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Intense NIR Absorbing Porphyrin based Dyes with BODIPY as Acceptor

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Supporting Information

Contents

1. INSTRUMENTATION AND REAGENTS:

NMR spectra were recorded on a Bruker Avance-400 and 500 MHz FT NMR spectrometers using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectral determinations were carried out by Bruker Maxis HRMS (Q-TOF analyzer) spectrometer by ESI techniques. UV-visible spectra were recorded on Perkin Elmer Lambda-35 spectrometer. Fluorescence spectra were recorded using Jasco FP-8500 spectrofluorometer. Spectroscopic grade solvents were used for all absorbance measurement.The standard approach of time-correlated single-photon counting (TCSPC) was used to study time resolved photoluminescence (TRPL). Using a picosecond pulsed diode laser with an output of 405 nm, TCSPC experiments were carried out. Dilute Ludox solution, a light scattering solution was used to measure the instrument response function (IRF). To estimate emission lifetimes, TRPL curves were fitted by mono-exponential fitting parameters using the deconvolution method accompanying with the IRF. The residual calculations ($\chi^{(2)}$) were used to estimate the fit's reliability. As the decay profile was multiexponential for both the dyes average lifetime was calculated using following equation[S1]

$$\tau_{av} = \sum c_i \tau_i$$

where τ_i lifetime of the i^{th} component and c_i is the fractional contribution of the i^{th} component to the total steady state intensity which was estimated via the following equation

$$c_i = \alpha_i \tau_i / \sum \alpha_i \tau_i$$

α_i is amplitude of the i^{th} component.

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were done using CH Instruments electrochemical analyser and electrodes were purchased from CH Instruments Inc. All measurements were done in THF under flow of nitrogen and 0.1M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) used as a supporting electrolyte. Platinum disc as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode were used. Ferrocenium/Ferrocene, Fc^+/Fc couple was used as external reference for calibration. All cyclic voltametric data were recorded at 100 mV/s scan rate at 298 K.

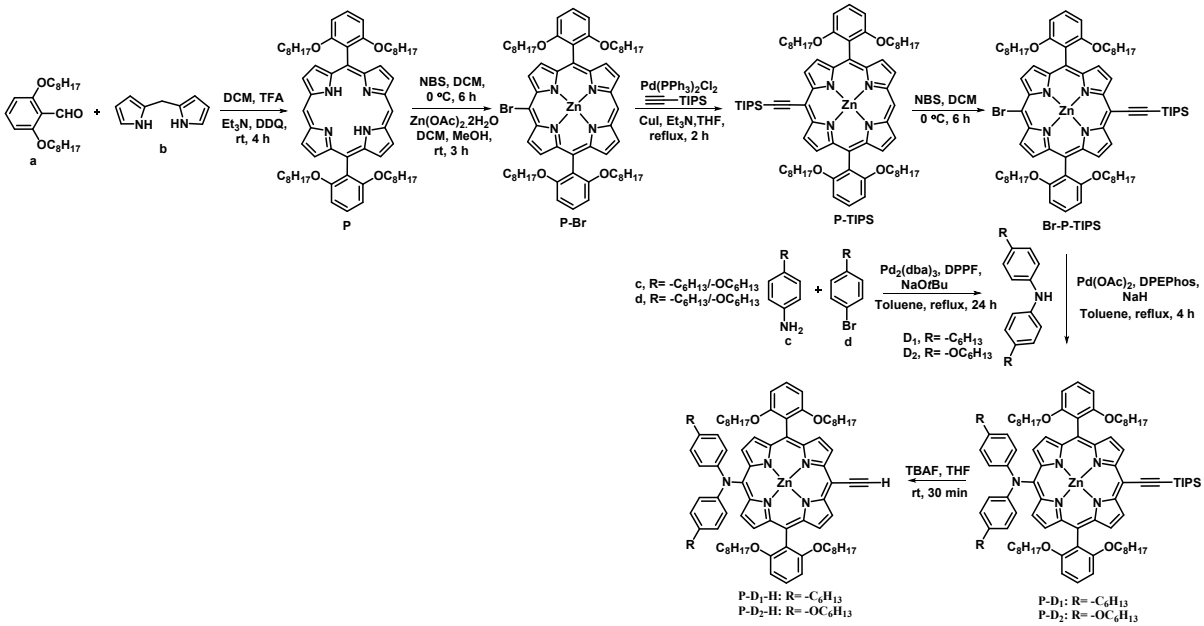
Commercially available solvents were distilled before use. Reagents were purchased from Sigma Aldrich and used as received without further purification unless otherwise stated. Solvents for the reactions were dried according to literature methods.

2. SYNTHESIS:

Experimental procedures:

2.1.1 Synthesis of Porphyrin-derived donor precursor:[S2]

Scheme S1



Synthesis of [5-Bis(4-hexyloxyphenyl)amino-15-(Triisopropylsilyl)ethynyl-10,20-bis(2,6-di-octoxyphenyl)porphyrinato] Zinc(II) ((P-D$_2$)): A mixture of bis(4-hexyloxyphenyl) amine, **D$_2$**[S3] (0.050 g, 0.135 mmol, 3.5 eq), and 60 % NaH (6.17 mg, 0.154 mmol, 4 eq), taken in a Schlenk tube in 10 mL toluene and heated for 15 min. Heat source was removed and after coming to room temperature followed by addition of porphyrin ***Br-P-TIPS*** (0.050 g, 0.038 mmol, 1 eq), DPEphos (0.0075 g, 0.014 mmol, 0.03 eq) and $Pd(OAc)_2$ (0.0002 g, 0.0093 mmol, 0.02 eqc) added to the reaction mixture and was gently refluxed for 4 h under nitrogen atmosphere. The solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) using DCM/hexanes: 20/80 as eluent to give the product ***(P-D$_2$)*** (0.037 g, 60%) as green solid.

Melting point: >300°C; FTIR data: 2921, 1457, 1275, 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 9.63 (d, *J*=4.5 Hz, 2H), 9.16 (d, *J*=4.5 Hz, 2H), 8.83 (d, *J*=4.5 Hz, 2H), 8.67 (d, *J*=4.5 Hz, 2H), 7.63 (t, *J*=8.5 Hz, 2H), 7.20 (d, *J*=8.4 Hz, 4H), 6.94 (d, *J*=8.5 Hz, 4H), 6.68 (d, *J*=8.8 Hz, 4H), 3.80 (t, *J*=6.5 Hz, 12H), 1.43 (m, 18H), 1.28-1.25 (m, 18H), 0.98-0.95 (m, 8H), 0.88-0.76 (m, 20H), 0.63-0.46 (m, 44H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 160.0, 152.9, 152.6, 152.0, 150.6, 150.1, 147.0, 132.1, 131.9, 130.6, 130.4, 129.8, 123.2, 121.0, 115.0, 114.2, 105.2, 99.2, 96.2, 96.1, 68.7, 68.3, 31.7, 31.4, 30.4, 29.8, 29.5, 28.6, 28.5, 25.8, 25.2, 22.7, 22.3, 19.2, 14.1, 13.9, 12.1. HRMS: m/z calcd for $[M]^+$ $C_{99}H_{137}N_5O_6SiZn$: 1583.9624, found 1583.9627.

Synthesis of [5-Bis(4-hexylphenyl)amino-15-ethynyl-10,20-bis(2,6-bis(octyloxy)phenyl) porphyrinato] Zinc (II) (P-D_1-H): To a solution of porphyrin **P-D_1** (20 mg, 0.013 mmol) in dry THF (3 mL) was added TBAF (65 µL, 1M in THF). The solution was stirred at 25 ºC for 30 min under nitrogen atmosphere. The mixture was quenched with water and then extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure and used as it is.

Synthesis of [5-Bis(4-hexyloxyphenyl)amino-15-ethynyl-10,20-bis(2,6-bis(octyloxy)phenyl) porphyrinato] Zinc (II) (P-D_2-H): To a solution of porphyrin **P-D_2** (20 mg, 0.013 mmol) in dry THF (3 mL) was added TBAF (65 µL, 1M in THF). The solution was stirred at 23 ºC for 30 min under nitrogen atmosphere. The mixture was quenched with water and then extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure and used as it is.

2.1.2 Synthetic routes for BODIPY-derived acceptor group:

Synthesis of 9-(ethoxycarbonyl)-3,8-diisopropyl-1,10-dihydrobenzo[e]pyrrolo[3,2-g]indole-2-carboxylic acid (2): Compound **1**[S4] (400 mg, 0.92 mmol, 1eq) was taken in a 50 mL two necked round bottom flask with a reflux condenser and a nitrogen inlet. It was dissolved in ethanol (20 mL) and aq. NaOH (37 mg, 0.92 mmol in 3.5 mL water, 1eq) and refluxed for 48 h. The reaction was quenched with addition of dil. HCl, and the precipitate formed was filtered, and washed properly with water. The residue was purified by column chromatography (silica gel) using EtOAc/hexane:30/70 to give napthobipyrrole monoester acid, **2** (205 mg, 55%) as white solid.

Melting point: >300°C; FTIR: 3473, 3357, 2924, 2123 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ_H 12.98 (s, br, 1H), 11.99 (s, 1H), 11.89 (s, 1H), 8.49-8.44 (m, 2H), 7.53-7.48 (m, 2H), 4.52-4.36 (m, 4H), 1.54 (dd, *J*=7.2 Hz, 1.05 Hz, 12H), 1.42 (t, *J*=7 Hz, 3H); ^{13}C NMR (DMSO d_6, 100 MHz) δ_C 160.7, 160.9, 145.6, 133.6, 132.8, 131.6, 131.2, 127.9, 127.1, 125.4, 123.6, 121.2, 120.2, 118.6, 118.4, 102.8, 63.4, 60, 24.8, 20.7, 14.4. HRMS: m/z calcd for $[M+H]^+$ $C_{24}H_{27}N_2O_4$: 407.1971, found 407.1974.

Synthesis of ethyl 3,8-diisopropyl-1,10-dihydrobenzo[e]pyrrolo[3,2-g]indole-2-carboxylate (3): Compound **2** (200 mg, 0.49 mmol,) was taken in a 10 mL two necked round bottom flask with a condenser dissolved in dry ethylene glycol (4 mL) and kept in vacuum for 0.5 h. After that refluxed for 3 h in a pre-heated oil bath. Heat source was removed and after cooling to room temperature the reaction mixture was poured in ice bath to give precipitate. Compound was filtered through a Buchner funnel and dried in desiccator to obtain napthobipyrrole monoester, **3** (173 mg, 97%) as white solid.

Melting point: >300°C; FTIR: 3364, 2958, 1631, 1461 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ_H 12.36 (s, 1H), 9.86 (s, 1H), 8.61 (m, 1H), 8.49 (m, 1H), 7.55-7.48 (m, 2H), 7.0 (d, *J*=1.8 Hz, 1H), 4.63-4.49 (m, 3H), 3.79-3.70 (m, 1H), 1.65 (d, *J*=7.5 Hz, 6H), 1.57 (t, *J*=7 Hz, 3H), 1.48 (d, *J*=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 164.5, 136.1, 128.6, 128.2, 126.9, 124.7, 123.7, 123.0, 122.3, 119.4, 119.3, 118.4, 117.1, 96.2, 61.4, 34.8, 31.7, 26.8, 26.0, 23.7, 21.3, 14.6, 14.3, 14.2. HRMS: m/z calcd for $[M+H]^+$ $C_{23}H_{27}N_2O_2$: 363.2073, found 363.2074.

Synthesis of diethyl 9,9'-((4-iodophenyl)methylene)bis(3,8-diisopropyl-1,10-dihydrobenzo[e]pyrrolo[3,2-g]indole-2-carboxylate) (4): Compound **3** (100 mg, 0.27 mmol, 1.9 eq) and 4-iodobenzaldehyde (32 mg, 0.14 mmol, 1 eq) were taken in a two necked round

bottom flask and kept in nitrogen atmosphere. DCM (10 mL) was added to it and stirred for 15 min to dissolve the solids, followed by addition of TFA (10 µL, 0.13 mmol, 0.9 eq). Reaction was monitored by checking TLC. After the consumption of all the starting material, the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using EtOAc/heaxane: 20/80 as eluent. Recrystallization from hexane yielded the napthobipyrrole based dipyrromethane, **4** (10 mg, 42%) as a white solid.

Melting point: >300°C; FTIR: 3349, 2958, 1702, 1666 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H 11.75 (s, 2H), 10.57 (s, 2H), 8.49-8.47 (m, 4H), 7.78 (d, *J*= 8.4 Hz), 7.47 (t, *J*= 3.8 Hz, 4H), 7.03 (d, *J*= 8.4 Hz, 2H), 6.48 (s, 1H), 4.47-4.34 (s, br, 2H), 4.35-4.31 (m, 4H), 1.55-1.54 (m, 12H), 1.44-1.40 (m, 12 H), 1.38-1.33 (m, 9H), 1.31-1.18 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 171.4, 138.5, 138.0, 134.0, 131.3, 130.9, 130.6, 128.7, 127.1, 126.1, 124.7, 123.3, 118.2, 96.2, 92.9, 64.6, 60.6, 31.0, 30.7, 29.8, 26.6, 25.4, 21.2, 14.3. HRMS: m/z calcd for $[M+H]^+$ $C_{53}H_{56}IN_4O_4$: 939.3346, found 939.3346.

Synthesis of Napthobipyrrole derived BODIPY Diester (5): Compound **4** (100 mg, 0.11 mmol, 1 eq) was dissolved in DCM (10 ml) and DDQ (24 mg, 0.11 mmol, 1 eq) was added to it and stirred. Reaction was monitored by checking and after all starting material consumed, solvent was reduced and a filter column is done. Without further purification it was kept for boron complexation. It was dissolved in DCM (5 mL) and Et_3N (0.5 mL, 3.52 mmol) added to it and the solution was stirred for 10 min before $BF_3.OEt_2$ (0.6 mL, 5.28 mmol) was added to the mixture and stirred for 4 h at rt. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using EtOAc/hexane: 20/80 as eluent. Recrystallization from hexane provided napthobipyrrole based BODIPY diester **5** (67.6 mg, 65%) as a green solid.

