# 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. 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 $\pi$-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 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 $\pi$ 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 resume, the following Pcs properties may be related to such a peculiar structure:

- The delocalized $\pi$ 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 mobilities 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 $\pi \rightarrow \pi^\star$ electronic transitions. Pc molecules can be used therefore as dye-sensitizers for hybrid organic-inorganic solar cells[1,11].
- 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].

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 1 (A)); 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 $\pi$ 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 1 (D). A first group of MOs is related to the skeletal $\sigma$ 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 $\pi$ 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, $\pi$ and $\pi^*$, electronic clouds are shown in Figures 1 (B) and

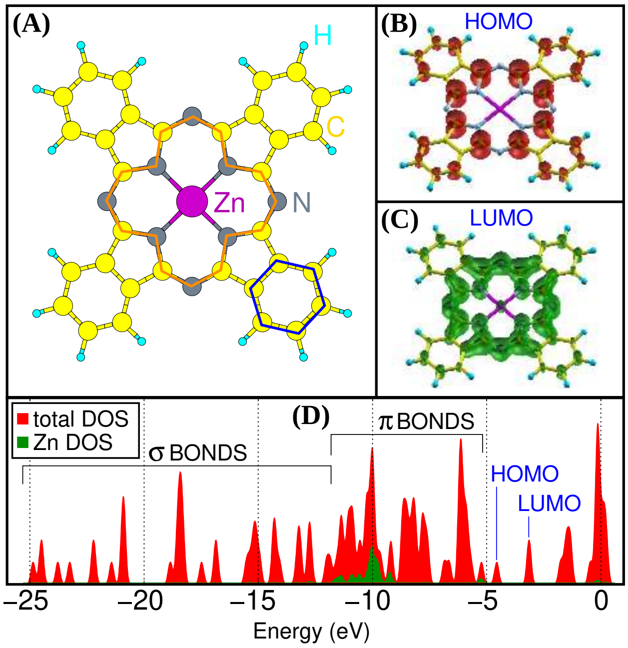


FIG. 1: (A) Top view of a ZnPc molecule. The orange and blue lines identify the inner pyrrole system and one of the outer benzene rings, respectively. (B) Electron density isosurface of the $\pi$ highest occupied molecular orbital (HOMO). (C) Electron density isosurface of the doubly degenerate $\pi^\star$ 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 labelled: the region of $\sigma$ bonds, formed by linear combinations of C $2s$, N $2s$, C $2p_{xy}$ and N $2p_{xy}$ atomic orbitals; the region of $\pi$ 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.

(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 $\pi$ zone of the DOS (see the major green feature in Figure 1 (D)). 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. 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 be characterized by the occurrence of two main conditions:

1. the formation of appreciable surface-molecule chemical bonds (possibly inducing an assembling of ordered interfaces due to a template effect of the surface structure).

2. the occurrence of a molecule-surface charge-transfer involving the $\pi$-electron clouds responsible of the Pc NLO and transport properties.

Such conditions have been chosen because their fulfilling 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(1*s*) 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 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 $\Gamma$ 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 H atoms. 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 don't undergo any reconstruction, don't 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 8 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 orthorombic crystal slab, formed by 6 atomic layers of bulk GaN cut along the $(000\overline{1})$ crystal axis, plus a Ga adlayer (i.e., supercells of 210 atoms). The 3*d* shells of Ga atoms have been explicitly considered as valence electrons in all of the calculations involving a GaN substrate, as suggested in Ref. 31. 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 6 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 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 $\Gamma$ point. The strength of a molecule-substrate bonding, i.e., the molecular adsorption energy, has been estimated by the total energy difference $E_{ads} = E[Pc/IS] - E[Pc] - E[IS]$. Difference electron density ($\rho_{diff}$) 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, $\rho_{diff}$[TiOPc/anatase] is given by $\rho$[TiOPc/anatase] − ($\rho$[TiOPc] + $\rho$[anatase]) where $\rho$[TiOPc/anatase] is the electron density of a supercell containing the molecule-semiconductor system, $\rho$[TiOPc] is the electron density of the same supercell with the molecule only, and the analogue for the $\rho$[anatase] density. Thus, a $\rho_{diff}$[TiOPc/anatase] map indicates the charge displacements induced by the interaction between the molecule and the surface.

