

PAPER

Porphyrin adsorbed on the (10 $\bar{1}$ 0) surface of the wurtzite structure of ZnO – conformation induced effects on the electron transfer characteristics†

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 17408

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Electron transfer at the adsorbate–surface interface is crucial in many applications but the steps taking place prior to and during the electron transfer are not always thoroughly understood. In this work a model system of 4-(porphyrin-5-yl)benzoic acid adsorbed as a corresponding benzoate on the ZnO wurtzite (10 $\bar{1}$ 0) surface is studied using density functional theory (DFT) and time-dependent DFT. Emphasis is on the initial photoexcitation of porphyrin and on the strength of coupling between the porphyrin LUMO or LUMO + 1 and the ZnO conduction band that plays a role in the electron transfer. Firstly, ZnO wurtzite bulk is optimized to minimum energy geometry and the properties of the isolated ZnO (10 $\bar{1}$ 0) surface model and the porphyrin model are discussed to gain insight into the combined system. Secondly, various orientations of the model porphyrin on the ZnO surface are studied: the porphyrin model standing perpendicularly to the surface and gradually brought close to the surface by tilting the linker in a few steps. The porphyrin model approaches the surface either sideways with hydrogen atoms of the porphyrin ring coming down first or twisted in a ca. 45° angle, giving rise to π -interactions of the porphyrin ring with ZnO. Because porphyrins are closely packed and near the surface, emerging van der Waals (vdW) interactions are examined using Grimme's D2 method. While the orientation affects the initial excitation of porphyrin only slightly, the coupling between the LUMO and LUMO + 1 of porphyrin and the conduction band of ZnO increases considerably if porphyrin is close to the surface, especially if the π -electrons are interacting with the surface. Based on the results of coupling studies, not only the distance between porphyrin and the ZnO surface but also the orientation of porphyrin can greatly affect the electron transfer.

Received 19th April 2013,
Accepted 21st August 2013

DOI: 10.1039/c3cp51685g

www.rsc.org/pccp

Introduction

Electron transfer (ET) from molecular adsorbates to semiconductor surfaces has been a subject of investigation for a few decades already but it has attracted even more attention in recent years.^{1–3} The reason for the rising interest in this reaction is its key role in many applications of molecular electronics and nanoscience including sensors and quantum dot devices, photocatalytic waste degradation, and solar energy

conversion.^{4,5} For example, dye sensitized solar cells (DSSCs) utilize the ET from photoexcited dye molecules to a nanocrystalline semiconductor, on which the dye is adsorbed for the photocurrent generation, and emerge as a potential cost efficient alternative to semiconductor cells.^{6,7} Power conversion efficiency of a DSSC consisting of a titanium dioxide nanocrystalline film sensitized with zinc porphyrin dye recently exceeded 12%.⁸

The photoinduced ET at the semiconductor organic interface must be fast to be efficient because it competes with other excitation deactivation processes. The ET of typical interfaces found in DSSCs, as studied using ultrafast optical spectroscopy techniques, was found to take place in the subpicosecond–picosecond time domain and to depend on the type of semiconductor and sensitizing dye.^{2,7,9,10} Although all factors affecting the ET are not yet completely understood, a fairly good ET description has been developed for the two extreme cases, *i.e.* the discrete donor–acceptor pairs and bulk systems, but the description is in the development stage for the ET phenomena at hybrid nanoscale interfaces.^{11–13} An important tool for

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† Electronic supplementary information (ESI) available: Used basis sets and additional calculation parameters, DOS and BAND plots, ZnO surface relaxation, adsorbate packing, dispersion effects and sample coupling strength assessment. See DOI: 10.1039/c3cp51685g

analyzing such interfaces is computational modelling. It can address many aspects of practical importance which are not experimentally accessible, such as conformations and arrangements of molecular adsorbates on semiconductor surfaces, mutual alignment of the energy levels of the semiconductor and the organic dye, electronic coupling between the two, and the rate of ET at different states of the relaxation of an excitation.^{3,14,15}

Among a relatively large choice of semiconductor surfaces ZnO has advantages both for experimental studies and computer modelling. ZnO is an inexpensive and environmentally friendly material. ZnO nanorods can be grown on different substrates in water solution and have well defined single-crystalline structures having wall surfaces with the same crystallographic orientation.¹⁶ The latter is an important factor for a quantitative comparison of the experimental measurements and computer modelling. As a semiconductor material, ZnO has almost the same band gap as TiO₂, and it is considered as a promising replacement of TiO₂ in DSSC applications¹⁷ and a nanoporous template structure for organic solar cells.¹⁸ ZnO has been computationally less studied than TiO₂, but lately, there has been considerable interest in an accurate description of the bulk and surface properties of ZnO,^{19–22} as well as in physisorption and adsorption of small molecules on various ZnO surfaces.^{23,24} Computational studies of large molecules on ZnO surfaces are still rare but already viable.^{25–28}

Porphyrin is used as the adsorbate molecule in this study. So far, porphyrin derivatives have yielded the highest energy conversion efficiencies in DSSCs.⁸ Moreover, they have been actively employed in both the complete device design²⁹ and the time-resolved ET studies in interface model systems.¹⁰ Porphyrin-based nano-structures used in molecular electronics applications have been recently reviewed in a number of publications.^{30–32} These highlight not only the particular electrochemical and photophysical properties of porphyrins but also how their performance is affected by surface chemistry, attachment and orientation. The structure–function relationship of porphyrins and their derivatives has also been investigated. Active research on this subject has been pursued since 1975 up to the present time.^{33–37} The first studies based on the post Hartree–Fock correlated methods were followed by density functional theory (DFT) calculations which allowed the modelling of both static and time-dependent properties of large porphyrin derivatives and assemblies. For a general review on applications of DFT on porphyrin–fullerene systems, see ref. 34. More recently, computational investigations of the porphyrin-based adsorbates on various materials have been reported in the context of molecular electronics. Many of these studies, in particular those involving porphyrins on metal oxide surfaces, draw their conclusions from comparing the electronic structure of isolated compounds without considering the organic–metal oxide interface. An overview of several aspects, such as intramolecular conformation, supramolecular ordering, electronic interaction, and the surface chemistry of tetrapyrroles on metal oxide substrates and ligand-related effects, is presented in ref. 38.

Herein, we present a computational study of 4-(porphyrin-5-yl)-benzoic acid adsorbed on the ZnO (10 $\bar{1}$ 0) surface. Our interest has been in the assessment of the coupling strengths of the porphyrin

LUMO and LUMO + 1 bands with the ZnO conduction band using various porphyrin to surface distances and orientations. We first test our methodologies with the ZnO bulk, followed by calculations and a relevant discussion about the isolated ZnO (10 $\bar{1}$ 0) surface and porphyrin. We then optimize a ZnO surface that is 1/3-filled with porphyrins standing at an angle of *ca.* 80 degrees with respect to the ZnO surface. Subsequently, we calculate a few porphyrin structures tilted towards the surface, with angles ranging from 80 degrees to all the way down to 20 degrees. Of these structures we calculate the coupling between the porphyrin LUMO or LUMO + 1 and the ZnO conduction band. We suggest that in the studied case, band coupling can predict the ET rate from porphyrin unoccupied orbitals to the ZnO conduction band. In addition, we study the effect of various orientations of porphyrin on the initial excitation of porphyrin adsorbed on the ZnO surface.

