

Transformation of a [4+6] Salicylbisimine Cage to Chemically Robust Amide Cages

Avinash S. Bhat, Sven M. Elbert, Wen-Shan Zhang, Frank Rominger, Michael Dieckmann, Rasmus R. Schröder, and Michael Mastalerz*

Abstract: In recent years, interest in shape-persistent organic cage compounds has steadily increased, not least because dynamic covalent bond formation enables such structures to be made in high to excellent yields. One often used type of dynamic bond formation is the generation of an imine bond from an aldehyde and an amine. Although the reversibility of the imine bond formation is advantageous for high yields, it is disadvantageous for the chemical stability of the compounds. Amide bonds are, in contrast to imine bonds much more robust. Shape-persistent amide cages have so far been made by irreversible amide bond formations in multiple steps, very often accompanied by low yields. Here, we present an approach to shape-persistent amide cages by exploiting a high-yielding reversible cage formation in the first step, and a Pinnick oxidation as a key step to access the amide cages in just three steps. These chemically robust amide cages can be further transformed by bromination or nitration to allow post-functionalization in high yields. The impact of the substituents on the gas sorption behavior was also investigated.

In recent years, the number and geometrical varieties of shape-persistent organic cages have dramatically increased due to the relative ease of synthesizing them, typically by applying dynamic covalent chemistry (DCC) reactions.^[1] The dynamic character of those reactions is a curse and a blessing at the same time. On the one hand it allows high-yielding access to rather complex molecules as a result of the self-correction mechanisms of the dynamically formed bonds, such as imine bonds,^[2] boronic esters,^[3] disulfide bonds,^[4] or

others.^[5] On the other hand, the dynamic nature of these bonds is based on low energetic stability, making them prone to be attacked, for example, by nucleophiles, and thus resulting in decomposition of the cage molecules into smaller fragments, decomposition products, or even the starting materials.

Whereas it is difficult to post-stabilize, for example, boronic ester units, imines are rich in chemistry and probably the simplest reaction is their reduction to amines.^[6] However, this is accompanied by a loss of shape-persistency because the former two sp²-hybridized imine bond atoms are now sp³-hybridized. This results in a higher conformational freedom of the cage, which is reflected, for example, in a loss of porosity. For instance, the specific surface area of 2071 m²g⁻¹ of the [4+6] salicylimine cage **1**^[2f,7] is decreased to less than 1 m²g⁻¹ in the reduced amine form.^[7b]

In contrast to an imine bond, an amide bond is chemically more robust and, as a result of the partial double bond character of the C–N bond, exhibits hindered rotation; it is therefore comparable to imines in terms of directionality and rigidity.^[8] Indeed, organic cages based on amide bonds have existed for quite a while,^[9] but larger amide cages in particular have to date been constructed through stepwise syntheses involving the formation of amide bonds, at least in the last crucial cage-forming step.^[10] As this bond formation is kinetically controlled, a self-correction is not possible, thus the cages are usually obtained in low overall yields.^[9b]

By using transition metals (Fe(III) or Ru(II)) as templates and applying high dilution conditions, the yields for small amide cages can even be increased to 70 %, compared to 27 % without.^[9c,11] It is worth mentioning that an exception is found for a smaller rigid [2+3] cage, which could be made in decent yields in one step by reacting three molecules of bis(acid chlorides) and two triamines to give the [2+3] hexaamide cage in 40 % yield because the number of statistically mismatching bond connections are very few as a result of the low number of necessary “correct” bond formations required to generate the cage.^[12] However, larger amide cages have been synthesized by multiple bond formations in one step, as well as by the above-mentioned stepwise approaches. Here, a template effect cannot be exploited and indeed the yields drop substantially, for example, to 7 % for a [2+4] octaamide cage based on resorcinarene tetrakis(acid chlorides) and *meta*-phenylenediamines.^[13] For comparison: The structurally related corresponding imine cage is synthesized by DCC in much higher yields of 45 %.^[2b] Certainly, the larger the molecular structures of amide-based cages are, the lower is the (overall) yield obtained by either the multiple stepwise approaches or one-pot procedures. Therefore, a more facile

[*] M. Sc. A. S. Bhat, Dr. S. M. Elbert, Dr. F. Rominger, Dr. M. Dieckmann, Prof. Dr. M. Mastalerz
Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: michael.mastalerz@oci.uni-heidelberg.de
M. Sc. A. S. Bhat, Dr. S. M. Elbert, Dr. W.-S. Zhang,
Prof. Dr. R. R. Schröder, Prof. Dr. M. Mastalerz
Centre for Advanced Materials
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 225, 69120 Heidelberg (Germany)

Supporting information (including experimental details) and the ORCID identification number for one of the authors of this article can be found under: <https://doi.org/10.1002/anie.201903631>.

