

Efficient coupling in organic-inorganic systems: a theoretical study

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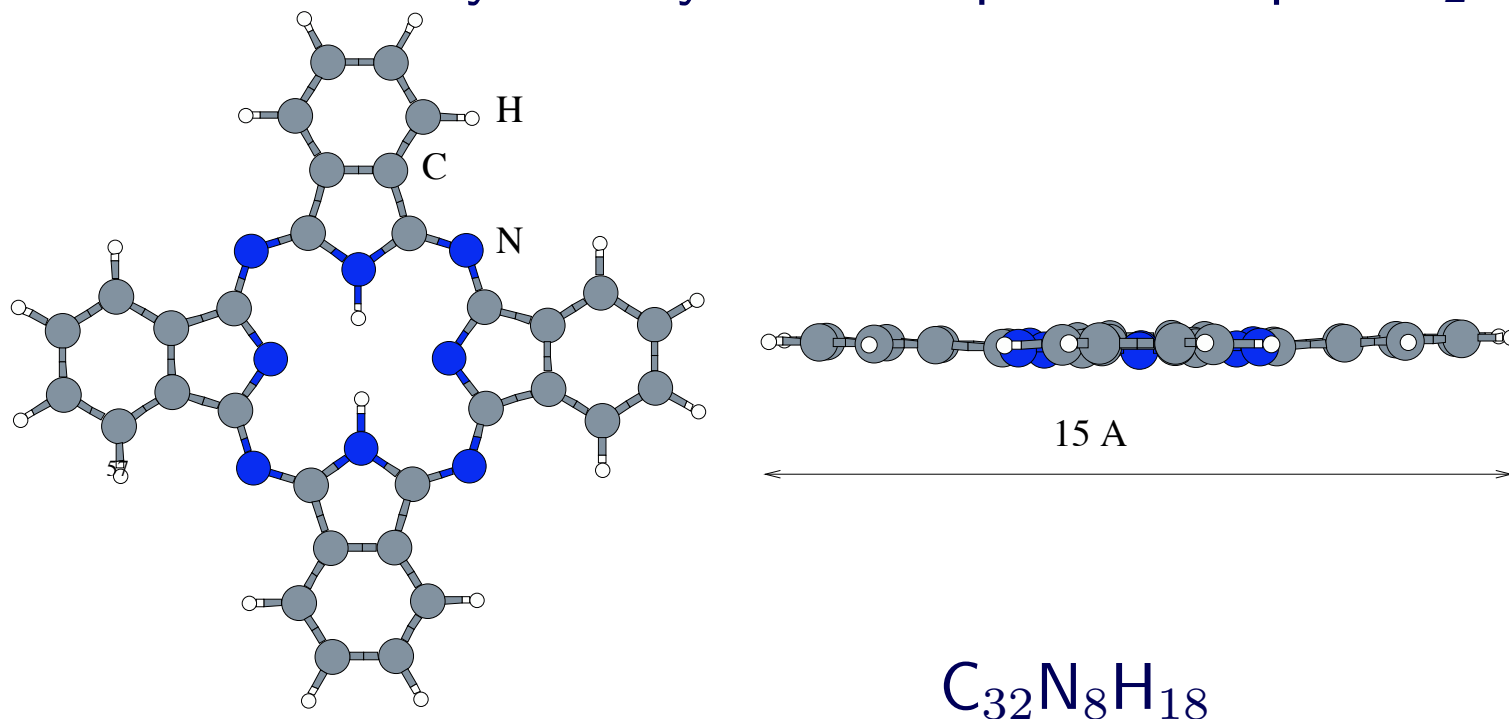
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Outline

- About Phtalocyanines (Pc's) and Pc's deposited over semiconductor surfaces
- The search for an *efficient coupling* between Pc's and semiconductor surfaces, i.e. a chemical binding that affects molecular properties
- DFT study of Pc's on TiO₂ anatase (101) surfaces, on GaAs (100) surfaces, on GaN surfaces,...
- Towards a general rule to predict coupling in Pc-semiconductor surfaces

Phthalocyanines

Phthalocyanines (Pc's) are a family of organic molecules characterized by the presence of a fourfold symmetry. The simplest example: H_2Pc

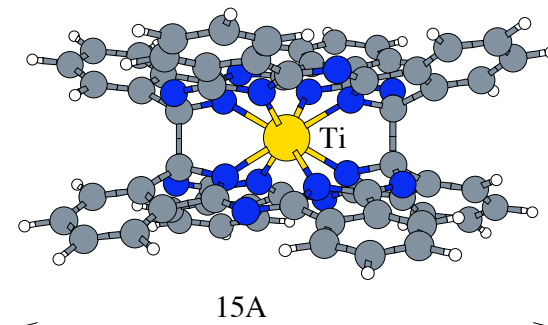
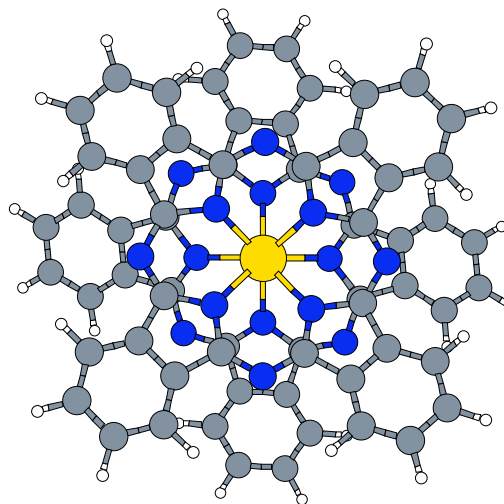
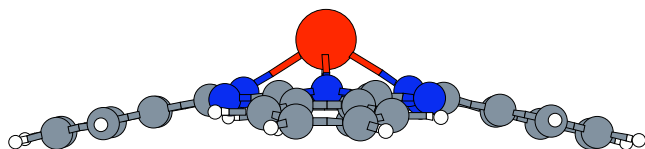
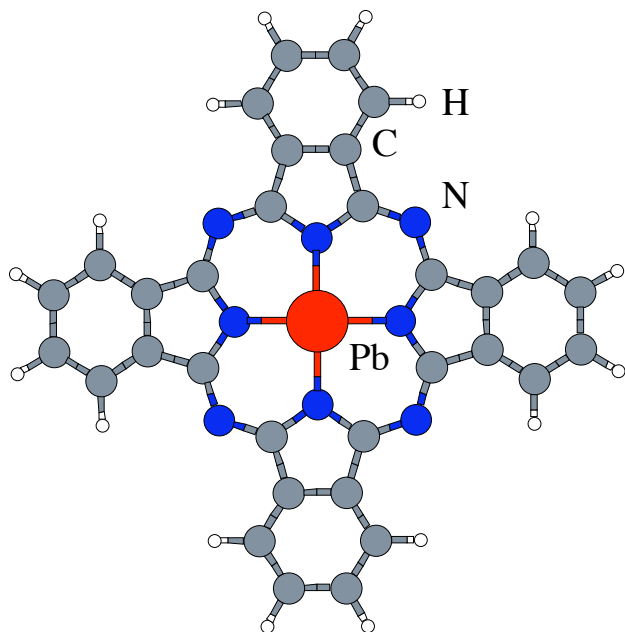


(blue=N, gray=C, white=H)

Metal Pc's have a metal atom in the center of the molecule.

