π-extended diketopyrrolopyrrole-porphyrin arrays: one- and two-photon photophysical investigations and theoretical studies

Md. Mehboob Alam,[a] *Frédéric Bolze,*[b] *Chantal Daniel,*[a]* *Lucia Flamigni,*[c] *Christophe Gourlaouen,*[a] *Valérie Heitz,*[d]* *Sébastien Jenni,*[d] *Julie Schmitt,*[d] *Angélique Sour* [d] *and Barbara Ventura* [c]*

Supporting Information

General information and experimental procedures

All chemicals were of the best commercially available grade and used without further purification. Tetrahydrofuran was dried using a dry solvent station GT S100. Column chromatographies were carried out on silica (Fluka 60, 70-230 mesh). NMR spectra were recorded at the ambient probe temperature using Bruker AVANCE 500 spectrometers. Chemical shifts are quoted as parts per million (ppm) relative to the residual peak of solvent and coupling constants (*J*) are quoted in Hertz (Hz). Where assignments of ^{1}H NMR spectra are given, they have been unambiguously established via COSY, HSQC, HMBC and ROESY experiments. In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s : singlet, d : doublet, t : triplet, m : multiplet, br s : broad signal), the number of protons implied, the value of the coupling constants in hertz if applicable, and finally the assignment. UV-vis spectra were recorded on a UVIKON XL spectrophotometer. Mass spectra were carried out on an Autoflex II TOF/TOF (Bruker) spectrometer, equipped with a Matrix Assisted Laser Desorption Ionization (MALDI) source. X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Cu-Kα radiation (λ = 1,54178 Å). Compounds **(TIPS)$_4$-ZnP** [1] and **DPP-Br** [2] were prepared according to the literature.

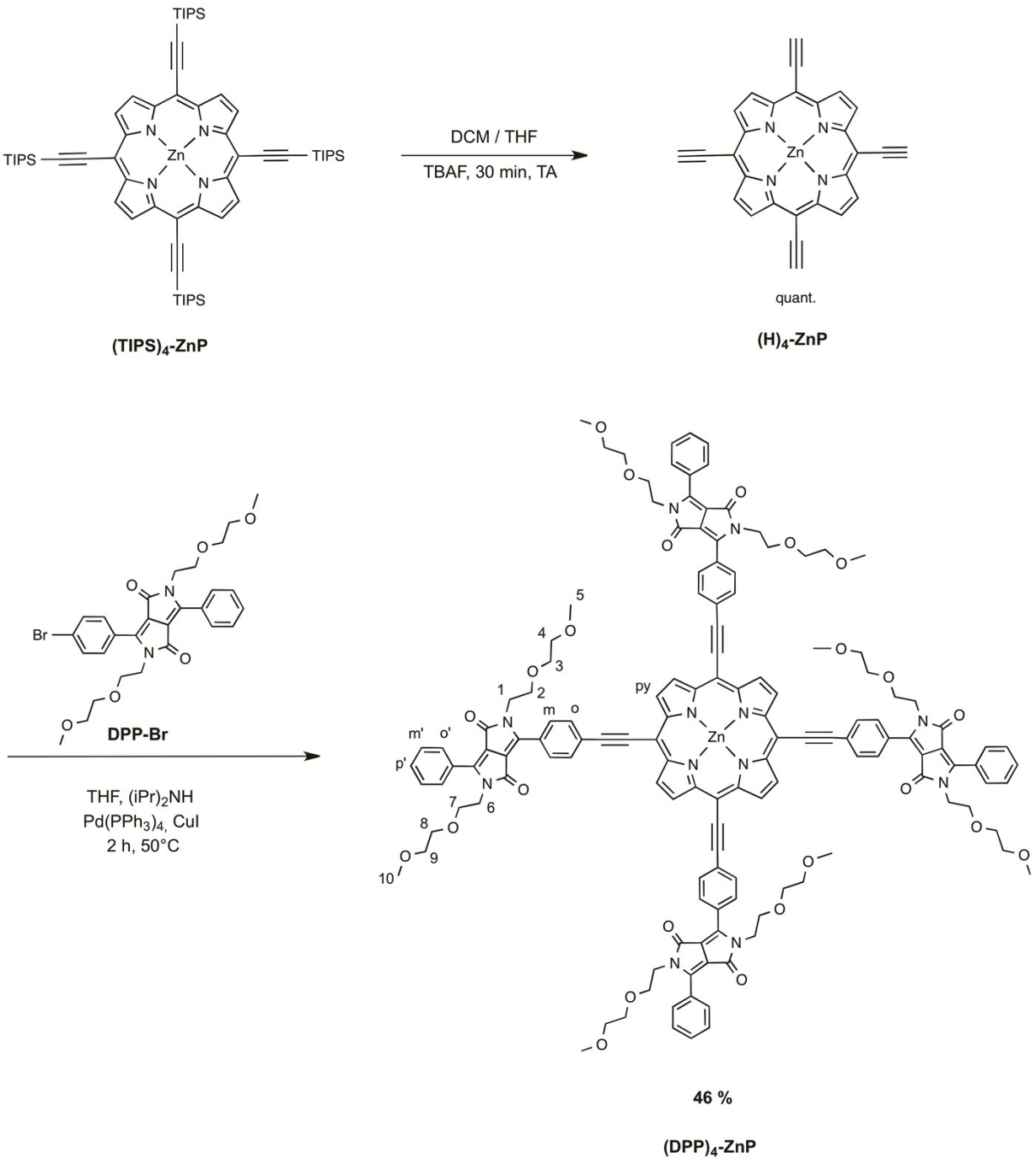


Figure S1. Synthesis of **$(DPP)_4$-ZnP**.

Synthesis of $(DPP)_4$-ZnP

To a degassed solution of **$(TIPS)_4$-ZnP** (126 mg, 115 μmol) in a mixture of dry THF (5.5 mL) and dry DCM (13 mL) was added, under argon, a solution of TBAF (218 mg, 690 μmol) in dry THF (1 mL). The reaction mixture was stirred at room temperature for 30 minutes and then a 1:1 mixture of water and ethanol (40 mL) was added. The solution was concentrated by evaporation of the solvent until the compound precipitated. The solid was filtered and washed with a cold mixture of water and ethanol (1:1). Due to its instability, the deprotected compound, obtained as a purple solid, was directly used for the next reaction.

$(H)_4$-ZnP , $Pd(PPh_3)_4$ (53 mg, 46 μmol), CuI (11 mg, 57.5 μmol) and DPP-Br (289 mg, 506 μmol) were dried under vacuum for 1 hour at 45°C. A solution of dry THF (10 mL) and $(iPr)_2NH$ (2 mL) degassed by four freeze-thaw cycles was transferred *via cannula* to the solids placed under argon. The resulting mixture was stirred at 50°C for 2 hours. The solvents were evaporated and the product was purified by silica gel column chromatography (DCM / pyridine 1%/ MeOH 1.5 to 3%). **$(DPP)_4$-ZnP** was obtained as a purple solid in 46% yield (130 mg).

^{1}H NMR (500 MHz, pyridine-d_5, 298K) : δ(ppm) = 3.29 (s, 12H, H_5 or H_{10}), 3.32 (s, 12H, H_5 or H_{10}), 3.46-3.51 (m, 16H, H_4 and H_9), 3.60-3.64 (m, 16H, H_3 and H_8), 3.86 (br s, 8H, H_2), 3.92-3.94 (m, 8H, H_7), 4.34 (br s, 8H, H_6), 4.45 (br s, 8H, H_1), 7.40-7.47 (m, 12H, $H_{m'+p'}$), 8.14 (d, J = 6.9 Hz, 8H, $H_{o'}$), 8.34 (d, J = 7.8 Hz, 8H, H_o), 8.44 (d, J = 7.3 Hz, 8H, H_m), 9.82 (s, 8H, py).

^{13}C NMR (125 MHz, pyridine-d_5, 298K) : δ(ppm) = 42.13, 42.19, 59.03, 59.06, 69.46, 70.64, 72.48, 97.16, 98.41, 102.67, 110.60, 110.39, 127.50, 128.32, 128.92, 129.18, 130.34, 130.50, 131.50, 131.55, 132.25, 148.68, 149.40, 151.80, 163.37, 163.04.

MALDI-TOF: *m/z* 2431.18 $[M]^+$ (calcd 2431.88 for $[C_{140}H_{132}N_{14}O_{24}Zn]$)

UV-vis. (DCM, 1% pyridine): λ_{max} (log ε) = 512 (5.32), 651 (4.34), 709 nm (4.96).

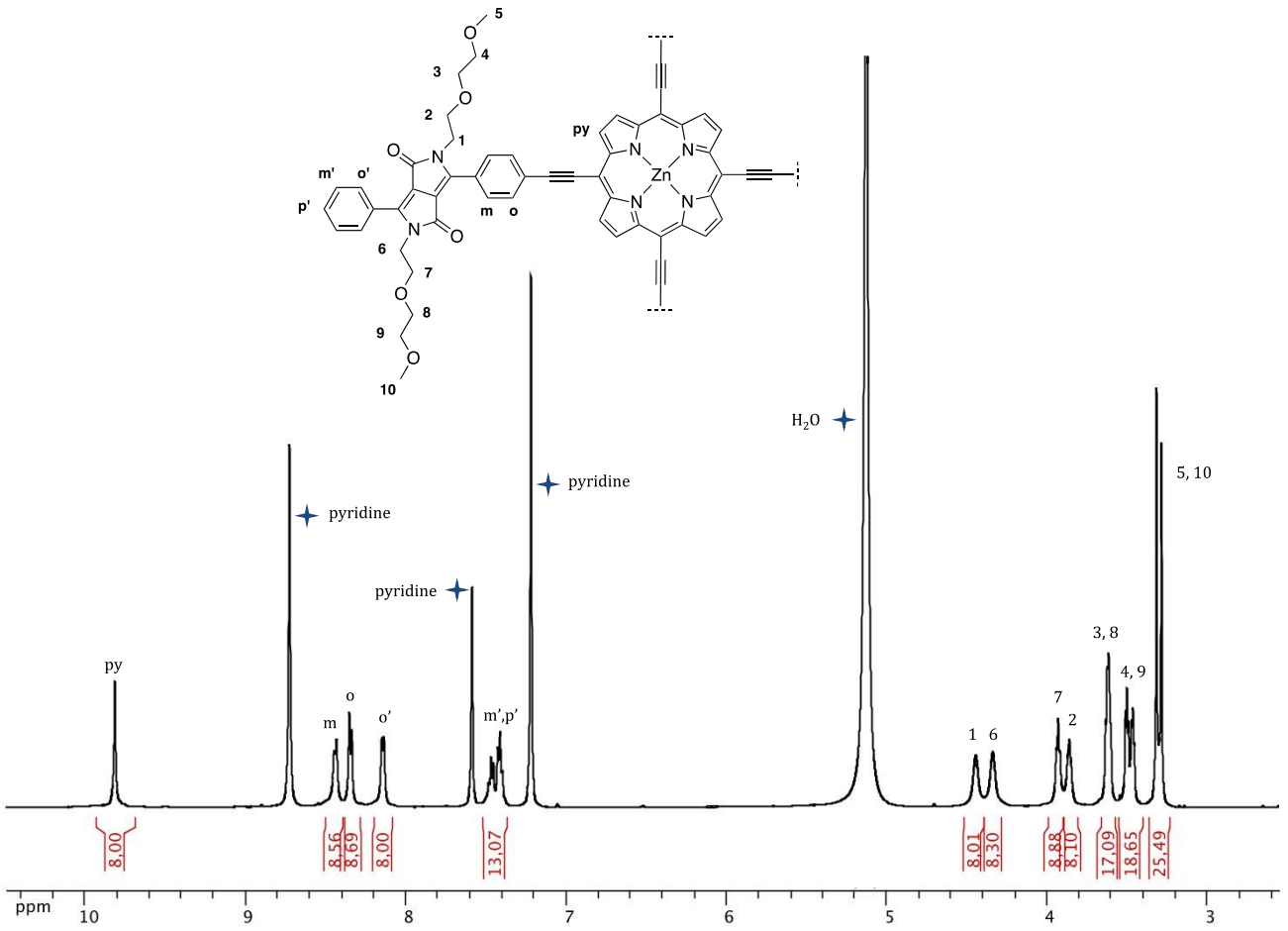


Figure S2. ^{1}H NMR (500MHz, pyridine-*d*5, 298K) spectrum of **(DPP)$_4$-ZnP**.

