Supporting Information

Benefits of Using BODIPY-Porphyrin Dyads for Developing Deep-Red Lighting Sources

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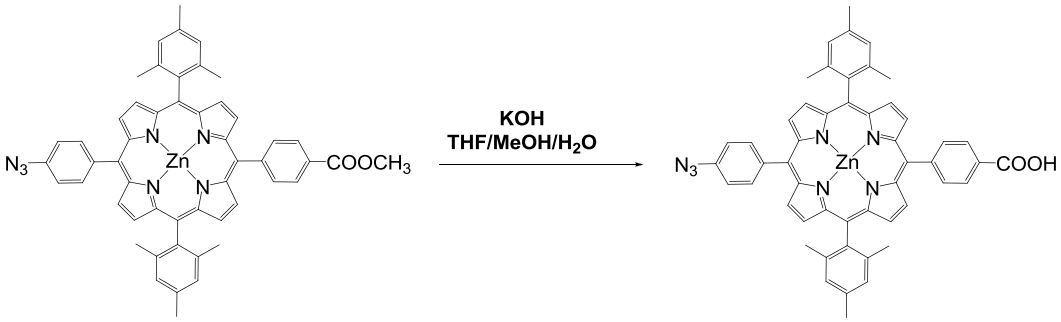
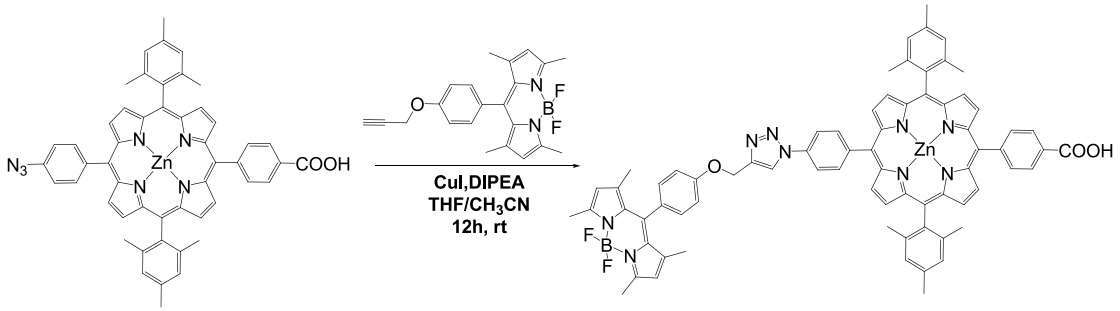
1. Synthesis



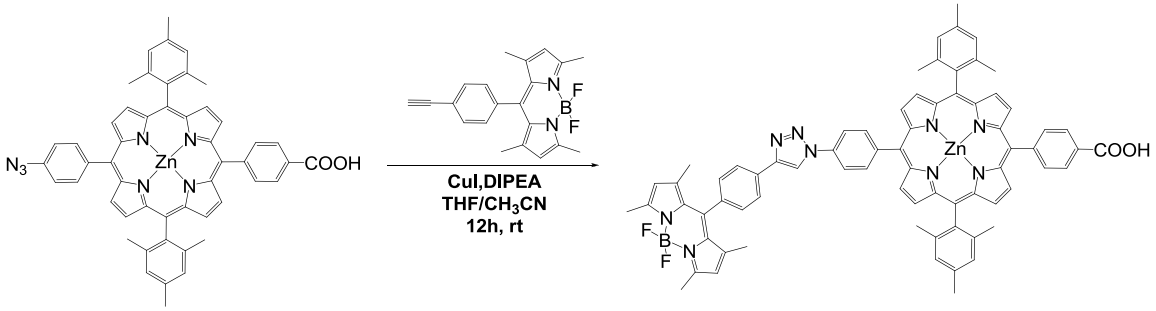
Scheme S1. Synthesis of **(Zn)DMP-N_3-COOH**.

Synthesis of **(Zn)DMP-N_3-COOH.** To a solution of [5-(4-methoxycarbonylphenyl)-15-(4-azidophenyl)-10,20-bis(2,4,6 trimethylphenyl) porphyrinato] zinc (50 mg, 0.058 mmol) in 20 mL of a THF MeOH mixture (2 : 1), an aqueous solution (7 mL) of KOH (300 mg, 5.35 mmol) was added and the mixture was stirred at room temperature overnight. The solvents were evaporated under reduced pressure and distilled H_2O (15 mL) was added to the resulting residue. After acidification of the mixture by addition of HCl (aq) 1 M, the product was precipitated, filtered, washed with distilled and dried resulting in 46 mg of porphyrin (0.054 mmol, yield: 94%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.2 (s, 1H), 8.74 (d, $^3J_{H,H}$ = 4.6 Hz, 2H), 8.71 (d, $^3J_{H,H}$ = 4.6 Hz, 2H), 8.59 (d, $^3J_{H,H}$ = 4.5 Hz, 4H), 8.33 (m, 4H), 8.22 (d, $^3J_{H,H}$ = 8.45 Hz, 2H), 7.52 (d, $^3J_{H,H}$ = 8.45 Hz, 2H), 7.31 (s, 4H), 2.58 (s, 6H), 1.78 (s, 12H). ^{13}C NMR (75 MHz, DMSO-d_6): ™ 167.5, 145.4, 139.5, 138.4, 138.0, 137.7, 137.3, 135.6, 134.5, 131.7, 130.7, 130.4, 127.9, 118.7, 118.3, 118.0, 117.8, 21.2, 21.1. UV/Vis (THF):λ_{max} (ε, $mM^{-1}cm^{-1}$) = 424 (368.2), 550 (19.1), 597 (2.8) nm. HRMS (MALDI-TOF): m/z calc for $C_{51}H_{40}N_7O_2Zn$ $[M + H]^+$ 846.2535, found 845.2522. Anal. Calc for $C_{51}H_{39}N_7O_2Zn$: C, 72.30; H, 4.64; N, 11.57. Found: C 72.26; H 4.68; N 11.60.



Scheme S2. Synthesis of **1**.

Synthesis of **1.** Equimolar amounts of porphyrin **(Zn)DMP-N3-COOH** (26 mg, 0.031 mmol) and **BDP-O-Triple** (11,7 mg, 0.031 mmol) were dissolved in a 1:1 mixture of THF/CH_3CN (5 mL) under nitrogen atmosphere. Next, CuI (6 mg, 0.032 mmol) and DIPEA (5 ⌈lt, 0.031 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, after diluted in CH_2Cl_2, was purified by column chromatography (silica gel, CH_2Cl_2) yielding the 20 mg of **1** (0.016 mmol, yield: 53%). ^{1}H (500 MHz, DMSO-d_6): ™ 13.17 (s, 1H), 9,29 (s, 1H), 8.79 (d, $^3J_{H,H}$ = 4.6 Hz, 2H), 8.72 (d, $^3J_{H,H}$ = 4.6 Hz, 2H), 8.61 (m, 4H), 8.42 (d, $^3J_{H,H}$ = 8.4Hz, 2H), 8.33 (m, 6H), 7.34 (s, 4H), 7.32 (s, 4H), 6.19 (s, 2H), 5.42 (s, 2H), 2.58 (s, 6H), 2.46 (s, 6H), 1.79 (s, 12H), 1.44 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): ™ 167.7, 158.7, 154.7, 149.2, 149.0, 148.8, 147.3, 143.8, 143.1, 142.8, 142.1, 139.1, 138.4, 137.0, 136.0, 135.3, 134.4, 131.9, 131.2, 130.5, 130.0, 129.3, 127.6, 127.5, 126.6, 123.5, 121.4, 118.6, 118.4, 118.3, 115.8, 61.4, 21.5, 21.1, 14.3. UV/Vis (THF): λ_{max} (ε, $mM^{-1}cm^{-1}$) = 425 (369.2), 500 (46.1), 557 (11.6), 598 (2.9) nm. HRMS (MALDI-TOF): *m/z* calcd. for $C_{73}H_{61}BFN_9O_3$ Zn $[M + H]^+$ 1224.4250, found 1224.4263. Anal. Calcd for $C_{73}H_{60}BF_2N_9O_3Zn$: C, 71.54; H, 4.93; N, 10.29. Found: C, 71.50; H 4.95; N 10.32.



Scheme S3. Synthesis of **2**.

Synthesis of **2.** Equimolar amounts of porphyrin **(Zn)DMP-N3-COOH** (26 mg, 0.031 mmol) and **BDP-Triple** (10,8 mg, 0.031 mmol) were dissolved in a 1:1 mixture of THF/CH_3CN (5 mL) under nitrogen atmosphere. In the next step, CuI (6 mg, 0.032 mmol) and DIPEA (5 µlt, 0.031 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, after diluted in CH_2Cl_2, was purified by column chromatography (silica gel, CH_2Cl_2) yielding the 22 mg of **2** (0.018 mmol, yield: 59%). ^{1}H (500 MHz, DMSO-d_6): ™ 13.09 (s, 1H), 9,76 (s, 1H), 8.83 (d, $^3J_{H,H}$ = 4.4 Hz, 2H), 8.73 (d, $^3J_{H,H}$ = 4.1 Hz, 2H), 8.63 (d, $^3J_{H,H}$ = 4.1 Hz, 2H), 8.61 (m, 2H), 8.47 (d, $^3J_{H,H}$ = 7.8 Hz, 2H), 8.35 (m, 6H), 8.28 (d, $^3J_{H,H}$ = 7.4 Hz, 2H), 7.60 (d, $^3J_{H,H}$ = 7.5 Hz, 2H), 7.32 (s, 4H), 6.22 (s, 2H), 2.58 (s, 6H), 2.50 (s, 6H) 1.79 (s, 12H), 1.50 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): ™ 167.7, 155.1, 149.4, 149.2, 149.1, 148.8, 147.3, 146.8, 143.2, 142.8, 141.6, 139.1, 138.4, 137.0, 136.0, 135.4, 134.4, 134.0, 132.0, 131.2, 130.8, 130.5, 129.8, 128.8, 127.6, 126.2, 121.5, 120.7, 118.6, 118.4, 118.3, 21.5, 21.1, 14.3. UV/Vis (THF): λ_{max} (ε, $mM^{-1}cm^{-1}$) = 425 (379.7), 500 (46.1), 557 (12.3), 598 (2.2) nm. HRMS (MALDI-TOF): *m*/*z* calc. for $C_{72}H_{59}BN_9O_2Zn$ $[M + H]^+$ 1194.4144, found 1194.4161. Anal. Calc. for $C_{72}H_{58}BF_2N_9O_2Zn$: C, 72.34; H, 4.89; N, 10.54. Found: C, 72.38; H 4.86; N 10.52.

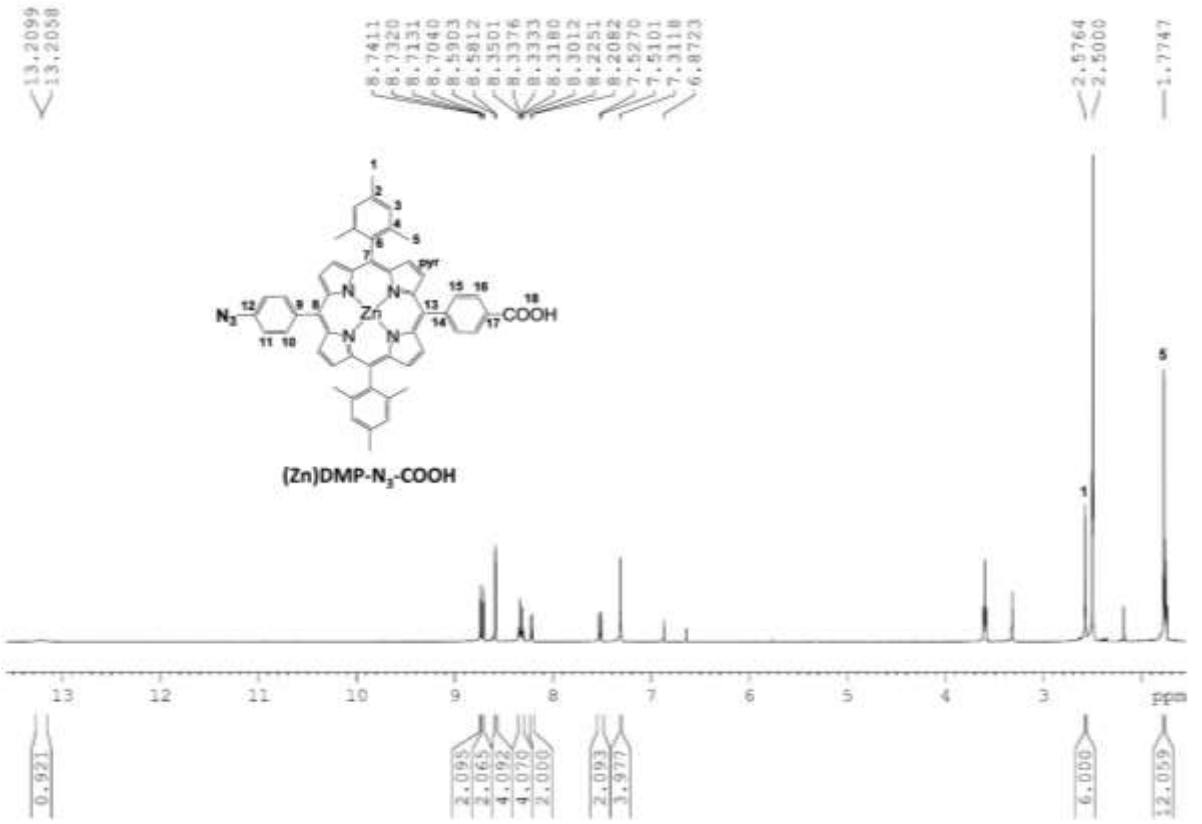


Figure S1. ^{1}H NMR spectrum of **(Zn)DMP-N_3-COOH** (500MHz, DMSO- d_6).

