Redefining the Robeson upper bounds for CO_2/CH_4 and CO_2/N_2 separations using a series of ultrapermeable benzotriptycene-based Polymers of Intrinsic Microporosity.

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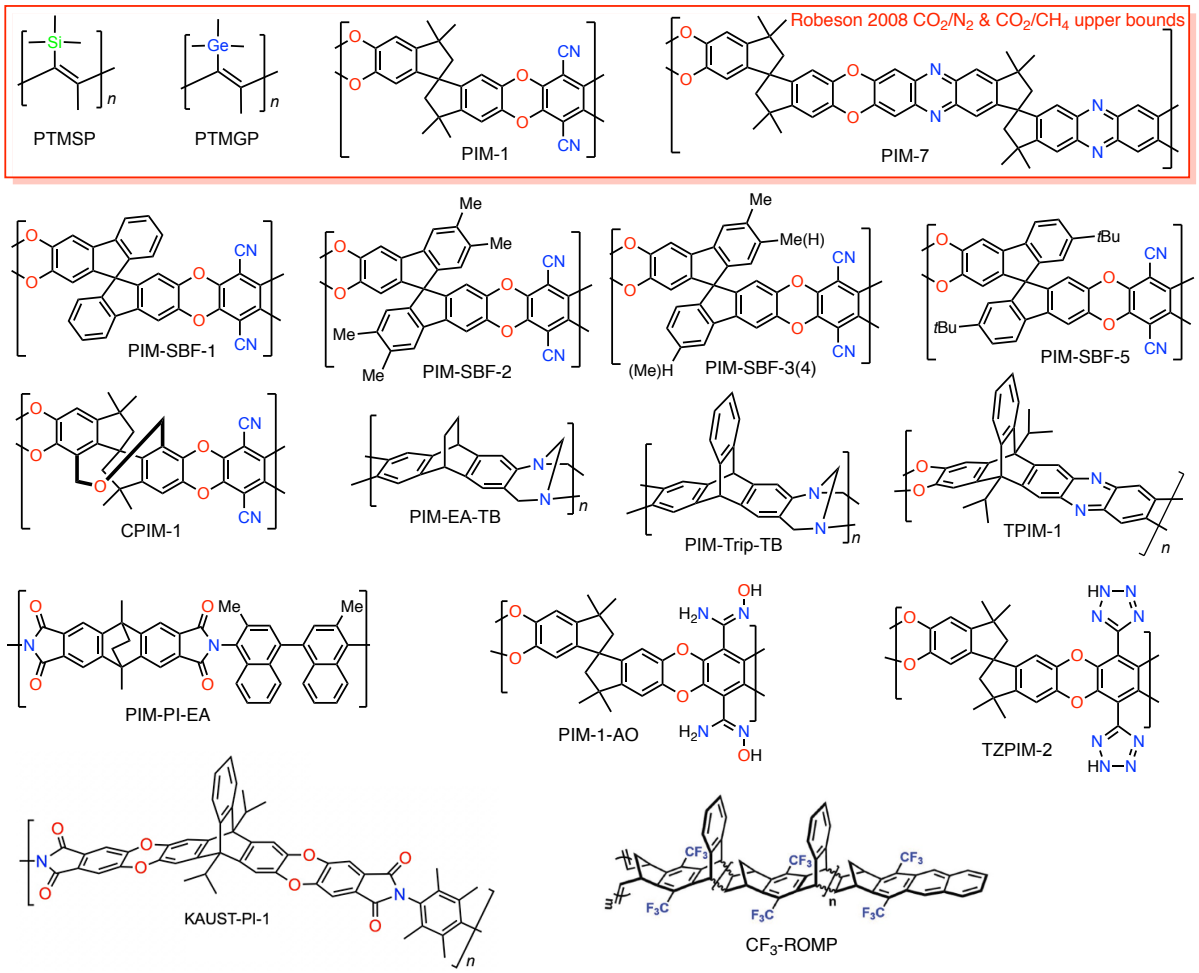
Table S1. The gas permeability data for polymers that were used to defined the 2008 Robeson upper bounds[1] for CO_2/N_2 and CO_2/CH_4 (PTMSP, PTMGP, PIM-1 and PIM-7) and those reported subsequently with data near or above these upper bounds.



Polymer	[a]Film history	P_{CO_2} (Barrer)	P_{CO_2}/P_{N_2}	P_{CO_2}/P_{CH_4}	Ref.
PTMSP	Fresh	29000	10.7	4.5	2
PTMGP	Fresh	14000	14.0	4.4	2
PIM-1	-[b]	2300	25.0	18.0	3
	MeOH	13600	16.6	10.0	4
PIM-7	-[b]	1100	26.2	17.7	3
PIM-SBF-1	MeOH	13900	17.7	12.6	4
	Aged 2088 d	2410	27.5	23.6	5
PIM-SBF-2	MeOH	22300	19.4	11.0	5
	Aged 1295 d	3870	23.3	21.0	5
PIM-SBF-3	MeOH	10900	23.5	12.4	5
	Aged 1295	4850	22.1	19.6	5

PIM-SBF-4	MeOH	10600	22.4	12.7	[5]
	Aged 1428	6410	22.4	19.4	[5]
PIM-SBF-5	MeOH	16400	15.2	6.6	[5]
	Aged 1439	10000	18.2	10.8	[5]
PIM-EA-TB	MeOH	7696	23.0	15.8	[6]
PIM-Trip-TB	MeOH	9709	15.4	10.7	[7]
	Aged 100 d	3951	20.9	18.1	[7]
TPIM-1	Aged 14 d	1549	28.7	31.0	[8]
KAUST-PI-1	Aged 14 d	2389	22.3	22.8	[9]
PIM-1-AO	Aged 7 d	1153	35.0	34.0	[10]
PIM-TZ	-[b]	1000	30.0	22.0	[11]
PIM-PI-EA	MeOH	7340	19.9	16.1	[12]
	Aged 273 d	3230	24.6	20.7	[12]
CPIM-1	MeOH	18900	19.3	14.4	[13]
PIM-TMN-Trip	MeOH	33300	14.9	9.7	[14]
	Aged 365 d	14100	19.3	14.9	[14]
CF_3-ROMP	EtOH	21266	9.0	5.4	[15]
	Aged 35 d	16148	8.8	5.5	[15]

[a]Film Histories. Methanol (MeOH) or ethanol (EtOH) treated film. Aged for stated number of day (d). [b]Film history not specified.

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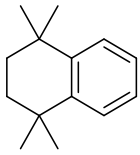
S.1 Materials and Methods

S1.1 General methods and equipment.

Commercially available reagents were used without further purification. Anhydrous dichloromethane and tetrahydrofuran were obtained from a Solvent Purification System. Anhydrous *N,N*-dimethylformamide was bought from Sigma 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 GF_{254}. Flash chromatography was performed on silica gel 60 Å (35-70 micron) chromatography grade (Fisher Scientific). Melting points were recorded using a Stuart Digital Melting Point Apparatus and are uncorrected. ^{1}H NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 (400 MHz) or DPX 500 (500 MHz) instruments, with ^{13}C NMR spectra recorded at 100 MHz or 125 MHz respectively. The solid state ^{13}C NMR were obtained using a Bruker Ultrashield ™ 300 WB spectrometer operating at 76 MHz. 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. Low-temperature (77 K) N_2 and CO_2 (273 K) adsorption/desorption isotherms were obtained using a Quantachrome Autosorb iQ surface area analyser. The powder samples were degassed for 800 mins at 125 °C under high vacuum prior to analysis. The powder samples were degassed for 600 min at 120 °C before the experiment. Gel permeation chromatography (GPC) analyses were performed on chloroform solutions (1 mg ml^{-1}) using a GPC MAX 1000 system equipped with two Viscotek CLM3012 LT 5000L columns and a RI(VE3580) detector, operating at a flow rate of 1 ml min^{-1}. Calibration was achieved using Viscotek polystyrene standards (M_w 1000 – 1,000,000 g mol^{-1}). Inherent viscosity measurements were made with an Ubbelohde capillary (Schott, Germany), maintained at 20 °C using quinoline solutions (~3.0 g cm^{-3}).

S1.2 Monomer and polymer synthesis.

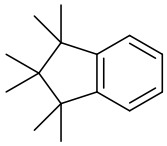
1,2,3,4-Tetrahydro-1,1,4,4-tetramethylnaphthalene (2a)



The compound 1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene (**2a**) was prepared according to the procedure reported by H. Toyama *et al*.[16] A solution of 2,5-dichloro-2,5-dimethylhexane (20.0 g, 109 mmol) in anhydrous benzene (250 mL, 2.80 mmol) was heated to 50 °C. To this, $AlCl_3$ (5.84 g, 44.0 mmol) was added portion wise over 30 min, which was then left at 50 °C for 24 h. The resulting solution

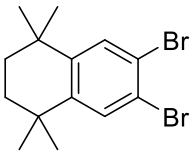
was cooled to room temperature, poured into dilute hydrochloric acid and extracted with DCM (3 x 100 mL). The organic layer was washed with water and dilute sodium carbonate solution before being dried over $MgSO_4$. The solvent was removed under vacuum and the resulting orange oil was purified by vacuum distillation to yield 1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene (**2a**) (14.5 g, 77.0 mmol, 71 %) as a colourless oil. ν_{max} (cm^{-1}): 3647, 2959, 2922, 2860, 1487, 1456, 1439, 1362, 1040, 754; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.33 (dd, 2H, *J* = 6.0, 3.4 Hz), 7.16 (dd, 2H, *J* = 5.9, 3.4 Hz), 1.71 (s, 4H), 1.31 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 144.8, 126.5, 125.5, 35.1, 34.2, 31.9; LRMS (EI, m/z): [M^+] calcd.: 188.16 found: 188.1.

2,3-Dihydro-1,1,2,2,3,3-hexamethyl-1H-indene (2b)



The compound 2,3,-dihydro-1,1,2,2,3,3-hexamethyl-1*H*-indene (**2b**) was synthesised according to the procedure reported by Baran *et al*.[17] (2-chloropropan-2-yl)benzene (17.5 g, 114 mmol) and 2,3-dimethyl-2-butene (23.9 g, 284 mmol) were dissolved in anhydrous DCM (100 mL) and cooled to -78 °C. $TiCl_4$ (4.31 g, 22.7 mmol) was added dropwise and left at -78 °C for 1 h. The resulting solution was allowed to warm to room temperature, poured into water:HCl (100 mL:50 mL) solution and extracted with DCM, dried over $MgSO_4$ and removed solvent under vacuum. Product was purified by distillation to yield 2,3-dihydro-1,1,2,2,3,3-hexamethyl-1*H*-indene (**2b**) (19.0 g, 93.9 mmol, 98 %) as colourless oil. ν_{max} (cm^{-1}): 2982, 2955, 2868, 1481, 1450, 1375, 1368, 1111, 1026, 752; ^1H NMR (601 MHz, $CDCl_3$): δ (ppm) 7.21-7.18 (m, 2H), 7.15-7.11 (m, 2H), 1.21 (s, 12H), 0.89 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 150.6, 126.7, 122.7, 48.5, 47.8, 27.6, 21.7; LRMS (EI, m/z): [M^+] calcd.: 202.17, found: 202.1.

