

Tribenzotriquinacene-based Polymers of Intrinsic Microporosity.

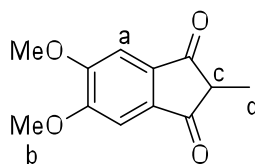
James Vile, Mariolino Carta, C. Grazia Bezzu, Neil B. McKeown*

1. Materials and Methods

Commercially available reagents were used without further purification. Anhydrous dichloromethane was obtained by distillation over calcium hydride under a 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. Flash chromatography was performed on silica gel 60A (35-70 micron) chromatography grade (Fisher Scientific). Melting points were recorded using a Gallenkamp Melting Point Apparatus and are uncorrected. Infrared spectra were recorded in the range 4000-600 cm^{-1} using a Perkin-Elmer 1600 series FTIR instrument either as a thin film or as a nujol mull between sodium chloride plates. The position of absorption bands are quoted in cm^{-1} . ^1H NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 instrument (400 MHz), with ^{13}C NMR spectra recorded at 100 MHz. Chemical shifts (δ_{H} and δ_{C}) were recorded in parts per million (ppm) from tetramethylsilane (or chloroform) and are corrected to 0.00 (TMS) and 7.26 (CHCl_3) for ^1H NMR and 77.00 (CHCl_3), centre line, for ^{13}C NMR. The abbreviations s, d, t, q, m and br. denote singlet, doublet, triplet, quartet, multiplet and broadened resonances; all coupling constants were recorded in Hertz (Hz). 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. Low-temperature (77 K) N_2 adsorption/desorption measurements of PIM powders were made using a Coulter SA3100. Samples were degassed for 800 min at 120 °C under high vacuum prior to analysis. Thermo Gravimetric Analysis (TGA) was performed using the device Thermal Analysis SDT Q600 at a heating rate of 10 °C/min from room temperature to 1000 °C. The solid state ^{13}C NMR was provided by the EPSRC Solid State NMR Research Service using a Varian VNMRs spectrometer operating at 100.56 MHz at Durham University. The acquisition conditions are provided with each spectrum.

2. Synthetic procedures

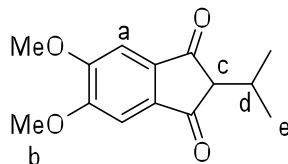
2.1. 5,6-Dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (5)



Methylmalonic acid (4.90 g, 41.5 mmol) and veratrole (4.58 g, 33.2 mmol) were added to polyphosphoric acid (50 g) and the mixture was stirred at 80 °C for 2 h. The mixture was poured into ice water (200 ml) and the product was extracted into DCM (2 x 200 ml). The solvent was removed under reduced pressure to leave a dark solid which was recrystallised from EtOH to give the desired product (4.10 g, 56%) as a light-brown solid, m.p. 225 – 227 °C (227 - 228 °C)¹. ^1H NMR (400 MHz, CDCl_3): δ = 7.33 (s, 2H, H_a), 4.02 (s, 6H, H_b), 2.99 (q, J = 7.7 Hz, 1H, H_c), 1.38 (d, J = 7.7 Hz, 3H, H_d). ^{13}C NMR (100 MHz; CDCl_3): δ = 200.3,

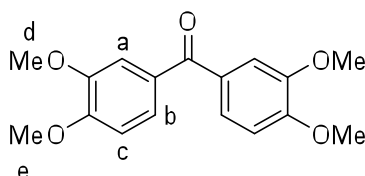
155.9, 136.9, 103.3, 56.7, 48.2, 11.0. LRMS (EI), m/z : 220 $[M]^+$. IR (DCM): 2934, 2835, 2343, 1698, 1581, 1502, 1461, 1312, 1218, 1122 cm^{-1} .

2.2. 2-Isopropyl-5,6-dimethoxy-1*H*-idene-1,3(2*H*)-dione (6)



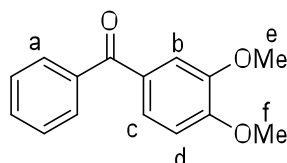
Isopropylmalonic acid (5.42 g, 37.1 mmol), veratrole (4.10 g, 29.7 mmol) and polyphosphoric acid (50 g) were stirred at 65 °C for 12 h. The mixture was poured into ice water (200 ml), stirred for 1 h, extracted into DCM (3 x 200 ml). The solvent was removed under reduced pressure and the crude product was recrystallised from EtOH to give the desired product (4.05 g, 44%) as a yellow solid, m.p. 145 - 147 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.29 (s, 2H, H_a), 4.01 (s, 6H, H_b), 2.82 (d, J = 3.6 Hz, 1H, H_c), 2.50 (m, 1H, H_d), 1.02 (d, J = 7.0 Hz, 6H, H_e). ^{13}C NMR (100 MHz; CDCl_3): δ = 200.3, 155.8, 137.9, 102.9, 58.1, 56.7, 29.2, 19.4. HRMS Calc for $\text{C}_{14}\text{H}_{16}\text{O}_4$ 248.1049, found 248.1050. IR (DCM): 2964, 2932, 2873, 2358, 1730, 1694, 1580, 1498, 1459, 1319, 1225, 1111, 1010 cm^{-1} .

2.3. 3,3',4,4'-Tetramethoxybenzophenone (7)



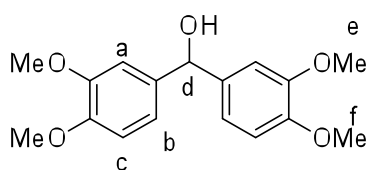
Veratrole (5.00 g, 36.2 mmol) and 3,4-dimethoxybenzoic acid (6.59 g, 36.2 mmol) were added to polyphosphoric acid (50 g). The mixture was stirred at 80 °C for 2 h, poured into water (200 ml) and extracted into DCM (2 x 200 ml). The solvent was removed under reduced pressure to give a dark solid which was recrystallized from EtOH to give the desired product (8.1 g, 74%) as a light-brown solid, m.p. 142 - 144 °C (147 °C)¹. ^1H NMR (400 MHz, CDCl_3): δ = 7.41 (d, J = 1.7 Hz, 2H, H_a), 7.36 (dd, J = 8.3 Hz, 1.6 Hz, 2H, H_b), 6.89 (d, J = 8.3 Hz, 2H, H_c), 3.94 (s, 6H, H_d), 3.92 (s, 6H, H_e). ^{13}C NMR (100 MHz; CDCl_3): δ = 194.5, 152.6, 148.8, 130.7, 124.8, 112.2, 109.7, 56.0. LRMS (EI), m/z : 302 $[M]^+$. IR (DCM): 3083, 2945, 2834, 2358, 1644, 1592, 1512, 1461, 1412, 1333, 1264, 1171, 1133, 1022 cm^{-1} .

2.4. 3,4-Dimethoxybenzophenone (8)



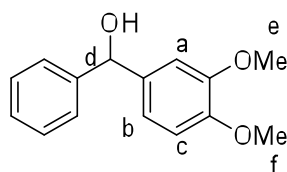
Polyphosphoric acid (100 ml) was stirred at 80 °C for 15 minutes then veratrole (6.03 g, 44.0 mmol) and benzoic acid (8.00 g, 65.6 mmol) were added and the mixture was stirred at 80 °C for 2 h. The mixture was poured into ice water (300 ml) and the white solid was filtered under suction and recrystallized from EtOH to give the desired product (7.13 g, 67%) as white needles, m.p. 96 – 98 °C (98 – 100 °C)². ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 7.3 Hz, 2H, H_a), 7.57 – 7.44 (m, 3H, H-Ar), 7.49 (d, *J* = 1.8 Hz, 1H, H_b), 7.37 (dd, *J* = 8.3 Hz, *J* = 1.8 Hz, 1H, H_c), 6.88 (d, *J* = 8.3 Hz, 1H, H_d), 3.94 (s, 3H, H_e), 3.93 (s, 3H, H_f). ¹³C NMR (100 MHz; CDCl₃): δ = 196.0, 153.4, 149.4, 138.7, 132.3, 130.6, 130.1, 128.6, 126.0, 112.5, 110.1, 56.5, 56.4. LRMS (EI), *m/z*: 242 [M]⁺. 3062, 3007, 2945, 2834, 1644, 1588, 1509, 1450, 1416, 1271, 1229, 1181, 1129, 1019 cm⁻¹.

2.5. Bis(3,4-dimethoxyphenyl)methanol (9)



3,3',4,4'-Tetramethoxybenzophenone (7) (2.00 g, 6.6 mmol) was dissolved in DCM (10 ml) and MeOH (60 ml). Sodium borohydride (0.38 g, 9.9 mmol) was added slowly with cooling in an ice-bath and the reaction was stirred at room temperature for 2 h. The reaction mixture was poured into water (100 ml) and extracted with DCM (2 x 100 ml). The solvent was removed under reduced pressure to obtain a yellow oil which was purified by column chromatography (hexane/EtOAc, 7:3) to give the desired product (0.81 g, 40%) as a yellow solid, m.p. 88 – 90 °C (84-85 °C)¹. ¹H NMR (400 MHz, CDCl₃): δ = 6.92 (d, *J* = 1.8 Hz, 2H, H_a), 6.87 (dd, *J* = 8.2 Hz, *J* = 1.8 Hz, 2H, H_b), 6.82 (d, *J* = 8.2 Hz, 2H, H_c), 5.31 (s, 1H, H_d), 3.86 (s, 6H, OMe), 3.79 (s, 6H, OMe), 1.81 (br s, 1H, OH). ¹³C NMR (100 MHz; CDCl₃): δ = 149.2, 148.5, 136.7, 119.2, 111.1, 110.0, 76.1, 56.0, 55.9. IR (DCM): 3422, 2947, 2837, 1591, 1512, 1456, 1413, 1259, 1132, 1025 cm⁻¹. LRMS (EI), *m/z*: 304 [M]⁺.

