P H Y S I C A L   R E V I E W   L E T T E R S

Theoretical Design of Coupled Organic-Inorganic Systems

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Metallo-organic molecules with highly conjugated π-electrons, like phthalocyanines (Pc's), are widely investigated for usage in electronic and electro-optic devices. However, their weak coupling with semiconductors is an obstacle to technological applications. Here we report a first-principle theoretical study of some fundamental features of the Pc-semiconductor interaction. Our results shed light on the general problem of organic-inorganic coupling and show that an effective coupling can be achieved by a careful choice of the Pc-substrate system and the semiconductor doping. Our results also reveal a universal alignment of the Pc electronic levels to the semiconductor band gap and suggest a general procedure for designing efficiently coupled organic-inorganic systems.

Hybrid materials containing both inorganic and organic components may give rise to a combination of the properties of each component or, most interestingly, to novel properties provided that a suitable degree of organic-inorganic coupling is achieved [1,2]. In this regard, a typical example is offered by metallo-organic macrocyclic complexes (MOMC) interacting with inorganic semiconductors. MOMC are a wide class of organic compounds characterized by a macrocycle carrying a metal (or a group containing a metal) in its center and including phthalocyanines (Pc's), metalloporphyrins and related biological molecules [3–7]. A peculiar feature of these MOMC is represented by the large hyperpolarizability of the π-electron clouds of the macrocycle [see the insets in Fig. 1(a)], which accounts for the transport and nonlinear optical properties (NLO) shown by these molecules. Such features would be of high interest for technological applications as, for instance, in a Pc-semiconductor *heterostructured junction* a tuning of the NLO properties of the organic film could be driven by its interaction with the inorganic substrate, thus opening new routes to design opto-electronic devices. Unfortunately, a very weak coupling characterizes the interaction of Pc's with semiconductor substrates, although ordered monolayers of different Pc's deposited on In-rich InAs and InSb surfaces were recently observed and related to the existence of some chemical bonding between the molecules and the surface atoms [8–11]. These results stress our insufficient understanding of the MOMC-semiconductor interactions and point to the general problem of how to achieve an efficient coupling between organic and inorganic components. Here, we have investigated such *fundamental* features of the organic-inorganic coupling in the case of Pc's-semiconductor systems, seen as representative of MOMC-semiconductor systems. We have assumed that

