In Silico Characterization of a Fourfold Magnesium Organometallic Compound in PTCDA Thin Films[†]

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In this contribution, using first principles calculations within a density functional theory framework, we report, for the first time, evidence for the formation of a fourfold magnesium organometallic compound upon metal deposition on perylene-3,4,9,10-tetracarboxyl dianhydride (PTCDA) organic semiconductor. Current investigation clearly indicates that in the bulk of the organic crystallographic structure the magnesium atom mainly interacts with three PTCDA molecules. The reactive metal is bound both to carboxylic oxygen atoms of the anhydride-end moieties and to a perylene carbon atom which changes its hybridization state, from sp^2 to sp^3, in the presence of metal impurities. In turn, the analysis of the electronic structure of the reacted system prevalently reveals the formation of four covalent bonds, as a consequence of a weak charge transfer toward the organic material. Such a result confirms the capability of the PTCDA thin films to host metal atoms providing, inside their structural empty channels, a rather accessible and soft chemical environment. Interestingly, in the light of these findings and of previous works, a relationship between first ionization potential of the doping metal and the character of the newly formed chemical bonds is confirmed.

I. Introduction

In the last few decades, organic molecular semiconductors have been attracting attention in science and technology, in view of their potential applications in electronic[1,2] and optoelectronic[3−6] devices. In this respect, organic light-emitting diodes (OLEDs) as arising from vacuum deposition techniques, showing relevant brightness and a relatively large range of colors coupled with a sufficient operating lifetime, represent an appealing alternative to liquid crystal-based flat panel displays. It is also worth emphasizing the relevant role of organic semiconductors in thin film transistor preparation as a key component of plastic circuitry or as memory elements in transaction cards and identification tags.[7−10]

In analogy to what happens in inorganic compounds such as zeolites[11] or mesostructured silica materials,[12] organic molecular semiconductors having periodic empty volumes capable of confining atomic species are easily doped by the incorporation of electron acceptors and/or donors; consequently, such a peculiar geometrical feature provides an intriguing chance for the optimization and fine-tuning of charge carrier transport properties which range from semiconduction regime to Ohmic behavior at room temperature. In this context, experimental observations have convincingly demonstrated that the introduction of lithium impurities within copper phthalocyanine (CuPc) induces electric changes in the bulk of the CuPc semiconductor, favoring the appearance of the band gap states, thus forming Ohmic contacts.[13] Many other interesting studies, including In,[14] Al,[15] Ti,[16] Na,[17] K,[17,18] and Mg[19] metals in interaction with organic-based supramolecular assembly have been confirming such a physical trend.

However, a better knowledge of the interaction patterns and related chemistry induced by electronic rearrangements in metal-doped organic semiconductors is fundamental for our understanding and future design of highly efficient optoelectronic devices: this requires a combination of experiments and first-principles atomistic simulations. Indeed, several theoretical and computational investigations on such a relevant issue are emerging with the aim to characterize the electronic properties of optoelectronic devices.[20] In this respect, in several computational applications, it was shown that ab initio approaches within DFT framework[21] are rather accurate in reproducing X-ray photoelectron spectroscopy and UV photoelectron spectroscopy spectra of metal-doped prototype systems such as (8-hydroxyquinoline)-aluminum (Alq3) with Mg atoms[19] and perylene-3,4,9,10-tetracarboxyl-dianhydride (PTCDA) with Ti[16] and K[18] impurities. Interestingly, and unexpectedly, in the latter application the formation of quasi-monodimensional O−K−O chains, which fill the empty channels in PTCDA crystallographic structure, were unequivocally shown, hence opening new perspectives for the future design of low dimensional nanostructures.[18] Having such an intriguing result in mind, in this contribution we address the binding affinity of PTCDA's structural empty channels toward magnesium atoms. In particular, to investigate microcavity effects and the nature of the chemical bonds involved in such an organic material for OLEDs devices, we report a detailed description of the chemical induced transformations upon metal deposition on both structural and electronic properties.

