Scientists image the charge distribution within a single molecule for the first time

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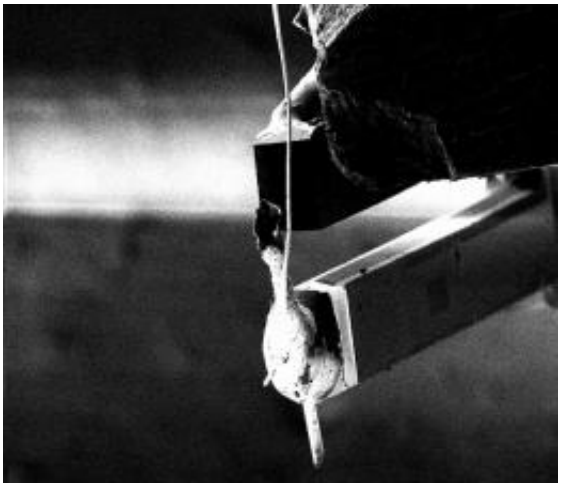


For their experiments the IBM scientists used their home-built combined scanning tunneling microscope (STM) and atomic force microscope (AFM). In this focused ion beam micrograph, the tip attached to a tuning fork can be seen. The tuning fork measures a few millimeters in length. The tiny tip measures only a single atom or molecule at its apex.

(PhysOrg.com) -- IBM scientists were able to measure for the first time how charge is distributed within a single molecule. This achievement will enable fundamental scientific insights into single-molecule switching and bond formation between atoms and molecules. Furthermore, it introduces the possibility of imaging the charge distribution within functional molecular structures, which hold great promise for future applications such as solar photoconversion, energy

storage, or molecular scale computing devices.

As reported in in the journal *Nature* Nanotechnology, scientists Fabian Mohn, Leo Gross, Nikolaj Moll and Gerhard Meyer of IBM Research – Zurich directly imaged the charge distribution within a single naphthalocyanine molecule using a special kind of atomic force microscopy called Kelvin probe force microscopy at low temperatures and in ultrahigh vacuum.

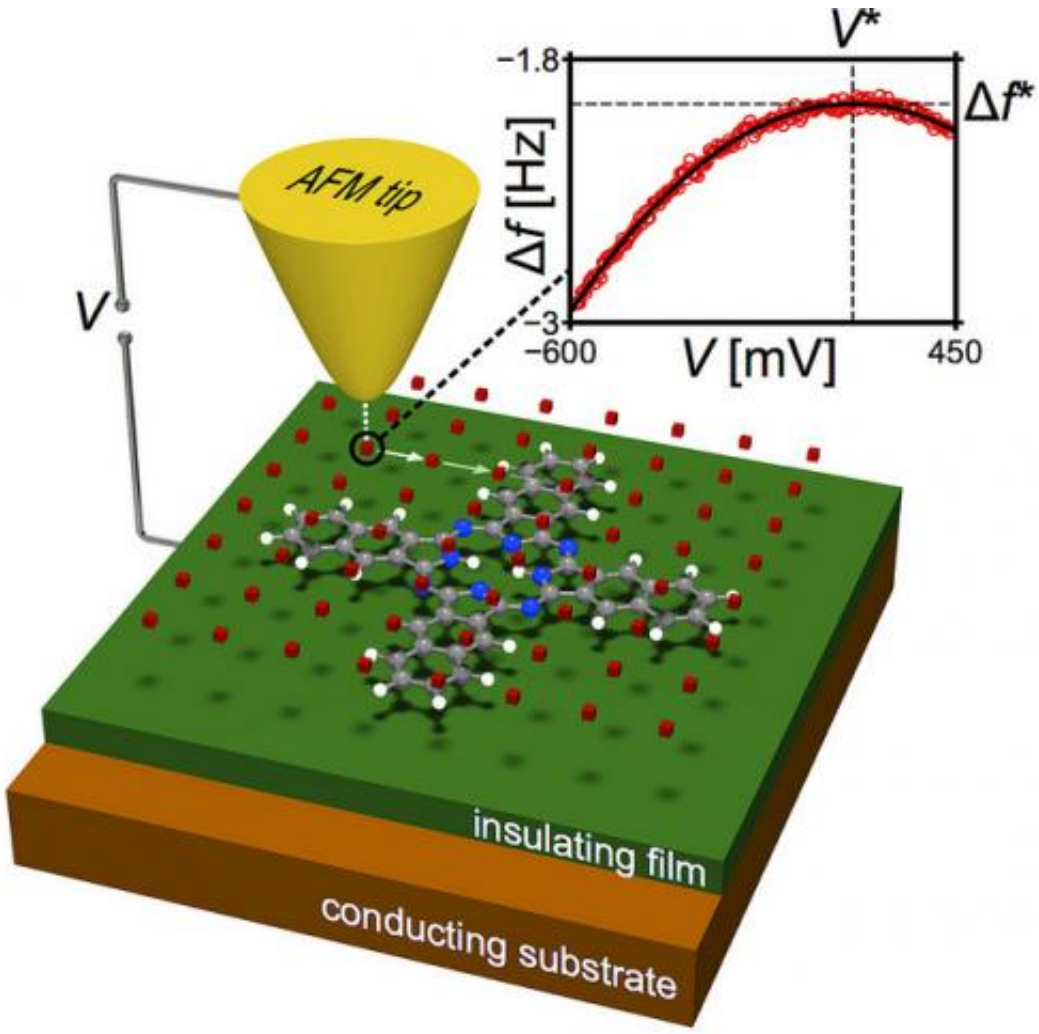
Whereas scanning tunneling microscopy (STM) can be used for imaging electron orbitals of a molecule, and atomic force microscopy (AFM) can be used for resolving its molecular structure, until now it has not been possible to image the charge distribution within a single molecule.

