

MS31. Tailored physical properties in molecular crystals

Chairs: Sebastien Pillet, Pilar Gomez-Sal

MS31-P1 Adaptive structural changes for increased sorption capacity

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A two-dimensional (2-D) metal-organic framework $\{[Zn(L)_4 \cdot DMF \cdot H_2O]_n\}$, (**1**), prepared by the reaction of 4-(1*H*-benzo[d]imidazol-1-yl)benzoic acid (**L**) with $Zn(NO_3)_2 \cdot 4H_2O$ under solvothermal conditions, can adapt its structure during supercritical carbon dioxide (CO_2) guest-exchange and CO_2 sorption. The 2-D layers of the framework are associated by weak interactions that enable the framework to undergo guest-induced expansion and contraction. At high pressure, additional space is created between adjacent layers resulting in a significant increase in the CO_2 sorption capacity (Figure 1). Moreover, the structural changes and gas uptake by the host occur preferentially for CO_2 at 25 °C while nitrogen (N_2) and methane (CH_4) are not adsorbed under the same conditions. Pressure differential scanning calorimetry (PDSC) and in situ single-crystal X-ray diffraction (SCD) experiments under gas loading were carried out to obtain insight into the dynamic behaviour of the framework.

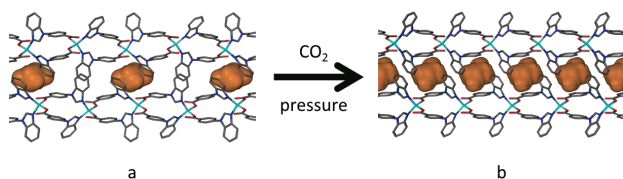


Figure 1. The framework viewed along [100]. a) Discrete mid-sized pockets of the structure observed at low pressure and b) the larger pockets observed at high pressure. Hydrogen atoms and guest molecules have been omitted for clarity.

Keywords: sorption, flexibility, carbon dioxide and hysteresis

MS31-P2 Crystal structure and gelation properties of naphthalene bioconjugates

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Low molecular mass gelators have been intensively researched in the past decade due to their ease of preparation and potential application in the field of soft and optical materials, transportation media, and as active media for organic reactions and catalysis.¹ Of special interests are chiral gelators where amplification of chiral or luminescent properties can be achieved via gelation.² We have successfully applied amino acid substituted benzene derivatives bearing phosphine moiety as ligands in Rh-catalyzed enantioselective hydrogenation reactions;³ it was shown that the enantioselectivity is strongly dependant of the amino acids used as well as the benzene substitution (*meta*- or *para*-). As an expansion of our research towards the field of soft materials, here we present an ongoing work on amino acid disubstituted naphthalene bioconjugates where solid state and gelation properties are influenced by small modifications of the molecule. Several crystal structures of bioconjugates were obtained. All compounds exhibit hydrogen bonding in their but no π - π stacking was observed. In the case of nonchiral glycine methyl ester derivative, two polymorphs were obtained by slow evaporation of different solvent solutions. It was shown by means of polycrystalline X-ray diffraction that in THF, a single phase is formed whilst in ethanol, both phases are present. The two polymorphs differ only in their characteristic torsion angles of the amide group. All derivatives were tested as gelators in various organic solvents. The results have shown that alanine derivative (Figure 1) with C6-aliphatic chains exhibit super-gelation of nonpolar aromatic solvents.

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MS31-P3 New hybrid materials via a combination of imidazolates and complex hydrides: first compounds and further perspectives

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Since the discovery of zeolites by Axel Frederik Cronstedt in 1756, microporous materials have received an always increasing attention. In this field, the great challenges for chemists were, and still are, to tune the pore size and the pore's surface chemical nature in order to obtain materials with targeted properties while keeping the stability window as large as possible to allow practical applications. Over the past 15 years, Metal-Organic Frameworks (MOFs) received most of the attention in this field thanks to the ease of synthesizing linkers with various sizes, chemical properties, or number of coordination sites.

The recently discovered porous polymorphs of magnesium and manganese borohydride show that the tetrahydroborate anion can also have a structure directing effect as many organic ligands by preferentially making linear metal-BH₄-metal units[1], [2]. The formation of compounds containing both an organic ligand, in this case imidazolate and BH₄ group could lead to the formation of new porous hydrides having the easily tunable properties of imidazolate frameworks.

Li₂ImBH₄ (Im = imidazolate) and Li₂bImBH₄ (bIm = benzimidazolate) were successfully synthesized by liquid assisted grinding and liquid synthesis. Both structures were solved using synchrotron radiation powder diffraction and neutron powder diffraction in the case of LiImBH₄. The main features of these structures are the formation of parallel positively charged [Li₂(b)Im]_∞ fibers extending perpendicular to the (benz)imidazolate plane. The charge balancing BH₄ units are located in between these fibers and coordinate to four Li atoms in a square planar environment. Anisotropic temperature factors refined from neutron diffraction data suggests high rotational disorder of the BH₄ unit perpendicular to the square plane. This disorder was investigated and confirmed by solid state NMR and theoretical studies.

This work clearly proves that it is possible to combine hydridic and classical ligands in the same structure and that the resulting materials have original and unique properties compared to the pure borohydride or imidazolate compound.

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[2] B. Richter, D. B. Ravnsbæk, N. Tumanov, Y. Filinchuk, and T. R. Jensen, *Dalton Trans*, vol. 44, no. 9, pp. 3988–3996, 2015.

Keywords: metal-organic frameworks, zeolitic imidazolate frameworks, borohydride, hydrogen storage, hybrid compounds

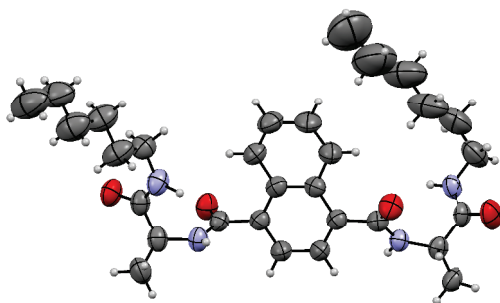


Figure 1. Molecular structure of the alanine bioconjugate.

Keywords: naphthalene, amino acid, bioconjugates, hydrogen bond