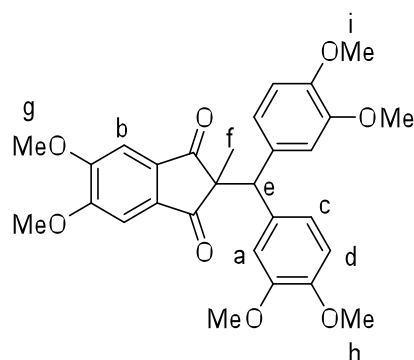
2.6 3,4-Dimethoxybenzhydrol (10)



3,4-Dimethoxybenzophenone (9) (6.50 g, 27 mmol) was dissolved in DCM (10 ml) and MeOH (100 ml). Sodium borohydride (2.35 g, 62 mmol) was added slowly with cooling using an ice-bath. Once the addition was complete, the reaction mixture was stirred at room temperature for 1 h, quenched with water (100 ml) and extracted with DCM (2 x 100 ml). The solvent was removed under reduced pressure to give the desired product (5.5 g, 85%) as a white solid, m.p. 97 – 99 °C (99 °C)³. ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (m, 5H, H-Ar), 6.93 (d, *J* = 1.8 Hz, 1H, H_a), 6.89 (dd, *J* = 8.2 Hz, *J* = 1.8 Hz, 1H, H_b), 6.83 (d, *J* = 8.2 Hz, 1H, H_c), 5.78 (s, 1H, H_d), 3.87 (s, 3H, H_e), 3.85 (s, 3H, H_f), 2.52 (s, 1H, OH). ¹³C NMR (100 MHz; CDCl₃): δ = 149.4, 148.8, 144.3, 137.0, 128.9, 127.9, 126.9, 119.4, 111.3, 110.1, 76.4,

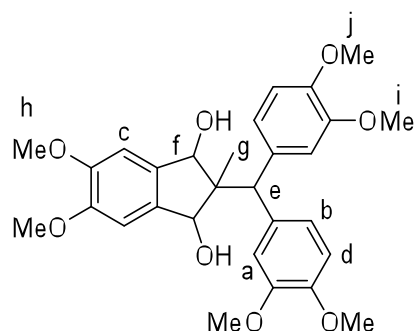
56.4, 56.3. LRMS (EI), m/z : 244 $[M]^+$. IR (DCM): 3483, 2937, 2837, 1599, 1512, 1453, 1417, 1259, 1235, 1136, 1025 cm^{-1} .

2.7. 2-[Bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (11)



A mixture of 5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (**5**) (1.93 g, 8.9 mmol) and *p*-toluenesulfonic acid monohydrate (small spatula tip) in toluene (75 ml) was heated to reflux. A solution of bis(3,4-dimethoxyphenyl)methanol (**8**) (2.93 g, 9.7 mmol) in dichloroethane (50 ml) was added dropwise over a period of 1 h. The mixture was heated at reflux for a further 2 h before being allowed to cool to room temperature. The mixture was washed with sodium hydroxide, 1M (2 x 100 ml) and water (2 x 100 ml) and the solvent was removed under reduced pressure. Recrystallization of the residue from EtOH furnished the desired product (3.33g, 75%) as a white solid, m.p. 161 - 162 °C (162 - 163 °C)¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.15 (d, J = 1.7 Hz, H_a), 7.14 (s, 2H, H_b), 6.91 (dd, J = 8.3 Hz, J = 1.7 Hz, 2H, H_c), 6.64 (d, J = 8.3 Hz, 2H, H_d), 4.44 (s, 1H, H_e), 3.92 (s, 6H, H_g), 3.82 (s, 6H, H_h), 3.73 (s, 6H, H_i), 1.23 (s, 3H, H_f). LRMS (EI), m/z : 506 $[M]^+$. IR (DCM): 2933, 2835, 1728, 1692, 1580, 1515, 1505, 1463, 1418, 1370, 1313, 1261, 1223, 1146, 1105, 1027 cm^{-1} .

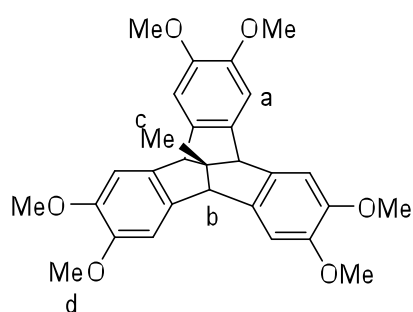
2.8. Bis(3,4-dimethoxyphenyl)methyl-5,6-dimethoxy-2-methyl-1,3-indanediol (15)



A solution of 2-[bis(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (**11**) (1.97 g, 3.89 mmol) in DCM (75 ml) was stirred under cooling in an ice-bath under a nitrogen atmosphere whilst a solution of di-*i*-butylaluminium hydride in cyclohexane, (15.6 ml, 1M, 15.6 mmol) was added dropwise. The mixture was stirred at room temperature for 24 h. The reaction was carefully quenched with water (100 ml), the precipitated solid was collected by suction filtration and washed repeatedly with DCM. The

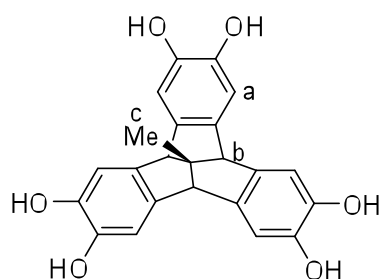
organic layer was separated and the aqueous layer extracted with DCM (2 x 50 ml). The combined organic layers were combined, dried with magnesium sulphate and the solvent removed under reduced pressure to give the desired product (1.61 g, 81%) as a white solid, m.p. 147 - 148 °C (148 - 149 °C)¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.14 (d, *J* = 2.0 Hz, 2H, H_a), 7.07 (dd, *J* = 8.3 Hz, *J* = 2.0 Hz, 2H, H_b), 6.97 (s, 2H, H_c), 6.86 (d, *J* = 8.3 Hz, 2H, H_d), 5.08 (s, 1H, H_e), 4.51 (d, *J* = 7.1 Hz, 2H, H_f), 3.89 (s, 6H, H_h), 3.88 (s, 6H, H_i), 3.88 (s, 6H, H_j), 2.24 (d, *J* = 7.1 Hz, 2H, OH), 0.85 (s, 3H, H_g). ¹³C NMR (100 MHz; CDCl₃): δ = 150.0, 148.8, 147.4, 136.6, 134.3, 121.4, 113.2, 110.9, 108.4, 82.2, 55.9, 55.8, 55.7, 54.3, 48.0, 20.8. LRMS (EI), *m/z*: 510 [M]⁺, 492 [M-H₂O]⁺, 474 [M-2H₂O]⁺. IR (DCM): 3472, 2936, 2360, 1606, 1506, 1464, 1261, 1141, 1101, 1026 cm⁻¹.

2.9. 2,3,6,7,10,11-Hexamethoxy-12d-methyltribenzotriquinacene (19)



Bis(3,4-dimethoxyphenyl)methyl-5,6-dimethoxy-2-methyl-1,3-indanediol (**12**) (1.70 g, 3.3 mmol) was stirred in Eaton's reagent (30 ml) for 12 h at room temperature. The reaction was poured carefully into water (100 ml) and extracted with DCM (2 x 100 ml). The organic layers were separated and the solvent removed under reduced pressure to give the crude product which was purified by column chromatography (hexane/EtOAc, 6:4) to give the desired product (0.90 g, 57 %) as a yellow solid, m.p. 238 - 240 °C (240 - 241 °C)¹. ¹H NMR (400 MHz, CDCl₃): δ = 6.69 (s, 6H, H_a), 4.08 (s, 3H, H_b), 3.86 (s, 18H, H_d), 1.45 (s, 3H, H_c). ¹³C NMR (100 MHz; CDCl₃): δ = 149.0, 137.1, 107.2, 63.3, 63.1, 56.1, 27.3. HRMS Calc. for C₂₉H₃₀O₆ 474.2042, found 474.2057. IR (DCM): 2938, 2858, 2358, 2342, 1607, 1506, 1464, 1408, 1336, 1303, 1277, 1248, 1222, 1190, 1146, 1087, 1026, 996 cm⁻¹.

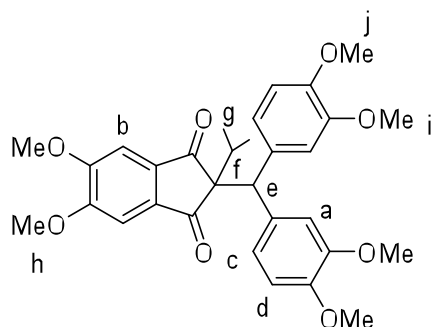
2.10. 2,3,6,7,10,11-Hexahydroxy-12d-methyltribenzotriquinacene (1)



A solution of 2,3,6,7,10,11-hexamethoxy-12d-methyltribenzotriquinacene (**13**) (0.40 g, 0.8 mmol) in DCM (30 ml) was stirred with cooling in an ice bath under a nitrogen atmosphere whilst boron tribromide (0.85 g, 3.7 mmol) was added slowly. The reaction was stirred at room temperature for 12 h, quenched with water (5 ml) and the solid was filtered under

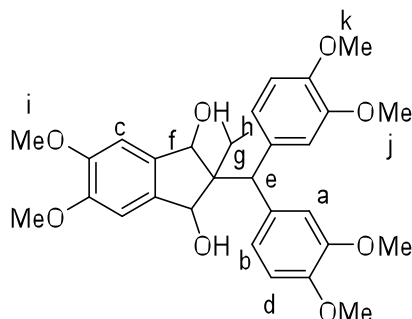
suction and dried under vacuum at room temperature for 12 h to give the desired product (0.24 g, 73%) as a grey solid, m.p. > 300 °C. ¹H NMR (400 MHz, MeOD): δ = 6.78 (s, 6H, H_a), 4.02 (s, 3H, H_b), 1.53 (s, 3H, H_c). ¹³C NMR (100 MHz; MeOD): δ = 148.8, 138.4, 111.6, 64.2, 64.1, 28.2. HRMS Calc for C₂₃H₁₈O₆ 390.1103, found 390.1104. IR (Nujol): 3392, 1678, 1164 cm⁻¹.

