CO$_2$ Adsorption

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A Shape-Persistent Organic Molecular Cage with High Selectivity for the Adsorption of CO$_2$ over N$_2$**

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The efficient separation of CO$_2$ from N$_2$, particularly at ambient temperature and pressure, is a key factor in the capture of carbon[1] from flue gas. In the past decade, the emergence of metal–organic frameworks (MOFs)[2] represented a milestone in the development of promising materials for adsorption-based gas separation. The pore size of MOFs can be controlled well, and certain functionalities can be introduced. Purely organic materials[3,4] and covalent organic frameworks (COFs)[5] have also been considered as candidate porous materials for gas storage and separation. The advantages of COFs are their light weight, thermal stability, and chemical robustness. Although MOFs and COFs show great promise, the exploitation of new absorbents is still essential to the advancement of cost-effective and environmentally benign gas separation. In contrast to the growing body of adsorption data for MOFs and COFs, only a few organic molecules (i.e. calixarenes,[6] cucurbit[6]uril,[7] *tris-o*-phenylenedioxycyclotriphosphazene,[8] imine-linked cages[9]) have been explored as porous materials for gas storage and separation. Porous organic molecules have the aforementioned advantages of COFs and are usually also highly soluble in a variety of solvents. Thus, they are solution-processable and can be purified by simple chromatography or recrystallization.

Among organic molecules with internal voids,[10] shape-persistent, rigid, three-dimensional, covalent cage molecules are of particular interest because of their well-defined pore dimensions and chemically and thermally robust backbone structures. Until now, shape-persistent 3D molecules have mainly been constructed by self-assembly processes driven by metal–ligand coordination.[11] The synthesis of covalent, shape-persistent 3D molecules that have higher thermal and chemical stability than metal-assisted self-assembled molecules is more challenging. Herein, we report the use of dynamic covalent chemistry (DCC)[12] in a highly efficient, one-pot synthesis of a shape-persistent 3D organic prismatic cage molecule. This new porous cage compound showed extraordinarily high ideal selectivity (73:1, v/v) for the adsorption of CO$_2$ over N$_2$ under ambient conditions (1 bar, 293 K), as well as high thermal stability up to 703 K. Control experiments indicated that this high, selective gas uptake was due to a significant extent to the porous nanostructure of the compound.

Although molecular trigonal-prismatic cages are among the simplest 3D constructs, they are relatively uncommon. The shape-persistent molecular prism **5** was prepared in a one-pot process from the readily accessible triamine **3** (as the top and bottom panels) and dialdehyde **4** (as the three lateral edges) through DCC (Scheme 1). Triamine **3** was synthesized from 1,3,5-trihexyl-2,4,6-triiodobenzene[13] (**1**) by Suzuki coupling followed by reductive hydrogenation. Imine formation[14] between the two building units **3** and **4** was explored in various solvents (CHCl$_3$, CH$_2$Cl$_2$, 1,2,4-trichlorobenzene, 1,2-dichloroethane) and at different temperatures (from room temperature up to 80 °C). The highest yield was attained by stirring the solution of **3** and **4** in a 2:3 stoichiometric ratio in chloroform for 16 h at room temperature under the catalysis of scandium(III) triflate. Because of the dynamic nature of imine metathesis, the condensation reaction between two equivalents of triamine **3** and three equivalents of dialdehyde **4** proceeds under thermodynamic control. Among all possible products, the desired 3D molecular prism **5** is enthalpy-favored owing to a lack of angle strain; it is also entropy-favored, as it consists of the minimum number of building units. Therefore, **5** is generated as the major product at equilibrium. The trigonal prism **5** was converted by hydride reduction into compound **6**, which contains more robust C–N single bonds. The product **6** was isolated in 74 % yield after column chromatography and was fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy as well as gel permeation chromatography and MALDI MS analysis.

The overall geometry of the proposed prismatic structure was confirmed by single-crystal X-ray analysis. Single crystals were obtained from a solution of **6** in a 1:1:4 mixture of dichloromethane, ethyl acetate, and hexane. X-ray diffraction analysis showed that **6** had the expected trigonal-prismatic structure, with six amine bonds and a large central cavity (Figure 1). The two trigonal panels are twisted about 22° with respect to each other; thus, the phenyl arms are not eclipsed but rotated toward a staggered geometry to minimize steric interactions. The distance between the top and bottom panels in this prism structure is about 5.6 Å, and the diameter at the widest point is 2.4 nm. To our knowledge, these dimensions determined by X-ray crystallography place compound **6** among the largest prismatic molecules constructed from

