

## Catalyst-free Preparation of Melamine-Based Microporous Polymer Networks through Schiff Base Chemistry

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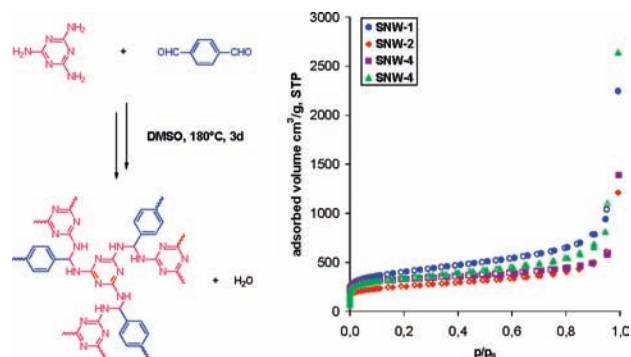
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Microporous materials derived from organic precursors have attracted considerable scientific interest due to applications in the fields of gas storage,<sup>1–4</sup> gas separation,<sup>5</sup> and heterogeneous catalysis.<sup>6,7</sup> Crystalline covalent-organic frameworks (COF) with regular porosity have been synthesized by the application of boronate ester formation.<sup>1,8</sup> Highly ordered materials with sheetlike structures were also obtained via the trimerization of nitrile monomers under ionothermal conditions.<sup>9</sup>

A well-established pathway for the generation of microporosity in amorphous polymers relies on a multiple Friedel–Crafts alkylation. Swollen polystyrene,<sup>10,11</sup> poly(chloromethylstyrene),<sup>2,11</sup> and polyaniline<sup>2,3</sup> as well as polyfunctional benzyl chlorides<sup>4</sup> have been used for the synthesis of hypercrosslinked polymers (HCP). By connecting sterically demanding building blocks, polymers of intrinsic microporosity (PIM) have been obtained.<sup>5,6</sup> Other cross-linking methods that have been applied to the synthesis of microporous polymers are based on the palladium-catalyzed Sonogashira–Hagihara<sup>12</sup> and Buchwald–Hartwig cross-coupling<sup>3</sup> of di- and trifunctional aromatic building blocks, the iron chloride mediated oxidative polymerization of thiophene monomers,<sup>7</sup> and the cross-linking of lithiated aryl species with silanes.<sup>13</sup> All of these methods lead to amorphous materials, although control over the porosity could be successfully demonstrated.<sup>2,12</sup> Nevertheless, it remains a great challenge to synthesize microporous organic polymers with a rational design at the molecular level using cheap and simple processes. Herein, a novel catalyst-free one-pot method toward the synthesis of nitrogen-rich polymer networks with high surface areas through Schiff base chemistry is reported.

Ever since its discovery in 1864 by Hugo Schiff,<sup>14</sup> this classical reaction has been a versatile tool in organic synthesis. The mechanism leading to the Schiff base is well understood and involves a number of steps that are reversible. The dynamic nature of the imine bond formation has been also helpful in the build-up of complex molecular architectures such as macrocyclic ligands<sup>15</sup> and interlocked molecules.<sup>16</sup> The imine double bond may be subsequently attacked by primary amines, resulting exclusively in the generation of an animal,<sup>17</sup> if appropriate experimental conditions are chosen.<sup>18</sup>

In view of the relevance of Schiff base chemistry and the search for nitrogen-rich polymers in material science, melamine (**1**) (A<sub>3</sub>), a large-scale industrial chemical, has been reacted with various di- (B<sub>2</sub>) and trialdehydes (B<sub>3</sub>) (**2–5**) in a one-pot polycondensation approach (Figure 1). Typically, the monomers were heated at 180 °C for 72 h in dimethyl sulfoxide under inert conditions to form a series of Schiff base networks (SNW) in 61–66% yield. After thoroughly washing the precipitated material with acetone, dichlo-



**Figure 1.** Schematic representation of the network structure of SNW-1 (left). Nitrogen sorption isotherms of SNW-1 (circles), SNW-2 (diamonds), SNW-3 (triangles) and SNW-4 (squares).

romethane, and tetrahydrofuran, all samples were obtained as off-white powders. No change in the material properties was observed upon exposure of the completely insoluble powders to humidity and/or acidic or alkaline conditions. The materials exhibited also high thermal stability as evidenced by thermogravimetric analysis ( $T_{\text{dec}} > 400$  °C).

