# Effects of orientation at the phthalocyanine–CdSe interface on the electron transfer characteristics

*V. V. Golovanov[1,3], B. V. Nazarchuk[1], V. V. Golovanova[1], N. V. Tkachenko[2], T. T. Rantala[3]*

[1] Center for Innovation Technologies, South-Ukrainian National University, Staroportofrankovskaya Str. 26, 65008, Odessa, Ukraine. E-mail: alban@te.net.ua

[2] Department of Chemistry and Bioengineering, Tampere University of Technology, P.O. Box 541, FI-33101, Tampere, Finland.

[3] Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101, Tampere, Finland.

## Abstract

Phthalocyanine molecule adsorbed on the $(10\bar{1}0)$ surface of wurtzite CdSe is theoretically modeled by DFT method. We have found that linker does not affect substantially redox properties of phthalocyanine, while saturation of the macrocycle with peripheral substituent groups causes downward shift in the energy position of its frontier orbitals that can hinder electron injection to the CdSe surface. Tilting of the phthalocyanine molecule to the surface also leads to the lowering of its molecular electronic levels relative to the bands of CdSe. At tilting angle of 30°, the LUMO level of the dye appears to be lower than the conduction band minimum of cadmium selenide, which makes unfavorable the electron transfer to its hybridized surface. By contrast, the HOMO level of the phenylbutyric acid linker provides a suitable intermediate channel for the hole transfer from the valence band of CdSe to the phthalocyanine that points to the possible acceptor behavior of the phthalocyanine molecule in its hybrids with CdSe nanostructures.

## Introduction

Semiconductor quantum dot (QD)–organic dye hybrids attract significant interest due to their wide application range in solar energy conversion, photonics, sensors and molecular electronics [1-4]. The new design paradigm to optoelectronic device engineering is based on photonic control of the electronic interactions in hybrid nanocomponents. Interest in these researches is motivated by the possibility to achieve a photoinduced electron transfer in both directions, from dye to QD and vice versa.

CdSe quantum dots are one of the most well developed and studied nanocomponents, which were found to act as electron donors in conjunction with acceptor molecules such as fullerene and viologen [5, 6]. Electron transfer to CdSe QDs was reported for their hybrids with rhodamine B, bithiophene and porphyrin derivatives [7-9]. Phthalocyanines (Pc) are another promising class of organic compounds, which possess a high extinction coefficient in the red spectral region and exhibit high thermal and chemical stabilities [10]. In the meantime, the QD–Pc hybrids are relatively unexplored due to the difficulties in synthesis of Pc with the adequate anchoring groups. According to estimations, the conduction band of CdSe QD is well matched to the lowest unoccupied molecular orbital (LUMO) of Pc [11, 12]. Results of the recent

investigation, [13] however, do not provide any evidence of electron transfer from the LUMO of Pc to the CdSe quantum dot. Instead, a hole transfer from the valence band of QD to the highest occupied molecular orbital (HOMO) of Pc occurs after photo-excitation of the quantum dot. Apparently the excited state energy of Pc is not sufficiently high for the electron transfer to take place from the LUMO of Pc to the QD conduction band.

Recent publications report that macrocyclic dyes adsorb on semiconductor surface with a wide distribution of tilt angles [14, 15]. Since electron transfer reaction is controlled by the QD–dye distance to a great extent, a detailed understanding of Pc orientation and molecular packing on the CdSe surface is critical for improving the charge transfer parameters, including the barrier for through-space charge tunneling. An important tool for analysis of such interfaces is computational modeling. It can address many aspects of practical importance such as conformations and arrangements of molecular adsorbates on semiconductor surfaces and the mutual alignment of their energy levels [16-19].

Herein, we present a computational study of Pc adsorbed on the CdSe $(10\bar{1}0)$ surface. We have found that the tilt angle of the dye to the surface has a strong effect on its redox properties and may be a reason for the unfavorable electron transfer from Pc to QD. On the other hand, a proper choice of the linker may substantially facilitate the hole transfer from QD to Pc. We also observe modulation of the redox properties of the phthalocyanine by modifying substituents in the periphery of the Pc ring. Understanding of the factors controlling Pc–CdSe binding geometry appears to be a route to engineering hybridized QDs with predictable properties, as well as provide a testing ground for interfacial electron transfer.

