Microporous Polymers

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Porous, Covalent Triazine-Based Frameworks Prepared by Ionothermal Synthesis**

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The synthesis of new porous architectures, assembled from simple molecular building blocks and with tailor-made functionalities, is a major goal in materials science.[1] It is highly desirable if such molecular building blocks already contain the structural information to generate a framework with regular and homogeneous porosity, thus avoiding the use of an auxiliary structure-directing agent.

In contrast to inorganic materials, only a few types of organic polymers exhibit permanent microporosity. The absence of microporosity is the other side of the "softness" of organic materials: Capillary pressures and high surface energies tend to close small pores by simple deformation of the framework.[2,3] Thus, it is very difficult to obtain microporous organic materials. Previously, pore collapse could be avoided by a very high degree of cross-linking, thereby yielding hard and rigid organic materials, for example, hypercross-linked polystyrene-derived resins[4] or polytriarylcarbinols,[5] and more recently polyanilines[6] or polyaryleneethynylenes.[7,8] Another approach is the introduction of stiff, bulky, contorted molecular motifs into an otherwise rigid linear polymer chain, resulting in space-inefficient packing of the chains and yielding polymers with intrinsic microporosity (PIMs).[9,10]

Besides the obstacles associated with the introduction of high surface areas, it seems even more difficult to achieve polymer materials with regular porosity, as it is widely accepted that the synthesis of extended, covalently bonded, regular organic structures relies on a reversible and self-optimizing polymerization under thermodynamic (rather than kinetic) control. Recently, Côté, Yaghi, et al. showed that the synthesis of crystalline covalent frameworks is possible by using the highly dynamic condensation reactions of boronic acids. Crystalline and highly porous 2D and 3D extended frameworks with high surface areas could be obtained.[11–13]

We report here on a promising new class of high-performance polymer frameworks with regular and irregular porosity, which are formed from simple, cheap, and abundant aromatic nitriles (Figure 1 a). By the dynamic trimerization reaction in ionothermal[14] conditions, that is, in molten zinc chloride at high temperature, triazine-based materials with high porosities and surface areas can be obtained that are similar in performance to zeolites, metal-organic frameworks (MOFs), or the covalent boron oxide based frameworks (COFs).[11,12]

Molten $ZnCl_2$ at 400 °C fulfils all the prerequisites to obtain crystalline porous polytriazines. First, nitriles show a good solubility in this ionic melt owing to strong Lewis acid–base interactions, and all of the monomers described here form clear solutions in this salt melt. Second, $ZnCl_2$ is a good catalyst for the trimerization reaction, which seems to be sufficiently reversible at this temperature. It is worth mentioning here that most aromatic and heterocyclic nitriles are temperature-stable compounds and start to decompose at temperatures often far above 400 °C, mainly through C–H bond cleavage and a subsequent loss of hydrogen.[15]

The polymers were synthesized by heating a mixture of the nitrile and $ZnCl_2$ in quartz ampules at 400 °C (see the Supporting Information). The yields of these reactions are generally close to quantitative. Figure 1 b shows a schematic representation of the formation of a triazine-based framework material by a trimerization reaction of 1,4-dicyanobenzene. The trimerization reaction can be followed by FTIR measurements of the products at different reaction times and temperatures (Figure 1 c). The disappearance of the otherwise intense carbonitrile band at 2218 cm^{-1} is indicative of a successful trimerization reaction, while the appearance of a strong absorption band at 1352 cm^{-1} points to the formation of triazine rings.[16] Reaction temperatures of less than 350 °C yield even after two days mainly soluble products. Incomplete polymerization was also observed for higher temperatures but shorter reaction times (e.g., 400 °C/10 h). For 400 °C and 40 h, FTIR spectroscopy indicates an almost complete conversion. Elemental analysis showed constant amounts of C, H, and N throughout the synthesis that are close to the theoretical values, as can be expected for this kind of reaction mechanism.