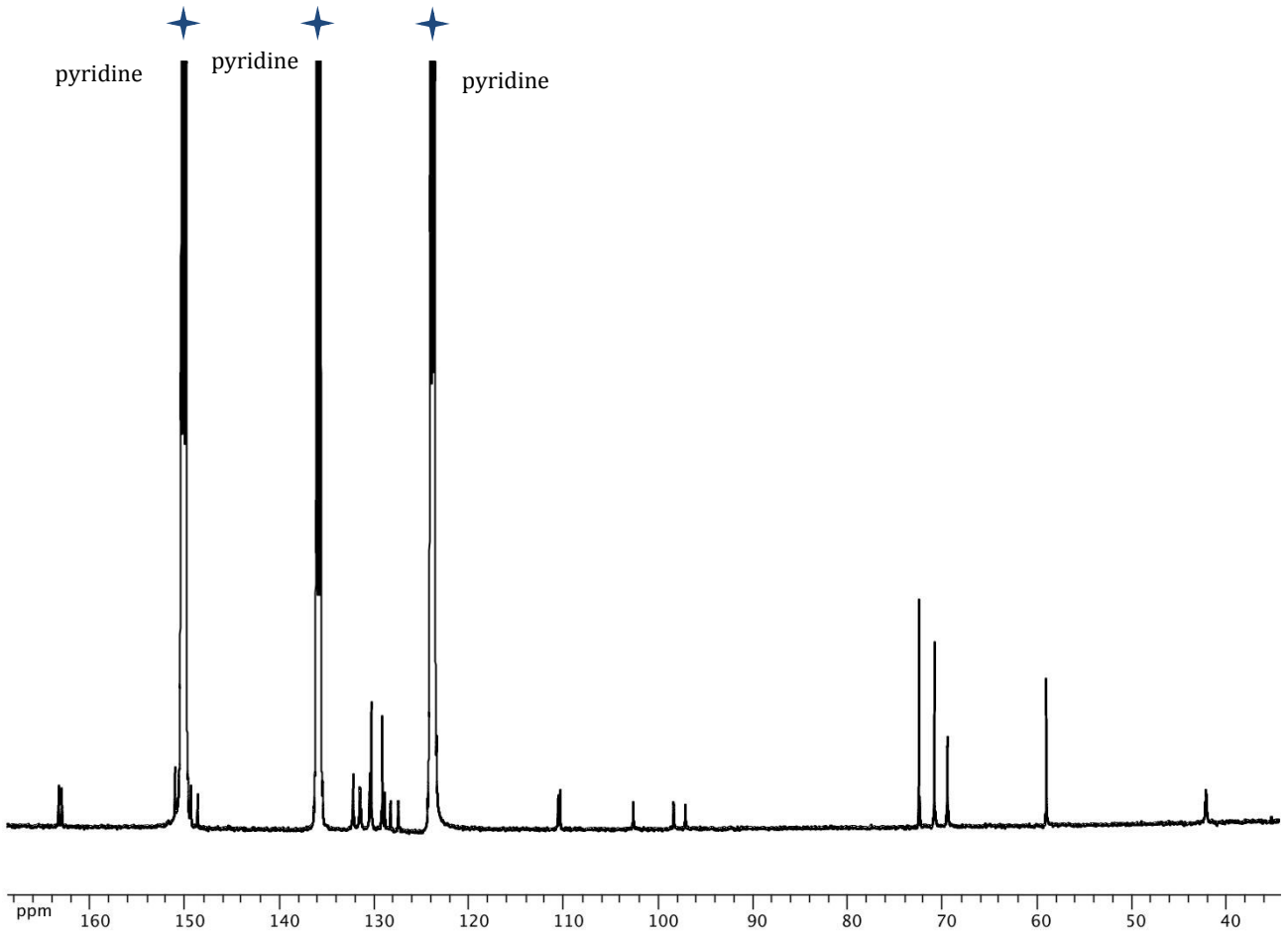


Figure S3. ^{13}C NMR (125 MHz, pyridine-d_5, 298 K) spectrum of **(DPP)$_4$-ZnP**.

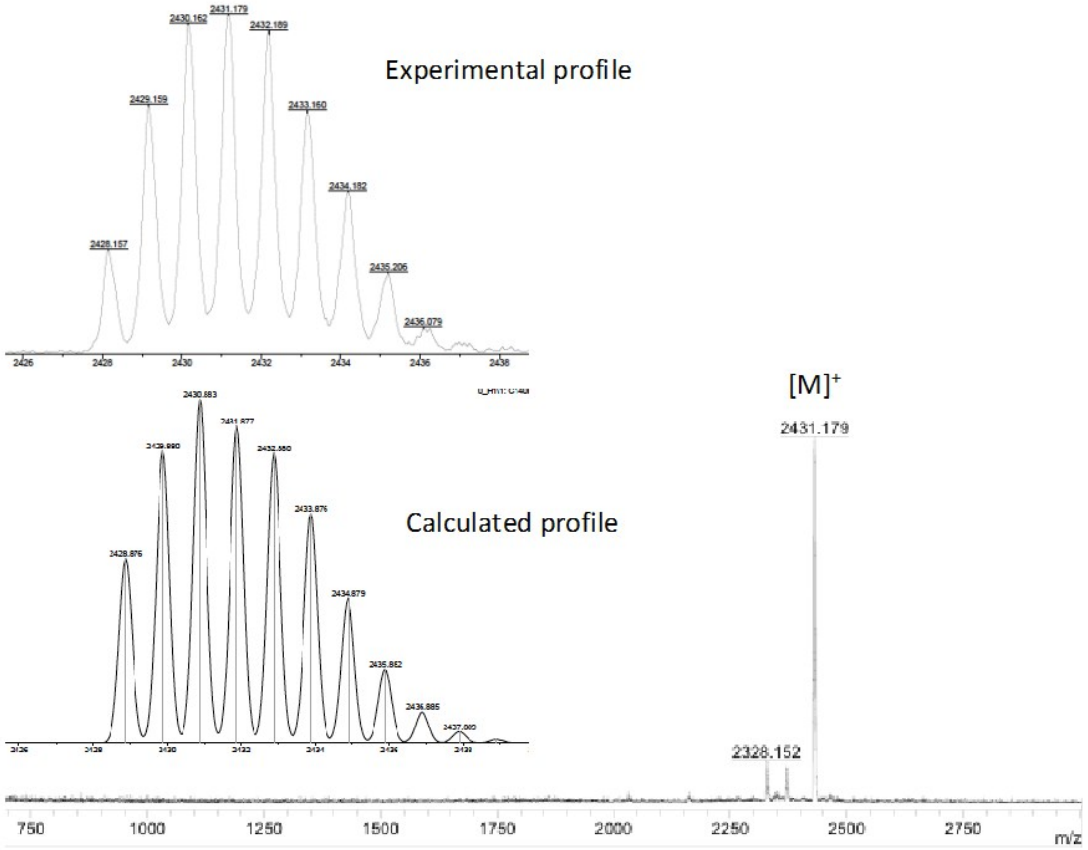


Figure S4. MALDI-TOF mass spectrum of **$(DPP)_4$-ZnP** and the corresponding calculated profile for $[M]^+$.

Absorption and emission data

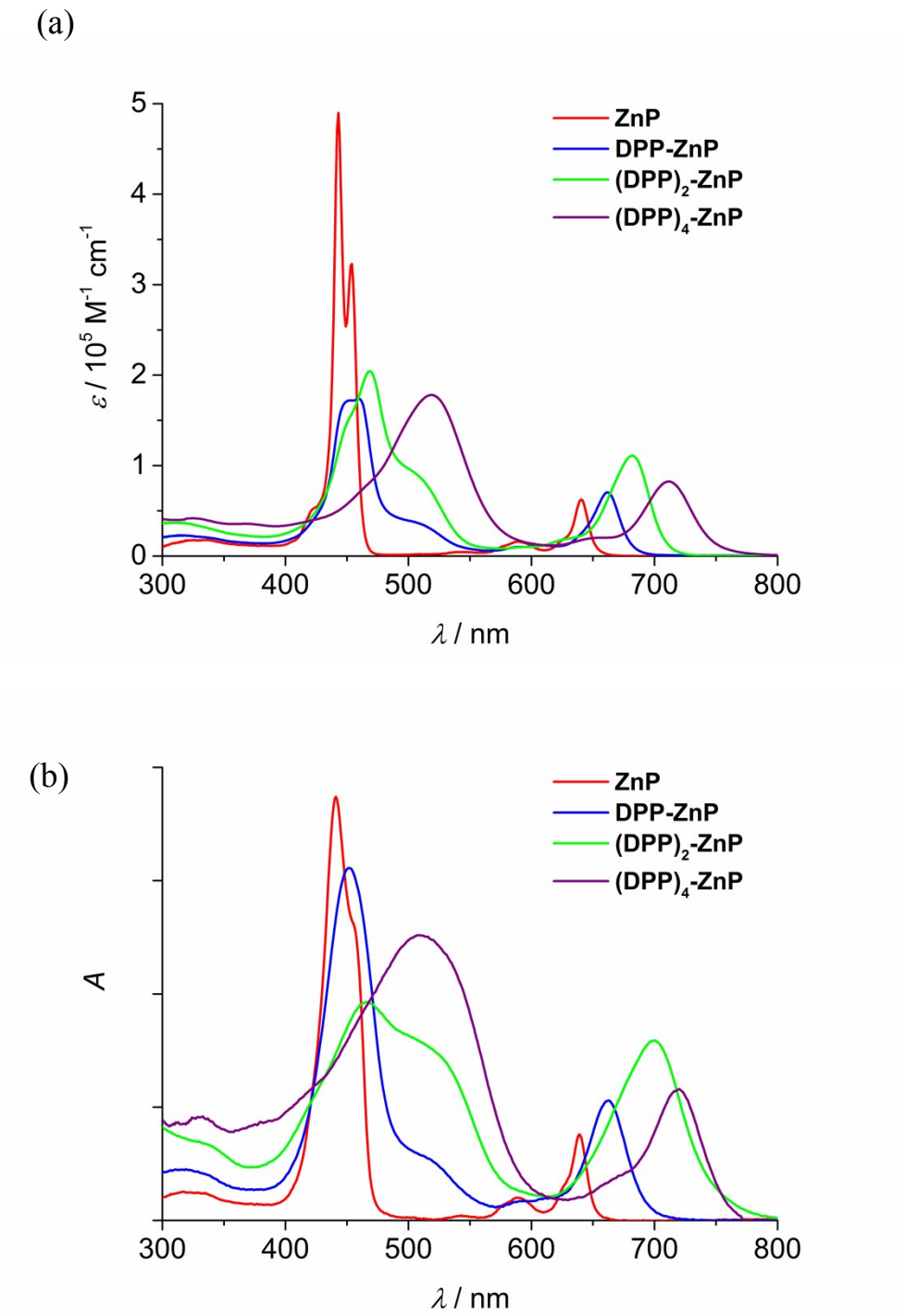


Figure S5. Absorption spectra of the four compounds in (a) DMSO and (b) H_2O + 1% DMSO.

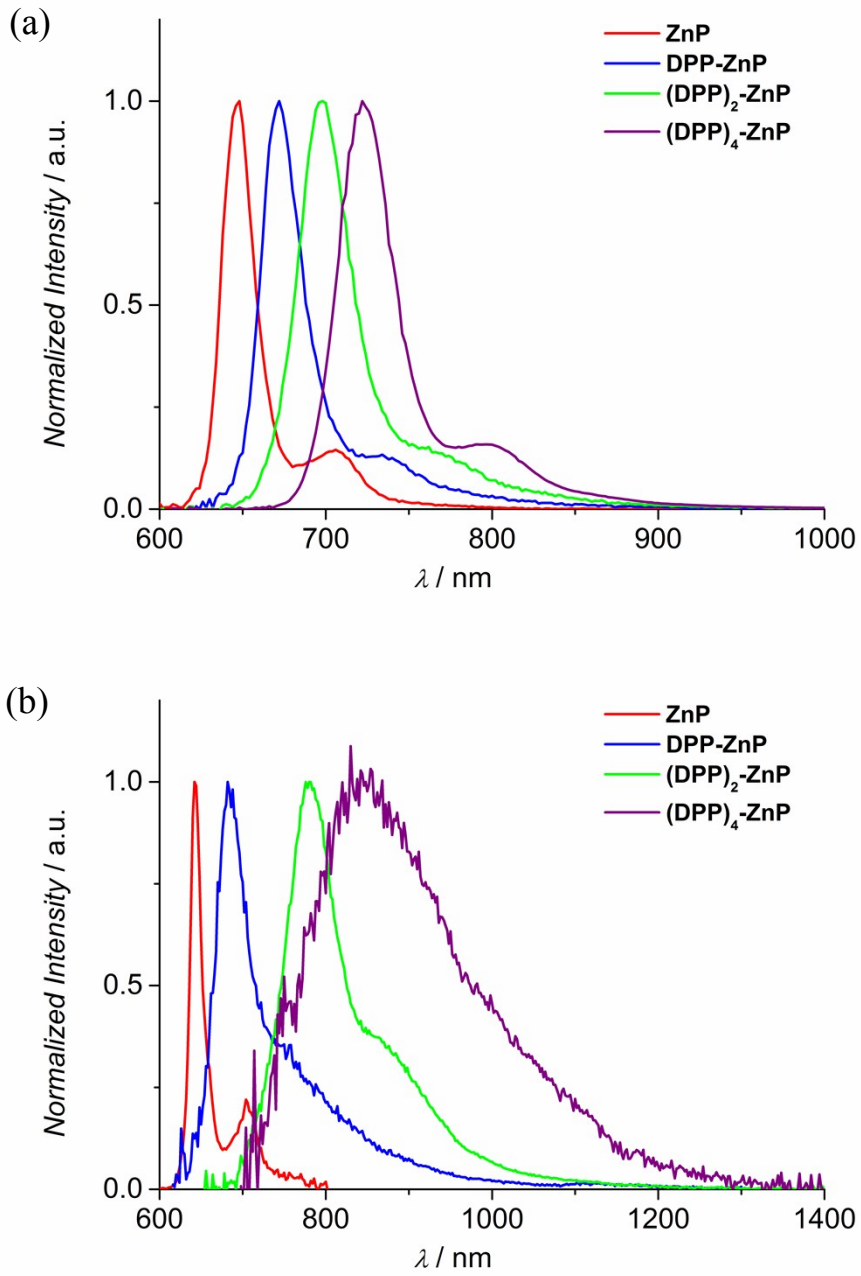


Figure S6. Normalized corrected room temperature emission spectra of the four compounds in (a) DMSO and (b) H_2O + 1% DMSO.

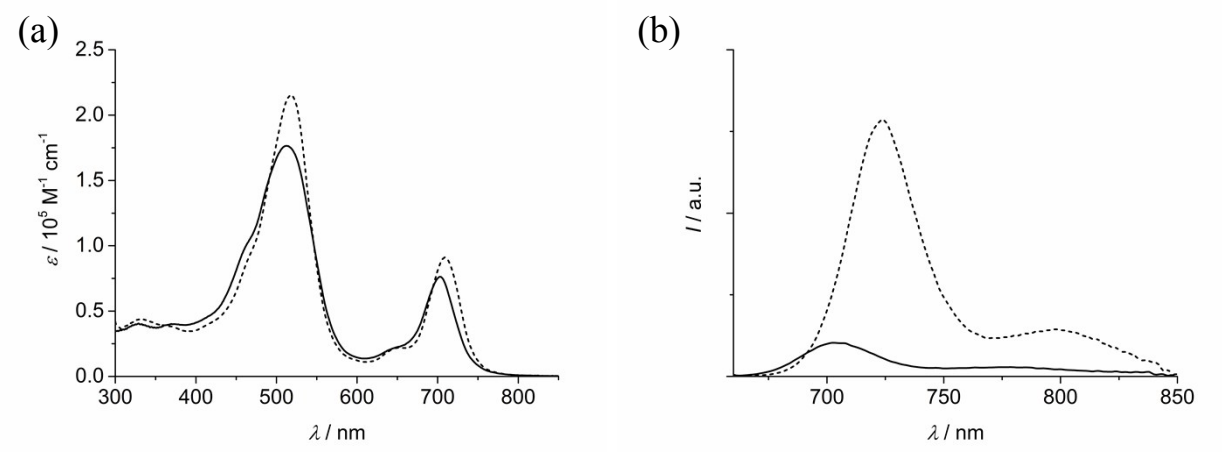


Figure S7. (a) Absorption spectra of **$(DPP)_4$-ZnP** in DCM (full line) and DCM + 1% pyridine (dashed line) and (b) emission spectra of isoabsorbing solutions of **$(DPP)_4$-ZnP** 6.3 × 10^{-7} M in the same solvents, excitation at 655 nm.

