Site-selective adsorption of naphthalene-tetracarboxylic-dianhydride on Ag(110): First-principles calculations

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The mechanism of adsorption of the 1,4,5,8-naphthalene-tetracarboxylic-dianhydride molecule on the Ag(110) surface is elucidated on the basis of extensive density functional theory calculations. This molecule, together with its perylene counterpart 3,4,9,10–perylene-tetracarboxylic-dianhydride (PTCDA), are archetype organic semiconductors investigated experimentally over the past 20 years. We find that the bonding of the molecule to the substrate is highly site selective, being determined by electron transfer to the lowest unoccupied molecular orbital of the molecule and local electrostatic attraction between negatively charged carboxyl oxygens and positively charged silver atoms in $[1\bar{1}0]$ atomic rows. The adsorption energy in the most stable site is 0.9 eV. A similar mechanism is expected to govern the adsorption of PTCDA on Ag(110) as well.

I. INTRODUCTION

The adsorption of functional organic molecules on metal surfaces is of wide current interest both from technological and fundamental points of view. Precise control of the first monolayer is a prerequisite for fabricating high-quality organic thin films, which are the basic constituents of hybrid organic-inorganic optical and electronic devices.[1] Understanding molecule-molecule and molecule-substrate interactions is necessary to explain different surface architectures,[2,3] and knowledge of the local electronic structure[4] and of mechanical properties is crucial for designing and controlling functionalities at the nanometer scale, for example, in the fields of molecular electronics[5,6] and molecular machines.[7]

Among the many molecules whose interaction with solid substrates has been studied, 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA) and its perylene counterpart, PTCDA, deserve special attention due to their unique properties. The aromatic cores of both molecules are terminated at opposite ends by two anhydride groups, as seen in Fig. 1 for NTCDA, and both of them have a D_{2h} symmetry. Upon room temperature deposition on silver surfaces they form commensurate superstructures, which depend on the orientation of the substrate.[3,8,9] Earlier near edge x-ray absorption fine structure (NEXAFS) studies[10–12] of the adsorbed monolayers indicated that both molecules are parallel to the substrate and exhibit substrate-dependent spectral changes which were interpreted as evidence for covalent π bonding.[3] The finding that such rather large molecules, which cover ∼10−15 substrate atoms, can lock into preferred adsorption sites, had no simple explanation for a long time. Chemisorption via π states delocalized over the aromatic core, claimed to favor the high surface mobility required for self-assembly,[9] cannot easily account for site selectivity. Recently, Eremtchenko, Schaefer, and Tautz[13,14] proposed an interesting experimental argument that PTCDA binds to Ag(111) via its central aromatic ring, but that this potential reaction center is inactive in the case of unsubstituted perylene. Later Hauschild et al.[15] reported synchrotron-quality normal incidence x-ray standing wave (NIXSW) measurements and density functional calculations on the same system, which revealed that anhydride side groups are slightly closer to the substrate than the aromatic core and also contribute to the bonding. Comparison of vibration spectra of adsorbed monolayers of PTCDA on different silver substrates by Tautz et al.[16–18] showed, however, that besides common features there are also notable differences in local adsorption properties on different surfaces. The Ag(110) surface consists of a regular array of atomic rows and grooves in the $[1\bar{1}0]$ direction, and one expects (a) the lateral variation of the adsorption energy to be larger for the (110) surface than for (001) and (111) surfaces and (b) charge transfer to be more pronounced (see below). Similar differences should also exist for the adsorption of NTCDA on silver substrates even though only the electronic structure of the NTCDA/Ag(111) interface has so far been studied in detail.[10,19]

Our work is directly motivated by the experiments of Fink et al.[8] who investigated the lateral ordering of NTCDA monolayers on several noble metal surfaces by means of low-energy electron diffraction (LEED), scanning tunneling microscopy (STM) and temperature-programmed desorption spectroscopy. Whereas two lateral superstructures were found for NTCDA on Ag(111) and Ag(001), only one sim-
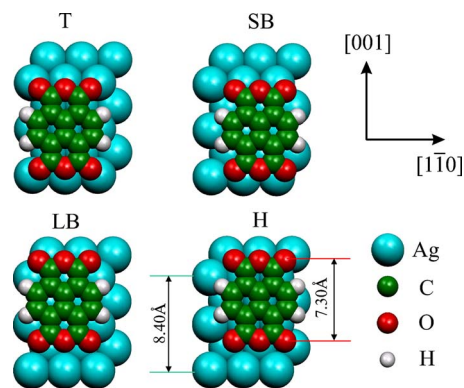