**Methods and models**

We employ the BAND/ADF software for DFT calculations with a linear combination of atomic orbitals approach and use a 3D periodic slab for surface modeling [20]. To describe the electron–electron exchange correlation two different DFT functionals were used: generalized gradient approximation with PBEsol [21] and the GLLB-SC [22]. The latter is based on the direct exchange potential approximation with the correlation potential from PBEsol and has been shown to yield good band gaps for bulk semiconductors [22]. The TZP basis set (a small frozen core) was chosen for all the types of atoms: H, C (1s), N (1s), O (1s), Se (3p), Cd (3d). The empirical dispersion correction to take into account the van der Waals interactions between phthalocyanine and surface was included in the calculations with Grimme DFT-D3 method [23]. The effective mass was obtained by numerical differentiation of the bands at the top of the valence band for holes and at the bottom of the conduction band for electrons.

The hexagonal wurtzite structure of CdSe is the most common phase under ambient conditions. The structure consists of tetrahedrally coordinated cadmium cations and selenium anions. Atomic positions and lattice constants of the cadmium selenide bulk were first fully relaxed for a supercell built out of 2×2×2 primitive cells of CdSe. The most energetically favorable nonpolar $(10\bar{1}0)$ surface has been chosen as our model surface [24]. The vacuum layer along the nonperiodic direction was 30 Å. The $(10\bar{1}0)$ surface slabs of 4, 6 and 8 layers were cut from the

optimized bulk structure and stabilities were assessed by allowing the atomic positions of the slabs to relax freely, but retaining the lateral lattice constants.

The six-layer slab with a single phthalocyanine molecule adsorbed per surface supercell of 13 Å ×21 Å has been chosen to study the surface–dye interaction. No appreciable differences in relaxed surface geometry were found in simulations with thicker slab. The surface coverage was 1/3 of monolayer. We chose this coverage to allow the dye to change its orientation and the tilt angle on the surface. The phthalocyanine molecule was anchored on the surface via a linker with phenyl and carboxylic acid groups attached onto two cadmium atoms in a bidentate bridging mode, which ensures a strongest chemical bonding and is predominant according to previous reports [25]. Hydrogen atom released from the carboxylic acid group was bound to the surface Se atom near the attached moiety to preserve the charge neutrality of the system. The models were optimized by allowing both surfaces of the slab, dye and linker, to relax.

**Results and discussion**

The lattice constants of CdSe bulk structure computationally optimized with PBEsol functional amount to $a$ = 4.38 Å and $c$ = 7.15 Å and are in agreement with experimentally measured values ($a$ = 4.38 Å and $c$ = 7.06 Å). The band gaps of cadmium selenide and energies of the frontier orbitals (HOMO and LUMO) of isolated phthalocyanine are listed in Table 1.

Table 1. Experimental and calculated band gaps of CdSe and frontier orbital energies (eV) of the isolated phthalocyanine.

| | CdSe band gaps | | | Isolated Pc molecule | | |
|---|---|---|---|---|---|---|
| | Bulk | 6-layers slab | 8-layers slab | HOMO | LUMO | HOMO/LUMO gap |
| PBEsol | 1.18 | 1.56 | 1.47 | -5.06 | -3.64 | 1.42 |
| GLLB-SC | 1.76 | 2.06 | 1.97 | -6.12 | -4.84 | 1.28 |
| Exp. [11,12] | 1.74 | -- | -- | -5.71 | -3.96 | 1.75 |

The band gap of CdSe bulk is underestimated by the PBEsol functional, whereas GLLB-SC improves the band gap of CdSe up to the experimental value. When slab thickness decreases, the band gap of CdSe increases above the bulk values. Taking into account the blueshift of the band gap energy for CdSe quantum dots due to the quantum confinement, we chose the six-layer slab with the band gap of 2.06 eV for further simulation of the CdSe QD–Pc interface phenomena as a compromise between accuracy and computational cost.

The change in atomic coordinates due to surface relaxation is in good agreement with prior studies of $(10\bar{1}0)$ surface of wurtzite structures [26]. With all the methods the relaxation is strongest for the surface Cd ion. During relaxation the surface Cd ions move toward the bulk and closer to the nearby surface selenium atoms. The surface Se atoms tend to move outward, resulting in a tilting of the surface CdSe bond relative to the horizontal plane. This relaxation behavior can be understood in terms of the transfer of electron density from the Cd atoms to the more electronegative Se atoms at the surface. The cadmium atoms at $(10\bar{1}0)$ surface donate their unshared electrons to the surface Se atoms, resulting in a more planar three-fold configuration around them accompanied by inward movement of surface cations.

The charge carrier effective masses calculated with PBEsol in CdSe bulk are $m_e$=0.11 and $m_h$=2.66 for electrons and holes, respectively. In the slab the electron effective mass increases up to $m_e$=0.18, while the effective mass for holes decreases down to $m_h$=0.27.