Melting point: >300°C; FTIR: 3429, 2957, 1719, 1684 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ_H 11.02 (t, *J*=7 Hz, 2H), 8.40 (dd, *J*=8 Hz, 1 Hz 1H), 7.97 (d, *J*=8.3 Hz, 2H), 7.51-7.46 (m, 2H), 7.45-7.39 (m, 4H), 4.55 (q, *J*=7.1 Hz, 4H), 4.36 (t, *J*=7.1 Hz, 2H), 2.81-2.72 (m, 2H), 1.62 (d, *J*=7.2 Hz, 12H), 1.47 (t, *J*=7.1 Hz, 6H), 1.26 (d, *J*=7.3 Hz, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 161.4, 149.7, 140.7, 140.5, 137.9, 136.0, 135.8, 134.2, 131.2, 129.3, 128.9, 128.0, 126.6, 126.2, 125.8, 124.4, 122.2, 95.1, 61.3, 25.7, 24.6, 21.1, 20.3, 14.5; HRMS: m/z calcd for $[M+H]^+$ $C_{53}H_{53}BF_2IN_4O_4$: 985.3173, found 985.3172.

Synthesis of Napthobipyrrole derived BODIPY Diacid (6): Compound **5** (15 mg, 0.02 mmol) was taken in a mixture of EtOH:THF (1:1, 6 mL) and KOH (170 mg, 3.04 mmol, 202 eq) in H_2O (0.8 mL) was added and stirred for 12 h at 80 ºC. After cooling to room temperature, the mixture was poured into dil. HCl, extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and then the residue was purified by recrystallization from DCM/Hexane to afford the compound **6** (11 mg, 78%) as green solid.

Melting point: >300°C; FTIR: 2959, 2856, 1599, 1459, 1065 cm^{-1}; ^1H NMR (THF-d_8, 500 MHz) δ_H 10.88 (s, 2H), 8.40 (d, *J*= 7.7 Hz, 2H), 8.35 (d, *J*=7.9 Hz, 2H), 8.06 (d, *J* =7.8 Hz, 2H), 7.69 (d, *J*=8.1 Hz, 2H), 7.63-7.53 (m, 4H), 4.35 (s, 2H), 3.59 (t, *J*=6.5 Hz, 2H), 1.56 (d, *J*=7.1 Hz, 12H), 1.21 (t, *J*=7.2 Hz, 12H); ^{13}C NMR (THF-d_8, 125 MHz) δ_C 150.4, 141.3, 139.0, 137.0, 136.6, 132.7, 130.7, 130.3, 130.0, 128.5, 127.2, 127.0, 126.6, 125.1, 96.1, 33.0, 30.7, 30.4, 26.6, 25.9, 25.8, 23.7, 21.4, 20.5, 14.5; HRMS: m/z calcd for $[M+H]^+$ $C_{49}H_{45}BF_2IN_4O_4$: 929.2547, found 929.2546.

Synthesis of Porphyrin-BODIPY Conjugate (Diester) (7): Compound **P-D_2-H** (15 mg, 0.0105 mmol, 1 eq) and BODIPY (**6)** (12.4 mg, 0.0125 mmol, 1.2 eq) were taken in a 10 mL Schlenk tube and dissolved in a mixture of dry THF (5 mL) and Et_3N (0.4 mL) and the solution was degassed with dinitrogen for 10 min, $Pd_2(dba)_3$ (2.8 mg, 0.0031 mmol, 0.3 eq) and $AsPh_3$ (6.5 mg, 0.021 mmol, 2 eq) were added to the mixture. The solution was refluxed for 4 h under nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was purified by recrystallization from hexane to give **7** (10 mg, 42%) as a green solid.

Melting point: >250°C (decomp); FTIR: 2957, 2922, 2859, 1718, 1461 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ_H 11.08(t, *J*= 7.0 Hz, 2H), 9.75(d, *J*= 4.5 Hz, 2H), 9.19 (d, *J*= 4.6 Hz, 2H), 8.92 (d, *J*= 4.6 Hz, 2H), 8.69 (d, *J*= 4.7 Hz, 2H), 8.42 (d, *J*= 8.9 Hz, 2H), 8.25 (d, *J*= 8.0 Hz, 2H), 7.85 (d, *J*= 8.1 Hz, 2H), 7.67 (t, *J*= 8.5 Hz, 2H), 7.49-7.41 (m, 4H), 7.21 (d, *J*= 9.2 Hz, 4H), 6.97 (d, *J*= 8.5 Hz, 4H), 6.70 (d, *J*= 9.2 Hz, 4H), 4.58-4.54 (m, 4H), 4.39-4.37 (m, 2H), 3.85-3.82 (m, 8H), 3.06-3.02 (m, 2H), 1.71-1.68 (m, 4H), 1.64 (d, *J*= 7.2 Hz, 12H), 1.53 (s, 18H), 1.48 (t, *J*= 7.1 Hz, 8H), 1.38 (d, *J*= 7.3 Hz, 16H), 1.29-1.25 (m, 14H), 1.02-1.00(m, 8H), 0.87-0.84 (m, 16H), 0.70-0.47(m, 50H); HRMS: m/z calcd for $[M+H]^+$ $C_{143}H_{170}BF_2N_9O_{10}Zn$: 2286.2379, found 2286.2325.

2.1.3 Synthetic routes for PBC1 and PBC2:

Synthesis of PBC1: Compound **P-D_1-H** (20 mg, 0.0203 mmol, 1.8 eq) and BODIPY-Diacid (**6)** (10 mg, 0.0107 mmol, 1 eq) were taken in a 25 mL Schlenk tube and dissolved in a mixture of dry THF (5 mL) and Et_3N (0.4 mL) and the solution was degassed with dinitrogen for 10 min, $Pd_2(dba)_3$ (2.8 mg, 0.003 mmol, 0.3 eq) and $AsPh_3$ (6.2 mg, 0.020 mmol, 2eq) were added to the mixture. The solution was refluxed for 4 h. The solvent was removed under reduced pressure. The residue was purified by recrystallization from hexane followed by methanol to give **PBC1** (16.8 mg, 60%) as a green solid.

Melting point: >250°C (decomp); FTIR: 2925, 2853, 1595, 1457 cm^{-1};^1H NMR (THF d_8, 500 MHz) δ_H 11.55 (s br, 2H), 9.73 (s, 2H), 9.73 (s, 2H), 9.07 (s, 2H), 8.83 (s, 2H), 8.58 (s, 2H), 8.46 (s, 2H), 8.35 (d, *J*= 6.5 Hz, 4H), 8.05 (s, 2H), 7.67 (s, 2H), 7.40 (s br, 4H), 7.22 (d, *J*= 7.5 Hz, 4H), 7.04 (t, *J*= 4.0 Hz, 4H), 6.94 (d, *J*= 7.5 Hz, 4H), 3.89 (s br, 8H), 3.50 (s br, 4H), 3.17 (s br, 4H), 2.48(s br, 4H), 2.04 (s, 2H), 1.57 (s br, 8H), 1.44 (s br, 8H), 1.10-1.03 (m, 12H), 0.96-0.85 (m, 44H), 0.75-0.63 (m, 33H); ^{13}C NMR (THF-d_8, 125 MHz) δ_C 161.1, 152.3, 152.6, 151.9, 151.5, 151.3, 141.1, 136.2, 132.7, 132.5, 132.1, 131.3, 130.7, 130.6, 130.3, 129.5, 129.2, 127.7, 127.2, 126.1, 124.3, 123.8, 122.7, 121.8, 115.3, 105.5, 98.3, 95.3, 69.1, 36.2, 33.0, 32.8, 32.8, 32.7, 30.8, 30.4, 30.4, 30.4, 30.2, 29.9, 29.8, 29.7, 28.1, 27.1, 24.3, 25.9, 23.7, 23.6, 23.4, 21.9, 20.8, 14.5; HRMS: m/z calcd for $[M]^+$ $C_{139}H_{160}BF_2N_9O_8Zn$: 2199.1780, found 2199.1701.

Synthesis of PBC2: Compound **P-D_2-H** (22.6 mg, 0.016 mmol, 1.8 eq) and BODIPY (**6)** (10 mg, 0.0107 mmol, 1eq) were taken in a 25 mL Schlenk tube and dissolved in a mixture of dry THF (5 mL) and Et_3N (0.4 mL) and the solution was degassed with dinitrogen for 10 min, $Pd_2(dba)_3$ (3 mg, 0.0032 mmol, 0.3 eq) and $AsPh_3$ (6.6 mg, 0.022 mmol, 2 eq) were added to the mixture. The solution was refluxed for 4 h under nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was purified by recrystallization from hexane followed by methanol to give **PBC2** (10 mg, 42%) as a green solid.

Melting point: >280°C (decomp); FTIR: 2924, 2854, 1595, 1457 cm^{-1}; ^{1}H NMR (THF-d_8, 500 MHz) δ_H 11.59 (s, br, 2H), 10.83 (s, 2H), 9.69 (d, J= 4.5 Hz, 2H), 9.07 (d, J=4.5 Hz, 2H), 8.80 (d, J=4.5 Hz, 2H), 8.55 (d, J=4.5 Hz, 2H), 8.46 (s, 4H), 8.33 (d, J= 7.2 Hz, 2H), 7.66 (t, J=8.5 Hz, 2H), 7.44-7.38 (m, 4H), 7.19-7.17 (m, 4H), 7.03 (d, J=8.5 Hz, 4H), 6.67 (d, J=9.5 Hz, 4H), 3.86-3.83 (m, 12H), 1.85 (s, 4H), 1.68-1.65 (m, 11H), 1.59 (s, 4H), 1.43-1.42 (m, 11H), 1.31-1.29 (m, 11H), 1.06-1.01 (m, 8H), 0.93-0.90 (m, 11H), 0.89-0.86 (m, 12H), 0.82-0.79 (m, 8H), 0.71-0.63 (m, 30H); ^{13}C NMR (THF-d_8, 125 MHz) δ_C 161.1, 154.1, 152.9, 151.4, 149.3, 148.1, 141.0, 138.8, 136.1, 133.1, 132.7, 132.3, 132, 130.7, 130.5, 129.2, 127.6, 127.1, 124.5, 124.3, 123.7, 121.8, 115.6, 115.2, 108, 105.5, 98.1, 95.3, 69.0, 33.0, 32.7, 32.5, 30.9, 30.7, 30.6, 30.5, 30.4, 29.9, 29.8, 29.7, 28.1, 26.8, 26.5, 26.4, 26.3, 25.9, 23.7, 23.6, 23.4, 21.9, 20.8, 14.5. HRMS: m/z calcd for $[M+H]^+$ $C_{139}H_{160}BF_2N_9O_{10}Zn$: 2230.1677, found 2230.1613.

3. ^{1}H, ^{13}C NMR and HRMS Spectra:

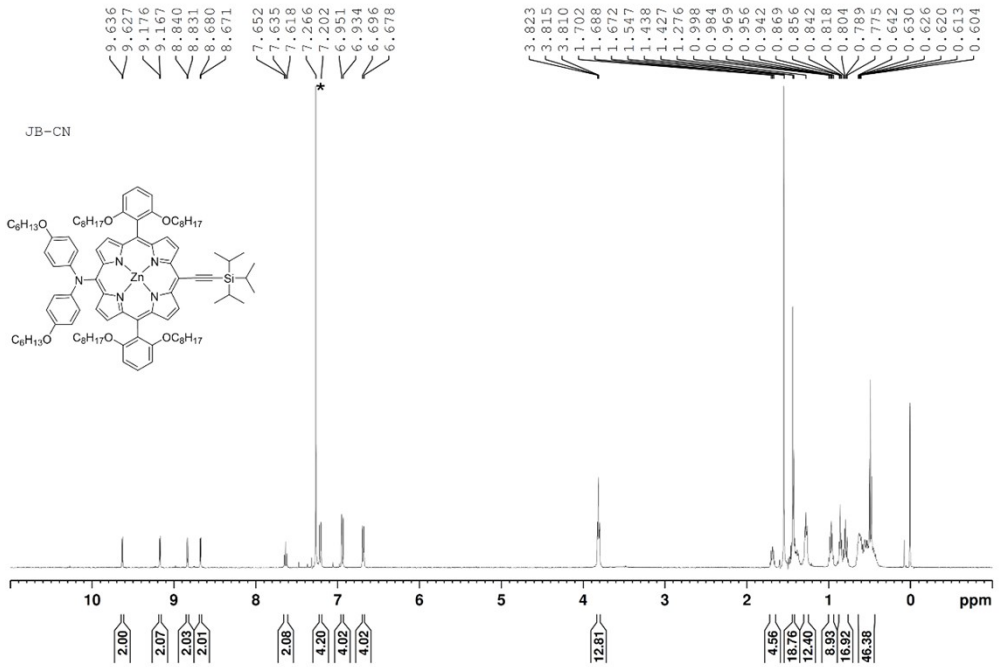


Figure S1. ^{1}H NMR spectrum of **P-D$_2$** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

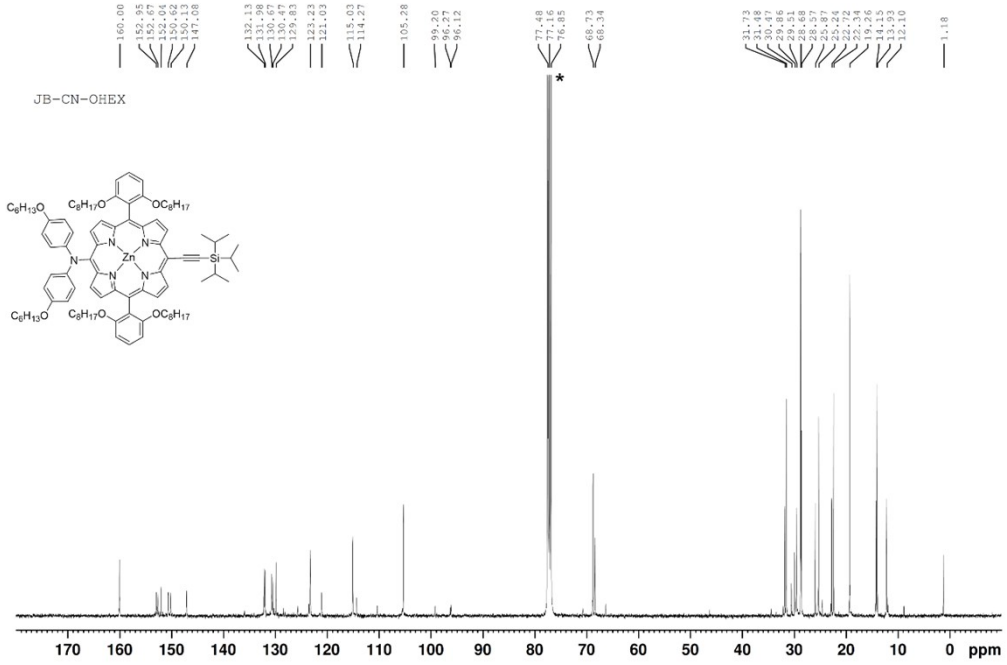


Figure S2. ^{13}C NMR spectrum of **P-D$_2$** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