Independent of the specific monomer used, the products were obtained as black monolithic materials (Figure S1 in the Supporting Information). For faster removal of the metal salt the samples were first crushed into powders and then the powders were extensively washed with a diluted HCl solution. Thermogravimetric analysis (TGA) revealed that a maximum amount of approximately 5 wt % residual $ZnCl_2$ stays in the material.

For the polymerization product of 1,4-dicyanobenzene using one equivalent of $ZnCl_2$, the XRD pattern of the products displays some intense reflection peaks (Figure 2 a). This observation can be explained by the formation of a

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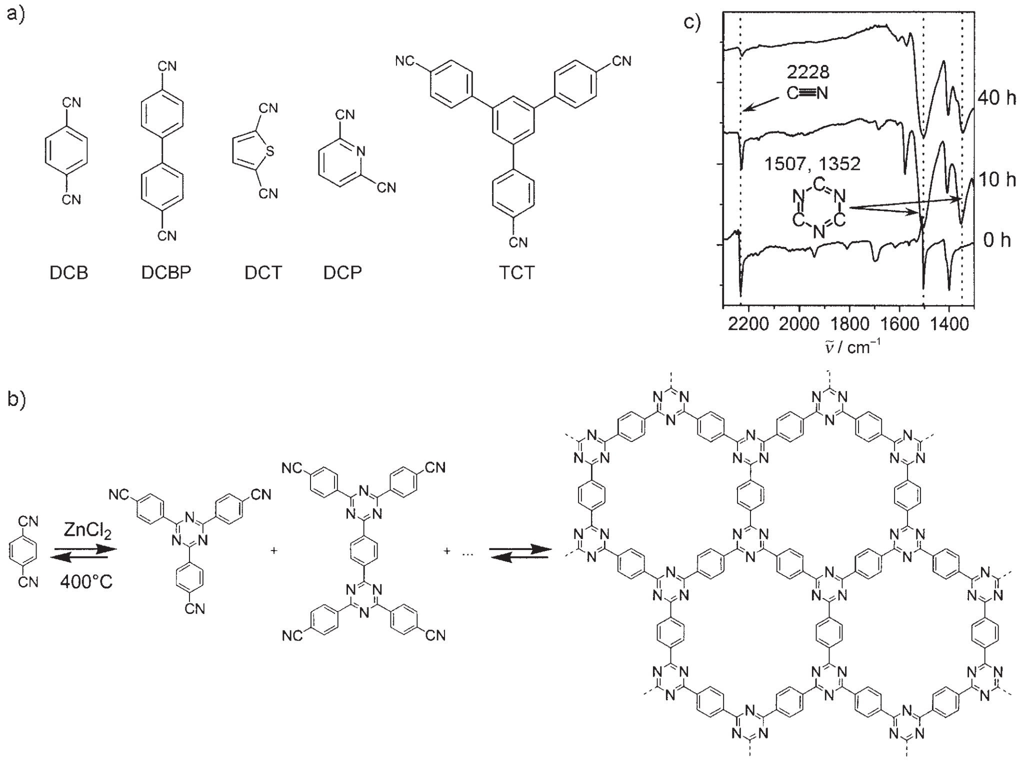

Figure 1. a) Nitrile monomers used for the ionothermal synthesis of polytriazine networks. b) Trimerization of dicyanobenzene in molten $ZnCl_2$ to trimers and oligomers and then to a covalent triazine-based framework (CTF-1). c) FTIR spectra following the progress of the condensation; transmission spectra recorded from the reactant (0 h) and the products after 10 h and 40 h are shown. The characteristic absorption bands for carbonitrile and triazine groups are highlighted.

