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Keywords: layered titanates, adsorption, reduction

MS.25.4

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Solid-State synthesis of mixed trihalides via reversible absorption of dihalogens by non porous onium salts

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1,6-Bis(trimethylammonium)hexane bis(trihalides) **1•(Br$_2$)$_2$** and mixed bis(trihalides) **2•(I$_2$)$_2$** and **2•(Br$_2$)$_2$** have been synthesized by treating the corresponding dihydrated halides **1•(H$_2$O)$_2$** and **2•(H$_2$O)$_2$** with molecular dihalogens (e.g., Br_2 and I_2) under gas-solid and solution conditions (Figure 1).[1] Despite the fact that the starting hexamethonium halides are non porous, the trihalides syntheses occur homogeneously, in quantitative yields, and reversibly. In all the cases the halogen bond [2] prevails over the hydrogen bond, and the hydrogen bonded water in the starting material is substituted by the halogen bonded dihalogens to form the crystalline trihalides. The stability of the trihalides is mainly due to cooperative halogen bond and cation templation effect [3]. Hexamethonium halides are proven effective solids for the clathration and storage of molecular dihalogens. While the starting salts are not isostructural, all the formed trihalides and mixed trihalides are isostructural. Single crystal X-ray diffraction, powder X-ray diffraction and Raman experiments have confirmed the formation of the solid trihalides. The method we describe is general and can be extended to the preparation of various uncommon trihalides species like interconversion of trihalides and mixed trihalides via solid-gas processes.

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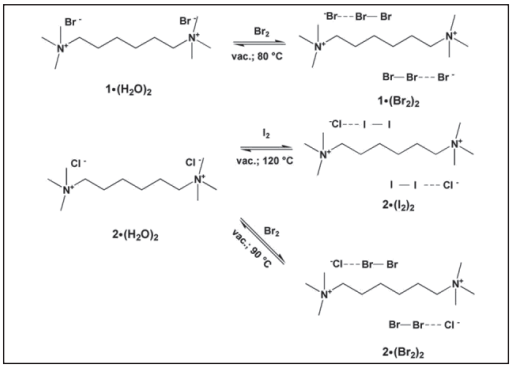

Figure 1. Synthesis of the complexes **1•(Br$_2$)$_2$**, **2•(I$_2$)$_2$** and **2•(Br$_2$)$_2$** via reversible gas-solid reactions and their reversion to **1•(H$_2$O)$_2$** and **2•(H$_2$O)$_2$**.

Keywords: gas-solid reactions, non porous salts, inclusion

MS.25.5

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Experimental visualization of breathing in fluorous metal-organic frameworks from single crystal diffraction - functionalized MOFs for gas storage and separation

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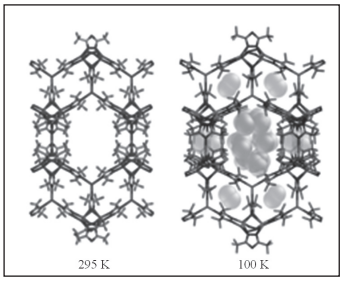
Fluorous metal-organic frameworks (FMOFs) are a new class of advanced porous material with fluorine-lined pore surface and hydrogen-free. Reaction of silver(I) and 3,5-bis(trifluoromethyl)-1,2,4-triazolate in toluene/acetonitrile yields FMOF-1, the first example in the FMOF family, that shows high-density gas uptake and unique hysteretic sorption of H_2 [1]. Variable single crystal X-ray diffraction measurements reveals that FMOF-1undergoes remarkable breathing and negative thermal expansion when the crystal is exposed to N_2 at ambient pressure [2]. Upon cooling a apparent negative thermal expansion takes place with very large changes in volume and unit-cell parameters during which multiple N_2 molecules are absorbed into channels and cages (see picture).

Details of the dynamic gas adsorption mechanism at the atomic level will be presented to illustrate the functional control and sequential filling of the multiple gas adsorption sites in both small and large pores within FMOF-1 and the consequent remarkable swelling of these framework cavities. Real-time 3D reciprocal space mapping technique employed at the SNS TOPAZ beam line for the analyses of guest-host interaction and structural transformation in MOFs will be introduced.



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[1] C. Yang, X.P. Wang, M.A. Omary *Journal of the American Chemical Society* **2007,** *129*, 15454. [2] C. Yang, X.P. Wang, M.A. Omary *Angewandte Chemie-International Edition* **2009**, *48*, 2500-2505.

