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Novel polymers of intrinsic microporosity (PIMs) derived from 1,1-spiro-bis(1,2,3,4-tetrahydronaphthalene)-based monomers

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ABSTRACT

The synthesis of novel monomers based upon the rigid 1,1′-spiro-bis(1,2,4,5-tetrahydro-6,7-dihydroxynaphthalene) framework is reported. These monomers can be used for the synthesis of polymers of intrinsic microporosity (PIMs) due to their reactive catechol units and nonlinear shape, which introduces the necessary sites of contortion into the resulting PIM.

Microporous materials contain interconnected pores that are less than 2 nm in diameter and are widely used as adsorbents, heterogeneous catalysts and for gas separation, purification and storage.[1] In the past few years there has been growing interest in the synthesis and applications of microporous materials derived from purely organic components.[2–4] Our approach involves the design of polymers with highly rigid and contorted macromolecular structures that cannot fill space efficiently thus leaving molecular-sized interconnected voids. These polymers of intrinsic microporosity (PIMs) are composed of fused rings that provide rigidity, and sites of contortion, which are provided by spiro-centres.[5–10] PIMs are organic microporous materials which combine the high internal surface areas of conventional microporous materials, such as zeolites or activated carbons, with the processability of polymers and have been studied as separation membranes,[11–13] hydrogen storage materials,[14–17] adsorbents[8,18] and heterogeneous catalysts.[19]

For example, the archetypal PIM, (PIM-1)[20,21] is prepared by the nucleophilic aromatic substitution reaction between commercially available 2,3,5,6-tetrafluoroterephthalonitrile and 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (Scheme 1). PIM-1 is a promising membrane material for gas and vapour separations and therefore we are interested in making novel PIMs in order to understand property-structure relationships and to optimise their performance in this important application. One simple modification of interest is the preparation of PIMs from a family of monomers based upon 1,1′-spiro-bis(1,2,4,5-tetrahydro-6,7-dihydroxynaphthalene). In particular, replacement of the fused five-membered spirocyclic rings of PIM-1 with six-membered rings was anticipated to increase the flexibility of the polymer framework, which may be beneficial to enhance solubility in a wider range of organic solvents and to improve film formation for membrane development. In analogy with the preparation of the analogous 1,1-spirobisindane monomers,[22] the key intermediate for the synthesis of the spiro-bis(tetrahydronaphthalene) monomers is the diester **1**, which was prepared via the route shown in Scheme 2.

After many unsuccessful attempts with a number of different reagents [e.g., cH_2SO_4 and polyphosphoric acid (PPA)], Eaton's reagent[23] facilitated the troublesome double addition of veratrole onto the ketone of diethyl-4-oxopimelate to give **1**, which was accompanied by partial hydrolysis of the ester groups. Hence it proved convenient to perform the aqueous hydrolysis of crude **1** to give the diacid **2**, which was isolated readily by precipitation with aqueous acid and then perform a re-esterification to obtain pure **1**. In order to make a direct comparison with PIM-1 and the analogous polymer containing a spirocyclic framework consisting of six-membered rings, the tetramethyl-containing spirobis(tetrahydronaphthalene) precursor **4** was prepared (Scheme 3). This was achieved by the addition of an excess of methylmagnesium bromide to diester **1**, followed by double cyclisation, in Eaton's reagent, of the dehydrated open-chain compound, which was isolated after acid work-up of the Grignard adduct. Demethylation of **4** using BBr_3 afforded the desired monomer **5**. By an identical route, the tetraphenyl spirobis(tetrahydronaphthalene) monomer **7** was prepared starting with the addition of phenylmagnesium bromide to **1**.

Of interest was the synthesis of a spirobis(tetrahydronaphthalene) monomer containing two ketone groups that can be used for further substitutions. This was achieved readily by treatment of diacid **2** with PPA to force a double intramolecular Friedel–Crafts acylation to give the desired spirocyclic diketone **9** (Scheme 4). BBr_3 facilitated the removal of the methoxy groups to give the monomer **10**.