Computational methods and models

Software and methodology

We employ the CRYSTAL09^{39,40} and GPAW^{41,42} software for DFT and use a slab model for the surface. Using two different computational codes allows us to exploit the strengths of both the codes and achieve a method-independent understanding of the structure and properties of ZnO. The CRYSTAL software uses a linear combination of atomic orbitals (LCAO) approach, and allows efficient use of hybrid density functionals for calculations with periodic boundary conditions. With GPAW we use the real space grid to describe wave functions with the help of the Projector Augmented Wave (PAW) method.⁴³ The PBE functional^{44,45} and the PBE0 hybrid functional,^{44–46} which incorporate 25% of exact Hartree–Fock exchange, are used in calculations done with CRYSTAL. With GPAW the PBE functional and the GLLB-SC potential, which have been shown to yield good band gaps for bulk semiconductors, are used.⁴⁷ GLLB-SC is based on the direct exchange potential approximation by Gritsenko *et al.*⁴⁸ called GLLB, but with the correlation potential from PBESol (SC stands for solid correlation). The potential is appealing, because it is almost as fast as GGA, but allows evaluation of the derivative discontinuity contribution to the Kohn–Sham band gap. This has been shown to be an important fraction of the total band gap.⁴⁹ We calculate the TD-DFT excitations with Casida's linear response equation⁵⁰ with GPAW TD-DFT implementation⁵¹ by using GLLB-SC wave functions and eigenvalues. The time dependent exchange correlation effects are taken into account by using adiabatic local density approximation (ALDA) f_{xc} kernel. Grimme's empirical DFT-D2 dispersion correction scheme⁵² is used in CRYSTAL to take into account the van der Waals interactions. Chemcraft is used for visualization of the structures.⁵³

We use both the all-electron (AE) and pseudopotential (PP) Gaussian basis sets for Zn and O in the case of the bulk ZnO wurtzite and the ZnO (10 $\bar{1}$ 0) surface slab in calculations done with CRYSTAL.⁵⁴ The contractions of the Zn and O all electron basis sets are (864111/64111/41) and (8411/411/1), respectively, and for the pseudopotential basis sets large core Hay and Wadt

pseudopotentials^{55–57} with contractions (111/111/41) are used for Zn and Durand and Barthelat large core pseudopotentials^{58–60} with (31/31) contractions for O. All electron basis sets are used for the porphyrin adsorbate.^{54,61,62} The contractions are (8411/411/1), (621/21/1), (621/21/1) and (511/1) for O, N, C and H, respectively. The PAW method employed with GPAW provides one-to-one mapping between the smooth wave functions represented in real space grids and rapidly varying all-electron wave functions with the help of atom centered augmentation spheres. Therefore, it can be considered an all-electron method, up to the frozen core approximation. The complete CRYSTAL basis sets and more detailed calculation options and parameters are given in the ESI.†

Bulk and surface models

The hexagonal wurtzite structure of ZnO is the most common phase under ambient conditions and its space group is $P6_3mc$. The structure consists of tetrahedrally coordinated zinc cations and oxygen anions (Fig. 1). Atomic positions and lattice constants of the ZnO bulk were fully relaxed.

Usually the ZnO nanorods grow fastest in polar directions, such as $\langle 0001 \rangle$, which means that the non-polar faces, *i.e.* either $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$, form most of the surface area of the nanorod arrays.^{63–65} Therefore, the nonpolar $\{10\bar{1}0\}$ surface has been chosen as our model surface. The $\{10\bar{1}0\}$ surface slabs of 4, 8 and 16 layers were cut from the optimized bulk structure and the stabilities were assessed by allowing the atomic positions and the lattice constants of the slabs to relax freely. In order to create a surface with a bulk-like core structure for adsorption studies, we relaxed the top three layers of the slabs of 8 layers while freezing the atomic positions of the two innermost layers and the lattice constants at the bulk values. The slab calculations were done with CRYSTAL only.

Model of the adsorbate on the ZnO surface

To study the adsorption, the slabs with relaxed surfaces were used to generate the $\{10\bar{1}0\}$ surface (2×3) supercells of *ca.* $7 \text{ \AA} \times 16 \text{ \AA}$, on which a single porphyrin was adsorbed. The surface coverage was 1/3. We chose this coverage to allow the adsorbate to change its orientation and the tilt angle on the surface. The various substituents of the porphyrin ring present in real dyes similarly affect the orientation and the tilting angle, although it is very hard to determine the exact dye geometries experimentally. Additionally, the surface coverages of 1/2 and 1/6 and their

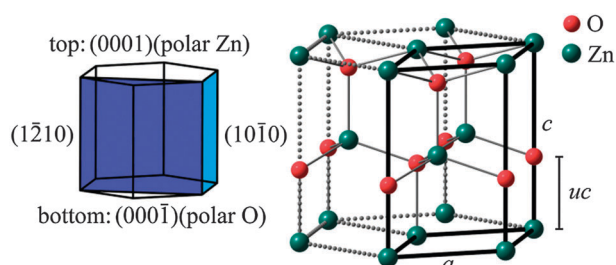


Fig. 1 Unit cell of the wurtzite structure of ZnO.

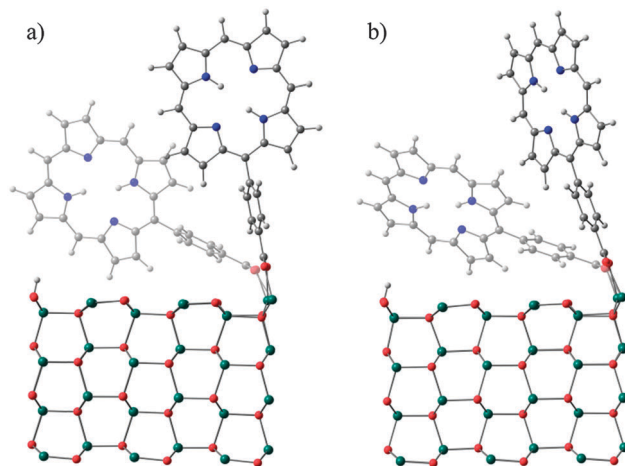


Fig. 2 Porphyrin tilted on the ZnO surface (a) sideways and (b) with twisting.

effects have been considered as presented in the ESI.† In the studies^{54,66} where carboxylic acids have been adsorbed on the ZnO $\{10\bar{1}0\}$ surface it has been concluded that the bidentate bridging (BB) adsorption of COO^- (the deprotonated COOH) onto two Zn sites results in the strongest chemical bonding and is predominant if not all of the surface sites are filled. Thus, we have considered this adsorption model in our studies. We first studied the linker and porphyrin at the upright position on the ZnO surface. The models were optimized by allowing the adsorbate and the top two surface layers to relax.

Next, we tilted porphyrin and the linker closer to the surface. We used two different models: porphyrin tilted towards the surface either (i) sideways with H atoms facing the surface (Fig. 2a), *i.e.* untwisted, or (ii) with twisting and π -electrons partially facing the surface (Fig. 2b), *i.e.* twisted. Because a porphyrin molecule is wide, interactions and steric repulsion arise between the twisted porphyrins, which prevent porphyrins from facing the surface horizontally. The tilted models were optimized by allowing the top two surface layers and the linker to relax. Additionally, an optimization was done where the twisted adsorbate and top two surface layers were fully relaxed. The optimizations were done with CRYSTAL and the properties were calculated with both CRYSTAL and GPAW using the optimized geometries.

Results and discussion

ZnO wurtzite bulk

The lattice constants a and c , the c/a ratio, and the internal parameter u of the computationally optimized and the experimentally measured bulk structure are listed in Table 1. The basis set and the functional affect the results only slightly. The PBE0 functional combined with the all-electron basis set gives the best match with the experimental results. The pure PBE functional gives slightly larger lattice constants a and c than its hybrid counterpart, but the c/a ratio and the internal parameter are unchanged. The basis set affects the lattice constants more than the functional. With the pseudopotential basis set the

Table 1 The calculated and experimental lattice constants a and c , their ratio c/a , and the internal parameter u of the hexagonal wurtzite ZnO lattice

	$a/\text{\AA}$	$c/\text{\AA}$	$ca.^{-1}$	u^a
CRYSTAL PBE/AE	3.27	5.28	1.61	0.379
CRYSTAL PBE/PP	3.37	5.25	1.56	0.391
CRYSTAL PBE0/AE	3.25	5.23	1.61	0.380
CRYSTAL PBE0/PP	3.33	5.19	1.56	0.390
GPAW PBE	3.29	5.32	1.62	0.378
Experimental ⁶⁷	3.25	5.20	1.60	0.382

^a The internal parameter u indicates the Zn–O displacement along the lattice constant c . In wurtzite structure the idealized value for u is $3/8$.

lattice constant a increases and the lattice constant c decreases, leading to a smaller c/a ratio compared to the all-electron, GPAW and experimental results. The internal parameter u increases as well.