“This work demonstrates an important new capability of being able to directly measure how charge arranges itself within an individual molecule”, states Michael Crommie, Professor for Condensed Matter Physics at the University of Berkeley. “Understanding this kind of charge distribution is critical for understanding how molecules work in different environments. I expect this technique to have an especially important future impact on the many areas where physics, chemistry, and biology intersect.”

In fact, the new technique together with STM and AFM provides complementary information about the molecule, showing different properties of interest. This is reminiscent of medical imaging techniques such as X-ray, MRI, or ultrasonography, which yield complementary information about a person’s anatomy and health condition.

“The technique provides another channel of information that will further our understanding of nanoscale physics. It will now be possible to investigate at the single-molecule level how charge is redistributed when individual chemical bonds are formed between atoms and molecules on

surfaces. This is essential as we seek to build atomic and molecular scale devices," explains Fabian Mohn of the Physics of Nanoscale Systems group at IBM Research – Zurich.



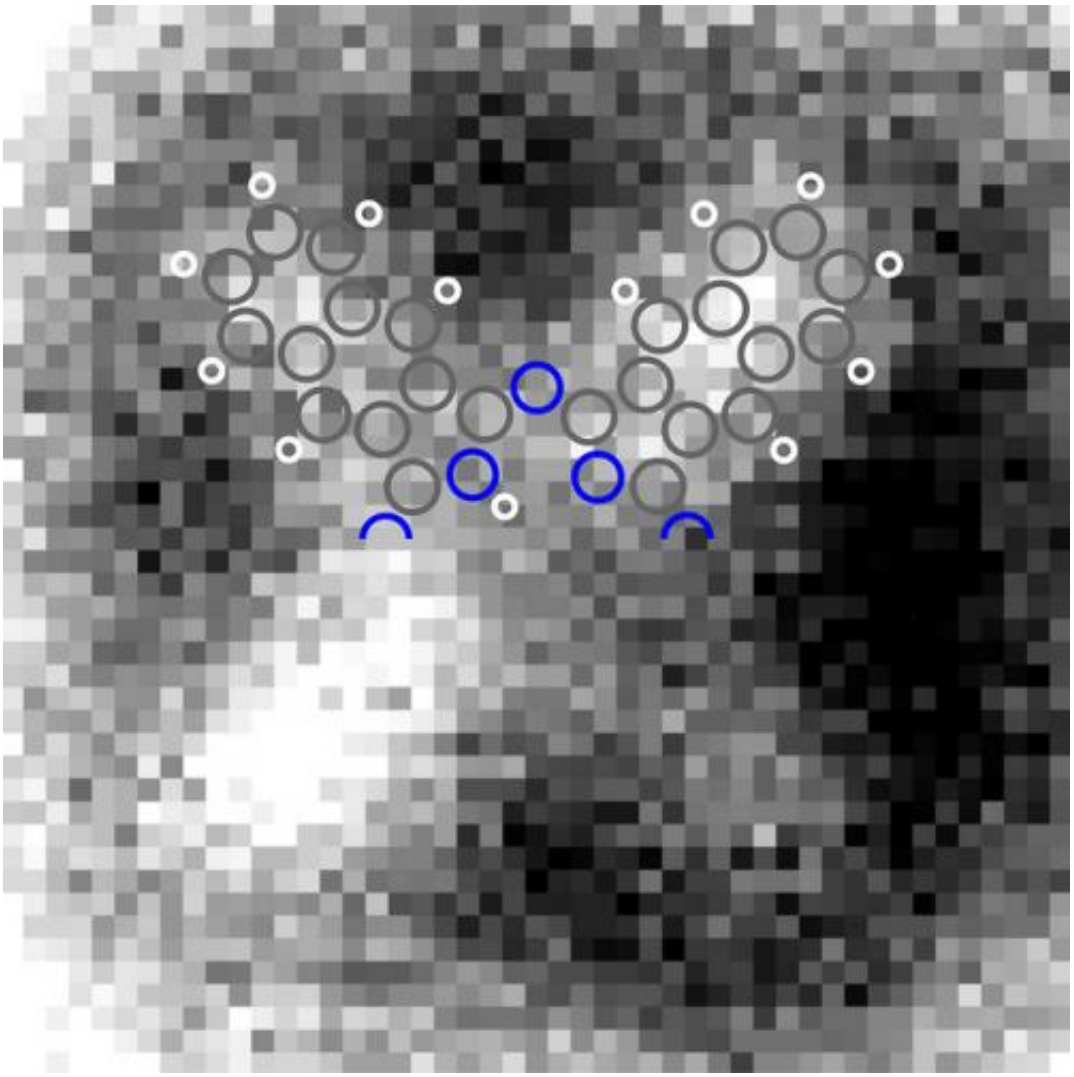
Schematic of the measurement principle. At each tip position, the frequency shift is recorded as a function of the sample bias voltage (inset, red circles). The maximum of the fitted parabola (inset, solid black line) yields the KPFM signal V* for that position. Image courtesy of IBM Research - Zurich