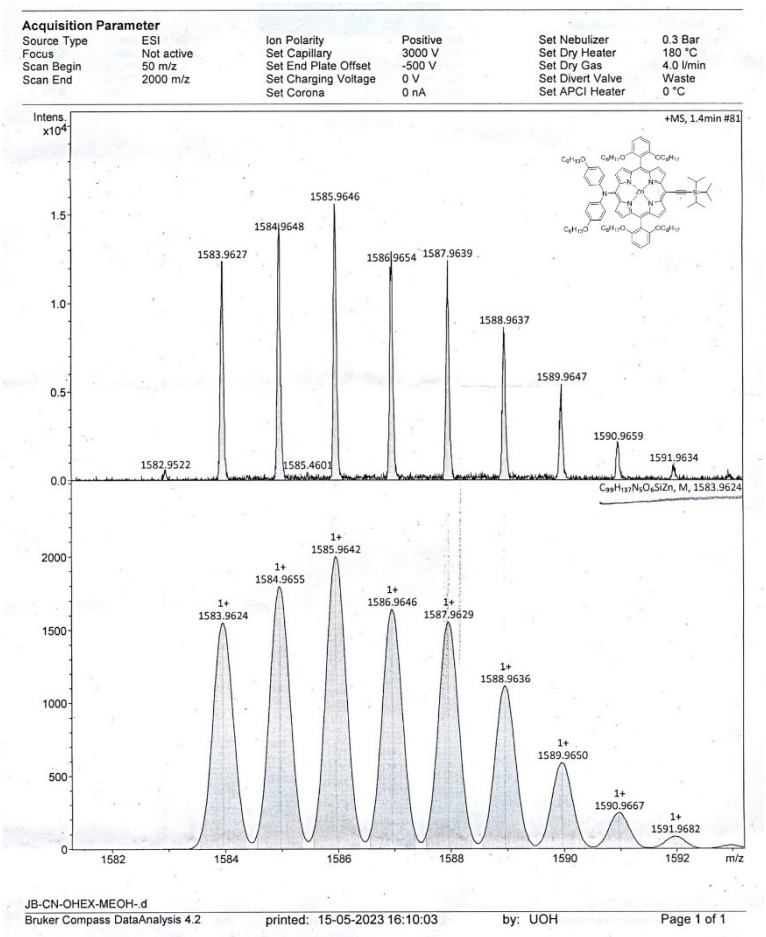


Figure S3. HR-ESI mass spectrum of **P-D$_2$**; m/z calculated for $[M]^+$ $C_{99}H_{137}N_5O_6SiZn$: 1583.9624, found 1583.9627

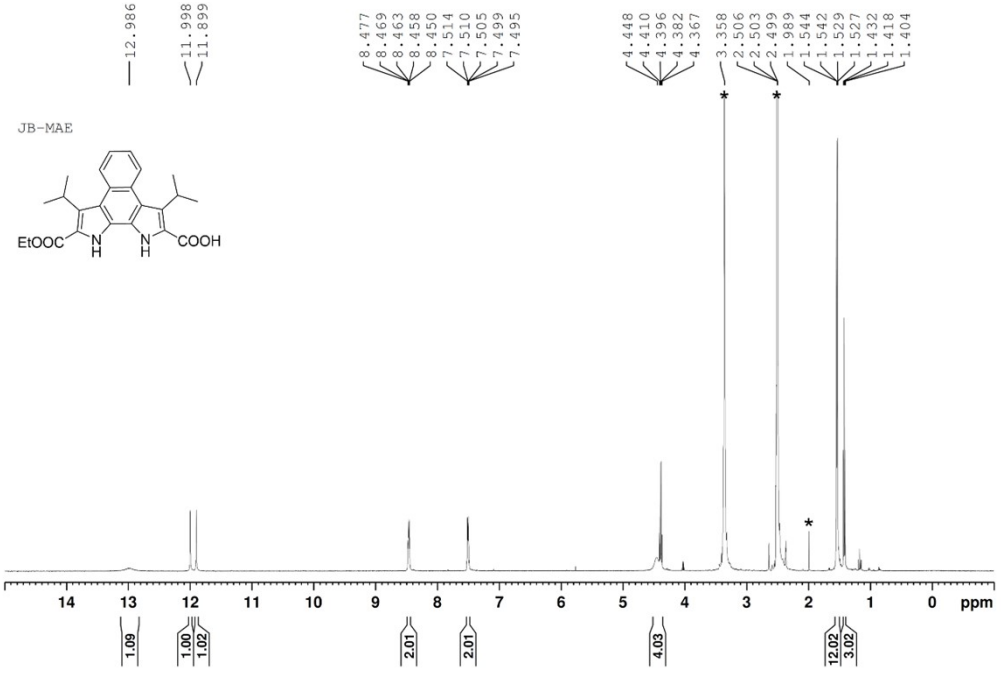


Figure S4: ^{1}H NMR spectrum of **2** in DMSO-d_6 recorded at 25 °C (*Asterisk indicates water and residual solvent impurity).

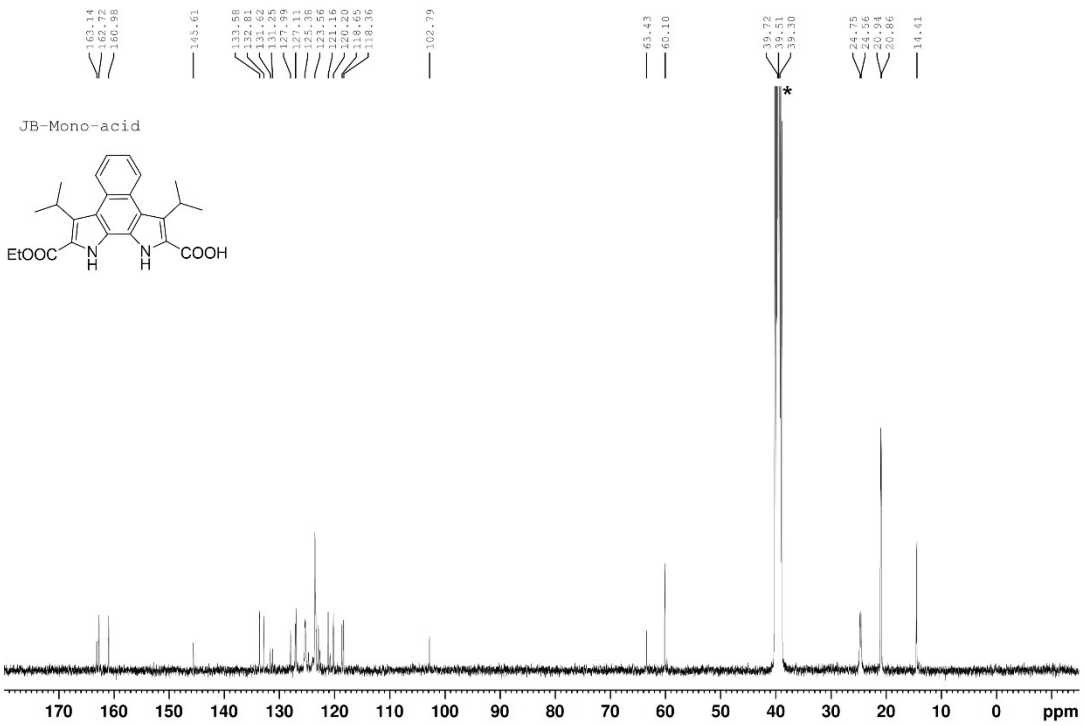


Figure S5. ^{13}C NMR spectrum of **2** in DMSO-d_6 recorded at 25 °C (*Asterisk indicates residual solvent impurity.

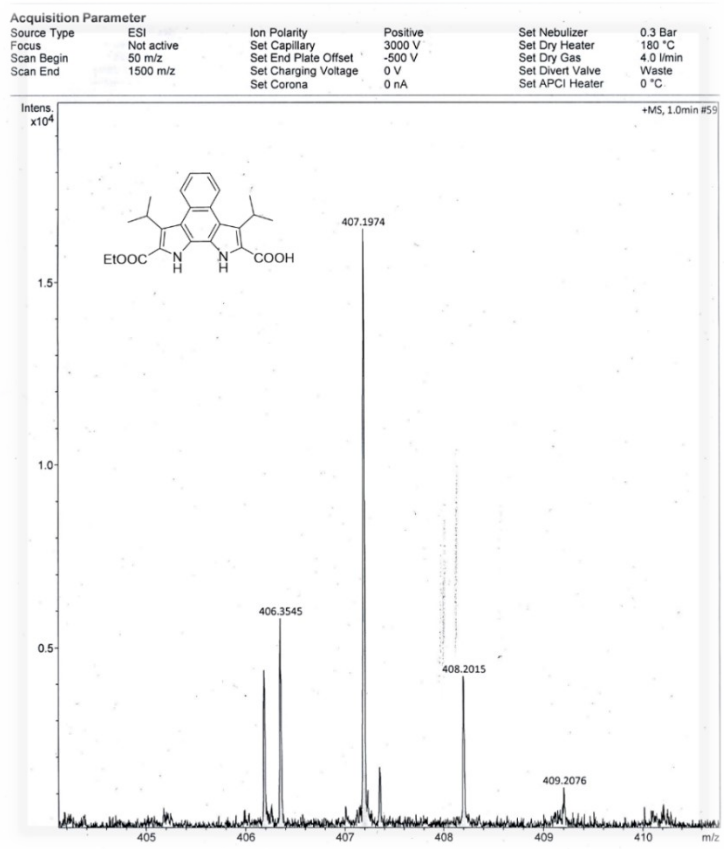


Figure S6. HR-ESI mass spectrum of **2**; m/z calculated for $C_{24}H_{27}N_2O_4$ $[M+H]^+$ 407.1971 found 407.1974.

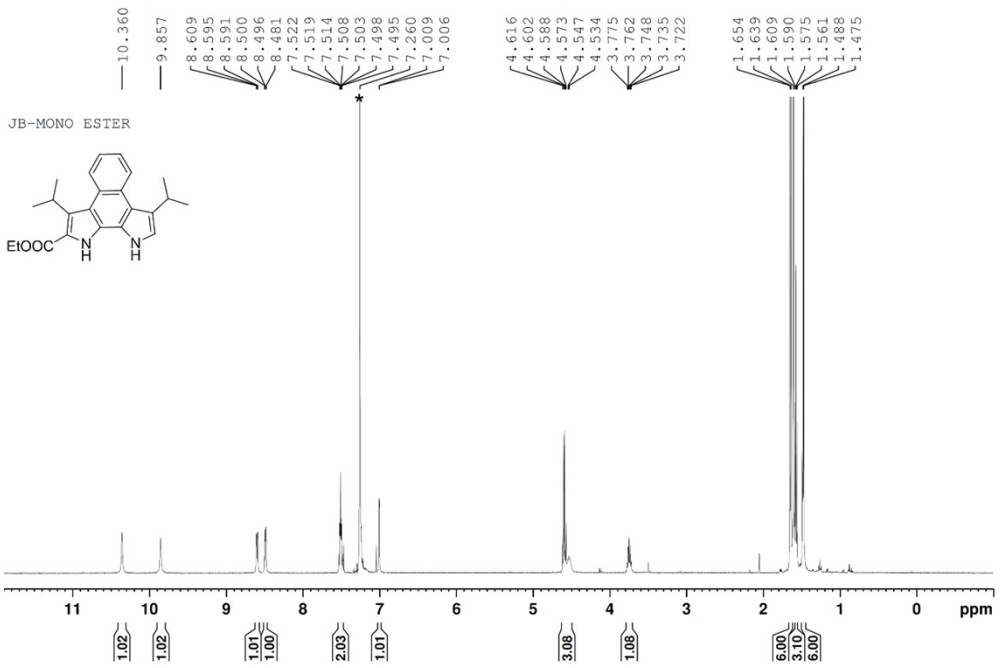


Figure S7. ^{1}H NMR spectrum of **3** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

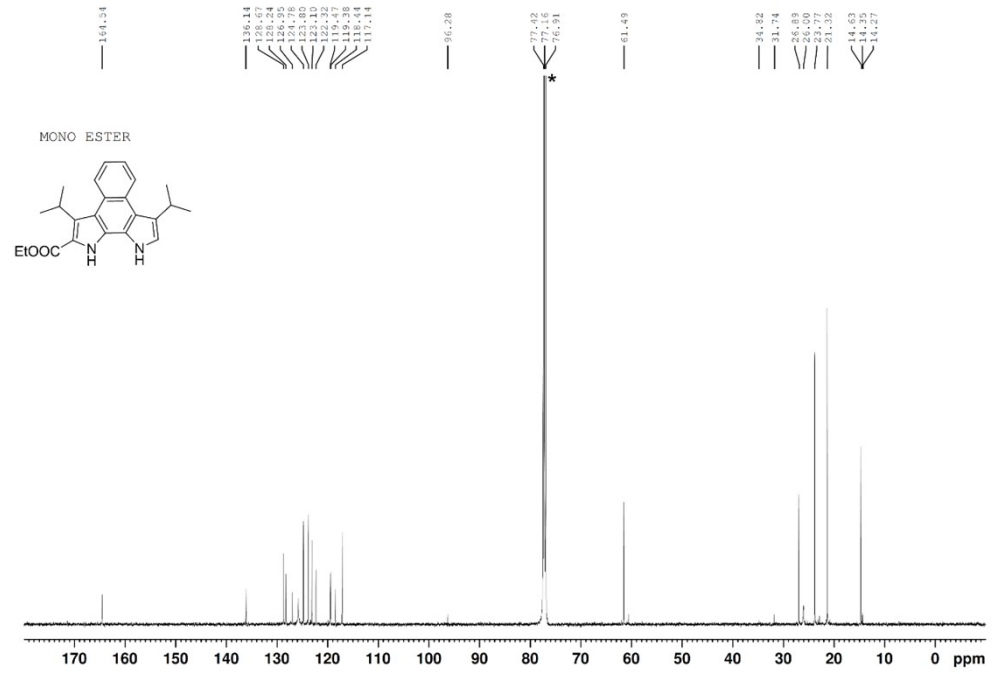


Figure S8. ^{13}C NMR spectrum of **3** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