Properties of Phtalocyanines

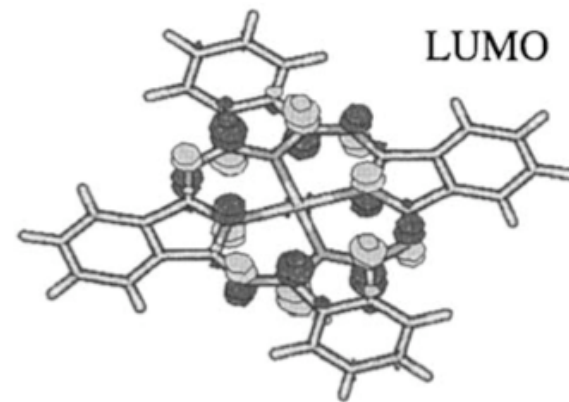
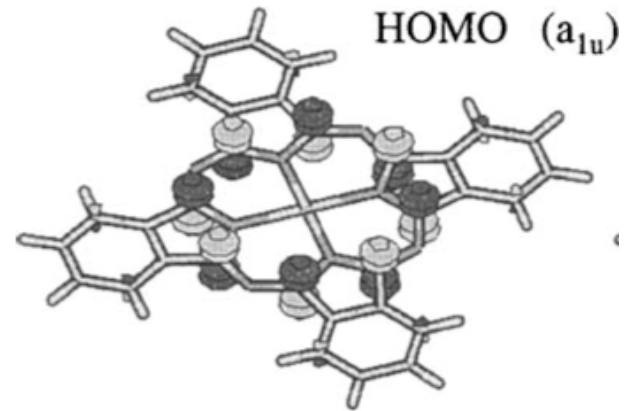
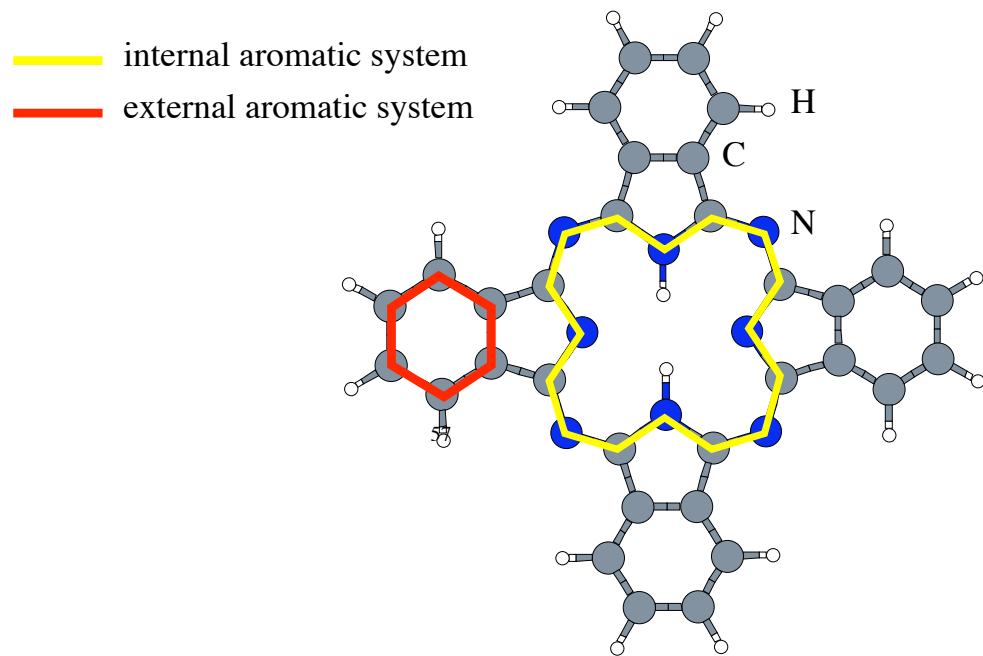
Pc's are often, but not always, flat. Lead Phtalocyanine (PbPc):



The electronic properties of Pc's can be tuned by varying the central metal atom. Pc's can form "sandwich" molecules, as in the above example:
 $\text{Ti}(\text{C}_{32}\text{N}_8\text{H}_{16})_2$

Properties of Phtalocyanines (2)

Pc's contain highly conjugated π -electron rings, giving them remarkable non-linear optic (NLO) properties



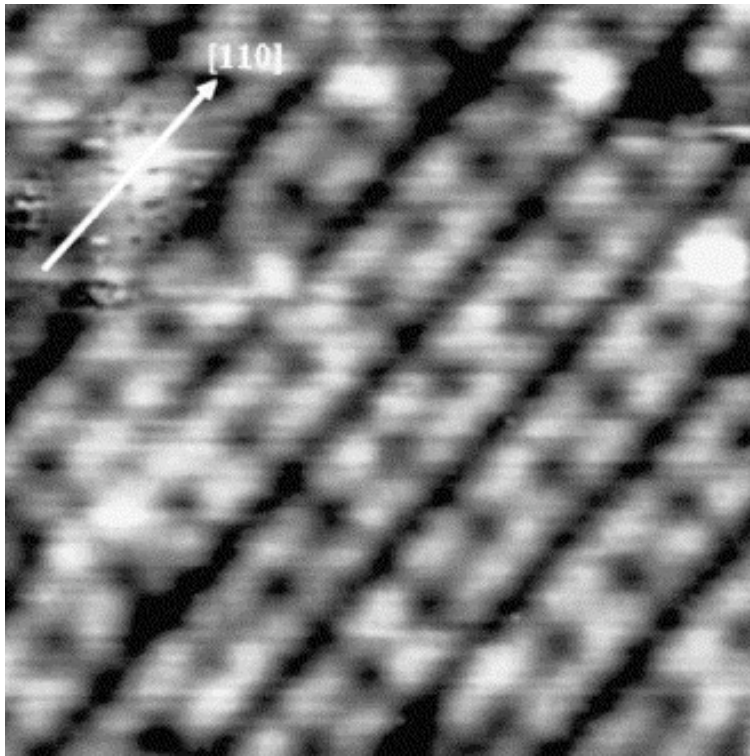
NLO properties are mostly determined by the frontier orbitals, HOMO and LUMO, formed by π states (from JCP 126, 124709 (2007))

