

FA4-MS29-T01

Dynamic Gas Separation on a Flexible Single-Crystal Host. Satoshi Takamizawa^{a,b}. ^aGraduate School of Nanobioscience, Yokohama City University. ^bJST-PRESTO

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Microporous materials, which have pores with diameters less than 20 Å, are attractive in both industry and scientific fields since they are applicable for gas separation, gas adsorption, and catalysis. I previously reported a porous single crystal of a metal complex [Cu₂(bza)₄(pyz)]_n **1**, which has structural flexibility as well as regularity. The single crystal **1** easily adsorbed various gases through narrow channels with a diameter of ca. 2-4 Å.

While the design of sorption selectivity in porosity is mostly based on pore structure and adsorption interaction, flexibility can enable tuning the adsorption state by adjusting the host structure. To develop the dynamic gas selectivity, three kinds of separation for various organic vapors and inorganic gases were carried out for **1**: (1) chromatography on a microcrystal packed column,¹ (2) sorption from a vapor mixture,² and (3) permeation through single crystal of for various organic vapors and inorganic gases.³ The analyses of these results demonstrated the novel dynamic separation on flexible porous solid: (1) strong entropy dependence,¹ (2) dynamic switch of gas selectivity,² and (3) smooth and high selective permeation through narrow channels.³

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Keywords: gas-solid inclusion reactions, adsorption kinetics, solid-state phase changes

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Structure and topology of novel zeolites and mesoporous materials. Junliang Sun^a, Charlotte Bonneau^a, Daliang Zhang^a, Yu Han^b, Corma Avelino^c, Xiaodong Zou^a. ^a*Inorganic and structural chemistry, Berzelii Center EXSELENT on Porous Materials, Stockholm University, Sweden.* ^b*King Abdullah University of Science and Technology, Saudi Arabia.* ^c*Instituto de Tecnología Química, Spain.*

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In the formation of mesoporous silica materials with surfactants, the interaction between inorganic species and surfactants plays a crucial role. The mesoporous materials commonly form a kind of interface which minimises the surface energy. It is quite often to see the silica wall follows so-called bi-continuous minimum surfaces, while no real example was found to present a tri-continuous minimum surface although it was predicted mathematically. IBN-9 is the first example which shows a tri-continuous pore structure with etc-c3 topology, and its silica wall follows a tri-continuous H-minimum surface.[1] IBN-9 was synthesized with a designed surfactant which enables the fine-tuning of the interface curvature. MCM-41-type and MCM-48-type mesostructures can also be synthesized with the same surfactant. The whole

system shows a good example of synthesizing mesostructures by controlling the interface curvature.

The minimum surfaces also appear in crystalline inorganic phases, especially for those with extra large pores, such as the germanate SU-M.[2] ITQ-37, a germanosilicate zeolite, is another example with its pore-size approaching the meso-scale.[3] Its structure was determined by a new approach: combining selected area electron diffraction (SAED) and powder X-ray diffraction (PXRD) in a charge-flipping algorithm. The framework of ITQ-37 follows the srs minimal net and its extra-large 30-rings form two unique cavities where each cavity is connected to three others to form a gyroidal channel system. These cavities describe the enantiomorphous srs net of the framework. Different from all known MCM-48-type mesostructures and other microporous structures, ITQ-37 is the first chiral zeolite with one single gyroidal channel and this channel is roughly separated from the framework by a G-minimum surface. It has the lowest framework density (10.3 T atoms per 1000 Å³) of existing 4-coordinated crystalline oxide frameworks, and the pore volume of the corresponding silica polymorph would be 0.38 cc.g⁻¹.

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Guest Ordering Inside MOF's Channels: Breathing Effect versus Steric Factors. Kirill Yussenko, Mikhail Meilikhov, Roland A. Fischer. *Inorganic Chemistry II, Ruhr-University Bochum, Germany.*

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The Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) are a unique class of hybrid solid-state materials with bright future due to their permanent porosity and high thermal stability. The use of these materials ranges from gas storage, separation and catalysis, to a number of diverse potential applications, including optoelectronics, sensors, smart membranes etc. Also aiming at applications in catalysis we have introduced the solvent-free gas-phase loading of MOFs via the adsorption of different volatile organometallic all-hydrocarbon precursors such as ferrocene, cobaltocene and their derivatives. Loading of the MOFs with different metal-organic guests opens a door for development of novel materials with tunable properties. Up to now, only a few examples of detailed structural characterization of the inclusion compounds like Guest@MOF have been described in the literature [1]. We have previously obtained adsorbate structures for numbers of inclusion compounds based on the home powder X-ray diffraction [2, 3]. Here, we present the results obtained in the course of analysis of the guest's ordering and packing inside the 1D-channels of two MOFs, [Al(OH)(bdc)]_n and [V(O)(bdc)]_n. As revealed, these two topologically similar structures have different adsorption properties. [Al(OH)(bdc)]_n shows a well-pronounced breathing effect on the contrary to [V(O)(bdc)]_n which demonstrates neither breathing effect nor appreciable guest capacity. To note, [Al(OH)(bdc)]_n exhibits a high loading rate

