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Uniform porous nanospheres of discrete shape-persistent organic cage compounds[†]

Markus W. Schneider,^a Lorenz G. Lechner^b and Michael Mastalerz^{*a}

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By mixing solutions of the reactants for shape-persistent cage compounds in a binary solvent mixture, spheres in the nanometre regime with controlled sizes can be generated, which show permanent porosities.

In recent years, the synthesis and investigation of porous materials have gained more and more attention due to the fact that they show various interesting properties, *e.g.* for separation or storage of gases¹ or as highly active homogeneous catalysts.² Porous materials became more diverse and can be divided into four main classes: (i) purely inorganic materials, such as zeolites;³ (ii) hybrids of organic linker molecules and metal clusters, so-called metal–organic frameworks (MOFs) or infinite coordination polymers (ICPs);⁴ (iii) purely organic materials, such as crystalline covalent organic frameworks (COFs)⁵ or amorphous conjugated microporous polymers (CMPs);⁶ and (iv) porous materials deriving from discrete molecules.⁷

The last one can be seen as a relatively new class of porous materials, because the specific surface areas did not exceed the value of 300 m² g⁻¹ till 2009.⁸ We and others have demonstrated that shapepersistent organic cage-compounds⁹ are superior within this class of permanent porous crystalline materials having specific surface areas of up to 2071 m² g⁻¹ (Brunauer–Emmett–Teller model, BET).¹⁰

For polymeric porous compounds, it is known that morphology has a high impact on the physical properties of the material.¹¹ To adjust such properties, controlling the morphology and size of the material particles in a defined manner is desired. For instance, Kitagawa and co-workers reported that the particle sizes of crystalline ICPs can be controlled by the addition of a modulator. Gas adsorption behaviour was evidently related to the particle size of the crystals.¹² In a similar fashion, the addition of ammonium salts to the reaction mixture led to the control of crystal-size and -shape, which influences the material properties dramatically when in the nanosized regime.¹³ Mirkin and Oh first showed that instead of the typical crystalline ICPs, defined amorphous globular assemblies can be generated from the same molecular building units.¹⁴ In comparison to their crystalline counterparts, nanospheric porous ICPs have *e.g.* good dispersibility, which is advantageous for processing the ICPs as thin films.¹¹

As already mentioned above, research activities in the field of discrete organic compounds as precursors for porous materials are still in a nascent state and need to be studied in a broader sense, including how morphology influences the porosity of the materials. To date, only a few examples of investigations on different crystalline polymorphs of cage-compounds were reported.^{10,15,16} For example, Cooper *et al.* revealed that the porosities of certain [4+6] cage compounds can be switched on and off by generating various polymorphs from different solvents.^{15a} Very recently, it was shown that the shape and porosities of particles of racemic mixtures of such cages can be controlled by defined mixing of the two enantiomeric cage compounds.¹⁶ However, to the best of our knowledge, no controlled method to generate smooth nanospheric assemblies of shape-persistent cage compounds *during* the synthesis was described to date.

Here, we communicate our first results on a synthetic procedure of [4+6] cage compounds, which form micro- or nanospheric particles by use of a well-balanced binary solvent mixture. Furthermore, we compare the nitrogen sorption and the derived surface areas of the amorphous nanospheric compounds with their crystalline counterparts.¹⁰

Recently, we introduced the one-pot synthesis of endo-functionalized adamantoid [4+6] cage compounds by the condensation of triptycene triamine and various salicyldialdehydes.^{10,17}

Previously, we reported that the cage compounds with bulkier groups in the periphery (**3a** and **3b**, Scheme 1) had to be precipitated through the addition of *n*-pentane to the THF solution after the reaction mixture reached the thermodynamic equilibrium (here, we call it method A), to obtain the pure products **3a**^A and **3b**^{A,10} Material properties of **3a** and **3b** revealed a strong dependency on the morphology of the material. The as-synthesized materials are amorphous with BET surface areas of approx. 700 m² g⁻¹ (**3a**^A and **3b**^A). When the compounds were crystalline, the specific surface areas were the lower, the bulkier the peripheral substituents are (SA = $22 \text{ m}^2 \text{ g}^{-1}$ for **3b**^{α}; SA = 309 m² g⁻¹ for **3a**^{α}). Method A was not sufficient for the synthesis of another cage compound, with an *n*-butyl chain in the periphery (**3c**). For this cage compound, we identified by screening of several conditions that a binary solvent mixture of THF/ MeCN (1.6 : 1 v/v) was the ideal reaction medium to get the product