Phthalocyanine-semiconductor heterostructures

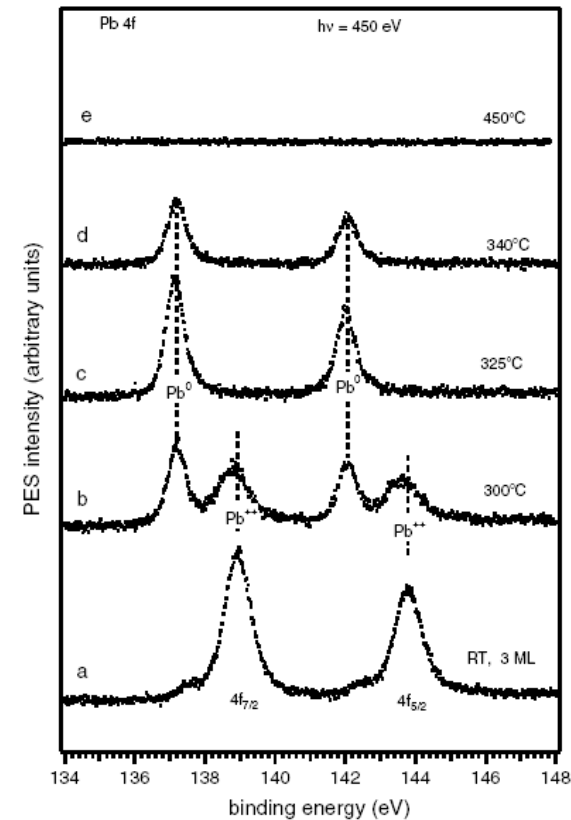
- Pc's are known to form thin ordered films over semiconductor surfaces
- Potentially useful for new kind of devices: OFETs, OLED, solar cells, limiting optical devices, 2nd and 3rd harmonic generation
- Possible tuning of properties via doping and charge transfer from/to the surface...
- ...but interaction of Pc's with semiconductor surfaces is often weak (van der Waals bonding) and the properties of Pc's are little changed wrt molecular case

Phthalocyanine-semiconductor heterostructures (2)

Evidence for ordered Pc monolayers on III-V surfaces with sizable Pc-substrate interaction exists (from Prog.Surf.Sci. **77**, 139 (2004))