In order to provide bulky substituents to enhance the solubility of the resulting polymers, phenyl and spirobisfluorene groups were joined to the spirobis(tetrahydronaphthalene) framework by the addition of the appropriate Grignard reagent to the bisketone **9** (Scheme 5). Thus, acid work-up of the product from the addition of phenylmagnesium bromide to **9** gave 1,1′-spirobis(4-phenyl-1,2-dihydro-6,7-dimethoxynaphthalene) **11**. Similarly, addition of

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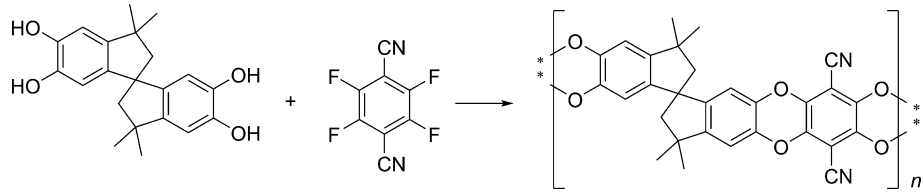
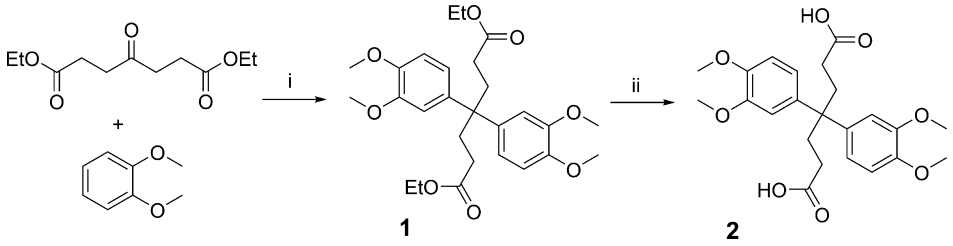
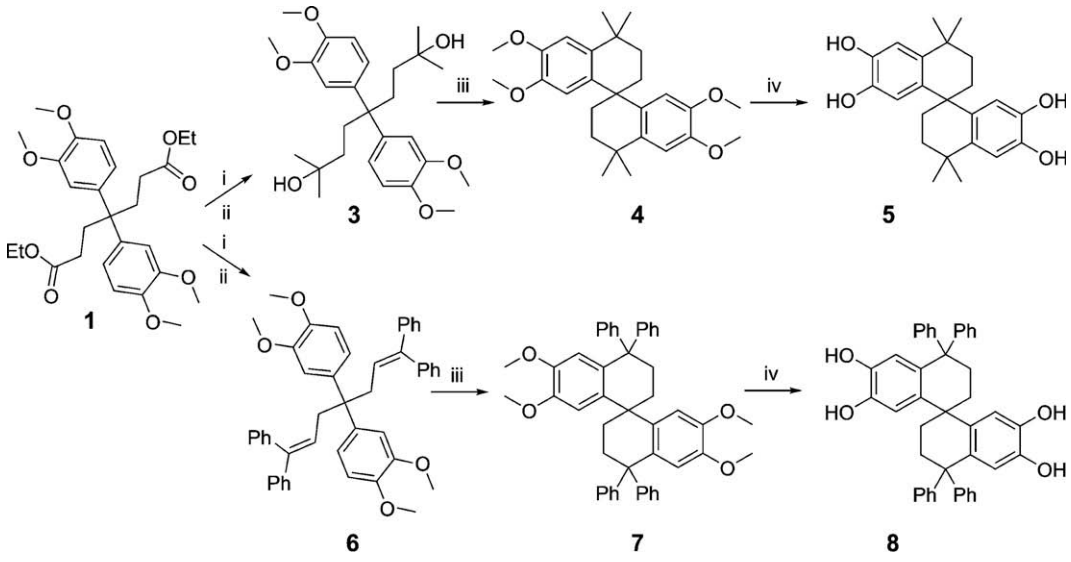


