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Ab initio Theoretical Investigation of Phthalocyanine−Semiconductor Hybrid Systems

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In the present study, an extensive investigation of the molecule−surface interaction in hybrid systems formed by phthalocyanines (Pcs) and inorganic semiconductors (IS) has been performed by using ab initio theoretical methods. The aim of this study is to provide a framework to design effectively coupled Pcs/IS systems, assumed here to be characterized by the formation of chemical bonds between the two components and by a molecule-surface charge-transfer involving the π-electron clouds responsible of the Pc optical and transport properties. The achieved results strengthen a crucial point for designing coupled Pc/IS structures, that is, the occurrence of a universal alignment of the Pc electronic levels with respect to the semiconductor band structure, previously suggested only on the ground of a limited set of results. Present results also confirm that an effective organic−inorganic coupling can be achieved through a careful choice of the Pc−substrate system and the semiconductor doping. In this regard, they trace also novel routes for designing hybrid Pc/IS systems by showing that the degrees of freedom for reaching an effective coupling can be increased by modifying the molecular architecture. Finally, present results predict that X-ray photoelectron spectroscopy (XPS) measurements can give an experimental evidence of molecule−surface charge-transfer processes occurring in coupled Pc/IS systems.

I. Introduction

Phthalocyanines (Pcs) present several properties of potential interest for technological applications. The structure of these molecules is characterized by one or more macrocyclic ligands carrying clouds of delocalized π electrons and by a central metal or group, e.g., Cu, Zn, Pb, Fe, Sn, TiO, Ru_2, $Si(OH)_2$, etc. Almost all of the metals appearing in the periodic table have been used to synthesize different kinds of Pc molecules where they generally play the role of electron donors to the ligands. In a short résumé, the following Pcs properties may be related to such a peculiar structure:

- The delocalized π clouds show a high-order polarizability and a marked nonlinear optical (NLO) activity.[1] Thus, Pcs films are suitable to be employed as limiting optical devices or photonic crystals for second and third harmonic frequency generation.[1−3]
- Oxidized[4] and reduced[5] Pc crystals are semiconducting. They show indeed high carrier mobility that can reach the value of 1 $cm^2\ V^{-1}\ s^{-1}$.[6−8] Pcs can be used as components of organic electronic devices like OFETs (organic field-effect transistors) and OLEDs (organic light-emitting devices).[4,7,9,10]
- High absorption coefficients have been measured in the visible light range for $\pi \rightarrow \pi^*$ electronic transitions. Pc molecules can be used therefore as dye-sensitizers for hybrid organic−inorganic solar cells.
- Transition metals with d electrons arranged in unpaired high-spin configurations (e.g., Fe, Co, Ni, Mn, Ru, V, etc.) induce local magnetic moments in Pc molecules.[12] In this regard, recent studies indicate that magnetic molecular films coupled to active substrates may open the way for a new class of electronically controlled magnetic devices.[13−15]

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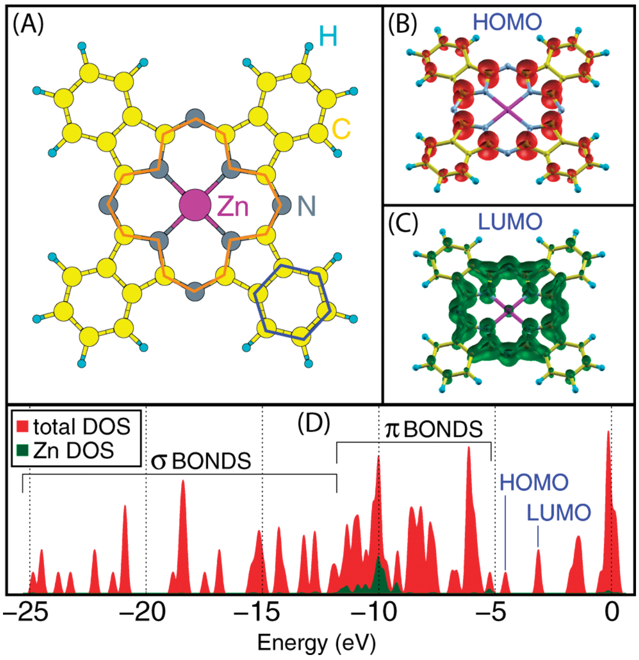

Figure 1. (A) Top view of a ZnPc molecule. The orange and blue lines identify the inner pyrrole system and one of the outer benzene rings, respectively. (B) Electron density isosurface of the π highest occupied molecular orbital (HOMO). (C) Electron density isosurface of the doubly degenerate π^* lowest unoccupied molecular orbital (LUMO). (D) Total density of states (DOS) for the valence molecular orbitals (red zone). Some relevant features of the DOS are labeled: the region of σ bonds, formed by linear combinations of C 2s, N 2s, C $2p_{xy}$, and N $2p_{xy}$ atomic orbitals; the region of π bonds, formed by linear combinations of C $2p_z$ and N $2p_z$ atomic orbitals; the HOMO and LUMO molecular orbitals. The green zone represents the projection of the total DOS over the 3d Zn atomic orbitals.

The ZnPc molecule is often chosen as a model because it shows most of the basic features of the Pc molecules as illustrated in Figure 1. Basically, the metallo−organic Pc complex is built by two units: (1) an organic macrocyclic ligand, schematically divided in an outer part formed by four benzene rings and an inner (pyrrole) part formed by a 16-atom closed C−N chain (see Figure 1A) and (2) a central metal (or group) in a typical (2+) oxidation state. According to the $4n + 2$ Huckel rule, the macrocycle structure could not be considered aromatic (it contains 40 π electrons). However, two electrons transferred from the central metal to the ligand make the metallo−organic complex an aromatic molecule. Valence electrons are typically arranged in groups of molecular orbitals (MOs) that can be ordered by following their increasing energies, as shown by the plot of the total density of states (DOS) in Figure 1D. A first group of MOs is related to the skeletal σ bonds. They are formed indeed by linear combinations of C 2s, N 2s, C $2p_{xy}$, and N $2p_{xy}$ orbitals (the z direction is perpendicular to the macrocycle plane), as shown by their projections over a basis of atomic orbitals (not reported here). At higher energies, there is another group of MOs related to the aromatic π bonds; actually, they are formed by linear combinations of C $2p_z$ and N $2p_z$ atomic orbitals. At the top of the valence MOs there is the highest occupied molecular orbital (HOMO), which is followed by the doubly degenerate lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO, π and π^*, electronic clouds are shown in Figures 1B and C, respectively. These two highly delocalized orbitals are responsible of most of the Pc properties mentioned above. Finally, the Zn contribution to the DOS of Figure 1 is basically given by its filled d shell, which is deeply embedded within the lower part of the π zone of the DOS (see the major green feature in Figure 1D). This fact is consistent with the formation of a Zn^{2+} ion as well as the mentioned statement that, at least in this simple case, the metal atom acts as a mere electron provider to the ligand, playing a minimal role in the above molecular properties.

In the last years, much experimental work has been devoted to the investigation of the Pcs interaction with different inorganic substrates in order to clarify the morphology, order, and assembly of deposited molecular films. More specifically, the balance between intermolecular and molecule−surface interactions can lead to a different assembling of the molecules deposited on the surfaces.[16] When the molecule−surface interactions prevail, the molecules can be arranged in ordered patterns which retain the same periodical order of the surface (template effect of the surface). They can otherwise form molecular crystals or clusters, when the intermolecular interactions dominate the hybrid system; examples of both conditions can be found in ref 16. Recent experimental studies have concerned also the properties of organic−inorganic hybrid interfaces.[16−19] Generally, these studies have shown that the Pc−semiconductor interaction is quite weak (see, e.g., refs 20−22 and most of the cases reported in ref 16.); although, in some promising cases involving In-rich InAs or InSb surfaces,[16,18,23−26] stronger organic−inorganic interactions have been observed. These experimental results have inspired a previous theoretical study[27] where we have investigated the properties of some selected phthalocyanine−inorganic semiconductor (Pc/IS) systems with the aim of identifying Pc/IS structures showing an effective organic−inorganic coupling, that we have assumed to

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be characterized by the occurrence of two main conditions:

1. The formation of appreciable surface−molecule chemical bonds (in order to favor a template effect of the surface structure).
2. The occurrence of a molecule−surface charge-transfer involving the π-electron clouds responsible of the Pc NLO and transport properties.

