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Interface properties and electronic structures of aromatic molecules with anhydride and thio-functional groups on Ag (111) and Au (111) substrates*

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First-principles calculations for several aromatic molecules with anhydride and thio groups on Ag (111) and Au (111) reveal that the self-assembly structures and the interface properties are mainly determined by the functional groups of aromatic molecules. Detailed investigations of the electronic structures show that the electrons in molecular backbone are redistributed and charge transfer occurs through the bond between the metal and the functional groups after these molecules have been deposited on a metal substrate. The interaction between Ag (111) (or Au (111)) and aromatic molecules with anhydride functional groups strengthens the π bonds in the molecular backbone, while that between Ag (111) (or Au (111)) and aromatic molecules with sulfur weakens the π bonds. However, the intrinsic electronic structures of the molecules are mostly conserved. The large-sized aromatic backbone has less influence on the nature of electronic structures than the small-sized one, either at the interface or at the molecules. These results are useful to build the good metal–molecule contact in molecule-based devices.

Keywords: aromatic molecules, electronic structures, metal surface, density functional theory

PACS: 31.15.V–, 31.10.+z, 68.43.–h, 71.15.Mb **DOI:** 10.1088/1674-1056/ab4276

1. Introduction

Organic conjugated molecular materials have been used as active components in the growing field of organic electronics and spin-based electronics, and in devices such as light-emitting displays,[1–3] field-effect transistors,[4] photovoltaic cells,[5–7] chemical sensors,[8] and ultra-high-density memory circuits.[9] Since all organic-based devices are integrated with metals or insulating or semi-conducting materials, many pivotal processes (*e.g.*, charge injection, exciton diffusion, light conversion, and spin injection) that determine the performance of the devices happen at the interface. Although a few experimental methods and theoretical calculations have revealed the interface structures and related properties, a detailed and unified understanding of the interface properties is still of great importance.[10–21] Molecules that consist of only aromatic rings and/or alkane structures have weak interactions with metal substrates.[14] However, molecules with functional groups can have strong interactions with substrates.[21] These interactions might influence the intrinsic electronic structures of the organic-based nano structures. This is very important for developing the means of constructing nano structures and for investigating the performances of organic-based devices.[22,23] Moreover, to better understand the interaction between molecules and the substrate, van der Waals interaction, which has been ignored in most of theoretical studies on molecule-substrate system,[14,21] cannot be neglected.[24–27]

In this work, we theoretically study the configurations and the electronic properties at the interface of molecules with different functional groups on Ag (111) and Au (111) substrates, by taking the van der Waals interaction into consideration. The 4,5,8-naphthalene-tetracaboxylic-dianhydride (NTCDA, Fig. 1(a)), 3,4,9,10, perylene-tetracarboxylicacid-dianhydride (PTCDA, Fig. 1(b)), and tetrathiafulvalene (TTF, Fig. 1(c)) are chosen in order to change the size of the aromatic ring system (naphthalene, perylene) and the functional group of anhydride and thio with the strong binding strength to noble metals. It is found that though the binding of molecules to metal substrates seems strong, the electron density difference and the density of states show that the electronic structures of molecules are mostly conserved regardless of the size of the aromatic ring and the functional group. We also find that the choice of a metal substrate will influence electronic properties at the interface slightly. These results offer useful information about metal–molecule contacts, electronic properties at the interface, and molecules themselves, which will influence the vital process that happens at the interface and determines the device performance.

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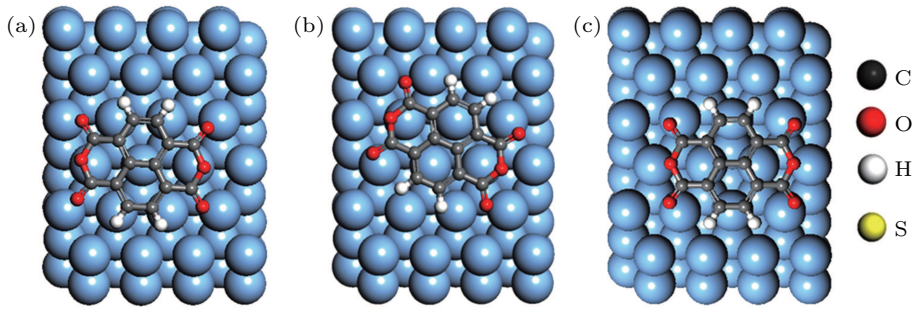


Fig. 1. Adsorption configurations with center of NTCDA molecule on (a) top, (b) bridge, and (c) hollow sites of Ag (111) substrate.