The technique could for example be used to study charge separation and charge transport in so-called charge-transfer complexes. These consist of two or more molecules and are subject of intense research activity because they hold great promise for applications such as energy storage or photovoltaics.

Gerhard Meyer, a senior IBM scientist who leads the STM and AFM research activities at IBM Research – Zurich adds:"The present work marks an important step in our long term effort on controlling and exploring molecular systems at the atomic scale with scanning probe microscopy." For his outstanding work in the field, Meyer recently received a European Research Council Advanced Grant. These prestigious grants support "the very best researchers working at the frontiers of knowledge" in Europe.*

Taking a closer look

To measure the charge distribution, IBM scientists used an offspring of AFM called Kelvin probe force microscopy (KPFM).



Kelvin probe force microscopy images of the tautomerization switching of naphthalocyanine. It is the first time that the charge distribution within a single molecule can be resolved. When a scanning probe tip is placed above a conductive sample, an electric field is generated due to the different electrical potentials of the tip and the sample. With KPFM this potential difference can be measured by applying a voltage such that the electric field is compensated. Therefore, KPFM does not measure the electric charge in the molecule directly, but rather the electric field generated by this charge. The field is stronger above areas of the molecule that are charged, leading to a greater KPFM signal. Furthermore, oppositely charged areas yield a different contrast because the direction of the electric field is reversed. This leads to the light and dark areas in the micrograph. Image courtesy of IBM Research - Zurich

