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Donor/Acceptor Properties of Aromatic Molecules in Complex Metal-Molecule Interfaces

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ABSTRACT: We present a comparative study, combining density functional theory (DFT) with scanning tunneling microscopy/spectroscopy (STM/STS), of two aromatic molecules bonded with a variable number of Cu adatom(s) on a Cu(111) surface. The two molecules, 1,3,5-tris(pyridyl)benzene (TPyB) and 1,3,5-tris(4-radical-phenyl)benzene (TPB), possess the same aromatic backbone but bond weakly vs. strongly to Cu with different terminal groups. We find that TPyB and TPB exhibit, respectively, small vs. large charge transfers between surface and molecule; this contrast results in opposite shifts in the calculated density of states distributions and thus explains the opposite STS peak shifts observed in our experiments. The two molecules exhibit weak donor vs. strong acceptor characters, respectively. This work provides fundamental understanding, at a single-molecule level, of the principle that selecting specific functional groups can effectively and intentionally modify the molecular electronic properties in a wider class of molecule-metal interfaces.

KEYWORDS: molecule-metal interface, donor/acceptor, self-assembly, scanning tunneling spectroscopy, density-functional theory

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INTRODUCTION

Molecule-metal interfaces (MMIs) play crucial roles in modulating the electronic properties of organic molecules\textsuperscript{1-21} that are in contact with metals and are therefore of great practical relevance for fabricating functional organic electronic devices. For example, a strong electron-accepting molecule adsorbed onto a metal electrode\textsuperscript{7} can increase the surface work function and reduce the hole-injection barrier so as to enhance the efficiency of organic light emitting diodes. Molecules and molecular layers adsorbed on metal surfaces are prototypical MMIs; they can be viewed as perpendicular MMIs since the molecules interact with the underlying surface. Various perpendicular MMIs have been studied extensively.\textsuperscript{22-23} Nevertheless, the real MMIs are much more complicated than this simplified picture. In particular, in addition to interacting with the underlying surface, the molecules frequently are bonded chemically to metal adatoms laterally, and thus can be viewed as lateral MMIs. For example, Wang et al.\textsuperscript{10} revealed that a lateral MMI formed with single Cu adatoms locally shifts molecular orbitals within single molecules. Hence, the molecular electronic properties are expected to be modulated by the combination of both types of MMIs. It is thus highly desirable to investigate the electronic structures of molecules that are subjected to such complex MMI configuration.

In this combined experimental and theoretical work, we address this issue by studying two molecules with similar aromatic backbones but different terminal groups. We use a molecular orbital as an indicator to demonstrate that the molecules exhibit donor-like vs. acceptor-like behavior depending on the nature of both the perpendicular and lateral MMIs. These results provide insights to understand the mechanism of molecular electronic properties in complex MMIs.

Sample preparation and scanning tunneling microscopy (STM) characterization were performed in a commercial ultrahigh vacuum tunneling microscope system (Omicron). A single-crystal Cu(111) was cleaned by cycles of Ar\textsuperscript{+} ion sputtering and annealing to 800 K. 1,3,5-tris(pyridyl)benzene (TPyB) and 1,3,5-tris(4-bromophenyl)benzene (TBB) molecules were deposited on the clean Cu(111) surface, which was held at room
temperature using an organic molecular beam deposition source at 210 and 250 °C respectively. After annealing at 120 °C, the samples were characterized at cryogenic temperature (4.9 K). The STM topographic data were acquired in constant current mode. The differential tunneling spectra dI/dV were measured using a lock-in amplifier with a sine modulation of 1.5 kHz at 5 mV.

As illustrated in Scheme 1, TPyB can directly bind with single Cu atoms diffusing on the surface (which we call Cu “adatoms” and label as Cu$_{\text{ada}}$) forming coordination N-Cu bonds (with now immobile Cu “adatoms” that act like anchors, being strongly bonded to the underlying surface in so-called three-fold hollow sites), as we already reported.$^{10}$ TBB, however, is first debrominated, leaving behind the 1,3,5-tris(4-radical-phenyl)benzene (TPB) that can also bind with Cu$_{\text{ada}}$ forming organometallic C-Cu bonds. Furthermore, similar twofold-coordinated honeycomb networks of both molecules with linking Cu$_{\text{ada}}$ can be formed when the deposited molecules are self-assembled on the surface, as illustrated in Scheme 2.

