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Microporous Materials

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Porous Organic Polymers: Distinction from Disorder?**

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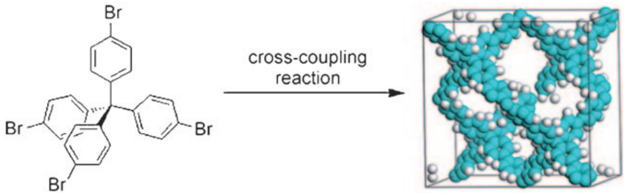
Microporous materials such as zeolites are of great importance in molecular separations and catalysis. Recently, a range of microporous crystalline zeolite analogues has been developed, in particular metal-organic frameworks (MOFs)[1] and covalent organic frameworks (COFs).[2] These materials can exhibit very large specific surface areas: for example, COF-103 was reported to have a Brunauer–Emmett–Teller surface area of 4210 $m^2 g^{-1}$ and a pore volume of 1.66 $cm^3 g^{-1}$.[2b] One practical drawback is that some of the most porous examples of MOFs and COFs also possess limited physicochemical stability. This results in part from the reversible coordination or covalent chemistry used to obtain crystalline products. By contrast, there is a growing range of microporous organic networks comprising very stable covalent C–C, C–H, and C–N bonds.[3] With a few exciting recent exceptions,[2d,e] these materials are generally amorphous in nature because of the irreversible reactions used in their synthesis.[3] It is nonetheless possible to obtain a degree of synthetic control over surface area and average micropore size in amorphous materials such as conjugated microporous polymers (CMPs),[4] although not with the long-range order and atomic precision that is possible in crystalline networks. Until now, however, none of these amorphous polymers has rivaled the largest surface areas exhibited by crystalline microporous materials; the maximum BET surface areas (> 1900 $m^2 g^{-1}$ for hypercrosslinked networks[3b,c]) fall short of those of leading MOFs and COFs.

Ben et al. have just described a microporous polyphenylene network, PAF-1, which is reported to have unprecedented surface area (BET surface area, 5640 $m^2 g^{-1}$; Langmuir surface area, 7100 $m^2 g^{-1}$ by N_2 sorption).[5] To our knowledge,[1–4,6] this exceeds surface areas measured for other materials, either crystalline or amorphous. The nitrogen sorption measurements are commensurate with the uptakes observed for gases such as H_2 (7.0 wt% excess at 77 K/48 bar) and CO_2 (1.3 $g g^{-1}$ at 40 bar, 298 K). These impressive sorption characteristics are combined with exceptional thermal and hydrothermal stability: for example, PAF-1 is thermally stable in air up to 520 °C and its sorption properties were unaffected by boiling in water for seven days.

The network was formed by nickel(0)-catalyzed Yamamoto-type Ullmann cross-coupling (Scheme 1), similar to the route described previously by Schmidt et al. for spirofluorene-based networks (BET surface area, 1275 $m^2 g^{-1}$).[7] A tetrahedral monomer, tetrakis(4-bromophenylmethane), was employed,[5] which is the bromo analogue of the monomer used recently in the synthesis of tetrahedral-linked polyarylenethynylene CMPs (BET surface area, 1213 $m^2 g^{-1}$).[8] Molecular structures for PAF-1 were confirmed by ^1H MAS NMR spectroscopy and elemental analysis. Despite some broad features in powder X-ray diffraction (PXRD) patterns, both diffraction and TEM analysis suggests that these networks are predominantly amorphous and that they exhibit little long-range order, in keeping with the irreversible coupling chemistry.



Scheme 1. Synthesis of the microporous polymer network PAF-1 by a Yamamoto cross-coupling reaction.

The combined physical properties of this material are outstanding with respect to other molecular networks and hence of strong practical interest. However, a key question, only partly addressed by the authors, is precisely why these networks are so much more microporous than other amorphous polyphenylenes[7] and related CMP networks.[4,8] A clue may lie in the elemental analyses for PAF-1 (calc. C 94.94, H 5.06; found C 94.73, H 5.27), which are very close to the ideal theoretical values. This result agrees with FTIR and ^1H MAS NMR analyses which show no signals assignable to halogen end groups. By contrast, residual halogen (and ethynyl) end groups were detected in microporous CMP networks,[4] both by ^1H MAS NMR spectroscopy and by elemental analyses, suggesting perhaps that this nickel(0)-catalyzed Yamamoto-type Ullmann cross-coupling may be more efficient under these conditions in forming highly condensed networks than analogous Sonogashira–Hagihara routes. Likewise, elemental

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analyses presented for other microporous Yamamoto-coupled networks[7] showed no residual halogen content.

