Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

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

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ELECTRONIC SUPPLEMENTARY INFORMATION

Software and methodology – Used basis sets

Zinc all electron basis set (for ZnO):

```
30 8
0 0 8 2.0 1.0
  417016.5    0.00023
   60504.2    0.00192
   12907.9    0.01101
    3375.74   0.04978
    1018.11   0.16918
     352.55   0.36771
     138.19   0.40244
      57.851  0.14386
0 1 6 8.0 1.0
    1079.2   -0.00620   0.00889
     256.52  -0.07029   0.06384
      85.999 -0.13721   0.22039
      34.318  0.26987   0.40560
      14.348  0.59918   0.41370
       4.7769 0.32239   0.34974
0 1 4 8.0 1.0
      60.891  0.00679  -0.00895
      25.082 -0.08468  -0.03333
      10.620 -0.34709   0.08119
       4.3076 0.40633   0.56518
0 1 1 0.0 1.0
       1.6868  1.0 1.0
0 1 1 0.0 1.0
       0.68300 1.0 1.0
0 1 1 0.0 1.0
       0.19000 1.0 1.0
0 3 4 10.0 1.0
      57.345   0.02857
      16.082   0.15686
       5.3493  0.38663
       1.7548  0.47766
0 3 1 0.0 1.0
       0.53100 1.0
```

Original: J. E. Jaffe, A. C. Hess, *Phys. Rev. B.* **1993**, *48*, 7903.
Modified in: F. Labat, I. Ciofini, C. Adamo *J. Chem. Phys.* **2009**, *131*, 044708-1.

Oxygen all electron basis set (for ZnO):

```
8 5
0 0 8 2.0 1.0
 8020.0       0.00108
 1338.0       0.00804
  255.4       0.05324
   69.22      0.1681
   23.90      0.3581
    9.264     0.3855
    3.851     0.1468
    1.212     0.0728
0 1 4 7.0 1.0
   49.43     -0.00883    0.00958
   10.47     -0.0915     0.0696
    3.235    -0.0402     0.2065
    1.217     0.379      0.347
0 1 1 0.0 1.0
    0.442     1.0        1.0
0 1 1 0.0 1.0
    0.160     1.0        1.0
0 3 1 0.0 1.0
    0.600     1.0
```

Original: F. Corá, *Mol. Phys.*, **2005**, *103*, 2483-2496.
Modified in: F. Labat, I. Ciofini, C. Adamo *J. Chem. Phys.* **2009**, *131*, 044708-1.

Zinc pseudopotential basis set (for ZnO):

```
230 5
HAYWLC
0 3 4 10 1.0
      68.8500000        0.0258532000
      18.3200000        0.1651195000
      5.92200000        0.4468212000
      1.92700000        0.5831080000
0 3 1 0 1.0
      0.568038041661          1.0000000000
0 1 1 0. 1.0
     1.74 1. 1.
0 1 1 0. 1.0
  0.939330573804 1. 1.
0 1 1 0. 1.
  0.125427391958 1. 1.
```

Original: a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270, b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 284, c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
Modified in: F. Labat, I. Ciofini, C. Adamo *J. Chem. Phys.* **2009**, *131*, 044708-1.

Oxygen pseudopotential basis set (for ZnO):

```
208 2
BARTHE
0 1 3 8. 1.
  19.591534  0.003424  0.036496
  4.432019  -0.189923  0.204118
  1.129740   0.593574  0.522515
0 1 1 0. 1.
  0.281551480361    1.0    1.0
```

Original: a) P. Durand, J.-C. Barthelat, *Theor. Chim. Acta*, **1975**, *38*, 283, b) J.-C. Barthelat, P. Durand, *Gazz. Chim. Ital.*, **1978**, *108*, 225. c) J. C. Barthelat, P. Durand, A. Serafini, *Mol. Phys.*, **1977**, *33*, 159.
Modified in: F. Labat, I. Ciofini, C. Adamo *J. Chem. Phys.* **2009**, *131*, 044708-1.

Oxygen all electron basis set (for porphyrin):

```
8 5
0 0 8 2.0 1.0
 8020.0       0.00108
 1338.0       0.00804
  255.4       0.05324
   69.22      0.1681
   23.90      0.3581
    9.264     0.3855
    3.851     0.1468
    1.212     0.0728
0 1 4 6.0 1.0
   49.43     -0.00883    0.00958
   10.47     -0.0915     0.0696
    3.235    -0.0402     0.2065
    1.217     0.379      0.347
0 1 1 0.0 1.0
    0.475960     1.0        1.0
0 1 1 0.0 1.0
    0.164585     1.0        1.0
0 3 1 0.0 1.0
    0.887339     1.0
```

Original: F. Corá, *Mol. Phys.*, **2005**, *103*, 2483-2496.
Modified in: F. Labat, I. Ciofini, C. Adamo *J. Chem. Phys.* **2009**, *131*, 044708-1.

Nitrogen all electron basis set (for porphyrin):

```
7 4
0 0 6 2.0 1.0
 4150.0     0.001845
  620.1     0.01416
  141.7     0.06863
   40.34    0.2286
   13.03    0.4662
    4.47    0.3657
0 1 2 5.0 1.0
    5.425 -0.4133 0.238
    1.149  1.224  0.859
0 1 1 0.0 1.0
    0.2832 1.0    1.0
0 3 1 0.0 1.0
    0.8    1.0    1.0
```

R. Dovesi, M. Causa, R. Orlando, C. Roetti, *J. Chem*. Phys **1990**, *92*, 7402-7411.

Carbon all electron basis set (for porphyrin):

```
6 4
0 0 6 2.0 1.0
 3048.0     0.001826
  456.4     0.01406
  103.7     0.06876
   29.23    0.2304
    9.349   0.4685
    3.189   0.3628
0 1 2 4.0 1.0
    3.665 -0.3959 0.2365
    0.7705 1.216  0.8606
0 1 1 0.0 1.0
    0.1959   1.0    1.0
0 3 1 0.0 1.0
    0.8    1.0
```

R. Dovesi, M. Causa, R. Orlando, C. Roetti, *J. Chem*. Phys **1990**, *92*, 7402-7411.

Hydrogen all electron basis set (for porphyrin):

```
1 4
0 0 5 1.0 1.0
 120.0     0.000267
  40.0     0.002249
  12.8     0.006389
   4.0     0.032906
   1.2     0.095512
0 0 1 0.0 1.0
   0.5     1.0
0 0 1 0.0 1.0
   0.13    1.0
0 2 1 0.0 1.0
   0.3     1.0
```

R. Dovesi, E. Ermondi, E. Ferrero, C. Pisani, C. Roetti *Phys. Rev. B*, **1983**, *29*, 3591-3600.

Software and methodology – Parameters used in CRYSTAL calculations

FINALRUN 4 option was used to ensure completely optimized structures. Larger than normal grid (LGRID) and TOLINTEG 7 7 7 7 14 keyword corresponding to extra fine integration (truncation of Coulomb and exchange series) were used, and additionally FMIXING values up to 90 were used to help in convergence.

In the calculations of bulk ZnO wurtzite, ZnO $(10\bar{1}0)$ surface and (2 × 3) supercell containing single absorbed 4-(porphyrin-5-yl)benzoic acid on the surface Monkhorst–Pack grids containing 50 k-points (corresponding to SHRINK 8 16), 34 k-points (SHRINK 8 16) and 10 k-points (SHRINK 4 8) in the irreducible part of the Brillouin zone (IBZ) were used, respectively.

