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# Polymers of Intrinsic Microporosity derived from a Carbocyclic analogue of Tröger's base.

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## Abstract

Tröger's base (TB) is often used as a building block for the synthesis of Polymers of Intrinsic Microporosity (PIMs) due to its rigid bicyclic V-shaped structure. In this study the TB component in the structure of a PIM is replaced by 2,3:6,7-dibenzobicyclo[3.3.1]nonane, a purely carbocyclic analogue of TB. This modification results in only a slightly reduced amount of microporosity as determined using nitrogen adsorption. Further comparisons with previously reported PIMs indicate that this building unit (and therefore TB) is significantly less effective for the generation of intrinsic microporosity than spirobisindane, a commonly used structural unit for PIM synthesis. It appears that the V-shape of the 2,3:6,7-dibenzobicyclo[3.3.1]nonane and TB units allows closer contact between polymer chains thereby enhancing packing efficiency.

## 1. Introduction

Over recent years there has been increasing interest in the preparation of new microporous materials using organic components.<sup>(1)</sup> For example, there are a number of different types of porous organic polymers including structurally ordered Covalent-Organic-Frameworks (COFs)<sup>(2)</sup> and amorphous network polymers such as Hypercrosslinked Polymers (HCPs),<sup>(3)</sup> Microporous Conjugated Polymers (MCPs)<sup>(4)</sup> and Porous Aromatic Frameworks (PAFs).<sup>(5)</sup> Polymers of Intrinsic Microporosity (PIMs) differ in that they do not possess a network structure and, hence, are often solution processable materials.<sup>(6)</sup> PIMs generate porosity from their rigid and contorted macromolecular chains that do not pack efficiently in the solid state.<sup>(7, 8)</sup> The solubility of PIMs allows them to be processed into self-standing films and

coatings and, therefore, they are suitable for making devices such as sensors<sup>(9, 10)</sup> or for the fabrication of polymer membranes, particularly for gas separations.<sup>(11)</sup> It is well established that increasing the rigidity of polymers used for gas separation membranes enhances their selectivity for one gas over another.<sup>(12)</sup> This prompted the recent development of PIMs derived from highly rigid bridged bicyclic structural units such as triptycene,<sup>(13-16)</sup> ethanoanthracene<sup>(17)</sup> and the amine-based bicyclic system 6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine,<sup>(17)</sup> which is more commonly known as Tröger's base (TB). The V-shaped TB unit is used in numerous applications including making components for supramolecular chemistry.<sup>(18)</sup> TB has been introduced into PIMs both by using polymerisation reactions that incorporate monomers that are TB derivatives, such as diamines suitable for PIM-polyimide synthesis,<sup>(19-26)</sup> or by using TB formation as the polymerisation reaction.<sup>(12, 14, 16, 27-29)</sup> The resulting TB-based PIMs have demonstrated excellent potential as gas separation membranes with high permeability and good selectivity for one gas over another, for which the latter can be partially attributed to the rigidity of TB.

Therefore, it is of interest to determine the structural contribution to the generation of intrinsic microporosity by the TB unit. With this objective, we report the synthesis of monomers and PIMs based on a purely hydrocarbon analogue of the TB unit – i.e. 2,3:6,7-dibenzobicyclo[3.3.1]nonane.<sup>(30-32)</sup> Comparisons are made between these polymers, structurally related TB PIMs,<sup>(21)</sup> and the more typical spirobisindane PIMs that have been described previously.<sup>(33)</sup>

## 2. Experimental

### 2.1. 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  $\text{cm}^{-1}$  using a Perkin-Elmer 1600 series FTIR instrument either as a thin film or as a nujol mull between sodium chloride plates. The positions of absorption bands are quoted in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded in the solvent stated using an Avance Bruker

DPX 400 instrument (400 MHz), with  $^{13}\text{C}$  NMR spectra recorded at 100 MHz. Chemical shifts ( $\delta H$  and  $\delta C$ ) were recorded in parts per million (ppm) from tetramethylsilane (or chloroform) and are corrected to 0.00 (TMS) and 7.26 ( $\text{CHCl}_3$ ) for  $^1\text{H}$  NMR and 77.00 ( $\text{CHCl}_3$ ), centre line, for  $^{13}\text{C}$  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) nitrogen 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. Single crystal XRD 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  $\text{K}(\alpha)$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

## 2.2. Synthetic procedures

The key diketone intermediate 2,3,8,9-tetramethoxy-6,12-methanodibenzo[a,e]cyclooctene-5,11(6H,12H)-dione **1** was prepared using a literature procedure<sup>(32)</sup> (see Supplemental Data). Crystallographic data for **1** is deposited in the Cambridge Structural Database (CCDC 1529466).