Finally, XPS C1*s* chemical shifts have been estimated by total energy differences between "standard" and "core hole" calculations.[32,33] In detail, in the case of the latter calculations, a C ultrasoft pseudopotential containing an 1*s* 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 C1*s* chemical shift and assumed to be equivalent to the XPS experimental $CO_2$ line observed at 291.90 eV.[34] 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:

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

A $\Gamma$ 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,[35] CuPc,[36] PbPc[37]), different central groups (TiOPc,[38] GaClPc[39]), or a multi-ligand sandwich structure ($Ti(Pc)_2$[40]) 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 $\beta2(2\times4)$ and Ga-rich $\zeta(4\times2)c(8\times2)$ GaAs surfaces,[41,42] the (001) As-rich $\beta2(2\times4)$ InAs surface,[43], the $(000\bar{1})$ $(1\times1)$ GaN surface,[31] and the (101) $TiO_2$ (anatase) surface,[44] 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.[45,46]

A couple of 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 non-metallic 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.

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.

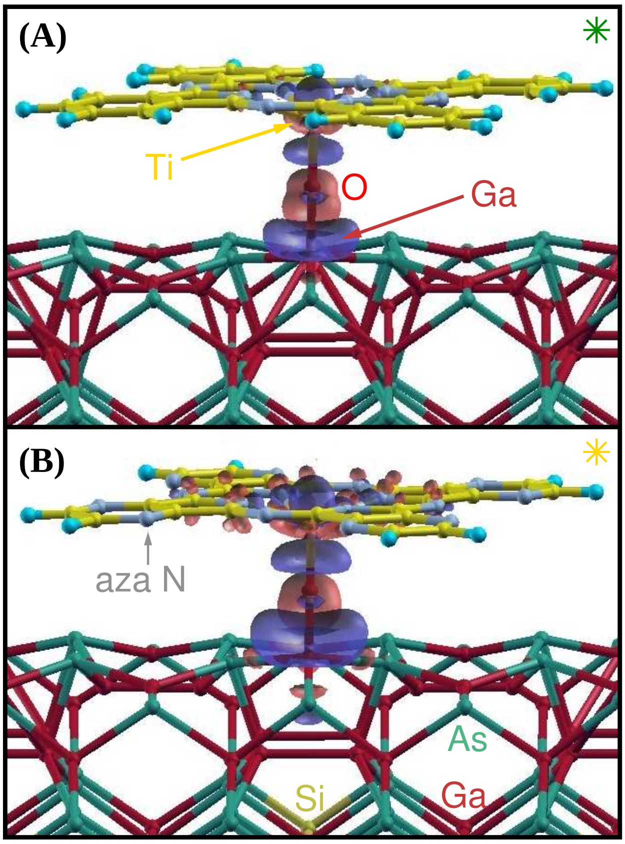


FIG. 2: Equilibrium geometries and isosurfaces of difference electron densities ($\rho_{\rm diff}$) of: (A) a TiOPc molecule bonded to a $\zeta(4\times2)/c(8\times2)$ Ga-rich GaAs surface; (B) a pyrazino-TiOPc molecule bonded to the same reconstructed surface in the case of $n$-doped GaAs. $\rho_{\rm diff}$ 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 green and yellow stars indicate a correspondence between the equilibrium configurations of the present Figure and the electronic levels of Figure 3.

### 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 three-fold coordinated $sp^2$ Ga atoms.[42,47] These surface atoms form an in-plane $\sigma$ structure with three neighbouring As atoms which carry dangling bonds pointing upwards in the (001) direction. The TiOPc molecule is strongly chemisorbed on this $\zeta$ surface, the surface $sp^2$ Ga atoms being the preferred adsorption sites, see Figure 2 (A). The molecular O atom forms a stable O-Ga bond characterized by a bond length of 1.77 Å and an adsorption energy ($E_{\rm ads}$) of 1.4 eV. As mentioned above, the TiOPc molecule weakly interacts, instead, with the As-As dimers characterizing the $\beta2(2\times4)$ (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 Figures 3 (A) 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 Figures 3 (A) 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 $\rho_{\rm diff}$[TiOPc/(Ga-rich)GaAs] map of Figure 2 (A) 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-