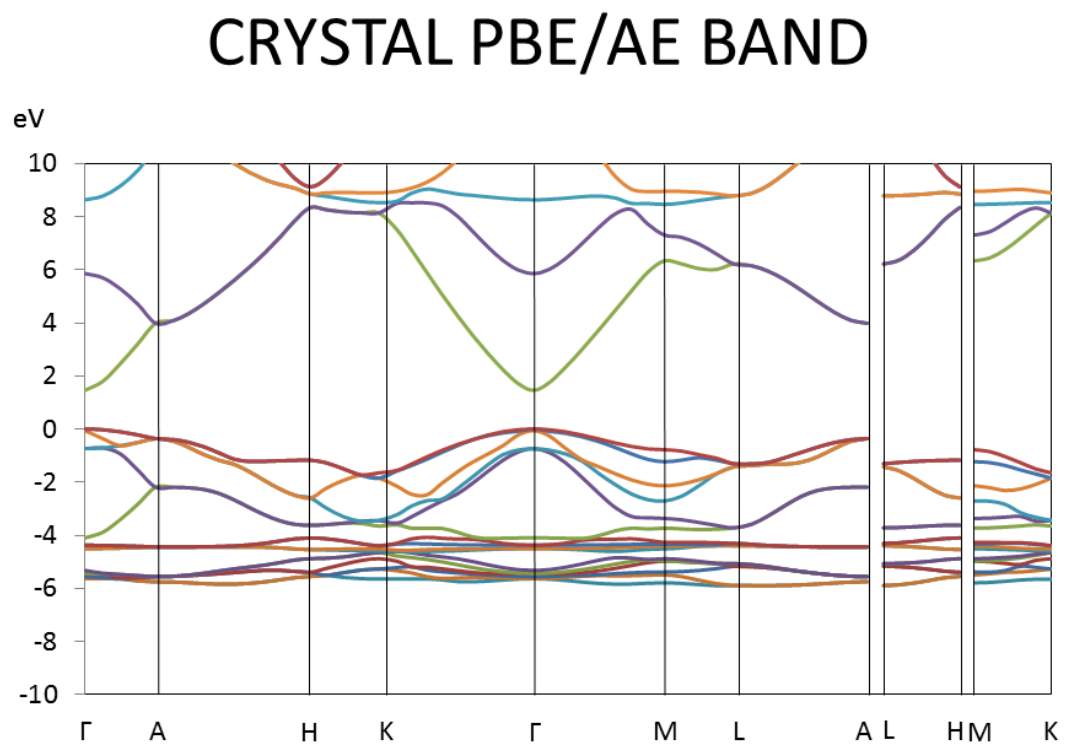
In calculations with adsorbate on the ZnO surface Grimme's D2 dispersion correction scheme was used with PBE0 functional using the following parameters:

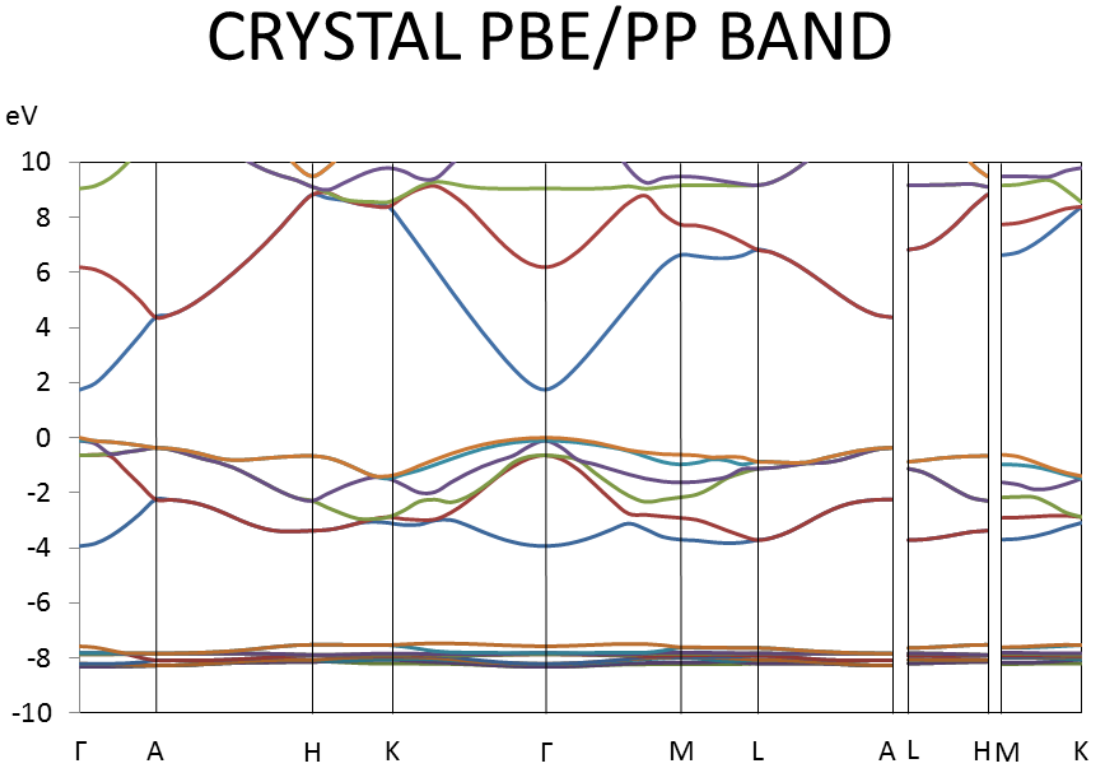
Scaling factor 0.60
Steepness 20
Cutoff distance to truncate direct lattice summation 25

Table S1: Used dispersion coefficients (Jnm^6mol^{-1}) and van der Waals radii (Å).

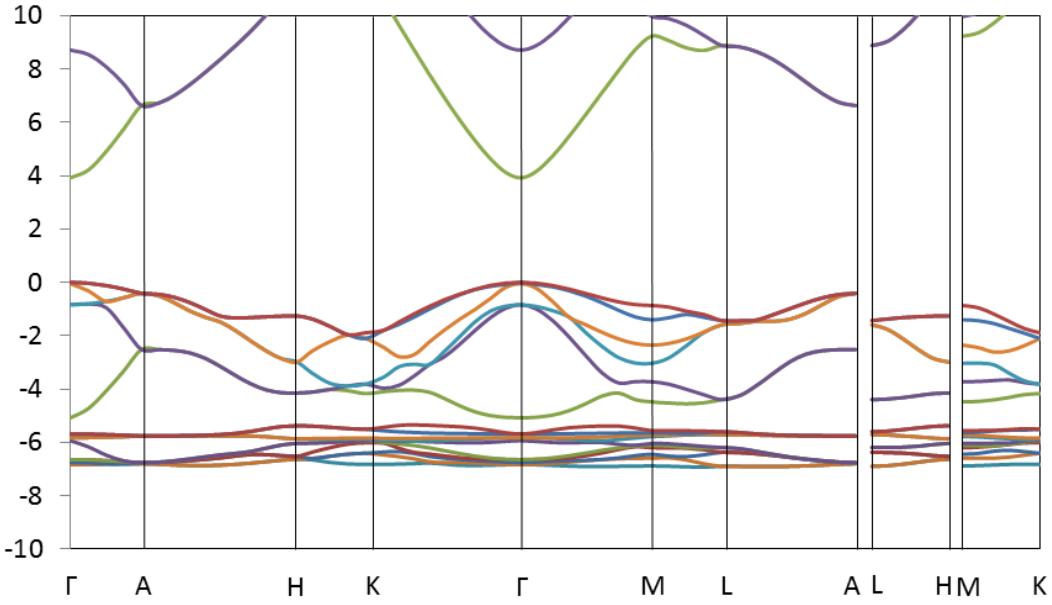
	dispersion coefficient	van der Waals radius
H	0.14	1.001
C	1.75	1.452
N	1.23	1.397
O	0.70	1.342
Zn	10.80	1.562

