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Cooperative Modulation of Electronic Structures of Aromatic Molecules Coupled to Multiple Metal Contacts

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We use cryogenic scanning tunneling microscopy and spectroscopy and density-functional theory calculations to inspect the modulation of electronic states of aromatic molecules. The molecules are self-assembled on a Cu(111) surface forming molecular networks in which the molecules are in different contact configurations, including laterally coupled to different numbers of coordination bonds and vertically adsorbed at different heights above the substrate. We quantitatively analyze the molecular states and find that a delocalized empty molecular state is modulated by these multiple contacts in a cooperative manner: its energy is down shifted by ~ 0.16 eV for each additional lateral contact and by ~ 0.1 eV as the vertical molecule-surface distance is reduced by 0.1 Å in the physisorption regime. We also report that in a molecule-metal-molecule system the bridging metal can mediate the electronic states of the two molecules.

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The electronic structure of a molecule is subject to the coupling of the molecule with its environment [1,2]. A thorough understanding of this issue is of great importance in the field of molecular electronics considering that the characteristics of molecular devices are determined by the molecular electronic structures and their contacts [3]. For example, a metal-molecule interface may strongly modify the molecular orbitals, and consequently, molecular conductance [3]. As one of the ultimate goals of molecular electronics is to realize single-molecule devices, wherein single molecules are connected to electrodes, one needs to understand how molecule-electrode coupling affects the molecular electronic structures at the level of individual molecules. Scanning tunneling microscopy and spectroscopy (STM-STs) have been used to address this challenging problem owing to their capability of resolving geometric details of molecule-metal contacts and simultaneously measuring the single-molecule electronic properties. These studies revealed in great detail that the molecular frontier orbitals are modulated when the molecules are coupled to metal atoms or a metal substrate [4–14]. So far, most of these studies focused on molecules coupled to one or at most two metal contacts. In future single-molecule devices, however, the molecules will be mostly connected to multiple electrodes, for example, to source, drain and gate electrodes in a field-effect transistor [15–20]. It is highly desirable to study individual molecules that are coupled to multiple metal contacts.

In this Letter, we report on a combined study with low-temperature STM-STs and density-functional theory (DFT) of the electronic structures of extended aromatic

molecules that are coupled with multiple metal contacts. The molecules are attached laterally to two or three neighboring molecules through metal-ligand coordination bonds and vertically to a metal surface at different distance. These parameters can be separately varied in the experiments, so this system provides an arena to inspect the contribution of different contacts individually and collectively. We used two-dimensional metal-organic coordination networks self-assembled on a Cu(111) surface as our model system [21]. As shown in Fig. 1(a), molecules of 1,3,5-tris(pyridyl)benzene (TPyB) self-assemble into a honeycomb network structure, wherein the adjacent TPyB molecules are linked via pyridyl-Cu-pyridyl coordination bonds involving the molecules' N atoms [22,23]. In the interior of the network domains each molecule is laterally coupled through three coordination bonds while at the edge of the network domains each molecule is coupled through two coordination bonds. Besides the lateral coupling, vertically the molecules are adsorbed at different sites of the Cu(111) atomic lattice (hollow or top) and at different adsorption heights, which gives rise to different coupling strengths ranging from weak physisorption to strong chemisorption. Hence the molecules are in contact with multiple metal contacts, which mimic multi-terminal single-molecule devices. We used low-temperature (4.9 K) STM to resolve the lateral and vertical contact configuration of the molecules and used STS to reveal the molecular electronic structures. We applied DFT calculations (with van der Waals interactions included) to simulate and interpret the experimental data [21].

FIG. 1 (color online). (a) STM topograph of TPyB-Cu coordination networks on the Cu(111) surface ($26 \times 15 \text{ nm}^2$, -0.1 V and 0.2 nA). The unit cells of the networks are shown as dashed rhombuses. (b)–(c) Top and side views of the DFT optimized structures of phase I and phase II, respectively.