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synthetic method is needed to solve this problem, which is reported herein.

The [4+6] imine cage **1** is synthesized in a twelvefold condensation of four molecules of triptycene triamine **2** and six molecules of salicyldialdehyde **5**, which occurs in yields of up to 86%.^[2f] However, as soon as triptycene triamine **2** is reacted with bis(acid chloride) **3** in a stoichiometric ratio, a large number of products are detected by HPLC, but no amide cage formation could be observed (Figure 1 a), which is

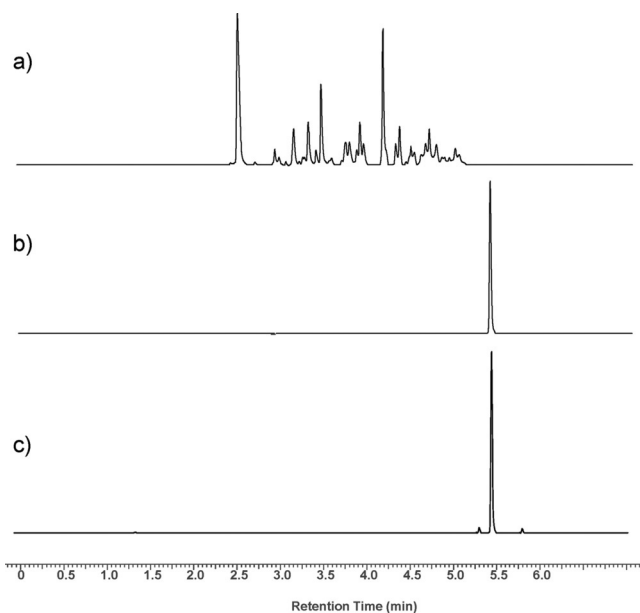
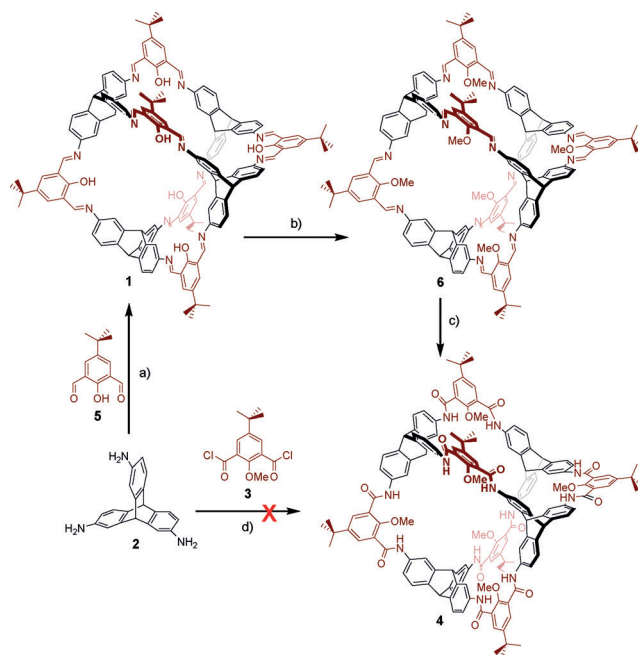


Figure 1. Comparison of HPLC traces (C-18 reverse-phase column (1.7 μm ethylene-bridged hybrid (BEH) particles), water/MeCN (90:10), 0.6 mL min⁻¹) of a) a crude product mixture of the reaction of bis(acid chloride) **3** and triamine **2**, b) pure amide cage **4**, and c) crude product of the Pinnick oxidation of cage **6**.

expected due to the irreversibility of the amide bond formation. The [4+6] amide cage **4** could be generated instead by first making salicylimine cage **1** by condensation of triamine **2** and salicyldialdehyde **5**, protection of the phenolic hydroxy groups as methyl ethers (cage **6**),^[14] and application of Pinnick oxidation conditions (Scheme 1).^[15,16]

