Porous Organic Materials

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Click Chemistry Finds Its Way into Covalent Porous Organic Materials**

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Porous organic materials are becoming increasingly important owing to their applications in catalysis and optoelectronics.[1] They are, however, best known for their gas adsorption/storage capacities.[2] Here, they clearly outperform their inorganic and metal–organic counterparts. As they are composed entirely of light elements, they have exceptionally low densities which are particularly appealing for the automotive sector where weight reduction is essential.

The development of permanently porous organic materials is challenging as nature tends to minimize pore volume because of the higher surface energies of porous materials. Upon solidification these materials either achieve efficient packing or existing voids collapse to give denser structures. Permanent porosity in wholly organic structures is obtained only by preventing efficient packing in the solid state. Hence, *rigid*, *sterically demanding*, and/or *contorted* organic building units have to be used to generate permanently porous organic materials.[3] Two different concepts are generally applied. The first relies on covalently bonded organic cages with intrinsic porosity which are prefabricated and then assembled to give crystalline porous materials.[4] The Cooper[5] and Mastalerz groups[6] independently used reversible imine condensation to produce cages that assemble to give microporous materials with surface areas comparable to those of classic polymeric or crystalline porous materials. The second approach involves the self-assembly of rigid but essentially nonporous building blocks, through either hydrogen bonding or covalent bonding. Examples of covalent materials reported by Yaghi et al. rely on reversible boronate or imine formation to generate three-dimensional crystalline networks.[7] Since crystallinity is not a prerequisite for molecular control over pore size in rigid frameworks, narrow pore size distributions have been obtained in three-dimensional porous organic polymers, showing that long-range order is not necessary for obtaining uniform pore sizes.[8] The essence is that thermodynamically and kinetically controlled processes can both be used to generate microporous organic frameworks. Thus, irreversible but high-yielding reactions such as organometallic cross-couplings[9] have been widely used to generate amorphous covalent porous networks. These reactions are a rather obvious choice, as the monomers, which are typically composed of aromatic rings and alkyne units, concurrently fulfill the stiffness requirement to allow for inefficient packing and subsequent permanent porosity.

However, neither boronate and imine formation nor organometallic cross-coupling reactions meet all the criteria outlined by Sharpless in 2001 for click reactions.[10] These reactions—mostly 1,3-dipolar cycloaddition reactions of organic azides and terminal alkynes—have had a strong impact on material sciences, especially polymer science.[11] Thus, it is all the more astonishing that click chemistry has until very recently not served in the preparation of porous organic materials. This has now been achieved: within a year's time two independent groups reported on "clicked" porous organic material.[12] The two studies are based on identical tetrahedral monomers. Cooper et al. prepared a conjugated microporous polymer (CMP) by reacting two complementary azido and alkyne tetrakisphenylmethanes (Scheme 1).[12a] The resulting CMP has a respectable Brunauer–Emmett–Teller (BET) surface area of 1128 $m^2 g^{-1}$. TGA analysis indicated the decomposition of residual azide and alkyne groups at 125 and 275 °C, respectively. Shortly afterwards, Nguyen and colleagues reported the first in-depth study of the same "clicked" network—termed this time porous organic polymer (POP)—using slightly modified reaction conditions (Scheme 1).[12b] They found that the surface area drastically increased at higher reaction temperature (440 $m^2 g^{-1}$ at 25 °C versus 1260 $m^2 g^{-1}$ at 100 °C), and that it decreased with the addition of sodium ascorbate. This finding was attributed to higher concentrations of Cu^I, the active catalyst, which led to more cross-linking and thus a lower surface area. When 10 mol% of sodium ascorbate was used, an essentially microporous material having a narrow pore size distribution with a primary pore width of 9.2 Å was suggested by nonlocal density functional theory (NLDFT) pore size distribution analysis. Since the pore width for a perfect diamond network lies around 21 Å, this finding constitutes strong evidence for interpenetrating networks. The optimized reaction protocol delivered a POP with a slightly higher surface area (1440 $m^2 g^{-1}$) than that of Cooper's CMP.