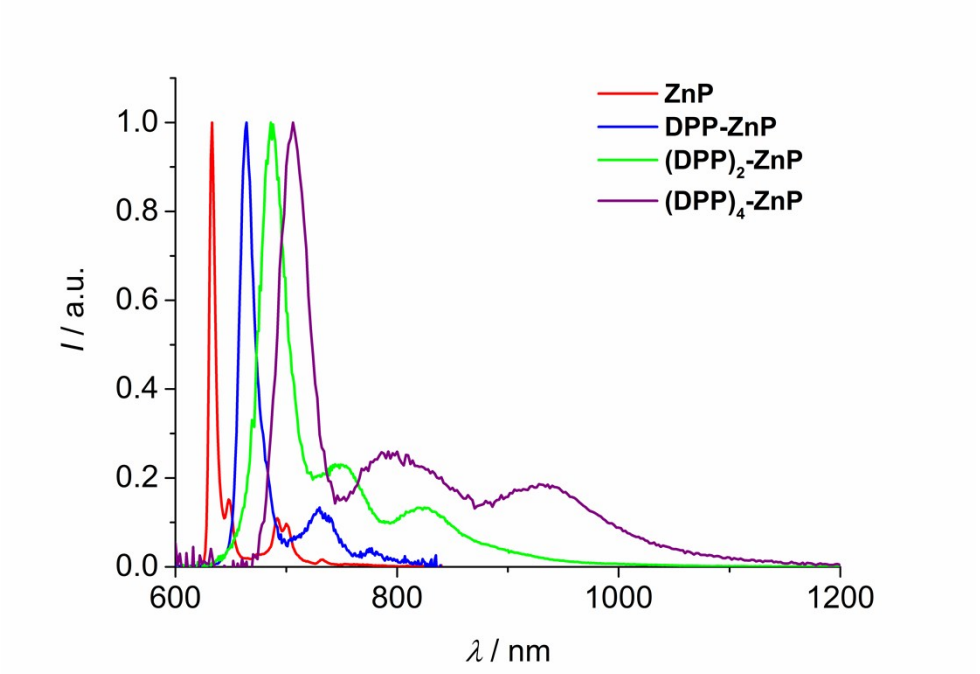


Figure S8: Normalized corrected fluorescence spectra of the four compounds at 77 K in DCM:MeOH (1:1).

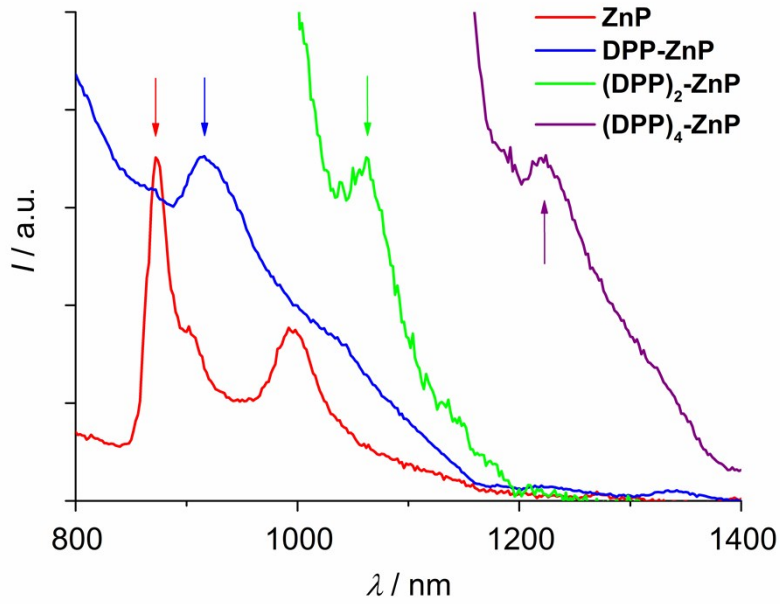


Figure S9. Arbitrarily scaled luminescence spectra of the four compounds at 77 K in DCM:MeOH:EtI (1:1:2).

Table S1. Fluorescence and phosphorescence data at 77 K in DCM:MeOH (1:1) and DCM:MeOH:EtI (1:1:2), respectively.

		λ_{max} / nm[a]	τ / ns [b]	E / eV
ZnP	*fluo*	633, 692, 732	1.90	1.96
	phos	872, 996	-	1.42
DPP-ZnP	*fluo*	664, 730, 776	1.22	1.87
	phos	914, 1034 sh	-	1.35
$(DPP)_2$-ZnP	*fluo*	687, 750, 824	0.86[c]	1.80
	phos	1062	-	1.16
$(DPP)_4$-ZnP	*fluo*	706, 792, 934	0.15 [20%]; 2.93 [80%]	1.76
	phos	1220	-	1.02

[a] From corrected emission spectra. [b] Fluorescence lifetimes, excitation at 465 nm. [c] Fluorescence bands at 750 and 824 nm show a second component (50% of the decay) with a lifetime of 4.05 ns.

Table S2. Triplet excited-state spectral features and lifetimes in air-free DMSO solutions.

	λ_{max} / nm	τ / μs
ZnP	470, 730	238.6
DPP-ZnP	570, 900	124.4
$(DPP)_2$-ZnP	570, 920	149.7
$(DPP)_4$-ZnP	590, 940	149.6

Singlet oxygen quantum yield determinations

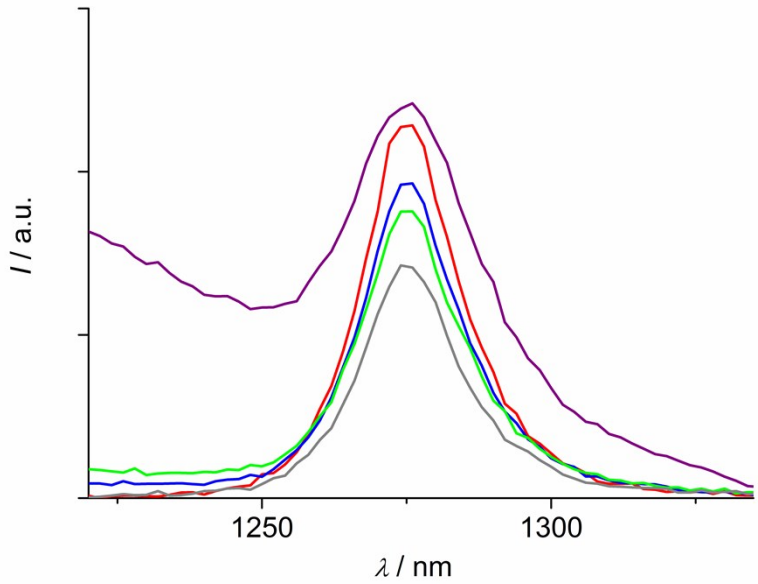


Figure S10. Singlet oxygen luminescence from optically matched solutions at 442 nm of **ZnP** (red), **DPP-ZnP** (blue), **$(DPP)_2$-ZnP** (green), **$(DPP)_4$-ZnP** (purple) and the standard Rose Bengal bis(triethyl-ammonium)salt (grey) in DCM (ϕ_Δ = 0.48). A_{442} = 0.505.

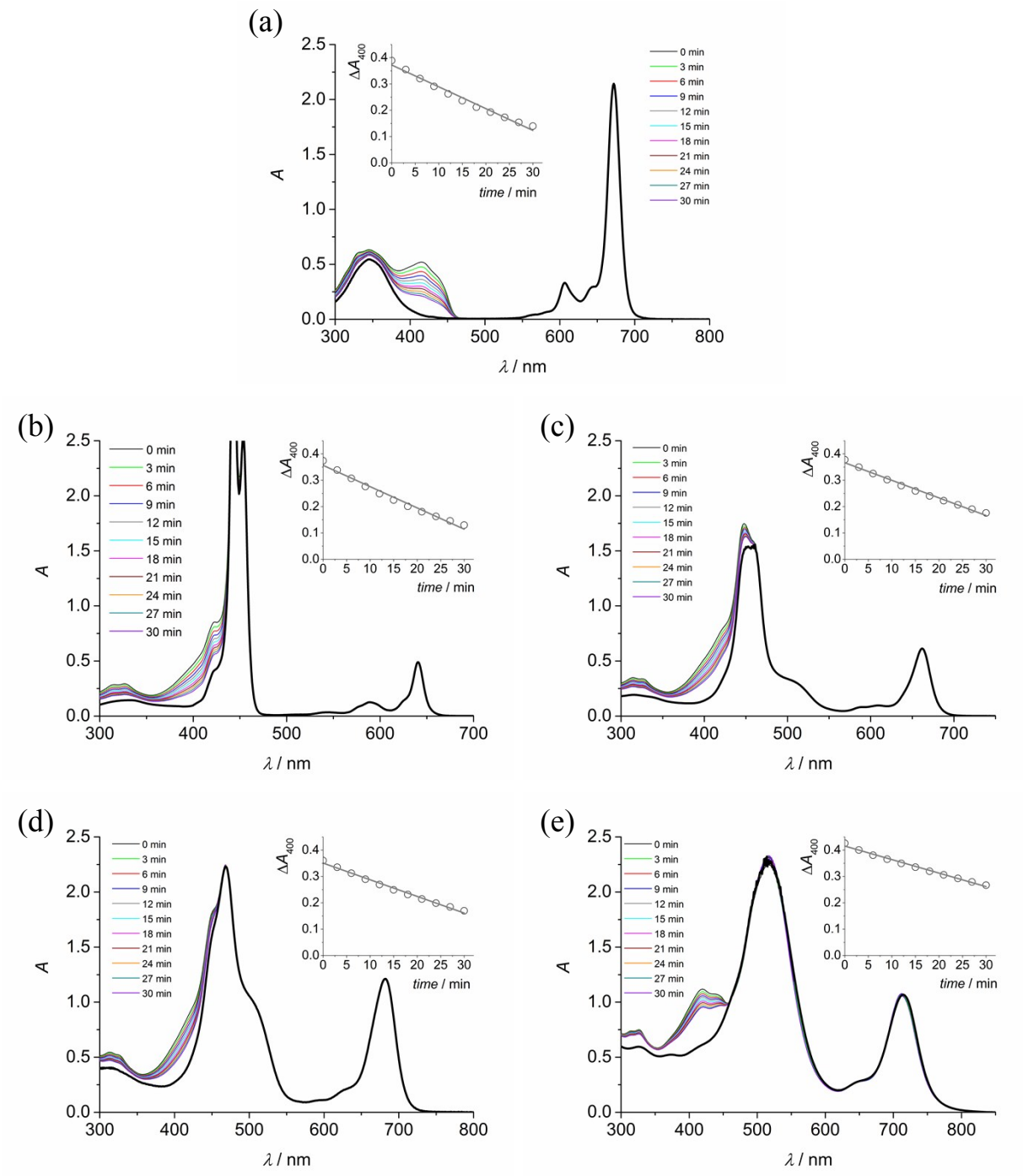


Figure S11. Absorption spectra of DMSO solutions containing (a) standard ZnPc, (b) **ZnP**, (c) **DPP-ZnP**, (d) **$(DPP)_2$-ZnP**, (e) **$(DPP)_4$-ZnP** and DPBF (2.2×10^{-5} M) upon irradiation at 646 nm (0-30 minutes). For comparison, the spectrum of a DMSO solution of each compound without DPBF is reported as a black thick curve. In the insets, DPBF absorbance at 400 nm is reported as a function of the irradiation time.

Computational data

Table S3. Vertical TD-DFT $S_0 \rightarrow T_n$ and $T_1 \rightarrow T_n$ transitions (in eV) of m-Zn-P, m-DPP-ZnP, m-$(DPP)_2$-ZnP and m-$(DPP)_4$-ZnP and associated wavelengths in nm.