To our delight, the HPLC trace of the crude product showed only one peak (Figure 1c). However, the ¹H NMR spectrum revealed that the compound was not pure and contained a lot of side products, which mainly stem from reactions of the scavenger 2-methylbutene (see Figure S103 in the Supporting Information). By washing the crude mixture with methanol and subsequent crystallization from DMF/MeOH, amide cage **4** was isolated in 21% yield. The complete conversion of imine to amide groups was confirmed by FTIR spectroscopy, with the imine band at $\tilde{\nu}$ = 1625 cm⁻¹ no longer being observed.^[14] Instead the carbonyl stretching mode of the amide group was clearly assigned to the peak at $\tilde{\nu}$ = 1655 cm⁻¹. Furthermore, MALDI-TOF mass spectrometry showed a signal at m/z 2495, which confirms the twelvefold oxidation. The ¹H NMR spectrum of cage **4** is rather simple, with only a few signals. Most characteristic are the



Scheme 1. a) THF, rt, 7 days, 83%; b) CH₃I, K₂CO₃, DMF, 80 °C, 16 h, 81%;^[14] c) NaClO₂, NaH₂PO₄, 2-methyl-2-butene, THF, H₂O, rt, 16 h, 21%; d) CH₂Cl₂/NEt₃, 16 h, rt.

amide protons resonating at δ = 10.31 ppm and the two signals at δ = 5.67 and 5.97 ppm from the triptycene bridgehead protons.

Single crystals of three different solvates were grown (see the Supporting Information), which were highly comparable in terms of their packing arrangements and cell parameters. Therefore, here, only the structure of single crystals of **4** that were grown by slowly cooling down a hot solution of **4** in DMF/MeOH is discussed. Enclathrated disordered solvent molecules could not be refined and, therefore, the SQUEEZE routine function had to be applied.^[17] Amide cage **4** crystallized in the monoclinic space group $P2_1$ with four molecules in the unit cell (Figure 2). The molecule is shape-persistent with the inner triptycene bridgehead carbon atoms forming a nearly regular tetrahedron with edge lengths between 12.3 and 12.6 Å. There are two types of amide bonds present. One is nearly in plane (dihedral angle between the

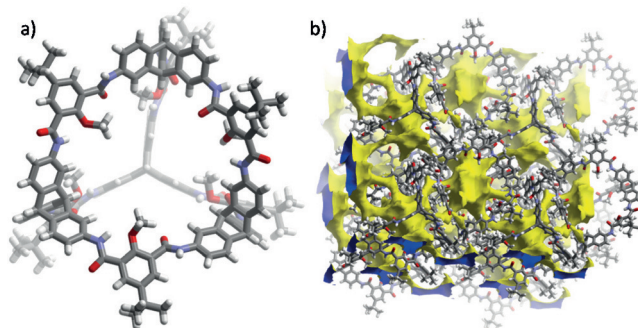
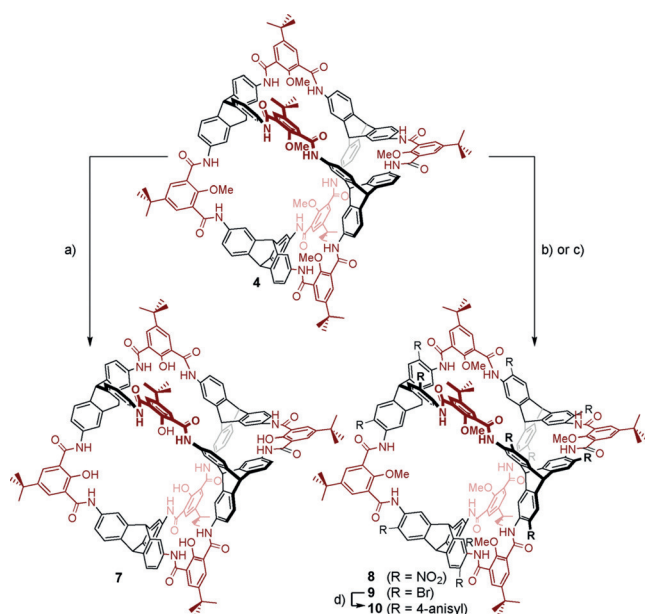


Figure 2. Single-crystal X-ray structure of amide cage **4**. a) Stick model; b) 2 \times 2 \times 2 unit cell showing the solvent-accessible pores as determined with a probe of 1.8 Å radius.

amide O and aromatic carbon atom attached to the amide N atom is between 0.56° and 6.85° with the two aryl rings, with the carbonyl oxygen atom pointing outside the cavity. This arrangement is stabilized by an intramolecular hydrogen bond between the amide NH group and the adjacent methoxy-O atom ($d_{\text{NH}\cdots\text{O}}$ is between 1.88 and 2.09 Å). The other amide bond is more deviated from planarity (5.69° to 12.58°) with the oxygen atom pointing inwards. In contrast to the corresponding imine cages **1** and **6**, the packing of **4** is not dominated by π - π stacking but rather by the formation of a more dense arrangement ($\rho = 0.80 \text{ g cm}^{-3}$, in comparison to 0.51 g cm^{-3} for cage **1** or 0.55 g cm^{-3} for **6**).^[7b,14] Analyzing the voids of the crystal structure with a probe of radius 1.8 Å revealed that it contains interconnected solvent-accessible pores within two-dimensional sheets with a volume of 7.9% of the cell volume. The surface is accessible for gases and was investigated by nitrogen gas sorption at 77 K (see below).

