Hexaphenylbenzene-based polymers of intrinsic microporosity

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Supporting information

1. Preparation of HPB-PIM-1

2. Preparation of HPB-PIM-2

3. General Methods

1. Preparation of HPB-PIM-1

1(a) 1,2-bis(3,4-dimethoxyphenyl)ethanone

To a dry two necked round bottom flask containing 2-(3,4-dimethoxyphenyl)acetic acid (16.50 g, 84.10 mmol) in dry DCM (30 ml) was added thionyl chloride (18.58 g, 156.14 mmol) drop-wise. The reaction mixture was heated to reflux for 1 h and then the DCM and excess thionyl chloride were removed by distillation. The resulting oil (16.80g, 78.38 mmol) was transferred to another two necked round bottom flask containing dry DCM (150 ml) and veratrole (16.01g, 117.58 mmol). Aluminium trichloride (15.68 g, 117.58 mmol) was added in small portions and the mixture was refluxed for 3 h after which the reaction was quenched by pouring into ice water (100 ml) containing 6M HCl (30 ml). The mixture was extracted with DCM (3x20 ml) and the combined organic layers reduced under vacuum. Recrystallisation from EtOH gave the desired product as a yellow solid (19.71g 79%). M.p. 103 – 105 ˚C (lit m.p. = 104 – 106 ˚C)[1]; IR (nujol) cm^{-1} 1679.2, 1152.2, 1018.2, 721.2; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.66 (dd, 1H, *J* = 8.4, 1.9 Hz, H_a), 7.56 (d, 1H, *J* = 1.9 Hz H_b), 6.88 (d, 1H, *J* = 8.4 Hz, H_c) 6.81 (m, 3H, H_{Ar}), 4.83 (s, 2H, CH_2), 3.94 (s, 3H, OMe), 3.92 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.85 (s, 3H, OMe). ^{13}C NMR (100 MHz; $CDCl_3$) δ 196.4, 153.1, 148.9, 148.8, 147.7, 129.5, 127.3, 123.3, 121.3, 112.2, 111.1, 110.4, 109.8, 77.3, 76.9, 76.6, 55.9, 55.8, 55.7, 55.7, 44.6. LRMS, *m/z*, (APCI$^+$): 317 (MH$^+$, 100%), 318 (20%).

1(b) 1,2-bis(3,4-dimethoxyphenyl)ethane-1,2-dione

To a round bottom flask containing 1,4-dioxane (150 ml), water (5 ml) and 1,2-bis(3,4-dimethoxyphenyl)ethanone (14.50 g, 45.84 mmol) was added selenium dioxide (5.09 g, 45.84 mmol) and the mixture heated at reflux for 15 hr. Once the reaction was cooled to room temperature the resulting solid was collected by filtration. The solid was washed with 1,4-dioxane to remove any traces of starting material then dissolved in DCM and filtered to remove residual selenium residue. The DCM was removed under vacuum to leave a green solid (12.32 g, 81%). M.p. 222 – 225 ˚C (lit m.p. = 223 – 224 ˚C)[1]; IR (nujol) cm^{-1} 1651.7, 1460.3, 1417.4, 1376.9, 1351.8, 1271.3, 1227.9, 1188.9, 1173.4, 1145, 1067.4, 1027.8, 1010, 971.4, 869.7, 816.2, 791.1; ^1H NMR (400 MHz; $CDCl_3$) δ 7.59 (d, 2H *J* = 1.9 Hz, H_a), 7.46 (dd, 2H, *J* = 8.4, 1.9 Hz, H_b), 6.87 (d, 2H, *J* = 8.4 Hz, H_c) 3.95 (s, 6H, OMe) 3.94 (s, 6H, OMe). ^{13}C NMR (100 MHz; $CDCl_3$) δ 193.9, 155.2, 150.0, 149.9, 126.9, 126.8, 110.7, 110.6, 56.7, 56.6. LRMS, *m/z*, ($APCI^+$) 331 (MH^+, 100%)

