Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for Computational Screening of Functionalized Zinc Porphyrins for Use in Dye Sensitized Solar Cells

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Table S1 gives a comparison between GPAW[1–3] and Gaussian09[4] calculated E_{HOMO}, E_{LUMO} and E_{gap} with the PBE[5;6] and B3LYP[7–9] functionals for the [H,H,H]-zinc porhyrin with the EthynPhA anchor group. For the Gaussian09 calculation the standard 6-311+G(d,p) Pople basis set has been used.[10–14] All calculations are based on the GPAW optimized geometry. The main differences between the two codes are the inclusion of core electrons in the Gaussian09 calculations and the use of the projector augmented-wave method in GPAW. Furthermore, the Gaussian09 calculations have been carried out using a triple-ζ basis set including polarization and diffuse functions as compared to the double-ζ basis set with polarization functions used in GPAW.

Table S1: Comparison of different methods to calculate E_{HOMO}, E_{LUMO} and E_{gap} for the [H,H,H]-zinc porhyrin with the EthynPhA anchor group. All calculations are based on the GPAW optimized geometry

Method	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
GPAW PBE	-6.53	-1.57	4.96
Gaussian09 PBE	-6.65	-1.75	4.90
Gaussian09 B3LYP	-6.70	-1.74	4.97

A comparison between values for E_{HOMO} (Figure S1), E_{gap} (Figure S2) and E_1 (Figure S3) for 60 various dye candidates calculated at the PBE (GGA) and B3LYP (hybrid) levels of theory is given to ensure that our chosen level of theory is acceptable. The PBE results have been calculated using GPAW and the B3LYP results have been calculated using the all-electron ADF code with a double-ζ Slater-type basis set with polarization functions.[15]

Table S2 furthermore gives a comparison between GPAW PBE and Molpro[16] CCSD(T)[17;18]/aug-cc-pVTZ[19] calculated E_{HOMO}, E_{LUMO} and E_{gap} for the bare zinc porphyrin. In contrast to Density Functional Theory, Coupled-Cluster is a high-end wave function method giving very accurate energies. However, the computational cost of Coupled-Cluster calculations are extremely high and thus only the simplest molecule has been investigated using Coupled-Cluster and used for validation of the Density Functional Theory results.

A comparison between singlet and triplet ΔSCF is given in Table S3.[20]

