Electronic Supplementary Material (ESI) for RSC Advances.

Shifting UV-Vis spectrum through rational structural modifications of zinc porphyrin photoactive compounds

Qudsia Arooj[1], Gregory Wilson[2] and Feng Wang[1]*

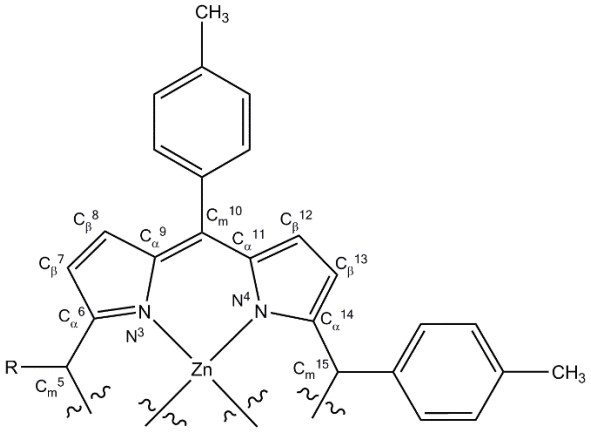
[1]Molecular model Discovery laboratory, Faculty of Science, Engineering and Technology, Department of Chemistry and Biotechnology, Swinburne University of Technology, Hawthorn, Melbourne, Victoria, 3122, Australia

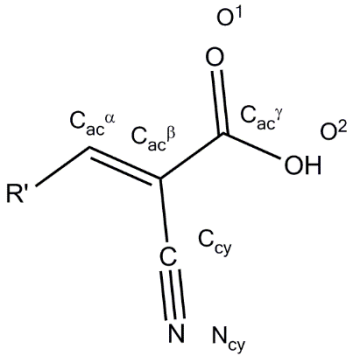
[2] CSIRO Energy, Newcastle Energy Centre, 10 Murray Dwyer Cct Mayfield West, NSW, 2304 Australia

*Corresponding author. Tel: +61 3 9214 5056; fax: +61-3-9214-5921

E-mail addresses: **fwang@swin.edu.au** (F.Wang)

Table S1. Selected Calculated Bond Lengths (Å) for the Four Oxidation States of the Porphyrin macrocycles (in Chloroform)





Bond	Bond length (Å)				
	Chloroform				
	Pzn-EDOT	Zn-P-π_1	Zn-P-π_2	Zn-P-π_3	Zn-P-π_4
C_R–C_m^5	1.495	1.493	1.492	1.481	1.481
C_m^5–C_α^6	1.409	1.410	1.410	1.409	1.412
C_α^6–C_β^7	1.446	1.447	1.448	1.446	1.446
C_β^7–C_β^8	1.361	1.359	1.359	1.360	1.360
C_β^8–C_α^9	1.445	1.446	1.446	1.446	1.445
C_α^9–C_m^{10}	1.408	1.405	1.405	1.406	1.406
C_m^{10}–C_α^{11}	1.409	1.411	1.411	1.411	1.410
C_α^{11}–C_β^{12}	1.445	1.444	1.444	1.444	1.445
C_β^{12}–C_α^{13}	1.361	1.362	1.362	1.362	1.362
C_β^{13}–C_α^{14}	1.445	1.444	1.444	1.444	1.445
C_α^{14}–C_m^{15}	1.409	1.409	1.408	1.409	1.408
C_α^6–N^3	1.376	1.374	1.374	1.374	1.374
C_α^9–N^3	1.378	1.380	1.380	1.379	1.379
C_α^{11}–N^4	1.377	1.375	1.375	1.376	1.376
C_α^{14}–N^4	1.377	1.378	1.378	1.377	1.378
N^3–Zn	2.051	2.050	2.051	2.050	2.052
N^4–Zn	2.049	2.051	2.051	2.047	2.050
C_R–C_{ac}^α	1.419	1.422	1.428	1.440	1.443
C_{ac}^α–C_{ac}^β	1.376	1.373	1.370	1.365	1.493
C_{ac}^β–C_{ac}^γ	1.487	1.490	1.487	1.491	1.426
C_{ac}^β–C_{Cy}	1.424	1.425	1.424	1.426	1.648
C_{Cy}–N_{Cy}	1.165	1.165	1.165	1.165	1.215
C_{ac}^γ–O^1	1.219	1.218	1.216	1.216	1.346
C_{ac}^γ–O^2	1.351	1.350	1.348	1.348	