1(c) 3,4-Bis(3,4-dimethoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone

To a mixture of 1,2-bis(3,4-dimethoxyphenyl)ethane-1,2-dione (2.00 g, 6.06 mmol) diphenylacetone (1.40 g, 6.67 mmol) and EtOH (12 ml) stirred at 85˚C was added KOH (0.17 g, 3.03 mmol) . After 1 h a further KOH (0.17g, 3.03mmol) was added and the reaction mixture stirred at 85 °C a further hour. The mixture was then filtered hot and the resulting solid washed with water and then EtOH, to give the desired product as a black powder (2.02 g, 67%) M.p. 171 – 173 ˚C; IR (nujol)cm^{-1} 1696.5, 1377.4, 1236.1, 1140.2, 1020.6, 963.2, 864.4, 827.3, 813.8, 781, 763.6; ^1H NMR (400 MHz; $CDCl_3$) δ 7.21 (m, 10H, H_{Ar}), 6.67 (d, 2H, *J* = 8.3 Hz, H_a), 6.49 (dd, 2H, *J* = 8.3, 1.9 Hz, H_b), 6.43 (d, 2H, *J* = 1.9 Hz, H_c), 3.83 (s, 6H, OMe), 3.42 (s, 6H, OMe); ^{13}C NMR (100 MHz; $CDCl_3$) δ 200,6; 154,6; 154,4; 149,6; 148,3; 133,9; 131,6; 131,1; 130,5; 129,8; 128,8; 128,5; 128,4; 127,8; 127,7; 126,0; 125,4; 124,8; 123,3; 113,3; 110,7; 56,1; 55,8; LRMS, *m/z*, (EI^+) 444 (M, 100%); HRMS Calc.for $C_{33}H_{28}O_5$ 504.1937, found 504.1946.

1(d) 1,2-(3,4-Dimethoxyphenyl)-3,4,5,6-tetraphenylbenzene

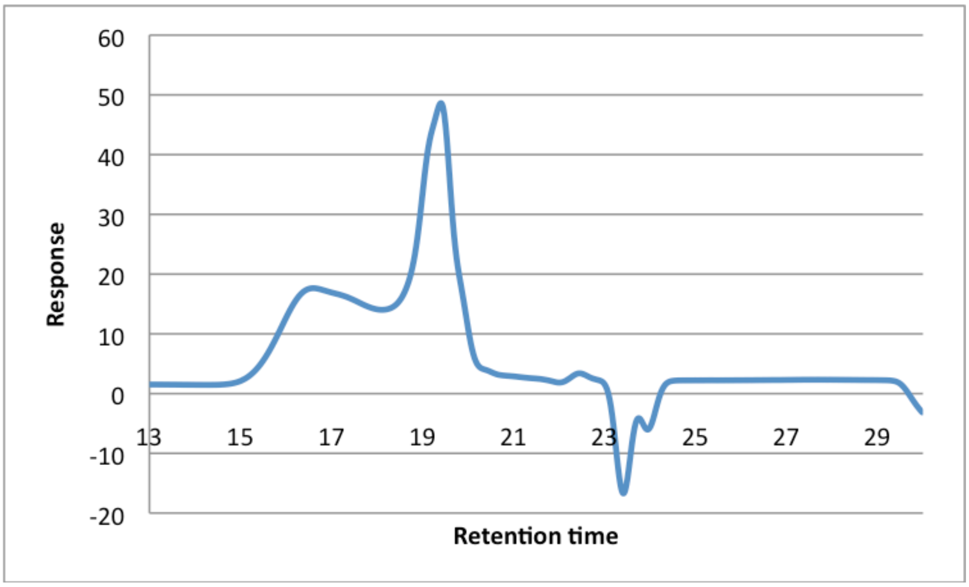
A mixture of diphenyl ether (8 ml), 3,4-bis(3,4-dimethoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone (2.00 g, 3.96 mmol) and diphenylacetylene (0.91 g, 4.76 mmol) was heated at reflux for 15 hrs. On cooling, the mixture was poured into cold MeOH. Hexane (50 ml) was added and the resulting solid collected by filtration. Purification was achieved by column chromatography (hexane : ethyl acetate, 7 : 3) followed by recrystalisation from MeOH to give an off-white powder (1.7g, 65%). M.p. 204 – 206 ˚C; IR (nujol)cm^{-1} 1600.1, 1517.7, 1312.8, 1255.4, 1176.8, 1135.8, 1070.7, 1026.4, 914.5, 857.6, 795.4, 770.9, 697.6; ^{1}H NMR (400 MHz; CDCl$_3$) δ 6.87 (m, 20H, H$_{Ar}$) 6.39 (m, 6H, H$_{Ar}$) 3.71 (s, 6H, OMe) 3.70 (s, 6H, OMe). ^{13}C NMR (100 MHz; CDCl$_3$) δ 147.7, 146.8, 141.3, 141.1, 140.8, 131.9, 131.8, 131.7, 131.7, 127.1, 127.0, 125.6, 125.6, 124.4, 115.9, 115.7, 109.9, 56.1, 55.9. LRMS, *m/z*, (EI$^+$) 654 (M, 100%); HRMS Calc.for $C_{46}H_{38}O_4$ 654.2770, found 654.2781.