To study the effect of linker between the Pc and QD on the redox properties of Pc moiety we created models with phenylbutyric acid linker connected to the dye either directly or through the ether linkage as it has been reported elsewhere [27, 28]. The corresponding schemes are represented in Figure 1(a, b).

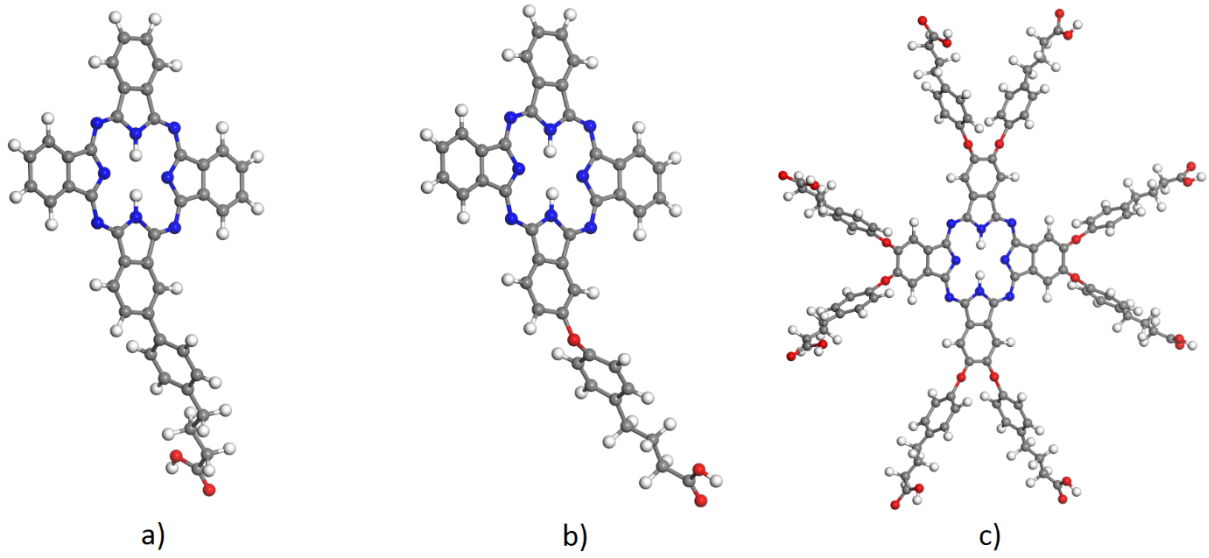


Figure 1. Scheme of the phthalocyanine molecules with phenylbutyric acid linker attached to the macrocycle a) directly and b) via oxygen atom. c) Functionalized phthalocyanine molecule with eight peripheral carboxyl containing linkers.

The effects of differently anchored linker and relative orientation of phenyl and Pc rings on the energies of HOMO and LUMO orbitals of the chromophore are listed in Table 2. It can be concluded that attachment of a single linker does not affect substantially positions of HOMO and LUMO orbitals, though linker connected via oxygen atom causes a slight (0.05 eV) upward shift in energy of the frontier orbitals of Pc. The most energetically favorable orthogonal orientation of the macrocycle plane with respect to phenyl ring of the linker results in slight separation between HOMO and LUMO orbitals of Pc.

Table 2. Calculated HOMO/LUMO energies (eV) of free phthalocyanine, Pc saturated with eight peripheral carboxyl groups (Fig.1c) and phthalocyanine molecule with C–C and C–O–C bond linkers (Fig.1a and Fig.1b, respectively).

| Linker type | Free Pc | | C–C bond linker | | C–O–C bond linker | | Pc with eight peripheral groups | |
|---|---|---|---|---|---|---|---|---|
| | PBEsol | GLLB | PBEsol | GLLB | PBEsol | GLLB | PBEsol | GLLB |
| HOMO | -5.06 | -6.12 | -5.05 | -6.12 | -5.01 | -6.10 | -5.16 | -6.41 |
| LUMO | -3.64 | -4.84 | -3.64 | -4.84 | -3.61 | -4.83 | -3.82 | -5.18 |
| HOMO/LUMO gap | 1.42 | 1.28 | 1.41 | 1.28 | 1.40 | 1.27 | 1.34 | 1.23 |

It is known that Pcs have a tendency to form aggregates owing to their planar aromatic structure that inhibit their properties at the molecular level [28]. One of the strategies employed to prevent

the formation of Pc aggregates is the functionalization of these compounds with peripheral groups as it is shown in Figure 1c. We have found (Table 2) that contrary to the effect of single linker, the saturation of Pc with peripheral groups attached via ether linkage causes significant downward shift in frontier orbital energies. This may hinder the electron injection to CdSe quantum dot in the combined system QD–Pc, since such functionalization may lead to lowering of the energy of the LUMO level with respect to the conduction band of CdSe QD.