The paper is organized as follows: in the first part we report the computational details regarding the simulation protocol adopted in this work. Afterward, we describe the main results of our theoretical and computational investigation trying to underline, as much as possible, the effects induced by local interaction patterns between Mg metal atoms and the hosting organic material (i.e., PTCDA thin films). Finally, by compari-

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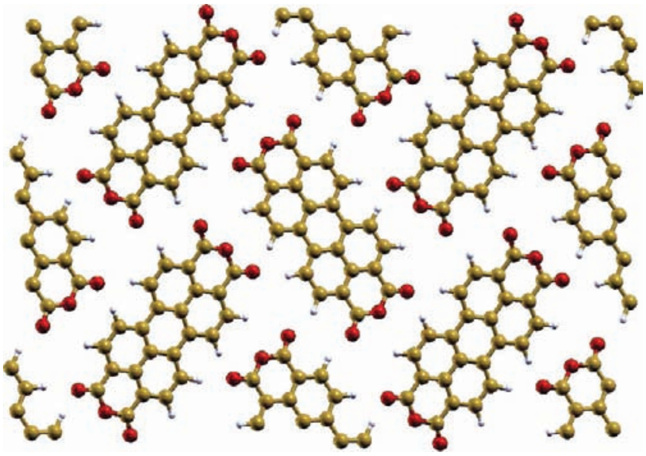

Figure 1. Crystallographic structure of PTCDA (top view). The monoclinic unit cell contains two organic molecules. Red balls represent oxygen atoms, white hydrogen atoms, and brown carbon atoms.

son of the basic features of the current interacting trend with those previously obtained in the presence of Ti,[16] Na,[17] and K[17,18] atoms, an intriguing general picture regarding the relationship between the first ionization potential (IP) of the introduced metal atom and the portion of the ionic character of the newly formed chemical bonds is observed, in line with previous results published in a recent work.[17b]

II. Methodology and Computational Details

The PTCDA thin films of interest for OLED devices usually have a thickness of 400−800 Å. These films are highly oriented when deposited under ultrahigh vacuum conditions on several substrates, and their molecular structures are believed to be very close to that of bulk PTCDA[16] whose unit cell contains two molecules. Therefore, in our calculations we consider bulk crystalline PTCDA, shown in Figure 1, as a realistic model of the thin film.

The metal deposition on PTCDA organic thin films is simulated by introducing Mg atoms into the empty channels of the organic crystal, subject to periodic boundary conditions (PBC). In particular, in order to avoid spurious effects due to interactions of magnesium atoms with their images, we have considered a double cell ($a = 7.44$ Å, $b = 11.96$ Å, $c = 17.34$ Å and, $\beta = 98.8°$) having four PTCDA molecules and a single interacting magnesium atom. Thus, the whole investigated molecular system consists of 153 atoms and 568 explicit valence electrons distributed over 284 bands. Mg atoms are introduced into the bulk of the organic semiconductor in positions strongly resembling ones previously sampled by potassium atom deposition.[18]

In the current simulations, all electronic and ionic degrees of freedom are simultaneously relaxed using damped[22] second-order ab initio molecular dynamics, within the classical scheme, proposed by Car and Parrinello.[23−25] The electronic structure is treated within density functional theory using the generalized gradient corrected approximation (GGA) to the PW91 functional for exchange and correlation energy.[26] We adopt a plane wave pseudopotential (PP) expansion[24,25] using ultrasoft[27] Vanderbilt PPs for all atoms (i.e., C, H, O, and Mg). 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; the equations of motions were integrated with a time step of 10 au (0.242 fs). The Γ point approximation has been used for Brillouin zone sampling, since this is adequate for a molecular crystal like that considered in this study, made of relatively large and weakly interacting submolecular units. The local minimum structure found has been further refined by sampling the reciprocal space using 8 *k* points.[28] For the structural optimizations the forces on each ion were relaxed (maximum force less than 10^{-4} au) and crystal cell parameters were kept fixed at their crystallographic values. Binding energies characterizing the local minima found in our simulations were calculated, as usual, with respect to the sum of the total energies of the isolated fragments (pure PTCDA crystal and Mg atom) in the same simulation cell.

