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

ELECTRONIC SUPPLEMENTARY INFORMATION

Determinants of the efficiency of photon upconversion by triplet-triplet annihilation in the solid state: zinc porphyrin derivatives in PVA

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I. SYNTHESES:

(i) Materials:

Oven-dried glassware was used for all syntheses. [5,10,15,20-tetraphenylporphyrinato]zinc(II) (ZnTPP) and [5,15-diphenylporphyrinato]zinc(II) (ZnDPP) were purchased from Sigma Aldrich and Frontier Scientific, respectively, and were used as received. Pyrrole was purchased from Sigma Aldrich and freshly distilled prior to use. A glass contour dry solvent dispensing system provided anhydrous CH_2Cl_2 for reaction solvents. 3,5-di-tert-butyltoluene, mesitaldehyde, paraformaldehyde, DDQ, $InCl_3$ and TFA were purchased from Sigma Aldrich and used without further purification. BF_3•OEt_2, propionic acid and $Zn(OAc)_2$•$2H_2O$ were purchased from Merck Schuchardt OHG, Scharlau and Univar respectively, and were all used without further purification.

(ii) General Synthesis Conditions:

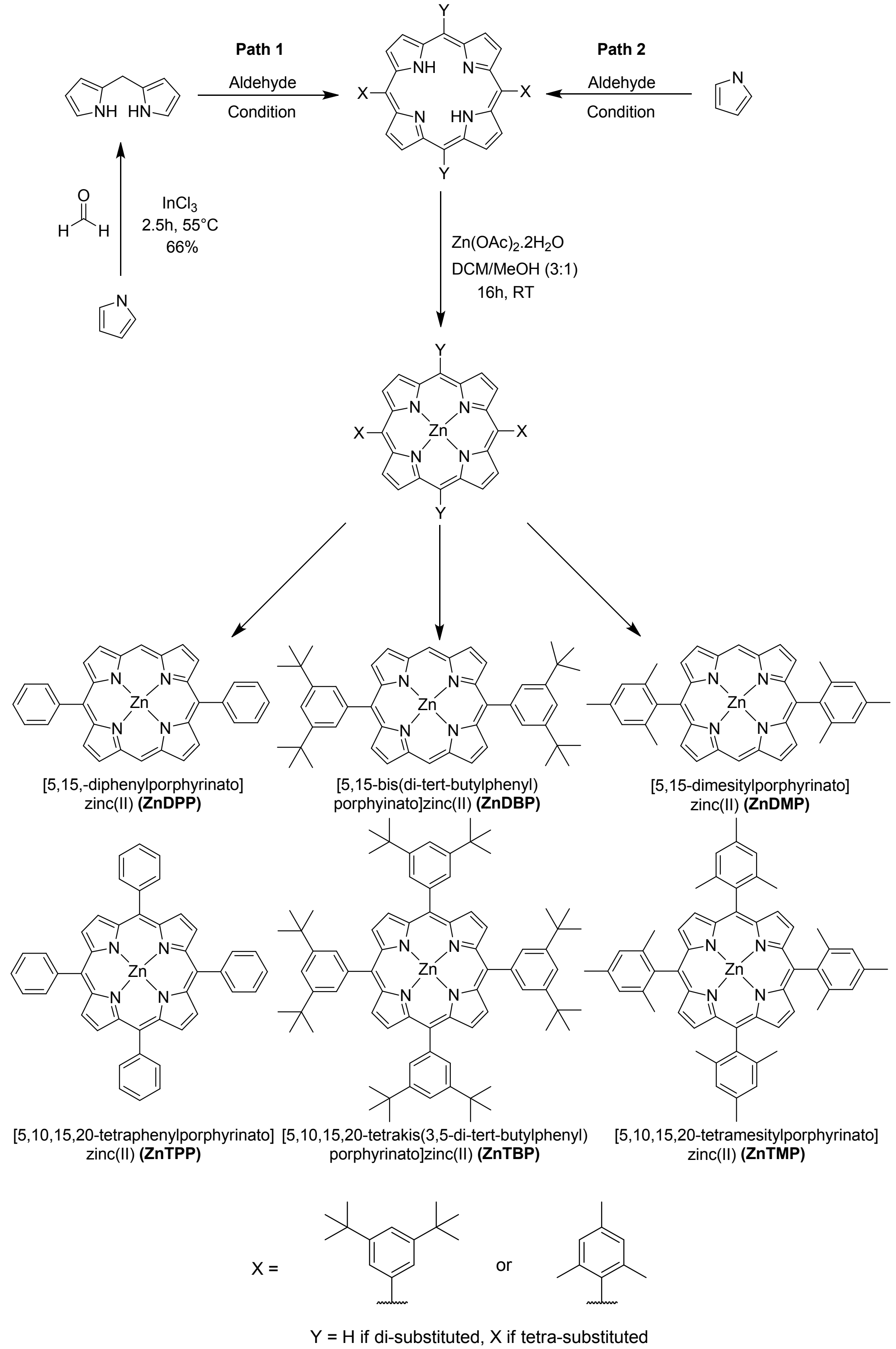
Di-(1H-pyrrol-2-yl)methane was synthesized from pyrrole and paraformaldehyde in the presence of $InCl_3$ catalyst according to the literature.[1] 3,5-di-tert-butylbenzaldehyde was synthesized via the Sommelet reaction[2, 3]; the intermediate 3,5-di-tert-butylbenzyl bromide was carried through the reaction conditions without isolation/purification. 5,10,15,20-tetrakis(di-*tert*-butylphenyl)porphyrin (TBP) was synthesized from 3,5-di-tert-butylbenzaldehyde and pyrrole in refluxing propionic acid according to Adler's method.[4] 5,10,15,20-tetramesitylporphyrin (TMP) was synthesized from mesitaldehyde and pyrrole in the presence of BF_3•OEt_2 according to

Lindsey's method.[5] 5,15-bis(di-*tert*-butylphenyl)porphyrin (DBP) was synthesized from 3,5-di-tert-butylbenzaldehyde and di-(1H-pyrrol-2-yl)methane in the presence of TFA via a modification of literature techniques.[6, 7] 5.15-dimesitylporphyrin (DMP) was synthesized from mesitaldehyde and di-(1H-pyrrol-2-yl)methane in the presence of BF_3•OEt_2 according to Lindsey's method.[8, 9] All free-base porphyrins were stirred with $Zn(OAc)_2$•$2H_2O$ (5 equivalents) in CH_2Cl_2/MeOH (3:1) for 16h at RT to afford the respective Zn-metalated derivatives.