Such conditions have been chosen because their fulfillment would give access to novel, hybrid organic−inorganic heterostructures where a tuning of the properties of the organic molecules (e.g., of NLO properties) could be driven by their interaction with the inorganic semiconductor, thus leading to a new class of functional materials.

The mentioned, previous study has improved our understanding of the Pc/IS charge-transfer mechanisms, suggested a *universal alignment* of the Pc electronic levels with respect to the semiconductor band gap and predicted the occurrence of an effective organic−inorganic coupling in the case of a peculiar Pc/IS system, i.e., a TiOPc molecule adsorbed on the anatase TiO_2 surface (hereafter referred to as a TiOPc/TiO_2 system). In this system, a molecule to surface charge-transfer was predicted which agrees with the donor character generally shown by the Pc molecules. A procedure for designing effectively coupled hybrid interfaces was also suggested.

The present study extends the previous one to a wide set of Pc/IS systems different for the molecular architecture and/or the semiconductor properties. More specifically, the investigation has been extended to Pc molecules having different central metals or central groups or a macrocycle structure modified through the introduction of peripheral acceptor (aza) groups. Regarding the inorganic semiconductor, novel doping conditions have been considered for, e.g., the GaAs substrate. Moreover, the wurtzite GaN ($000\bar{1}$) surface, which presents quite peculiar electronic properties, has been considered in addition to the previously investigated GaAs, InAs, and TiO_2 surfaces. The achieved results strengthen those of our previous study and show that both the molecular architecture and the semiconductor properties can play a significant role in the tuning of the Pc/IS interaction. In detail, present results: (i) confirm a *universal alignment* of the Pc electronic levels; (ii) indicate further Pc/IS systems showing an effective organic−inorganic coupling; (iii) indicate that the direction of the Pc/IS charge-transfer, from the molecule to the substrate, can be reversed by inducing an acceptor behavior of the Pcs, through a modification of the molecular architecture, and by realizing a suitable doping of the semiconductor; this result significantly increases the degrees of freedom for designing effectively coupled hybrid interfaces; (iv) give theoretical estimates of the XPS (X-ray photoelectron spectroscopy) C (1s) chemical shifts for some selected Pc/IS systems, which suggest that surface−molecule charge-transfer processes can be revealed by this spectroscopic technique.

II. Methods

The Pc−semiconductor systems have been investigated by using ab initio density functional theory methods in the generalized gradient approximation (GGA) and a supercell approach.[28] Total energies have been calculated by using ultrasoft pseudopotentials,[29] plane-wave basis sets, and the PBE gradient corrected exchange-correlation functional.[30] Satisfactorily converged results have been achieved by using cutoffs of 25 Ry on the plane waves and of 150 Ry on the electronic density as well as the Γ point for the **k**-point sampling of the Brillouin zone.

Surface supercells have been modeled from bulk structures by adding an adequate portion of empty space ($\approx$15 Å) to a crystal slab. This implies the presence of a possibly reconstructed (upper) surface interacting with a given molecule and an opposite (lower) surface. Two different ways have been chosen to arrange the atoms of this latter surface in order to avoid the appearance of spurious surface electronic states in the semiconductor energy gap. In the case of III−V semiconductors, which generally undergo severe surface reconstruction, the atoms of the lower surface have been initially located in their unrelaxed bulk positions and saturated by pseudo-H atoms, i.e., H atoms carrying an electronic charge of 1.25 (0.75) when saturating cationic (anionic) layers.[31−33] Once optimized, this saturated atomic layer has been kept fixed in further calculations. On the other hand, the surfaces of TiO_2 slabs, which generally do not undergo any reconstruction, do not need saturation layers. Once optimized, the corresponding lower surfaces have been simply kept fixed in their relaxed configuration. The GaAs and InAs surface supercells have been modeled by adding empty space to a 4×4 crystal slab, formed by eight atomic layers of bulk GaAs or InAs cut along the (001) crystal axis (i.e., supercells of 128 atoms). The GaN surface supercells have been modeled by adding empty space to a 6×5 orthorhombic crystal slab, formed by six atomic layers of bulk GaN cut along the ($000\bar{1}$) crystal axis, plus a Ga adlayer (i.e., supercells of 210 atoms). The 3d shells of Ga atoms have been explicitly considered as valence electrons in all of the calculations involving a GaN substrate, as suggested in ref 34. The same shells have been instead included into the Ga pseudopotential in the calculations involving a GaAs substrate. The TiO_2 surface supercells have been modeled by adding empty space to a 4×4 crystal slab, formed by six atomic layers of bulk TiO_2 (i.e., supercells of 192 atoms) cut along the (101) crystal axis. The above supercells have been used to

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investigate the properties of molecule−surface hybrid systems.

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 slab. The electronic properties of the molecule−surface systems, considered as a whole, have been investigated by analyzing the electronic eigenvalues calculated at the Γ point. Eigenvalues related to different systems have been aligned by using, as a common reference, the electronic levels of a He atom placed inside the flat potential region of the corresponding supercells. The strength of a molecule−substrate bonding, i.e., the molecular adsorption energy, has been estimated by the total energy difference $E_{\mathrm{ads}} = E[\mathrm{Pc/IS}] - E[\mathrm{Pc}] - E[\mathrm{IS}]$. 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 TiOPc/anatase system, ρ_{diff}[TiOPc/anatase] is given by ρ[TiOPc/anatase] − (ρ[TiOPc] + ρ[anatase]) where ρ[TiOPc/anatase] is the electron density of a supercell containing the molecule−semiconductor system, ρ[TiOPc] is the electron density of the same supercell with the molecule only, and the analogue for the ρ[anatase] density. Thus, a ρ_{diff}[TiOPc/anatase] map indicates the charge displacements induced by the interaction between the molecule and the surface.

The surface−molecule charge-transfers investigated in the present study are controlled by an energy balance closely related to the relative positions of the semiconductor and molecule electronic levels. These positions could be affected, in principle, by two limits of the DFT-GGA methods: (i) a wrong ordering of the frontier molecular orbitals in certain Pcs, due to a self-interaction error inducing a bad description of the strongly localized d orbitals of the central metal[35] and (ii) the well-known GGA limit leading to too small values of the molecule and semiconductor energy gaps. However, the former limit does not affect our main results. Our study is focused indeed on Pc molecules involving empty d orbitals of the central metal, which are found quite high above the ligand LUMO, or fully occupied d shells, which are quite deeply embedded in the region of the occupied ligand orbitals, as shown in Figure 1D. In both cases, the frontier HOMO−LUMO belong to the Pc macrocycle and are not affected by the d orbitals of the central atom. As an exception, the VOPc and CuPc molecules, which involve open d shells, have been investigated by using a Hubbard U correction in order to take into account the self-interaction error.[36] These molecules are considered here only for generalizing some properties of the HOMO and LUMO orbitals, which result once more related to the macrocycle. Regarding the latter limit, the GGA error on the energy gaps, let us consider first the relative positions of filled levels. In the cases of the HOMO and the level at the top of the valence band (VB), we assume that their relative positions are estimated well by present DFT-GGA methods. Such an assumption is supported by the results we achieved in the case of the CuPc/GaAs system, where the HOMO results to be located at about 1.0 eV below the VB both by the experiment[18] and by our results. On the other hand, regarding the relative positions of empty levels, like the LUMO and the bottom of the semiconductor conduction band (CB), our estimates could be affected by too small energy gaps. Then, when empty states are involved in charge transfers, we have compared the calculated LUMO−CB relative positions to the positions estimated by adding the experimental HOMO−LUMO and GaAs energy gaps to the calculated HOMO and top of the VB, respectively. The two estimates fully agree, thus suggesting that a systematic error affects the molecule and semiconductor energy gaps. This make us confident on the results regarding the energy balance which controls the molecule−surface charge-transfer processes, in all of the systems investigated here.

Finally, XPS C 1s chemical shifts have been estimated by total energy differences between "standard" and "core hole" calculations.[37,38] In detail, in the case of the latter calculations, a C ultrasoft pseudopotential containing an 1s core hole has been generated and used in place of the regular pseudopotential, one C atom at a time. Then, the energy differences between the standard and core-hole calculations have been compared with an analogue quantity obtained for the C atom of a CO_2 molecule embedded in the supercell and not interacting with the surface or the Pc molecules. The latter quantity is used as a reference C 1s chemical shift and assumed to be equivalent to the XPS experimental CO_2 line observed at 291.90 eV.[39] Such an approach has given results in a very good agreement with experimental findings in the case of small aromatic molecules, like benzene and pyrimidine. Plots simulating XPS spectra have been obtained by fitting numerical data with Lorentzian functions peaked on the core shift values. The functions are written in a standard form:

$$f(x) = \frac{\Gamma/2}{(\Gamma/2)^2 + (x_0 - x)^2} \tag{1}$$

A Γ parameter of 0.3 eV has been used in all of the plots.