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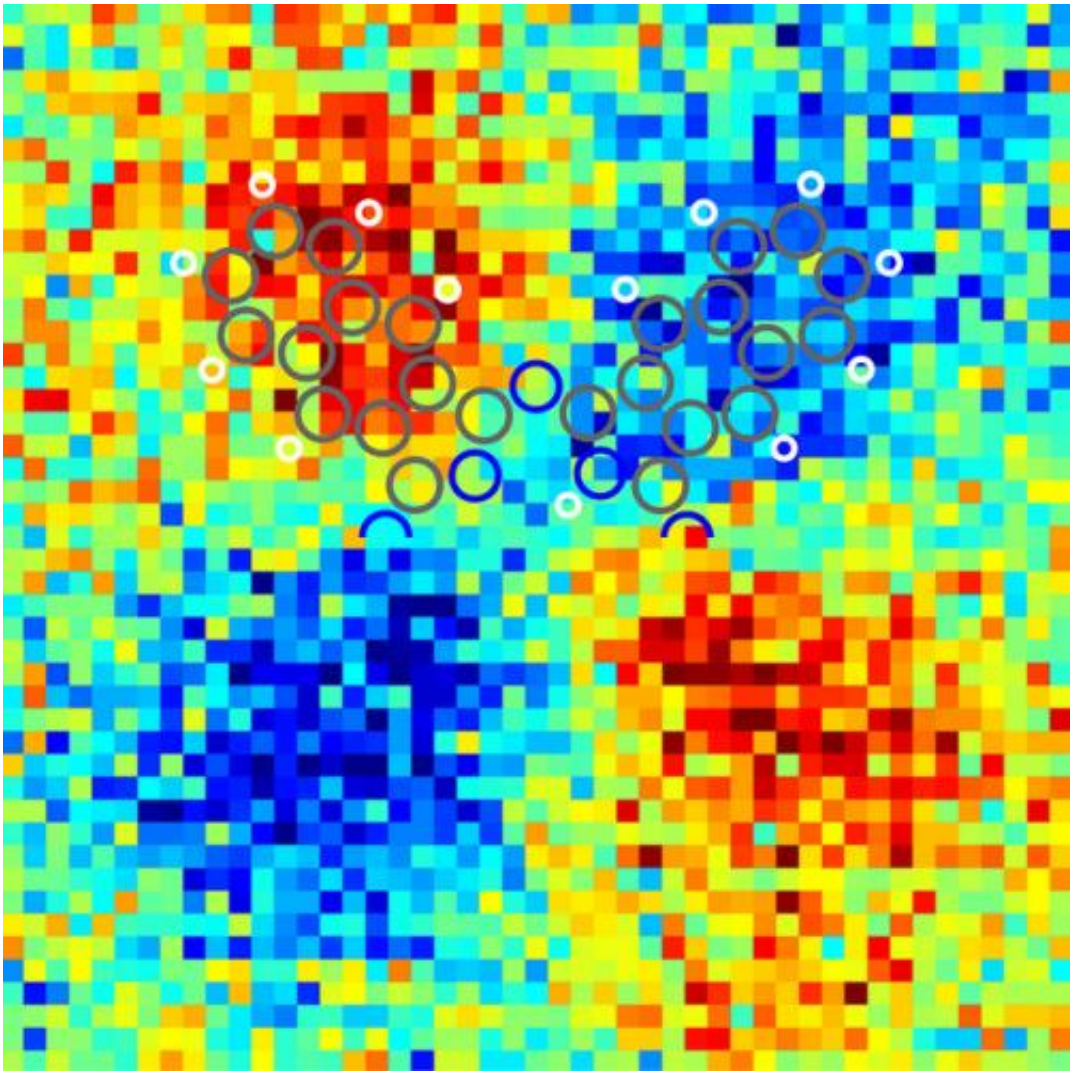

Asymmetry in the Kelvin probe force microscopy images of the tautomerization switching of naphthalocyanine. It is the first time that the charge distribution within a single molecule can be resolved. When a scanning probe tip is placed above a conductive sample, an electric field is generated due to the different electrical potentials of the tip and the sample. With KPFM this potential difference can be measured by applying a voltage such that the electric field is compensated. Therefore, KPFM does not measure the electric charge in the molecule directly, but rather the electric field generated by this charge. The field is stronger above areas of the molecule that are charged, leading to a greater KPFM signal. Furthermore, oppositely charged areas yield a different contrast because the direction of the electric field is reversed. This leads to the red and blue areas in the micrograph. Image courtesy of IBM Research - Zurich

