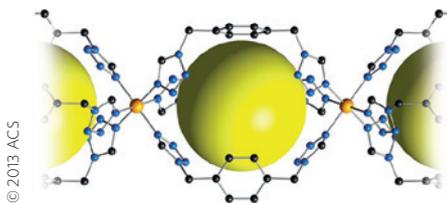


SPIN-CROSSOVER TRANSITION

Disruption on adsorption

J. Am. Chem. Soc. **135**, 15986–15989 (2013)



Stimuli-responsive materials are attractive for the development of devices such as sensors or for memory storage, and with this in mind, molecules that display spin-crossover phenomena have received much interest. Spin-crossover arises when metal complexes can exist either in low-spin or high-spin electronic ground states; it involves a transition from one to the other. This causes changes in the magnetic properties of the compound and can be induced by an external stimulus — typically a temperature variation. Guillermo Mínguez Espallargas from the University of Valencia, Spain, and co-workers have now observed that the spin-crossover

transition of an iron(II) coordination polymer is affected by the physisorption of CO₂ gas molecules.

Single-crystal X-ray characterization shows that both the low-spin and high-spin states, at 120 K and 240 K, respectively, adopt the same structure. The material consists of one-dimensional coordination polymer chains, [Fe(II)(btzx)₃]²⁺ (where btzx is a flexible ligand comprising two tetrazole units grafted on a phenyl core), closely packed in a parallel manner and separated by counteranions (ClO₄⁻). An interesting feature of the material is that it exhibits empty internal cavities between two iron centres, but no permanent channels. Nevertheless, the flexibility of the btzx ligands enables gas molecules to find their way to these cavities, presumably through rotation of the central phenyl ring. Measurements show that the material selectively adsorbs CO₂ over N₂, most likely owing to the smaller kinetic diameter of CO₂ and its stronger affinity for the cationic polymer chains.

The researchers observed that this CO₂ adsorption affected the material's spin-crossover transition temperature — it increased to 209 K for the CO₂-loaded

material from 200 K for the unloaded material — and that this effect is reversible. Characterization of the CO₂-loaded material by X-ray powder diffraction crystallography showed that the material retained the same structure, and under ambient conditions (1 bar, 273 K) accommodated one CO₂ molecule per cavity through O=C=O...π interactions with the ligands' tetrazole units. This increases the framework's electron density, stabilizing the low-spin state, which in turn increases the spin transition temperature. *AP*

BIOCHEMISTRY

Gene self-replication

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Before the evolution of polymerase enzymes, it is likely that the first cells on Earth relied on self-replicating genetic material, using an inherent chemical reactivity to facilitate copying. Cells now possess sophisticated biocatalytic mechanisms for this, but the original self-replication process presents an attractive concept for the creation of simple artificial cells and recent research

2013 NOBEL PRIZE IN CHEMISTRY

Model citizens

Computational chemistry has developed rapidly over the past 40 years, with advances in computing power being matched by breakthroughs in the methods used to model molecules and their behaviour. Such theoretical techniques come in two popular flavours; one is based on classical Newtonian physics and the other on quantum mechanics. Now, for making advances in developing both methods, and more specifically for combining these two approaches, Martin Karplus of the University of Strasbourg and Harvard University, Michael Levitt from the Stanford University School of Medicine and Arieh Warshel of the University of Southern California, have been awarded the 2013 Nobel Prize in Chemistry.

Although the award is for numerous advances over their respective careers, it will be associated mostly with the development of the computational method known as QM/MM (quantum mechanics/molecular mechanics), which combines both quantum and classical mechanics to simulate large molecules — such as proteins — with high computational efficiency. Classical techniques treat atoms and bonds like balls



and springs, using force-fields to simulate their interactions. These methods are relatively simple and thus quite quick to carry out, but they are unable to model chemical reactions. For that, you need quantum-based calculations, but scaling these up to study large molecules is unfeasible because of their computational expense — they would simply take far too long.

In QM/MM, the chemically active region of the molecule — for example the active site of an enzyme — is treated quantum

mechanically, and the rest of the molecule is treated classically, significantly speeding up the calculations while still describing the chemistry using a high-level of theory. Since these methods were pioneered in the 1970s, they have been applied to many multiscale problems, from drug discovery to understanding materials for solar cells. The continuing development of these computational strategies will undoubtedly lead to deeper chemical insights into bigger and more complex problems. *GA*