III. Results and Discussion

In this study, we have considered Pc molecules having different central metals (ZnPc,[40] CuPc,[41] PbPc[42]), different

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central groups (TiOPc,[43] GaClPc,[44] VOPc,[44]), or a multiligand sandwich structure ($Ti(Pc)_2$[45]) as well as Pc molecules modified through the introduction of acceptor aza groups in the macrocycle. In the investigated Pc/IS systems, these molecules interact with the (001) As-rich $\beta2$ (2×4) and Ga-rich $\zeta(4\times2)c(8\times2)$ GaAs surfaces,[31,46] the (001) As-rich $\beta2(2\times4)$ InAs surface,[47] the $(000\bar{1})$ (1×1) GaN surface,[34] and the (101) TiO_2 (anatase) surface,[48] belonging to intrinsic or doped substrates (doping conditions have been simulated by suitable substitutions of host atoms with donor or acceptor species). We did not consider the In-rich InAs and InSb surfaces mentioned above because their reconstruction models are still uncertain.[32,49]

Some preliminary remarks should be taken into account when discussing the present results:

- None of the above Pc molecules shows a chemical affinity for As-rich surfaces, like the $\beta2(2\times4)$ reconstructed GaAs and InAs surfaces. These surfaces seem characterized indeed by a low reactivity and give always rise to very weak interactions with all of the above Pcs.
- The formation of appreciable molecule–surface bonds occurs only when reactive nonmetallic atoms (like the O atom of a TiOPc molecule or the Cl atom of the similar GaClPc molecule) are present in the central Pc group and act as bridging atoms between the Pc molecules and the surfaces.
- Different starting geometries have been tested in order to find the stable adsorption sites of a Pc molecule on a given semiconductor. In all of the investigated systems, the molecular macrocycle has been assumed parallel to the semiconductor surface. Pc molecules with a central group carrying a nonmetallic atom are highly site-selective, that is, they form a bond with the surface only at sites permitting the interaction of the nonmetallic atom with a surface cation. Configurations corresponding to rotations of these molecules around their molecule-surface bond are almost degenerate (≈0.1 eV). On the other hand, Pc molecules carrying only a central metal atom weakly interact with the surface and give rise to almost degenerate configurations even when located at different surface sites. It has to be noted that, in the case of weak interactions, present results could be partially affected by the neglect of van der Waals interactions in our DFT methods.

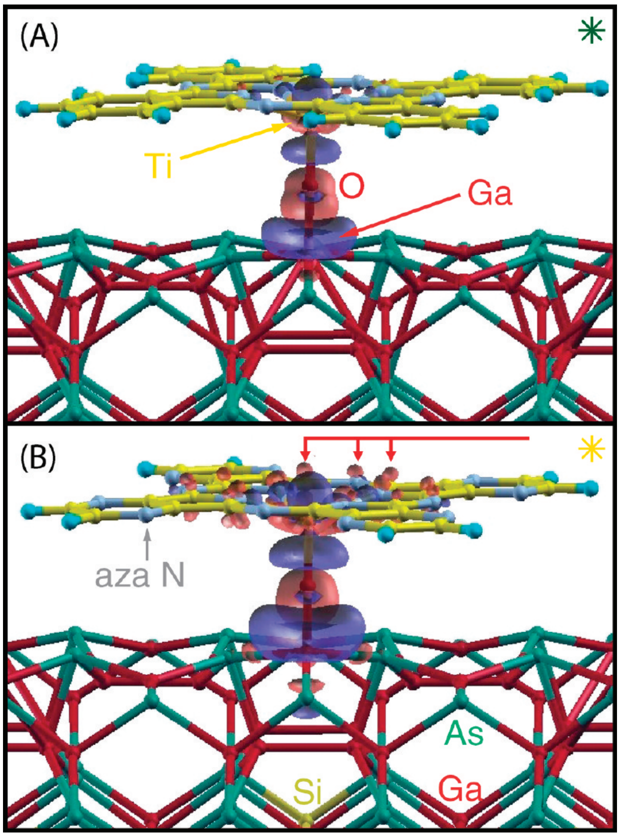

Figure 2. Equilibrium geometries and isosurfaces of difference electron densities (ρ_{diff}) of (A) a TiOPc molecule bonded to a $\zeta(4\times2)/c(8\times2)$ Ga-rich GaAs surface and (B) a pyrazino-TiOPc molecule bonded to the same reconstructed surface in the case of *n*-doped GaAs. ρ_{diff} maps show 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. The red arrows in the lower frame indicate some of the N and C pyrrole atoms where the electronic charge increases. The green and yellow stars indicate a correspondence between the equilibrium configurations of the present figure and the electronic levels of Figure 3.

- Molecule–surface interaction patterns which require some breaking of the double bonds in the aromatic macrocycle have not been considered here. There is a vast literature concerning the experimental investigation of Pc molecules deposited on inorganic substrates (even quite reactive ones), and the occurrence of a molecular dissociation is rarely reported.[1,16]

In the following, first, we focus on the Pc/IS systems where our results indicate the occurrence of an effective coupling. Then, we discuss some general features of the molecule–surface coupling emerging from present results like, e.g., the mentioned universal alignment of the Pc frontier orbitals, which can play a significant role when designing Pc/IS hybrid interfaces. Some results of our previous study,[27] regarding the interaction of TiOPc with GaAs and TiO_2 surfaces, will be reported here with further details in order to give a comprehensive theoretical picture of the Pc/IS interactions.

A. TiOPc Molecule on GaAs Surfaces. The $\zeta(4\times2)/c(8\times2)$ (001) Ga-rich GaAs surface is characterized by the formation of surface and subsurface Ga dimers as well as by the presence of parallel lines of 3-fold coordinated sp^2

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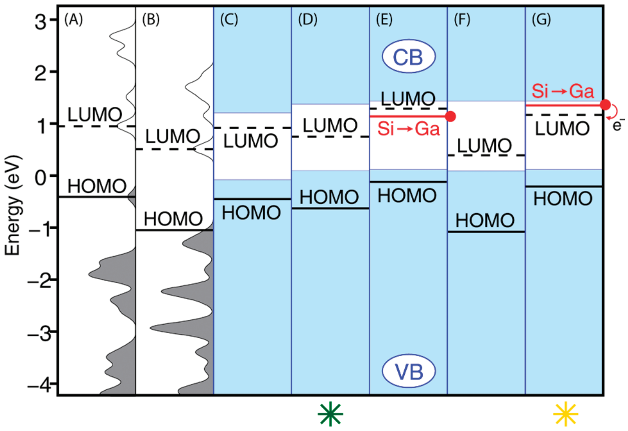

Figure 3. DOS and sketched electronic levels of a TiOPc and its pyrazino-derivative as isolated molecules or when interacting with different GaAs surfaces. All of the levels are aligned to a common reference. The HOMO and LUMO are represented by full and dashed black lines, respectively. The color background delimits the valence and conduction band regions relative to the semiconductor electronic structure. Dopant donor levels are indicated by a red line and a solid circle.[51] (A) Isolated TiOPc molecule. (B) Isolated pyrazino-TiOPc molecule. (C) TiOPc weakly interacting with an As-rich GaAs surface. (D) TiOPc bonded to a Ga-rich GaAs surface. (E) TiOPc bonded to an *n*-doped Ga-rich GaAs surface. In this figure, the Si donor level has been artificially lowered to make clear the relative positions of the donor level, of the LUMO and of the bottom of the conduction band. (F) Pyrazino-TiOPc bonded to a Ga-rich GaAs surface. (G) Pyrazino-TiOPc bonded to an *n*-doped Ga-rich GaAs surface. The green and yellow stars indicate a correspondence between electronic levels of the present figure and equilibrium configurations of Figure 2.