FIG. 1. (Color online) Local adsorption geometries studied: T (top), SB (short bridge), LB (long bridge) and H (hollow). The names refer to the position of the midpoint of the central C═C bond with respect to the underlying Ag(110) surface.

pler superstructure was observed for Ag(110) and Cu(001). The NTCDA/Ag(110) interface, having a well-defined geometry and a relatively small number of atoms per unit cell, is therefore appealing for computational work.

Density functional theory (DFT) calculations[20] have proven quite successful in describing covalent and ionic bonding of small molecules at surfaces.[21] However, it is not obvious whether bonding of large closed-shell organic adsorbates on noble metals, where van-der-Waals interactions can play a significant role, will be adequately grasped by current semilocal implementations of DFT, like the local density approximation (LDA) and various generalized gradient approximations (GGA).[22] In general, since dispersion interactions are not taken into account when constructing the current density functionals,[23,24] one cannot expect a good performance of DFT for pure van-der-Waals-bonded systems. It is unclear, however, how much van-der-Waals character do the molecule-metal bonds possess in the systems that concern us here. Even though the first DFT study of a large organic molecule interacting with a metal appeared almost ten years ago,[25] still few such works exist. In the case of molecules like C_{60}, which bond strongly to some noble metal substrates,[26] or when a single head group is involved in the bonding, as for alkane-thiols on Au(111),[27] or when reactive metals such as Ni[28] are used as substrates, present-day DFT is largely successful. However, a recent study[29] showed that calculated DFT adsorption energies of inert hydrocarbons are much smaller than experimental ones. For PTCDA, sometimes no bonding was found, [30,31] even though experiments suggest a weak chemisorption. On the more open and reactive Ag(110) surface the molecule-metal bond may exhibit a more covalent (or ionic) character for which current density functionals perform rather well. Fortunately, we *do* find that in our case DFT is successful, because much of the relevant experimental data, some extrapolated from related systems, are reproduced by calculations.

II. COMPUTATIONAL DETAILS

Calculations were performed with the ABINIT code,[32] using the Perdew-Burke-Ernzerhof (PBE) GGA exchange-correlation functional.[33] Light atoms were described with Goedecker-Teter-Hutter pseudopotentials,[34] and silver atoms were treated within the Troullier–Martins scheme[35] (*s*-component taken as local to avoid ghost states). The simulated system consisted of a NTCDA molecule on one side of a six-layer silver slab and a vacuum region equivalent to eight silver layers. Thus the total computational box included 78 atoms and a pool of 690 electrons, making it already a quite demanding system. Wave functions were expanded in plane waves with a 50 Ry kinetic energy cutoff (60 and 70 Ry for test calculations—the results changed little). The Brillouin zone of the 3×3 surface unit cell was sampled by six special *k* points[36] together with a Fermi broadening of 0.01 Ha.

The bottom three silver layers were fixed in their calculated bulk positions (PBE lattice constant 4.20 Å), and the top three silver layers and the molecular degrees of freedom were relaxed according to Hellmann–Feynman forces, pre-

serving the initial local symmetry. Geometry optimization was performed using damped molecular dynamics until the maximum force was below 10^{-3} Ha/bohr. The potential energy surface describing the metal-molecule interaction is rather shallow, meaning that a substantial change in geometry leads only to a minor change in total energy. This motivated our strict convergence criterion. As test calculations, we calculated surface energies of clean silver surfaces, and obtained 0.32, 0.41 and 0.62 eV per surface atom for (111), (001) and (110) faces in accord with previous GGA results and the experimental trend. The calculated work functions for these surfaces were 4.47, 4.27 and 4.13 eV, respectively, typical values for PBE using Troullier–Martins pseudopotentials. These values are also in accord with the experimental trend: the closed-packed (111) surface has the highest work function (4.46–4.74 eV) while the open (110) has the lowest work function among the low-index silver surfaces (4.14–4.52 eV). This is quite important for the present system: the Ag(110) surface, having a smaller work function, can donate more charge to electron acceptor molecules like NTCDA. These differences in work functions are certainly relevant for an interpretation of adsorption properties of the molecules of interest on different substrates.[16–18]