2.11. 2-(Bis(3,4-dimethoxyphenyl)methyl)-2-isopropyl-5,6-dimethoxy-1H-indene-1,3(2H)-dione (12)



A solution of 2-isopropyl-5,6-dimethoxy-1H-indene-1,3(2H)-dione (**6**) (2.17 g, 8.8 mmol) and *p*-toluenesulfonic acid (0.1 g) in toluene (70 ml) was heated to reflux. Then a solution of bis(3,4-dimethoxyphenyl)methanol (**8**) (4.00g, 13.0 mmol) in dichloroethane (70 ml) was added dropwise. The mixture was refluxed for 2 h, cooled to room temperature and washed with water (2 x 100 ml). The organic layer was evaporated under vacuum leaving a crude red solid which was purified by column chromatography (hexane/EtOAc, 7:3) to give the desired product (1.40 g, 30%) as a yellow solid, m.p. 156 – 160 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.28 (d, *J* = 0.9 Hz, 2H, H_a), 7.12 (s, 2H, H_b), 6.97 (dd, *J* = 7.7 Hz, *J* = 0.9 Hz, 2H, H_c), 6.65 (d, *J* = 7.7 Hz, 2H, H_d), 4.67 (s, 1H, H_e), 3.95 (s, 6H, H_h), 3.87 (s, 6H, H_i), 3.76 (s, 6H, H_j), 2.55 (m, 1H, H_f), 0.84 (d, *J* = 6.8 Hz, 6H, H_g). ¹³C NMR (100 MHz; CDCl₃): δ = 203.9, 155.6, 148.2, 147.2, 137.8, 133.0, 122.0, 112.9, 110.7, 102.2, 65.4, 56.5, 55.7, 55.6, 54.4, 32.3, 18.2. LRMS (EI), *m/z*: 534 [M]⁺. IR (DCM): 2934, 2360, 2342, 1726, 1685, 1579, 1514, 1464, 1331, 1303, 1265, 1146, 1114, 1027, 863 cm⁻¹.

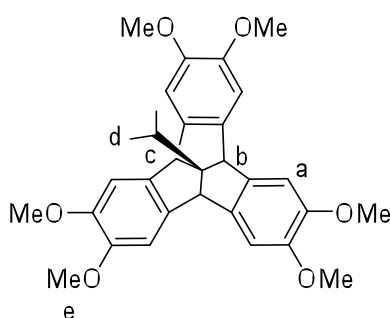
2.12. 2-(Bis(3,4-dimethoxyphenyl)methyl)-2-isopropyl-5,6-dimethoxy-2,3-dihydro-1H-indene-1,3-diol (16)



A solution of 2-(bis(3,4-dimethoxyphenyl)methyl)-2-isopropyl-5,6-dimethoxy-1H-indene-1,3(2H)-dione (**14**) (0.73 g, 1.4 mmol) in DCM (30 ml) was stirred under nitrogen at 0 °C whilst a solution of di-*i*-butylaluminium hydride in cyclohexane, 1M (5.47 ml, 5.5 mmol) was added dropwise. The mixture was stirred at room temperature for 24 h. The mixture was

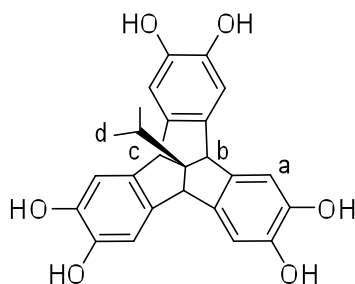
poured into water (200 ml) and the precipitated solid was collected by suction filtration and washed repeatedly with DCM. The organic layer was separated and the aqueous one extracted with DCM. The combined organic layers were dried with magnesium sulphate and the solvent removed under reduced pressure to give the desired product (0.65 g, 88%) as a white solid, m.p. 143 – 147 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.14 (d, J = 1.7 Hz, 2H, H_a), 7.00 (dd, J = 8.3 Hz, J = 1.7 Hz, 2H, H_b), 6.96 (s, 2H, H_c), 6.83 (d, J = 8.3 Hz, 2H, H_d), 5.21 (s, 1H, H_e), 4.97 (d, J = 7.3 Hz, 2H, H_f), 3.89 (s, 6H, H_i), 3.88 (s, 6H, H_j), 3.88 (s, 6H, H_k), 2.72 (m, 1H, H_g), 2.39 (d, J = 7.3 Hz, 2H, OH), 0.29 (d, J = 6.9 Hz, 6H, H_h). ^{13}C NMR (100 MHz; CDCl_3): δ = 150.1, 148.8, 147.5, 137.9, 134.7, 121.5, 113.2, 110.9, 107.1, 58.0, 55.9, 55.8, 55.7, 53.4, 49.1, 29.3, 20.2. LRMS (EI), m/z : 538 $[\text{M}]^+$. IR (DCM): 3501, 2938, 2834, 2359, 1511, 1464, 1262, 1142, 1102, 1027 cm^{-1} .

2.13. 2,3,6,7,10,11-Hexamethoxy-12d-isopropyltribenzotriquinacene (20)



2-(Bis(3,4-dimethoxyphenyl)methyl)-2-isopropyl-5,6-dimethoxy-2,3-dihydro-1H-indene-1,3-diol (**15**) (0.26 g, 0.5 mmol) was stirred in Eaton's reagent (15 ml) for 2 h. The mixture was quenched with water (100 ml) and extracted with DCM. The solvent was removed under reduced pressure leaving a crude red solid which was purified by column chromatography (Hexane/EtOAc, 1:1) to give the desired product (0.18 g, 75%) as a light-yellow solid, m.p. 232 – 236 °C. ^1H NMR (400 MHz, CDCl_3): δ = 6.88 (s, 6H, H_a), 4.50 (s, 3H, H_b), 3.86 (s, 18H, H_c), 2.16 (m, 1H, H_d), 1.01 (d, J = 6.7 Hz, H_d). ^{13}C NMR (100 MHz; CDCl_3): δ = 148.9, 137.5, 107.0, 72.1, 58.2, 56.1, 34.7, 17.6. HRMS Calc for $\text{C}_{31}\text{H}_{34}\text{O}_6$ 502.2355, found 502.2347. IR (DCM): 2956, 2830, 2360, 2341, 2256, 1607, 1507, 1465, 1408, 1388, 1370, 1338, 1300, 1275, 1245, 1222, 1190, 1140, 1089, 1026, 997 cm^{-1} .

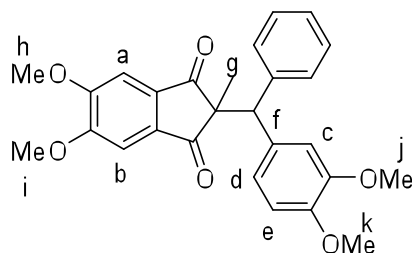
2.14. 2,3,6,7,10,11-Hexahydroxy-12d-isopropyltribenzotriquinacene (2)



A solution of **16** (0.35 g, 0.7 mmol) in dry DCM (20 ml) was stirred under nitrogen at 0 °C whilst boron tribromide (0.70 ml, 2.8 mmol) was added slowly. The mixture was stirred at room temperature for 2 h, quenched with water (50 ml) and the solid that formed was

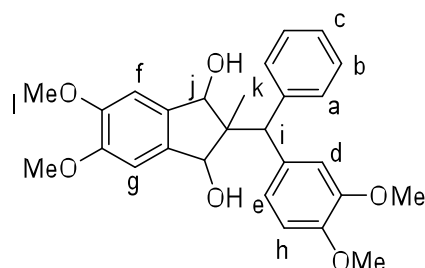
collected by filtration and dried under vacuum at room temperature to give the desired product (0.20 g, 70%) as a grey solid, m.p. > 300 °C. ^1H NMR (400 MHz, MeOD): δ = 6.77 (s, 6H, H_a), 4.26 (s, 3H, H_b), 2.02 (m, 1H, H_c), 0.96 (d, J = 6.7 Hz, H_d). ^{13}C NMR (100 MHz; MeOD): δ = 145.7, 138.7, 111.4, 73.1, 59.1, 36.3, 18.0. HRMS calc for $\text{C}_{25}\text{H}_{22}\text{O}_6$ 418.1416, found 418.1427. IR (Nujol): 3395, 3180, 1677, 1311, 1161 cm^{-1} .

2.15. 2-[(Phenyl-(3,4-dimethoxyphenyl))methyl]-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (13)



A mixture of 5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (**5**) (2.20 g, 10.0 mmol) and *p*-toluenesulfonic acid (0.6 g) in toluene (75 ml) was heated to reflux in a two-necked flask. Then a solution of 3,4-dimethoxybenzhydrol (**10**) (3.66 g, 15 mmol) in 1,2-dichloroethane (75 ml) was added dropwise. The mixture was refluxed for 2 h, allowed to cool, washed with water and the solvent removed under reduced pressure to give a dark solid which was recrystallized from EtOH to give the desired product (3.47 g, 78%) as a yellow solid, m.p. 181–183 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.45 (s, 1H, H_a), 7.43 (s, 1H, H_b), 7.21 (d, J = 1.7 Hz, 1H, H_c), 7.18 – 7.16 (m, 5H, H-Ar), 6.97 (dd, J = 8.3 Hz, J = 1.7 Hz, 1H, H_d), 6.68 (d, J = 8.3 Hz, 1H, H_e), 4.51 (s, 1H, H_f), 3.97 (s, 3H, H_h), 3.96 (s, 3H, H_i), 3.86 (s, 3H, H_j), 3.78 (s, 3H, H_k), 1.28 (s, 3H, H_g); ^{13}C NMR (100 MHz; CDCl_3) δ = 203.2, 155.8, 148.3, 147.4, 140.2, 136.4, 132.6, 129.4, 128.2, 126.6, 122.0, 112.8, 110.6, 103.0, 57.9, 57.1, 56.5, 55.7, 55.6, 20.2; HRMS calc for $\text{C}_{27}\text{H}_{26}\text{O}_6$ 446.1729, found 446.1728. IR (DCM): 2934, 1730, 1694, 1581, 1504, 1459, 1312, 1146, 1105, 1004, 871, 702 cm^{-1} .