Ga atoms.[31,50] These surface atoms form an in-plane σ structure with three neighboring As atoms which carry dangling bonds pointing upward in the (001) direction. The TiOPc molecule is strongly chemisorbed on this ζ surface, the surface sp^2 Ga atoms being the preferred adsorption sites; see Figure 2A. The molecular O atom forms a stable O−Ga bond characterized by a bond length of 1.77 Å and an adsorption energy (E_{ads}) of 1.4 eV. As mentioned above, the TiOPc molecule weakly interacts, instead, with the As−As dimers characterizing the $\beta 2(2 \times 4)$ (001) As-rich GaAs surface. Regarding the electronic structure of these TiOPc/GaAs systems, Figure 3 shows the electronic levels of an isolated TiOPc as well as the HOMO and LUMO locations with respect to the semiconductor band gap when the molecule interacts with the two above GaAs surfaces. The weak TiOPc/(As-rich)GaAs interaction leaves the ligand molecular orbitals substantially unperturbed; see Figure 3A and C. Noticeably, in the case of the TiOPc/(Ga-rich)GaAs system, despite of the quite strong bond forming in this system, the HOMO−LUMO pair is only slightly lowered in energy; see Figure 3A and D. This supports the description of the metallo−organic Pc complex discussed in section I: the central metal or group acts often as a mere electron donor and has a small influence on the macrocyclic ligand properties. Accordingly, the ρ_{diff}-[TiOPc/(Ga-rich)GaAs] map of Figure 2A shows a charge displacement from the molecular Ti atom and the Ga atom involved in the Ga−O bond toward the bridging O atom and the region where the bond forms, thus clearly indicating that only the central TiO group is involved in the molecule−surface bonding and acts as an anchoring group.

The chemical bonding characterizing the TiOPc/(Ga-rich)GaAs system represents a potential condition for the occurrence of a surface−molecule charge transfer. In this regard, the electronic levels of Figure 3D show that the HOMO falls *inside the valence band* (VB) while the LUMO is located *in the energy gap* of GaAs.[52] 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(III) atom in the supercell with a Si(IV) donor. The introduction of a shallow donor level has remarkable effects on the electronic structure of the TiOPc/GaAs system, as shown in Figure 3E. In fact, the HOMO−LUMO pair rigidly shifts upward 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. Actually, a ρ_{diff}[TiOPc/*n*-GaAs] (not reported here) is very similar to the ρ_{diff}[TiOPc/GaAs] shown in Figure 2A, thus confirming that the LUMO refuses a charge transfer from the GaAs surface. These results indicate that the formation of molecule−surface chemical bonds is not a sufficient condition to produce an effective substrate−molecule coupling.

Then, we have investigated the influence of the *molecular architecture* on charge-transfer processes by substituting the TiOPc molecule adsorbed on the Ga-rich GaAs surface with its electron−acceptor pyrazino-derivative (py-TiOPc). A py-TiOPc molecule is obtained by substituting two C−H pairs with two N atoms in each of the outer benzene rings (see the “aza N” label in Figure 2B). The N atoms are more electronegative than the C ones, thus they can stabilize electrons on π conjugated orbitals. The py-TiOPc molecule forms a chemical bond with the Ga-rich GaAs surface similar to that formed by the TiOPc molecule, with an E_{ads} value of 1.2 eV. The HOMO and LUMO positions of the py-TiOPc, both for the isolated molecule and the molecule−surface system are slightly lower than the TiOPc ones (compare Figure 3A and B for the isolated molecules, and Figure 3D and F for the two molecules interacting with the same undoped GaAs surface) in agreement with the different architectures of the two molecules; see ref 44. A remarkable difference between the properties of the same two molecules is found instead when they interact with the surface of *n*-doped GaAs (*n*-GaAs). In fact, at variance with the

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(51) It is worth noticing that the position of the dopant levels in Figures 3, 5, and 7 is the position of such levels calculated in the case of doped surfaces non interacting with any molecule. There is only one exception to this statement: in Figure 3E, the dopant level corresponds to the level calculated when the molecule is bonded to the surface because the TiOPc molecule refuses a charge transfer from the semiconductor and the donor level remains occupied.

(52) The calculated value of the GaAs energy gap is 1.2 eV to be compared with an experimental value of 1.52 eV.

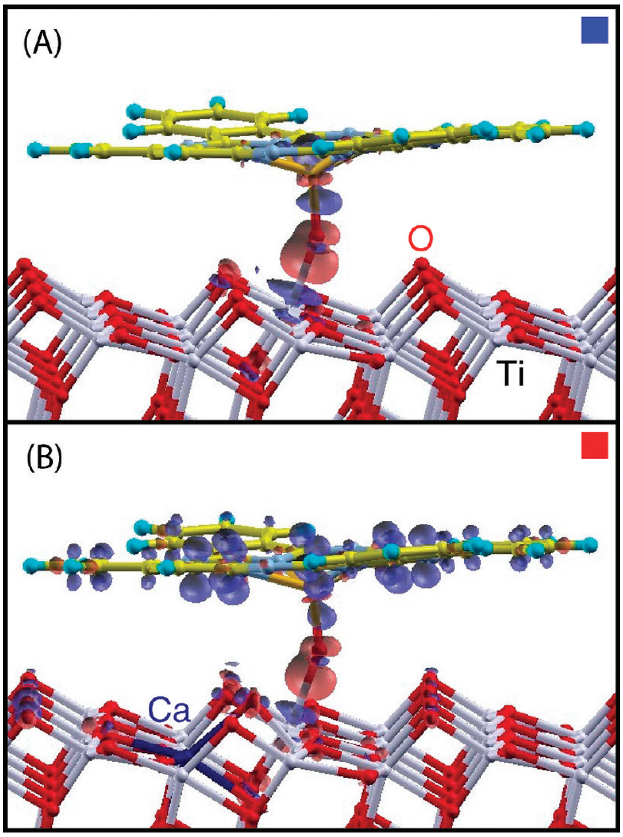

Figure 4. Equilibrium geometries and isosurfaces of difference electron densities (ρ_{diff}) of (A) a TiOPc molecule bonded to the (101) anatase surface and (B) a TiOPc molecule bonded to a *p*-doped anatase surface. ρ_{diff} maps show the displacements of electronic charge induced by the molecule−surface interaction. Red surfaces cover areas where the difference is positive, blue surfaces, where it is negative. The blue and red squares indicate a correspondence between the TiOPc/anatase configurations of the present figure and the electronic levels of Figure 5.

TiOPc/*n*-GaAs system, in the case of the py-TiOPc/*n*-GaAs the LUMO maintains a position below the donor-induced level and becomes populated with some extra electronic density, as shown by the electronic structure of Figure 3G and by the ρ_{diff}[py-TiOPc/*n*-GaAs] map drawn in Figure 2B, respectively. In the latter figure, red spots representing an increase of charge appear indeed around the pyrrole N and C atoms on which the py-TiOPc LUMO is mainly localized (compare with Figure 1C). This surface to molecule charge-transfer involves the LUMO π^* orbital, thus showing that the py-TiOPc/*n*-GaAs system satisfies the two conditions mentioned above for the achievement of an effective organic−inorganic coupling.

All together, the above results are especially instructive. They show that the usual donor character of Pcs may represent a trouble for reaching an effective coupling in Pc/IS systems. However, such trouble can be overcome by modifying the Pc architecture, which permits the Pc character to be reversed from a donor to an acceptor one.

B. TiOPc Molecule on the TiO_2 (101) Surface. The (101) anatase surface presents rows of 5-fold coordinated Ti_{5c} atoms, which are undercoordinated atoms with

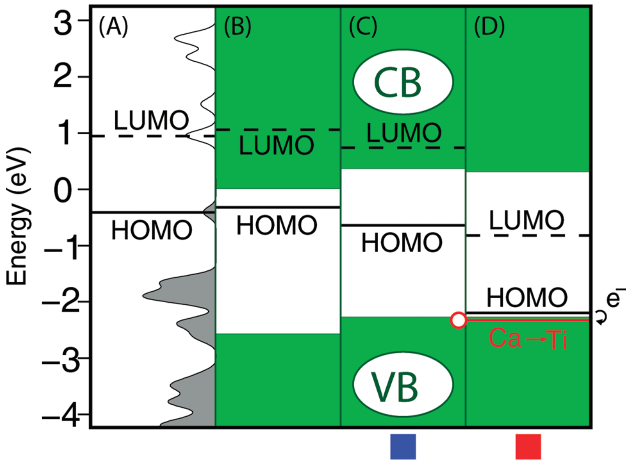

Figure 5. DOS and sketched electronic levels of a TiOPc molecule interacting with the (101) anatase surface. All of the levels are aligned to a common reference. The HOMO and LUMO are represented by full and dashed black lines, respectively. The color background delimits the valence and conduction band regions relative to the semiconductor electronic structure. A dopant acceptor level is indicated by a red line and an empty circle.[51] (A) Isolated TiOPc molecule. (B) TiOPc weakly interacting with the anatase surface (i.e., with the O atom pointing upward). (C) TiOPc bonded to the anatase surface. (D) TiOPc bonded to a *p*-doped anatase surface. The blue and red squares indicate a correspondence between the electronic levels of the present figure and the equilibrium configurations of Figure 4.