### General procedure for demethylation using $\text{BBr}_3$

The tetramethoxy compound (i.e. one of **1**, **5**, **6**, **8**) was dissolved in DCM (30 ml) under a nitrogen atmosphere at 0 °C. Boron tribromide (5 molar equivalents) was added slowly and the reaction was stirred at room temperature for 12 h. The reaction was quenched with water (5 ml) and the solid was collected by suction filtration and dried under vacuum for 12 h at 30 °C to give the desired biscatechol product.

### 2,3,8,9-tetrahydroxy-6,12-methanodibenzo[a,e]cyclooctene-5,11(6H,12H)-dione (**2**)

Using the general procedure diketone **1**<sup>(32)</sup> gave **2** (0.44 g, 80%) as a grey solid, m.p. > 300 °C.  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  7.27 (s, 2H<sub>c</sub>), 6.76 (s, 2H), 3.65 (m, 2H), 2.87 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz; MeOD)  $\delta$  197.1, 153.8, 147.6, 136.8, 122.5, 115.8, 115.2, 57.1, 35.3. HRMS Calc for  $\text{C}_{17}\text{H}_{12}\text{O}_6$  312.0634, found 312.0631. IR (DCM): 3200, 1653, 1596, 1517, 1348, 1299  $\text{cm}^{-1}$ .

### **5,6,11,12-tetrahydro-2,3,8,9-tetrahydroxy-5,11-methanodibenzo[a,e]cyclooctene (3)**

Using the general procedure diketone **5** gave **3** (0.4 g, 86%) as a white solid, m.p. > 300 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.56 (s, 2H), 6.31 (s, 2H), 3.05 (m, 4H), 2.54 (m, 2H), 1.98 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz; MeOD)  $\delta$  144.1, 143.9, 133.4, 126.6, 116.0, 115.9, 39.8, 33.3, 26.0. HRMS Calc for  $\text{C}_{17}\text{H}_{16}\text{O}_4$  284.1049, found 284.1047. IR (DCM): 3386, 1630, 1520, 1266  $\text{cm}^{-1}$ .

### **Tetracyclo[7.7.1.0<sup>2,7</sup>.0<sup>10,15</sup>]heptadecane-16',9''-fluorene]-2'(7'),3',5',10',12',14'-hexaene-4',5',12',13'-tetrol (4)**

Using the general procedure diketone **6** gave **4** (0.43 g, 81%) as a light brown solid, M.p. > 300 °C.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  8.34 (s, 2H), 8.18 (s, 2H), 7.00 (m, 16H), 5.44 (s, 2H), 5.39 (s, 2H), 2.99 (m, 2H), 2.79 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz;  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  156.7, 152.2, 144.2, 142.6, 140.3, 138.6, 130.8, 128.0, 127.9, 127.2, 127.1, 127.0, 125.9, 124.0, 120.0, 119.3, 119.1, 114.3, 60.0, 42.6, 25.8. HRMS Calc for  $\text{C}_{41}\text{H}_{28}\text{O}_4$  584.1988, found 584.1989. IR (DCM): 3523, 3046, 2914, 1602, 1516, 1443, 1267  $\text{cm}^{-1}$ .

### **2,3,8,9-Tetrahydroxy-6H,12H-5,11-methanodibenzo[1,5]-diazocine (7)**

Using the general procedure diketone **8** gave **7** (2.57 mg, 88%). Mp >300 °C;  $^1\text{H}$  NMR (400 MHz; MeOD)  $\delta$  6.53 (s, 2H), 6.32 (s, 2H), 4.45 (d, 2H,  $J = 16.5$  Hz), 4.21 (s, 2H), 3.89 (d, 2H, 16.5 Hz);  $^{13}\text{C}$  NMR (100 MHz; MeOD)  $\delta$  145.9, 145.2, 144.0, 139.9, 119.4, 113.6, 112.2, 111.4, 67.8, 58.9, 49.0; HRMS Calc. for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_4$  287.1032, found 287.1026.