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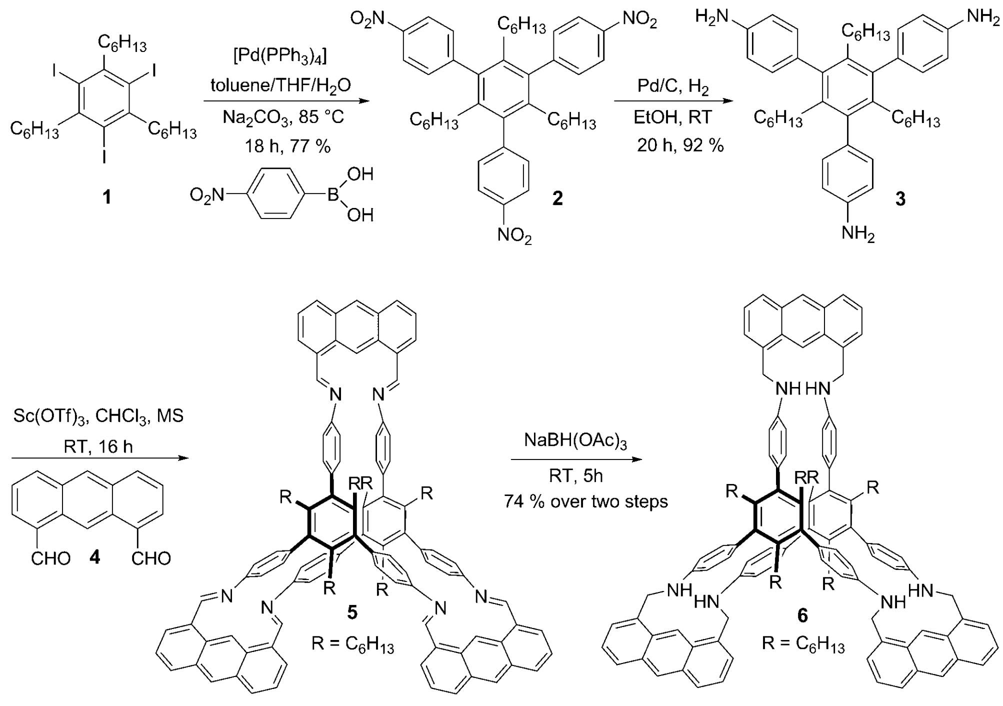


Scheme 1. Covalent assembly of the cage molecule **6** from triamine **3** and dialdehyde **4**. MS = molecular sieves, Tf = trifluoromethanesulfonyl.

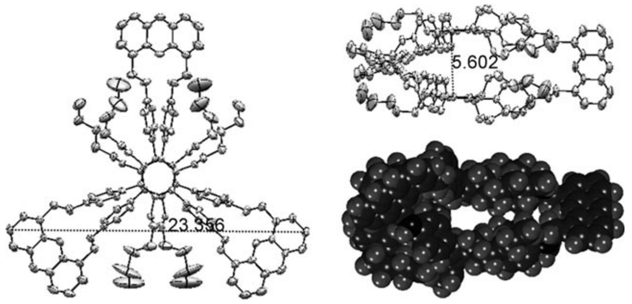


Figure 1. X-ray crystal structure of compound **6**. Left: ellipsoid model as viewed down the C_3 axis. Top right: ellipsoid model as viewed down the C_2 axis. Hydrogen atoms are omitted for clarity. Bottom right: space-filling model as viewed down the C_2 axis.

purely organic building blocks. Compounds of this type thus have great potential for studies of host–guest interactions and supramolecular chemistry.

The packing diagram shows that the molecular prisms stack on top of each other along the [100] direction in an offset fashion and that the layers do not interpenetrate. A layered structure results (Figure 2). The distance between the two layers, as defined by the distance between the top and bottom panels of neighboring cages, is 4.6 Å; the distance reaches 10.4 Å at the widest point, which is defined by two anthracene side moieties. In addition to the internal voids, the cage material has a one-dimensional pore channel running between the cages. The pore channel is shown as an orange Connolly surface in Figure 2.

To demonstrate the potential of the cage molecule **6** in CO_2/N_2 gas separation, we measured its ideal selectivity in the adsorption of these two gases. High selectivity and reversible loading are highly desired characteristics for a good adsorbent. A solvent-free sample of **6** was obtained by drying the crystal sample under high vacuum. Powder X-ray diffraction (PXRD) analysis showed that desolvation under vacuum at room temperature for a prolonged time period (4 days) results in a slight loss of crystallinity, and heating to 80 °C accelerates the process. The adsorption isotherms of CO_2 and N_2 at 20 °C were measured with a desolvated sample under high vacuum at room temperature (Figure 3). The uptake value of CO_2 was $4.46\,cm^3\,g^{-1}$ (amount of gas at standard temperature and pressure (STP: 20 °C, 1 bar) per gram of compound **6**), which corresponds to $0.20\,mmol\,g^{-1}$, whereas N_2 was hardly adsorbed at all ($0.061\,cm^3\,g^{-1}$). Although the CO_2-adsorption capacity at 1 bar is lower than that of some other recently reported organic cage molecules ($1.2–3.0\,mmol\,g^{-1}$ at 275 K and 1.12 bar),[9] the material showed an excellent ideal CO_2/N_2 adsorption selectivity of 73 at STP.[15] One reason for the low gas uptake is presumably the presence of six hexyl chains for each cage molecule. These groups occupy a large portion of void space and thus decrease the accessible pore volume. A similar effect—a decrease in CO_2 adsorption due to the presence of side chains—was observed previously for MOFs.[16] The loading was completely reversible: when we applied a vacuum to the sample at room temperature and repeated the adsorption test multiple times, we observed a similar loading capacity (see Figure S5 in the Supporting Information). To our knowledge, no purely organic porous materials with such high CO_2/N_2 adsorption selectivity have been described previously.

