

First-principles electronic structure study of Ti-PTCDA contacts

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We investigate the interaction of Ti atoms with thin films made of 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) molecules by means of self-consistent electronic structure calculations within a generalized gradient approximated density-functional theory framework. Following experimental suggestions, we model the thin films in terms of the bulk crystallographic structure of PTCDA. We fully optimize the atomic PTCDA structures in the presence of Ti impurities by local minimizations of the electronic total energy. We find that the Ti atoms react with the anhydride groups of PTCDA and form additional bridge-type bonds with the surrounding molecules. This process is accompanied by an electronic charge transfer from the metal atoms to the organic molecules, which provides a consistent interpretation of the experimentally observed C 1s core-level shifts upon metal deposition. As a consequence of the chemical reaction, electronic states are induced in the gap above the highest occupied molecular orbital level of the organic semiconductor, in good agreement with photoemission studies.

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I. INTRODUCTION

High-quality organic semiconductor layers with good optoelectronic properties can be deposited on a variety of substrates, including metals and conventional semiconductors (like Si and GaAs). These systems are at the basis of many novel device applications,¹⁻³ such as light emitting diodes (LED's) and field effect transistors (FET's). Perylenetetracarboxylic dianhydride (PTCDA) is one of the organic molecules that are commonly used in these devices. PTCDA molecules can be stacked together to form a van der Waals-(vdW-) bonded molecular crystal, which can be grown in vacuum with a high degree of orientation to a substrate, even in the presence of a large lattice mismatch, by a phenomenon called quasiepitaxy.⁴⁻⁶

Bulk properties of organic molecular thin films such as electroluminescence, photoconductivity, and carrier transport have been extensively investigated. More recently, experimental studies have focused on the properties of metal contacts and heterojunctions in organic-based electronics.^{7,8} In particular, the chemistry and the electronic properties of interfaces between metals and thin films of PTCDA, having a thickness in the 400–800 Å range, have been investigated with synchrotron radiation photoemission spectroscopy (PES).⁷ These experiments showed that reactive metals like In, Ti, Al, and Sn, when deposited at room temperature on PTCDA films, give rise to electronic states in the band gap of PTCDA. These results are further corroborated by core-level spectroscopy data indicating that these metals react with the anhydride groups of PTCDA. The appearance of “chemistry-induced” gap states strongly affects the conductivity by allowing charge carriers to tunnel through the junction. As a consequence, contacts between reactive metals and PTCDA show Ohmic behavior, in sharp contrast with the blocking character typically observed in junctions made by nonreactive noble metals, like Au and Ag. In addition, the PES data

showed that the reactive metals diffuse initially into the PTCDA film without surface accumulation.

In spite of the technological importance of the contacts between metals and organic thin films, only few theoretical investigations of these systems have been reported to date. In view of the fact that charge transfer effects are likely to occur in these systems, a self-consistent treatment of electronic and atomic relaxation effects is expected to play a crucial role. This has been done in the investigations by Curioni and Andreoni who have studied Alq₃ (tris-8-hydroxyquinilino-aluminum) complexes with single metal atoms (Li, Al, Ca) using gradient-corrected functionals based on density-functional theory (DFT).⁹

In this paper, we study the interaction of Ti, taken as a prototypical reactive metal, with bulk PTCDA, using a theoretical formalism in which atomic and electronic relaxations are fully and self-consistently taken into account. Our approach is based on density-functional theory within a generalized gradient approximation for the exchange and correlation energy. This theory provides an accurate description of chemical bonding. After introducing Ti impurities at selected locations in the unit cell of bulk PTCDA, we fully optimize the local atomic geometries using a damped Car-Parrinello molecular dynamics scheme.¹⁰ We find that, in the most stable configurations, Ti atoms bind to the oxygen atoms of the anhydride groups of PTCDA. This bond formation process is accompanied by the transfer of electronic charge from Ti to PTCDA and leads to the appearance of electronic states in the band gap of the organic semiconductor, in good agreement with the experimental data. We find that the gap states have a substantial amount of π character on the aromatic rings of the organic molecule to which Ti binds. In addition, we have carried out calculations of C 1s core-level shifts. The calculated shifts agree with experiment and allow us to interpret the main effects observed in the PES spectra subsequent to Ti deposition.⁷

The paper is organized as follows. First, the computational method is outlined in Sec. II. Then we present our results for atomic and electronic structures in Sec. III. Section IV is devoted to the calculation of C $1s$ core-level shifts. Finally, we provide a brief summary and concluding remarks in Sec. V.