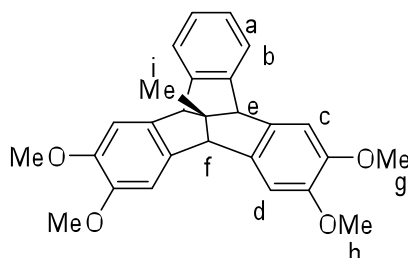
2.16. 2-[(Phenyl-(3,4-dimethoxyphenyl))methyl]-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-diol (17)



A solution of the 2-[(phenyl-(3,4-dimethoxyphenyl))methyl]-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-dione (**17**) (0.38g, 0.9 mmol) in DCM (20 ml) was stirred under nitrogen in at 0 °C whilst a solution of di-*i*-butylaluminium hydride in cyclohexane, 1M (3.40 ml, 3.4 mmol) was added dropwise. The mixture was stirred at room temperature for 24 h. After

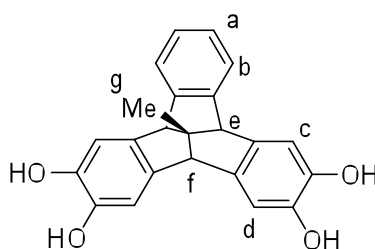
careful addition of saturated aqueous ammonium chloride (15 ml), the precipitated solid was collected by suction filtration and washed repeatedly with dichloromethane. The organic layer was separated and the aqueous one extracted with dichloromethane. The combined organic solutions were washed with water, dried with sodium sulfate and evaporated under vacuum. The solid residue was purified by column chromatography (hexane/EtOAc, 6:4) to give the desired product (0.25 g, 65%) as a white solid, m.p. 195-197 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.56 (d, J = 7.2 Hz, 2H, H_a), 7.36 (t, J = 7.2 Hz, 2H, H_b), 7.26 (m, 1H, H_c), 7.13 (d, J = 2.0 Hz, 1H, H_d), 7.07 (dd, J = 8.3 Hz, J = 2.0 Hz, 1H, H_e), 6.98 (s, 1H, H_f), 6.96 (s, 1H, H_g), 6.85 (d, J = 8.3 Hz, 1H, H_h), 5.16 (s, 1H, H_i), 4.51 (d, 2H, J = 12.8 Hz, H_j), 3.88 (s, 12H, H_k), 2.23 (m, 2H, OH), 0.87 (s, 3H, H_l); ^{13}C NMR (100 MHz; CDCl_3) δ = 149.6, 148.4, 147.1, 141.6, 136.4, 136.3, 133.8, 129.3, 128.2, 126.1, 121.3, 113.0, 110.6, 108.1, 108.0, 81.9, 81.6, 55.5, 55.5, 53.9, 48.1, 20.4; HRMS calc for $\text{C}_{27}\text{H}_{30}\text{NaO}_6$ 473.1940, found 473.1943. IR (DCM): 3484, 2935, 2361, 1604, 1506, 1462, 1265, 1143, 1101, 1026, 846, 734 cm^{-1} .

2.17. 2,3,6,7-Tetramethoxy-12d-methyltribenzotriquinacene (21)



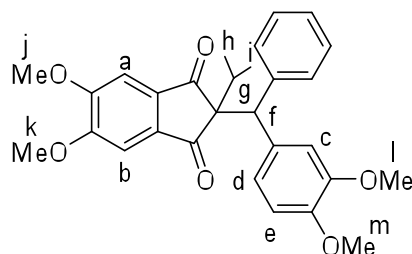
2-[(Phenyl-(3,4-dimethoxyphenyl)methyl]-5,6-dimethoxy-2-methyl-1*H*-indene-1,3(2*H*)-diol (**18**) (2.54 g, 5.6 mmol) was dissolved in Eaton's reagent (50 ml) and stirred at room temperature for 2 h. The reaction mixture was quenched with water (200 ml) and extracted with DCM (2 x 100 ml). The organic layers were evaporated under vacuum and the solid residue was purified by column chromatography (hexane/EtOAc, 7:3) and recrystallized from MeOH to give the desired product (1.18 g, 50%) as a white solid, m.p. 110 – 114 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.43 (dd, J = 5.5 Hz, J = 3.2 Hz, 2H, H_a), 7.22 (dd, J = 5.5 Hz, J = 3.2 Hz, 2H, H_b), 6.94 (s, 2H, H_c), 6.90 (s, 2H, H_d), 4.39 (s, 2H, H_e), 4.33 (s, 1H, H_f), 3.90 (s, 6H, H_g), 3.89 (s, 6H, H_h), 1.69 (s, 3H, H_i). ^{13}C NMR (100 MHz; CDCl_3): δ = 149.7, 149.6, 146.1, 137.7, 137.5, 127.8, 124.8, 107.7, 107.5. HRMS calc for $\text{C}_{27}\text{H}_{26}\text{O}_4$ 414.1831, found 414.1830. IR (DCM): 2936, 1605, 1503, 1461, 1311, 1258, 1222, 1087, 1028 cm^{-1} .

2.18. 2,3,6,7-Tetrahydroxy-12d-methyltribenzotriquinacene (3)



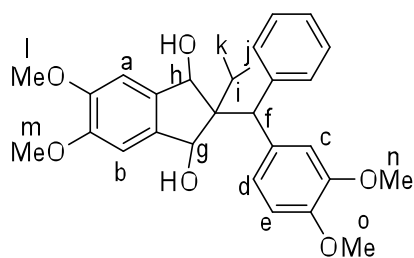
2,3,6,7-Tetramethoxy-12d-methyltribenzotriquinacene (**19**) (1.00 g, 2.4 mmol) was dissolved in DCM (20 ml) at 0 °C under a nitrogen atmosphere and boron tribromide (1.82 g, 7.3 mmol) was added slowly and stirred at room temperature for 4 h. The reaction mixture was quenched with water (10 ml), the DCM was evaporated and the solid was filtered and dried under vacuum at room temperature to give the desired product (0.65 g, 70%) as a grey solid, m.p. decomposes 240 – 250 °C. ¹H NMR (400 MHz, (CD₃)₂CO): δ = 7.67 (s, 2H, OH), 7.66 (s, 2H, OH), 7.42 (dd, *J* = 5.5 Hz, *J* = 3.3 Hz, 2H, H_a), 7.14 (dd, *J* = 5.5 Hz, *J* = 3.3 Hz, 2H, H_b), 6.93 (s, 2H, H_c), 6.85 (s, 2H, H_d), 4.23 (s, 2H, H_e), 4.13 (s, 1H, H_f), 1.59 (s, 3H, H_g). ¹³C NMR (100 MHz; CDCl₃): δ = 147.9, 146.7, 146.6, 139.0, 138.2, 128.7, 126.1, 112.4, 112.3, 64.9, 64.7, 63.8, 29.0. HRMS calc for C₂₃H₁₈O₄ 358.1205, found 358.1193. IR (Nujol): 3395, 3159, 2714, 1680, 1161 cm⁻¹.

2.19. 2-((3,4-Dimethoxyphenyl)(phenyl)methyl)-2-*i*-propyl-5,6-dimethoxy-1*H*-indene-1,3(2*H*)-dione (**14**)



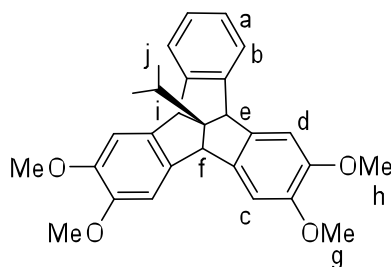
To a refluxing solution of 2-*i*-propyl-5,6-dimethoxy-1*H*-indene-1,3(2*H*)-dione (**6**) (2.80 g, 11.3 mmol) and *p*-toluenesulfonic acid (0.5 g) in toluene (100 ml) was added dropwise a solution of 3,4-dimethoxybenzhydrol (**10**) (4.13 g, 16.9 mmol) in dichloroethane (100 ml). The mixture was refluxed for 3 h, cooled to room temperature and washed with water (2 x 100 ml). The organic layer was evaporated under vacuum leaving a crude red solid which was purified by column chromatography (hexane/EtOAc, 7:3) to give the desired product (3.44 g, 60%) as a yellow solid, m.p. 167 – 169. ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (s, 1H, H_a), 7.47 (s, 1H, H_b), 7.33 (d, *J* = 1.9 Hz, 1H, H_c), 7.14 – 7.02 (m, 5H, H-Ar), 6.99 (dd, *J* = 8.3 Hz, *J* = 1.9 Hz, 1H, H_d), 6.65 (d, *J* = 8.3 Hz, 1H, H_e), 4.71 (s, 1H, H_f), 3.94 (s, 3H, H_j), 3.93 (s, 3H, H_k), 3.88 (s, 3H, H_l), 3.76 (s, 3H, H_m), 2.56 (m, 1H, H_g), 0.86 (d, *J* = 6.8 Hz, 3H, H_h), 0.81 (d, *J* = 6.8 Hz, 3H, H_i). ¹³C NMR (100 MHz; CDCl₃): δ = 204.4, 204.0, 156.1, 156.0, 148.7, 147.7, 140.9, 138.3, 133.2, 130.0, 128.7, 126.9, 122.7, 113.6, 111.2, 102.8, 102.7, 65.7, 57.0, 56.2, 56.1, 55.4, 32.7, 18.8, 18.5. HRMS Calc for C₂₉H₃₀O₆ 474.2042, found 474.2032. IR (DCM): 3060, 2966, 2937, 2836, 2360, 2342, 1727, 1689, 1579, 1516, 1503, 1464, 1422, 1389, 1372, 1332, 1301, 1266, 1246, 1223, 1186, 1146, 1114, 1079, 1028, 1009 cm⁻¹.