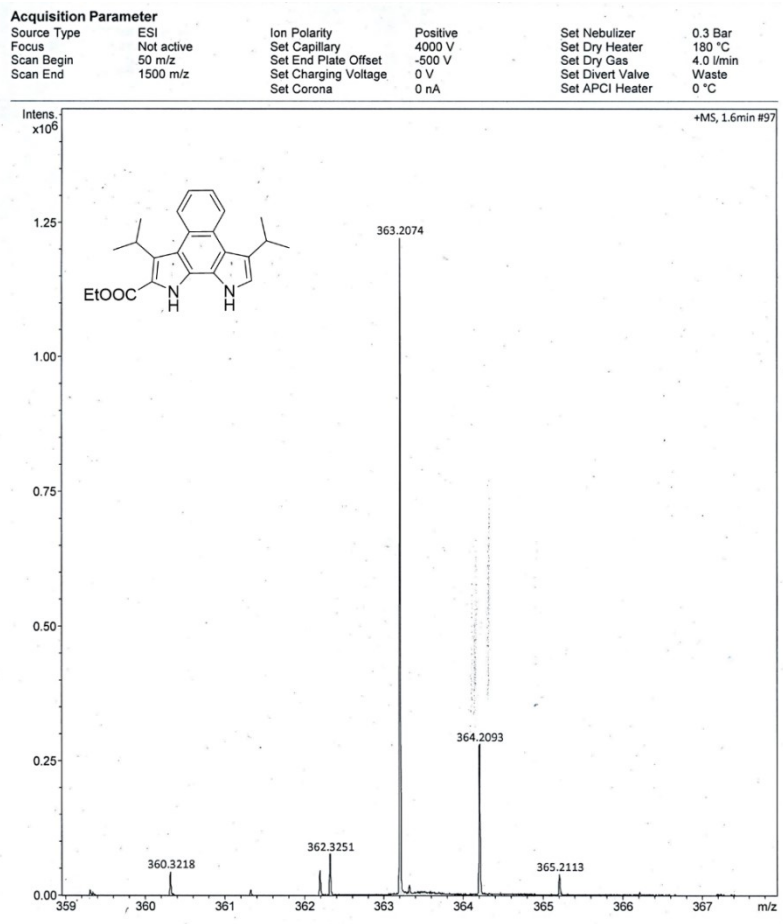


Figure S9. HR-ESI mass spectrum of **3;** m/z calculated for $[M+H]^+$ $C_{23}H_{27}N_2O_2$ 363.2073, found 363.2074.

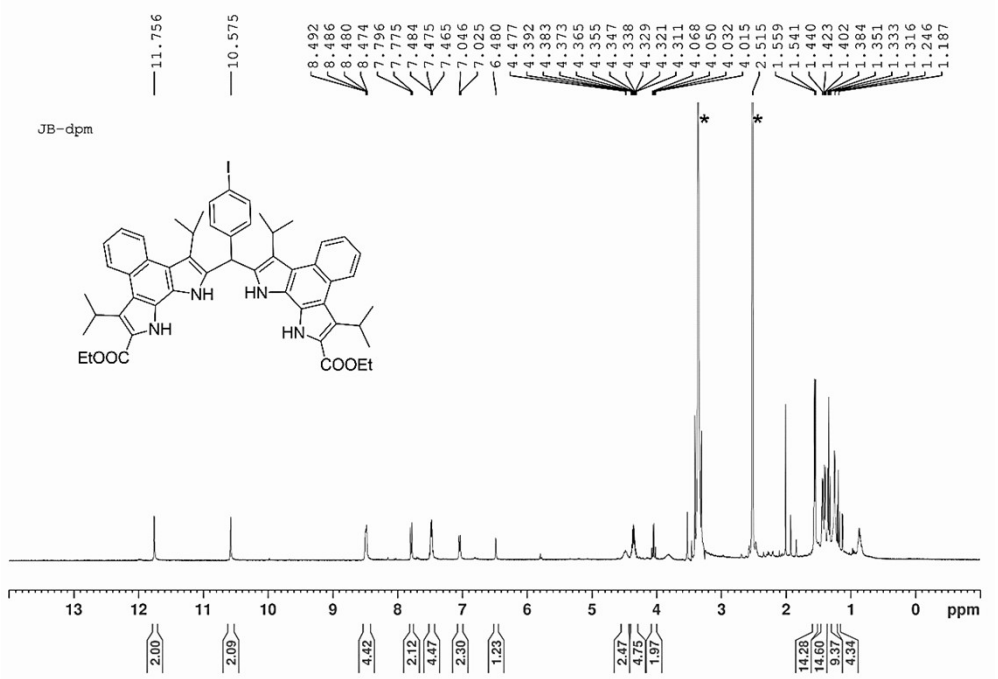


Figure S10. ^{1}H NMR spectrum of **4** in DMSO-d_6 recorded at 25 °C (*Asterisk indicates residual solvent impurity).

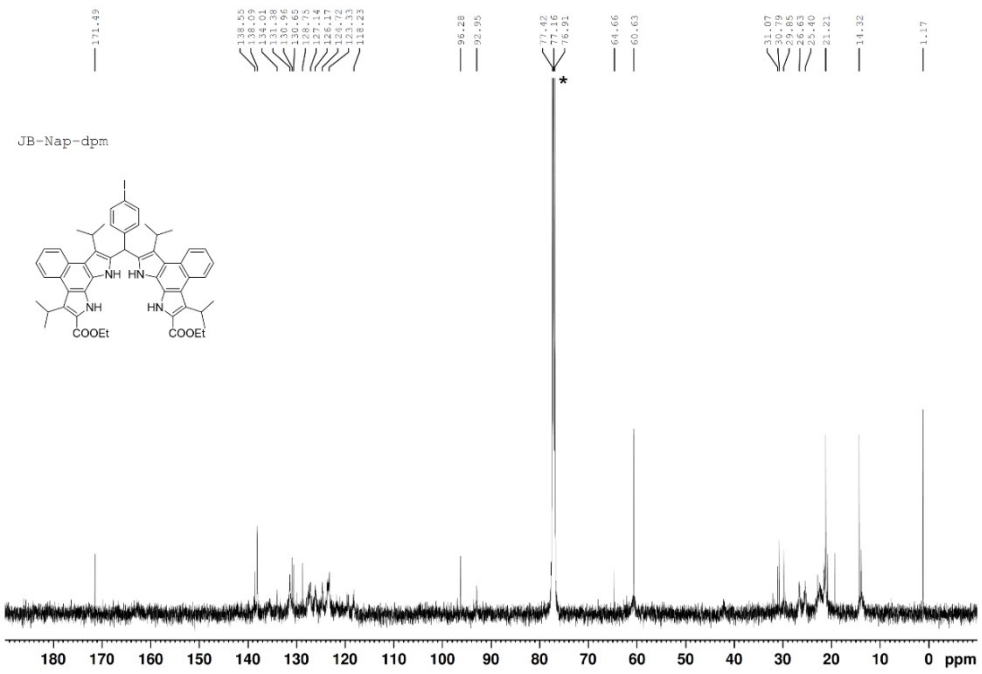


Figure S11. ^{13}C NMR spectrum of **4** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

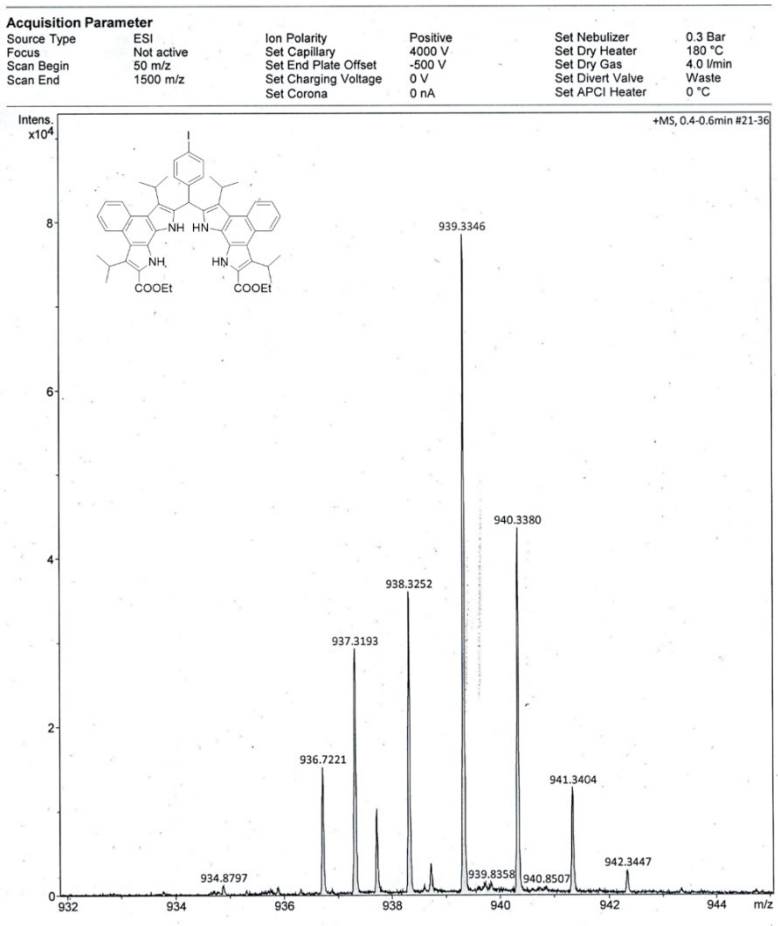


Figure S12. HR-ESI mass spectrum of **4**; m/z calculated for $[M+H]^+$ $C_{53}H_{56}IN_4O_4$ 939.3346, found 939.3346.

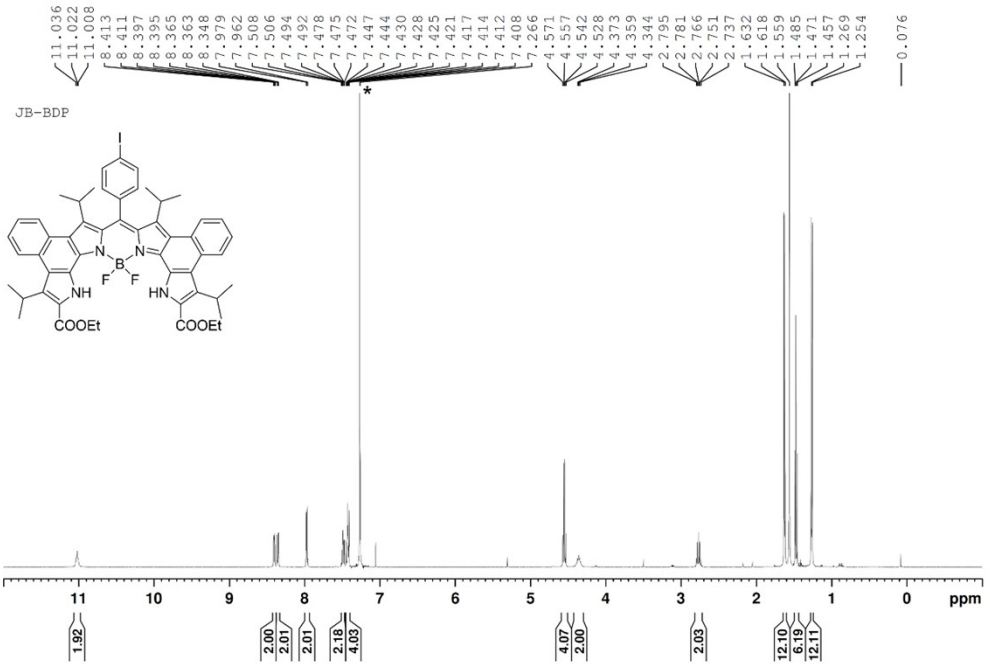


Figure S13. ^{1}H NMR spectrum of **5** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

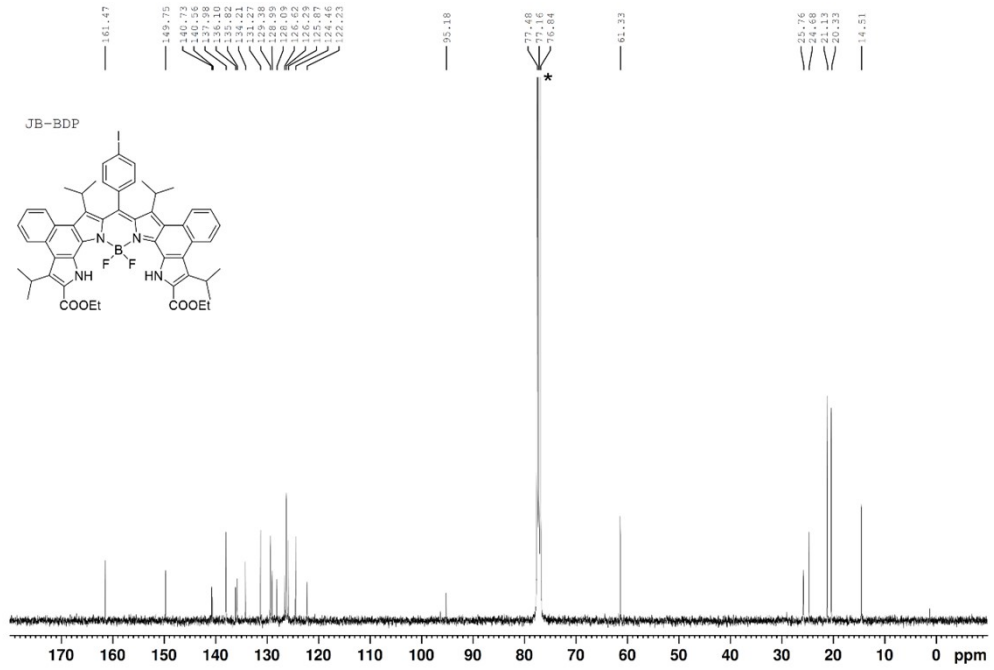


Figure S14. ^{13}C NMR spectrum of **5** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