Based on the experimental measurements of recombination kinetics for porphyrin–$TiO_2$ system, Imahori *et al*. [15] suggested heterogeneous geometry where the dye molecules are attached to the surface with distribution of tilt angles. By contrast, computations constrained by the experimentally measured dye layer thickness using X-ray reflectometry [29], points to a narrow distribution of the individual dye orientations for close packed monolayers with tilt angle of 35° – 40°. According to Ye *et al.* [14], the charge transfer occurs by tunneling through space, rather than through the spacer connecting the macrocycle core and anchoring carboxyl group.

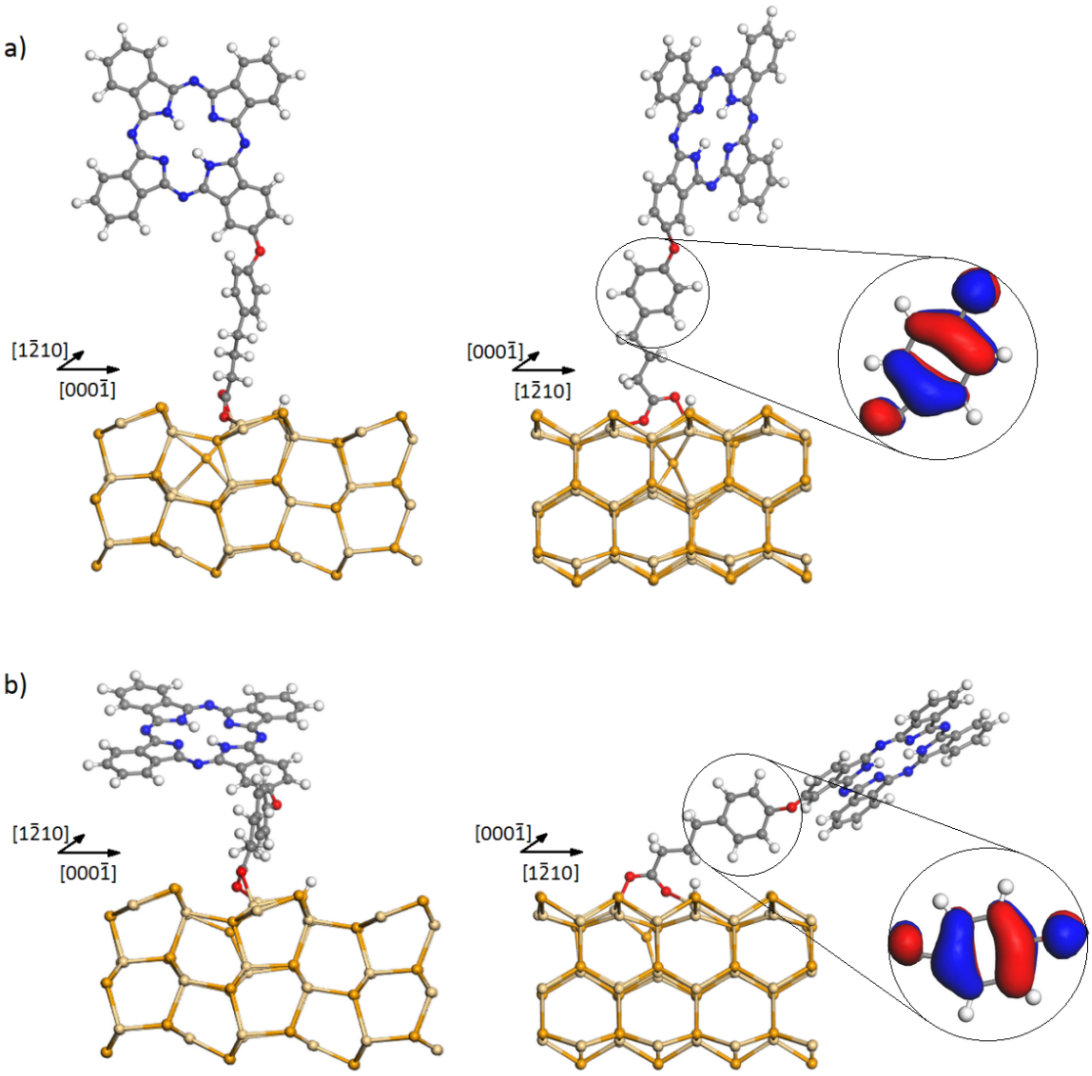


Figure 2. Relaxed geometries of the phthalocyanine molecule adsorbed on the (10$\bar{1}$0) surface of CdSe in upright (a) (*ca.* 80°) and titled (b) (*ca.* 30°) positions along the [000$\bar{1}$] (left) and [1$\bar{2}$10] (right) directions. Inset depicts HOMO orbital of the phenyl ring in the linker.