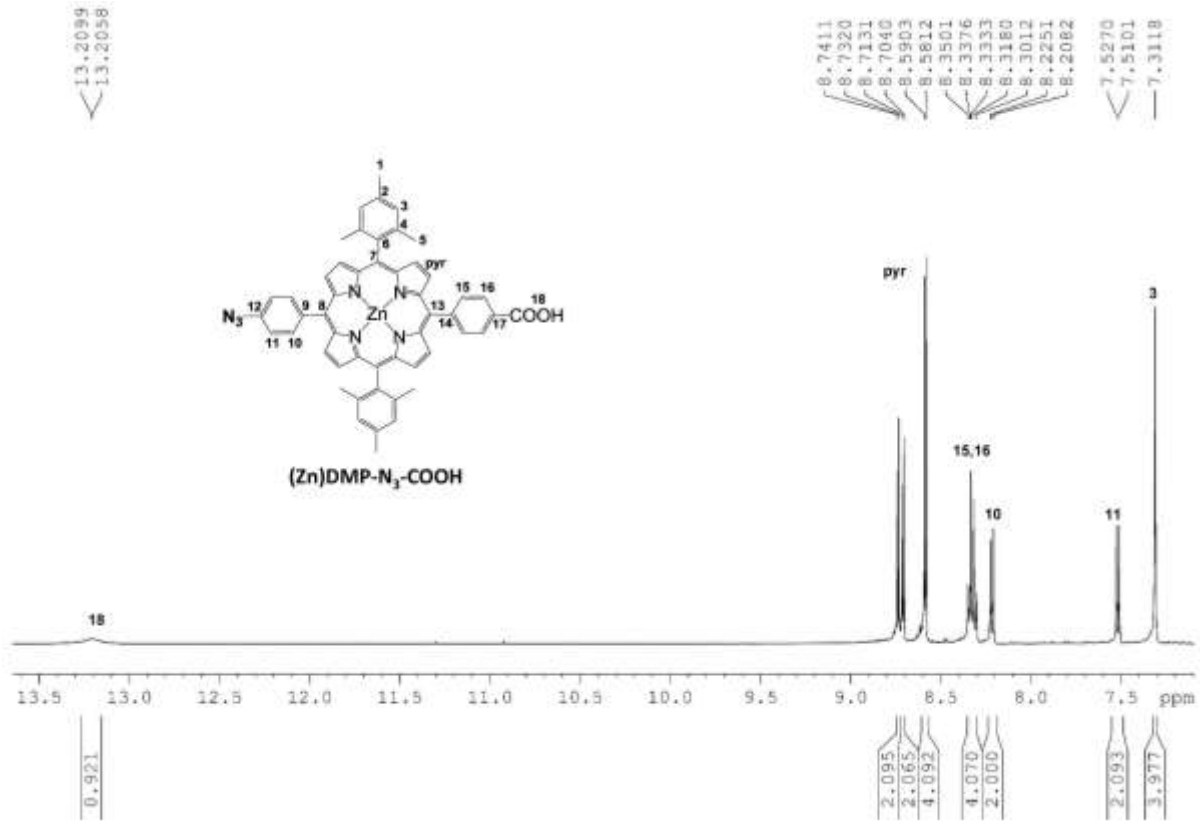


Figure S2. Aromatic region of ^{1}H NMR of **(Zn)DMP-N_3-COOH** (500MHz, DMSO- d_6).

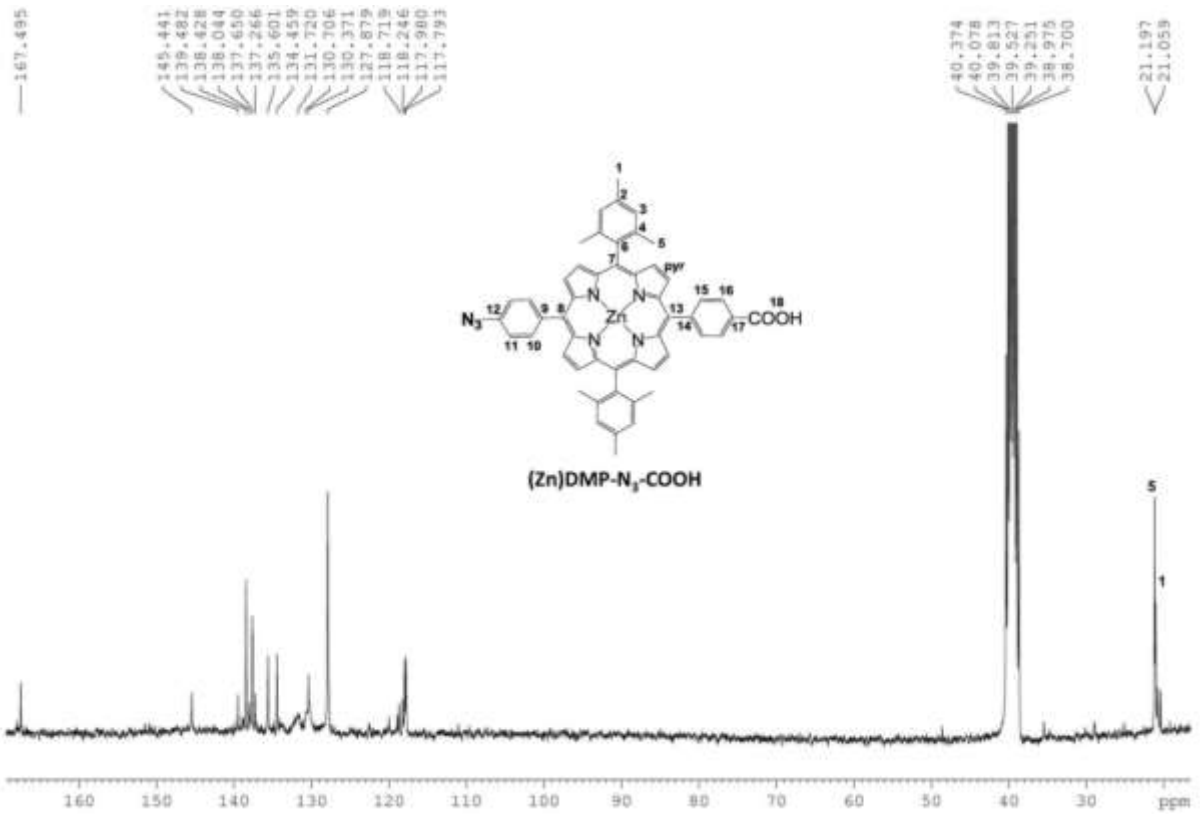


Figure S3. ^{13}C NMR spectrum of **{Zn}DMP-N_3-COOH** (75MHz, DMSO- d_6).

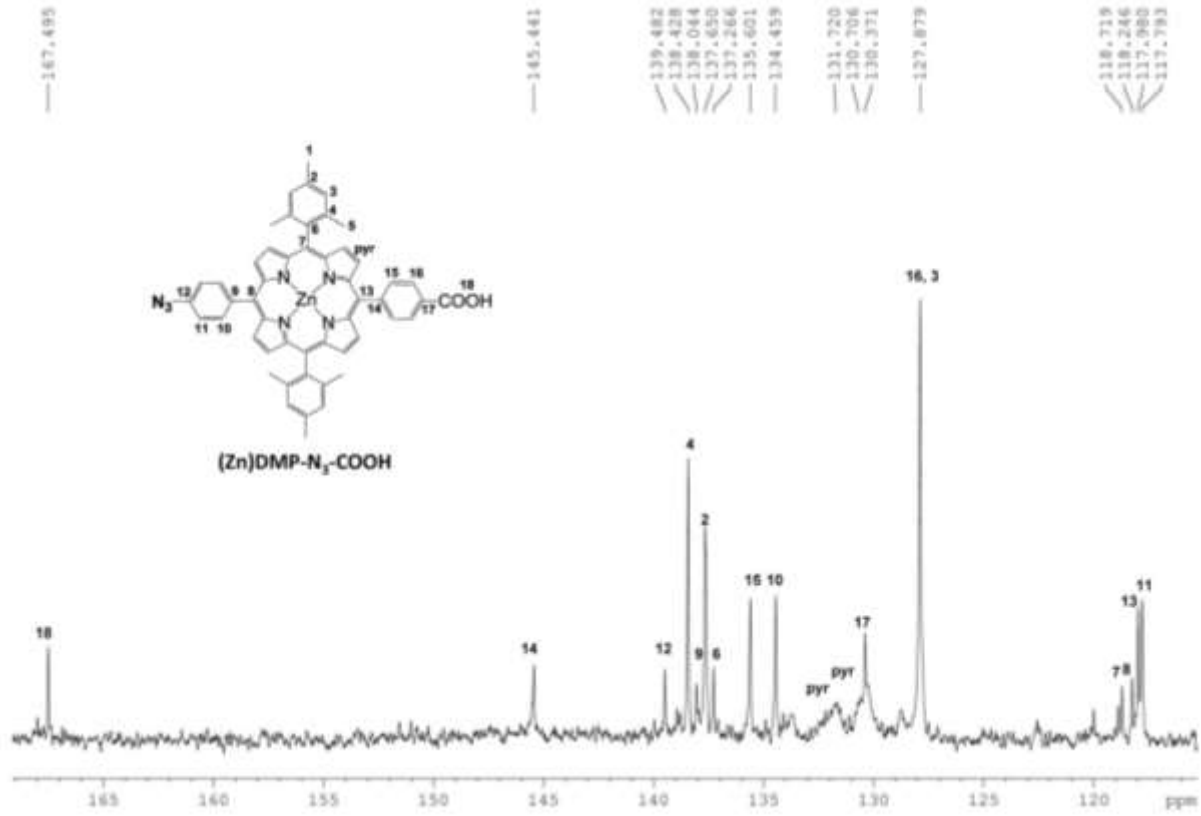


Figure S4. Aromatic region of ^{13}C NMR spectrum of **{Zn}DMP-N_3-COOH** (75MHz, DMSO- d_6).

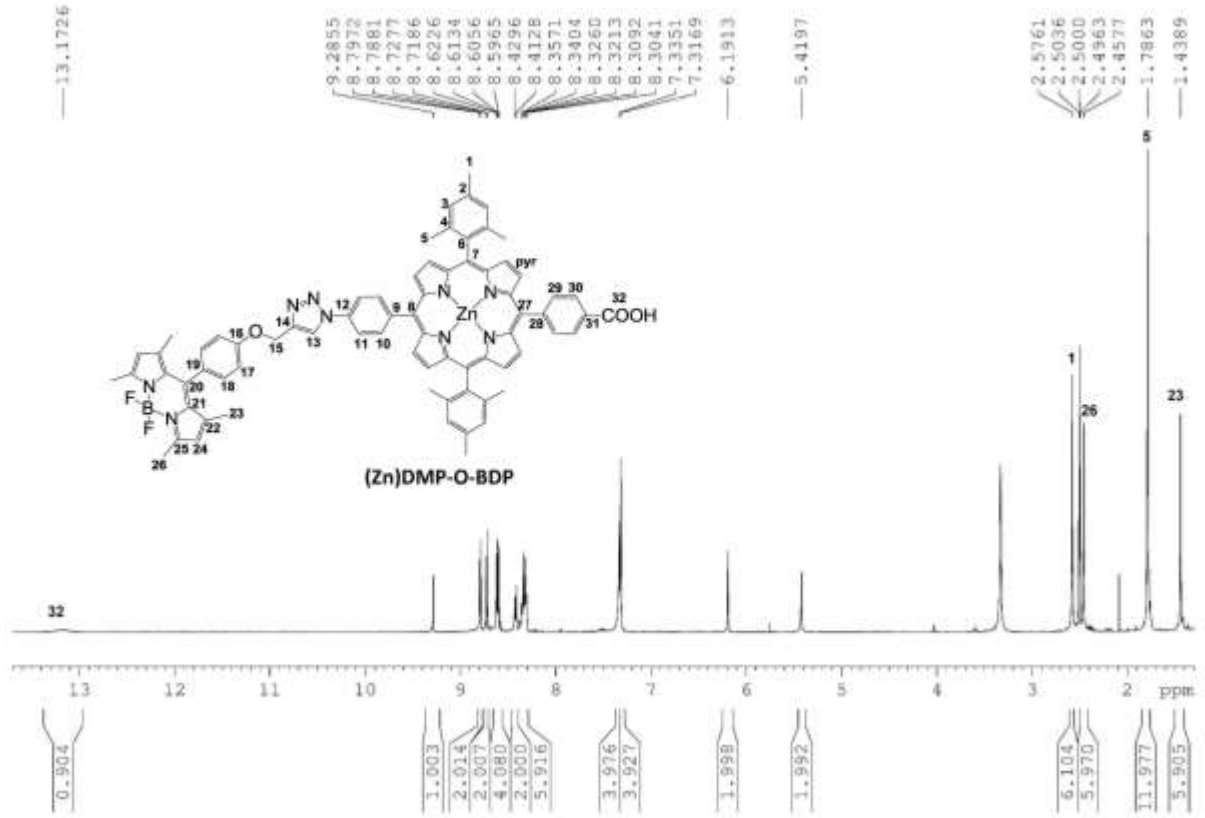


Figure S5. ^{1}H NMR spectrum of **1** (500MHz, DMSO- d_6).

