

**P08.03.05***Acta Cryst.* (2008). **A64**, C420**Monte Carlo simulations of fullerene-cubane**Bart Verberck<sup>1,2</sup>, Gerrit A Vliegthart<sup>2</sup>, Gerhard Gompper<sup>2</sup><sup>1</sup>University of Antwerp, Department of Physics, Groenenborgerlaan 171, Antwerp, Antwerp, 2020, Belgium, <sup>2</sup>Theorie der weichen Materie und Biophysik, Institut fuer Festkoerperforschung, Forschungszentrum Juelich, 52425 Juelich, Germany, E-mail: bart.verberck@ua.ac.be

Macroscopic amounts of C<sub>60</sub>.C<sub>8</sub>H<sub>8</sub> (fullerene-cubane) can nowadays be synthesised [1]. By means of powder and single crystal x-ray diffraction the structure of C<sub>60</sub>.C<sub>8</sub>H<sub>8</sub> has been inferred to be face-centered cubic (fcc) at room temperature. The fcc phase exhibits freely rotating fullerene molecules. Below 140 K the crystal lattice is orthorhombic and the fullerene molecules adopt fixed orientations. The cubane molecules are orientationally ordered in both phases, an observation deduced from proton NMR measurements [1]. Recent x-ray scattering experiments have confirmed the existence of different solid phases of this unique molecular crystal [2]. Here we present Monte Carlo simulation results confirming a structural phase transition in C<sub>60</sub>.C<sub>8</sub>H<sub>8</sub>. Our simulations reproduce the crystal lattices, but have in addition been designed to provide precise information about the rotational and translational motions of the fullerene and cubane molecules. In particular, we not only observe the transition from freely-rotating to non-rotating fullerenes, but we obtain the orientations of the C<sub>60</sub> molecules in the ordered (low-temperature) phase, a characteristic which has up to now not been directly obtained from experiments [1,2].

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[2] B. Verberck, V. Heresanu, S. Rouziere, J. Cambedouzou, P. Launois, E. Kovats, S. Pekker, G.A. Vliegthart, K.H. Michel, and G. Gompper, to appear in *Fuller. Nanotub. Car. N.* (2008).

Keywords: fullerenes, cubane, Monte Carlo simulations

**P08.03.06***Acta Cryst.* (2008). **A64**, C420**Effect of selenium incorporation on crystal structure of arsenic sulfide (As<sub>4</sub>S<sub>4</sub>)**

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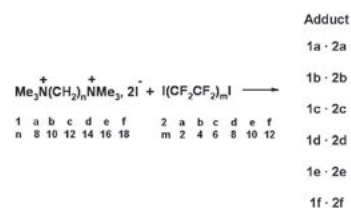
A new solid solution series of crystalline arsenic chalcogenide As<sub>4</sub>(S,Se)<sub>4</sub> was prepared by sublimation method using arsenic, sulfur and selenium powder as evaporation source materials. The crystalline materials obtained by the technique exhibited a shape of an elongated prism up to approximately 3.0 mm in length. The effect of Se substitution on the As<sub>4</sub>S<sub>4</sub> molecular structure has been investigated by single-crystal X-ray diffraction method and electron microprobe analysis. These products crystallized in monoclinic system with P2<sub>1</sub>/n space group, whose molecular packing corresponds to the low-temperature phase of As<sub>4</sub>S<sub>4</sub> cage-like molecule. The variation of Se concentration is continuous throughout the solid solution series, confirming a random substitution of Se for S in the molecular structure. Substitution of S in the As<sub>4</sub>S<sub>4</sub> by Se to form As<sub>4</sub>(S,Se)<sub>4</sub> preserves the initial As<sub>4</sub>S<sub>4</sub> type configuration in the primitive monoclinic lattice, and leads to an increase of As-(S,Se) bonds and an expansion of As<sub>4</sub>(S,Se)<sub>4</sub> molecules. The expansion of the molecules implies that Vegard's law is obeyed over the whole range of As<sub>4</sub>S<sub>4</sub>-