As stated in the introduction, amide bonds are more stable than imine bonds and, therefore, it is not surprising that amide cage **4** is highly stable under basic or acidic conditions at room temperature, such as in 3M NaOH_{aq} (pH 14.5), 2M HCl (pH -0.3), and even in oxidizing acids, such as 4M H₂SO₄ (pH -0.9) or conc. HNO₃ (pH -1). Only in conc. H₂SO₄ (36M) does the amide cage decompose (see Table S1 and Figure S44 in the Supporting Information).

In contrast to the imine cages **1** and **6**, the robustness of amide cage **4** now allows its chemical post-functionalization under harsh conditions (Scheme 2). When **4** is treated with Lewis-acidic AlCl₃ in toluene at 70 °C for 4 h, the methyl ether groups are selectively cleaved to give amide cage **7** in 60% yield. Thus, a cage can be generated with an extraordinarily high polarity in the interior, with six phenolic hydroxy and



Scheme 2. a) AlCl₃, toluene, 70 °C, 4 h, 60%; b) KNO₃, TFA, rt, 3 h, 84% (**8**); c) NBS, DMF, 80 °C, 16 h, 83% (**9**); d) 4-Methoxyphenylboronic acid, 4 mol% Pd₂dba₃, 25 mol% tBu₃P HBF₄, K₂CO₃ (2 N), THF, 80 °C, 16 h, 56%. TFA = trifluoroacetic acid, NBS = *N*-bromosuccinimide, dba = dibenzylideneacetone.

twelve amide groups, in four steps from simple building blocks. Nitronium ions are among the most reactive electrophiles generated under an “aggressive” chemical environment, such as using concentrated or fuming nitric acid in combination with acetic or trifluoroacetic acid.^[18] When amide cage **4** was treated with KNO₃ and trifluoroacetic acid, a selective twelvefold substitution at the triptycene moieties *ortho* to the amide groups and *meta* to the triptycene bridgeheads occurred, thereby giving nitrated cage **8** in 84% yield. The positions of the introduced nitro groups were clearly assigned by 2D NMR experiments (see Figures S13–S15 in the Supporting Information). This substitution pattern is in line with the fused *ortho*-effect that is often observed in triptycene chemistry.^[19] Amide cage **4** can also be brominated with NBS in DMF at the same position as where the nitration took place. The yield for this twelvefold reaction to brominated cage **9** is 83%, which is nearly the same as for the nitration. Although the twelve bromo substituents are sterically surrounded by the amide groups, it was possible to exchange these by a twelvefold Suzuki–Miyaura cross-coupling reaction with 4-anisylboronic acid to give cage **10** in 56% yield (Scheme 2).

As discussed above, the single-crystal X-ray structure of amide **4** suggests that the compound is more rigid and, therefore, more shape-persistent than the corresponding amine cage investigated previously.^[7b] Therefore, it is expected to have a decent specific surface area. A porous sample was generated by dissolving cage **4** in DMF and pouring it into a cold and stirred solution of methanol to obtain a colorless precipitate. This was immersed in 2-propanol and then diethyl ether before activation at 150 °C under vacuum. According to the Brunauer–Emmett–Teller model, a specific surface area of 275 m²g⁻¹ was determined by N₂ sorption at 77 K. The shape of the isotherms can best be described as mainly type I with a narrow pore-size distribution with a maximum at 17.8 Å, as calculated by QS-DFT.^[20] In comparison to the parent amide cage **4**, the brominated and the nitrated cages **8** and **9** have the same functional groups surrounding the interior cavity, but the presence of the electron-withdrawing nature of the *ortho*-positioned substituents (Br, NO₂) should result in the amide bonds varying in strength and thus polarity. The IR spectra shows the CO stretching bands of the amide units to be shifted from $\tilde{\nu} = 1655 \text{ cm}^{-1}$ for the parent cage **4** to $\tilde{\nu} = 1668 \text{ cm}^{-1}$ for the brominated cage **9** to $\tilde{\nu} = 1678 \text{ cm}^{-1}$ for the nitrated cage **8**. This change in polarity should affect the gas sorption behavior towards polar gases such as CO₂. Therefore, cages **8** and **9** were treated in the same way (pouring a solution of DMF into methanol, washing, and activation) as **4** to generate porous materials. Whereas the brominated cage **9** shows a significantly smaller specific surface area of 102 m²g⁻¹, the nitrated cage gave a very similar isotherm and thus specific surface area of 260 m²g⁻¹ with a maximum pore diameter of 17.2 Å while the demethylated cage **7** showed a specific surface area of 398 m²g⁻¹. All the cages adsorb similar amounts of CO₂ (**4**: 9.4 wt%; **7**: 9.0 wt%; **8**: 9.1 wt%, **9**: 9.0 wt%), and CH₄ (**4**: 0.98 wt%; **7**: 0.80 wt%; **8**: 0.87 wt%, **9**: 0.86 wt%) at 273 K and 1 bar. The comparable specific surface areas as well as the pore-size distributions of cages **4** and **8** allowed us to study,