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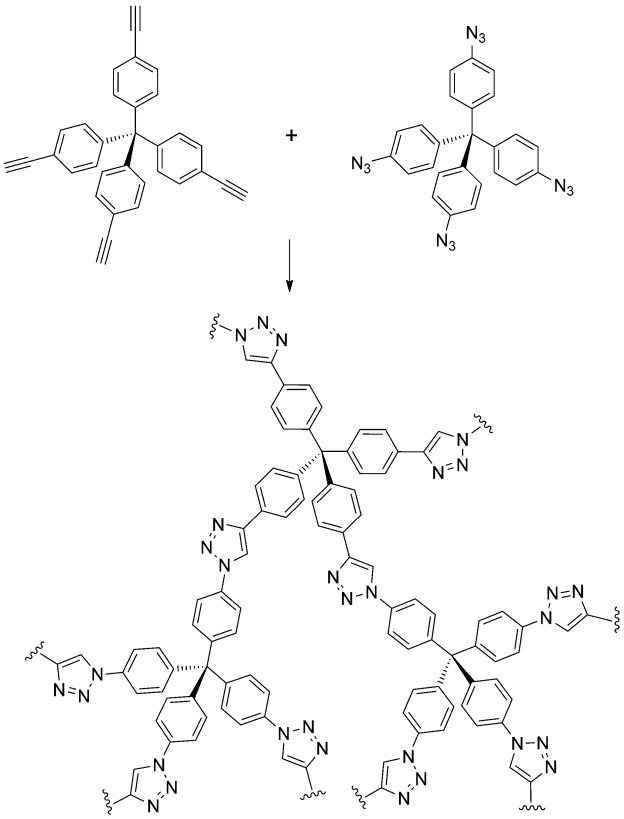

Scheme 1. Reaction conditions used by Cooper et al.:[12a] THF/NEt_3 (10:1), 10 mol% $CuSO_4$, 20 mol% sodium ascorbate, 60°C, 84 h; reaction conditions used by Nguyen et al.:[12b] DMF, 10 mol% $CuSO_4 \cdot 5H_2O$, 10 mol% sodium ascorbate, 100°C, 24 h, quant.

Both groups observed unreacted azide functions and significant amounts of physisorbed water. Nguyen's material proved to be thermally stable (loss of only 20 wt% upon heating to 500°C) and showed excellent resistance to strongly acidic and basic conditions. Its N_2 and H_2 adsorption capacities (1.6 wt% at 77 K and 1 bar) are comparable with those of materials having similar surface areas (Figure 1).

These first two studies clearly show the potential of click reactions for the generation of covalent porous organic materials. As porous organic networks are typically obtained in a "shake-and-bake" process requiring extensive optimization studies, click chemistry with its ease of operation seems particularly suited for this kind of approach. We are convinced that further "clicked" covalent organic materials will soon join these first examples. Thiol–ene and thiol–yne coupling reactions occupy a front seat in this context as they can be UV-activated without any side-product generation, and for the thiol–yne reaction, the starting alkyne monomers from the 1,3-dipolar cycloaddition can be used.

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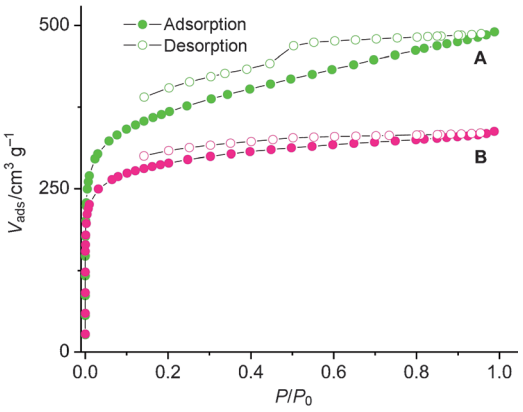

Figure 1. N_2 adsorption–desorption isotherms at 77 K for two POP materials. **A**: 10 mol% and **B**: 70 mol% sodium ascorbate.

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