Since the tilt angle determines the dye–semiconductor electron transfer distance and due to the expected exponential distance dependence of electron transfer dynamics even a modest change of distance (and thus, the angle) may have a drastic impact on the transfer rate.

In order to clarify the effect of the conjugated linker and dye binding geometries on the electronic levels of the combined hybrid CdSe–Pc system, we have performed calculations of the phthalocyanine molecule bound to the CdSe surface via phenylbutyric acid linker with angles ranging from almost upright position on the surface at *ca.* 80° to all the way down to *ca.* 30°, see Figure 2. The model geometries were optimized by allowing the adsorbate and the surface layers to relax including twisting of the Pc molecule where π-electrons of the core are facing the surface (Figure 2b). From these structures we calculated relative positions of the HOMO/LUMO levels of the phthalocyanine molecule and the CdSe energy bands.

The distance between the core of Pc and the surface for differently tilted molecule geometries varies from 16 Å to 9 Å (Figure 2a and 2b, respectively). The most pronounced surface relaxation upon adsorption of Pc with linker is observed at the adsorption sites for surface Cd ions that move upwards and retain the more bulk-like positions, while the nearest to Pc Se atom shifts inwards, closer to the second layer. This relaxation can be understood in terms of charge redistribution from Se anions to more electronegative oxygen atoms of binding moiety on top of the Cd cations.

The adsorption energies of the differently tilted Pc models from Figure 2 are represented in Table 3. The adsorption energy ($E_{ads}$) of the phthalocyanine molecule on the CdSe surface is calculated from the following equation:

$$E_{ads} = E_{comb} - E_{Pc} - E_{slab} - (E_{Se-H} - E_{O-H}),$$

where $E_{comb}$ is the calculated formation energy of the combined CdSe–Pc system, $E_{Pc}$ and $E_{slab}$ are these of the isolated Pc and CdSe slab, respectively, and $E_{Se-H}$ and $E_{O-H}$ are energies of Se–H and O–H bonds. The value of $E_{Se-H}$ has been obtained as difference in formation energies of the CdSe slab with and without hydrogen atom adsorbed on top of the surface Se anion. The value of $E_{O-H}$ was calculated as 1/2 formation energy of the $H_2O$ molecule.

When the phthalocyanine molecule is twisted and tilted towards the surface its adsorption energy increases due to attractive porphyrin–surface interactions until the energy minimum is reached close to the surface (at a *ca.* 30° tilting angle).

Table 3. Calculated adsorption energies (eV) of the Pc molecule adsorbed on CdSe surface with carboxyl linker with PBEsol functional and Grimme D3 dispersion correction.

| | PBEsol | | PBEsol + Grimme D3 correction | |
|---|---|---|---|---|
| Tilting angle | *ca.* 80° | *ca.* 30° | *ca.* 80° | *ca.* 30° |
| $E_{ads}$ | 4.43 | 5.17 | 4.78 | 5.76 |

The energies are then corrected by including the empirical dispersion correction to take into account the van der Waals interactions between phthalocyanine and surface and between the neighboring phthalocyanine rings. We note that the dispersion correction stabilizes the twisted

and tilted porphyrin model more than the upright model. The main reason for this is larger interaction of the π-orbital of the dye's core with the CdSe surface, which is supported by the slight broadening (*ca.* 0.02 eV) of the frontier orbitals of Pc upon tilting. Indeed, moving the phthalocyanine closer to the surface strongly affects its frontier orbital energies and modifies their position relative to the bands of CdSe, see Figure 3.