1 (e) 1,2-(1,2-Dihydroxyphenyl)-3,4,5,6-tetraphenylbenzene (Monomer 1)

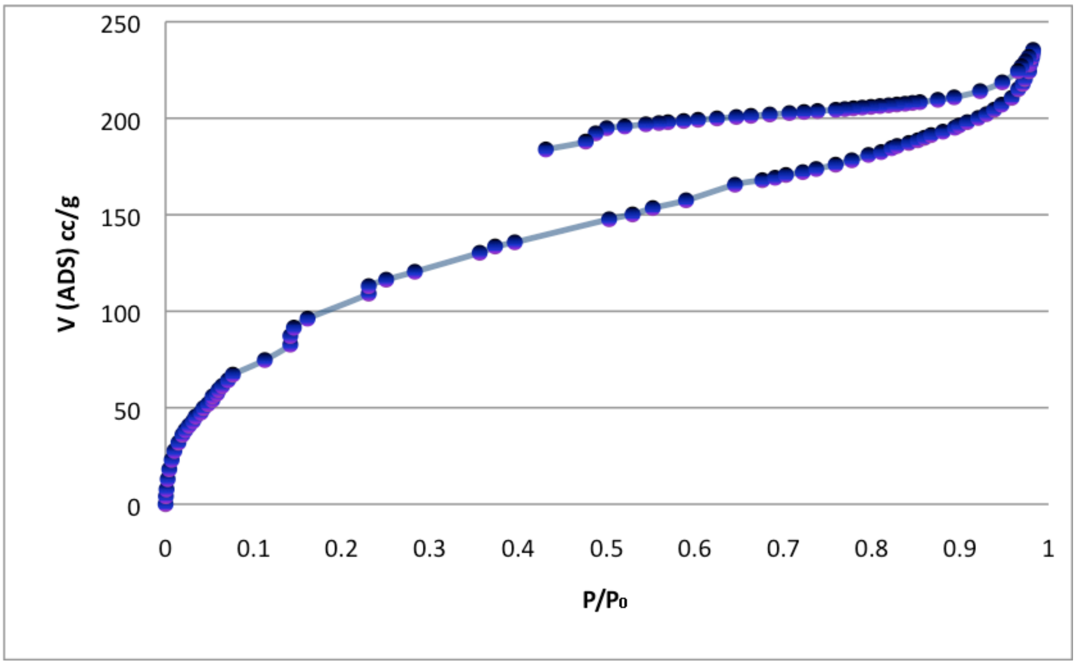
To a cooled (0 °C) solution of 1,2-(3,4-dimethoxyphenyl)-3,4,5,6-tetraphenylbenzene (0.50 g, 0.76 mmol) in dry dichloromethane (30 ml) was added boron tribromide (0.60 g, 2.29 mmol) dropwise, under a dry nitrogen atmosphere. The mixture was then stirred at room temperature for a further 30 min. The reaction was poured into ice and left under vigorous stirring to allow the evaporation of the dichloromethane. The resulting precipitate was collected by filtration, washed with water and dried. Recrystallisation from dichloromethane/hexane (1/1) gave the desired compound as a off-white solid (0.4 g, 89%) M.p. + 360 ˚C; IR (film) cm^{-1} 3055.1, 2305.4, 1599.1, 1517.2, 1439.6, 1265, 1109.8, 1071.7, 1019.1, 896.2, 739, 425.2; ^{1}H NMR (400 MHz; Acetone d^{6}) δ 7.46 (dd, 4H, OH) 6.84 (m, 20H, H_{Ar}) 6.35 (m, 2H, H_{Ar}) 6.22 (m, 2H, H_{Ar}). ^{13}C NMR (100 MHz; $CDCl_3$) 145.2, 144.2, 143.0, 142.9, 142.4, 141.7, 134.5, 133.1, 128.2, 126.8, 126.7, 125.0, 124.9, 120.3, 120.2, 115.0. HRMS Calc.for $C_{42}H_{30}O_4$ 598.2144 , found 598.2158.

1 (f) HPB-PIM-1 from 1,2-(3’,4’-dihydroxyphenyl)-3,4,5,6-tetraphenylbenzene

Monomer 1,2-(3’,4’-dihydroxyphenyl)-3,4,5,6-tetraphenylbenzene **1** (500 mg, 0.84 mmol) and 2,3,5,6-tetrafluoroterephthalonitrile (167 mg, 0.84 mmol) were added to dry DMF (20 ml). This mixture was heated to 65 °C, then dry K_2CO_3 (0.92 g, 6.68 mmol) was added and the mixture stirred for 96 hrs. The reaction mixture was quenched with water (100 ml), and the resulting solid collected by filtration and dried in a vacuum oven to remove any traces of solvent. (654 mg, 86 % based on the molecular weight of the repeated unit). IR (nujol)cm^{-1} 2340.4, 1262.6, 1020.6, 1004.7, 815.7, 721.2, 697.6; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.57 (br m, 20H, H_{Ar}), 6.40 (br m, 6H, H_{Ar}); BET surface area = 425 m^{2} g^{-1}; total pore volume = 0.36 cm^{3} g^{-1} at p/p^{0} = 0.98, adsorption. GPC ($CHCl_3$) *Mn* = 20,000, *Mw* = 33,000 mol g^{-1} (Minor peak), *Mn* = 2,400 and *Mw* = 3,000 (Major peak); TGA (nitrogen): 3% loss of weight occurred at ~ 350 °C. Initial weight loss due to thermal degradation commences at ~ 535 °C.