### **5,6,11,12-tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]cyclooctene (5)<sup>(32)</sup>**

Potassium hydroxide (3.04 g, 54.4 mmol) and ethylene glycol (75 ml) were heated to 80 °C and to this mixture hydrazine monohydrate (2.72 g, 54.4 mmol) and diketone **1** (2.50 g, 6.8 mmol) were added and the mixture was refluxed at 200 °C for 16 h. The mixture was cooled to room temperature, quenched with water (200 ml) and acidified slowly with aqueous hydrochloric acid until neutral. The solid was collected by suction filtration and purified by column chromatography (hexane/EtOAc, 7:3) and recrystallized from MeOH to give the

desired product (0.92 g, 40%) as a white solid, m.p. 206 – 208 °C (209 – 210 °C)<sup>(32)</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.68 (s, 2H), 6.44 (s, 2H), 3.86 (s, 6H), 3.77 (s, 6H), 3.17 (m, 4H), 2.72 (m, 2H), 2.07 (m, 2H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>) δ 147.7, 147.4, 133.0, 126.5, 112.0, 111.9, 56.0, 55.6, 38.9, 32.7, 29.2. HRMS Calc For C<sub>21</sub>H<sub>24</sub>O<sub>4</sub> 340.1675, found 340.1664. IR (DCM): 2907, 1609, 1514, 1464, 1355, 1258, 1216, 1125, 1033 cm<sup>-1</sup>. Crystals were prepared by a slow diffusion of hexane into THF solution of monomer. Crystal size: 0.4 x 0.15 x 0.02 mm, orthorhombic, space group P 21 21 21, *a* = 7.6363(4), *b* = 8.2848(6), *c* = 27.736(2) Å,  $\alpha = \beta = \gamma = 90^\circ$ , *V* = 1754.7(2) Å<sup>3</sup>, *Z* = 4:  $\mu = 0.088\text{mm}^{-1}$ , 1828 reflections measured, 1828 unique reflections (*R*<sub>int</sub> = 0.0000), 1596 reflections with *I* > 2σ(*I*), *R* = 0.057 and ω*R*<sup>2</sup> = 0.1179 (observed data), *R* = 0.0706 and ω*R*<sup>2</sup> = 0.1127 (all data). Crystallographic data was deposited in the Cambridge Structural Database (CCDC 1529467).

**4',5',12',13'-tetramethoxydispiro[fluorene-9,8'-tetracyclo[7.7.1.0<sup>2,7</sup>.0<sup>10,15</sup>]heptadecane-16',9''-fluorene]-2'(7'),3',5',10',12',14'-hexaene (6)**

In a two-necked round bottom flask was added diketone **1** (2.00 g, 5.4 mmol) and dry THF (60 ml). 2-Biphenyl magnesium bromide (5.54 g, 21.6 mmol) in dry THF (60 ml) was added slowly at 0 °C under vigorous stirring and the mixture was refluxed for 48 h. The reaction was quenched with water (150 ml) and the THF was evaporated under reduced pressure. The precipitate was filtered under suction and dried. The crude product was stirred in Eaton's reagent (50 ml) for 16 h, quenched carefully with water (150 ml) and extracted with DCM (2 x 150 ml). The organic layers were evaporated under reduced pressure to give the crude product. Purification by column chromatography (hexane/EtOAc) yielded **6** (1.04 g, 30 %) as a white solid. M.p. 175 – 180 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.96 (m, 16H), 5.68 (s, 2H), 5.45 (s, 2H), 3.35 (s, 6H), 3.33 (s, 6H), 3.05 (t, *J* = 3.0 Hz, 2H), 2.93 (t, *J* = 3.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ 156.1, 152.1, 148.1, 145.8, 140.8, 139.0, 132.4, 129.4, 128.3, 127.2, 127.1, 127.0, 126.2, 124.3, 120.0, 119.4, 114.9, 110.5, 61.1, 55.6, 55.0, 43.9, 25.5. HRMS Calc for C<sub>45</sub>H<sub>36</sub>O<sub>4</sub> 640.2614, found 640.2636. IR (DCM): 3059, 2936, 1507, 1443, 1361, 1256, 1212 cm<sup>-1</sup>. Crystals were prepared by a slow diffusion of hexane into Toluene solution of monomer. Crystal size: 0.4 x 0.15 x 0.02 mm, monoclinic, space group P 21, *a* = 14.221 (5), *b* = 10.214 (5), *c* = 15.384 (5) Å,  $\beta = 115.536 (5)^\circ$ , *V* = 2016.3 (14) Å<sup>3</sup>, *Z* = 2:  $\mu = 0.08\text{mm}^{-1}$ , 4640 reflections measured, 4640 unique reflections (*R*<sub>int</sub> = 0.0000), 3809 reflections with *I* > 2σ(*I*), *R* = 0.070 and ω*R*<sup>2</sup> = 0.1834 (observed data), *R* = 0.0895 and ω*R*<sup>2</sup> = 0.1666 (all data). Crystallographic data was deposited in the Cambridge Structural Database (CCDC 1529468).