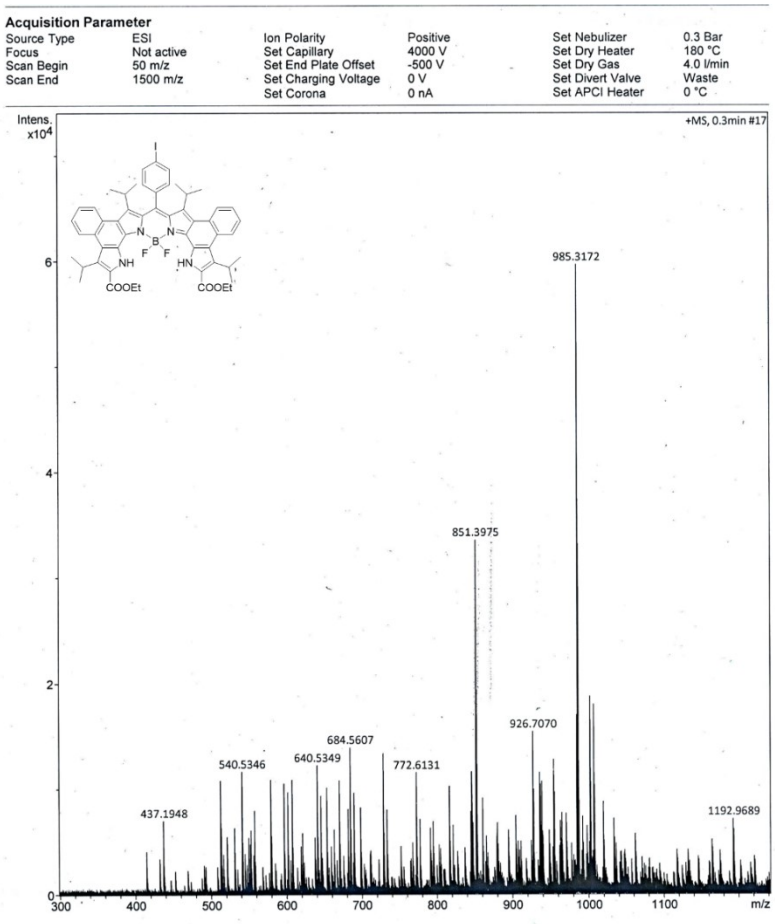


Figure S15. HR-ESI mass spectrum of **5**; m/z calculated for $[M+H]^+$ $C_{53}H_{53}BF_2IN_4O_4$ 985.3173, found 985.3172.

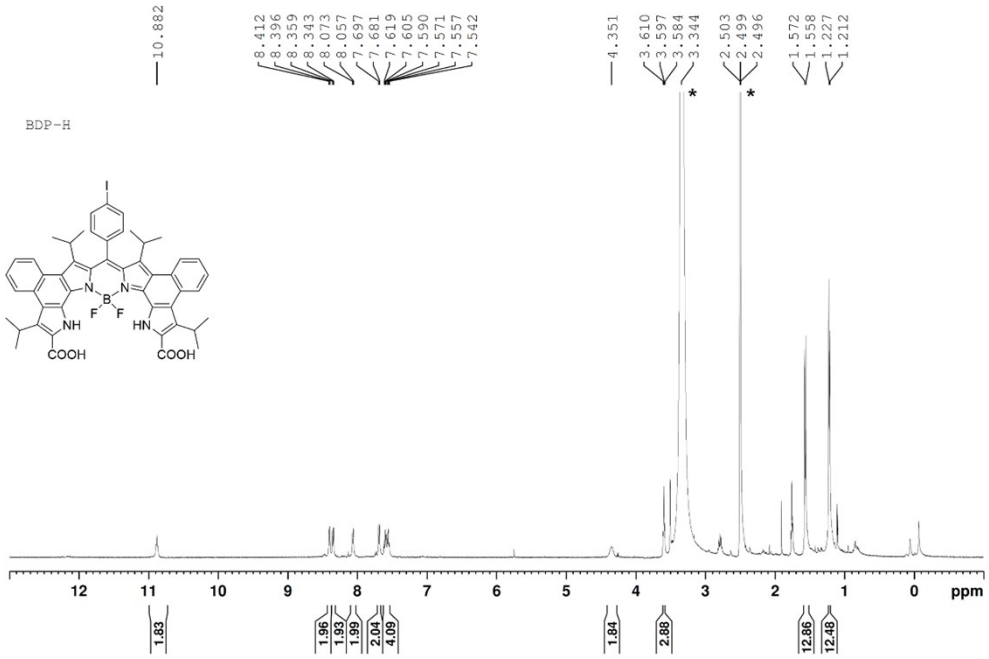


Figure S16. ^{1}H NMR spectrum of **6** in THF-d_8 recorded at 25 °C (*Asterisk indicates residual solvent impurity).

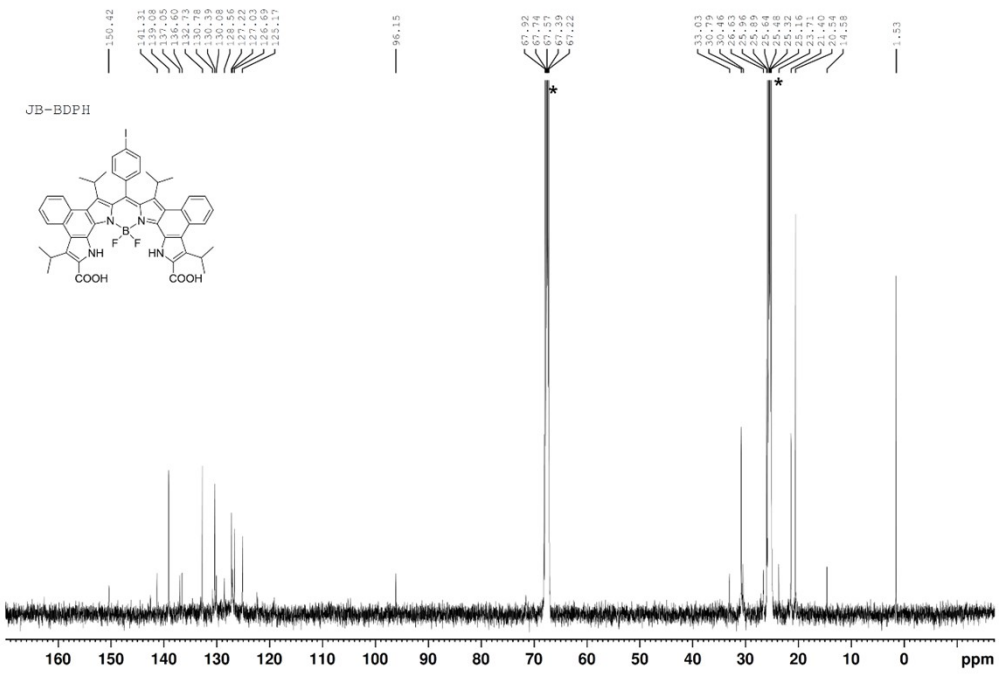


Figure S17. ^{13}C NMR spectrum of **6** in THF-d_8 recorded at 25 °C (*Asterisk indicates residual solvent impurity).

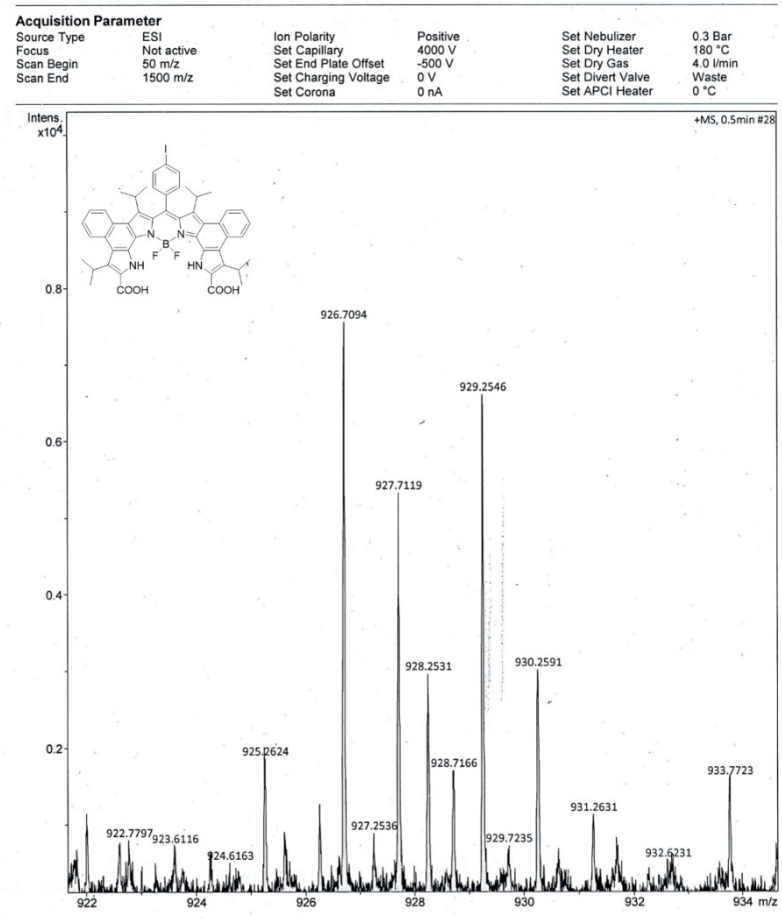


Figure S18. HR-ESI mass spectrum of **6**; m/z calculated for $[M+H]^+$ $C_{49}H_{45}BF_2IN_4O_4$ 929.2547, found 929.2546.

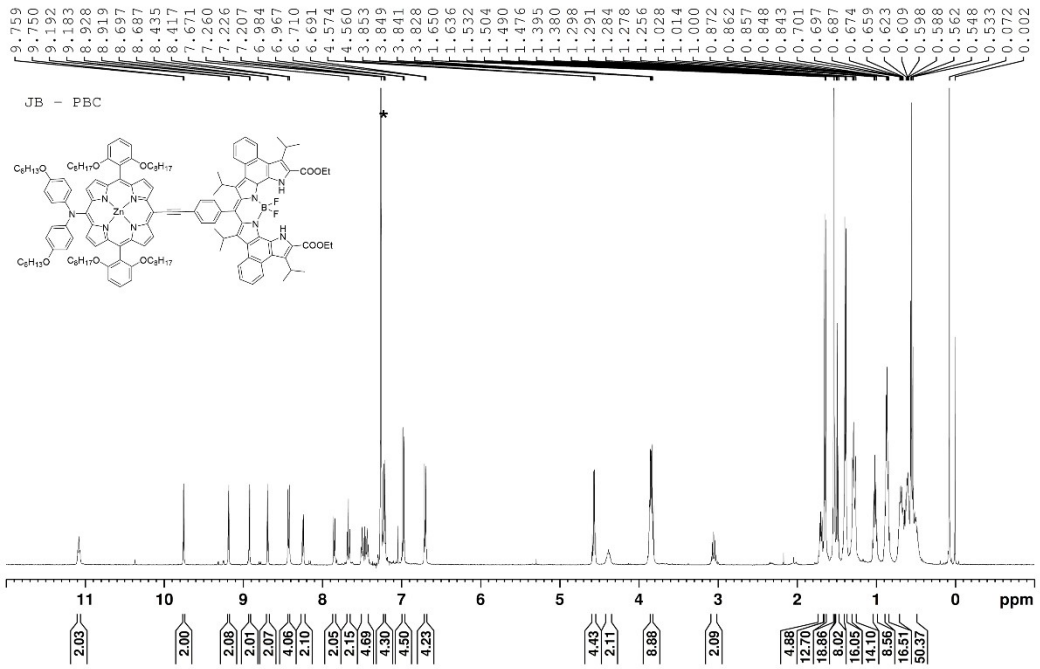


Figure S19. ^{1}H NMR spectrum of **7** in $CDCl_3$ recorded at 25 °C (*Asterisk indicates residual solvent impurity).

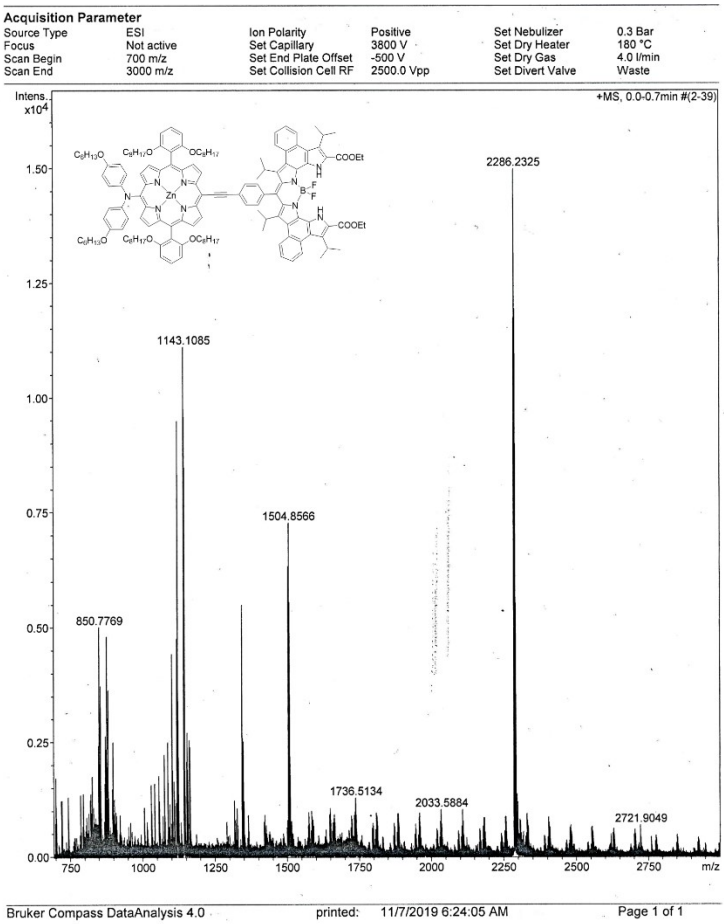


Figure S20. HR-ESI mass spectrum of **7**; m/z calculated for $[M+H]^+$ $C_{143}H_{170}BF_2N_9O_{10}Zn$ 2286.2379, found 2286.2325.