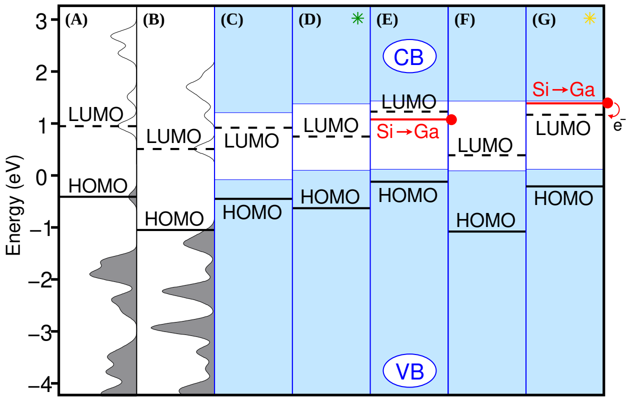


FIG. 3: DOS and sketched electronic levels of a TiOPc and its pyrazino- derivative as isolated molecules or when interacting with different GaAs surfaces. All of the levels are aligned to a common reference. The HOMO and LUMO are represented by full and dashed black lines, respectively. The colour background 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. (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; (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.

rich)GaAs system represents a potential condition for the occurrence of a surface-molecule charge transfer. In this regard, the electronic levels of Figure 3 (D) show that the HOMO falls *inside the valence band* (VB) while the LUMO is located *in the energy gap* of GaAs.[48] 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 3 (E). 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. Actually, a $\rho_{\rm diff}$[TiOPc/$n$-GaAs] (not reported here) is very similar to the $\rho_{\rm diff}$[TiOPc/GaAs] one shown in Figure 2 (A), 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 2 (B)). The N atoms are more electronegative than the C ones, thus they can stabilize electrons on $\pi$ 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 $E_{\rm ads}$ 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 Figures 3 (A) and (B) for the isolated molecules, and Figures 3 (D) 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. 39. 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 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 3 (G) and by the $\rho_{\rm diff}$[py-TiOPc/$n$-GaAs] map drawn in Figure 2 (B), 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 1 (C)). This surface to molecule charge-transfer involves the LUMO $\pi^\star$ 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 a trouble can be overcome by modifying the Pc architecture, which permits to reverse the Pc character from a donor to an acceptor one.

### B. TiOPc Molecule on the $TiO_2$ (101) Surface

The (101) anatase surface presents rows of five-fold coordinated $Ti_{5c}$ atoms, which are under-coordinated atoms with respect to the six-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 ($O_{\rm mol}$) of the TiOPc molecule. A $Ti_{5c}$-$O_{\rm mol}$ bond[49] 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 $TiO_2$[44]) and by an $E_{\rm ads}$ equal to 1.3 eV. Moreover, the difference density map of Figure 4 (A) shows a displacement of electronic charge toward the region of the $Ti_{5c}$-$O_{\rm mol}$-Ti bridge quite similar to that found in the case of the TiOPc/GaAs system (cf Figure 2 (A)).

The electronic structures of the isolated molecule, of a TiOPc molecule weakly interacting with the anatase surface (i.e., having the O atom pointing upwards) and of the same molecule bonded to the surface are sketched in Figures 5(A), 5(B) and 5(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 5 (C)) is characterized by a HOMO located in the $TiO_2$ band gap[50] 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 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 5(D). 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 4(B) clearly shows that electronic charge moves from the molecular orbital involving C atoms of the macrocyclic ligand (i.e., the HOMO $\pi$ 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,[1,39] 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,.