Naphthalocyanine, a cross-shaped symmetric organic molecule which was also used in IBM's single-molecule logic switch**, was found to be an ideal candidate for this study. It features two hydrogen atoms opposing each other in the center of a molecule measuring only two nanometers in size. The hydrogen atoms can be switched controllably between two different configurations by applying a voltage pulse. This so-called tautomerization affects the charge distribution in the molecule, which redistributes itself between opposing legs of the molecules as the hydrogen atoms switch their locations.

Using KPFM, the scientists managed to image the different charge distributions for the two states. To achieve submolecular resolution, a high degree of thermal and mechanical stability and atomic precision of the instrument was required over the course of the experiment, which lasted several days. Moreover, adding just a single carbon monoxide molecule to the apex of the tip enhanced the resolution greatly. In 2009, the team has already shown that this modification of the tip allowed them to resolve the "anatomy"—the chemical structures—of molecules

with AFM. The present experimental findings were corroborated by first-principle density functional theory calculations done by Fabian Mohn together with Nikolaj Moll of the Computational Sciences group at IBM Research – Zurich.

Pushing the frontiers of nanoscience with scanning probe techniques

“With the emergence of scanning probe microscopy and related techniques in the 1980s, the door to the nanoworld was pushed wide open,” stated the introductory article in the first edition of Nature Nanotechnology in 2006***.

The STM and its offspring the AFM are the two workhorses of atomic and molecular scale research. The STM, which was invented by Gerd Binnig and Heinrich Rohrer at IBM Research – Zurich in 1981, allowed scientists for the first time to image individual atoms on a surface. The revolutionary microscope, for which the two scientists received the 1986 Nobel Prize in physics, has expanded the boundaries of our knowledge by revealing the properties of surfaces and molecules or atoms adsorbed thereon with atomic resolution.

The STM, however, is not a traditional microscope. Rather than showing a direct image, it uses a very sharp tip—having only a single or a few atoms at its apex—to scan the surface of a material. By bringing the tip very close to the sample surface and applying a bias voltage, a flow of current can be measured between the tip and the sample due to the quantum mechanical effect of electron tunneling. Keeping this tunneling current constant and recording the vertical movement of the tip across the surface makes it possible to study the structure of the surface, atom by atom. See video demonstration

The STM can even be used to manipulate individual atoms and molecules. In 1989, IBM scientist Don Eigler in a famous experiment used his newly developed low-temperature STM to position 35 xenon atoms to spell "IBM". See video demonstration

In 1985, the AFM was invented by Gerd Binnig. Rather than measuring a tunneling current, the AFM uses a sharp tip attached to a cantilever to measure the tiny forces between the tip and the sample to create an image. See video demonstration

As the STM and AFM evolved, their capabilities and those of related scanning probe techniques have greatly enhanced the abilities of scientists to explore a wide variety of atomic-scale structures and properties. They offer amazing potential for prototyping complex functional structures and for tailoring and studying their electronic and chemical properties on the atomic scale, which will be essential to create new nanoscale devices and systems that will outperform those that exist today in information technology, medicine, environmental technologies, the energy industry and beyond.

More information: The scientific paper entitled "Imaging the charge distribution within a single molecule" by F. Mohn, L. Gross, N. Moll, and G. Meyer was published online in *Nature Nanotechnology*, DOI 10.1038/NNANO.2012.20 (26 February 2012).

* cited from the ERC press release, January 24, 2012: erc.europa.eu/sites/default/fi … _adg2011_results.pdf

** P. Liljeroth, J. Repp, and G. Meyer, "Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules", Science 317, p.1203–1206 (2007), DOI: 10.1126/science.1144366

*** C. Gerber, H. P. Lang, “How the doors to the nanoworld were opened”, Nature Nanotechnology 1, p.3 - 5 (2006), DOI: 10.1038/nnano.2006.70

Provided by IBM