The successful build-up of a three-dimensional polymeric network as well as high conversion of the functional groups initially present in the monomers was confirmed by Fourier transform infrared (FTIR) spectroscopy of all four materials (Supporting Information). Bands which can be attributed to the primary amine group of melamine at 3470 and 3420 (NH<sub>2</sub> stretching) and 1650 cm<sup>-1</sup> (NH<sub>2</sub> deformation) as well as to the carbonyl function of the aldehydes at 2870 (C–H stretching) and 1690 cm<sup>-1</sup> (C=O stretching) are absent or strongly attenuated in the spectra of the SNW materials. The nodal lines derived from standing vibrational waves are used to define the quadrant and semicircle vibrations of heteroaromatic ring systems. The distinct bands corresponding to the quadrant (1550 cm<sup>-1</sup>) and semicircle stretching (1480 cm<sup>-1</sup>) of the triazine ring are present in the spectra of the SNW materials, indicating the successful incorporation of the melamine into the network. No bands that may be attributed to imine linkages such as the C=N stretching vibration around 1600 cm<sup>-1</sup> are found in the FTIR spectra.

A detailed analysis of the material's chemical structure was performed by <sup>13</sup>C and <sup>15</sup>N solid-state NMR spectroscopy (Supporting Information). The <sup>13</sup>C cross-polarization magic angle spinning (CP-MAS) NMR spectrum of SNW-1 shows three resonances at 167, 129, and 55 ppm. The first can be assigned to the carbon atoms present in the triazine ring of the melamine, whereas the signal at 129 ppm originates from the CH aromatic carbons of the benzene. The latter resonance at 55 ppm can be correlated to the tertiary carbon atoms formed upon the addition of the primary amine groups

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of melamine to the newly formed carbon–nitrogen double bond leading to aminal structures.<sup>17,18</sup> In addition to the results from the <sup>13</sup>C CP-MAS analysis, the <sup>15</sup>N CP-MAS spectrum of **SNW-1** shows two major resonances at –205 and –283 ppm, respectively. The first signal is assigned to the nitrogen atoms in the triazine ring, whereas the second signal can be attributed to the secondary amine present in the aminal motif. Hence, the assumption of the aminal formation in the secondary cross-linking step mentioned before can be supported, as no resonance around –55 ppm corresponding to an imine nitrogen is found. In accordance with the results from the FTIR analysis, no signals from unreacted aldehyde or primary amine groups are detected in the <sup>13</sup>C and <sup>15</sup>N CP-MAS NMR spectra of **SNW-1**.

The porous properties of the **SNW** materials were then analyzed by nitrogen sorption analysis. As seen in Figure 1, the adsorption isotherms show a steep gas uptake at low relative pressures and a flat course in the intermediate section, thus reflecting the microporous nature of the polymer networks. A hysteresis is not observed upon desorption which is usually found for microporous polymer networks.<sup>19</sup> This indicates a very high degree of cross-linking of small structural motifs. Remarkably, the highest Brunauer–Emmet–Teller (BET) surface areas of 1377 and 1213 m<sup>2</sup>/g were obtained in the case of **SNW-1** and **SNW-4**, respectively (Table 1). These two materials possess similar network geometries

**Table 1.** Composition and Porosity of the **SNW** Materials

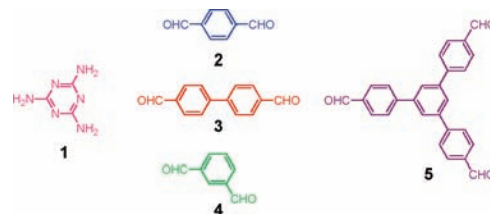
network	composition	S <sub>BET</sub> (m <sup>2</sup> /g) <sup>a</sup>	PV (cm <sup>3</sup> /g) <sup>b</sup>	MPV (cm <sup>3</sup> /g) <sup>c</sup>
<b>SNW-1</b>	<b>1+2</b>	1377	1.01	0.41
<b>SNW-2</b>	<b>1+3</b>	842	0.62	0.28
<b>SNW-3</b>	<b>1+4</b>	1133	0.84	0.35
<b>SNW-4</b>	<b>1+5</b>	1213	0.69	0.41

<sup>a</sup> Surface area calculated from nitrogen adsorption isotherms using the BET equation. <sup>b</sup> Pore volume calculated from nitrogen adsorption at  $p/p_0 = 0.8$ . <sup>c</sup> Micropore volume calculated from NLDFT.

and pore sizes although they were derived from two different monomer combinations. A semilogarithmic representation of the low pressure regime of the adsorption isotherms (Supporting Information) and the micropore volumina derived from nonlocal density functional theory (NLDFT) of 0.41 cm<sup>3</sup>/g for both materials further illustrate the similar microporosity of **SNW-1** and **SNW-4**. The lower BET surface area for **SNW-2** (842 m<sup>2</sup>/g) as well as the NLDFT micropore volume of 0.28 cm<sup>3</sup>/g can be attributed to a higher conformational flexibility of the network due to the biphenyl linker between the cross-linking melamine units.