Figure 1(a) reveals that there are two types of coordination networks, denoted as phase I (upper part) and phase II (lower part). Both phases have the same honeycomb shape and are stabilized by the same type of coordination bonds but have different periodicity and orientation with respect to the Cu(111) atomic lattice. The molecules in phase I exhibit uniform apparent height of $1.40 \pm 0.05 \text{ \AA}$ above the surface, while in phase II the molecules residing in two triangular sublattices have heights of 1.53 ± 0.05 and $0.95 \pm 0.05 \text{ \AA}$, respectively. We denote the molecules in phase I as type A molecules and the molecules with higher and lower apparent heights in phase II as type B and type C molecules, respectively; we also use subscripts to denote the number of coordination bonds formed by a molecule, as indicated in Fig. 1(a). Phase I has a periodicity (the distance between two neighboring cavities) of $2.652 \pm 0.025 \text{ nm}$ along the $\langle 11\bar{2} \rangle$ directions of the Cu(111) surface, corresponding to a $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ unit cell. The centers of two adjacent A molecules are separated by $6a$ along $\langle 10\bar{1} \rangle$ directions, implying that all the A molecules adsorb at equivalent sites on the Cu(111) atomic lattice. By contrast, phase II has a periodicity of $2.531 \pm 0.058 \text{ nm}$ along the $\langle 10\bar{1} \rangle$ directions, corresponding to a (10×10) unit cell. Accordingly, the B and C molecules are registered at two different surface sites, as shown below, top vs hollow sites. The DFT optimized structures with one-layer Cu substrate (for details, see Supplemental Material [21]) of phase I and phase II on a Cu(111) surface are shown in Figs. 1(b) and 1(c), respectively. The A₃ molecule is physisorbed with its central benzene ring at a hollow site and has an adsorption height of $3.29 \text{ \AA}$. The B₃ molecule is also physisorbed but with its central benzene ring at a top site and an adsorption height of $3.40 \text{ \AA}$. The C₃ molecules are

FIG. 2 (color online). Experimentally measured typical STS (a) and DFT calculated PDOS (Fermi level is aligned with respect to the vacuum level of a six-layer slab system) (b) at the central benzene of *M* (noncoordinated), A₂, A₃, and B₃ molecules, respectively. The curves are shifted vertically for clarity. (c) STS and DFT simulated PDOS maps of A₃ at indicated bias voltages and energies ($4 \times 4 \text{ nm}^2$, 0.4 nA); the dashed outline marks one unit cell of phase I.

chemisorbed with their central benzene ring at a hollow site and forming chemical bonds with three underlying Cu atoms in the surface layer. The distance between the central benzene of the C₃ molecule and the Cu surface is $2.59 \text{ \AA}$, which is $0.81 \text{ \AA}$ smaller than for B₃ molecules, in fair agreement with the experimental observed apparent height difference of $0.6 \text{ \AA}$.

Figure 2(a) shows typical STS spectra measured with the tip positioned at the center of four types of molecules: A₂, A₃, B₃ and noncoordinated molecules (*M*) that can be found in the network cavities (the measured height of *M* is $1.42 \pm 0.05 \text{ \AA}$ and the calculated height is $3.30 \text{ \AA}$). The common STS features of these species are a strong peak at $\sim 2.0 \text{ V}$ and a shoulder at $\sim 1.5 \text{ V}$. We used STS mapping to elucidate the origin of the 2.0 and 1.5 V features. Figure 2(c) shows the STS mappings of A₃ molecules at 1.50 and 2.05 V. One can see that the 1.50 V mapping exhibits a hexagonal ring shape with a depression at the center of the molecule, whereas the 2.05 V mapping has a protrusion at the center position surrounded by a truncated hexagonal ring. These characteristics suggest that the 1.5 V shoulder might be assigned to the pyridyl states (STS acquired with the tip positioned at the pyridyl arms show a more pronounced 1.5 V feature; see Supplemental Material [21]) and the 2.0 V peak to the states that are delocalized at the central aromatic ring and the pyridyl arms. We carried out DFT calculations to verify this

assignment. As shown in Fig. 2(b), the central benzene ring of an A_3 molecule contributes a local projected density of states (PDOS) peak at 2.10 eV (the pyridyl arms contribute to a peak at 1.20 eV; see Supplemental Material [21]). The simulated PDOS maps at 1.20 and 2.10 eV are shown in Fig. 2(c). The 1.20-eV PDOS map exhibits six dots in a hexagonal arrangement, which corroborates the STS mapping at 1.50 V. The 2.10-eV PDOS map exhibits three closely spaced dots at the central aromatic ring and two dots at each pyridyl arm, which resembles the STS mapping at 2.05 V. Based on the combined STS and DFT results, we conclude that the strong peak at ~ 2.0 V resolved in the STS spectra originates from a molecular state that is delocalized at the central benzene ring and the three pyridyl arms.