II. COMPUTATIONAL METHODOLOGY

We take Ti as a typical example of a metal which chemically reacts with PTCDA. According to experiment,⁷ other reactive metals exhibit a very similar behavior. The PTCDA films of interest have a thickness in the 400–800 Å range, are highly oriented when deposited in ultrahigh-vacuum conditions on several substrates, and their molecular structure is believed to be very close to that of bulk PTCDA.⁷ Therefore, in our calculations, we consider bulk crystalline PTCDA, whose unit cell contains two molecular units. Then, to investigate how Ti interacts with PTCDA, we introduce a small number of impurities, ranging from one to four Ti atoms, in the unit cell of bulk PTCDA.

The PTCDA molecule has a central perylene core with two anhydride end groups (O=C—O—C=O). Two such molecular units are contained in the monoclinic unit cell (space group $P2_1/c$) of the bulk PTCDA solid, as shown in Fig. 1(a). The intermolecular distance in the $[102]$ direction is 3.21 Å [Fig. 1(b)]. In our calculations, all electronic and atomic degrees of freedom are simultaneously relaxed using a damped¹¹ *ab initio* molecular dynamics scheme.^{10,12} The electronic structure is treated within density-functional theory, using the Perdew-Wang generalized gradient approximation for exchange and correlation (PW91).¹³ We adopt a plane-wave pseudopotential approach,¹² using ultrasoft pseudopotentials¹⁴ (PP's) with cutoff radii of 0.8 bohr for H, 1.2 bohr for C and O, and 1.8 bohr for Ti atoms, respectively. The $3s$ orbital of Ti is included in the valence shell. We use energy cutoffs of 25 and 200 Ry to truncate the plane-wave expansion of the pseudo wave functions and of the augmented charge density, respectively. We use only the Γ point for Brillouin zone sampling, since this is adequate for a molecular crystal like PTCDA, made of relatively large and weakly interacting molecular units.

We previously used this approach to optimize the structure of ethylene oxide,¹⁵ a molecule made of the same atomic species as PTCDA. In the present case, the results of the optimization of the internal coordinates of a PTCDA crystal, whose unit cell is kept fixed at the experimental values of the lattice parameters,^{16,17} are summarized in Table I. The interatomic distances and bond angles agree with experiment¹⁶ within errors of 2% at most. Our calculated average C-H distance is 1.10 Å. No experimental value is available for the C-H distance in PTCDA but one should expect a typical value of about 1.08 Å for a C-H bond in aromatic compounds.¹⁸ We notice that the approximate exchange-correlation energy functional that we use is capable of good accuracy in the description of chemical bonds but is not expected to describe properly weak physical interactions, like the vdW bonds between different PTCDA molecules. This limitation is irrelevant in the present context since we do not

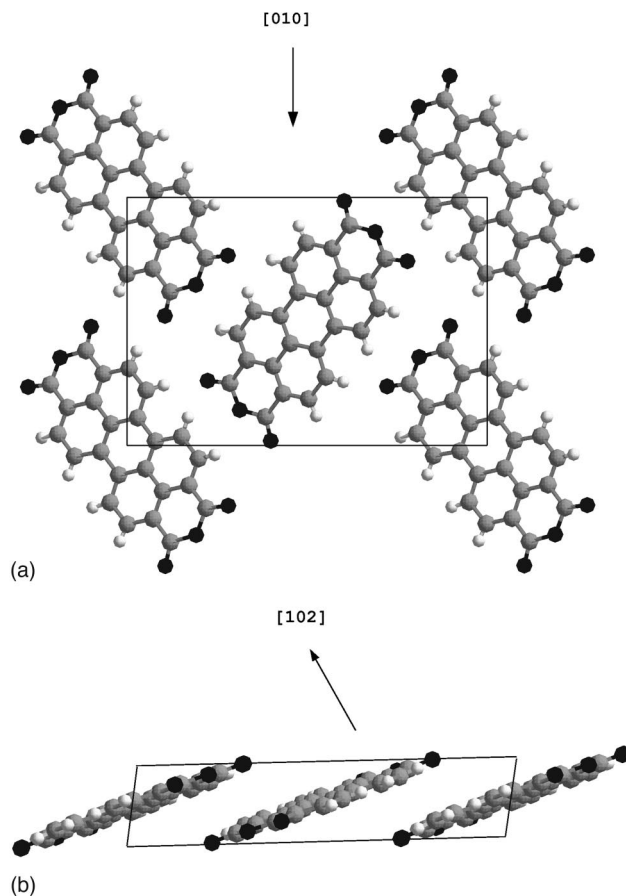


FIG. 1. PTCDA crystallographic structure, viewed from a direction orthogonal (a) and parallel (b) to the molecular planes. Black, gray, and white balls represent O, C, and H atoms, respectively. The solid lines show the unit cell.

optimize the crystalline unit cell of PTCDA and our main interest is in describing the chemical interaction between a reactive metal and PTCDA.