Scheme 1. Top: TPyB binds incrementally with Cu adatoms. Bottom: TBB first debrominates to form TPB, which then binds incrementally with Cu adatoms. Some C atoms are labeled 1-6 representing C$_1$-C$_6$, while the N atoms are labeled explicitly N$_4$-N$_6$. 

Scheme 2. Twofold coordination of Cu adatoms: TPyB (left) and TPB (right) can form similar repeating honeycomb networks with linking Cu adatoms. The atomic labels correspond to those in Scheme 1.

Figure 1. STM topographs and STS spectra measured at the center of TPB (corresponding data for TPyB are reported in Reference 10). (a) A large-scale STM topograph of islands of networks formed out of TPB and Cu_ada on a Cu(111) surface (80 × 160 nm²). (b) Zoomed-in STM topograph of the ladder-like (L) dimer phase (16 × 16
of the honeycomb (H) phase (16 × 16 nm$^2$). The STM topographs were scanned at 1.2 V and 1.5 nA. (d) Further zoomed-in STM topographs of TPB attachment configurations with Cu$_{\text{ada}}$ (3.2 × 3.2 nm$^2$). To avoid confusion, it should be noted that the bottom panel is not part of the ladder phase, but is a defect in the ladder phase which has 3 unshared Cu atoms. (e) From top to bottom, STS spectra measured at the center of the TPB molecules of the five structures shown in (d) from top to bottom.

The structures formed by TPyB were reported before. Here we present the structures formed by TPB. Figure 1a shows that the TPB molecules on Cu(111) mainly form 2D ladder-like (L) structures (enlarged in Figure 1b) and honeycomb-like (H) structures (enlarged in Figure 1c). The L phase contains pairs of molecules that are bonded by a bridging Cu$_{\text{ada}}$ forming a dogbone structure; the dogbone structures are linked together at each of their four terminal groups via bonding to single Cu$_{\text{ada}}$. In the H phase, each Cu$_{\text{ada}}$ is bonded to two molecules and each molecule is bonded to three Cu$_{\text{ada}}$ through its three terminal groups. Moreover, besides the extended phases, there exist additional clusters on the surface in which the molecules are isolated, or bonded to single Cu$_{\text{ada}}$ at one, two or three of their terminal groups. Figure 1d shows five different bonding configurations; these configurations were calculated as described in the following.

We used scanning tunneling spectroscopy (STS) to probe the molecular electronic structures. Figure 1e displays the tunneling spectra acquired with the tip positioned above the central phenyl ring of the molecule in each of these five configurations. The molecules in all these configurations exhibit a broad main peak above the Fermi level. From top to bottom, the main STS peak shifts to higher energy with increasing number of bonded Cu$_{\text{ada}}$ except for that corresponding to the H phase. This shifting trend is opposite to TPyB, where the peak shifts to lower energy with increasing number of bonded Cu$_{\text{ada}}$ as reported in Reference 10. The opposite shifting trend indicates that the lateral Cu$_{\text{ada}}$ bonding makes TPB more acceptor-like while making TPyB more donor-like.

This contrasting behavior motivated our theoretical investigation. We modeled both the TPyB and the TPB molecules in five Cu$_{\text{ada}}$-bonded configurations on an equal footing in the H phase, so as to compare binding energies, atomic populations, densities of states,
and geometries, including un-coordinated (m=0), singly-coordinated (m=1), doubly-coordinated (m=2), triply-coordinated (m=3) single molecules, as well as extended networks (m=1.5), as shown in Figure 1d. Here m represents the number of bonded Cuada for each molecule. The singly and shared bondings with Cuada coexisting in the L structure are already considered in our five models. Thus, there is no need to separately calculate the L structure, which has a different unit cell size that would raise other complications in the comparisons.