^aInstitute of Organic Chemistry II & Advanced Materials, Ulm University, Albert-Einstein-Allee 11, Ulm, Germany. E-mail: michael.mastalerz@ uni-ulm.de; Fax: +49 731-40-22840; Tel: +49 731-40-22844

^bCentral Facility of Electron Microscopy, Electron Microscopy Group of Materials Science, Ulm University, Albert-Einstein-Allee 11, D-89069 Ulm, Germany

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Scheme 1 One-pot synthesis of shape-persistent adamantoid cage compounds **3a–3c**. (i) *Reaction conditions*: THF, reflux, three days, then precipitation with *n*-pentane (**3a^A** and **3b^A**);¹⁰ reaction in THF/acetoni-trile, reflux, 2–3 days (**3a^B–3c^B**).

as an orange powder in high yields. The authenticity and purity of $3c^{B}$ (here, we term the binary solvent approach method B) was proved by NMR-, IR-, and mass-spectroscopy as well as by elemental analysis

(see ESI[†]). Investigation of the morphology by means of powder X-ray diffraction revealed that the material is amorphous. Surprisingly, by scanning electronic microscopy (SEM) imaging, we found that nearly homodisperse spheres were formed with an average diameter of 374 nm \pm 76 nm (s.d., n = 60) (Fig. 1a and b). Since this cage compound with *n*-butyl groups is a new derivative in the row of endo-functionalized [4+6] cage compounds,^{96,10} it was not clear if the formation of the nanospheres can be deduced as a unique property to the less bulky peripheral n-butyl substituents of the molecular structure, or if the nanospheres derive from method B. Therefore, 1 and 2a as well as 1 and 2b were reacted under conditions similar to method B, to figure out, whether it is possible to control the morphology of synthesized cage compounds, independently from their molecular structure. To our delight, cage compounds $3a^B$ and $3b^B$ could be synthesized as nanospheres from THF/MeCN (1:1.36 v/v and 1:1 v/v) according to the procedure described above for 3c^B. By SEM imaging (Fig. 1e and f), nanospheric assemblies can be detected for both compounds $3a^{B}$ and $3b^{B}$ with average sphere diameters of $142 \pm$ 43 nm (s.d., n = 60) for $3a^{B}$ and 274 ± 70 nm (s.d., n = 60) for $3b^{B}$. This is in contrast to the amorphous material generated by protocol A, where the resulting particles are also amorphous, but much less structured.10 Analysis of the compounds by 1H NMR-, IR- and massspectroscopy are in agreement to those synthesized before by method A, showing that the molecular composition is identical,¹⁰ although the morphology is different.

It is known for ICPs that the amorphous nanospheric assemblies are less porous than the crystalline ones.¹ To analyze the porosities of the generated nanospheres $3c^{B}$ by N₂-sorption, we investigated the thermal stability by thermogravimetrical analysis (TGA) first, which suggested that the material is stable up to 400 °C (see ESI†). A sample of the compound was degassed at 200 °C and 6×10^{-2} mbar for 23 h



Fig. 1 Scanning electron microscopic (SEM) images of nanospheres of $3c^{B}$ (a and b) having an average diameter of 374 nm \pm 76 nm (s.d., n = 60), crystallized $3c^{er}$ (c and d) by slow diffusion of acetonitrile into a saturated THF-solution, and nanospheres of $3a^{B}$ (e) and $3b^{B}$ (f) with average diameters of 142 \pm 43 nm (s.d., n = 60) and 274 \pm 70 nm (s.d., n = 60). The white frames in (a) and (c) mark the zoomed-in sections depicted in (b) and (d), respectively.





Fig. 2 Nitrogen sorption isotherms of 3c at 77 K. Top: amorphous, nanospheric material $3c^{B}$; bottom: crystalline material $3c^{cr}$. Filled symbols: adsorption isotherms; open symbols: desorption isotherms.

before N₂-sorption measurements were performed. The sorption isotherm (Fig. 2, top) of nanospheric **3**c^B can be classified as a hybrid of a type-II and a type-I isotherm, revealing that the material is mainly macroporous. The pore volume is calculated to be 0.11 cm³ g⁻¹. From the *t*-plot analysis, a micropore contribution of only 11% of the overall surface is estimated. The calculated specific surface area is 148 m² g⁻¹ (BET-model) or 182 m² g⁻¹ (Langmuir-model) (Table 1).