Band structures and densities of states (DOS) were calculated to examine the accuracy of the methods further. Shapes of the calculated bands were almost identical regardless of the method and are given as ESI.† The main differences in DOS are in the widths of the bands and band gaps, which are listed in Table 2. The DOS plots obtained with the PBE functional are shown in Fig. 3. The DOS plots calculated with GPAW/GLLB-SC and with CRYSTAL/PBE0 are given as ESI.†

The band gap is underestimated by the pure PBE functional and somewhat overestimated with the hybrid PBE0 functional. GPAW/PBE predicts a smaller band gap than CRYSTAL/PBE. A likely reason for this is a better relaxation of the conduction bands when the GPAW grids are used compared to the relaxation when the valence based basis sets are employed in CRYSTAL. More importantly, CRYSTAL/PBE and GPAW give similar valence band structures (Fig. 3) with only slight differences meaning that the methods have comparable accuracy. GPAW/PBE has no separation between the Zn 3d band and the first valence band, whereas CRYSTAL/PBE/AE has a very small and PBE0/AE a bit larger separation (Table 2). Use of the pseudo-potential basis set leads to a wide separation between the 1st valence band and the Zn 3d band. The PBE/AE, PBE0/AE and GPAW/PBE methods yield similar widths for the Zn 3d band

Table 2 Calculated and experimental band gaps, the valence and Zn 3d band positions, and their band separations

	Band gap/eV	1st Valence band/eV	Band separation/eV	Zn 3d band/eV
CRYSTAL PBE/AE	1.46	0 ↔ −3.98	0.10	−4.08 ↔ −5.90
CRYSTAL PBE/PP	1.74	0 ↔ −3.92	3.55	−7.47 ↔ −8.29
CRYSTAL PBE0/AE	3.92	0 ↔ −4.80	0.55	−5.34 ↔ −6.93
CRYSTAL PBE0/PP	3.94	0 ↔ −4.54	3.48	−8.01 ↔ −9.00
GPAW PBE	0.77	0 ↔ −3.96	0.00	−3.98 ↔ −6.00
GPAW GLLB-SC	2.18	0 ↔ −4.12	0.36	−4.57 ↔ −6.54
Experimental ⁷¹	3.37–3.44			
Experimental ^{a68}		0 ↔ −5.4	1.0	−6.4 ↔ −8.2
Experimental ^{a69}		0 ↔ −5.7	0.8	−6.5 ↔ −8.1

^a Estimates from XES figures in ref. 68 and 69.

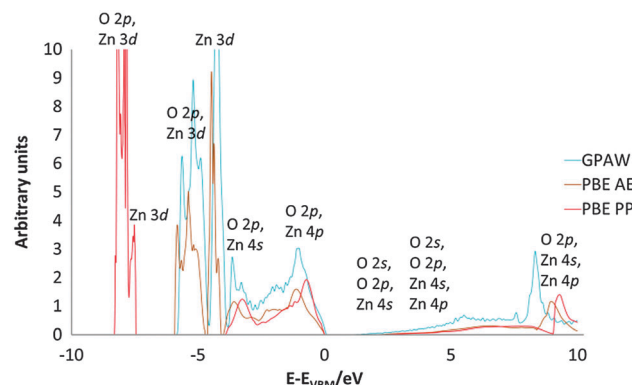


Fig. 3 Densities of states calculated with GPAW and CRYSTAL using the PBE functional. Energy of the valence band maximum (E_{VBM}) has been set to 0 eV.

that is split into two distinct parts. The PP basis set narrows the band, but it still consists of two parts. However, the parts are no longer distinctly separated (Fig. 3).

Compared to the O 2p peaks from the experimental resonant X-ray emission spectroscopy (RXES)^{68,69} the 1st valence band calculated with the pure PBE functional and with PBE0 are both too narrow, though the PBE0 functional predicts a width that is in better agreement with the experiment. The position of the Zn 3d band depends strongly on the representation of the electron structure: the AE and GPAW/PBE methods yield too high and the PP methods too low energies. The orbital contributions to the peaks agree with the experimental assignments of O 2p: the first strong peak in the 1st valence band has mostly the O 2p and Zn 4p contributions and the second peak the O 2p and Zn 4s contributions while the first part of the Zn 3d band consists solely of the Zn 3d contributions and the second part consists of both the O 2p and Zn 3d contributions (Table 2 and Fig. 3).⁶⁸

Using GLLB-SC improves the band positions in the GPAW calculations. This has been also observed with the Ag 3d band energies.⁷⁰ GLLB-SC gives ~ 0.6 eV lower Zn 3d band energies than PBE, improving the description, but still leaves the bands somewhat above the experimental values. Additionally, the band gap is better than with PBE but it is still too low compared to the experiment and a small band separation between the valence band and the Zn 3d band appears (Table 2). GPAW/PBE lattice constants were used in the GPAW/GLLB-SC calculation.

Overall, CRYSTAL PBE0/AE results match the experimental values best, although the band gap is slightly overestimated, the first valence band is a bit too narrow and the Zn 3d band position is ~ 1 eV too high in energy. However, all methods yield good qualitative results.

ZnO (10 $\bar{1}$ 0) surface

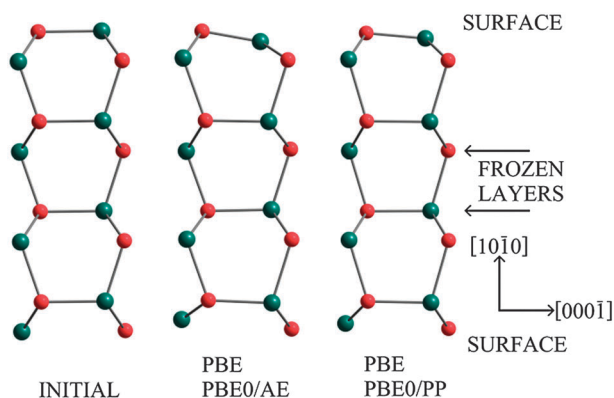
The effect of the thickness of the ZnO slab model on the optimized lattice constants is demonstrated in Table 3. The lattice constants approach the bulk values when the slab thickness increases and are in a rather good agreement in the model of 16 layers. The band gap values decrease below the bulk band gaps, as expected from the fully relaxed models with bulk-like core structures and relaxed top and bottom surfaces.

Table 3 Lattice constants (*a* and *b*) and the band gaps of the ZnO slab models of various thicknesses optimized with CRYSTAL

	PBE/AE			PBE/PP		
	<i>a</i> /Å	<i>b</i> /Å	Band gap/eV	<i>a</i> /Å	<i>b</i> /Å	Band gap/eV
4 Layers	3.38	5.39	2.24	3.79	5.24	2.31
8 Layers	3.33	5.31	1.62	3.44	5.29	1.70
8 Layers ^a	3.27	5.28	1.56	3.37	5.25	1.76
16 Layers	3.31	5.29	1.32	3.41	5.27	1.57
Bulk	3.27	5.28	1.46	3.37	5.25	1.74

	PBE0/AE			PBE0/PP		
	<i>a</i> /Å	<i>b</i> /Å	Band gap/eV	<i>a</i> /Å	<i>b</i> /Å	Band gap/eV
4 Layers	3.37	5.33	4.77	3.74	5.16	4.57
8 Layers	3.31	5.25	4.03	3.40	5.22	3.95
8 Layers ^a	3.25	5.23	3.97	3.33	5.19	3.86
16 Layers	3.29	5.23	3.73	3.37	5.21	3.75
Bulk	3.25	5.23	3.92	3.33	5.19	3.94

^a Lattice constants and the atomic positions of the two innermost layers frozen at the bulk values.

**Fig. 4** Initial and relaxed surface slabs.

The PP basis set reconstructed the wurtzite structure in the slabs of 4 layers into two layers of ions in a trigonal planar structure, which explains why the slab parameter *a* increased considerably compared to the AE basis set which did not cause reconstruction.