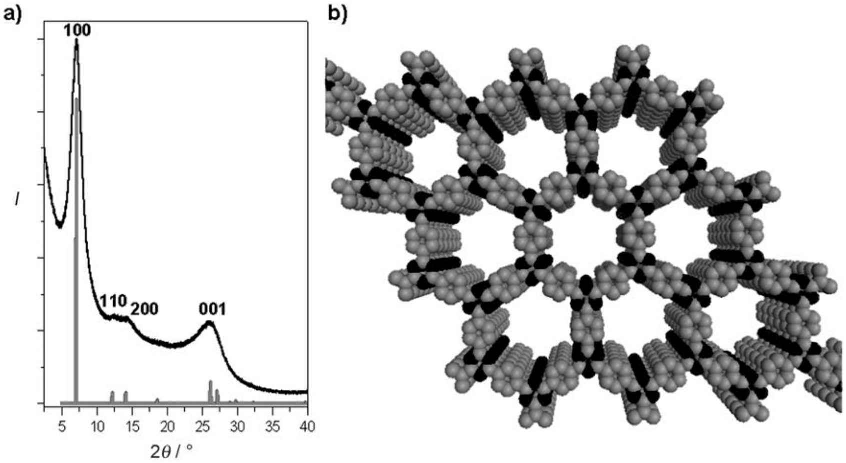

Figure 2. a) Observed PXRD pattern of CTF-1 (black) and calculated PXRD pattern from an optimized structure (eclipsed conformation AAA⋯) of CTF-1 calculated with MS Modeling (gray). b) Schematic representation of the structure of CTF-1 (C gray, N black); H atoms are omitted for clarity.

crystalline triazine-based organic framework (CTF-1) with hexagonal packing of pores (Figures 1 b and 2 b). Besides the intense (100) peak at lower angles and two additional peaks (attributable to the (110) and (200) reflections), a broad peak at 26.1° corresponding to an interlayer distance of 3.4 Å for the (001) aromatic sheets is also found.

The proposed sheetlike structure of CTF-1 resembles nicely the boron oxide based covalent organic frameworks (COF-1) introduced by Côté, Yaghi, et al.,[9] and a comparison of COF-1 with CTF-1 shows that they are isoelectronic. Indeed, purified COF-1 shows a similar XRD pattern to CTF-1. For COF-1 with incorporated mesitylene, it was reported that the layers form a staggered ABA structure. After removal of the guest molecules, however, some shifting of the layers to an eclipsed (AAA) structure was observed.

For the CTF-1 described here, a geometry optimization of a section of the sheets was carried out (MS Modeling 3.1 software suite). The resulting periodicities (for example, the void-to-void distance) were used to assemble a hexagonal unit cell ($a = b = 14.574$ Å), while the distance of the (001) peak in the diffraction pattern was used for the layer distance between the sheets ($c = 3.4$ Å). An eclipsed AAA structure, in which the atoms of each layer are placed above their analogues in the next layer with *P6/mmm* symmetry, was found to be very close to the experimental structure (Figure 2 a). The assumed structure from CTF-1 derived from this geometry optimization and the comparison with the XRD pattern are shown in Figure 2b. However, it should be noted that a broadening of the diffraction peaks probably points to a limited long-range order.

As measured by nitrogen-sorption experiments, CTF-1 shows a surface area of 791 $m^2 g^{-1}$ with a total pore volume of 0.40 $cm^3 g^{-1}$. These values are close to those found for COF-1 (711 $m^2 g^{-1}$ and 0.32 $cm^3 g^{-1}$).[9] From the pore size distribution determined by nonlocal DFT (NLDFT), a pore size of 1.2 nm is found, which is in agreement with the pore size measured from the optimized model of CTF-1.

Higher amounts of $ZnCl_2$ in the reaction mixtures still yielded highly porous, yet amorphous materials. As seen from Table 1, these materials have even higher surface areas, probably as a result of the lower overall density of amorphous compared to crystalline materials.

Table 1: Surface area and pore volume of different aromatic carbonitriles trimerized in $ZnCl_2$ melts.

