Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for Optimizing Porphyrins for Dye Sensitized Solar Cells using Large-Scale Ab-initio Calculations

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Table S1: Largest and smallest E_{HOMO}, E_{LUMO}, E_{gap} and E_1 values obtained in the screening

Backbone	A	R1	R2	R3	E_{HOMO}	E_{LUMO}	E_{gap}	E_1
H_2P	EthynPhA	MOTPA	MOTPA	MOTPA	-4.94[a]	-1.76	3.18	1.21
FZnP	2CyanoPropenA	F	F	F	-7.21[b]	-2.41	4.80	1.54
ZnP	EthynPhA	TMP	TMP	TMP	-5.54	-1.46[a]	4.08	1.59
FZnP	2CyanoPropenA	F	DTA	F	-6.26	-2.74[b]	3.52	1.07
ZnP	EthynPhA	H	H	H	-6.53	-1.57	4.96[a]	1.65
FZnP	2CarboxyPropenA	DTA	MOTPA	MOTPA	-5.15	-2.58	2.57[b]	0.97
FZnP	2CyanoPropenA	DTBP	DTBP	DMP	-6.51	-2.24	4.26	1.65[a]
TiO_2BAP	2CyanoPropenA	DTA	DTA	MOTPA	-5.38	-2.66	2.72	0.90[b]

[a] Largest value of all candidates.
[b] Smallest value of all candidates.

Table S2: Statistics for E_{LUMO} values as the side groups are changed but the anchor group retained. $\langle E_{\mathrm{LUMO}} \rangle$ is the mean value, $\sigma = \sqrt{\langle E_{\mathrm{LUMO}}^2 \rangle - \langle E_{\mathrm{LUMO}} \rangle^2}$ is the standard deviation and RSD = $\frac{\sigma}{|\langle E_{\mathrm{LUMO}} \rangle|} \cdot 100\%$ is the relative standard deviation

Backbone	A	$\langle E_{\mathrm{LUMO}} \rangle$ (eV)	σ (eV)	RSD (%)
Zn	EthynPhA	-1.70	0.09	5.13
Zn	2CarboxyPropenA	-2.26	0.07	3.08
Zn	2CyanoPropenA	-2.26	0.08	3.40
TiO	EthynPhA	-1.86	0.09	4.58
TiO	2CarboxyPropenA	-2.38	0.07	2.96
TiO	2CyanoPropenA	-2.38	0.08	3.32
H2	EthynPhA	-1.77	0.09	4.93
H2	2CarboxyPropenA	-2.32	0.07	3.14
H2	2CyanoPropenA	-2.34	0.07	3.06
TiO2R	EthynPhA	-2.11	0.07	3.25
TiO2R	2CarboxyPropenA	-2.52	0.09	3.61
TiO2R	2CyanoPropenA	-2.50	0.13	5.03
FZn	EthynPhA	-2.08	0.09	4.49
FZn	2CarboxyPropenA	-2.51	0.08	3.19
FZn	2CyanoPropenA	-2.49	0.10	4.14

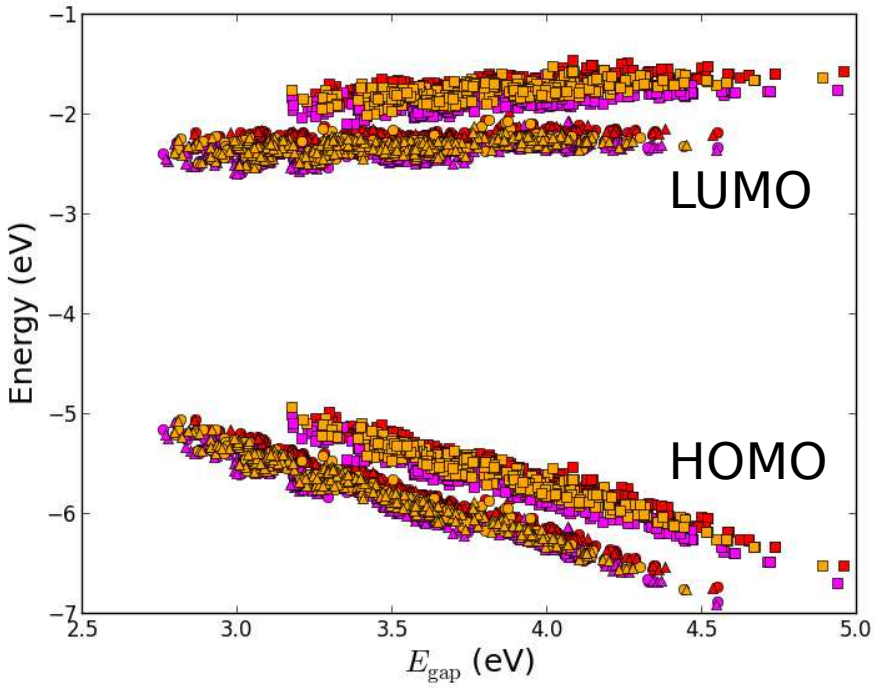

Figure S1: Calculated E_{HOMO} and E_{LUMO} relative to vacuum ordered by the resulting E_{gap} of functionalized porphyrins with the ZnP (red), H_2P (orange) and TiOP (magenta) backbones and the EthynPhA (square), 2CarboxyPropenA (circle) and 2CyanoPropenA (triangle) anchor groups.