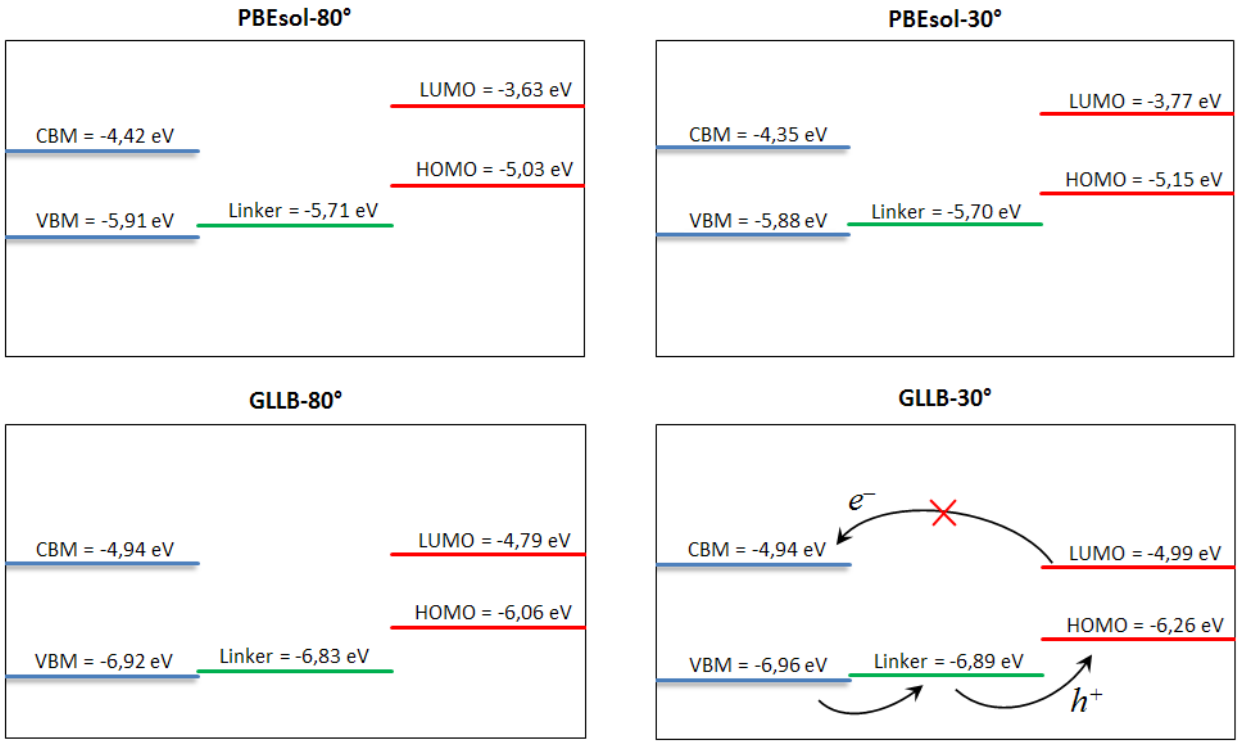


Figure 3. Energy diagram of the phthalocyanine molecule adsorbed at different tilt angles via carboxyl linker on the $(10\bar{1}0)$ CdSe surface.

Tilting of the Pc towards the surface leads to a lowering of the dye's LUMO and HOMO relative to the bands of CdSe. Calculations of the tilted molecule with GLLB-SC potential resulted in configuration, where energy level of the dye's LUMO becomes lower than conduction band minimum of the slab. Thus, tilting of the molecule inhibits an electron transfer from phthalocyanine to CdSe surface. On the other hand, the occupied energy state associated with phenyl group of the linker is located between the valence band maximum of CdSe and HOMO of Pc that ensures a suitable wiring pathway for the hole transfer from a cadmium selenide to Pc in their hybrids structures. The LUMO of the phenyl group is found high in energy (*ca.* 4.2 eV above its HOMO) that rules out its contribution to the Pc–CdSe electron transfer.

It is worth noting, that quantum confinement increases the band gap of QDs compared to that of bulk material. For smaller QDs the energy of the conduction band will be higher, thus the electron transfer form an excited Pc will be energetically less favorable. However, the energy of the valence band will be lower and smaller QDs are expected to be better hole donors. From this view point, our results are consistent with findings of Arvani *et al.* [13], where experimental evidences of the hole transfer from CdSe quantum dots to phthalocyanine molecules have been observed using time resolved spectroscopic methods.

We have found that the linker can play a substantial role in charge transfer dynamics for phthalocyanine–CdSe hybrid nanostructures. The binding surface geometry can be considered as one of the key factors in attempts to achieve an efficient electron transfer from the Pc to the CdSe quantum dots. Our calculations indicate that the increasing number of peripheral ether groups in phthalocyanine molecule makes unfavorable an electron transfer from Pc to cadmium selenide QD due to lowering of the HOMO/LUMO system of the chromophore.