ZnO wurtzite bulk – BAND and DOS plots

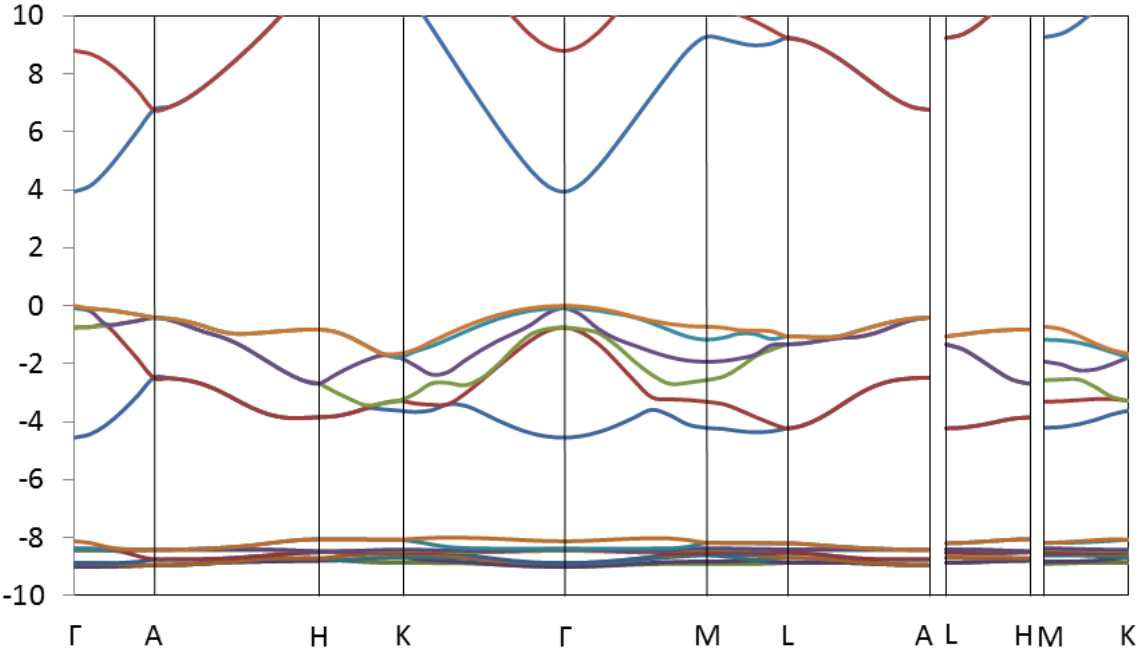




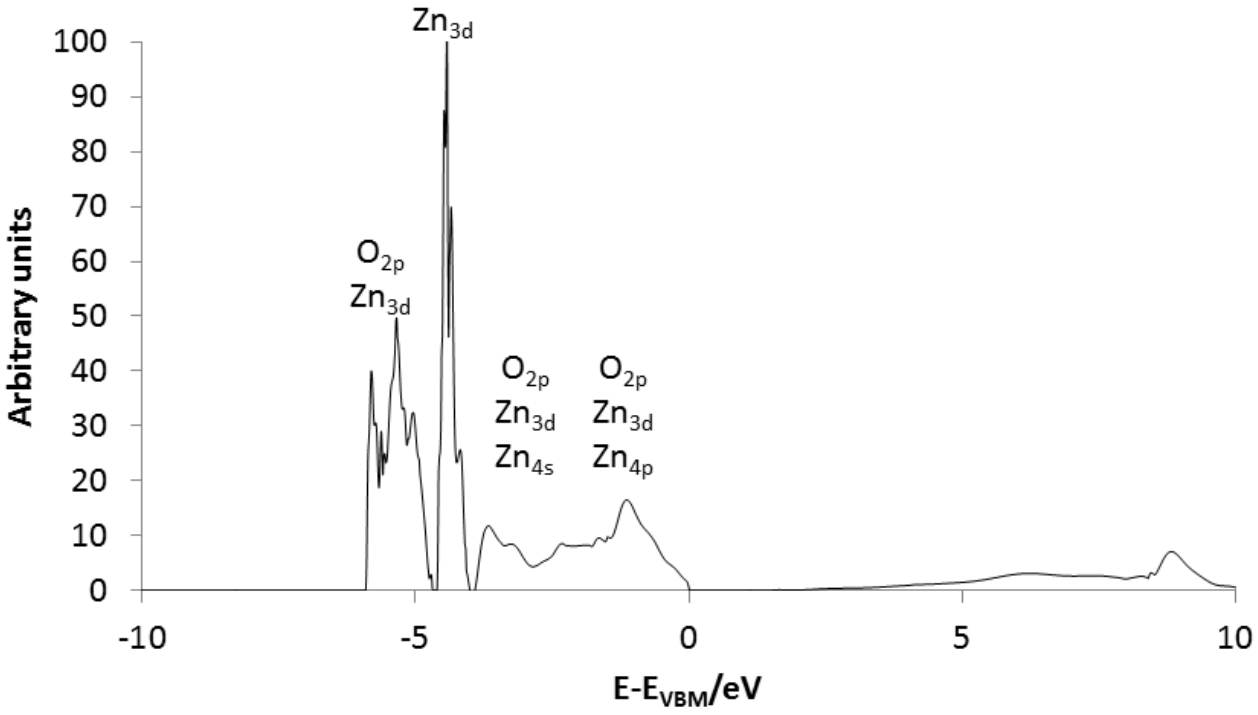
CRYSTAL PBE0/AE BAND



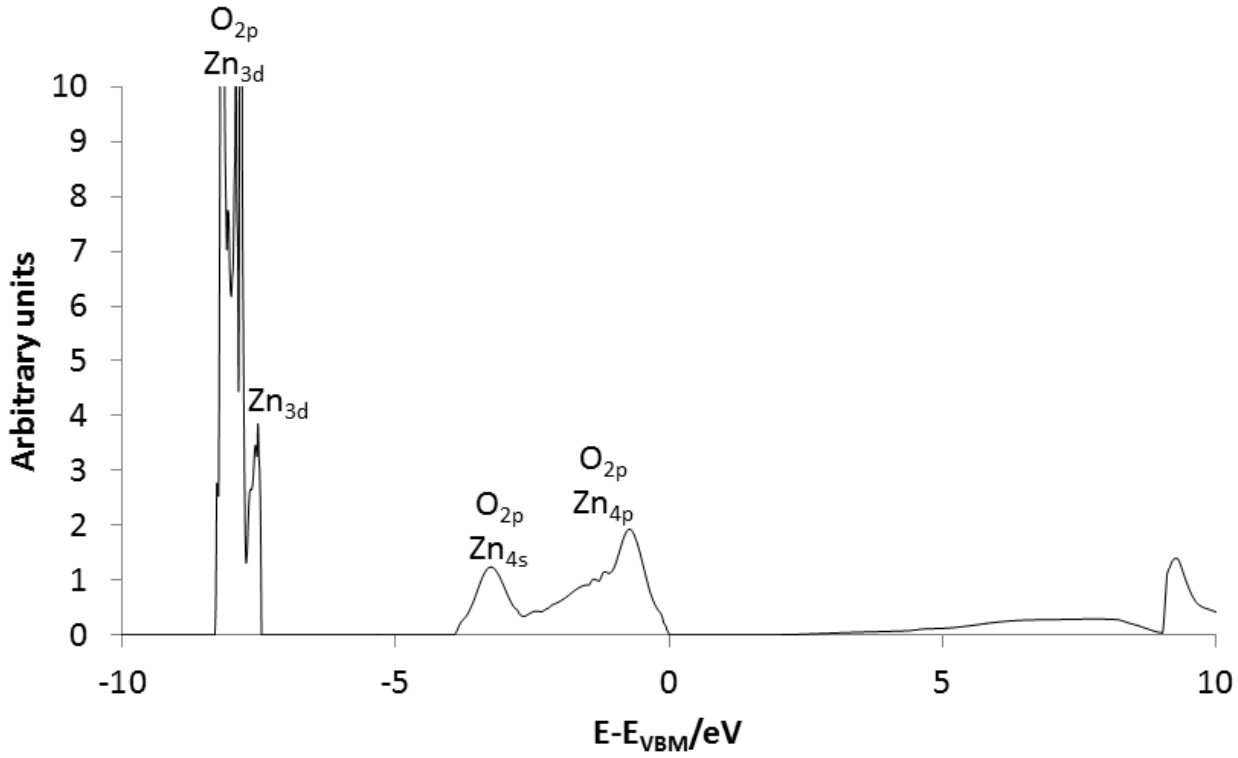
CRYSTAL PBE0/PP BAND



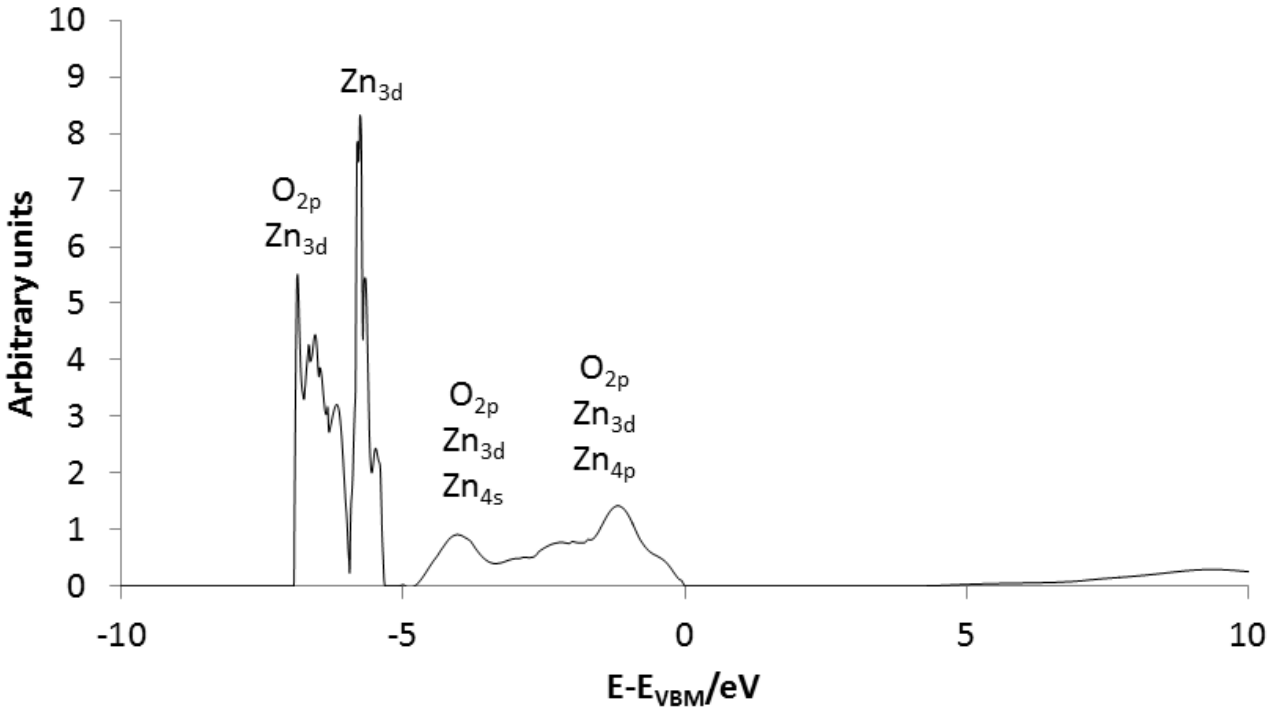
CRYSTAL PBE/AE DOS



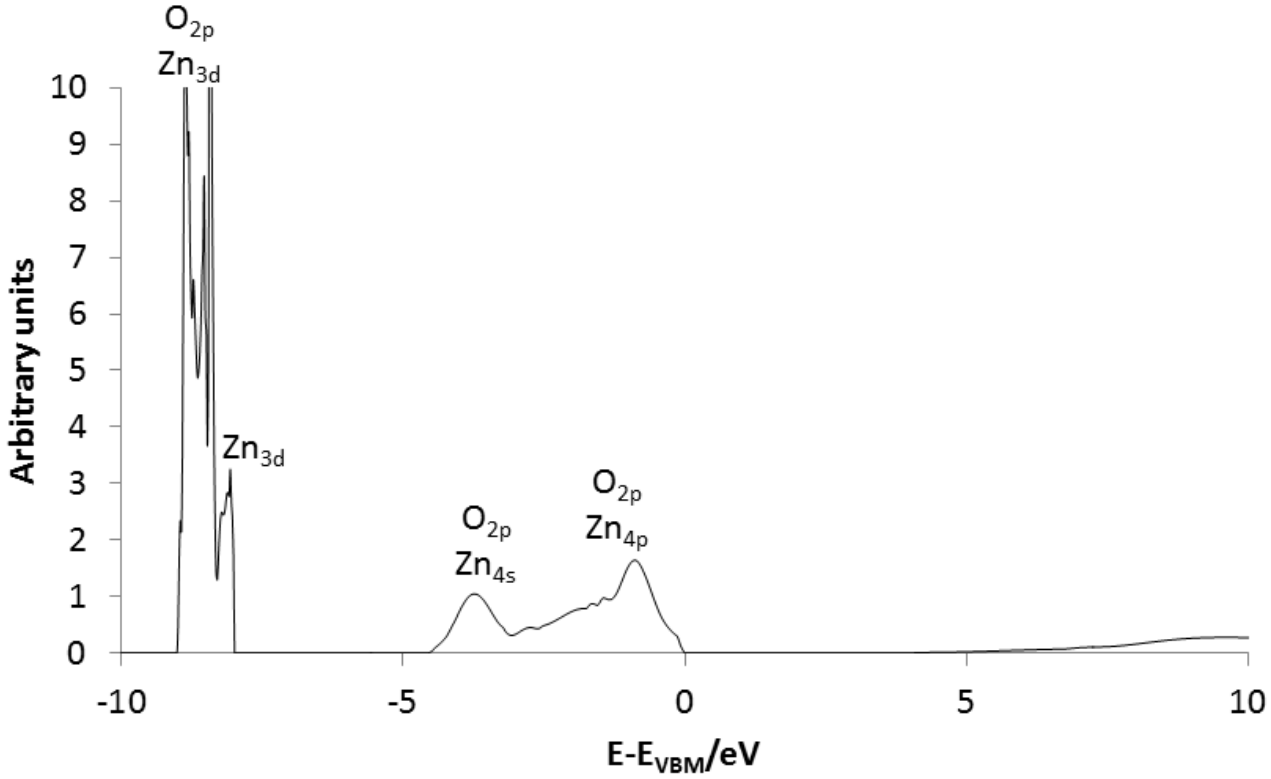
CRYSTAL PBE/PP DOS



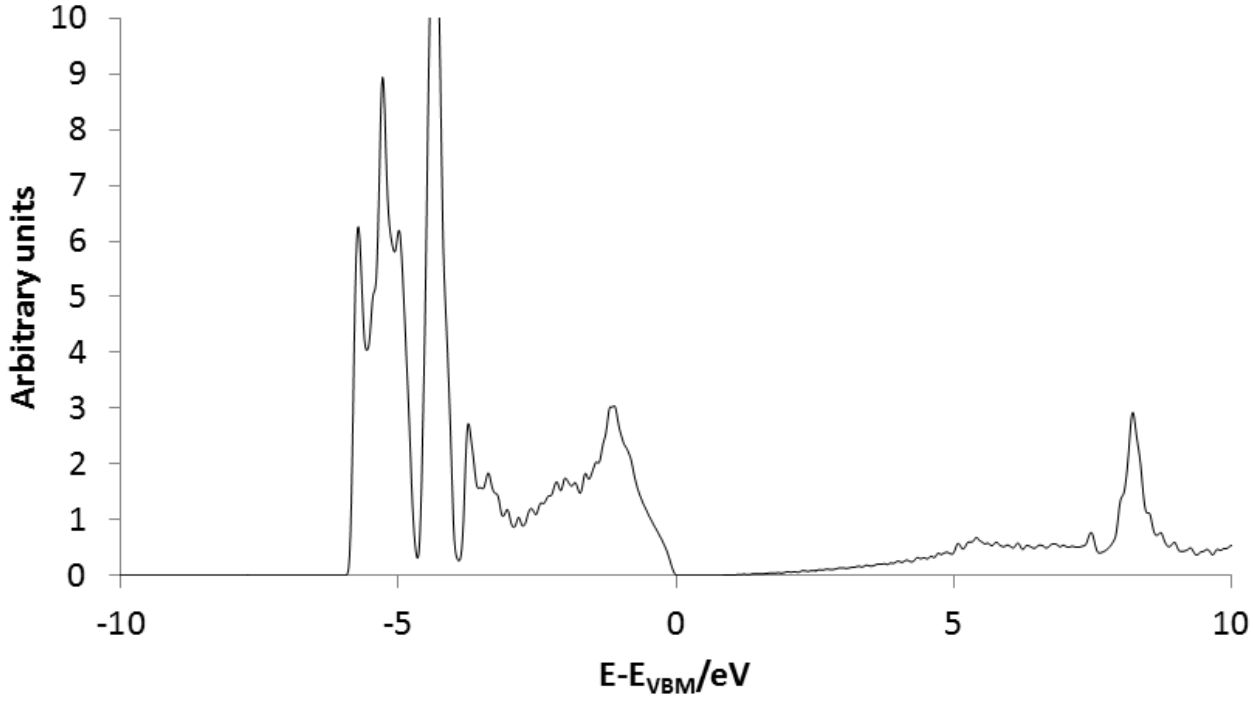
CRYSTAL PBE0/AE DOS



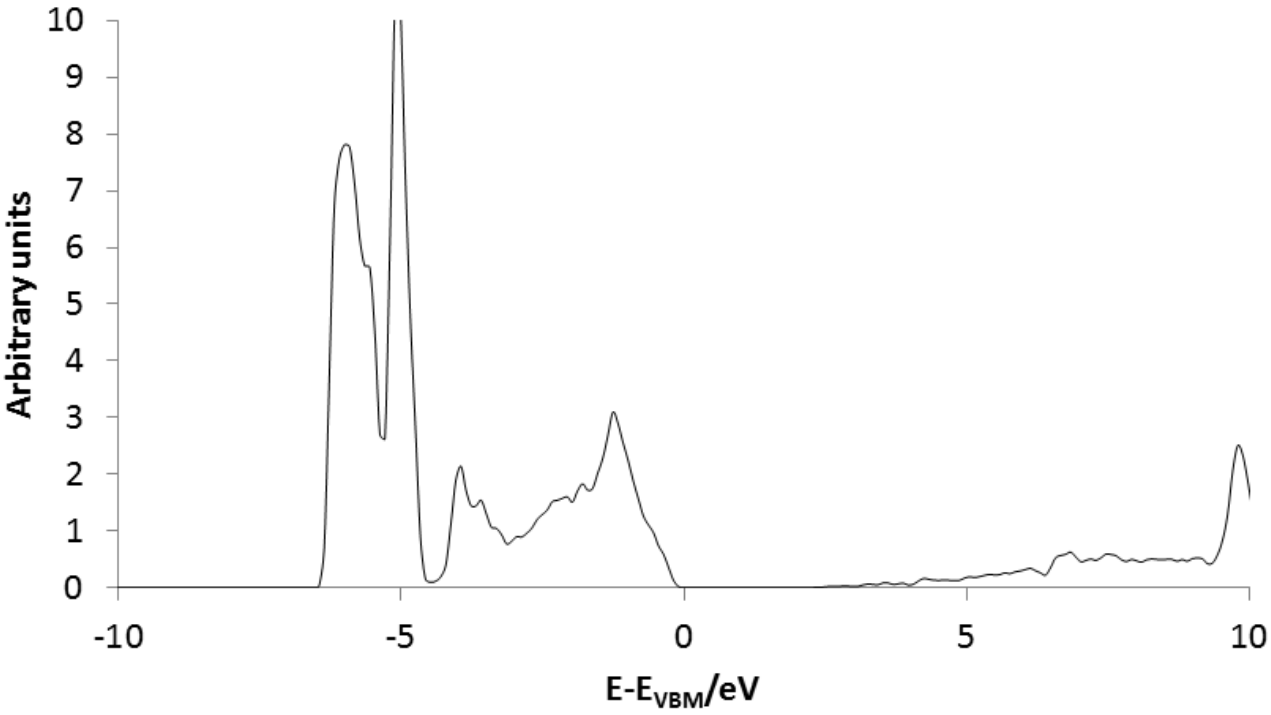
CRYSTAL PBE0/PP DOS



GPAW PBE DOS



GPAW GLLB-SC DOS



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

The change in atom coordinates due to surface relaxation is presented in Table S2. The x-coordinate did not change noticeably. With all the methods the relaxation is strongest