We evaluated the modulation of this delocalized state in response to the lateral contacts through comparing the STS spectra of A_2 , A_3 , and M molecules as these species possess different numbers of coordination bonds. This state is at 2.54 V for an M molecule [Fig. 2(a)], and shifted to 2.25 V (2.07 V) for an A_2 (A_3) molecule. Hence the molecular state is down shifted towards the Fermi level cumulatively with an increasing number of coordination bonds. Figure 2(b) shows the calculated PDOS of the central benzene of M , A_3 and A_2 molecules. One can see that the PDOS peaks are at 2.83, 2.50, and 2.10 eV for M , A_2 , and A_3 , respectively, which corroborates the peak down shift observed in STS. Shifts of molecular states induced by metal-molecule contact have been reported in different systems [4–14], but cumulative shifts by multiple contacts have rarely been reported. To our knowledge, the only example is that in K_xC_{60} complexes the C_{60} states are down shifted cumulatively due to stepwise charge transfer (each attached K atom donates $\sim 0.6e$ to the C_{60} host) [10]. DFT calculations conclude that there is no significant charge transfer between the TPyB molecule and the coordinated Cu atoms (less than 0.1 electrons from Bader charge analysis), thus excluding that the observed energy level shifts are caused by charging effects. The STS map at 2.05 V and the PDOS map at 2.10 eV confirm that the shifted state is delocalized over the entire molecule, thus, when a pyridyl ligand forms a bond with Cu, the orbital hybridization modulates (down shifts) this delocalized state. This state is further down shifted when the second and third pyridyl ligands form bonds with Cu [21]. Therefore the cumulative shifts of the molecular states can be attributed to hybridization between the delocalized molecular orbital and the multiple coordinated Cu atoms.

The different adsorption heights and adsorption mechanisms of the three types of molecules (A , B , and C) allow inspecting the influence of vertical couplings on the molecular electronic states. To exclude the effects of lateral coupling, we focus on the molecules that form the same number of coordination bonds. First we compare A_3 with B_3 . As shown in Figs. 2(a) and 2(b), both experimental STS

and theoretical PDOS reveal that the B_3 molecule has a major peak at higher energy than A_3 does (STS: 2.23 vs 2.07 V; PDOS: 2.53 vs 2.10 eV). Because both species are weakly adsorbed on the surface at a distance larger than 3.2 Å, the effects of registration site (A_3 at a hollow site and B_3 at a top site) is negligible. The observed different electronic characteristics exemplify that a subtle change of the molecular adsorption height (0.13 Å measured and 0.11 Å calculated) effectively modulates the molecular states [24]. Furthermore, we observed that some C molecules (denoted as C^H) have an apparent height higher than the normal C_3 molecules, as revealed in the line profile of Fig. 3(a). DFT calculations confirm that C_3 molecules can exist in a metastable adsorption configuration at a larger height. Figure 3(b) shows the structure of this metastable configuration, which is physisorbed and has an adsorption height of 3.10 Å. Since both the normal C and the C^H molecules are adsorbed at hollow sites, these two species allow us to compare directly molecules adsorbed at the same site but at different heights, and, most interestingly, to evaluate how the molecule-to-contact

FIG. 3 (color online). (a) Upper panel: STM topograph showing a C_3^H molecule within a phase-II network (8×8 nm², -0.1 V and 0.2 nA); Lower panel: Profile along line shown in upper panel. (b) Top and side views of the DFT calculated metastable structure of phase II. (c) Experimentally measured STS at the central benzene of C_3^H and C_3 molecules. The curves are shifted vertically for clarity. (d) Experimentally measured energy levels of the delocalized molecular state for molecules of different configurations (square for M , circle for A , triangle for B , and diamond for C). (Note that the measured peak positions of different molecules of the same type fall in a range as indicated by the multiple data points.) The sloping lines are plotted to guide the eye.

distance influences the molecular electronic structures. Figure 3(c) shows STS spectra measured at the centers of C_3 and C_3^H molecules. The STS spectrum of C_3 is rather different from those for the other species [cf. Fig. 2(a)]: it does not show the pronounced peak around 2.0 V; instead, it has a shoulder feature around 2.0 V. Apparently the molecular states of C_3 are highly hybridized with the substrate as a result of the chemisorptions. In contrast, the STS spectrum of the physisorbed C_3^H molecule has a peak at 2.0 V resembling those of M , A , and B molecules.

