VIP Cage Compounds

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A Salicylbisimine Cage Compound with High Surface Area and Selective CO_2/CH_4 Adsorption**

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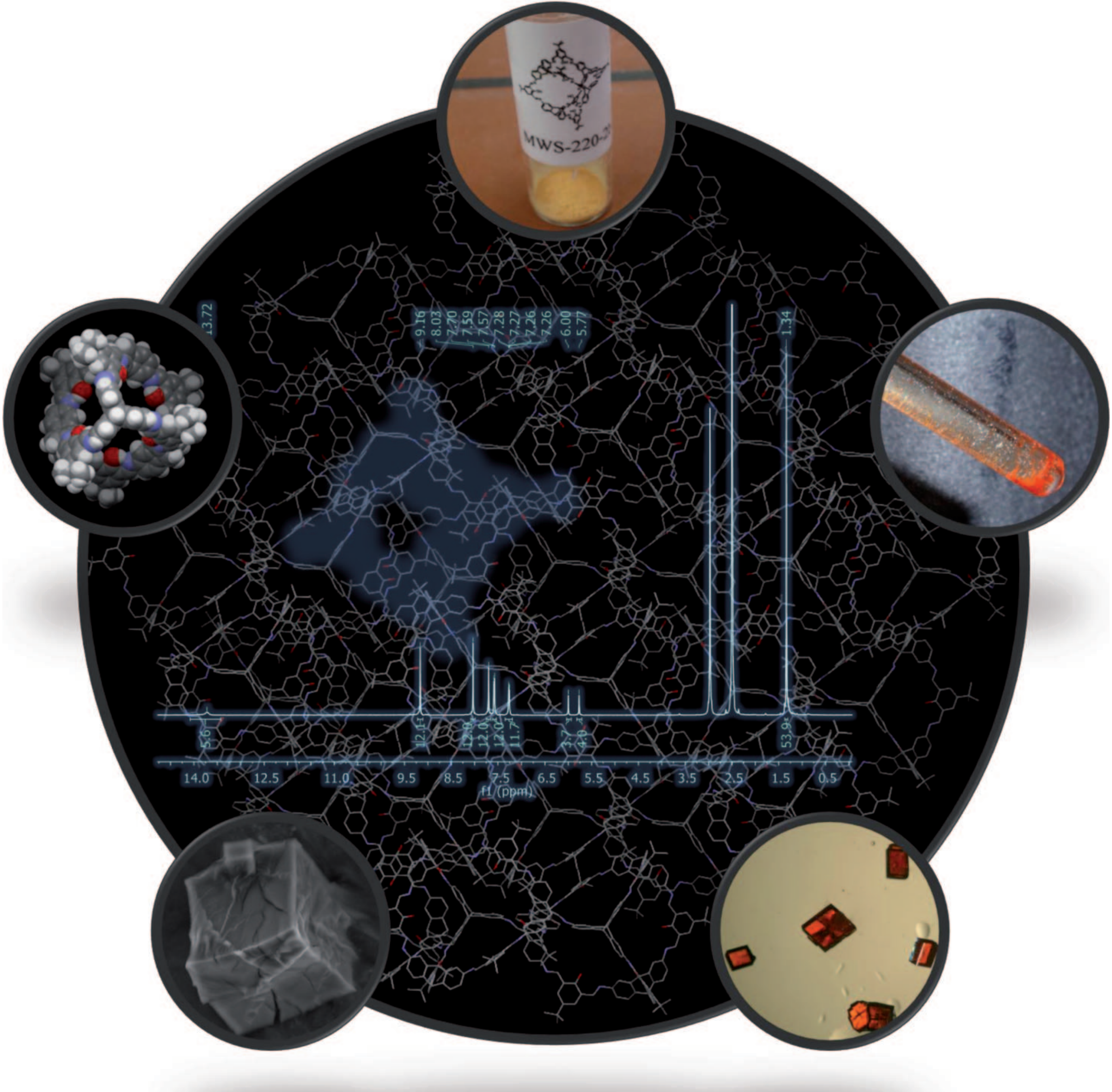

Porous organic compounds[1] are a new class of materials beside the well-investigated zeolites[2] and metal organic frameworks[3] (MOFs). They can be synthesized under relatively mild conditions, in principle allowing the introduction of sensitive functional groups into the frameworks. Because they are light-weight compounds a priori, they are promising materials for the storage of gases, such as H_2 or methane, and for the separation of gas mixtures, for example, for the removal of CO_2 from methane-rich natural gases.[4] In addition to investigations on gas adsorption, some catalytic applications of porous organic compounds have been described recently.[5]

In general, two classes of porous organic materials can be distinguished: extended polymeric structures and materials consisting of discrete molecules assembled by weak supramolecular interactions.