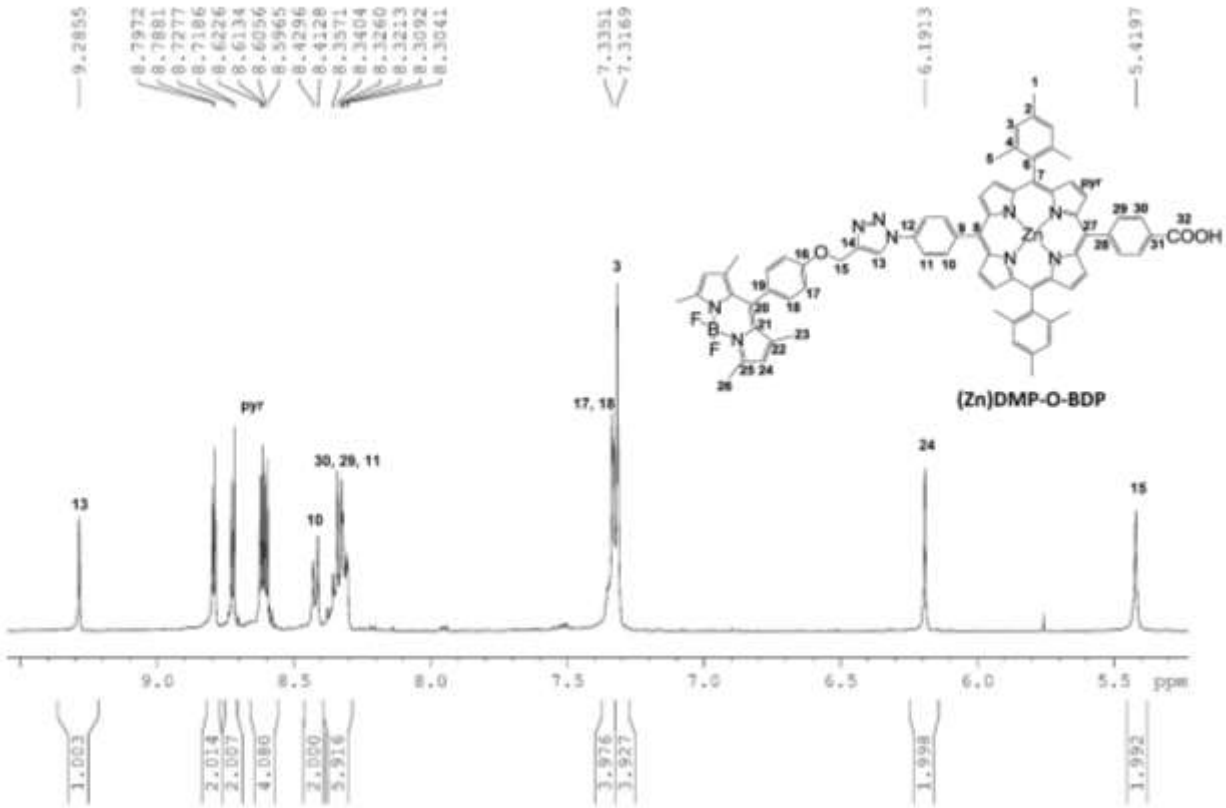


Figure S6. Aromatic region of ^{1}H NMR of **1** (500MHz, DMSO- d_6).

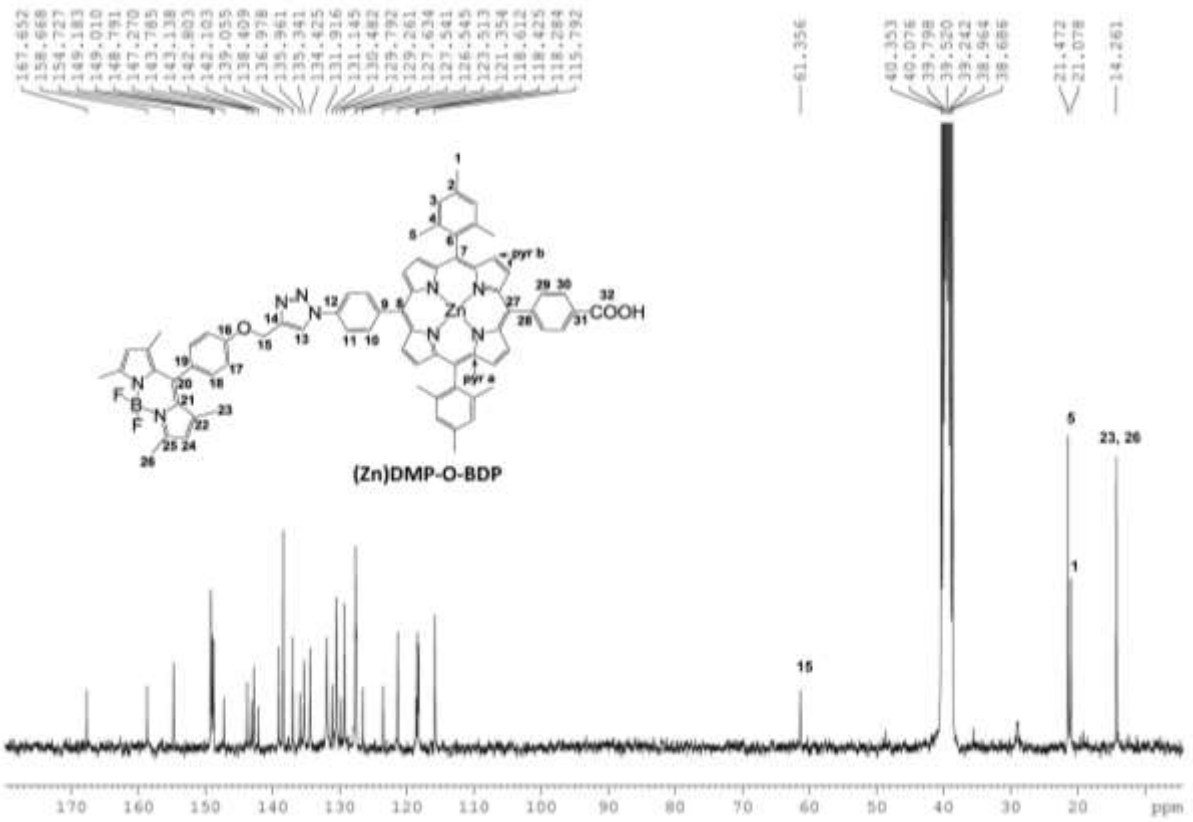


Figure S7. ^{13}C NMR spectrum of **1** (75MHz, DMSO- d_6).

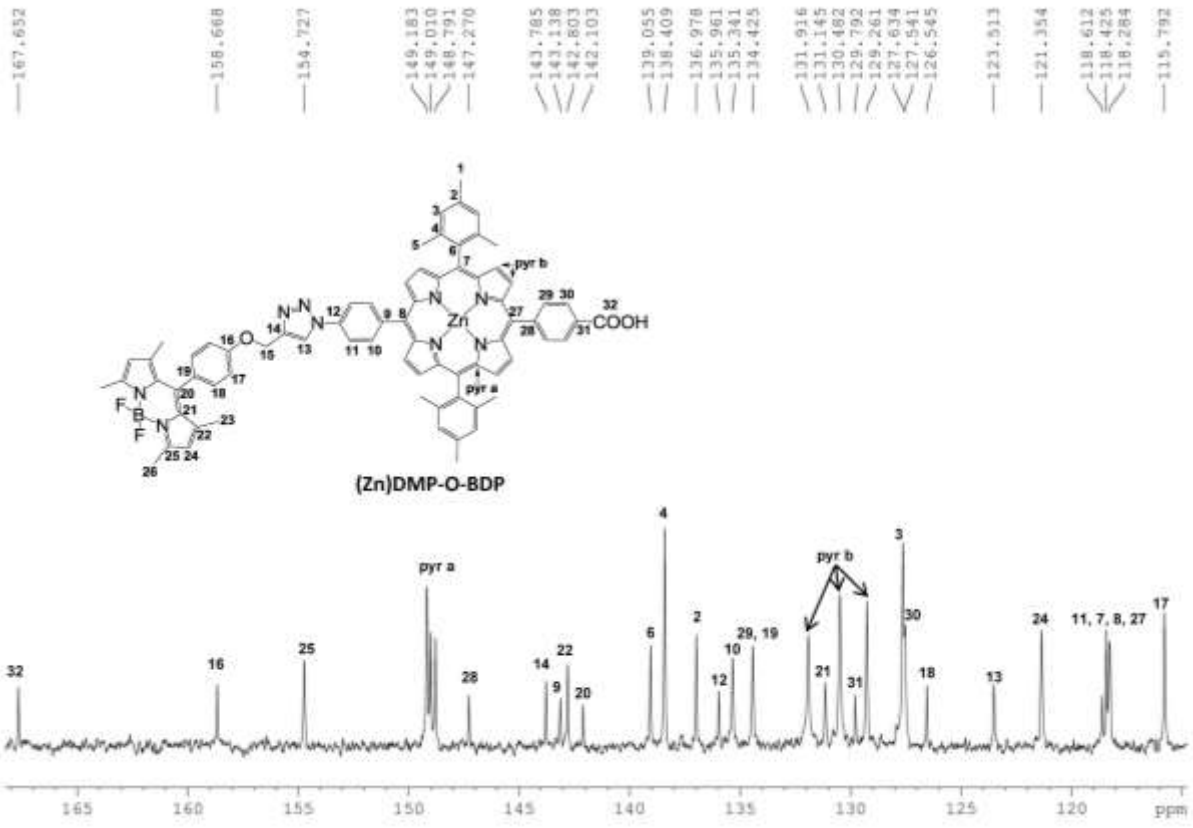


Figure S8. Aromatic region of ^{13}C NMR spectrum of **1** (75MHz, DMSO- d_6).

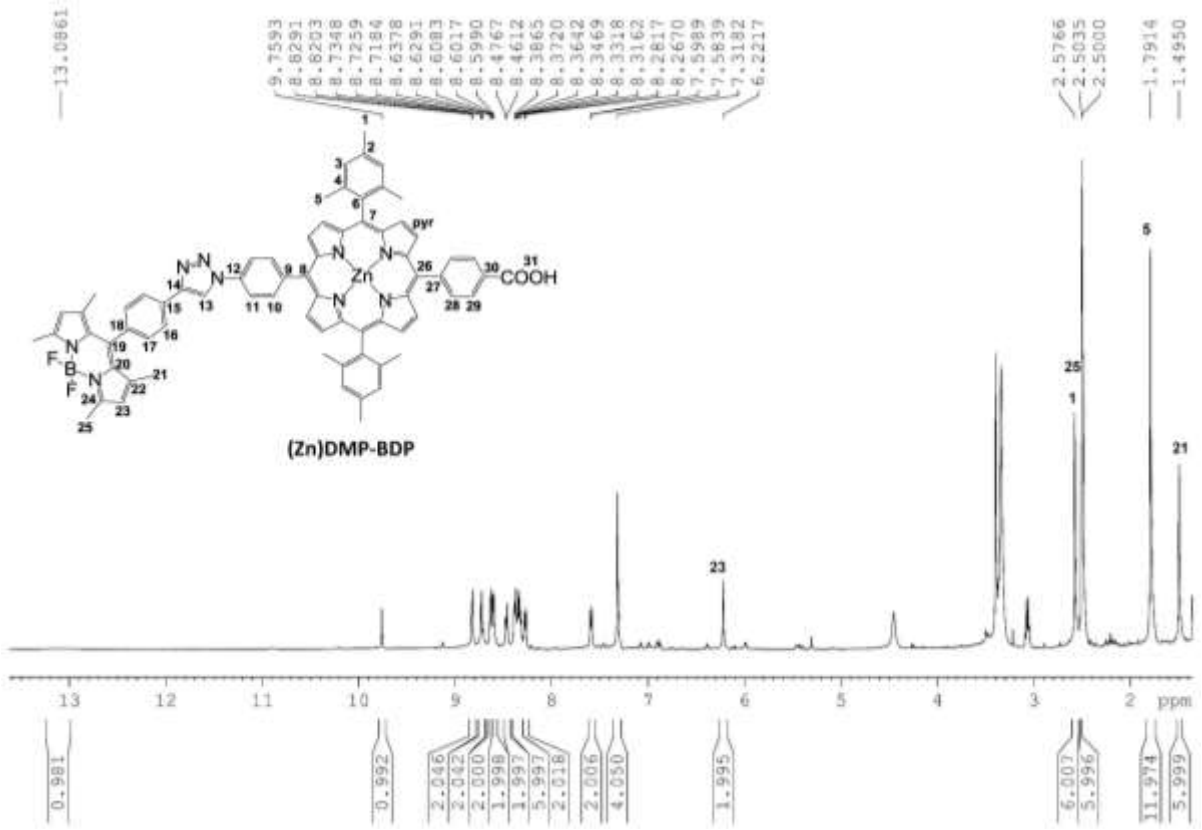


Figure S9. ^{1}H NMR spectrum of **2** (500MHz, DMSO- d_6).

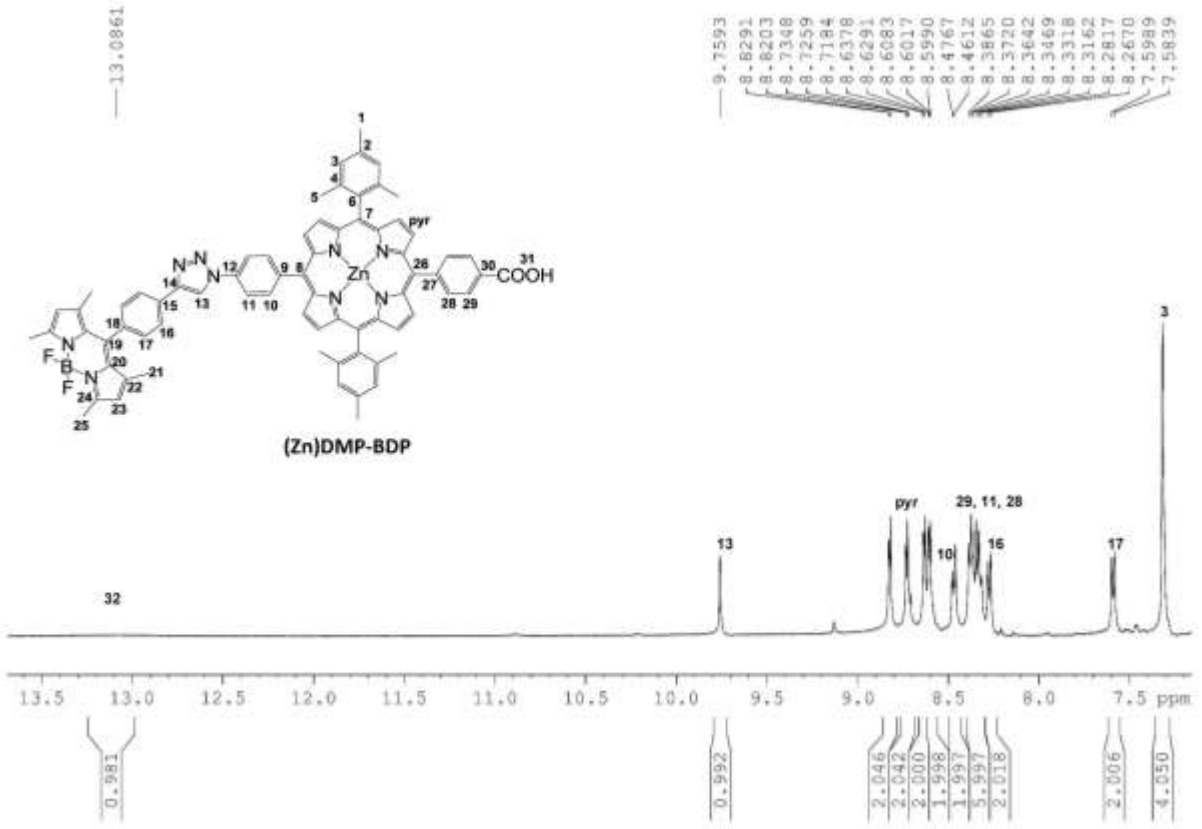


Figure S10. Aromatic region of ^{1}H NMR of **2** (500MHz, DMSO- d_6).