To reduce the computational time, we adopted a Cu(111) surface with a single Cu monolayer as the substrate. This single-layered substrate model has already been used in our earlier study of TPyB attachment on Cu(111),\textsuperscript{10} where the calculation results were shown to be largely insensitive to the number of Cu layers, whether four or one. As the experimental observation is basically the same for TPyB and TPB attachment on Cu(111), the resulting (10 × 10) unit cell contains 100 Cu atoms with lattice constants a=b=25.56 Å, c=30.0 Å, α=β=90°, γ=120°. These surface Cu (Cu_{surf}) atoms were fixed during structural optimization so as to better represent a solid metal surface. Prior work\textsuperscript{10} has shown that a [TPyB\textsubscript{2}-Cu\textsubscript{3}]_{net} network on Cu(111) presents slightly distorted molecules and that each coordinating Cu_{ada} bonds strongly to one hollow site of the surface, with near-bulk-like Cu-Cu distances between Cu_{ada} and Cu_{surf}. We here use this type of attachment for both TPyB and TPB as initial geometries before further optimization.

Our calculations were performed using the atomic orbital-based DFT method available in the SIESTA code.\textsuperscript{24} We adopted the DRSLL exchange-correlation functional which includes Van der Waals (VdW) interactions\textsuperscript{25,26} and the double zeta plus polarization orbitals basis set. The detailed parameters used in the calculations include an energy cutoff of 300 Ry, a maximal force threshold of 0.02 eV/Å, a projected atomic orbital energy shift of 100 meV, a maximal displacement tolerance of 1.0×10^{-4} Å, and a k point sampling of 1×1×1. Note that SIESTA has been successfully applied in many simulations of organic molecule-surface interfaces.\textsuperscript{27-29}

### RESULTS AND DISCUSSION

#### RESULS AND DISCUSSION
As shown in Figures 2a and 2f, a single TPyB molecule adsorbed without linking to Cu_{ada} (m=0) on a Cu(111) surface tends to maintain a near-planar structure, while a TPB molecule is strongly warped. Three dihedral angles reflecting the molecular warping are listed in Table S1 to quantify this structural feature, with values of ~175° and ~130°, respectively, for nearly flat vs. strongly warped molecules. In order to show the structural difference in detail, we additionally measured the distances from three terminal N or C atoms (N4-N6 or C4-C6, as labeled in Schemes 1-2) of TPyB vs. TPB to the nearest Cu_{ada} or Cu_{surf} atoms, as well as the attachment heights, i.e. the average interlayer spacings between C1-C3 for TPyB vs. TPB and three Cu_{surf} atoms below them, as illustrated in Figures 3a and 3b. It can be seen that the near-planar TPyB is only weakly attached on Cu(111), with a molecule-surface interlayer spacing over 3.5 Å (see Figure 3b), while three terminal C atoms of the TPB radical approach the Cu_{surf} at internuclear distances of ~2.12 Å (see Figure 3a), so the TPB is strongly arched, maintaining a VdW spacing of ~4.2 Å (see Figure 3b) between its central phenyl ring and the substrate. The three C atoms carrying unpaired electrons are responsible for the strong bending of the TPB, while also strongly bonding the TPB to the Cu_{surf}.

However, when bonded to Cu_{ada} atoms, the geometries of the two molecules are dramatically changed (see Figure 2). When a Cu_{ada} bonds to TPyB, the corresponding N-Cu_{ada} bond length becomes 2.0-2.1 Å, much shorter than the distance between N and Cu_{surf} (over 3.4 Å, see Figure 3a). The backbone of the molecule becomes slightly distorted as compared with the nearly flat geometry when m=0. As a result, the central phenyl ring is elevated with respect to the Cu surface (see Figure 3b). Such a geometrical distortion is enhanced with increasing number of bonded Cu_{ada}. Note that in the fully networked TPyB (m=1.5), the molecule backbone is distinctly warped, as clearly seen in Figure 2e and in Table S1. By contrast, TPB actually becomes more planar when increasing the number of the bonded Cu_{ada} (see Figure 3b and Table S1), since the raised Cu_{ada} help maintain a VdW distance between the molecule and the substrate. Summarizing, the TPyB and TPB initially are, respectively, nearly planar vs. strongly warped when not bonded to Cu_{ada}; such bonding induces a similarly warped backbone when m=3 or 1.5.
The geometric structure comparison reflects the differences in relative binding energies (see Figure 3c) as calculated according to “lateral” molecule-atom binding:

\[ \Delta E \text{ (mol-atom)} = [E_{a+mol} - E_{mol} - E_a]/n_1 \]

and “perpendicular” molecule-substrate binding:

\[ \Delta E \text{ (mol-substrate)} = [E_{s+a+mol} - E_{a+mol} - E_{a+s + a} + E_a]/n_2 \]

Here, except for the fully optimized energy \( E_{s+a+mol} \) of the complete system, all energies are obtained from those of the frozen geometries subtracted from those of the original adsorption structures formed among the substrate, the atom, and the molecule. Here \( n_1 \) (\( n_1 = 1, 2, 3, \) or 6) represents the bond number of Cu\(_{\text{ada}}\) with N or C, while \( n_2 \) (\( n_2 = 1 \) or 2) represents the number of TPyB/TPB molecules. The lateral interaction between the molecule and each Cu\(_{\text{ada}}\) actually represents the N-Cu or C-Cu coordination bond strength. When Cu\(_{\text{ada}}\) is onefold coordinated with a molecule, the C-Cu bond energy is stabilized at about -3.9 eV, while the N-Cu bond energy remains about -0.8 eV. In twofold coordination, each C-Cu bond energy is found to be lifted to -2.3 eV, still larger than that for N-Cu (-0.7 eV). This implies that the bonding of TPyB with Cu\(_{\text{ada}}\) is not as firm as for TPB and thus TPyB is more likely to form the diverse observed intermediates with Cu\(_{\text{ada}}\).

Remarkably, the perpendicular interaction energy between TPyB and the surface is basically kept constant at around -2 eV with an increasing number of bonded Cu\(_{\text{ada}}\), m, while that between TPB and substrate is dramatically and linearly reduced. This is mainly due to the terminal C radicals binding with more Cu\(_{\text{ada}}\) instead of Cu\(_{\text{surf}}\). By comparing the bond energies between the terminal C and each Cu\(_{\text{ada}}\) or Cu\(_{\text{surf}}\) (-3.9 eV or -2.2 eV, where -2.2 eV is calculated from the perpendicular molecule-substrate binding energy for TPB on Cu(111) divided by 3), we realize that the TPB molecule binds with Cu\(_{\text{ada}}\) more stably than with Cu\(_{\text{surf}}\). This is because of the stronger molecular warping as the TPB is attached to the substrate, leading to less orbital overlap between C and Cu\(_{\text{surf}}\). It is thus clear that the molecular deformation on the surface can potentially affect the physical properties of MMIs.
Figure 2. Optimized geometries in top views (top image in each frame) and side views (bottom image in each frame) of (a-e) TPyB and (f-j) TPB monolayers on Cu(111), obtained by surface-constrained VdW/DRSLL with the lattice constants $a=b=25.56$ Å, $c=30.0$ Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, for increasing numbers of Cu$_{ada}$ (a-d, f-i) and for molecular networks (e,j). Orange, green, blue, white, and red atom colors represent Cu$_{surf}$, C, N, H, and Cu$_{ada}$, respectively. Cu$_{ada}$ are enlarged for clearer identification.
Figure 3. (a) Bond length from N (blue triangles) or C (black squares) at the molecular vertices of TPyB or TPB, resp., to the nearest Cu, whether it is a Cu adatom Cu_{ada} (filled symbols for m=1, 2, 3 and 1.5) or a Cu surface atom Cu_{surf} (open symbols for m=0, 1 and 2). The larger values around 3.4 Å correspond to N atoms of TPyB that are not covalently bonded to Cu, but undergo Van der Waals bonding. (b) Average interlayer spacings between TPyB (blue triangles) or TPB (black squares) and the surface, defined as the average distances between the planes of atoms C1-C3 (see the labels in Schemes 1 and 2) of TPyB/TPB and the plane of three Cu_{surf} atoms below them. (c) Frozen binding energies of TPyB (blue triangles) or TPB (black squares) with Cu(111) from VdW/DRSLL calculations. Filled symbols correspond to “lateral” molecule-adatom binding, while open symbols correspond to “perpendicular” molecule-substrate binding. All data are arranged according to the number of bonded Cu_{ada}, namely m = 0, 1, 2, 3, 1.5.