for the surface Zn ion. During the relaxation the Zn ion moves towards the center of the slab and closer to the nearby surface oxygen. The relaxation is stronger with all-electron basis set than with pseudopotential basis set.

TableS2. Relaxation of the surface layers (Å)

atom #	PBE_PP		PBE_AE	
	Δy	Δz	Δy	Δz
1 (O)	+0.011	-0.077	+0.073	-0.004
2 (Zn)	+0.149	-0.258	+0.246	-0.371
3 (Zn)	+0.008	+0.040	+0.039	+0.093
4 (O)	-0.005	-0.009	+0.033	-0.027
5 (O)	+0.003	-0.015	+0.020	+0.006
6 (Zn)	+0.018	-0.042	+0.033	-0.063

atom #	PBE0_PP		PBE0_AE	
	Δy	Δz	Δy	Δz
1 (O)	0	-0.093	+0.053	-0.038
2 (Zn)	+0.136	-0.247	+0.212	-0.336
3 (Zn)	+0.010	+0.039	+0.033	+0.080
4 (O)	-0.001	-0.009	+0.032	-0.023
5 (O)	+0.002	-0.017	+0.015	-0.003
6 (Zn)	+0.016	-0.041	+0.028	-0.061

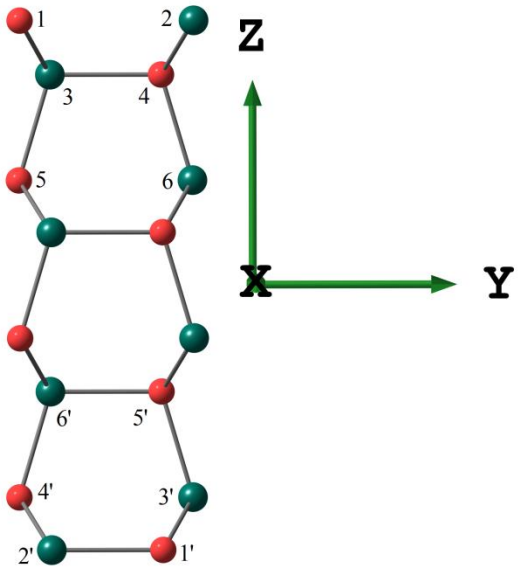


Figure S1. Surface model atom numbering and axes. The Z axis is nonperiodic direction.

Porphyrin adsorbed via the COO^- anchor group on the ZnO $(10\bar{1}0)$ surface – Surface packing

In addition to 1/3 surface packing the more densely packed surface with coverage of 1/2 and sparse surface with coverage of 1/6 have been analyzed. The 1/2 coverage has been studied with geometry optimizations of the adsorbate and the top two ZnO surface layers using PBE0 density functional. Optimizations of the 1/6 coverage model converged slowly so we took the geometry for the adsorbate from the 1/3 surface coverage model and studied the model using single point calculations.