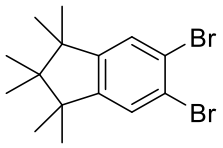
6,7-Dibromo-1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene (3a)



1,2,3,4-Tetrahydro-1,1,4,4-tetramethylnaphthalene (**2a**) (23.8 g, 126 mmol) was dissolved in anhydrous DCM (200 mL) and Fe powder (catalytic amount) was added. To this solution, bromine (60.6 g, 379 mmol) was added dropwise over 1 h and the mixture was left at room temperature 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 $MgSO_4$ and the solvent was removed under reduced

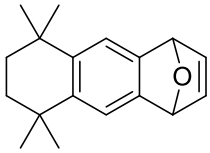
pressure. The crude product was purified by column chromatography (hexane) to yield **3a** (33.0 g, 75 %) as a white crystalline solid. Mp 111 – 112 ºC; ν_{max} (cm^{-1}): 2953, 2936, 2922, 2862, 1460, 1387, 1362, 1348, 1296, 1261, 1211, 1190, 1132, 1105, 1070, 1047, 1020, 887, 860, 839, 756, 685; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.50 (s, 2H), 1.66 (s, 4H), 1.25 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 146.4, 131.8, 121.4, 34.7, 34.3, 31.6; HRMS (EI, m/z): [M^+] calcd.: 345.9749, found: 345.9751.

5,6-Dibromo-2,3-dihydro-1,1,2,2,3,3-hexamethyl-1H-indene (3b)



The compound 2,3,-dihydro-1,1,2,2,3,3-hexamethyl-1*H*-indene (**2b**) (5.00 g, 24.7 mmol) was dissolved in anhydrous DCM (60 mL) and Fe powder (catalytic amount) was added. To this solution, bromine (11.8 g, 74.1 mmol) was added dropwise over 1 h and was left at room temperature for 3 h. The resulting reaction mixture was poured into water, organic layer was separated and washed with sodium carbonate solution. The organic layer was dried over $MgSO_4$ and solvent was removed under vacuum. The crude was purified by column chromatography in hexane and then recrystallized from ethanol to yield 5,6-dibromo-2,3-dihydro-1,1,2,2,3,3-hexamethyl-1*H*-indene (**3b**) (4.08 g, 46 %) as a white crystalline solid. Mp 118 – 119 °C; ν_{max} (cm^{-1}): 2982, 2945, 2909, 2868, 1474, 1456, 1449, 1396, 1381, 1368, 1350, 1288, 1161, 1119, 1103, 1067, 872, 854, 756, 673, 584, 538; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.34 (s, 2H), 1.18 (s, 12H), 0.86 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 152.1, 128.1, 122.3, 49.1, 47.8, 27.3, 21.5; HRMS (EI, m/z): [M^+] calcd.: 357.9926, found: 357.9930.

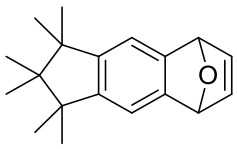
1,4,5,6,7,8-Hexahydro-5,5,8,8-tetramethyl-1,4-epoxyanthracene (4a)



Following the general procedure reported by Luo *et al.*[18], compound **3a** (13.2 g, 38.0 mmol) and anhydrous furan (25.0 mL, 344 mmol) were dissolved in anhydrous THF (30 mL) and cooled to -78 °C. To this solution, *n*-BuLi (19.8 mL, 50.0 mmol) in anhydrous THF (10 mL) was added dropwise over 0.5 h and the reaction was left to stir at -78 °C for 1.5 h. The resulting solution was allowed to warm to room temperature and water was added (100 mL). The organic layer was extracted with DCM and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting solid was washed with a small amount of hexane, filtered off and dried to yield the desired product **4a** (7.62 g, 79 %) as a white powder. Mp 124 – 126 ºC; ν_{max} (cm^{-1}): 2961, 2920, 2857, 1464, 1360, 1283, 1161, 1001, 968, 868, 853,

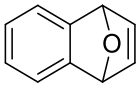
833, 694, 660; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.20 (s, 2H), 6.98 (t, 2H, J = 1.1 Hz), 5.65 (t, 2H, J = 1.1 Hz), 1.64 (s, 4H), 1.24 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 145.3, 142.6, 140.9, 118.6, 82.3, 35.2, 34.4, 31.8, 31.7; HRMS (EI, *m/z*): [M^+] calcd.: 254.1665, found: 254.1677.

2,3-Dihydro-1,1,2,2,3,3-hexamethyl-1H-5,8-epoxybenz[f]indene (4b)



The compound 2,3-dihydro-1,1,2,2,3,3-hexamethyl-1H-5,8-epoxybenz[f]indene (**4b**) was prepared according to the general procedure reported by Luo *et al.*[18] 5,6-Dibromo-2,3-dihydro-1,1,2,2,3,3-hexamethyl-1*H*-indene (**3b**) (4.00 g, 11.1 mmol) and anhydrous furan (7.27 mL, 100 mmol) were dissolved in anhydrous THF (15 mL) and cooled to -78 °C. To this, a solution of *n*-BuLi (5.78 mL, 14.4 mmol) in anhydrous THF (5 mL) was added dropwise and left to stir at -78 °C for 1.5 h. The resulting solution was allowed to warm to room temperature and water was added. The organic layer was extracted with DCM and dried over $MgSO_4$. The solvent was removed under vacuum and the precipitated solid was washed with hexane, filtered off and dried to yield **4b** (1.68 g, 56 %) as a white powder. Mp 132 – 133 °C; ν_{max} (cm^{-1}): 3003, 2986, 2947, 2864, 1447, 1375, 1368, 1281, 1148, 1123, 999, 897, 889, 866, 849, 772, 748, 704, 652, 613, 550, 538, 527, 505; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.02 (t, 2H, J = 1.1 Hz), 7.00 (s, 2H), 5.65 (t, 2H, J = 1.1 Hz), 1.15 (s, 6H), 1.14 (s, 6H), 0.86 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 147.6, 147.0, 143.1, 115.3, 82.6, 48.9, 47.4, 27.6, 27.3, 21.8, 21.5; HRMS (EI, m/z): [M^+] calcd.: 268.1822, found: 268.1831.

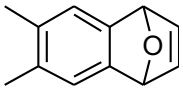
1,4-Dihydro-1,4-epoxynaphthalene (4c)



The compound 1,4-dihydro-1,4-epoxynaphthalene (**4c**) was prepared according to the general procedure reported by Luo *et al.*[18] 1,2-Dibromobenzene (30.0 g, 127 mmol) and anhydrous furan (83.1 mL, 1143 mmol) were dissolved in anhydrous THF (40 mL) and cooled to -78 °C. *n*-BuLi (66.2 mL, 165 mmol) in anhydrous THF (20 mL) was added dropwise and left to stir at -78 °C for 1.5 h. The solution was allowed to warm to room temperature and water was added. The organic layer was extracted with DCM and dried over $MgSO_4$. The resulting solid after solvent removal was washed with hexane, filtered off and dried to yield **4c** (7.34 g, 40 %) as a white solid. Mp 56 – 57 ºC; ν_{max} (cm^{-1}): 3021, 1450, 1279, 987, 871, 845; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.25 (dd, 2H, J = 5.0, 2.9 Hz),

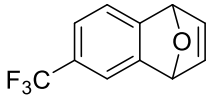
7.03 (t, 2H, J = 1.1 Hz), 6.97 (dd, 2H, J = 5.1, 3.0 Hz), 5.71 (t, 2H, J = 1.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 149.2, 143.2, 125.1, 120.4, 82.5; LRMS (EI, m/z): [M^+] calcd.: 144.06, found: 144.0.

1,4-Dihydro-6,7-dimethyl-1,4-epoxynaphthalene (4d)



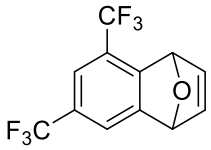
Following the general procedure reported by Luo *et al*.[18] 1,2-dibromo-4,5-dimethylbenzene (20.0 g, 75.8 mmol) and anhydrous furan (49.6 mL, 682 mmol) were dissolved in anhydrous THF (40 mL) and cooled to -78 °C. *n*-BuLi (39.4 mL, 98.5 mmol) in anhydrous THF (20 mL) was added dropwise and left to stir for 1.5 h. The solution was allowed to reach room temperature and water was added. The organic layer was extracted with DCM and dried over $MgSO_4$. After solvent removal, the resulting solid was washed with hexane, filtered off and dried to yield 1,4-dihydro-6,7-dimethyl-1,4-epoxynaphthalene (**4d)** (10.1 g, 77 %) as a white solid. Mp 67 – 68 ºC; ν_{max} (cm^{-1}): 2920, 1458, 1389, 1277, 1072, 1038, 976, 868, 841, 694, 637; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.06 (s, 2H), 7.00 (t, 2H, J = 1.0 Hz), 5.66 (t, 2H, J = 1.0 Hz), 2.20 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 146.8, 143.3, 132.7, 122.3, 82.4, 19.9; LRMS (EI, m/z): [M^+] calcd.: 172.09, found: 172.1.

6-Trifluoromethyl-1,4-dihydro-1,4-epoxynaphthalene (4e)



The compound 6-(trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene (**4e**) was synthesised according to the procedure reported by Bailly *et al*.[19] 4-Chlorobenzotrifluoride (10.0 g, 55.4 mmol) was dissolved in anhydrous THF (80 mL) and cooled to -78 °C. *n*-BuLi (29.0 mL, 72.0 mmol) was added dropwise and left to stir at -78 °C for 1 h. The reaction solution was transferred dropwise into furan (40.0 mL, 552 mmol) and left at room temperature for 2 h. After solvent removal, the crude product was filtered through a pad of basic aluminium using diethyl ether as eluent. The resulting oil was distilled under vacuum to yield pure 1,4-dihydro-6-(trifluoromethyl)-1,4-epoxynaphthalene (**4e**) as a colourless oil (5.68 g, 48 %). ν_{max} (cm^{-1}): 3019, 2359, 2324, 1427, 1354, 1323, 1275, 1198, 1167, 1140, 1049, 995, 897, 872, 853, 839, 750, 700, 654, 637, 544; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.46 (s, 1H), 7.32 (d, 1H, J = 7.4 Hz), 7.30 (d, 1H, J = 7.4 Hz), 7.07-7.03 (m, 2H), 5.57-5.76 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 153.4, 150.5, 143.3, 142.8, 127.6 (q, J = 33 Hz), 127.0, 125.3, 123.4, 123.2 (q, J = 4 Hz), 121.6, 120.1, 117.1 (q, J = 4 Hz), 82.3; LRMS (EI, m/z): [M^+] calcd.: 212.04, found: 212.0.

5,7-Bis(trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene (4f)

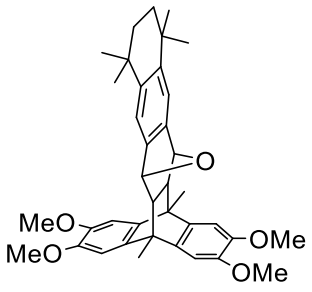


The compound 5,7-bis(trifluoromethyl)-1,4-dihydro-1,4-epoxynaphthalene (**4f**) was obtained according to the procedure reported by Bailly *et al.*[19] 2,4-Bis(trifluoromethyl)chlorobenzene (10.0 g, 40.2 mmol) was dissolved into anhydrous THF (80 mL) and cooled to -78 °C. To this, a solution of *n*-BuLi was added dropwise and left to stir at -78 °C for 1 h. The resulting solution was transferred into anhydrous furan (88.0 mL, 1207 mmol) and kept at room temperature for 24 h. Solvent was removed under vacuum and the resulting oil was filtered through a pad of basic aluminium (diethyl ether as eluent). The desired product **4f** was obtained by distillation under vacuum as colourless oil (4.5 g, 40 %). ν_{max}(cm^{-1}): 3036, 1389, 1325, 1287, 1256, 1192, 1175, 1142, 1069, 899, 872, 843, 820, 752, 704, 667, 635, 625; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (s, 1H), 7.49 (s, 1H), 7.11 (dd, 1H, *J* = 5.5, 1.9 Hz), 7.06 (dd, 1H, *J* = 5.5, 1.9 Hz), 6.08 – 6.01 (m, 1H), 5.87 – 5.81 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 152.5, 144.0, 142.3, 128.8 (q, *J* = 33 Hz), 126.8, 126.6, 124.6, 124.4, 124.0 (q, *J* = 35 Hz), 122.5, 122.3, 119.5 (dt, *J* = 8, 4 Hz), 81.9, 81.6 (q, *J* = 2 Hz); HRMS (EI, m/z): [M^+] calcd.: 280.0317, found: 280.0317.