In addition to optimizing atomic geometries and computing the corresponding ground-state electronic structures, we calculate the vertical C $1s$ core-level shifts for a PTCDA crystal with Ti impurities. Approaches based on DFT have been successfully used to evaluate the core-electron binding energies in the oxidation of pyrrolidone analogs¹⁹ or core-hole x-ray-absorption spectra of fullerenes.²⁰ We use here a

TABLE I. Structural parameters of the pure PTCDA structure. Interplane distance d (Å), average bond lengths (Å) and angles resulting from the structural relaxation, compared to experiment (Ref. 16).

	Present theory	Expt. ^a
C-O	1.31	1.29
C-C	1.41	1.40
C-H	1.10	
C-O-C	117.7°	118.5°
d	3.14	3.21

^aReference 16.

TABLE II. Calculated C $1s$ core-level shifts (eV) of small molecules compared to the results of another DFT calculation (Ref. 33) and to experiment (Ref. 32). We consider vertical excitations. The shifts are given with respect to the C $1s$ core level of the CO molecule.

Molecule	Theory		Expt.
	Present	Ref. 33	Ref. 32
CO	0.00	0.00	0.00
CH ₄	5.59	5.7	5.33
C ₂ H ₂	5.03	4.83	5.04
HCHO	1.89	2.06	1.86

methodology which proved successful for the evaluation of Si $2p$ (Refs. 21–27) and N $1s$ core-level shifts^{28–30} in inorganic materials. Having optimized the ground-state geometry of a Ti_{*n*}-PTCDA ($n = 1, \dots, 4$) system, we replace the PP of the C atom where the ionization is supposed to occur with a PP that describes a C atom having a screened $1s$ hole in its core.^{31,22} We repeat this procedure for all the C atoms at inequivalent lattice sites and calculate each time the total energy. Then, the relative binding energy (BE) of the $1s$ core levels belonging to a pair of C atoms at inequivalent lattice sites is given by the corresponding total energy difference. In this way, we fully take into account electronic relaxation effects in the final state.

We tested the above approach with calculations on small molecules taking the C $1s$ level in the CO molecule as a reference. We performed these calculations on a periodically repeated simple cubic cell with a lattice size of $L = 22$ bohrs, which we found adequate to give only a negligible interaction between periodic images.^{22,23} In Table II, the results of these calculations are compared with experiment³² and with theoretical values for vertical core-level shifts, obtained with an all-electron nonlocal DFT formulation based on a Gaussian expansion of the electronic orbitals.³³ The accuracy of our method is clearly shown by the excellent agreement of our results with experiment and the calculation of Ref. 33. A similar approach has recently been applied to the calculation of the C $1s$ core-level shifts in poly-ethylene-terephthalate (PET).³⁴

III. ELECTRONIC STRUCTURE OF TITANIUM IMPURITIES IN A PTCDA CRYSTAL

We considered first a single Ti impurity per unit cell. A Ti atom is expected to interact with the electrophilic oxygen atoms of the anhydride groups and with the aromatic rings of the perylene core of PTCDA. We have therefore considered five different local configurations in which a Ti atom was either placed in the neighborhood of an oxygen atom or of an aromatic ring. After local geometry optimization by damped molecular dynamics, the most stable configuration corresponded to a Ti atom bound simultaneously to a side oxygen atom of an anhydride group and to several carbon atoms of two other PTCDA molecules [Fig. 2(a)]. All the other local minima that we found were significantly higher in energy. For instance, structures in which the Ti atom interacts with