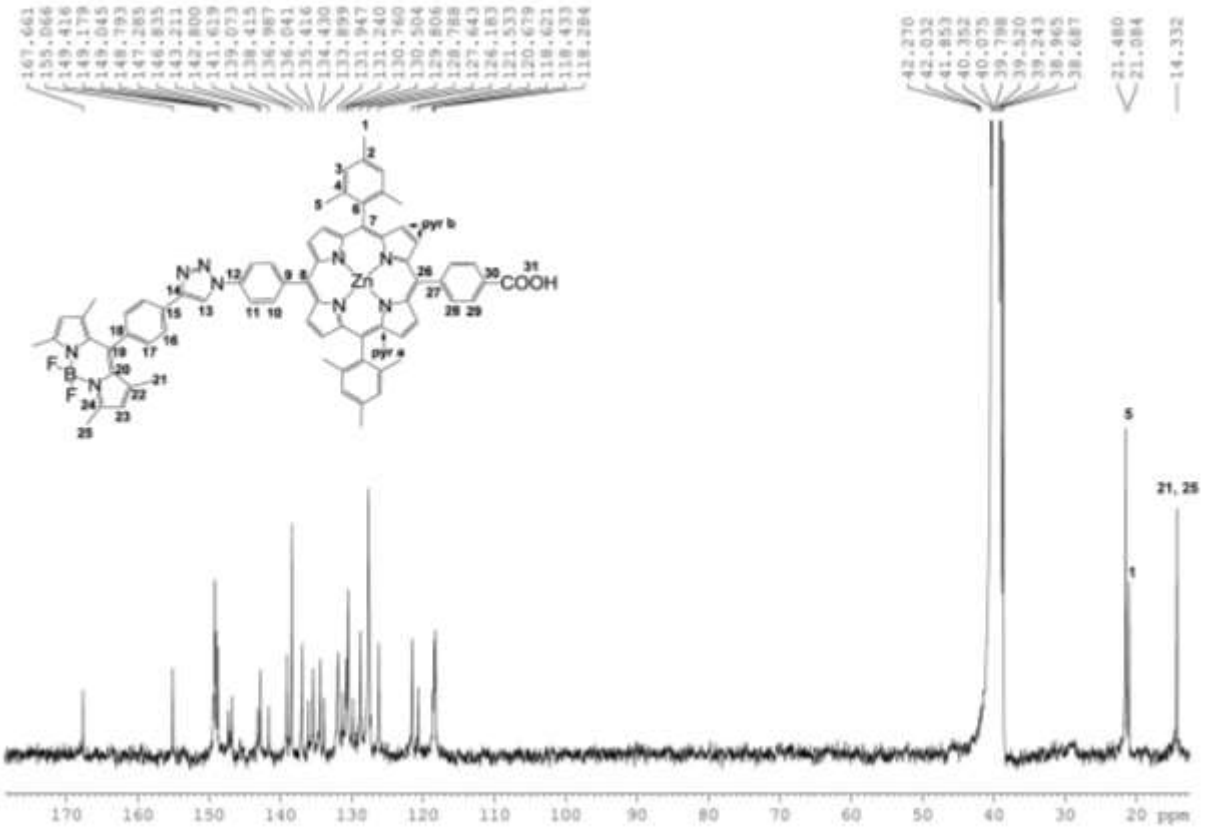


Figure S11. ^{13}C NMR spectrum of **2** (75MHz, DMSO- d_6).

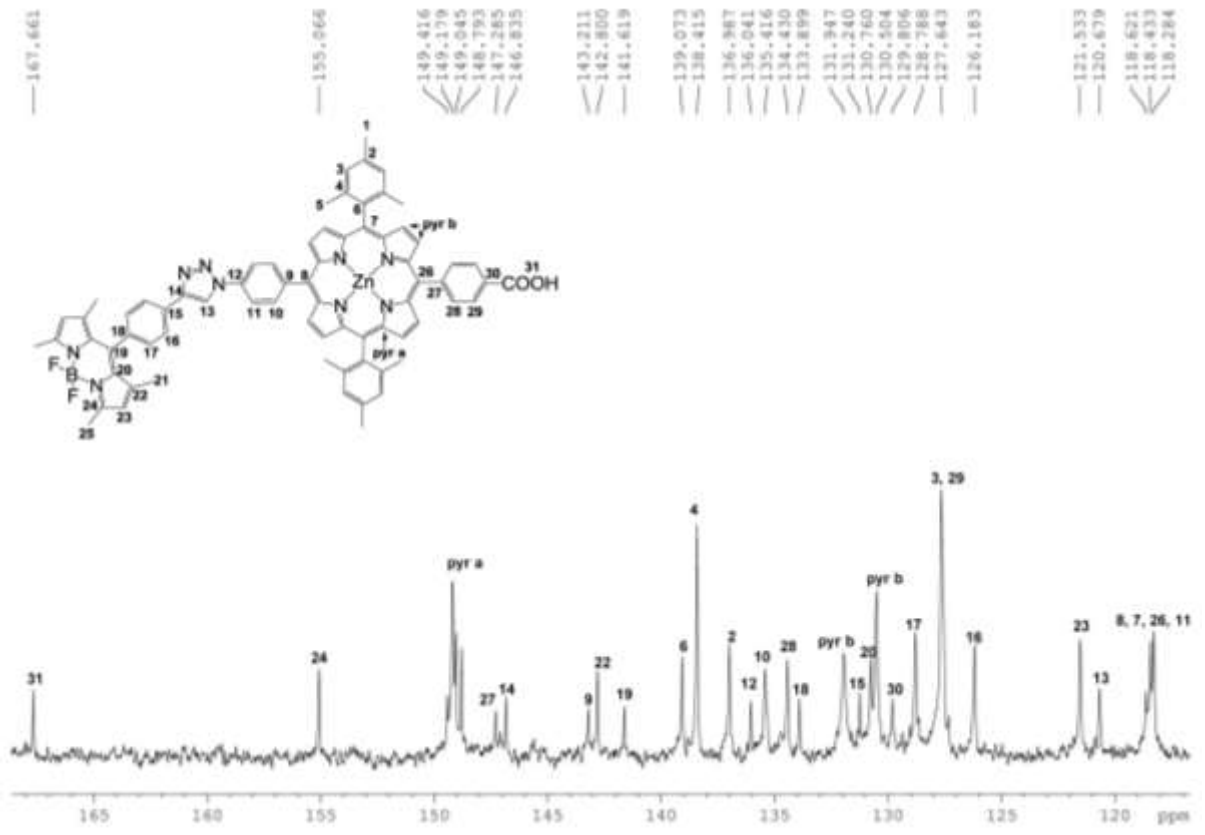


Figure S12. Aromatic region of ^{13}C NMR spectrum of **2** (75MHz, DMSO- d_6).

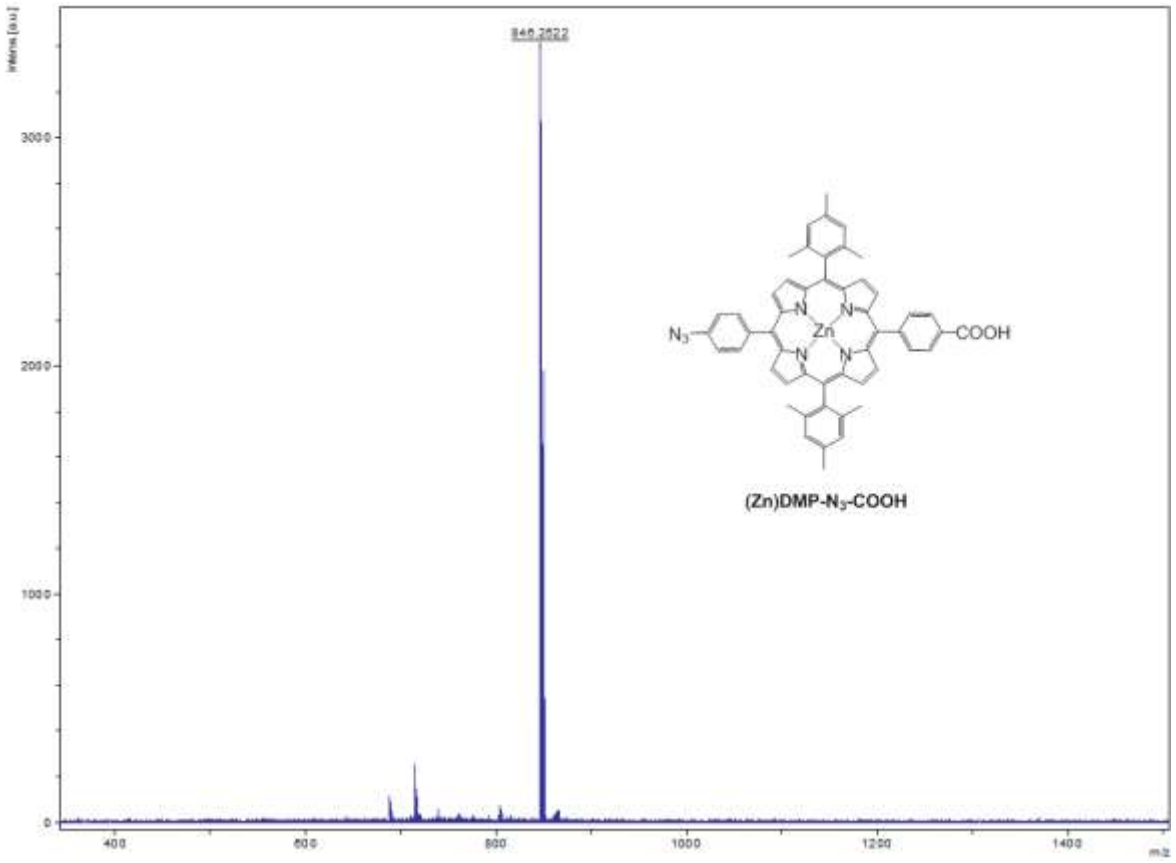


Figure S13. Maldi-TOF spectrum of **Zn-DMP-N_3-COOH**.

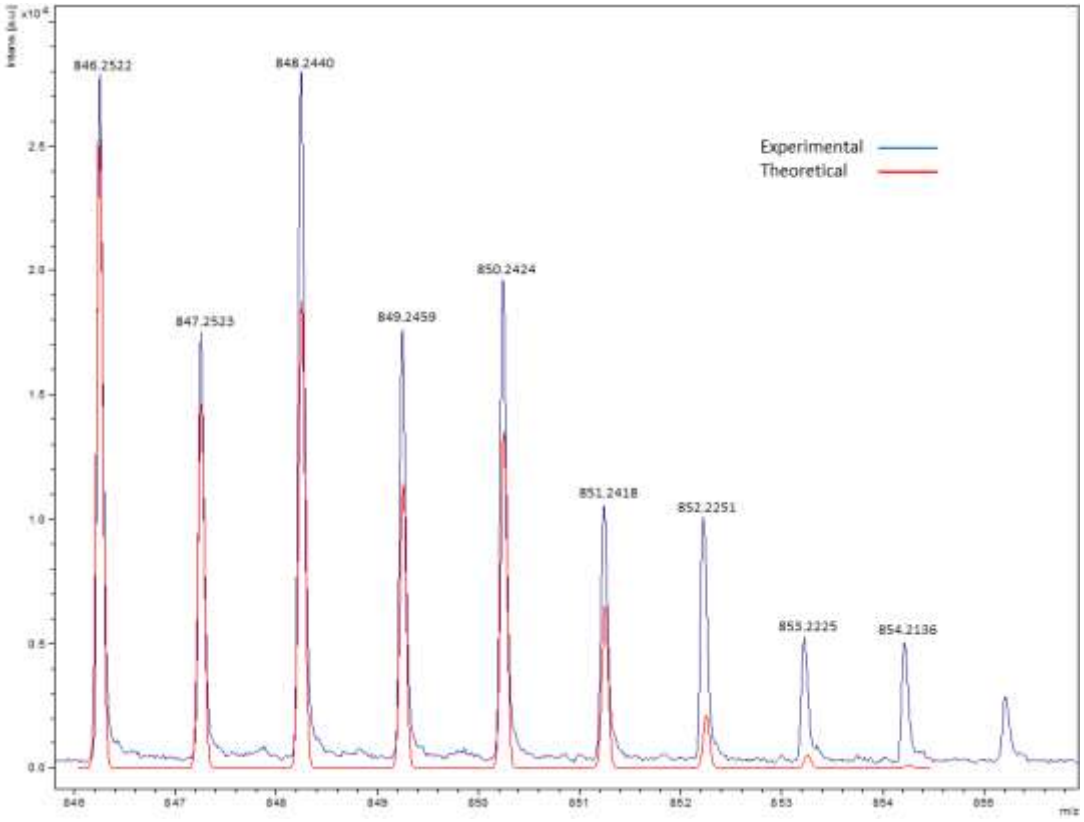


Figure S14. Isotope pattern of the mass peak of MALDI-TOF spectrum for **Zn-DMP-N_3-COOH**, experimental (blue line), theoretical (red line).