### **2,3,8,9-Tetramethoxy-6H,12H-5,11-methanodibenzo[1,5]-diazocine (8)<sup>(34)</sup>**

3,4-Dimethoxyaniline (3.00 g, 19.58 mmol) and paraformaldehyde (1.17 g, 39.16 mmol) were added in portions and under vigorous stirring to trifluoroacetic acid (20 ml) at 0 °C. The mixture was allowed to cool down to room temperature and left under stirring for 16 h. The mixture was quenched with water and a 30% aqueous NH<sub>3</sub> solution was added until pH~9. The resulting precipitate was collected under suction and repeatedly washed with water and MeOH. The solid was dried under vacuum to obtain **8** as light purple powder (2.50 g, 75%). Mp 198-200 °C; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ 6.65 (s, 2H), 6.37 (s, 2H), 4.60 (d, 2H, J = 16.3 Hz), 4.27 (s, 2H), 4.06 (d, 2H, 16.3 Hz), 3.85 (s, 6H), 3.77 (s, 6H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ 148.3, 146.1, 140.4, 118.8, 108.8, 107.9, 67.1, 57.9, 55.9; HRMS Calc. for C<sub>19</sub>H<sub>23</sub>O<sub>4</sub>N<sub>2</sub> 343.1658, found 343.1669.

### **General procedure for Polymer synthesis.**

In a two-necked round bottom flask was added, under inert atmosphere, equimolar amount of the bis-catechol monomer (**2**, **3**, **4** or **5**) and 2,3,5,6-tetrafluoroterephthalonitrile, were added to anhydrous dimethylformamide (25 ml per g of catechol). The mixture was heated to 65 °C, until the two starting materials were completely dissolved, then dry potassium carbonate (8 equivalents) was added and the mixture kept to stirring for 96 h. The solution was quenched with water (80 ml per g of catechol), filtrated and washed repeatedly with water and acetone. For the insoluble polymers **P1**, **P2** and **P4**, the crude polymer was washed under reflux using solvent in the following sequence: THF, CHCl<sub>3</sub>, acetone and methanol. The product was then refluxed overnight in methanol, filtered off and dried under vacuum. For soluble polymer **P3**, the solid was dissolved in CHCl<sub>3</sub> (15 ml per g of solid), the solution filtered through cotton wool and poured into a mixture of acetone/methanol (2/1, 40 ml/g). The product was dried and refluxed with methanol overnight, collected and dried under vacuum.

### **Polymer P1**

Monomer **2** (0.503 g, 1.61 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.322 g, 1.61 mmol) and dry potassium carbonate (1.78 g, 12.90 mmol) were reacted according to the general procedure to give a yellow solid (521 mg, 75% based on the molecular weight of the repeated unit). Apparent BET surface area = 46 m<sup>2</sup> g<sup>-1</sup>; total pore volume = 0.15 cm<sup>3</sup> g<sup>-1</sup> estimated from nitrogen adsorption at  $P/P_0 = 0.98$ ; TGA analysis (nitrogen): 4.55% loss of weight

occurred at ~ 100 °C. Initial weight loss due to thermal degradation commences at ~ 416 °C. IR (DCM): 3200, 2250 (CN), 1653, 1596, 1517, 1348, 1299.