2. Method

All geometric relaxation and total energy minimization were carried out by using the Vienna *ab initio* simulation package (VASP).[28] The projector augmented wave (PAW) potential is used to describe core electrons and the interaction between exchange and correlation is described by Perdew, Burke, and Ernzerhof (PBE) functional.[29] A van der Waals (vdW) interaction was taken into account by using the Grimme's empirical correction, which is highly accurate for predicting structural and energetic properties if a proper exchange functional is used.[30–33] The plane-wave expansion was truncated at cutoff energy of 400 eV. Due to the numerical limitations, a single Γ point is employed for Brillouin zone matrix integrations. The adsorption structures of NTCDA, PTCDA, and TTF on Ag (111) or Au (111) substrates were investigated. They all have aromatic backbones but different functional groups. Large super-cells containing four layers of metal atoms and a vacuum space of at least 12 angstroms were used. Each molecule was placed on one side of the surface and all atoms except for those at the bottom of two metal layers were relaxed until the net force on every atom was smaller than 0.02 eV/Å. The robustness of the results with respect to all computational parameters was thoroughly tested.

3. Results and discussion

3.1. NTCDA on Ag (111) and Au (111)

NTCDA has a naphthalene core with anhydride groups at both ends (Fig. 1(a)). First, we investigate the interface properties of NTCDA on Ag (111). On Ag (111), we consider several adsorption configurations with the molecules centered on the top, bridge and hollow sites of the substrate (see Figs. 1(a)–1(c)). The most stable structure is one with the molecule centered on the bridge site of substrate. Molecular plane is parallel to the substrate, and four anhydride oxygen atoms bind directly to the Ag atoms in the first layer of the substrate (see the left part of Fig. 2(a).). The distances between Ag and O are all around 2.4 Å, which is smaller than that between the center of the molecule and the substrate. So the molecule bends a little along the lateral side. The right part of Fig. 2(a) shows the planar integration (x–y plane) of electron density difference of NTCDA/Ag (111) according to the following equation:

$$\Delta q(z) = \int_S \Delta\rho\,(r)\,\mathrm{d}S,$$

where $\Delta\rho$ is the electron density difference obtained by subtracting electron density of NTCDA/Ag (111) from that of NTCDA and Ag (111) separately, and S is the area of the plane. A negative value means losing electrons, while a positive one refers to obtaining electrons. We find a negative peak near the first layer of Ag (111), which indicates the electrons transfer from first-layer Ag atoms to the interface between the molecule and the substrate. There is a small negative peak in molecular plane and two small positive peaks below and above the molecular plane respectively, all of which indicate that the electrons of in-plane orbitals transfer to out-of-plane ones within the molecule. Since electrons that transfer from the substrate to the molecule are mainly from the first layer of Ag (111), we carefully investigate the electron density difference on each Ag atom of the first layer. Figure 2(b) shows the electron density differences at a certain electron density ($\pm 0.012\ e/\text{Å}^3$) in real space, in which the blue parts indicate a decrease of electron density, while the yellow parts indicate an increase of electron density. We find that the Ag atoms directly under the oxygen atoms and under the two C–C bonds (marked with red arrows in Fig. 2(b)) have charge reduction, corresponding to the peak near the first layer of Ag (111) in the right part of Fig. 2(a). The sigma bonds of C–H and C–O also have charge reduction, corresponding to the small peak in the molecular plane in the right part of Fig. 2(a). The C–C π bonds and p_z orbitals of oxygen atoms have charge accumulation. It can be concluded that the C–C π bonds are strengthened after being deposited on Ag (111) substrate from the view of electron density difference and the reduction of 1% of the bond length. And the NTCDA molecule is an electron acceptor in this system. Integration of $\Delta q(z)$ along the z direction shows that the maximum electron transfer is about 0.34 electrons per unit cell. Considering the size of the unit cell, the electron transfer is rather small, indicating a weak interaction between NTCDA and Ag (111).

