

A facile synthesis of a novel triptycene-containing A–B monomer: precursor to polymers of intrinsic microporosity†

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A new synthetic approach affords the first example of a triptycene-containing A–B monomer bearing both phenazine activating aromatic *o*-dichloride and a catechol group which can be used for the synthesis of a novel polymer of intrinsic microporosity (PIM) has been developed. The new polymer was characterized by GPC, IR, and ¹H NMR, elemental analysis and demonstrated good porosity, thermal stability and solubility in common organic solvents such as chloroform from which a self-supporting and transparent film could be cast.

Over the past few decades, extensive research in the field of microporous materials (pore size < 2 nm) has been conducted. These materials have attracted great interest by chemists and material chemists due to their technological importance for various applications and commercial interests.¹ Recently, purely organic materials with network and non-network structures, called polymers of intrinsic microporosity (PIMs)² have been extensively studied and show high internal surface area, solubility and thermal stability. Applications of PIMs include adsorption,³ gas and liquid separation,⁴ hydrogen storage⁵ and catalysis.⁶ The microporosity in PIMs is intrinsic due to their highly rigid (no single bonds about which free rotation can occur) and contorted molecular structures which prohibit close packing of the polymer chains and trap sufficient internal free volume resulting in the formation of porous materials with relatively high surface area. The major advantage of PIMs over the conventional porous materials (zeolites and activated carbon) is the great ability to tailor these materials for various applications through incorporation of different functional groups in the polymer repeat unit. In principle, PIMs can be prepared *via* polycondensation reaction (a double aromatic nucleophilic substitution) using a combination of a bifunctional hydroxylated aromatic monomer and an activated fluorinated or chlorinated aromatic monomer to form rigid dibenzodioxane linking groups. For example, soluble non-network polymers **PIM-1** and **PIM-7** were prepared by the polymerization reaction between the commercially available 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane (**1**) and the

activated tetrafluoroterephthalonitrile monomer (**2**) or the specially prepared tetrachloride monomer (**3**) in basic medium, respectively (Scheme 1). Analysis by N₂ adsorption demonstrated that these materials are microporous with surface areas of >700 m² g⁻¹ as calculated using the Brunauer–Emmett–Teller (BET) method. The microporosity in these polymers is due to the great rigidity and the non-planar moiety resulting from the presence of the spiro-centre as a site of contortion.⁷

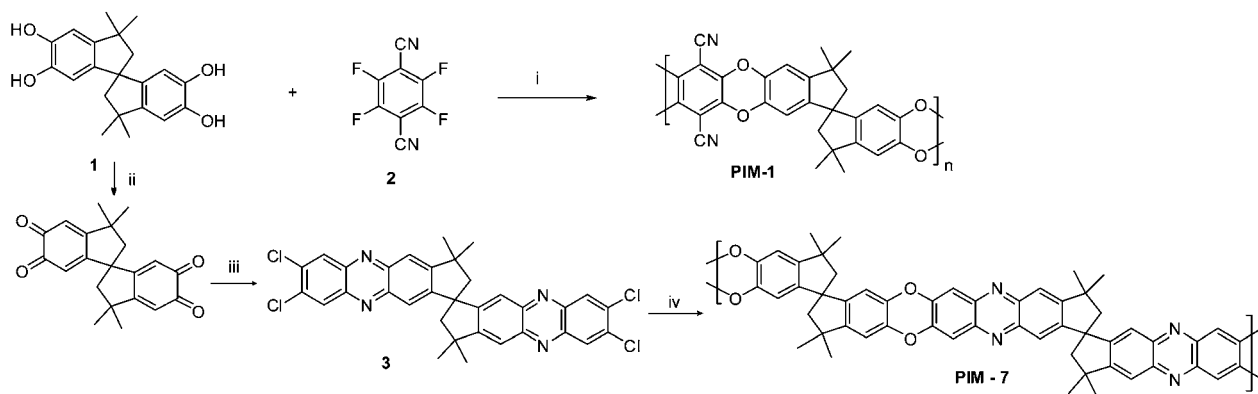
Recently, the synthesis of triptycene-containing insoluble network PIMs with a different alkyl chain length at the bridgehead position of the triptycene and which exhibited high apparent surface area ranging from 618 (R = octyl) to 1760 m² g⁻¹ (R = methyl) was reported. Interestingly, these materials showed a high uptake of hydrogen when R = methyl (about 3% by mass at 10 bar).^{5b}