Extended three-dimensional polymeric structures with exceptional high surface areas and narrow pore size distributions have been synthesized by thermodynamically as well as kinetically driven reactions. Reversible condensation reactions of boronic acids and diols,[6] and of amines and aldehydes,[7] and trimerization of nitriles[8] have resulted in (mostly) crystalline covalent organic frameworks (COFs). These frameworks exhibit exceptional high Brunauer–Emmett–Teller (BET) surface areas of up to $3620\,m^2\,g^{-1}$ and narrow pore size distributions. The reversibility of the reactions allows the material to self-correct the structure until the thermodynamically most stable structure is formed, which is often crystalline.

Irreversible reactions, such as palladium-catalyzed cross-coupling reactions, have also been used for the synthesis of porous compounds.[9] Even though no correction processes are possible, the material properties (surface areas and pore size distributions) are comparable with those of the above mentioned COFs. Although these materials are usually amorphous, very high BET surface areas of $5600\,m^2\,g^{-1}$ were achieved with such synthetic methods.[9f]

The second type of porous organic material is composed of discrete molecules, which self-assemble through certain supramolecular interactions, forming defined pores in the crystalline state.[10] Recently, it was demonstrated that such crystals show reasonable material properties in terms of surface area and selective gas uptake.[11] One of the first examples of porous crystals of a low-molecular-weight organic compound, which retains its channel-like structure after the guest is removed, is tris(*o*-phenylenedioxy)cyclophosphazene (TPP).[11a–c] TPP adsorbs CO_2 and methane (ca. 4 and 0.6 wt %, respectively, at 800 mbar and 298 K) even at ambient conditions.[11b] McKeown and co-workers found another porous organic crystal by a systematic survey of the Cambridge Structural Database (CSD): 3,3′,4,4′-tetra(trimethylsilylethynyl)biphenyl (TTEB).[11d] TTEB has a higher BET surface area ($278\,m^2\,g^{-1}$) than TPP and adsorbs 0.8 wt % hydrogen at 10 bar and 77 K.

The precise prediction of the assembly of small molecules in the crystalline state is still one of the most challenging topics in crystal engineering. Therefore it is more reasonable to construct organic molecules that contain shape-persistent clefts, cavities, or voids, thus leading to a high intrinsic molecular free volume.[12] For instance, salphene derivatives of rigid triptycenes and their metal complexes gave materials with surface areas (BET) of up to $499\,m^2\,g^{-1}$.[13] Cucurbituril and calix[4]arene derivatives were investigated with respect to the storage of various gases, such as methane, hydrogen, CO_2, and acetylene.[14]

Shape-persistent organic cage compounds with defined cavities display intrinsic volumes a priori,[15] making these compounds ideal candidates for the construction of materials with defined pores. In this context, only a few compounds have been studied to date. For example, Atwood and co-workers demonstrated that an organic cage compound called noria[16] adsorbs reasonable amounts of gases although it is in an amorphous state. The compound can selectively take up CO_2 ($2.5\,mmol\,g^{-1}$ at 30 bar and 298 K) in preference to N_2 despite the relatively small measured surface area of $350\,m^2\,g^{-1}$ (BET) and pore volume of $0.13\,cm^3\,g^{-1}$.[17] Zhang et al. synthesized a cage compound (ZC) that forms one-dimensional channels in the crystalline state and is able to adsorb CO_2 ($0.2\,mmol\,g^{-1}$ at 1 bar and 298 K) selectively over N_2.[18] In a detailed study Cooper et al. described the influence of peripheral side chains on small organic cage compounds (CC1–CC3) on crystal packing. Depending on the side chains, surface areas of up to $624\,m^2\,g^{-1}$ (BET) were achieved, and good gas adsorption properties were measured for a variety of gases at different conditions (e.g. CC2 adsorbs 3.0 mmol CO_2 per gram at 273 K and 1 bar).[19]