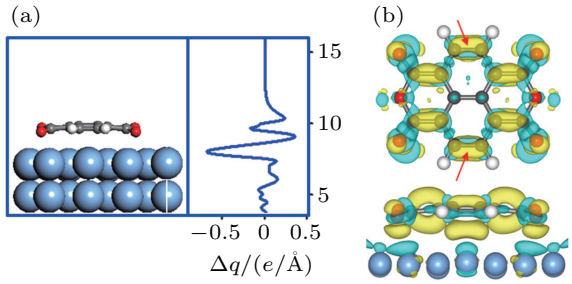


Fig. 2. Configurations and interface properties of NTCDA on Ag (111) and Au (111). (a) Left part: side view for NTCDA on Ag (111); right part: planar integration (x–y plane) of electron density difference ($\Delta q(z)$, e/Å). (b) Detailed distribution of electron density difference of NTCDA/Ag (111).

The above results show that the NTCDA has a weak interaction with the Ag (111) substrate. Because Au and Ag are in the same group in the periodic table, and Au is often used as electrodes in devices, the interface properties of organic molecules on Au surfaces are also important. In the following, the interface properties of NTCDA on Au (111) are investigated. Like the scenario on Ag (111), the most stable configuration for NTCDA on Au (111) surface is one with the center of the molecule being on the bridge site of Au (111) substrate as shown in Fig. 3(a). However, the molecule on Au (111) is more planar than that on Ag (111), which is clearly shown in Fig. 3(b). The distance between Au and O is 2.8 Å, larger than those between Ag and O in NTCDA/Ag (111). This suggests a weaker interaction between NTCDA and Au (111) than between NTCDA and Ag (111). The planar integration (x–y plane) of electron density difference (the right part of Fig. 3(c)) shows a line shape very similar to that of NTCDA/Ag (111) with a much smaller electron density. Moreover, there is no obvious peak near the first layer of Au (111), suggesting a negligible electron density difference on the first layer of the substrate before and after molecular adsorption. Figure 3(d) shows the detailed information about the electron redistribution. It seems that most of the redistributed electrons coming from the Au atoms under the acetone oxygen transfer to the C–C π bonds and the anhydride oxygen. The electrons transfer from the substrate to the molecule, with a maximum of 0.08 electron per unit cell, which is much smaller than that for NTCDA/Ag (111).

