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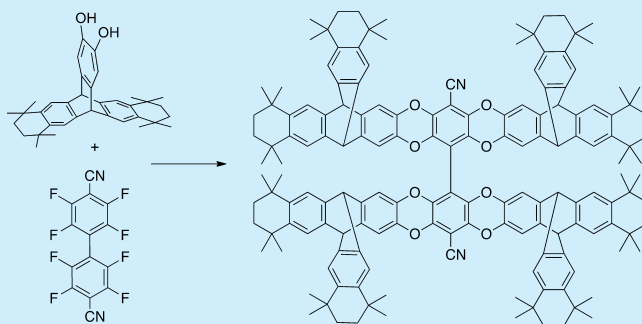


Triptycene-Based Organic Molecules of Intrinsic Microporosity

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Supporting Information

ABSTRACT: Four Organic Molecules of Intrinsic Microporosity (OMIMs) were prepared by fusing triptycene-based components to a biphenyl core. Due to their rigid molecular structures that cannot pack space efficiently, these OMIMs form amorphous materials with significant microporosity as demonstrated by apparent BET surface areas in the range of 515–702 m² g⁻¹. Bulky cyclic 1',2',3',4'-tetrahydro-1',1',4',4'-tetramethylbenzo units placed on the triptycene termini are especially efficient at enhancing microporosity.



Most microporous materials are based on crystalline¹ or amorphous² network structures with porosity arising from the presence of interconnected voids. In order to allow for solution processability, there has been intense recent interest in the preparation of microporous materials without network structures derived from either discrete small molecules or macromolecules. In most cases microporosity derived from discrete molecules is generated from their self-assembly into ordered porous crystals with cage structures being particularly successful for generating porosity.³ In contrast, microporosity from non-network macromolecules originates from the inability of rigid contorted polymer chains to pack space efficiently, as demonstrated by the much-studied Polymers of Microporosity (PIMs).⁴ The analogous generation of amorphous microporous materials from well-defined discrete molecules has been achieved mainly by using prefabricated pores derived from macrocycles or cage molecules.⁵ However, to date, very few discrete molecules have been demonstrated to generate porosity solely from inefficient packing.⁶ Recently, we introduced the concept of Organic Molecules of Intrinsic Microporosity (OMIMs) based upon the design of well-defined, rigid molecules with awkward shapes that cannot pack efficiently in the solid state.⁷ Molecular packing simulation studies of various OMIMs, including triptycene-based examples OMIM-1 and OMIM-4 (Scheme 1), suggest that the addition of bulky substituents (e.g., ^tBu on OMIM-4) increases both the amount and accessibility of microporosity.⁷ Here we describe for the first time the synthetic realization of some of the OMIMs used in these packing simulations and investigate the effect of bulky substituents, including a bulky cyclic unit (1',2',3',4'-tetrahydro-1',1',4',4'-tetramethylbenzo), on the amount of intrinsic microporosity generated.

The use of triptycene as a component for microporous polymers is commonplace due to their relative ease of synthesis,

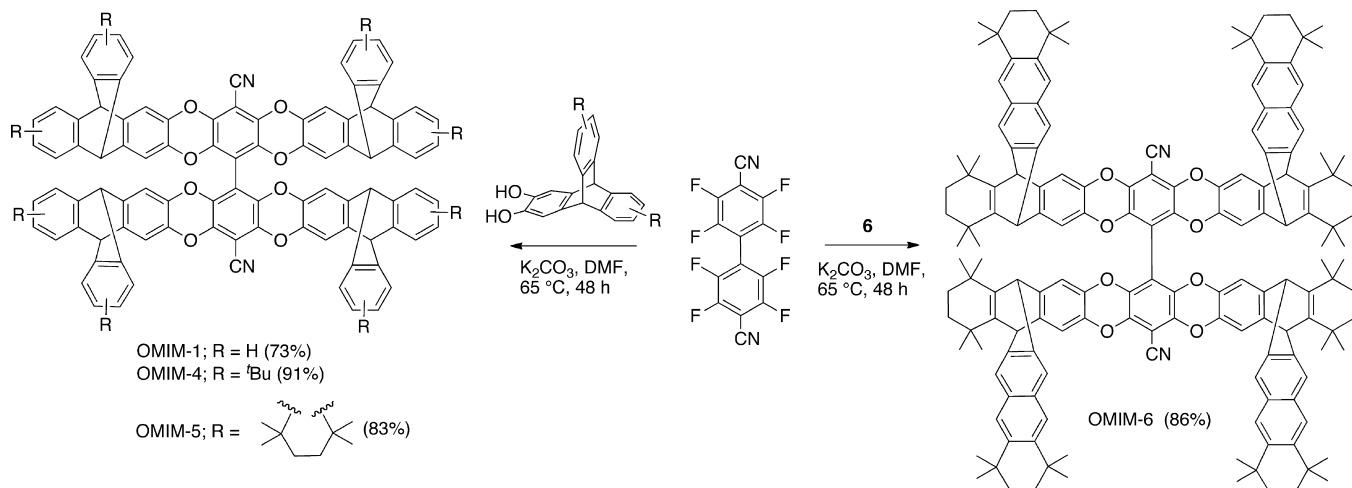
rigidity, and high internal molecular free volume.⁸ Packing simulations predicted that fusing four triptycene units to a central biphenyl core would also produce OMIMs with significant microporosity.⁷ This was achieved synthetically by an efficient aromatic nucleophilic substitution reaction, similar to that used for the construction of PIMs,⁴ between 4,4'-dicyano-2,2',3,3',5,5',6,6'-octafluorobiphenyl⁹ and 2,3-dihydroxytriptycene¹⁰ (for OMIM-1). Suitably substituted triptycenes, 2,7-di-*tert*-butyl-12,13-dihydroxytriptycene **1** and [1,2],[6,7]-di-[1',2',3',4'-tetrahydro-1',1',4',4'-tetramethylbenzo-12,13-dihydroxytriptycene **2** were used to make OMIM-4 and OMIM-5, respectively (Scheme 1).