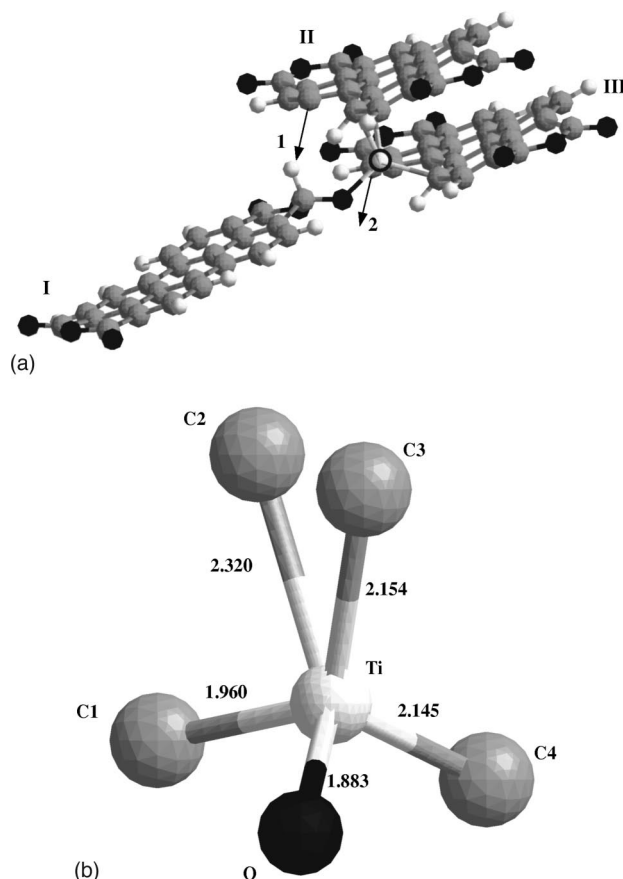


FIG. 2. Most stable structure found for a single Ti impurity in the PTCDA unit cell. (a) Ti, indicated by a thick circle, binds to O and C atoms belonging to three different molecules, labeled I, II, and III, respectively. H displacements (see text) are indicated by two arrows, labeled 1 and 2, respectively. Notice that, as a consequence of the cell periodicity, each one of these displacements is the periodic image of the other. (b) View of Ti and its nearest neighbors. Bond lengths (in Å) are given. Atom C2 and C3 belong to the same aromatic ring. Atom C1 has lost its H to a neighboring PTCDA molecule.

the aromatic rings of two adjacent PTCDA molecules are less stable by about 2.5 eV. A structure in which Ti interacts with the central O atom of an anhydride group is even less stable, having an energy about 4 eV higher than that of the most stable configuration. The local environment of Ti in the most stable configuration is shown in Fig. 2(a). As we can see Ti binds to atoms belonging to three different PTCDA molecules. The strongest bonds have lengths shorter than 2.4 Å and occur with an O atom of molecule I and with four C atoms, two of which belong to molecule II and two other to molecule III. Bond lengths less than 2.4 Å are typical of single bonds between Ti and carbon in organic complexes.^{35,36} The Ti-O bond is shorter than Ti-C bonds, reflecting the higher electroaffinity of oxygen compared to carbon. Our calculated value for the Ti-O bond (1.88 Å) agrees well with typical values reported in the literature.^{35,37,38} Finally, by eliminating from Fig. 2(a) all the atoms whose distance from Ti is larger than 2.4 Å we obtain the local bonding structure shown in Fig. 2(b). This geom-

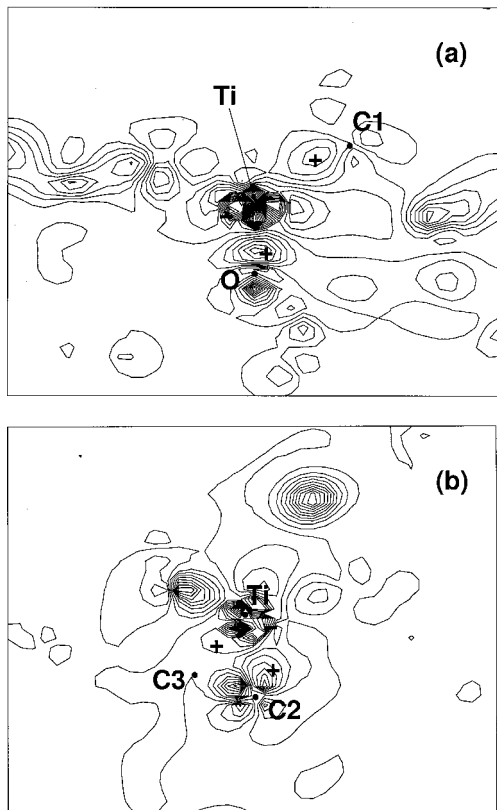


FIG. 3. Difference between the valence electron density in the Ti-PTCDA system and the sum of the valence electron densities of its noninteracting components, PTCDA and Ti: $\Delta\rho = \rho(\text{Ti-PTCDA}) - \rho(\text{PTCDA}) - \rho(\text{Ti})$. (a) Contour map in the plane defined by the O-Ti-C1 atoms. The positive signs identify positive $\Delta\rho$. The contour lines correspond to charge densities between -0.08 and 0.07 a.u. with strides of 0.0075 a.u. (b) Same as (a) in the plane defined by the C2-Ti-C3 atoms. The contour lines correspond to charge densities between -0.06 and 0.05 a.u. with strides of 0.0055 a.u.