Despite the tremendous progress in the field of PIMs synthesis, there is still a need for the development of these materials that can exhibit higher free volume and which can be tailored for more applications. This can be accomplished *via* designing new monomers that can be utilized for their synthesis. Described herein is the facile synthesis and characterization of a novel 9,10-dibutyl triptycene-based A–B monomer **8** containing phenazine units and its use as a precursor for the synthesis of PIMs. It is noteworthy that this triptycene-containing monomer is suitable for making PIMs, since both a catechol group and an aromatic dichloride unit, suitably activated towards nucleophilic aromatic substitution reaction by the pyrazine ring in the phenazine structure, are present in the same molecule.^{7b} Such an A–B monomer has a significant advantage in step-growth polymerization over AA–BB used previously in the preparation of PIMs, due to the lack of the requirement for strict control over stoichiometric balance for attaining high molecular weight polymer. Triptycene is an attractive building block for the construction of microporous organic materials due to its high 'internal free volume'.⁸ Moreover, it has been proven that triptycene derivatives can serve as 'spacers' in guest–host complexes,^{14,15} chemical and biological activities,^{16,17} liquid crystalline materials^{18,19} and molecular rotors/gyroscopes.^{20,21}

The A–B monomer **8** was synthesised using a multi-step synthetic sequence as depicted in Scheme 2. First, 9,10-dibutyl-2,3,6,7-tetramethoxyanthracene **4** was prepared according to the procedure described by Shklyayev *et al.* *via* the acid mediated reaction of veratrol (1,2-dimethoxybenzene) with the valeraldehyde.¹⁰ By adapting Zong's procedure, 9,10-dibutyl-2,3,6,7-tetramethoxytriptycene **5** was prepared in good yield by the conventional Diels–Alder reaction

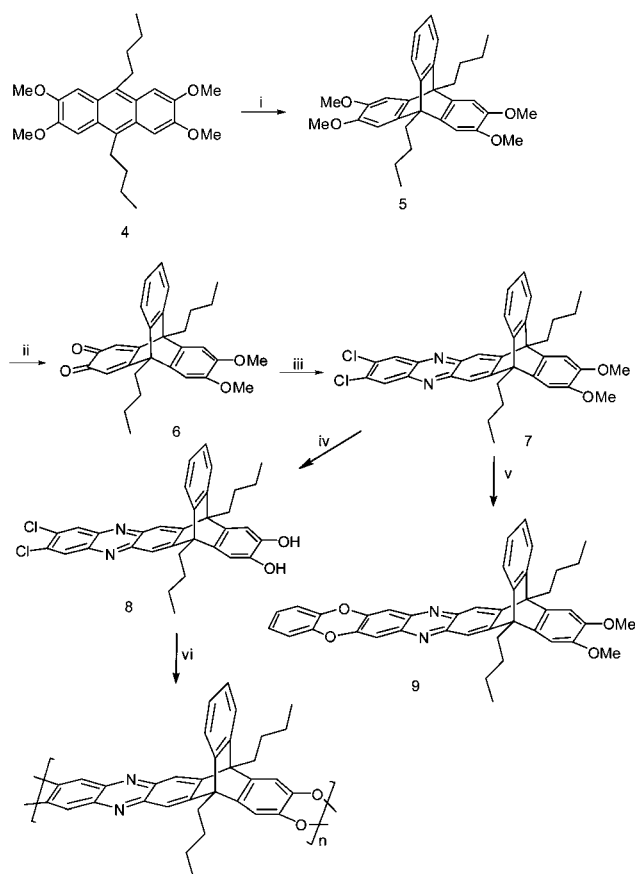
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Scheme 1 Synthesis of **PIM-1** and **PIM-7**. *Reagents and conditions:* (i) K_2CO_3 , DMF, 65°C , 48 h; (ii) nitric acid, AcOH, $\text{C}_2\text{H}_5\text{OH}$, 0°C , 24 h; (iii) 4,5-dichloro-1,2-diaminobenzene, AcOH, reflux, 3 h; (iv) bis catechol (A), K_2CO_3 , 18-crown-6, DMF, 150°C , 48 h.

between 9,10-dibutyl-2,3,6,7-tetramethoxyanthracene and the benzyne formed *in-situ* from 2-amino-4,5-dimethoxy benzoic acid.¹¹ The *o*-quinone **6** was prepared as a dark red solid in good yield by selective oxidation of **5** with dilute nitric acid in dichloromethane and glacial acetic acid (1 : 1, v/v) using the procedure of Zhao *et al.*¹² Finally, condensation reaction of the *o*-quinone **6** with 4,5-dichloro-



Scheme 2 *Reagents and conditions:* (i) 2-carboxy-benzenediazonium chloride, 1,2-dichloroethane, propylene oxide, reflux, 4 h; (ii) 0.25 M HNO₃, AcOH and CH₂Cl₂ (1 : 1, v/v), 5 minutes; (iii) 4,5-dichloro-1,2-diaminobenzene, AcOH, reflux, 2 h; (iv) BBr₃, CH₂Cl₂, 2 h. K₂CO₃, DMF, 150 °C; (v) catechol, K₂CO₃, DMF, 150 °C; (vi) K₂CO₃, DMF, 18-crown-6, 150 °C.