### **Polymer P2**

Monomer **3** (0.304 g, 1.07 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.214 g, 1.07 mmol) and dry potassium carbonate (1.78 g, 12.90 mmol) were reacted according to the general procedure to give a yellow solid (367 mg, 85% based on the molecular weight of the repeated unit). Apparent BET surface area = 437 m<sup>2</sup> g<sup>-1</sup>; total pore volume = 0.36 cm<sup>3</sup> g<sup>-1</sup> estimated from nitrogen adsorption at  $P/P_0 = 0.98$ ; TGA analysis (nitrogen): 5.51% loss of weight occurred at ~ 100 °C. Initial weight loss due to thermal degradation commences at ~ 505 °C. IR (Nujol): 2924, 2238 (CN), 1600 cm<sup>-1</sup>. SS <sup>13</sup>C NMR (100.5 MHz):  $\delta = 138.3, 133.9, 94.0, 67.8, 39.1, 32.3, 25.7$ .

### **Polymer P3**

Monomer **4** (0.338 g, 0.58 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.116 g, 0.58 mmol) and dry potassium carbonate (0.64 g, 4.62 mmol) were reacted according to the general procedure to give a yellow solid (0.224 g, 55% based on the molecular weight of the repeat unit). Apparent BET surface area = 684 m<sup>2</sup> g<sup>-1</sup>; total pore volume = 0.63 cm<sup>3</sup> g<sup>-1</sup> estimated from nitrogen adsorption at  $P/P_0 = 0.98$ ; TGA analysis (nitrogen): 0.80% loss of weight occurred at ~ 100 °C. Initial weight loss due to thermal degradation commences at ~ 477 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.6-7.2$  (br m, 20H), 2.5-3.3 (br m, 6H). Analysis by GPC (THF):  $M_n = 3,700$   $M_w = 10,300$  g mol<sup>-1</sup> relative to polystyrene. IR (CHCl<sub>3</sub>): 3062, 2923, 2852, 2240 (CN), 1501, 1450, 1324, 1265 cm<sup>-1</sup>.

### **Polymer P4**

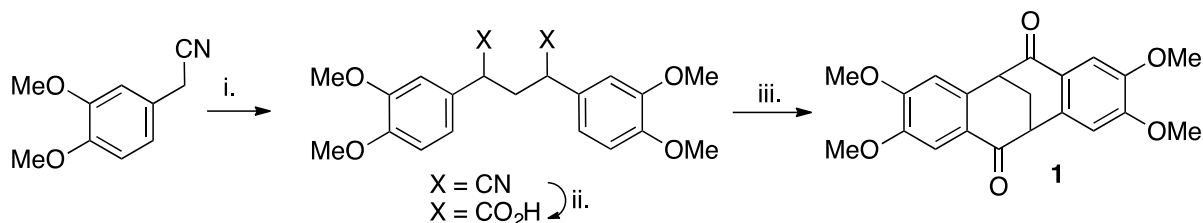
Monomer **7** (1.000 g, 3.49 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (698 mg, 3.49 mmol), and dry potassium carbonate (3.85 g, 27.92 mmol) were reacted according to the general procedure to give a yellow solid (1.13 g, 80% based on the molecular weight of the repeated unit). Apparent BET surface area = 570 m<sup>2</sup> g<sup>-1</sup>; total pore volume = 0.35 cm<sup>3</sup> g<sup>-1</sup> estimated from nitrogen adsorption at  $P/P_0 = 0.98$ ; TGA analysis (nitrogen): 5% loss of weight occurred at ~ 380 °C. Initial weight loss due to thermal degradation commences at ~ 440 °C.