The approximate exchange-correlation density functional used is capable of good accuracy in the description of chemical bonds but is not expected to describe properly weak physical interactions, like the van der Waals interactions between different PTCDA molecules (see Figure 1). This limitation is irrelevant in the present context since we do not optimize the crystalline unit cell of PTCDA and our main interest is in describing the chemical interaction between Mg and PTCDA. Moreover, it is worth noting that, with this computational procedure, where the cell parameters are kept fixed during the simulations, we are able to reproduce the bulk PTCDA structure with an error less than 3%.[16]

III. Structural and Electronic Properties of the Mg−PTCDA Complex

In the present calculations we will examine the permeability of PTCDA's empty channels toward magnesium atoms. To this end, a Mg metal atom was introduced in a PTCDA supercell in order to avoid spurious effects of the imposed periodicity of the crystal structure. As usual,[18,20a] the metal atom concentration in the solid phase is expressed as the number of Mg atoms divided by the number of PTCDA molecules in the simulation cell, e.g., $Mg_{x=0.25}$−PTCDA, one Mg atom, and four PTCDA molecules. In this context, in the current simulated model system we are considering the presence of low concentration of such a reactive metal within the organic material; this is because we would like to highlight, through first-principles electronic structure calculations, the actual chemical changes involved in the reactive process between Mg atoms and PTCDA molecules.

The geometry optimization procedure was carried out starting from local minimum conformations as obtained for the $K_{x=0.25}$−PTCDA doped system. In turn, the optimized structure of the $Mg_{x=0.25}$−PTCDA interacting system, in singlet spin multiplicity, is reported in Figure 2 where, for the sake of clarity, the PBC are also reported. Moreover, geometry optimizations considering different positions for the Mg atom within the empty channel basically end up to the same local minimum structure as shown in Figure 2. Extension to Mg−π complexation was also investigated in the present work. To this end, in the initial conformation the Mg metal atom was introduced in the middle position between two PTCDA molecules, hence in strict interaction with the π molecular orbitals of the perylene core of the organic molecules (see the upper panel reported in Figure 3). However, in this case our results clearly indicate that Mg−π complexation, being accompanied by a remarkable deformation of the perylene rings (see the bottom panel in Figure 3), is strongly endothermic having a binding energy of almost 74 kcal/mol. Similar results were found also in similar systems (Ti−PTCDA[16] and K−PTCDA[18]).

The resulting relaxed conformation unequivocally shows that Mg metal atoms are basically confined within PTCDA's empty channels, in close interaction with the anhydride end groups (see Figure 2). A deeper inspection of our data reveals the

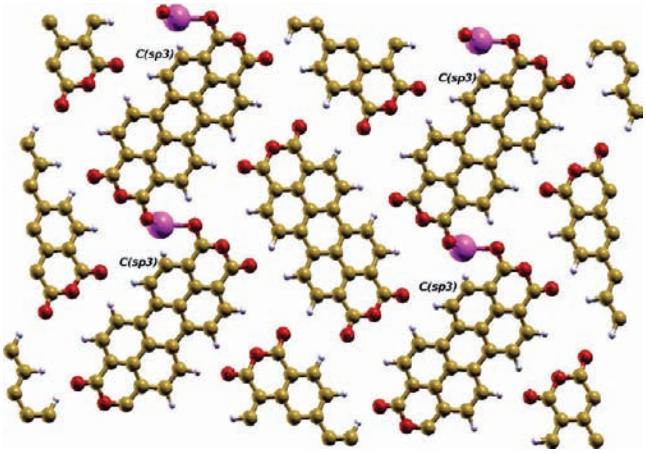

Figure 2. Lowest local minimum structure found for Mg_x-PTCDA interacting system at Mg concentration $x = 0.25$ (see text). Red balls represent oxygen atoms, white hydrogen atoms, brown carbon atoms, and magenta magnesium atoms. Our simulation cell contains four PTCDA molecules and a single Mg atom. Distance between Mg atoms is 7.44 Å (twice the *a* crystallographic cell parameter). Note that C(sp^3) labels carbon atoms which undergo a change in the hybridization state upon deposition of metal impurities.