III. RESULTS AND DISCUSSION

After minimizing the residual forces, we obtained the following adsorption energies: 0.92 eV for the *T* site, 0.45 eV for SB, and practically zero for LB and H. The adsorption energies were determined using the relationship $E_{ad} = -(E_{tot} - E_{sub} - E_{mol})$, where E_{sub} is the total energy of the bare slab (calculated using the same computational box), E_{mol} is the total energy of an isolated NTCDA molecule (calculated using a large enough computational box), and E_{tot} is the total energy of substrate-adsorbate system. Positive adsorption energy means exothermic adsorption. The experimental adsorption energy for NTCDA on Ag(110) is not known. For a superstructure of NTCDA on Ag(001) with a similar area per molecule (100.2 vs 106.4 Å^2) a value of about 1.0 eV was obtained from the temperature-programmed desorption spectrum,[8] while for a denser superstructure of NTCDA on Ag(111) an adsorption energy of 1.1 eV was deduced.[9] Thus, our value of 0.92 eV is reasonable, but is most probably an underestimate, keeping in mind that usually GGA functionals tend to underbind adsorbates on noble metals and that the adsorption energy on the Ag(110) face should be even larger than those two values. It is expected, however, that the *differences* between adsorption energies in different adsorption configurations should be more accurate.

These differences are quite significant. The top site is predicted to be by far the most stable one. Fink *et al.*,[8] in fact, also proposed that the top site, with all oxygens sitting almost on top of silver atoms underneath, should be the most favorable adsorption configuration (see Fig. 4 in Ref. 8). The proposal was motivated by analogy with the local adsorption geometry of PTCDA on Ag(110), which had been determined in an elegant STM experiment,[37] and noting that both PTCDA and NTCDA fit the Ag(110) template (PTCDA

spans four, and NTCDA spans three atomic rows—see Fig. 1, T site, and Fig. 4 in Ref. 37). Our DFT calculations fully confirm this hypothesis. For NTCDA on Ag(110) the most favorable adsorption geometry is that for which oxygens lie directly above silver atoms in the $[1\bar{1}0]$ rows, just like for PTCDA on Ag(110). For the latter system an earlier computational study based on the empirical universal force field (UFF),[38] predicted instead an equilibrium configuration equivalent to LB. The second most stable configuration, SB (Fig. 1), is also characterized by oxygen atoms on top of atomic rows but shifted half a lattice constant in the $[1\bar{1}0]$ direction. Although this remains to be explored in detail, configuration SB is likely a transition state for diffusion along the Ag rows. In the case of the least favorable sites, LB and H, oxygen atoms sit between the close-packed rows. During the geometry optimization, carboxyl oxygens moved towards the substrate, causing a bending of the molecule, just like for PTCDA on Ag(111).[15] In the relaxed geometries, carboxyl oxygens were approximately 0.25 and 0.30 Å closer to the silver substrate than the naphthalene core for the T and SB sites, respectively. For the T site, the carboxyl oxygens were situated 2.40 Å, the anhydride oxygens 2.50 Å, the carbons in the anhydride groups 2.54 Å, the carbons and hydrogens in the naphthalene core 2.62 Å from the topmost Ag(110) plane. An average distance of ∼3.0 Å was obtained for NTCDA on the less reactive Ag(111) surface in a recent NIXSW experiment.[39] On one hand, the distance between the NTCDA molecule and the more reactive Ag(110) surface should indeed be smaller than on the close-packed Ag(111) surface. On the other hand, since the potential energy around the equilibrium molecule-metal distance is quite shallow in DFT, changes in that distance only lead to a tiny variation of the adsorption energy. Thus we conclude that the calculated distances are subject to larger errors than the adsorption energies themselves. During the geometry optimization, in the case of the favorable sites (T and SB), silver atoms just below the carboxyl oxygens moved upwards by 0.07 and 0.03 Å with respect to the average level of the top layer, thus further reducing the corresponding Ag−O distances. This naturally leads to the hypothesis that the interaction which leads to site-selectivity occurs between the carboxyl oxygens and the silver atoms in the $[1\bar{1}0]$ rows. If this is so, then what is the physical nature of this interaction?

