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Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy

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We report a real-space visualization of the formation of hydrogen bonding in 8-hydroxyquinoline (8-hq) molecular assemblies on a Cu(111) substrate, using noncontact atomic force microscopy (NC-AFM). The atomically resolved molecular structures enable a precise determination of the characteristics of hydrogen bonding networks, including the bonding sites, orientations, and lengths. The observation of bond contrast was interpreted by ab initio density functional calculations, which indicated the electron density contribution from the hybridized electronic state of the hydrogen bond. Intermolecular coordination between the dehydrogenated 8-hq and Cu adatoms was also revealed by the submolecular resolution AFM characterization. The direct identification of local bonding configurations by NC-AFM would facilitate detailed investigations of intermolecular interactions in complex molecules with multiple active sites.

Intermolecular bonding has been experimentally characterized mainly through crystallography via x-ray and electron diffractions, as well as through infrared, Raman, nuclear magnetic resonance, and near-edge extended absorption fine-structure spectroscopy (1, 2). At the single-molecule level, state-of-the-art scanning tunneling microscopy (STM) is a technique widely used to elucidate the molecular structure and chemical specificity of surface-immobilized species (3–5). The bonding interactions between molecules in self-assemblies were also evidenced in scanning tunneling hydrogen microscopy (6). Nevertheless, most of the characterization techniques are, thus far, more sensitive to the covalent structures of the molecules, and in many cases, theoretical calculations of intermolecular interaction are also not as precise as those for covalently bound species.

Recently, noncontact atomic force microscopy (NC-AFM) has achieved superior resolution in real-space that has enabled the identification of the chemical structure, adsorption configurations, and chemical transformation of individual molecules (7–10). For example, the difference in bond order in aromatic molecules was distinguished via electron-density-dependent Pauli repulsion with CO-functionalized NC-AFM tips (11), and AFM tomography revealed the angular symmetry of a chemical bond on surface (12). Herein, we used NC-AFM to investigate the intermolecular interactions in 8-hydroxyquinoline (8-hq) (Fig. 1A) molecular assemblies formed on Cu(111) at liquid helium (LHe) and room temperatures (RTs). The hydrogen bonds (H bonds) formed between 8-hq molecules were characterized by high-resolution AFM images, and the local bonding configuration was determined with the atomic precision. We also observe the coordination complex composed of dehydrogenated 8-hq and Cu adatoms. The observations were validated with ab initio density functional theory (DFT) calculations.

The 8-hq molecules deposited on Cu(111) at LHe temperature appeared as individual molecules or randomly assembled aggregates (fig. S1) (13). For the single 8-hq molecules, DFT calculations suggest that the molecular plane is slightly tilted with respect to the substrate because of the weak interactions between the OH group and the N atom of 8-hq and Cu(111) surface. Compared with the calculated total electron density of the molecule shown in Fig. 1B, the STM image (Fig. 1C) exhibits no internal features of the heterocycle because the tunneling current is primarily sensitive to the local density of states near the Fermi level. In contrast, the AFM images with a CO-functionalized tip revealed the submolecular structure of 8-hq through the short-range Pauli repulsive force (Fig. 1, D to F). The calculated electron density map (Fig. 1B) qualitatively reproduces the observed contrast in frequency shift (Δf) in the AFM image. Here, the AFM sensor measured the total force of three components (7, 14): (i) the long-range attractive electrostatic forces, responsible for the overall negative Δf background in the images; (ii) the attractive van der Waals force, which contributed to the dark halo surrounding the molecule without atomic corrugation; and (iii) the short-range Pauli repulsion, which contributed to the atomic contrast of molecular structure with respect to the metal substrate. When the tip height was decreased (Fig. 1, D to F), the increasing proportion of Pauli repulsion in the total force enhanced contrast in the AFM images. Although a quantitative understanding of the AFM imaging mechanism is nontrivial, a direct correlation between the AFM images and the chemical structure of a molecule can still be rationalized. In our case, the heterocyclic skeleton and the hydroxyl group of 8-hq were readily distinguished. The pyridine ring in the heterocycle is slightly pronounced, which may be caused by tilting of the molecular plane on the substrate. A further interpretation of the topography need also take into account the difference in electron density of the phenol ring and the pyridine ring.

The AFM images of the 8-hq molecular aggregates (Fig. 2, A and B) reveal bonding-like...
features between adjacent molecules in the assemblies that were reproduced in all of the observations, whereas these features were not observed in the corresponding STM images at the same regions [see fig. S3 and (13)]. A close examination of the position and orientation of the bonding-like structures indicated that they coincide very well with the expected locations of H bonds formed between 8-hq molecules (Fig. 2, C and D). The results from recent theoretical and experimental investigations suggest that the H bond has both an electrostatic origin and a partly covalent character (15, 16). Despite extensive studies of H bonding in supramolecular and biological systems using various techniques, direct identification of the bonding configuration of the H bond in real-space is elusive (17).