After the initial assessment, we chose the slab of 8 layers for modelling the surface as a compromise between accuracy and computational cost. The top three surface layers on both sides of the slab were allowed to relax while the atomic positions of the two innermost layers and the lattice constants were frozen at the bulk values. We also studied the surface relaxation briefly with this model, noting that the position of the Zn atom on both surfaces changes somewhat when the PP basis set is used and even more when the AE basis set is used, see Fig. 4. The numerical values describing the surface relaxation are given as ESI.†

Porphyrin

Porphyrin compounds have typically a very strong absorption band in the near UV region, called the Soret band, and four

Table 4 Frontier orbital energies (eV) of porphyrin with respect to the HOMO

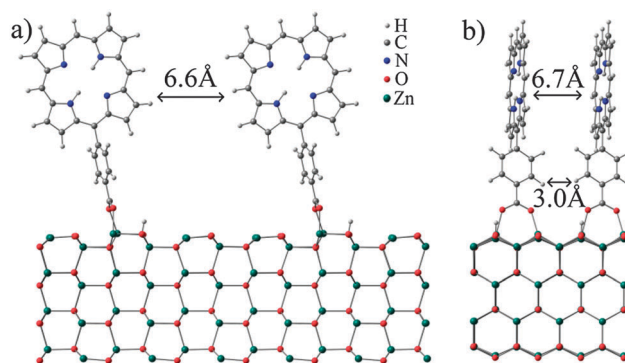
	H - 2	H - 1	HOMO	LUMO	L + 1	L + 2
GPAW/PBE	-0.86	-0.23	0.00	1.83	1.92	2.53
CRYSTAL/PBE	-0.86	-0.29	0.00	1.82	1.92	2.54
CRYSTAL/PBE0	-1.43	-0.17	0.00	2.84	2.93	4.00

weak bands in the visible region, called the Q bands. Out of the latter, two peaks are attributed to pure electronic transitions while the other two are interpreted in terms of vibrational contributions.^{72,73} Upon interaction with other molecular compounds or substrates, the positions of both the Soret and Q bands shift and the spacing between the peaks within the Q band changes. These modifications, which depend on the orientation and distance of the porphyrin ring with respect to the interacting moiety, originate mainly from the energy variation of the molecular orbitals involved in the electronic transitions.^{35–37} In this respect, computational studies have identified only few frontier molecular orbitals of porphyrin, *i.e.* HOMO, HOMO - 1, LUMO and LUMO + 1, to be truly relevant for the Q bands. The Q bands are also the most important regarding the electron transfer from porphyrin to surface in DSSC applications.

To obtain the orbital energies of 4-(porphyrin-5-yl)benzoic acid, we use a slab model constructed of only a single porphyrin in a *ca.* 7 Å × 16 Å unit cell in a similar fashion to when porphyrin is adsorbed on the ZnO surface. The relevant energy levels of porphyrin are listed in Table 4. The calculated energies can be compared to the energies of porphine, the simplest porphyrin, and 4-(10,15,20-triphenylporphyrin-5-yl)benzoic acid, both of which have a Soret band absorption peak at *ca.* 3.0 eV and Q-band absorption peaks in the range of 2.4–1.9 eV.^{74,75} The PBE frontier orbital energies are in a range that is comparable to the experimental excitation energies but in the case of the PBE0 functional the TD formalism would be needed for obtaining the correct excitation energy.

Porphyrin adsorbed *via* the COO⁻ anchor group on the ZnO (1010) surface

The optimizations with the PBE/AE, PBE0/AE and PBE0/PP methods gave similar porphyrin orientations, where porphyrin

**Fig. 5** Adsorbate packing shown along the (a) $[1\bar{1}0]$ and (b) $[00\bar{1}]$ directions predicted by the PBE0/PP method.

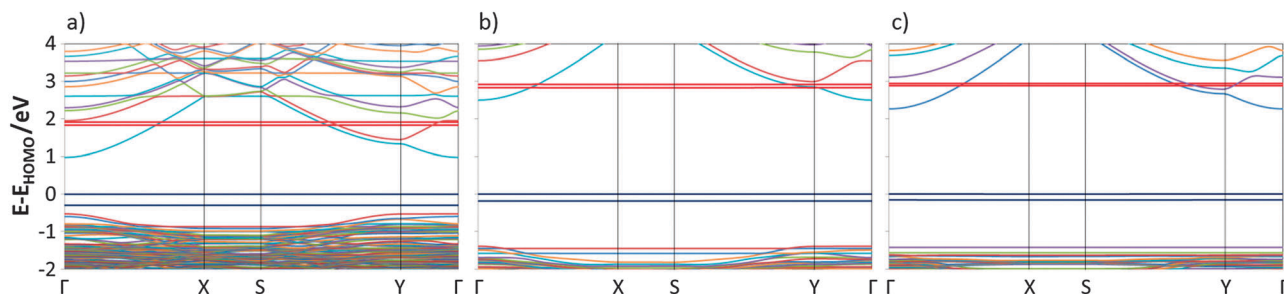


Fig. 6 Band structure of the ZnO surface-porphyrin adsorbate model calculated with (a) PBE/AE, (b) PBE0/AE and (c) PBE0/PP. Energy of the porphyrin HOMO level (E_{HOMO}) is set at 0 eV.

stands at a *ca.* 80° angle on the surface (Fig. 5). It is also worthwhile to note that the Zn ions at the adsorption site move upwards due to the adsorption of the linker and regain the more bulk-like positions. Optimizing the structure of the surface-adsorbate model with the PBE/PP method did not converge due to SCF problems.

The band energies are approximately the same as in the case of the isolated porphyrin and ZnO models, regardless of the functional used. The band structures of the surface-adsorbate models are presented in Fig. 6. The LUMO bands of porphyrin and the conduction bands of ZnO overlap with all the methods, although the energy difference between the porphyrin LUMO band and ZnO conduction band minimum varies. In the PBE0 results the separation between the porphyrin HOMO level and the ZnO valence band maximum is wider than with PBE due to a larger ZnO band gap. The PBE0/PP predicts the porphyrin HOMO – 2 and some of the lower states to lie above the ZnO valence band.

As the overlap of the LUMO bands of porphyrin and the conductance band of ZnO is similar with all the methods, it is assumed that the choice of the functional does not affect the further analysis of the system much. However, it should be noted that in the case of PBE, the ZnO band gap is smaller than the porphyrin HOMO–LUMO gap, which is not the case experimentally.

Next we tilted porphyrin closer to the ZnO surface to study the change in the total energy of the model and coupling between the porphyrin LUMO or LUMO + 1 and the ZnO conduction band. The structures were partially optimized using the PBE0/PP method. When porphyrin is tilted towards the surface its energy increases, first slowly but faster near the surface (Fig. 7a). The standing, twisted porphyrin has a somewhat higher total energy than the standing, untwisted porphyrin. However, when the twisted porphyrin is tilted, the energy decreases due to the attractive porphyrin–surface interactions until the energy minimum is reached close to the surface (at a *ca.* 25° tilting angle). Finally we relaxed the porphyrin on the surface and then changed the tilting angle. In this model there is a steep energy minimum due to optimal porphyrin–surface interactions. This third case describes the porphyrin model best, whereas the first two energy curves are relevant in cases where substituents restrict the porphyrin orientation. In the minimum energy orientation the π -orbitals

