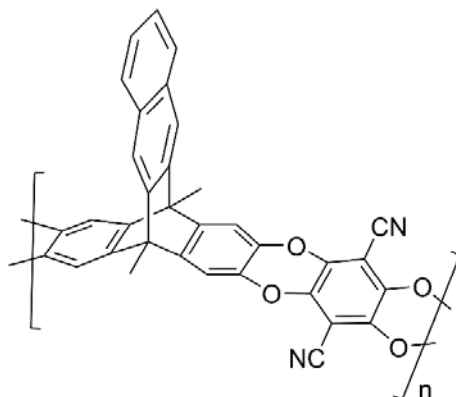
Following the general procedure reported by Swager *et al.*²⁴, 2,3,6,7-tetramethoxy-9,10-dimethylantracene (2.00 g, 6.0 mmol), prepared according to the method reported by McKeown *et al.*²⁵, and 1,4-dihydro-1,4-epoxynaphthalene (1.56 g, 6.00 mmol) were dissolved in DMF (15 mL) and heated in microwave reactor at 250 °C for 2 h at a pressure of 7 bar. The resulting solution was poured into water and the precipitate collected by filtration and washed with water. The crude product was purified by column chromatography DCM/ ethyl acetate (9:1, v/v) to yield (5*s*,12*s*)-2,3,16,17-tetramethoxy-5,12-dimethyl-5,5*a*,6,11,11*a*,12-hexahydro-5,12-[1,2]benzeno-6,11-epoxytetracene (2.38 g, 5.05 mmol, 83 %) as a light brown crystalline solid. Mp: 110–112 °C; ν_{max} (cm⁻¹): 2932, 1508, 1485, 1458, 1404, 1331, 1281, 1242, 1223, 1192, 1153, 1045, 1018, 949, 922, 841, 752, 606, 575; ¹H NMR (500 MHz, CDCl₃): δ H (ppm) = 7.13–7.10 (m, 2H, Ar *H*), 7.04–7.01 (m, 2H, Ar *H*), 6.88 (s, 2H, Ar *H*), 6.84 (s, 2H, Ar *H*), 4.99 (s, 2H, CH), 3.89 (s, 6H, CH₃), 3.83 (s, 6H, CH₃), 2.08 (s, 6H, CH₃), 2.01 (s, 2H, CH); ¹³C NMR (126 MHz, CDCl₃) δ C (ppm) = 147.1, 147.1, 146.6, 140.5, 136.9, 126.4, 118.7, 106.8, 106.2, 79.8, 77.2, 56.6, 43.2, 17.3; HRMS (EI, *m/z*): Calculated: 470.21 found: 470.2108 [M⁺].

2,3,6,7-Tetramethoxy-9,10-dimethylbenzenotriptycene (12).

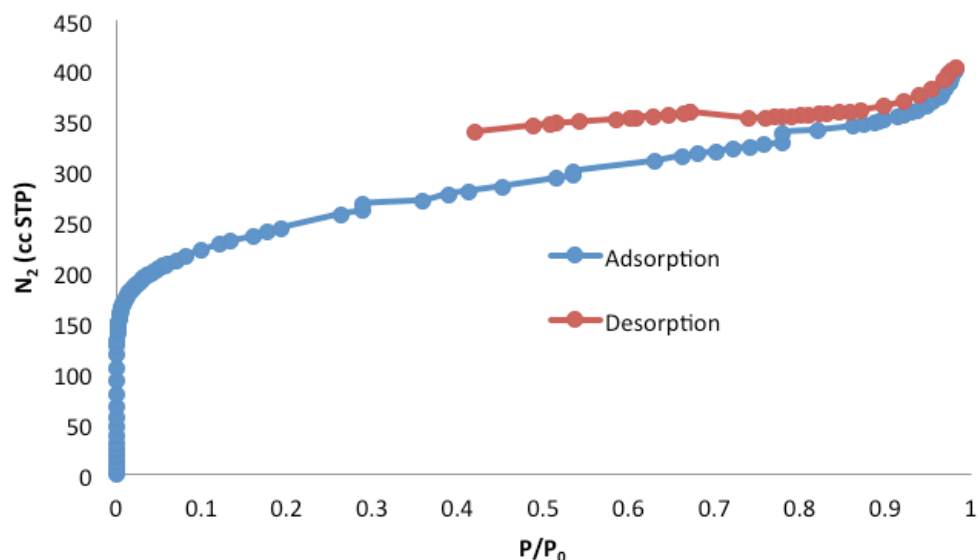
Adduct **11** (1.87 g, 4.0 mmol) was dissolved in TFA (40.0 mL) and left at room temperature for 24 h. The reaction mixture was poured into water and filtered off. The precipitate was washed with water. The crude product was purified by column chromatography DCM/ ethyl acetate (9:1, v/v) to yield 2,3,6,7-tetramethoxy-9,10-dimethylbenzenotriptycene (**12**) (1.32 g, 2.91 mmol, 73 %) as a light brown crystalline solid. Mp: 123–125°C; $\nu_{\max}$ (cm⁻¹): 2967, 2936, 1601, 1485, 1458, 1431, 1404, 1281, 1223, 1192, 1165, 1146, 1042, 1018, 945, 883, 860, 756, 617, 579; ¹H NMR (500 MHz, CDCl₃): δ H (ppm) = 7.72–7.68 (m, 2H, Ar *H*), 7.65 (s, 2H, Ar *H*), 7.38–7.34 (m, 2H, Ar *H*), 6.98 (s, 4H, Ar *H*), 3.85 (s, 12H, CH₃), 2.50 (s, 6H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ C (ppm) = 146.2, 145.9, 140.8, 131.3, 127.4, 125.7, 118.2, 106.0, 56.4, 47.5, 14.2; HRMS (EI, m/z): Calculated: 452.20 found: 452.1969 [M⁺].

2,3,6,7-Tetrahydroxy-9,10-dimethylbenzenotriptycene (13).

Compound **12** (1.32 g, 2.91 mmol) was dissolved in anhydrous DCM (40 mL) and cooled to 0 °C. BBr₃ (2.18 g, 8.74 mmol) was added drop-wise and the solution left at 0 °C for 0.5 h, then allowed to warm to rt for 2.5 h. The reaction mixture was poured into ice-water and the DCM allowed to evaporate. The solid was collected by filtration, washed with water and dried under N₂ to yield the desired product **13** (0.84 g, 2.13 mmol, 73 %) as a white powder. Mp: Above 300 °C; $\nu_{\max}$ (cm⁻¹): 3326, 2981, 1695, 1612, 1491, 1440, 1378, 1293, 1248, 1170, 983, 882, 800, 764, 665, 619; ¹H NMR (500 MHz, (CD₃)₂CO): δ H (ppm) = 7.77–7.73 (m, 2H, Ar *H*), 7.67 (s, 2H, Ar *H*), 7.48 (bs, 3H, OH), 7.37–7.33 (m, 2H, Ar *H*), 6.91 (s, 4H, Ar *H*), 2.34 (s, 6H, CH₃); ¹³C NMR (126 MHz, (CD₃)₂CO) δ C (ppm) = 148.0, 142.3, 141.0, 132.3, 128.2, 126.2, 118.5, 109.9, 47.6, 29.8, 14.6; HRMS (EI, m/z): Calculated: 396.14 found: 396.1361 [M⁺].