As mentioned above, the specific surface area of ICP compounds was shown to depend strongly on the morphology with usually lower surface areas of the amorphous materials. This is not necessarily the same trend for porous cage compounds.^{10,16} To compare crystalline and nanospheric amorphous cage compound **3c**, we crystallized cage compound **3c**^{α} as red crystals by slow diffusion of MeCN into a saturated THF-solution. As can be seen by SEM imaging (Fig. 1c and d), there are still some nanospheres left, sitting on top of the crystals. The crystalline material was treated the same as the nanospheric one (200 °C and 6 × 10⁻² mbar for 23 h) prior to N₂-sorption measurements. Most interestingly, the isotherm is very similar to that of the amorphous polymorph (Fig. 2, bottom). One minor difference

Table 1 Comparison of selected materials properties of 3a-3c derived from various synthetic methods

| | BET surface area/m ² g ⁻¹ | | | |
|---------------------------------|---|-------------------------|---------------------------|--------------------------------------|
| Compound | Crystalline | Amorphous (method A) | Nanospheres (method B) | Average nanosphere diameter/nm |
| 3a | 309 ^a | 727 ^a | 38 | 142 |
| 3b | 22^a | 690 ^a | 36 | 274 |
| 3c | 174 | n.d. | 148 | 374 |
| ^{<i>a</i>} Values take | en from ref. 10 |). | | |

is that the small hysteresis between adsorption and desorption is located in the region between $P/P_0 = 0.4$ and 1.0, whereas for the amorphous material $3c^B$ the hysteresis is located in the low P/P_0 regime below 0.4. As reported for similar cages (amorphous/crystalline) the micropore contribution in the crystalline material is higher than in the amorphous porous material. From the *t*-plot method, a micropore contribution of 48% on the overall surface can be calculated, which is expected for a more ordered structure and complements trends described before for similar pairs of polymorphs.¹⁰ The calculated specific surface area is with 174 m² g⁻¹ (BET-model) or 196 m² g⁻¹ (Langmuir-model) comparable to that of the amorphous material of $3c^B$. This strengthens the observation that there is no general "rule of thumb" for cage compounds that crystalline or amorphous materials will have higher specific surface areas.

We also measured the specific surface areas of nanospheres $3a^{B}$ and $3b^{B}$. First investigations of the material by nitrogen sorption revealed specific surface areas of $38 \text{ m}^{2} \text{ g}^{-1}$ (BET) and $42 \text{ m}^{2} \text{ g}^{-1}$ (Langmuir) for $3a^{B}$, and $36 \text{ m}^{2} \text{ g}^{-1}$ (BET) and $39 \text{ m}^{2} \text{ g}^{-1}$ (Langmuir) for $3b^{B}$. Those values are substantially lower than those measured for amorphous $3a^{A}$ and $3b^{A}$.¹⁰ It is worth mentioning that the surface area of crystalline $3b^{er}$ was in the same range ($22 \text{ m}^{2} \text{ g}^{-1}$) as that of the nanospheres.¹⁰ If we compare bulk amorphous, nanospheric amorphous and bulk crystalline materials of those compounds, it seems for now that the nanospheric materials properties are closer to the bulk crystalline ones. This finding for adamantoid [4+6] cage compounds complements those published recently for the racemic mixtures of the Cooper cages.¹⁶ However, these first results have to be proofed further by a more detailed study, which will be published in due course.

To conclude, we introduced a new procedure to control the morphology of shape-persistent organic cage compounds during their syntheses to generate uniform spheres in the nanometre regime, which were shown to be permanently porous. Most interestingly, for **3b** and **3c**, the sorption behaviour for nitrogen gas seems not to differ whether the material is nanospheric or bulk crystalline.

These types of nanospheres are, to the best of our knowledge, not described to date for one-component materials of discrete cage compounds¹⁶ and open the opportunity to further study the materials properties, *e.g.* for processing the cage structures into thin films. Furthermore, the influence of the reaction parameters (*e.g.* medium and reaction temperatures, concentration and mixing rates) on shape and porosity of such nanoparticles will be studied in more detail.