To reveal the electronic structures, we next examine the charge transfer in more detail. Table 1 lists the Bader charges of the six C of the central phenyl ring, the molecules, Cu_{ada} and Cu(111) substrate in the five structures presented in Figure 2. In general, the total charge of the central phenyl ring is positive for TPyB but negative for TPB, indicating that the two molecules exhibit donor vs. acceptor character, respectively, as they have lost or gained electrons. TPB-Cu$_3$ on Cu(111) is an exception with positive charge on the central phenyl ring. However, it has significant amounts of negative charge localized on three C vertices with charge values -0.3022, -0.3579 and -0.4436, confirming that TPB is an acceptor.

Considering the whole molecule, we find very little charge transfer to TPyB with an increasing number of bonded Cu_{ada}, less than +0.1 |e|, implying weak donor character and weak coordination bonds between N and Cu_{ada}. By contrast, a large electron transfer to TPB of approximately -1.0 |e| reflects the acceptor character of the TPB and the occurrence of strong electronic interactions between C and Cu_{ada} or Cu_{surf}. In fact, TPyB is a closed-shell molecule unlike the TPB radical which easily binds with Cu as it carries a single unpaired electron. A single TPyB molecule does not bind with the Cu as strongly as a TPB radical does and thus forms weaker N-Cu bonds than C-Cu in TPB. For the
shared twofold coordination in the networks, the electron transfer to TPB, of approximately -0.7 |e| is again much larger than the TPyB case, where it is close to 0. The distinct charge transfer properties of TPB and TPyB will definitely alter the electron filling in the electronic structure and thus induce characteristic shifts in STS, which can be confirmed by the following projected density of states (PDOS) calculations of the molecule.

Table 1 Bader charge analysis of different parts of the listed surface systems from DFT calculations; T3 indicates top site adsorption of the molecular center.

<table>
<thead>
<tr>
<th>Surface system</th>
<th>m</th>
<th>Six central C (T3 site)</th>
<th>TPyB or TPB (T3 site)</th>
<th>Bonded Cu_{ada} *</th>
<th>Cu(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPyB on Cu(111)</td>
<td>0</td>
<td>-0.2267</td>
<td>-0.0675</td>
<td>-</td>
<td>+0.1488</td>
</tr>
<tr>
<td>TPyB-Cu on Cu(111)</td>
<td>1</td>
<td>+0.0109</td>
<td>-0.0653</td>
<td>+0.3600</td>
<td>-0.3860</td>
</tr>
<tr>
<td>TPyB-Cu_{2} on Cu(111)</td>
<td>2</td>
<td>+0.2219</td>
<td>+0.0086</td>
<td>+0.2986</td>
<td>-0.6201</td>
</tr>
<tr>
<td>TPyB-Cu_{3} on Cu(111)</td>
<td>3</td>
<td>+0.2910</td>
<td>+0.0536</td>
<td>+0.3230</td>
<td>-1.1911</td>
</tr>
<tr>
<td>[TPyB_{2}-Cu_{3}]_{net} on Cu(111)</td>
<td>1.5</td>
<td>+0.0766</td>
<td>-0.0051</td>
<td>+0.4424</td>
<td>-1.7495</td>
</tr>
<tr>
<td>TPyB on Cu(111)</td>
<td>0</td>
<td>+0.1896</td>
<td>-0.9698</td>
<td>-</td>
<td>+0.9962</td>
</tr>
<tr>
<td>TPyB-Cu on Cu(111)</td>
<td>1</td>
<td>-0.0788</td>
<td>-1.0491</td>
<td>+0.2500</td>
<td>+0.6097</td>
</tr>
<tr>
<td>TPyB-Cu_{2} on Cu(111)</td>
<td>2</td>
<td>-0.0900</td>
<td>-0.9607</td>
<td>+0.3282</td>
<td>+0.4452</td>
</tr>
<tr>
<td>TPyB-Cu_{3} on Cu(111)</td>
<td>3</td>
<td>+0.2190</td>
<td>-0.9447</td>
<td>+0.2767</td>
<td>-0.0844</td>
</tr>
<tr>
<td>[TPyB_{2}-Cu_{3}]_{net} on Cu(111)</td>
<td>1.5</td>
<td>-0.1271</td>
<td>-0.6717</td>
<td>+0.4079</td>
<td>-0.3614</td>
</tr>
</tbody>
</table>