Synthetic pathways for the Zn porphyrins are outlined in Scheme 1, with conditions and yields presented in Table 1.

(iii) Purities:

All compounds were purified via column chromatography using Silicycle Silia Flash® P60 silica gel grade 230-400 mesh, using various ratios of EtOAc, CH_2Cl_2 and petroleum spirits. ^{1}H NMR spectroscopy were performed using an Aglient DD2 500MHz spectrometer and a Varian 600 MHz spectrometer. All chemical shifts are expressed in parts per million (δ) using residual solvent as reference. ^{1}H NMR data was reported in the format: chemical shift (δ) followed by (integration, multiplicity, coupling constant (Hz), assignment). Low resolution mass spectra were taken using an Agilent LC ESI-TOF mass spectrometer.



Scheme S1: Synthesis of di- and tetra-substituted Zn porphyrin derivatives.

Table S1: Synthetic conditions and yields for bis- and tetra-substituted porphyrins.

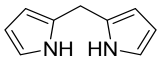
Product	Aldehyde	Conditions	Free base Porphyrin yield	Reaction Path	Porphyrin metalation yield
[5,15-bis(3,5-di-*tert*-butylphenyl) porphyrinato]zinc(II) (ZnDBP)	3,5-(di-*tert*-butyl) benzaldehyde	1)TFA, DCM, RT, 3h 2) DDQ, RT, 20 min	17%	1	94%
[5,15-dimesitylporphyrinato] zinc(II) (ZnDMP)	mesitaldehyde	1) BF_3•OEt_2, 1% EtOH in DCM, RT, 1h 2)DDQ, RT, 20 min	27%	1	90%
[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl) porphyrinato]zinc(II) (ZnTBP)	3,5-(di-*tert*-butyl) benzaldehyde	CH_3CH_2COOH, Reflux 30 min	8%	2	94%
[5,10,15,20-tetramesitylporphyrinato] zinc(II) (ZnTMP)	mesitaldehyde	1) BF_3•OEt_2, 1% EtOH in DCM, RT, 1h 2)DDQ, RT, 20 min	11%	2	98%

(iv) Synthesis Details:

General Synthetic procedure for Zn metalation of free-base porphyrins

Generic amounts are indicated by X. $Zn(CH_3COO)_2.2H_2O$ (Xg, X mmol) was added to a solution of porphyrin (X g, X mmol) dissolved in a mixture of CH_2Cl_2 (X mL) and MeOH (X mL) and the reaction mixture was stirred at RT for 16h in the dark. The reaction mixture was then washed with 5% (w/v) aq. $NaHCO_3$ (X mL) and brine (X mL) and subsequently dried over Na_2SO_4, filtered and the solvent removed by rotary evaporation. The residue was purified by column chromatography (silica gel, 1:1 CH_2Cl_2/hexane as eluent) to yield the Zn(II) metalated porphyrin.

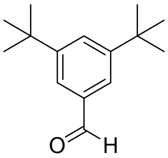
Synthesis of di-(1H-pyrrol-2-yl)methane



Paraformaldehyde (1.94 g, 64.8 mmol) was added to freshly distilled pyrrole (450 mL, 6478 mmol) and degassed with N_2 for 10 min while being stirred at RT. The mixture was heated to 55°C and $InCl_3$ (1.43 g, 6.48 mmol) was added in one portion. The mixture was stirred at 55°C for 2h 30 min, after which it was quenched by the addition of powdered NaOH (7.8 g, 195 mmol) and stirred for a further 45 min. The mixture was vacuum filtered and the residual solid washed with a small amount of pyrrole (*ca* 50 mL). The filtrate was concentrated under reduced pressure to produce an off-white solid, which was left overnight to remove remaining pyrrole. The crude solid was purified via column chromatography (silica gel, 14:5:1

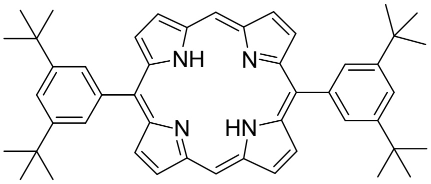
hexane/CH_2Cl_2/EtOAc as eluent) to yield di-(1H-pyrrol-2-yl)methane as a white solid (6.17 g, 66%). ^{1}H NMR (600MHz, $CDCl_3$) δ 4.00 (2H, s, -C**H**$_2$), 6.03 - 6.07 (2H, m, C**H**CNH), 6.16 (2H, dd, J = 5.6, 2.8 Hz, C**H**CHNH), 6.67 – 6.70 (2H, m, C**H**NH), 7.92 ppm (2H, s, br., -N**H**).

Synthesis of 3,5-di-tert-butylbenzaldehyde



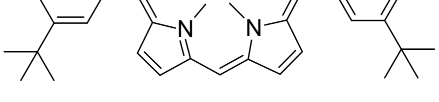
A solution of 3,5-di-tert-butyltoluene (11.9 g, 58.0 mmol), N-bromosuccinimide (15.5 g, 87.0 mmol) and azobisisobutyronitrile (AIBN) (0.50 g, 3.04 mmol) in C_6H_5Cl (400 mL) was heated at reflux and stirred for 4 h. The reaction mixture was cooled, filtered through paper and the solvent was removed by rotary evaporation. The residue was dissolved in 70 mL of a solvent mixture composed by EtOH/H_2O (1:1) and hexamethylenetetramine (25.0 g, 179 mmol) was added and the solution was heated at reflux for 4 h. Concentrated HCl was added (12 mL) and the mixture was refluxed for a further 30 min. The ethanol was removed via rotary evaporation and the remaining aqueous layer was extracted with ether. The ether layer was dried over Na_2SO_4 and the solvent removed by rotary evaporation. Recrystallization from EtOH afforded 3,5-di-*tert*-butylbenzaldehyde as white crystals (6.55 g, 52%). ^{1}H NMR (600MHz, $CDCl_3$) δ 1.38 (18H, s, *tert*-butyl-**H**), 7.71 – 7.73 (1H, m, Ar-**H**, *p-)*, 7.73 – 7.75 (2H, m, Ar-**H**, *o-*), 10.02 pm (1H, s, C**H**O).