etry bears resemblance to known structures of Ti in organometallic compounds.^{35,36,39}

In the structural optimization that led to the geometry described above, we observed a spontaneous migration of a H atom (per unit cell) between pairs of adjacent PTCDA molecules, as indicated by the arrows 1 and 2 in Fig. 2(a). As a consequence of the process represented by arrow 2, the carbon atom C1 in the Ti neighborhood loses its H atom to a C atom belonging to a different PTCDA molecule, which does not belong to the Ti neighborhood and is not shown in the picture. In order to check that this process is not an artifact of periodic boundary conditions, we performed additional calculations on a model finite system that included a Ti atom and its three nearest-neighbor PTCDA molecules. These three molecules and the Ti atom were placed in a supercell large enough to avoid spurious interactions between periodic images. In one case, we considered a local Ti environment like the one in Fig. 2(b) but without H migration; i.e., the atom C1 retained its H neighbor and the three PTCDA molecules retained their regular stoichiometry. In another case, we removed the H neighbor of the atom C1 and we added a

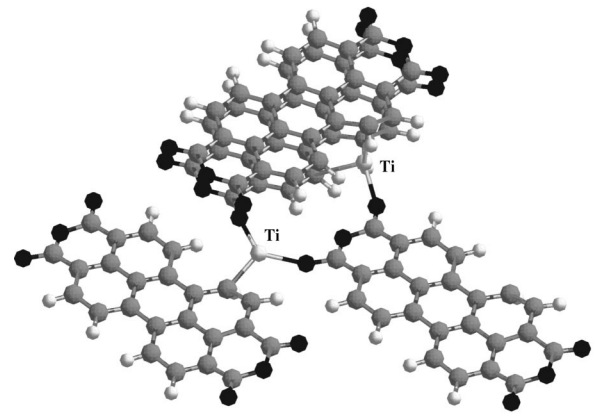


FIG. 4. Local minimum structure found for the Ti_2 -PTCDA system.

H atom to molecule I in the position indicated by arrow 1 in Fig. 2(a). Interestingly, after full relaxation we found that the two structures, with and without H migration, had essentially the same energy (within 0.02 eV). This suggests that H migration between adjacent PTCDA molecules can indeed occur upon Ti incorporation in a PTCDA crystal. This process makes possible the formation of a stronger bond between Ti and C. At the same time it stabilizes a change from sp^2 to sp^3 hybridization in an anhydride C following the formation of a Ti-O bond.

To better visualize the formation of the chemical bonds in the structure of Fig. 2(b), we report, in Figs. 3(a) and 3(b), electron density maps on planes defined by triplets of atoms participating in the bonds. The contour plots show the difference between the valence electron density of a Ti-PTCDA system and the sum of the valence electron densities of a PTCDA crystal and an isolated Ti atom in the same geometry of the Ti-PTCDA system. In Fig. 3(a) the contour map is plotted in the plane defined by O, Ti, and C1. One notices a substantial amount of charge transfer from Ti to both the O and the C1 atoms. In Fig. 3(b) the contour map is plotted in the plane defined by Ti and the atoms C2 and C3 belonging to the same aromatic ring. This figure shows a significantly smaller charge transfer consistent with the weaker character of the bonds between Ti and the two atoms C2 and C3.

By performing additional geometry optimizations we found local minimum structures for two, three, and four Ti atoms in the unit cell. In all cases the most stable structures occur when at least two Ti atoms are bound to the side oxygens of the anhydride groups, as shown, e.g., in Fig. 4 which reports the most stable structure found for Ti_2 -PTCDA. In this structure, one Ti atom has a bonding configuration similar to the one described above for a single Ti impurity per cell. The other Ti atom is in a different local configuration in which it binds to two oxygen and one carbon atoms, each of which belonging to a different PTCDA molecule. When more than two Ti atoms are present in the unit cell, the binding energy per Ti atom is significantly reduced compared to the case when only one or two Ti atoms are present, suggesting that such highly concentrated configurations may be unlikely.