## **3. Results and discussion**

### **3.1. Monomer synthesis**

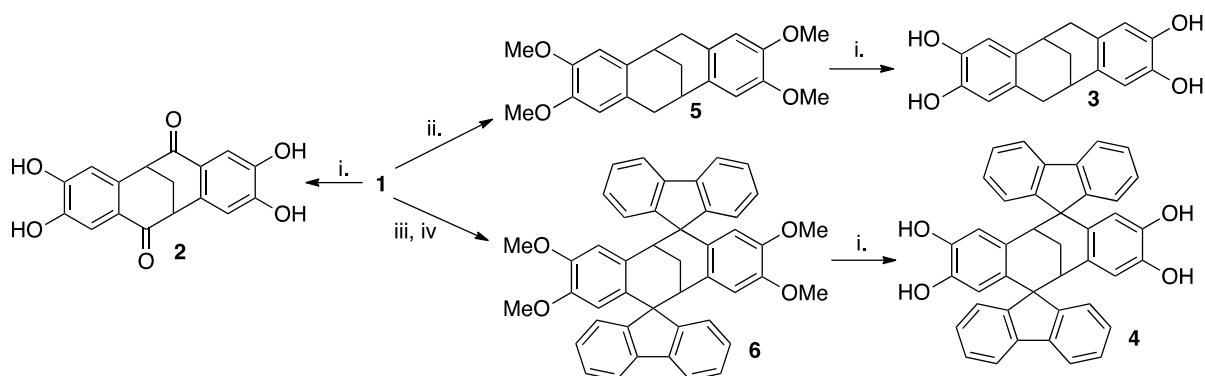


Following the work of Ogura *et al.*,<sup>(32)</sup> the key intermediate diketone **1** was conveniently prepared from commercially available (3,4-dimethoxyphenyl)acetonitrile in three steps in a good overall yield of 40 % (Scheme 1; Supplementary Data).



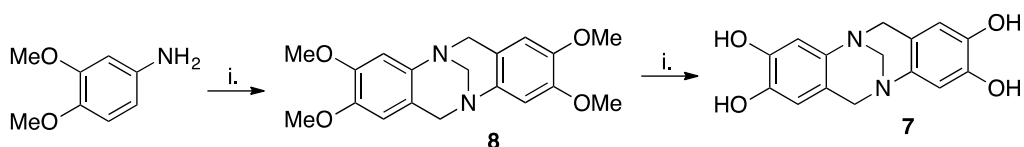
**Scheme 1.** Reagents and conditions. i.  $\text{CH}_2\text{I}_2$ , NaOMe, THF, reflux 2 h; ii. KOH, EtOH, 88%. iii. PPA, 80 °C,

Biscatechol monomers **2-4**, which are suitable for PIM synthesis via polymerisation using dibenzodioxine formation, were prepared from diketone **1** as outlined in Scheme 2. Simple removal of the methyl groups from **1** using boron tribromide gave the diketone monomer **2**. Wolff-Kishner reduction was successfully performed on **1** to give **5** followed by methyl group removal ( $\text{BBr}_3$ ) to give biscatechol monomer **3**, which contains the simplest carbocyclic analogue to the TB unit. Fused fluorene substituents were introduced by the reaction of **1** with the Grignard reagent derived from 2-bromobiphenyl to give **6**, which was demethylated to give monomer **4**.



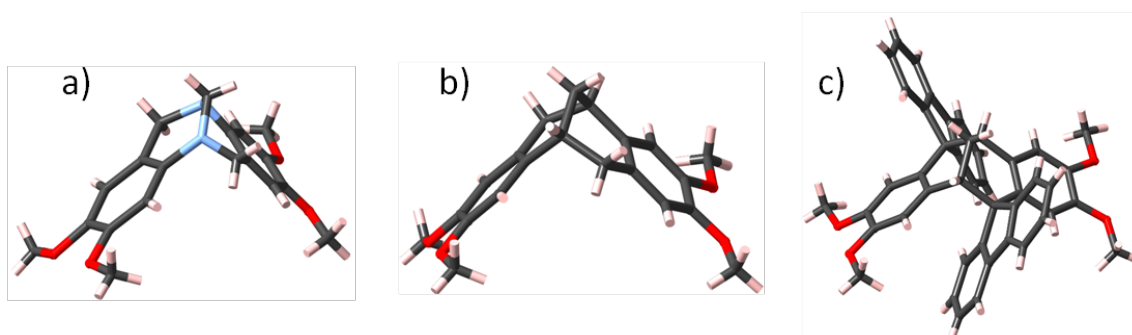
**Scheme 2.** Reagents and conditions. i.  $\text{BBr}_3$ , DCM, 4 h; ii. Hydrazine, KOH, ethylene glycol, 200 °C, 24 h; iii. Grignard reagent from 2-bromobiphenyl, THF, reflux, 24 h; iv. Eaton's reagent 12 h 30%.