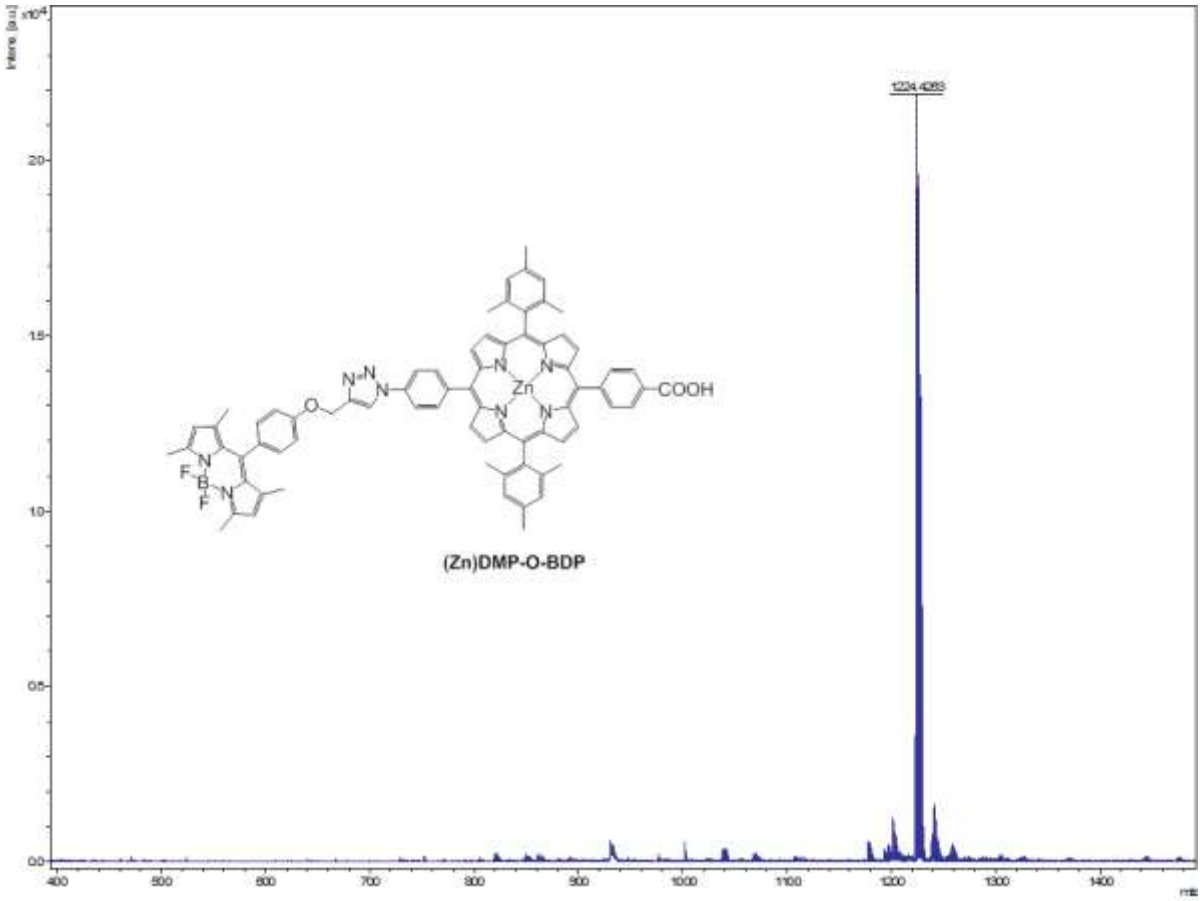


Figure S15. Maldi-TOF spectrum of **1**.

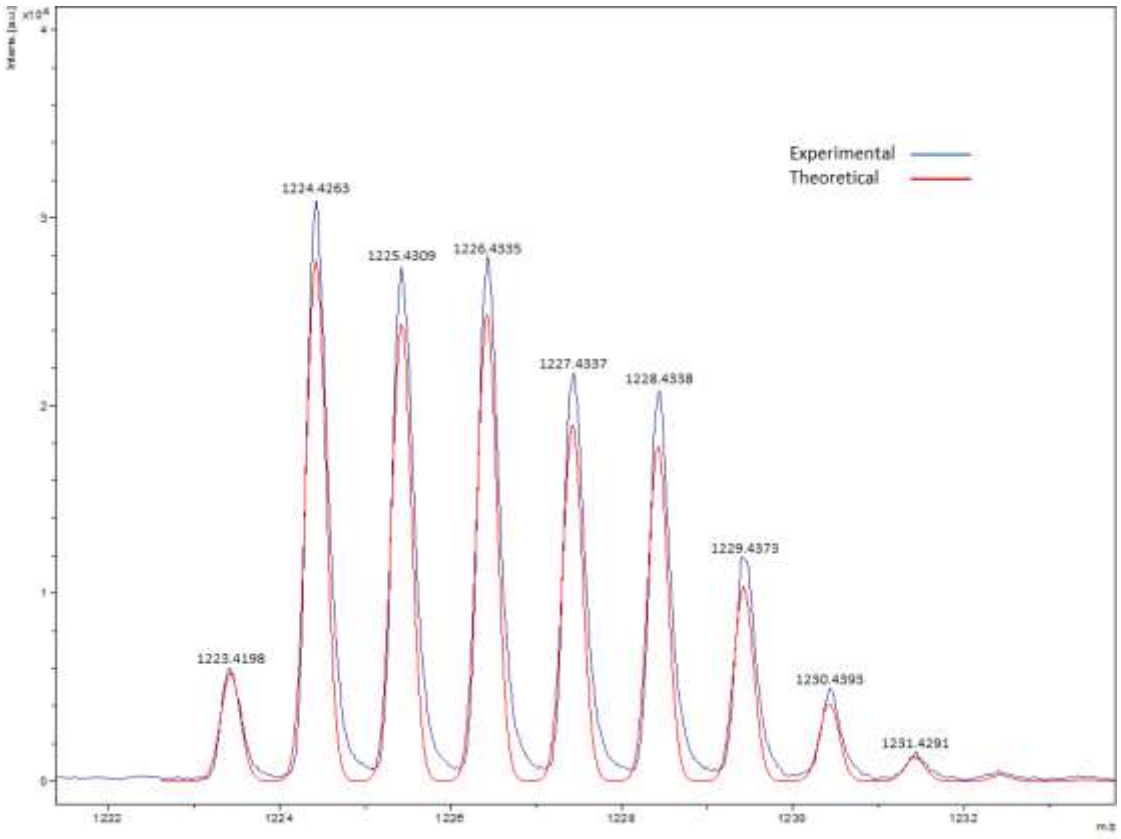


Figure S16. Isotope pattern of the mass peak of MALDI-TOF spectrum for **1**, experimental (blue line), theoretical (red line).

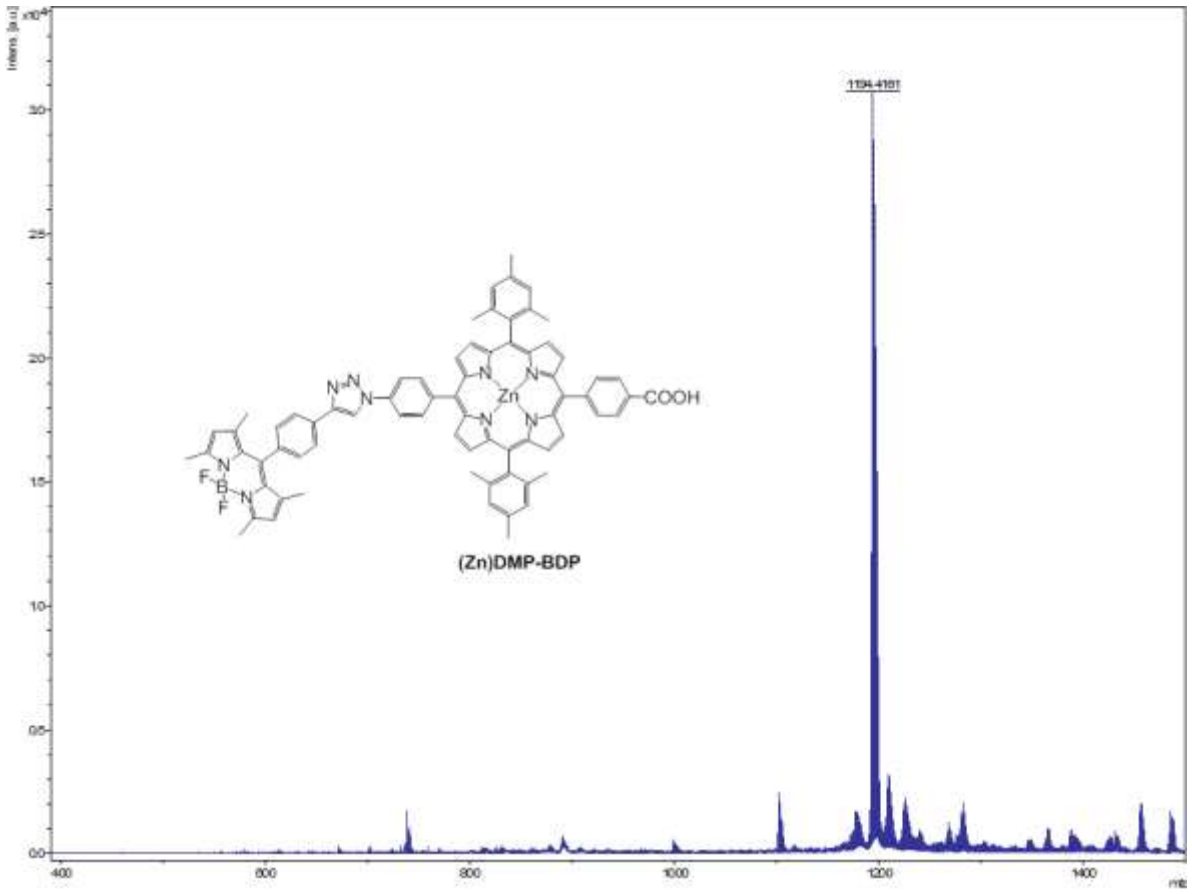


Figure S17. Maldi-TOF spectrum of **2**.

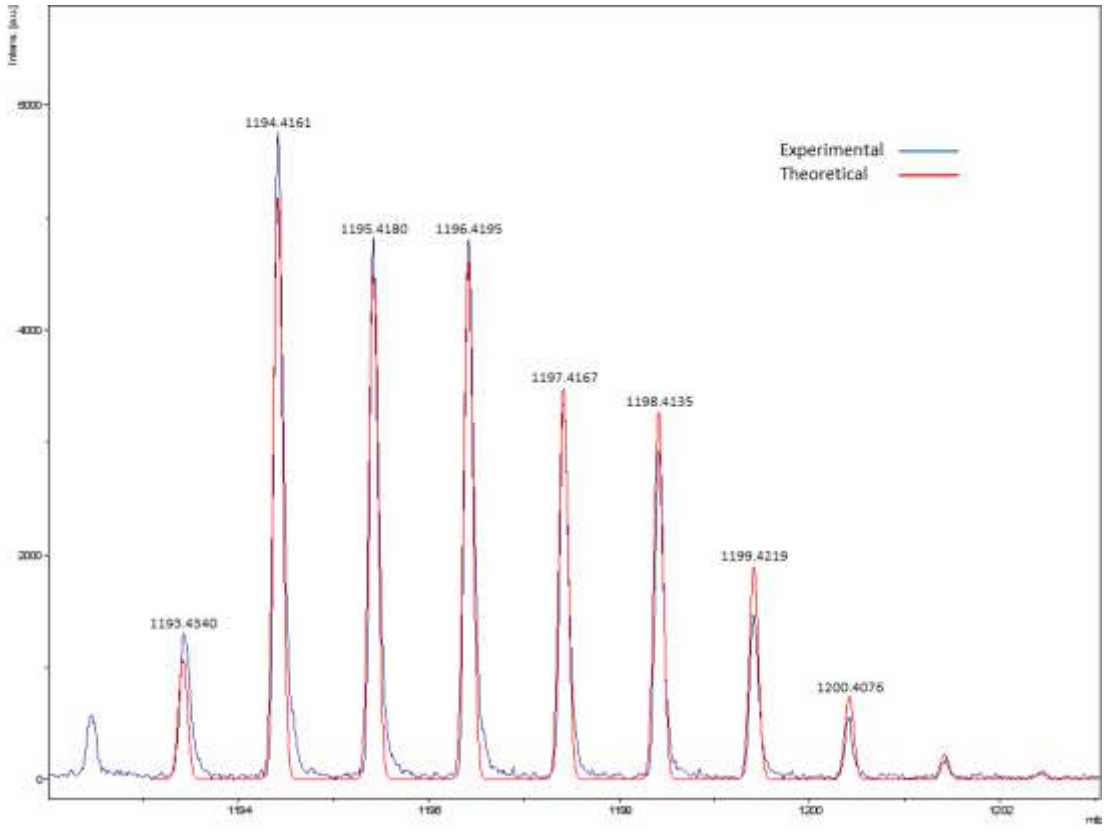


Figure S18. Isotope pattern of the mass peak of MALDI-TOF spectrum for **2**, experimental (blue line), theoretical (red line).

2. Materials and techniques.

All manipulations were carried out using standard Schlenk techniques under nitrogen atmosphere. CuI, KOH, diisopropylethylamine (DIPEA) and other chemicals and solvents were purchased from usual commercial sources and used as received, unless otherwise stated. Tetrahydrofuran (THF) was distilled from Na/benzophenone while acetonitrile (CH_3CN) was kept over activated 3 Å molecular sieves for 24 hours prior use. [5-(4-methoxycarbonylphenyl)-15-(4-azidophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato]zinc was prepared according to literature procedure. [1]

NMR spectra. NMR spectra were recorded on Bruker AVANCE III-500 MHz and Bruker DPX-300 MHz spectrometers using solutions in deuterated solvents and the solvent peak was chosen as the internal standard.

Mass spectra. High-resolution mass spectra (HRMS) were recorded on a Bruker UltrafleXtreme MALDI-TOF/TOF spectrometer, using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile as Matrix.

Photophysical measurements. UV-vis absorption spectra were measured on a Shimadzu UV-1700 spectrophotometer using 10 mm path-length cuvettes. Emission spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red sensitive WRE-343 photomultiplier tube (wavelength range 200-850 nm). The solid-state characterization was carried out on quartz slides. The films consisted of the same composition as those used for device characterization and were prepared using the same procedure.

Microscopic studies: AFM images were performed with VEECO DIMENSION 5000, and the probe head is from NanoScope V.