2.20. 2-((3,4-Dimethoxyphenyl)(phenyl)methyl)-2-*i*-propyl-5,6-dimethoxy-2,3-dihydro-1*H*-indene-1,3-diol (**18**).



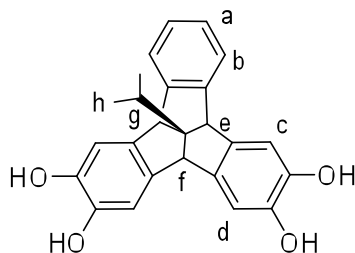
A solution of 2-((3,4-dimethoxyphenyl)(phenyl)methyl)-2-isopropyl-5,6-dimethoxy-1*H*-indene-1,3(2*H*)-dione (**20**) (2.59 g, 5.5 mmol) in DCM (70 ml) was stirred under nitrogen at 0 °C whilst a solution of di-*i*-butylaluminium hydride in cyclohexane, 1M (22 ml, 22.0 mmol) was added slowly. The mixture was stirred at room temperature for 16 h. The reaction was quenched with water (100 ml) and the precipitated solid was collected by suction filtration and washed repeatedly with dichloromethane. The organic layer was separated and the aqueous one extracted with dichloromethane. The combined organic solutions were washed with water, dried with sodium sulfate and removed under reduced pressure to give the desired product (2.40 g, 90%) as a yellow solid, m.p. 195-197 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (s, 1H, H_a), 7.50 (s, 1H, H_b), 7.35 – 6.95 (m, 5H, H-Ar), 7.13 (d, *J* = 1.8 Hz, 1H, H_c), 7.00 (dd, *J* = 8.3 Hz, *J* = 1.8 Hz, 1H, H_d), 6.83 (d, *J* = 8.3 Hz, 1H, H_e), 5.29 (s, 1H, H_f), 4.99 (d, *J* = 7.2 Hz, 1H, H_g), 4.95 (d, *J* = 7.2 Hz, 1H, H_h), 3.89 (s, 3H, H_i), 3.88 (s, 3H, H_m), 3.87 (s, 3H, H_n), 3.86 (s, 3H, H_o), 2.75 (m, 1H, H_i), 2.38 (m, 2H, OH), 0.30 (d, *J* = 7.0 Hz, 3H, H_j), 0.23 (d, *J* = 7.0 Hz, 3H, H_k). ¹³C NMR (100 MHz; CDCl₃): δ = 150.1, 148.8, 147.5, 142.4, 138.1, 137.9, 134.5, 129.7, 128.4, 126.3, 121.6, 113.3, 110.9, 107.1, 107.0, 79.0, 78.7, 58.0, 55.9, 55.9, 55.8, 55.7, 53.4, 49.5, 29.2, 20.1. HRMS Calc for C₂₉H₃₄O₆ 478.2355, found 478.2357. IR (DCM): 3466, 2957, 2358, 1605, 1506, 1464, 1308, 1264, 1144, 1101, 1028 cm⁻¹.

2.21. 2,3,6,7-Tetramethoxy-12*d*-*i*-propyltribenzotriquinacene (**22**)



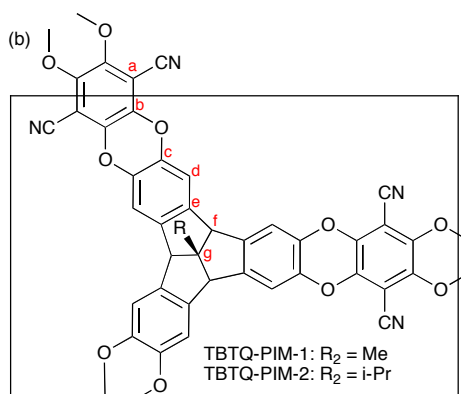
2-((3,4-Dimethoxyphenyl)(phenyl)methyl)-2-isopropyl-5,6-dimethoxy-2,3-dihydro-1*H*-indene-1,3-diol (**21**) (2.30 g, 4.8 mmol) was stirred in Eaton's reagent (40 ml) for 12 h. The reaction mixture was poured into water (100 ml), extracted into DCM (2 x 200 ml) and the organic layer was evaporated under reduced pressure. The solid residue was purified by column chromatography (hexane/EtOAc, 7:3) to give the desired product (0.96 g, 45%) as a yellow solid, m.p. 102 – 104 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.40 (dd, *J* = 5.5 Hz, *J* = 3.3 Hz, 2H, H_a), 7.18 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 2H, H_b), 6.92 (s, 2H, H_c), 6.87 (s, 2H, H_d), 4.57 (s, 2H, H_e), 4.52 (s, 1H, H_f), 3.87 (s, 6H, H_h), 3.86 (s, 6H, H_g), 2.16 (m, 1H, H_i), 1.01 (d, *J* = 6.7 Hz), 6H, H_j). ¹³C NMR (100 MHz; CDCl₃): δ = 148.9, 145.7, 137.3, 127.2, 124.0, 106.9, 71.2, 58.4, 56.1, 56.0, 34.8, 17.6. HRMS Calc for C₂₉H₃₀O₄ 442.2144, found 442.2157. IR (DCM): 2958, 1606, 1505, 1464, 1303, 1223, 1112, 1089, 998, 850 cm⁻¹.

2.22. 2,3,6,7-Tetrahydroxy-12d-*i*-propyltribenzotriquinacene (4)



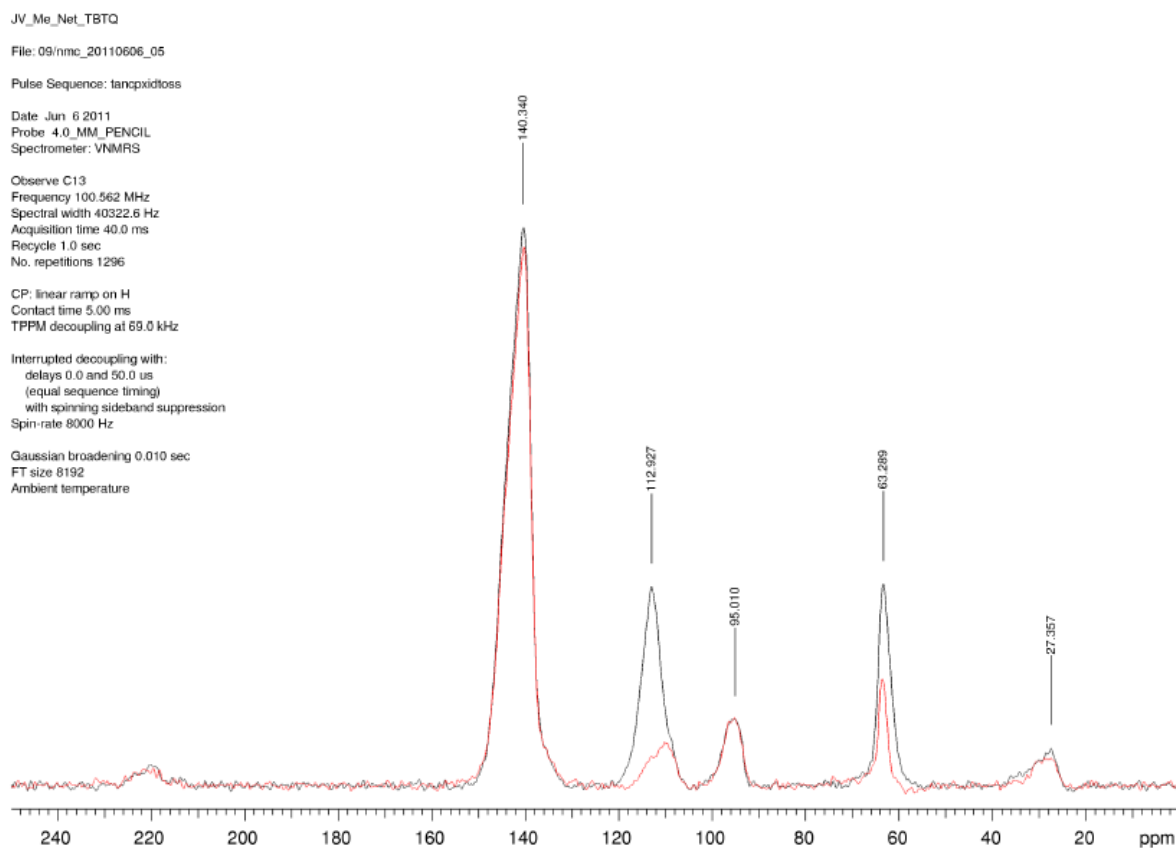
2,3,6,7-Tetramethoxy-12d-*i*-propyltribenzotriquinacene (**22**) (0.53 g, 1.2 mmol) was dissolved in DCM (20 ml) under a nitrogen atmosphere and boron tribromide (0.90 g, 3.6 mmol) was added slowly with cooling in an ice-bath and then stirred at room temperature for 4 h. The reaction mixture was quenched with water (10 ml), the DCM was evaporated under reduced pressure and the solid was collected by filtration and dried under vacuum at room temperature to give the desired product (0.33 g, 72%) as a grey solid, m.p. 216 – 220 °C. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 7.62 (s, 4H, OH), 7.41 (dd, J = 5.5 Hz, J = 3.3 Hz, 2H, H_a), 7.12 (dd, J = 5.5 Hz, J = 3.3 Hz, 2H, H_b), 6.93 (s, 2H, H_c), 6.85 (s, 2H, H_d), 4.49 (s, 2H, H_e), 4.39 (s, 1H, H_f), 2.10 (m, 1H, H_g), 0.98 (d, J = 6.7 Hz, 6H, H_h). ^{13}C NMR (100 MHz; MeOD): δ = 148.0, 146.4, 146.3, 139.2, 138.5, 128.4, 125.5, 111.9, 111.8, 72.7, 59.8, 36.7, 18.4. HRMS calc for $\text{C}_{25}\text{H}_{22}\text{O}_4$ 386.1518, found 386.1525. IR (Nujol): 3374, 3151, 2722, 1677, 1304, 1161 cm^{-1} .

