

## Inspecting Cu-Coordination Induced Perturbation of Molecular Ligand Orbitals in Supramolecular Assemblies at a Sub-molecular Resolution

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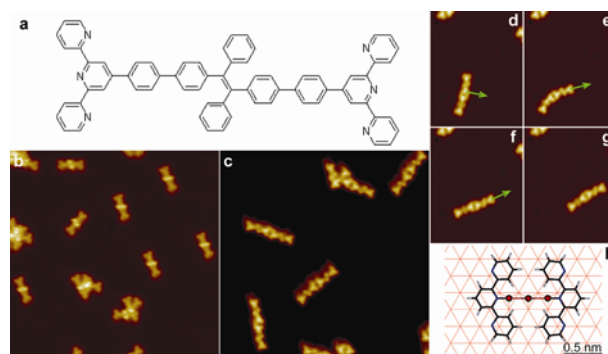
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The use of metal–ligand coordination for the formation of complex supramolecular structures, including polygonal clusters, polyhedrons, cages, grids and frameworks, has evolved into one of the most widely used strategies in designing new materials.<sup>1,2</sup> Besides structural design, coordination also bestows new electronic characteristics to the metal centers as well as the molecular ligands, leading to new properties, including catalytic, magnetic and optical properties.<sup>2</sup>

In recent years, metal–ligand coordination has been employed on surfaces to assemble low-dimensional supramolecular systems.<sup>3</sup> This approach has generated a wide range of coordinative architectures, for example, one-dimensional chains, two-dimensional polygons and networks.<sup>4</sup> In the meantime, the electronic properties of the metallic coordination centers have been studied by advanced physical techniques such as X-ray photoemission spectroscopy, scanning tunneling spectroscopy and density functional theory calculations.<sup>5</sup> However, the influence of the metal coordination on the electronic properties of the molecular ligands is rarely addressed in these low-dimensional coordination systems.<sup>6</sup> Here we report on a low-temperature (5K) scanning tunneling microscopy/spectroscopy (STM/STS) study of the electronic states of molecular ligands in a metal–ligand coordination system. Sub-molecular resolved molecular states manifest a localized perturbation of molecular orbitals induced by the metal coordination.

The molecule used in our study is 1,2-bis(4'-(4'-2,2':6',2''-terpyridyl)-biphenyl-4-yl)-1,2-tetraphenylethene (BTP-TPE), as shown in Figure 1a. This molecule has two symmetric terpyridine (*tpy*) end moieties that are attached to a central tetra-phenyl ethylene (*tpe*) moiety through phenyl moieties. As deposited on a Cu(111) surface which was cooled down to 200 K, single molecules were observed exclusively as shown in Figure 1b. (The clusters are formed due to the presence of *cis*-conformers). As deposited at the same surface held at 300 K, chain-like structures were observed, as shown in Figure 1c. Since Cu adatom density increases exponentially with the surface temperature, the different assembly behavior observed on the surface at 300 K and 200 K suggests that Cu adatoms play a crucial role in the formation of the chain-like structures. (Note that the observed molecular mobility is appreciable at 150 K). It is known that the *tpy* moiety coordinates with transition metals, including Cu,<sup>7,8</sup> so we conclude that the Cu adatoms present on the 300-K surface coordinated the *tpy* moieties of the BTP-TPE molecules, forming the chain-like structures.<sup>4c,9</sup>

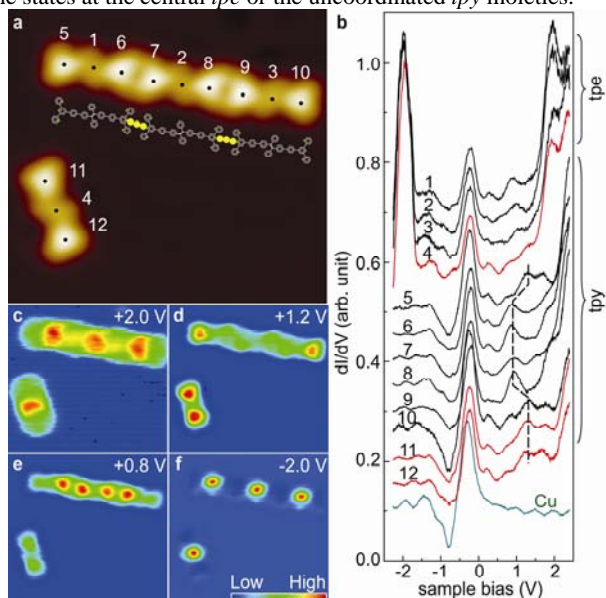


**Figure 1.** (a) Structure of BTP-TPE molecule. (b and c) STM topograph (30×30 nm<sup>2</sup>, -0.5 V, 0.5 nA) of single molecules and molecular chains. (d)–(g) (16×20 nm<sup>2</sup>, -0.2 V, 0.5 nA) Manipulating a dimer. The green arrows indicate the lateral tip displacement for each manipulation. (h) DFT calculated *tpy*-Cu trimer-*tpy* coordination.