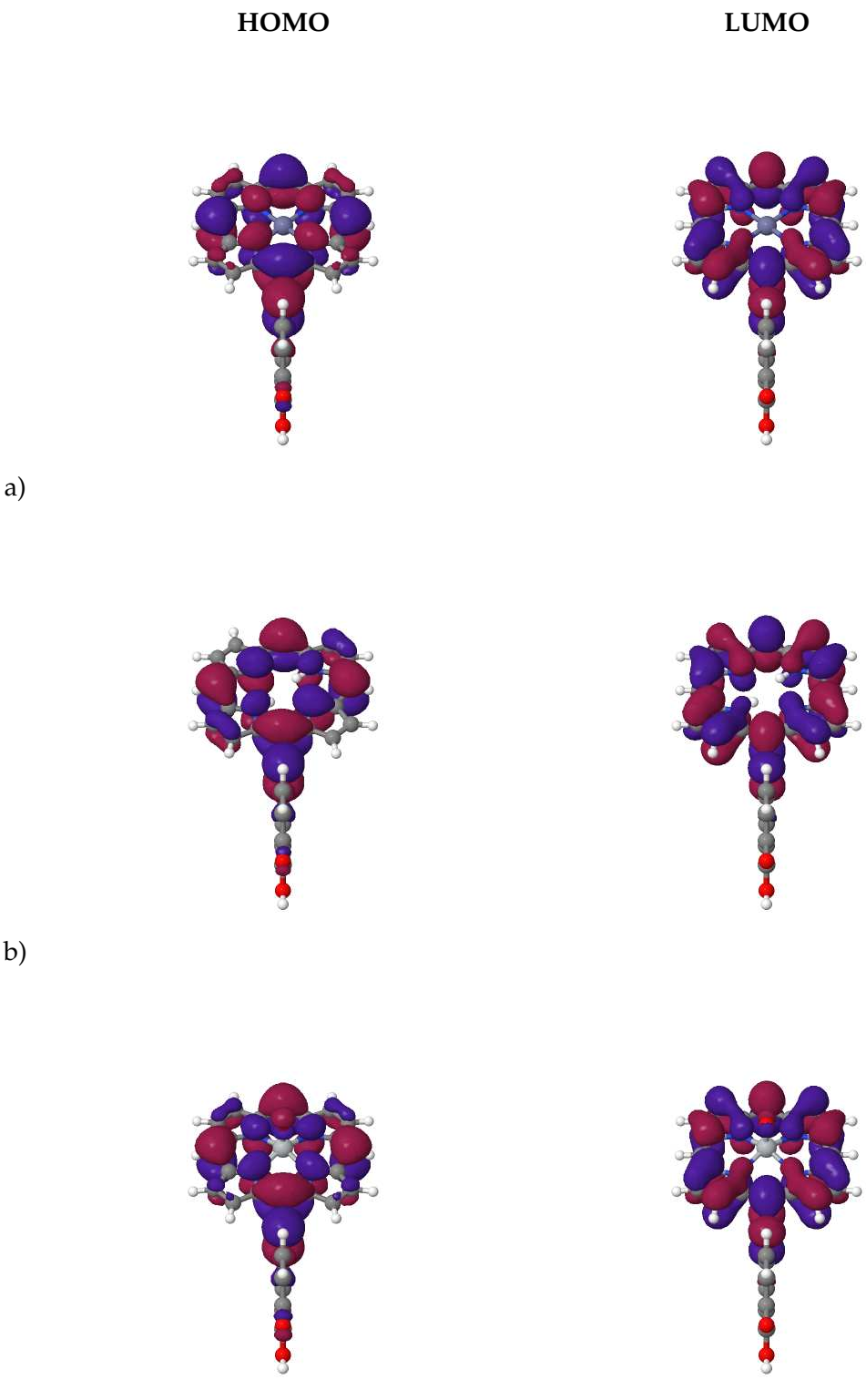

Figure S2: Comparison of the spatial shape of the HOMO and LUMO of dyes using only the H side group and the EthynPhA anchor group together with the ZnP (top), H_2P (middle) and TiOP (bottom) backbones.