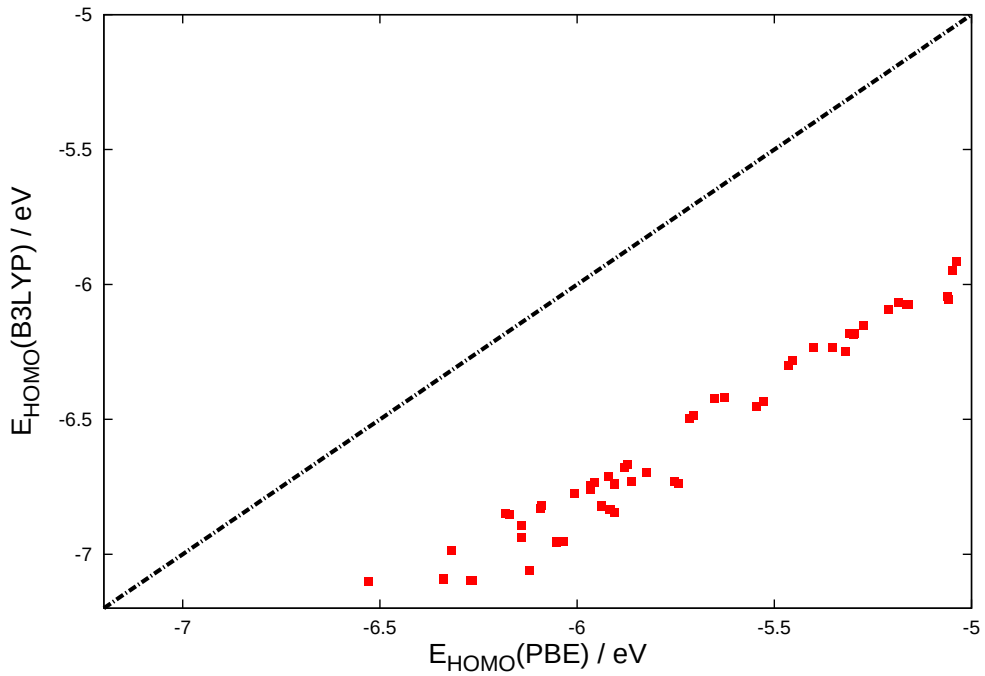

Figure S1: Comparison of E_{HOMO} values for various zinc porphyrins calculated at the PBE and B3LYP levels of theory.

Table S2: Comparison of different methods to calculate E_{HOMO}, E_{LUMO} and E_{gap} for the bare zinc porhyrin. All calculations are based on the GPAW optimized geometry

Method	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
GPAW PBE	-6.79	-1.35	5.43
CCSD(T)	-6.73	-1.09	5.64

The standard ASTM G-173-03 (AM 1.5 G) solar spectrum is given in Figure S4.

A Visualization of the HOMOs (top) and LUMOs (bottom) for zinc [H,H,H]-porphyrin (left), zinc [DMP, DMP, DMP]-porphyrin (middle) and zinc [DTA, DTA, DTA]-porphyrin (right) respectively is given in Figure S5. In the figure all dyes are functionalized with the EthynPhA anchor group.

A visual comparison between E_1 values for zinc porphyrins with the EthynPhA (red cross), 2CarboxyPropenA (green x) and 2CyanoPropenA (blue star) anchor groups calculated using the triplet ΔSCF method and E_{gap} is given in Figure S6.

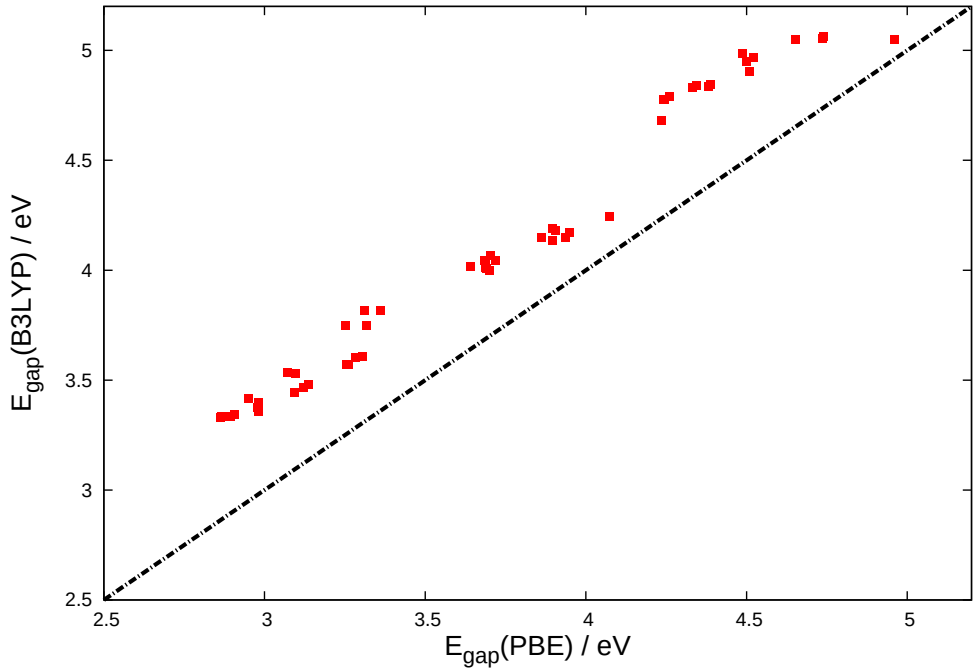

Figure S2: Comparison of E_{gap} values for various zinc porphyrins calculated at the PBE and B3LYP levels of theory.