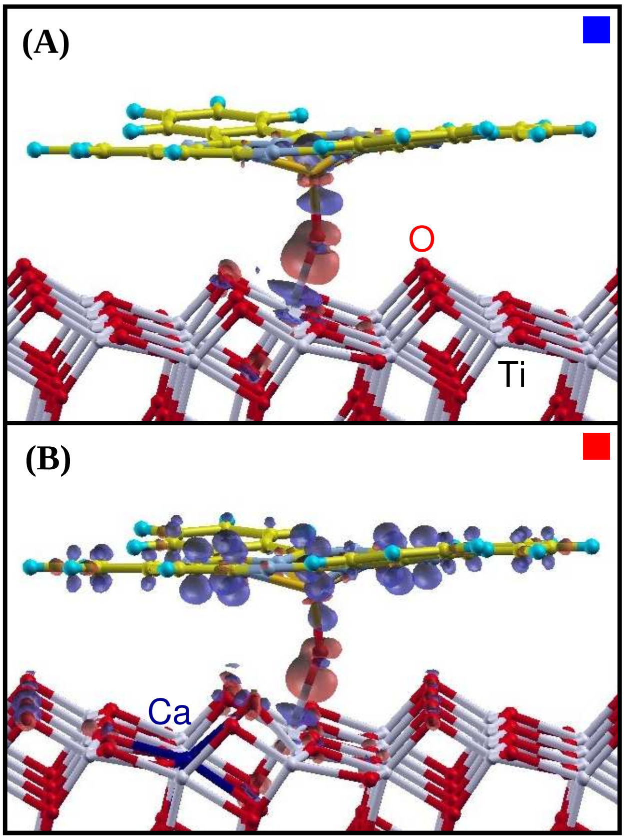


FIG. 4: Equilibrium geometries and isosurfaces of difference electron densities ($\rho_{\rm diff}$) of: (A) a TiOPc molecule bonded to the (101) anatase surface; (B) a TiOPc molecule bonded to a *p*-doped anatase surface. $\rho_{\rm diff}$ maps show the displacements of electronic charge induced by the 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 4 and the electronic levels of Figure 5.

### 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.[51] 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 $(1\times1)$ 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.[31,52] These Ga atoms are indeed close enough each other to share their valence electronic levels, thus giving rise to a partially filled metallic band spanning the entire energy gap.[53]

Two different Pc molecules, the already discussed TiOPc molecule and the alogenide GaClPc one, together 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 inter-

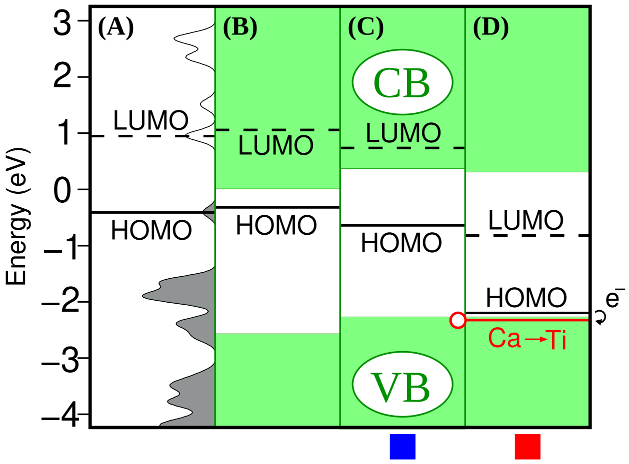


FIG. 5: DOS and sketched electronic levels of a TiOPc molecule interacting with the (101) anatase surface. All of the levels are aligned to a common reference. The HOMO and LUMO are represented by full and dashed black lines, respectively. The colour background delimits the valence and conduction band regions relative to the semiconductor electronic structure. A dopant acceptor level is indicated by a red line and an empty circle. (A) isolated TiOPc molecule; (B) TiOPc weakly interacting with the anatase surface (i.e., with the O atom pointing upwards); (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.

actions. Both molecules are characterized by a (metal)-(non-metal) 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[54] and arranged in a distorted tetrahedral configuration $ClGa_4$, see Figure 6 (A). 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 Figures 6 (A) 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 6 (A)) to the Cl atom and the new $Ga_{surf}$-Cl bonds (see the red zones in Figure 6 (B)). 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 Figures 7 (A) 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.[55] 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 which may be useful when designing hybrid Pc-semiconductor structures. It should be also noted that 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., Figures 7 (D) 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 7 (F), thus permitting a surface to molecule charge transfer. Such a transfer actually occurs, as clearly shown in Figures 6 (C) and (D) which indicate a charge displacement toward the pyrrole N and C atoms contributing to the LUMO with their $2p$ atomic orbitals. Thus, once again, a change of the Pc architecture permits to achieve 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