To answer this question, we analyze the electron density redistribution caused by the adsorption of NTCDA at different sites by calculating the density difference

$$\Delta n = n^{\text{tot}} - n^{\text{sub}} - n^{\text{mol}}, \qquad (1)$$

where n^{tot} is the total density of the system, and n^{sub} and n^{mol} are the densities of the substrate and molecule in their relaxed geometries. This function shows the charge rearrangement caused by adsorption of the molecule on the surface. Averages of the total densities and the density differences along the $[1\bar{1}0]$ and $[001]$ directions, as well as xy-integrated densities and density differences, are shown in Fig. 2. From these plots and three-dimensional (3D) representations of the
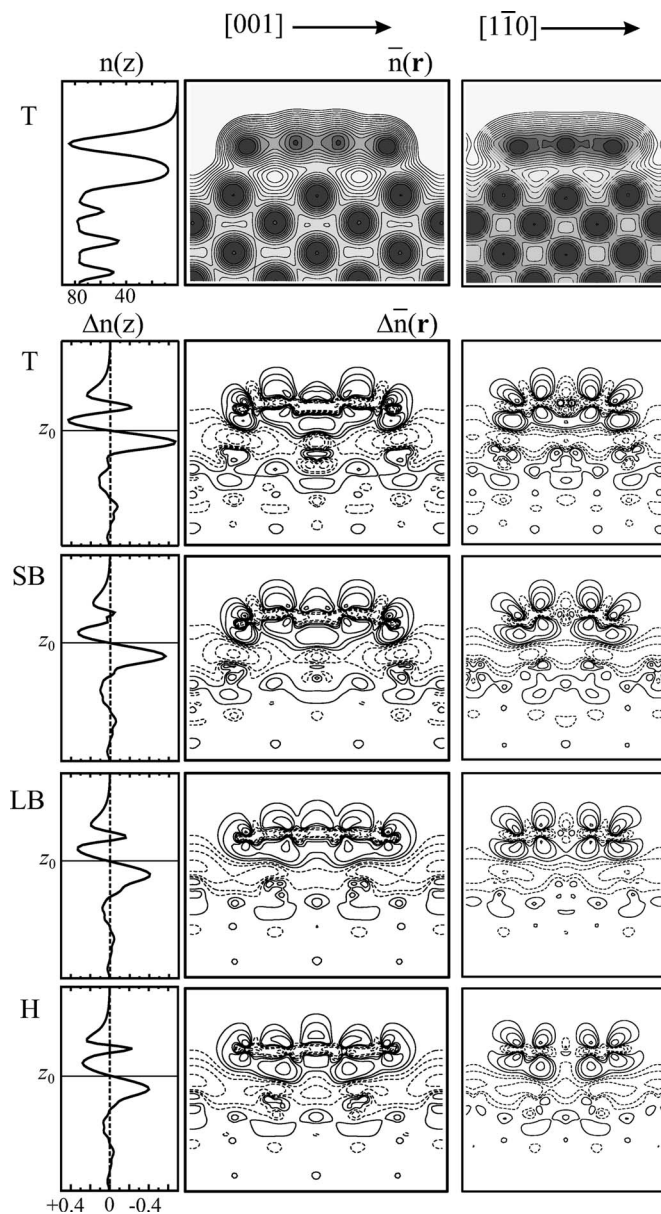

FIG. 2. Total electron density for the top site (upper row) and density differences for all four adsorption sites. Left column: xy-integrated densities (the units are $e\text{Å}^{-1}$). Central column: averages over the $[1\bar{1}0]$ direction. Right: averages over the $[001]$ direction. Solid contours represent electron charge accumulation regions, broken contours = charge depletion.