Synthesis of 5,15-bis(3,5-di-tert-butylphenyl)porphyrin (DBP)



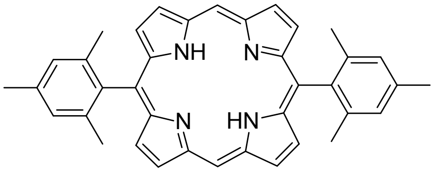
3,5-di-*tert*-butylbenzaldehyde (0.90 g, 4.11 mmol) and di-(1H-pyrrol-2-yl)methane (0.60 g, 4.11 mmol) were dissolved in anhydrous CH_2Cl_2 (700 mL). The solution was purged with N_2 for 15 min, then TFA (0.63 mL, 8.22 mmol) was added and the mixture was stirred for 3h in the dark at RT. DDQ (1.71 g, 7.52 mmol) was then added and the mixture stirred at RT for a further 20 min. Et_3N (4 mL) was added to quench the acid, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, 4:1 hexane/CH_2Cl_2 as eluent) to yield 5,15-bis(3,5-di-tert-butylphenyl)porphyrin (DBP) as a deep reddish-purple solid (238 mg, 17%). ^{1}H NMR (600MHz, $CDCl_3$) δ -3.00 (2H, s, -NH inner ring, 1.59 (36H, s, *tert*-butyl-**H**), 7.84 – 7.87 (2H, m, Ar-**H**, meso-(3,5-di-*tert*-butylphenyl) *–p*), 8.15 – 8.18 (4H, m, Ar-**H**, meso-(3,5-di-*tert*-butylphenyl) *–o*), 9.15 (4H, d, J = 4.5 Hz, **H**-pyrrole β-), 9.41 (4H, d, J = 4.5 Hz, **H**-pyrrole β-), 10.32 ppm (2H, s, meso-**H**). LRMS (ESI)$^+$ *m/z* 687.4488 ($C_{48}H_{54}N_4$ $[M+H]^+$ requires 687.4426).

Synthesis of [5,15-bis(3,5-di-tert-butylphenyl)porphyrinato]zinc(II) (ZnDBP)



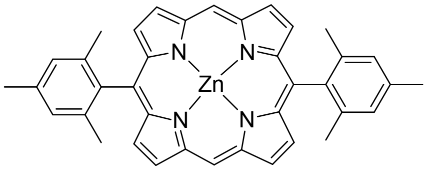
See general Zn(II) metalation procedure. Product obtained as dark red solid (103 mg, 94%). ^{1}H NMR (500MHz, $CDCl_3$) δ 1.59 (36H, s, *tert*-butyl-**H**), 7.84 – 7.87 (2H, m, Ar-**H**, meso-(3,5-di-*tert*-butylphenyl) –*p*), 8.15 – 8.18 (4H, m, Ar-**H**, meso-(3,5-di-*tert*-butylphenyl) –*o*), 9.22 (4H, d, J = 4.5 Hz, **H**-pyrrole β-), 9.47 (4H, d, J = 4.5 Hz, **H**-pyrrole β-), 10.36 ppm (2H, s, meso-**H**). LRMS (ESI)$^+$ *m/z* 749.3560 ($C_{48}H_{52}N_4Zn$ [M+H]$^+$ requires 749.3561).

Synthesis of 5,15-dimesitylporphyrin (DMP)



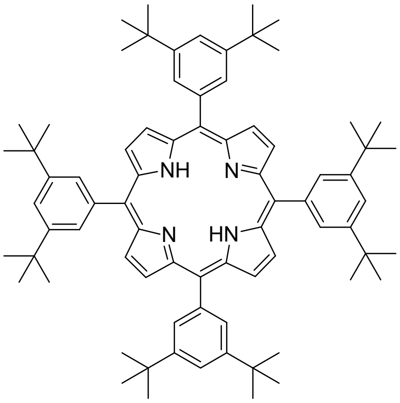
Mesitaldehyde (0.74 mL, 5.00 mmol) and di-(1H-pyrrol-2-yl)methane (0.73 g, 5.00 mmol) were dissolved in anhydrous CH_2Cl_2 (500 mL). EtOH (3.75 mL) was added and the solution was purged with N_2 for 15 min. BF_3•OEt_2 (1.30 mL, 1.25M solution in anhydrous CH_2Cl_2, 1.63 mmol) was added and the mixture was stirred for 1h in the dark at RT. DDQ (0.91 g, 4.00 mmol) was then added and the mixture stirred at RT for a further 20 min. Et_3N (0.3 mL) was added to quench the acid, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, 1:1 hexane/CH_2Cl_2 as eluent) to yield 5,15-dimesitylporphyrin (DMP) as a deep purple solid (366 mg, 27%). ^{1}H NMR (600MHz, $CDCl_3$) δ -3.05 (2H, s, -N**H** inner ring), 1.86 (12H, s, meso-mesityl-C**H**$_3$-*o*), 2.67 (6H, s, meso-mesityl-C**H**$_3$-*p*), 7.34 (8H, s, Ar-**H**, meso-mesityl-*m*), 8.89 (4H, d, J = 4.3 Hz, **H**-pyrrole β-), 9.34 (4H, d, J = 4.3 Hz, **H**-pyrrole β-), 10.23 ppm (2H, s, meso-**H**). LRMS (ESI)$^+$ *m/z* 547.2916 ($C_{38}H_{34}N_4$ [M+H]$^+$ requires 547.2861).

Synthesis of [5,15-dimesitylporphyrinato]zinc(II) (ZnDMP)



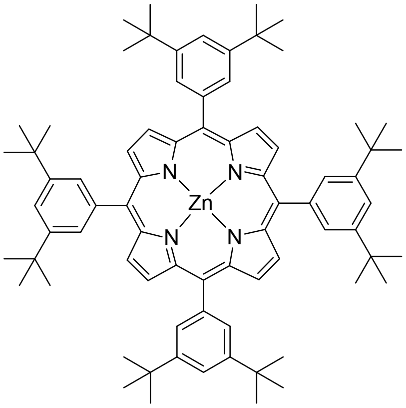
See general Zn(II) metalation procedure. Product obtained as reddish-pink solid (100 mg, 90%). ^{1}H NMR (500MHz, CDCl$_3$) δ 1.84 (12H, s, meso-mesityl-C**H**$_3$-*o*), 2.68 (6H, s, meso-mesityl-C**H**$_3$-*p*), 7.33 (8H, s, Ar-**H**, meso-mesityl-*m*), 8.97 (4H, d, J = 4.3 Hz, **H**-pyrrole β-), 9.39 (4H, d, J = 4.3 Hz, **H**-pyrrole β-), 10.25 ppm (2H, s, meso-**H**). LRMS (ESI)$^+$ *m/z* 609.1999 ($C_{38}H_{32}N_4Zn$ [M+H]$^+$ requires 609.1996).