respect to the 6-fold coordinated Ti atoms of the anatase TiO_2 bulk. The Ti_{5c} atoms are suitable therefore for the formation of chemical bonds with the O atom (O_{mol}) of the TiOPc molecule. A $Ti_{5c}-O_{mol}$ bond[53] actually forms in the TiOPc/TiO_2 system as indicated by a bond length of 2.09 Å (to be compared with a Ti−O distance of about 2.0 Å measured in bulk anatase and rutile TiO_2[48]) and by an E_{ads} equal to 1.3 eV. Moreover, the difference density map of Figure 4A shows a displacement of electronic charge toward the region of the $Ti_{5c}-O_{mol}-Ti$ bridge quite similar to that found in the case of the TiOPc/GaAs system (cf. Figure 2A).

The electronic structures of the isolated molecule, of a TiOPc molecule weakly interacting with the anatase surface (i.e., having the O atom pointing upward) and of the same molecule bonded to the surface, are sketched in Figure 5A−C, respectively. In the case of the weakly interacting molecule, the HOMO−LUMO levels are still quite aligned with the ones found for an isolated molecule. In the case of the bonded molecule, they are just slightly lowered in energy by the formation of the $Ti_{5c}-O_{mol}$ bond. Moreover, the bonded molecule (see Figure 5C) is characterized by a HOMO located in the TiO_2 band gap[54] and a LUMO placed above the minimum of the conduction band (CB). Such a configuration appears suitable therefore for an electron transfer from the molecule to a *p*-type doped anatase. Then, an unoccupied, shallow acceptor level has been introduced in the anatase band gap by substituting a Ti(IV) atom

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(53) We indicate surface Ti atoms with the label Ti5c to avoid mistakes over the TiOPc Ti atom, which is also differently colored (yellow instead of white) in all of the figures related to TiOPc/TiO_2 systems.

(54) The calculated value of the TiO_2 band gap is 2.8 eV, to be compared with an experimental value of 3.2 eV.

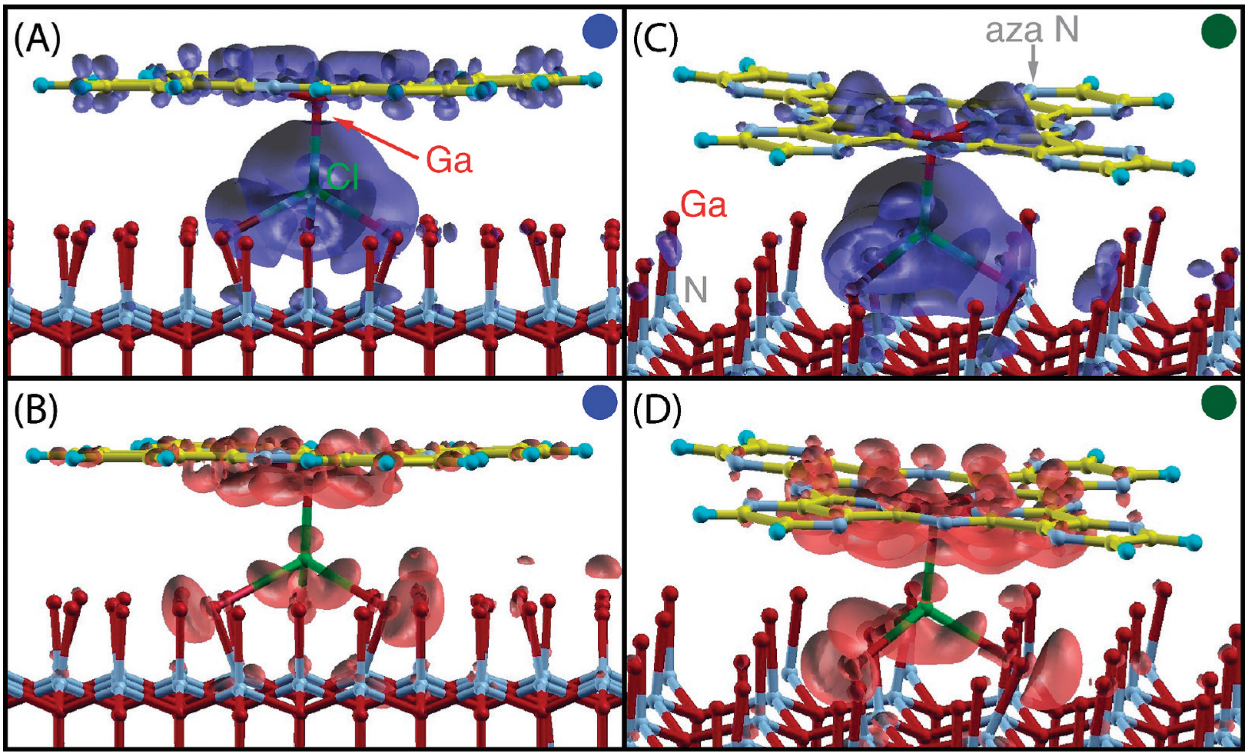

Figure 6. Equilibrium geometries and isosurfaces of difference electron densities (ρ_{dif}) for a GaClPc molecule and its pyrazino derivative adsorbed on the $(000\bar{1})$ GaN surface. Parts A and B show the geometry of the GaClPc molecule adsorbed on the GaN surface together with the regions of negative and positive charge density difference, respectively; C and D show the geometry of the pyrazino-GaClPc molecule adsorbed on an *n*-doped GaN surface together with the regions of negative and positive charge density difference, respectively. The blue and green circles indicate a correspondence between the GaClPc/GaN configurations of the present figure and the electronic levels of Figure 7.

with a Ca(II) atom. As found in the case of the TiOPc/GaAs system, 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 Figure 5D. However, in the present case, the HOMO looses 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. Accordingly, the difference density map of Figure 4B clearly shows that electronic charge moves from the molecular orbital involving C atoms of the macrocyclic ligand (i.e., the HOMO π orbital) to surface atoms, that is, electrons are transferred from the orbital most affecting the molecular properties to the substrate. This realizes again an effective Pc−semiconductor coupling.

The above results and those achieved for the TiOPc/*n*-GaAs system indicate that a surface−molecule charge transfer actually occurs only if allowed by the corresponding energy balance given, e.g., in the TiOPc/*p*-TiO_2 system, 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 TiOPc/*p*-TiO_2 system, a favorable energy balance is induced by the usual donor character of Pc molecules,[1,44] while, in the TiOPc/GaAs system, an opposing energy balance leads to the translation of the molecular levels in order to hinder the surface to molecule charge transfer. In the latter case, the energy balance can be inverted and a charge transfer process from the surface to the molecule takes place only when the TiOPc architecture is modified in order to induce an electron-attractive behavior of the molecule, as in the case of the TiOPc pyrazino-derivative.