Recently, we introduced the functionalized adamantoid cage compound **3**,[20] which is accessible in a one-pot Schiff base condensation reaction of triamine **1** and salicylbisaldehyde **2** (58 % yield; Scheme 1).[20] Simple reduction of the imine bonds with sodium borohydride results in the corresponding cage compound **4**. Analysis of the AM1-optimized model of cage compound **3** reveals that the hydroxy groups directing into the cage interior form an octahedron with an estimated volume of approximately 678 Å^3. The calculated value of the void space in cage compound **3** exceeds the values

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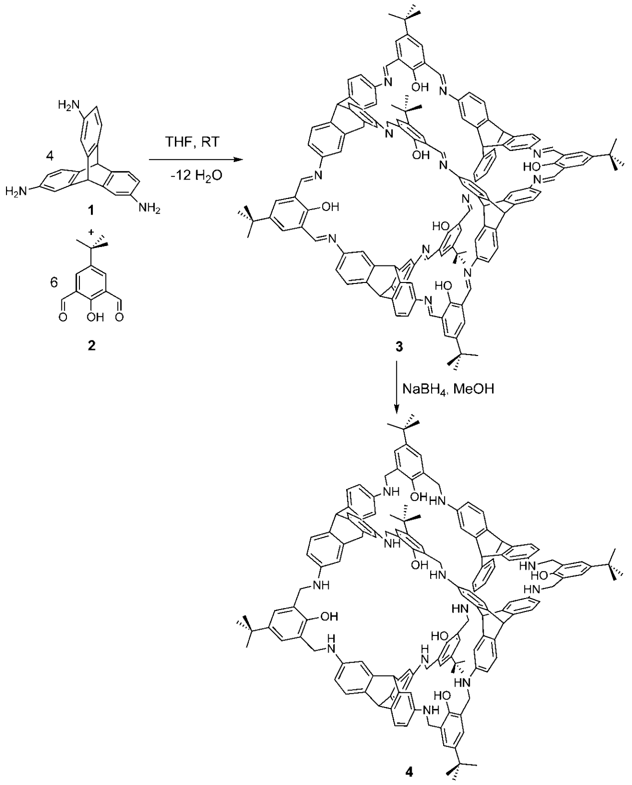

Scheme 1. Synthesis of cage compounds **3** and **4**.[20]

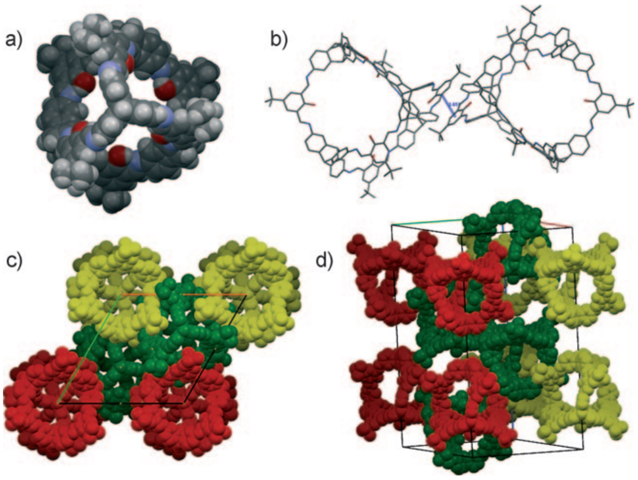

Figure 1. Crystal structure of cage compound **3**. a) Single molecule along the crystallographic *c* axis (gray: carbon; white: hydrogen; red: oxygen; blue: nitrogen); b) arrangement of two adjacent molecules interacting by π–π stacking (depicted as stick model); c) and d) packing of cage molecules in the unit cell. For b)–d) hydrogen atoms are omitted for clarity.

for CC1–CC3 and noria, which prompted us to investigate the material properties of our cage compounds with respect to porosity, surface area, and gas adsorption.