Synthesis of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (TBP)



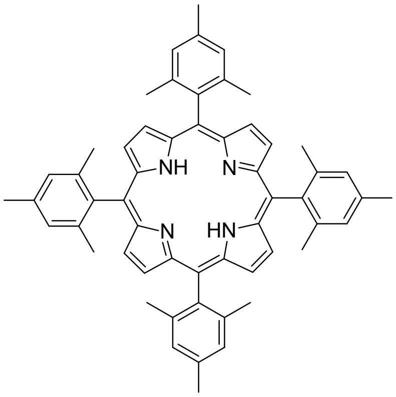
Freshly distilled pyrrole (2.88g, 43.0 mmol) and 3,5-di-*tert*-butylbenzaldehyde (9.38g, 43.0 mmol) were added to refluxing propionic acid (160 mL) and the mixture allowed to reflux for 30 min while stirring. The reaction mixture was then cooled to room temperature, filtered, and the filter cake washed with methanol until the filtrate was clear. The filter cake was washed then with hot water (200 mL) and the purple solid dried at the pump before drying *in vacuo* to remove adsorbed acid. The crude product was purified via column chromatography (silica gel, 1:1 CHCl$_3$/hexane as eluent) to yield 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (TBP) as a dark purple solid (0.96g, 8%). ^{1}H NMR (600MHz, $CDCl_3$) δ -2.66 (2H, s, -NH inner ring), 1.53 (72H, s, *tert*-butyl-**H**), 7.80 (4H, s, Ar-**H**, *meso*-(3,5-di-*tert*-butylphenyl *p-),* 8.10 (8H, s, Ar-**H**, -(3,5-di-*tert*-butylphenyl *o-)*, 8.90 ppm (8H, s, **H**-pyrrole β-).

Synthesis of [5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato]zinc(II) (ZnTBP)



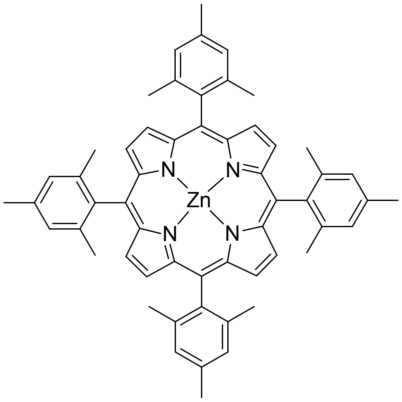
See general Zn(II) metalation procedure. Product obtained as deep pink solid (199 mg, 94%). ^{1}H NMR (500MHz, $CDCl_3$) δ 1.53 (72H, s, *tert*-butyl-**H**), 7.80 (4H, s, Ar-**H**, *meso*-(3,5-di-*tert*-butylphenyl *p-),* 8.10 (8H, s, Ar-**H**, -(3,5-di-*tert*-butylphenyl *o-)*, 9.02 ppm (8H, s, **H**-pyrrole β-).

Synthesis of 5,10,15,20-tetramesitylporphyrin (TMP)



Mesitaldehyde (0.75 mL, 5.06 mmol) and pyrrole (0.35 mL, 5.06 mmol) were dissolved in anhydrous CH_2Cl_2 (500 mL). EtOH (3.75 mL) was added and the solution was purged with N_2 for 15 min. BF_3•OEt_2 (1.30 mL, 1.25M solution in anhydrous CH_2Cl_2, 1.63 mmol) was added and the mixture was stirred for 1h in the dark at RT. DDQ (0.90 g, 3.96 mmol) was then added and the mixture stirred at RT for a further 20 min. Et_3N (0.3 mL) was added to quench the acid, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, 1:1 hexane/CH_2Cl_2 as eluent) to yield 5,10,15,20-tetramesitylporphyrin (TMP) as a deep purple solid (105 mg, 11%). ^{1}H NMR (500MHz, $CDCl_3$) δ -2.49 (2H, s, -N**H** inner ring), 1.86 (24H, s, meso-mesityl-C**H**$_3$-*o*), 2.63 (12H, s, meso-mesityl-C**H**$_3$-*p*), 7.28 (8H, s, Ar-**H**, meso-mesityl-*m*), 8.63 ppm (8H, s, **H**-pyrrole β-). LRMS (ESI)$^+$ *m/z* 783.4253 ($C_{56}H_{54}N_4$ $[M+H]^+$ requires 783.4426).

Synthesis of [5,10,15,20-tetramesitylporphyrinato]zinc(II) (ZnTMP)



See general Zn(II) metalation procedure. Product obtained as deep pink solid (85 mg, 98%). ^{1}H NMR (500MHz, $CDCl_3$) δ 1.85 (24H, s, meso-mesityl-C**H**$_3$-*o*), 2.63 (12H, s, meso-mesityl-C**H**$_3$-*p*), 7.28 (8H, s, Ar-**H**, meso-mesityl-*m*), 8.69 ppm (8H, s, **H**-pyrrole β-). LRMS (ESI)$^+$ *m/z* 845.3351 ($C_{56}H_{52}N_4Zn$ $[M+H]^+$ requires 845.3561).