It seems that the gas-adsorption selectivity can be attributed to the combination of a well-defined, porous 3D cage structure and a strong chemical interaction of CO_2 with secondary amine groups in the pores through reversible carbamate formation.[17] The porous nanostructure not only ensures the highly regular 3D porosity, but also promotes the favored interaction between amine groups and CO_2 molecules. As a control experiment, compound **5** was used instead of cage **6** as the adsorbent. The ideal CO_2/N_2 adsorption selectivity at 1 bar and 293 K decreased from 73 to 39, presumably as a result of the weaker interaction of CO_2 with the imine groups (−CH=N−) than with secondary amines (see

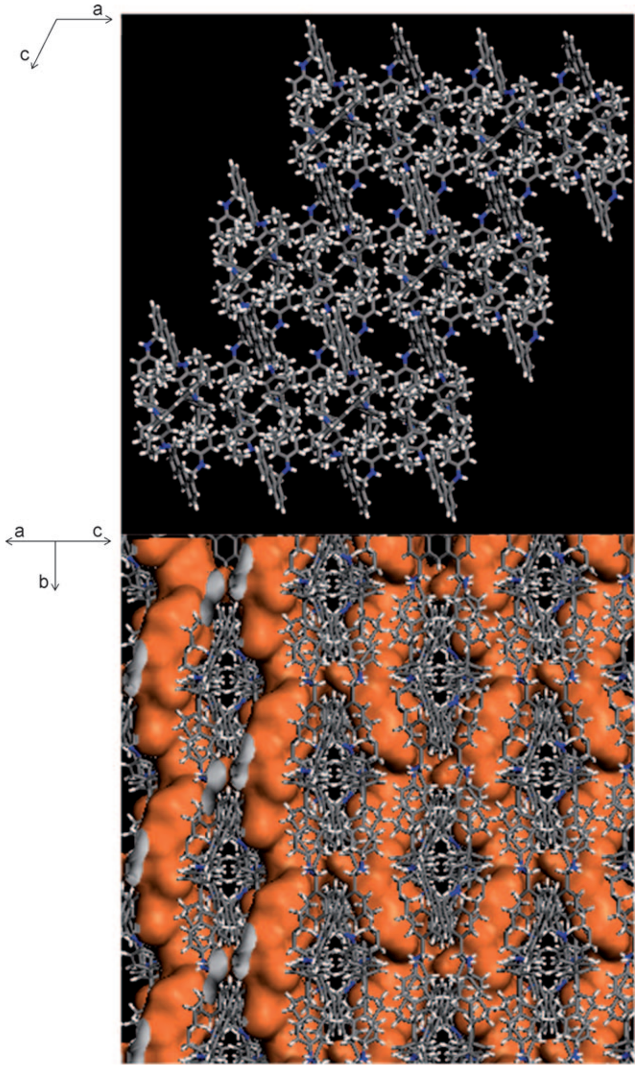


Figure 2. Crystal-packing diagram of **6**. The 1D pore channel between the cages is shown as an orange Connolly surface (probe radius = 1.82 Å).

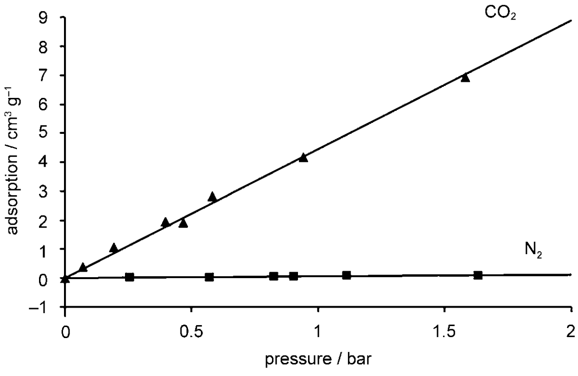
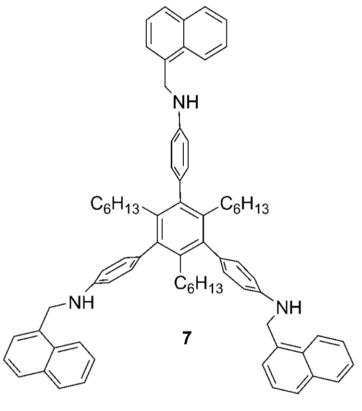


Figure 3. CO_2- and N_2-adsorption isotherms at 20 °C for compound **6**.