2.23. TBTQ-PIM-1

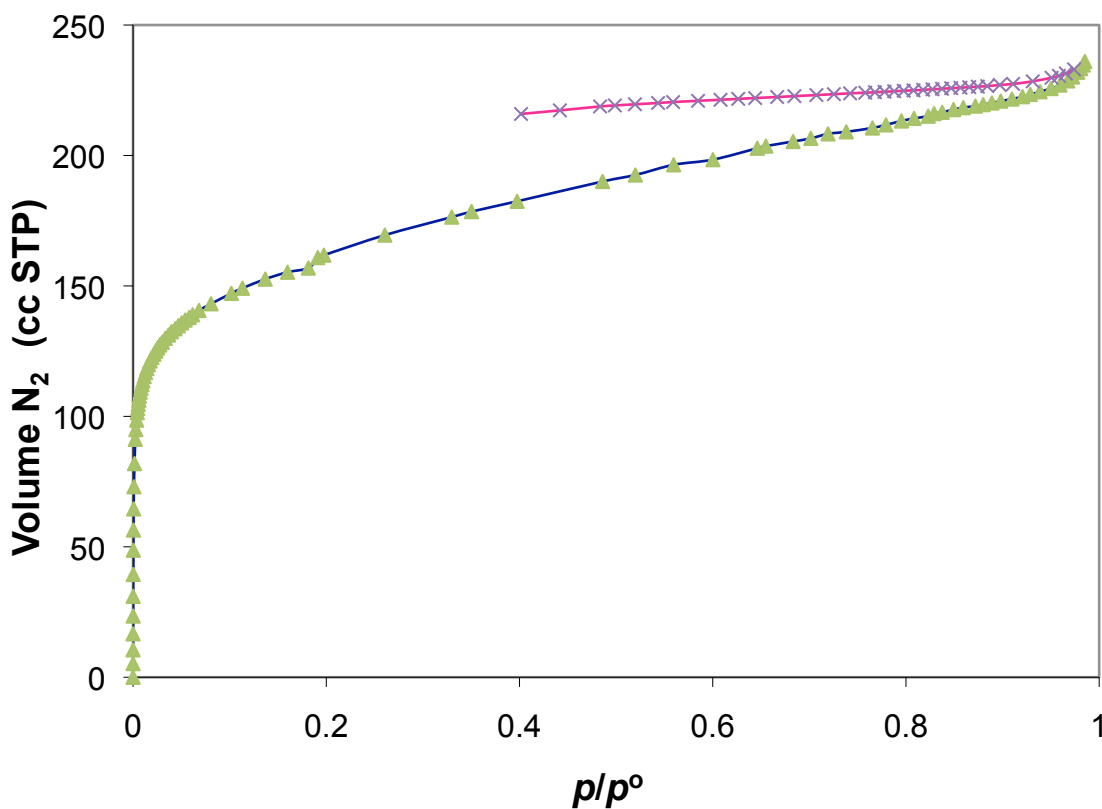


In a two-necked round bottom flask was added under a dry nitrogen atmosphere monomer **1** (0.202 g, 0.518 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.155 g, 0.777 mmol) and dry dimethylformamide (20 ml). The mixture was heated to 80 °C then dry potassium carbonate (0.86 g, 6.22 mmol) was added and the mixture was stirred at 80 °C for 16 h. The solution was quenched with water (100 ml), the solid collected by filtration and washed repeatedly with water and acetone. The product was washed with refluxing chloroform (12 h), acetone (12 h) and MeOH (12 h). The purified product was dried at 100 °C under vacuum (12 h) to give a yellow solid (0.175 g, 72% based on the molecular weight of the repeat unit). BET surface area = 565 $\text{m}^2 \text{g}^{-1}$; total pore volume = 0.36 $\text{cm}^3 \text{g}^{-1}$ at $p/p^0 = 0.98$, adsorption; TGA analysis (nitrogen): 3.3% loss of weight occurred at ~ 86 °C. Initial weight loss due to thermal degradation commences at ~ 526 °C. IR (Nujol): 2922, 2858, 2241 (CN), 1680 cm^{-1} .

SS ^{13}C NMR (100.5 MHz): $\delta = 27.4$ (R = CH_3); 63.3 (C_f and C_g); 95.0 (C_a); 110. (CN); 112.9 (C_d), 140.3 (C_b , C_c and C_e). (note the peak at 220 is a side band)

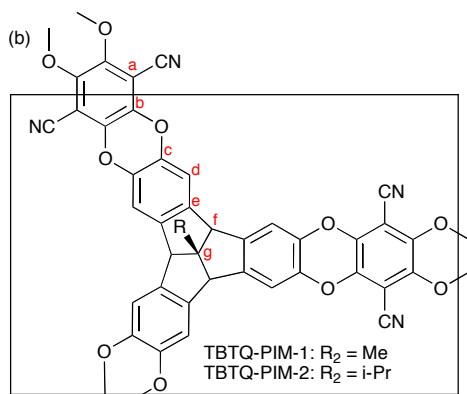


ESI Fig 1. Solid state ^{13}C NMR spectra for **TBTQ-PIM-1**. The black spectrum is the full cross-polarisation spectrum and the red spectrum is with interrupted decoupling, which removes signals from carbons attached to single hydrogens.



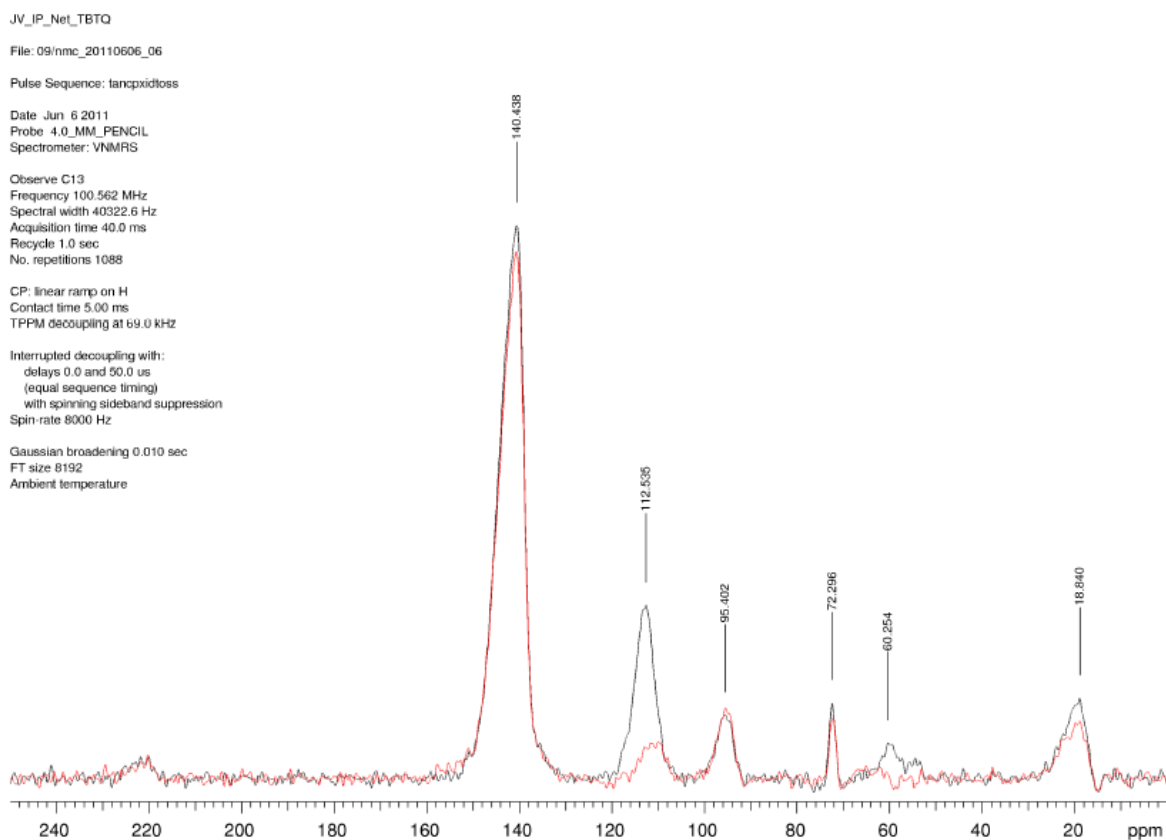
ESI Fig. 2. Nitrogen isotherm of TBTQ-PIM-1 at 77 K.