II. FIGURES:

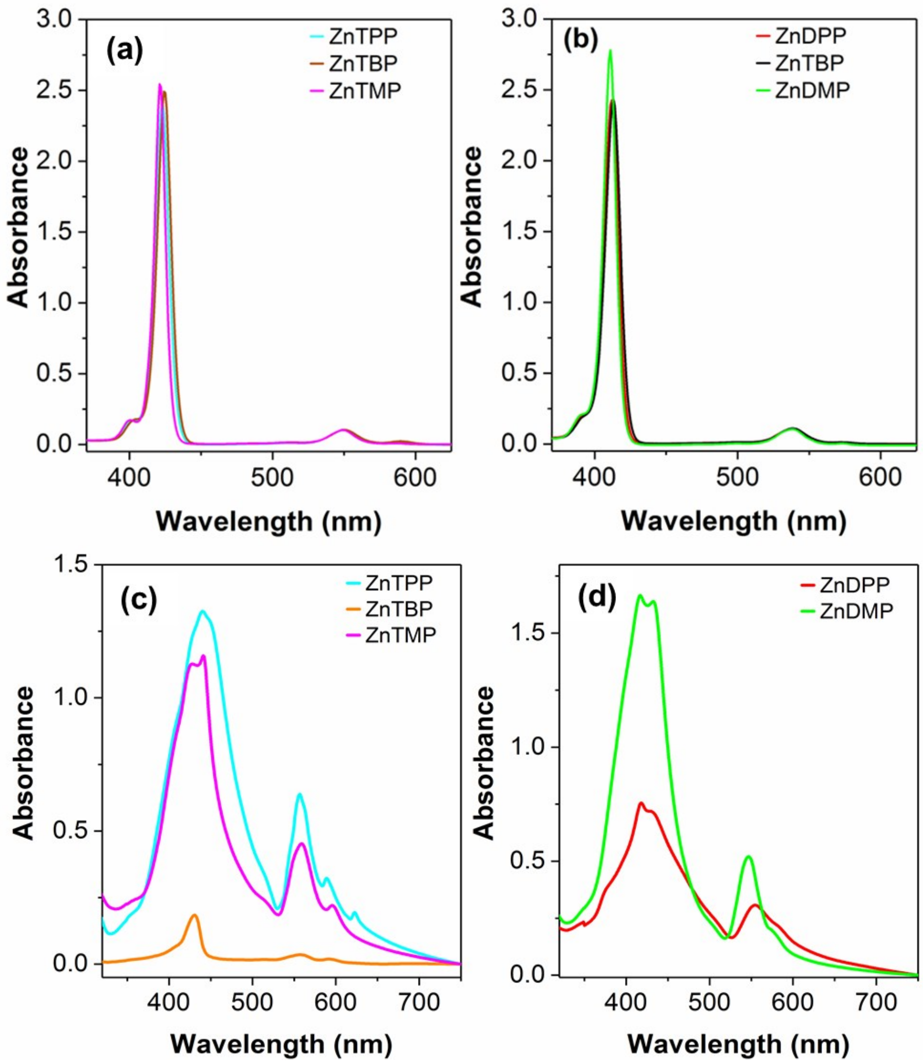


Figure S1: Absorption spectra (a) the tetraphenyl derivatives (group G1) and (b) the diphenyl derivatives (group G2) in toluene. The spectra were taken in solutions prepared with identical absorbances of 0.10 at the Q band absorption maxima. Absorption spectra of (c) G1 and (d) G2 dual absorber-upconverters in PVA (0.1 wt.%).

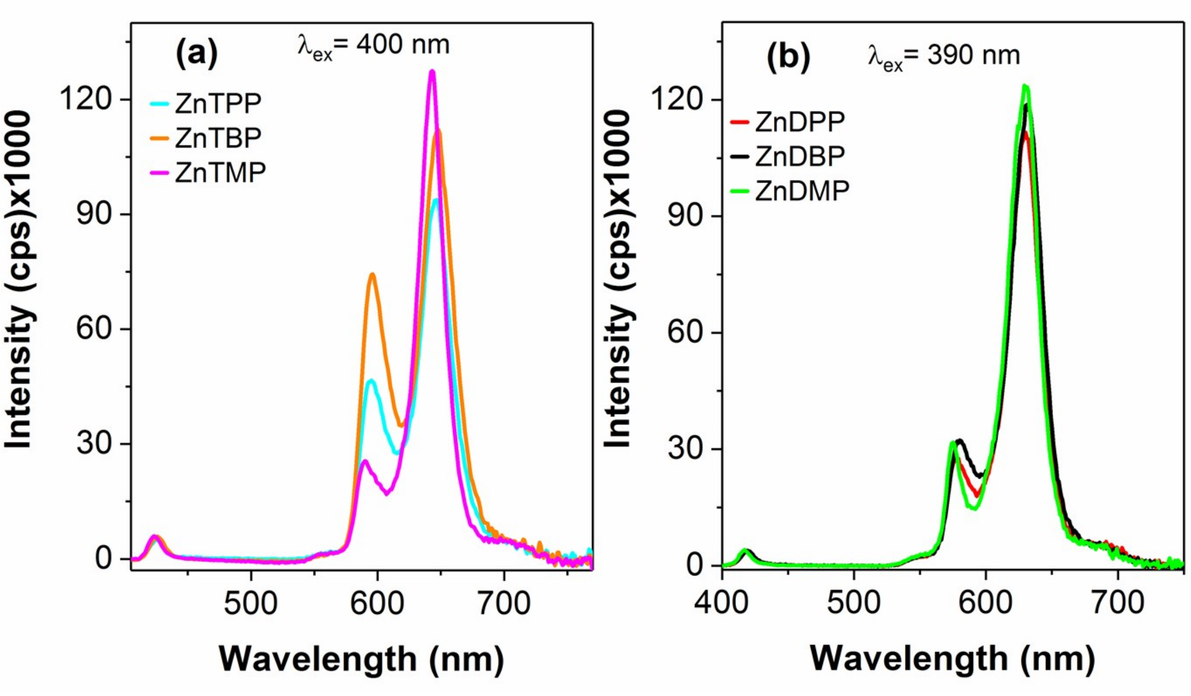


Figure S2: Corrected emission spectra in toluene. (a) Group G1, excited at 400 nm and (b) Group G2 excited at 390 nm.