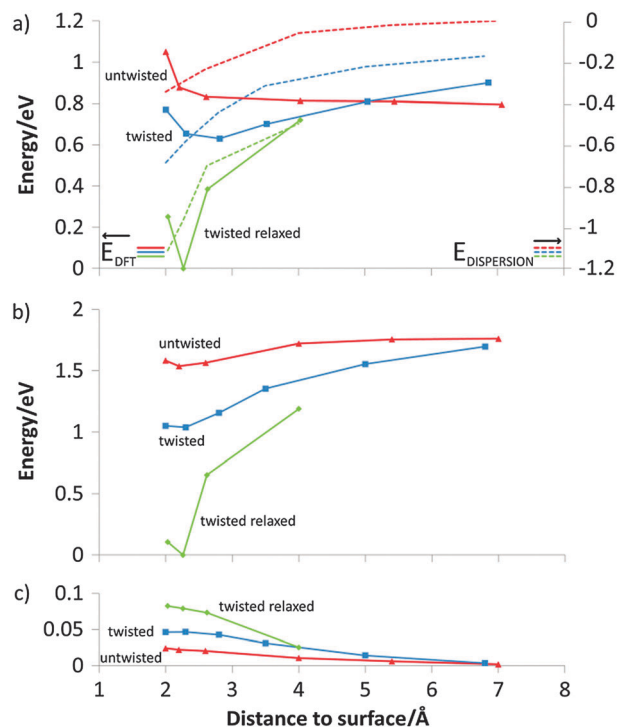


Fig. 7 (a) Relative energies of porphyrin models calculated with DFT and the amount of dispersion correction and (b) the sum of the previous. (c) The coupling strengths of porphyrin and ZnO (in eV).

of the porphyrin rings interact and the distances to the neighbouring porphyrin rings are *ca.* 3.6 Å. Similar porphyrin–porphyrin distances have been found for porphyrin moieties tilted (35° – 40°) on a TiO_2 surface.⁷⁶

The energies were then corrected by including the empirical dispersion correction to take into account the van der Waals interactions between porphyrin and surface and between the neighbouring porphyrin rings. However, the empirical DFT-D2 method may cause overbinding as analysed in ref. 77 and 78. For this reason we limited the dispersion correction to the adsorbate and the first ZnO layer and the dispersion corrected energies should be considered only qualitatively.

We first note that the dispersion correction stabilizes the twisted porphyrin model more than the untwisted model and the twisted relaxed model is stabilized the most (Fig. 7a). The main reason for this is the π -orbital interaction between

neighbouring porphyrins in the twisted models and the shorter porphyrin–porphyrin distance in the twisted relaxed model compared to the twisted model. Additionally, when porphyrin is tilted near the surface the twisted models are stabilized more due to a larger interaction area with the surface. We also note that the standing geometry of porphyrin is no longer a local minimum geometry (Fig. 7b). When the untwisted porphyrin is tilted towards the surface the total energy decreases until the minimum energy is reached near the surface. The twisted porphyrin has initially a similar total energy as the untwisted porphyrin but the energy of this orientation decreases further when the porphyrin is tilted towards the surface. The relaxed tilted porphyrin has the steepest energy curve.

Full optimization using the dispersion correction was also performed. For this structure the porphyrin–ZnO distance was *ca.* 2.4 Å and the porphyrin–porphyrin distance *ca.* 3.1 Å. However, the electronic structure is not at the minimum DFT energy when the dispersion corrected minimum energy geometry is adopted, because the empirical dispersion correction only affects the total energy and the gradients. As such we do not analyse the electronic properties of this structure. It is also obvious that there is a distribution of various porphyrin–surface distances and porphyrin orientations close to the surface caused by the thermal motion, but this is out of the scope of our current study.

When porphyrin is tilted closer to the surface, the ZnO bands and porphyrin orbital energies remain mostly unchanged. However, the coupling strength between the bands is stronger when porphyrin is close to the surface (Fig. 7c). The coupling strength is of specific interest, as it affects the charge transfer from the excited porphyrin to the ZnO. The coupling strength is estimated from the vertical distance of the ZnO conduction band and porphyrin LUMO or LUMO + 1 bands (Fig. 8) at the “avoided crossing” for each porphyrin orientation. Thus, this is the usual two degenerate level coupling in perturbation theory. The distance (the coupling strength) at “avoided crossing” between the bands increases as the bands interact more strongly. Coupling is stronger with the twisted porphyrin models than with the untwisted porphyrin model and increases as the porphyrin is tilted closer to the surface. Similarly, the distance between porphyrin and the TiO₂ surface

has been seen to affect the through-space electron transfer rates.⁷⁹ Based on this, the band coupling can be used to predict ET from the porphyrin unoccupied orbitals to the ZnO conduction band. It is also worth noting that, when porphyrin is brought closer to the surface, the coupling strength does not change much after a certain porphyrin–surface distance in the case of the twisted porphyrin. Additionally, the porphyrin–porphyrin interactions cause widening of the porphyrin LUMO and LUMO + 1 when the porphyrin is twisted. The porphyrin–porphyrin coupling allows electron migration between porphyrins as well. Sample figures that show how the coupling strength changes with the changing porphyrin orientation are given as ESI.†

Based on the estimated coupling strengths, a dye near the ZnO surface in the twisted orientation has the highest relative ET rate. Obtaining a dye layer with this orientation experimentally is challenging due to tight surface packing that prevents dyes from tilting as far towards the surface as in our models. One might obtain a tilted dye layer by altering the linker, for example using a *meta*-substituted benzoate instead of a *para*-substituted one as in our model case. Another possibility would be to use temporary supramolecular spacers around the dyes leading to a sparser surface packing. After surface adsorption of porphyrins the spacers could be removed by heating, chemical reaction or by other means to give the dye molecules the space to tilt towards the surface.

Excitation of porphyrin is needed before ET can take place. The effect of tilting of porphyrin closer to the surface on the excitation energies was examined by comparing the GPAW/TD-DFT/GLLB-SC results of the standing porphyrin models and the porphyrin models tilted close to the surface. The tilted porphyrin model had a surface–porphyrin distance of 2.6 Å and the tilted and twisted porphyrin model a distance of 2.8 Å. The obtained TD-DFT excitation energies are given in Table 5.

In all cases porphyrin has two similar excitations comparable to those of the isolated porphyrin. The excitation energies differ only slightly with different porphyrin orientations. Most notably the 2nd excitation has a somewhat lower energy in the tilted porphyrin orientation than in the standing orientation. The excitations are composed of transitions from HOMO – 1 and HOMO to LUMO and LUMO + 1. However, the first excitation (*ca.* 2.3 eV) of the tilted porphyrin contains only 66% of these transitions and the tilted twisted porphyrin 49%, while the rest of the excitation consists of ZnO–ZnO transitions. Additionally, the second excitation of the tilted twisted porphyrin contains 67% of porphyrin states. The deviation from the isolated porphyrin case is due to a too low ZnO band gap, which allows mixing of the surface excitations occurring at lower energies than they should with the first two porphyrin

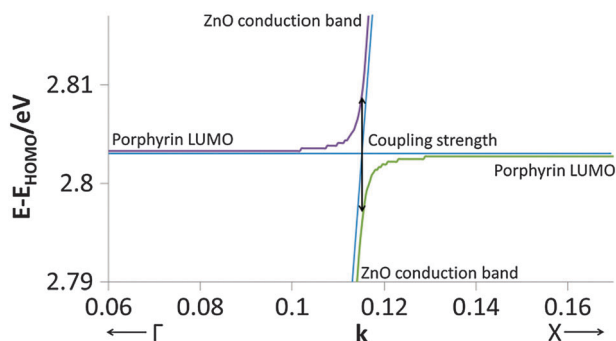


Fig. 8 Coupling strength between the porphyrin LUMO and the ZnO conduction band measured from a magnified band structure.

Table 5 Excitation energies (eV) of the 1st and 2nd excitations of porphyrin calculated with GPAW/TD-DFT/GLLB-SC

	Free porphyrin	Standing	Standing twisted	Tilted	Tilted twisted
1st Excitation	2.24	2.31	2.33	2.30	2.33
2nd Excitation	2.46	2.58	2.56	2.53	2.54

excitations. With GPAW/TD-DFT/PBE the mixing of the surface and porphyrin contributions in excitations is even greater. In other words, GLLB-SC mixes the excitations less and helps in assigning them. In addition, it slightly increases (~ 0.1 eV) the excitation energies compared to those calculated with GPAW/PBE. However, a method that yields a correct ZnO band gap would be superior to both of the tested TD-DFT methods. To summarize, based on the TD-DFT calculations the excitation energies of porphyrin change only slightly when the orientation of porphyrin is changed on the surface.