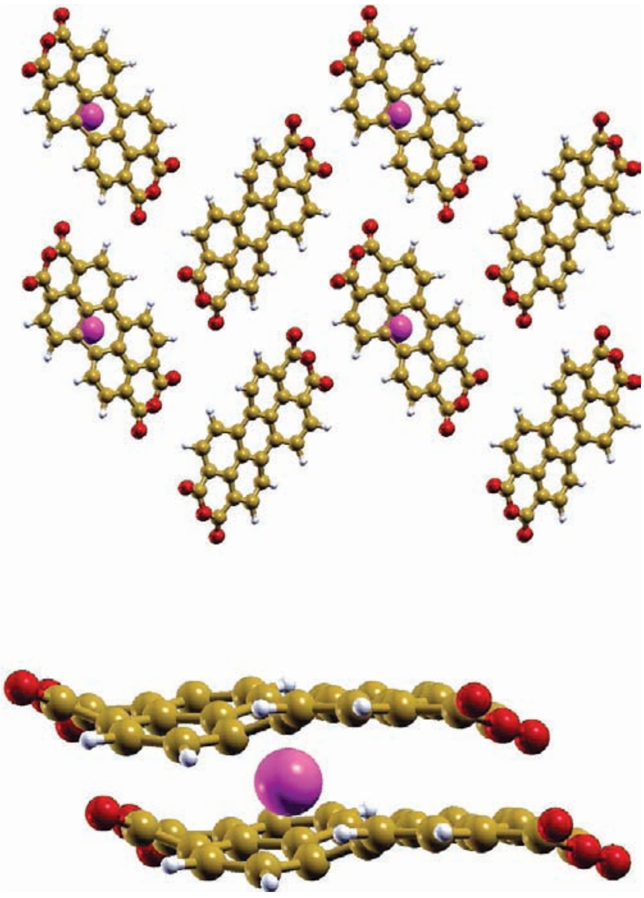

Figure 3. Upper panel: Another stationary point structure found, at higher energy, for Mg metal atom in interaction with the π molecular orbitals widespread along the perylene moiety of the PTCDA organic semiconductor; the concentration of Mg atoms is $x = 0.25$ (see text). Bottom panel: Local geometrical deformation of the pyrelene rings as a consequence of the metal complexation. Colors are the same as those used in Figure 2.

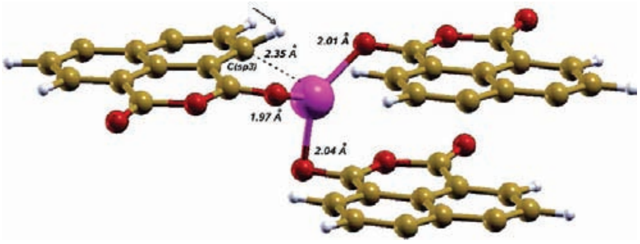

Figure 4. Local connectivity (nearest neighbors) of the Mg metal atom interacting with PTCDA organic semiconductor in the lowest local minimum structure found. The corresponding interatomic distances are also shown. The arrow indicates the hydrogen atom which moves out of the perylene core of the organic molecule, as a consequence of a change in hybridization of the carbon atom which binds to Mg in a concerted mechanism. Colors are the same as those used in Figure 2.