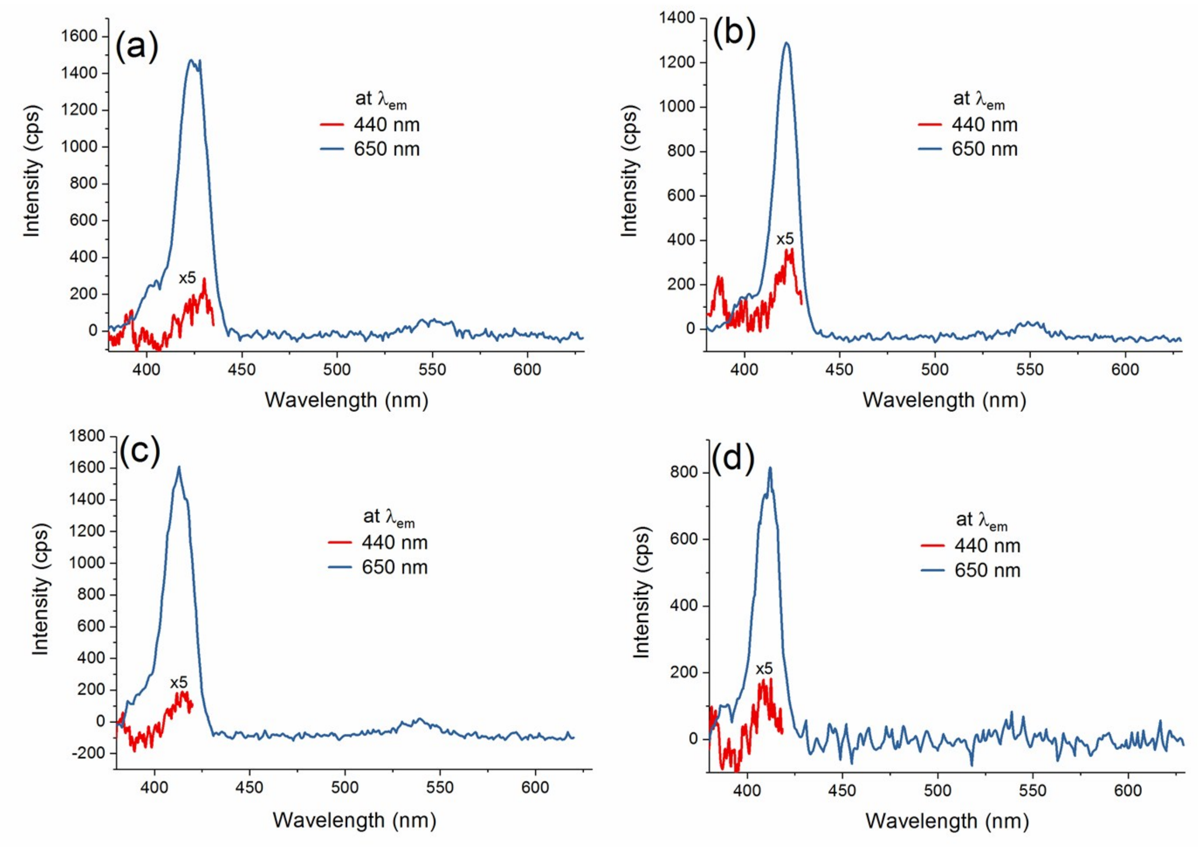


Figure S3. Corrected emission-excitation spectra of ZnTBP (a), ZnTMP (b), ZnDBP (c), and ZnDMP (d) in toluene. Emission is detected from S_1 (blue) and S_2 (red).

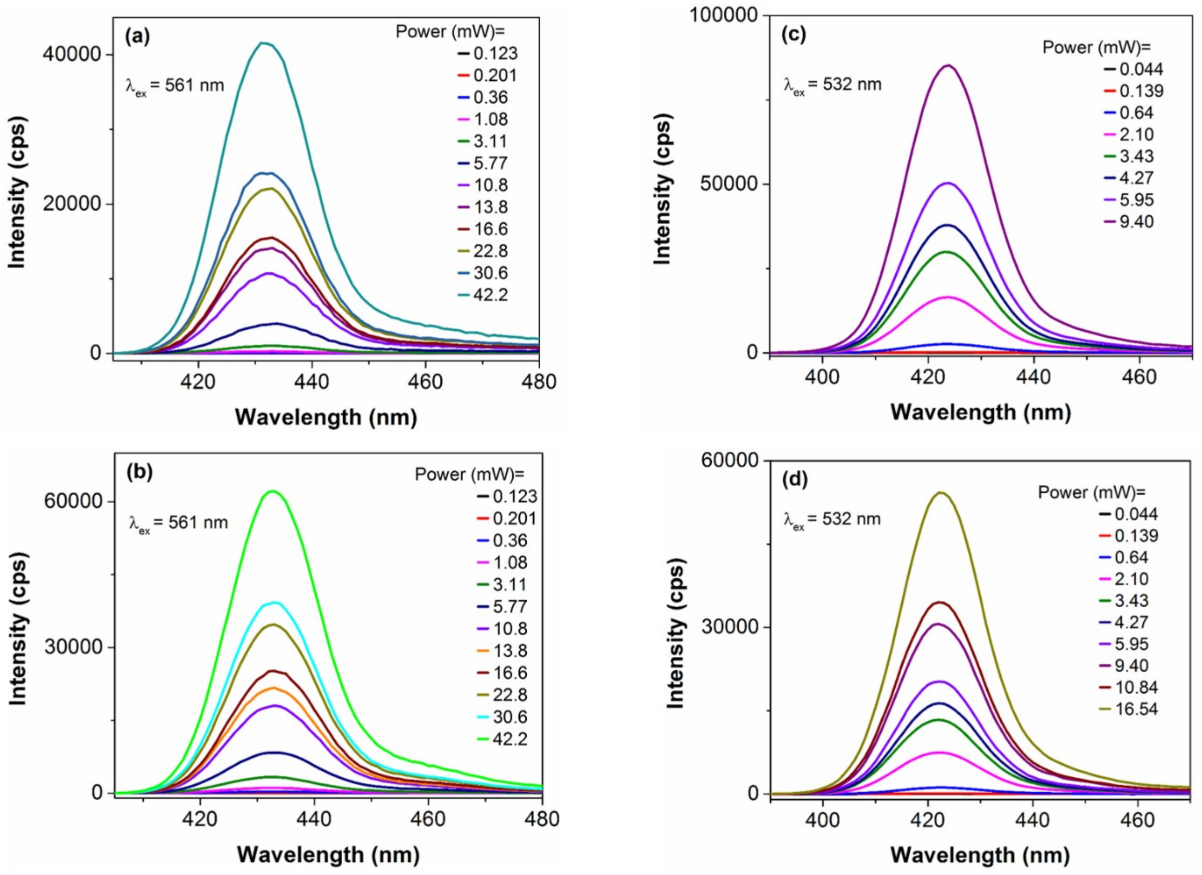


Fig. S4. Power dependent upconverted emission of ZnTPP (a), ZnTBP (b), ZnDPP (c) and ZnDMP (d) in toluene in degassed condition.