To allow the direct comparison between a TB PIM and a PIM derived from a carbocyclic TB analogue, the biscatechol-containing TB monomer **7** was prepared using a previously reported procedure (Scheme 3) via tetramethoxy-substituted TB derivative **8**.<sup>(19, 21, 34)</sup>



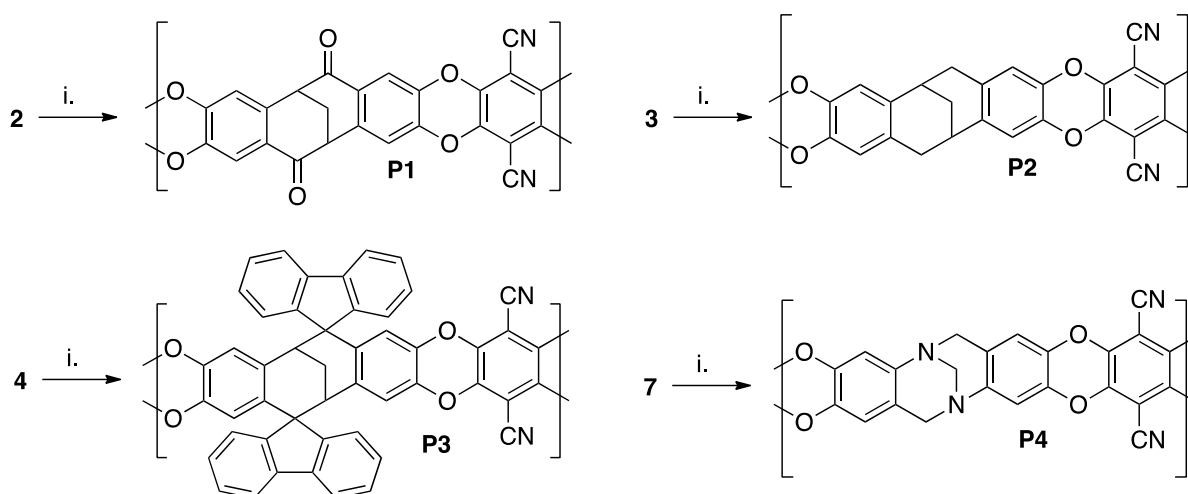
**Scheme 3.** Reagents and conditions. i. Dimethoxymethane, TFA, RT; ii. BBr<sub>3</sub>, DCM.

The structure of the 2,3:6,7-dibenzobicyclo[3.3.1]nonane units within the novel monomers was confirmed by growing crystals suitable for x-ray diffraction analysis from intermediates **5** and **6** and this was compared with the structure reported by Bu *et al.*<sup>(34)</sup> of the related tetramethoxy derivative of Tröger's base **8** (Fig. 1).



**Fig. 1.** Solid state crystal structures of (a) tetramethoxy Tröger's base **8**, (b), **5** (b) and (c) **6**.

There is a clear similarity between the TB unit (Fig. 2a) and the TB analogous structures (Fig. 2b and c). For example, for **5** and **8** the angle between the two planes formed by the dimethoxy benzene moieties was found to be 88° for both structures. For monomer **6**, instead, the same angle was found of 114° presumably due to the bulky fluorene substituents.



**Scheme 4.** Reagents and conditions. i. 2,3,5,6-tetrafluoroterephthalonitrile, K<sub>2</sub>CO<sub>3</sub>, DMF, 65 °C, 3 days.