two main conditions must be both satisfied to achieve such an efficient coupling: (i) the formation of appreciable surface-molecule chemical bonds, and (ii) a molecule-surface charge-transfer involving the π-electron clouds responsible of the Pc NLO and transport properties. Then, we have verified the occurrence of such conditions by performing a systematic study of different Pc-semiconductor systems investigated, for the first time, by *ab initio* theoretical methods. Our results clarify the surface-molecule charge-transfer mechanisms and permit to propose a new Pc-semiconductor system, i.e., the OTiPc molecule adsorbed on the (101) TiO_2 anatase surface [see Fig. 1(a)], for which they predict an effective organic-inorganic coupling never reported before (to the best of the authors knowledge). In detail, present results reveal a *universal alignment* of the Pc electronic levels to a semiconductor band gap and show that the successful organic-inorganic coupling in the OTiPc-anatase system is founded on: (i) the chemical affinity of the Pc central group with the surface atoms, which permits the formation of surface-molecule chemical bonds, (ii) the above alignment of the Pc electronic levels, and (iii) a suitable doping of the inorganic semiconductor. They indicate also that the last two conditions play a key role in the molecule-surface charge-transfer processes. Finally, our results suggest a general procedure for a theoretical design of efficiently coupled molecule-semiconductor systems. The two main features of the Pc's architecture involved in the realization of an efficient organic-inorganic coupling, i.e., the π-electron clouds and the central metal, are present in many organic and biological systems. Thus, the indications given by present results for achieving an efficient coupling in the case of the Pc-semiconductor systems can apply to many different organic- or biological-semiconductor systems.
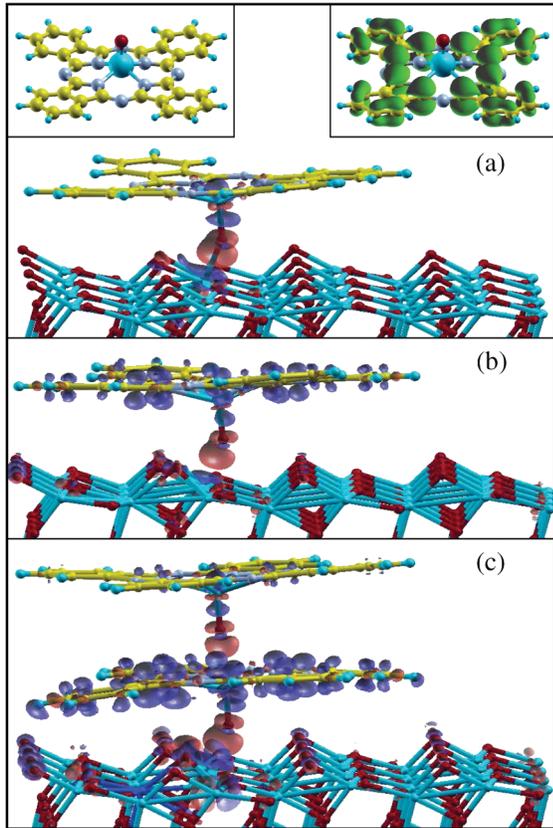
FIG. 1 (color).   Stable configurations and isosurfaces of difference electron densities (ρ_{diff}) of: (a) OTiPc-anatase system (structure and π-electron clouds of an isolated OTiPc molecule in the left and right insets, respectively); (b) OTiPc-(p-doped) anatase system; (c) 2(OTiPc)-(p- doped) anatase system. ρ_{diff} maps show the displacements of electronic charge at the molecule-surface interaction. Red surfaces cover areas where the difference is positive, blue surfaces where it is negative. C, N, and H atoms of the Pc molecule are represented by yellow, gray, and light blue spheres, respectively. Ti and O atoms by (big) light blue and red spheres, respectively.

The Pc-semiconductor systems have been investigated by using first-principles Density Functional Theory methods in the generalized gradient approximation and a supercell approach [12]. Total energies have been calculated by using ultrasoft pseudopotentials,[13] planewave basis sets, and the PBE [14] exchange-correlation functional. Electronic properties have been investigated by analyzing the electronic eigenvalues calculated at the Γ point. Satisfactorily converged results have been achieved by using cutoffs of 25 Ry on the plane waves. The supercells are formed by ≈ 15 Å of empty space added to a bulk supercell simulated by six (eight, H-saturated at the bottom) atomic planes, i.e., 192 (108 + 32) atoms, of TiO$_2$ (GaAs) bulk. The strength of a molecule-surface bonding, i.e., the molecular adsorption energy, has been estimated by the total energy difference $E_{\text{ads}} = E[\text{Pc} + \text{surface}] - E[\text{Pc}] - E[\text{surface}]$. Geometry optimization procedures have been

performed by fully relaxing the positions of all of the atoms in a supercell, except for the atoms of the bottom layer of the semiconductor, which have been kept fixed to their optimized positions. *Difference* electron density (ρ_{diff}) maps have been analyzed to unravel the formation of chemical bonds and the occurrence of charge-transfer processes. For example, in the OTiPc-anatase system, $\rho_{\text{diff}}[\text{OTiPc} - \text{anatase}]$ is given by $\rho[\text{OTiPc} - \text{anatase}] - (\rho[\text{OTiPc}] + \rho[\text{anatase}])$ where $\rho[\text{OTiPc} - \text{anatase}]$ is the electron density of a supercell containing the molecule-semiconductor system, $\rho[\text{OTiPc}]$ is the electron density of the same supercell with the molecule only, and the analogue for the $\rho[\text{anatase}]$ density. Thus, a $\rho_{\text{diff}}[\text{OTiPc} - \text{anatase}]$ map indicates the charge displacements induced by an interaction between the molecule and the surface. Further details on the theoretical methods are given in Refs. [15,16].