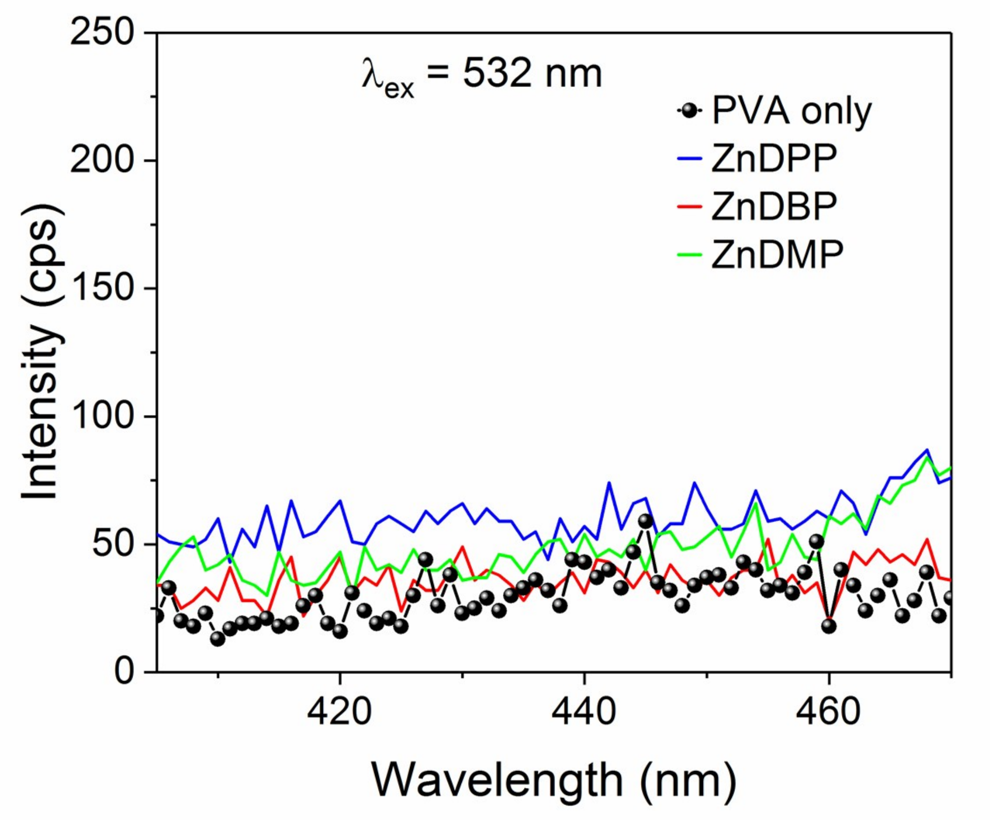


Figure S5. Non-occurrence of NCPU-TTA in G2 compounds in degassed PVA (excitation power = 16.54 mW).

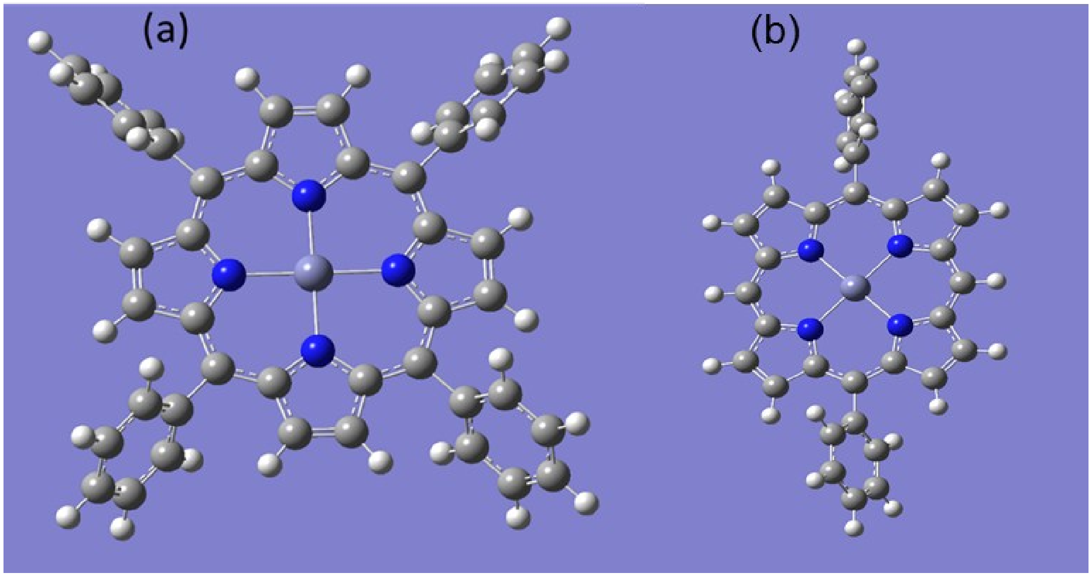


Figure S6. DFT-optimized structures of monomers of (a) ZnTPP and (b) ZnDPP at the B3LYP/6-31G(d) level in the gas phase.

