

Recognition of Weak Interactions at the Gas-crystal Interface

Angiolina Comotti, Silvia Bracco, Roberto Simonutti, *Department of Materials Science, University of Milano-Bicocca, Milan, Italy*. E-mail: piero.sozzani@mater.unimib.it

Molecular self-assembled materials are promising in several fields such as gas storage, selective recognition, separation and modulation of the functions of active molecules. The application of the principles of self-assembly and crystal engineering permit the shaping of specific nanoscale environments where guest molecules, through new weak interactions, are entrapped. We could obtain an empty-pore hexagonal structure (solved by single-crystal analysis) held together by a network of weak interactions and fabricate supramolecular architectures that cooperatively stabilize gases that diffuse in. The molecular crystal can store large amounts of carbon dioxide and methane selectively over nitrogen, oxygen and hydrogen [1]. NMR spectroscopy could measure intermolecular distances and recognize the specific interactions that contribute to the overall stabilization. The impressive upfield shifts caused by the aromatic ring currents on gas molecules at the van der Waals contacts provide a tool for understanding the preferred topology of the gases interacting with the inner surface of the porous crystal. A variety of conjugated molecules can be encapsulated in the infinite nanochannels of 0.5 nm of the host matrix. Weak host-guest $\text{CH}\cdots\pi$ and $\pi\cdots\pi$ interactions form collectively a stable architecture with all the active molecules aligned along the crystallographic c axis in thermally stable single crystals.

[1] Sozzani P., Bracco S., Comotti A., Ferretti L., Simonutti R., *Angew. Chem. Int. Ed.*, 2005, **44**, 2. [2] Sozzani P., Comotti A., Bracco S., Simonutti R., *Angew. Chem. Int. Ed.*, 2004, **43**, 2811.

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