Conclusions

A model system constructed of 4-(porphyrin-5-yl)benzoic acid adsorbed on the ZnO wurtzite (10 $\bar{1}0$) surface was studied with the focus on the coupling strength between the porphyrin unoccupied orbitals and the ZnO conduction band and the initial photoexcitations of porphyrin in various porphyrin orientations. The PBE and PBE0 functionals perform well in optimizing the model systems. The energy of the porphyrin LUMO level is higher than that of the ZnO conduction band minimum, which is in agreement with ET observed experimentally in similar systems. However, the PBE functional underestimates the ZnO band gap and PBE0 overestimates the porphyrin HOMO–LUMO gap. The porphyrin LUMO–ZnO conduction band coupling strength increases steadily as the porphyrin approaches the surface. If porphyrin is twisted so that the π -electrons face the surface, at least partially, the coupling strength increases further. The strength of the band coupling can be used to predict the relative rate of the ET from the porphyrin LUMO to the ZnO conduction band. Both the distance between porphyrin and the ZnO surface and the orientation of porphyrin with respect to the surface affect the coupling. In our models the coupling is highest when the porphyrin is the closest to the surface and aligned with it. Based on our results it might be possible to enhance the rate of the ET from the dye molecules to the ZnO surface by dyes where a linker has a distinct tilting angle that orients the dye close to the surface. Alternatively, the dyes could be surrounded by temporary supramolecular or loosely bound spacers prior to adsorption which would be later removed by heating, a chemical reaction or by other means to give the dyes the room needed for the tilting. Based on the TD-DFT calculations the nature of the porphyrin excitations changes only slightly with the changing orientation of porphyrin.

In this paper, we have investigated the effect of the orientation of porphyrin on the ZnO surface on the initial excitation of porphyrin and on the coupling between the porphyrin LUMO or LUMO + 1 and the ZnO conduction band, both of which are relevant to ET. Our next goals are to examine dyes on other semiconductor surfaces and to examine the ET and the coupling more closely.

Acknowledgements

Computing resources provided by the CSC – IT Center for Science Ltd, administrated by the Finnish Ministry of

Education, are gratefully acknowledged. This work was supported by the FP7-PEOPLE Marie Curie International Incoming Fellowship Program (project MOEBIUS) and the National Doctoral Programme in Material Physics (NGSMP), which are acknowledged. Financing of the computational research by the Academy of Finland is greatly appreciated.

Notes and references

- 1 A. J. Nozik and R. Memming, Physical chemistry of semiconductor–liquid interface, *J. Phys. Chem.*, 1996, **100**, 13061–13078, DOI: 10.1021/jp953720e.
- 2 J. B. Asbury, E. Hao, Y. Wang, H. N. Ghosh and T. Lian, Ultrafast Electron Transfer Dynamics from Molecular Adsorbates to Semiconductor Nanocrystalline Thin Films, *J. Phys. Chem. B*, 2001, **105**, 4545–4557, DOI: 10.1021/jp003485m.
- 3 O. V. Prezhdo, W. R. Duncan and V. V. Prezhdo, Photoinduced electron dynamics at the chromophore–semiconductor interface: A time-domain *ab initio* perspective, *Prog. Surf. Sci.*, 2009, **84**, 30–68, DOI: 10.1016/j.progsurf.2008.10.005.
- 4 H. E. Katz and J. Huang, Thin-Film Organic Electronic Devices, *Annu. Rev. Mater. Res.*, 2009, **39**, 71–92, DOI: 10.1146/annurev-matsci-082908-145433.
- 5 D. V. Talapin, J.-S. Lee, M. V. Kovalenko and E. V. Shevchenko, Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications, *Chem. Rev.*, 2010, **110**, 389–458, DOI: 10.1021/cr900137k.
- 6 M. Grätzel, Recent Advances in Sensitized Mesoscopic Solar Cells, *Acc. Chem. Res.*, 2009, **42**, 1788–1798, DOI: 10.1021/ar900141y.
- 7 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, Dye-Sensitized Solar Cells, *Chem. Rev.*, 2010, **110**, 6595–6663, DOI: 10.1021/cr900356p.
- 8 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, Md. K. Nazeeruddin, E. W.-G. Diao, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, Porphyrin-Sensitized Solar Cells with Cobalt(II/III)-based Redox Electrolyte Exceed 12 Percent Efficiency, *Science*, 2011, **334**, 629–634, DOI: 10.1126/science.1209688.
- 9 L. Gundlach, R. Ernstorfer and F. Willig, Ultrafast interfacial electron transfer from the excited state of anchored molecules into a semiconductor, *Prog. Surf. Sci.*, 2007, **82**, 355–377, DOI: 10.1016/j.progsurf.2007.03.001.
- 10 H. Imahori, S. Kang, H. Hayashi, M. Haruta, H. Kurata, S. Isoda, S. E. Canton, Y. Infahsaeng, A. Kathiravan, T. Pascher, P. Chabera, A. P. Yartsev and V. Sundström, Photoinduced Charge Carrier Dynamics of Zn–Porphyrin–TiO₂ Electrodes: The Key Role of Charge Recombination for Solar Cell Performance, *J. Phys. Chem. A*, 2011, **115**, 3679–3690, DOI: 10.1021/jp103747t.
- 11 D. M. Adams, L. Brus, C. E. D. Chidsey, S. Creager, C. Creutz, C. R. Kagan, P. V. Kamat, M. Lieberman, S. Lindsay, R. A. Marcus, R. M. Metzger, M. E. Michel-Beyerle, J. R. Miller, M. D. Newton, D. R. Rolison, O. Sankey, K. S. Schanze, J. Yardley and X. Zhu, Charge Transfer on the Nanoscale: Current Status, *J. Phys. Chem. B*, 2003, **107**, 6668–6697, DOI: 10.1021/jp0268462.