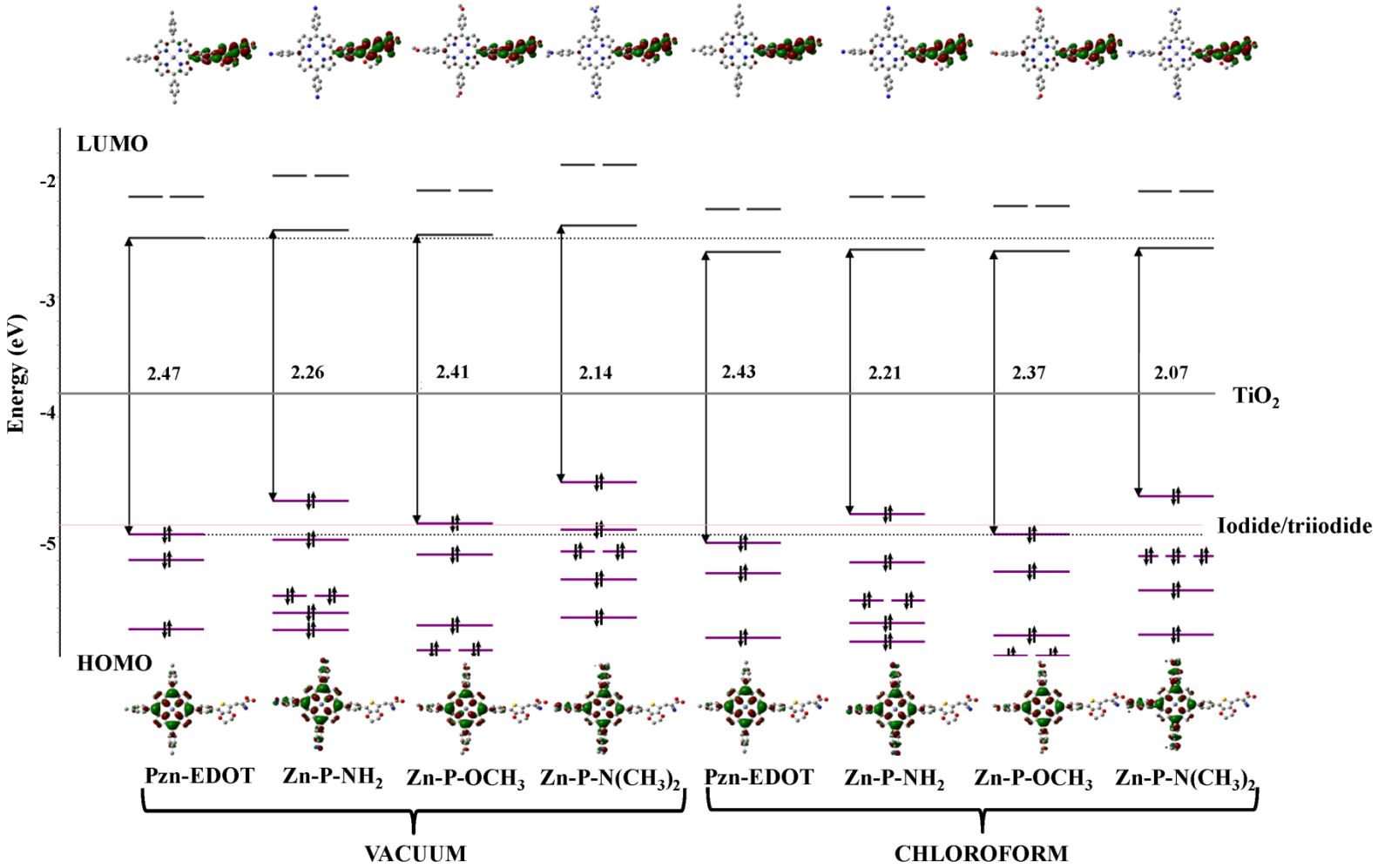


Figure S2. Single point calculated frontier MO (Molecular orbitals) using B3LYP/6-31G* model in vacuum and Chloroform along with the comparison of charge density of HOMOs and LUMOs with the reference dye Pzn-EDOT and *meso*-substituted zinc porphyrin dyes.