STM image of an ordered Pb-Pc monolayer on (001) InSb surface

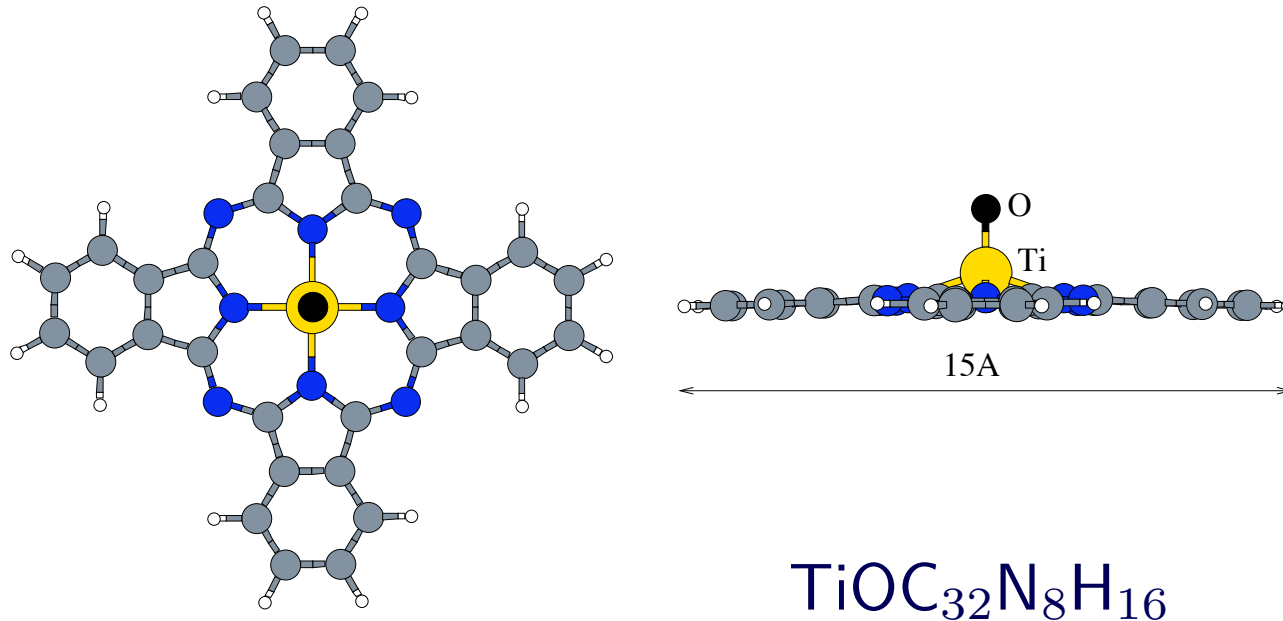


Pb core level spectra of PbPc molecules deposited on InSb

Wanted: sizable surface-Pc interactions

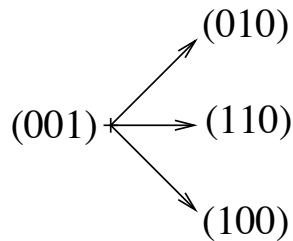
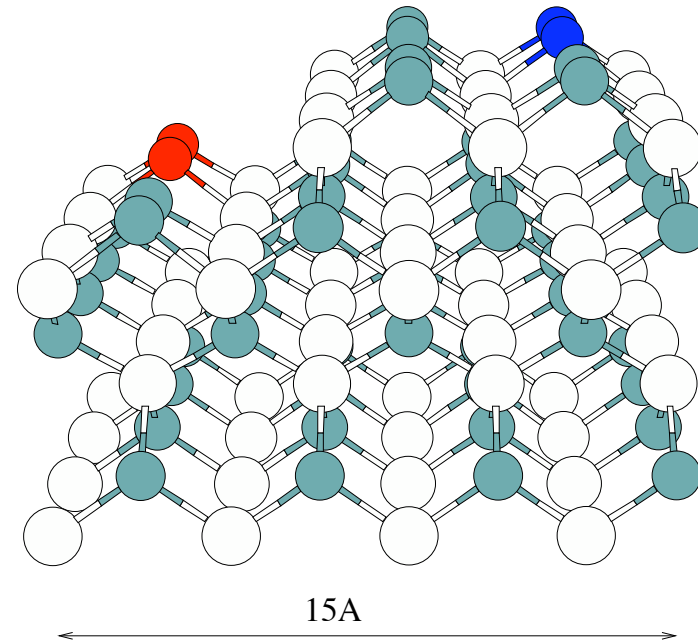
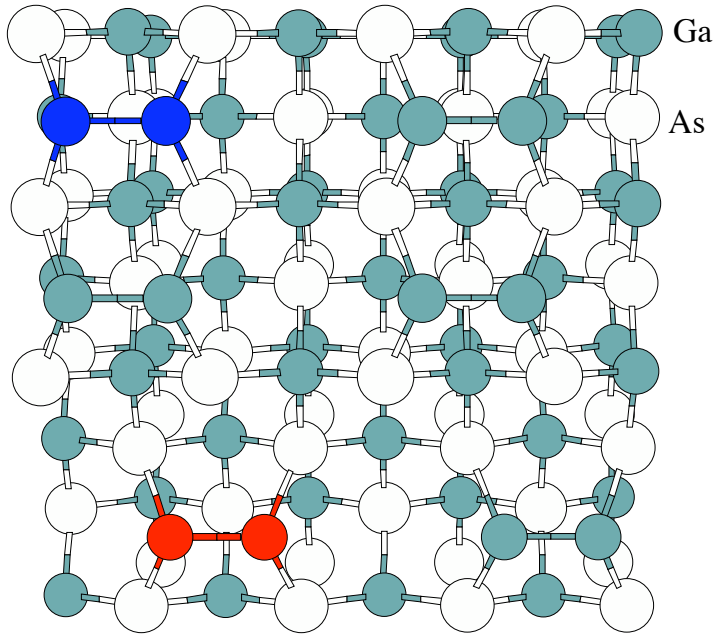
We have examined several potential candidates. An incomplete list:

- *PbPc (also ZnPc, CuPc) on reconstructed GaAs or InAs surfaces*
Can Ga/As dimers on the surface bind to protruding Pb atom?
- *OTiPc (and its modifications) on GaAs or TiO₂ surfaces*
Can O atom bind to the surface and act as a bridge?



GaAs surface (As-rich)

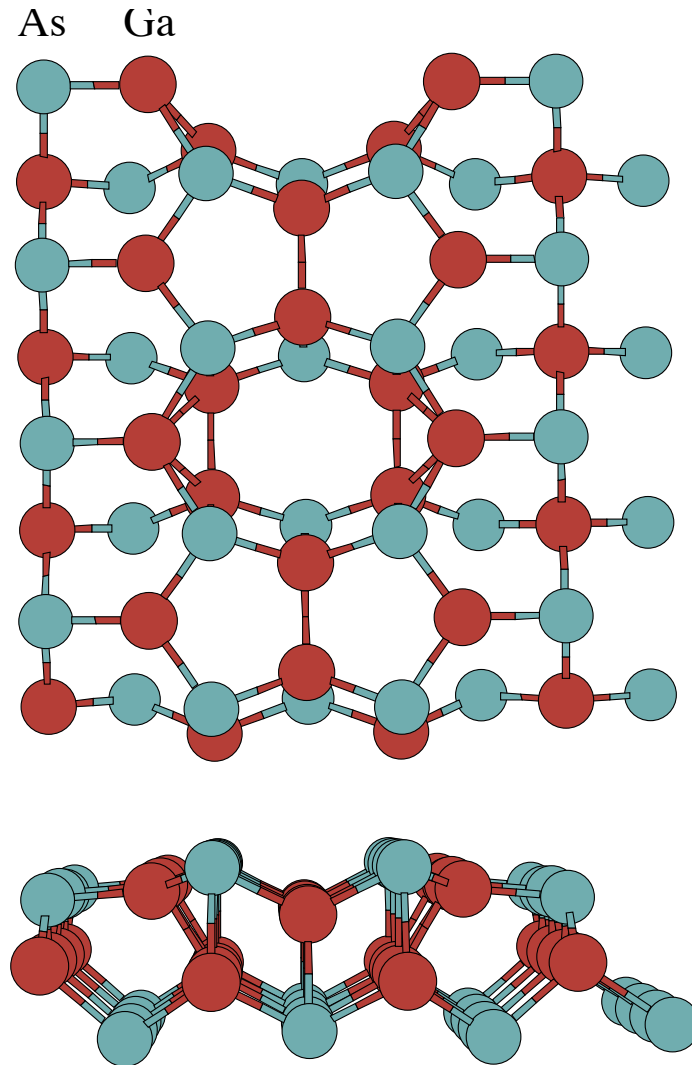
(100) GaAs $\beta_2(2 \times 4)$ (As-rich) reconstructed surface:



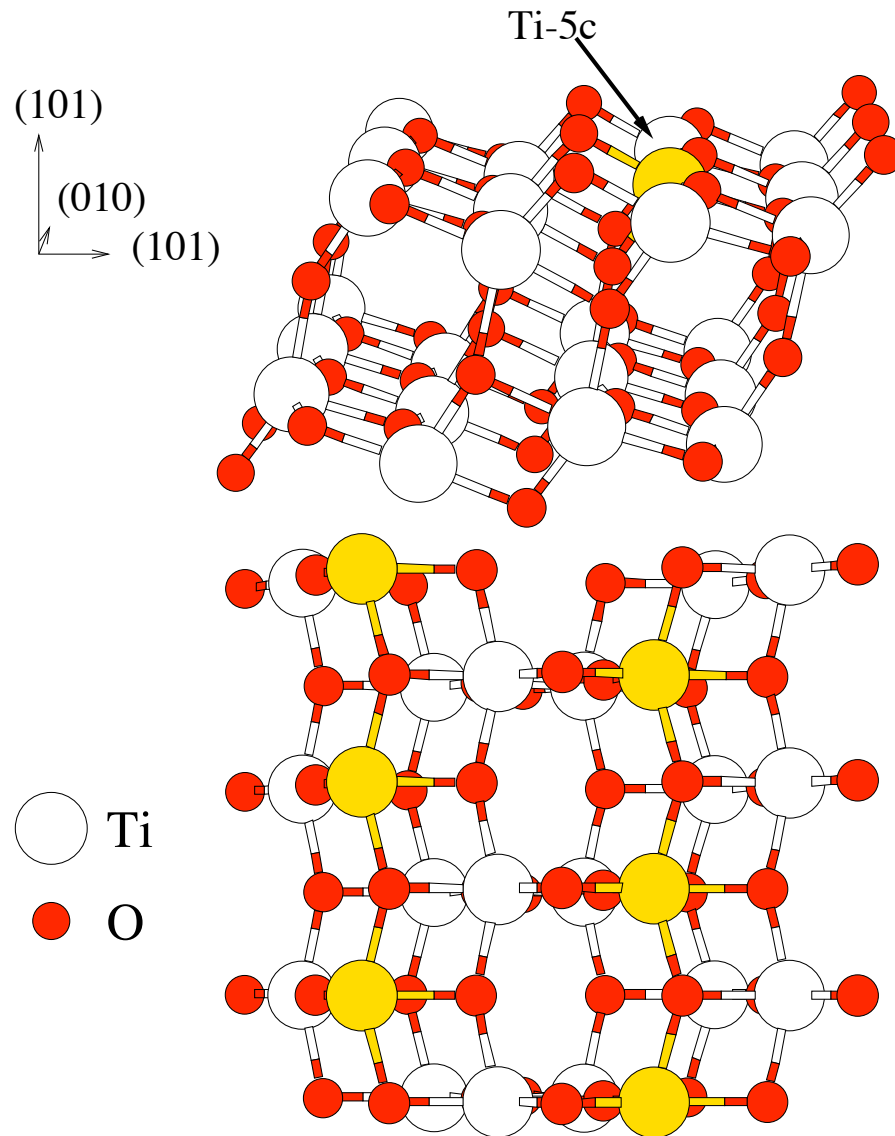
  As dimers along the (110) direction

GaAs surface (Ga-rich)

(100) GaAs $\zeta(4 \times 2)c(8 \times 2)$ (Ga-rich) reconstructed surface:



TiO₂ Anatase (101) surface



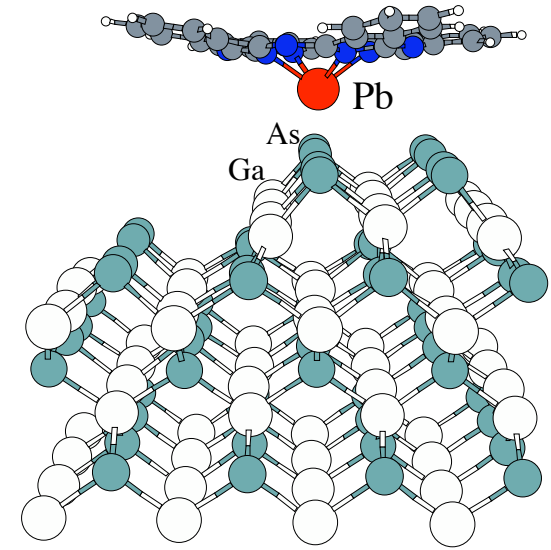
Theoretical Methodology

- Density Functional Theory, GGA-PBE exchange-correlation functional
- Plane Waves and Ultrasoft Pseudopotentials
- Supercell geometry: H saturators + semiconductor slab + molecule + empty space. Minimum size: $\sim 150 \div 200$ -atom cells!
- Structural optimization: requires 8-16 processors of a IBM SP5

All calculations performed using PWscf: <http://www.pwscf.org>
a package of the Quantum-ESPRESSO distribution:
<http://www.quantum-espresso.org>

What doesn't work

- PbPc on either As-rich or Ga-rich GaAs surface
- PbPc on the same (hypothetical) InAs surfaces
- OTiPc on As-rich GaAs surface



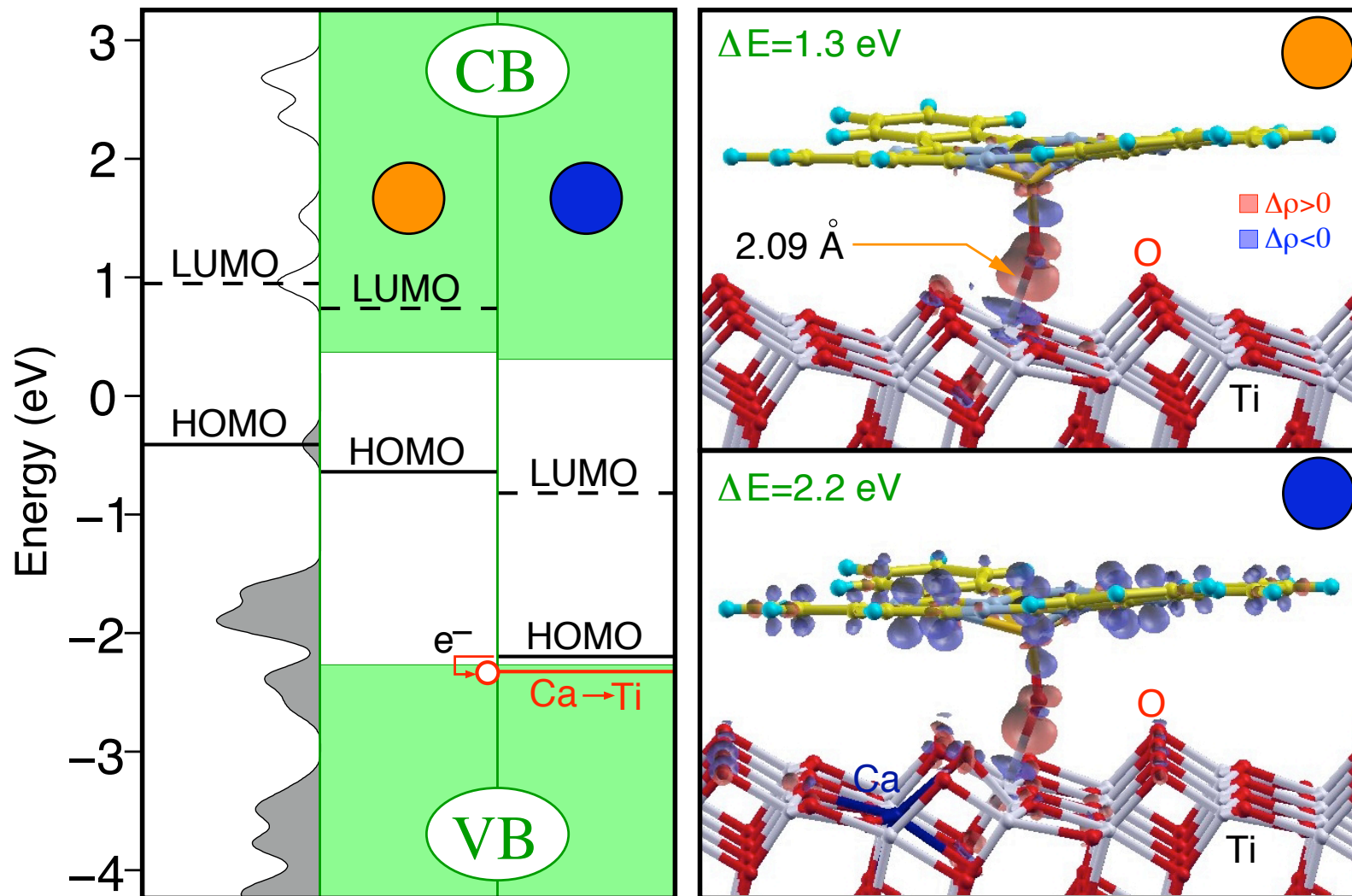
No evidence of chemical bonding in any of the above: $E_b < 0.1\text{eV}$
(remember: no van der Waals interactions in DFT-GGA)

- OTiPc on Ga-rich GaAs surface

Sizable chemical bonding: $E_b \simeq 1.4\text{ eV}$, but no transfer of electrons from n -doped GaAs to the LUMO of Pc is observed.