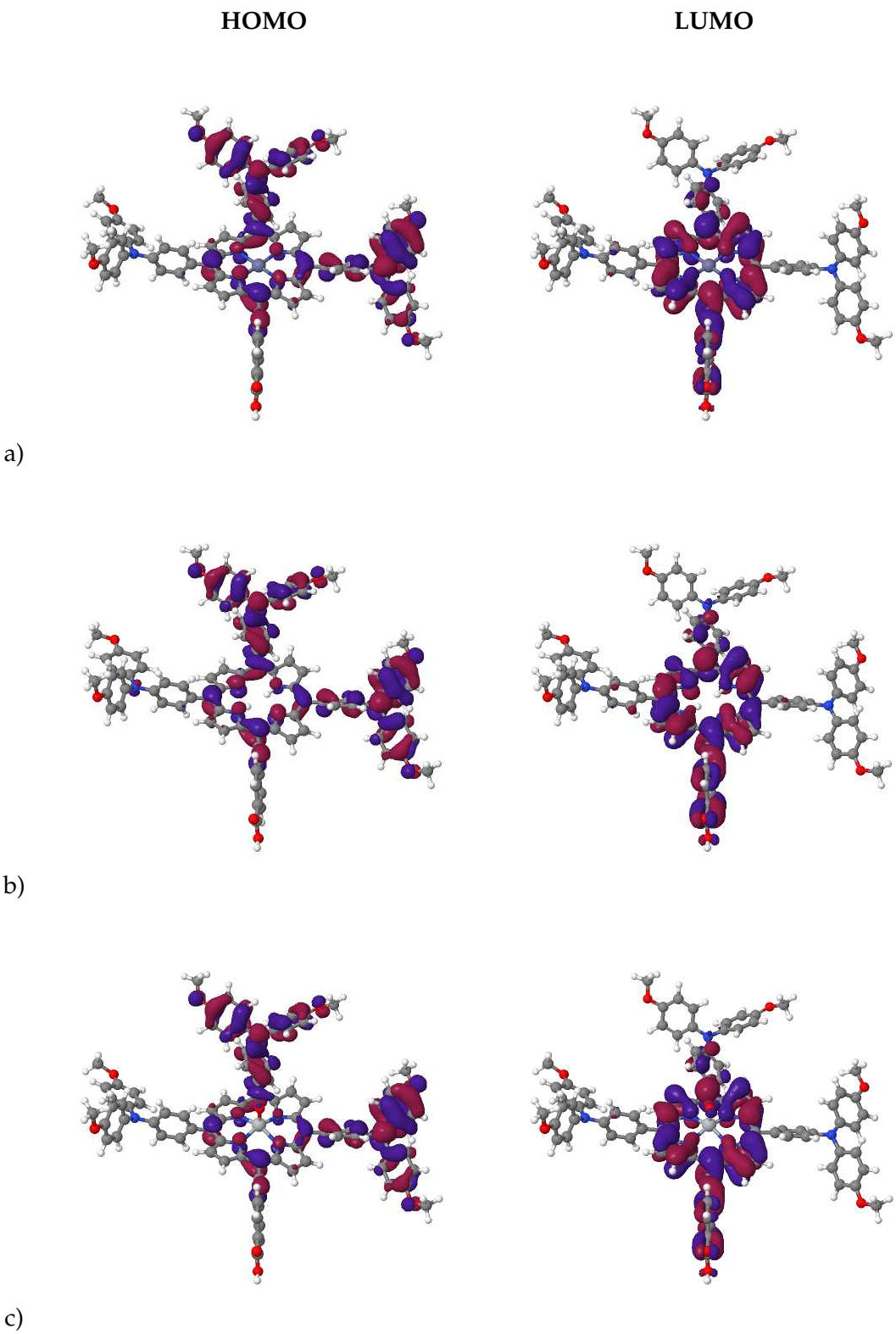

Figure S3: Comparison of the spatial shape of the HOMO and LUMO of dyes using only the MOTPA side group and the EthynPhA anchor group together with the ZnP (top), H_2P (middle) and TiOP (bottom) backbones.

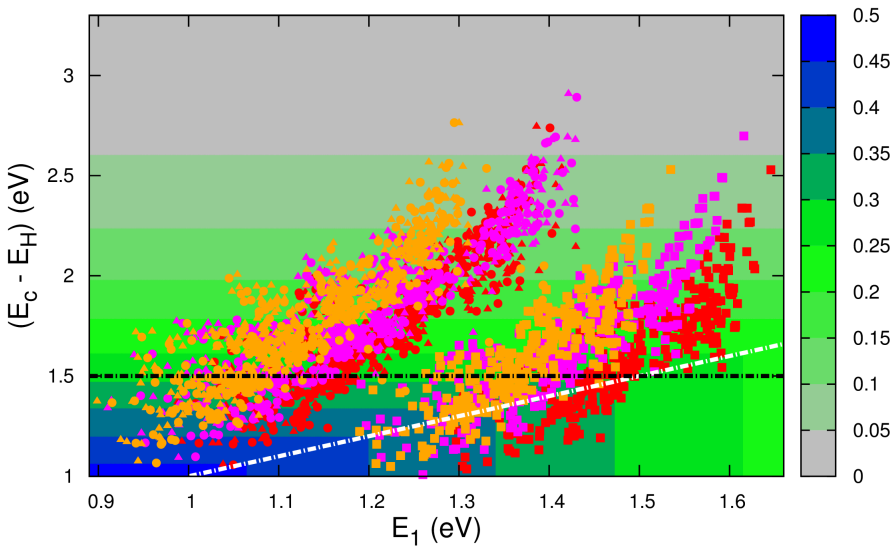

Figure S4: Calculated level alignment quality as function of the optical gap, E_1, and the energy difference between the conduction band for functionalized porphyrins with the ZnP (red), H_2P (orange) and TiOP (magenta) backbones and the EthynPhA (square), 2CarboxyPropenA (circle) and 2CyanoPropenA (triangle) anchor groups. The black dotted line indicates the lower limit of $E_c - E_H$ for dyes to be used with the I^-/I_3^- electrolyte and the white dotted line indicates where $E_c - E_H = E_1$.