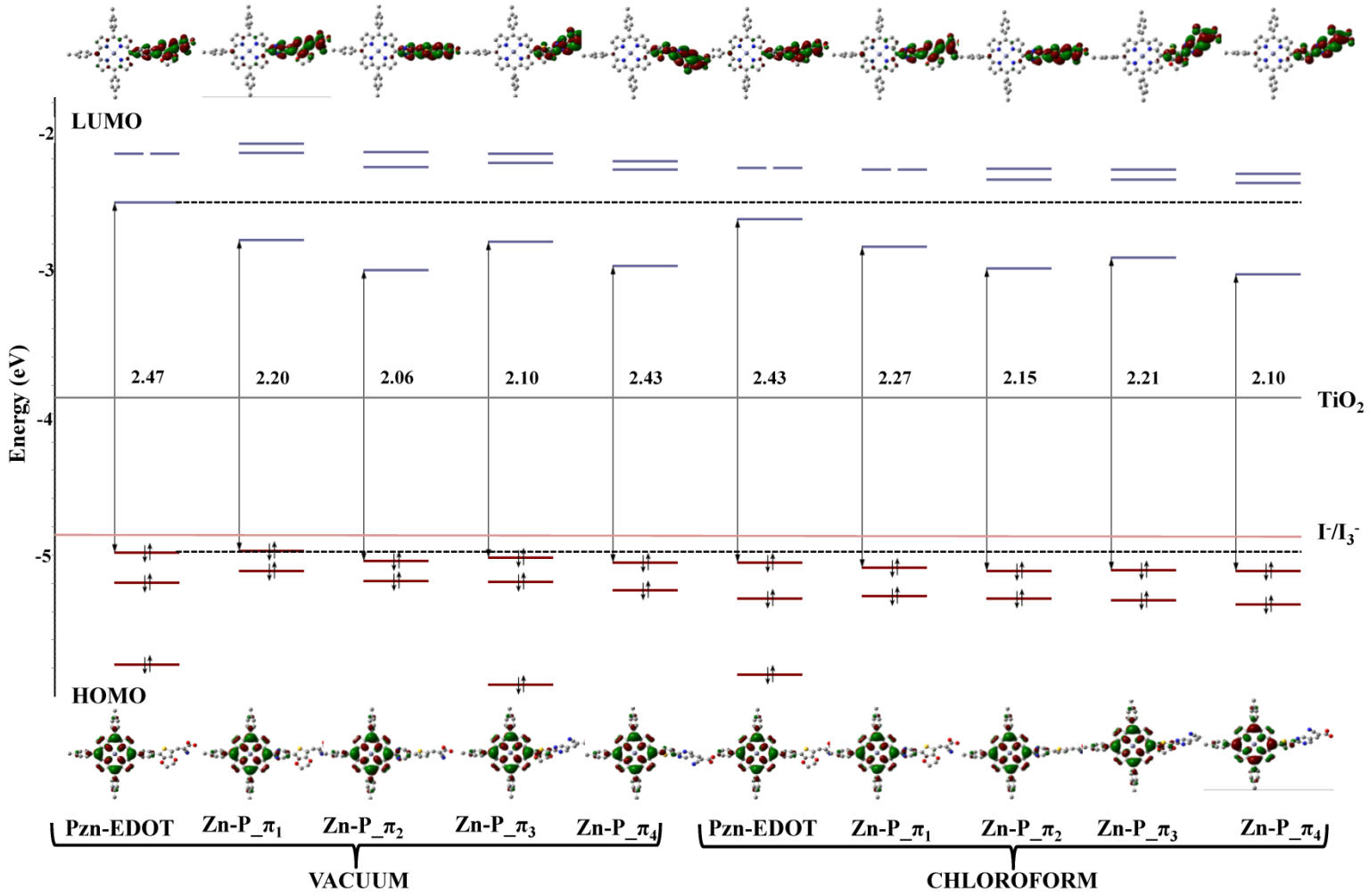


Fig. S3 Single point calculated frontier MO (Molecular orbitals) using B3LYP/6-31G* model in vacuum and Chloroform along with the comparison of charge density of HOMOs and LUMOs with the reference dye Pzn-EDOT and π-substituted zinc porphyrin dyes.