The N_2 sorption for PAF-1 was found to correlate with a simulated gas sorption isotherm derived from a perfectly crystalline diamondoid model (P2; Figure 1 a) with a simulated density of 0.315 g cm^{-3},[5] despite the fact that PXRD analysis suggests little long-range order. The authors highlight that the tetrahedral node-to-node distance in PAF-1 is long enough to give a high degree of microporosity but not so long as to promote interpenetration or to render the network mesoporous. These findings contrast with molecular simulations presented recently for CMP networks[9] where good agreement between simulated and measured micropore surface area was observed only for amorphous, interpenetrated models that matched the relatively high experimental bulk density for these solids (0.83 g cm^{-3}). These molecular simulations for amorphous CMPs also incorporated halogen end groups:[9] indeed, it proved difficult to construct plausible models with a density of 0.83 g cm^{-3} without the introduction of end groups and network interpenetration.

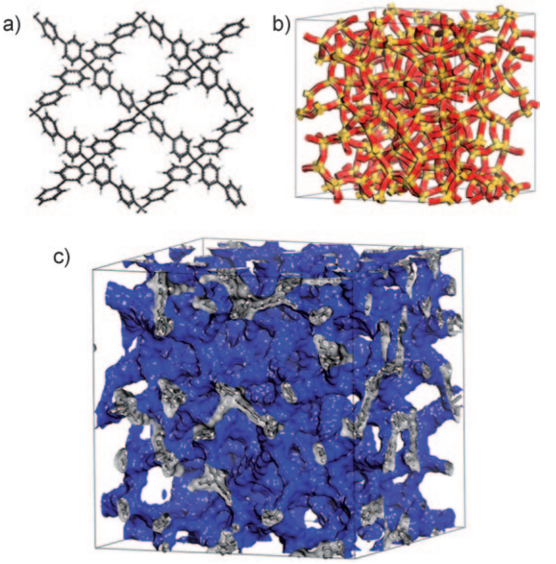

Figure 1. a) Diamondoid crystalline structure P2 proposed for PAF-1.[5] b) Model for amorphous silica (Accelrys Materials Studio 4.0); silicon atoms in yellow, oxygen in red. c) Model of amorphous PAF-1 built using amorphous silica (b) as the template. The Connolly surface shown in blue was created using a probe radius of 1.82 Å.

In principle, the lack of sharp diffraction peaks in the PXRD pattern for PAF-1 could be explained, for example, by multiple stacking faults in an otherwise locally ordered extended structure similar to P2. It is, however, also possible to rationalize the surface area and apparent lack of end groups in PAF-1 without invoking a periodic crystalline structure at all. As an illustration, we have constructed an alternative simulation by using a model for amorphous silica as a template (Figure 1 b,c). To build this model, silicon atoms were replaced with the tetrahedral carbon nodes for PAF-1 and oxygen atoms were replaced with the biphenyl struts in the network, followed by energy minimization. Only one bromine end group was included in the amorphous unit cell, and high levels of condensation were satisfied mostly by “loops” in the structure. This amorphous “expanded silica analogue” model has a simulated density of 0.292 g cm^{-3}, which is slightly lower than that of the crystalline P2 model (0.315 g cm^{-3}) presented by Ben et al.[5] The calculated elemental composition for this amorphous simulation (C 94.82, H 5.06, Br 0.12) is comparable with experimental analysis for PAF-1;[5] the bromine content is rather too low to detect by FTIR or ^{1}H MAS NMR spectroscopy. A Connolly surface area of 4900 m^2 g^{-1} and a solvent-accessible surface of 6100 m^2 g^{-1} were calculated from this simulation using a probe radius of 1.82 Å. As for the crystalline model, P2, these simulated values compare well with the experimentally determined surface areas for PAF-1. Silica is known to have a number of amorphous or glassy phases as well as various crystalline polymorphs.[10] Structural analogies with such phases—or with materials such as silicon or germanium—may prove fruitful in understanding networks such as PAF-1 that are based on tetrahedral linkers.

To summarize, PAF-1 combines high physicochemical stability with the potential synthetic diversification offered by organic polymers. This material and other analogues merit further investigation because these results challenge the notion that exceptionally high surface areas are the preserve of molecular networks with high degrees of long-range crystalline order.

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