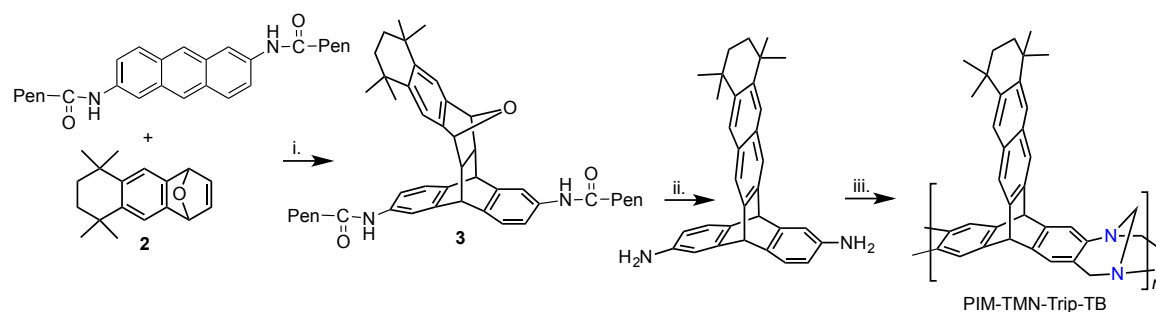
PIM-BTrip

Monomer **13** (0.84 g, 2.13 mmol) and tetrafluoroterephthalonitrile (0.43 g, 2.13 mmol) were dissolved in anhydrous DMF (15.0 mL). To this, anhydrous K_2CO_3 (2.35 g, 17.0 mmol) was added and the mixture heated to 65 °C for 96 h. The reaction mixture was poured into water, neutralised with dilute HCl solution and the solid collected by filtration then washed with water, acetone and methanol. The purified polymer was collected by filtration and dried under vacuum at 100 °C to yield a yellow powder (0.86 g, 1.66 mmol, 78 %). v_{max} (cm^{-1}): 2974, 1435, 1296, 1269, 1007, 885, 752, 582; $T_d = 436^\circ C$; BET surface area = $791\text{ m}^2\text{g}^{-1}$; pore volume = $0.61\text{ cm}^3\text{g}^{-1}$ at ($P/P_0 = 0.98$); Solid state ^{13}C NMR (100 MHz) δ_c (ppm) = 144.9, 139.9, 138.2, 131.8, 48.0, 16.4, 13.1.



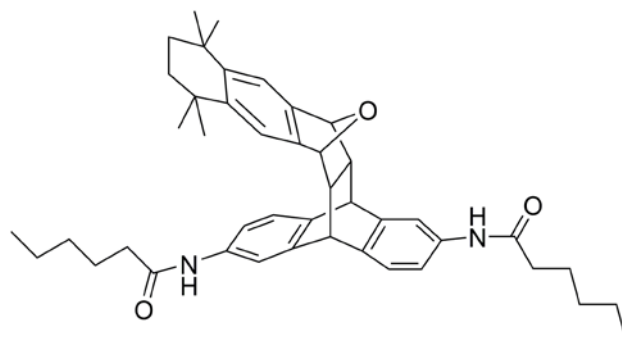
Supplementary Figure 6. The N_2 adsorption and desorption isotherms for PIM-BTrip.

S1.5 Synthesis of PIM-TMN-Trip-TB



Supplementary Scheme 3. Synthesis of PIM-TMN-Trip-TB. Reagents and conditions: i. DMF, 250 °C, 7 bar, 2 h, microwave irradiation, ii. Conc. HCl, MeOH, reflux, 24 h.; iii. Dimethoxymethane, TFA, rt, 2.5 h

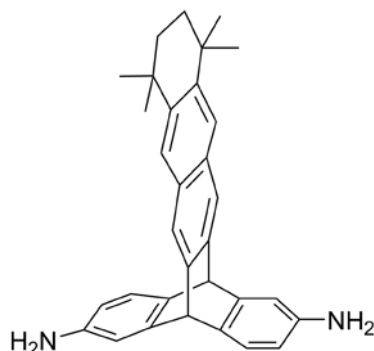
N,N'-((5*R*,14*R*)-8,8,11,11-tetramethyl-5,5*a*,6,8,9,10,11,13,13*a*,14-decahydro-5,14-[1,2]benzeno-6,13-epoxypentacene-2,18-diyl)dihexanamide (**14**)



N,N'-(anthracene-2,6-diyl)dihexanamide²⁶ (3.00 g, 7.42 mmol) and 5,5,8,8-tetramethyl-1,4,5,6,7,8-hexahydro-1,4-epoxyanthracene (**2**) (1.89 g, 7.42 mmol) were dissolved in DMF (18.0 mL) and heated to 250 °C in a microwave reactor for 2 h. After this time the solvent was removed under vacuum and the crude product washed with cold chloroform. The crude product was dissolved in hot methanol, filtered and the solvent removed under reduced pressure and then recrystallised from acetonitrile to yield **14** (2.60 g, 3.93 mmol, 53 %) as a white solid. Mp: 278–280 °C; ν_{max} (cm⁻¹): 3283, 2955, 2928, 2859, 2359, 2340, 1676, 1651, 1597, 1537, 1483, 1420, 1267, 1213, 1184, 980, 883, 860, 837, 827, 735, 586, 544; ¹H NMR (500 MHz, (CD₃)₂SO): δ_{H} (ppm) = 9.69 (s, 1H, NH), 9.68 (s, 1H, NH), 7.58 (d, 1H, *J* = 2.0 Hz, Ar *H*), 7.55 (s, 1H, Ar *H*), 7.21–7.09 (m, 6H, Ar *H*), 4.87 (s, 1H, CH), 4.86 (s, 1H, CH), 4.35 (s, 2H, CH), 2.29–2.19 (m, 4H, CH₂), 1.98 (m, 2H, CH), 1.62–1.49 (m, 8H, CH₂), 1.37–1.20 (m, 8H, CH₂), 1.17 (s, 12H, CH₃), 0.90–0.81 (m, 6H, CH₃); ¹³C NMR (126 MHz, (CD₃)₂SO) δ_{C} (ppm) = 171.4, 171.3, 145.3, 144.7, 142.8, 142.3, 139.3, 137.4, 137.2, 136.9, 124.0, 123.8, 116.9, 116.3, 116.2, 115.7, 115.4, 80.9,

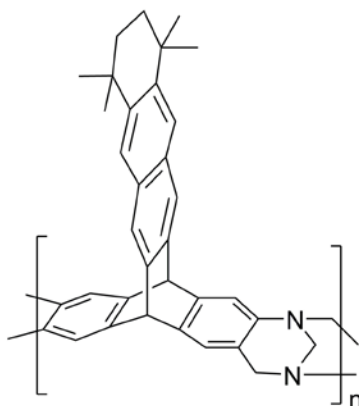
80.8, 49.8, 49.4, 46.6, 46.6, 36.9, 36.8, 35.1, 34.5, 32.4, 32.0, 31.4, 31.3, 25.4, 25.3, 22.4, 22.4, 14.3; HRMS (EI, m/z): Calculated: 658.41 found: 658.4133 [M^+].