Theoretical calculations. In order to further explore the molecular structures of 1 and 2, as well as to get insight into their electron density distribution of their frontier molecular orbitals (FMOs) theoretical calculations were carried out using the Gaussian 03 program suite.[2] Density functional theory (DFT)[3] with hybrid B3LYP functionals[4,5] and the 6-31G(d) basis sets were performed for gas phase geometry optimization of **1** and **2** (Figure S11, Table S1 and Figure S12 table S2, respectively). TDDFT calculations were carried out using geometry optimized coordinates in the same level of theory and basis sets. The input geometries as well as the computed structures and molecular orbitals were modeled using ChemCraft software.[6]

3. Device fabrication and characterization

Double layer LECs were fabricated as follows. ITO coated glass plates were patterned by conventional photolithography (Naranjo Substrates). The substrates were cleaned by using sequential ultrasonic baths, namely in water-soap, water, ethanol, and propan-2-ol solvents. After drying, the substrates were placed in a UV–ozone cleaner (Jelight 42-220) for 10 min. An 100 nm layer of PEDOT:PSS was doctor-bladed onto the ITO-glass substrate to increase the device preparation yield (400 □m substrate distance and a speed of 10 mm/s). The luminescent layer comprised a mixture of the dyads, reference and equimolar mixture of the references with $LiCF_3SO_3$ dissolved in trimethylolpropane ethoxylate (TMPE) with the mass ratio of 1:0.06:0.2, respectively. The solutions were stirred in a sealed vial over time. The active layer was deposited by means of doctorblading (850 □m substrate distance and a speed of 12 mm/s) and spincoating technique (800 rpm, 15 s; 1200 rpm, 20 s, 3000 rpm, 10 s) reaching a thickness of 80-130 nm. These conditions resulted in homogenous thin films with a roughness less than 5 %, having no apparent optical defects. The latter was determined using the profilometer DektakxT from Bruker. Once the active layer was deposited, the samples were transferred into an inert atmosphere glovebox (<0.1 ppm O_2 and H_2O, Innovative Technology). Aluminum cathode electrode (90 nm) was thermally evaporated using a shadow mask under high vacuum ($<1 \cdot 10^{-6}$ mbar) using an Angstrom Covap evaporator integrated into the inert atmosphere glovebox. Time dependence of luminance, voltage, and current was measured by applying constant and/or pulsed voltage and current by monitoring the desired parameters simultaneously by using Avantes spectrophotometer (Avaspec-ULS2048L-USB2) calibrated in conjunction with a sphere Avasphere 30-Irrad using Default parameters and Botest OLT OLED Lifetime-Test System. Electroluminescence spectra were recorded using the above mentioned spectrophotometer.

Table S1. Photoluminescence and redox features of the BODIPY and Porphyrin reference as well as the dyads **1** and **2**.

Compound	Absorption	Emission			Redox[e]			
	λ_{max}/ nm[a] (ε/$M^{-1}cm^{-1}$)	Emission[a/b] λ_{max}/ nm	ϕ^c %	ϕ^d %	$E^1_{1/2red}$ V	$E^2_{1/2red}$ V	$E^1_{1/2ox}$ V	$E^2_{1/2ox}$ V
Zn-Porphyrin	424(368222);550(19064); 597(2824)	607; 657[a]/ 660[b]	-	4.4	-1.15	-1.52	1.03	1.38
BODIPY-O-Triple	500(46856); 359(4071); 307(4377)	512 [a]/-[b]	57	-	-1.13	-	1.38	-
BODIPY-Triple	499(42761); 361(3482); 306(2342)	514[a]/-[b]	51	-	-1.09		1.41	
1	425(369248);500(46095); 557(11550); 598(2942)	514;607;656[a]/656[b]	1.1	4.8	-1.18	-1.4	0.98	1.34
2	426(379729);501(41149); 557(12259); 598(2165)	515;607;655[a]/659[b]	4.4	4.3	-1.11	-1.39	1.03	1.40

[a]Absorption and emission maxima measured in THF. [b]Emission maxima of the thin films. [c]Photoluminescence quantum yields using rhodamine (Φ = 49% in ethanol) as standard measured in THF upon excitation at 490 nm. [d]Photoluminescence quantum yields using ZnTPP (Φ = 0.03 in toluene) as standard measured in THF upon excitation at 550 nm. [e]Electrochemical redox data measured in THF, reported *vs*. SCE with Fc/Fc^+ as internal standard ($E_{1/2\ ox}$ is 0.55V).

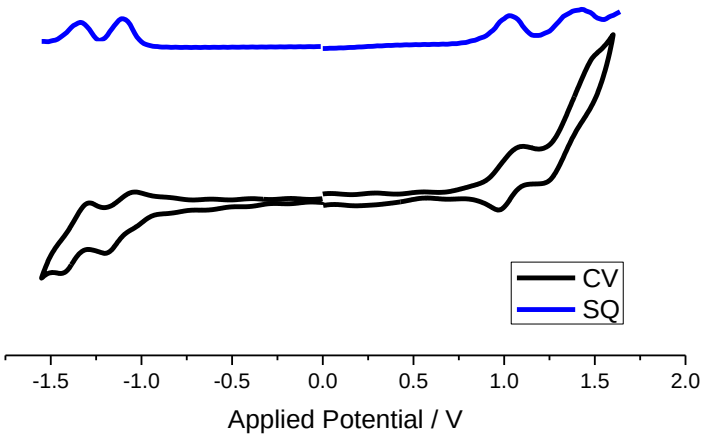


Figure S19. Cyclic (CV) and square wave (SQ) voltammograms of **1** in THF. All potentials are reported vs. SCE and FcH/FcH^+ was used as internal standard ($E_{1/2}$Ox = 0.55 V).

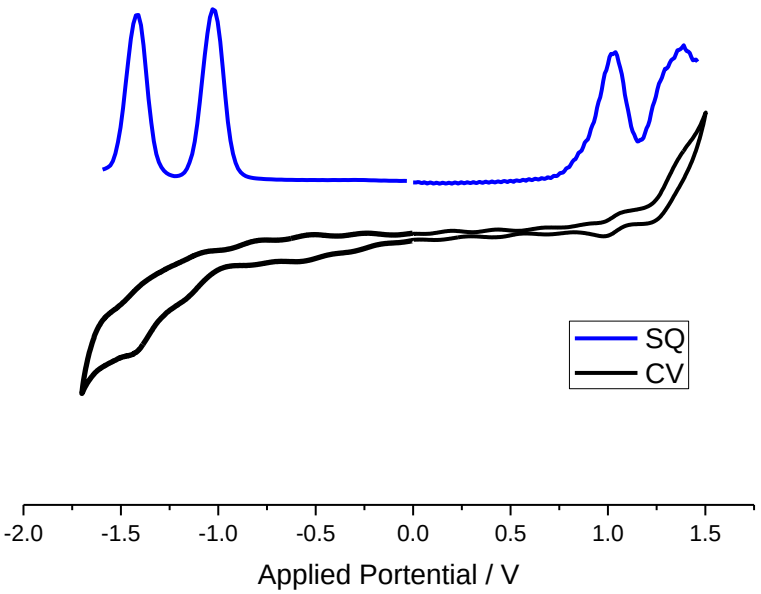


Figure S20. Cyclic (CV) and square wave (SQ) voltammograms of **2** in THF. All potentials are reported vs. SCE and FcH/FcH^{+} was used as internal standard ($E_{1/2}Ox = 0.55$ V).

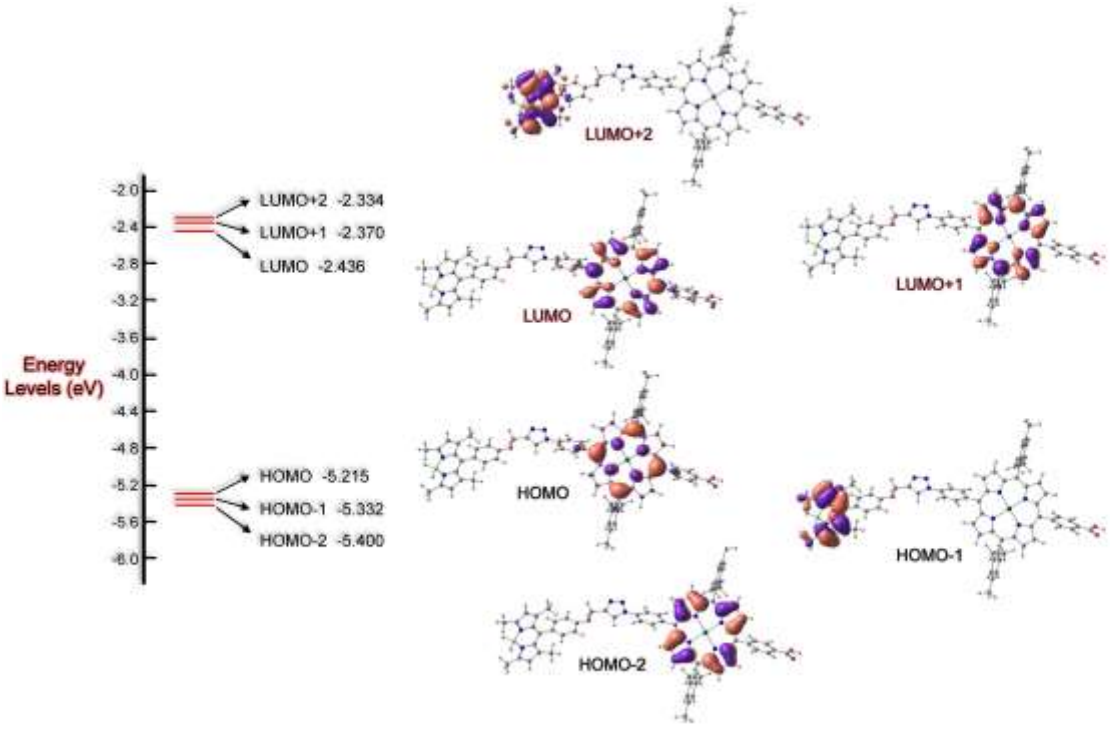


Figure S21. Frontier molecular orbitals of **1** with the corresponding energy levels.

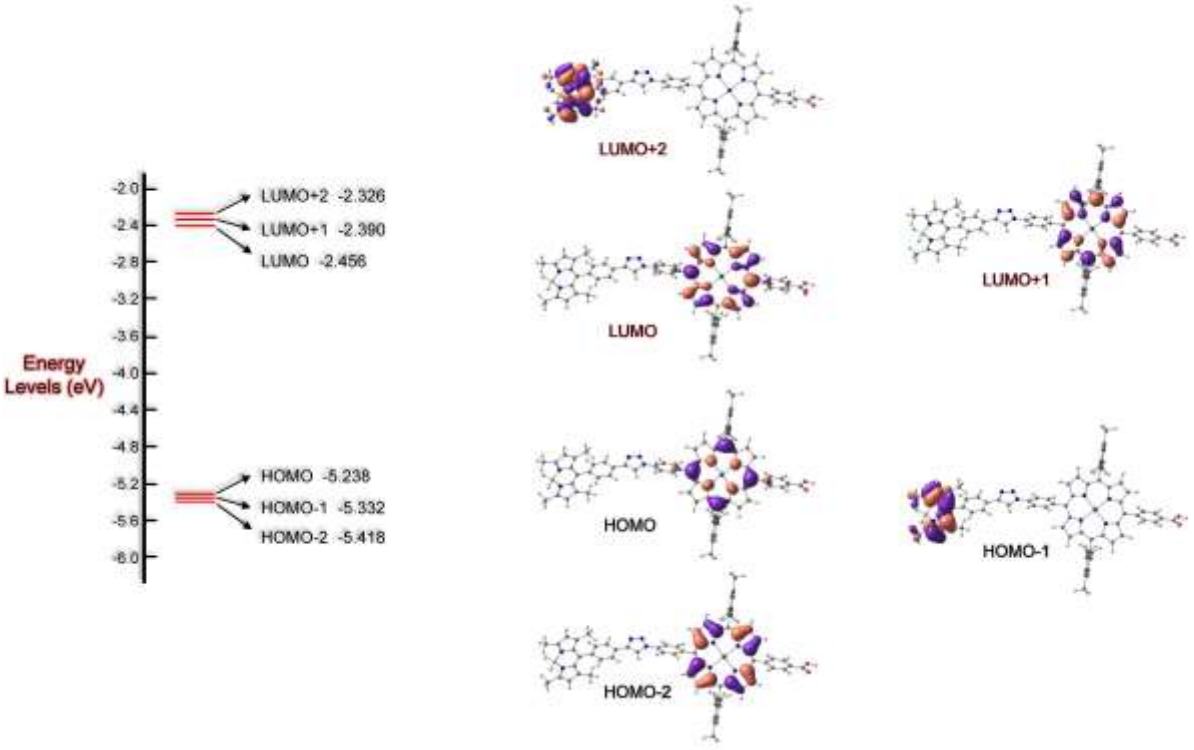


Figure S22. Frontier molecular orbitals of **2** with the corresponding energy levels.

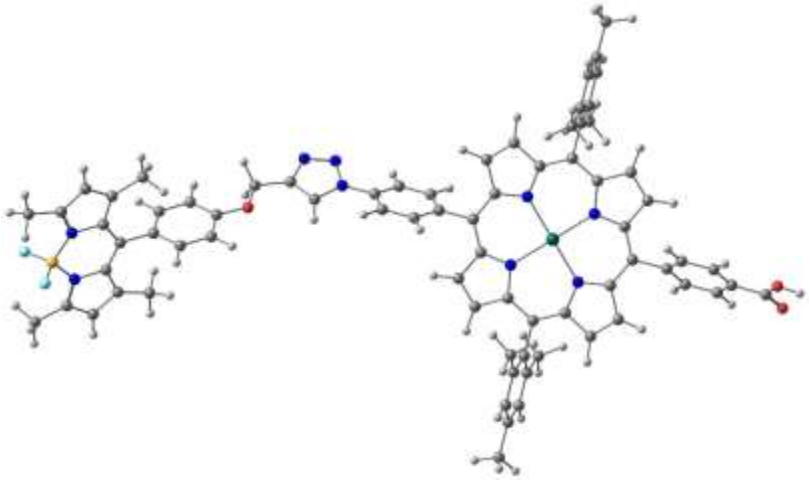


Figure S23. Gas phase geometry optimized structure of **1**. Carbon, nitrogen, hydrogen, oxygen, fluoro, zinc and boron atoms correspond to grey, blue, white, red, light blue, green and yellow spheres, respectively.