The dihydroxytriptycene precursors were prepared by the Diels–Alder addition of 4,5-dimethoxybenzynes (obtained by the reaction of commercial 2-amino-4,5-dimethoxybenzoic acid with isoamyl nitrite) to the appropriate anthracene, followed by subsequent boron tribromide mediated demethylation.¹⁰ The synthesis of **2** from 1,1,4,4,8,8,11,11-octamethyl-1,2,3,4,8,9,10,11-octahydropentacene¹¹ **3** gave, in addition to the desired triptycene **4**, the naphthobenzobarrelene **5** (Scheme 2). Regioisomers **4** and **5** were readily separated by column chromatography, and both products were characterized by X-ray crystallography. Surprisingly, it was found that naphthobenzobarrelene **5** was the major product, being formed in approximately double the yield of triptycene **4** (33% and 15% yields, respectively), suggesting that each of the three rings of anthracene **3** is equally reactive as a diene toward the cycloaddition of benzyne.

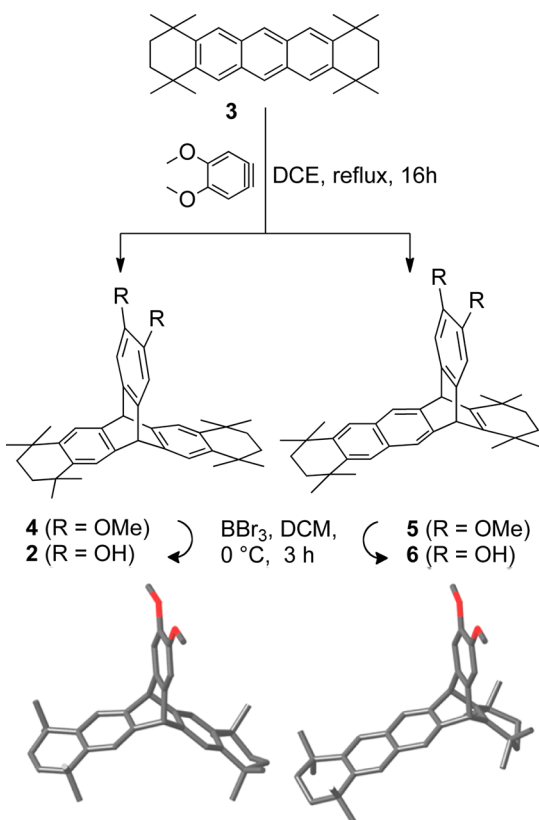
Other examples of naphthobenzobarrelene adducts have been reported, but few have been isolated due to difficulty in

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Scheme 1. Synthesis of the Triptycene-Based OMIMs^a

^aSee Supporting Information for further details.

Scheme 2. Synthesis of the Extended Triptycene **2** and the Naphthobenzobarrelene **6** Precursors to OMIM-5 and OMIM-6, Respectively;^a (Bottom) Single Crystal X-ray Diffraction Structures of Intermediates **4** and **5**

^aSee Supporting Information for further details.

separating them from the triptycene coproducts.¹² Diels–Alder reactions are known to be influenced by steric crowding, so it is perhaps surprising that naphthobenzobarrelene **5** is the major product. For example, a recent report describes the exclusive synthesis of a naphthobenzobarrelene adduct by blocking addition across the central ring by placing bulky ferrocenyl groups at the 9,10 positions of anthracene and using the

sterically crowded 3-trifluoromethylbenzyne as a coreactant.^{12c} However, previous studies of benzyne addition to 2,3,5,6-tetramethylantracene also reported naphthobenzobarrelene byproducts, and therefore, in the case of anthracene **3**, it appears that the electronic effect of substitution outweighs the potential steric hindrance to addition at the outer rings. The unforeseen formation of **5** facilitated the preparation of OMIM-6 from the demethylated naphthobenzobarrelene **6** and comparison of its properties to those of the isomeric triptycene-based OMIM-5 (Scheme 1).