As<sub>4</sub>Se<sub>4</sub> solid solution. Site occupancy refinements revealed that S atoms are preferentially replaced by Se atoms at the (S,Se)<sub>2</sub> site, whereas the substitution of S by Se is hard to occur in the (S,Se)<sub>3</sub> site. The a few substitution at the (S,Se)<sub>3</sub> site yields an extremely short As-(S,Se) bonds around (S,Se)<sub>3</sub> site. The difference in the As-(S,Se) bond distances brings about a deformation of the As<sub>4</sub>(S,Se)<sub>4</sub> cage-like molecule. The molecular features of the anionic substitution are similar to those of the photoinduced transition of As<sub>4</sub>S<sub>4</sub> molecule, which is characterized by the dissociated S<sub>2</sub> atom and the surviving S<sub>3</sub> atom during the transformation.

Keywords: As<sub>4</sub>S<sub>4</sub> molecular crystal, arsenic chalcogenide, solid solution

**P08.03.07***Acta Cryst.* (2008). **A64**, C420**Dynamic porous networks capable of diiodoperfluoroalkanes' mixtures separation**Pierangelo Metrangolo<sup>1</sup>, Yvan Carcenac<sup>1</sup>, Manu Lahtinen<sup>2</sup>, Tullio Pilati<sup>3</sup>, Giuseppe Resnati<sup>1,3</sup>, Kari Rissanen<sup>2</sup><sup>1</sup>Politecnico di Milano, CMIC, Via Mancinelli 7, Milano, Milano, 20131, Italy, <sup>2</sup>Department of Chemistry, University of Jyväskylä, Finland, <sup>3</sup>ISTM-CNR, Milan, Italy, E-mail: pierangelo.metrangolo@polimi.it

In this presentation we report the application of supramolecular methods and crystal engineering to the resolution of diiodoperfluoroalkanes' (DIPFAs) mixtures through selective and reversible incorporation in the crystal lattice of dynamic porous organic solids. Surprisingly, the transformation of the densely packed (non-porous) methonium iodides **1** occur rapidly and selectively in the solid state by exposition of the microcrystalline powder to the vapors of the convenient alfa,omega-DIPFAs **2**, a process that would be expected to involve surmounting a considerable energy barrier. Reminiscent of the low affinity DIPFAs have for hydrocarbons (HCs), the cations and the superanions tend to stack separately in columns. As a result of this, each superanion is surrounded by four columnar stacks of HC cations, leading to a well-defined cavity in which the DIPFA **2** is trapped thanks to strong halogen bonding. A comparison with the structure of pure decamethonium iodide **1b** suggests a 'sliding doors' mechanism to create room to the diiodoperfluorocarbon.



Keywords: halogen bonding, porous networks, supramolecular chemistry

**P08.03.08***Acta Cryst.* (2008). **A64**, C420-421**Dynamic change in emission mode of ammonium anthracenedisulfonate in crystalline state**

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Efficient regulation of luminescence output induced by external stimuli is a significant issue in the development of chemical

or physical sensing devices. On-off switching of solid-state luminescence intensity have been achieved by adsorption and desorption of guest molecules or thermal stimuli. However, there has been few reports on the switching of luminescence mode. Here, we report the regulation of luminescence mode of organic salts of anthracene-2,6-disulfonic acid (ADS) with *sec*-butylamine by external stimuli. The organic salts yielded inclusion crystals with 1,4-dioxane, 1,4-thioxane or benzene. Whereas emission spectra of inclusion crystal with 1,4-thioxane or benzene have vibrational structure, that of inclusion crystal with 1,4-dioxane are broad and redshifted by 20 nm. This indicate that the latter exhibited excimer-like emission derived from the large  $\pi/\pi$  overlap of the anthracene moieties. Powder X-ray diffraction (PXRD) analyses indicated that the inclusion crystals with 1,4-dioxane showed supramolecular isomerization by chemical and physical stimuli. When the inclusion crystal with 1,4-dioxane was heated until 473 K, 1,4-dioxane was released completely from the crystal. The emission spectrum of the resulting crystal was similar to inclusion crystal with 1,4-thioxane or benzene. PXRD pattern and emission spectra suggest the rearrangement of ADS. By the exposure of the crystal to 1,4-dioxane, the PXRD peak shifted to the longer distance. After cooling of the crystal until 253 K, the peak in PXRD pattern and emission spectrum became similar to that of original crystal. These date confirm that the inclusion crystal with 1,4-dioxane changes the emission mode from monomer emission to excimer-like one through the reversible structure transition by external stimuli.