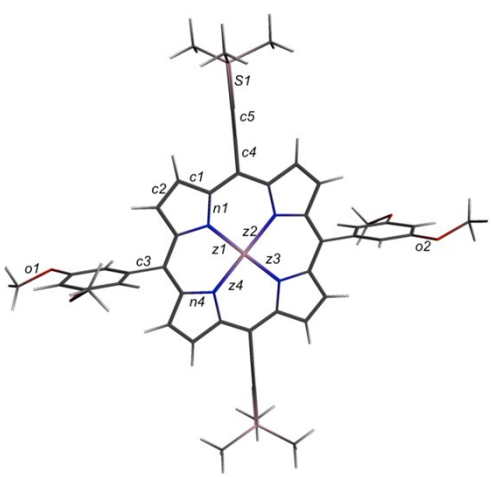
	$S_0 \rightarrow T_n$ on the geometry of the a^1A_g or a^1A electronic ground state	$S_0 \rightarrow T_n$ on the geometry of the lowest T_1 (a^3A_u or a^3A) excited state	$T_1 \rightarrow T_n$ on the geometry of the lowest T_1 (a^3A_u or a^3A) excited state
m-ZnP	1.466 $a^1A_g \rightarrow a^3A_u$	1.249 $a^1A_g \rightarrow a^3A_u$ **1000 nm**	0.500 $a^3A_u \rightarrow b^3A_u$
	1.692 $a^1A_g \rightarrow b^3A_u$	1.641 $a^1A_g \rightarrow b^3A_u$	0.569 $a^3A_u \rightarrow c^3A_u$
	1.870 $a^1A_g \rightarrow c^3A_u$	1.822 $a^1A_g \rightarrow c^3A_u$ 686 nm	1.226 $a^3A_u \rightarrow a^3A_g$ **1019 nm** f=0.012
	2.031 $a^1A_g \rightarrow d^3A_u$	2.099 $a^1A_g \rightarrow d^3A_u$	1.310 $a^3A_u \rightarrow d^3A_u$
	2.644 $a^1A_g \rightarrow a^3A_g$	2.485 $a^1A_g \rightarrow a^3A_g$	1.332 $a^3A_u \rightarrow e^3A_g$ **938 nm** f=0.025
			1.633 $a^3A_u \rightarrow f^3A_g$ **765 nm** f=0.39
			1.766 $a^3A_u \rightarrow g^3A_u$
			1.771 $a^3A_u \rightarrow h^3A_g$ **705 nm** f=1.77
			1.791 $a^3A_u \rightarrow i^3A_g$ **697 nm** f=0.001
			1.798 $a^3A_u \rightarrow j^3A_u$
m-DPP-ZnP[a]	1.276 $a^1A \rightarrow a^3A$	0.828 $a^1A \rightarrow a^3A$ 1509 nm 1.015 1231 nm[b]	0.846 $a^3A \rightarrow b^3A$
	1.433 $a^1A \rightarrow b^3A$	1.374 $a^1A \rightarrow b^3A$	1.222 $a^3A \rightarrow c^3A$
	1.659 $a^1A \rightarrow c^3A$	1.637 $a^1A \rightarrow c^3A$	1.261 $a^3A \rightarrow d^3A$ 991 nm f=0.009
	1.830 $a^1A \rightarrow d^3A$	1.801 $a^1A \rightarrow d^3A$	1.338 $a^3A \rightarrow e^3A$

			934 nm f=0.003
	2.029 $a^1A \rightarrow e^3A$	1.991 $a^1A \rightarrow e^3A$	1.504 $a^3A \rightarrow f^3A$ **831 nm** f=0.021
	2.280 $a^1A \rightarrow f^3A$		1.740 $a^3A \rightarrow g\ ^3A$ 718 nm f=0.002
	2.310 $a^3A \rightarrow g^3A$		1.746 $a^3A \rightarrow h\ ^3A$ 715 nm f=0.003
			1.763 $a^3A \rightarrow i\ ^3A$ **709 nm** f=0.099
			1.830 $a^3A \rightarrow j^3A$ 683 nm f=0.002
			1.882 $a^3A \rightarrow k^3A$ **664 nm** f=0.038
m-$(DPP)_2$-ZnP	1.252 $a^1A_g \rightarrow a^3A_u$	1.068 $a^1A_g \rightarrow a^3A_u$ **1170 nm**	0.566 $a^3A_u \rightarrow b^3A_u$
	1.331 $a^1A_g \rightarrow b^3A_g$	1.300 $a^1A_g \rightarrow b^3A_g$	0.646 $a^3A_u \rightarrow c^3A_u$
	1.425 $a^1A_g \rightarrow b^3A_u$	1.370 $a^1A_g \rightarrow b^3A_u$	0.751 $a^3A_u \rightarrow a^3A_g$ 1665 nm f=0.0008
	1.632 $a^1A_g \rightarrow c^3A_u$	1.584 $a^1A_g \rightarrow c^3A_u$ 789 nm	0.880 $a^3A_u \rightarrow d^3A_u$
	1.806 $a^1A_g \rightarrow d^3A_u$		0.986 $a^3A_u \rightarrow b^3A_g$ 1268 nm f=1.989
	2.030 $a^1A_g \rightarrow c^3A_g$	1.977 $a^1A_g \rightarrow c^3A_g$	1.138 $a^3A_u \rightarrow e^3A_u$
	2.134 $a^1A_g \rightarrow e^3A_u$		
m-$(DPP)_4$-ZnP	1.250 $a^1A_g \rightarrow a^3A_u$	1.062 $a^1A_g \rightarrow a^3A_u$ **1177 nm**	0.216 $a^3A_u \rightarrow b^3A_u$
	1.251 (^3A_u)	1.225 (^3A_u)	0.688 $a^3A_u \rightarrow c^3A_u$
	1.343 (^3A_g)	1.314 (^3A_g)	0.755 $a^3A_u \rightarrow a^3A_g$ 1657 nm f=0.097
	1.349 (^3A_g)	1.321 (^3A_g)	0.843 $a^3A_u \rightarrow b^3A_g$

			1483 nm f=0.34
	1.409 (^3A_u)	1.358 (^3A_u)	0.906 $a^3A_u \rightarrow c^3A_g$ 1380 nm f=1.099
	1.412 (^3A_u)		
	1.778 (^3A_u)		
	1.781 (^3A_u)		
	2.087 (^3A_g)		
	2.094 (^3A_g)		
	2.118 (^3A_u)		
	2.122 (^3A_u)		

Table S4. Optimized important bond lengths (in Å) of m-ZnP, m-DPP-ZnP, m-$(DPP)_2$-ZnP and m-$(DPP)_4$-ZnP in the electronic ground state. The X-ray structure of **ZnP** is reported for comparison, as well as its symmetric structure with Ci (Centre of inversion). (Bonds labels according to Scheme S1).

	ZnP X-ray	m-ZnP		m-ZnP with Ci	m-DPP-ZnP	m-$(DPP)_2$-ZnP with Ci	m-$(DPP)_4$-ZnP with Ci
z1	2.083	2.047		2.047	2.048	2.049	2.052
z2	2.060	2.049		2.049	2.047	2.048	2.051
z3	2.070	2.047		2.047	2.049	2.049	2.052
z4	2.071	2.049		2.049	2.048	2.048	2.051
n1	1.366	1.365		1.365	1.366	1.363	1.367
n4	1.378	1.374		1.373	1.375	1.374	1.367
c1	1.439	1.439		1.439	1.439	1.439	1.437
c2	1.349	1.357		1.357	1.358	1.357	1.358
c3	1.501	1.501		1.501	1.500	1.500	-
c4	1.441	1.425		1.425	1.425	-	-
c5	1.204	1.216		1.216	1.216	-	-
o1	1.434	1.433		1.433	1.433	1.434	-
o2	1.370	1.366		1.366	1.367	1.367	-
s1	1.843	1.853	1.853	1.854	-		



Scheme S1. Labels of the important bond lengths.

Table S5. Cartesian coordinates (in Å) of the DFT(B3LYP) optimized structures of the model systems m-ZnP, m-DPP-ZnP, m-$(DPP)_2$-ZnP and m-$(DPP)_4$-ZnP.

m-ZnP	m-DPP-ZnP	m-DPP-ZnP-DPP	m-$(DPP)_4$-ZnP
C 4.60365 2.96352 3.82194	Zn -0.056912 0.106837 -0.001188	Zn 0.013891 0.29719 0.275826	C -0.055574 -2.60568 -1.62238
C 5.30122 2.59858 2.61736	N -1.4812 1.27329 -0.899544	N -1.42359 1.42007 -0.656871	C -0.02356 -3.10635 -2.96884
H 5.21945 1.64724 2.12161	N 1.40828 1.09296 -1.03964	N 1.46982 1.26856 -0.788842	H -0.056843 -4.14485 -3.24596
C 6.05619 3.66757 2.25707	N 1.36673 -1.06054 0.894555	N 1.45091 -0.830807 1.20329	C 0.058894 -2.02756 -3.78877
H 6.71102 3.75682 1.40743	N -1.52186 -0.878814 1.03676	N -1.44142 -0.670414 1.34437	H 0.105585 -2.01723 -4.86324
C 5.82459 4.69736 3.23844	C -1.26668 2.27183 -1.80358	C -1.22027 2.38343 -1.59998	C 0.07431 -0.86395 -2.94604
C 6.41595 5.9655 3.21587	C -2.83654 1.22455 -0.675807	C -2.77768 1.36771 -0.428492	C 0.151671 0.463769 -3.41533
C 6.19606 6.97856 4.15581	C 2.72527 -0.980237 0.707785	C 2.80937 -0.73763 1.01775	C 0.166723 1.61842 -2.6052
C 6.79995 8.28635 4.10886	C 1.1526 -2.04709 1.81402	C 1.24688 -1.8008 2.13943	C 0.242571 2.96408 -3.10345
H 7.4891 8.62409 3.35403	C 1.23113 2.09033 -1.95297	C 1.28112 2.23102 -1.73609	H 0.29107 3.23937 -4.14186
C 6.33179 8.97874 5.17871	C 2.75927 0.847419 -0.976895	C 2.82375 1.04608 -0.712867	C 0.23797 3.78538 -2.02231
H 6.56337 9.98903 5.46783	C -2.87361 -0.647467 0.960104	C -2.79519 -0.446418 1.26997	H 0.283371 4.8598 -2.00877
C 5.43969 8.1011 5.88929	C -1.34748 -1.91345 1.9112	C -1.25808 -1.68216 2.23977	C 0.158747 2.94408 -0.860189
C 4.74255 8.44706 7.06554	C -2.51843 2.88355 -2.1625	C -2.47854 2.96733 -1.98174	C 0.134706 3.41432 0.468961
C 3.87089 7.59513 7.77574	C -3.48774 2.24055 -1.46341	C -3.44043 2.34374 -1.25502	C 0.055574 2.60568 1.62238
C 3.17741 7.9582 8.98329	C 2.41065 -2.6077 2.2294	C 2.50995 -2.33869 2.56953	C 0.02356 3.10635 2.96884
H 3.24537 8.91562 9.46928	H -2.63386 3.70039 -2.85277	H -2.6034 3.75454 -2.70403	H 0.056843 4.14485 3.24596
C 2.45009 6.87694 9.36321	H -4.5465 2.43299 -1.47544	H -4.50123 2.52426 -1.27276	C -0.058894 2.02756 3.78877
H 1.80737 6.7822 10.2215	H 2.52524 -3.39938 2.94877	H 2.63611 -3.11345 3.3048	H -0.105585 2.01723 4.86324
C 2.68987 5.84359 8.38761	H 4.44662 -2.09681 1.60839	H 4.54142 -1.81357 1.94711	C -0.07431 0.86395 2.94604
C 2.11402 4.56871 8.421	C 3.38248 -1.94742 1.54956	C 3.47573 -1.679 1.88081	C -0.151671 -0.463769 3.41533
C 2.32184 3.56125 7.47236	C -2.62492 -2.3588 2.40041	C -2.53019 -2.1205 2.74905	C -0.166723 -1.61842 2.6052
C 1.71171 2.2562 7.51476	H -2.77131 -3.16371 3.09933	H -2.67267 -2.90792 3.46763	C -0.242571 -2.96408 3.10345
H 1.0359 1.91253 8.27885	C -3.5679 -1.57901 1.81251	C -3.47995 -1.35704 2.1512	H -0.29107 -3.23937 4.14186
C 2.15163 1.57644 6.42508	H -4.63559 -1.62673 1.93875	H -4.5464 -1.40413 2.288	C -0.23797 -3.78538 2.02231
H 1.90657 0.57216 6.12632	C -3.49572 0.333476 0.178005	C -3.4267 0.504449 0.460867	H -0.283371 -4.8598 2.00877
C 3.03778 2.4568 5.71042	C -0.106852 -2.46622 2.29127	C -0.010997 -2.22278 2.62263	C -0.158747 -2.94408 0.860189
C 3.7136 2.11992 4.51913	C 3.38374 -0.103279 -0.162566	C 3.45862 0.126556 0.129341	C -0.134706 -3.41432 -0.468961
C 7.34502 6.26935 2.07724	C 3.44726 1.72219 -1.892	C 3.50256 1.90162 -1.6521	C 0.202374 4.81618 0.665319
C 6.8215 6.79937 0.89218	H 4.51151 1.74045 -2.05123	H 4.56721 1.93197 -1.80654	C 0.262899 6.00904 0.853303
H 5.76156 6.98361 0.818863	C 2.50318 2.48973 -2.49347	C 2.5493 2.6327 -2.28396	C -0.202374 -4.81618 -0.665319
C 7.68112 7.07542 -0.166464	H 2.6487 3.25372 -3.23647	H 2.68661 3.37328 -3.05174	C -0.262899 -6.00904 -0.853303
C 9.05521 6.82833 -0.055403	C -0.00948 2.65706 -2.31833	C 0.033112 2.76275 -2.12797	N 0.004772 -1.24017 -1.6335
H 9.68859 7.05481 -0.899452	C -4.98937 0.440931 0.258741	C -4.92036 0.60313 0.551514	N 0.114701 1.63163 -1.2393
C 9.55964 6.30284 1.12694	C -5.57957 1.09328 1.33644	C -5.50351 1.32012 1.5915	N -0.004772 1.24017 1.6335
C 8.70145 6.02179 2.19986	C -5.77967 -0.101332 -0.749824	C -5.71718 -0.021168 -0.402942	N -0.114701 -1.63163 1.2393
H 9.11232 5.61153 3.11157	C -6.9692 1.20363 1.40279	C -6.89348 1.41129 1.6753	Zn 0.0 0.0 0.0
C 4.92992 9.76343 7.57856	H -4.97617 1.5208 2.12447	H -4.89451 1.81022 2.33803	C -0.342428 -7.40706 -1.07021
C 5.08531 10.8839 8.0236	C -7.16851 0.015651 -0.679945	C -7.10657 0.074835 -0.314604	C -0.406109 -7.92168 -2.37692
C 1.2119 4.25247 9.57777	H -5.33275 -0.609245 -1.59252	H -5.27539 -0.581667 -1.21458	C -0.365391 -8.30601 0.010079
C 1.76797 3.72876 10.7505	C -7.77573 0.667684 0.395939	C -7.70712 0.790534 0.724123	C -0.513759 -9.28171 -2.59204
H 2.83185 3.5602 10.801	H -8.84762 0.756386 0.447914	H -8.77947 0.862914 0.790338	H -0.370788 -7.24649 -3.21871