2,6-Diamino-[12,13]-(5',5',8',8'-tetramethyl-5',6',7',8',-tetrahydronaphthyl)-tritycene (15)



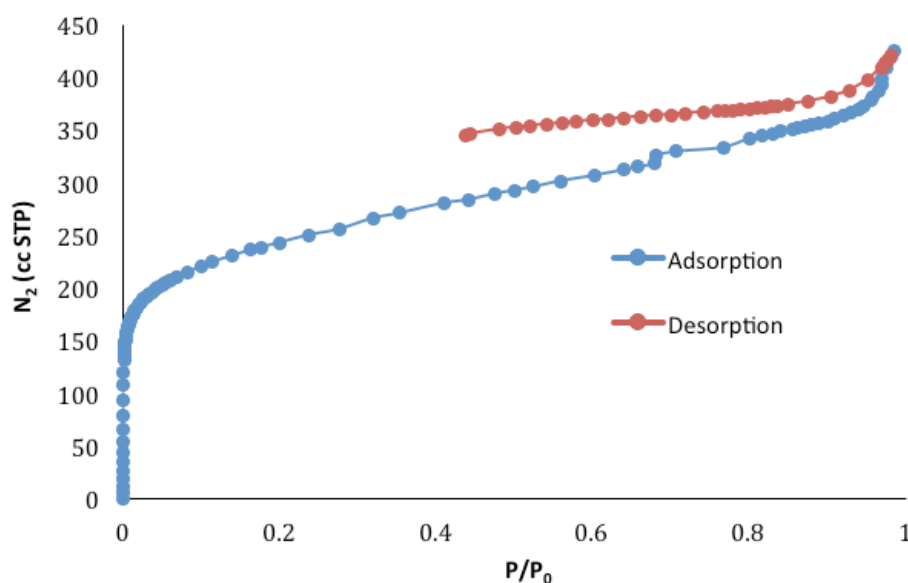
The compound **14** (1.08 g, 1.63 mmol) was dissolved in anhydrous, degassed methanol (40.0 mL) and conc. HCl (20.0 mL) was added dropwise and subsequently heated to reflux for 24 h. The resulting precipitate was filtered off and washed with water. The precipitate was suspended in water (100.0 mL), which was neutralised with ammonium hydroxide solution. The crude product was collected by filtration, washed with water and dried under N_2 to yield **13** (0.55 g, 1.22 mmol, 74 %) as an off white solid. Mp: Above 300 °C; $\nu_{\max}$ (cm^{-1}): 3298, 2951, 2928, 1661, 1595, 1533, 1477, 1458, 1410, 1265, 1190, 1109, 910, 841, 814, 748, 727, 637, 529; ^1H NMR (500 MHz, $(CD_3)_2SO$): δ_H (ppm) = 7.65 (s, 2H, Ar H), 7.60 (s, 2H, Ar H), 7.01 (d, 2H, J = 7.8 Hz, Ar H), 6.65 (d, 2H, J = 2.2 Hz, Ar H), 6.14 (dd, 2H, J = 7.8, 2.2 Hz, Ar H), 5.17 (s, 2H, CH), 4.82 (bs, 4H, NH_2), 1.67 (s, 4H, CH_2), 1.29 (s, 12H, CH_3); ^{13}C NMR (126 MHz, $(CD_3)_2SO$) δ_C (ppm) = 171.1, 146.1, 145.2, 143.4, 143.0, 142.5, 141.3, 139.1, 136.6, 129.5, 51.8, 36.3, 34.6, 34.1, 32.2, 30.8, 24.9, 21.9, 13.9; HRMS (EI, m/z): Calculated: 444.26 found: 444.2530 [M^+].

PIM-TMN-Trip-TB



Following the general procedure for the preparation of Tröger's base (TB) polymers reported by Carta et al.¹³ monomer **13** (0.55 g, 1.22 mmol), DMM (0.54 mL, 6.12 mmol) and DCM (1.5 mL) were combined. TFA (4.37 mL) was added and the reaction mixture was left to stir at room temperature for 2.5 h. The resulting viscous yellow mixture was poured into aqueous ammonium hydroxide solution and stirred vigorously for 2 h. The solid was collected by filtration, washed

with water and then acetone. The resulting powder was dissolved in chloroform and reprecipitated from methanol. This reprecipitation procedure from chloroform was repeated twice to provide PIM-TMN-Trip-TB as a pale yellow powder (0.24 g, 0.49 mmol, 40 %). $v_{\max}$ (cm^{-1}): 2955, 1464, 1437, 1418, 1362, 1339, 1213, 1184, 1107, 1078, 1032, 1022, 935, 903, 615, 604, 534; BET surface area = $847 \text{ m}^2\text{g}^{-1}$; pore volume = $0.63 \text{ cm}^3\text{g}^{-1}$ at ($P/P_0 = 0.98$); ^1H NMR (500 MHz, CDCl_3) δ 7.61-7.16 (m, 4H, Ar *H*), 7.04-6.83 (m, 2H, Ar *H*), 6.81-6.57 (m, 2H, Ar *H*), 5.24-4.92 (m, 2H, CH), 4.42 (bs, 2H, CH_2), 4.15-3.59 (m, 4H, CH_2), 1.58 (bs, 4H, CH_2), 1.43-0.83 (m, 12H, CH_3); ^{13}C NMR (126 MHz, CDCl_3) δ_c (ppm) = 145.0, 143.4, 140.5, 139.8, 130.0, 124.5, 121.8, 120.4, 58.5, 52.6, 35.2, 34.3, 32.5.



Supplementary Figure 7. The N_2 adsorption and desorption isotherms for PIM-TMN-Trip-TB.

S2. Computational Models and Method

S2.1 Molecular Models

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was used to conduct all Molecular dynamics (MD) simulations.²⁹ The generalized amber force field (GAFF)³⁰ bonded parameters combined with the transferable potential for phase equilibria (TraPPE)^{31–36} non-bonded Lennard-Jones parameters (with cutoff = 15 Å, and cross-interaction LJ parameters with the Lorentz–Berthelot combining rules) were used to model both PIM-TMN-Trip and PIM-TMN-SBI polymer frameworks. The partial charges of both PIM-TMN-Trip and PIM-TMN-SBI were obtained through *ab initio* calculations using HF/6–31G* level of theory combined with the restrained electrostatic potential (RESP) charge fitting procedure.^{37,38} Gaussian 03 (M. Frisch *et al.*, revision C. 02.; 2008) was used to conduct all *ab initio* calculations. For MD simulations, long-range electrostatics were calculated using the particle-particle particle-mesh solver.³⁹ The velocity–Verlet algorithm was employed for all MD simulations with a time step of 1 fs. To calculate the mean and standard deviations of the molecular simulations, eight independently generated samples starting from different configurations were used. The modeling consists of periodic cubic simulation boxes with a box length of at least of 8.5 nm in order to minimize possible finite-size effects.