for all types of guest molecules which are ordered in the middle of the channel, whereas inflexible $[V(O)(bdc)]_n$ can adsorb only a little amount of the guest (5-10 mol. %). In the first case, the stoichiometry of inclusion compound is $Guest_{0.5}@[Al(OH)(bdc)]_n$ or $Guest_{0.25}@[Al(OH)(bdc)]_n$. In the case of $[V(O)(bdc)]_n$, only cobaltocene forms inclusion phase composition cobaltocene $_{0.5}@[V(O)(bdc)]_n$ due to the formation of charge-transfer complex [4]. Hydrogen bonds, host-guest and guest-guest interactions as well as structural effects of the substitute group inside the guest molecule have been studied in details for all inclusion compounds.

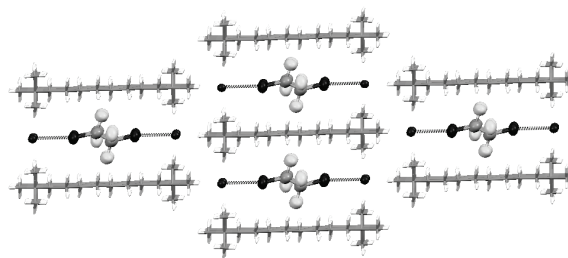
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Keywords: coordination polymers, host-guest complexes, powder structure determination

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Dimensional Encapsulation of Halogen-Bonded Supramolecular Anions. Pierangelo Metrangolo^{a,b}, Gabriella Cavallo^a, Manu Lahtinen^c, Tullio Pilati^d, Kari Rissanen^e, Giuseppe Resnati^{a,b,d}, Giancarlo Terraneo^{a,b}. ^aNFMLab - D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy. ^bCNST - IIT@POLIMI, Politecnico di Milano, Via G. Pascoli 70/3, 20133 Milan, Italy. ^cDepartment of Chemistry, University of Jyväskylä, Post Office Box 35, Jyväskylä FI-40014, Finland. ^dC.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy. ^eDepartment of Chemistry, Nanoscience Center, University of Jyväskylä, Post Office Box 35, Jyväskylä FI-40014, Finland.
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Halogen bonding [1] has increasingly facilitated the assembly of diverse host-guest solids. In this contribution, we show that a well-known class of organic salts, bis(trimethylammonium) alkane diiodides, can reversibly encapsulate I_2 [2] and a series of α,ω -diiodoperfluoroalkanes (DIPFAs) through intermolecular interactions between the host's Γ anions and the guest's terminal iodine substituents [3]. In particular, bis(trimethylammonium)hexane diiodide encapsulates I_2 yielding in a predictable and controllable manner the selective formation of the rare polyiodide species $\Gamma \cdots I-I \cdots \Gamma$. Similarly, the process is highly selective for the DIPFA that forms an $\Gamma \cdots I(CF_2)_m I \cdots \Gamma$ superanion, which matches in length to the chosen dication. DIPFAs that are 2 to 12 carbons in length can thereby be isolated from mixtures by means of crystallization from solution upon addition of the dissolved size-matched ionic salt. The solid-state salts can also selectively capture I_2 and the DIPFAs from the vapour phase, yielding the same product formed from solution despite a lack of porosity of the starting lattice structure.



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Keywords: Halogen Bonding, Dynamic Porous Materials, Anions

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Towards docking-based prediction of host-guest framework systems Peter A. Wood, Oliver Korb. Cambridge Crystallographic Data Centre, Cambridge, UK.
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The design and prediction of multi-component organic crystal structures is of interest to many areas of the chemical industry. Host-guest framework structures can, for example, be used to tune the physicochemical properties of a solid form, to achieve selective separation and even as catalysts. Current design and prediction methods have limitations though; crystal structure prediction (CSP) can be very computationally expensive for each individual multi-component system and there is also a limit to the number of experimental screens that can be carried out.

These multi-component structures do, however, essentially represent a form of host-guest binding related to that seen when a ligand interacts with a protein binding site. In this study we investigate whether established techniques for predicting protein-ligand binding can be applied to the challenge of modelling small molecule host-guest crystalline frameworks.

In order to examine the general applicability of this technique, an off-the-shelf docking package (GOLD [1]) is used with a standard scoring function (CHEMPLP [2]) that has been trained for interactions in protein-ligand binding sites. A range of experimentally-determined channel-based test structures are used to evaluate the effectiveness of the docking package. The test structures include API frameworks, well-known organic inclusion compounds and metal-organic frameworks. This work shows that the principles of docking can be successfully applied to the crystal engineering problem of predicting host-guest systems.

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Keywords: crystal engineering, docking, guest-host structures