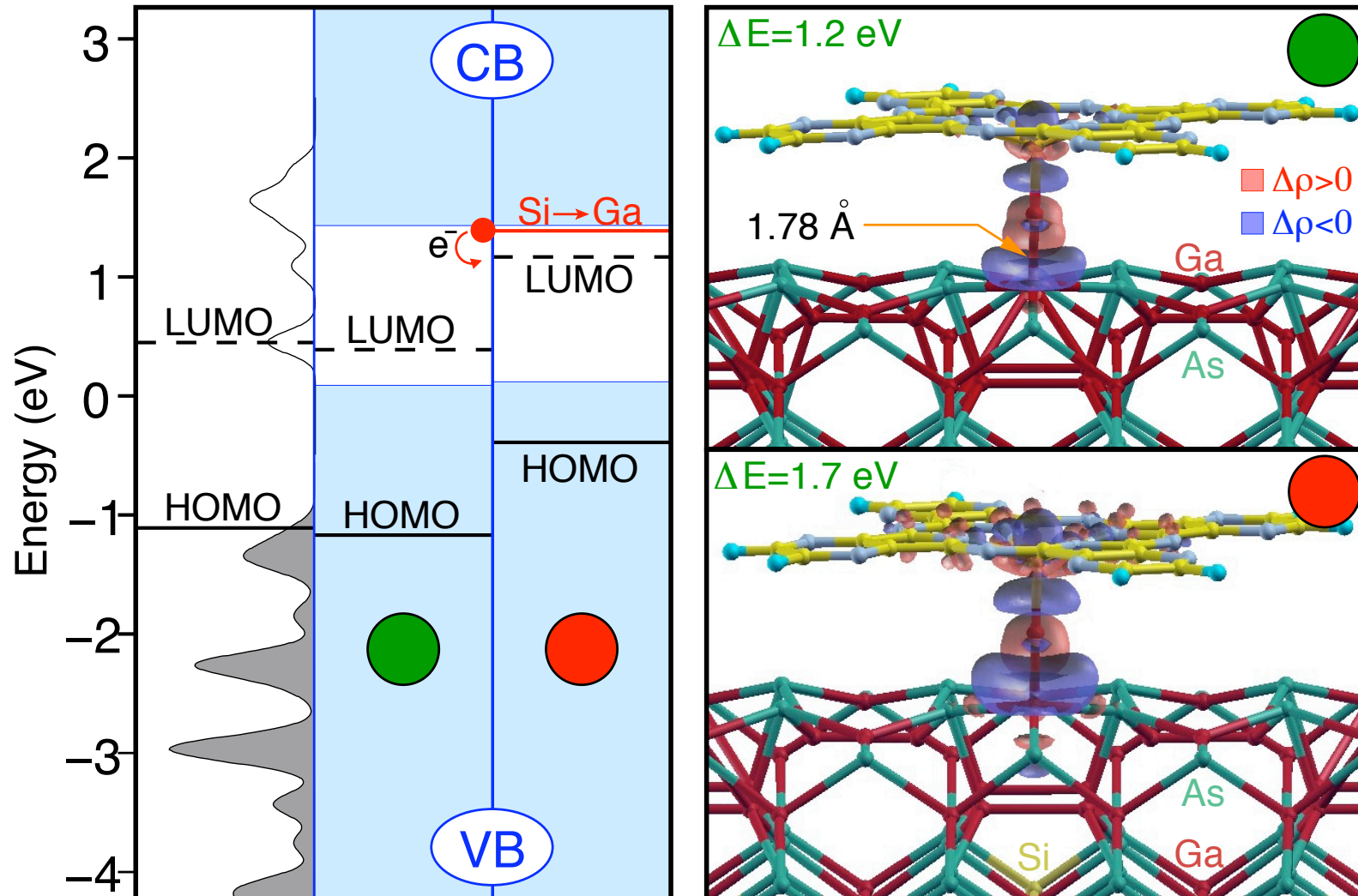
What works (*p*-doping)

OTiPc on (101) TiO₂ (anatase) surface. Ti-O-TiPc bond is formed, charge transfer from molecular HOMO to *p*-doped TiO₂ takes place



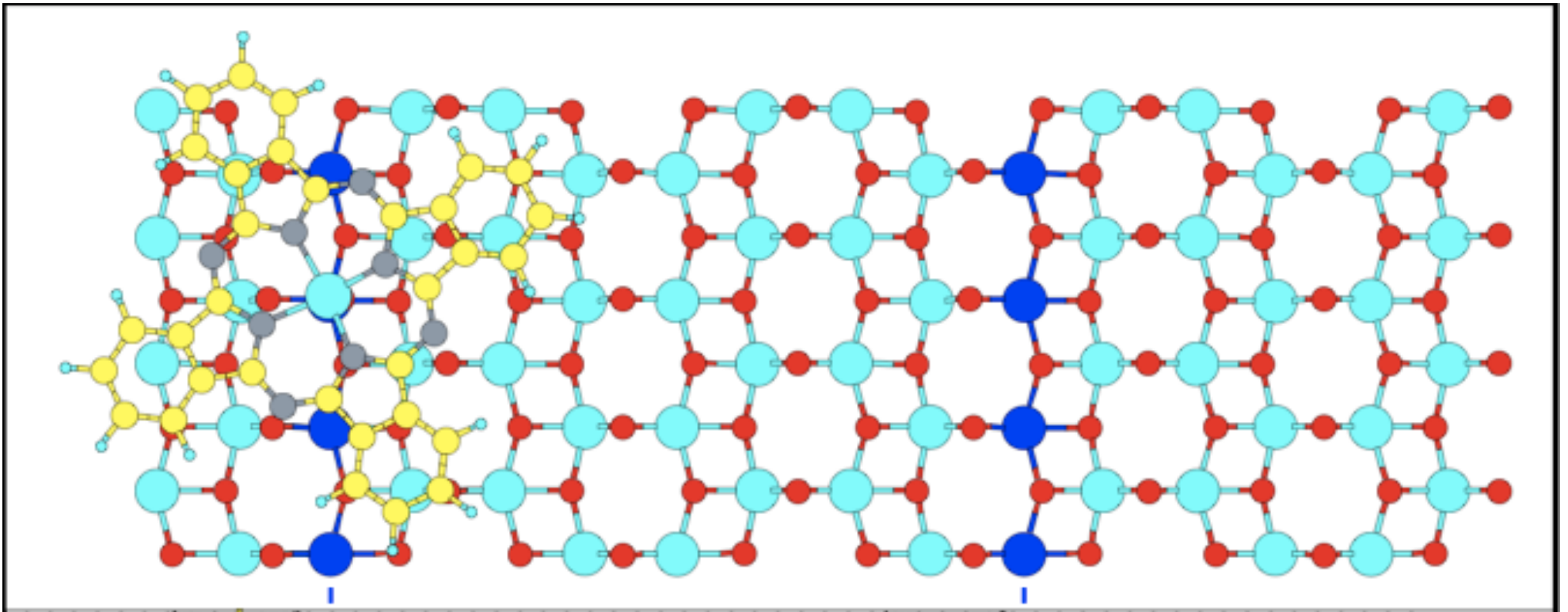
Is *n*-doping possible?