C 0.934981 3.43809 11.8264	C 4.87937 -0.190341 -0.232556	C 4.95545 0.056498 0.069613	C -0.457681 -9.66645 -0.211065
C -0.444804 3.66423 11.7445	C 5.65964 0.728595 0.462116	C 5.72016 0.993176 0.757722	H -0.31326 -7.92832 1.02034
H -1.0571 3.42649 12.6009	C 5.4817 -1.18433 -0.997192	C 5.57413 -0.944553 -0.672631	C -0.547996 -10.1784 -1.51347
C -0.981604 4.1838 10.5741	C 7.05099 0.652076 0.38739	C 7.1129 0.92595 0.701083	H -0.543728 -9.65207 -3.60523
C -0.150355 4.47971 9.48408	H 5.20306 1.50557 1.05873	H 5.25071 1.77448 1.33855	H -0.473281 -10.3444 0.628667
H -0.58638 4.88455 8.58187	C 6.87367 -1.25733 -1.06581	C 6.9672 -1.0075 -0.724108	C 0.342428 7.40706 1.07021
C 3.47842 0.824489 3.97343	H 4.88616 -1.90241 -1.5428	H 4.99052 -1.67697 -1.2122	C 0.406109 7.92168 2.37692
C 3.27463 -0.275428 3.4977	C 7.67057 -0.340679 -0.375587	C 7.74881 -0.074002 -0.038886	C 0.365391 8.30601 -0.010079
N 4.93651 4.23832 4.18039	H 8.74442 -0.398111 -0.43125	H 8.82368 -0.124433 -0.080363	C 0.513759 9.28171 2.59204
N 5.3737 6.89492 5.25271	O 7.73588 1.5977 1.09785	O 7.78214 1.88701 1.40561	H 0.370788 7.24649 3.21871
N 3.55991 6.31061 7.43288	O 7.37727 -2.26525 -1.83929	O 7.48767 -2.02413 -1.47492	C 0.457681 9.66645 0.211065
N 3.12547 3.65341 6.36234	O -7.4604 1.85914 2.49654	O -7.37778 2.13412 2.72937	H 0.31326 7.92832 -1.02034
O 7.27908 7.59234 -1.36642	O -7.86348 -0.540361 -1.71701	O -7.80906 -0.567289 -1.29548	C 0.547996 10.1784 1.51347
O 10.8798 6.02449 1.33845	C 8.80022 -2.39891 -1.9448	C 8.91278 -2.14808 -1.56198	H 0.543728 9.65207 3.60523
O 1.36981 2.92524 13.0164	H 9.24889 -2.58617 -0.968453	H 9.35147 -2.31663 -0.577784	H 0.473281 10.3444 -0.628667
O -2.3103 4.44137 10.3908	H 8.9675 -3.25453 -2.59087	H 9.09438 -3.01225 -2.19261	C -0.636559 -11.6178 -1.71774
Si 5.29834 12.598 8.69367	H 9.24437 -1.51013 -2.39483	H 9.35514 -1.26299 -2.02062	C 0.012993 -12.6257 -1.03831
Si 2.96375 -1.94368 2.75363	C 9.16785 1.58543 1.04669	C 9.21508 1.87482 1.38559	C -0.308136 -13.8724 -1.64942
Zn 4.24917 5.27433 5.80719	H 9.56603 0.655017 1.4532	H 9.6044 0.950113 1.81326	C 0.522602 -14.8451 -1.13693
C 4.62127 -2.69996 2.29373	H 9.52391 1.72851 0.02572	H 9.59322 2.00445 0.370818	C 0.636559 11.6178 1.71774
H 5.14941 -2.0836 1.56319	H 9.49063 2.4179 1.66328	H 9.52419 2.71574 1.9978	C -0.012993 12.6257 1.03831
H 5.25922 -2.8222 3.16796	C -9.29231 -0.429599 -1.71844	C -9.24029 -0.498466 -1.26671	C 0.308136 13.8724 1.64942
H 4.46736 -3.74678 1.87025	H -9.60308 0.615615 -1.73214	H -9.58387 0.5332 -1.35086	C -0.522602 14.8451 1.13693
C 2.06021 -3.02114 4.06811	H -9.62382 -0.918447 -2.62863	H -9.57866 -1.06462 -2.12825	C 1.22591 13.6179 2.73831
H 2.67157 -3.10682 4.97704	H -9.72498 -0.93581 -0.854893	H -9.63574 -0.949761 -0.356071	C -1.07462 12.8543 0.080752
H 1.09479 -2.57908 4.35112	C -8.88061 1.99953 2.6278	C -8.79794 2.25799 2.87676	C 1.07462 -12.8543 -0.080752
H 1.8685 -4.0369 3.69171	H -9.29464 2.57764 1.80096	H -9.23804 2.76517 2.01637	C -1.22591 -13.6179 -2.73831
C 1.8412 -1.80012 1.21168	H -9.36656 1.02476 2.68109	H -9.26385 1.2804 3.01223	N 1.39463 12.205 2.7221
H 0.87723 -1.33533 1.4601	H -9.03786 2.53449 3.55856	H -8.9486 2.85871 3.76847	N -1.39463 -12.205 -2.7221
H 2.32701 -1.1757 0.449147	C 0.008822 3.69403 -3.28505	C 0.038025 3.75498 -3.13982	N 1.33662 -14.2488 -0.185588
H 1.63962 -2.78538 0.765343	C -0.12435 -3.53391 3.2349	C -0.024395 -3.2828 3.56282	N -1.33662 14.2488 0.185588
C 11.8377 6.84329 0.34439	C 0.022095 4.57744 -4.11146	C 0.039299 4.58556 -4.01904	C 2.44505 11.5777 3.5152
H 12.8329 6.74967 0.784906	C 0.052281 5.60689 -5.08495	C -0.036659 -4.18775 4.36526	H 2.07592 11.2653 4.49101
H 11.7322 6.12524 -0.480637	C -1.13859 6.12591 -5.62513	C 0.050637 5.55816 -5.04915	H 2.84273 10.7177 2.98463
H 11.6996 7.86451 -0.037085	C 1.27743 6.13034 -5.53568	C -1.1461 5.98032 -5.65495	H 3.234 12.3098 3.6641
C 5.80142 7.29983 -1.83917	C -1.10166 7.11626 -6.58673	C 1.26195 6.11627 -5.49342	C -2.19006 14.9181 -0.788012
H 5.33523 6.31994 -1.66885	H -2.09012 5.74196 -5.28686	C -1.12726 6.91216 -6.67374	H -2.12844 14.3685 -1.72368
H 5.31034 8.05491 -1.2106	C 1.30926 7.11357 -6.50533	H -2.08665 5.56543 -5.32391	H -3.22933 14.932 -0.462182
H 5.69756 7.57592 -2.89103	H 2.20229 5.76125 -5.1169	C 1.27636 7.03935 -6.52078	H -1.84357 15.9365 -0.939776
C 2.66959 3.28213 13.4475	C 0.12147 7.61942 -7.05863	H 2.1888 5.82166 -5.02426	C 2.19006 -14.9181 0.788012
H 3.16629 2.5263 12.8245	H -2.02616 7.50596 -6.98536	C 0.083785 7.448 -7.13783	H 3.22933 -14.932 0.462182
H 3.13125 4.26346 13.2733	H 2.26457 7.50902 -6.81399	H -2.05523 7.2259 -7.12684	H 2.12844 -14.3685 1.72368
H 2.77172 3.01226 14.501	C 0.122562 8.6676 -8.06848	H 2.21908 7.46573 -6.8266	H 1.84357 -15.9365 0.939776
C -3.3623 3.69276 11.2435	C -0.781838 9.69418 -8.24684	C 0.068108 8.43171 -8.21049	C -2.44505 -11.5777 -3.5152
H -4.35661 3.7784 10.7995	C -0.333945 10.5267 -9.31211	C -0.859295 9.4237 -8.45507	H -2.84273 -10.7177 -2.98463
H -3.21916 2.67392 11.6293	C -1.13469 11.6476 -9.37223	C -0.417934 10.2031 -9.56293	H -2.07592 -11.2653 -4.49101
H -3.26401 4.41455 12.066	N 1.11938 8.81695 -9.02782	C -1.21821 11.3206 -9.66873	H -3.234 -12.3098 -3.6641
C 6.54423 13.5297 7.55679	N -2.10369 11.5253 -8.38441	N 1.0679 8.54503 -9.168	O 1.81413 14.3507 3.53058
H 7.51818 13.0492 7.38767	C -3.31687 12.3203 -8.23494	N -2.18086 11.2465 -8.67385	O -1.66285 12.1214 -0.711333
H 6.03204 13.6055 6.58729	H -4.10062 11.6628 -7.8691	C -3.38324 12.0609 -8.54818	O 1.66285 -12.1214 0.711333
H 6.73039 14.5507 7.92183	H -3.18002 13.1272 -7.51656	H -4.19023 11.4184 -8.20756	O -1.81413 -14.3507 -3.53058
C 6.42623 12.393 10.4553	H -3.60718 12.7347 -9.19626	H -3.24767 12.8609 -7.82206	C -0.617344 16.2516 1.51625
H 7.39437 11.8911 10.3221	C 2.12355 7.83504 -9.42042	H -3.63953 12.487 -9.51335	C 0.554431 16.9684 1.7942
H 6.61396 13.3852 10.892	H 3.07007 8.0019 -8.90829	C 2.10288 7.56815 -9.48583	C -1.85619 16.8925 1.65493
H 5.84323 11.8089 11.1808	H 1.76511 6.83221 -9.20634	H 3.04665 7.81383 -9.00131	C 0.48806 18.2985 2.18361
C 3.82292 13.3849 9.06935	H 2.28811 7.94232 -10.4887	H 1.78244 6.5773 -9.17757	H 1.51182 16.4795 1.69514
H 3.26616 13.4617 8.12523	C -1.93512 10.3256 -7.64063	H 2.25481 7.58293 -10.5614	C -1.91741 18.219 2.0584
H 3.20458 12.8159 9.77759	C 0.894439 9.96627 -9.83325	C -2.00824 10.0832 -7.8724	H -2.77067 16.3465 1.47637
H 3.95144 14.4004 9.47292	O -2.69252 9.99062 -6.73182	C 0.826467 9.64291 -10.0412	C -0.746727 18.9274 2.31714
	O 1.6339 10.2854 -10.7624	O -2.75963 9.79666 -6.94271	H 1.39948 18.8438 2.38435
	C -1.01758 12.8044 -10.2541	O 1.57002 9.92507 -10.9783	H -2.87876 18.6984 2.17454
	C -0.58648 12.617 -11.5758	C -1.10158 12.4383 -10.6006	H -0.797187 19.9624 2.62479
	C -1.28091 14.1075 -9.80518	C -0.748092 12.1871 -11.9332	C 0.617344 -16.2516 -1.51625
	C -0.441612 13.7014 -12.4288	C -1.29051 13.764 -10.1853	C -0.554431 -16.9684 -1.7942
	H -0.370214 11.6195 -11.9277	C -0.604797 13.2354 -12.8309	C 1.85619 -16.8925 -1.65493
	C -1.12478 15.1898 -10.66	H -0.594848 11.1691 -12.259	C -0.48806 -18.2985 -2.18361
	H -1.57973 14.2789 -8.78212	C -1.1328 14.8096 -11.0843	H -1.51182 -16.4795 -1.69514
	C -0.711479 14.9907 -11.9749	H -1.53148 13.9788 -9.15492	C 1.91741 -18.219 -2.0584
	H -0.116554 13.5409 -13.4473	C -0.796513 14.5488 -12.4099	H 2.77067 -16.3465 -1.47637
	H -1.32164 16.1893 -10.298	H -0.34203 13.0278 -13.8582	C 0.746727 -18.9274 -2.31714
	H -0.596034 15.835 -12.6399	H -1.26867 15.8279 -10.7492	H -1.39948 -18.8438 -2.38435
	C -0.13867 -4.44564 4.03866	H -0.680626 15.3647 -13.1093	H 2.87876 -18.6984 -2.17454

	Si -0.150567 -5.84554 5.25428	C -0.076012 -5.25404 5.29709	H 0.797187 -19.9624 -2.62479
	C -1.93767 -6.32479 5.57181	C 1.10573 -5.888 5.71967	C 0.227917 0.652597 -4.81786
	C 0.672884 -5.25424 6.83474	C -1.30316 -5.70805 5.81147	C -0.227917 -0.652597 4.81786
	C 0.800783 -7.2794 4.5025	C 1.05747 -6.94341 6.60896	C -0.302424 -0.80751 6.01467
	H -2.50396 -5.48884 5.98781	H 2.05797 -5.54894 5.33962	C -0.412289 -0.986817 7.41606
	H -2.43103 -6.64407 4.65132	C -1.34697 -6.77277 6.69013	C -0.62936 -2.26535 7.95791
	H -1.98511 -7.15247 6.2849	H -2.21924 -5.21946 5.51521	C -0.315973 0.108571 8.29164
	H 0.140139 -4.40233 7.26265	C -0.169167 -7.41731 7.09829	C -0.774028 -2.43543 9.32108
	H 0.681557 -6.05614 7.57832	H 1.97405 -7.41877 6.92304	H -0.685578 -3.12054 7.3014
	H 1.70633 -4.95068 6.65388	H -2.30141 -7.08882 7.08198	C -0.445519 -0.06928 9.65522
	H 0.343755 -7.60909 3.56702	C -0.187083 -8.53213 8.03436	H -0.143007 1.09699 7.89307
	H 1.83653 -7.00274 4.29403	C 0.701669 -8.81997 9.04943	C -0.692607 -1.34019 10.1939
	H 0.810279 -8.1281 5.1922	N -1.18742 -9.49483 8.06474	H -0.924937 -3.42957 9.71258
		C 0.235433 -9.96474 9.75805	H -0.369406 0.781725 10.3146
		C 1.81877 -8.26308 9.78192	C -0.822797 -1.49741 11.6363
		C -2.18546 -9.76435 7.0364	C -0.113117 -0.871375 12.6387
		C -0.984483 -10.419 9.12811	N -1.70338 -2.38858 12.235
		C 0.991548 -10.1201 10.9003	C -0.525345 -1.40332 13.8947
		N 1.95093 -9.1193 10.9113	C 1.04406 -0.031127 12.8646
		O 2.57347 -7.31582 9.57131	C -1.56256 -2.3822 13.6514
		H -3.14011 -9.29726 7.27445	C 0.337412 -0.955549 14.8719
		H -1.83217 -9.40117 6.0755	N 1.26616 -0.121835 14.2674
		H -2.33129 -10.8401 6.98742	O 1.73151 0.667149 12.1231
		O -1.73478 -11.3698 9.33653	O -2.25363 -3.07687 14.3933
		C 0.837421 -11.1055 11.9663	C 0.302424 0.80751 -6.01467
		C 3.11856 -9.02622 11.779	C 0.412289 0.986817 -7.41606
		C 0.501178 -12.4258 11.6371	C 0.62936 2.26535 -7.95791
		C 0.974505 -10.755 13.3168	C 0.315973 -0.108571 -8.29164
		H 3.94577 -8.6437 11.1888	C 0.774028 2.43543 -9.32108
		H 2.9434 -8.34559 12.6102	H 0.685578 3.12054 -7.3014
		H 3.36946 -10.0098 12.1628	C 0.445519 0.06928 -9.65522
		C 0.325483 -13.3752 12.6337	H 0.143007 -1.09699 -7.89307
		H 0.387049 -12.7017 10.5995	C 0.692607 1.34019 -10.1939
		C 0.784274 -11.7054 14.3103	H 0.924937 3.42957 -9.71258
		H 1.20073 -9.73515 13.5909	H 0.369406 -0.781725 -10.3146
		C 0.466744 -13.0186 13.9722	C 0.822797 1.49741 -11.6363
		H 0.077312 -14.3928 12.3661	C 0.113117 0.871375 -12.6387
		H 0.880488 -11.4202 15.348	N 1.70338 2.38858 -12.235
		H 0.326006 -13.7583 14.7478	C 0.525345 1.40332 -13.8947
			C -1.04406 0.031127 -12.8646
			C 1.56256 2.3822 -13.6514
			C -0.337412 0.955549 -14.8719
			N -1.26616 0.121835 -14.2674
			O -1.73151 -0.667149 -12.1231
			O 2.25363 3.07687 -14.3933
			C 2.21299 0.767836 14.9286
			H 1.86041 0.998588 15.9295
			H 3.20477 0.32121 14.9861
			H 2.27938 1.68244 14.345
			C -2.82769 -3.07285 11.6074
			H -3.15427 -2.51907 10.732
			H -2.56555 -4.08967 11.3188
			H -3.63614 -3.11822 12.3318
			C 2.82769 3.07285 -11.6074
			H 2.56555 4.08967 -11.3188
			H 3.15427 2.51907 -10.732
			H 3.63614 3.11822 -12.3318
			C -2.21299 -0.767836 -14.9286
			H -3.20477 -0.32121 -14.9861
			H -1.86041 -0.998588 -15.9295
			H -2.27938 -1.68244 -14.345
			C 0.356152 -1.29168 16.2926
			C -0.855701 -1.40035 16.9883
			C 1.55574 -1.55104 16.9703
			C -0.864707 -1.74113 18.3335
			H -1.7838 -1.20784 16.4712
			C 1.53995 -1.90637 18.3119
			H 2.49646 -1.50387 16.4419
			C 0.331753 -1.99496 18.999
			H -1.80481 -1.80975 18.8624
			H 2.47011 -2.11706 18.8201
			H 0.3226 -2.26412 20.0459

