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Organic molecules of intrinsic microporosity: Characterization of novel microporous materials

Annalaura Del Regno, Flor R. Siperstein *

School of Chemical Engineering and Analytical Science, The University of Manchester, Manchester M13 9PL, United Kingdom

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A B S T R A C T

Molecular simulations were used in this work to characterise a new class of microporous material: organic molecules of intrinsic microporosity (OMIMs). Molecular dynamics simulations were used to generate the material's samples, and grand canonical Monte Carlo simulations of argon adsorption were used to ascertain the relationship between the different structures and the observed properties. Packing behavior, porosity and adsorption capacity have been determined for each system. The final density of the material, as well as the surface area and pore volume depend on the ending group's bulkiness. Bulkier molecules lead to materials with lower densities, but it was found that the adsorption behavior is not just related to the material's density, but also to the pore size and shape, which are determined by the way the molecules pack. The relationship between adsorption capacity and physical properties were analyzed and the role of surface area, free volume and enthalpic interaction were used to identify different adsorption regimes. It was found that the uptake of argon at low pressure is proportional to the strength of the adsorbent-adsorbate interaction while at moderate pressure it is dependent on the free volume and surface area.

1. Introduction

Microporous materials are solids that contain interconnected pores of the order of molecular dimensions (less than 2 nm), property that makes them interesting for a series of applications such as heterogeneous catalysis, adsorption, separation and gas storage. During the past decade many materials have been explored, from traditional microporous materials like zeolites, silica and activated carbons to a wide new range of organic based networks like metal–organic frameworks (MOFs) [1–3], covalent organic frameworks (COFs) [4–6] and hyper-crossed-linked polymers (HCP) [7,8].

Crystalline materials have the advantage of a well controlled pore size and shape, nevertheless, many adsorbents used in industry are amorphous, as they can have other desirable properties. New microporous polymers, such as polymers of intrinsic microporosity (PIMs) [9–13], behave in part as typical adsorbents due to their rigid structure, but also as polymers with a higher flexibility than most carbons and silicas. Careful selection of the monomers has led to a variety of microporous polymers: spirobifluorene based polyamydes [14], conjugated microporous polymers [15] and element organic frameworks [16,17].

Crystalline and amorphous microporous materials can also be obtained with molecules. For instance, ordered cage-like materials can be synthesized through dynamic covalent interactions [18], where a group of atoms (such as a coordination compound or simply an imine) create a temporary bond with the organic cage during its formation, but they are not part of the final compound. The cages then assemble to form crystalline porous materials. Other ordered materials can exploit hydrogen bonding between small molecules leading to microporous molecular crystals, as shown by Mostarlerz and Oppel [19]. Intrinsic microporosity is also observed in triptycene-based materials [20–22] due to their high internal molecular free volume which pack inefficiently. Microporosity therefore, can be generated by chemical–physical interactions and also by a clever manipulation of the structure geometry, both for relatively small molecules and polymers.

Organic molecules of intrinsic microporosity (OMIMs) [13,23] are a new class of molecules formed with similar building block than those used to prepare PIMs, but with a significantly lower molecular weight. They have similar chemistry to PIMs and pack inefficiently due to their highly concave, “awkward” shape.

Mathematical studies of two dimensional disks and three dimensional superballs [24,25] proved that a system's packing density can be modulated by changing the grade of its members concavity; the lowest system's density corresponds to the highest number of concave faces of its units. The building blocks of OMIMs were therefore designed to imitate this concave geometry [13,23]; they consist of a core which determines the geometry, and termini that provide the general environment for these materials (Fig. 1).

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* Corresponding author.
E-mail address: flor.siperstein@manchester.ac.uk (F.R. Siperstein).

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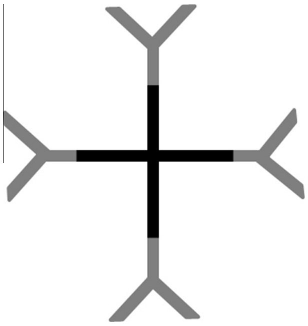

Fig. 1. Schematic representation of a generic OMIM structure; the core is represented in black, the termini in gray.

A series of biphenyl core OMIMs have been recently reported by Abbott et al. [23]; in this work a series of packing protocols were compared to determine a realistic and consistent model in order to represent accurately these new materials. Three different type of OMIMs were investigated, exploring different termini conformations but preserving the core structure and the aromaticity of each system; trigonal (2,3-dihydroxytriptycene (OMIM-1)), tetrahedral (2,3-dihydroxy-9,9′-spirobisfluorene (OMIM-2)) and octahedral configurations (2,3-dihydroxyhexabenzopropellane (OMIM-3)) were analyzed and the properties of simulated samples compared with experimental wide-angle X-ray scattering (WAXS). This work showed that the relationship between the OMIM structure and the materials properties is complex. Therefore, a better understanding of the packing behavior is essential in order to efficiently screen series of possible termini that will lead to the desired material's performances.