Small red crystals of compound **3** were grown by slowly cooling a hot (100 °C) saturated DMSO solution to room temperature. When the crystals were removed from the mother liquor, they started to crack immediately (see Figures S1 and S2 in the Supporting Information). Cracking also occurred within a few minutes when the crystals were frozen in a perfluoroalkane matrix cooled by a N_2 stream. This is already an indication that substantial amounts of loosely bound solvent molecules are located in the lattice voids. The high volatility of the inclathrated solvent is also confirmed by thermogravimetric analysis (TGA, see Figure S3 in the Supporting Information): Freshly prepared crystals collected by suction filtration showed a weight loss of roughly 22 % when they were heated to 200 °C. This corresponds to eight DMSO molecules per cage molecule.[21]

Although the crystals are not very durable, we succeeded in collecting in a very short period of time a satisfactory data set by X-ray diffraction through the use of a highly sensitive detector.[22] The trigonal unit cell ($a = b = 29.149(3)$ Å, $c = 58.518(5)$ Å, $V = 43\,060(7)$ Å^3, space group $R\bar{3}$) was found containing six cage molecules. Each is located on a threefold axis, so only one-third of **3** is found in the asymmetric unit (Figure 1). Even though the resolution reached is approximately 1 Å, the *R* values indicate that the connectivity is as depicted ($R1 = 0.3603$, $wR2$ (all data) = 0.7525). On account of the great amount of disordered solvent molecules and the resulting low scattering power of the crystals of **3**, we corrected the observed data by using the SQUEEZE routine in PLATON.[23] We found 8477 electrons in 29 150 Å^3, which means that around 67.7 % of the unit cell is filled with disordered solvent molecules. After that we were able to refine all non-hydrogen atoms anisotropically, resulting in *R* values of $R1 = 0.0585$ and $wR2$ (all data) = 0.1642.[22] Each cage molecule is C_3-symmetric and can be seen as a regular tetrahedron, in which three adjacent edges are twisted around the common vertex by about 32° (see Figure 1 a). In the crystalline state two different types of imine bonds can be distinguished: one forms a hydrogen-bond-stabilized six-membered ring, whereas the other does not.[24] The hydroxy groups are directed into the cavity of the cage, forming a slightly distorted octahedron with an average edge length of $d(\mathrm{O}\cdots\mathrm{O}) = 10.53$ Å and a volume of roughly 550 Å^3. The cages self-assemble through π–π interactions between the phenolic arene rings, which are orientated coplanar to each other at a distance of 3.65 Å, which is a typical distance for π–π interactions (Figure 2). Additionally, there are weak interactions between the phenolic hydroxy groups and the protons of the *tert*-butyl groups of adjacent cage molecules ($d(\mathrm{OH}\cdots\mathrm{H}^{t\mathrm{Bu}}) = 2.26$ Å). The assembly of eight adjacent cage molecules results in additional voids with a diameter of approximately 22.3 Å. All cavities are interconnected in three dimensions, building a porous framework (Figure 1 c and 1 d). The calculated density of the framework after removal of residual solvent molecules is 0.51 g cm^{-3}, which is very low for a solid compound, again indicating that the material is porous.

Scanning electron microscopy (SEM) images of the crystals show their fast decay into a microcrystalline powder (see Figure S2 in the Supporting Information). ^{1}H NMR, MALDI-TOF MS, and IR spectra of a dried sample held at 200 °C and 6×10^{-2} mbar for several hours do not differ from those of the as-synthesized material, confirming the compound's stability.

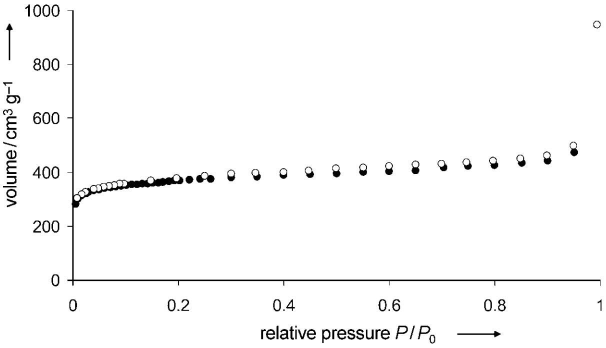

Figure 2. N_2 adsorption (●) and desorption (○) isotherms for **3** measured at 77 K.