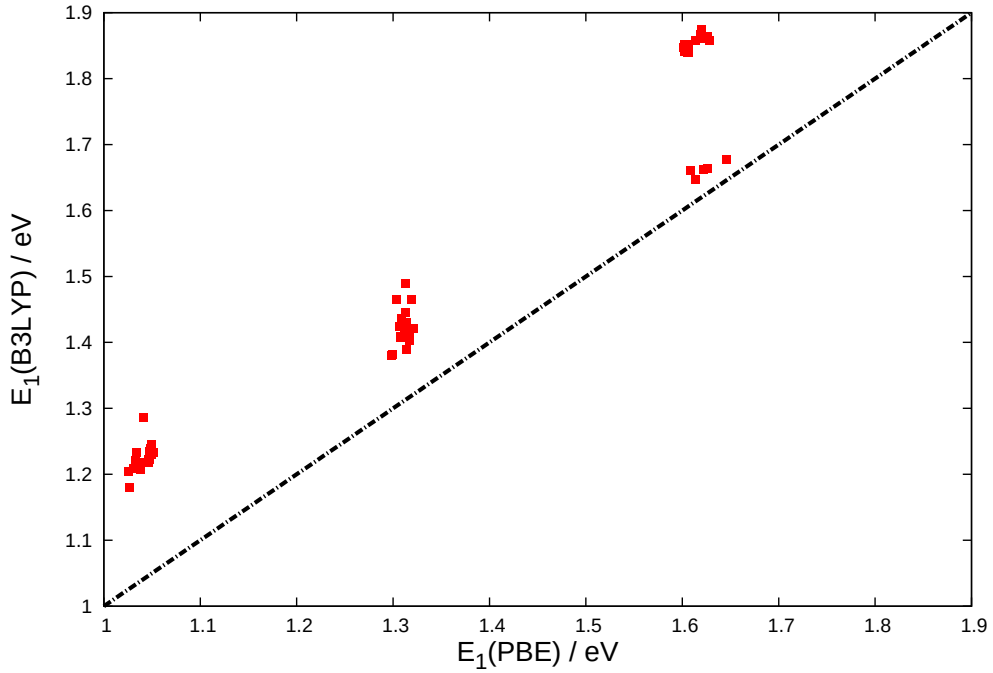

Figure S3: Comparison of E_1 values for various zinc porphyrins calculated at the PBE and B3LYP levels of theory.

Table S3: Comparison between singlet and triplet ΔSCF[20] for different zinc porhyrins

A	R1	R2	R3	E_1^{triplet} (eV)	E_1^{singlet} (eV)
EthynPhA	H	H	H	1.65	1.97
EthynPhA	TPA	H	TPA	1.54	1.76
EthynPhA	TPA	TPA	TPA	1.41	1.63
EthynPhA	MOTPA	H	MOTPA	1.49	1.70
EthynPhA	MOTPA	MOTPA	MOTPA	1.35	1.56
EthynPhA	TPA	TMP	TPA	1.46	1.67
2CyanoPropenA	MOTPA	DTA	MOTPA	1.01	1.06

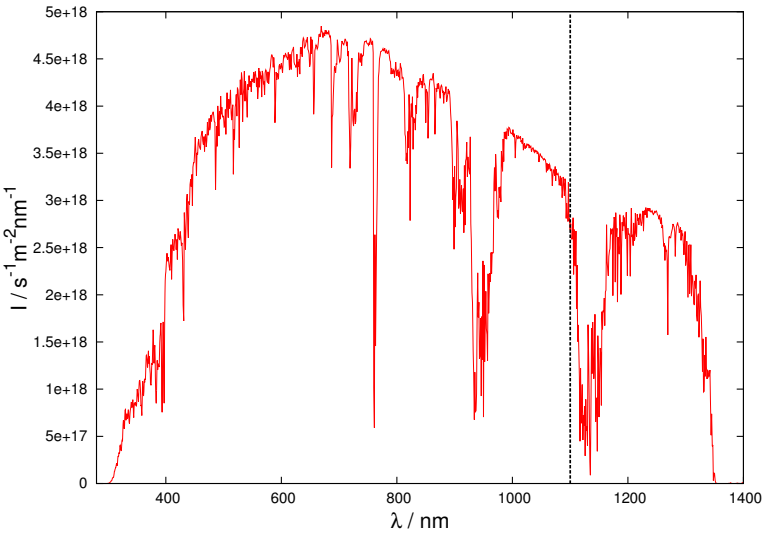

Figure S4: The standard ASTM G-173-03 (AM 1.5 G) solar spectrum. The dotted line indicates the approximately optimal value of the optical gaps E_1.