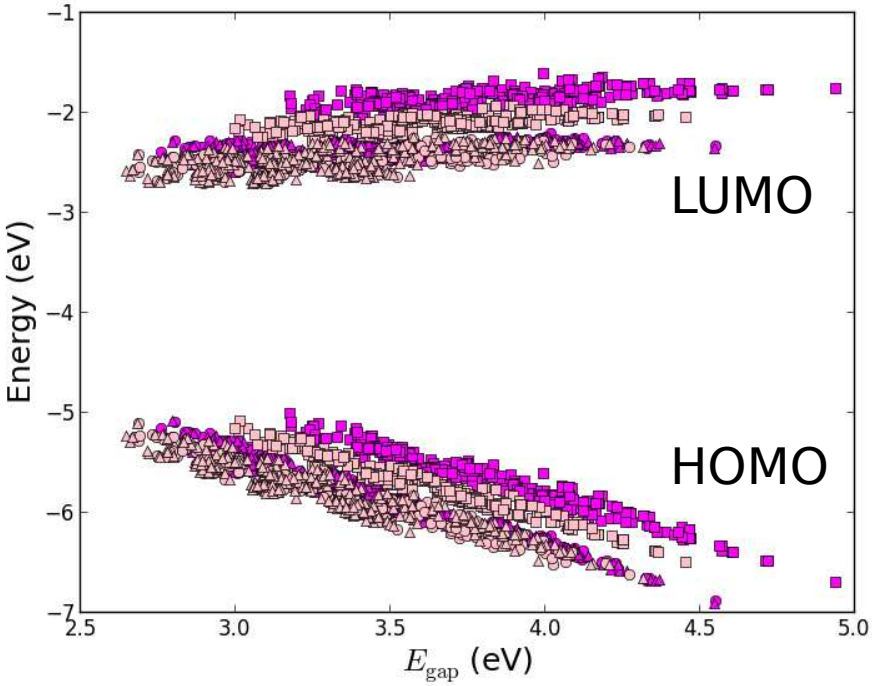

Figure S5: Calculated E_{HOMO} and E_{LUMO} relative to vacuum ordered by the resulting E_{gap} of functionalized porphyrins with the TiOP (magenta) and TiO_2BAP (pink) backbones and the EthynPhA (square), 2CarboxyPropenA (circle) and 2CyanoPropenA (triangle) anchor groups.

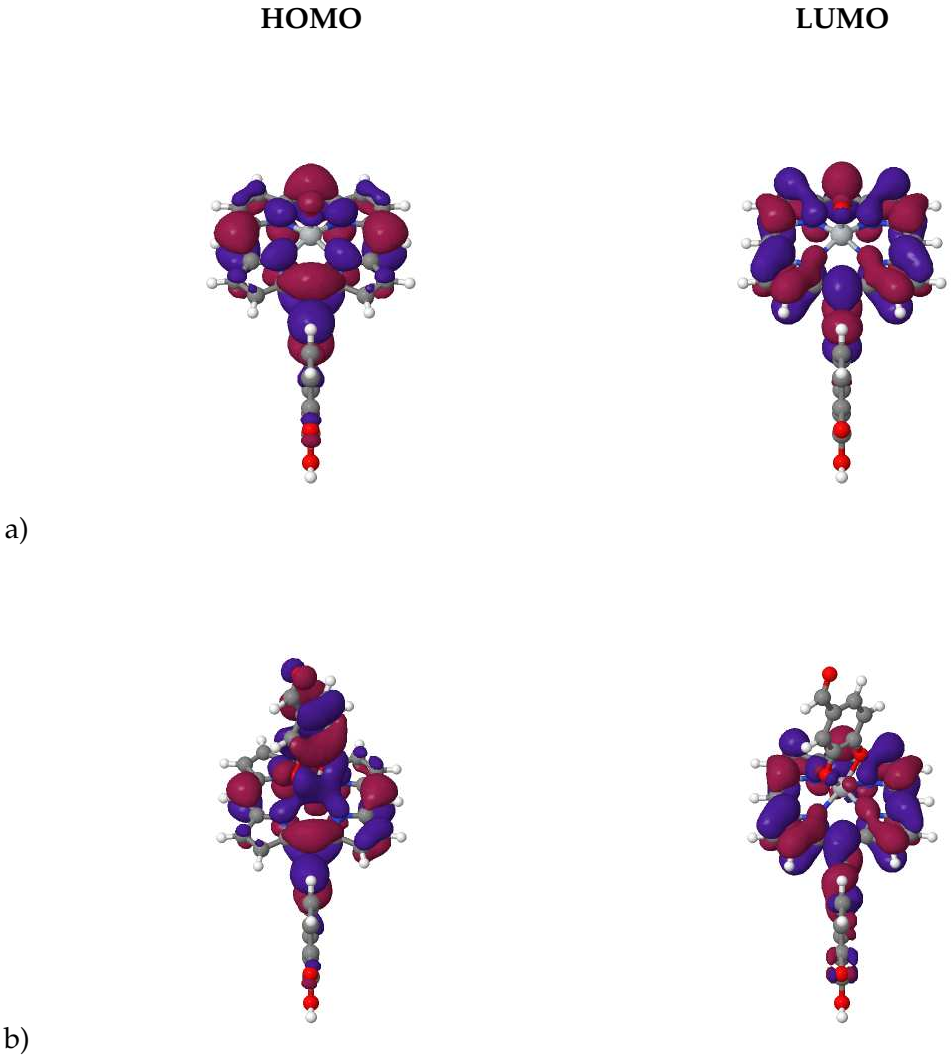

Figure S6: Comparison of the spatial shape of the HOMO and LUMO of dyes using only the H side group and the EthynPhA anchor group together with the TiOP (top) and TiO_2BAP (bottom) backbones.