General procedure for the synthesis of the oxygen-bridged tetramethoxy benzotriptycenes (5a-f)

The oxygen-bridged tetramethoxy benzotriptycenes (**5a-f**) were synthesised according to a modified procedure reported by Sydlik *et al.*[20] In a sealed vessel, 2,3,6,7-tetramethoxy-9,10-dimethylanthracene (2.00 g, 6.13 mmol) prepared following the method reported by Ghanem *et al.*[21], and the required epoxyarene (**4a-f**) (6.13 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 was collected by filtration and thoroughly washed with water.

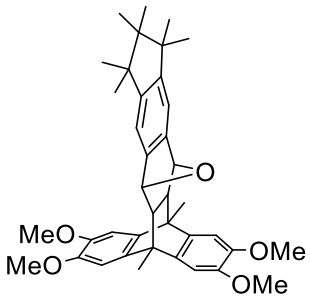
2,3,6,7-Tetramethoxy-9,10-(1',3',4',5',6',8'-hexahydro-2',2',5',5'-tetramethyl-1',8'-epoxyanthryl)-9,10-dimethylanthracene (5a)



Following the general procedure described above, the crude product was purified by column chromatography DCM/ethyl acetate (9:1 v/v) to yield adduct **5a** (77 %) as a light brown crystalline

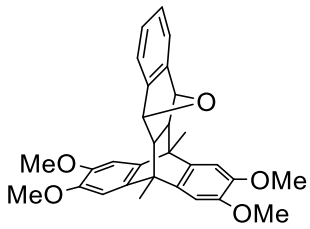
solid. Mp 288 – 290 ºC; ν_{max} (cm^{-1}): 2934, 1506, 1489, 1437, 1404, 1279, 1242, 1227, 1196, 1163, 1049, 1032, 854, 835, 822, 785, 748; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.03 (s, 2H), 6.87 (s, 2H), 6.84 (s, 2H), 4.92 (s, 2H), 3.89 (s, 6H), 3.83 (s, 6H), 2.07 (s, 6H), 1.99 (s, 2H), 1.60 (s, 4H), 1.19 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): 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.: 580.3183, found: 580.3180.

2,3,6,7-Tetramethoxy-9,10-(2',8'4',5'-tetrahydro-4',4',5',5',6',6'-hexamethyl-3'H-1',8'-epoxyindenyl)-9,10-dimethylanthracene (5b)



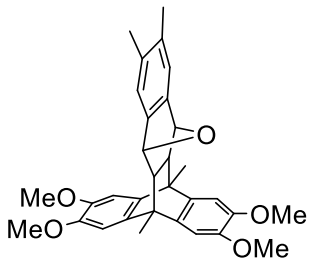
Following the general procedure, the crude product was purified by trituration with hexane to yield adduct **5b** as an off white solid (63 %). Mp 125 – 127 °C; ν_{max} (cm^{-1}): 2936, 1485, 1458, 1281, 1242, 1196, 1150, 1045, 1022, 853, 748, 610, 567; ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.87 (s, 2H), 6.84 (s, 2H), 6.83 (s, 2H), 4.92 (s, 2H), 3.89 (s, 6H), 3.83 (s, 6H), 2.07 (s, 6H), 2.01 (s, 2H), 1.10 (s, 12H), 0.81 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 148.6, 147.0, 146.5, 145.9, 140.7, 137.0, 113.1, 106.8, 106.1, 79.8, 56.9, 56.6, 56.5, 48.7, 47.5, 43.3, 27.9, 27.4, 21.8, 21.5, 17.3; HRMS (EI, m/z): [M^+] calcd.: 594.3340, found: 594.3339.

2,3,6,7-Tetramethoxy-9,10-(2',7'-dihydro-2',7'-epoxynaphthalene)-9,10-dimethylanthracene (5c)



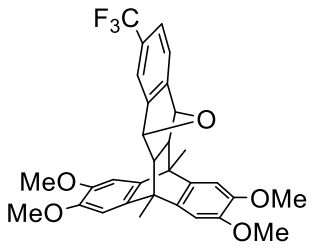
Following the general procedure, the crude product was purified by trituration with methanol to yield adduct **5c** (83 %) as an off-white solid. Mp 110 – 112 ºC; ν_{max} (cm^{-1}): 2932, 1508, 1485, 1458, 1404, 1331, 1281, 1242, 1223, 1192, 1153, 1045, 1018, 949, 922, 841, 752, 606, 575; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.12 (dd, 2H, *J* = 5.3, 3.0 Hz), 7.02 (dd, 2H, *J* = 5.3, 3.0 Hz), 6.87 (s, 2H), 6.84 (s, 2H), 4.99 (s, 2H), 3.89 (s, 6H), 3.83 (s, 6H), 2.08 (s, 6H), 2.01 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 147.1, 147.1, 146.6, 140.5, 136.9, 126.4, 118.7, 106.8, 106.2, 79.8, 56.6, 56.5, 56.4, 43.2, 17.3; HRMS (EI, m/z): [M^+] calcd.: 470.2088, found: 470.2108.

2,3,6,7-Tetramethoxy-9,10-(2',7'-dihydro-4',5'-dimethyl-2',7'-epoxynaphthalene)-9,10-dimethylanthracene (5d)



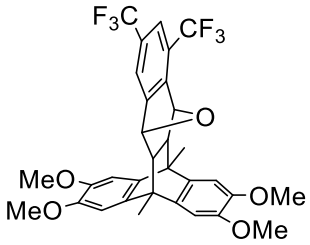
Following the general procedure described above, the crude product was purified by trituration with hexane to yield adduct **5d** (78 %) as an off-white solid. Mp 238 – 240 ºC; ν_{max} (cm^{-1}): 2936, 1491, 1464, 1406, 1292, 1246, 1196, 1161, 1043, 856, 821, 783, 752, 673, 611, 570; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.90 (s, 2H), 6.86 (s, 2H), 6.82 (s, 2H), 4.93 (s, 2H), 3.88 (s, 6H), 3.82 (s, 6H), 2.16 (s, 6H), 2.05 (s, 2H), 1.96 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 147.0, 146.5, 145.0, 140.6, 136.9, 134.3, 120.1, 106.7, 106.1, 79.6, 56.9, 56.6, 56.5, 43.2, 20.0, 17.3; HRMS (EI, m/z): [M^+] calcd.: 498.2401, found: 498.2410.

2,3,6,7-Tetramethoxy-9,10-(4'-trifluoromethyl-2',7'-dihydro-2',7'-epoxynaphthalene)-9,10-dimethylanthracene (5e)



Following the general procedure, the crude product was purified by column chromatography DCM/ethyl acetate (20:1 v/v) to yield adduct **5e** as light brown crystalline solid (52 %). Mp 138 – 140 °C; ν_{max} (cm^{-1}): 2938, 1506, 1485, 1462, 1437, 1404, 1319, 1292, 1279, 1196, 1148, 1113, 1045, 1020, 951, 885, 843, 818, 783, 746, 677, 669, 660, 606, 579; ^{1}H NMR (601 MHz, $CDCl_3$): δ (ppm) 7.38 (s, 1H), 7.34 (d, 1H, J = 7.7 Hz), 7.22 (d, 1H, J = 7.6 Hz), 6.88 (s, 1H), 6.87 (s, 1H), 6.84 (s, 2H), 5.05 (d, 2H, J = 1.9 Hz), 3.89 (s, 3H), 3.89 (s, 3H), 3.84 (s, 6H), 2.08 (s, 6H), 2.04 – 2.00 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 150.9, 148.0, 147.1, 146.7, 146.7, 140.2, 140.1, 136.6, 136.6, 128.9 (q, J = 32 Hz), 127.6, 125.4, 124.1 (t, J = 4 Hz), 123.3, 121.1, 118.9, 115.8 (q, J = 4 Hz), 106.7, 106.7, 106.2, 106.1, 79.6, 79.6, 56.6, 56.5, 56.0, 55.8, 43.1, 17.3, 17.2; HRMS (EI, m/z): [M^+] calcd.: 538.1962, found: 538.1969.

2,3,6,7-Tetramethoxy-9,10-(3',5'-bis(trifluoromethyl)-2',7'-dihydro-2',7'-epoxynaphthalene)-9,10-dimethylanthracene (5f)

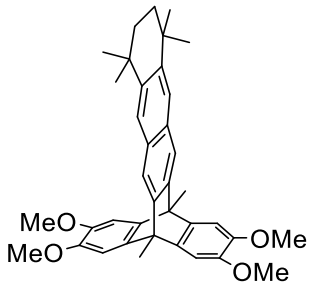


Following the general procedure, the crude product was purified by trituration with MeOH to adduct **5f** as light brown powder (58 %). Mp 166 – 168 °C; ν_{max} (cm^{-1}): 2965, 2938, 2830, 1506, 1487, 1464, 1404, 1385, 1327, 1277, 1254, 1242, 1194, 1159, 1121, 1074, 1045, 1020, 949, 895, 870, 835, 820, 783, 752, 687, 673, 633, 608, 571; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (s, 2H), 6.90 (s, 1H), 6.88 (s, 1H), 6.85 (s, 1H), 6.84 (s, 1H), 5.31 (s, 1H), 5.14 (s, 1H), 3.90 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.03 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 149.9, 147.3, 147.3, 146.9, 146.8, 139.9, 136.4, 136.3, 130.1, 122.4, 120.7, 119.0, 106.9, 106.8, 106.3, 106.2, 79.4, 79.2, 56.6, 56.6, 56.5, 56.5, 55.7, 55.0, 43.1, 43.1, 17.2, 16.9; HRMS (EI, m/z): [M^+] calcd.: 606.1835, found: 606.1855.

General procedure for the synthesis of the tetramethoxy benzotriptycenes (6a-f)

The required oxygen-bridged benzotriptycene (**5a-f**) was dissolved in TFA (or $MeSO_4H$ in the case of the adducts with CF_3 groups) and left at room temperature for 24 h. The reaction mixture was poured into ice – water bath, neutralised with aqueous sodium hydroxide (2N), extracted with DCM and dried over $MgSO_4$. The crude product was obtained after solvent removal.