In the present study, we consider Pc molecules having a different central metal (PbPc, lead phthalocyanine,[17] and Ti(Pc)$_2$ [18]), or a central group (OTiPc [19]) interacting with the well defined (001) GaAs As-rich $\beta 2(2 \times 4)$ [20] and Ga-rich $\zeta(4 \times 2)c(8 \times 2)$ [21] surfaces, as well as with the (101) TiO$_2$ (anatase) surface [22]. However, the main focus is on the OTiPc-GaAs and OTiPc-TiO$_2$ systems, which exemplify well the conditions permitting to achieve an effective organic-inorganic coupling. Results achieved for other Pc-semiconductor systems will be reported elsewhere. [23] We did not consider the mentioned In-rich InAs and InSb surfaces because their reconstruction is still uncertain [24,25].

In all the cases here reported, the energetically favorable orientation of the molecules presents the macrocycle plane parallel to the surface [see Fig. 1(a)]. In the PbPc-GaAs and Ti(Pc)$_2$-GaAs systems, the molecules give rise to very weak interactions with both the As-rich and Ga-rich surfaces (E_{ads} less than 0.1 eV). Even the OTiPc-GaAs(As-rich) system is characterized by a weak molecule-surface interaction. On the contrary, an appreciable O-Ga bond forms in the case of the OTiPc-GaAs(Ga-rich) system (E_{ads} equal to 1.39 eV). It may be noted that the different interactions shown by the above Pc-GaAs systems are mainly related to the structure and chemical properties of the molecule rather than the surface properties, e.g., OTiPc is the only molecule having a reactive O atom which is also more aggressive toward (metallic) Ga atoms than (nonmetallic) As atoms. In the OTiPc-GaAs system, the formation of an O-Ga bond represents a promising condition for charge-transfer processes. The corresponding electronic structure is given in Fig. 2(b), which shows the position of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital), i.e., the π orbital and its antibonding π^* counterpart, in the order, with respect to the top of the valence band (VB) and the bottom of the conduction band (CB) of GaAs. This figure shows that the HOMO is located in the VB while the

LUMO is in the band gap close to the top of the VB. This implies that a charge transfer may occur only from an *n*-doped substrate to the Pc molecule. The *n*-doping of GaAs has been simulated by substituting a Ga atom in the supercell with a Si donor. The introduction of a Si donor level has remarkable effects on the electronic structure of the OTiPc-GaAs system, as shown in Fig. 2(a). In fact, the HOMO-LUMO pair rigidly shifts upwards by leading the HOMO close to the top of the VB and the LUMO above the Si donor level, that is, the Pc molecule responds to the presence of the Si donor by hindering an electron transfer from the substrate. Such a result shows that the formation of molecule-surface chemical bonds and a suitable position of the electronic levels may be not sufficient to produce a substrate-molecule charge transfer.