*: the Bader charge on the linked Cu_{ada} is an average value when there are inequivalent Cu_{ada}. 
Figure 4. PDOS of the central phenyl ring of TPyB (a) or TPB (b) in five adsorption structures (m=0,1,2,3,1.5) from DFT calculations.

The experimental STS curves were recorded with the STM tip positioned above the central phenyl ring of the molecule at positive bias voltage. This process thus corresponds to the electron tunneling to the unoccupied molecular orbitals (MOs) which are mainly localized on the central phenyl ring of the molecule. First-principles calculations can provide detailed information of the MOs (see Figures S1 and S2). In particular, their energy levels relative to the Fermi level can be compared with the STS peak positions. Figure 4 shows the PDOS of central phenyl ring of TPyB or TPB molecule adsorbed at the T3 top position in all five structures. The first peaks above the Fermi levels in the TPyB-Cu\textsubscript{m} (m=0,1,2,3) series appear, respectively, at 1.29, 0.78, 0.70, and 0.45 eV, down-shifting with an increasing number of N-Cu bonds. This trend matches the direction of the dI/dV peak obtained from the STS. By contrast, the PDOS peaks in the TPB-Cu\textsubscript{m} (m=0,1,2,3) series appear at 1.62, 1.76, 2.26, and 2.28 eV, showing a trend that
is qualitatively consistent with the experimental dI/dV peaks at 0.89, 1.00, 1.20, and 1.40 V. The clear consistency in the trends of the calculated and experimental peak positions supports a common underlying mechanism.

To further reveal the donor vs. acceptor character of the two molecules, we derive the orbital overlap and energy levels of the N-Cu or C-Cu interactions from the calculated PDOS of 2s and 2p orbitals of the three vertex N or C atoms, as well as of 4s, 4p, and 3d orbitals of the bonded Cu$_{ada}$, as shown in Figure 5.

In the two series of TPyB-Cu$_m$ and TPB-Cu$_m$ (m=0,1,2,3) clusters, we find that the occupied MOs below the Fermi level dominating the N-Cu$_{ada}$/C-Cu$_{ada}$ interaction are mainly from 2p of N/C and 3d of Cu$_{ada}$. The orbital overlap between 2p of N and 3d of Cu$_{ada}$ is relative small. This indicates a weak interaction in the N-Cu$_{ada}$ bond and therefore a small charge transfer between them. Moreover, Figure 5a shows that the main N 2p peak is gradually reduced and spreads towards lower energy with increasing m (top to bottom panels). This reflects that TPyB plays a donor-like role by the lone pair electrons of N, but through weak N-Cu$_{ada}$ bonds that donate relatively little charge. By contrast, the C-Cu$_{ada}$ interacting occupied MOs have a significant overlap between 2p of C and 3d/4s of Cu$_{ada}$, as shown in Figure 5b. The substantial interaction of the vertex C radical of TPB with Cu$_{ada}$ facilitates electron transfer to TPB, which exhibits acceptor-like character.