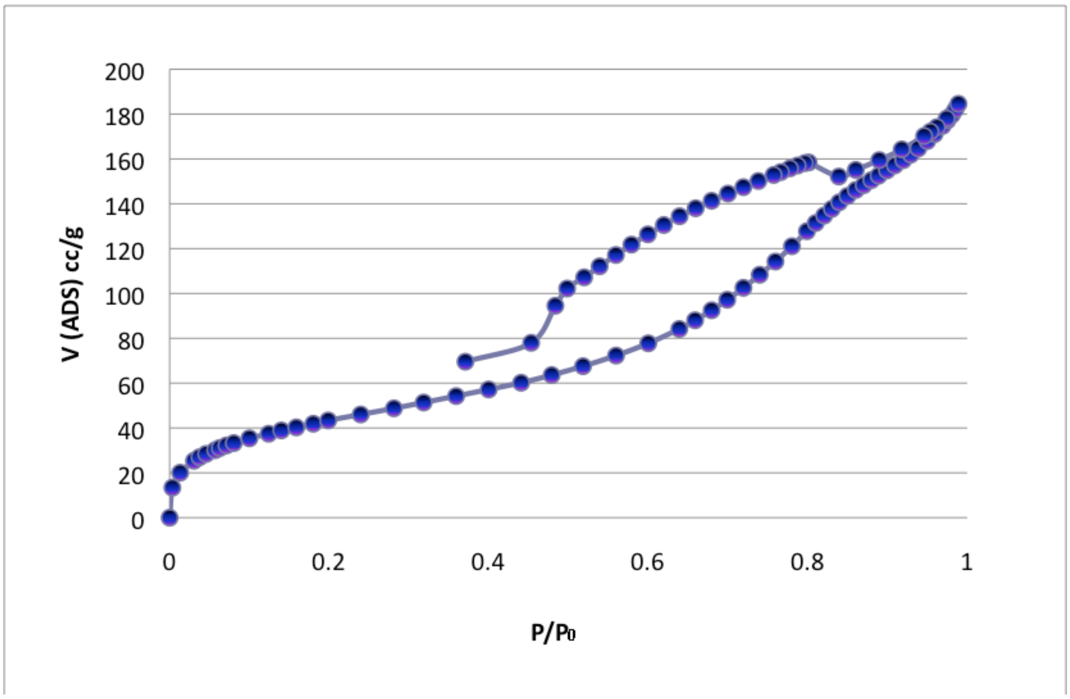
GPC trace of **HPB-PIM-1**



Nitrogen adsorption isotherm of **HPB-PIM-1** at 77 K.

1(g) [2+2] cyclic of HPB-PIM-1 (3)

Under a dry nitrogen atmosphere, 1,2-(3',4'-dihydroxyphenyl)-3,4,5,6-tetraphenylbenzene **1** (250 mg, 0.17 mmol) and 2,3,5,6-tetrafluoroterephthalonitrile (18 mg, 0.09 mmol) were added to anhydrous DMF (40 ml) and the mixture was heated to 65 °C dissolving the two starting materials. Anhydrous K_2CO_3 (76 mg, 1.36 mmol) was added and the mixture stirred for 15 hrs after which the reaction was quenched with water (100 ml). The mixture was extracted with DCM (3 x 20 ml), the organic phases combined and the solvent removed under reduced pressure. The crude product was purified by repeated application of column chromatography using a mixed solvent system of hexane: ethyl acetate (8:2) as eluent with the fastest moving fraction being collected in each case. The solvent was removed under partial pressure and the solid dried in a vacuum oven to give a yellow powder (654 mg, 14 %). M.p > 350°C; IR (nujol) cm^{-1} 2340.4, 1273.4, 1236.7, 1134.5, 1023.8, 901.4, 711.3, 701.9 683.1; ^1H NMR (400 MHz; $CDCl_3$) δ 6.57 (br m, 40H, H_{Ar}), 6.40 (br m, 12H, H_{Ar}); HRMS, *m/z*, (ES^+) Calc.for $C_{100}H_{52}N_4O_8$ ^{39}K 1475.3422, found 1475.3372 ($M + K^+$); BET surface area = 162 m^2 g^{-1}; total pore volume = 0.28 cm^3 g^{-1} at p/p^0 = 0.98, adsorption, (nitrogen). Crystals were prepared by a slow diffusion of methanol into chloroform solution of **3**. Data were collected at Cardiff University using a Bruker-Nonius Kappa CCD area-detector diffractometer equipped with an Oxford Cryostream low temperature cooling device operating at 150(2) K, Mo *K*α radiation (λ = 0.71073 Å). Crystal size: 0.3 x 0.4 x 0.1 mm, monoclinic, space group *C2/c*, a = 49.3119(12), b= 25.9637(8), c= 15.3295(4) Å , β= 94.7630(10), V = 19558.9(9)$Å^3$, Z = 8: μ= 0.18 mm^{-1}, 13685 reflections measured, 9296 unique reflections (*Rint* = 0.0528), 6555 reflections with $I > 2\sigma(I)$, R = 0.1494 and $\omega R2$ = 0.3863 (observed data), R = 0.1928 and $\omega R2$ = 0.4199 (all data). The asymmetric unit contains one molecule of the dimer and there is disorder solvent ($MeOH/CHCl_3$) in the voids.