Now, we focus on the OTiPc-anatase system shown in Fig. 1. The (101) anatase surface presents rows of Ti atoms under coordinated with respect to the sixfold coordinated Ti atoms of the anatase bulk. They are suitable therefore for the formation of a chemical bond with the O atom of the OTiPc molecule. Such an O-Ti$_{surface}$ bond actually forms as indicated by an E_{ads} equal to 1.25 eV and by the difference density map of Fig. 1(a) showing a displacement of elec-
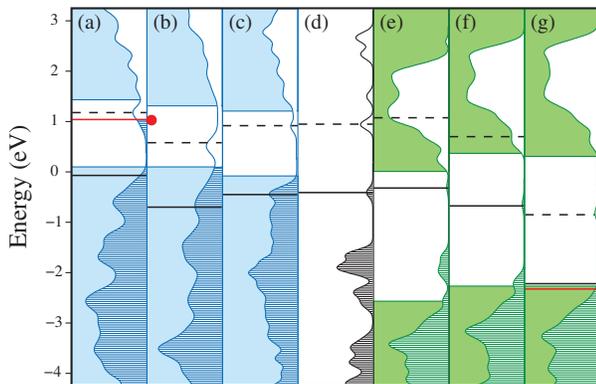
FIG. 2 (color). Density of states (DOS) and molecular electronic levels of a OTiPc molecule interacting with different GaAs and anatase surfaces. All the levels and the bands are aligned to a common reference. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are represented by full and dashed black lines, respectively. The filled and empty areas represent the valence band (VB) and conduction band (CB) DOS' of a molecule-semiconductor system, respectively. The color background (either blue or green) delimit the VB and CB regions relative to the semiconductor band structures only. Dopant levels are indicated by a red line and a solid (open) circle for the donor (acceptor) level. (a) OTiPc bonded to an *n*-doped Ga-rich GaAs surface, (b) OTiPc bonded to a Ga-rich GaAs surface (c) OTiPc weakly interacting with an As-rich GaAs surface, (d) isolated OTiPc molecule, (e) OTiPc weakly interacting with an anatase surface, (f) OTiPc bonded to an anatase surface, (g) OTiPc bonded to a *p*-doped anatase surface. The molecule-surface coupling increases when moving from the middle panel to the left or right ends.

tronic charge towards the region of the O-Ti$_{surface}$ pair. The electronic structure of the OTiPc-anatase system is characterized by a HOMO in the anatase band gap and a LUMO above the bottom of the CB [see Fig. 2(f)], suitable for an electron transfer from the molecule to a *p*-type doped anatase. Then, we have introduced an unoccupied, shallow acceptor level in the anatase band gap by substituting a Ti atom with a Ca atom. Once more, the introduction of a dopant level has relevant effects on the positions of the molecular levels by leading to a downward rigid translation of the HOMO-LUMO pair; see Fig. 2(g). However, in this case, the HOMO loses its electrons by remaining located above a fully occupied acceptor level, that is, a charge transfer occurs from the molecule to the *p*-doped substrate. Moreover, the difference density maps of Fig. 1(b), clearly shows that electronic charge moves from the molecular π orbital involving C atoms of the macrocycle (i.e., the HOMO) to surface atoms, that is, electrons are transferred *from the π orbital* affecting the molecular NLO properties *to the substrate*, thus realizing an *effective Pc-semiconductor coupling*. Such a charge-transfer process matches a stronger molecule-surface bonding, as underlined by an E_{ads} equal to 2.20 eV, calculated in the case of the OTiPc-*p*-doped system. A comparison of these results with those achieved for the OTiPc-GaAs (*n*-type) system indicates that a surface-molecule charge transfer actually occurs only if allowed by the corresponding energy balance given, e.g., in the OTiPc-TiO$_2$, by the sum of the energies paid to remove an electron from the molecule and gained by adding an electron to the semiconductor. In the OTiPc-TiO$_2$, a favorable energy balance is related to the usual Pc donor character,[3] while, in the OTiPc-GaAs system, an opposing energy balance leads to the translation of the molecular levels discussed above.

Present results give also suggestions on the properties of an OTiPc film on the (101) anatase surface. This surface presents rows of fivefold Ti atoms compatible with an ordered assembling of a first molecular layer, which should be favored by the moderate strength of the O-Ti bond. Regarding the structure of a second molecular layer, the stable configuration for a two-molecules system is shown in Fig. 1(c). The second OTiPc molecule forms a weak O-Ti bond with the molecule adsorbed on the surface (E_{ads} equal to 0.44 eV). Figure 1(c) also shows a difference density map corresponding to the two OTiPc molecules interacting with a Ca-doped *p*-type anatase. The second molecule enhances the charge transfer from the first molecule to the substrate [compare Figs. 1(b) and 1(c)]. The Ca acceptor strengthens the bonding between the two molecules (E_{ads} equal to 0.84 eV). All together, these results suggest that the first OTiPc molecular layers should present a certain degree of order and a stronger organic-inorganic coupling in presence of a *p*-type doped anatase.