possibility of formation of an organometallic compound as arising from the chemical interaction between the Mg atom and different PTCDA molecules. As a matter of fact, we obtained a binding energy equal to −44.7 kcal/mol for the Mg−PTCDA complex formation. In turn, the local connectivity as reported in Figure 4, shows that the Mg atom in the organic semiconductor reacts with three carboxylic oxygen atoms of the anhydride end groups of different PTCDA molecules, along a direction perpendicular to the molecular stack. The predicted Mg−O bonds have a length of almost 2.0 Å (see data reported in Figure 4). Interestingly, in a further analysis of the local atomistic environment, we identify a hydrogen atom bound to perylene-conjugated moiety lying out of the plane (by about 20°) of the aromatic ring. Such evidence clearly suggests that a carbon atom of the perylene group in proximity of the Mg atom changes its hybridization state, from sp^2 to sp^3, favoring the Mg−C bond formation upon introduction of metal impurities. A similar interaction pattern was observed in the Mg−Alq3 system, where the Mg atom was found to interact with both oxygen and carbon atoms, thus forming, like in the current case, a four-coordinated organometallic compound.[19] As a comparison, the Mg−C bond length in Mg−PTCDA complex is equal to 2.35 Å (see Figure 4) and is very close to that observed in the Mg−Alq3 system (2.40 Å).[19] On the other hand, the current Mg−O distances ranging from 1.97 to 2.04 Å are systematically shorter that those previously reported in Mg−Alq3 where the two Mg−O both had a length of 2.30 Å. Such a difference suggests that Mg−PTCDA complex has relatively stronger Mg−O interactions and this fact could explain the increase in binding energy.

Furthermore, to better understand the local interaction in terms of electronic structure rearrangements upon doping, we evaluated the three-dimensional (3D) plot of the difference ($\Delta\rho$) between the electronic density of the Mg−PTCDA complex and the sum of the electronic density of the two separated fragments (i.e., Mg atom and bulk PTCDA) at the same molecular geometry (see Figure 2). The 3D plot of $\Delta\rho$ is displayed in Figure 5 in which the red clouds represent the excess electronic charge, while the blue ones represent depletion of electronic charge. The changes in electronic structure, arising from the Mg−PTCDA complex formation, partially remove charge density around the metal atom, as well as from the lone pairs of the carboxylic oxygen atoms belonging the anhydride moieties of the organic semiconductor (blue clouds). This means that both Mg and O atoms donate electronic charge along the Mg−O direction (red lobes) as a consequence of the local interaction. In other words, Mg and O atoms in Mg−PTCDA complex form prevalently covalent bonds. In this context, a similar behavior was observed in the Ti−PTCDA system.[16] Interestingly, the 3D plot of $\Delta\rho$ as reported in Figure 5 indicates that the same trend occurs along the Mg−C(sp^3) bonds. Moreover, the Löwdin charge analysis[29] suggests that the Mg

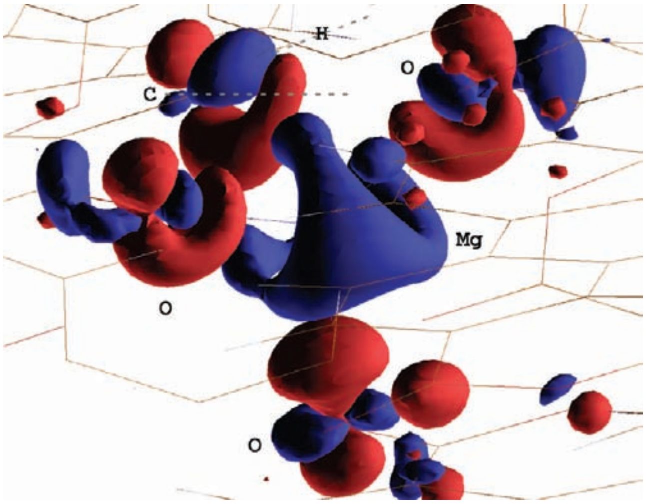

Figure 5. 3D difference density plot ($\Delta\rho$) for Mg−PTCDA interacting system at concentration of $x = 0.25$ Mg atom (see text) in the reaction region of the lowest local minimum structure found. Red and blue volumes indicate excess and depletion of electronic charge, respectively.

metal atom, in interaction with three PTCDA molecules (see Figure 2 and Figure 4), does not change its oxidation state, transferring 0.28 electrons to the hosting organic matrix. A rather different picture was observed in the K−PTCDA interacting system,[18,20a] where the K atom was found ionically bound to PTCDA semiconductor. In particular, in such a case was evident the appearance of singly occupied induced band gap states, which strongly resemble virtual π molecular orbitals of pristine PTCDA molecules.[18,20a] Therefore, this result suggested a net charge transfer process from K atoms to the lowest unoccupied molecular orbitals of the bulk PTCDA.