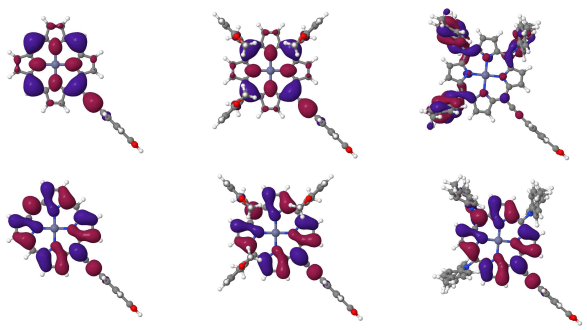

Figure S5: Visualization of the HOMOs (top) and LUMOs (bottom) for zinc [H,H,H]-porphyrin (left), zinc [DMP, DMP, DMP]-porphyrin (middle) and zinc [DTA, DTA, DTA]-porphyrin (right) respectively. All with the EthynPhA group as anchor group.

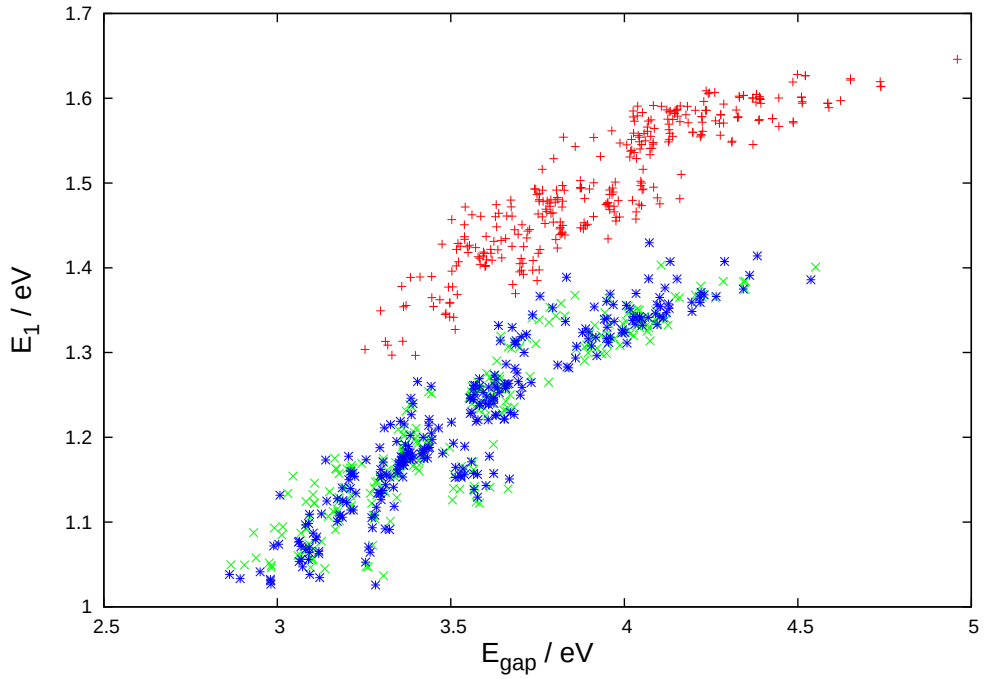

Figure S6: E_1 values for zinc porphyrins with the EthynPhA (red cross), 2CarboxyPropenA (green x) and 2CyanoPropenA (blue star) anchor groups calculated using the triplet ΔSCF method vs E_{gap}.

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