C. GaClPc and TiOPc Molecules on the $(000\bar{1})$ GaN Surface. GaN and its $(000\bar{1})$ surface have been considered in the present study due to their peculiar properties. At variance with GaAs, GaN is indeed a wide-band gap III−V semiconductor (the E_g value is 3.46 eV) characterized by a lower energy value of the VB maximum and a higher one of the CB minimum.[55] Thus, in a hybrid junction, *n*- and *p*-type doped GaN may represent in principle a stronger donor and a stronger acceptor, respectively, than the correspondingly doped GaAs materials. Moreover, several GaN surface reconstructions present very special features which may introduce further degrees of freedom when designing hybrid interfaces. For instance, in the (1×1) reconstruction of the $(000\bar{1})$ GaN surface considered here, the presence of a metallic overlayer of Ga atoms, single bonded to the N atoms of an underlying plane heavily affects the surface properties.[34,35] These Ga atoms are indeed close enough to each other to share their valence electronic levels, thus giving rise to a partially filled metallic band spanning the entire energy gap.[57]

Two different Pc molecules, the already discussed TiOPc molecule and the halogenide GaClPc one, together

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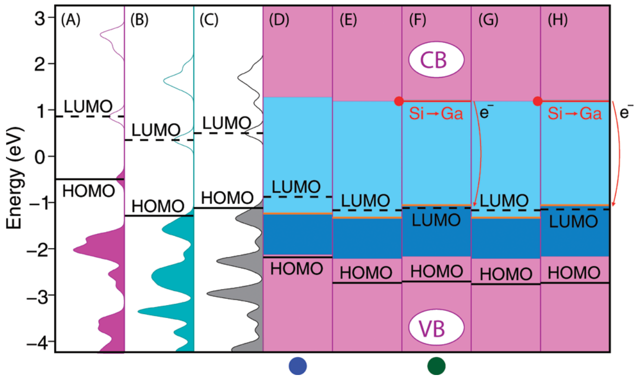

Figure 7. DOS and sketched electronic levels of GaClPc, pyrazino-GaClPc, and pyrazino-TiOPc molecules and of the same molecules interacting with the (000$\bar{1}$) GaN surface. All of the levels are aligned to a common reference. The HOMO and LUMO are represented by full and dashed black lines, respectively. The magenta color background delimits the valence and conduction band regions relative to the semiconductor electronic structure. The GaN band gap is filled by a metallic band arising from the Ga overlayer. The occupied and unoccupied parts of this band are indicated by dark and light blue colors, respectively. The Fermi energy levels of all of the molecule−surface systems are indicated by an orange line. A dopant donor level is indicated by a red line and a filled circle.[51] (A) Isolated GaClPc molecule. (B) Isolated pyrazino-GaClPc molecule. (C) Isolated pyrazino-TiOPc molecule. (D) GaClPc adsorbed on the GaN surface. (E) Pyrazino-GaClPc adsorbed on the GaN surface. (F) Pyrazino-GaClPc adsorbed on an *n*-doped GaN surface. (G) Pyrazino-TiOPc molecule adsorbed on the GaN surface. (H) Pyrazino-TiOPc molecule adsorbed on an *n*-doped GaN surface. The blue and green circles indicate a correspondence between present electronic levels and GaClPc/GaN configurations of Figure 6.

with their pyrazino-derivatives, have been considered here in order to investigate the effects of the peculiar properties of the (000$\bar{1}$) GaN surface on the Pc/IS interactions. Both molecules are characterized by a (metal)−(nonmetal) pair as a central group. Moreover, the corresponding Pc/GaN systems present quite similar properties. Thus, in the following, we will discuss in detail only the GaClPc/GaN case.

The GaClPc molecule forms a strong molecule−surface bond (E_{ads} equal to 2.1 eV) characterized by the Cl atom placed in a triangular surface site[58] and arranged in a distorted tetrahedral configuration $ClGa_4$; see Figure 6A. The chemisorbed GaClPc molecule undergoes relevant changes in its axial structure. The Ga−Cl bond length is stretched indeed from the value of 2.21 Å, calculated for an isolated molecule, to the value of 2.43 Å (10% larger), while the four Ga−N molecular bonds are shortened from the value of 2.03 Å to the value of 1.99 Å. Such strong molecular modifications are accompanied by the massive displacement of the charge density shown in Figure 6A and B where, for the sake of clearness, the negative and positive charge displacements are separately shown, respectively. These figures show a displacement of the electronic charge from the molecular Ga−Cl bond region (the big blue spot in Figure 6A) to the Cl atom and the new Ga_{surf}−Cl bonds (see the red zones in Figure 6B). The same figures show also that the charge displacement involving the central group is accompanied by a rearrangement of the electronic charge inside the macrocycle which leads to a piling up of electronic charge on the N atoms involved in the shortened, molecular Ga−N bonds. The above structural and charge-distribution changes indicate that the GaClPc/GaN interaction induces a weakening of the molecular Ga−Cl bond, an increase of the $Ga^{\delta+}$−$Cl^{\delta-}$ polarization, and a decrease of the electronic charge on the Pc macrocycle. This last feature accounts for a marked lowering of the HOMO−LUMO pair of the adsorbed molecule with respect to the isolated one; see Figure 7A and D. In detail, the HOMO becomes resonant with the GaN valence band, while the LUMO is located in the GaN energy gap, just above the filled part of the GaN surface metallic band. Likely, the lowering of the HOMO−LUMO pair induced by the interaction with the GaN surface is affected by the above-mentioned donor character of the Pc molecules. Such a character hinders a lowering of the LUMO below the top of the surface metallic band in order to prevent a surface to molecule charge transfer.[59] Accordingly, even in the case of an *n*-doped GaN substrate (obtained once more by substituting a Ga atom with a Si atom), the LUMO level stays over the Fermi level, i.e., no surface to molecule charge transfer occurs. In both cases, the Pc−GaN interaction seems to induce a sort of pinning of the LUMO above the top of the surface metallic band. Such a pinning may be useful when designing hybrid Pc−semiconductor structures, although its occurrence has to be carefully checked. It could be affected indeed by the equilibration of the surface electronic structure with that of the bulk, an effect which cannot be taken into account in the present slab calculations.

A considerable shift of the HOMO−LUMO levels has been met so far only when a Pc molecule was being adsorbed on a doped semiconductor surface in order to induce a charge transfer process. Thus, on one hand, the above results indicate that even in the case of highly reactive GaN surfaces, the donor character of the Pc molecules can hinder charge transfer processes. On the other hand, they show that a particular care has to be used when designing hybrid Pc/IS interfaces involving such highly reactive GaN surfaces because they can heavily perturb the Pc HOMO−LUMO pair also in the case of undoped substrates.

Quite similar results have been found for the GaClPc pyrazino-derivative interacting with the same GaN surface; see, e.g., Figure 7D and E. However, at variance with the case of the GaClPc molecule, in the case of the py-GaClPc/*n*-GaN system, the LUMO level becomes degenerate with the Fermi level; see Figure 7F, thus permitting a surface to molecule charge transfer. Such a transfer actually occurs, as clearly shown in Figures 6C and D which indicate a charge displacement toward the pyrrole

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(58) Actually, the E_{ads} is almost degenerate with the one calculated for a similar hexagonal site, and quite lower (0.7 eV) than the one calculated if the molecule is placed straight over a top-layer Ga atom. Such results are consistent with other ones described for the adsorption of Ga, N, Mg, and O adatoms.[63−65]

(59) A calculation involving a *p*-doped GaN surface, obtained by substituting a Ga atom with a Ca atom, has confirmed the absence of any surface−molecule charge transfer.

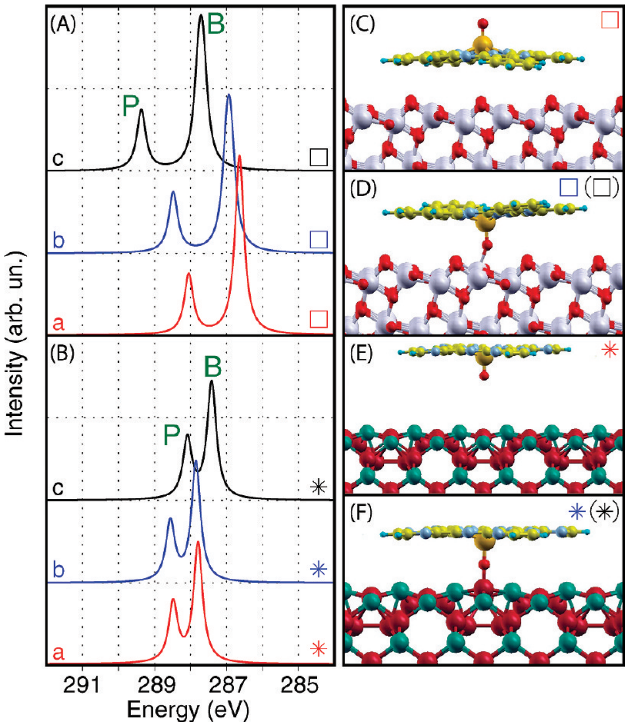

Figure 8. Theoretical spectra of the C 1s core shifts of a TiOPc molecule adsorbed on the anatase (101) TiO_2 surface and of a py-TiOPc molecule adsorbed on the (001) $\xi(4 \times 2)/c(8 \times 2)$ GaAs surface (left side) presented together with the corresponding equilibrium geometries (right side). (A) XPS spectra of (a) TiOPc weakly interacting with the anatase surface; (b) TiOPc chemisorbed on the anatase surface; (c) TiOPc chemisorbed on a *p*-doped anatase surface. (B) XPS spectra of (a) py-TiOPc weakly interacting with the GaAs surface; (b) py-TiOPc chemisorbed on the GaAs surface; (c) py-TiOPc chemisorbed on a *n*-doped GaAs surface. The P and B labels indicate peaks assigned to the inner pyrrole and outer benzene C atoms (see Figure 1), respectively. Stable configurations of (C) TiOPc weakly interacting with the anatase surface (the molecule has been turned over); (D) TiOPc chemisorbed on the anatase surface; (E) py-TiOPc weakly interacting with the GaAs surface (the molecule has been constrained to stay far from the surface); (F) py-TiOPc chemisorbed on the GaAs surface. The stable configurations of molecules adsorbed on doped surfaces are not shown because they are very similar to those chemisorbed on undoped surfaces. Stars and squares indicate a correspondence between XPS spectra and atomic structures.