Monomer	Monomer/$ZnCl_2$	Surface area[a] [$m^2 g^{-1}$]	Pore volume[b] [$cm^3 g^{-1}$]
DCB	1.0	791	0.40
DCB	0.1	1123	0.58
DCBP	0.1	2475	2.44
DCT	0.1	584	0.29
DCP	0.1	730	0.36
TCT	0.033	975	0.66

[a] Determined by the BET equation over a relative pressure range as described in reference [17]. [b] Determined for $P/P_0 = 0.99$.

Monomers with higher molecular weights (such as DCBP), however, yield no porous materials in reactions with a monomer/$ZnCl_2$ ratio of 1, probably because the low mass of $ZnCl_2$ is not sufficient in such a reaction mixture to fully dissolve the monomers and the produced oligomers. Thus, a higher amount of $ZnCl_2$ was used to compare the products of reactions for the other nitriles (monomer/$ZnCl_2$ = 0.1). The surface areas and pore volumes for all networks polymerized under similar synthetic conditions are summarized in Table 1. The absence of comparable pore regularity in our experiments can presumably be explained by the structure of the monomers. DCBP, and TCT do not feature a planar but a slightly contorted structure, while DCT and DCP do not have a linear arrangement of the nitrile groups. Thus, comparable planar sheets as found for DCB are not achieved with these monomers. However, these materials still exhibit very high surface areas and porosities. A striking result is obtained for frameworks made from DCBP, which exhibit a surface area of 2475 $m^2 g^{-1}$ and a total pore volume of 2.44 $cm^3 g^{-1}$ (Table 1).

For the materials derived from DCBP a high amount of mesopores (>2 nm) is also found in the samples (see the Supporting Information; the relative contributions of the mesopore volume and surface area are about 1.9 $cm^3 g^{-1}$ and 1530 $m^2 g^{-1}$). Unlike the other polymers, elemental analysis of this sample showed a rather low nitrogen content. Thus, a significant amount of triazine cleavage has to be taken into account. The loss of some of these triazine knots from the network can also explain the existence of larger mesopores (ca. 4 nm, see the Supporting Information).

TGA measurements on all samples indicate that the ionic solvent system can easily be removed (residual zinc salts below 5 wt %). This observation also justifies the view that the resulting materials are pure organic polymer frameworks, rather than metal–organic frameworks.

Owing to their low density, microporous polymers are regarded as potential hydrogen storage materials.[18–20] To estimate the potential of the materials shown here for this application, hydrogen-sorption measurements at low pressure were carried out on the DCBP network, as it exhibits the highest surface area (Figure 3). It was found that the latter can adsorb 1.55 wt % H_2 at 1.00 bar and 77 K. With this value, the DCBP network can compete with most MOFs, mesoporous carbon materials, and zeolites,[21] and it can provide at the same time high thermal, chemical, and mechanical stability and the formability of a thermoset polymer material. The latter point, in conjunction with the more flexible functionality of the bridging units, makes the triazine-based materials very promising for potential applications in gas storage or as sensors, sorption materials, or catalyst supports.

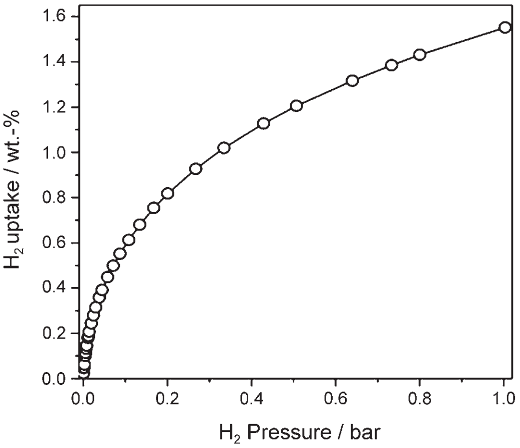

Figure 3. Hydrogen adsorption of the DCBP polymer at 77 K.

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