1,2-diaminobenzene in refluxing glacial acetic acid afforded compound **7** in good yield, which was then demethylated with BBr_3 in CH_2Cl_2 to give the corresponding 1,2-hydroxylated triptycene **8**. The structures of all new compounds were confirmed by ^1H and ^{13}C NMR, FTIR, MS spectra and elemental analysis.

In order to confirm the feasibility of using the pyrazine-activated dichloride monomer in the dioxane formation reaction and to optimize the reaction conditions for polymerisation, the model compound **9** was prepared from the reaction of the catecholate anion with *o*-dichloro compound **7** in 91% yield (Scheme 2). This model compound also aids the structural characterization of the polymer derived from monomer **8**. Similarly, the A–B monomer **8** was polymerized in anhydrous DMF containing 18-crown and excess anhydrous potassium carbonate (Scheme 2). The resulting polymer was isolated and purified by repeated precipitation from CHCl_3 solution into methanol to give a yellow-orange powder with spectral properties corresponding to the expected structure that match the spectroscopic data of the model compound **9**.¹³ The elemental analysis data of the polymer are in close agreement with the theoretical values. The ^1H NMR corroborates the proposed structure and shows broad signals for the aromatic and aliphatic protons, indicating a high molecular weight polymer. The aromatic signals appear as three resolved broad absorptions at δ 7.07, 7.36, and 7.81 ppm, whereas the aliphatic ones range from δ 2.90–1.14 ppm. Infrared measurements showed diagnostic absorbances at 1290 for the C–O function, and 1419–1610 for the C=N and C=C skeletal bands. In addition, the polymer is readily soluble in chloroform from which a self-supporting and transparent film could be cast. The good solubility was attributed to the presence of a flexible side butyl chains and the highly rigid three-dimensional structure of the triptycene unit, which prevent close packing of the polymer chains. The gel permeation chromatography (GPC) measurements using chloroform as eluent demonstrated that the polymer exhibited reasonably high average molecular masses with $M_n = 30\,000$, $M_w = 56\,000\text{ g mol}^{-1}$ and a polydispersity index of 1.9 as calibrated against polystyrene standards. Standard nitrogen adsorption analysis for the powdered polymer obtained at 77 K provides an apparent BET surface area of $523\text{ m}^2\text{ g}^{-1}$ and significant adsorption at low relative pressure ($p/p^\circ < 0.1$), which confirm that these materials are microporous (Fig. 1). TGA analysis (nitrogen) indicated that the polymer exhibited relatively high thermal stability and initial weight loss due to thermal degradation which commences at $\sim 460^\circ\text{C}$.

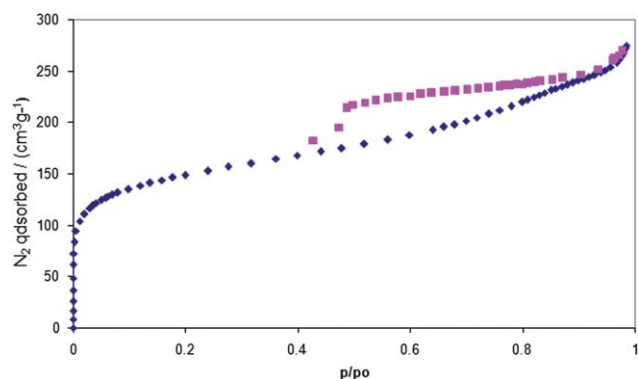


Fig. 1 Nitrogen adsorption (solid circles) and desorption (open circles) isotherms at 77 K for the polymer obtained from A–B monomer **8**.

In summary, we have successfully developed an efficient synthetic route for the preparation of a novel 9,10-dibutyl triptycene-based A–B monomer that contains both a pyrazine-activated dichloride group and a catechol group and used it efficiently as a precursor for the synthesis of a non-network PIMs. All synthetic procedures are simple, efficient and are suitable for scale-up. Further study on the synthesis and the use of other 9,10-dialkyl precursors for preparation of PIMs is in progress. To the best of our knowledge, this report describes the first example of a triptycene A–B monomer to be used as a precursor for the synthesis of PIMs. It is also worth noting that the presence of phenazine subunits as N-donor ligands suggests the introduction of appropriate metal ions for potential catalytic activity.⁹

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Notes and references

- 1 *Handbook of Porous Solids*, ed. F. Schuth, K. Sing and J. Weitman, Wiley-VCH, Berlin, 2002, vol. 1–5.