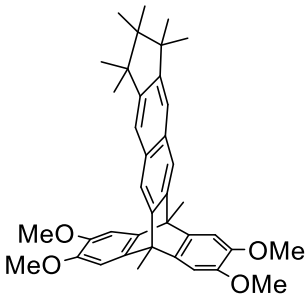
2,3,6,7-Tetramethoxy-9,10-dimethyl-[12,13]-(3',3',6',6'-tetramethyl-3',4',5',6'-tetrahydronaphtho)triptycene (6a)



Following the general procedure, the crude product was then purified by column chromatography ($CHCl_3$) to yield compound **6a** (62 %) as a white powder. Mp above 300 ºC; ν_{max} (cm^{-1}): 2955, 2928, 2859, 1601, 1489, 1462, 1439, 1404, 1285, 1250, 1165, 1146, 1042, 903, 868, 856, 764, 752, 633, 621, 536; ^{1}H NMR (500 MHz, $CDCl_3$): 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); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 146.1, 145.0, 143.9, 140.8,

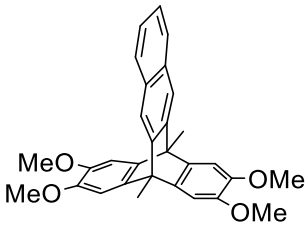
129.5, 124.5, 117.4, 106.0, 56.4, 47.4, 35.1, 34.4, 32.5, 14.2; HRMS (EI, *m/z*): [M^+] calcd.: 562.3077, found: 562.3068.

2,3,6,7-Tetramethoxy-9,10-dimethyl-[12,13]-(3',3',4',4',5',5'-hexamethyl-3',4'-dihydro-1'H-indeno)triptycene (6b)



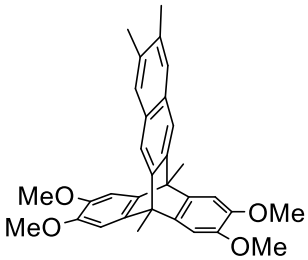
Following the general procedure, the crude product was then purified by trituration with hexane to yield compound **6b** (78 %) as a white powder. Mp 180 – 182 °C; ν_{max} (cm^{-1}): 2947, 1485, 1458, 1435, 1404, 1281, 1227, 1165, 1146, 1042, 1022, 899, 752, 621; ^{1}H NMR (601 MHz, $CDCl_3$): δ (ppm) 7.63 (s, 2H), 7.43 (s, 2H), 6.96 (s, 4H), 3.84 (s, 12H), 2.48 (s, 6H), 1.24 (s, 12H), 0.85 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 150.5, 146.2, 145.1, 141.1, 131.2, 120.5, 118.0, 106.1, 56.6, 48.9, 47.6, 47.5, 28.0, 21.6, 14.3; HRMS (EI, m/z): [M^+] calcd.: 576.3234, found: 576.3239.

2,3,6,7-Tetramethoxy-9,10-dimethylbenzotriptycene (6c)



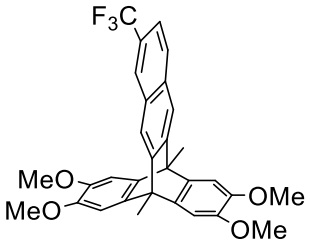
Following the general procedure, the crude product was then purified by trituration with ethanol to yield compound **6c** (84 %) as a white powder. Mp 123 – 125 ºC; ν_{max} (cm^{-1}): 2967, 2936, 1601, 1485, 1458, 1431, 1404, 1281, 1223, 1192, 1165, 1146, 1042, 1018, 945, 883, 860, 756, 617, 579; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.70 (dd, 2H, J = 6.1, 3.3 Hz), 7.65 (s, 2H), 7.36 (dd, 2H, J = 6.2, 3.2 Hz), 6.98 (s, 4H), 3.85 (s, 12H), 2.50 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 146.3, 146.0, 140.9, 131.4, 127.6, 125.8, 118.4, 106.2, 56.5, 47.7, 14.3; HRMS (EI, m/z): [M^+] calcd.: 452.1982, found: 452.1969.

2,3,6,7-Tetramethoxy-9,10-dimethyl-13,14-dimethylbenzotriptycene (6d)



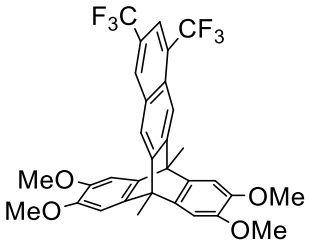
Following the general procedure, the crude product was then purified by column chromatography DCM/metanol (100:1 v/v) to yield compound **6d** (84 %) as a white powder. Mp 278 – 280 ºC; ν_{max} (cm^{-1}): 2936, 1483, 1435, 1402, 1278, 1224, 1147, 1042, 1018, 895, 752, 617, 549; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.53 (s, 2H), 7.44 (s, 2H), 6.97 (s, 4H), 3.84 (s, 12H), 2.47 (s, 6H), 2.34 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 146.1, 144.9, 141.0, 135.1, 130.1, 127.1, 117.3, 106.0, 56.4, 47.5, 20.1, 14.2; HRMS (EI, m/z): [M^+] calcd.: 480.2295, found: 480.2277.

2,3,6,7-Tetramethoxy-9,10-dimethyl-13-trifluoromethylbenzotriptycene (6e)



Following the general procedure, the crude product was purified by column chromatography DCM/ethyl acetate (40:1 v/v) to afford compound **6e** (93 %) as a white solid. Mp 289 – 291 °C; ν_{max} (cm^{-1}): 2951, 1604, 1585, 1516, 1489, 1443, 1408, 1384, 1327, 1281, 1258, 1223, 1184, 1146, 1111, 1065, 1038, 934, 903, 887, 872, 837, 814, 795, 752, 698, 679, 667, 640, 617, 598, 559; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.01 (s, 1H), 7.80 (d, 1H, J = 8.6 Hz), 7.72 (s, 1H), 7.70 (s, 1H), 7.54 (dd, 1H, J = 8.6, 1.8 Hz), 6.99 (s, 4H), 3.86 (s, 6H), 3.86 (s, 6H), 2.51 (s, 3H), 2.51 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 148.6, 147.7, 146.5, 146.5, 140.5, 140.4, 132.9, 130.4, 128.5, 128.0, 127.9, 127.6 (q, J = 32 Hz), 125.7, 125.2 (q, J = 4 Hz), 123.6, 121.5 (q, J = 3 Hz), 119.0, 118.2, 106.2, 106.2, 56.5, 47.8, 47.7, 14.3; [M^+] calcd.: 520.1856, found: 520.1881.

2,3,6,7-Tetramethoxy-9,10-dimethyl-12,14-bis(trifluoromethyl)benzotriptycene (6f)



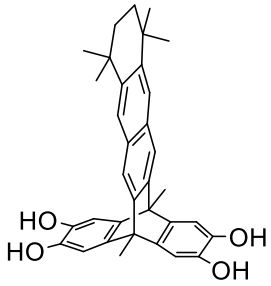
Following the general procedure, the crude product was purified by column chromatography (DCM) to yield **6f** as a white solid (93 %). Mp 272 – 274 °C; ν_{max} (cm^{-1}): 2970, 2940, 2830, 1607, 1582, 1487, 1449, 1439, 1406, 1385, 1344, 1275, 1209, 1186, 1152, 1115, 1088, 1042, 1016, 959, 899, 887, 870, 762, 752, 733, 667, 613; ^{1}H NMR (601 MHz, $CDCl_3$): δ(ppm) 8.20 (s, 1H), 8.04 (s, 1H), 7.92 (s, 1H), 7.80 (s, 1H), 7.01 (s, 2H), 6.99 (s, 2H), 3.87 (s, 6H), 3.86(s, 6H), 2.54 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 150.6, 148.6, 146.7, 146.7, 140.1, 140.0, 131.5, 129.7 (q, J = 4 Hz), 128.7 (q, J = 33 Hz), 126.4 (q, J = 33 Hz), 125.4, 125.0, 123.2, 122.8, 120.4 (dt, J = 8, 4 Hz), 119.7, 114.8,

106.3, 106.2, 56.6, 56.5, 48.2, 47.7, 14.1, 14.1; HRMS (EI, m/z): [M^+] calcd.: 588.1730, found: 588.1746.

General procedure for the synthesis of the biscatechol monomers (1a-f)

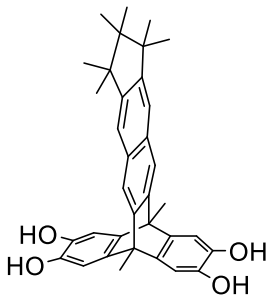
The required biscatechol monomers were synthesised according to the general procedure reported by Ghanem *et al*. [21] The tetramethoxy benzotriptycene precursor (**6a-f**) (2.00 mmol) was dissolved in anhydrous DCM (40 mL) and cooled to 0 °C. BBr_3 (6.00 mmol) was added dropwise and left at 0 °C for 30 minutes, then allowed to warm to room temperature for 2.5 h. The resulting reaction was poured into ice – water and allowed DCM to evaporate. Then, the precipitate was filtered off, washed with water and dried. The crude product was dissolved in ethyl acetate and dried over $MgSO_4$. After most of the solvent removal, the product was precipitated from hexane and filtered off.

2,3,6,7-Tetrahydroxy-9,10-dimethyl-[12,13]-(3',3',6',6'-tetramethyl-3',4',5',6'-tetrahydronaphtho)triptycene (Monomer TMN-Trip) (1a)



This compound was attained as a white powder in a 92 % yield. ν_{max} (cm^{-1}): 3121, 2951, 2228, 1592, 1491, 1442, 1376, 1299, 1265, 1163, 969, 865, 763, 680; ^{1}H NMR (500 MHz, $(CD_3)_2CO$): 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, $(CD_3)_2CO$): 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*): [M^+] calcd.: 506.2451, found: 506.2455.

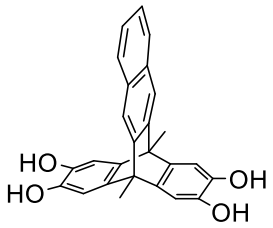
2,3,6,7-Tetrahydroxy-9,10-dimethyl-[12,13]-(3',3',4',4',5',5'-hexamethyl-3',4'-dihydro-1'H-indeno)triptycene (Monomer HMI-Trip) (1b)



This compound was obtained as a white powder in a 77 % yield. ν_{max} (cm^{-1}): 3368, 2955, 1612, 1485, 1447, 1377, 1296, 1169, 984, 903, 876, 837, 814, 760, 621; ^{1}H NMR (601 MHz, $(CD_3)_2CO$): δ (ppm) 7.61 (s, 2H), 7.49 (s, 2H), 7.44 (*b*s, 4H), 6.88 (s, 4H), 2.32 (s, 6H), 1.25 (s, 12H), 0.87 (s, 6H); ^{13}C NMR

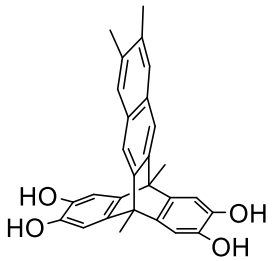
(126 MHz, $(CD_3)_2CO$): δ (ppm) 150.6, 146.8, 142.2, 141.2, 132.2, 121.2, 118.4, 109.8, 49.3, 48.0, 47.5, 28.2, 21.8, 14.6; HRMS (EI, m/z): [M^+] calcd.: 520.2608, found: 520.2608.