density difference (not shown) one recognizes that (a) electron charge flows mainly from the metal to the molecule and (b) the charge accumulation distribution is closely related to the lowest unoccupied molecular orbital (LUMO) of the isolated molecule. This can clearly be seen in Fig. 3, where the total electron density along with density difference in a plane 0.5 Å below the molecule (in the T configuration) is compared to the LUMO (b_{1g} symmetry), the highest occupied molecular orbital (HOMO) (b_{3g}) and the HOMO-1 (a_u) orbitals of the free NTCDA molecule.[40] Practically no back donation from occupied orbitals occurs. For NTCDA on Ag(111) NEXAFS studies of Gador et al..[10,11] showed a partial filling of the π-type LUMO. Our results are consistent
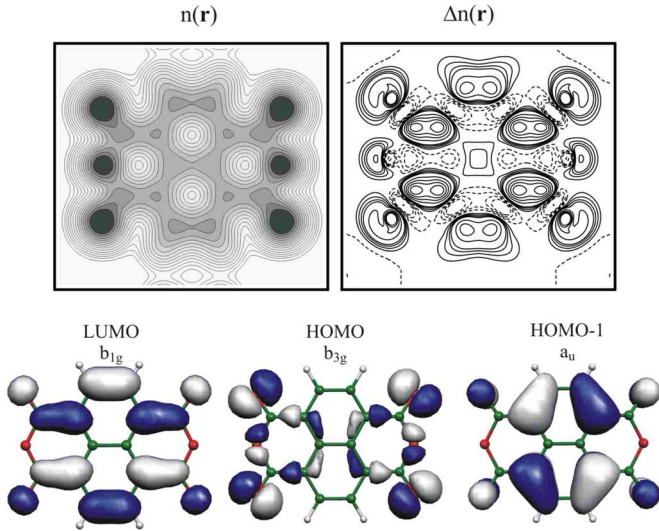
FIG. 3. (Color online) Top: Contours of the total electron density (left) and of the electron density difference (right) in a plane 0.5 Å below the NTCDA molecule at the top site; for Δn solid contours represent electron charge accumulation regions, broken contours = charge depletion. Bottom: 3D views of the LUMO (b_{1g} symmetry), HOMO (b_{3g}), and HOMO-1 (a_u) orbitals of the isolated NTCDA molecule.[40] The distribution of accumulated charge closely resembles that of the LUMO of isolated NTCDA.

with this finding. Various approximate charge partitioning schemes exist which associate charge with particular subsystems of the total system. We define the net electron charge on the molecule as

$$\Delta N = \int_{z_0}^{z_1} \Delta n(z)dz, \qquad (2)$$

where $\Delta n(z)$ is the xy-integrated density difference, z_0 is the coordinate for which $\Delta n(z_0)$ is zero (see Fig. 2), and z_1 lies in the middle of the vacuum region, where all densities are practically zero. The net electron charge, as well as the adsorption energies for all four sites, are summarized in Table I. NTCDA acquires about 0.3–0.4 e charge upon adsorption. The charge transfer can be rationalized by the following simple argument. To a first approximation, the overall charge transfer is proportional to the difference of the chemical potentials of the substrate (referred to the vacuum level close to the surface of the metal) and of the molecule. The former is $\mu_{sub} = -\Phi_{sub}$, Φ_{sub} being the work function of the Ag(110) surface, namely 4.13 eV (computed value). The latter, the so-called charge neutrality level,[41] is approximately equal to the midgap position[42]

TABLE I. Adsorption energies and net electron charges on the molecule determined from Eq. (2) after adsorption in four different sites.

Site	T	SB	H	LB
Adsorption energy E_{ad} [eV]	0.92	0.45	~0	~0
Charge ΔN [electrons]	0.38	0.37	0.34	0.35

$$\mu_{mol} \approx \frac{e_{HOMO} + e_{LUMO}}{2} \approx -\frac{IP + EA}{2}, \qquad (3)$$

where e_{HOMO}, e_{LUMO} are computed Kohn–Sham eigenvalues while IP and EA are the ionization potential and the electron affinity of the isolated molecule. According to the last expression on the right hand side, μ_{mol} is just the negative of the absolute electronegativity defined by Mulliken.[43] In our case, $\mu_{NTCDA} \approx -5.9$ eV, which agrees very well with the experimental value −6.0 eV.[44] Interestingly, the so-calculated absolute electronegativities are almost equal for NTCDA and PTCDA, even though the band gap is smaller for PTCDA than NTCDA. Thus, $\mu_{sub} > \mu_{NTCDA}$, so that electrons are transferred to the molecule, mainly to its LUMO. Such an interpretation is in agreement with chemical studies, since NTCDA is known to be an electron acceptor.[45]