PIM-TMN-Trip and PIM-TMN-SBI polymer frameworks were constructed using the Polymatic simulated polymerization algorithm⁴⁰ and the ‘21-step’ compression/decompression scheme.⁴¹ The polymatic simulated polymerization algorithm involves virtual polymerization through artificially bonding adjacent chemical repeat units together in cycles along with molecular dynamics simulations to form long polymer chains. First, 500 repeat monomers of PIM-TMN-Trip or PIM-TMN-SBI (see Fig. 1A and Fig. 1D) were randomly packed into a simulation box under periodic boundary conditions at a low arbitrary density of 0.3–0.4 g/cm³ following polymerization via Polymatic. In order to obtain the final simulation box at relevant experimental conditions, the ‘21-step’ compression/decompression scheme was used.⁴¹ During the polymerization steps, additional charges on ‘reactive atoms’ ($q_{\text{polym}} = \pm 0.5e$) were used to accelerate the polymerization process. During polymerization, ‘reactive atoms’ on neighboring monomers within a cutoff distance of 6 Å or less were bonded together.⁴⁰ The polymerization of neighboring monomers was carried out until no more bonds could be found within the specified cutoff distance for at least 500 ps following the compression/decompression scheme where $T_{\text{max}} = 1000$ K, $P_{\text{max}} = 5 \times 10^4$ atm, $T_{\text{final}} = 300$ K, and $P_{\text{final}} = 1$ atm were employed according to previous work.⁴¹

S2.2 Gas Adsorption

Unary gas adsorption of CH₄, CO₂, N₂, H₂, O₂, and He on PIM-TMN-Trip and PIM-TMN-SBI frameworks were conducted using the Cassandra Monte Carlo (MC) simulation software.⁴² Gas molecules were modeled using previously parameterized force field parameters.^{33,43–46}

The isobaric-isothermal (*NPT*) version of the Gibbs Ensemble Monte Carlo simulation (*NPT-GEMC*)^{47,48} technique was used for gas adsorption simulations where total number of particles, pressure, and temperature are kept constant while allowing the volume of the ‘gas box’ to fluctuate. During MC simulations, gas molecules were allowed to translate, rotate and swap between simulation boxes while PIM-TMN-Trip and PIM-TMN-SBI frameworks were held

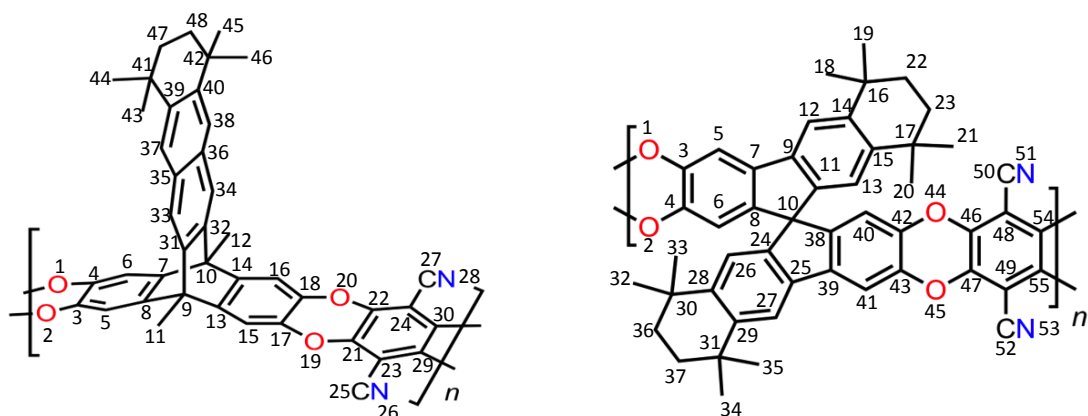
rigid. The MC simulations consist of at least 1.5×10^7 MC steps where the last 1×10^7 MC steps were considered a production run and were used to calculate the mean and standard deviation of simulations.

S2.3 Structure Characterization

The total free volume (V_f) and pore size distributions (PSDs) of either PIM-TMN-Trip or PIM-TMN-SBI frameworks were calculated using the Poreblazer software.⁴⁹ The V_f was measured using a probe size of 0.0 Å in combination with the van der Waals radius of the atoms in the PIM-TMN-Trip or PIM-TMN-SBI frameworks. The geometric surface area (SA_{geo}) was calculated by measuring the accessible surface area between the polymer framework and a spherical probe with a size of 3.681 Å (similar to a N₂ molecule). Fractional free volume (FFV) of the frameworks were calculated using where $V_{\text{sp}} (1/\rho_{\text{bulk}})$ is the specific volume of the polymer framework. The surface area of both PIM-TMN-Trip or PIM-TMN-SBI frameworks were calculated according to BET theory⁵⁰ applied to N₂ adsorption isotherm at 77 K according to Hart *et al.*⁵¹

S2.4 Permselectivity and Permeability Estimation

Similar to previous simulation work done by Hart *et al.*⁵², the permeability of gas molecules were estimated using the solution-diffusion model, where P_i , D_i , and S_i are permeability, diffusivity, and solubility of gas i inside PIM-TMN-Trip or PIM-TMN-SBI frameworks. Gas diffusivity was estimated using the empirical correlation presented by Thornton *et al.*⁵³, where the authors have presented a correlation between diffusivity and fractional free volume using a wide range of polymers. PIM-1 was included in the correlation, though it is the only PIM included. The D_i was calculated using the following relationship, where c_i is the gas concentration inside the PIM-TMN-Trip or PIM-TMN-SBI framework.⁵⁴ S_i was calculated using the amount of either CH₄, CO₂, N₂, H₂, O₂, or He adsorbed in each polymer framework (at 298 K and 1 bar by GEMC simulations).



Supplementary Figure 8. Chemical structures of PIM-TMN-Trip and PIM-TMN-SBI. Numbers of each atom is consistent with Supplemental Table 2.

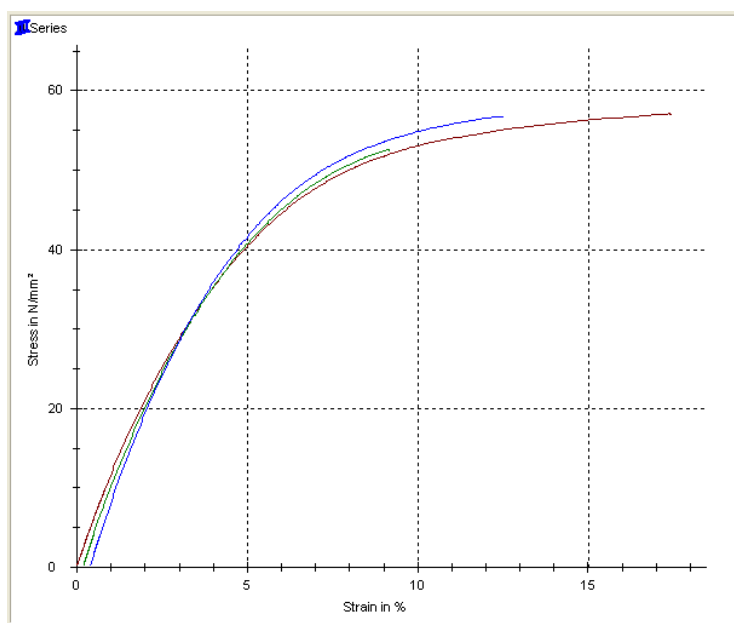
Atom Number	PIM-TMN-Trip Charge	PIM-TMN-Trip Atom Type	PIM-TMN-SBI Charge	PIM-TMN-SBI Atom Type
1	-0.188560	os	-0.21837	os
2	-0.188560	os	-0.24435	os
3	0.119969	ca	0.17065	ca
4	0.119969	ca	0.23127	ca
5	-0.102152	ca	-0.14539	ca
6	-0.102152	ca	-0.11171	ca
7	-0.053558	ca	0.03112	ca
8	-0.053558	ca	0.05689	ca
9	0.249604	c3	0.06517	ca
10	0.249604	c3	0.14826	c3
11	0.192694	c3	0.05605	ca
12	0.192694	c3	-0.11573	ca
13	-0.093586	ca	-0.13226	ca
14	-0.093586	ca	0.00425	ca
15	-0.007267	ca	0.02135	ca
16	-0.007267	ca	0.24905	c3