The formation of covalent bonds in unimolecular reactions has recently been reported (10). The bond contrast in the AFM images has been qualitatively compared with the bond order, where the higher local electron density leads to stronger Pauli repulsion exerted on the tip (10, 11). In our observations, the Δψ contrast of these intermolecular bonds is comparable to that of intramolecular covalent bonds in the constant-height images, as also evident in the force spectroscopy measurements (fig. S4) (13). Given the clearly identified bonding sites, we could perform a detailed analysis of the H bond configurations (18).

The apparent bond lengths of the intermolecular H bonds were measured, as summarized in fig. S5 (13), and can be used as a reference for data acquired through other characterization methods to understand the effect of the substrate on H bonding (19).

Our study also revealed differences in the H bond configurations in the 8-hq self-assemblies on surface and those in the bulk crystal. In addition to the conventional H bond, which involves only the OH group and N atom of 8-hq, we also observed H bond formation between the aromatic rings and the OH group or N atom. These results provide direct evidence for the influence of substrate on the intermolecular bonding characteristics (1, 20).

We performed DFT calculations on two types of molecular clusters to further understand the origin of the contrast of intermolecular H bonds in our observation. In Fig. 3A, the paired 8-hq molecules were bonded by two H bonds of O-H···N, as illustrated by the black dotted lines in Fig. 3B (21). The calculated total electron density plotted in Fig. 3C shows a bright spot at the position of the O atom and a protrusion toward the adjacent molecule around the position of the N atom. The in-plane plot of the differential charge density (Fig. 3D), which is defined as $\rho_{\text{DCD}} = \rho_{\text{Total}} - \rho_{\text{Substrate}} - \sum \rho_{\text{Molecule}}$ (where $\rho_{\text{Total}}$ is the electron density of 8-hq adsorbed on the Cu substrate, $\rho_{\text{Substrate}}$ is the electron density of the Cu substrate, and $\sum \rho_{\text{Molecule}}$ is the electron density of 8-hq), reflects the charge redistribution after the bond forms between two 8-hq molecules and indicates that covalent-like characteristics developed from charge reductions near the H and N atoms that led to charge accumulation between them. As expected, the enhanced charge density at N and O is consistent with the charge transfer from H to N and O atoms, whereas the charge accumulation offers an additional repulsive force to the tip at the region along the H bonding direction. Thus, the observed line feature between the two 8-hq molecules in the AFM image is attributed to a joint effect that results from both the covalent charge in H···N and the charge transferred from H to N and O. The above interpretation is primarily based on the simplified mechanism of tip-to-sample Pauli repulsion (22). A quantitative understanding of the image contrast of an H bond may require further consideration of the relaxation of the CO molecule attached on the tip apex (11). In another configuration (Fig. 3, E to H), DFT calculations also concluded electron density redistribution in the proximity of the newly formed bond. In this unconventional C-H···N hydrogen bond, the effect of charge accumulation between N and H atoms is much weaker compared with that in the O-H···N hydrogen bond (1, 15).

When 8-hq was deposited onto Cu(111) at RT, the molecules formed highly ordered dimers and trimers, which are distinct from the H-bonded aggregates formed at the LHes temperature. No internal structures of these dimers and trimers could be resolved in the high-resolution STM images (fig. S8). The size of these molecular aggregates did not correspond to those of the H-bonded clusters from DFT calculations. The AFM images of the dimers and trimers (Fig. 4, A and B) allowed the identification of the outer edge of the molecules corresponding to the positions of H or C atoms, but the inner edge was blurred.

The dehydrogenation of the hydroxyl group on Cu(111) at RT has been widely reported (23). Our experimental and theoretical calculation results also suggest that the individual 8-hq molecules exist as radical species that are weakly bound to the substrate by O and N atoms in a tilted orientation (fig. S7). Alternatively, the highly mobile 8-hq radicals coordinate with Cu adatoms on surface to form an organometallic complex (24). The proposed chemical structures of a dimer and trimer, respectively, in which the dehydrogenated 8-hq is assembled via an O(N)-Cu bond, are shown in Fig. 4, C and D. The calculated geometric sizes of these 8-hq complexes agree well with the AFM observations.

When the AFM is operated in the Pauli repulsion regime, the repulsive force from the outermost-shell valence electrons is also relevant to $V^2 \varphi_\text{ electrons}(r)$, which is in the form of kinetic energy. Here, $\varphi_\text{ electrons}(r)$ is the electron wave function of the nth eigenstate of the sample. The kinetic energy reflects the localization property of electrons, which can be estimated by the electron localization function (ELF) (25). The ELF of the dimer
and trimer exhibited strongly localized electron density donation from N to Cu, whereas the electrons between the Cu-Cu bonding are rather delocalized (Fig. 4, E and F). We attributed the bonding features in the central regions of the dimer and trimer to N-Cu coordination bonding, similar to the observed formation of the metal-organic coordinate bond excited by inelastic electrons (9, 26). According to the ELF, the O-Cu bond is strongly polarized, and the most shared electrons of the bond are localized around O; thus, the AFM signal is negligible. The C-H···O hydrogen bonds formed in the dimer and trimer were detectable in AFM because of the localized electrons around O and H.