- 12 K. L. Sebastian and M. Tachiya, Theory of photoinduced heterogeneous electron transfer, *J. Chem. Phys.*, 2006, **124**, 064713, DOI: 10.1063/1.2171238.
- 13 S. Varaganti and G. Ramakrishna, Dynamics of Interfacial Charge Transfer Emission in Small Molecule Sensitized TiO₂ Nanoparticles: Is It Localized or Delocalized?, *J. Phys. Chem. C*, 2010, **114**, 13917–13925, DOI: 10.1021/jp102629u.
- 14 K. K. Liang, C.-K. Lin, H.-C. Chang, M. Hayashi and S. H. Lin, Theoretical treatments of ultrafast electron transfer from adsorbed dye molecule to semiconductor nanocrystalline surface, *J. Chem. Phys.*, 2006, **125**, 154706, DOI: 10.1063/1.2359445.
- 15 F. Rissner, G. M. Rangger, O. T. Hofmann, A. M. Track, G. Heimel and E. Zojer, Understanding the Electronic Structure of Metal/SAM/Organic-Semiconductor Heterojunctions, *ACS Nano*, 2009, **3**, 3513–3520, DOI: 10.1021/nn9010494.
- 16 S.-H. Hu, Y.-C. Chen, C.-C. Hwang, C.-H. Peng and D.-C. Gong, Development of a wet chemical method for the synthesis of arrayed ZnO nanorods, *J. Alloys Compd.*, 2010, **500**, L17–L21, DOI: 10.1016/j.jallcom.2010.03.235.
- 17 S. H. Ko, D. Lee, H. W. Kang, K. H. Nam, J. Y. Yeo, S. J. Hong, C. P. Grigoropoulos and H. J. Sung, Nanoforest of Hydrothermally Grown Hierarchical ZnO Nanowires for a High Efficiency Dye-Sensitized Solar Cell, *Nano Lett.*, 2011, **11**, 666–671, DOI: 10.1021/nl1037962.
- 18 J. Bouclé, H. J. Snaith and N. C. Greenham, Simple Approach to Hybrid Polymer/Porous Metal Oxide Solar Cells from Solution-Processed ZnO Nanocrystals, *J. Phys. Chem. C*, 2010, **114**, 3664–3674, DOI: 10.1021/jp909376f.
- 19 A. R. H. Preston, B. J. Ruck, L. F. J. Piper, A. Demasi, K. E. Smith, A. Schleife, F. Fuchs, F. Bechstedt, J. Chai and S. M. Durbin, Band structure of ZnO from resonant X-ray emission spectroscopy, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 155114, DOI: 10.1103/PhysRevB.78.155114.
- 20 J. Wróbel, K. J. Kurzydowski, K. Hummer, G. Kresse and J. Piechota, Calculations of ZnO properties using the Heyd–Scuseria–Ernzerhof screened hybrid density functional, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **80**, 155124, DOI: 10.1103/PhysRevB.80.155124.
- 21 H. Dixit, R. Saniz, D. Lamoén and B. Partoens, Accurate pseudopotential description of the GW bandstructure of ZnO, *Comput. Phys. Commun.*, 2011, **182**, 2029–2031, DOI: 10.1016/j.cpc.2011.02.001.
- 22 N. L. Marana, V. M. Longo, E. Longo, J. B. L. Martins and J. R. Sambrano, Electronic and Structural Properties of the (10 $\bar{1}0$) and (11 $\bar{2}0$). ZnO Surfaces, *J. Phys. Chem. A*, 2008, **112**, 8958–8963, DOI: 10.1021/jp801718x.
- 23 M. Breedon, M. J. S. Spencer and I. Yarovsky, Adsorption of NO and NO₂ on the ZnO (2 $\bar{1}\bar{1}0$) surface: A DFT study, *Surf. Sci.*, 2009, **603**, 3389–3399, DOI: 10.1016/j.susc.2009.09.032.
- 24 J. D. Prades, A. Cirera and J. R. Morante, *Ab initio* calculations of NO₂ and SO₂ chemisorption onto non-polar ZnO surfaces, *Sens. Actuators, B*, 2009, **142**, 179–184, DOI: 10.1016/j.snb.2009.08.017.
- 25 F. D. Sala, S. Blumstengel and F. Henneberger, Electrostatic Field Driven Alignment of Organic Oligomers on ZnO Surfaces, *Phys. Rev. Lett.*, 2011, **107**, 146401, DOI: 10.1103/PhysRevLett.107.146401.
- 26 F. Labat, I. Ciofini, H. P. Hratchian, M. Frisch, K. Raghavachari and C. Adamo, First Principles Modelling of Eosin-Loaded ZnO Films: A Step Toward the Understanding of Dye-Sensitized Solar Cell Performances, *J. Am. Chem. Soc.*, 2009, **131**, 14290–14298, DOI: 10.1021/ja902833s.
- 27 T. Le Bahers, F. Labat, T. Pauporté, P. P. Lainé and I. Ciofini, Theoretical Procedure for Optimizing Dye-Sensitized Solar Cells: From Electronic Structure to Photovoltaic Efficiency, *J. Am. Chem. Soc.*, 2011, **133**, 8005–8013, DOI: 10.1021/ja201944g.
- 28 N. Sai, K. Leung and J. R. Chelikowsky, Hybrid density functional study of oligothiophene/ZnO interface for photovoltaics, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 121309(R), DOI: 10.1103/PhysRevB.83.121309.
- 29 H. Imahori, T. Umeyama and S. Ito, Large π -Aromatic Molecules as Potential Sensitizers for Highly Efficient Dye-Sensitized Solar Cells, *Acc. Chem. Res.*, 2009, **42**, 1809–1818, DOI: 10.1021/ar900034t.
- 30 M. Jurow, A. E. Schuckman, J. D. Batteas and C. M. Drain, Porphyrins as molecular electronic components of functional devices, *Coord. Chem. Rev.*, 2010, **254**, 2297–2310, DOI: 10.1016/j.ccr.2010.05.014.
- 31 M. G. Waltera, A. B. Rudine and C. C. Wamser, Porphyrins and phthalocyanines in solar photovoltaic cells, *J. Porphyrins Phthalocyanines*, 2010, **14**, 759–792, DOI: 10.1142/S1088424610002689.
- 32 C. Di Natale, D. Monti and R. Paolesse, Chemical sensitivity of porphyrin assemblies – review article, *Mater. Today*, 2010, **13**, 46–52, DOI: 10.1016/S1369-7021(10)70127-9.
- 33 M. Gouterman and G. H. Wagniere, Spectra of porphyrins: part II. Four orbital model, *J. Mol. Spectrosc.*, 1963, **11**, 108–127, DOI: 10.1016/0022-2852(63)90011-0.
- 34 M. E. Zandler and F. D'Souza, The Remarkable Ability of B3LYP/3-21G(*) Calculations to Describe Geometry, Spectral and Electrochemical Properties of Molecular and Supramolecular Porphyrin-Fullerene Conjugates, *C. R. Chim.*, 2006, **9**, 960–981, DOI: 10.1016/j.crci.2005.12.008.
- 35 O. Cramariuc, T. I. Hukka and T. T. Rantala, Time-dependent Density Functional Calculations on the Electronic Absorption Spectra of an Asymmetric *meso*-substituted Porphyrin and its Zinc Complex, *J. Phys. Chem. A*, 2004, **108**, 9435–9441, DOI: 10.1021/jp048291b.
- 36 O. Cramariuc, T. I. Hukka, T. T. Rantala and H. Lemmetyinen, A TD-DFT description of photoabsorption and electron transfer in a covalently bonded porphyrin–fullerene dyad, *J. Phys. Chem. A*, 2006, **110**, 12470–12476, DOI: 10.1021/jp062834v.
- 37 O. Cramariuc, T. I. Hukka, T. T. Rantala and H. Lemmetyinen, *Ab initio* description of photoabsorption and electron transfer in a doubly-linked porphyrin–fullerene dyad, *J. Comput. Chem.*, 2009, **30**, 1194–1201, DOI: 10.1002/jcc.21143.