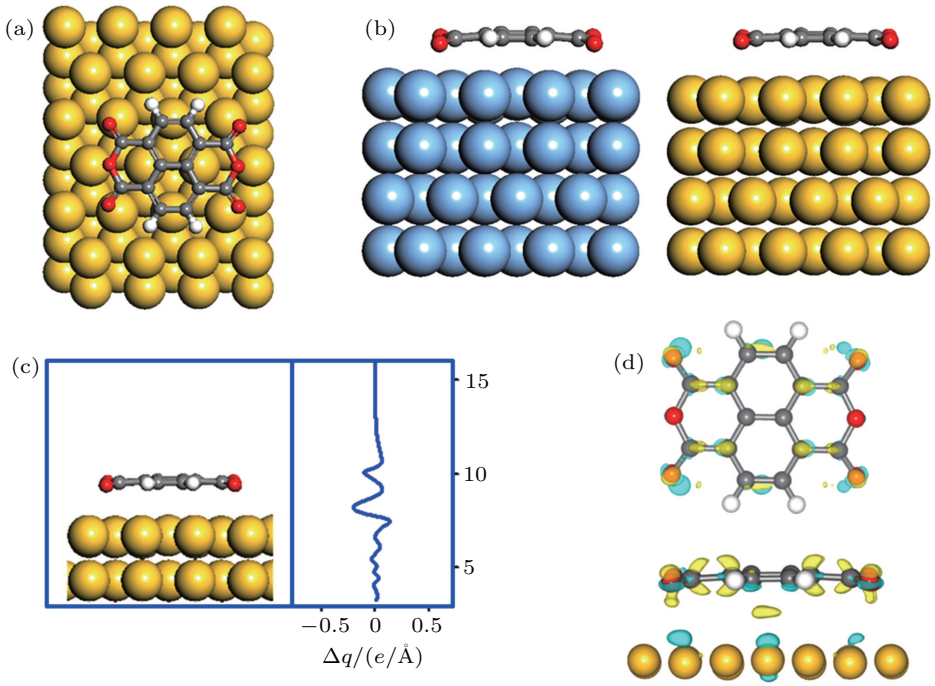


Fig. 3. (a) Adsorption configuration with center of NTCDA molecule on bridge site of Au (111) substrate; (b) side view of molecule on Au (111) and on Ag (111); (c) Left part: side view for NTCDA on Au (111); right part: planar integration (x–y plane) of electron density difference ($\Delta q(z)$, e/Å); (d) Detailed distribution of electron density difference of NTCDA/Au (111). Isosurfaces for panels (c) and (d) are ± 0.012 e/Å^3.

The projected density of states (PDOS) on carbon and oxygen atoms of free molecules and the molecules on Ag (111) are shown in Figs. 4(a) and 4(b), respectively. Due to electrons transferring from the substrate to the molecule, the lowest unoccupied state of a free molecule (indicated by red arrow in Fig. 4(a) is split into several peaks with the major peaks (the blue arrow in Fig. 4(b)) shifting below the Fermi level of NTCDA/Ag (111), which means that the p_z orbitals of carbon and oxygen atoms have charge accumulation. Because the π orbitals are contributed from the electrons on p_z orbitals, this is also evidence that the π bonds are strengthened. It is in agreement with what we found in the electron density difference, and the electrons transfer from the substrate to the molecule. Unlike the NTCDA/Ag (111) system, the PDOS of NTCDA/Au (111) (Fig. 4(c)) shows that the splitting of the lowest unoccupied state is very small and the major peak (the green arrow in Fig. 4(c)) is still above the Fermi level of NTCDA/Au (111) with a tiny peak below it. This suggests

that a little electron transfer happens between molecule and substrate. Therefore, according to the electron redistribution and the density of states, we find that the electronic structure of NTCDA will less influence Au (111) than Ag (111).

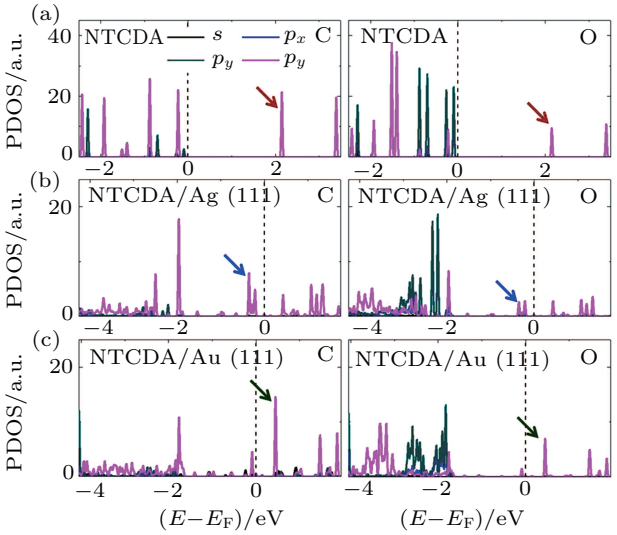


Fig. 4. Projected density of states on carbon and oxygen atoms for (a) free NTCDA molecule, (b) NTCDA/Ag (111), and (c) NTCDA/Au (111). The unit a.u. is short for arbitrary units.