17	0.144555	ca	0.24538	c3
18	0.144555	ca	-0.07062	c3
19	-0.188560	os	-0.08106	c3
20	-0.188560	os	-0.08483	c3
21	0.056121	ca	-0.06759	c3
22	0.056128	ca	-0.02525	c3
23	-0.046310	ca	-0.03454	c3
24	-0.046310	ca	0.05605	ca
25	0.344786	c1	0.06517	ca
26	-0.453924	n1	-0.13226	ca
27	0.344786	c1	-0.11573	ca
28	-0.453924	n1	0.02135	ca
29	0.040298	ca	0.00425	ca
30	0.040298	ca	0.24538	c3
31	-0.019501	ca	0.24905	c3
32	-0.019501	ca	-0.08782	c3
33	-0.079611	ca	-0.06592	c3
34	-0.079610	ca	-0.06876	c3
35	0.132798	ca	-0.08066	c3
36	0.132798	ca	-0.03476	c3
37	-0.178446	ca	-0.02577	c3
38	-0.178446	ca	0.05689	ca
39	0.031659	ca	0.03112	ca
40	0.031659	ca	-0.14539	ca
41	0.196232	c3	-0.11171	ca
42	0.196232	c3	0.23127	ca
43	-0.045562	c3	0.17065	ca

44	-0.045562	c3	-0.21837	os
45	-0.045562	c3	-0.24435	os
46	-0.045562	c3	0.16531	ca
47	-0.006121	c3	0.16254	ca
48	-0.006121	c3	-0.10476	ca
49			-0.10476	ca
50			0.31248	c1
51			-0.40929	n1
52			0.31248	c1
53			-0.40929	n1
54			0.16531	ca
55			0.16254	ca

Supplementary Table 2. Atom information of PIM-TMN-Trip and PIM-TMN-SBI. Numbers of each atom is consistent with Supplemental Figure 8.

S3. Physical Characterization



Supplementary Figure 9. Stress/strain curves of three MeOH treated PIM-TMN-Trip samples after thermal conditioning at 140°C.

S3.1 Pure gas permeation

Pure gas permeation experiments were carried out on a custom made fixed-volume/pressure increase instrument constructed by Elektro & Elektronik Service Reuter (Geesthacht, Germany), equipped with a turbomolecular pump and a membrane-backing pump. In standard experiments, the feed gas pressure was regulated at 1 bar (the actual value was read with a resolution of 0.1 mbar); the permeate pressure was measured in the range from 0 to 13.3 mbar (maximum), with a resolution of 0.0001 mbar. The gases were generally tested in the same order (H_2 , He, O_2 , N_2 , CH_4 , and CO_2). Nevertheless, it was verified by repeating a measurement cycle, that the measurement order for these materials was irrelevant at a feed pressure of 1 bar, provided that sufficiently long vacuum was applied to completely remove the previous gas.

Feed pressure, permeate pressure, and temperature were continuously recorded during each measurement run. The temperature was controlled at a constant temperature of 25 ± 1 °C. Before the first measurement, the membrane was evacuated for sufficient time inside the cell (at least 1 h). Between two subsequent measurements, the system was evacuated for a period of at least ten times the time lag of the previous species in order to guarantee the complete removal of the previous gas. In repeated cycles, changes between the first and second cycle were generally much less than 5%. Circular membranes, with an effective exposed surface area of 2.14 cm^2 were used.

S3.1.1 Data fitting

The pressure increase on the permeate side was recorded as a function of time from the moment that the membrane was exposed to the feed gas. The whole permeation curve takes the following form.⁵⁵

$$p_t = p_0 + (d_p/d_t)_0 \cdot t + \frac{RT \cdot A \cdot \ell}{V_p \cdot V_m} \cdot p_f \cdot S \left(\frac{D \cdot t}{\ell^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D \cdot n^2 \cdot \pi^2 \cdot t}{\ell^2}\right) \right) \quad \text{Eq.1}$$

in which p_t is the permeate pressure at time t and p_0 is the starting pressure, typically less than 0.002 mbar. The baseline slope $(d_p/d_t)_0$ is usually negligible for a defect-free membrane after sufficient evacuation. R is the universal gas constant, T is the absolute temperature, A is the exposed membrane area, V_p is the permeate volume, V_m is the molar volume of a gas in standard conditions (0 °C and 1 atm), p_f is the feed pressure, S is the gas solubility, D the gas diffusion coefficient, and ℓ is the membrane thickness. The time lag method was applied to the recorded data to determine the gas diffusion coefficient.⁵⁶

The permeability coefficient, P , is calculated from the following equation, describing the steady state permeation:

$$P_t = P_0 + (dp/dt)_0 \cdot t + \frac{RT \cdot A}{V_p \cdot V_m} \cdot \frac{p_f \cdot P}{\ell} \left(t - \frac{\ell^2}{6D} \right) \quad \text{Eq.2}$$

the last term in Equation (2) corrects for the so-called permeation time lag, Θ , which is inversely proportional to the diffusion coefficient of the gas:

$$\Theta = \frac{\ell^2}{6D} \quad \text{Eq.3}$$

the approximate gas solubility coefficient, S , was obtained indirectly as the ratio of the permeability to the diffusion coefficient by assuming the solution-diffusion transport mechanism:

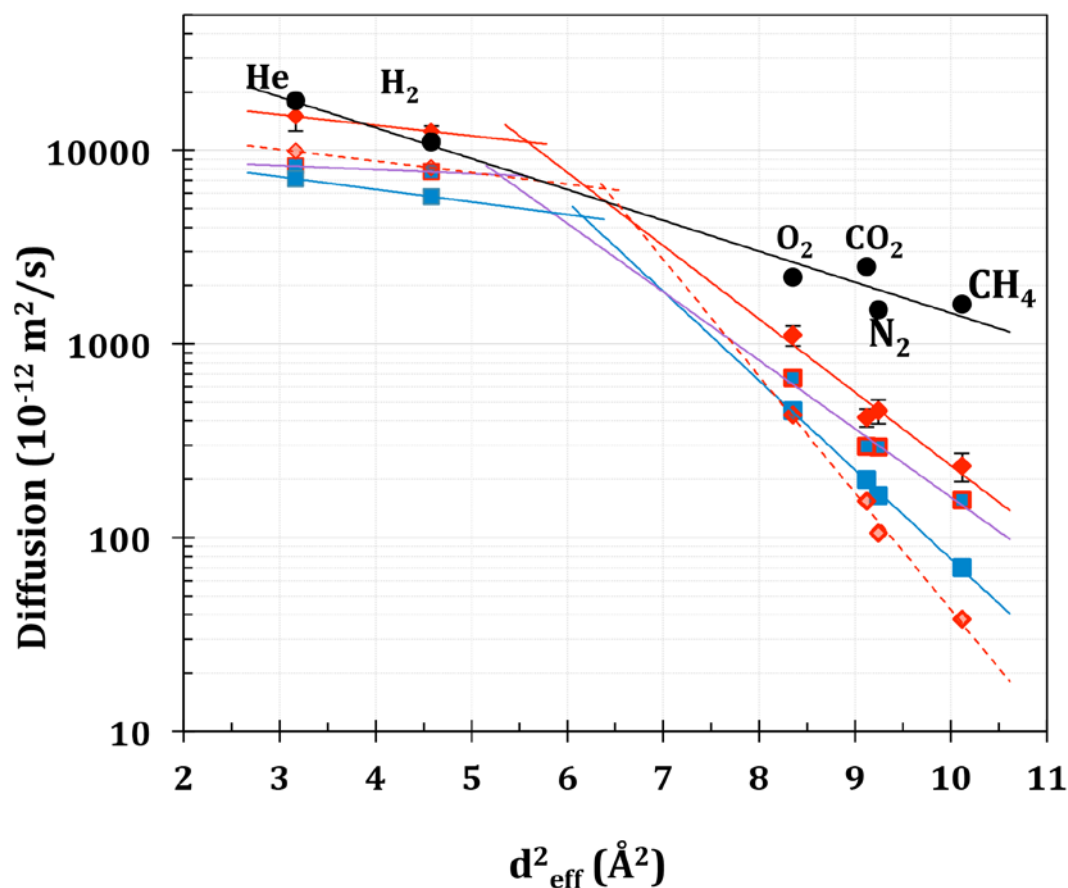
$$S = P / D \quad \text{Eq.4}$$

Permeabilities are reported in Barrer [$1 \text{ Barrer} = 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$].

Supplementary Table 3. Gas Diffusion Coefficients (D_x , 10^{-12} m²/s) and selectivities (D_x/D_{N_2}) for PIM-TMN-Trip, PIM-TMN-SBI and PIM-TMN-Trip-TB measured from films with different processing histories.

Polymer	Film history	D_{He} (D_{He}/D_{N_2})	D_{H_2} (D_{H_2}/D_{N_2})	D_{O_2} (D_{O_2}/D_{N_2})	D_{CO_2} (D_{CO_2}/D_{N_2})	D_{N_2}	D_{CH_4} (D_{CH_4}/D_{N_2})
PIM-TMN-Trip	1	16092 (28.1)	13931 (24.3)	1160 (2.03)	421 (0.74)	572	325 (0.57)
	2	12532 (40.0)	10971 (35.0)	934 (2.98)	351 (1.12)	313	159 (0.51)
	3	12299 (44.2)	11517 (41.4)	882 (3.17)	357 (1.28)	278	114 (0.41)
	4	9869 (94.0)	8131 (77.4)	430 (4.1)	154 (1.47)	105	37.7 (0.36)
	5	16900 (32.1)	14746 (28.0)	1355 (2.58)	497 (0.95)	526	297 (0.57)
	6	12521 ±827 (33.3 ±4.54)	14952 ±2385 (28.0 ±2.98)	1108 ±133 (2.46 ±0.09)	417 ±45 (0.92 ±0.04)	451 ±64	233 ±39 (0.51 ±0.01)
PIM-TMN-SBI	8	8280 (28.3)	7740 (26.4)	665 (2.27)	295 (1.00)	295	160 (0.53)
	9	4350 (73.7)	3060 (51.8)	150 (2.54)	72.9 (1.23)	59	25.5 (0.43)
PIM-TMN-Trip-TB	10	8680 (177)	5510 (112)	266 (5.43)	68.5 (1.4)	48.9	14.8 (0.30)

1. Methanol treated 195 μ m thick film; 2. Methanol treated 192 μ m thick film aged 39 days; 3. Methanol treated 193 μ m thick film heated at 120 °C for 24 h then aged for 14 days; 4. Aged film 187 μ m thick film heated at 120 °C for 24 h then aged for 365 days; 5. Aged 195 μ m thick film after second methanol treatment; 6. Average values $\pm$ standard deviation of 4 samples: methanol treated 156 $\pm$ 5 μ m thick films and subsequently heated at 140 °C for 4 h; 8. Methanol treated 166 μ m thick film, 9. Methanol treated 110 μ m thick film heated at 120 °C for 24 h then aged for 14 days. 10. Methanol treated 125 μ m thick film of PIM-TMN-Trip-TB, for which the molecular structure is shown in Supplementary Fig. 1.



Supplementary Figure 10. Size-dependence of the diffusion coefficient for methanol treated films of PTMSP (black)²⁷, methanol treated 150 μm thick film heated at 140 $^{\circ}\text{C}$ for 4h of PIM-TMN-Trip (red and error bars, lightly shaded is data for 365 day aged film), PIM-TMN-SBI and PIM-1, based on the effective gas diameter defined by Teplyakov.²⁸ The single gently sloped correlation for PTMSP is consistent with its larger pore size relative to PIMs (Fig. 2c). For PIMs, especially aged PIM-TMN-Trip, the steeper gradient for the larger gases indicates size-sieving consistent with smaller micropores (Fig. 2c). Note that for He and H₂ all PIMs generally show a different correlation related to a lower size-selectivity for small species.

Supplementary Table 4. Gas permeability values (P_x , Barrers) and ideal selectivities (P_x/P_{N_2}) for PIM-TMN-Trip measured from methanol treated 156 ± 5 μ m thick film heated at 140 °C for 4h (data used to give point 6 in Table 1 and Fig. 3).

Polymer	Film	P_{He} (P_{He}/P_{N_2})	P_{H_2} (P_{H_2}/P_{N_2})	P_{O_2} (P_{O_2}/P_{N_2})	P_{CO_2} (P_{CO_2}/P_{N_2})	P_{N_2}	P_{CH_4} (P_{CH_4}/P_{N_2})
PIM-TMN-Trip	1	6000 (2.44)	16600 (6.76)	7990 (3.24)	40700 (16.5)	2460	4490 (1.12)
	2	6040 (2.35)	16700 (6.48)	8040 (3.12)	41300 (16.0)	2570	4750 (1.85)
	3	5430 (2.53)	15100 (7.02)	7000 (3.27)	35600 (16.6)	2140	3840 (1.79)
	4	5420 (2.48)	15000 (6.88)	7060 (3.23)	36100 (16.6)	2180	3840 (1.76)
Average $P \pm \sigma$		5720 ± 343 (2.45 ± 0.08)	15800 ± 942 (6.79 ± 0.23)	7520 ± 573 (3.22 ± 0.06)	38400 ± 2980 (16.4 ± 0.27)	2340 ± 211	4230 ± 464 (1.81 ± 0.04)

Supplementary Table 5. Ideal Permselectivities $\pm$ standard deviation (σ) for PIM-TMN-Trip measured from methanol treated 156 ± 5 μ m thick film heated at 140 °C for 4h.

x/y	P_x/P_y	$\sigma P_x/P_y$
CO ₂ /O ₂	5.11	0.02
CO ₂ /CH ₄	9.11	0.31
H ₂ /CO ₂	0.41	0.008
He/CO ₂	0.15	0.002
He/H ₂	0.36	0.001
H ₂ /CH ₄	3.76	0.19
He/CH ₄	1.36	0.07
N ₂ /CH ₄	0.55	0.01
He/O ₂	0.76	0.01
H ₂ /O ₂	2.11	0.04

Supplementary Table 6. Gas Diffusion Coefficients (D_x , 10^{-10} m²/s) and selectivities (D_x/D_{N_2}) for PIM-TMN-Trip measured from methanol treated 156 ± 5 μ m thick film heated at 140 °C for 4h.