Nitrogen adsorption isotherm of **3** at 77 K.

2. Preparation of HPB-PIM-2

2(a) 1,2-dimethoxy-4-(phenylethynyl)benzene

A mixture of 4-bromoveratrole (0.61 g, 2.82 mmol), Et_3N (4 ml) and DMF (4 ml) were deoxygenated by use of a nitrogen atmosphere. Ethynylbenzene (0.32 g, 3.10 mmol) was added and the reaction heated to°C90 after which CuI (53.7 mg, 0.28 mmol) and $[P(Ph)_3]_2PdCl_2$ (0.198g, 0.28 mmol) were added. The reaction mixture was stirred at 65 °C for 15 hrs and then quenched with water (40 ml) and allowed to stir for 1hr. The product was extracted with DCM (3 x 20 ml) and the organic layers were combined washed with water (3 x 20 ml) and dried with $MgSO_4$. The solvent was removed under reduced pressure and purification was achieved by column chromatography to give the desired product as a yellow solid (0.47, 70%) M.p 94 - 95 ˚C (lit m.p 93 - 95 ˚C)[2]; IR(film)/cm^{-1} 2362.8, 1594.3, 1512.3, 1465.1, 1327.7, 1251, 1225, 1138.2, 1124.3, 1024.5, 849, 810.4, 763.6, 692.8; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.98 (m, 1H, H_{Ar}), 7.96 (m, 1H, H_{Ar}), 7.64 (m, 2H, H_{Ar}), 7.50 (m, 3H, H_{Ar}), 6.89 (d, 1H, H_{Ar}), 3.96 (s, 3H, OMe) 3.95 (s, 3H, OMe). ^{13}C NMR (100 MHz; $CDCl_3$) δ 149.360, 148.506, 131.379, 128.263, 127.958, 124.815, 123.344, 115.315, 114.107, 110.892, 89.415, 87.884, 55.820, 55.810. LRMS, *m/z*, (APCl$^+$) 239 (M$^+$, 100%) 240 (M^{2+}, 20%)

2(b) 1-(3,4-dimethoxyphenyl)-2-phenylethanone

To a stirred solution of 2-phenylacetic acid (5.00 g, 36.72 mmol) in dry DCM (20 ml). thionyl chloride (13.80 g, 73.42 mmol) was added drop-wise and the mixture was heated to reflux for 1 hr. Once completed the reaction was distilled firstly to remove any DCM and thionyl chloride. Then the temperature was increased to distil of the acid chloride, which was a reddish oil. This oil (5.50 g, 35.62 mmol) was transferred to another two necked round bottom flask containing dry DCM (150 ml) and veratrole (7.35 g, 53.20 mmol). Aluminium trichloride (7.09g, 53.20 mmol) was added carefully to the mixture, once added the mixture was refluxed for 3 hrs. After refluxing the reaction was quenched by pouring into iced water (100 ml) containing 6M HCl (30 ml). This was separated using DCM (3x20 ml) and the combined organic layers reduced under vacuum. Recrystallisation from EtOH gave the desired product as a yellow solid (6.23g 68%). M.p. 85 – 87 ˚C (lit m.p 82 ˚C)[3]; IR (nujol)cm^{-1} 1673.9, 1451.6, 1377.8, 1346.5, 1264.5, 1152.7, 1071.7, 1026.1; ^{1}H NMR (400 MHz; $CDCl_3$) 7.59 (dd, 1H, H_a, $J = 8.3, 2.0$ Hz), 7.48 (d, 1H, H_b, $J = 2.0$ Hz), 7.21 (m, 6H, H_{Ar}), 6.83 (d, 1H, H_c, $J = 8.3$ Hz), 4.16 (s, 2H, CH_2), 3.86 (s, 3H, OMe), 3.83 (s, 3H, OMe). 13C NMR (100 MHz; $CDCl_3$) δ 196.3, 153.2, 149.0, 135.0, 129.6, 129.2, 128.6, 126.7, 123.4, 110.5, 109.9, 56.0, 55.9, 45.2, LRMS, *m/z*, (APCl$^+$): 257 (MH$^+$, 100%), 258 (20%).