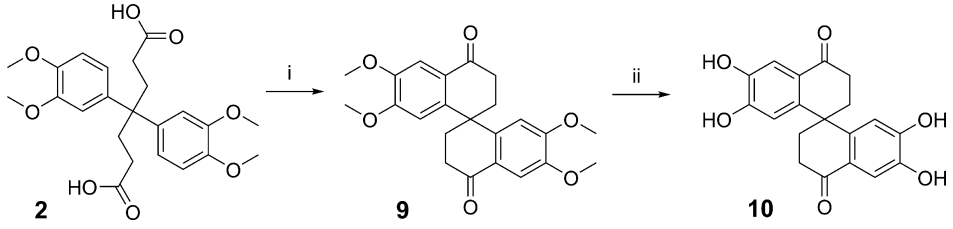
Scheme 1. PIM-1 synthesis.



Scheme 2. Reagents and conditions: (i) Eaton's reagent, 20 °C (7 d, 32%); (ii) aq NaOH (20%), MeOH (2 h, 95%).



Scheme 3. Reagents and conditions: (i) MeMgBr, THF, reflux; (ii) 10% HCl (1 h, 91% for **3** and 1 h, 75% for **6**) and (iii) Eaton's reagent (overnight, 20% for **4** and 73% for **7**); (iv) BBr_3, CH_2Cl_2 (1 h, 94% for **5** and 4 h, 73% for **8**).

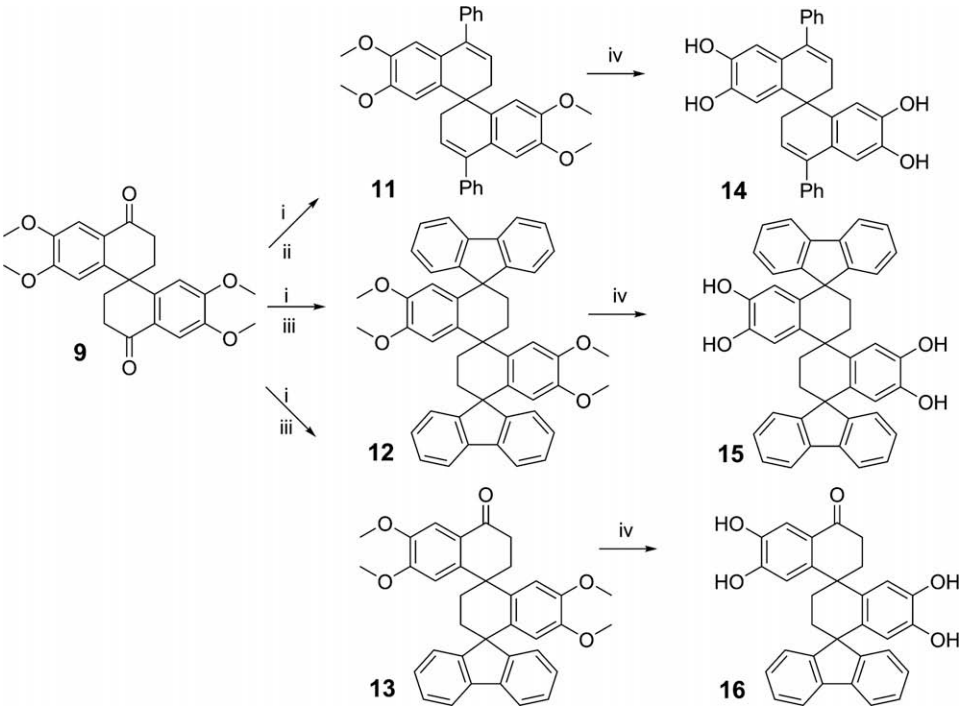


Scheme 4. Reagents and conditions: (i) PPA, 80 °C (3 h, 68%) and (ii) BBr_3, CH_2Cl_2 (2 h, 73%).