The cage compound **3** synthesized in THF is also microcrystalline, although its powder X-ray diffraction (PXRD) pattern is different from that calculated from the reflections of the X-ray single-crystal structure. We suggest that the as-synthesized compound is a thermodynamically more stable polymorph, whereas the crystals from DMSO are a kinetically formed polymorph.

Thermogravimetric analysis (TGA) of the as-synthesized cage compound **3** showed no weight loss at temperatures below 450 °C (see the Supporting Information). We measured the adsorption of N_2 at 77 K of a sample, which had previously been treated 3 h at 200 °C and 6×10^{-2} mbar (Figure 2). The isotherm can be classified as a hybrid of a type I isotherm (typically for microporous systems) with a small fraction of a type II isotherm.[25] The *t*-plot analysis of the measurement revealed that the micropore contribution of the surface area is roughly 80 %. The calculated surface area of the material is 1566 $m^2 g^{-1}$ (Langmuir) and 1375 $m^2 g^{-1}$ (BET). These values are to the best of our knowledge the highest reported for materials consisting of discrete organic compounds; they even exceed the values reported for the discrete metal–organic polyhedron MOP-28 (Langmuir surface area: 1100 $m^2 g^{-1}$, BET surface area: 919 $m^2 g^{-1}$).[26] Furthermore, our values are higher than those of most conjugated microporous polymers (CMPs)[9] and comparable to those of COF-8,[6d] COF-300,[7a] and SNW-1.[7b] Micropore analysis for the pore-size distribution shows a maximum at 8.8 Å (Horvath–Kawazoe model, see Figure S14 in the Supporting Information), which is in good agreement with the estimated pore size of the AM1 calculated model and the diameter of the cavity in the X-ray crystal structure. The micropore volume is estimated to 0.42 $cm^3 g^{-1}$. Comparison of IR and ^1H NMR spectra as well as the PXRD pattern of the material heated at 200 °C at 6.2×10^{-2} mbar for several hours with those of the as-synthesized compound show no differences, again demonstrating the thermal stability of the microcrystalline material. It is worth mentioning that a two-year-old sample of the cage compound **3** stored in a vial under air showed no decomposition, as indicated by MALDI-TOF MS, ^1H NMR, and IR analysis.

Compound **3** has polar functional groups inside the cavity, which might be advantageous for selective gas adsorption. Initial experiments were carried out with H_2, CO_2, and methane (Figure 3). Cage compound **3** adsorbs 5.6 mmol H_2 per gram at 77 K and 1 bar, which corresponds to 1.1 wt %. This value is comparable to the uptake of H_2 by the cage compounds CC2 and CC3 that Cooper et al. reported recently (see Table 1)[19] and higher than those of porous crystals of TTEB, where the data were collected at even higher pressure (3.9 $mmol\,g^{-1}$ at 77 K and 10 bar).[11d] For CO_2, we measured an adsorption of 2.1 $mmol\,g^{-1}$ at 273 K and 1 bar, which equates to 9.4 wt %. Again, this value is comparable to those of CC2 and CC3 and is ten times higher than the overall uptake of a imine cage compound (ZC) recently reported by the Zhang group (Table 1).[18]

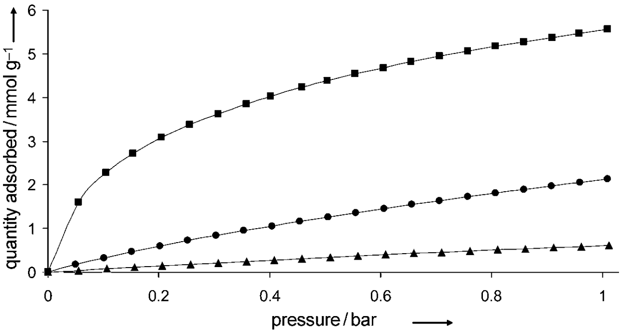

Figure 3. Gas adsorption isotherms of H_2 (■, 77 K), CO_2 (●, 273 K), and CH_4 (▲, 273 K) for cage compound **3**.

We also examined the adsorption of methane at 273 K and 1 bar. Indeed, only 0.6 $mmol\,g^{-1}$ (0.98 wt %) of the less polar methane is adsorbed, which is significantly less than the values reported for CC2 (1.13 $mmol\,g^{-1}$) and CC3 (1.53 $mmol\,g^{-1}$). More important than the absolute values of

Table 1: Comparison of surface areas (SA), micropore volume (V_{micro}), and uptake of gases for selected materials consisting of only discrete organic molecules.

