SCANNING PROBE MICROSCOPY

Seeing the charge within

The distribution of electric charge within a single naphthalocyanine molecule has been revealed by researchers using a combination of three types of microscopy and theoretical modelling.

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Atomic force microscopy is a well-established tool that can image surfaces with atomic resolution and, in some cases, even allow individual bonds to be visualized[1]. In a spectacular experiment, reported in *Nature Nanotechnology*, researchers at IBM Research-Zurich have now directly imaged the charge distribution within a molecule[2] using Kelvin probe force microscopy[3]. This opens the door to using a combination of atomic force microscopy and Kelvin probe force microscopy to make quantitative measurements of the charge distribution in individual molecules. Such measurements will lead to a deeper understanding of fundamental processes that are relevant to catalysis, organic photovoltaic materials and molecular electronics.

The IBM team — Fabian Mohn, Leo Gross, Nikolaj Moll and Gerhard Meyer — used three forms of microscopy, plus *ab initio* modelling, to investigate the charge distribution in a simple model system: naphthalocyanine. Kelvin probe force microscopy allows the local contact potential difference between the tip and the sample[4] — which is closely related to the distribution of charge on the surface — to be measured (Fig. 1). Previously, Kelvin probe force microscopy has been used by a number of groups to measure the charge states of nanoscale objects: the IBM group measured the charge state of an atom on a surface[5], whereas a collaboration between researchers in Berlin and Milan measured the charge state of a point defect[6], and a group in Toulouse measured the charge state of a molecule[7]. What sets the latest work apart is that Mohn and co-workers have observed charge distribution with submolecular resolution and elegantly shed new light on the origin of the contrast in the images produced by a Kelvin probe force microscope.

The IBM team imaged a naphthalocyanine molecule on a thin insulating layer of sodium chloride on a copper substrate using three forms of microscopy, and compared the results with electron density maps calculated by *ab initio* methods, leading to a textbook example of the different contrast mechanisms and, therefore, the different types of information