Charge transfer from the metal to the molecule leads to an increase of the work function Φ of the combined system. From the total charge density distribution we obtain an induced negative electric dipole moment per NTCDA of 0.6 e Å which corresponds to an increase $\Delta\Phi = +1.0$ eV. This dipole is slightly smaller than the crude estimate 0.4 e × 2.5 Å partially because the relaxation of the ion cores makes an opposite contribution to the net dipole. No measurements of the work function for NTCDA/Ag(110) are available at present. Hill, Schwartz, and Kahn[46] found that the work function increases by +0.2 eV upon adsorption of a related molecule, 3,4,9,10-perylene-tetracarboxylic bis-imidazole on polycrystalline Ag. A similarly small value was found for NTCDA on Ag(111).[19,47] Since the Ag(110) surface has a smaller work function than the Ag(111) surface, charge donation can be more substantial and $\Delta\Phi$ larger on the Ag(110) surface. However, our value of +1.0 eV is probably overestimated for two reasons. First, the calculated work function of the Ag(110) surface is slightly lower than the experimental one, and this favors charge donation to the LUMO of NTCDA. Second, as is well known, the band gaps of semiconductors[48] and of organic molecules[49] are underestimated in both LDA and GGA. The Kohn–Sham LUMO eigenvalue is usually lower in energy than the corresponding electron affinity level and this also leads to a stronger charge donation to the LUMO and thus to a larger $\Delta\Phi$. To cure these problems, expensive calculations at the level of self-consistent many-body perturbation theory, e.g., the GW-approximation,[50] must be performed. We believe, however, that the abovementioned issues will not affect the proposed model for the site-selective adsorption of NTCDA on the Ag(110) surface.

Table I shows that the overall charge on the molecule is very similar for all the adsorption sites studied and does not reflect the significant differences in adsorption energies. However, one notices from Fig. 2 that in the case of the favorable T and SB sites the charge transfer is stronger and more localized between the carboxyl oxygens and silver atoms underneath. Furthermore, the electrostatic energy gain crudely estimated by treating the molecule-metal system as a plane-parallel capacitor amounts to only 0.12 eV, i.e., much less than the actual electrostatic contribution to the adsorption energy in those favorable sites. This also speaks for the

fact that site selectivity is determined by the proximity of carboxyl oxygens and silver atoms.

Our results suggest the following adsorption scenario of NTCDA on Ag(110) surface which leads to site-specific bonding. As a result of charge transfer to the LUMO of the molecule, silver atoms in the topmost layer become slightly positively charged. Carboxyl oxygens, being negatively charged even in the free molecule (~0.2 electron excess), are then attracted by electrostatic forces to the substrate. This attraction is maximal when the Ag−O distance is minimal, that is in the T and SB configurations. Thus, changes in the electron density are bigger and more localized for these two sites (Fig. 2), as compared to the unfavorable LB and H configurations. The local Ag−O attraction leads to a distortion of NTCDA from planarity, i.e., the carboxyl oxygens move closer to the substrate than the naphthalene core. Most of these effects, together with changes in bond lengths which reflect the density distribution of the LUMO, have been found and discussed for PTCDA on Ag(111).[15] It is interesting to note the qualitative similarity between those two systems despite the fact that both molecules and substrates are different. Bonds which are cut by the nodal planes of the LUMO are slightly elongated (maximum 0.03 Å for the C=O bond), while the other bonds are slightly contracted. However, as mentioned in the introduction, the bonding is stronger and more site specific for the more open Ag(110) surface. Furthermore, free electron-like surface states of the Ag(111) surface might also play a role in adsorption on that substrate. Figure 4 summarizes the mechanism of the bonding and bending of the molecule on the Ag(110) surface.