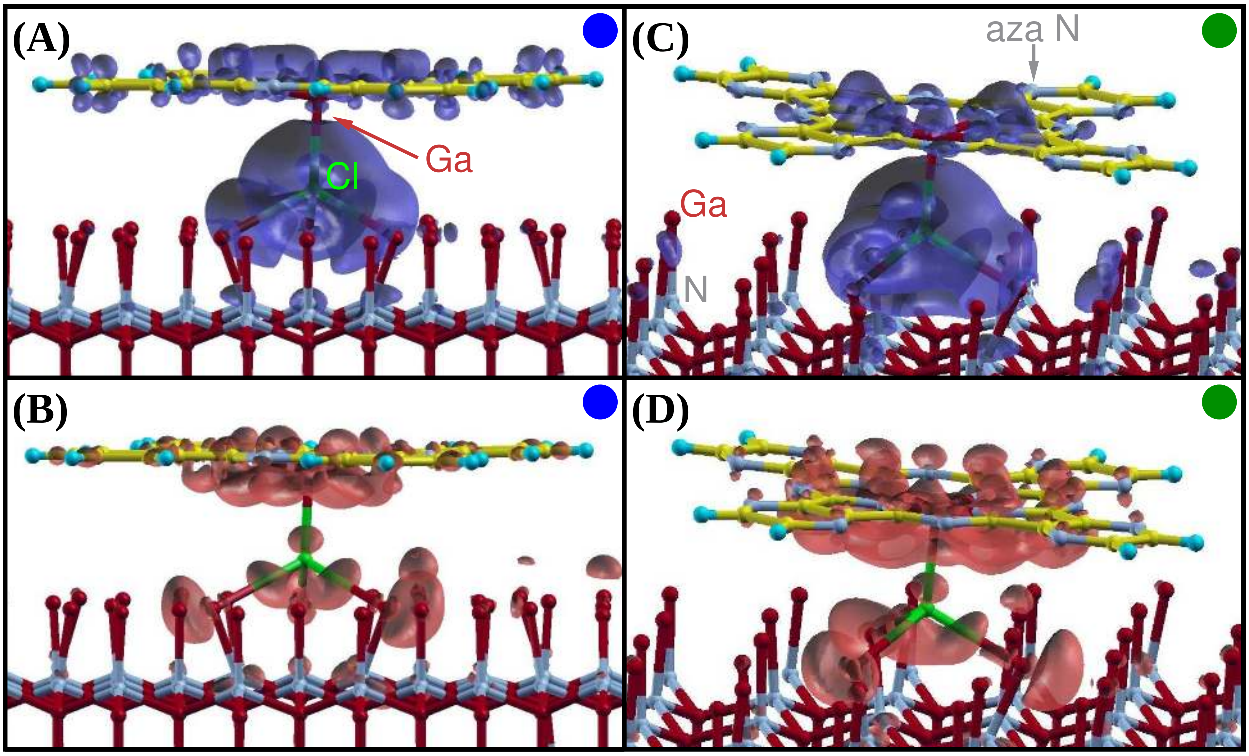


FIG. 6: Equilibrium geometries and isosurfaces of difference electron densities ($\rho_{\rm diff}$) for a GaClPc molecule and its pyrazino derivative adsorbed on the $(000\bar{1})$ GaN surface. (A) and (B) show the geometry of the GaClPc molecule adsorbed on the GaN surface together with the regions 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.

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, Figures 7 (G) 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 1$s$ 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 1$s$ 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(1$s$) 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 upwards, see Figure 8 (C). 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 8 (D). A clear trend can be recognized by looking at the C 1$s$ 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 doesn't interact with the surface (red curve in Figure 8 (A)), the spectrum is almost identical to the one (not shown) calculated for an isolated TiOPc molecule. Such spectrum is characterized by two peaks corresponding to the C 1$s$ 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.[36,37] 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 8 (A)) towards 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 5 (B) 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 8 (A)) has been calculated instead for the molecule adsorbed on the

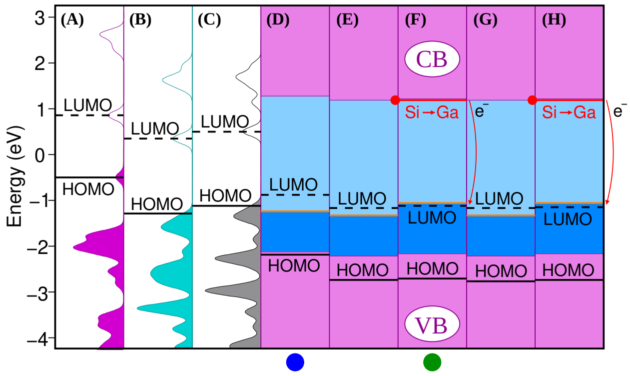


FIG. 7: DOS and sketched electronic levels of GaClPc, pyrazino-GaClPc, and pyrazino-TiOPc molecules and of the same molecules interacting with the $(000\bar{1})$ GaN surface. All of the levels are aligned to a common reference. The HOMO and LUMO are represented by full and dashed black lines, respectively. The magenta colour 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. (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.

