

MS26-02 Porous Crystalline Materials from Discrete Organic Molecules. Michael Mastalerz, *Institute of Organic Chemistry II & Advanced Materials, Ulm University, Germany*, E-mail: Michael.mastalerz@uni-ulm.de

Research on porous materials focussed in the last two decades mainly on extended framework materials, like metal-organic frameworks (MOFs) zeolites and some three-dimensional polymeric organic networks.^[1]

In contrast, research on porous materials consisting of discrete organic molecules exclusively were long time neglected, although in 1976 it was already shown that Dianin's compound can act as an "organic zeolite".^[2] The lower interest in porous organic molecular crystals might be mainly attributed to the low reported specific surface areas, which rarely exceeded 300 m²/g. However, in 2009 the situation changed, when Atwood et al. and Cooper et al. reported on porous organic cage compounds with surface areas up to 624 m²/g.^[3] Since then, the new field rapidly developed.

We showed that on the basis of the rigid triptycene scaffold we were able to construct shape-persistent cage compounds with intrinsic porosities.^[4] In the crystalline state inlathrated solvents can be removed from the voids without collapsing of the porous structure. The measured specific surface area of 2071 m²/g (Brunauer-Emmett-Teller model), these porous cage compounds can compete with MOFs and other porous materials.^[5]

Besides introducing intrinsic porous cage compounds, we were able to rationally construct an extrinsic porous organic crystal with an even higher accessible surface area of 2796 m²/g.^[6] This material adsorbs high amounts of CO₂ (15.9 wt% at 273 K and 1 bar) and H₂ (2.2 wt% at 77 K and 1 bar) and is comparable to some of the best performing MOFs in this respect.

- [1] a) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334, b) A. Thomas, *Angew. Chem.* **2010**, *122*, 8506 c) N. B. McKeown, P. M. Budd, *Macromolecules* **2010**, *43*, 5163, d) Introduction to Zeolite Science and Practice, 3rd ed. (Eds.: H. Cejka, H. van Bekkum, A. Corma, F. Schüth) Elsevier, Amsterdam, Netherlands **2007**
- [2] R. M. Barrer, V. H. Shanson, *J. Chem. Soc. Chem. Comm.* **1976**, 333.
- [3] a) J. Tian, P. K. Thallapally, S. J. Dalgarno, P. B. McGrail, J. L. Atwood, *Angew. Chem. Int. Ed.* **2009**, *48*, 5492; b) T. Tozawa et al., *Nat. Mater.* **2009**, *8*, 973.
- [4] M. Mastalerz, *Chem. Commun.* **2008**, 4756
- [5] a) M. Mastalerz, M. W. Schneider, I. M. Oppel, O. Presly, *Angew. Chem. Int. Ed.* **2011**, *50*, 1046; b) M. W. Schneider, I. M. Oppel, H. Ott, L. G. Lechner, H.-J. S. Hauswald, R. Stoll, M. Mastalerz, *Chem. Eur. J.* **2012**, *18*, 837; c) M. W. Schneider, I. M. Oppel, M. Mastalerz, *Chem. Eur. J.* **2012**, *18*, 4156-4160;
- [6] M. Mastalerz, I. M. Oppel, *Angew. Chem.* **2012**, DOI: 10.1002/anie.201201174

Keywords: porous solids; organic molecular crystals; surface adsorption

MS26-03 Thermo and solvatochromic coordination frameworks with 4-(pyridin-4-yl)benzoic acid. Gaëlle Ramon, Gift Mehlanga, Susan A. Bourne, *Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town, Rondebosch, 7701, South Africa* E-mail: gaelle.ramon@uct.ac.za

Two novel metal-organic frameworks were synthesised solvothermally using the ditopic ligand : 4-(pyridin-4-yl)benzoic acid (44pba) (**1**) with either cobalt or nickel nitrate salts. Isostructural porous 3D-networks were obtained: [Co₄(44pba)₈]_n[(DMF)₃·(EtOH)_{0.25}·(H₂O)₄]_n (**2**) and [Ni₄(44pba)₈]_n[(DMF)_{3.5}·(EtOH)·(H₂O)_{1.5}]_n (**3**). Their crystal structures were solved and their thermal behaviours studied. Both **2** and **3** displayed dramatic colour change when exposed to air and we showed that they readily absorb traces of water from the moist air. The reversibility of the water uptake and associated colour change were observed upon heating and fully characterised with hot stage microscopy (HSM- Figure 1), thermogravimetric analysis (TGA), Powder X-ray Diffraction (PXRD) and UV-Vis spectrometry.

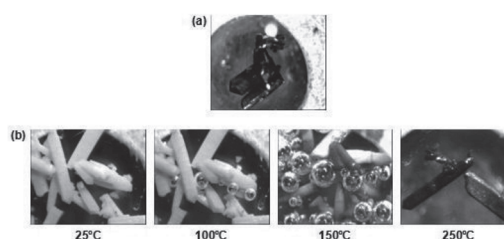


Figure 1: (a) single crystals of **2**, as synthesized. (b) **2** after exposure to water vapour (yellow crystals). On heating, water is released from the channels and the sample reverts to a purple colour.

This and further solvatochromic properties were investigated using **2** (**3** could not be synthesised in large enough quantities).

To study the ability of our material to absorb different solvents, **2** (purple) was dried under vacuum at 200°C for 10h and resulted in **2d** (purple), the empty network: [Co₄(44pba)₈]_n.

Under controlled conditions of temperature, **2d** was exposed to water vapour resulting in **2d-water** (yellow). The uptake was recorded using a specially designed balance at different temperatures (20 - 30°C range). The absorption mechanism was identified as D4 3-dimensional diffusion with an activation energy of 84.5 ± 5 kJ·mol⁻¹.

Additional studies were carried out with water and a range of dry solvents in which **2d** crystals were immersed. The solvated forms of **2** displayed a range of colours: the non-polar or aprotic solvents resulted in crystals which retained the original purple colour (DMF, DMSO or benzene) while the polar protic solvents resulted in pink (methanol), orange-brown (ethanol) or yellow (water) crystals. All solvated forms of **2** were characterised by HSM, TGA, PXRD and UV-Vis spectroscopy.

Keywords: kinetics; porous network; sorption