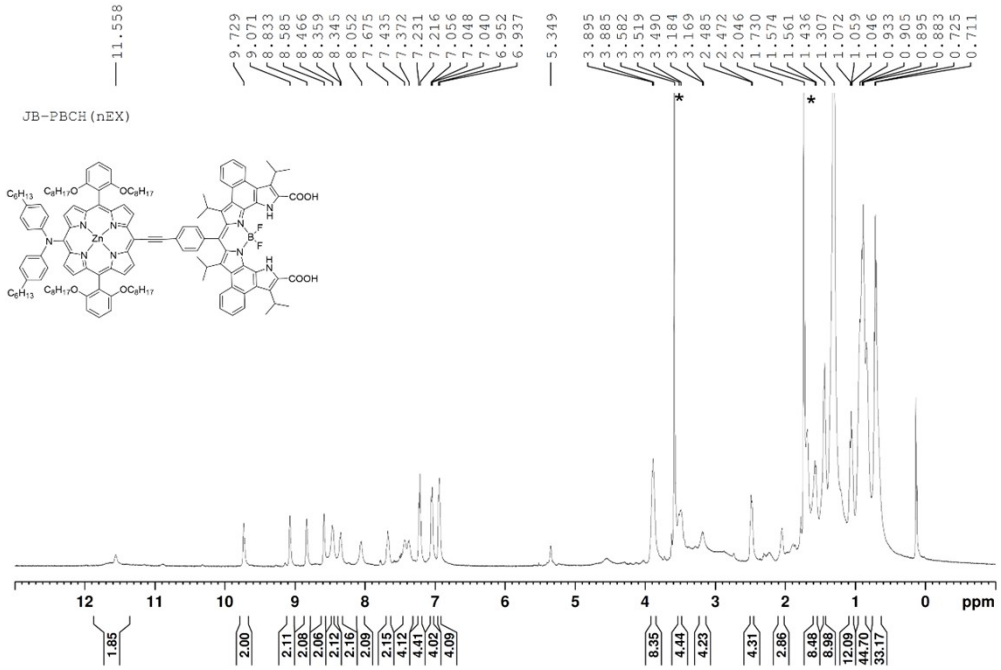


Figure S21. ^{1}H NMR spectrum of **PBC1** in THF-d_8 recorded at 25 °C (*Asterisk indicates water and residual solvent impurity).

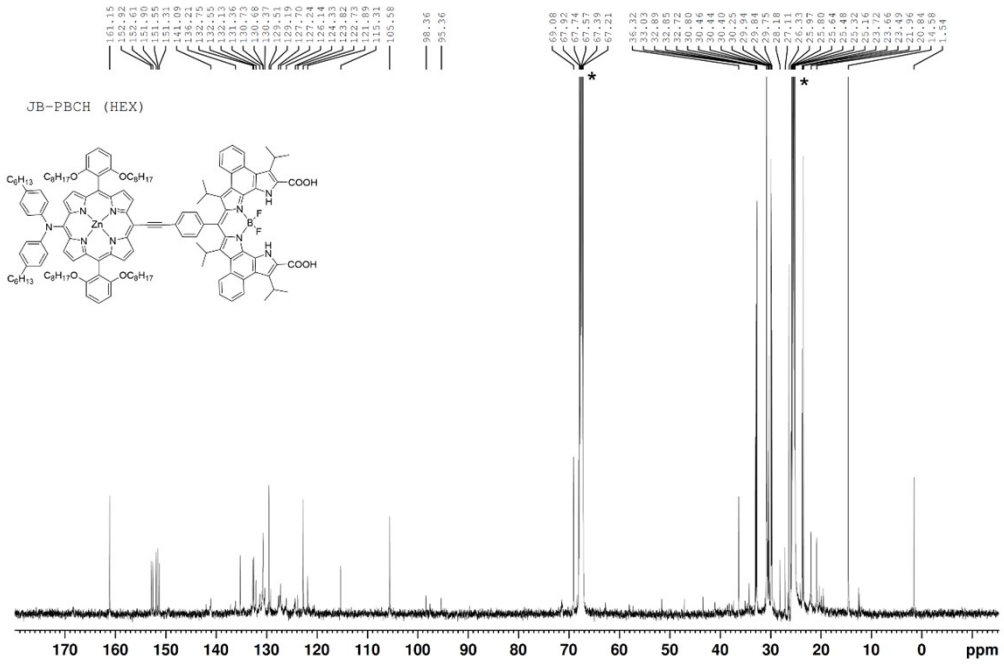


Figure S22. ^{13}C NMR spectrum of **PBC1** in THF-d_8 recorded at 25 °C (*Asterisk indicates residual solvent impurity).

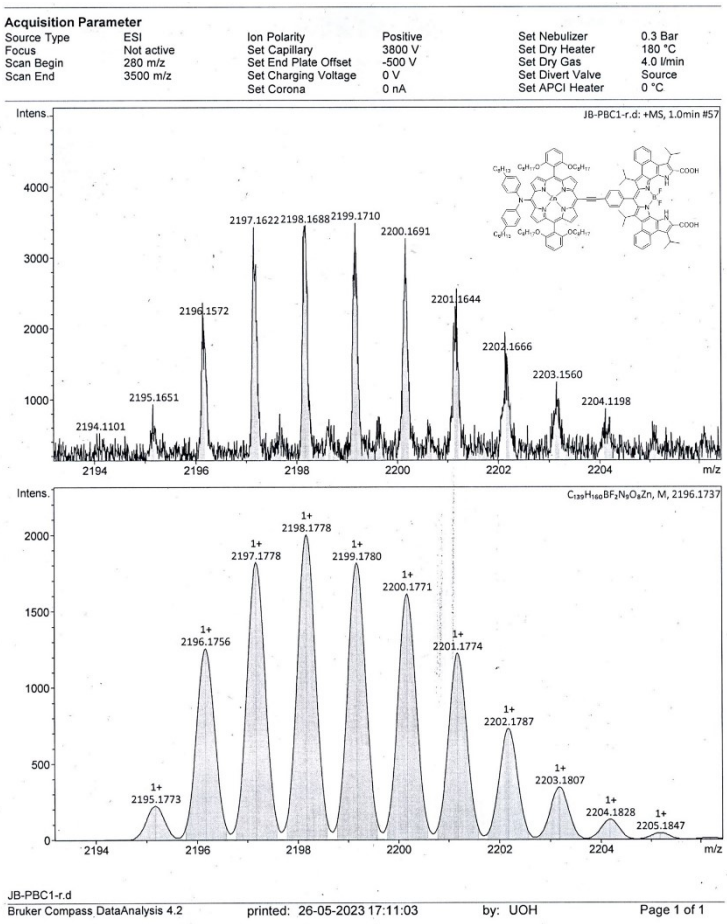


Figure S23. HR-ESI mass spectrum of **PBC1**; m/z calculated for $[M+H]^+ C_{139}H_{161}BF_2N_9O_8Zn$: 2199.1780, found 2199.1710.

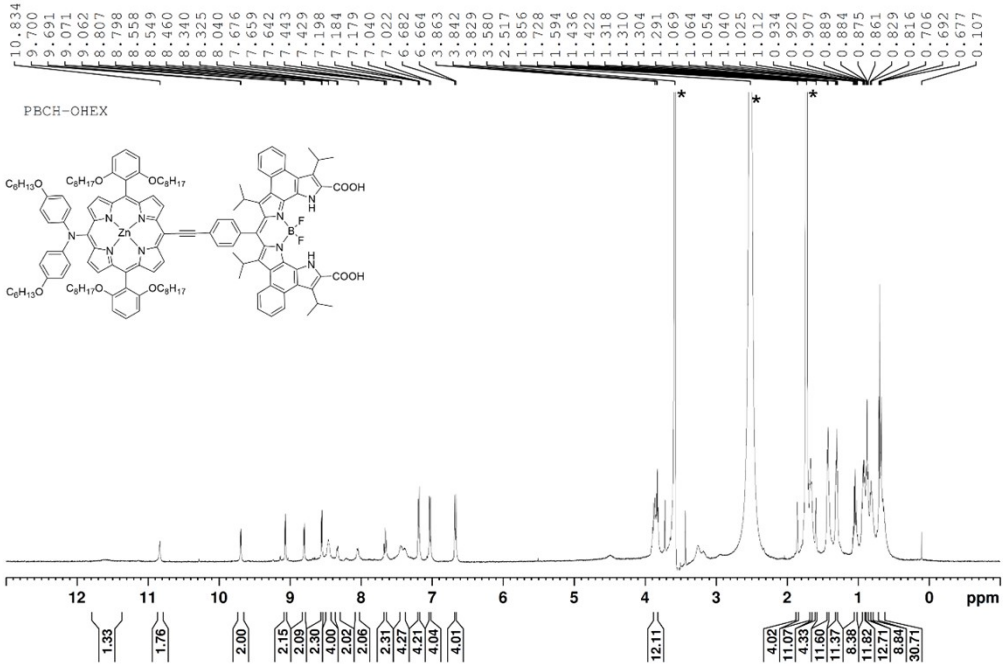


Figure S24. ^{1}H NMR spectrum of **PBC2** in THF-d_8 recorded at 25 °C (*Asterisk indicates residual solvent impurity).

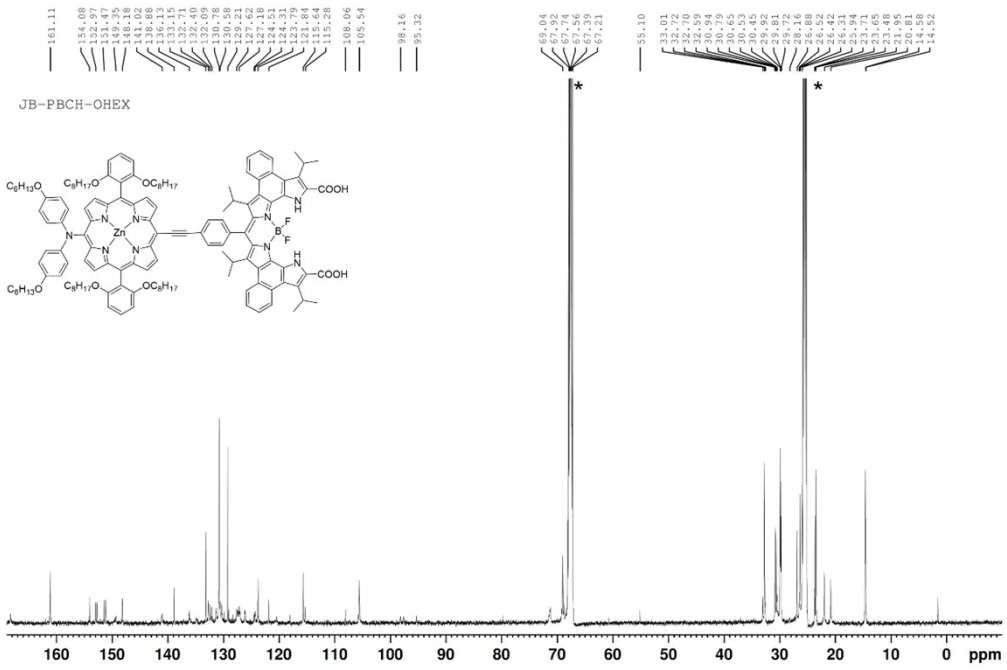


Figure S25. ^{13}C NMR spectrum of **PBC2** in THF-d_8 recorded at 25 °C (*Asterisk indicates residual solvent impurity).

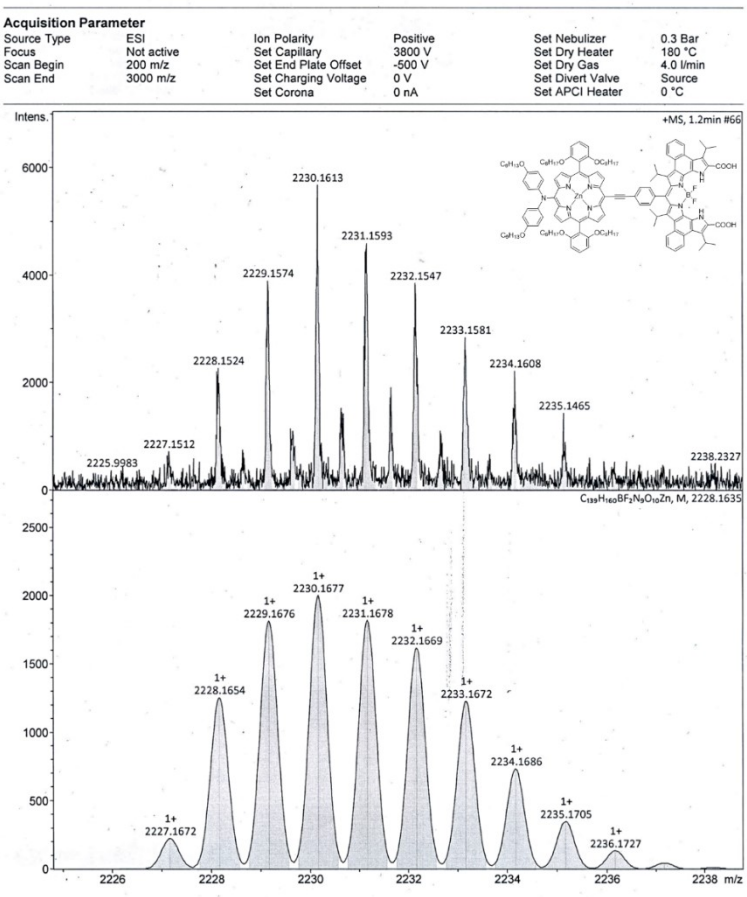


Figure S26. HR-ESI mass spectrum of **PBC2**; m/z calculated for $[M+H]^+ C_{139}H_{161}BF_2N_9O_{10}Zn$ 2230.1677, found 2230.1613.