N and C atoms contributing to the LUMO with their 2p atomic orbitals. Thus, once again, a change of the Pc architecture permits achieving an effective Pc/IS coupling. It may be noted that the E_{ads} of the py-GaClPc is to 1.5 eV when the molecule interacts with the doped surfaces, against a value of 2.0 eV calculated for the molecule interacting with the intrinsic surface, likely because some extra charge on the molecular LUMO and the charge related to the surface metallic band give rise to a repulsive interaction between the molecule and the topmost surface layer.

As mentioned above, a similar theoretical picture has been achieved for the TiOPc and its pyrazino-derivative interacting with the same GaN surface; see, e.g., the electronic structure calculated for the pyrazino-derivative, Figure 7G and H.

D. Calculated XPS Spectra and Molecule−Surface Charge-Transfer Processes. Simulations of XPS spectra have been performed in the cases of the $TiOPc/TiO_2$ and py-TiOPc/*n*-GaAs systems by focusing on the core shift of the C 1s electrons. In the macrocyclic ligand, the HOMO and LUMO orbitals span indeed the whole network of the conjugated C (and N) atoms. Thus, surface-molecule charge transfers involving such molecular orbitals are expected to induce appreciable variations of the C 1s core shifts.

In the first Pc/IS system, formed by a TiOPc molecule interacting with the (101) TiO_2 surface (see section III.B), the XPS C (1s) spectrum has been calculated for three different molecule−semiconductor configurations. In the first one, the molecule is weakly interacting with the surface, i.e., turned over with the O atom pointing upward, see Figure 8C. In the second and third configurations, the molecule is bonded to the surfaces of intrinsic and *p*-doped TiO_2, respectively; see, e.g., Figure 8D. A clear trend can be recognized by looking at the C 1s chemical shifts of these three Pc/IS systems, which closely agrees with the corresponding electronic structures; see Figure 5. In the first configuration, when the molecule does not interact with the surface (red curve in Figure 8A), the spectrum is almost identical to the one (not shown) calculated for an isolated TiOPc molecule. Such a spectrum is characterized by two peaks corresponding to the C 1s binding energies of the carbon atoms belonging to the pyrrole and benzene rings (see Figure 1), respectively. The pyrrole C atoms correspond to the higher energy peak, as expected. Moreover, the two peaks have a distance of 1.3 eV each other, in agreement with a common feature of the XPS spectra measured in the case of Pc molecules like, e.g., CuPc and PbPc.[41,42] In the case of the TiOPc molecule adsorbed on the intrinsic TiO_2 surface, a small shift (0.3 eV, see the blue curve in Figure 8A) toward higher binding energies is found due to a slight stabilization of the molecular levels induced the formation of a molecule−surface bond; see also Figures 5B and C. A more relevant blue-shift (0.9 eV for the pyrrole peak and 0.7 eV for the benzene peak; see the black curve in Figure 8A) has been calculated instead for the molecule adsorbed on the *p*-doped surface, due to the charge transfer induced from the molecule to the surface. Such a shift agrees with a reduction of electronic charge on the HOMO orbital also responsible of its lowering in energy; see Figures 5C and D.

Calculated XPS spectra give clear evidence also of a charge transfer occurring in an opposite way, from the surface to the molecule, like that predicted here for the second Pc/IS system, that is, the py-TiOPc interacting with a GaAs surface (see section III.A). Once again, the XPS C 1s spectrum has been calculated for three

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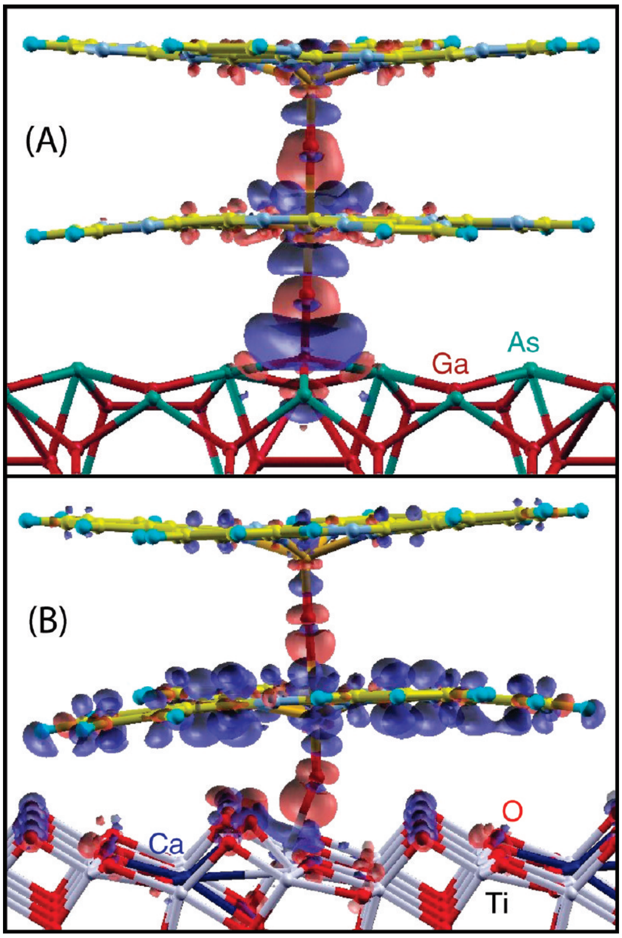

Figure 9. Stable configurations and isosurfaces of difference electron densities (ρ_{diff}) of (A) two pyrazino-TiOPc molecules piled up on an *n*-doped GaAs Ga-rich surface and (B) two TiOPc molecules piled up on a *p*-doped anatase surface. ρ_{diff} maps show the displacements of electronic charge at the molecule−surface interaction. Red surfaces cover areas where the difference is positive, blue surfaces, where it is negative.

different Pc−semiconductor arrangements, that is, a molecule noninteracting with the surface (i.e., constrained to stay far from the surface); see Figure 8E, and a molecule bonded to the surface of an intrinsic or an *n*-doped GaAs; see Figure 8F. When the molecule does not interact with the surface (red curve in Figure 8B), the spectrum is still identical to the one (not shown in the figure) calculated for an isolated py-TiOPc molecule. In this spectrum, the presence of eight extra N atoms in the macrocyclic system leads to a blue shift of both the spectral features with respect to the isolated TiOPc molecule (red curve in Figure 8A). Such changes of the spectrum are characterized by a larger blue shift of the outer benzene peak with respect to the pyrrole one (1.3 vs 0.7 eV, respectively), because the −aza− substitutions affect their nearest benzene C neighbors more than the inner pyrrole ones. These different shifts lead to an energy difference between the pyrrole and benzene peaks that shrinks to the value of 0.7 eV. The spectrum of the noninteracting py-TiOPc undergoes a small blue-shift (about 0.1 eV, see the blue curve) toward higher binding energies when the same molecule is adsorbed on intrinsic GaAs, due to a slight stabilization of the molecular levels produced by the formation of a molecule−surface bond. A more relevant shift toward *lower* binding energies (0.5 eV for the pyrrole peak and 0.4 eV for the benzene peak; see the black curve) is calculated instead for the molecule adsorbed on the doped surface, due to the charge transfer induced from the surface to the molecule. In fact, at variance with the TiOPc/TiO_2case, the C atoms are now surrounded by some extra electronic density belonging to the LUMO level.

The above results indicate that XPS investigations can provide an experimental evidence of the molecule−semiconductor charge-transfer processes theoretically predicted here for coupled Pc−semiconductor systems.