Table S2. Coordinates of gas phase geometry optimized structure of **1** at the B3LYP/LANL2DG/6-31G* level with energy E = -3826.71253198 Hartree/particle.

C	-3.841126000	-2.097396000	3.472486000
C	-2.807861000	-2.748323000	4.077336000
C	-3.374976000	-3.856581000	4.813437000
C	-4.740324000	-3.861077000	4.645004000
C	-5.055547000	-2.803754000	3.825251000

C	-9.753430000	-3.583857000	3.940933000
C	-8.877331000	-2.731593000	3.337926000
C	-7.550926000	-3.084788000	3.800088000
N	-7.643363000	-4.152577000	4.660733000
C	-8.975460000	-4.478571000	4.768933000
C	-6.355777000	-2.441165000	3.409863000
C	-8.310692000	-8.135029000	7.737383000
C	-9.345118000	-7.472927000	7.147041000
C	-8.770482000	-6.429464000	6.326959000
N	-7.399365000	-6.475110000	6.430513000
C	-7.086747000	-7.510454000	7.278782000
C	-9.516374000	-5.519389000	5.550919000
C	-2.379802000	-6.811547000	7.057268000
C	-3.253465000	-7.682007000	7.636854000
C	-4.588344000	-7.253282000	7.272483000
N	-4.501052000	-6.142712000	6.467279000
C	-3.165671000	-5.846150000	6.321033000
C	-2.627703000	-4.777704000	5.575221000
C	-5.783886000	-7.893091000	7.667864000
C	-11.014638000	-5.670131000	5.558429000
C	-5.660354000	-9.076383000	8.576655000
C	-1.131970000	-4.604926000	5.596560000
C	-6.475782000	-1.279228000	2.473616000
C	-11.645430000	-6.527904000	4.631121000
C	-13.038137000	-6.653406000	4.658674000
C	-13.826542000	-5.953178000	5.577359000
C	-13.181449000	-5.113316000	6.488468000
C	-11.790331000	-4.956266000	6.495686000
C	-6.031061000	-10.360365000	8.139596000
C	-5.917551000	-11.460821000	8.982788000
C	-5.430080000	-11.303351000	10.287174000
C	-5.057282000	-10.028471000	10.735080000

C	-5.172305000	-8.930267000	9.886474000
C	-0.334008000	-5.209637000	4.601728000
C	1.053315000	-5.032878000	4.641619000
C	1.674817000	-4.275600000	5.639011000
C	0.865370000	-3.681970000	6.611245000
C	-0.525878000	-3.833470000	6.610752000
C	-5.962932000	-1.349520000	1.167462000
C	-6.077436000	-0.280414000	0.283549000
C	-6.704342000	0.896255000	0.705428000
C	-7.209690000	0.997333000	2.004545000
C	-7.100205000	-0.087388000	2.872718000
Zn	-6.070797000	-5.158913000	5.549848000
C	-15.332002000	-6.086877000	5.568181000
C	-11.145402000	-4.032479000	7.505421000
C	-10.841185000	-7.310511000	3.616228000
C	-0.952720000	-6.039817000	3.498622000
C	-1.352971000	-3.166158000	7.687831000
C	-6.822296000	1.987676000	-0.198441000
N	-5.949384000	2.125759000	-1.231666000
N	-6.286266000	3.196994000	-1.889864000
C	-7.376173000	3.765440000	-1.296457000
C	-7.733718000	3.002307000	-0.210712000
C	-11.571508000	11.374900000	-1.333319000
C	-10.344076000	11.748122000	-0.688030000
C	-10.414181000	13.123901000	-0.500981000
C	-11.644860000	13.584022000	-1.013821000
N	-12.332183000	12.537151000	-1.509456000
C	-15.260086000	10.796560000	-3.179487000
C	-15.238985000	9.403024000	-3.395867000
C	-14.039437000	8.898130000	-2.906939000
C	-13.322055000	10.025460000	-2.381690000
N	-14.114227000	11.163644000	-2.574072000

C	-12.063239000	10.131990000	-1.766338000
C	-11.235148000	8.904115000	-1.565953000
C	-11.358589000	8.139574000	-0.394329000
C	-10.585815000	7.001213000	-0.200365000
C	-9.665648000	6.598033000	-1.179760000
C	-9.531947000	7.348475000	-2.353795000
C	-10.316415000	8.491753000	-2.534819000
C	-9.184108000	10.892151000	-0.270161000
C	-12.173383000	14.981402000	-1.041472000
C	-13.643396000	7.451157000	-2.955402000
C	-16.333589000	11.773796000	-3.533500000
B	-13.744761000	12.618717000	-2.159913000
F	-13.707255000	13.440937000	-3.284614000
F	-14.669032000	13.102339000	-1.234462000
C	3.178121000	-4.124602000	5.677867000
C	-8.003627000	5.006085000	-1.847232000
O	-8.952675000	5.469778000	-0.892995000
C	-5.330245000	-12.510521000	11.147045000
O	-5.642923000	-13.635241000	10.808423000
O	-4.843588000	-12.242956000	12.386832000
H	-3.786710000	-1.213655000	2.853463000
H	-1.756464000	-2.500310000	4.039163000
H	-10.828170000	-3.616548000	3.830046000
H	-9.107302000	-1.942708000	2.636625000
H	-8.371149000	-8.963883000	8.427574000
H	-10.403195000	-7.663129000	7.259633000
H	-1.300288000	-6.822934000	7.110281000
H	-3.015858000	-8.541386000	8.246722000
H	-13.518585000	-7.318434000	3.943246000
H	-13.774749000	-4.564174000	7.217095000
H	-6.402028000	-10.489163000	7.127134000
H	-6.197023000	-12.454141000	8.647187000

H	-4.685136000	-9.901041000	11.745651000
H	-4.890742000	-7.942822000	10.240116000
H	1.663133000	-5.499726000	3.870277000
H	1.326867000	-3.081506000	7.392910000
H	-5.481467000	-2.264402000	0.835436000
H	-5.691575000	-0.344859000	-0.726859000
H	-7.662421000	1.921730000	2.348958000
H	-7.488153000	-0.002164000	3.883272000
H	-15.642157000	-7.121347000	5.382036000
H	-15.782297000	-5.468850000	4.779763000
H	-15.768215000	-5.769263000	6.520977000
H	-11.897467000	-3.594042000	8.168693000
H	-10.609021000	-3.211495000	7.014674000
H	-10.413385000	-4.561662000	8.126679000
H	-10.141988000	-8.001215000	4.102332000
H	-10.241766000	-6.648395000	2.980406000
H	-11.498404000	-7.897518000	2.967278000
H	-1.648652000	-5.448903000	2.891443000
H	-1.523238000	-6.884846000	3.902004000
H	-0.181467000	-6.440222000	2.833488000
H	-0.716126000	-2.594177000	8.369762000
H	-1.908865000	-3.901035000	8.282186000
H	-2.093264000	-2.479501000	7.260580000
H	-8.537709000	3.089772000	0.500254000
H	-9.658335000	13.747461000	-0.040513000
H	-16.030554000	8.833121000	-3.865786000
H	-12.067517000	8.443835000	0.370811000
H	-10.676480000	6.407901000	0.704142000
H	-8.828271000	7.061151000	-3.126372000
H	-10.206044000	9.070491000	-3.447835000
H	-9.478645000	10.113814000	0.441990000
H	-8.419917000	11.514221000	0.206635000

H	-8.720102000	10.379409000	-1.119652000
H	-11.462814000	15.669481000	-0.576211000
H	-13.131312000	15.039796000	-0.513870000
H	-12.362386000	15.300971000	-2.071980000
H	-14.440041000	6.866498000	-3.426413000
H	-13.464768000	7.036479000	-1.957463000
H	-12.723889000	7.292672000	-3.529255000
H	-17.183738000	11.260919000	-3.990721000
H	-15.952106000	12.528999000	-4.229281000
H	-16.672330000	12.311155000	-2.641436000
H	3.606394000	-4.110391000	4.669635000
H	3.648195000	-4.957945000	6.217453000
H	3.475291000	-3.200695000	6.185373000
H	-8.500583000	4.796318000	-2.805857000
H	-7.232510000	5.766578000	-2.033175000
H	-4.825936000	-13.100433000	12.851118000

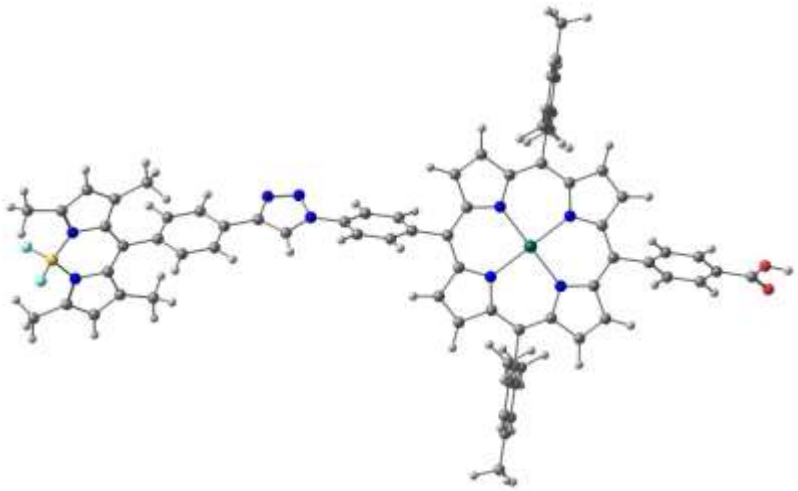


Figure S24. Gas phase geometry optimized structure of **2**. Carbon, nitrogen, hydrogen, oxygen, fluoro, zinc and boron atoms correspond to grey, blue, white, red, light blue, green and yellow spheres, respectively.

Table S3. Coordinates of gas phase geometry optimized structure of **2** at the B3LYP/LANL2DG/6-31G* level with energy E = -3712.19862069 Hartree/particle.

C	-1.695180000	0.219894000	-0.794216000
C	-0.743634000	-0.720705000	-1.053218000

C	0.543251000	-0.088653000	-0.862396000
7	0.353634000	1.221478000	-0.488349000
C	-1.002335000	1.439052000	-0.430994000
C	-0.628057000	6.020225000	0.821065000
C	-1.610458000	5.101270000	0.601828000
C	-0.961259000	3.866300000	0.213118000
7	0.400458000	4.052907000	0.216182000
C	0.635209000	5.358307000	0.581265000
C	-1.627605000	2.659967000	-0.095639000
C	5.376488000	5.045694000	0.365087000
C	4.425284000	5.985556000	0.627300000
C	3.139444000	5.332069000	0.519229000
7	3.329605000	4.007879000	0.198586000
C	4.684970000	3.800181000	0.102844000
C	1.898110000	5.971175000	0.712559000
C	4.312736000	-0.808448000	-1.042734000
C	5.295259000	0.107757000	-0.814475000
C	4.644110000	1.369902000	-0.529276000
7	3.281605000	1.195463000	-0.577359000
C	3.047929000	-0.123493000	-0.890554000
C	1.785131000	-0.731706000	-1.040265000
C	5.310566000	2.577257000	-0.225062000
C	1.922416000	7.429036000	1.088732000
C	6.807557000	2.559293000	-0.253442000
C	1.760797000	-2.188942000	-1.418656000
C	-3.124412000	2.676217000	-0.062182000
C	1.976432000	7.808312000	2.447147000
C	1.998758000	9.168814000	2.772932000
C	1.967566000	10.165467000	1.793140000
C	1.918791000	9.767440000	0.454228000
C	1.893783000	8.418421000	0.082992000
C	7.552501000	2.736222000	0.925758000

C	8.943234000	2.718386000	0.899349000
C	9.624078000	2.524538000	-0.310112000
C	8.892701000	2.348115000	-1.492805000
C	7.500481000	2.365136000	-1.460415000
C	1.728077000	-3.179049000	-0.414055000
C	1.703225000	-4.527564000	-0.788002000
C	1.711579000	-4.923888000	-2.127983000
C	1.739604000	-3.926140000	-3.107078000
C	1.766273000	-2.566578000	-2.778831000
C	-3.834578000	1.942676000	0.902874000
C	-5.225634000	1.959855000	0.949809000
C	-5.935860000	2.712210000	0.008790000
C	-5.253501000	3.437881000	-0.971762000
C	-3.860232000	3.422526000	-0.995504000
Zn	1.841636000	2.619010000	-0.161794000
C	1.961570000	11.628701000	2.171589000
C	1.843268000	8.043720000	-1.381920000
C	2.012851000	6.771905000	3.548628000
C	1.717524000	-2.806446000	1.052207000
C	1.794134000	-1.529043000	-3.879538000
N	-7.356582000	2.731798000	0.059704000
N	-8.042164000	1.709514000	0.643455000
N	-9.305900000	1.987031000	0.558498000
C	-9.477990000	3.189440000	-0.081217000
C	-8.223613000	3.672970000	-0.403070000
C	-15.253820000	6.355504000	-0.013943000
C	-14.698475000	6.916813000	1.185615000
C	-15.659211000	7.793541000	1.676742000
C	-16.770644000	7.773152000	0.808704000
N	-16.524467000	6.913399000	-0.198356000
C	-17.288922000	5.013299000	-3.391666000
C	-16.349213000	4.112201000	-3.934033000