The formation of Ti bonds, both with oxygens and

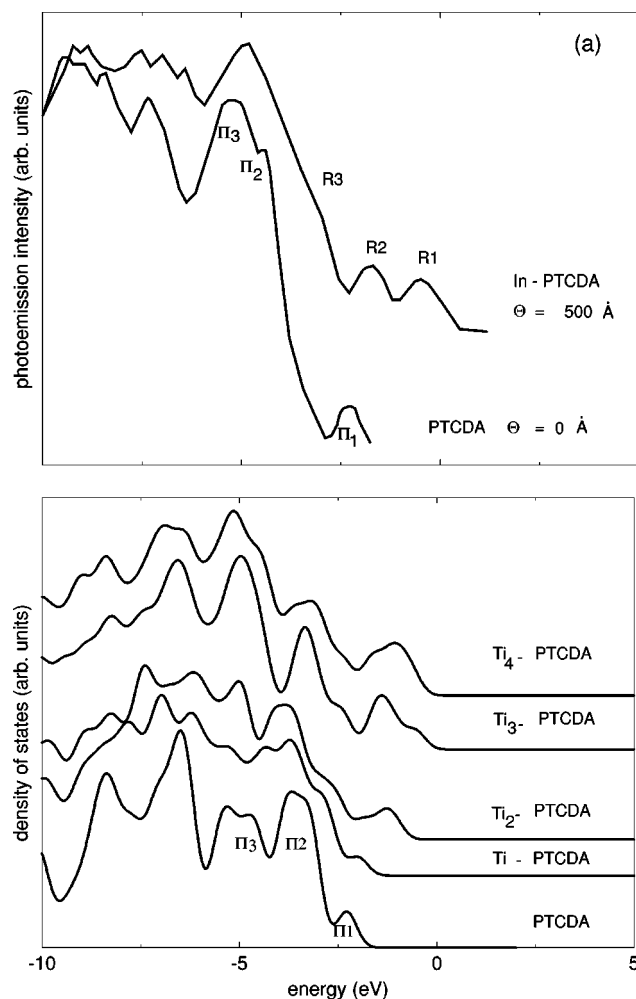


FIG. 5. (a) Photoemission spectra from Ref. 7 of the extended valence band of the pure PTCDA film (bottom curve) and under In coverage (Θ) of 500 \AA . Use of Ti gives a similar behavior. (b) Calculated density of states from Kohn-Sham eigenvalues for PTCDA (bottom curve) and for the Ti_n -PTCDA systems ($n = 1, \dots, 4$), where n indicates the number of Ti atoms introduced in the PTCDA unit cell.

peryleneic carbons, modifies the electronic structure of PTCDA in an important way. In particular, when a finite volume concentration of Ti is present, Ti-related features appear in the valence electronic density of states (DOS) of PTCDA, which can be associated to corresponding changes observed in the photoemission spectra upon metallic deposition. Experimental spectra corresponding to pure PTCDA films and to a PTCDA film under a metallic coverage of 500 \AA are reproduced in Fig. 5(a) from Ref. 7. In these experiments, the reactive metal was In, but similar spectra could be obtained also with Ti.⁷ Our calculated DOS, corresponding to different volume concentrations of Ti impurities in crystalline PTCDA, are shown in Fig. 5(b) for comparison. To generate this plot we considered only the most stable configurations found for each Ti concentration. The DOS have been obtained by convoluting the calculated Kohn-Sham (KS) eigenvalues at the Γ point with a Gaussian broadening function having a standard deviation of 0.35 eV. The three