2,3,6,7-Tetrahydroxy-9,10-dimethylbenzotriptycene (Monomer BTrip) (1c)



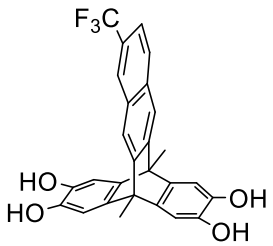
This compound was accomplished as a white powder in a 73 % yield. ν_{max} (cm^{-1}): 3326, 2981, 1695, 1612, 1491, 1440, 1378, 1293, 1248, 1170, 983, 882, 800, 764, 665, 619; ^1H NMR (500 MHz, $(CD_3)_2CO$): δ (ppm) 7.75 (dd, 2H, *J* = 6.1, 3.3 Hz), 7.67 (s, 2H), 7.48 (*b*s, 4H), 7.35 (dd, 2H, *J* = 6.2, 3.2 Hz), 6.91 (s, 4H), 2.34 (s, 6H); ^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ (ppm) 148.0, 142.3, 141.0, 132.3, 128.2, 126.2, 118.5, 109.9, 47.6, 14.6; HRMS (EI, m/z): [M^+] calcd.: 396.1356, found: 396.1361.

2,3,6,7-Tetrahydroxy-9,10-dimethyl-13,14-dimethylbenzotriptycene (Monomer DM-BTrip) (1d)



This compound was attained as a white powder in a 76 % yield. ν_{max} (cm^{-1}): 3363, 2968, 1622, 1497, 1446, 1379, 1290, 1173, 897, 835, 765, 615, 548; ^1H NMR (601 MHz, $(CD_3)_2CO$): δ (ppm) 7.54 (s, 2H), 7.48 (s, 2H), 7.44 (*b*s, 4H), 6.88 (s, 4H), 2.33 (s, 6H), 2.31 (s, 6H); ^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ (ppm) 147.2, 142.3, 141.4, 136.6, 131.2, 128.1, 117.8, 110.0, 47.7, 20.2, 14.7 ; HRMS (EI, m/z): [M^+] calcd.: 424.1669, found: 424.1662.

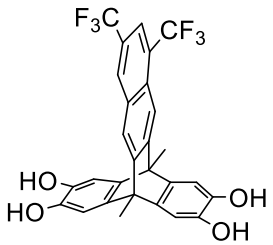
2,3,6,7-Tetrahydroxy-9,10-dimethyl-13-trifluoromethylbenzotriptycene (Monomer TFM-BTrip) (1e)



This compound was obtained as a white powder in a 65 % yield. ν_{max} (cm^{-1}): 3352, 2970, 1612, 1487, 1443, 1379, 1329, 1298, 1263, 1186, 1155, 1117, 1065, 986, 934, 907, 843, 812, 762, 619, 598; ^1H NMR (601 MHz, MeOD): δ (ppm) 8.04 (s, 1H), 7.84 (d, 1H, *J* = 9.0 Hz), 7.69 (s, 1H), 7.65 (s, 1H), 7.51(dd, 1H, *J* = 8.6, 1.9 Hz), 6.84 (s, 4H), 2.31 (s, 6H); ^{13}C NMR (151 MHz, MeOD): δ (ppm) 151.1,

150.1, 142.9, 142.8, 141.1, 141.0, 134.3, 131.6, 129.7, 127.9, 127.0, 126.0 (q, J = 4 Hz), 121.7 (q, J = 4 Hz), 119.2, 118.4, 110.1, 110.1, 48.1, 48.0, 14.5, 14.5; HRMS (EI, m/z): [M^+] calcd.: 464.1229, found: 464.1229.

2,3,6,7-Tetrahydroxy-9,10-dimethyl-12,14-bis(trifluoromethyl)benzotriptycene (Monomer DTFM-BTrip) (1f)



This compound was attained as a white powder in a 92 % yield. ν_{max} (cm^{-1}): 3429, 2974, 1614, 1489, 1445, 1383, 1342, 1298, 1277, 1207, 1188, 1157, 1117, 1088, 1015, 988, 957, 924, 903, 889, 880, 841, 775, 762, 669, 617; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ (ppm) 8.53 (s, 1H), 8.08 (s, 1H), 8.01 – 7.98 (m, 2H), 7.63 (*b*s, 4H), 6.96 (s, 2H), 6.95 (s, 2H), 2.39 (s, 6H); ^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ(ppm) 153.0, 150.7, 142.7, 140.2, 140.0, 132.5, 131.3 (q, J = 5 Hz), 129.1, 127.4, 127.2, 126.8 – 125.8 (m), 124.2, 123.9, 120.6, 114.3, 110.3, 110.2, 48.2, 47.8, 14.3, 14.2; HRMS (EI, m/z): [M^+] calcd.: 532.1104, found: 532.1128.

General procedure for synthesis of polybenzodioxin polymers.

The synthesis of the polybenzodioxin polymers (**PIMa-f**) was conducting according to the procedure described by Budd *et al.*[22] The required biscatechol (**1a-f**) (3.00 mmol) and tetrafluoroterephthalonitrile (3.00 mmol) were dissolved in anhydrous DMF (20 mL). Once both monomers were dissolved, K_2CO_3 (24 mmol) was added and the resulting mixture was heated to 65 °C for 72 h. After this time, polymer solution was poured into water, acidified with HCl and filtered off. The crude solid was washed thoroughly with water, acetone and methanol, refluxed twice in THF for 12 h to further remove oligomers and subsequently refluxed in MeOH twice for 12 h to remove traces of residual solvent. Finally, the resulting polybenzodioxin-based PIMs were collected by filtration and dried under vacuum at 120 °C for 12 h.

PIM-TMN-Trip (PIMa): This polymer was obtained as a yellow powder in a 67 % yield (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; ^{1}H NMR (601 MHz, $CDCl_3$): δ (ppm) 7.66 (s, 2H), 7.56 (s, 2H), 6.96 (s, 4H), 2.35 (s, 6H), 1.70 (s, 4H), 1.31 (s, 12H); ^{13}C NMR (76 MHz, solid state): δ (ppm) 143.4, 136.9, 129.8, 123.6, 117.3, 108.7, 94.0, 46.9, 33.5, 30.6, 12.2; 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}; Temperature at the maximum point of the weight loss ascribed to the generalized decomposition (T_d) is 510 °C.

PIM-HMI-Trip (PIMb): This polymer was obtained as a yellow powder in a 58 % yield (based on the molecular weight of the repeated unit); ν_{max} (cm^{-1}): 2980, 1435, 1396, 1379, 1296, 1271, 1171, 1155, 1005, 903, 883, 752, 552; ^{1}H NMR (500 MHz, ($CDCl_3$): δ (ppm) 7.63 (s, 2H), 7.45 (s, 2H), 6.96 (s, 4H), 2.35 (s, 6H), 1.23 (s, 12H), 0.83 (s, 6H); ^{13}C NMR (76 MHz, solid state): δ (ppm) 149.6, 144.7, 140.8, 137.0, 131.4, 118.8, 108.8, 94.2, 46.9, 26.1, 19.4, 12.4; BET surface area = 1033 m^2 g^{-1}; total pore volume = 0.71 cm^3 g^{-1} at P/P_o = 0.98 from N_2 adsorption at 77 K; GPC ($CHCl_3$): M_n = 61,300 g mol^{-1}, M_w = 147,800 g mol^{-1}; Temperature at the maximum point of the weight loss ascribed to the generalized decomposition (T_d) is 500 °C.

PIM-BTrip (PIMc): This polymer was obtained as a yellow powder in a 78 % yield (based on the molecular weight of the repeated unit); ν_{max} (cm^{-1}): 2974, 1435, 1296, 1269, 1007, 885, 752, 582; ^{13}C NMR (76 MHz, solid state): δ (ppm) 144.3, 137.4, 131.1, 125.6, 117.9, 108.9, 94.1, 47.1, 12.4; BET surface area = 911 m^2g^{-1}; total pore volume = 0.63 cm^3g^{-1} at (P/P_o = 0.98); Temperature at the maximum point of the weight loss ascribed to the generalized decomposition (T_d) is 585 °C.

PIM-DM-BTrip (PIMd): This polymer was obtained as a yellow powder in a 82 % yield (based on the molecular weight of the repeated unit); ν_{max} (cm^{-1}): 2974, 1435, 1294, 1269, 1005, 900, 885, 752, 548; ^{13}C NMR (76 MHz, solid state): δ (ppm) 145.2, 141.2, 136.7, 130.0, 126.0, 117.0, 108.8, 94.4, 47.2, 17.8, 12.4. BET surface area = 920 m^2g^{-1}; total pore volume = 0.73 cm^3g^{-1} at (P/P_o = 0.98); Temperature at the maximum point of the weight loss ascribed to the generalized decomposition (T_d) is 580 °C.

PIM-TFM-BTrip (PIMe): This polymer was obtained as a yellow powder in a 79 % yield (based on the molecular weight of the repeated unit); ν_{max} (cm^{-1}): 2974, 1439, 1329, 1294, 1269, 1186, 1163, 1124, 1067, 1005, 885; ^{13}C NMR (76 MHz, solid state): δ (ppm) 144.9, 137.3, 129.7, 127.6, 118.9, 109.3, 94.3, 47.2, 12.5; BET surface area = 848 m^2g^{-1}; total pore volume = 0.66 cm^3g^{-1} at (P/P_o = 0.98); Temperature at the maximum point of the weight loss ascribed to the generalized decomposition (T_d) is 545 °C.

PIM-DTFM-BTrip (PIMf): This polymer was obtained as a yellow powder in an 84 % yield (based on the molecular weight of the repeated unit); ν_{max} (cm^{-1}): 2980, 1439, 1298, 1271, 1206, 1188, 1161, 1128, 1088, 1007, 905, 885, 671; ^{13}C NMR (76 MHz, solid state): δ (ppm) 144.9, 137.6, 131.2, 127.6, 119.3, 114.3, 109.2, 94.7, 47.4, 11.7; BET surface area = 964 m^2g^{-1}; total pore volume = 1.02 cm^3g^{-1} at (P/P_o = 0.98); Temperature at the maximum point of the weight loss ascribed to the generalized decomposition (T_d) is 555 °C.