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Notes and references

- 1 R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **120**, 4044.
- 2 (a) D. Farrusseng, S. Aguado and C. Pinel, Angew. Chem., Int. Ed., 2009, 48, 7402; (b) P. Kaur, J. T. Hupp and S. T. Nguyen, ACS Catal., 2011, 1, 819.
- 3 Introduction to Zeolite Science and Practice, ed. H. Ceijka, H. van Bekkum, A. Corma and F. Schüth, Elsevier, Amsterdam, Netherlands, 3rd edn, 2007.
- 4 (a) S. Kitagawa, R. Kitaura and S.-i. Noro, Angew. Chem., Int. Ed., 2004, 43, 2334; (b) G. Férey, Chem. Soc. Rev., 2008, 37, 191.

- 5 For reviews, see: (a) N. B. McKeown and P. M. Budd, Macromolecules, 2010, 43, 4163; (b) M. Mastalerz, Angew. Chem., Int. Ed., 2008, 47, 444; (c) A. Thomas, Angew. Chem., Int. Ed., 2010, 49, 8328.
- 6 J.-X. Jiang and A. I. Cooper, *Top. Curr. Chem.*, 2010, 293, 1.
 7 For reviews, see: (a) N. B. McKeown, J. Mater. Chem., 2010, 20, 10588; (b) J. R. Holst, A. Trewin and A. I. Cooper, *Nat. Chem.*, 2010, 2, 914; (c) A. I. Cooper, *Angew. Chem., Int. Ed.*, 2011, 40, 996; (d) G. Couderc and J. Hulliger, *Chem. Soc. Rev.*, 2010, 39, 1545; (e) P. J. Langley and J. Hulliger, *Chem. Soc. Rev.*, 1999, 28, 279; (f) C. H. Görbitz, *Chem.-Eur. J.*, 2007, 13, 1022.
- 8 (a) J. Tian, P. K. Thallapally, S. J. Dalgarno, P. B. McGrail and J. L. Atwood, Angew. Chem., Int. Ed., 2009, 48, 5492; Angew. Chem., Int. Ed., 2009, 34, 3423; (b) T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner and A. I. Cooper, Nat. Mater., 2009, 8, 973.
- 9 (a) M. Mastalerz, Angew. Chem., Int. Ed., 2010, 49, 4042; (b)
 M. Mastalerz, M. W. Schneider, I. M. Oppel and O. Presly, Angew. Chem., Int. Ed., 2011, 40, 1046; (c) J. T. A. Jones, T. Hasell, X. Wu,
 J. Basca, K. E. Jelfs, M. Schmidtmann, S. Y. Chong, D. J. Adams,

A. Trewin, F. Schiffman, F. Cora, B. Slater, A. Steiner, G. M. Day and A. I. Cooper, *Nature*, 2011, **474**, 367.

- 10 M. W. Schneider, I. M. Oppel, H. Ott, L. G. Lechner, H.-J. S. Hauswald, R. Stoll and M. Mastalerz, *Chem.-Eur. J.*, 2012, 18, 837.
- 11 A. M. Spokoyny, D. Kim, A. Sumrein and C. A. Mirkin, *Chem. Soc. Rev.*, 2009, **38**, 1218.
- 12 S. Diring, S. Furukawa, Y. Takashima, T. Tsuruoka and S. Kitagawa, *Chem. Mater.*, 2010, **22**, 4431.
- 13 M. Ma, D. Zacher, X. Zhang, R. A. Fischer and N. Metzler-Nolte, *Cryst. Growth Des.*, 2011, 11, 184.
- 14 M. Oh and C. A. Mirkin, Nature, 2004, 438, 641.
- (a) J. T. A. Jones, D. Holden, T. Mitra, T. Hasell, D. J. Adams, K. E. Jelfs, A. Trewin, D. J. Willock, G. M. Day, J. Bacsa, A. Steiner and A. I. Cooper, *Angew. Chem., Int. Ed.*, 2011, **40**, 749;
 (b) M. Mitra, X. Wu, R. Clowes, J. T. A. Jones, K. E. Jelfs, D. J. Adams, A. Trewin, J. Basca, A. Steiner and A. I. Cooper, *Chem.-Eur. J.*, 2011, **17**, 10234;
 (c) M. J. Bojdys, M. E. Briggs, J. T. A. Jones, D. J. Adams, S. Y.-I. Chong, M. Schmidtmann and A. I. Cooper, *J. Am. Chem. Soc.*, 2011, **133**, 16466.
- 16 T. Hasell, S. Y. Chong, K. E. Jelfs, D. J. Adams and A. I. Cooper, J. Am. Chem. Soc., 2012, 134, 588.
- 17 M. Mastalerz, Chem. Commun., 2008, 4756.