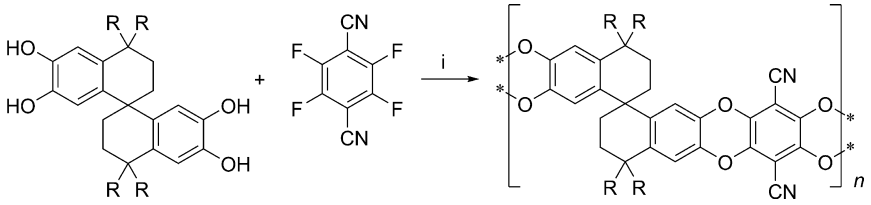
2-biphenylmagnesium bromide to **9**, followed by treatment of the crude product with Eaton's Reagent,[24,25] gave the spiro-fused bis-fluorene derivative **12** together with a mono-fluorene containing derivative **13** originating from the single addition of the Grignard reagent to **9**. Removal of the methoxy groups from **11**, **12** and **13** gave the desired biscatechol monomers **14**, **15** and **16**, respectively.

Polymers were prepared from the monomers by reaction with 2,3,5,6-tetrafluoroterephthalonitrile (Scheme 6) using the optimised procedure developed for the synthesis of PIM-1.[20]

The method of purification of the crude polymers was dependent on their solubility, with the soluble polymers being reprecipitated from a good solvent (e.g., $CHCl_3$ or THF) into a poor solvent (e.g., MeOH or acetone) and the insoluble polymers being washed sequentially in refluxing solvents (THF, acetone, then MeOH). The physical properties of the novel polymers along with the relevant physical properties of the analogous spirobisindane-containing polymers are given in Table 1. With one exception (the polymer of the bisketone monomer **10**, which might preferentially undergo



Scheme 5. Reagents and conditions: (i) appropriate Grignard reagent, THF, reflux; (ii) 10% HCl (24 h, 78% for **11**); (iii) Eaton's reagent (3 d, 19% for **12**, 3 d, 50% for **13**) and (iv) BBr_3, CH_2Cl_2 (6 h, 88% for **14**, 1 h, 90% for **15** and 2 h, 85% for **16**).



Scheme 6. Reagents and conditions: (i) DMF, K_2CO_3, 65 °C (typically 3 d, yields between 74% and 90%).

Table 1
Summary of the physical properties of PIMs

Polymer from	Surface area (m^2/g)	M_w /10^3 (g/mol)	T_{onset}[b] (°C)	Solubility
5	432 (780)[c]	22	490	+ (THF, $CHCl_3$)
8	395	93	495	+ (THF)
10	713 (501)[c]	—[a]	445	—
14	203 (560)[c]	—[a]	466	—
15	590 (895)[c]	16	495	+ (THF, $CHCl_3$)
16	300 (656)[c]	—[a]	486	—

[a] Not soluble therefore incompatible with characterisation by gel permeation chromatography.
[b] Onset of degradation temperature measured by thermogravimetric analysis.
[c] Comparison of the surface area of the parent spiro bisindane polymers.[22]

a base-catalysed aldol reaction during polymerisation resulting in extensive cross-linking), it should be noted that the Brunauer, Emmett and Teller (BET) surface areas of the polymers in their powdered form, calculated from the nitrogen adsorption isotherms obtained at 77 K, are in each case lower than the analogous spirobisindane-containing polymers.[22] This might be expected due to the greater flexibility of the six-membered spirocyclic ring unit. Nevertheless, each polymer demonstrated significant microporosity with the fluorene-containing polymer derived from monomer **15** demonstrating a very respectable BET surface area of 590 $m^2\ g^{-1}$ and excellent solubility in organic solvents, which will facilitate membrane fabrication. A full assessment of the membrane properties of these polymers is in progress.

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Supplementary data

Supplementary data (synthesis of compounds **1**–**16** and the polymers derived from monomers **5**, **8**, **10**, **14**, **15** and **16**) associ-

ated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.032.

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