S2. Pure gas permeation measurements

All the gases used for pure gas permeation tests were supplied by Sapio at a minimum purity of 99.9995%. Permeation tests were carried out at 1 bar of feed gas pressure and at a constant temperature of 25 ± 1 °C on a fixed volume/pressure increase instrument, constructed and customized by Elektro & Elektronik Service Reuter (Geesthacht, Germany). Between two consecutive measurements, the membrane is evacuated for at least ten times the time lag of the previously measured gas, in order to guarantee a complete degassing. Before the first measurement the membrane is degassed for approximately 1 hour, or more if needed, to guarantee complete removal of absorbed species. The degassing of the membranes is performed under high vacuum conditions by a turbomolecular pump. The permeability coefficient, P, is expressed in Barrer (1 Barrer = 10^{-10}×cm^3 (STP)×cm×cm^{-2} ×s^{-1} ×cm Hg^{-1}) and calculated from the steady state of the permeation curve. Diffusion is calculated by the so-called time-lag method and the approximate gas solubility coefficient by assuming the validity of the diffusion-solution model. A more detailed description of the method and calculation procedures is reported elsewhere.[23]

S3. References

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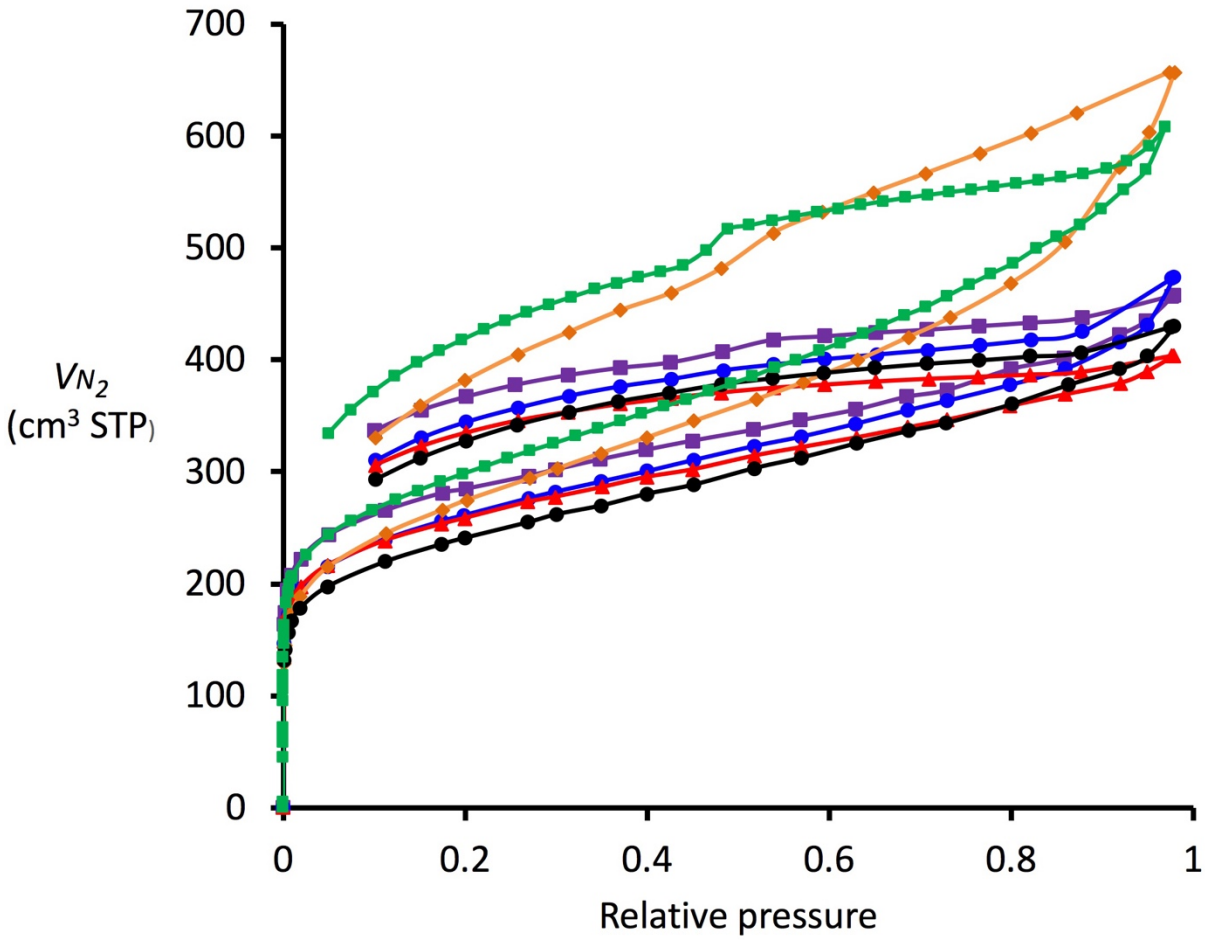

Fig. S1. Nitrogen adsorption isotherms acquired at 77 K for powdered samples of PIM-BTrip (▲), PIM-TMN-Trip (■), PIM-HMI-Trip (■), PIM-DM-BTrip (●), PIM-TFM-BTrip (●) and PIM- DTFM-BTrip (◆).

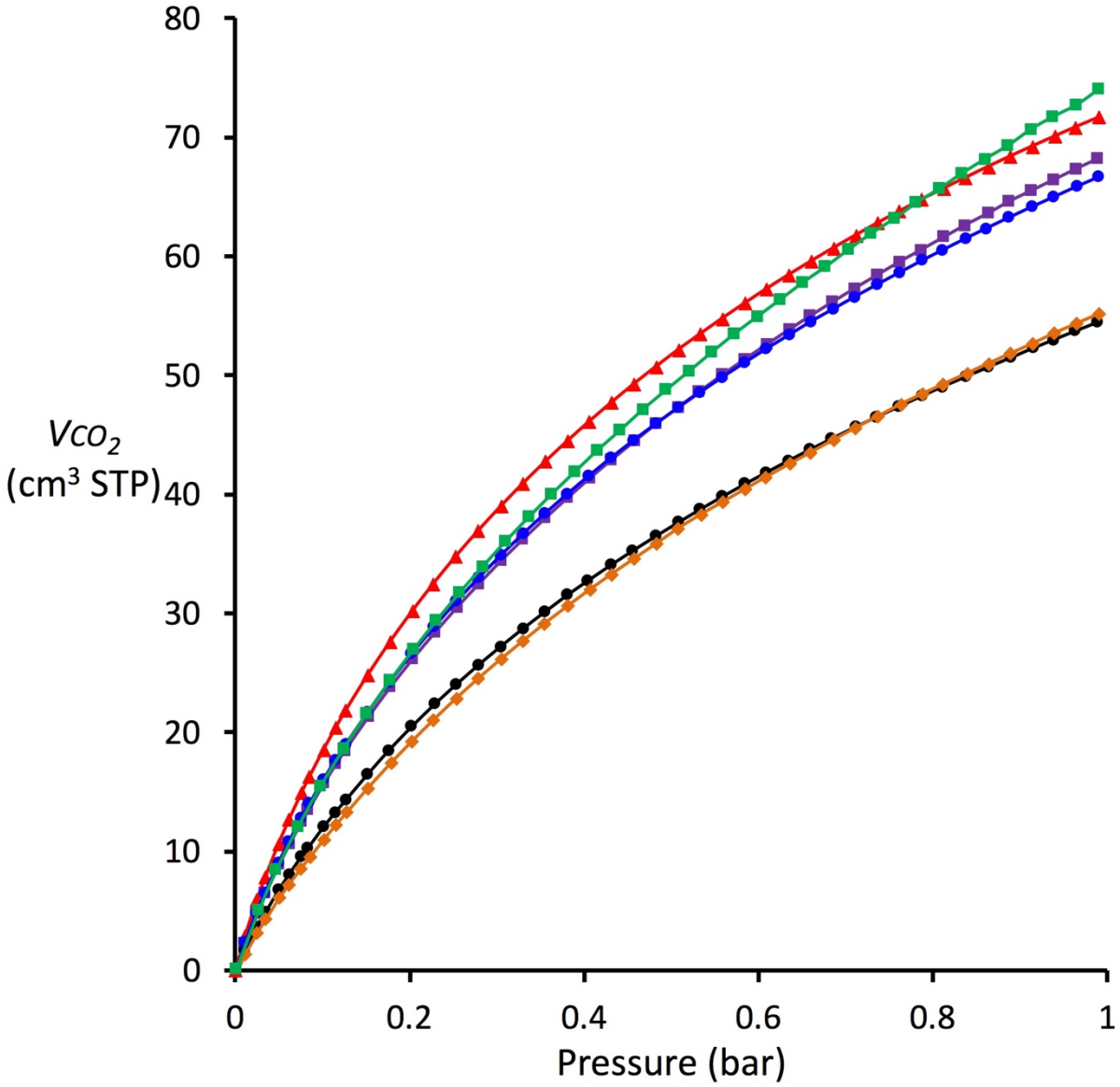

Fig. S2. Carbon dioxide adsorption isotherms acquired at 273 K for powdered samples of PIM-BTrip (▲), PIM-TMN-Trip (■), PIM-HMI-Trip (■), PIM-DM-BTrip (●), PIM-TFM-BTrip (●) and PIM- DTFM-BTrip (◆).

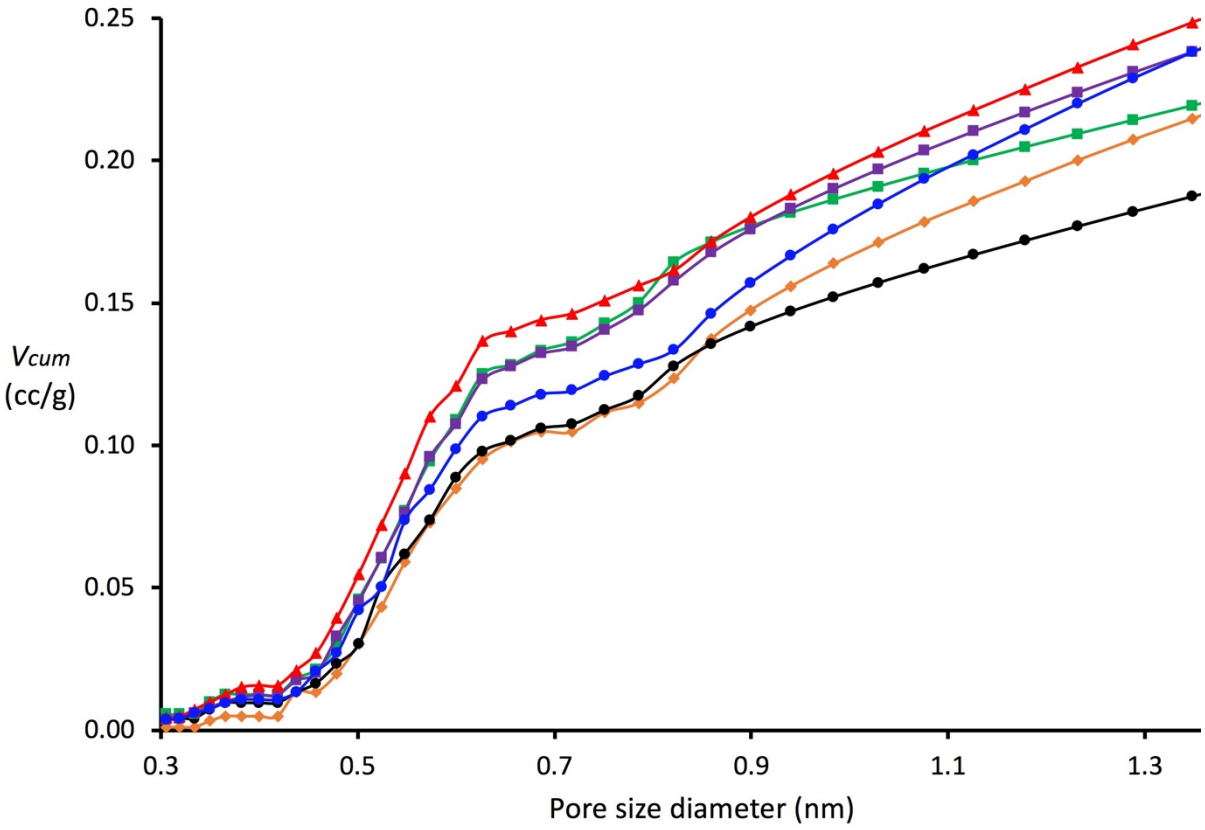

Fig. S3. Cumulative pore volume calculated from CO_2 adsorption data for PIM-BTrip (▲), PIM-TMN-Trip (■), PIM-HMI-Trip (■), PIM-DM-BTrip (●), PIM-TFM-BTrip (●) and PIM-DTFM-BTrip (◆).

Fig. S4. Photographs of solvent cast films.