4. ABSORPTION AND EMISSION STUDIES:

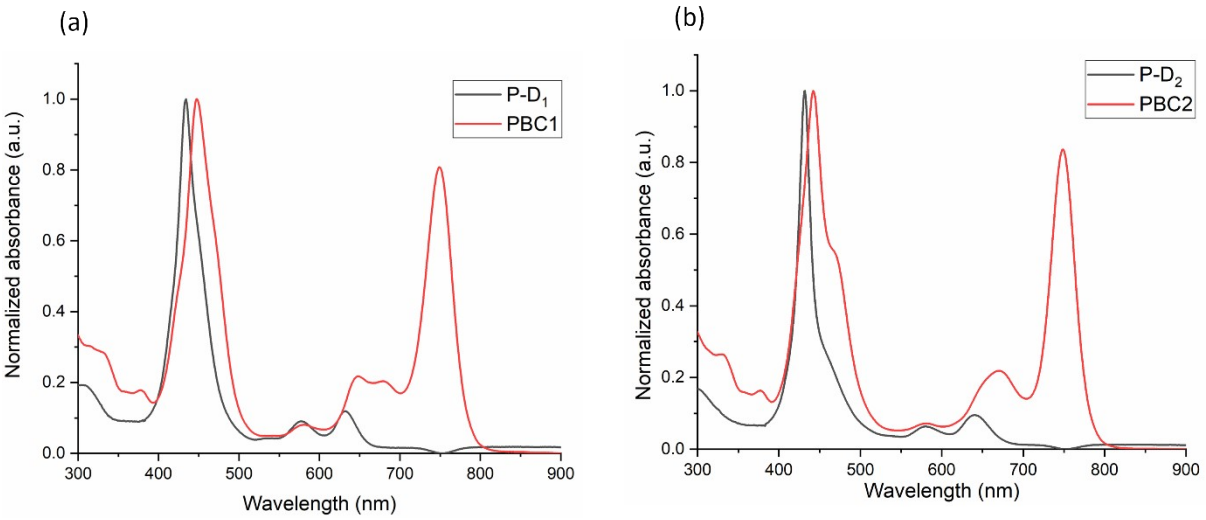


Figure S27 Comparative UV-Vis-NIR spectra of donor porphyrins (with hexyl and hexloxy chains) with **PBC1** and **PBC2** in THF solvent respectively.

Table S1 Absorption data for different porphyrins, BODIPY analogues and porphyrin-BODIPY conjugates.

Dye	Absorption peaks (nm)
5,15-diaryl porphyrin (**P**)	412 (λ_{max}), 502, 535, 576, 631
Porphyrin donor (hexyl) (**P-D$_1$**)	434 (λ_{max}), 578, 632
Porphyrin donor (hexyloxy) (**P-D$_2$**)	432 (λ_{max}), 581, 641
Meso-free BODIPY [3]	727 (λ_{max})
Acceptor BODIPY (**9**)	748 (λ_{max})
PBC1	448 (λ_{max}), 648, 750
PBC2	442 (λ_{max}), 670, 750

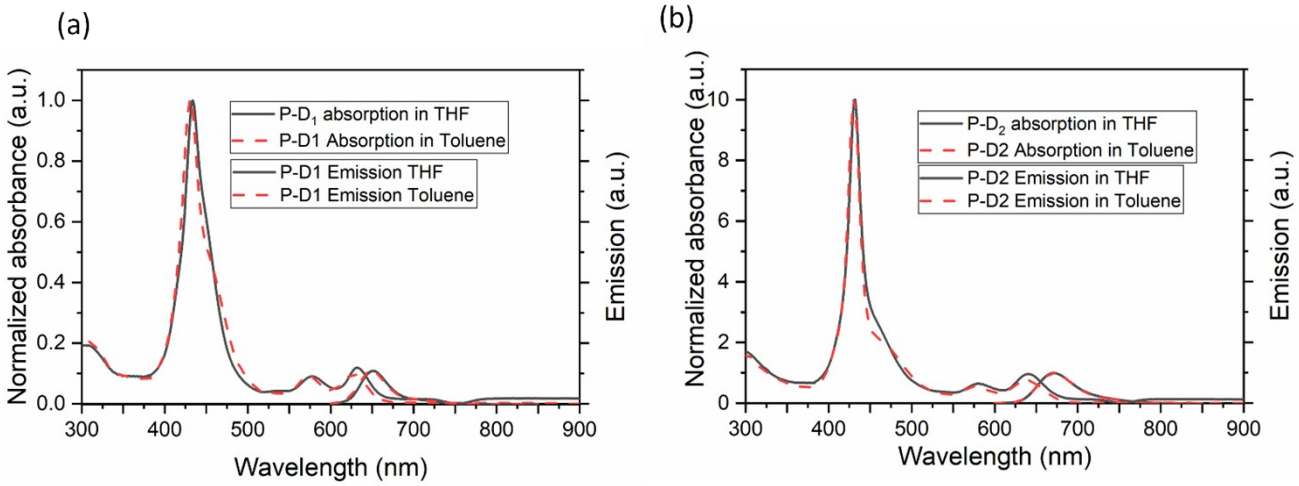


Figure S28. UV-Vis-NIR absorption and emission spectra (straight lines) in THF and dotted lines in toluene for (a) **P-D$_1$** (b) **P-D$_1$**.

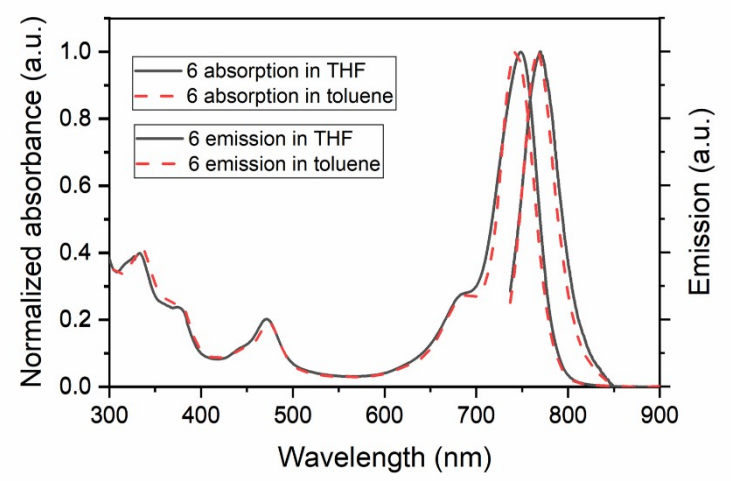


Figure S29. UV-Vis-NIR absorption and emission spectra (straight lines) in THF and dotted lines in toluene for **6** (BODIPY Acceptor).

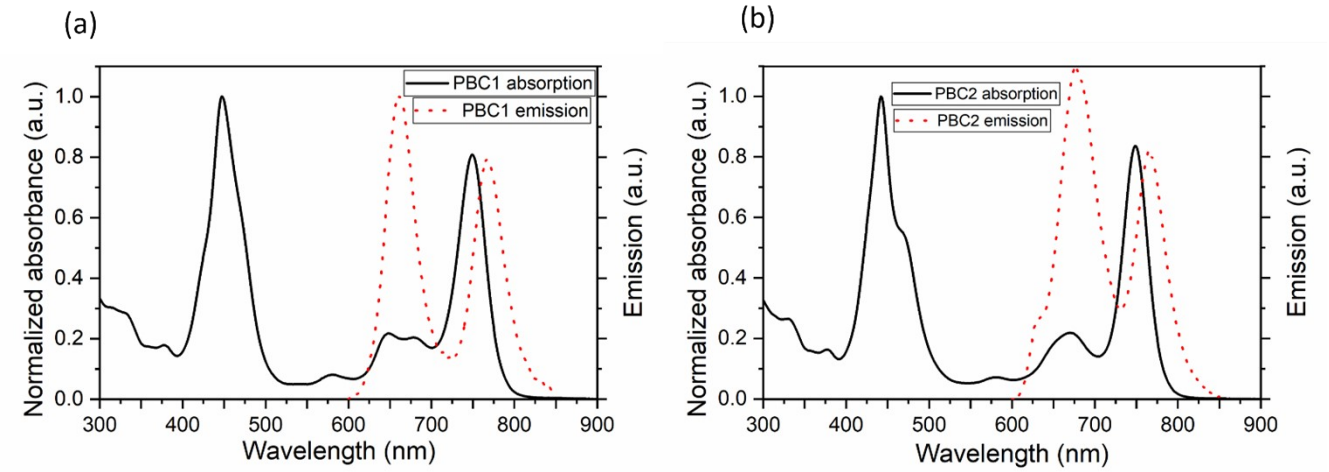


Figure S30. UV-Vis-NIR absorption spectra (straight lines) and emission spectra (dotted lines) for (a) **PBC1** (b) **PBC2** in THF.

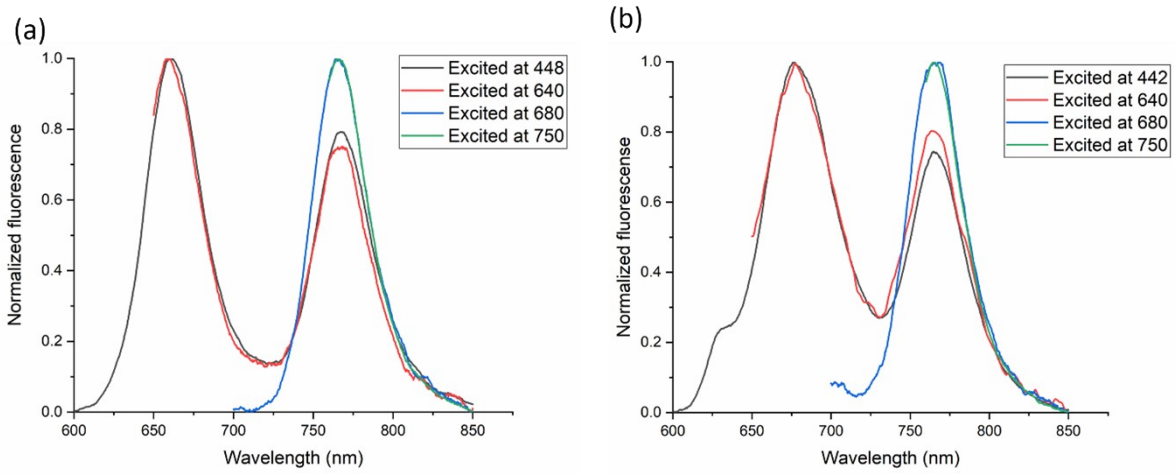


Figure S31. Emission spectra excited at different wavelengths for (a) **PBC1** (b) **PBC2** in THF.

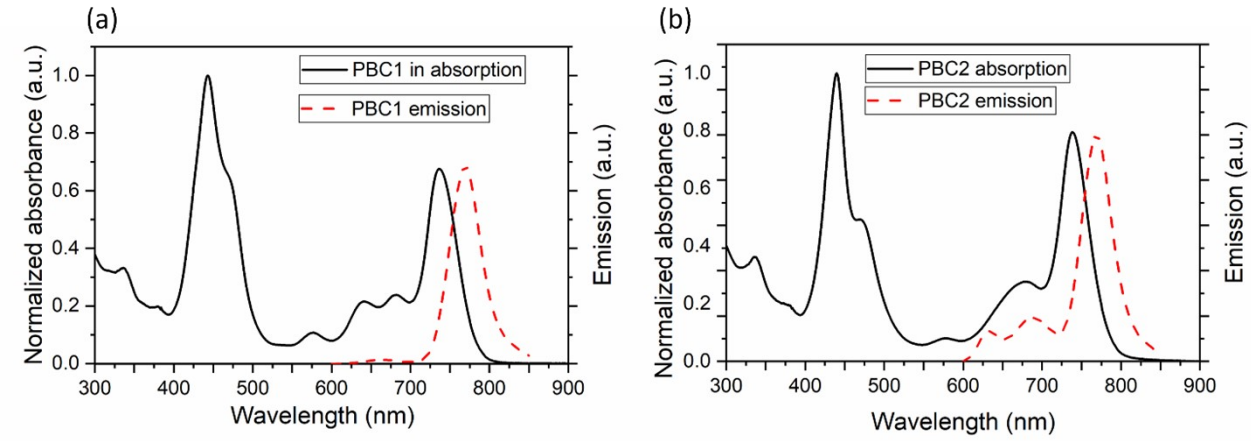


Figure S32. UV-Vis-NIR absorption spectra (straight lines) and emission spectra (dotted lines) for (a) **PBC1** (b) **PBC2** in toluene.

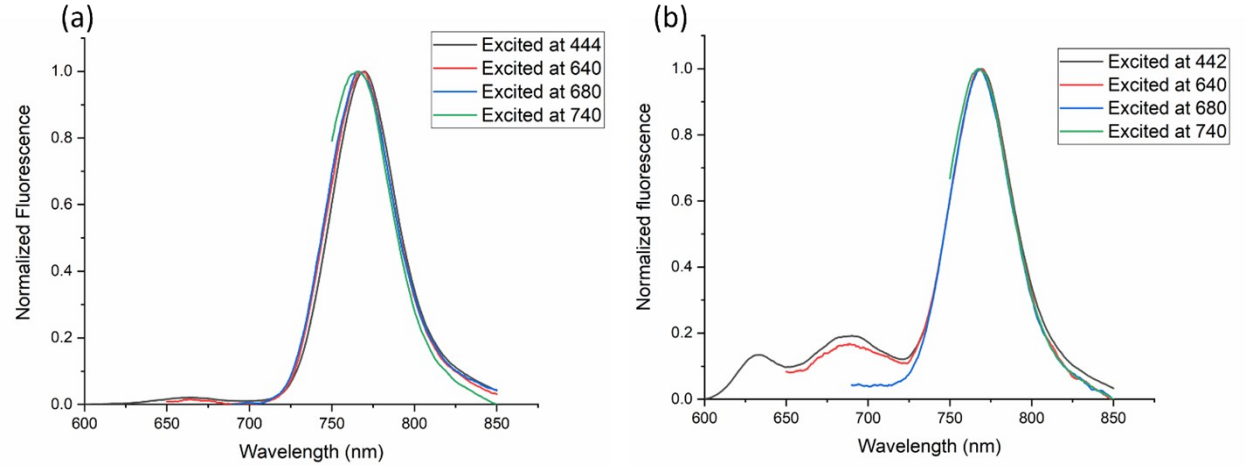


Figure S33. Emission spectra excited at different wavelengths for (a) **PBC1** (b) **PBC2** in toluene.