Structural details—including the molecular conformation, the bond configuration, and the interacting sites on the functional groups—acquired from high-resolution noncontact AFM images provided useful insights into the mechanisms of molecular assembly and recognition. Because the H bond is ubiquitous in nature and central to biological functions, the present technique may provide an important and complementary characterization method for unraveling the fundamental aspects of molecular interactions at the single-molecule level. The observation of H bonding in real-space may also stimulate theoretical discussion about the nature of this intermolecular interaction.

References and Notes

One-Dimensional Electrical Contact to a Two-Dimensional Material

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Heterostructures based on layering of two-dimensional (2D) materials such as graphene and hexagonal boron nitride represent a new class of electronic devices. Realizing this potential, however, depends critically on the ability to make high-quality electrical contact. Here, we report a contact geometry in which we metalize only the 1D edge of a 2D graphene layer. In addition to outperforming conventional surface contacts, the edge-contact geometry allows a complete separation of the layer assembly and contact metallization processes. In graphene heterostructures, this enables high electronic performance, including low-temperature ballistic transport over distances longer than 15 micrometers, and room-temperature mobility comparable to the theoretical phonon-scattering limit. The edge-contact geometry provides new design possibilities for multilayered structures of complimentary 2D materials.

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tomically thin two-dimensional (2D) materials (1, 2)—such as graphene, hexagonal boron nitride (BN), and the transition metal dichalcogenides (TMDCs)—offer a variety of outstanding properties for fundamental studies and applications. More recently, the capability to assemble multiple 2D materials with complementary properties into layered heterogeneous structures presents an exciting new opportunity in materials design (2–11), but several fundamental challenges remain, including making good electrical contact to the encapsulated 2D layers. Electrically interfacing 3D metal electrodes to 2D materials is inherently problematic. For graphene devices, the customary approach is to metalize the 2D surface. However, graphene lacks surface bonding sites, so the lack of chemical bonding and strong orbital hybridization leads to large contact resistance (12–19). In multilayer structures, the requirement to expose the surface for metallization presents additional restrictive demands on the fabrication process. For example, encapsulated BN/graphene BN heterostructures (BN-G-BN) need to be assembled sequentially so as to leave the graphene surface accessible during metallization, because no process to selectively remove the BN layers has been identified. Moreover, polymers used during both the layer assembly and lithography steps are difficult to remove (20). Their presence can degrade the electrical contact (21, 22) and channel mobility (23) and contaminate the layer interfaces, causing bubbles and wrinkles that multiply with each successive layer, limiting typical device size to ~1 μm (2, 4, 24).

We demonstrate a new device topology where 3D metal electrodes are connected to a 2D graphene layer along the 1D graphene edge (14, 19, 25–27). We first encapsulate the graphene layer in BN. The entire multilevel stack is then etched to expose only the edge of the graphene layer, which is in turn metalized. This contact geometry is similar to that in conventional semiconductor field-effect transistors (FETs), where doped 3D bulk regions make lateral contact to a 2D electron gas. Although carrier injection is limited only to the 1D atomic edge of the graphene sheet, the contact resistance is remarkably low (as low as 100 ohm μm in some devices). The edge-contact process also allows a complete separation of the layer assembly and contact metallization processes, which permits implementation of a polymer-free layer assembly method. Combining these two techniques, we fabricated graphene devices with unprecedented performance exhibiting room-temperature mobility up to 140,000 cm2/Ns and sheet resistivity below 40 ohms per square at n > 4 × 1013 cm−2, comparable to the theoretical limit imposed by acoustic phonon scattering. At temperatures below 40 K, we observed ballistic transport over length scales longer than 15 μm.

The edge-contact fabrication process is illustrated in Fig. 1A. Beginning with a BN-G-BN heterostructure, a hard mask is defined on the top BN surface by electron-beam lithography (EBL) of a hydrogen-silsesquioxane (HSQ) resist. The regions of the heterostructure outside of the mask are then plasma-etched (see supplementary materials section 1.2) to expose the graphene edge. Finally, metal leads (1 nm Cr/15 nm Pd/60 nm Au) are deposited by electron beam evaporation to make electrical contact along this edge (other metal combinations showed inferior performance) (table S1). In Fig. 1B, a cross section scanning transmission electron microscope (STEM) image of a representative device shows the resulting geometry of the edge-contact. In the magnified region, electron energy-loss spectroscopy (EELS) mapping confirms that the graphene and metal overlap at a well-defined interface. From the angle of the etch profile (−45°), we expect that the graphene terrace is exposed only 1 to 2 atoms deep. Within the resolution of the STEM image, there is no evidence of metal diffusion into the graphene/BN interface, confirming the truly edge