			C -0.356152 1.29168 -16.2926
			C 0.855701 1.40035 -16.9883
			C -1.55574 1.55104 -16.9703
			C 0.864707 1.74113 -18.3335
			H 1.7838 1.20784 -16.4712
			C -1.53995 1.90637 -18.3119
			H -2.49646 1.50387 -16.4419
			C -0.331753 1.99496 -18.999
			H 1.80481 1.80975 -18.8624
			H -2.47011 2.11706 -18.8201
			H -0.3226 2.26412 -20.0459

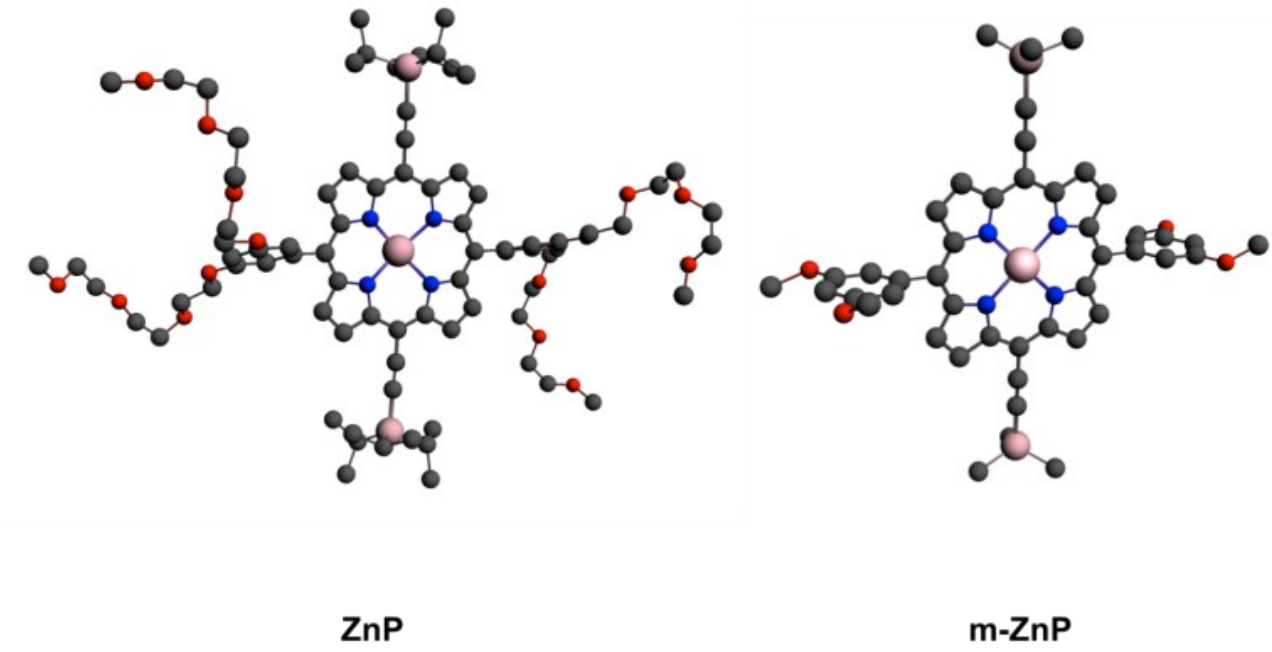


Figure S12. DFT optimized structure of m-ZnP in the electronic ground state, as compared to the X-ray structure of **ZnP** (the DMSO coordinated to the Zn metal centre is not shown, for the complete structure see Fig. S16). H atoms are hidden for the sake of clarity.

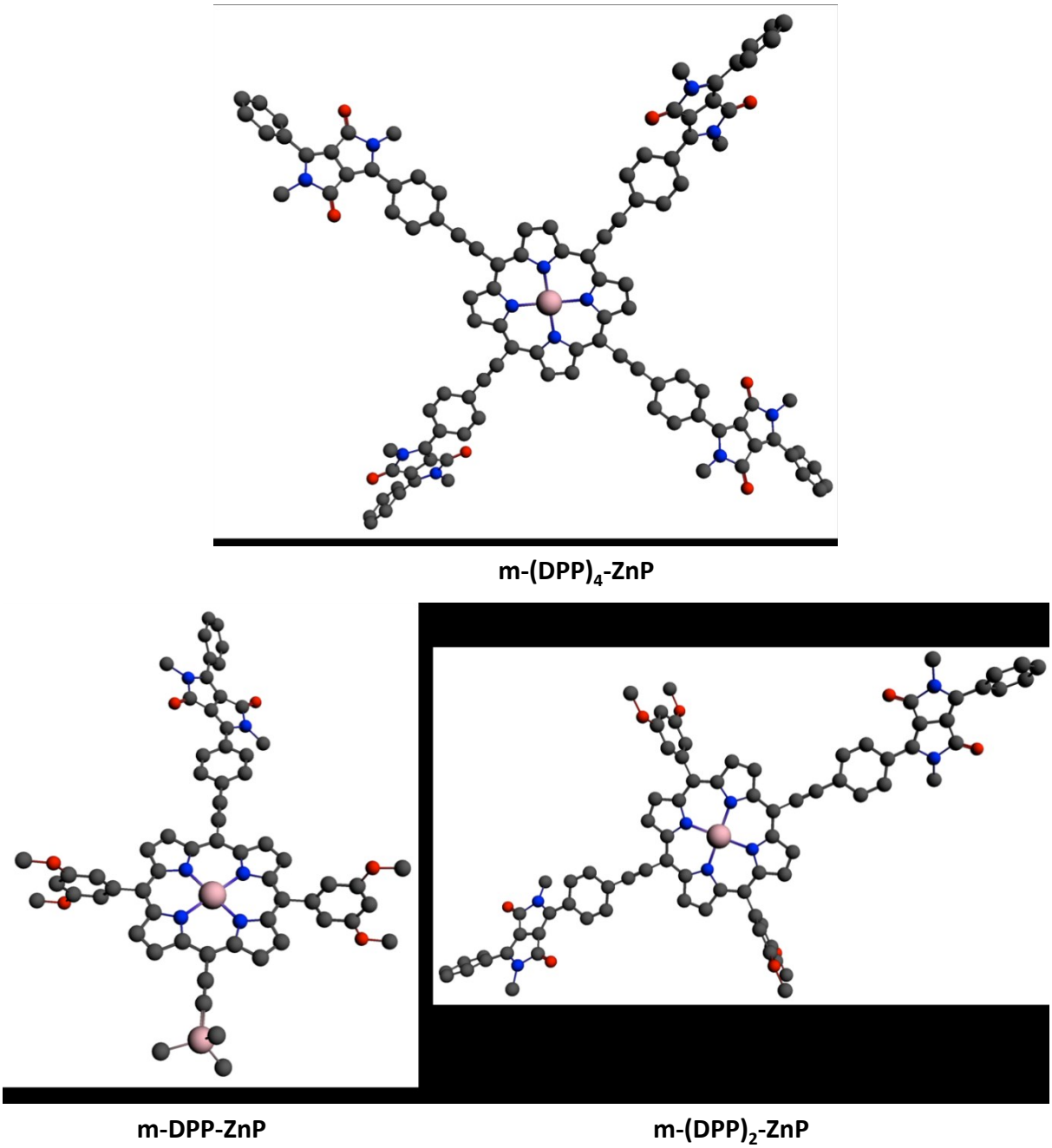
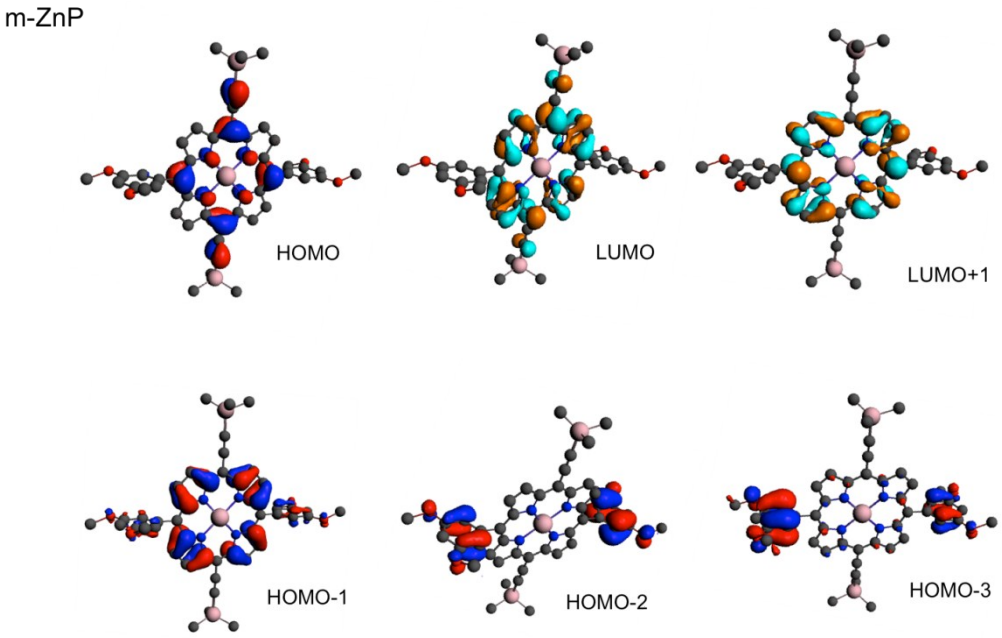
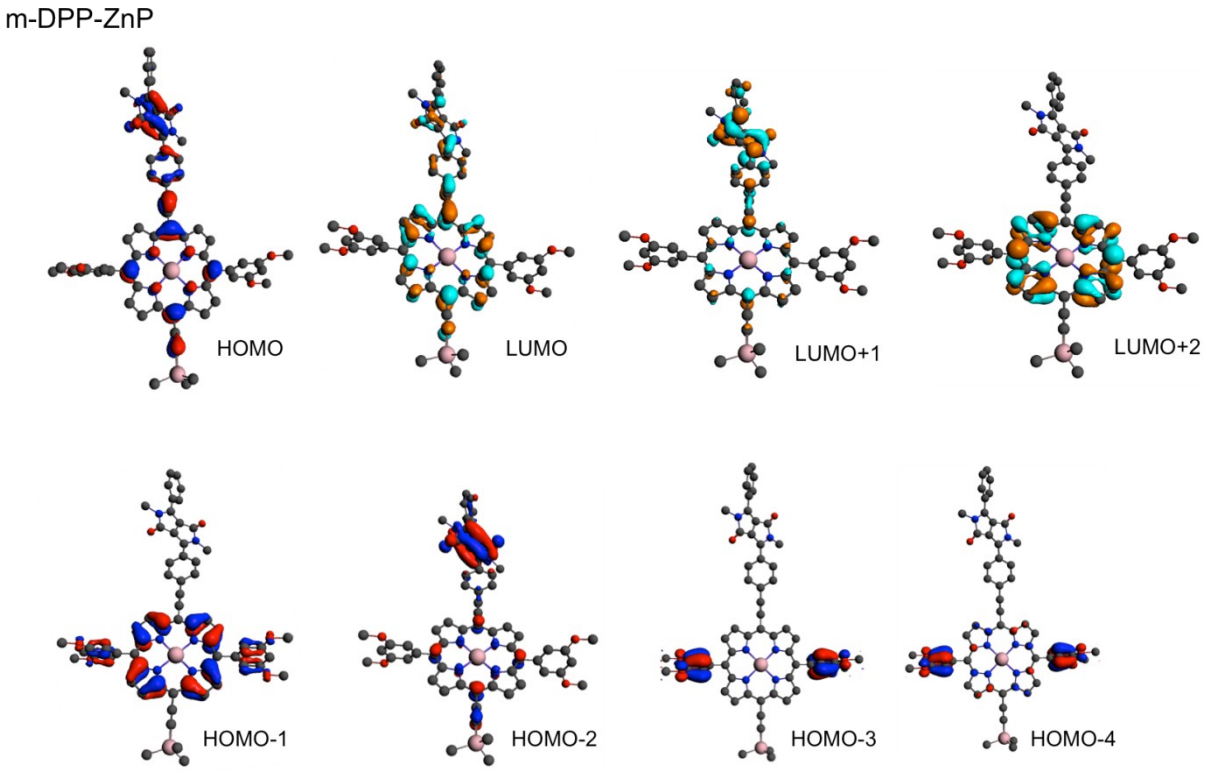


Figure S13. DFT(B3LYP) optimized structures of m-DPP-ZnP, m-$(DPP)_2$-ZnP and m-$(DPP)_4$-ZnP.