Table S1 in the Supporting Information). To further investigate the importance of the intrinsic porosity of the molecular cage structure for gas-adsorption selectivity, we synthesized compound **7**, which is the noncage analogue of **6**, by subjecting the top panel **3** to reaction with 1-naphthaldehyde (3 equiv). The lower CO_2/N_2 adsorption selectivity of 38 observed for **7** indicated that the 3D cage structure is responsible for the high selectivity of **6** in the adsorption of CO_2 over N_2 (see Table S1 in the Supporting Information).



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In summary, we efficiently synthesized a shape-persistent, prismatic molecular cage **6** in one step from readily accessible, solely organic building blocks. The material exhibited high selectivity in the adsorption of CO_2 over N_2 and thus shows great potential for gas-separation applications. The cage molecule showed excellent solubility in a variety of solvents and thus also holds great promise for the fabrication of membranes or thin films for gas-separation purposes. A range of molecular cages with controllable pore sizes and shapes as well as surface functionalities can be synthesized readily by selection of the appropriate building blocks. This ready accessibility of a range of structures opens many new possibilities for the use of such shape-persistent molecular-cage-based porous materials in gas adsorption, catalysis, and chemical sensing. The structure–property relationships and detailed mechanism of gas-adsorption selectivity of this class of materials are under investigation.

Experimental Section

A solution of $Sc(OTf)_3$ (32 mg, 0.087 mmol) in CH_3CN (10 mL) was added dropwise to a solution of 1,3,5-trihexyl-2,4,6-tris(4-aminophenyl)benzene (**3**; 350 mg, 0.58 mmol) and 1,8-diformylanthracene (**4**; 204 mg, 0.87 mmol) in chloroform (193 mL). The yellow solution was stirred at room temperature for 16 h, and the resulting red solution was concentrated to give **5**. Fresh chloroform (50 mL) was added, followed by $NaBH(OAc)_3$ (3.69 g, 17.4 mmol), and the resulting yellow suspension was stirred at room temperature for 5 h. The reaction was quenched by the addition of saturated $NaHCO_3$ (50 mL), and the mixture was extracted with $CHCl_3$ (3 × 75 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated to give the crude product. Purification by flash column chromatography (with CH_2Cl_2 as the eluent) yielded the molecular cage **6** (387 mg, 74 %) as a yellow solid.

5: ^1H NMR (crude product, 500 MHz, $CDCl_3$): $\delta = 11.67$ (s, 3H), 9.65 (s, 6H), 8.59 (s, 3H), 8.26 (d, $J = 6.9$ Hz, 6H), 8.19 (d, $J = 8.3$ Hz, 6H), 7.81 (d, $J = 7.1$ Hz, 6H), 7.66 (app t, $J = 7.7$ Hz, 6H), 7.59 (d, $J = 8.0$ Hz, 6H), 7.53 (d, $J = 8.7$ Hz, 6H), 7.30 (d, $J = 8.0$ Hz, 6H), 2.30–2.22 (m, 12H), 1.26–1.17 (m, 12H), 0.95–0.87 (m, 12H), 0.84–0.76 (m, 24H), 0.57 ppm (t, $J = 7.2$ Hz, 18H).

6: ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 9.07$ (s, 3H), 8.51 (s, 3H), 8.01 (d, $J = 8.5$ Hz, 6H), 7.56 (d, $J = 6.6$ Hz, 6H), 7.46 (dd, $J = 8.5$, 6.7 Hz, 6H), 7.19 (dd, $J = 8.2$, 1.7 Hz, 6H), 6.94–6.86 (m, 10H), 6.66 (dd, $J =$ 8.1, 2.2 Hz, 6H), 4.82 (br s, 12H), 3.80 (s, 6H), 2.24–2.28 (m, 12H), 1.25 (m, 12H), 1.07–0.99 (m, 12H), 0.94–0.85 (m, 24H), 0.68 ppm (t, $J = 7.2$ Hz, 18H); ^{13}C NMR (CDCl$_3$, 101 MHz): $\delta = 146.6$, 139.7, 135.6, 132.2, 131.9, 130.4, 119.4, 114.5, 111.3, 47.3, 32.3, 31.4, 31.3, 29.9, 22.7, 14.4 ppm; MS (MALDI): m/z calcd for $C_{132}H_{134}N_6$: 1814.15 $[M]^+$; found: 1814.74.

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