- 38 J. M. Gottfried and H. Marbach, Surface-Confined Coordination Chemistry with Porphyrins and Phthalocyanines: Aspects of Formation, Electronic Structure, and Reactivity, *Z. Phys. Chem.*, 2009, **223**, 53–74, DOI: 10.1524/zpch.2009.6024.
- 39 R. Dovesi, R. Orlando, B. Civalieri, C. Roetti, V. R. Saunders and C. M. Zicovich-Wilson, CRYSTAL: a computational tool for the *ab initio* study of the electronic properties of crystals, *Z. Kristallogr.*, 2005, **220**, 571–573, DOI: 10.1524/zkri.220.5.571.65065.
- 40 R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalieri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco and M. Llunell, *CRYSTAL09, CRYSTAL09 User's Manual*, University of Torino, Torino, 2009.
- 41 J. J. Mortensen, L. B. Hansen and K. W. Jacobsen, Real-space grid implementation of the projector augmented wave method, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 035109, DOI: 10.1103/PhysRevB.71.035109.
- 42 J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Møller, M. Strange, G. A. Tritsarlis, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, K. S. Thygesen and K. W. Jacobsen, Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method, *J. Phys.: Condens. Matter*, 2010, **22**, 253202, DOI: 10.1088/0953-8984/22/25/253202.
- 43 P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979, DOI: 10.1103/PhysRevB.50.17953.
- 44 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868, DOI: 10.1103/PhysRevLett.77.3865.
- 45 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 1997, **78**, 1396, DOI: 10.1103/PhysRevLett.78.1396.
- 46 C. Adamo and V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, *J. Chem. Phys.*, 1999, **110**, 6158–6170, DOI: 10.1063/1.478522.
- 47 M. Kuisma, J. Ojanen, J. Enkovaara and T. T. Rantala, Kohn–Sham potentials with discontinuity for band gap materials, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 115106, DOI: 10.1103/PhysRevB.82.115106.
- 48 O. Gritsenko, R. van Leeuwen, E. van Lenthe and E. J. Baerends, Self-consistent approximation to the Kohn–Sham exchange potential, *Phys. Rev. A*, 1995, **51**, 1944–1954, DOI: 10.1103/PhysRevA.51.1944.
- 49 R. W. Godby, M. Schlüter and L. J. Sham, Accurate Exchange–Correlation Potential for Silicon and Its Discontinuity on Addition of an Electron, *Phys. Rev. Lett.*, 1986, **56**, 2415–2418, DOI: 10.1103/PhysRevLett.56.2415.
- 50 M. E. Casida, Time-dependent density-functional response theory for molecules, in *Recent advances in density functional methods part I*, ed. D. P. Chong, World Scientific, Singapore, 1995, p. 155.
- 51 M. Walter, H. Häkkinen, L. Lehtovaara, M. Puska, J. Enkovaara, C. Rostgaard and J. J. Mortensen, Time-dependent density-functional theory in the projector augmented-wave method, *J. Chem. Phys.*, 2008, **128**, 244101: 1–10, DOI: 10.1063/1.2943138.
- 52 S. Grimme, Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction, *J. Comput. Chem.*, 2006, **27**, 1787–1799, DOI: 10.1002/jcc.20495.
- 53 G. A. Zhurko, *Chemcraft Version 1.60*, www.chemcraftprog.com.
- 54 F. Labat, I. Ciofini and C. Adamo, Modelling ZnO phases using a periodic approach: from bulk to surface and beyond, *J. Chem. Phys.*, 2009, **131**, 044708, DOI: 10.1063/1.3179752.
- 55 P. J. Hay and W. R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, *J. Chem. Phys.*, 1985, **82**, 270–283, DOI: 10.1063/1.448799.
- 56 P. J. Hay and W. R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potentials for main group elements Na to Bi, *J. Chem. Phys.*, 1985, **82**, 284–298, DOI: 10.1063/1.448800.
- 57 P. J. Hay and W. R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.*, 1985, **82**, 299–310, DOI: 10.1063/1.448975.
- 58 P. Durand and J.-C. Barthelat, A Theoretical Method to Determine Atomic Pseudopotentials for Electronic Structure Calculations of Molecules and Solids, *Theor. Chim. Acta*, 1975, **38**, 283–302, DOI: 10.1007/BF00963468.
- 59 J.-C. Barthelat and P. Durand, Recent progress of pseudopotential methods in quantum chemistry, *Gazz. Chim. Ital.*, 1978, **108**, 225–236.
- 60 J.-C. Barthelat, P. Durand and A. Serafini, Non-empirical pseudopotentials for molecular calculations, *Mol. Phys.*, 1977, **33**, 159–180.
- 61 R. Dovesi, M. Causa, R. Orlando, C. Roetti and V. R. Saunders, *Ab initio* approach to molecular crystals: A periodic Hartree–Fock study of crystalline urea, *J. Chem. Phys.*, 1990, **92**, 4702–4711, DOI: 10.1063/1.458592.
- 62 R. Dovesi, C. Ermondi, E. Ferrero, C. Pisani and C. Roetti, Hartree–Fock study of lithium fluoride with the use of a polarizable basis set, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1983, **29**, 3591–3600.
- 63 I. Gonzalez-Valls and M. Lira-Cantu, Vertically-aligned nanostructures of ZnO for excitonic solar cells: a review, *Energy Environ. Sci.*, 2009, **2**, 19–34, DOI: 10.1039/B811536B.
- 64 K. S. Kim, H. Jeong, M. S. Jeong and G. Y. Jung, Polymer-Templated Hydrothermal Growth of Vertically Aligned Single-Crystal ZnO Nanorods and Morphological Transformations Using Structural Polarity, *Adv. Funct. Mater.*, 2010, **20**, 3055–3063, DOI: 10.1002/adfm.201000613.

- 65 H. Saarenpää, E. Sariola-Leikas, A. P. Perros, J. M. Kontio, A. Efimov, H. Hayashi, H. Lipsanen, H. Imahori, H. Lemmetyinen and N. V. Tkachenko, Self-Assembled Porphyrins on Modified Zinc Oxide Nanorods: Development of Model Systems for Inorganic–Organic Semiconductor Interface Studies, *J. Phys. Chem. C*, 2012, **116**, 2336–2343, DOI: 10.1021/jp2104769.
- 66 N. H. Moreira, A. L. da Rosa and T. Frauenheim, Covalent functionalization of ZnO surfaces: a density functional tight binding study, *Appl. Phys. Lett.*, 2009, **94**, 193109, DOI: 10.1063/1.3132055.
- 67 K. Kihara and G. Donnay, Anharmonic thermal vibrations in ZnO, *Can. Mineral.*, 1985, **23**, 647–654.
- 68 C. L. Dong, C. Persson, L. Vayssieres, A. Augustsson, T. Schmitt, M. Mattesini, R. Ahuja, C. L. Chang and J.-H. Guo, Electronic structure of nanostructured ZnO from X-ray absorption and emission spectroscopy and the local density approximation, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 195325, DOI: 10.1103/PhysRevB.70.195325.
- 69 A. R. H. Preston, B. J. Ruck, L. F. J. Piper, A. DeMasi, K. E. Smith, A. Schleife, F. Fuchs, F. Bechstedt, J. Chai and S. M. Durbin, Band Structure of ZnO from resonant X-ray emission spectroscopy, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 155114, DOI: 10.1103/PhysRevB.78.155114.
- 70 J. Yan, K. W. Jacobsen and K. S. Thygesen, First-principles study of surface plasmons on Ag(111) and H/Ag(111), *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 235430, DOI: 10.1103/PhysRevB.84.235430.
- 71 A. Janotti and C. G. Van de Walle, Fundamentals of zinc oxide as a semiconductor, *Rep. Prog. Phys.*, 2009, **72**, 126501, DOI: 10.1088/0034-4885/72/12/126501.
- 72 A. Stradomska and J. Knoester, Shape of the Q band in the absorption spectra of porphyrin nanotubes: vibronic coupling or exciton effects?, *J. Chem. Phys.*, 2010, **133**, 094701, DOI: 10.1063/1.3481654.
- 73 J. M. Beames, T. D. Vaden and A. J. Hudson, The spectroscopy of jet-cooled porphyrins: an insight into the vibronic structure of the Q band, *J. Porphyrins Phthalocyanines*, 2010, **14**, 314–323, DOI: 10.1142/S1088424610002094.
- 74 Y.-H. Zhang, Z.-Y. Li, Y. Wu, Y.-Z. Zhu and J.-Y. Zheng, DFT study on the geometric, electronic structure and Raman spectra of 5,15-diphenylporphine, *Spectrochim. Acta, Part A*, 2005, **62**, 83–91, DOI: 10.1016/j.saa.2004.12.009.
- 75 V. Cantonetti, D. Monti, M. Venanzi, C. Bombelli, F. Ceccacci and G. Mancini, Interaction of a chirally functionalised porphyrin derivative with chiral micellar aggregates. Construction of a system with stereoselective cytochrome-P450 biomimetic activity, *Tetrahedron: Asymmetry*, 2004, **15**, 1969–1977, DOI: 10.1016/j.tetasy.2004.05.020.
- 76 M. J. Griffith, M. James, G. Triani, P. Wagner, G. G. Wallace and D. L. Officer, Determining the Orientation and Molecular Packing of Organic Dyes on a TiO₂ Surface Using X-ray Reflectometry, *Langmuir*, 2011, **27**, 12944–12950, DOI: 10.1021/la202598c.
- 77 O. Anatole von Lilienfeld and A. Tkatchenko, Two- and three-body interatomic dispersion energy contributions to binding in molecules and solids, *J. Chem. Phys.*, 2010, **132**, 234109, DOI: 10.1063/1.3432765.
- 78 T. Risthaus and S. Grimme, Benchmarking of London Dispersion-Accounting Density Functional Theory Methods on Very Large Molecular Complexes, *J. Chem. Theory Comput.*, 2013, **9**, 1580–1591, DOI: 10.1021/ct301081n.
- 79 H. Imahori, S. Kang, H. Hayashi, M. Haruta, H. Kurata, S. Isoda, S. E. Canton, Y. Infahsaeng, A. Kathiravan, T. Pascher, P. Chábera, A. P. Yartsev and V. Sundström, Photoinduced Charge Carrier Dynamics of Zn–Porphyrin–TiO₂ Electrodes: The Key Role of Charge Recombination for Solar Cell Performance, *J. Phys. Chem. A*, 2011, **115**, 3679–3690, DOI: 10.1021/jp103747t.