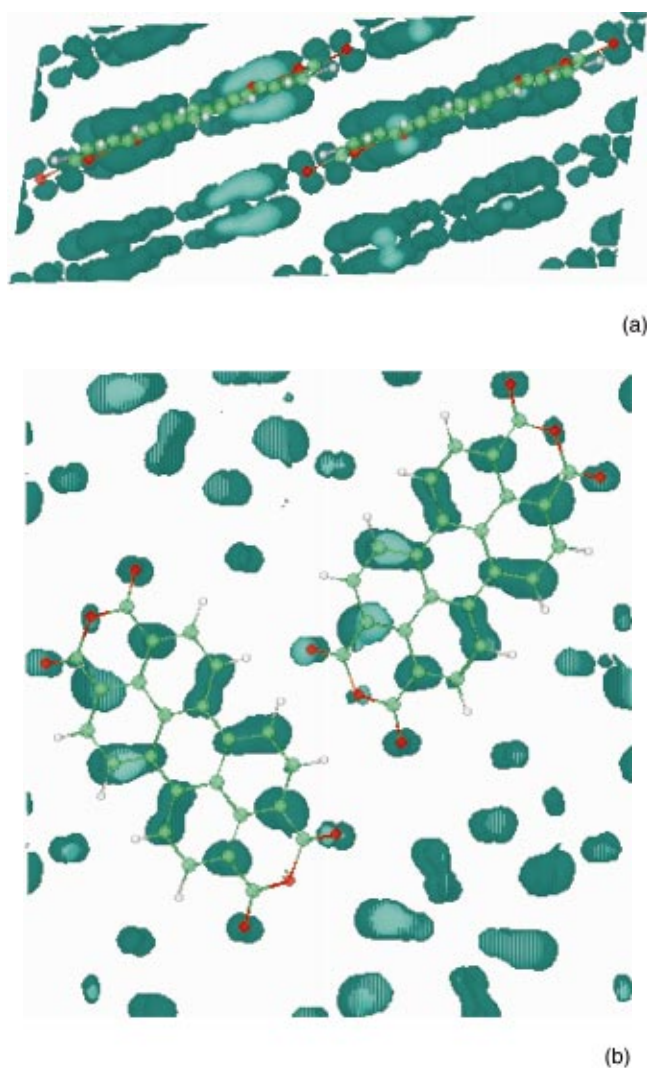


FIG. 6. (Color) HOMO of PTCDA, as seen from directions (a) parallel and (b) orthogonal to the molecular planes. The isodensity threshold has been fixed at 0.001 a.u. The atomic structure of only two molecules is shown.

peaks labeled Π_1 , Π_2 , and Π_3 in the DOS of pure PTCDA correspond to the highest-lying π orbital states. The DOS of systems with different Ti concentrations have been aligned at their respective O $2s$ peaks. This is a reasonable criterion since the O $2s$ peak is essentially unaffected by the presence of a small (atomic) concentration of Ti impurities in a PTCDA crystal. Overall, there is a good qualitative agreement between theory and experiment. In particular, the formation of metal-induced gap states is evident at increasing metallic concentration.

Finally, we give in Fig. 6 three-dimensional isodensity plots of the electronic charge density corresponding to the highest occupied molecular orbital (HOMO) of pure PTCDA. The π character of this state is evident in Fig. 6(a). A view in the direction orthogonal to the molecular planes [Fig. 6(b)] shows that the HOMO is quite delocalized over the perylene groups with some participation of the oxygens. These results are in qualitative agreement with recent semi-

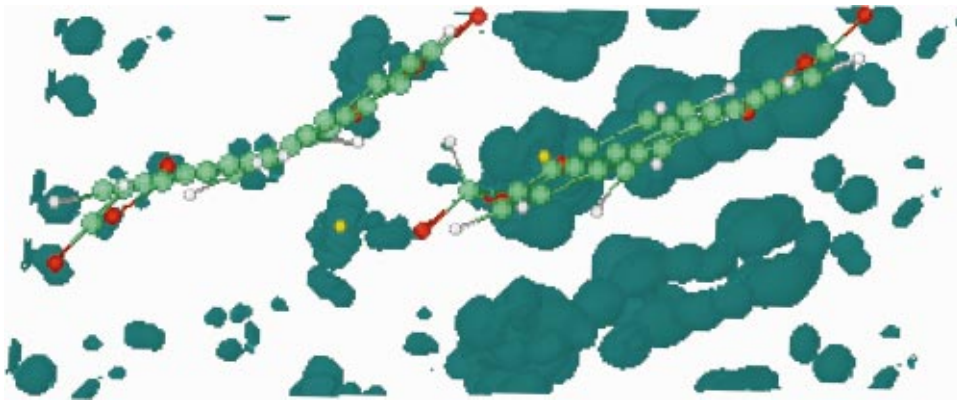


FIG. 7. (Color) HOMO of the Ti_2 -PTCDA system. The Ti atoms are represented by yellow balls.

empirical INDO calculations.⁴⁰ Figure 7 shows how the HOMO is modified when two Ti atoms are added to the unit cell of PTCDA. As in the case of pure PTCDA, the HOMO is delocalized on the aromatic rings, but now a fraction of the charge is also present on the Ti-O bond.