2(c) 1-(3,4-dimethoxyphenyl)-2-phenylethane-1,2-dione

Selenium dioxide (0.86 g, 7.80 mmol) was added to a stirred mixture of 1,4-dioxane (150 ml), water (5 ml) and 1-(3,4-dimethoxyphenyl)-2-phenylethanone (2.00 g, 7.80 mmol) which was then heated to reflux for 15 hr. On cooling, the resulting solid was collected by filtration and washed with 1,4-dioxane to remove any traces of starting material. The filtrate was added to DCM (30 ml) and the solution filtered to remove the selenium residue. The DCM was removed under partial pressure and the solid dried in a vacuum oven to give a pink solid (2.05g, 97%). M.p. 113-136 ˚C (lit m.p. = 114 – 115 ˚C) [4]; IR (nujol) cm^{-1} 1663.3, 1460.31418.8, 1376.9, 1303.6, 1283.8, 1240, 1146.4, 1022, 932.8, 875, 834.5, 809.4, 787.2, 764.6, 749.2, 716.9, 683.6, 673.1; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.98 (m, 1H, H_{Ar}), 7.96 (m, 1H, H_{Ar}), 7.64 (m, 2H, H_{Ar}), 7.50 (m, 3H, H_{Ar}), 6.89 (d, 1H, H_{Ar}), 3.96 (s, 3H, OMe), 3.95 (s, 3H, OMe). ^{13}C NMR (100 MHz; $CDCl_3$) δ194.6, 193.2, 154.8, 149.5, 134.7, 133.1, 129.9, 128.8, 126.3, 126.1, 110.2, 110.0, 56.2, 56.0,. LRMS, *m/z*, (APCI^{+}) 271 (MH^{+}, 100%) 272 (20%)

2(d) 3-(3,4-dimethoxyphenyl)-2,4,5-triphenylcyclopenta-2,4-dienone

KOH (0.06 g, 1.13 mmol) was added to a solution of 1-(3,4-dimethoxyphenyl)-2-phenylethane-1,2-dione (1.00 g, 2.25 mmol) and diphenylacetone (0.52 g, 2.48 mmol) in EtOH (12 ml), which was then stirred at 85˚C for 1 h, after which time a further 0.5 eq of KOH (0.06 g, 1.13 mmol) was added and the reaction continued for 1 h. The reaction mixture was then filtered hot and the resulting dark solid washed with water and then EtOH to give the desired product as a black powder. M.p. 180 – 184 ˚C; IR (nujol)cm^{-1} 1700.4, 1597.7, 1576.5, 1510.4, 1490.7, 1412.6, 1377.4, 1353.7, 1316.6, 1301.7, 1275.6, 1253, 1233.2, 1186.9, 1161.9, 1139.2, 1116.1, 1090, 1077, 1019.1, 1002.3, 971.9, 937.7, 917.4, 871.6, 841.2, 817.1, 803.2, 790.6, 769.4, 760.7, 744.3, 735.2, 714, 691.3, 638.3, 625.7, 616.1; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.18 (m, 13H, H_{Ar}) 6.90 (m, 2H, H_{Ar}) 6.57 (d, 1H, *J* = 8.3 Hz, H_a) 6.45 (dd, 1H, *J* = 8.3, 2.0 Hz, H_b) 6.24 (d, 1H, *J* = 2.0 Hz, H_c) 3.77 (s, 3H, OMe) 3.29 (s, 3H. OMe); ^{13}C NMR (100 MHz; $CDCl_3$) δ 200,6; 154,6; 154,4; 149,6; 148,3; 133,9; 131,6; 131,1; 130,5; 129,9; 129,8; 129,1; 128,8; 128,5; 128,4; 127,8; 127,7; 126,0; 125,4; 124,8; 123,3; 113,3; 110,7; 56,1; 55,8; LRMS, *m/z*, (EI$^+$) 444 (M, 100%); HRMS Calc.for $C_{31}H_{24}O_3$ 444.1725, found 444.1736.