Polymer	Film	D_{He} (D_{He}/D_{N_2})	D_{H_2} (D_{H_2}/D_{N_2})	D_{O_2} (D_{O_2}/D_{N_2})	D_{CO_2} (D_{CO_2}/D_{N_2})	D_{N_2}	D_{CH_4} (D_{CH_4}/D_{N_2})
PIM-TMN-Trip	1	176 (32.2)	136 (24.8)	12.9 (2.36)	4.79 (0.88)	5.45	2.89 (0.53)
	2	121 (27.6)	116 (26.5)	11.3 (2.58)	4.21 (0.96)	4.38	2.30 (0.52)
	3	161 (38.4)	122 (29.1)	10.2 (2.43)	3.88 (0.92)	4.19	2.13 (0.51)
	4	140 (34.9)	127 (31.6)	9.96 (2.47)	3.81 (0.95)	4.03	2.01 (0.50)
Average D $\pm$ σ		150 $\pm$ 24 (33.3 $\pm$ 4.54)	125 $\pm$ 8 (28.0 $\pm$ 2.98)	11.1 $\pm$ 1.3 (2.46 $\pm$ 0.09)	4.17 $\pm$ 0.45 (0.92 $\pm$ 0.04)	4.51 $\pm$ 0.64	2.33 $\pm$ 0.39 (0.51 $\pm$ 0.01)

Supplementary Table 7. Ideal selectivities for diffusivity $\pm \sigma$ for PIM-TMN-Trip measured from methanol treated 150 μ m thick film heated at 140 °C for 4h.

x/y	D_x/D_y	$\sigma D_x/D_y$
CO ₂ /O ₂	0.38	0.01
CO ₂ /CH ₄	1.80	0.10
H ₂ /CO ₂	30.2	2.7
He/CO ₂	34.1	4.6
He/H ₂	1.19	0.14
H ₂ /CH ₄	54.5	7.3
He/CH ₄	64.8	10.1
N ₂ /CH ₄	1.94	0.05
He/O ₂	13.6	2.1
H ₂ /O ₂	11.4	1.2

Supplementary Table 8. Time-lag (Θ)(s) for PIM-TMN-Trip, PIM-TMN-SBI and PIM-TMN-Trip-TB measured from films with different processing histories.

Polymer	Film history	l (μm)	Θ_{He}	Θ_{H_2}	Θ_{O_2}	Θ_{CO_2}	Θ_{N_2}	Θ_{CH_4}
PIM-TMN-Trip	1	195	0.39	0.45	5.46	15.1	11.1	19.5
	2	192	0.49	0.56	6.55	17.4	19.5	38.5
	3	193	0.50	0.54	7.04	17.4	22.3	54.5
	4	187	0.59	0.72	13.5	37.7	55.5	155
	5	195	0.38	0.43	4.68	12.7	12.0	21.3
	6a	152	0.22	0.28	2.99	8.03	7.05	13.3
	6b	151	0.31	0.33	3.37	9.06	8.7	16.6
	6c	154	0.25	0.32	3.90	10.2	9.47	18.6
	6d	161	0.31	0.34	4.33	11.3	10.7	21.5
PIM-TMN-SBI	8	166	0.55	0.60	6.90	15.6	15.7	29.3
	9	110	0.46	0.66	13.5	27.7	34.2	79.2
PIM-TMN-Trip-TB	10	125	0.30	0.47	9.81	66.6	53.3	176

1. Methanol treated 195 μm thick film; 2. Methanol treated 192 μm thick film aged 39 days; 3. Methanol treated 193 μm thick film heated at 120 $^{\circ}\text{C}$ for 24 h then aged for 14 days; 4. Aged film 187 μm thick film heated at 120 $^{\circ}\text{C}$ for 24 h then aged for 365 days; 5. Aged 195 μm thick film after second methanol treatment; 6. Average values $\pm$ standard deviation of 4 samples: methanol treated 156 ± 5 μm thick films and subsequently heated at 140 $^{\circ}\text{C}$ for 4 h; 8. Methanol treated 166 μm thick film, 9. Methanol treated 110 μm thick film heated at 120 $^{\circ}\text{C}$ for 24 h then aged for 14 days. 10. Methanol treated 125 μm thick film of PIM-TMN-Trip-TB, for which the molecular structure is shown in Supplementary Fig. 1.

S3.6 High temperature permeability measurements.

The permeability of pure gases at high temperature was measured using the constant volume-variable pressure method in a purpose built cell. Helium, hydrogen and carbon dioxide were tested at 25°C and CO₂ and H₂ were also tested at higher temperature (up to 120 °C) for potential pre-combustion carbon capture applications. Prior the measurement, all the sample were freshly treated in MeOH and dried over night at 120 °C in a vacuum oven. The sample was then mounted in the permeation cell and completely evacuated before the measurement. After exposing the feed side of the membrane to the pure gas, the increase in pressure on the permeate side was recorded over time with a pressure transducer (MKS Baratron 615); knowing the volume of the downstream chamber the permeability can be calculated from the increment in pressure.

S3.7 Mixed gas permeation

Single gases were supplied by Pirossigeno at a minimum purity of 99.9995%. Certified gas mixtures were supplied by Sapio at a purity of $\pm 0.01\%$ from the certified concentration (CO₂/CH₄ mixture with 47.89 mol.% CH₄ and N₂/CO₂/O₂ mixture with 10.10 mol.% CO₂ and 10.02 mol.% O₂), or the mixtures were prepared in-line by calibrated mass flow controllers (Bronkhorst).

Mixed gas permeation experiments were carried out on a custom made constant pressure / variable volume instrument, equipped with a modified Millipore permeation cell (diameter 47 mm). The experiments were carried out at a feed flow rate of 100-200 cm³ min⁻¹ and a feed pressure of 0-5 bar(g), using EL-FLOW electronic Mass Flow Controllers (Bronkhorst) in the feed line and a EL-PRESS electronic back pressure controller in the retentate line. Argon (30 cm³ min⁻¹) was used as the sweeping gas at ambient pressure. The actual temperature and pressure were recorded to convert the measured flow rates to standard temperature and pressure conditions (STP, 1 atm at 0°C). Highly permeable samples were masked with an adhesive aluminium tape with a smaller aperture to limit the total permeate flow rate and to keep the stage cut close to or below 1%.