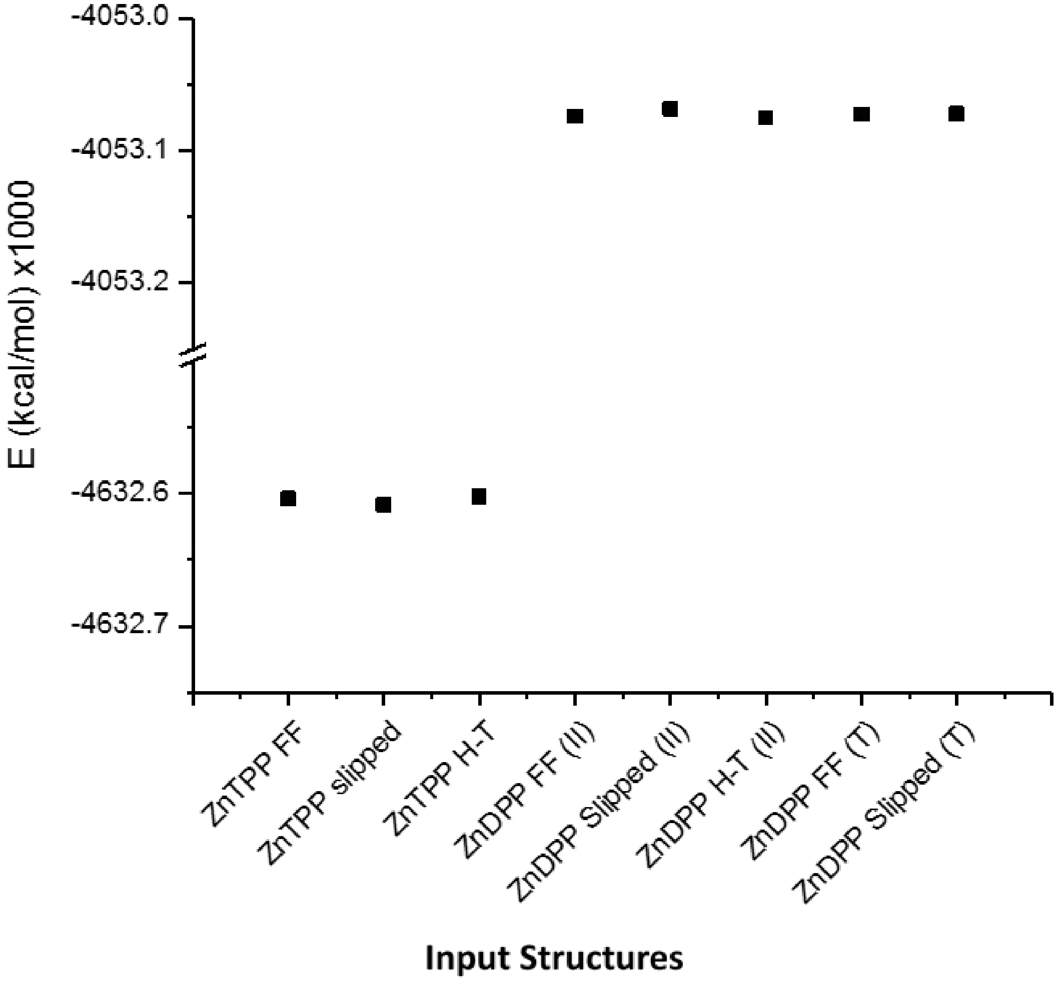


Figure S7. The absolute energies of the optimized structures of the ZnTPP and ZnDPP dimers obtained at the B97D/6-31G(d,p) level in the gas phase.

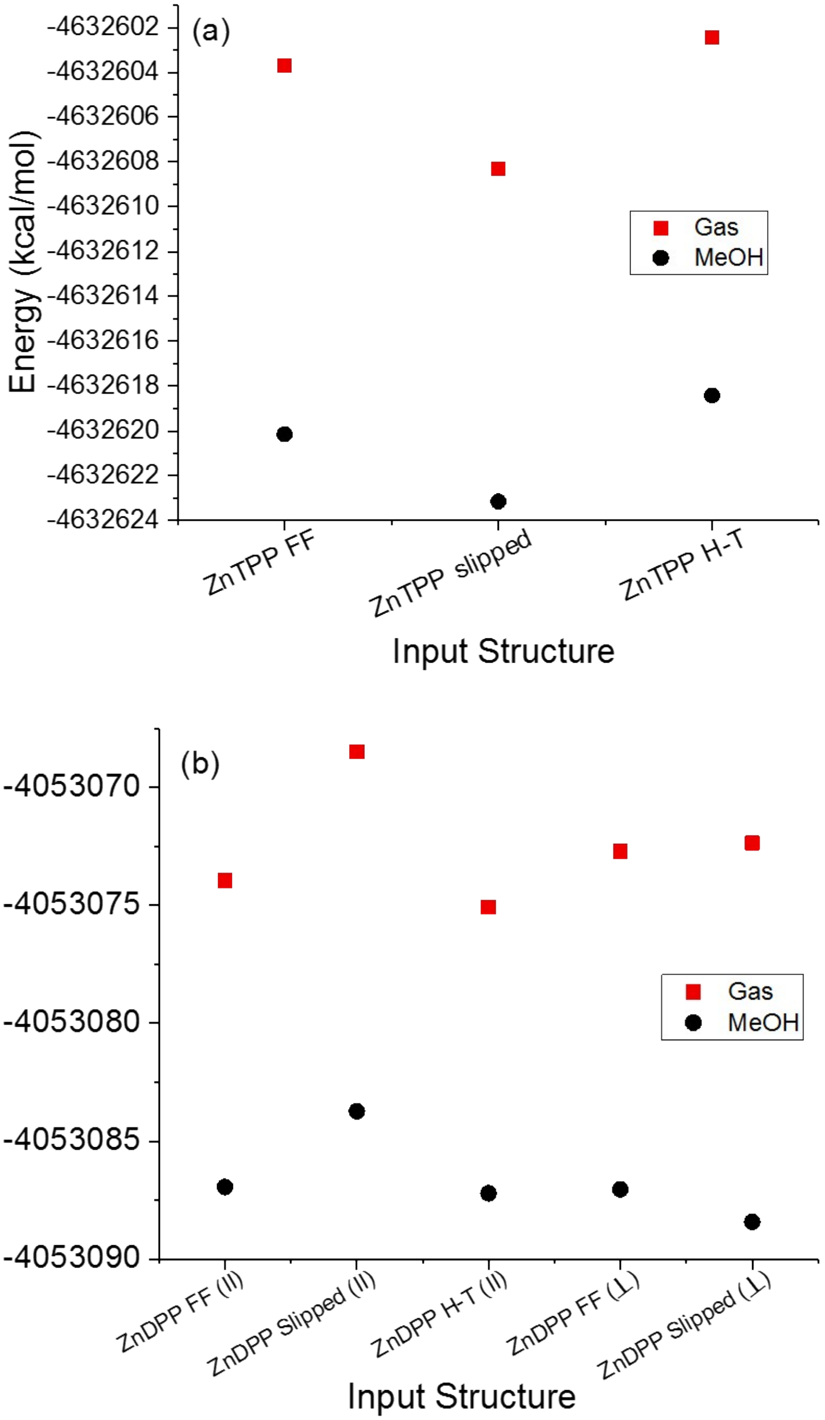


Figure S8. The absolute energies of the optimized structures of dimers of ZnTPP (a) and ZnDPP (b) obtained at the B97D/6-31G(d,p) level in the gas phase and in methanol.

References:

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