Our next goal is to examine important question not yet considered in this study. In practice, the QDs are capped with shield molecules that protect QDs from aggregation and degradation. The dyes are equipped by stronger anchoring groups that replace the capping molecules on the surface of QDs. However, the environment of dyes can be enriched by capping molecules that may restrict orientational flexibility of Pc in real conditions.

## Conclusions

A model system constructed for phthalocyanine molecule attached to $(10\bar{1}0)$ CdSe surface in various orientations through the linker consisting of phenyl and carboxyl groups is studied with the focus on the relative position of the electronic levels of dye and CdSe bands. The energy of the phthalocyanine LUMO level becomes lower than that of the CdSe conduction band minimum upon tilting of the molecule at *ca.* 30$^{o}$ that makes unfavorable an electron transfer from Pc to CdSe. This can be explained by stabilization of dye with CdSe, when the π-electrons face the surface of semiconductor. The obtained results are consistent with recently reported lack of an electron transfer from LUMO of Pc to CdSe quantum dot [13].

The calculated charge carrier effective masses indicates, that surface conductivity sufficiently increases for holes and decreases for electrons relative to the bulk conductivity. The HOMO level of the linker consisting of phenyl groups may provide a suitable intermediate state to accelerate the hole transfer from the valence band of CdSe to the Pc, that points to the possible acceptor behavior of the phthalocyanine molecule in its hybrids with CdSe nanostructures.

## Acknowledgments

This work was supported by NATO SPS MYP project NANEOS, Grant No. 985043. Computational resources were provided by the CSC – IT Center for Science, Espoo, Finland.

## References

[1] B. Guzelturk, P. Ludwig H. Martinez, Q. Zhang, Q. Xiong, H. Sun, X. Sun, A. Govorov, H.i Demir, Excitonics of semiconductor quantum dots and wires for lighting and displays, *Laser & Photonics Reviews*, Vol. 8, Issue 1 (2014) 73–93.

[2] C. Chuang, P. Brown, V. Bulović, M. Bawendi, Improved performance and stability in quantum dot solar cells through band alignment engineering, *Nature Materials*, 13, (2014) 796–801.

[3] P. Docampo, S. Guldin, T. Leijtens, N. Noel, U. Steiner, H. Snaith, Lessons learned: from dye-sensitized solar cells to all-solid-state hybrid devices. *Adv. Mat.*, 26 (2014) 4013-4030.

[4] V. Smyntyna, V. Golovanov, S. Kasiulis, G. Mattogno, G. Righini, Influence of chemical composition on sensitivity and signal reproducibility of CdS sensors of oxygen, *Sensors and Actuators* B 24-25 (1995) 628-630.

[5] K. Virkki, S. Demir, H. Lemmetyinen and N. Tkachenko, Photoinduced electron transfer in CdSe/ZnS quantum dot–fullerene hybrids, *J. Phys. Chem*. C, 119(31) (2015) 17561–17572.

[6] A. Morris-Cohen, M. Frederick, L. Cass, E. Weiss, Simultaneous determination of the adsorption constant and the photoinduced electron transfer rate for a CdS quantum dot-viologen complex, *J Am. Chem. Soc.*, 133(26) (2011) 10146-54.

[7] A. Boulesbaa, Z. Huang, D. Wu and T. Lian, Competition between energy and electron transfer from CdSe QDs to adsorbed rhodamine B, *J. Phys. Chem*. C, 114(2) (2010) 962–969.

[8] A. Iagatti, R. Flamini, M. Nocchetti, and L. Latterini, Photoinduced formation of bithiophene radical cation via a hole-transfer process from CdS nanocrystals, *J. Phys. Chem*. C, 117(45) (2013) 23996–24002.

[9] S. Jin, M. Tagliazucchi, H. Son, R. Harris, K. Aruda, D. Weinberg, A. Nepomnyashchii, O. Farha, J. Hupp, and E. Weiss, Enhancement of the yield of photoinduced charge separation in zinc porphyrin–quantum dot complexes by a bis(dithiocarbamate) linkage, *J. Phys. Chem.* C, 119(9) (2015) 5195–5202.

[10] L. Martín-Gomis, F. Fernández-Lázaroa and Á. Sastre-Santos, Advances in phthalocyanine-sensitized solar cells (PcSSCs), *J. Mater. Chem*., A, 2 (2014) 15672-15682.

[11] O. Madelung, Semiconductors Data Handbook, Berlin: Springer (2004) 815-835.

[12] D. Guldi, I. Zilbermann, A. Gouloumis, P. Vazquez, T. Torres, Metallophthalocyanines: versatile electron-donating building blocks for fullerene dyads, *J. Phys. Chem.* B 108(48) (2004) 18485-18494.