2.24. TBTQ-PIM-2

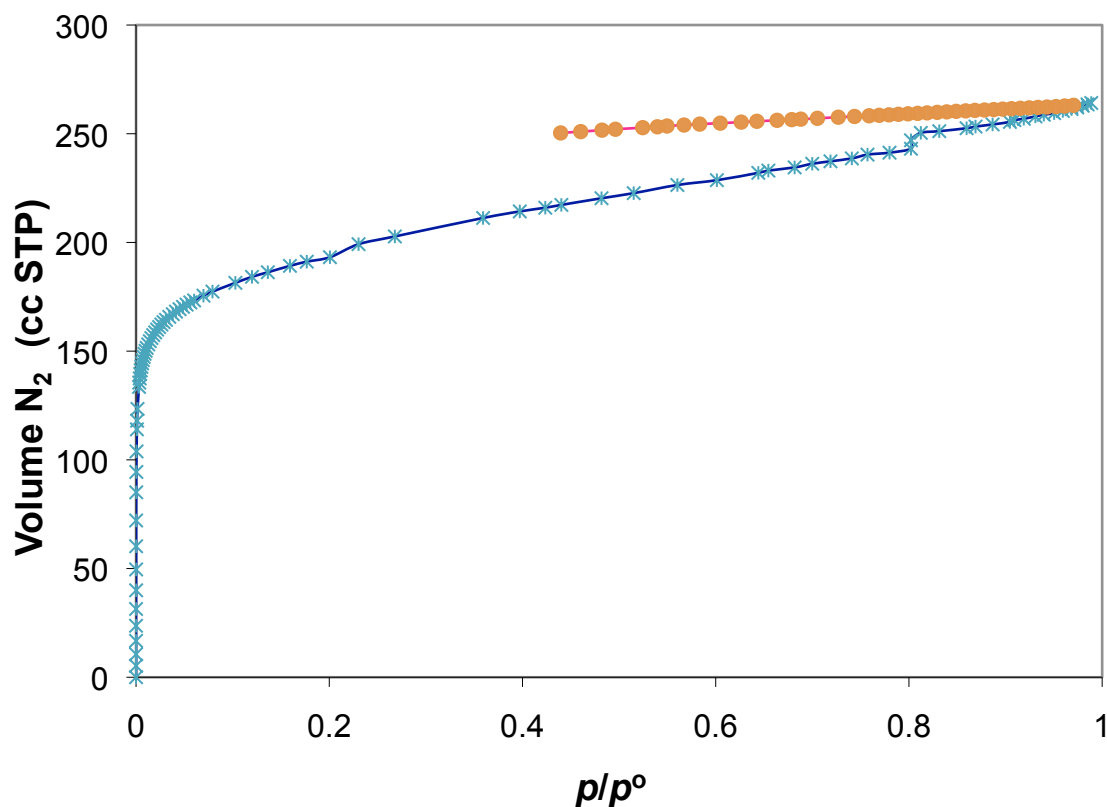


In a two-necked round bottom flask was added under a dry nitrogen atmosphere monomer **2** (0.179 g, 0.428 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.129 g, 0.642 mmol) and dry dimethylformamide (20 ml). The mixture was heated to 80 °C then dry potassium carbonate (0.71 g, 5.14 mmol) was added and the mixture was stirred at 80 °C for 16 h. The solution was quenched with water (100 ml), the solid collected by filtration and washed repeatedly with water and acetone. The product was washed with refluxing chloroform (12 h), acetone (12 h) and MeOH (12 h). The purified product was dried at 100 °C under vacuum (12 h) to give a brown solid (0.145 g, 68% based on the molecular weight of the repeat unit). BET

surface area = $673 \text{ m}^2 \text{ g}^{-1}$; total pore volume = $0.41 \text{ cm}^3 \text{ g}^{-1}$ at $p/p^o = 0.98$, adsorption; TGA analysis (nitrogen): 2.2% loss of weight occurred at $\sim 110 \text{ }^\circ\text{C}$. Initial weight loss due to thermal degradation commences at $\sim 483 \text{ }^\circ\text{C}$. IR (Nujol): 2916, 2239 (CN) cm^{-1} . SS ^{13}C NMR (100.5 MHz): $\delta = 18.8$ (R, CH_3); 54-64 (R, CH and C_f); 72.3 (C_g); 95.4 (C_a); 110.0 (CN); 112.5 (C_d), 140.3 (C_b , C_c and C_e). (note the peak at 220 is a side band).

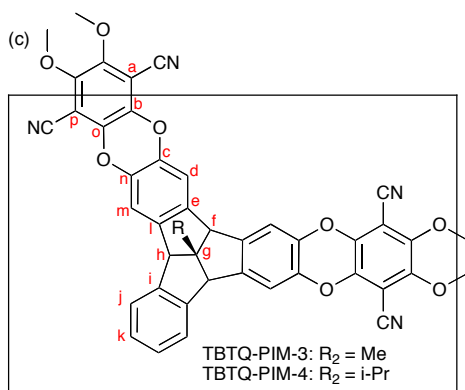


ESI Fig 3. Solid state ^{13}C NMR spectra for **TBTO-PIM-2**. The black spectrum is the full cross-polarisation spectrum and the red spectrum is with interrupted decoupling, which removes signals from carbons attached to single hydrogens.



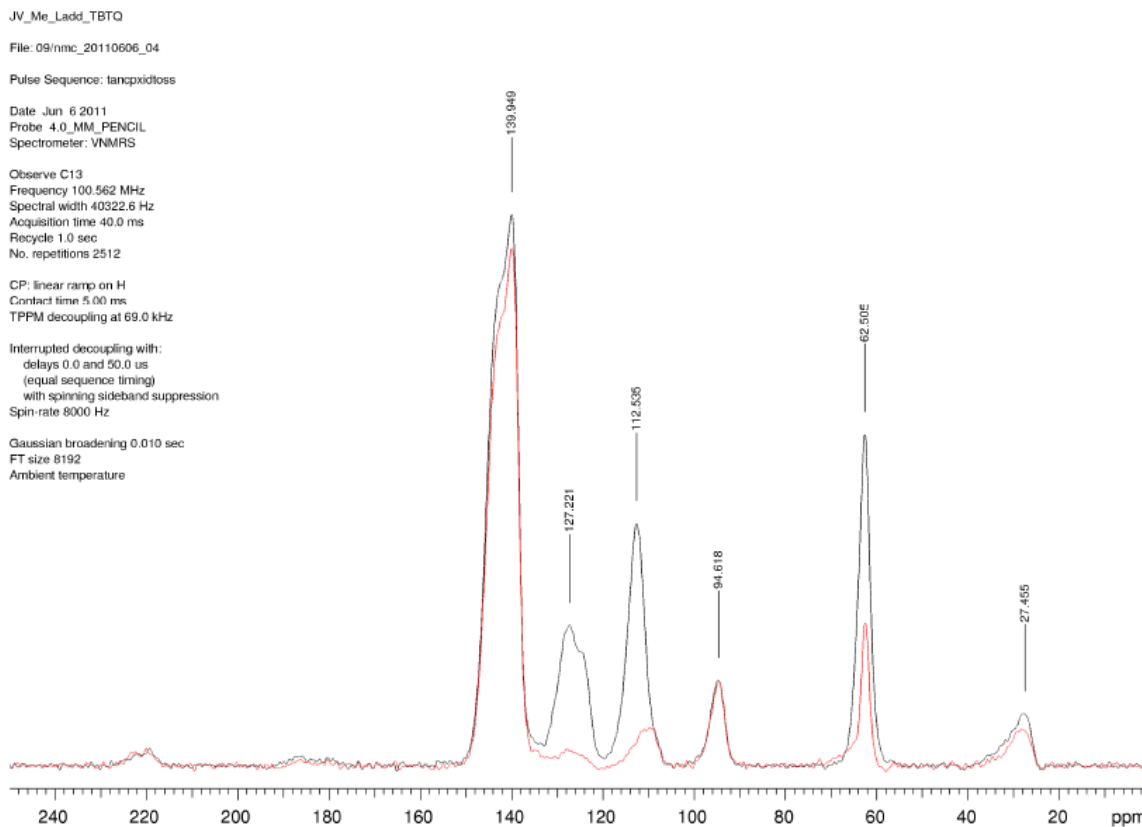
ESI Fig. 4. Nitrogen isotherm of TBTQ-PIM-2 at 77 K.

2.25. TBTQ-PIM-3

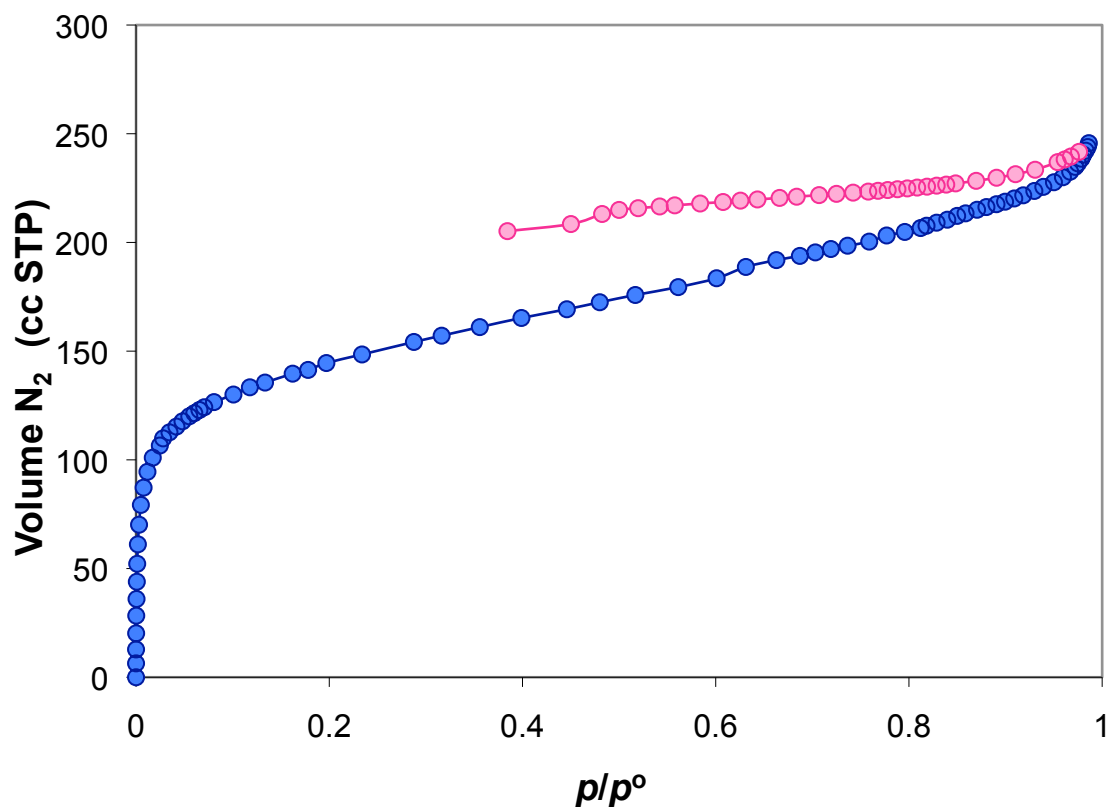


In a two-necked round bottom flask was added under a dry nitrogen atmosphere monomer **3** (0.364 g, 1.017 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.203 g, 1.017 mmol) and dry dimethylformamide (30 ml). Dry potassium carbonate (1.12 g, 8.14 mmol) was added and the mixture was heated to 65 °C and stirred for 96 h. The solution was quenched with water (100 ml), collected by filtration and washed repeatedly with water and acetone. Due to its poor solubility, the product was purified by refluxing in acetone (12 h) and MeOH (12 h). The purified product was dried at 100 °C under vacuum (12 h) to give a yellow solid (0.360 g, 74% based on the molecular weight of the repeat unit). BET surface area = 511 m² g⁻¹; total

pore volume = $0.37 \text{ cm}^3 \text{ g}^{-1}$ at $p/p^o = 0.98$, adsorption; TGA analysis (nitrogen): 0.6% loss of weight occurred at $\sim 100 \text{ }^\circ\text{C}$. Initial weight loss due to thermal degradation commences at $\sim 531 \text{ }^\circ\text{C}$. IR (Nujol): 2923, 2855, 2238 (CN), 1677 cm^{-1} . SS ^{13}C NMR (100.5 MHz): $\delta = 27.4$ (R = CH_3); 62.5 (C_f , C_g and C_h); 94.6 (C_a and C_p); 110.0 (CN); 112.5 (C_d , C_m); 127.2 (C_i , C_j and C_k); 138-148 (C_b , C_c , C_e , C_l , C_n , C_o). (note the peak at 220 is a side band).