E. Outlook to Molecular Layers. An investigation of the horizontal assembling of the first molecular layer in a Pc/IS system is somehow out of reach of the theoretical methods used in the present study. Notwithstanding, a glance to the properties of molecular layers coupled with semiconductor substrates has been given here by investigating the properties of a vertical arrangement of two Pc molecules interacting with an IS surface; see, e.g., the geometries found for the py-TiOPc/*n*-GaAs and TiOPc/*p*-TiO_2 systems shown in Figure 9A and B, respectively.

In detail, in the case of the py-TiOPc/*n*-GaAs system (simulated by substituting two Ga atoms with Si atoms), when a second py-TiOPc molecule is adsorbed upon the first one, the most favorable adsorption site corresponds to the formation of an $\mathrm{O{-}Ti_{lower}{-}O{-}Ti_{upper}}$ chain where the Ti atom of the lower molecule reaches a distorted octahedral coordination; see Figure 9A. The upper molecule forms a quite stable Ti−O bond with the lower molecule characterized by a length of 2.15 Å, and by an E_{ads} of 0.7 eV. Moreover, the ρ_{diff} map in Figure 9A indicates the occurrence of a charge transfer process from the *n*-doped GaAs to the molecular LUMOs of both the adsorbed molecules. Such a charge transfer can be also deduced by the opposite bending direction of the corresponding macrocyclic-ligand planes, both carrying a negative charge, although it has to be taken into account that such electrostatic bending could be counterbalanced by van der Waals interactions, not included in the present calculations.

Similar results have been obtained when a second TiOPc molecule is placed upon a first molecule absorbed on the surface of a *p*-doped TiO_2 (simulated by substituting two Ti atoms with Ca atoms); see Figure 9B. A somewhat larger charge transfer seems to occur in this case than in the GaAs one; compare Figures 9A and B. A larger polarization of the system can be also appreciated by a comparison with the case of a single molecule adsorbed on the *p*-doped anatase surface; see the ρ_{diff} maps shown in Figures 9B and 4B (the displayed isosurfaces have been plotted by using the same value of charge density).

In the two Pc/IS systems above, the molecule−semiconductor coupling seems extended to the second-layer molecule, thus suggesting that an efficient organic−inorganic coupling could be achieved in the

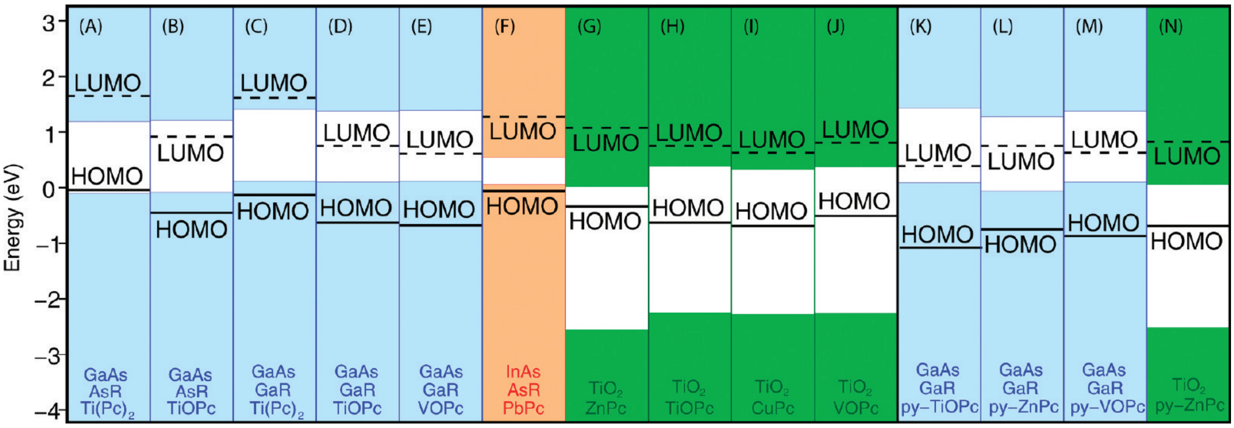

Figure 10. HOMO−LUMO energy levels related to the macrocyclic ligand(s) of different Pc molecules interacting with different undoped semiconductor surfaces. Filled areas represent semiconductor band structures, separated by an energy gap between the valence and conduction band. All of the levels are aligned to a common reference. Different colors indicate different semiconductor substrates: (A) Ti(Pc)$_2$ on As-rich GaAs. (B) TiOPc on As-rich GaAs. (C) Ti(Pc) on Ga-rich GaAs. (D) Ti(Pc)$_2$ on Ga- rich GaAs. (E) VOPc on Ga-rich GaAs. (F) PbPc on As-rich InAs. (G) ZnPc on TiO$_2$. (H) TiOPc on TiO$_2$. (I) CuPc on TiO$_2$. (J) VOPc on TiO$_2$. (K) Pyrazino(py)-TiOPc on Ga-rich GaAs. (L) py-ZnPc on Ga-rich GaAs. (M) py-VOPc on Ga-rich GaAs. (N) py-ZnPc on TiO$_2$.

case of thin Pc films deposited on doped semiconductors.

F. Universal Alignment of the Pc Electronic Levels. Figure 10 displays an extensive set of results regarding the electronic structure of different Pc molecules interacting with different semiconductors. These results firmly confirm an indication given in our previous study[27] regarding the occurrence of a sort of universal alignment of the Pc electronic levels with respect to the band structure of different *undoped* semiconductors. The different panels of Figure 10 show indeed that the HOMO−LUMO pair of different Pc molecules (full and dashed black lines in the figure) maintains an almost common alignment with respect to the band gap of the GaAs, InAs, and TiO$_2$ substrates, independently of the strength of the molecule−surface chemical interaction, more specifically, independently of the formation of chemical bonds involving the molecular central group. This general property can be related to the weak effect that the central group involved in a molecule−surface bond has on the highly delocalized π orbitals, as shown by the quite similar HOMO−LUMO electronic transitions and ionization potentials found by both present theoretical results and experimental measurements[1,44,60−62] for different Pc molecules. An exception to the above general rule is represented by systems where the molecule is strongly perturbed by an interaction with highly reactive surfaces, like the $(000\bar{1})$ GaN surface discussed above.

A universal alignment of the Pc HOMO−LUMO represents a *key point* when designing Pc−semiconductor systems. Such a property implies indeed that, in the 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 (or the HOMO peak position, depending upon the measure technique; see ref 44) and the semiconductor work function (or band potential). Thus, as a first step, ionization potentials and work functions can be used to select a Pc−semiconductor pair where the HOMO (LUMO) is located in the semiconductor energy gap, which is a necessary, although not sufficient, condition to realize a molecule to surface (surface to molecule) charge-transfer. Then, in a second step, the occurrence of the first condition for an effective Pc−semiconductor coupling (see section I), represented by the formation of a molecule−surface bond, can be favored by the choice of a Pc central group having some chemical affinity with a particular semiconductor surface. Such a choice does not affect the HOMO−LUMO positions in the semiconductor band gap due to the above universal alignment. Finally, theoretical calculations can be performed to verify that a *p*-type (*n*-type) doping of the semiconductor, possibly combined with changes to the molecular architecture, can actually induce a molecule to surface (surface to molecule) charge transfer involving the HOMO (LUMO) orbital, as required by the second condition for an effective Pc−semiconductor coupling. Thus, present results significantly extend the procedure proposed in our previous work for a theoretical design of efficiently coupled organic−inorganic systems.

IV. Conclusions

In the present study, the interaction of Pc molecules with inorganic semiconductors has been extensively investigated by using ab initio DFT methods. The achieved results strengthen a crucial point for designing Pc−semiconductor hybrid structures, that is, the occurrence of a universal alignment of the Pc electronic levels with respect to the semiconductor band structure, previously suggested on the grounds of a limited set of results. Present results also predict that the achievement of an effective Pc/IS coupling is not a rare event. In this regard, they trace novel routes for designing hybrid systems by showing that the degrees of freedom for such a design can be increased by modifying the molecular architecture. Present results predict indeed that a suitable functionalization of the Pc molecules permits to realize charge transfer processes in both directions, from the molecule to the surface and viceversa, thus involving both the HOMO and LUMO orbitals, respectively. Furthermore, they provide a sound theoretical framework for designing effectively coupled hybrid systems. Finally, present results predict that XPS measurements can give an experimental evidence of molecule–surface charge-transfer processes occurring in effectively coupled Pc/IS systems.

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