$p$-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 5 (C) and (D).

Calculated XPS spectra give clear evidences 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(1$s$) spectrum has been calculated for three different Pc-semiconductor arrangements, that is, a molecule non-interacting with the surface (i.e., constrained to stay far from the surface), see Figure 8 (E), and a molecule bonded to the surface of an intrinsic or an $n$-doped GaAs, see Figure 8 (F). When the molecule doesn't interact with the surface (red curve in Figure 8 (B)), 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 8 (A)). Such changes of the spectrum

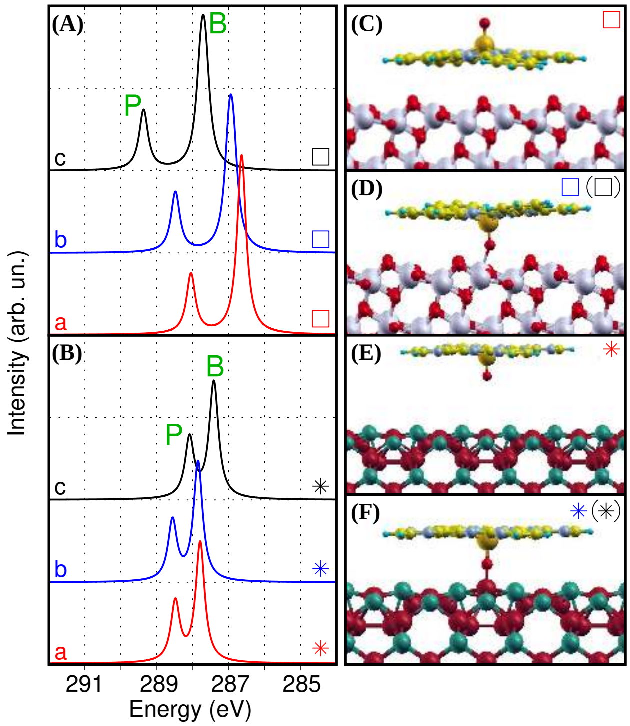


FIG. 8: Theoretical spectra of the C 1s core shifts of a TiOPc molecule adsorbed on the anatase (101) $TiO_2$ surface and of a py-TiOPc molecule adsorbed on the (001) $\zeta(4\times2)$/c$(8\times2)$ GaAs surface (left side) are presented together with the corresponding equilibrium geometries (right side). (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.

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 non interacting py-TiOPc undergoes a small blue-shift (about 0.1 eV, see the blue curve) towards 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 towards *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/$TiO_2$ case, 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. An 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 Figures 9 (A) 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 O-$Ti_{lower}$-O-$Ti_{upper}$ chain where the Ti atom of the lower molecule reaches a distorted octahedral coordination, see Figure 9 (A). 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 $\rho_{diff}$ map in Figure 9 (A) 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.

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 9 (B). A somewhat larger charge transfer seems to occur in this case than in the GaAs one, compare Figures 9 (A) 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 $\rho_{diff}$ maps shown in Figures 9 (B) and 4 (B) (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 case of thin Pc films deposited on doped semiconductors.