To examine the intermolecular bonding nature of the chains, we carried out manipulation experiments on the individual chains. First the STM tip was located above a molecule within a chain at a short tip-to-molecule distance, then the STM feedback loop was opened and the tip was moved laterally by few nanometers. Figure 1d to 1g shows a sequence of such manipulations. One can see that the chain was displaced, rotated and even bent as an entity under the manipulations. This experiment evidences that the lateral inter-molecular interaction within the chain is strong enough to overcome the diffusion barrier of the molecules on the surface. Hydrogen bonds and metal coordination are two candidates for such a strong inter-molecular interaction. A careful inspection of the geometry and chemistry of the adjacent molecules excludes that the chains are stabilized by inter-molecular hydrogen bonds (cf. Figure 1h). The Cu-*tpy* coordination is further supported by our density functional theory (DFT) calculations. As shown in Figure 1h, the calculation shows that two *tpy* ligands form a stable coordination with three Cu atoms.<sup>10</sup> Figure 2a is a STM image showing a trimeric chain along with a single molecule. A structural model is plotted at the same scale as the STM topograph. The Cu atoms were not resolved in the STM topograph at this image condition, presumably due to the electronic and (or) geometric effects that were reported before.<sup>11</sup>

We measured STS  $dI/dV$  spectra of the single molecule and of the trimeric chain at specific positions, i.e., the left, right and central sites of each molecule, as indicated by the numbers in Figure 2a, which correspond to the side *tpy* and the central *tpe* moieties of each molecule. These site-dependent STS spectra

reveal the local electronic characteristics of individual molecules. As shown in Figure 2b, on the single molecule, the spectra taken at the two *tpy* exhibit similar features, namely two peaks at 1.3 V and 1.5 V, and a rise above 2.0 V, while at the central *tpe* STS shows a peak at -2.0 V and another peak at 2.0 V. The -2.0-V peak can be assigned as the highest occupied molecular orbital (HOMO) and the peaks at 1.3 V, 1.5 V (*tpy*) and 2.0 V (*tpe*) can be assigned as the low-lying unoccupied orbitals. On the trimeric chain, the STS at the two terminal *tpy* (positions 5 and 10) exhibits the same features as those of the single molecule's *tpy*, while at positions 6, 7, 8 and 9 STS show a peak at 0.9 V, which is 0.4 V down-shifted compared with those of the single molecule's *tpy*, as highlighted by the dashed line. At the central *tpe* positions 2, 3 and 4, the spectra are the same as for the single molecule's *tpe*. Figure 2b clearly indicates that the Cu coordination modifies the electronic states locally at the *tpy* moieties which are coordinated to Cu atoms, but does not affect the states at the central *tpe* or the uncoordinated *tpy* moieties.



**Figure 2.** (a) ( $12.5 \times 11.5 \text{ nm}^2$ ,  $-0.2 \text{ V}$ ,  $0.5 \text{ nA}$ ) STM topograph of a BTP-TPE trimer and a single molecule. A tentative model of the trimer is shown, with yellow dots representing the Cu atoms. The black dots indicate the tip positions while measuring the STS curve. (b)  $dI/dV$  tunneling spectra measured at the positions indicated by the numbers in (a). The spectra measured on the trimer and on the single molecule are shown in black and red lines, respectively. The peak at  $-0.5 \text{ V}$  is from the tip. (c)–(f) STS maps of the same area as (a) at the indicated bias voltages.

The modified electronic characteristics can be visualized in STS spatial maps as shown in Figure 2c to 2f. At a bias voltage of  $-2.0 \text{ V}$  or  $2.0 \text{ V}$ , the single molecule and the molecules in the trimeric chain show a common feature – a bright protrusion at the center of the molecules, which is given by the strong STS signal at the central *tpe*. At a bias voltage of  $0.8 \text{ V}$ , the two *tpy* at the chain terminals show similar contrast as the single molecule's *tpy*, while other *tpy* in the chain appear brighter. This STS contrast is reversed at a bias voltage of  $1.2 \text{ V}$ . These maps clearly reveal that the Cu coordination only perturbs the ligand orbitals of the coordinated moieties. It is worthwhile to note that on the sample of chain-like structures, there exist single molecules too. Some of these single molecules also exhibit the similar modified *tpy* states, which indicates the attachment of Cu atom(s) to single molecules.

The downwards shift of the low-lying unoccupied orbital can be understood conceptually within ligand field theory: the overlap of the *tpy* orbitals and the Cu atomic orbital lowers the energy level of the former. The fact that the Cu-coordination induced perturbation is of a local nature appears through the breaking of

the symmetry of the BTP-TPE molecular orbitals. It can be explained by the particular orbital configuration of the BTP-TPE molecule. The molecule has two degenerate low-lying unoccupied orbitals that are localized at the two *tpy* moieties (Supporting Figure S1). When a Cu atom (ion) coordinates to one of the *tpy* moieties, the orbital localized at this moiety is lowered (bonding orbital). The degenerate orbital which is localized at the opposite *tpy* moiety, however, is not affected because the spatial overlap of this state with the Cu atomic states is negligible, while the orbitals localized at the *tpe* moiety are only slightly affected. (Supporting Figures S2, S3). Further analysis is being conducted to clarify the details of the coordination.

In summary, we have demonstrated that the low-lying molecular orbitals of the *tpy* ligand are downshifted by the Cu coordination. Due to the localized character of the orbitals, the perturbation only occurs at the moieties that are directly involved in the coordination. Our results exemplify, for the first time to our knowledge, the effects of metal-coordination on the ligand electronic states at a sub-molecular level.

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Supporting Information Available: Methods. Supporting Figures. Full author list of Reference 5(c). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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