C	-15.226408000	4.097832000	-3.114418000
C	-15.504721000	5.019062000	-2.048539000
N	-16.780867000	5.552156000	-2.266648000
C	-14.750465000	5.419215000	-0.932774000
C	-13.388230000	4.842633000	-0.720135000
C	-12.256644000	5.472351000	-1.256127000
C	-10.985708000	4.938910000	-1.055322000
C	-10.808627000	3.761946000	-0.310545000
C	-11.944656000	3.130841000	0.222911000
C	-13.214597000	3.664738000	0.019913000
C	-13.371075000	6.659469000	1.837323000
C	-18.046375000	8.543555000	0.915872000
C	-14.005281000	3.260347000	-3.359608000
C	-18.643160000	5.367894000	-3.913970000
B	-17.502140000	6.600933000	-1.369709000
F	-18.690310000	6.068882000	-0.871681000
F	-17.757271000	7.760624000	-2.100851000
C	1.714992000	-6.386467000	-2.508943000
C	11.109306000	2.514546000	-0.282926000
O	11.789124000	2.665332000	0.713293000
O	11.663214000	2.315759000	-1.507282000
H	-2.767384000	0.101335000	-0.853304000
H	-0.892858000	-1.747848000	-1.355093000
H	-0.741082000	7.050435000	1.128178000
H	-2.676421000	5.243470000	0.704945000
H	6.447610000	5.184505000	0.342826000
H	4.573788000	7.029761000	0.864004000
H	4.426911000	-1.856151000	-1.282810000
H	6.362748000	-0.057606000	-0.827887000
H	2.043211000	9.455894000	3.821893000
H	1.901075000	10.526184000	-0.325893000
H	7.030074000	2.879364000	1.867043000

H	9.521704000	2.848252000	1.808165000
H	9.415248000	2.203582000	-2.431963000
H	6.937235000	2.235225000	-2.379824000
H	1.675255000	-5.286971000	-0.008940000
H	1.739307000	-4.211806000	-4.157420000
H	-3.285222000	1.363156000	1.638672000
H	-5.767759000	1.403040000	1.704751000
H	-5.800028000	3.990423000	-1.729448000
H	-3.334109000	3.982908000	-1.762391000
H	2.513735000	11.805029000	3.101060000
H	0.938022000	11.995427000	2.328194000
H	2.410960000	12.247565000	1.387553000
H	1.819537000	8.937741000	-2.012747000
H	0.955889000	7.442759000	-1.613044000
H	2.714760000	7.446502000	-1.675461000
H	2.890795000	6.120932000	3.460803000
H	1.131529000	6.120349000	3.517717000
H	2.044739000	7.249782000	4.532663000
H	0.843536000	-2.195132000	1.306216000
H	2.603400000	-2.220802000	1.325135000
H	1.697738000	-3.701249000	1.681974000
H	1.782489000	-2.005652000	-4.864668000
H	2.691067000	-0.901245000	-3.818854000
H	0.931425000	-0.854896000	-3.820079000
H	-7.890968000	4.586234000	-0.868386000
H	-15.579150000	8.394546000	2.573707000
H	-16.490016000	3.533516000	-4.838140000
H	-12.375308000	6.384438000	-1.834577000
H	-10.126487000	5.444232000	-1.488565000
H	-11.816274000	2.219530000	0.797233000
H	-14.083047000	3.165466000	0.440935000
H	-13.243770000	5.608119000	2.116964000

H	-13.283993000	7.263183000	2.746200000
H	-12.531043000	6.913003000	1.181611000
H	-18.902269000	7.862475000	0.971490000
H	-18.196454000	9.163620000	0.025630000
H	-18.035799000	9.182463000	1.802710000
H	-14.134863000	2.679697000	-4.278407000
H	-13.812823000	2.557994000	-2.541435000
H	-13.100993000	3.868677000	-3.469211000
H	-19.416112000	5.119027000	-3.178771000
H	-18.847638000	4.833580000	-4.845398000
H	-18.715074000	6.446020000	-4.092229000
H	1.271417000	-7.006638000	-1.722851000
H	2.737365000	-6.752350000	-2.674566000
H	1.155958000	-6.561337000	-3.434803000
H	12.627718000	2.330192000	-1.363331000

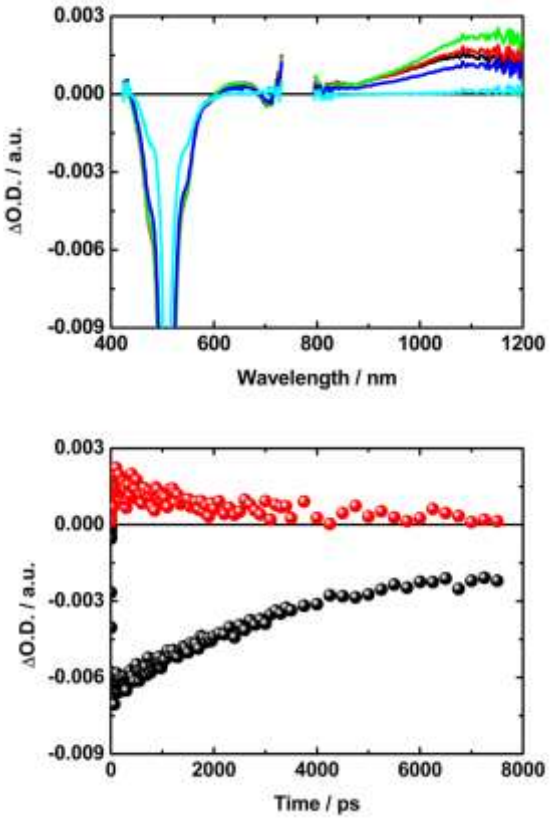


Figure S25. Top: Femtosecond transient absorption spectra of the BODIPY reference compound in argon saturated THF; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue), and 7500 ps (cyan) after excitation at 505 nm. Bottom: Corresponding time absorption profiles at 485 nm (black) and 1100 nm (red).

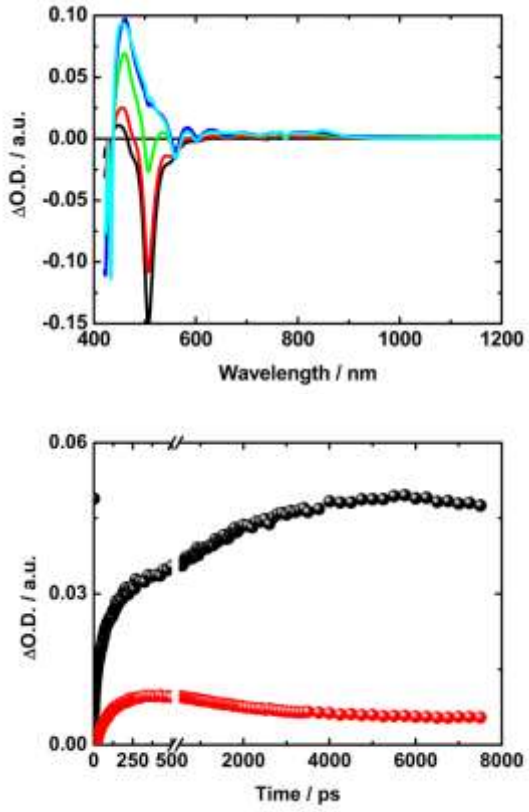


Figure S26. Top: Femtosecond transient absorption spectra of the BODIPY-ZnP dyad **1** in argon saturated THF; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue), and 7500 ps (cyan) after excitation at 505 nm. Bottom: Corresponding time absorption profiles at 460 nm (black) and 580 nm (red).

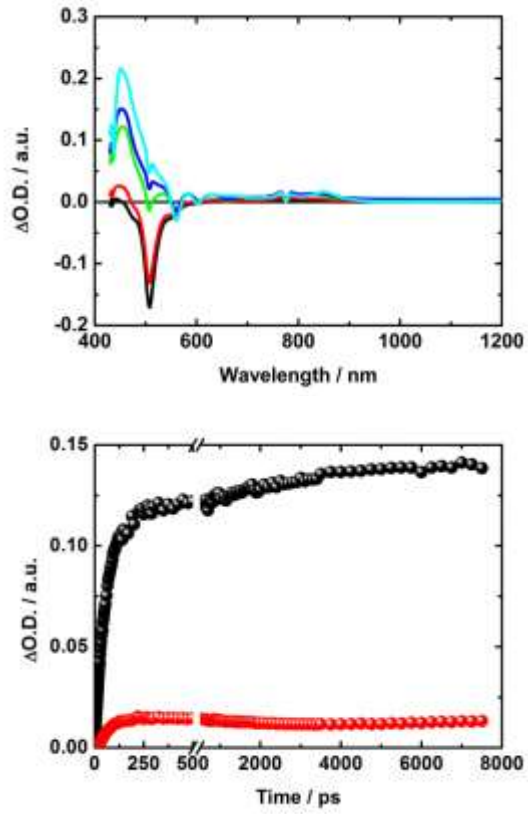


Figure S27. Top: Femtosecond transient absorption spectra of the BODIPY-ZnP dyad **2** in argon saturated THF; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue), and 7500 ps (cyan) after excitation at 505 nm. Bottom: Corresponding time absorption profiles at 440 nm (black) and 580 nm (red).

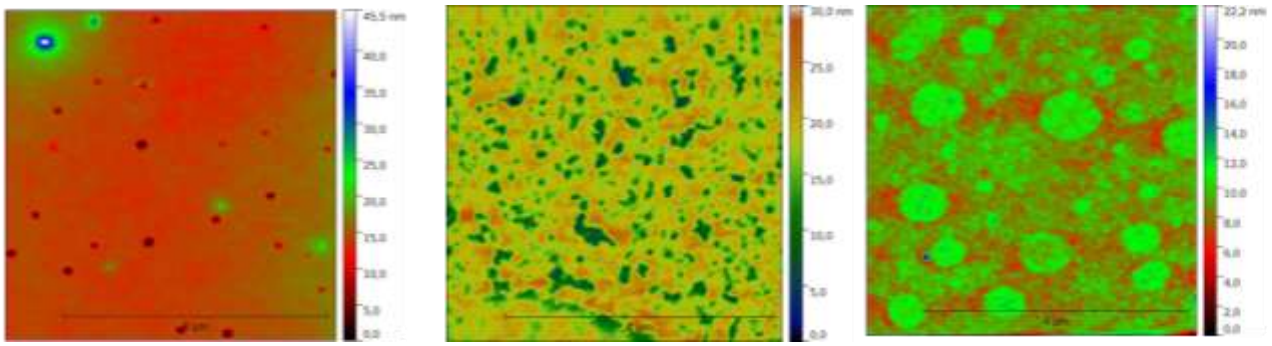


Figure S28. AFM images of 1 (left), Zn-porphyrin (middle), and 1:1 molar ratio mixture of BODIPY:Zn-Porphyrin films with a thickness of 110 nm.

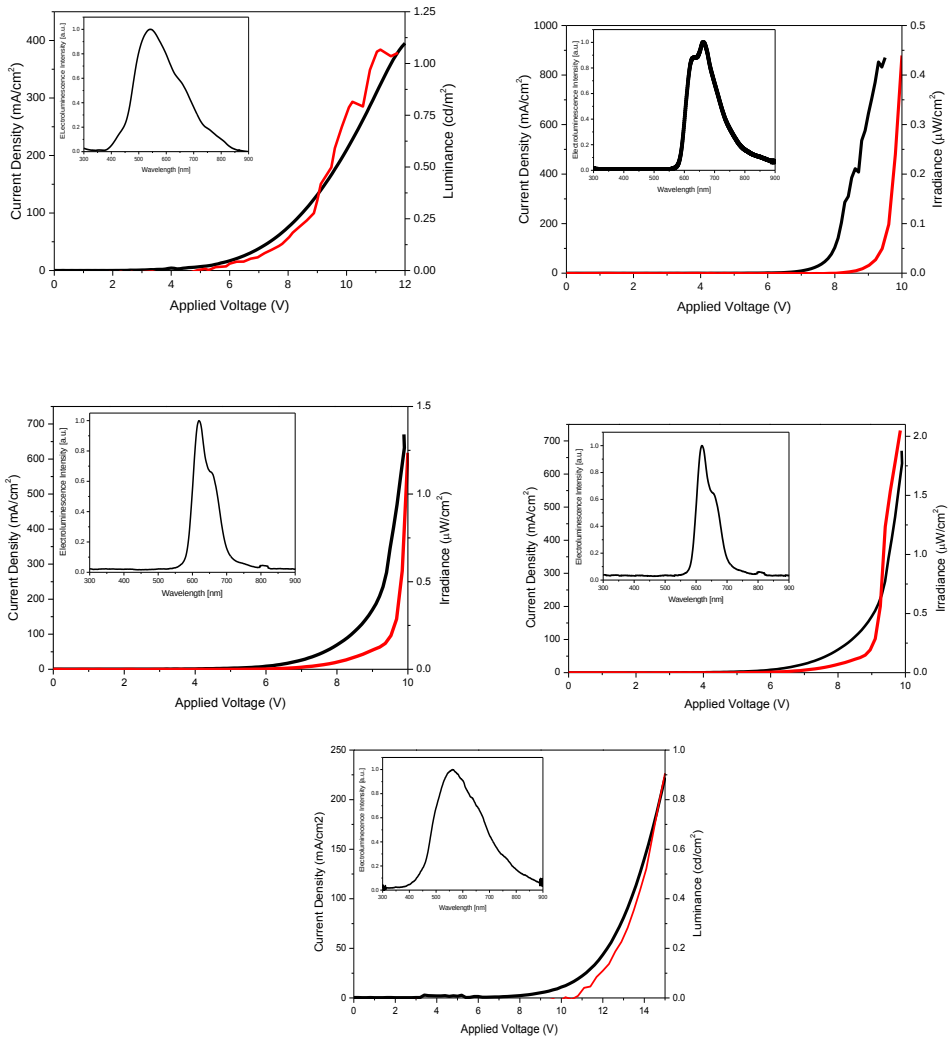


Figure S29. Current density (black) and brightness (red) versus applied voltage assays for devices with BODIPY (top left) and Zn-porphyrin (top right) reference devices, **1** (central left), **2** (central right), and 1:1 molar ratio Zn-porphyrin: BODIPY (bottom) devices. The inset shows the EL spectra recorded at 10 V.

References

[1] Nikolaou, V.; Angaridis, P. A.; Charalambidis, G.; Sharma, G. D.; Coutsolelos, A. G. *Dalton Trans.* **2015**, *44*, 1734

[2] G. W. Trucks, M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Lyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, nJ. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al- Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision D.01)*, Gaussian Inc., Wallingford, CT, **2004**.

[3]. L. S. W. Kohn, *Phys. Rev.*, **1965**, *140*, A1133.

[4] A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, **1988**, *38*, 3098.

[5] C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **1988**, *37*, 785.

[6] D. A. Zhurko and G. A. Zhurko, *ChemCraft 1.6*, Plimus, San Diego, CA, available at http://www.chemcraftprog.com.