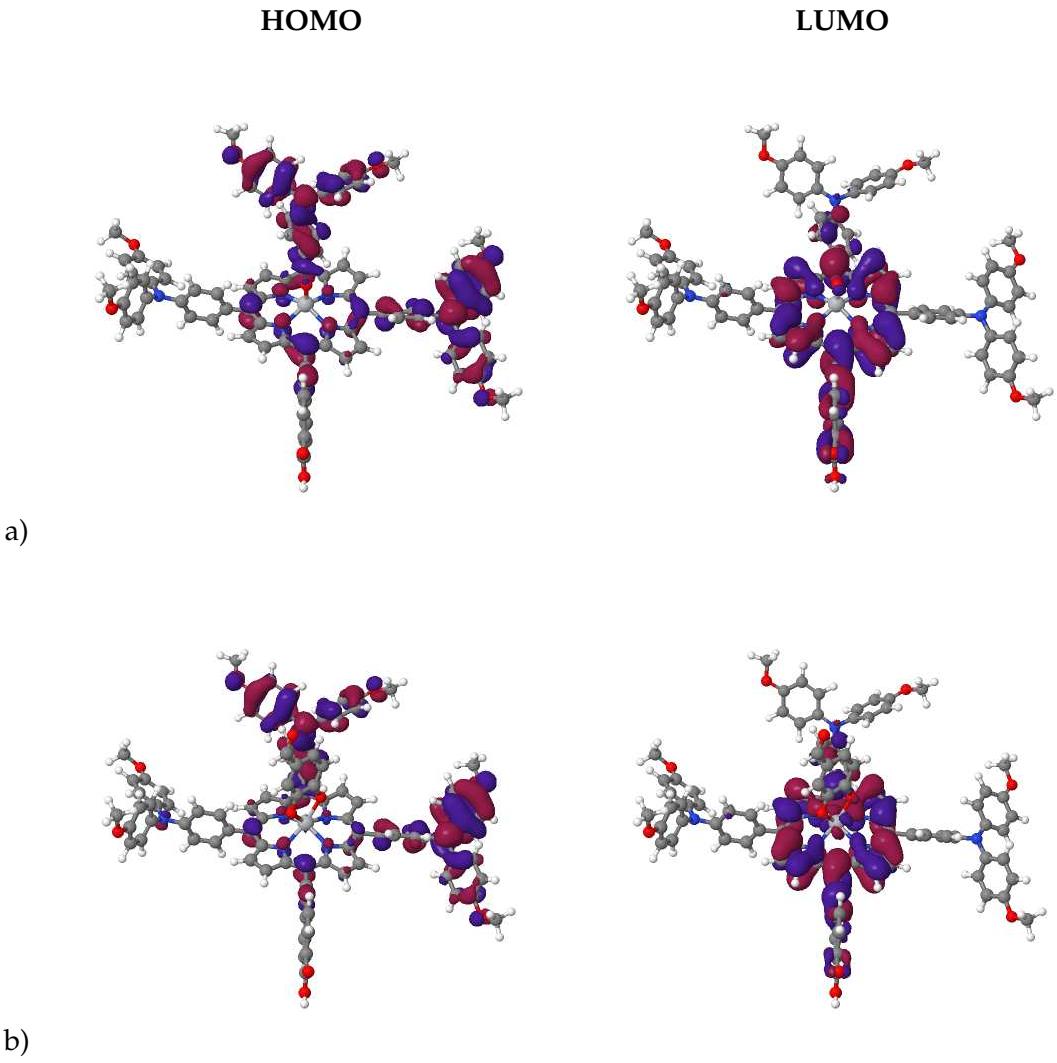

Figure S7: Comparison of the spatial shape of the HOMO and LUMO of dyes using only the MOTPA side group and the EthynPhA anchor group together with the TiOP (top) and TiO_2BAP (bottom) backbones.