2(e) 1,4-di(3’,4’-dimethoxyphenyl)-2,3,5,6-tetraphenylbenzene

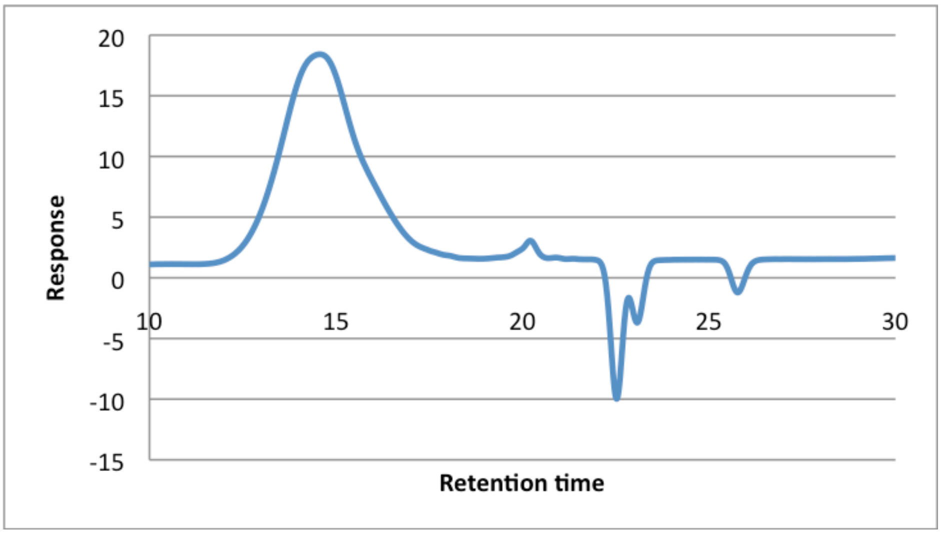
A mixture of 3-(3,4-dimethoxyphenyl)-2,4,5-triphenylcyclopenta-2,4-dienone (1.55 g, 3.50 mmol), 1,2-dimethoxy-4-(phenylethynyl)benzene (1.00 g, 4.20 mmol) and Ph_2O (8 ml) were refluxed for 15 hrs. On cooling, the mixture was poured into cold MeOH and the resulting precipitate collected by filtration. The solid was added to warm hexane (50 ml) to dissolve residual Ph_2O and the crude product was collected by fitration and purified by column chromatography (hexane:ethyl acetate) and finally by recrystallisation from MeOH to give the product as a cream powder (1.46 g, 61%). M.p. 204 – 208 ˚C; IR (nujol) cm^{-1} 1584.2, 1518.1, 1417.4, 1377.4, 1330.1, 1313.7, 1254.4, 1231.3, 1176.3, 1136.8, 1071.2, 1028.3, 910.2, 892.3, 856.2, 808, 768, 699.5, 665.8, 634.4; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.86 (m, 20H, H_{Ar}) 6.32 (m, 6H, H_{Ar}) 3.68 (s, 6H, OMe) 3.40 (s, 6H, OMe). ^{13}C NMR (100 MHz; $CDCl_3$) δ147.2, 146.4, 140.9, 140.5, 139.7, 132.9, 131.5, 131.4, 131.3, 131.2, 126.8, 126.7, 126.7, 126.6, 126.5, 125.1, 124.2, 115.4, 109.3, 55.5, 55.4,. LRMS, *m/z*, (EI$^+$) 654 (M, 100%); HRMS Calc.for $C_{46}H_{38}O_4$ 654.2770, found 654.2784.

2(f) 1,4-Di(3’,4’-dihydroxyphenyl)-2,3,5,6-tetraphenylbenzene (Monomer 2)