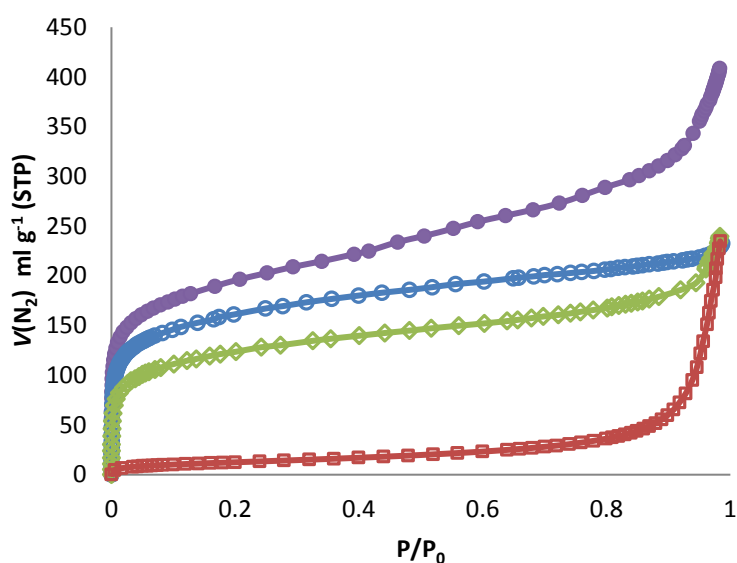
### 3.2. Polymer synthesis

Monomers **2-4** and **7** were polymerised using the typical conditions optimised previously for PIM preparation using dibenzodioxin formation to give polymers **P1-P4**, respectively (Scheme 4).<sup>(6, 35)</sup> With the exception of **P3**, all of the polymers proved to be insoluble in common organic solvents preventing their structural characterisation via solution-based techniques such as Gel Permeation Chromatography (GPC). In contrast, **P3** is fully soluble in THF and chloroform, presumably due to the bulky fused fluorene groups enhancing solubility. Hence **P3** was readily characterised by <sup>1</sup>H NMR and GPC (THF), which revealed a value for  $M_w$  of 10,300 g mol<sup>-1</sup> relative to polystyrene standards (Table 1). This modest molecular mass was insufficient for the formation of robust self-standing films.

**Table 1.** Physical properties of polymers **P1-P4**.

Polymer	Monomer	Solubility	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume <sup>a</sup> (ml g <sup>-1</sup> )	$M_w$	PDI
<b>P1</b>	<b>4</b>	No	45	0.15	n/a	n/a
<b>P2</b>	<b>3</b>	No	440	0.36	n/a	n/a
<b>P3</b>	<b>7</b>	Yes (CHCl <sub>3</sub> )	685	0.63	10,300	2.78
<b>P4</b>	<b>2</b>	No	570 <sup>b</sup>	0.35	n/a	n/a

<sup>a</sup>Calculated from the amount of nitrogen adsorbed at 77 K and relative pressure  $P/P_0 = 0.98$ . <sup>b</sup>This apparent BET surface area is in good agreement with the previously reported value of 565 m<sup>2</sup> g<sup>-1</sup>.<sup>(21)</sup>



**Fig. 2.** N<sub>2</sub> adsorption isotherms for polymers **P1-P4** obtained at 77 K.

### 3.3. Analysis of Microporosity

Nitrogen adsorption isotherms obtained at 77 K from powdered samples of the polymers (Fig. 2; Supplementary Data) allowed apparent BET surface area and pore volumes to be estimated (Table 1). Isotherms from polymers **P2**, **P3** and **P4** all show significant nitrogen adsorption at low relative pressure ( $P/P_o < 0.01$ ), which indicates the presence of intrinsic microporosity. In contrast, polymer **P1** proved non-porous, which may be attributed to the large cohesive interactions between polymer chains due to the polar ketone groups. Polymer **P3** displays relatively high surface area, which suggests that the rigid, spiro-fused fluorine units increase free volume by maintaining a larger distance between polymer chains. The larger hysteresis between the nitrogen adsorption and desorption isotherms (Fig. 2: Supplemental data) for Polymer **P3** relative to **P2** or **P4** suggests swelling during analysis that indicates weaker cohesion between chains, which is consistent with the solubility of Polymer **P3** in organic solvents. A direct comparison of the nitrogen adsorption isotherms of the structurally related polymers **P2** and **P4**, shows that 2,3:6,7-dibenzobicyclo[3.3.1]nonane of **P2** appears to be only slightly less efficient at generating intrinsic microporosity than the TB unit of **P4**. In addition, previous work demonstrated that the equivalent spirobisindane-based PIMs to polymers **P1** and **P3**, containing ketone and fused fluorene substituents, had apparent BET surface areas of 501 and 895 m<sup>2</sup> g<sup>-1</sup>, respectively.<sup>(33)</sup> Therefore, it can be deduced that 2,3:6,7-dibenzobicyclo[3.3.1]nonane unit is significantly less efficient at inducing intrinsic microporosity than the spirobisindane unit, which is an often used component in the synthesis of PIMs.

### 4. Conclusions.

Replacing the TB component in the structure of a PIM with 2,3:6,7-dibenzobicyclo[3.3.1]nonane, a purely carbocyclic analogue of TB, results in only a slightly reduced microporosity as determined using nitrogen adsorption. Indeed direct comparison with previously reported PIMs indicates that this building unit (and therefore TB) is significantly less effective for the generation of intrinsic microporosity than spirobisindane, a common structural unit used in PIM synthesis. It appears likely that the shape of the 2,3:6,7-dibenzobicyclo[3.3.1]nonane unit allows closer contact between polymer chains thereby enhancing packing efficiency. Greater cohesive interaction between chains is apparent from the lack of solubility of the resulting polymers, although placing bulky fused fluorene substituents onto the polymer improves solubility and microporosity, presumably by increasing the distance between chains in the solid state.

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