Keywords: gas storage, neutron diffraction, metal-organic framework

MS.26.1

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Understanding hydrogenation properties of various hydrogen storage materials from their local structure

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Hydrogen has been considered as a promising alternative fuel for transportation, provided we can find a way to store a large amount of it in a compact way [1]. The realization of such a storage system can be achieved by developing materials that can easily absorb, safely store, and rapidly release hydrogen and have durable reversibility. However, there is currently no material to meet all the requirements for on board storage. Great efforts have been made to understand hydrogenation properties of currently available hydrogen storage materials to look for a way to improve properties or to prepare new materials. However, investigating some of these materials is challenging since their hydrides are only stable under hydrogen gas pressure. We have investigated the structure of conventional hydrogen storage materials using in-situ neutron experiments. In this talk, I will present our average and local structural studies on various hydrogen storage materials by using Rietveld and the atomic pair distribution function analysis [2] on neutron and synchrotron X-ray total scattering data. The systems of interest are mechanically alloyed MgCo, Ti-V-Mn binary and ternary alloys and (Mg, Pr)Ni_2.

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Keywords: hydrogen storage materials, local structure, total scattering

MS.26.2

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Analysis of isotropic nanostructured systems using SAS

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Small-angle scattering (SAS) of X-rays and neutrons experiences a renaissance in the studies of isotropic nanostructured systems. Novel data analysis methods significantly enhanced resolution and reliability of structural models provided by the technique [1]. Especially noticeable is the progress in the studies of biomacromolecular solutions allowing one to study the structure of native particles and to rapidly analyze structural changes in response to variations in external conditions. Emerging automation of the experiment, data processing and interpretation make SAS using synchrotron radiation a streamline tool for large scale structural studies in molecular biology. The SAS method provides low resolution macromolecular shapes *ab initio* and is readily combined with other structural and biochemical techniques in multidisciplinary studies to build rigid body models of complexes and to characterize oligomeric mixtures and flexible systems.

The novel approaches also became very useful for other types of isotropic objects, in particular for the studies of formation and structural properties of functional nanoparticles fabricated with different procedures. The recent developments in the SAS data analysis will be presented and illustrated by applications to biomacromolecular solutions and metal nanoparticle systems.

[1] H.D. Mertens, D.I. Svergun *J Struct Biol.* **2010,** *172*,128-141.

Keywords: Macromolecule, Nanoanalysis, Scattering

MS.26.3

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Competition between PCBM Aggregation and P3HT crystallization in thin films upon annealing

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Concomitant development of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) aggregation and poly(3-hexylthiophene) (P3HT) crystallization in bulk heterojunction (BHJ) thin film (ca. 85 nm) solar cells has been revealed using simultaneous grazing-incidence small-/wide-angle X-ray scattering (GISAXS/GIWAXS). With enhanced time and spatial resolutions (5 s/frame; minimum $q \approx 0.004$ Å^{-1}), synchrotron GISAXS has captured in detail the fast growth in size of PCBM aggregates from 7 to 18 nm within 100 s of annealing at 150 °C. Simultaneously observed is the enhanced crystallization of P3HT into lamellae oriented mainly perpendicular but also parallel to the substrate. An Avrami analysis of the observed structural evolution indicates that the faster PCBM aggregation follows a diffusion-controlled growth process, whereas the slower development of crystalline P3HT nanograins is characterized by constant nucleation rate. These two competing kinetics result in local phase separation with space-filling PCBM and P3HT nanodomains less than 20 nm in size when annealing temperature is kept below 180 °C. Accompanying the morphological development is the synchronized increase in electron and hole mobilities of the BHJ thin-film solar cells, revealing the sensitivity of the carrier transport of the device on the structural features of PCBM and P3HT nanodomains. Optimized structural parameters, including the aggregate size and mean spacing of the PCBM aggregates, are quantitatively correlated to the device performance; a comprehensive structural model for the optimized BHJ thin film solar cells is presented.

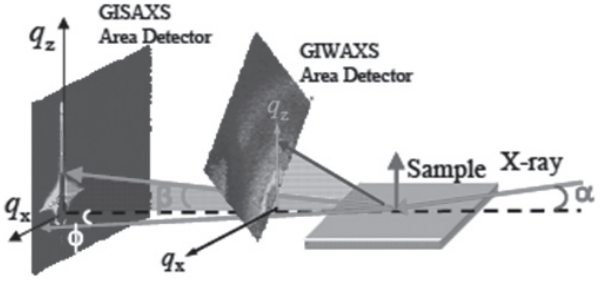

Figure 1. Schematic of the setup for synchronized GISAXS/GIWAXS

Figure 2. A structural model for an optimized P3HT/PCBM thin-film solar cells. The intercalated PCBM aggregates (large spheres) and P3HT crystallites (blocks) are immersed in the matrix of P3HT chains (wires) and dispersed PCBM molecules (small spheres).

Keywords: GISAXS/GIWAXS, PCBM/P3HT, BHJ solar cells