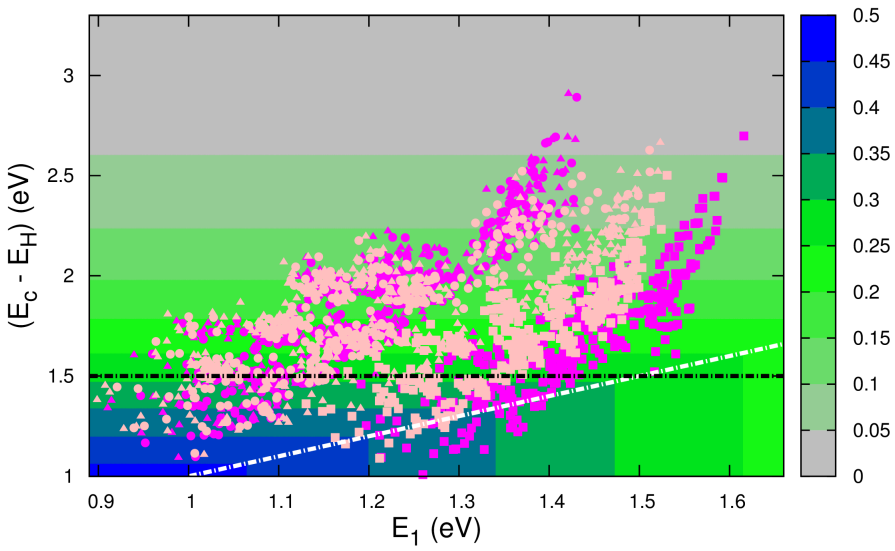

Figure S8: Calculated level alignment quality as function of the optical gap, E_1, and the energy difference between the conduction band for functionalized porphyrins with the TiOP (magenta) and TiO_2BAP (pink) backbones and the EthynPhA (square), 2CarboxyPropenA (circle) and 2CyanoPropenA (triangle) anchor groups. The black dotted line indicates the lower limit of $E_c - E_H$ for dyes to be used with the I^-/I_3^- electrolyte and the white dotted line indicates where $E_c - E_H = E_1$.

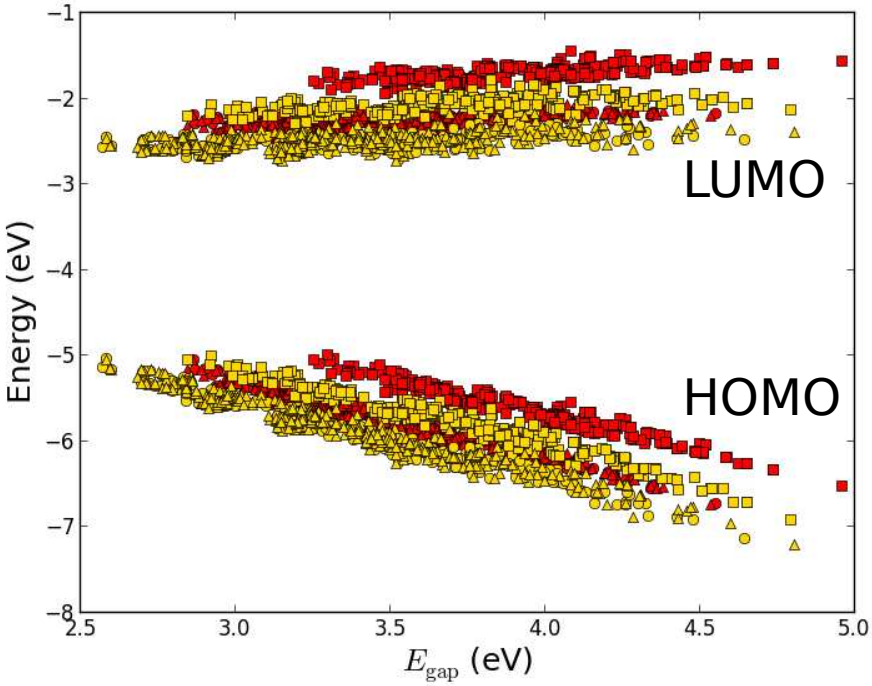

Figure S9: Calculated E_{HOMO} and E_{LUMO} relative to vacuum ordered by the resulting E_{gap} of functionalized porphyrins with the ZnP (red) and FZnP (yellow) backbones and the EthynPhA (square), 2CarboxyPropenA (circle) and 2CyanoPropenA (triangle) anchor groups.