- 2 (a) N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675; (b) N. B. McKeown, P. M. Budd, B. S. Ghanem and K. J. Msayib, *UK Pat.*, appl. 0317557, 2005; *International pat.*, appl. PCT/GB2004/003166.
- 3 (a) P. M. Budd, B. S. Ghanem, K. J. Msayib, N. B. McKeown and C. E. Tattershall, *J. Mater. Chem.*, 2003, **13**, 2721; (b) A. V. Maffei, P. M. Budd and N. B. McKeown, *Langmuir*, 2006, **22**, 4225.
- 4 (a) P. M. Budd, K. J. Msayib, C. E. Tattershall, B. S. Ghanem, K. J. Reynolds, N. B. McKeown and D. J. Fritsch, *J. Membr. Sci.*, 2005, **251**, 263; (b) B. S. Ghanem, N. B. McKeown, P. M. Budd, J. D. Selbie and D. J. Fritsch, *Adv. Mater.*, 2008, **20**, 2766.
- 5 (a) N. B. McKeown, B. S. Ghanem, K. J. Msayib, P. M. Budd, C. E. Tattershall, K. Mahmoud, D. Book and A. Walton, *Angew. Chem., Int. Ed.*, 2006, **45**, 1804; (b) B. S. Ghanem, M. Hashem, K. Harris, K. J. Msayib, M. Xu, P. M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton and N. B. McKeown, *Macromolecules*, 2010, **43**, 5287.
- 6 H. J. Mackintosh, P. M. Budd and N. B. McKeown, *J. Mater. Chem.*, 2008, **18**, 573.
- 7 (a) P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chem. Commun.*, 2004, 230; (b) B. S. Ghanem, N. B. McKeown, P. M. Budd and D. Fritsch, *Macromolecules*, 2008, **41**, 1640.
- 8 (a) B. S. Ghanem, K. J. Msayib, N. B. McKeown, K. D. M. Harris, Z. Pan, P. M. Budd, A. Butler, J. Selbie, D. Book and A. Walton, *Chem. Commun.*, 2007, 67; (b) N. T. Tsui, A. J. Paraskos, L. Torun, T. M. Swager and E. L. Thomas, *Macromolecules*, 2006, **39**, 3350; (c) X. Z. Zhu and C. F. Chen, *J. Org. Chem.*, 2005, **70**, 917; (d) C. E. Godinez, G. Zepeda and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2002, **124**, 4701; (e) Z. Chen and T. M. Swager, *Macromolecules*, 2008, **41**, 6880.
- 9 N. B. McKeown, P. M. Budd, K. J. Msayib, B. S. Ghanem, H. J. Kingston, C. E. Tattershall, S. Makhseed, K. J. Reynolds and D. Fritsch, *Chem.–Eur. J.*, 2005, **11**, 2610.
- 10 Yu. V. Shklyayev and Yu. V. Nifontof, *Russ. Chem. Bull.*, 2002, **51**, 844.
- 11 Q. S. Zong and C.-F. Chen, *Org. Lett.*, 2006, **8**, 211.
- 12 J.-M. Zhao, H.-Y. Lu, J. Cao and C.-F. Chen, *Tetrahedron Lett.*, 2009, **50**, 219.
- 13 See ESI†.
- 14 M. E. Rogers and B. A. Averill, *J. Org. Chem.*, 1986, **51**, 3308.
- 15 X. Z. Zhu and C. F. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 13158.
- 16 X. Z. Zhu and C. F. Chen, *J. Org. Chem.*, 2005, **70**, 917.
- 17 N. J. Xanthopoulou, A. P. Kourounakis, S. Spyridis and P. N. Kourounakis, *Eur. J. Med. Chem.*, 2003, **38**, 621.
- 18 S. J. Norvez, *J. Org. Chem.*, 1993, **58**, 2414.
- 19 T. M. Long and T. M. Swager, *J. Mater. Chem.*, 2002, **12**, 3407–3412.
- 20 C. E. Godinez, G. C. Zepeda, J. Mortko, H. M. A. Dang and M. A. Garcia-Garibay, *J. Org. Chem.*, 2004, **69**, 1652–1662.
- 21 S. M. Hou, T. Sagara, D. C. Xu, T. R. Kelly and E. Ganz, *Nanotechnology*, 2003, **14**, 566.