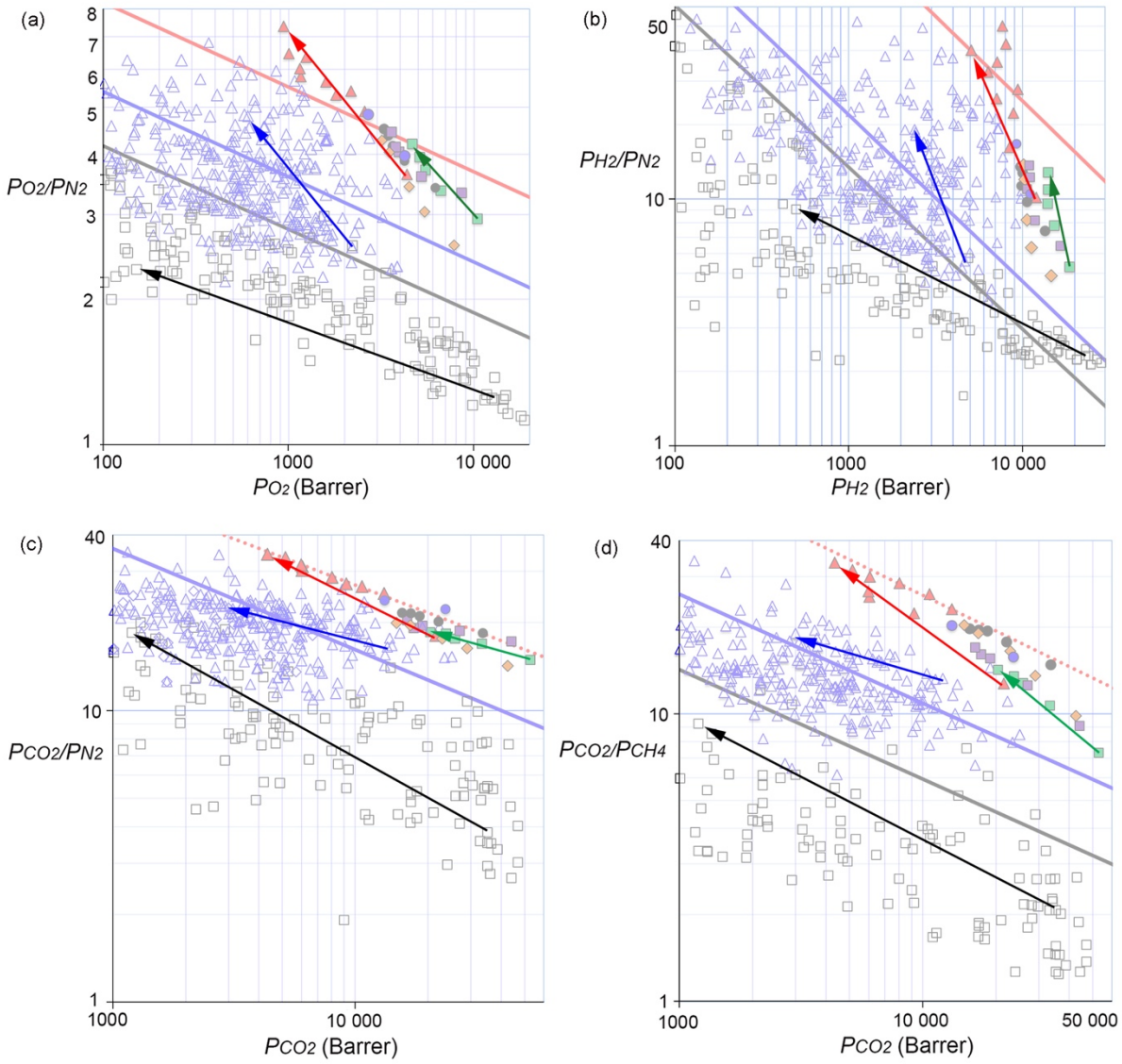

Fig. S5. The Robeson plots from Fig. 2 redrawn to show the ageing trends for some key highly permable polymers: PTMSP over four years (black arrow)[24]; PIM-1 over 3 years (blue arrow)[25]; PIM-TMN-Trip over 1 year (green arrow) and PIM-BTrip over 1 year (red arrow).

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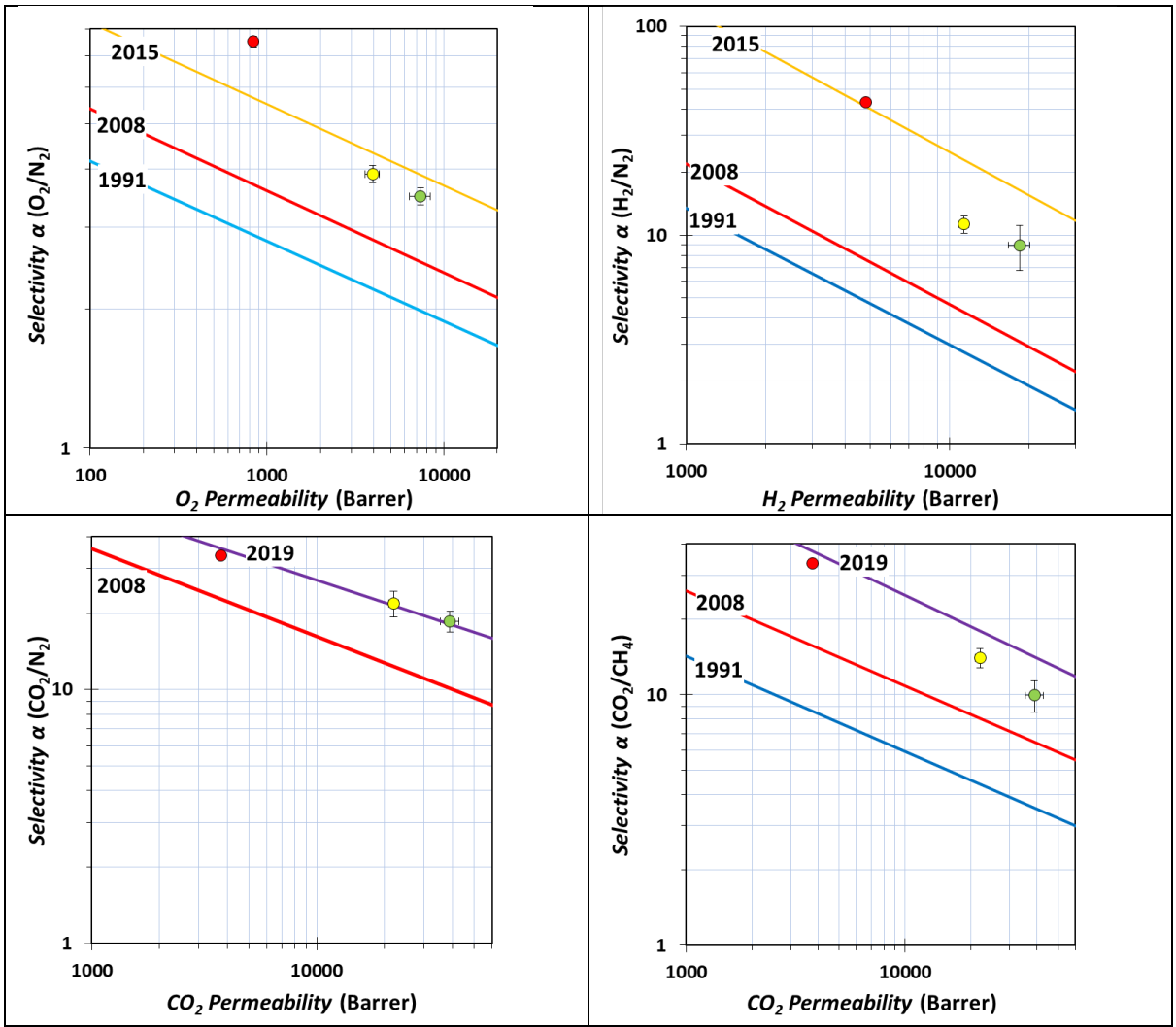

Fig. S6. Robeson plots for the (a) O_2/N_2, (b) H_2/N_2, (c) CO_2/N_2 and (d) CO_2/CH_4 gas pairs showing the gas transport properties for 718 aged PIM-BTrip (●), PIM-DM-BTrip (●), and PIM-HMI-Trip (●) after methanol treatment used for reproducibility measurements with error bars. Horizontal bars represent the standard deviation in Permeability and vertical bars in selectivity. In the case of PIM-BTrip the error bars are smaller than symbols.

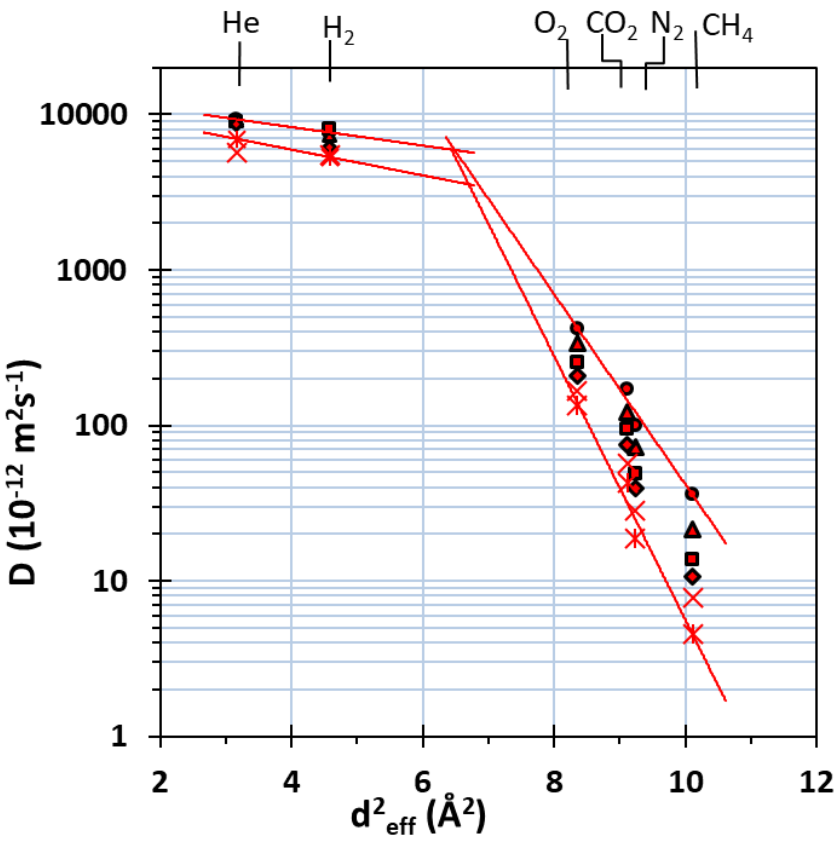

Fig. S7. Correlation of the diffusion coefficient with the square of the effective gas diameter for PIM-BTrip after methanol treatment (●), and after ageing for 130 (▲), 253 (■), 365 (◆), 490 (X), and 633 (ж) days.