Keywords: solid-state dynamics, luminescence, organic crystals

### P08.03.09

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#### Computational studies of relationships between structure and lattice dynamics in organic crystals

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There is an increasing demand for accurate assignments of the vibrational modes in molecular organic crystals at terahertz frequencies (1 THz = 33 cm<sup>-1</sup>), due to the rapidly growing number of experimental activities using terahertz time-domain spectroscopy (THz-TDS). The vibrational modes in this region are largely due to whole-molecule motions and are therefore dictated by the intermolecular interactions in the crystal. To date, a number of approaches have been developed to calculate vibrational spectra in the terahertz range, including lattice dynamics based on atom-atom model potentials [1] and on periodic electronic structure theory [2]. We have been applying the two methods to develop an understanding of relationships between structure and lattice dynamics in molecular organic crystals and to characterise observed THz-TDS spectra. Computational investigations of the vibrational modes in several series of small molecules with well-characterised crystal structures will be presented, along with the observed spectra. We find that the computational efficiency of the atom-atom approach can be exploited to rapidly investigate the effect of structural changes on lattice dynamics, while the more demanding electronic structure calculations must be used when the mixing of low-frequency molecular modes with the lattice modes becomes significant. Their combined use can be a successful approach to characterising

observed spectra and is leading to an understanding of the influence of both molecular structure and intermolecular interactions on the dynamics in molecular crystals in the terahertz region.

[1] G.M.Day, J.A.Zeitler, W.Jones, T.Rades, and P.F.Taday, *J.Phys. Chem. B*, v.110, p.447, 2006.

[2] D.G. Allis, D.A. Prokhorova, and T.M. Korter, *J. Phys. Chem. A*, v.110, p.1951, 2006.

Keywords: dynamics, theoretical calculations, vibrational spectra

### P08.03.10

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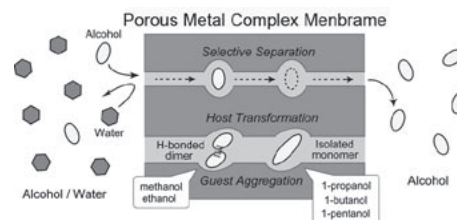
#### Alcohol vapor inclusion in transformable crystal hosts and application to separation membrane

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The vapor absorbency of series of alcohols from methanol to 1-pentanol was characterized on single crystal adsorbents, [M<sup>II</sup>(bza)<sub>4</sub>(pyz)]<sub>n</sub> (bza = benzoate; pyz = pyrazine; M = Rh (1), Cu (2)). The crystal structures for all alcohol-inclusions were determined by single-crystal X-ray crystallography at 90 K. The crystal phase transition induced by the guest adsorption occurred in the inclusion crystals except for the 1-propanol. A hydrogen-bonded dimer of adsorbed alcohol was found in the methanol and ethanol inclusion-crystals. In contrast, an isolated monomer existed in the channel for 1-propanol, 1-butanol, and 1-pentanol inclusions. Alcohol/water separation was characterized by a pervaporation (PV) technique using microcrystals of 2 dispersed in a poly(dimethylsiloxane) membrane [1].

[1] S. Takamizawa, C. Kachi-Terajima, T. Akatsuka, M. Kohbara, T. Jin, *Chem. Asian J.*, 2 (7), 837-848 (2007).



Keywords: gas-solid inclusion reaction, solid-state structural changes, single-crystal applications

### P08.03.11

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#### Gas-conforming ability of [M<sup>III</sup>(en)<sub>3</sub>]Cl<sub>3</sub> as transformable ionic-single crystal hosts

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Single crystal of [Co(en)<sub>3</sub>]Cl<sub>3</sub> shows gas adsorbency for various gases