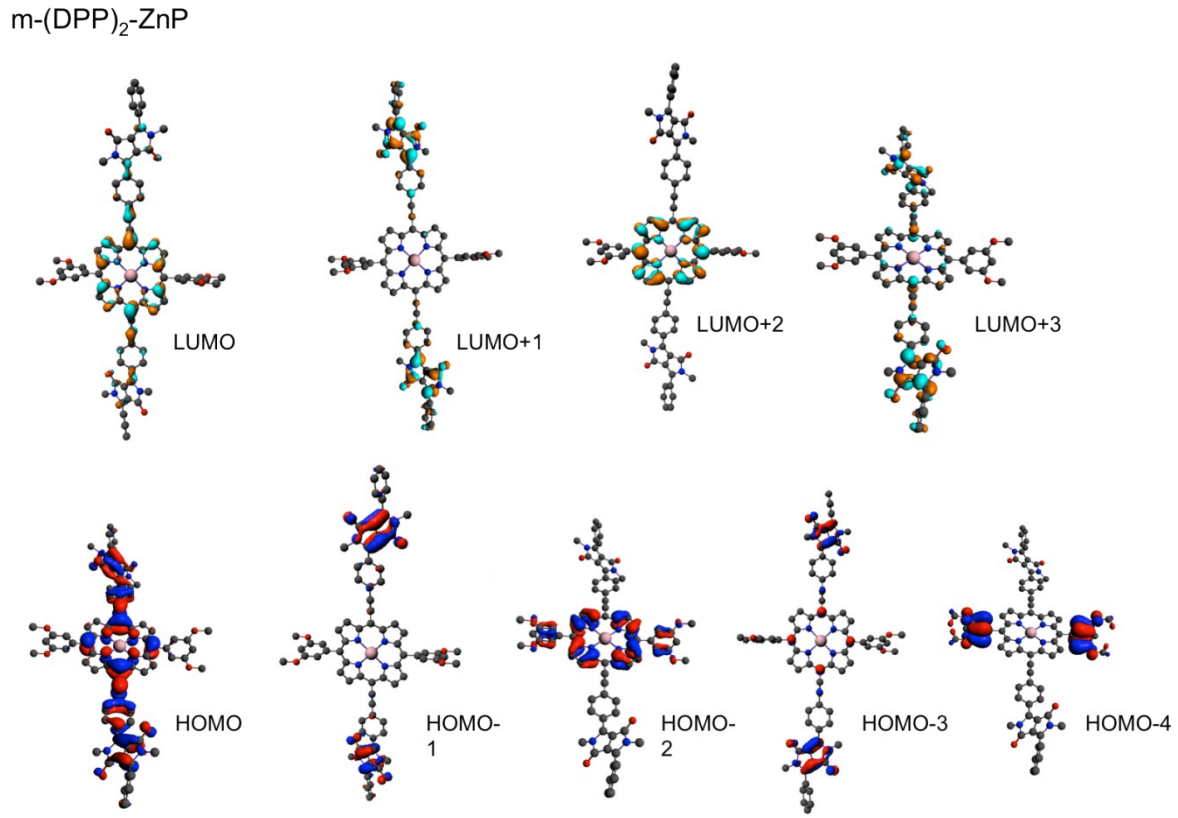
(a)


m-ZnP
HOMO
LUMO
LUMO+1
HOMO-1
HOMO-2
HOMO-3

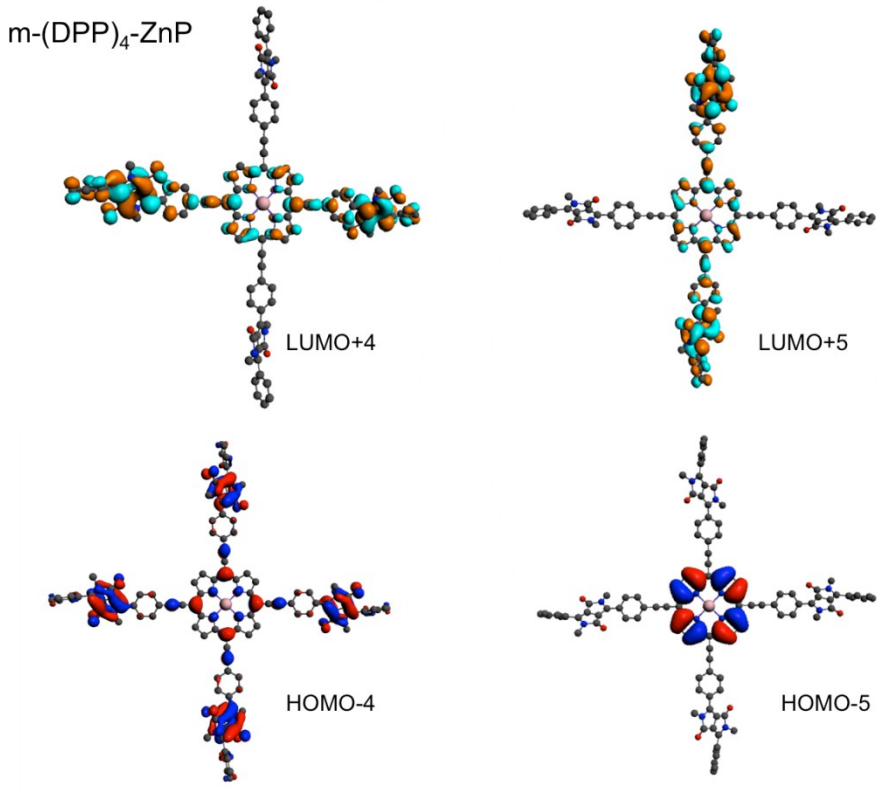
(b)


m-DPP-ZnP
HOMO
LUMO
LUMO+1
LUMO+2
HOMO-1
HOMO-2
HOMO-3
HOMO-4

(c)


m-(DPP)2-ZnP
LUMO
LUMO+1
LUMO+2
LUMO+3
HOMO
HOMO-1
HOMO-2
HOMO-3
HOMO-4

(d)


m-(DPP)4-ZnP
LUMO+4
LUMO+5
HOMO-4
HOMO-5

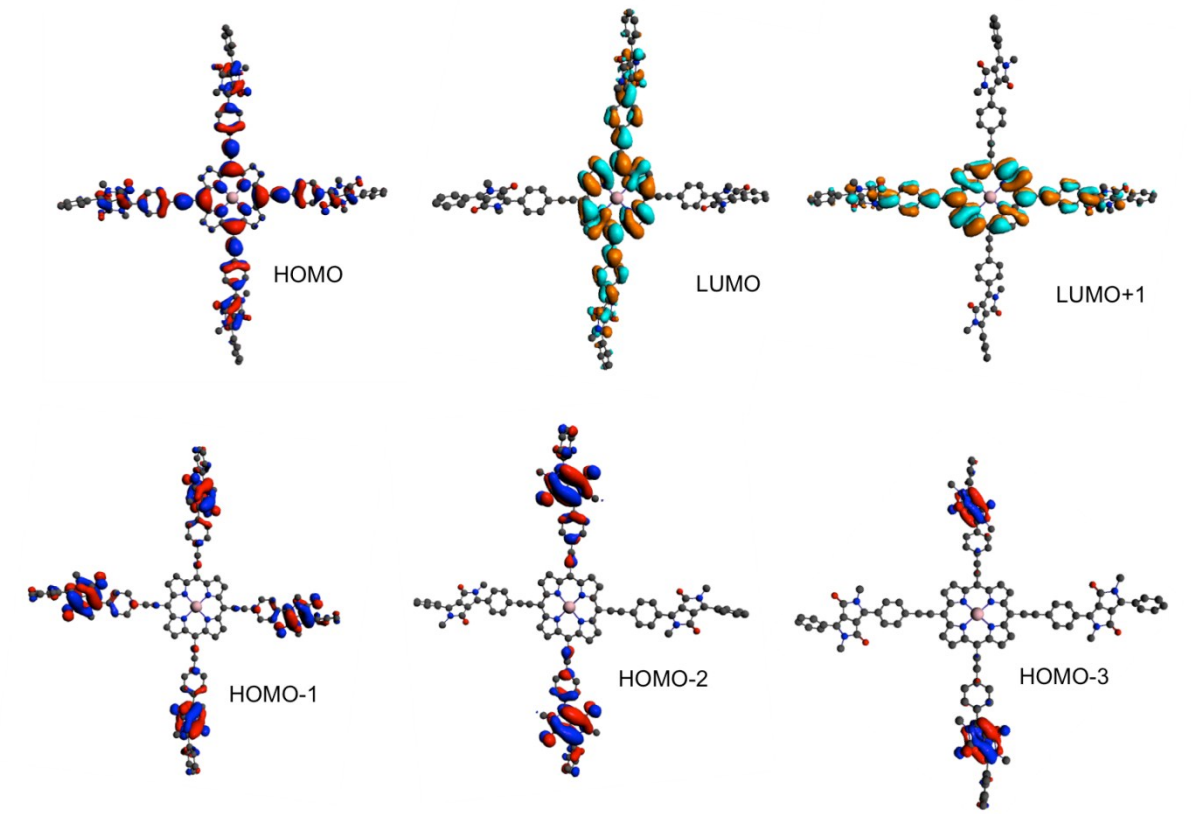


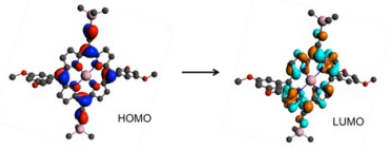
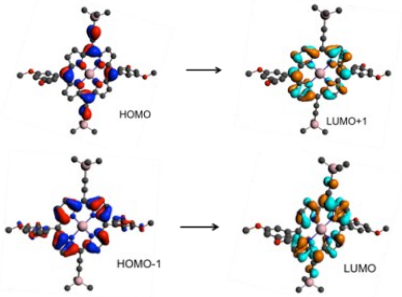
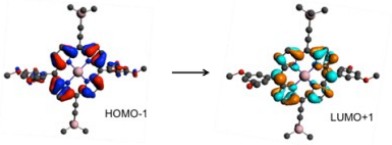
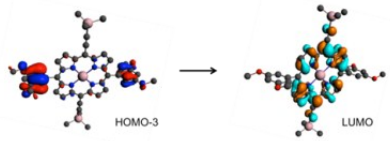
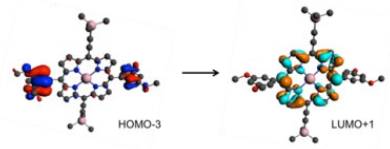
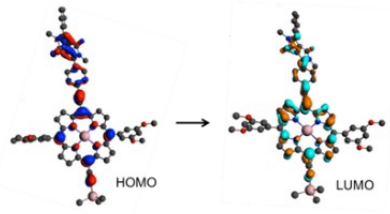
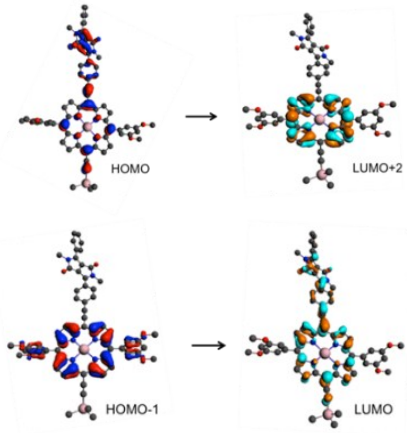
Figure S14. KS orbitals describing the electronic ground state of (a) m-ZnP, (b) m-DPP-ZnP, (c) m-$(DPP)_2$-ZnP and (d) m-$(DPP)_4$-ZnP.

Table S6. TD-DFT transition energies (in eV) and absorption wavelengths (in nm) of m-ZnP, m-DPP-ZnP, m-$(DPP)_2$-ZnP and m-$(DPP)_4$-ZnP calculated in DCM and associated oscillator strengths (only the values > 0.05 are reported here).