Considering the lateral ordering of the molecules, we studied adsorption in the favored T configuration for two different lateral surface unit cells: (3,0/0,3) and the experimentally found (3,0/1,3).[8] Both unit cells contain one molecule and the same number of substrate atoms and both structures are rather open. We found that the adsorption energies in both of these arrangements are essentially the same. This happens, most probably, because semilocal GGA functionals fail to describe long-range van-der-Waals interactions,[22] which are likely to be important for the preference of one superstructure over the other.

CONCLUSIONS

In conclusion, we have studied site-selective adsorption properties of NTCDA on the Ag(110) surface by means of density functional calculations. The interaction of the molecule with the substrate can be summarized by the following scenario: (1) NTCDA, being an electron acceptor, takes ~0.4 e from the silver substrate and the LUMO is partially filled; (2) this transfer leads to a slight positive charging of the silver atoms in the topmost layer and weakening of the C=O bonds, thus enhancing the local electrostatic interaction between Ag atoms in the Ag$[1\bar{1}0]$ rows and carboxyl oxygens (this is the main difference between favorable and unfavorable sites); (3) the Ag−O attraction distorts the molecule from the planar configuration. Being quite similar to the mechanism recently established for PTCDA on
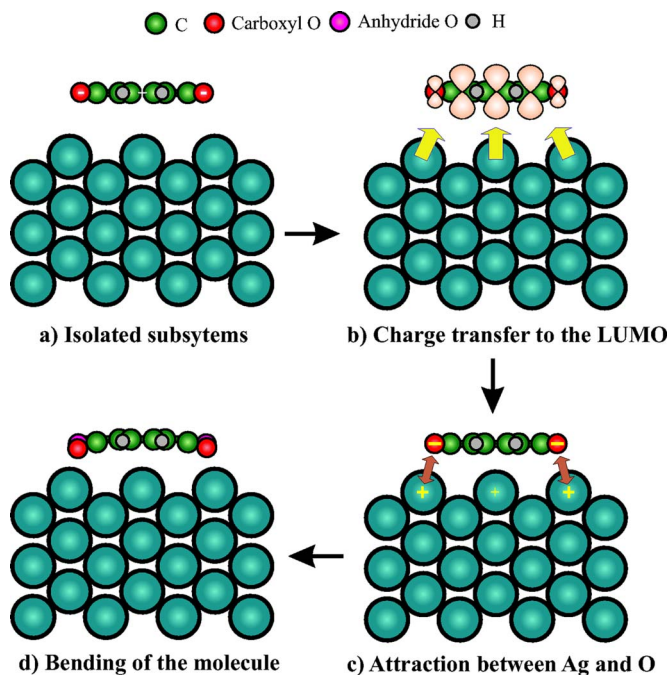

FIG. 4. (Color online) Sketch of the mechanism of adsorption of NTCDA on Ag(110), viewed along the $[1\bar{1}0]$ direction. (a) The two isolated subsystems: note the electron excess on the peripheral oxygens and the positive charge on the naphthalene core. (b) Charge transfer from the substrate to the molecule, mainly to its LUMO. (c) This transfer causes positive charging of the topmost silver layer and a local electrostatic attraction between silver atoms in the $[1\bar{1}0]$ rows below the negatively charged carboxyl oxygens. (d) The Ag−O attraction causes a distortion of NTCDA from planarity, with peripheral oxygens moving closer to the Ag rows than the naphthalene core.

Ag(111),[15] we believe that the proposed scenario is also applicable to the adsorption of PTCDA on Ag(110).[37] Experimentally found differences between different substrates[16–18] are still to be explored in detail. Very recently, a single polar N−Cu bond was found to be responsible for bonding of inclined adenine on Cu(110),[51] like for alkane-thiols on Au(111),[27] suggesting that local electrostatic bonding can occur for many organic molecules on open fcc(110) surfaces. In the case of aromatic acceptor molecules with several peripheral electronegative atoms (O, N, halogens) adsorbed flat on noble metal fcc(110) surfaces, the origin of site selectivity is less obvious. Our results suggest that observed commensurate superstructures can arise from the close match of those atoms and electron-depleted substrate atoms. DFT computations appear capable of grasping lateral variations of the resulting electrostatic interactions.

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