3.2. PTCDA on Ag (111) and Au (111)

In order to learn more about the effect of aromatic structure on the interaction between molecules and substrate, we further investigate the interface properties of PTCDA on Ag (111). The PTCDA is similar to NTCDA with anhydride groups at the ends. Unlike NTCDA with a naphthalene core structure, the PTCDA has a larger-sized aromatic core structure, perylene, instead. A configuration with one molecule in one unit cell with 4×7 Ag atoms per substrate layer (the left part of Fig. 5(a)) is used.

The right part of Fig. 5(a) shows the planar integration of electron density difference. We find that electrons transfer from first-layer Ag atoms to the molecules and the electrons are redistributed in the molecule, which is similar to the case in NTCDA/Ag (111). The electron density difference on each atom (in the right part of Fig. 5(a)) shows that the Ag atoms directly under the oxygen atoms, the C–C bonds marked by red arrows in Fig. 5(b), the sigma bonds of C–H, C–O, and the lone-pair electrons of oxygen atoms all have charge reduction. The C–C π bonds and p_z orbitals of oxygen atoms have charge accumulation. Unlike NTCDA/Ag (111), the Ag atoms directly under the oxygen atoms contribute a lot compared with the ones under C–C bonds. It is obvious that the electron transfer is mainly through oxygen atoms. The C–C π bonds have charge accumulation through oxygen atoms, and the electrons on different molecular orbitals are redistributed. It can be concluded that the C–C π bonds are strengthened after being deposited on Ag (111) substrate from the view of electron density difference. The electron transfer from the substrate to the molecule is about 0.25 electrons per unit cell, which is smaller than that in NTCDA/Ag (111), suggesting that a large-sized aromatic core structure (PTCDA) will be less influenced by the substrate compared with a small-sized ones (NTCDA).