In the 1/2 packed surface in the non-twisted orientation the porphyrin adsorbate is standing in ca. 75 degree angle on the surface and cannot tilt closer to the surface due to close packing of adsorbates. We did not calculate the twisted orientation but it is likely that the porphyrins tilt somewhat in this orientation. However, the porphyrin–surface interactions cannot be as strong as in 1/3 packing as the benzoate linker in next porphyrin prevents tilting down to the surface.

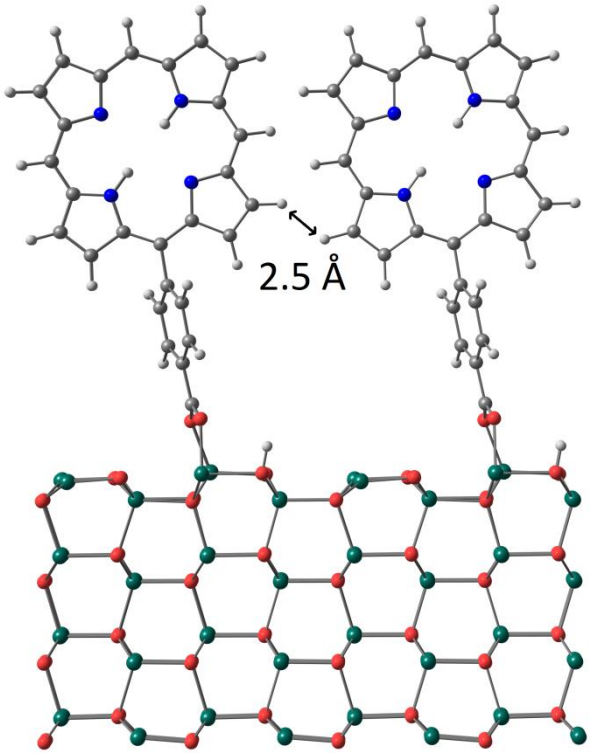
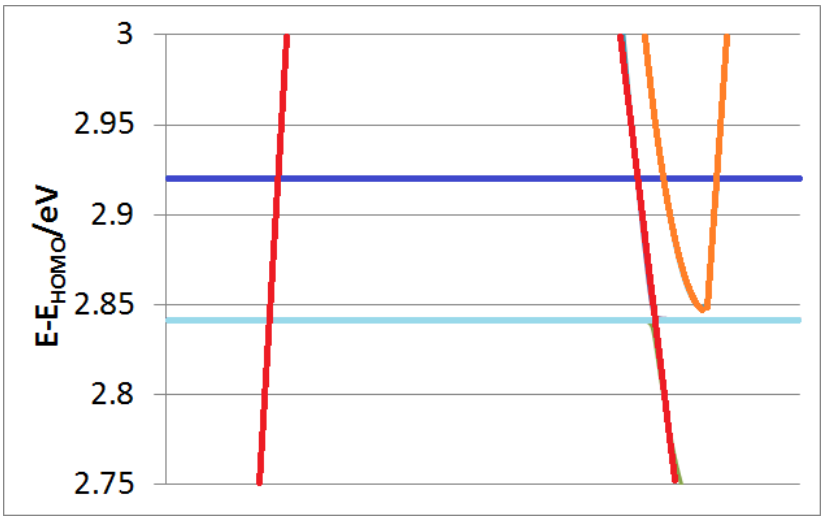


Figure S2. Adsorbate packing in 1/2 surface coverage, non-twisted orientation

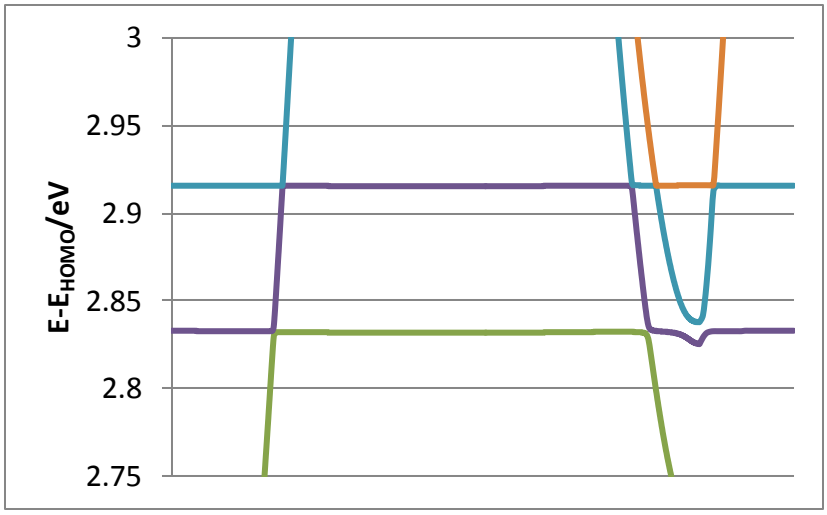
In 1/6 surface coverage model the porphyrin is likely to tilt on the surface because this is already possible with 1/3 coverage. However, in this packing the broadening of porphyrin HOMO-1, HOMO, LUMO and LUMO+1 that was seen in twisted orientation in 1/3 packing disappears. This means that there are no porphyrin-porphyrin interactions or they are very weak. (porphyrin-porphyrin interactions in band structure with 1/3 packing can be seen in ESI section "Samples of magnified porphyrin LUMO bands, ZnO conduction bands and porphyrin HOMO bands (path Γ-X-S-Y-Γ)".

Porphyrin adsorbed via the COO^- anchor group on the ZnO $(10\bar{1}0)$ surface – Samples of magnified porphyrin LUMO bands, ZnO conduction bands and porphyrin HOMO bands (path Γ-X-S-Y-Γ)



KEY:
light blue – porphyrin LUMO
dark blue – porphyrin LUMO+1
red – ZnO conduction band
orange – ZnO conduction band+1

The measured coupling strengths are always from the first porphyrin LUMO/LUMO+1 and ZnO conduction band avoided crossing because the ZnO conduction band +1 sometimes pushes down the porphyrin LUMO at the second avoided crossing

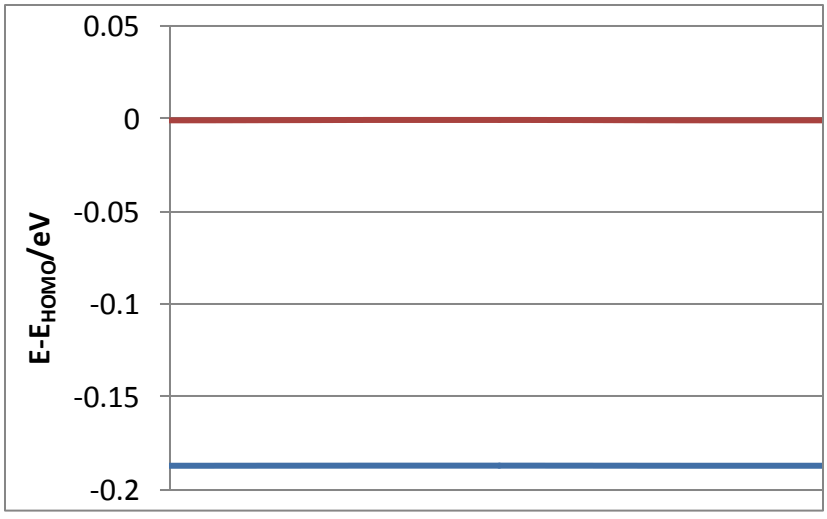


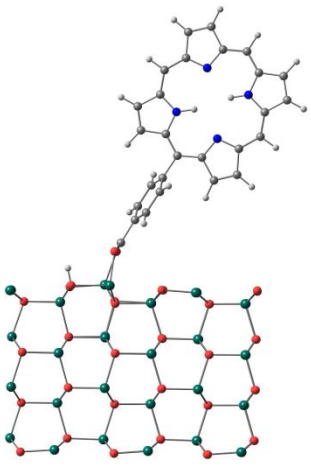
Sample1:
"untwisted" porphyrin
5.4 Å porphyrin–surface distance