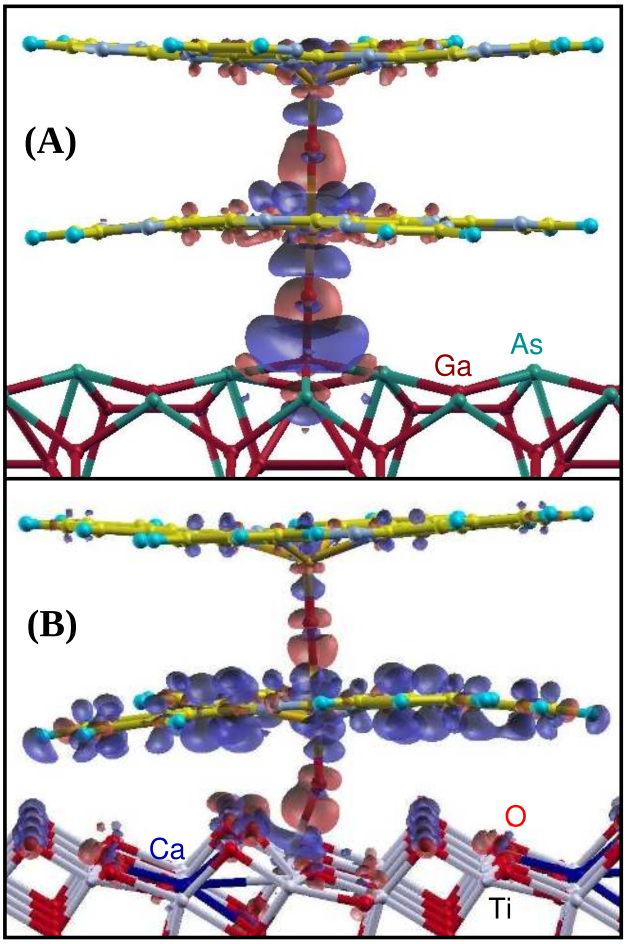


FIG. 9: Stable configurations and isosurfaces of difference electron densities ($\rho_{diff}$) of: (A) two pyrazino-TiOPc molecules piled up on an *n*-doped GaAs Ga-rich surface; (B) two TiOPc molecules piled up on a *p*-doped anatase surface. $\rho_{diff}$ maps show the displacements of electronic charge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

### 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 on the strength of the molecule-

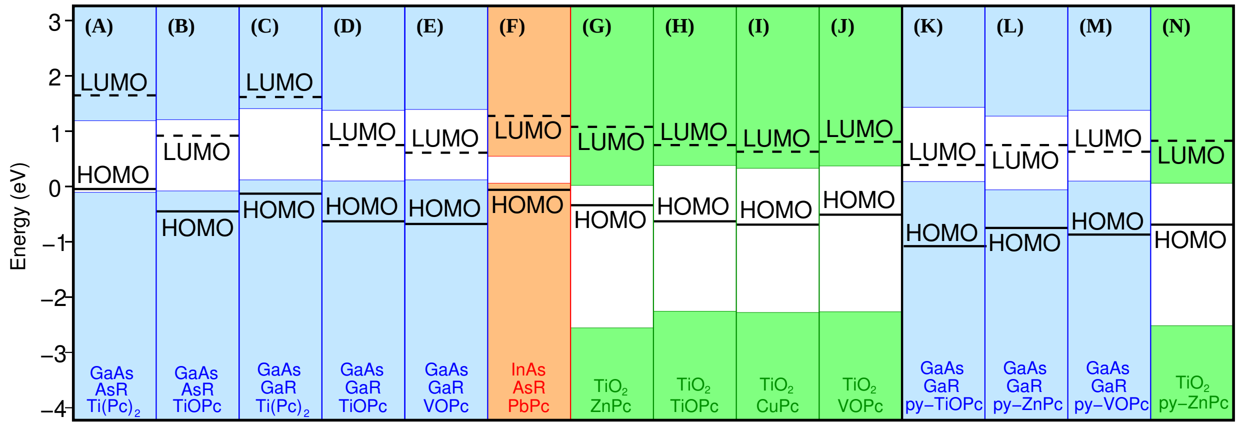


FIG. 10: HOMO-LUMO energy levels related to the macrocyclic ligand(s) of different Pc molecules interacting with different undoped semiconductor surfaces. Filled areas represent semiconductor band structures, separated by an energy gap between valence and conduction band. All of the levels are aligned to a common reference. Different colours indicate different semiconductor substrates: (A) $Ti(Pc)_2$ on As-rich GaAs; (B) TiOPc on As-rich GaAs; (C) $Ti(Pc)_2$ 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 $TiO_2$.

surface chemical interaction, more specifically, independently on 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 $\pi$ orbitals, as shown by the quite similar HOMO-LUMO electronic transitions and ionization potentials found by both present theoretical results and experimental measurements[1,39,56–58] 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 $(000\overline{1})$ 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 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. 39) 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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