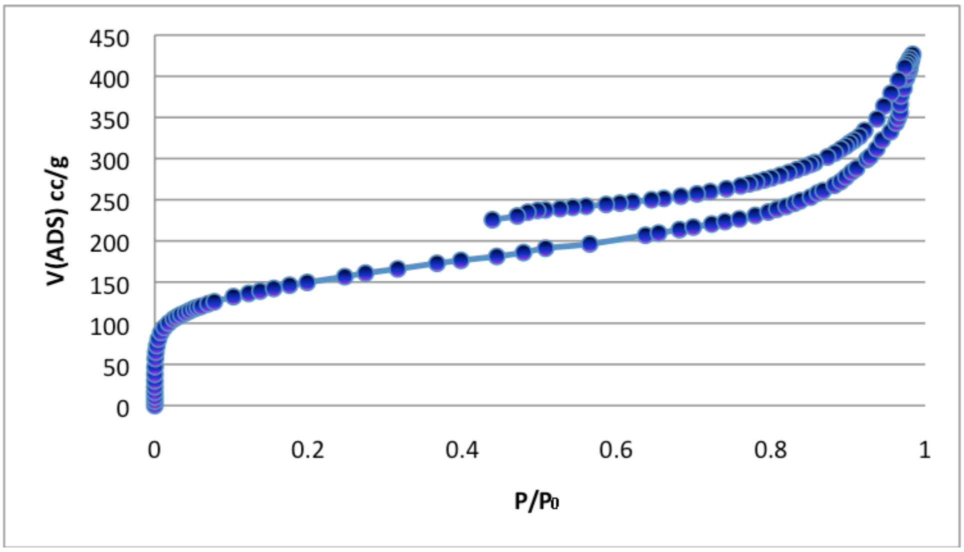
To a solution of 1,3(4)-di(3’,4’-dimethoxyphenyl)-2,3,5,6-tetraphenylbenzene **15** (1.00 g, 1.52 mmol) in dry dichloromethane (30 ml), boron tribromide (1.50 g, 3.80 mmol) was added dropwise under a dry nitrogen atmosphere. The mixture was maintained at 0 °C during the addition and for the following 0.5 h. The reaction mixture was poured into ice and the excess dichloromethane allowed to evaporate. The resulting precipitate was collected by filtration, washed with water and dried. Recrystallization from dichloromethane/hexane (1/1) gave the desired compound as a off-white solid (0.82 g, 91%) M.p. 352 – 355 ˚C; IR (film) cm^{-1} 3054.6, 1598.7, 1520.1, 1265, 896.2, 738.6; ^{1}H NMR (400 MHz; Acetone d^6) δ 7.40 (m, 4H, OH) 6.87 (m, 20H, H_{Ar}) 6.29 (m, 6H, H_{Ar}). ^{13}C NMR (100 MHz; $CDCl_3$). 145.3, 144.3, 143.0, 142.5, 142.3, 142.1, 141.8, 134.4, 133.2, 133.1, 128.2, 126.8, 125.1, 120.4, 115.5. HRMS Calc.for $C_{42}H_{30}O_4$ 598.2144, found 598.2136.

2(g) HPB-PIM-2 from 1,4-(3’,4’-dihydroxyphenyl)-2,3,5,6-tetraphenylbenzene

A mixture of 1,2-(3’,4’-dihydroxyphenyl)-3,4,5,6-tetraphenylbenzene **8** (500 mg, 0.84 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (167 mg, 0.84 mmol) and anhydrous DMF (20 ml) was stirred under a dry nitrogen atmosphere. The mixture was heated to 65 °C and anhydrous K_2CO_3 (0.92 g, 6.68 mmol) was added and the mixture stirred for 96 hrs. After the addition of water (100 ml), filtered and washed repeatedly with water and acetone. The solid was dissolved in $CHCl_3$ (20 ml) and, throughout filtration by cotton wool, poured in a flask containing a mixture of acetone/methanol (2/1, 80 ml). The product was dried under high vacuum overnight to give the final product as yellow solid (699 mg, 92% based on the molecular weight of the repeated unit); IR (nujol) cm^{-1} 1258.4, 1109.5, 998.6, 834.6, 801.9, 768.9, 702.3, 651.3; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.58 (br s, 20H, H_{Ar}), 6.40 (br s, 6H, H_{Ar}); BET surface area = 537 m^2 g^{-1}; total pore volume = 0.65 cm^3 g^{-1} at p/p^0 = 0.98, adsorption; GPC ($CHCl_3$) M_n = 40,000, M_w = 106,000; TGA analysis (nitrogen): 1% loss of weight occurred at ~ 350 °C. Initial weight loss due to thermal degradation commences at ~ 525 °C.



GPC trace of **HPB-PIM-2**



Nitrogen adsorption isotherm of **HPB-PIM-1** at 77 K.

3. General Methods

(a) Gas permeability measurements.[5] Thick polymer films were obtained by solution casting from chloroform solution (5–10% wt/vol) into an accurately leveled Teflon circular dish. Solvent exchange was achieved by methanol treatment overnight. The treated membranes were dried in high, oil-free vacuum for 16 h at 120 °C and stored for measurement in a desiccator over silica gel. Gas permeation data were measured at 30 °C with pure gases, using a proprietary developed pressure increase time-lag apparatus operated at low feed pressure (typically 200–700 mbar), starting with oil free vacuum ($<10^{-4}$ mbar). Permeability coefficient P was calculated from the slope in the steady-state region and apparent diffusion coefficient D, from the time-lag, θ, using $D = l^2/6\theta$, where l is the membrane thickness.

(b) Nitrogen adsorption measurements. Basic volumetric N_2 sorption studies were undertaken at 77 K using a Beckman Coulter 3100 Surface Area Analyzer (Fullerton, California, USA). Apparent surface areas were calculated from N_2 adsorption data by multipoint BET analysis.

(c) Gel Permeation Chromatography (GPC). This was carried out using a Viscotek GPC Max1000 system which includes a refractive index detector and two 2 columns (KF-805L Shodex). The analysis used dilute solution of polymer in chloroform.

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