The calculated density of states (DOS) for the fourfold Mg organometallic complex in PTCDA matrix is reported in the upper panel of Figure 6. The reported DOS have been computed by convoluting the Kohn−Sham (KS) eigenvalues at the Γ point with a Gaussian broadening function with a standard deviation of 0.35 eV. Note that, for the sake of clarity, in the same panel the calculated DOS for the crystalline PTCDA in its lowest local minimum is also shown. In this context, photoemission measurements carried out on the PTCDA semiconductor show a characteristic peak (termed in literature as P3 and mainly composed by molecular orbitals having a π character[18]) at almost 2 eV below the Fermi level, which is correctly reproduced by our calculations (see Figure 6). Moreover, always taking into account the organic system, the calculated band dispersion of 0.2 eV, evaluated using 11 k points along the direction perpendicular to molecular plane, is found in excellent agreement with experimental data reported in literature.[30]

In the case of Mg−PTCDA system, the calculated DOS clearly indicates the presence of a chemistry induced electronic band which is located into the band gap of the organic semiconductor at +0.9 eV with respect to the highest occupied molecular orbital, HOMO, of the pristine PTCDA (see upper panel in Figure 6). The 3D electronic density plot of this induced band gap state (i.e., the HOMO of the Mg−PTCDA system) is shown in Figure 6 (bottom panel). It can be seen that such a newly formed molecular orbital shows a hybrid character resulting from the combination of a Mg 3s orbital and PTCDA unoccupied orbitals having basically a π character. Moreover, the presence of electronic charge on the Mg atom supports the idea of a partial charge-transfer process toward the organic material and the prevalent formation of covalent bonds. It is worth noting that present results are qualitatively in line with the character of the induced band gap states previously described in a Mg−Alq3 organometallic complex.[19]