In the [TPyB$_2$-Cu$_3$]$_{net}$ or [TPB$_2$-Cu$_3$]$_{net}$ networks, Cu$_{ada}$ is bridged between two N or C atoms, forming a N-Cu$_{ada}$-N or C-Cu$_{ada}$-C twofold bond. We find that the Fermi level of [TPB$_2$-Cu$_3$]$_{net}$ lies in the overlapping PDOS of Cu$_{ada}$ and C, quite different from the onefold C-Cu coordination cases. The partially unfilled C-Cu$_{ada}$-C reflects electron deficiency. The electron transfer occurring in the twofold case (-0.7|e|) appears to be smaller than the onefold coordination cases (-1.0|e|), see Table 1. By contrast, in N-Cu$_{ada}$-N, the electron-rich state leads to excess electrons and thus shifts the Fermi level to the right. Overall, the electron filling is different for the onefold and twofold coordination cases of both TPyB and TPB.
Figure 5. PDOS of interacting N or C and bonded Cu$_{ada}$ in all configurations from DFT calculations for TPyB (a, left column) and TPB (b, right column). The calculated STS peaks are marked by blue arrows and the original Fermi levels are labeled with dash-dotted lines.

In addition, our calculations (shown in Figure 5) can explain the contrasting STS peak shifts of the two molecules. It is found that the 2p levels of N at lower energies cause an up-shift of the total MO levels (see Figure S3), as well as a rise of the Fermi levels (by about 0.07-0.09 eV rise per Cu$_{ada}$, see Figure 5a), thus narrowing the corresponding energy range as the number of bonded Cu$_{ada}$ increases. By contrast, the stronger C-Cu bonds with increasing number of bonded Cu$_{ada}$ lead to a negligible shift of the overall MO levels (see Figure S3), and a slight lowering of the Fermi levels (by about 0.02-0.03 eV reduction per Cu$_{ada}$, see Figure 5b). However, unoccupied orbital levels of three vertex C of TPB lying between Fermi level and STS peaks can force the STS peak to be
up-shifted as C binds to Cu_{ada} instead of Cu_{surf}. As shown in Figure 5b, there are weak peaks in the PDOS below the main STS peaks. They are actually mainly from three C atoms interacting with Cu_{ada}/Cu_{surf}, as identified in Figure S4, which exhibits 39 atomic PDOS curves from the TPB molecule in all calculated TPB coordination configurations. Although TPB can strongly bind with Cu_{ada}/Cu_{surf} due to the strong acceptor character, unoccupied anti-bonding orbital levels of vertex C resulting from binding with Cu_{ada} are higher than those with Cu_{surf} in the cluster configurations. This reveals a stronger C-Cu_{ada} bond than C-Cu_{surf} bond as higher anti-bonding MO levels are formed from a stronger atom-atom interaction. This also coincides with the above binding energy results which show that TPB binds with Cu_{ada} more stably than with Cu_{surf} owing to different molecular deformations on the surface. Thus, the STS peaks of TPB configurations for m=2, 3 are dramatically raised to higher energies at 2.26 and 2.28 eV compared to those for m=0, 1.

**CONCLUSIONS**

DFT calculations and experimental STM/STS results reveal the distinct interactions between Cu adatoms and two aromatic molecules of TPyB and TPB through different types of bonds. While TPyB and TPB form almost identical supramolecular structures on Cu(111), they differ in significant ways due to very different charge transfer behaviors: the radical TPB interacts much more strongly than does TPyB with the Cu adatoms. As the number of the bonded Cu adatoms increases, the STS peak of TPyB is down-shifted while that of the TPB series is up-shifted with respect to the Fermi level. Our comparative experimental and theoretical study reveals that the extended networks exhibit different charge transfer behavior between the molecules and the Cu substrate from those in the single-molecule clusters because of different electron filling in the one-fold and two-fold coordination cases.

These results are particularly useful in selecting and synthesizing electron acceptors or donors for fabricating functional organic electronic devices. By appropriate choice of molecules with suitable electron affinity and metal atoms to induce assembly into clusters or networks, molecular electronic structures can be modulated on purpose.
ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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The TPyB (left) vs. TPB (right) clusters on Cu(111) showing the planar vs. warped attaching structures, which result from their donor vs. acceptor character.