Compound	$SA_{Langmuir}$ [$m^2 g^{-1}$]	SA_{BET} [$m^2 g^{-1}$]	V_{micro} [$cm^3 g^{-1}$] N_2, $P/P_0 \approx 1$	CO_2 [$mmol\,g^{-1}$] at 1 bar, 273 K	CH_4 [$mmol\,g^{-1}$] at 1 bar, 273 K	H_2 [$mmol\,g^{-1}$] at 1 bar, 77 K
3	1566	1377	0.42	2.1	0.61	5.6
CC2[19]	600	533	0.26	3.0	1.13	5.9
CC3[19]	730	624	0.28	2.5	1.53	5.0
ZC[18]	–[a]	–[a]	–[a]	0.2[b]	–[a]	–[a]
noria[17]	–[a]	350	0.13	2.5[c]	–[a]	–[a]
TTEB[11a]	–[a]	278	0.16	–[a]	–[a]	3.9[d]

[a] Not reported. [b] At 298 K. [c] At 30 bar and 298 K. [d] At 10 bar.

gas adsorption is the good selectivity for CO$_2$ over methane. Natural gas reserves contain, besides methane, roughly 40 % CO$_2$ and N$_2$, which must be removed prior to combustion.[4d] In principle, cage compound **3** could be used to remove CO$_2$ from natural gas and to enrich the methane content. The higher selectivity of **3** for CO$_2$/CH$_4$ (10:1 w/w) compared to that of similar systems might be attributed to the polar hydroxy groups directed into the cavities of the cages. This assumption will be tested by further experiments in which the interior of the cavity is varied by derivatization of the hydroxy moieties.

We investigated the adsorption of nitrogen by cage compound **4**, where the imine bonds are reduced to amine bonds. Because cage compound **4** is less temperature stable than the corresponding imine compound, we performed BET measurements to evaluate the surface areas and nitrogen adsorption properties of a sample heated in vacuum at 80 °C for 6 h. For several samples surface areas were less than 1 m^2 g^{-1}, revealing that the more flexible cage structure **4** collapses in the solid state and does not allow gas penetration. This indicates that a shape-persistent rigid structure might be advantageous for gas adsorption.

In conclusion, cage compound **3** has the highest surface area (1566 m^2 g) reported to date for a material consisting of a discrete purely organic compound and is even comparable to the surfaces areas of some described extended structures like CMPs[9] and COFs.[6] Our material is able to take up 9.4 wt % CO$_2$ and 0.94 wt % methane, which corresponds to a CO$_2$/CH$_4$ selectivity of 10:1 (w/w). This selectivity might be influenced by the polar functional groups inside the cavity. A more detailed investigation of the influence of the cage interior on gas-sorption properties is in progress in our research group. We are also synthesizing derivatives of the cage compound with various substituents on the periphery in order to study the effect on packing and porosity.[19]

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[21] In the ^{1}H NMR spectrum of the as-synthesized, air-dried cage compound **3** we found four THF molecules per cage molecule, suggesting that those are inclathrated inside the cavity of the cage molecule.

[22] Data were collected on an Oxford Diffraction SuperNova Atlas Dual system with a (Cu) microfocus source and focusing multilayer mirror optics. The structure was solved by direct methods and refined by full matrix least squares using SHELXTL-97.[27] All non-hydrogen atoms were refined using anisotropic thermal parameters. X-ray data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-789520). Crystal Data for **3a**: $T = 120(2)$ K, $C_{152}H_{128}N_{12}O_6$, $M = 2218.66$, trigonal space group $R\bar{3}$, $a = b = 29.149(3)$ Å, $c = 58.518(5)$ Å, $V = 43060(7)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 0.513$ g cm^{-3}, $\mu = 0.246$ mm^{-1}, $3.03° < \Theta < 62.14°$, reflections collected/unique 49155/14857 [$R(\text{int}) = 0.0454$], data/restrains/parameters 14857/0/517 GOF 0.866, final $R[I > 2\sigma(I)]$ $R1 = 0.0585$, $wR2$ (all data) = 0.1642, residual density 0.131 and −0.192 e A^{-3}.

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