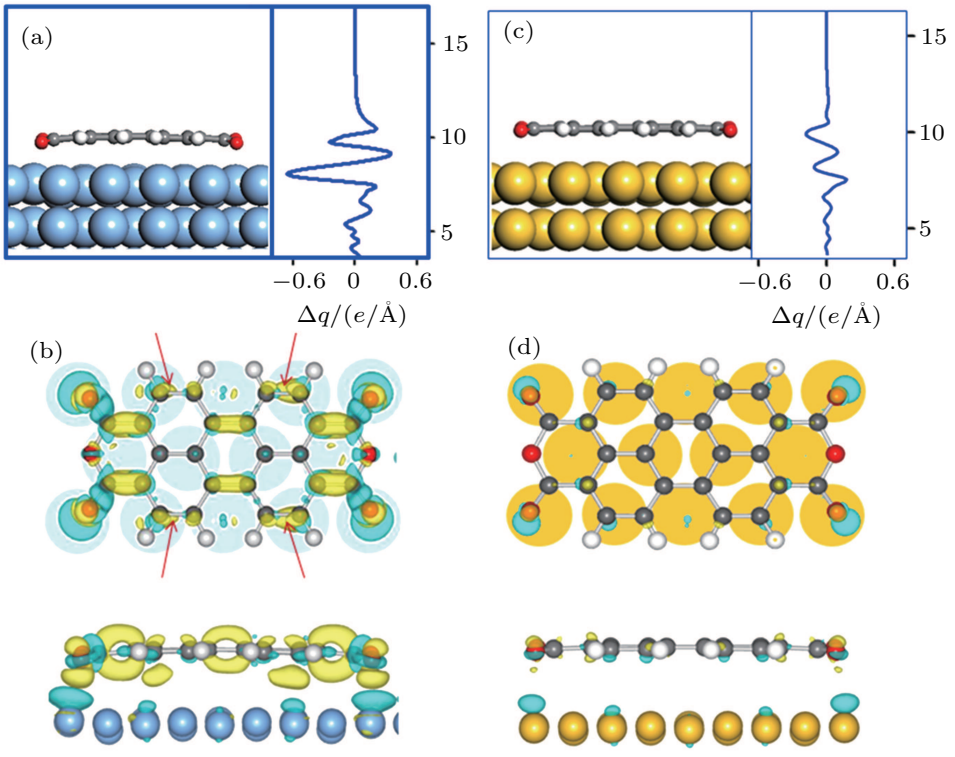


Fig. 5. Configurations and interface properties of PTCDA on Ag (111) and on Au (111): Side view (left part) and $\Delta q(z)$ (right part) for PTCDA (a) on Ag (111) and (b) on Au (111); (c) detailed distribution of electron density differences of PTCDA/Ag (111) and PTCDA/Au (111). The isosurfaces for panels (c) and (d) are ± 0.012 $e/\text{Å}^3$ and ± 0.008 $e/\text{Å}^3$, respectively.

Both the electron redistribution details and charge transfer show that the interaction between PTCDA and the Ag (111) substrate is mainly through oxygen atoms and is weaker than that between NTCDA and the Ag (111); the molecule conserves its electronic structure; the C–C π bonds are strengthened a little after molecules have been deposited on Ag (111). Thus, the functional groups of an aromatic molecule determine the nature of the interaction between molecules and the Ag (111) substrate, especially for a molecule with large-sized aromatic structures.[34,35]

The PTCDA/Au (111) is also investigated, and the results are shown in Figs. 5(c) and 5(d). The electron transfer from Au (111) to PTCDA, 0.1 electron, is much smaller than that from Ag (111) to the same molecule (0.25 electron), which is similar to the case of NTCDA molecules. A similarity between the behaviors of NTCDA and PTCDA suggests that Au (111) is an idea substrate that will not influence the electronic structure of aromatic molecules with anhydride groups.

3.3. TTF on Ag (111) and Au (111)

The investigation above shows that the adsorption of PTCDA and NTCDA molecules on both Ag (111) and Au (111) involve transferring electrons, and the intrinsic electronic structures of molecules are influenced little by adsorption. We find that a combination of Au (111) and molecules with a large-sized aromatic backbone is a better choice when we need a weak molecule-substrate interaction. However, both molecules have anhydride groups as functional groups, which controls the adsorption. We need to further investigate how the interaction changes when molecules with different functional groups are used. The TTF with sulfur atoms in the aromatic cycles is chosen.

The configuration of TTF on Ag (111) substrate is shown in the left part of Fig. 6(a). Because two sulfur atoms on one side bind to the substrate, the TTF molecule tilts a little. The right part of Fig. 6(a) shows the planar integration of electron density difference. There are three main peaks. One is near the substrate which indicates an increase of electron density. The other two are near the molecular plane, which indicates that the out-of-plane molecular orbitals have charge reduction and the in-plane molecular orbitals have charge accumulation. It seems that the TTF molecule loses electrons when it is deposited on Ag (111) substrate, unlike NTCDA and PTCDA. Carefully analyzing the details of the electron density changes on each atom (Fig. 6(b)), we find that the π orbital of C–C and lone-pair electrons on S atoms have charge reduction. The two Au atoms directly connected to the S atoms also have charge reduction through the dz orbital. The electron density between molecule and substrate increases. The electron transfer is mainly through sulfur atoms. At the same time, electron redistributions within the molecule are also found. Though the C–C bond between the two five-member rings is weakened when deposited on Ag (111) substrate, the sigma bonds are strengthened a little through electron redistributions. It suggests that the π bonds are weakened when TTF is deposited on Ag (111). The electron transfer is about 0.28 electrons per unit cell. Considering that there are only two Au atoms directly under the sulfur atoms, this implies that the interaction between TTF and Ag (111) is larger than that between NTCDA (or PTCDA) and Ag (111).