Yes! one needs to select a Pc with acceptor character, such as the pyrazino modification (2 N replacing C-H in benzene rings) of TiOPc:



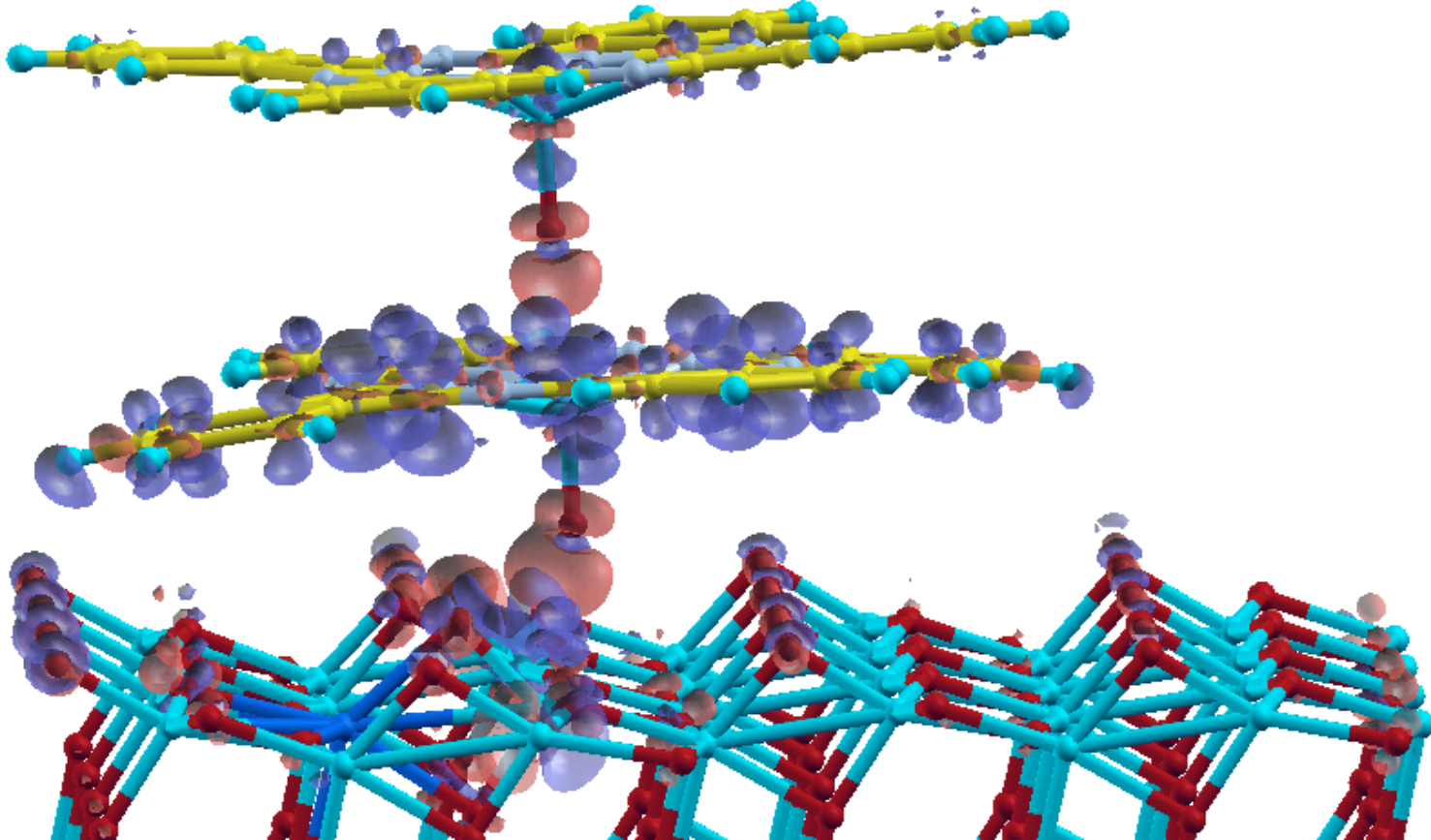
Are ordered films possible?

The morphology of TiO_2 anatase surface, containing rows of under-coordinated Ti atoms to which the OTiPc can bind, suggests so:



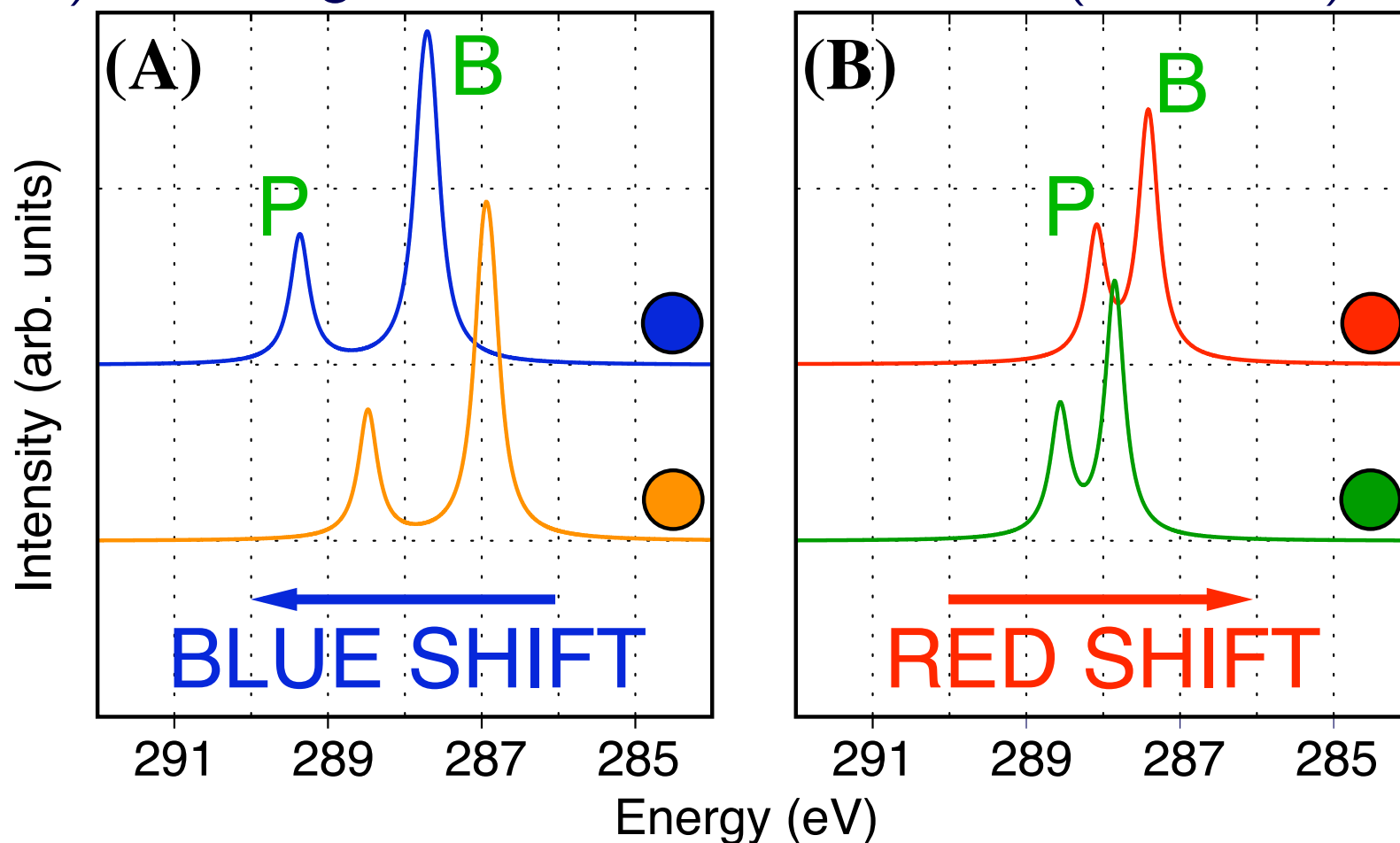
What about multilayers?

Second OTiPc molecule is weakly bound ($E_b \simeq 0.44$ eV) but p -doping enhances binding energy ($E_b \simeq 0.84$ eV) and charge transfer from first layer to surface



Theoretical XPS spectra

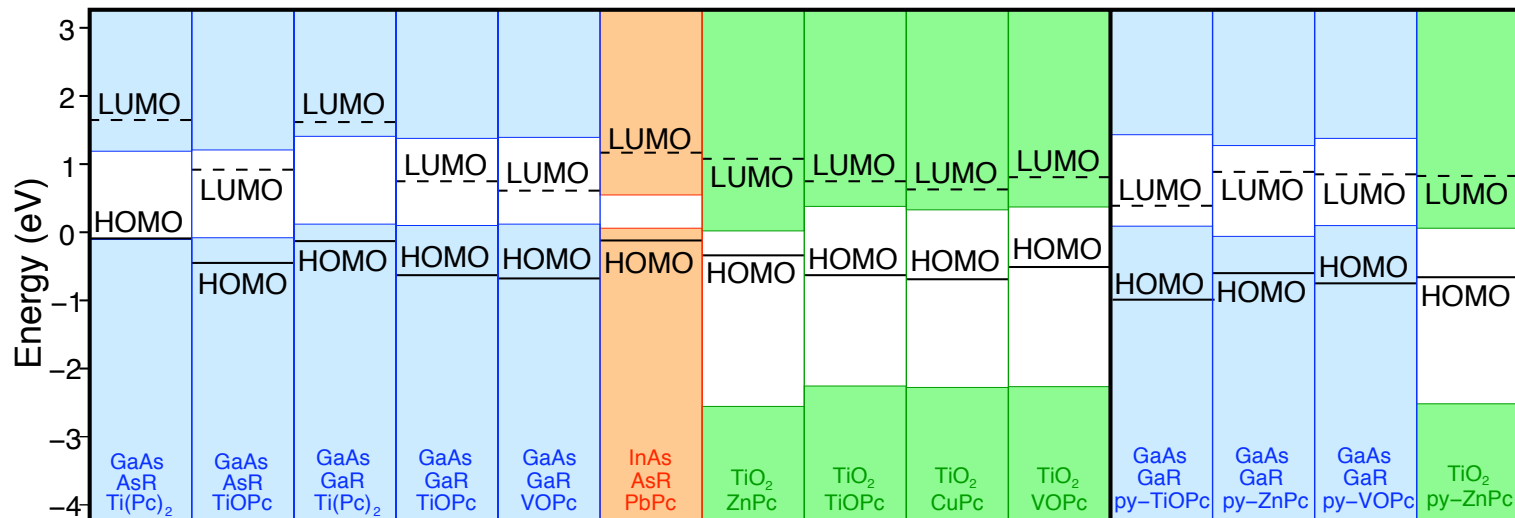
Marked blue shift (red shift) of C1s spectra when the surface is *p*-doped (*n*-doped) and charge is transferred from HOMO (to LUMO)



P: C atoms in inner pyrrole ring. **B**: C atoms in outer benzene ring.

Rationalizing the results

- In absence of charge transfer, HOMO and LUMO stay where they are, irrespective of chemical bonding
- Position of HOMO and LUMO is determined by the molecule IP and by the Work Function (W_f) of the surface
- HOMO and LUMO move only in presence of *charge transfer*



A general rule for tunable Pc-semiconductor interfaces?

Conditions for the charge transfer to take place:

- W_f and the IP should be such as to bring the HOMO (or the LUMO) in the gap
- The X group in XPc should be chemically "similar" to the surface in order to maximize interactions

Conditions above may be necessary but not sufficient!

Conclusions

- Several occurrences of sizable chemical bonding between a Pc and a semiconductor surface found:
 - OTiPc on (100) GaAs $\zeta(4 \times 2)c(8 \times 2)$ (Ga-rich) surface
 - OTiPc on (101) TiO₂ anatase surface
 - py-OTiPc on (100) GaAs $\zeta(4 \times 2)c(8 \times 2)$ (Ga-rich)
- ...but tuning the Pc-semiconductor heterostructure via doping may be possible only in the last two cases
- A general rule for effective coupling has been deduced