$CHCl_3$ Vacuum

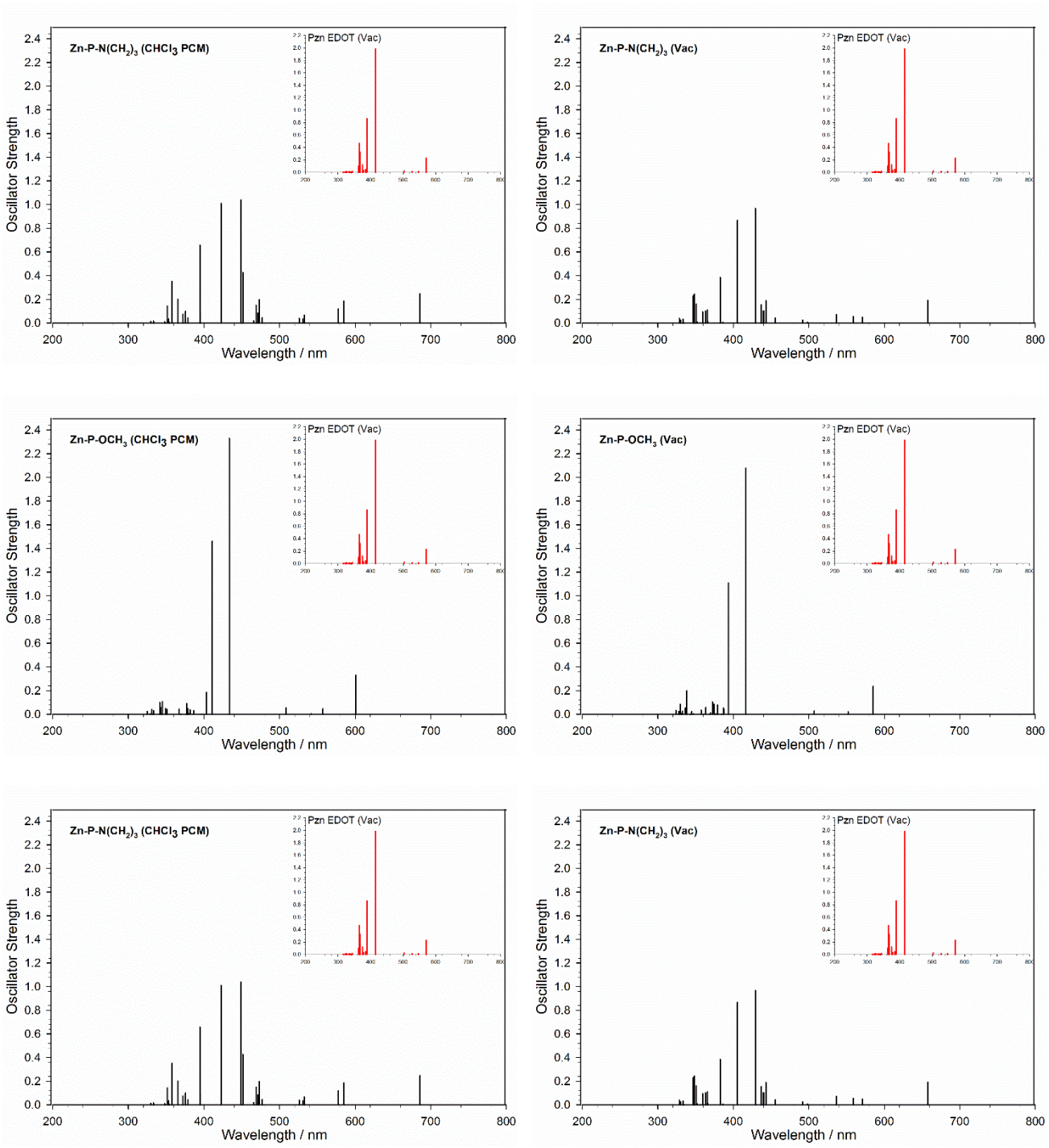


Fig. S4. Calculated excitations of three examples of meso-substituted porphyrins (black vertical lines) in polarised continuum and vacuum. The *y* axes for are scaled to the maximum oscillator strength for the examples studied. Inset: calculated excitations for the parent EDOT porphyrin (red vertical lines).

