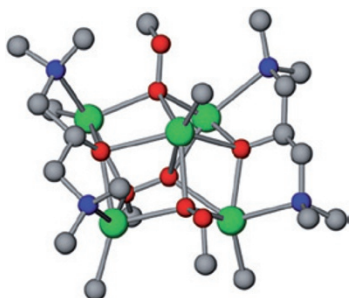


ORGANOCADMIUM COMPOUNDS

Preparing peroxides

Angew. Chem. Int. Ed. <http://doi.org/fz4psr> (2012)

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The reactivity of organometallic compounds with oxygen has been explored since the early days of organometallic chemistry. Peroxides — in which the metal centre bears an $-OOR$ ligand (where R is an alkyl group) — are very reactive, rendering the insertion of dioxygen into metal–carbon bonds difficult to control, and intermediates and mechanisms difficult to identify. Studies on zinc complexes have shown that peroxides could be stabilized, and in turn isolated, with chelating ligands. But although the *in situ* generation of cadmium

peroxides has also been suggested, their characterization has remained elusive.

Kieran Molloy and co-workers at the University of Bath have now obtained crystals of organo-cadmium peroxides, and unambiguously characterized them by X-ray diffraction. They relied on a tridentate ligand featuring two stabilizing dimethyl-amino groups and a hydroxyl moiety (bdmap), previously shown to support the formation of an organozinc peroxide.

The complex $\{[MeCd(bdmap)_3]_2 \cdot CdMe_2\}$ was first produced by reaction of dimethyl cadmium and bdmap in a 4:3 ratio, and subsequently submitted to an atmosphere of dry oxygen at low temperature. This yielded a double peroxide in which two $\{MeCd(bdmap)_2\}$ units are held together by a $\{Cd(OOMe)\}$ moiety. This complex was in turn subjected to an O_2 -insertion step, this time at room temperature, which led to a triple peroxide complex in which the central cadmium ion adopts a $\{MeCdO_3\}$ coordination environment. Such a pentadentate peroxy unit has not been observed previously with zinc, presumably because it can't accommodate the higher coordination numbers that cadmium can.

Both organo-cadmium peroxides rapidly decompose into oxo clusters.

AP

BULLVALENES

Shape-shifting sensors

Chem. Sci. <http://doi.org/hr7> (2012)

Bullvalene is a small hydrocarbon molecule that exists as a mixture of degenerate isomers that rapidly interconvert through a series of rearrangement reactions. Although it contains only 10 carbon atoms and 10 hydrogen atoms, there are more than a million different arrangements that those atoms can adopt to form the same skeletal structure.

Jeffrey Bode and co-workers at ETH Zürich have previously shown that bullvalene derivatives with two porphyrin substituents exhibit a relatively high affinity for C_{60} . These derivatives dynamically adapt to form a larger population of isomers in which the porphyrins are capable of sandwiching a C_{60} molecule. Identifying a specific high-binding isomer in a system with so many similar structures is not straightforward, but by including a ^{13}C label in the bullvalene core, Bode and co-workers are now able to perform pattern-based sensing with NMR spectroscopy. The

MICROSCOPY

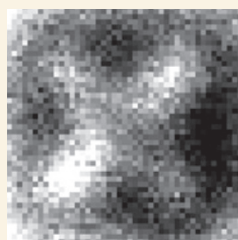
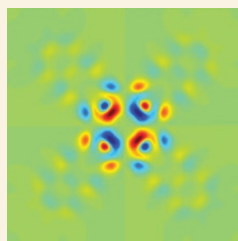
Force microscopy takes charge

Nature Nanotech. **7**, 227–231 (2012)

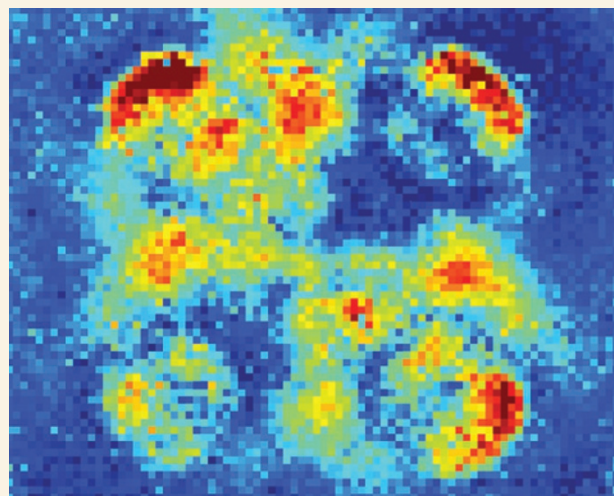
In the past few years, advances in scanning and force microscopies have enabled scientists to view individual molecules with unprecedented clarity. As well as providing stunning pictures of molecular features few thought it would ever be possible to 'see', the techniques have already been used to identify a natural product.

Now, Fabian Mohn and colleagues at IBM Research in Zürich have probed within a molecule and revealed its charge distribution. They used a combination of scanning tunnelling microscopy (STM), atomic force microscopy and Kelvin probe force microscopy (KPFM) to study naphthalocyanine. This molecule, which can be electrically switched between tautomers that differ in the position of hydrogen atoms in the central ring, was placed on an insulating sodium chloride layer on a copper surface.

On examining naphthalocyanine using STM, Mohn and colleagues found that increasing the bias voltage meant they could see an asymmetry in the centre of the molecule, reflecting the position of the



hydrogen atoms (pictured, top left). Moving to using KPFM with a copper probe tip, they found extra charge density in the regions of the molecule perpendicular to the hydrogen atoms (pictured, bottom left). Mohn and colleagues electrically switched the position of the hydrogen atoms and saw the charge density swap to the other regions.



To obtain even more resolution, they used a CO-functionalized tip. The images obtained (such as that pictured on the right) reveal the location of the charge density more precisely, showing that the outermost aromatic ring and the four outer nitrogen atoms take the lion's share. NW
Corrected after print: 26 April 2012

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Correction

In the Research Highlight 'Force microscopy takes charge' (N. Withers *Nature Chem.* **4**, 336; 2012), Fabian Mohn's surname was spelled incorrectly. Corrected in the HTML and PDF versions after print, 26 April 2012.