In this work the influence of the termini's chemical nature on gas adsorption was studied. The cross-shaped core was preserved (Fig. 2 – Core) and the environment of the termini was systematically changed. Starting from the simplest OMIMs type, the benzene and the naphthalene based OMIMs (Fig. 2 – termini A and E), different substituents such as tert-butilate, adamantan and triptycene were added to the basic aromatic linear terminus (Fig. 2 – termini B, C, D for the benzene family, F and G for the naphthalene one).

We aim to understand the packing behavior of these two families, determine the relationship between the terminus chemistry and/or bulkiness with the packing ability and the adsorption properties in order to anticipate the properties of the final material knowing the nature of cores and termini. Different representative samples of each material were generated using molecular dynamics simulation. The structural properties (density, surface area, pore size distribution and porosity) were characterized. We used grand canonical Monte Carlo (GCMC) simulations of argon to investigate the role of the surface area and pore size distribution as well as adsorbent/guest energetics in determining adsorption of small molecules in these novel materials. We found many similarities in the adsorption behavior compared to other porous materials, such as MOFs, where different adsorption regimes can be identified: those proportional to the surface area or pore volume, which suggest that the knowledge developed for other porous materials is transferable to OMIMs despite the disordered nature of the structures they form.

2. Methodology

2.1. OMIMs structure

The two families of OMIMs, the benzene and the naphthalene based OMIMs (Fig. 2 – pink and blue blocks) were represented using fully atomistic models. The interactions between atoms were described using the OPLS force field [26] and the charges were calculated through the charge equilibration algorithm (QEq) [27].

The Qeq method, introduced by Rappe et al. in 1996, has been widely used as it provides a rapid method for estimating point charges located on each atom. The point charges are calculated based on the molecular geometry and experimental atomic properties: atomic electron affinity and ionization potential. In this method, the potential energy of an atom is described as a Taylor expansion of its partial charge. The first and second derivatives

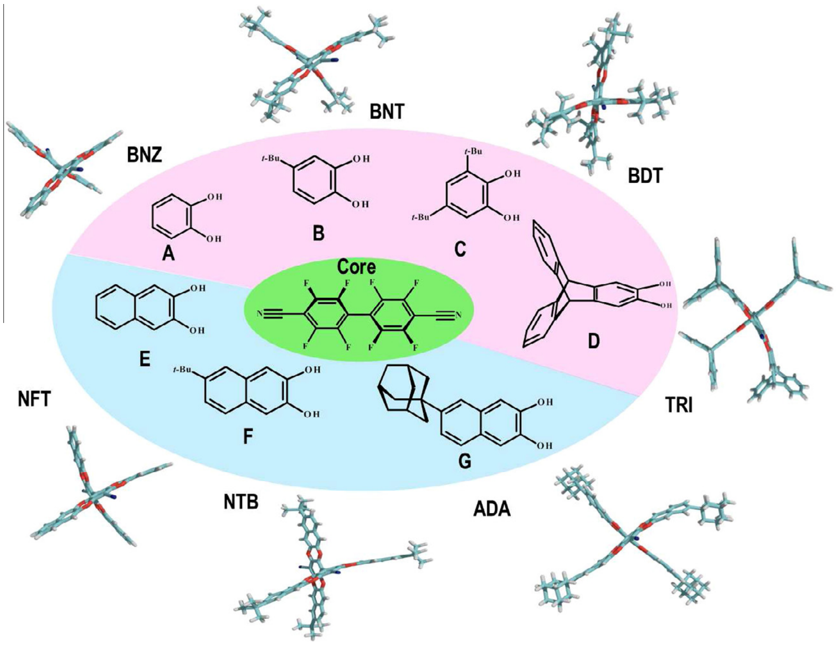

Fig. 2. Chemical structures of termini for benzene family (pink block; A – benzene-1,2-diol, B – 4-tert-butylbenzene-1,2- diol, C – 3,5-di-tert-butylbenzene-1,2-diol, D – 2,3-dihydroxy-triptycene), naphthalene family (blue block, E – naphthalene-2,3-diol, F – 6-tert-butylnaphthalene-2,3-diol, G – 6-adamantannaphathalene-2,3-diol) and core (green block; 4,4′-dicyano-biphenyl) precursors and the resulting cross-shaped OMIMs with related acronyms.