Overall, B_3 , A_3 , C_3^H , and C_3 molecules experience gradually increased coupling with the Cu substrate, leading to a gradual shift of the molecular states towards lower energy, which finally hybridize with the Cu substrate states. These results are consistent with the general understanding that the stronger the coupling, the more severe is the perturbation of the intrinsic molecular states. As the adsorption of benzene on Cu(111) has been well documented [25–30], here we attempt to understand our results using benzene as a reference. Benzene is weakly adsorbed with an adsorption height of $3.6 \sim 3.7 \text{ \AA}$ [27,29,30]. Toyoda *et al.* predicted that a reduction of the benzene-Cu distance lowers the work function at a rate of $\sim 0.1 \text{ eV}/0.1 \text{ \AA}$ when the distance falls in the range of $2.5\text{--}3.5 \text{ \AA}$ [29]. Our data allow us to test this prediction since the energy position of the STS resolved states depends on the effective work function. Figure 3(d) summarizes the shifting trend of the delocalized molecular state in different contact configurations as illustrated by the inset model. One can see that the energy levels of M , A_2 , and A_3 (these species have the same adsorption height but are laterally coupled to different numbers of bonds) down shift at a rate of $\sim 0.16 \text{ eV}/\text{bond}$, while the energy levels of B_3 , A_3 , and C_3^H (these species are laterally coupled to the same number of bonds but adsorbed at different adsorption heights) down shift at a rate of $\sim 0.1 \text{ eV}/0.1 \text{ \AA}$ as the adsorption height is reduced in the physisorption regime, in good agreement with the theoretical prediction.

We found that some C molecules exhibit a bistable character; i.e., they may switch their state between the metastable C_3^H state and the stable C_3 state under stimulation of tunneling electrons. We made use of this switching behavior to investigate molecular state modulation in response to a *trans* effect. Trans effect refers to a ligand-metal-ligand (L-M-L) system in which the L-M bond on one side can be modified by the M-L bond at the opposite (trans) position [31,32]. The inset in Fig. 4(a) shows that the B_3 molecule in the center is surrounded by two normal C_3 molecules [C_3 (I) and C_3 (II)] and one C_3^H molecule [C_3^H (III)], as confirmed by the STS spectra in Fig. 4(a). This B_3 molecule shows a peak at 2.07 V, which is 0.16 V down shifted compared with the standard B_3 molecules that are surrounded by three C_3 molecules. As this B_3 molecule has the same height as the standard B_3 molecules

FIG. 4 (color online). (a) STS acquired at the centers of a B_3 molecule and its surrounding three C_3 molecules two normal C_3 (I&II) molecules and one C_3^H (III) molecule, shown and identified in the inset STM topograph ($4 \times 4 \text{ nm}^2$, 1.0 V, and 0.2 nA). (b) As (a) but molecule C_3 (II) has converted to a high geometry: C_3^H (II). The curves are shifted vertically for clarity.

[cf. Fig. 3(a)], the 0.16 V down shift is not ascribed to the vertical coupling effect. In addition, laterally the coordination number remains unchanged as well. We thus attribute the 0.16 V down shift of the molecular state of this B_3 molecule to a trans effect, that is, as the C molecule changes its state from normal C_3 to C_3^H , or vice versa, the states of the B_3 molecule that coordinate to the Cu at the trans position are modulated accordingly. The inset in Fig. 4(b) shows a B_3 molecule surrounded by one C_3 molecule and two C_3^H molecules. The B_3 molecule shows a peak centered at 1.78 V, which is 0.45 V down shifted compared with the standard B_3 molecules. This example, on one hand, confirms the trans effect and, on the other hand, demonstrates that the trans effect is cumulative as well; i.e., the B_3 states can be stepwise down shifted when coordinated with an increasing number of trans C_3^H ligands. As discussed before, the energy down shift of the delocalized state accompanies stronger molecule-contact coupling and the observed trans effect suggests that a C_3^H molecule enhances the pyridyl-Cu coupling of the B_3 molecule at the trans position. The mechanism of the trans effect is not fully understood and requires further study.

In summary, these coordination networks self-assembled on a Cu(111) surface provide a unique model system for systematic examination of molecules coupled with multiple metal contacts. Our studies, which discriminate the contribution of different contacts, reveal that a delocalized molecular state is modulated cooperatively by the electrodes.

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