A similar relation between monomer structure and resulting porosity has also been observed for other systems where the monomer strut length could be correlated to the surface area of the materials.<sup>2,12</sup> In the case of **SNW-3**, the kinked geometry of isophthalaldehyde leads to a more distorted network structure and results in a BET surface area of 1133 m<sup>2</sup>/g and a NLDFT micropore volume of 0.39 cm<sup>3</sup>/g. On the contrary, the monomers used for the other **SNW** materials lead to linear struts that connect the triazine rings. The high amount of cross-linking, however, to somewhat flexible secondary amines make the **SNW** networks rather comparable to HCPs than to PIMs (even though it should be stated that the difference between these networks is not always clear-cut).

Summarizing, we have presented a novel synthetic protocol for the design and build-up of highly cross-linked microporous polymers based on Schiff base chemistry. Several unique characteristics make the materials promising candidates for potential applications in material science: (i) the proposed condensation



**Figure 2.** Molecular structures of building units for **SNW** materials.

approach leads to materials with high BET surface areas and a tailorable microporosity which has only been observed in few cases;<sup>2,12</sup> (ii) cheap materials are obtained due to the low price starting compounds and the easy way of synthesis, whereas other synthetic pathways often rely on costly reaction conditions and/or building blocks;<sup>1,5,6,8,12</sup> (iii) no catalyst is needed for the formation of the polymeric networks, so that the **SNW** materials are not contaminated with inorganic remains or byproduct as this is observed in other systems;<sup>3,4,7,9,11–13</sup> (iv) the use of melamine as amine component leads to materials with a nitrogen content of up to 40 wt %, which has never been obtained for a microporous material. Significant amounts of nitrogen have only scarcely been incorporated into comparable materials<sup>2,3,9</sup> and may be beneficial for the storage of gases<sup>2</sup> or the stabilization of metal species. Finally, the nitrogen-rich polymer scaffold of the networks may also be helpful for the development of novel proton conducting materials.

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**Supporting Information Available:** Synthetic protocols, elemental analysis, TGA data, FTIR data, <sup>13</sup>C and <sup>15</sup>N CP-MAS NMR data, SEM micrographs, nitrogen sorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Han, S. S.; Furukawa, H.; Yaghi, O. M.; Goddard, W. A. *J. Am. Chem. Soc.* **2008**, *130*, 11580–11581.
- Germain, J.; Fréchet, J. M. J.; Svec, F. *J. Mater. Chem.* **2007**, *17*, 4989–4997.
- Germain, J.; Svec, F.; Fréchet, J. M. J. *J. Chem. Mater.* **2008**, *20*, 7069–7076.
- Wood, C. D.; Tan, B.; Trewin, A.; Niu, H.; Bradshaw, D.; Rosseinsky, M. J.; Khimiyak, Y. Z.; Campbell, N. L.; Kirk, R.; Stöckel, E.; Cooper, A. I. *J. Chem. Mater.* **2007**, *19*, 2034–2048.
- McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2006**, *35*, 675–683.
- Mackintosh, H. J.; Budd, P. M.; McKeown, N. B. *J. Mater. Chem.* **2008**, *18*, 573–578.
- Schmidt, J.; Weber, J.; Epping, J. D.; Antonietti, M.; Thomas, A. *Adv. Mater.* **2009**, *21*, 702–705.
- Coté, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170.
- Kuhn, P.; Antonietti, M.; Thomas, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3450–3453.
- Davankov, V. A.; Tsyurupa, M. P. *React. Polym.* **1990**, *13*, 27–42.
- Schwab, M. G.; Senkovska, I.; Rose, M.; Klein, N.; Koch, M.; Pahnke, J.; Jonschker, G.; Schmitz, B.; Michael, H.; Kaskel, S. *Soft Matter* **2009**, *5*, 1055–1059.
- Jiang, J. X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimiyak, Y. Z.; Cooper, A. I. *Angew. Chem., Int. Ed.* **2007**, *46*, 8574–8578.
- Rose, M.; Böhlmann, W.; Sabo, M.; Kaskel, S. *Chem. Commun.* **2008**, 2462–2464.
- Schiff, H. *Justus Liebig’s Ann. Chem.* **1864**, *131*, 118–119.
- Borisova, N. E.; Reshetova, M. D.; Ustyynyuk, Y. A. *Chem. Rev.* **2007**, *107*, 46–79.
- Rowan, S. J.; Stoddart, J. F. *Org. Lett.* **1999**, *1*, 1913–1916.
- Layer, R. W. *Chem. Rev.* **1963**, *63*, 489–510.
- Forlani, L. S., M.; Todesco, P. E. *Gazz. Chim. Ital.* **1986**, *116*, 229–232.
- Weber, J.; Antonietti, M.; Thomas, A. *Macromolecules* **2008**, *41*, 2880–2885.

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