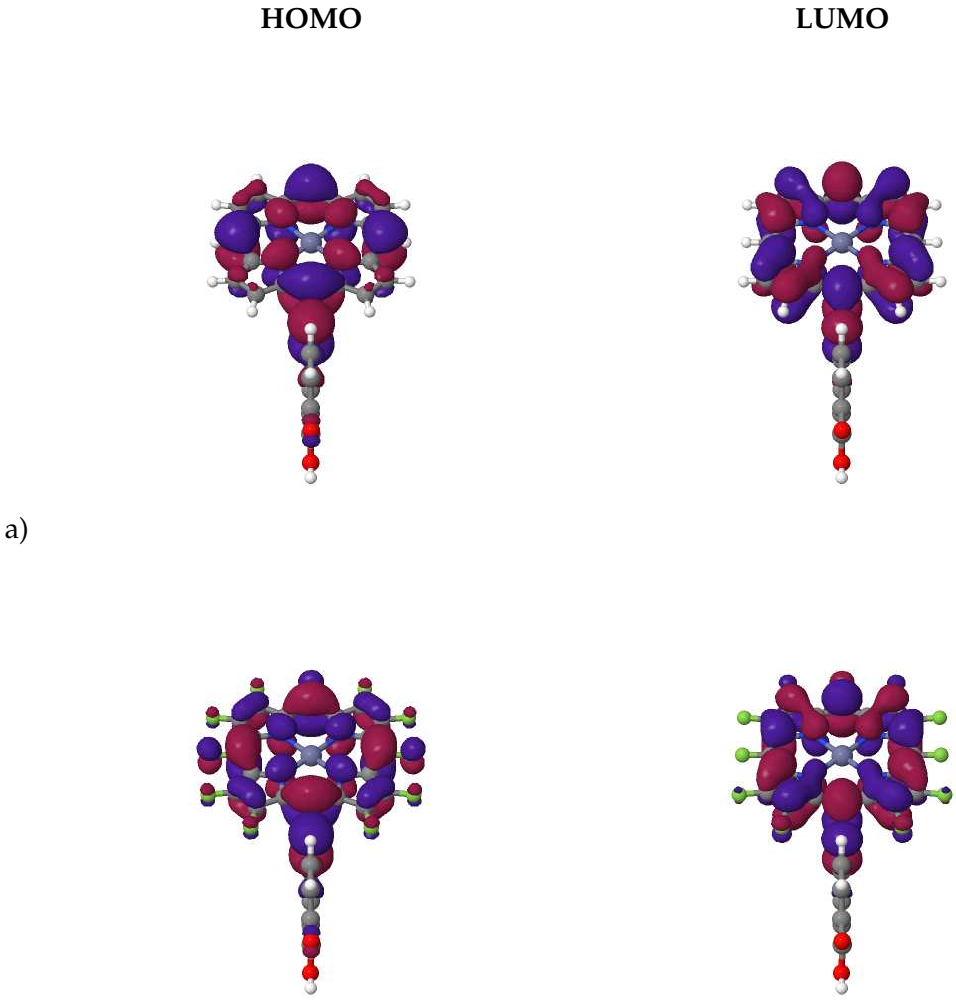

Figure S10: Comparison of the spatial shape of the HOMO and LUMO of dyes using only the H side group and the EthynPhA anchor group together with the ZnP (top) and FZnP (bottom) backbones.

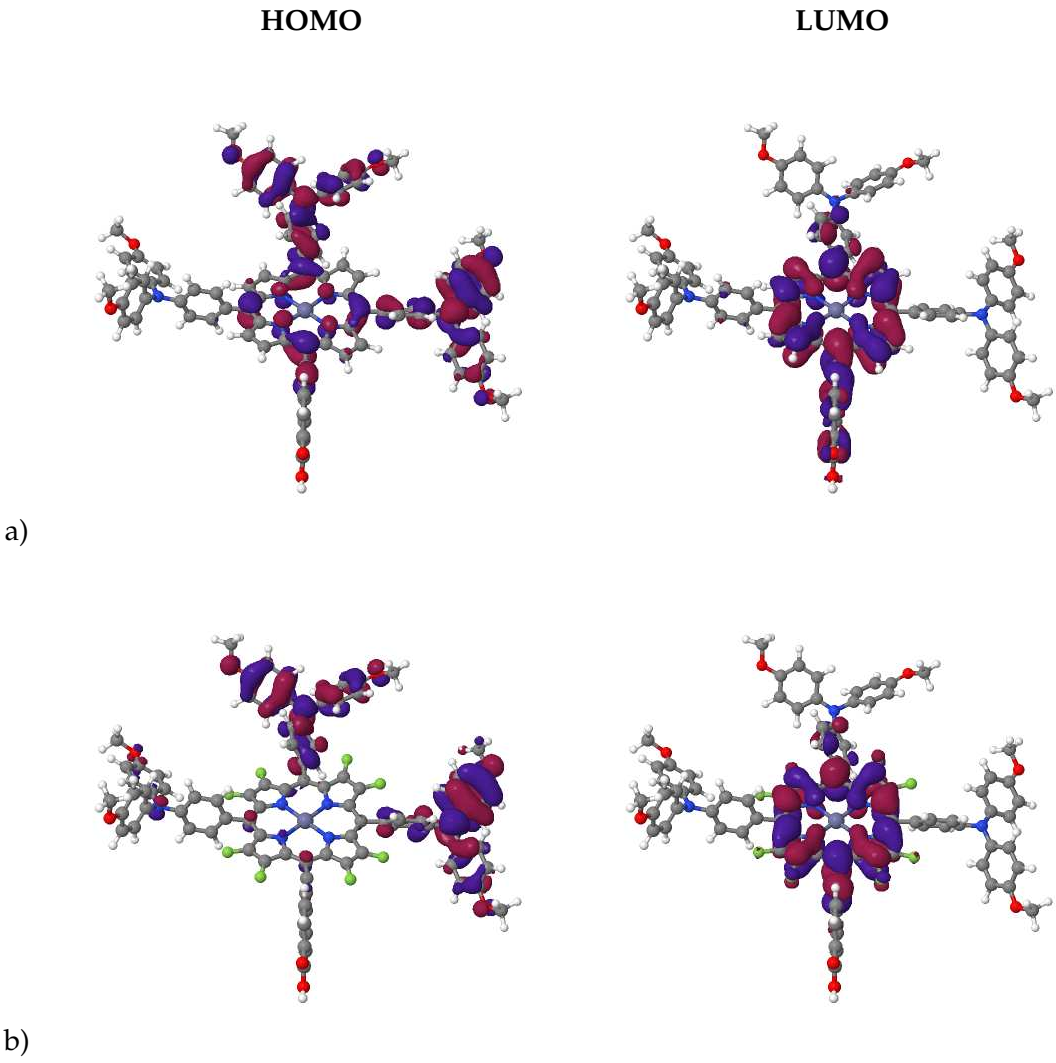

Figure S11: Comparison of the spatial shape of the HOMO and LUMO of dyes using only the MOTPA side group and the EthynPhA anchor group together with the ZnP (top) and FZnP (bottom) backbones.