	Transition[a]	Energies (in eV)	Wavelength (in nm)	f
m-ZnP ^{1}A				
	HOMO → LUMO	2.094	596	0.536
	60% HOMO-1 → LUMO 36% HOMO → LUMO+1	2.152	580	0.062
	44% HOMO → LUMO+1 29% HOMO-1 → LUMO	2.595	481	1.06
	HOMO-1 → LUMO+1	2.646	472	1.433
	HOMO-2 → LUMO	2.674	467	0.112
	77% HOMO-3 → LUMO 15% HOMO → LUMO+1	2.802	446	0.526
	HOMO-2 → LUMO+1	2.897	431	0.050
	HOMO-3 → LUMO+1	3.005	415	0.525
m-DPP-ZnP ^{1}A				
	HOMO → LUMO	1.861	670	1.71
	62% HOMO-1 → LUMO 30% HOMO → LUMO+2	2.082	600	0.057

	HOMO-2 → LUMO	2.232	560	0.136
	HOMO → LUMO+1	2.350	532	0.181
	50% HOMO→ LUMO+2 31% HOMO-1→ LUMO	2.432	514	0.67
	63% HOMO-1→ LUMO+2 23% HOMO-2 → LUMO+1	2.588	482	0.60
	HOMO-2 → LUMO+1	2.715	460	0.387
	40% HOMO-2 → LUMO+2 33% HOMO-3 → LUMO+2 19% HOMO-1→ LUMO+1	2.792	448	0.547
	65% HOMO-3 → LUMO+2 21% HOMO-2 → LUMO+2	2.828	442	0.275
	HOMO-4 → LUMO+2	2.933	426	0.732
m-$(DPP)_2$-ZnP ^1A				
	HOMO → LUMO	1.736	720	2.45
	66% HOMO-2 → LUMO 29% HOMO → LUMO+2	2.034	614	0.07
	HOMO-3 → LUMO	2.236	559	0.13
	52% HOMO → LUMO+2 28% HOMO-2 → LUMO	2.369	527	0.593
	73% HOMO → LUMO+3	2.388	523	0.66
	HOMO-1 → LUMO+1	2.539	492	0.107
	HOMO-4 → LUMO	2.557	488	0.214
	60% HOMO-2 → LUMO+2 21% HOMO → LUMO+3	2.614	478	0.750
	57% HOMO-3 → LUMO+1 40% HOMO-1 → LUMO+3	2.649	471	0.106
m-$(DPP)_4$-ZnP ^1A_u				
	HOMO (a_u) → LUMO (a_g)	1.648	758	1.633
	HOMO (a_u) → LUMO+1 (a_g)	1.650	757	1.638
	HOMO-1 (a_u) → LUMO (a_g)	2.080	600	0.627
	HOMO-1 (a_u) → LUMO+1 (a_g)	2.080	600	0.629
	43% HOMO-4 (a_u)→ LUMO (a_g) 34% HOMO-5 (a_u) → LUMO+1 (a_g)	2.214	565	0.306
	43% HOMO-4 (a_u) → LUMO+1 (a_g) 34% HOMO-5 (a_u) → LUMO (a_g)	2.218	565	0.300
	45% HOMO-4 (a_u) → LUMO (a_g) 33% HOMO (a_u) → LUMO+4 (a_g)	2.319	540	0.749
	45% HOMO-4 (a_u) → LUMO+1 (a_g) 32% HOMO (a_u) → LUMO+3 (a_g)	2.321	540	0.782
	37% HOMO (a_u) → LUMO+4 (a_g) 31% HOMO-5 (a_u) → LUMO+1 (a_g)	2.443	510	0.343
	36% HOMO (a_u) → LUMO+3 (a_g) 30% HOMO-5 (a_u) → LUMO (a_g)	2.445	510	0.171
	63% HOMO-3 (a_g) → LUMO+2 (a_u)	2.514	497	0.462
	64% HOMO-2 (a_g) → LUMO+2 (a_u)	2.517	498	0.392
	HOMO-5 (a_u) → LUMO+4 (a_g)	3.014	415	0.307
	HOMO-5 (a_u) → LUMO+5 (a_g)	3.016	415	0.302

Table S7. TD-DFT absorption wavelengths (λ, in nm) and associated main one-electron excitations (> 20%) corresponding to the most intense OP ^1A_u transitions (f > 0.5) depicted in the theoretical spectra of Fig. 6 for m-ZnP and m-DPP-ZnP.

	Transition	λ	*f*
m-ZnP > 90%		596	0.54
44% 29%		481	1.06
> 90%		472	1.43
78% CT		446	0.53
> 90% CT		415	0.53
m-DPP-ZnP > 90%		670	1.71
50% 31%		514	0.67

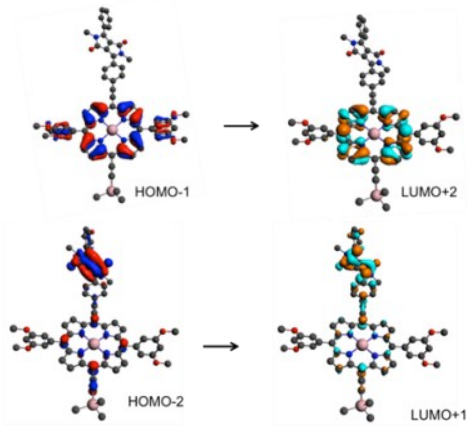
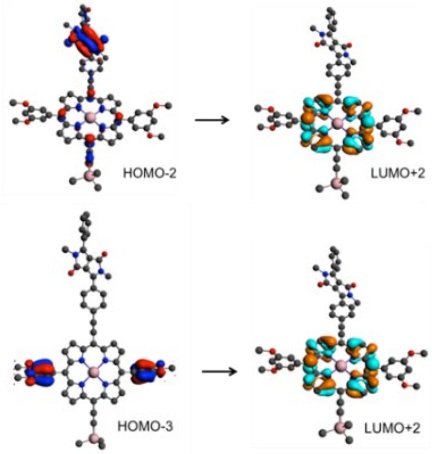
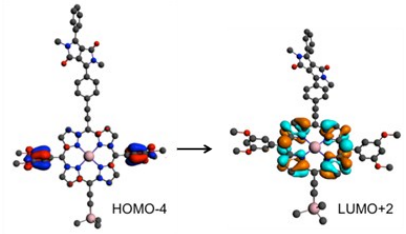
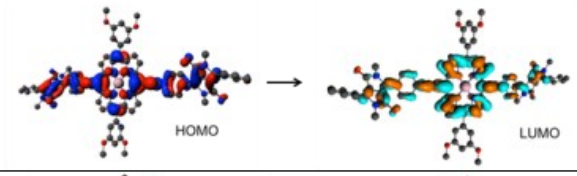
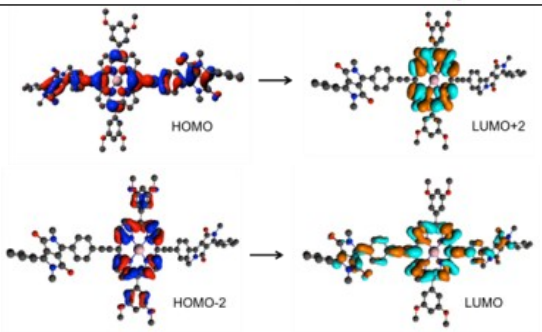
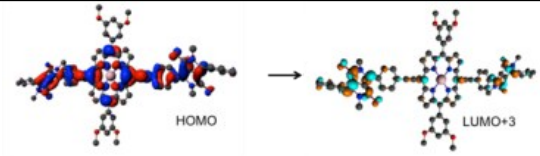
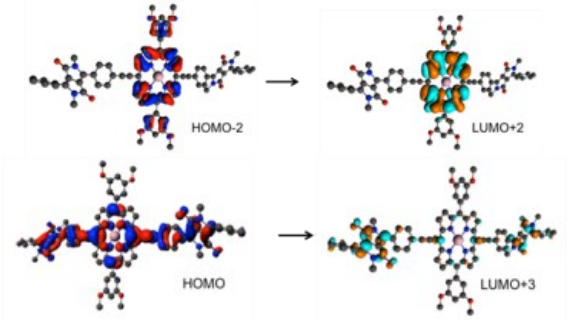
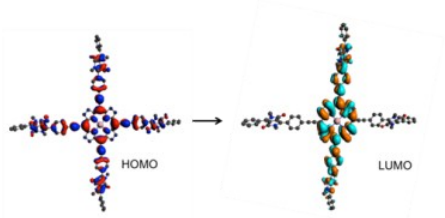
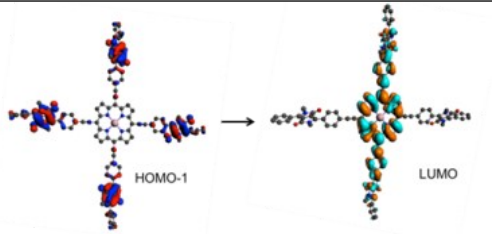
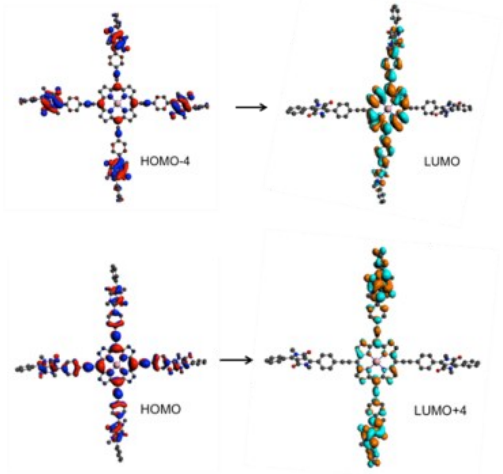
63% 23%		482	0.60
40% CT 33% CT		448	0.55
90% CT		426	0.73

Table S8. TD-DFT absorption wavelengths (λ, in nm) and associated main one-electron excitations (> 20%) corresponding to the most intense OP ^1A_u transitions (f > 0.5) depicted in the theoretical spectra of Fig. 6 for m-$(DPP)_2$-ZnP and m-$(DPP)_4$-ZnP.

	Transition	λ	f
m-$(DPP)_2$-ZnP > 90%		720	2.45
52% 28%		527	0.59
73%		523	0.66
60% 21%		478	0.75
m-$(DPP)_4$-ZnP[a] > 90%		758	1.63
> 90%		600	0.63

45% 32%		540	0.76
65%		498	0.50

[a] In the case of m-$(DPP)_4$-ZnP, only one component of the degenerate transitions is reported (see Table S5).

Two-photon excitation spectra

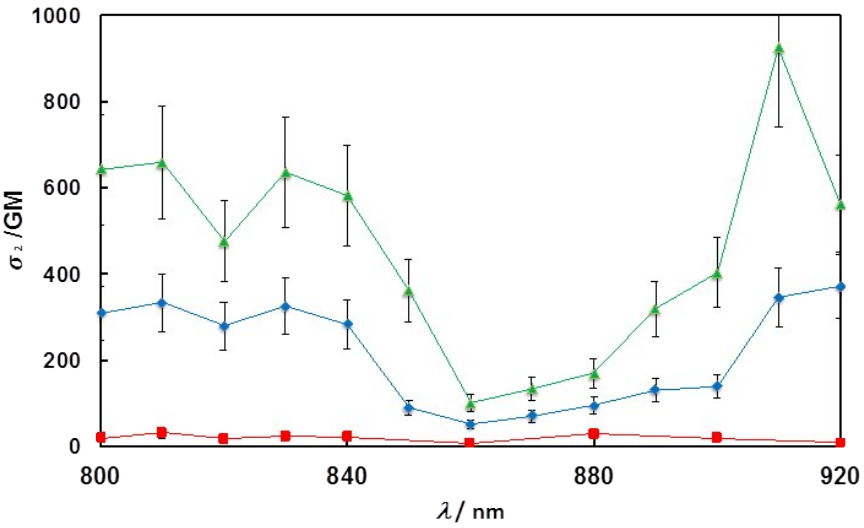


Figure S15. Two-photon excitation spectra of **ZnP** (red), **DPP-ZnP** (blue) and **$(DPP)_2$-ZnP** (green) in DMSO.

Crystallographic data

***X-ray crystal structure determination*.** The crystal-detector distance was 40 mm. The cell parameters were determined (APEX2 software) [3] from reflections taken from three sets of 20 frames, each at 10s exposure. The structure was solved by Direct methods using the program SHELXS-97.[4] The refinement and all further calculations were carried out using SHELXL-2013.[5] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2. A semi-empirical absorption correction was applied using SADABS in APEX2.[6]

CCDC 1451986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

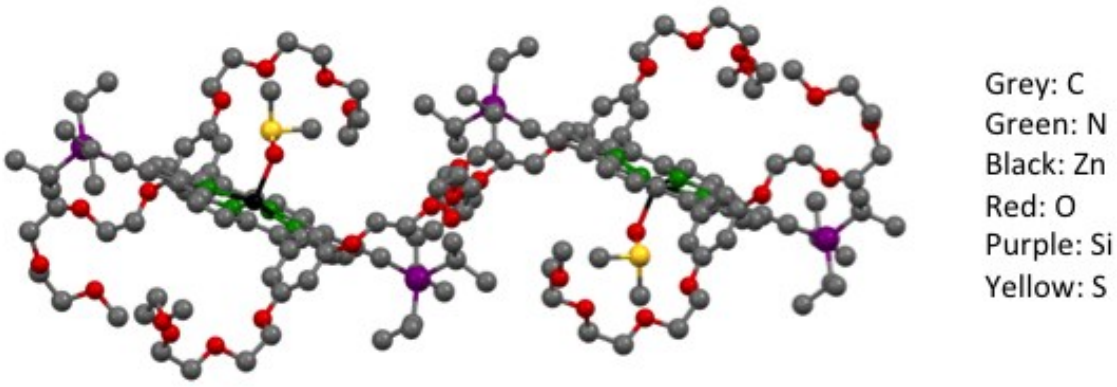


Figure S16. Representation of the crystal packing of **ZnP**. Hydrogens are omitted for clarity. One DMSO molecule is linked to each zinc metal centre.

Table S9. Crystal data and structure refinement for **ZnP**.

Identification code	shelx
Empirical formula	C84 H122 N4 O17 S Si2 Zn
Formula weight	1613.46 g/mol
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 11.4105(3) Å α = 79.762(2)°. b = 17.6824(4) Å β = 89.224(2)°. c = 22.7971(6) Å γ = 74.592(2)°.
Volume	4361.0(2) $Å^3$
Z, Calculated density	2, 1.229 Mg/m^3
Absorption coefficient	1.408 mm^{-1}
F(000)	1728
Crystal size	0.250 x 0.060 x 0.040 mm^3
Theta range for data collection	2.635 to 66.733°.
Limiting indices	-13<=h<=13, -20<=k<=16, -27<=l<=26
Reflections collected / unique	42050 / 15092 [R(int) = 0.0540]
Completeness to theta = 67.679	95.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6889
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15092 / 0 / 994
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1076
R indices (all data)	R1 = 0.0740, wR2 = 0.1187
Extinction coefficient	n/a
Largest diff. peak and hole	0.895 and -0.822 $e.A^{-3}$

References

[1] M. John Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2415-2422.

[2] H. Ftouni, F. Bolze, H. de Rocquigny and J.-F. Nicoud, *Bioconjugate Chem*., 2013, **24**, 942-950.

[3] "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.

[4] G. M. Sheldrick, "SHELXS-97 Program for Crystal Structure Determination", *Acta Crystallogr.* 1990, *A46*, 467-473.

[5] G. Sheldrick, "A short history of SHELX", *Acta Crystallogr.* 2008, *A64,* 112-122.

[6] "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.