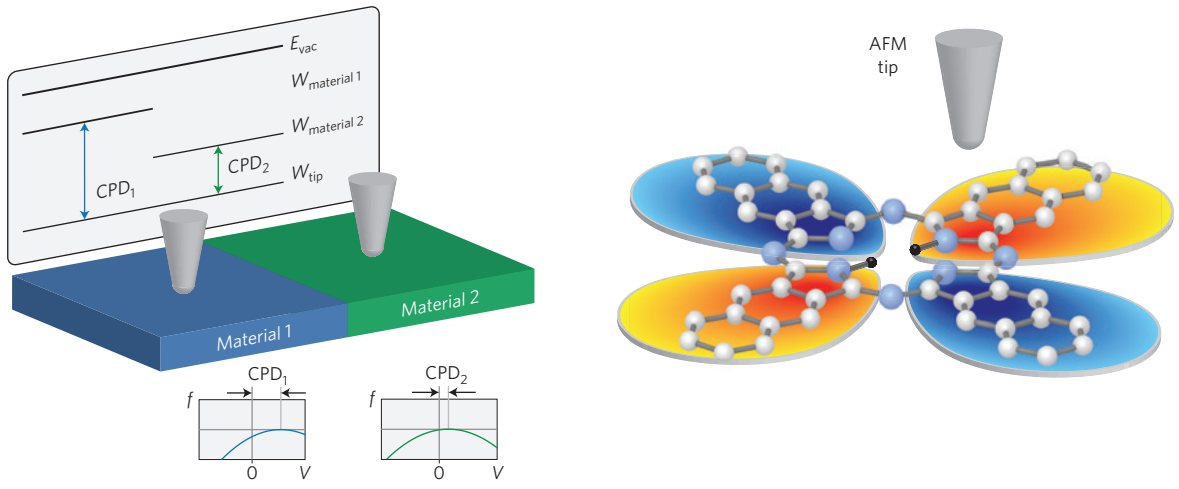

Figure 1 | Kelvin probe force microscopy. Mohn and co-workers measured the resonant frequency f of an atomic force microscope (AFM) as a function of the electrical bias V between the AFM and the sample at each point on a 64 × 64 grid covering an area of 2.5 nm × 2.5 nm above a naphthalocyanine molecule ($C_{48}H_{26}N_8$) on a surface (right: the carbon atoms in the molecule are shown in white; the nitrogen atoms are blue and the two inner hydrogen atoms are black; the other hydrogens are not shown). At each point on the grid the resulting curve is a parabola, with f reaching a maximum value when V is equal to the local contact potential difference (CPD). Mohn and co-workers used the values of the CPD at each point in the grid to build up an image of the charge distribution within the molecule (see Figs 2 and 3 in ref. 2). The main experimental challenge was to maintain stability and correct for drift for long enough to acquire an image, which currently takes 30 h. The Kelvin probe force microscopy technique used by Mohn and co-workers seems to measure the electrical field generated by the charge distribution within the molecule: this electric field is slightly stronger along one axis of the naphthalocyanine molecule (blue lobes) and slightly weaker along the other axis (yellow–red lobes). The CPD is equal to $W_{material}$–W_{tip}, where $W_{material}$ is the workfunction of the sample material (that is, the energy needed to move an electron at the Fermi energy to infinity, E_{vac}) and W_{tip} is the workfunction of the material used to make the tip of the AFM. Two materials can have different workfunctions, and hence different CPDs, even when atomic force microscopy or scanning tunnelling microscopy suggest that they have the same structure: in this example, the blue material has a larger workfunction (and, therefore, a larger CPD) than the green material. Figure courtesy of J. Hedberg, McGill University.

that can be extracted using these techniques. In brief, scanning tunnelling microscopy measures the electron density of states at the Fermi energy; atomic force microscopy measures the total electron density; and Kelvin probe force microscopy seems to measure the electrical field generated within a molecule.

The naphthalocyanine molecule has two hydrogen atoms at its centre and four lobes that form a cross shape (Fig. 1). There are small differences between the axis defined by the two lobes that are parallel to the two inner hydrogen atoms (the H lobes) and the axis defined by the lobes that are perpendicular (the N lobes). Moreover, these axes can be switched back and forth by using a scanning tunnelling microscope to move the two hydrogen atoms to new positions: this process is known as tautomeric switching. (There are four positions where a hydrogen atom can sit at the centre of a naphthalocyanine molecule, but two hydrogen atoms cannot sit at adjacent positions, so the molecule has two different structures, which are known as tautomers.)

Switching from one state to the other led to significant changes in the Kelvin probe force microscope images. This strongly supports the conclusion that the local contact potential measured by Kelvin probe force microscopy reflects the charge distribution within the molecule. Moreover, it leads to an intuitive interpretation of the submolecular contrast seen by the IBM team: local variations in the charge density lead to a locally varying electric field, and thus to local variations in the contact potential between the tip and the sample. The contrast in Kelvin probe force microscopy thus reflects the distribution of all electrons and nuclei within the molecule. This makes Kelvin probe force microscopy much more sensitive to small asymmetries in the charge distribution than atomic force microscopy, where the contrast is a function of the total electron density.

Just as in ultrahigh-resolution atomic force microscopy, the key to obtaining submolecular resolution is to attach a carbon monoxide molecule to the tip of the atomic force microscope and to use very small oscillation amplitudes (to maximize the effect of the tip–sample interaction on the oscillation frequency). The IBM team compared images collected by an atomic force microscope with a single-atom tip and an atomic force microscope with a carbon monoxide molecule attached to its tip: the images were similar for large tip–sample separations, but they were noticeably different at smaller separations. The quantitative interpretation of Kelvin probe force microscopy data thus remains an open challenge.

The prospect of using Kelvin probe force microscopy to study charge-transfer complexes at the molecular scale seems bright. In fact, with a calculated quadrupole moment of 0.14 e nm^2, naphthalocyanine could be viewed as a classical charge-transfer complex because one of its axes is positively charged (that is, donor-like) and the other is negative (acceptor-like). Exposing a charge-transfer complex to light, and then imaging the resulting charge separation with submolecular resolution, now looks to be a realistic possibility, although there are a number of challenges to overcome. For example, it took ~10^5 s (30 h) to collect the data for the images reported by Mohn and co-workers, whereas typical timescales for charge separation are ~10^{-12} s (although recombination times are typically much slower). However, some of the pump–probe and stroboscopic techniques that are currently used in ultrafast electrostatic force microscopy might be able to bring this dream closer to reality.

In the shorter term, it should be possible to use Kelvin probe force microscopy to visualize the redistribution charge caused by the formation and breaking of chemical bonds, which could prove invaluable in catalysis. ❐

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