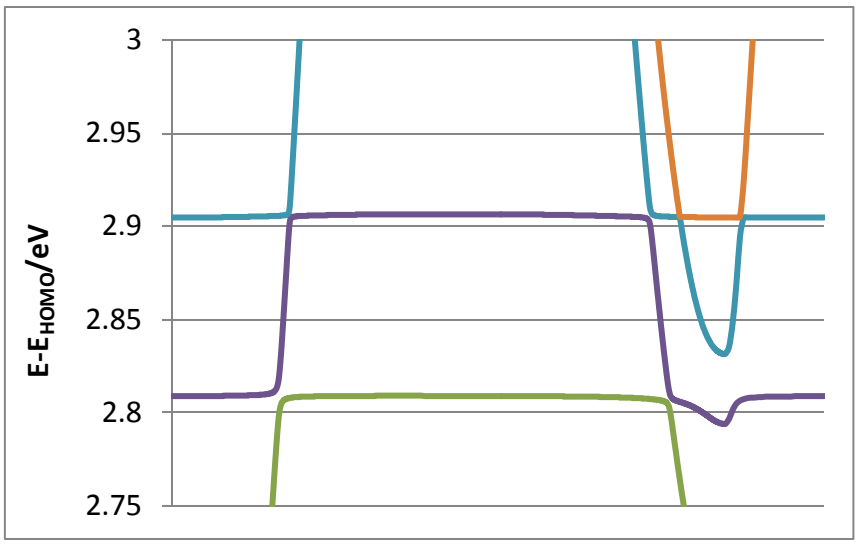
measured coupling strength
0.006 eV

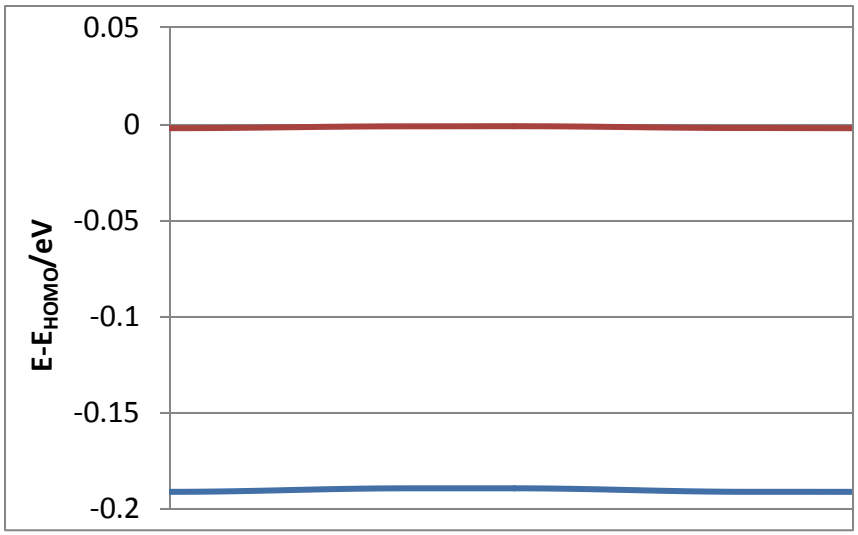
The ZnO conduction band+1 causes a "dent" in porphyrin LUMO as well

The HOMO and HOMO-1 levels are straight







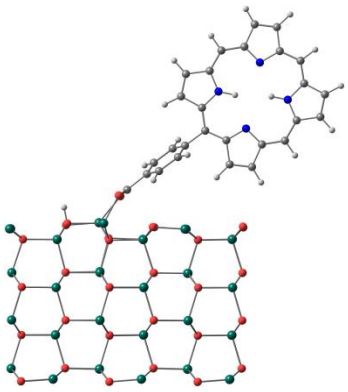


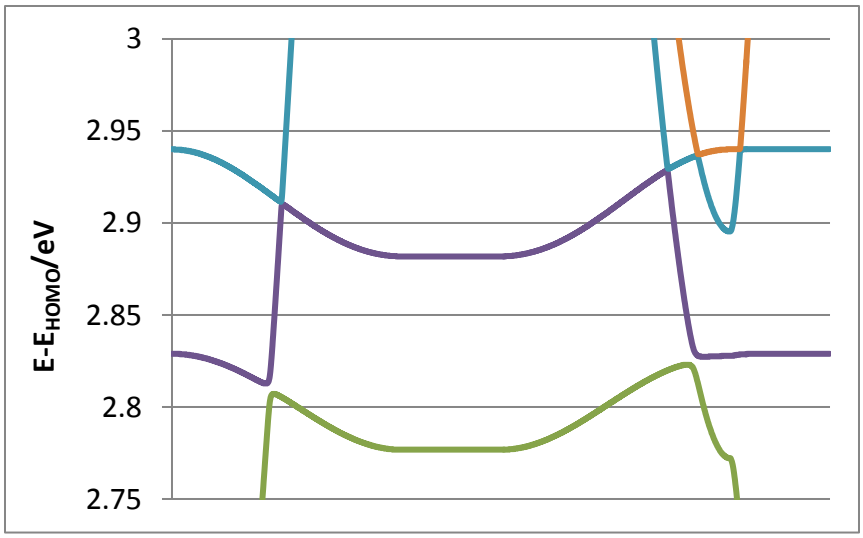
Sample 2:
"untwisted" porphyrin
2.6 Å porphyrin–surface distance