Data from matrix assisted laser desorption ionization mass spectrometry, solution NMR, elemental analysis, and analytical gel permeation chromatography are consistent with each of the anticipated OMIM structures. OMIM-1 and OMIM-5 demonstrate simple ¹H/¹³C NMR spectra, whereas those of OMIM-4 and OMIM-6 are complex indicating the presence of regioisomers (also enantiomers for OMIM-4), as expected due to the less symmetrical nature of the precursors **2** and **6**, respectively. OMIM-5 was also characterized by single crystal X-ray diffraction (Figure 1).

Nitrogen adsorption isotherms measured at 77 K from amorphous powdered samples of the OMIMs each demonstrate significant uptake at low relative pressures indicative of microporosity (up to 8 mmol g⁻¹ at *p/p*^o < 0.1; Figure 2). Apparent BET surface areas calculated from these isotherms are 480, 626, 702, and 622 m² g⁻¹ for OMIM-1, OMIM-4, OMIM-5, and OMIM-6, respectively. These results validate predictions from molecular packing studies that suggest placing rigid bulky groups on the termini of OMIMs will enhance microporosity.⁷ In addition, the rate of nitrogen adsorption is faster for OMIM-4, OMIM-5, and OMIM-6 as compared to OMIM-1. This suggests that the microporosity is also more readily accessible for those OMIMs with bulky terminal substituents due to the more open conformation adopted by the molecules, also as predicted.⁷ Although the apparent microporosity is modest as compared to many recently described microporous molecular materials based on crystalline order,³ the BET surface area of OMIM-5 is comparable to microporous amorphous materials based on cages⁵ or many PIMs (e.g., PIM-1 ≈ 760 m² g⁻¹).⁴ In addition, it seems reasonable to conclude from this study that bulky cyclic substituents, such as 1',2',3',4'-tetrahydro-1',1',4',4'-tetramethylbenzo, may be of general utility for the

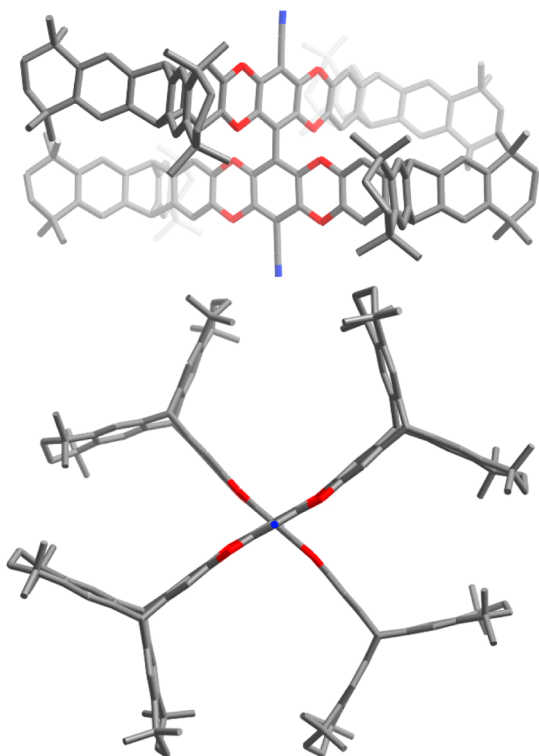


Figure 1. Two views of the X-ray single crystal structure of OMIM-5 (hydrogen atoms have been removed for clarity).

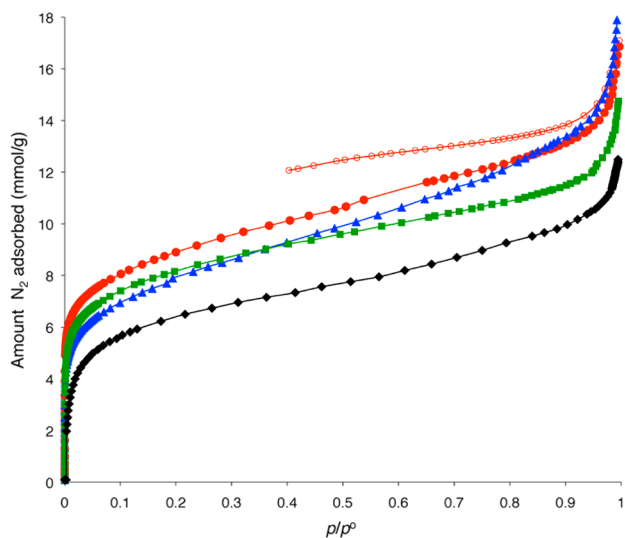


Figure 2. Nitrogen sorption isotherms as measured at 77 K for OMIM-1 (black \blacklozenge), OMIM-4 (green \blacksquare), OMIM-5 (red \bullet), and OMIM-6 (blue \blacktriangle). The partial desorption isotherm for OMIM-5 is also shown (orange \circ).

enhancement of molecular microporous materials, as demonstrated by OMIM-5. Such symmetrical substituents also avoid the formation of regioisomers, ensuring that the molecular structure is well-defined, thus conforming to one of the key OMIM design criteria.

■ ASSOCIATED CONTENT

📄 Supporting Information

Complete experimental details and data characterizing all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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