[13] M. Arvani, K. Virkki, F. Abou-Chahine, A. Efimov, N. V. Tkachenko and D. Lupo, Photoinduced hole transfer in QD–phthalocyanine Q1 hybrids, *Phys. Chem. Chem. Phys*., 18, (2016) 27414-27421.

[14] S. Ye, A. Kathiravan, H. Hayashi, Y. Tong, Y. Infahsaeng, P. Chabera, T. Pascher, A. Yartsev, S. Isoda, H. Imahori, and V. Sundström, Role of adsorption structures of Zn-porphyrin on $TiO_2$ in dye-sensitized solar cells studied by sum frequency generation vibrational spectroscopy and ultrafast spectroscopy, *J. Phys. Chem*. C 117 (2013) 6066−6080.

[15] H. Imahori, S. Kang, H. Hayashi, M. Haruta, H. Kurata, S. Isoda, S. Canton, Y. Infahsaeng, A. Kathiravan, T. Pascher, P. Chabera, A. Yartsev, and V. Sundstrom, Photoinduced charge carrier dynamics of Zn-porphyrin-$TiO_2$ electrodes: The key role of charge recombination for solar cell performance, *J. Phys. Chem*. A, 115 (2011) 3679–3690.

[16] V**.** Golovanov, V**.** Golovanova, T. T. Rantala**,** Thermal desorption of molecular oxygen from $SnO_2$ (110) surface: Insights from first-principles calculations, *Journal of Chemical Physics in Solids*, 89 (2016) 15-22.

[17] V. Golovanov, T. Kortelainen and T. T. Rantala, Stability of siloxane couplers on pure and fluorine doped $SnO_2$ (110) surface: a first principles study, *Surface Science,* 604(19-20) (2010) 1784-1790.

[18] M. Viitala, O. Cramariuc, T. T. Rantala, V. Golovanov, Small hydrocarbon adsorbates on $SnO_2$(110) surfaces: Density functional theory study, *Surface Science*, 602(18) (2008) 3038-3042.

[19] J. Solis, V. Golovanov, V. Lantto and S. Leppavuori, A study of dual conductance response to carbon monoxide of CdS and α-$SnWO_4$ thin films, *Physica Scripta,* T54 (1994) 248-251.

[20] BAND2014, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[21] J. Perdew, A. Ruzsinszky, G. Csonka, O. Vydrov, G. Scuseria, L. Constantin, X. Zhou, and K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett*., 102 (2009) 039902.

[22] M. Kuisma, J. Ojanen, J. Enkovaara, and T. T. Rantala, Kohn-Sham potential with discontinuity for band gap materials, *Phys. Rev*. B 82 (2010) 115106.

[23] S. Grimme, J. Antony, S. Ehrlich1 and H. Krieg1, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys*. 132 (2010) 154104.

[24] I. Csik, S. Russo, P. Mulvaney, Density functional study of non-polar surfaces of wurtzite CdSe, *Chemical Physics Letters* 414 (2005) 322–325.

[25] N. Moreira, A. da Rosa and T. Frauenheim, Covalent functionalization of ZnO surfaces: a density functional tight binding study, *Appl. Phys. Lett*., 94 (2009) 193109.

[26] G. Pilania, T. Sadowski, and R. Ramprasad, Oxygen adsorption on CdSe surfaces: case study of asymmetric anisotropic growth through ab initio computations, *J. Phys. Chem*. C, 113 (2009) 1863–1871.

[27] M. Niskanen, M. Kuisma, O. Cramariuc, V. Golovanov, T. Hukka, N. Tkachenko and T. Rantala, Porphyrin adsorbed on the $(10\bar{1}0)$ surface of the wurtzite structure of ZnO – conformation induced effects on the electron transfer characteristics, *Phys. Chem. Chem. Phys*., 15 (2013) 17408.

[28] V. Blas-Ferrando, J. Ortiz, V. González-Pedro, R. Sánchez, I. Mora-Seró, F. Fernández-Lázaro and Á. Sastre-Santos, Synergistic interaction of dyes and semiconductor quantum dots for advanced cascade cosensitized solar cells, *Adv. Funct. Mater*., 25(21) (2015) 3220–3226.

[29] M. Griffith, M. James, G. Triani, P. Wagner, G. Wallace, and D. Officer, Determining the orientation and molecular packing of organic dyes on a $TiO_2$ surface using X-ray reflectometry, *Langmuir*, 27 (2011) 12944–12950.