The permeate composition was determined with a Mass Spectrometric device equipped with a quadrupole mass filter (Hiden Analytical, HPR-20 QIC Benchtop residual gas analysis system, max. 200 AMU) and a sampling capillary with a typical flow rate of ca. 10-20 cm³ min⁻¹ at ambient pressure, depending on the gas sampled. The electron ionization energy was 70 eV and the gases were detected with the SEM ion detector. Nitrogen was detected at 14 AMU to avoid overlap of N₂ with the CO fragments from CO₂ at 28 AMU in CO₂/N₂ mixtures; methane was detected at 15 AMU (as CH₃) to avoid overlap of the molecular CH₄ peak with the O fragment from CO₂ at 16 AMU in the case of CO₂/CH₄ mixtures. All sensitivity ratios were previously calibrated against the weaker ³⁶Ar isotope at 36 AMU (ca. 0.3% abundancy). During the permeation experiments, this signal was used as the internal standard for calculation of the gas concentrations in the sweep/permeate.

Before each analysis, the membrane was flushed for at least 1 hour at both sides with two independent argon streams until the MS signal was sufficiently stable. Subsequently, two experiments were carried out. In the first experiment, the argon flux at the feed side was replaced by the pure gas or gas mixture at atmospheric pressure (absolute pressure 1 bar(a)) to determine the time needed to reach steady state permeation. In the second experiment, the feed pressure was stepwise changed from 1-5 bar(g) and back, with sufficiently long time intervals

to reach steady state permeation in each step. The background signals were determined just before switching from argon to the gas or gas mixture at the feed side, and were subtracted from the measured signal during data processing.

S.3.7.1 Data fitting

All measured data were recored with the MASsoft software package supplied with the mass spectrometer and with the FlowPlot software supplied with the pressure and mass flow controllers. The measured data were processed by self-written elaboration program, taking good care to synchronize the two sources of data.

The mixed gas selectivity, $\alpha_{i/j}$ was evaluated as the ratio of the individually calculated gas permeances (Π_i) in the mixture:

$$\alpha_{\text{CO}_2/\text{N}_2} = \frac{\Pi_{\text{CO}_2}}{\Pi_{\text{N}_2}} \quad \text{Eq. 5}$$

$$\alpha_{\text{CO}_2/\text{CH}_4} = \frac{\Pi_{\text{CO}_2}}{\Pi_{\text{CH}_4}} \quad \text{Eq. 6}$$

where the individual gas permeance, Π_i , of the i^{th} species in the mixture is obtained as the ratio of its volumetric permeate flux, J_i^{Permeate} , to the partial pressure difference between the feed and permeate sides, Δp_i :

$$\Pi_i = \frac{x_i^{\text{Permeate}} J_i^{\text{Permeate}}}{x_i^{\text{Feed}} p^{\text{Feed}} - x_i^{\text{Permeate}} p^{\text{Permeate}}} \quad \text{Eq. 7}$$

in which x_i is the mole fraction of the i^{th} species, p^{Feed} and p^{Permeate} are the total feed and permeate pressures, respectively. The permeate flux is the flow rate per unit area, defined as:

$$J_i^{\text{Permeate}} = \frac{Q_i^{\text{Permeate}}}{A} \quad \text{Eq. 8}$$

The volumetric permeate flow rate, Q_i^{Permeate} , is calculated from the known Argon sweep flow rate, Q_{Ar} and from the signal ratio of the gas and argon in the permeate/sweep mixture.

$$Q_i^{\text{Permeate}} = Q_{\text{Ar}} \frac{I_i \times RS_i}{I_{\text{Ar}} \times RS_{\text{Ar}}} \quad \text{Eq. 9}$$

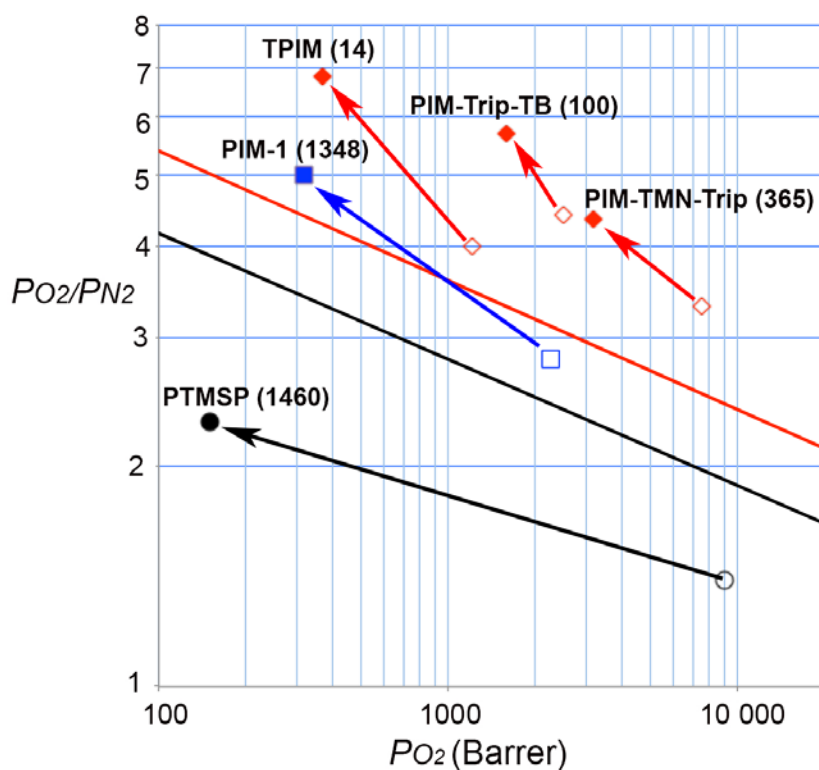
Where I_i and I_{Ar} are the measured intensities of the gas and of argon by the mass spectrometer, and RS_i and RS_{Ar} are the relative sensitivities of the gas and argon, respectively.

Supplementary Table 9. Mixed gas permeability data of 1 year aged sample PIM-TMN-Trip for gas mixture N₂/O₂/CO₂ (79.9/10.1/10.0) mol%.

Pressure bar(a)	Permeability (Barrer)		Selectivity (-) CO ₂ /N ₂
	N ₂	CO ₂	
1.02	582	12500	21.5
1.99	583	12120	20.8
2.99	583	11880	20.4
3.99	584	11670	20.0
4.99	581	11410	19.7
5.99	574	11140	19.4

Supplementary Table 10. Mixed gas permeability data of 1 year aged sample PIM-TMN-Trip for gas mixture CH₄/CO₂ (47.89/52.11) mol%.

Pressure Bar(a)	Permeability (Barrer)		Selectivity (-) CO ₂ /CH ₄
	CH ₄	CO ₂	
1.01	693	11740	17.0
1.99	703	11260	16.0
2.99	739	11100	15.0
3.99	758	10860	14.3
4.99	779	10650	13.7
5.99	799	10490	13.1



Supplementary Figure 11. Robeson plot for O₂/N₂ gas pair showing ageing trends for selected polymers. Empty symbols show freshly methanol treated data and filled symbols show data following ageing after the indicated number of days. It appears that PIM-TMN-Trip ages at a similar rate to PIM-1 with a similar commensurate increase in selectivity. Data and references are given in Table S1.

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