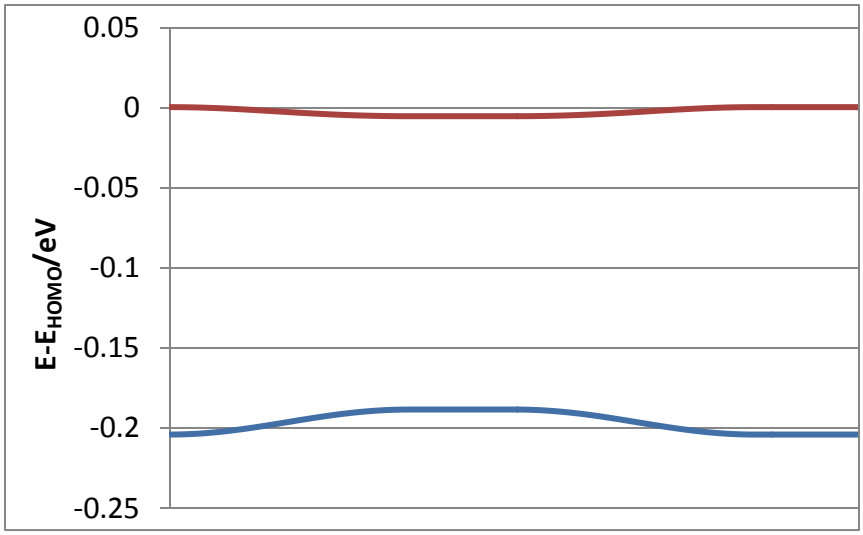
measured coupling strength 0.020 eV

The ZnO conduction band+1 causes deeper "dent" in porphyrin LUMO as well

The HOMO and HOMO-1 levels are not completely straight





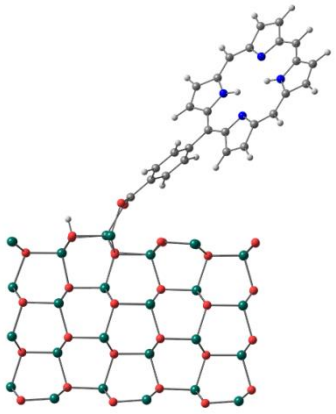


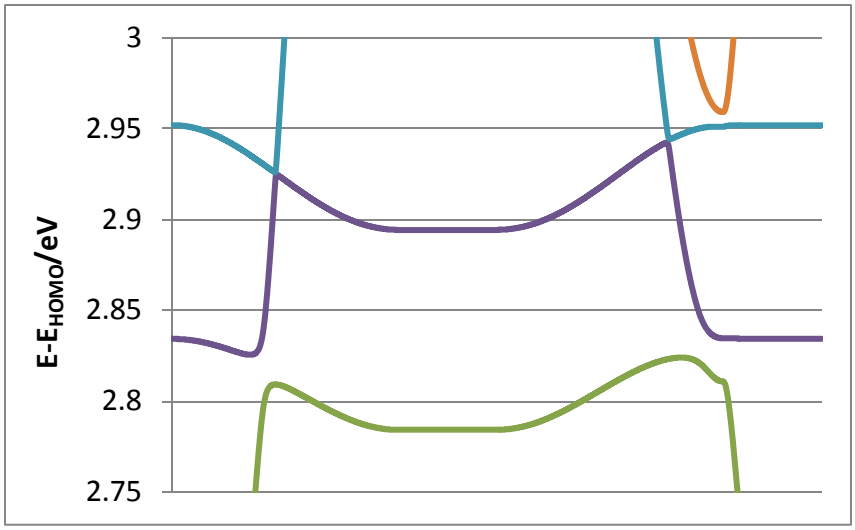
Sample 3:
"twisted" porphyrin
5.0 Å porphyrin–surface distance

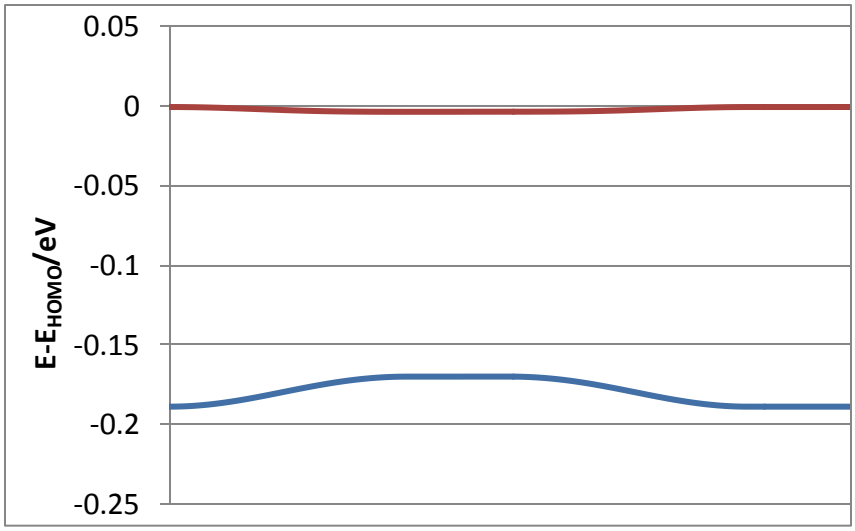
measured coupling strength 0.014 eV

The porphyrin bands curve due to porphyrin–porphyrin interactions

Porphyrin LUMO+1 band is less affected by tilting than porphyrin LUMO





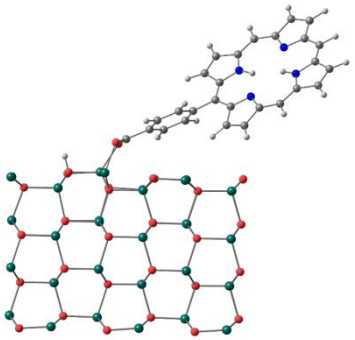


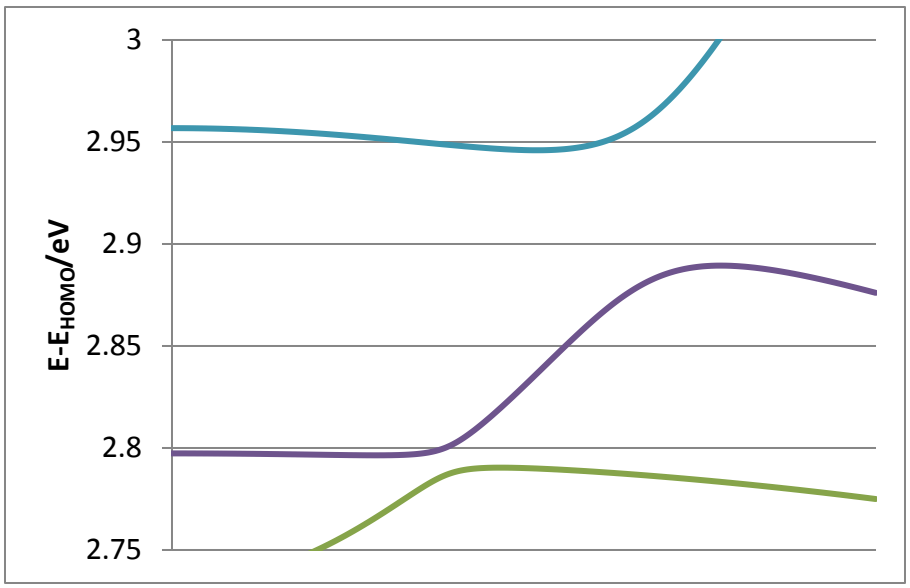
Sample 4:
"twisted" porphyrin
2.8 Å porphyrin–surface distance

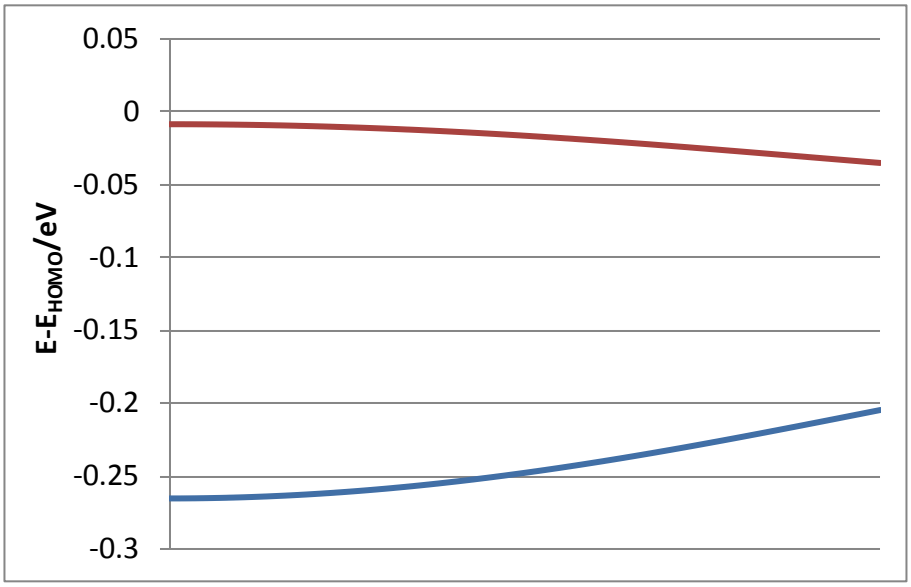
measured coupling strength 0.043 eV

The porphyrin bands curve due to porphyrin–porphyrin interactions

Porphyrin LUMO+1 band is less affected by tilting than porphyrin LUMO







Sample 5:
"Relaxed twisted" porphyrin 2.3 Å porphyrin–surface distance (part of path Γ-X)

measured coupling strength 0.079 eV (Cond&LUMO+1)

The porphyrin bands curve due to porphyrin–porphyrin interactions

Porphyrin LUMO+1 band interacts strongly with the surface.