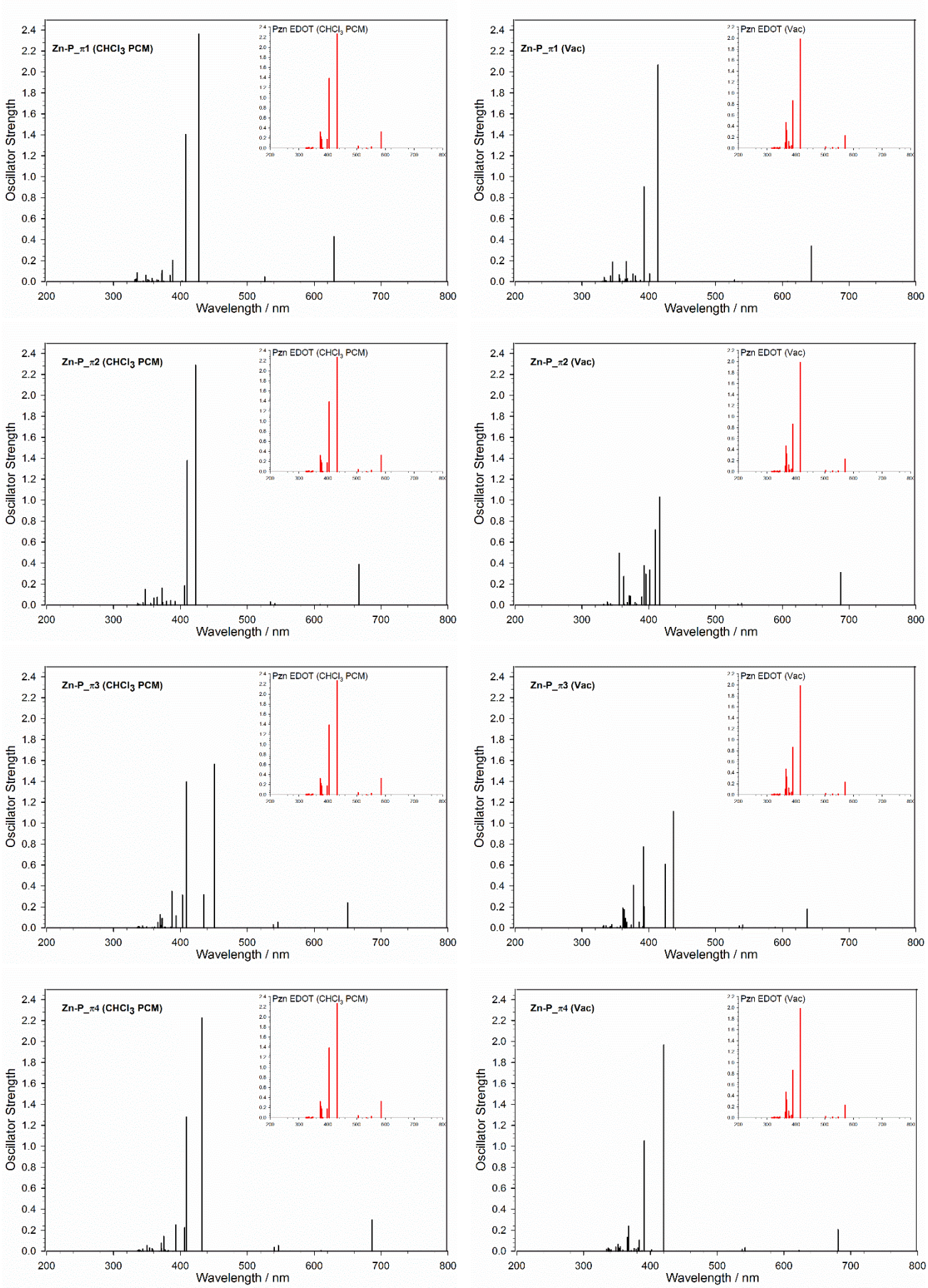


Fig. S5. Calculated excitations of four examples of Pi Bridge porphyrins (black vertical lines) in polarised continuum and vacuum. The *y* axes for are scaled to the maximum oscillator strength for the examples studied. Inset: calculated excitations for the parent EDOT porphyrin (red vertical lines).