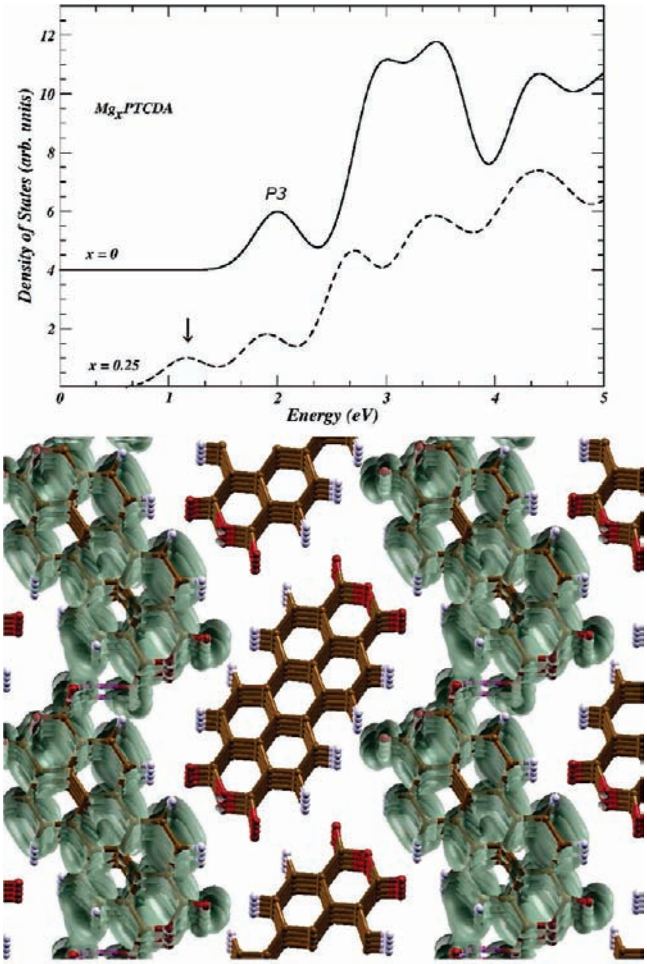

Figure 6. Upper panel: Calculated DOS from Kohn−Sham eigenvalues for bulk PTCDA (solid line) and for the $Mg_{x=0.25}$−PTCDA (dashed line) systems; the arrow indicates the chemistry induced band gap state corresponding to the HOMO of the investigated reacted system. Bottom panel: 3D electronic density plot of the HOMO for the Mg−PTCDA interacting system. Colors are the same as those used in Figure 2.

Finally, it should be noted that our data confirm the necessity of including molecular packing found in the crystal structure of the hosting matrix to obtain a reliable theoretical picture able to describe the metal doping process within the organic semiconductor (or thin films). On the other hand, a theoretical modeling in gas phase considering only a single PTCDA molecule and the Mg atom represents a rather unrealistic situation.[19a] Unfortunately, at least to our knowledge, no experimental data are available in literature for Mg-doped PTCDA thin films, even though this system seems to present, in the configurational space sampled, an appealing and sensitive electronic response which, promoting electronic density into the band gap region of the organic matrix, is expected to improve ohmicity of the Mg/PTCDA contacts.

IV. Concluding Remarks

PTCDA, an organic semiconductor, has been modeled by its crystallographic structure, and a Mg atom has been introduced in a double monoclinic cell, in order to mimic the doped material. This model represents a low metal concentration in the organic semiconductor and has the advantage of avoiding spurious effects due to periodic boundary conditions, to which the supercell is subject in the DFT calculations. The system is a reliable model for organic thin films, used in OLED devices, since their structure is believed to be similar to that of a PTCDA crystal.

DFT based calculations, with plane wave ultrasoft pseudopotentials, show that the Mg atom reacts with oxygen atoms of the anhydride terminal groups of three PTCDA molecules and with a carbon atom of the perylene core of the organic molecule, forming prevalently covalent bonds. This picture is corroborated by electron density plots by difference and, as well, by Löwdin population analysis: a weak charge transfer (0.28 e)$^-$ is observed from a Mg metal atom toward the organic system. Interestingly, looking at previous published results on similar systems we can, one more time, reinforce the hypothesis proposed by Wüsten and co-workers (see ref 17b) which states that the nature of the chemical bonds between metal and PTCDA end groups is related to the first ionization potential (IP) of the metal atom. In fact the entity of the charge transfer is major for K[17,18] and Na,[17] which form essentially ionic bonds having a relatively low IP (419 and 496 kJ/mol, respectively);[31] on the contrary, in metals like Mg and Ti, having higher IP (737 and 656 kJ/mol, respectively),[31] the charge transfer is smaller and covalent bond formation is unequivocally confirmed by our analysis. Further proof of this behavior is provided by inspection of the 3D plot of the HOMO of the doped system: the higher the metal's IP, the lower is the electronic involvement of metal atom in this molecular orbital. At last, it is interesting also to emphasize that the HOMO of the metal−PTCDA system is usually reminiscent of the LUMO of pristine PTCDA solid.

Further studies are in progress to extend the sampling of configurational space in order to locate other local minima of the Mg−PTCDA system and to access effects of metal concentration on electronic structure in the band gap region. In this respect, preliminary calculations carried out introducing two Mg atoms into the simulation cell suggest that the binding of the second Mg atom to already reacted PTCDA molecules is energetically favorable by about 3.4 kcal/mol. Moreover, at high Mg concentration inside the semiconductor, metal nanoclusters might be formed thanks to the hosting capabilities of the flexible, π conjugated organic matrix.

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