The electronic structure of an OTiPc molecule interacting with different semiconductor surfaces reveals further

interesting features; see Fig. 2. In its middle panel (d), this figure reports the HOMO-LUMO pair of the isolated OTiPc molecule. Moving from this panel to the left or right ends, the figure shows the location of the HOMO-LUMO pair with respect to semiconductor band gaps *for an increasing molecule-surface interaction* (the electronic structure given in panel (e) corresponds to a weak OTiPc-anatase interaction, achieved by locating the OTiPc molecule on the surface with its O atom upwards). A significant result shown by the panels (b)–(f) (undoped substrates) is that the HOMO-LUMO pair of the OTiPc molecule (full and dashed black lines in the figure) maintains an almost *common alignment* with respect to the band gap of the GaAs and TiO$_2$ substrates *independently* on the strength of the molecule-surface chemical interaction. More specifically, such an alignment is independent on the formation of chemical bonds involving the molecule central group. This is related to the weak effect that this group has on the highly delocalized π orbitals and implies that, in absence of a semiconductor doping perturbing the HOMO-LUMO pair, that alignment is basically *controlled* by the relative positions of the first molecular ionization potential and the semiconductor work functions. Then, the HOMO-LUMO positions change only when a donor or an acceptor are introduced in the substrate to induce some charge-transfer process involving *these orbitals*; see panels (a) and (g). These results represent a general feature of the Pc-semiconductor interaction, not affected by the presence of a metal-oxygen pair in the OTiPc in place of a metal central atom. Quite similar theoretical results have been achieved indeed for Pc-semiconductor systems where the Pc carries a single central metal atom [23]. Thus, the above results suggest a common alignment of the HOMO-LUMO levels of a *same* Pc interacting with *different* semiconductors. In addition, *different* Pc's should present similar locations of their levels with respect to the band gap of a *same* semiconductor. In fact, quite similar π-π^* electronic transitions and ionization potentials are indicated by both theoretical results [23] and experimental findings [26] achieved for different Pc molecules, that is, such transitions and potentials are almost independent on the nature of the Pc central group. All together, the above results suggest a *universal* alignment of the Pc electronic levels with respect to the band structure of different (undoped) semiconductors.

On the ground of the above results and common features of the Pc-semiconductor systems, a general procedure can be proposed for a theoretical design of coupled organic-inorganic systems sketched in three steps: (i) comparison of the value of the semiconductor work function with the ionization potentials of a given family of Pc molecules, in order to identify Pc-semiconductor systems where the Pc HOMO should be located in the semiconductor band gap. Such a condition is likely satisfied in semiconductors having large work function and band gap, like metal oxides

and nitrides. (ii) selection of a Pc central group and of a particular semiconductor surface by looking only at their chemical affinity, in order to favor a surface-molecule chemical bonding. Such an approach is permitted by the present prediction that a chemical bonding does not affect the HOMO position in the band gap. (iii) theoretical investigation of the molecule-surface chemical bonding and the effects of a *p*-type doping of the semiconductor, in order to check the occurrence of an energy balance favoring an effective molecule-surface coupling.

In conclusion, our results clarify the charge-transfer mechanisms occurring in Pc-semiconductor systems, reveal a universal alignment of the Pc electronic levels to a semiconductor band gap, indicate a Pc-semiconductor system exemplifying the achievement of an effective coupling, and propose a general procedure for a theoretical design of coupled organic-inorganic systems. They can apply to a wide class of MOMC including Pc's, metal-loporphyrins and similar biological systems and aim at opening the way towards thoroughly novel hybrid heterostructures.

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