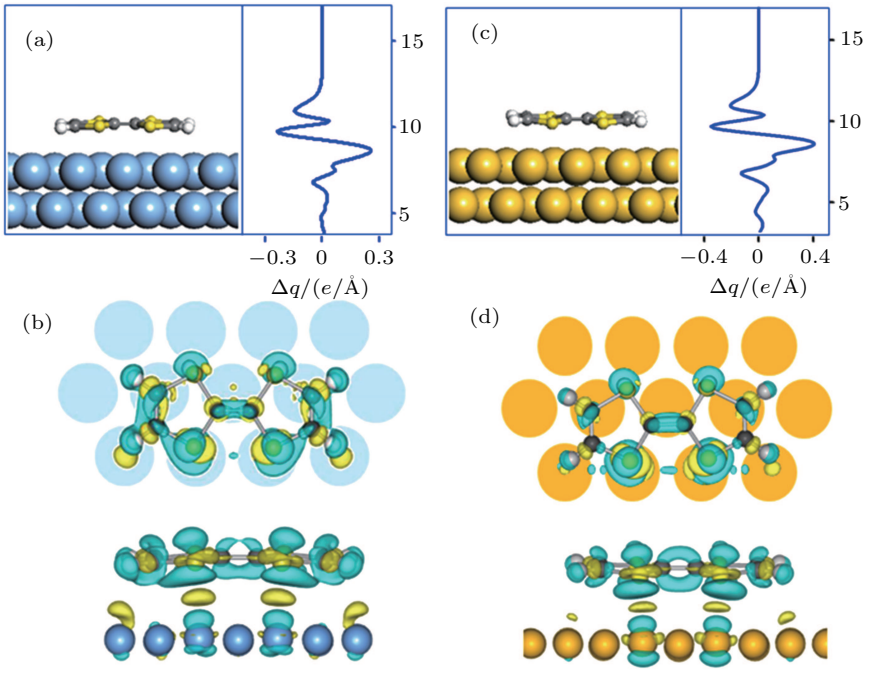


Fig. 6. Configurations and interface properties of TTF on Ag (111) and Au (111): side view (left part) and $\Delta q(z)$ (right part) for TTF (a) on Ag (111) and (b) on Au (111); detailed distribution of the electron density difference of (c) TTF/Ag (111) and (d) TTF/Au (111). Isosurfaces for panels (c) and (d) are ± 0.012 $e/\text{Å}^3$ and ± 0.008 $e/\text{Å}^3$, respectively.

Considering the difference between behaviors of NTCDA on Ag (111) and Au (111), we compare the interface properties of TTF on Ag (111) with those of TTF on Au (111) (as shown in Fig. 6(b)). The most stable configuration is similar to that for TTF/Ag (111): the two sulfur atoms on one side bind to the substrate. However, the TTF molecule on Au (111) tilts much more than it does on Ag (111). The electron redistribution details and the electron transfer show characteristics similar to those of TTF on Ag (111), but with a much greater electron transfer, 0.41 electrons per unit cell, which shows a stronger interaction between TTF and Au (111). This is totally different from NTCDA/PTCDA on Ag (111)/Au (111), which shows a stronger interaction between molecule and Ag (111). It implies that the functional group plays a vital role in determining the molecule-substrate interactions.

4. Conclusions

Our simulation of aromatic molecules with different functional groups reveals that the self-assembly structures and the interface properties are mainly determined by the functional groups of aromatic molecules. When deposited on metal substrates, the electrons in molecular backbone are redistributed, and electron transfer occurs mainly through the bonds between metal and the functional groups, but the intrinsic electronic structures of the molecules are mostly conserved. The interaction between Ag (111)/Au (111) and molecules with anhydride functional groups is weaker than that between Ag (111)/Au (111) and molecules with sulfur. Though Ag and Au belong to the same group in the periodic table and the lattice parameters are similar, the electronic properties at the interfaces of molecule/Ag (111) and molecule/Au (111) differ from each other slightly. For molecules with anhydride groups, the adsorption strengthens C–C π bonds and Au (111) has less influence on the molecular electronic structure than Ag (111). For TTF, the adsorption weakens the C–C π bonds and Au (111) has a greater influence on the molecular electronic structure, which is different from the molecules with anhydride groups. Though the adsorption energy shows a strong interaction between molecule and substrate. The electronic structures are not strongly affected.

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