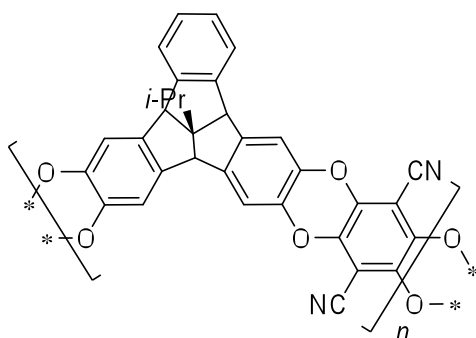


ESI Fig 5. Solid state ^{13}C NMR spectra for **TBTQ-PIM-3**. The black spectrum is the full cross-polarisation spectrum and the red spectrum is with interrupted decoupling, which removes signals from carbons attached to single hydrogens.



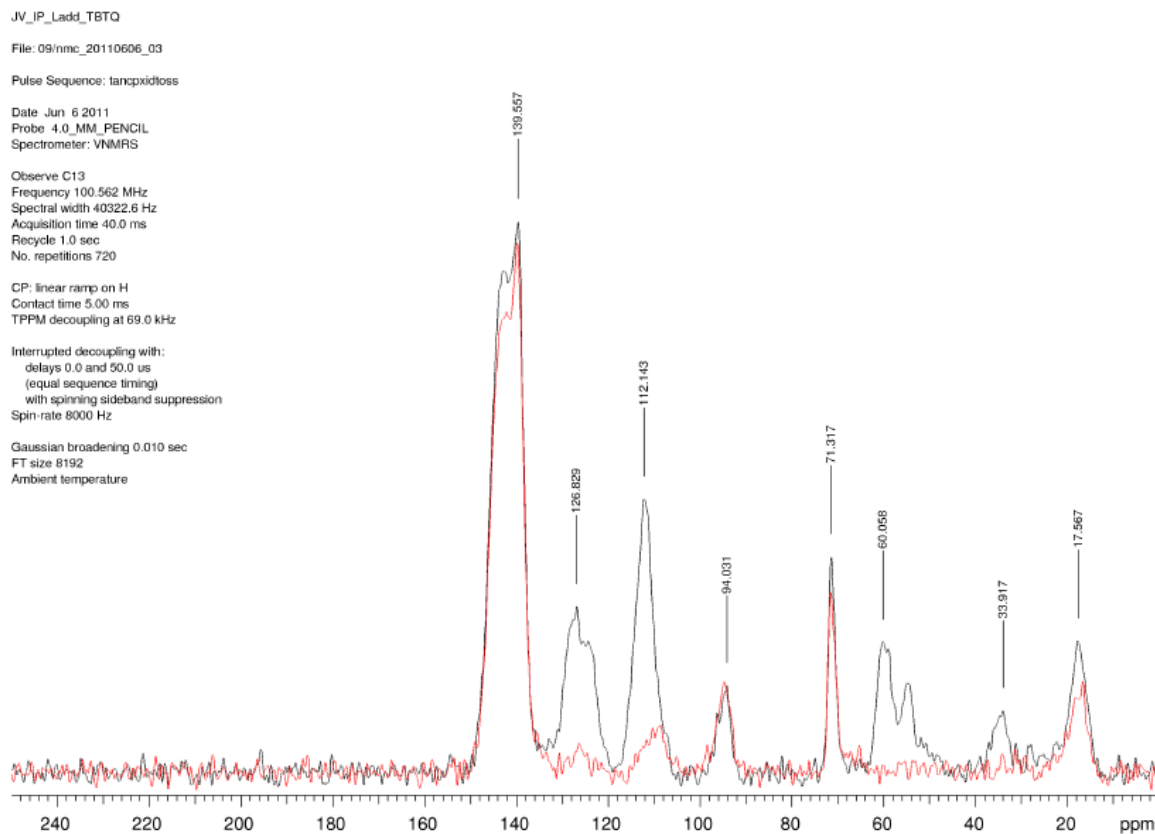
ESI Fig. 6. Nitrogen isotherm of TBTQ-PIM-3 at 77 K.

2.26. TBTQ-PIM-4

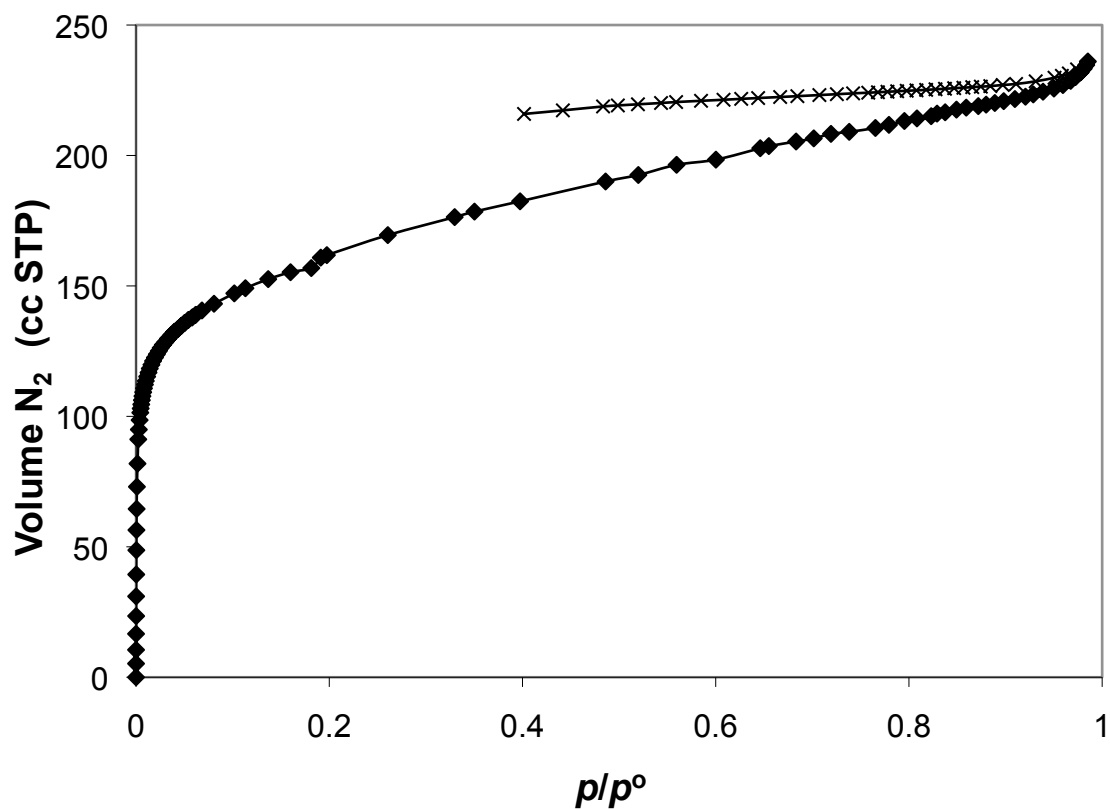


In a two-necked round bottom flask was added under a dry nitrogen atmosphere monomer **4** (0.253 g, 0.655 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.131g, 0.655 mmol) and dry dimethylformamide (30 ml). Dry potassium carbonate (0.72g, 5.22 mmol) was added and the mixture was heated to 65 °C and stirred for 96 h. The solution was quenched with water (100 ml), collected by filtration and washed repeatedly with water and acetone. Due to its poor solubility, the product was purified by refluxing in acetone (12 h) and MeOH (12 h). The purified product was dried at 100 °C under vacuum (12 h) to give a yellow solid (0.222 g, 67% based on the molecular weight of the repeat unit). BET surface area = 568 m² g⁻¹; total pore volume = 0.37 cm³ g⁻¹ at $p/p^o = 0.98$, adsorption; TGA analysis (nitrogen): 0.5% loss of weight occurred at ~ 75 °C. Initial weight loss due to thermal degradation commences at ~

472 °C. IR (Nujol): 2922, 2857, 2239 (CN), 1679, 1299 cm^{-1} . SS ^{13}C NMR (100.5 MHz): δ = 17.6 (R = CH_3); 33.9 (R = CH); 54-62 (C_f and C_h); 71.3 (C_g); 94.6 (C_a and C_p); 110.0 (CN); 108-118 (C_d , C_m); 122-132 (C_i , C_j and C_k); 138-148 (C_b , C_c , C_e , C_l , C_n , C_o).



ESI Fig 7. Solid state ^{13}C NMR spectra for **TBTQ-PIM-4**. The black spectrum is the full cross-polarisation spectrum and the red spectrum is with interrupted decoupling, which removes signals from carbons attached to single hydrogens.



ESI Fig. 8. Nitrogen isotherm of TBTQ-PIM-4 at 77 K.

3. ESI References

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