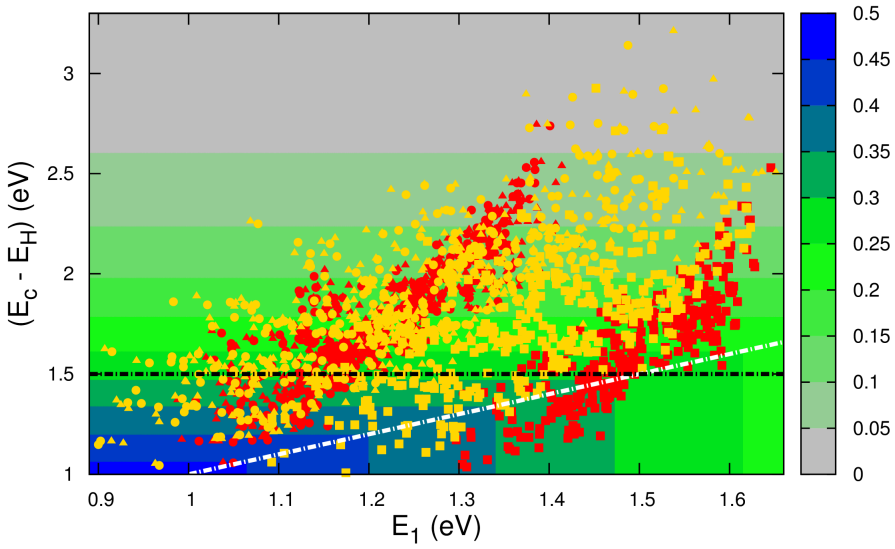

Figure S12: Calculated level alignment quality as function of the optical gap, E_1, and the energy difference between the conduction band for functionalized porphyrins with the ZnP (red) and FZnP (yellow) backbones and the EthynPhA (square), 2CarboxyPropenA (circle) and 2CyanoPropenA (triangle) anchor groups. The black dotted line indicates the lower limit of $E_c - E_H$ for dyes to be used with the I^-/I_3^- electrolyte and the white dotted line indicates where $E_c - E_H = E_1$.

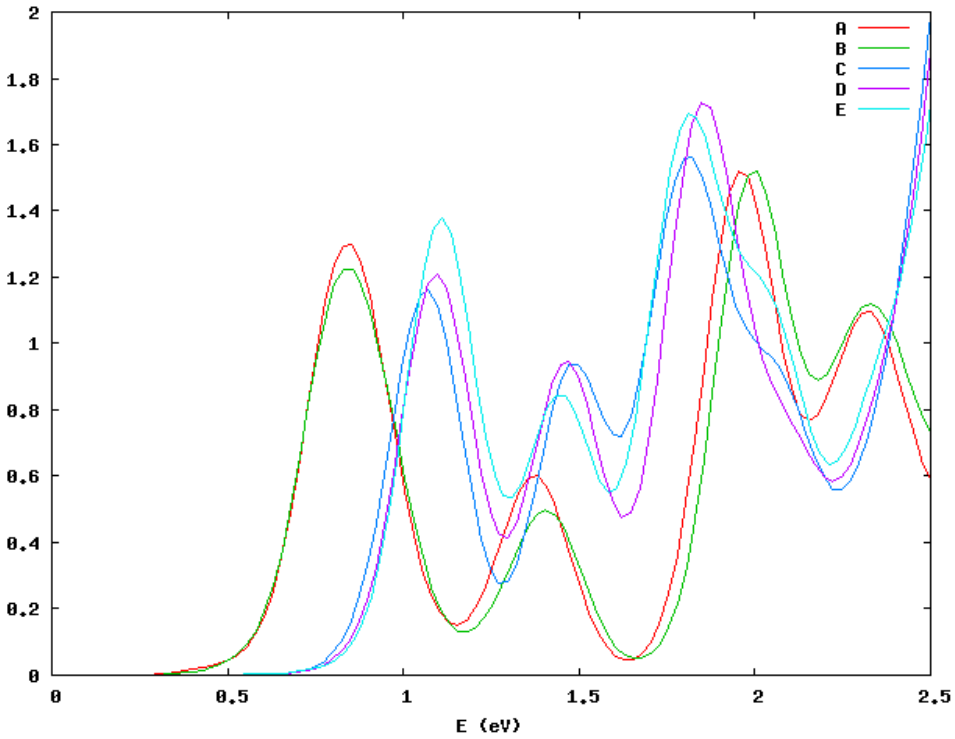

Figure S13: TD-DFT spectra with an added width of 0.1 eV of the top five candidates. With a sufficiently amount of dye layers, all dyes will have a step-function absorption spectrum above the absorption edge since the absorption here is non-zero for all dyes. However, the absorption edge is poorly predicted by TD-DFT due to the charge-transfer character of Donor-π-Acceptor porphyrin dyes.