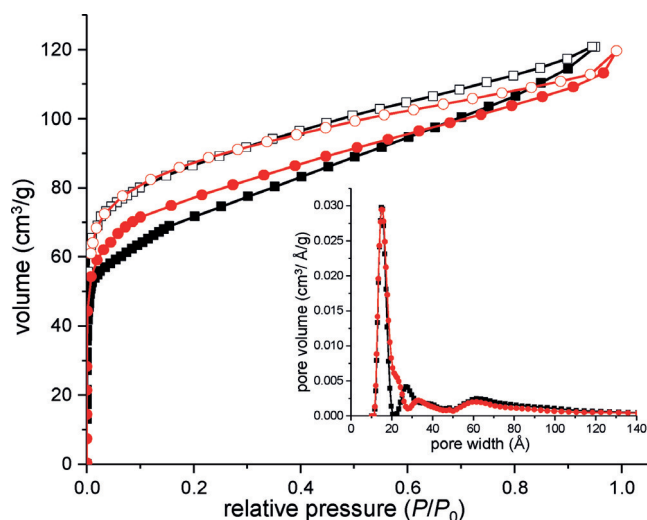


Figure 3. Nitrogen sorption isotherms of cages **4** (black) and **8** (red) at 77 K. Filled symbols: adsorption; open symbols: desorption. Inset: QSDFT pore-size distribution.

whether the substituents have an influence on the interaction of the compounds with the gases and ultimately have an impact on gas-sorption selectivities (Figure 3). Whereas the heat of adsorption (Q_{st}) of CO_2 rises from 26 kJ mol^{-1} for cage **4** to 35 kJ mol^{-1} for nitrated cage **8** at 0.1 mmol g^{-1} uptake, the difference for CH_4 is smaller (**4**: 15 kJ mol^{-1} ; **8**: 19 kJ mol^{-1}). The calculated Henry selectivities for CO_2 versus CH_4 rises from $S_H = 20.4$ for **4** to 28.5 for **8** (Table S2).

To summarize, a large shape-persistent [4+6] amide cage **4** was synthesized in 21% yield by transforming in just two steps an imine cage **1** that was accessible in high yields. A twelvefold Pinnick oxidation was the key step in the synthesis. To the best of our knowledge, larger amide cages have thus far only been made by multiple-step approaches, mainly in low overall yields. The amide cage **4** is chemically robust in both acidic and basic media over a large pH range from -1 to 14.5 , which is to the best of our knowledge, the largest range.^[21] This chemical robustness allowed post-functionalization under harsh conditions, such as a twelvefold bromination and nitration to give the cages **8** and **9** in yields of 84% each, which has not been described to date for similar compounds. The ease of this approach allows large quantities of **8** and **9** to be generated for further reactions, thereby opening up the access to a large variety of cage derivatives. Furthermore, it has been demonstrated that the nitro groups enhance the gas sorption selectivity towards polar CO_2 . Currently, we are investigating the scope of the reaction for other types of shape-persistent imine cages.^[22]

Acknowledgements

We thank the European Research Council (ERC) for funding this project in the frame of the consolidators grant CaTs n DOCs (grant agreement no.725765).

Conflict of interest

The authors declare no conflict of interest.

Keywords: amides · dynamic covalent chemistry · imines · organic cage compounds · shape-persistency

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 8819–8823
Angew. Chem. **2019**, *131*, 8911–8915

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Manuscript received: March 25, 2019

Accepted manuscript online: April 9, 2019

Version of record online: May 20, 2019