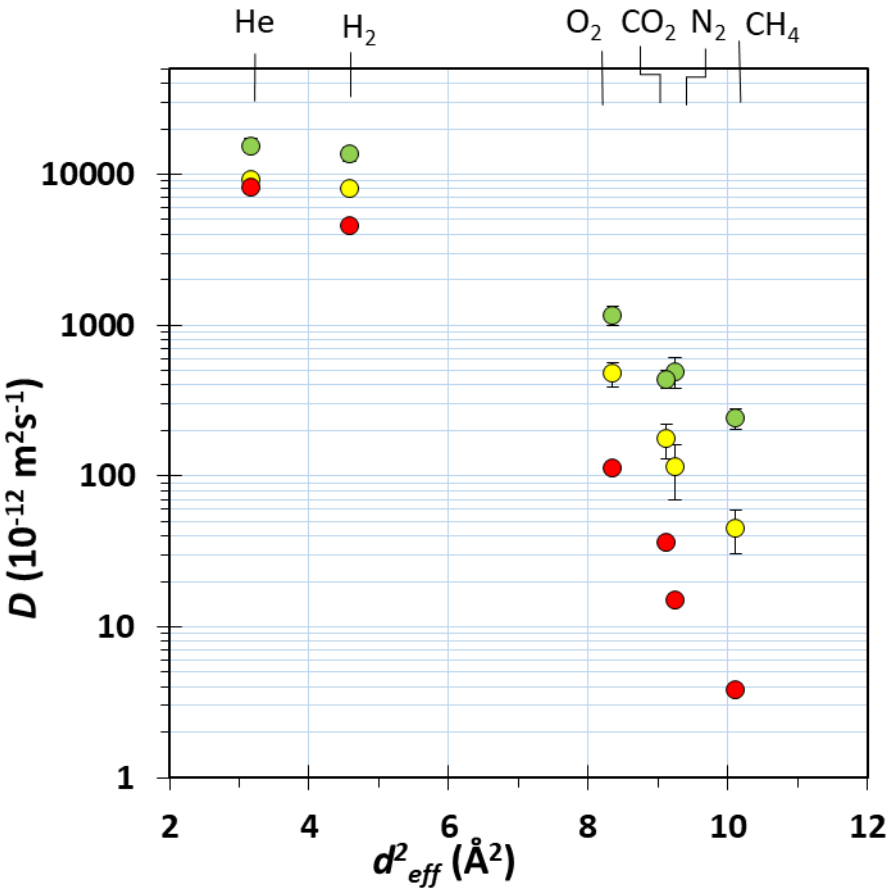

Fig. S8. Correlation of the diffusion coefficient with the square of the effective gas diameter for 718 aged PIM-BTrip (●), PIM-DM-BTrip (●), and PIM-HMI-Trip (●) after methanol treatment. Error bars represent the standard deviation, which is smaller than symbols for some case.

Table S2. Ideal gas diffusion coefficients (10^{-12} m^2s^{-1}) of freshly methanol treated and aged films measured at 25 °C and 1 bar of feed pressure

PIM-[a]	l (μm)[b]	D_{N2}	D_{O2}	D_{CO2}	D_{CH4}	D_{H2}	D_{He}	D_{O2}/D_{N2}	D_{H2}/D_{N2}	D_{CO2}/D_{N2}	D_{CO2}/D_{CH4}
BTrip	160	100	422	172	36.1	7660	9300	4.22	76.6	1.72	4.76
(130)	"	72.0	339	122	21.2	7310	9110	4.71	101	1.69	5.75
(253)	"	48.6	255	94.1	13.6	8040	8930	5.25	165	1.94	6.92
(365)	"	39.2	209	74.8	10.7	6180	8630	5.34	158	1.91	6.99
(490)	"	28.3	167	56.4	7.76	5520	8400	5.90	195	1.99	7.27
(633)	"	18.7	135	43.0	4.5	5320	8230	7.25	285	2.30	9.55
(718)[c]	"	15.2 (±1.2)	113 (±6)	36.0 (±1.9)	3.79 (±0.29)	4600 (±243)	8170 (±295)	7.44 (±0.17)	304 (±9.58)	2.38 (±0.07)	9.51 (±0.22)
BTrip	64	48.6	274	88.3	11.9	5230	5440	5.64	108	1.82	7.42
(120)	"	30.2	183	61.6	9.3	4160	4980	6.07	138	2.04	6.62
(253)	"	36.6	218	70.9	10.5	6870	4980	5.95	187	1.94	6.75
(371)	"	18.9	122	34.7	4.7	6311	3788	6.44	334	1.84	7.38
TMN-Trip	166	803	1700	641	413	15900	20600	2.12	19.8	0.80	1.55
(120)	"	303	1020	418	113	18800	12800	3.37	62.0	1.38	3.70
(253)	"	234	854	346	89.6	12500	14900	3.65	53.55	1.48	3.86
(358)	"	195	762	302	73.0	12100	14400	3.92	62.1	1.55	4.13
(426)	"	160	667	271	58.8	11600	15900	4.17	72.6	1.69	4.61
HMI-Trip[d]	135	494 (±110)	1160 (±172)	439 (±62)	241 (±36)	13700 (±1490)	15500 (±1680)	2.39 (±0.29)	29.3 (±9.6)	0.90 (±0.09)	1.83 (±0.11)
(120)	"	320	964	383	127	11500	14300	3.01	35.9	1.20	3.02
(253)	"	184	690	266	63.9	10200	12000	3.75	55.6	1.45	5.72
(358)	"	144	593	241	51.0	10100	11400	4.13	70.5	1.68	4.73
(426)	"	134	584	218	43.5	10000	11800	4.35	74.8	1.63	5.01
TFM-BTrip	176	542	1130	464	264	13800	16700	2.08	25.5	0.86	1.76
(123)	"	189	710	277	61.4	11300	13200	3.76	59.8	1.47	4.51
(255)	"	145	579	216	44.3	8290	12800	3.99	57.7	1.49	4.87
(367)	"	124	531	197	39.0	9530	13300	4.28	107	1.59	5.05
(496)	"	103	474	186	32.6	9455	13500	4.60	91.7	1.80	5.70
DTFM-BTrip	112	375	1110	430	165	10300	11100	2.96	27.5	1.15	2.61
(119)	"	317	859	347	108	9080	12300	2.71	28.6	1.09	3.21
(366)	"	196	672	273	60.7	8920	11600	3.42	45.4	1.39	4.50
(490)	"	131	518	195	37.8	9030	9380	3.95	68.9	1.49	5.16
(636)	"	111	473	170	31.1	8910	9960	4.25	80.0	1.52	5.46
DM-BTrip[d]	114	115 (±46)	478 (±87)	176 (±46)	44.8 (±14.2)	8140 (±592)	9300 (±701)	4.41 (±0.91)	77.1 (±21.7)	1.59 (±0.21)	4.00 (±0.51)
(128)	"	61.9	313	113	19.2	7700	10000	5.06	124	1.83	5.88

[a] The number in parentheses is the ageing time in days. [b] The thickness did not exhibit significant changes upon ageing. [c] Average and standard deviation (between parentheses) of four independent measurements of the same aged sample. [d] Average and standard deviation (between parentheses) of four independent samples.

Table S3. Ideal gas solubility coefficients (cm^3_{STP} cm^{-3} bar^{-1}) of freshly methanol treated and aged films at 25 °C and 1 bar of feed pressure

PIM-[a]	l (μm)[b]	S_{N2}	S_{O2}	S_{CO2}	S_{CH4}	S_{H2}	S_{He}	S_{O2}/S_{N2}	S_{H2}/S_{N2}	S_{CO2}/S_{N2}	S_{CO2}/S_{CH4}
BTrip	160	8.85	7.69	94.1	35.2	1.18	0.37	0.87	0.13	10.6	2.67
(130)	"	5.44	5.68	80.8	20.1	0.87	0.26	1.04	0.16	14.8	4.02
(253)	"	6.19	6.39	85.1	22.6	0.83	0.29	1.03	0.13	13.7	3.77
(365)	"	5.35	5.66	80.4	19.8	0.87	0.24	1.06	0.16	15.0	4.06
(490)	"	5.17	5.57	80.6	19.5	0.87	0.24	1.08	0.17	15.6	4.13
(633)	"	5.12	5.18	76.0	21.6	0.72	0.20	1.01	0.14	14.8	3.52
(718)[c]	"	5.53 (±0.23)	5.58 (±0.03)	78.4 (±0.71)	22.3 (±0.90)	0.79 (±0.02)	0.20 (±0.01)	1.01 (±0.04)	0.14 (±0.01)	14.2 (±0.5)	3.52 (±0.12)
BTrip	64	5.23	4.92	78.2	26.1	1.35	0.55	0.94	0.26	14.9	3.00
(120)	"	4.98	4.75	73.6	19.1	1.29	0.46	0.95	0.26	14.7	3.84
(253)	"	3.90	3.94	63.4	16.0	0.88	0.53	1.01	0.23	16.3	3.96
(371)	"	6.10	6.14	111	25.8	0.92	0.72	1.01	0.15	18.3	4.30
TMN-Trip	166	3.31	4.60	61.8	13.2	0.89	0.24	1.39	0.27	18.7	4.68
(120)	"	4.87	4.85	59.9	20.8	0.61	0.33	1.00	0.13	12.3	2.88
(253)	"	4.71	4.78	56.0	17.0	0.84	0.26	1.02	0.18	11.9	3.31
(358)	"	4.97	5.00	58.7	18.0	0.88	0.28	1.01	0.18	11.8	3.27
(426)	"	5.17	5.20	56.6	18.3	0.91	0.25	1.00	0.18	10.9	3.09
HMI-Trip[d]	135	3.28 (±0.47)	4.77 (±0.22)	67.1 (±6.1)	12.5 (±1.6)	1.01 (±0.04)	0.32 (±0.03)	1.48 (±0.23)	0.31 (±0.05)	20.6 (±1.85)	5.41 (±0.49)
(120)	"	3.37	4.03	52.8	12.7	0.77	0.22	1.20	0.23	15.7	4.16
(253)	"	3.97	4.28	53.4	14.3	0.78	0.25	1.08	0.20	13.5	3.73
(358)	"	4.74	4.75	54.1	15.9	0.83	0.28	1.00	0.17	11.4	3.40
(426)	"	4.50	4.59	56.5	16.7	0.82	0.26	1.02	0.18	12.6	3.38
TFM-BTrip	176	2.53	4.11	54.4	6.47	0.74	0.23	1.62	0.29	21.5	8.41
(123)	"	4.33	4.47	59.9	15.2	0.71	0.23	1.03	0.16	13.8	3.94
(255)	"	4.53	4.71	64.0	16.1	0.89	0.24	1.04	0.20	14.1	3.96
(367)	"	4.79	4.87	64.7	16.8	0.80	0.23	1.02	0.17	13.5	3.85
(496)	"	5.26	5.16	63.1	18.2	0.77	0.22	0.98	0.15	12.0	3.47
DTFM-BTrip	112	6.00	5.26	74.3	19.7	1.07	0.40	0.88	0.18	12.4	3.77
(119)	"	4.26	4.72	62.8	15.0	0.94	0.28	1.11	0.22	14.7	4.19
(366)	"	4.99	4.97	62.7	17.2	0.90	0.30	1.00	0.18	12.6	3.65
(490)	"	4.96	5.06	65.1	17.7	0.87	0.38	1.02	0.17	13.1	3.67
(636)	"	4.99	5.03	65.42	17.55	0.86	0.36	1.01	0.17	13.1	3.69
DM-BTrip[d]	114	7.23 (±2.04)	6.31 (±1.03)	97.0 (±17.7)	28.1 (±7.8)	1.05 (±0.10)	0.32 (±0.03)	0.91 (±0.20)	0.15 (±0.04)	13.9 (±2.7)	3.57 (±0.67)
(128)	"	6.31	6.33	81.0	23.4	0.96	0.26	1.00	0.15	12.8	3.46

[a] The number in parentheses is the ageing time in days. [b] The thickness did not exhibit significant changes upon ageing. [c] Average and standard deviation (between parentheses) of four independent measurements of the same aged sample. [d] Average and standard deviation (between parentheses) of four independent samples.