IV. CARBON $1s$ CORE-LEVEL SHIFTS

Core-level photoemission spectroscopy is a powerful tool for chemical analysis as the binding energy of a core level strongly depends on the local chemical environment of the atom to which the level belongs. In the case of pure PTCDA, photoemission spectra show two peaks, approximately 3.9 eV apart, in the energy range corresponding to C $1s$ states.⁷ The peak at lower binding energy is attributed to the carbon atoms of the perylene core, while the peak at higher binding energy is attributed to the carbon atoms of the anhydride end groups of the PTCDA molecule. The core electrons of these atoms have comparatively higher binding energy because the screening of valence electrons is less effective in the presence of the strongly electronegative O atom nearby. We can reproduce these results using the method outlined in Sec. II. We find, on average, a relative binding energy shift of 3.12 eV between the $1s$ levels of the C atoms in the aromatic rings and those of the C atoms having an O neighbor. In this case the agreement with experiment is less impressive than for the small molecules in Sec. II, but still within the accuracy of our approach.^{21–30} Vertical ionization was assumed in the above calculations. This assumption is further corroborated by additional calculations in which we fully relaxed the atomic geometry of the system in the presence of a core hole. This resulted only in minor changes in the geometry, less than 1% in the bond lengths, and the corresponding change in the average core-level shift due to adiabatic processes was of about 0.1 eV.

Photoemission measurements⁷ performed *in situ* during metal deposition show that (i) the peak attributed to carbon of the anhydride group disappears from the spectra and (ii) the peak attributed to perylenic carbon is shifted to higher kinetic energies, i.e., lower binding energies, by about 0.7 eV. Our calculations give an interpretation of both experimental observations. We consider here a PTCDA crystal with zero, one, or two Ti atoms per unit cell bound to oxygen atoms. For any given Ti_n ($n=0,1,2$)-PTCDA system, our procedure gives the relative core-level shifts. In order to

compare core-level shifts corresponding to PTCDA crystals with different Ti impurity concentrations, we proceed as in Sec. III by aligning the O $2s$ peaks of the different systems. Our results are as follows. First, when one or two Ti atoms are present in the PTCDA unit cell the perylenic carbon peak shifts to lower binding energies by about 0.18 eV and 0.87 eV, respectively, in good qualitative agreement with experiment. The shift to lower binding energy is due to a more effective screening of the core hole by the valence electrons in the presence of charge transfer from Ti to the aromatic rings. As we have seen in Sec. III this charge is quite delocalized over the aromatic rings. Thus the shift is spread almost uniformly over all the perylenic carbons and the width of the corresponding peak in the core-level spectra essentially does not change with Ti concentration. On the other hand, the charge transfer from Ti to O is strongly localized on the O atom to which Ti binds. Thus the $1s$ levels of the anhydride carbons also shift to lower binding energies, but this time the shift is more unevenly distributed, resulting in a significant broadening of the peak due to anhydride carbon atoms. In our calculations we find that, although, on average, the relative shift between anhydride and perylenic C $1s$ peaks remains close to 3.1 eV at different Ti concentrations, the standard deviation of the anhydride C peak goes from about 0.1 eV in pure PTCDA to about 0.3 eV and 0.5 eV in the presence of one and two Ti atoms in the unit cell, respectively. This suggests that the disappearance of the anhydride peak observed in the experimental spectra following metallic deposition should be due to a broadening of the corresponding peak which is less intense than the perylenic peak and less distinct from the background than the latter already in the case of pure PTCDA.⁷ These results should be considered as merely indicative, since the actual distribution of metal atoms in a PTCDA film is unknown and a simple uniform periodic distribution has been assumed here. Disorder present in the real material is expected to broaden even further the peak attributed to the carbon atoms of the anhydride end groups.

V. CONCLUSIONS

We have investigated the interaction of a reactive metal (titanium) with PTCDA on the basis of DFT calculations on crystalline bulk PTCDA in the presence of a finite concentration of periodically repeated Ti impurities. This provides a

computationally accessible system to model the substantial incorporation of Ti atoms that is experimentally observed to occur in thin PTCDA films upon deposition of reactive metals like Ti. Although our assumed periodic distribution of Ti impurities is far from realistic, we are able to reproduce and interpret the main results of recent photoemission experiments.⁷ We find, in particular, that reactive metals like Ti bind strongly to the anhydride end groups of the PTCDA molecules and can form additional bridge type bonds with the aromatic carbons of neighboring molecules. This process is accompanied by a significant transfer of electronic charge from the metal atoms to the organic molecules, which may sometimes result in H migration from one molecule to another. The net outcome is the formation of metal-induced gap states, in good agreement with experimental photoemission

data. These states are responsible for the Ohmic behavior of the Ti-PTCDA interfaces. Work is in progress to further extend this investigation to study the indiffusion processes of the metal deep into the PTCDA films at room temperature.

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