5. SINGLET STATE LIFE TIME ANALYSIS

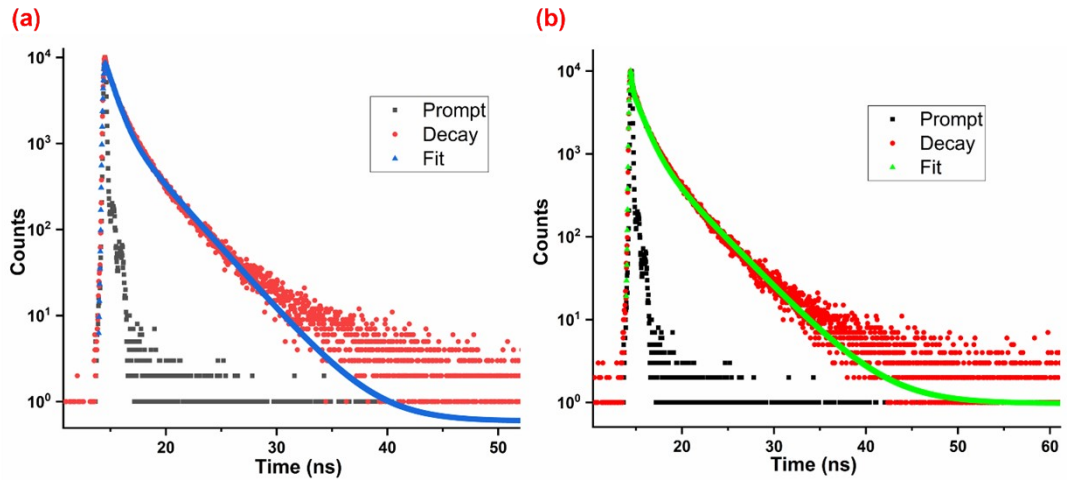


Figure S34. Fluorescence decay profile of: a) **PBC1**; b) **PBC2** recorded in chloroform (λ_{exc}= 405 nm).

6. COMPUTATIONAL STUDIES:

Quantum mechanical calculations were performed using Gaussian 09 program provided by CMSD facility of University of Hyderabad.[S5] All calculations were carried out by density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) was used. LANL2DZ basis set was used for Zn and 6-31G basis set was used for all other atoms in calculations and the molecular orbitals were visualized using Gauss view 5. Electronic spectra were calculated using time-dependent density functional theory (TD-DFT) in THF solvent using PCM model. The result of TD-DFT was analyzed using GaussSum programme.[S6]

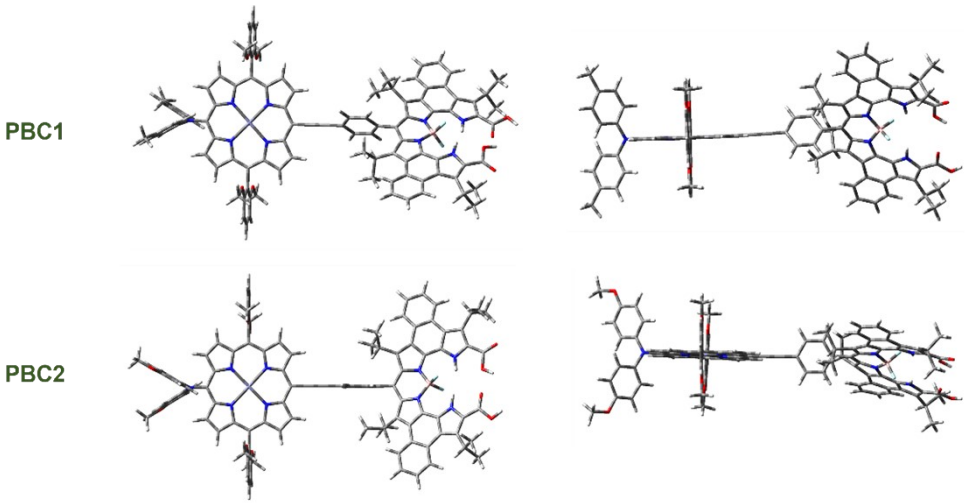


Figure S35. DFT optimized structures of dyes **PBC1** and **PBC2**.

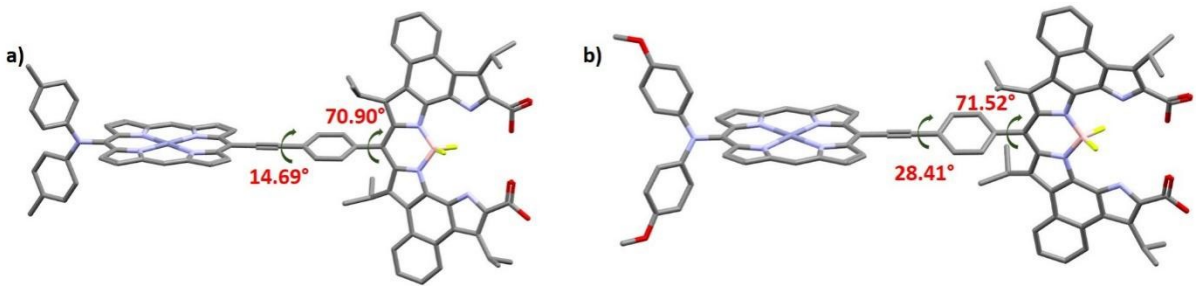


Figure S36. DFT optimized structures of dyes (a) **PBC1** (b) **PBC2** with dihedral angle between porphyrin, phenyl and BODIPY planes.

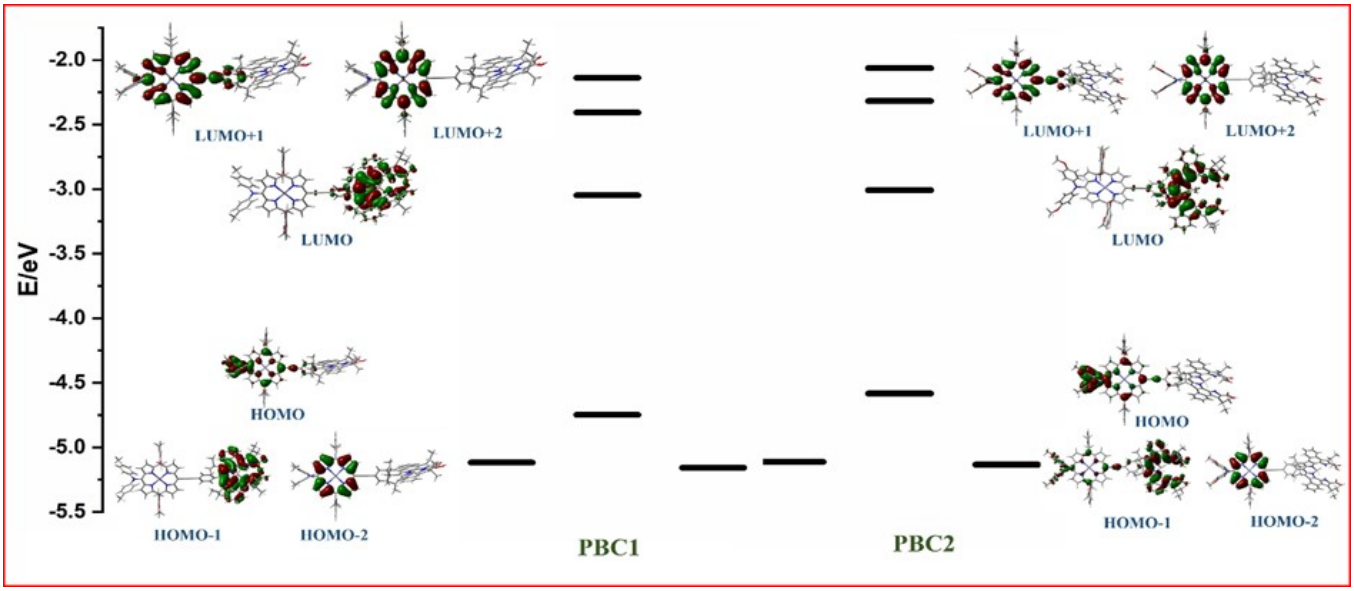


Figure S37. Frontier molecular orbital profiles of **PBC1** and **PBC2** calculated with LANL2DZ for Zn and B3LYP 6-31G(d) basis set for other atoms.

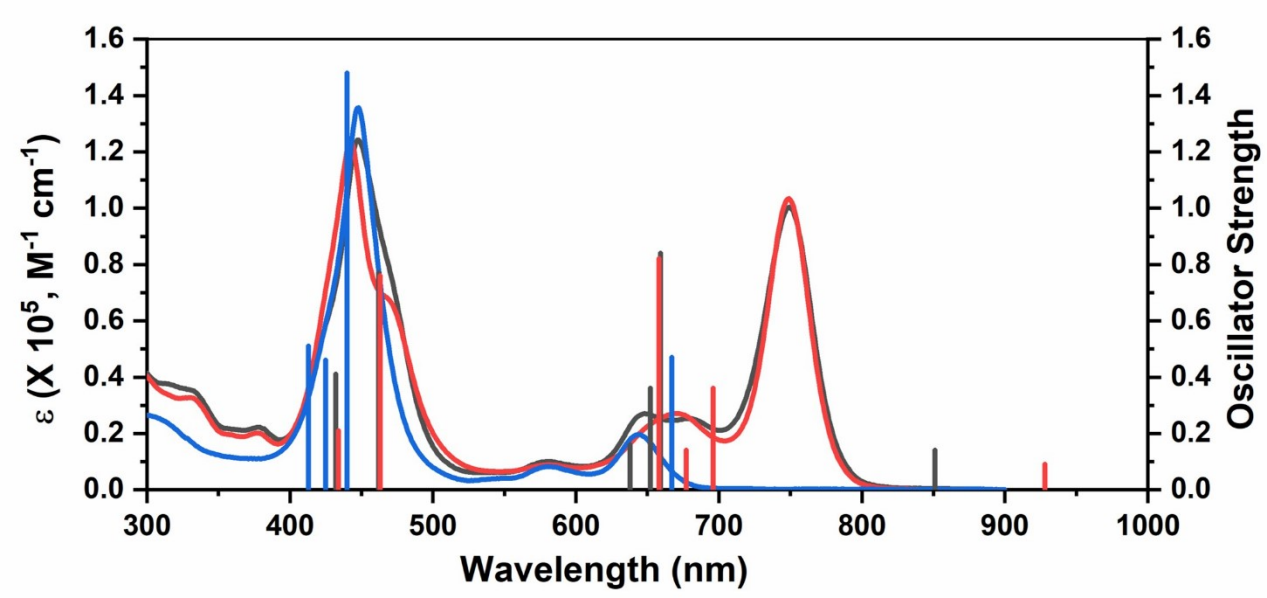


Figure S38. Theoretical (vertical bars) and experimental (continuous lines) UV-Vis-NIR absorption spectra of **PBC1** (black) and **PBC2** (red) in THF along with YD2-o-C8 (blue) for comparison.

Table S2: Selected transitions, oscillator strength, symmetry calculated (H = HOMO, L =LUMO) from DFT analysis for **PBC1**, **PBC2** and **YD2-*o*-C8**.

Dye	Wavelength (nm)	Oscillator Strength	Symmetry	Major Contribution
PBC1	851	0.14	Singlet-A	H→L (98%)
	659	0.84	Singlet-A	H-1→L (100%)
	652	0.36	Singlet-A	H→L+1 (87%)
	638	0.16	Singlet-A	H-3→L (93%)
	462	0.77	Singlet-A	H-8→L (64%), H-9→L (13%)
	432	0.41	Singlet-A	H-13→L (22%), H-13→L (15%), H-11→L (28%)
PBC2	928	0.09	Singlet-A	H→L (98%)
	696	0.36	Singlet-A	H→L+1 (94%)
	658	0.82	Singlet-A	H-2→L (99%)
	463	0.76	Singlet-A	H-9→L (49%), H-11→L (19%), H-10→ L (17%)
	434	0.21	Singlet-A	H-12→L (41%). H-14→ L (19%), H-13→ L (15%)
YD2-*o*-C8	667	0.47	Singlet-A	H→L (91%)
	440	1.48	Singlet-A	H-1→L+1 (43%), H→L+2 (39%)
	425	0.76	Singlet-A	H-2→L+1 (45%), H-1→L (34%)
	413	0.51	Singlet-A	H→L+2 (54%), H-1→L+1 (23%)

7. ELECTROCHEMICAL STUDIES:

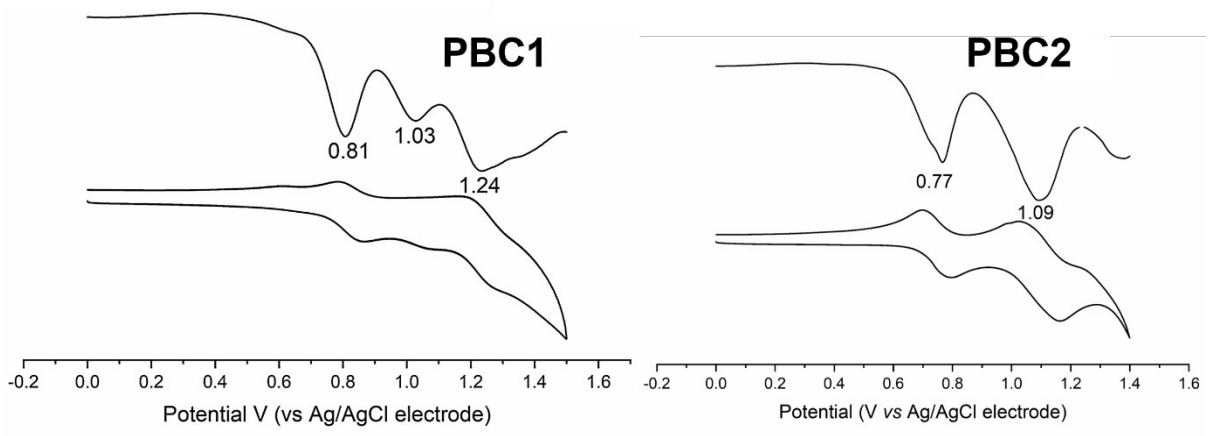


Figure S39. Cyclic voltammograms and differential pulse voltammograms of PBC1 and PBC2 in THF (scan rate: 0.1 V s^{-1}; electrolyte: 0.1 M $TBAPF_6$; working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag/AgCl).

Table S3: Absorption spectral and electrochemical data for **PBC1** and **PBC2**.

Dye	Absorption λ_{max}/nm ($\varepsilon/10^5$ M^{-1} cm^{-1})	Emission in nm	$E_{0\text{-}0}$	Oxidation E_{ox}(from DPV) vs. NHE	Reduction E_{red} (from DPV) vs. NHE	E_{ec}	Φ_f[S7]
PBC1	448 (1.94), 649 (0.41), 753 (1.64)	661, 767	1.64 eV	1.02V	-0.64 V	1.66 eV	0.025
PBC2	443 (1.93), 670 (0.43), 750 (1.53)	676, 765	1.64 eV	0.98 V	- 0.67 V	1.65 eV	0.016

$E_{0\text{-}0}$= Optical band gap, E_{ec}= Electrochemical gap

8. PHOTOSTABILITY:

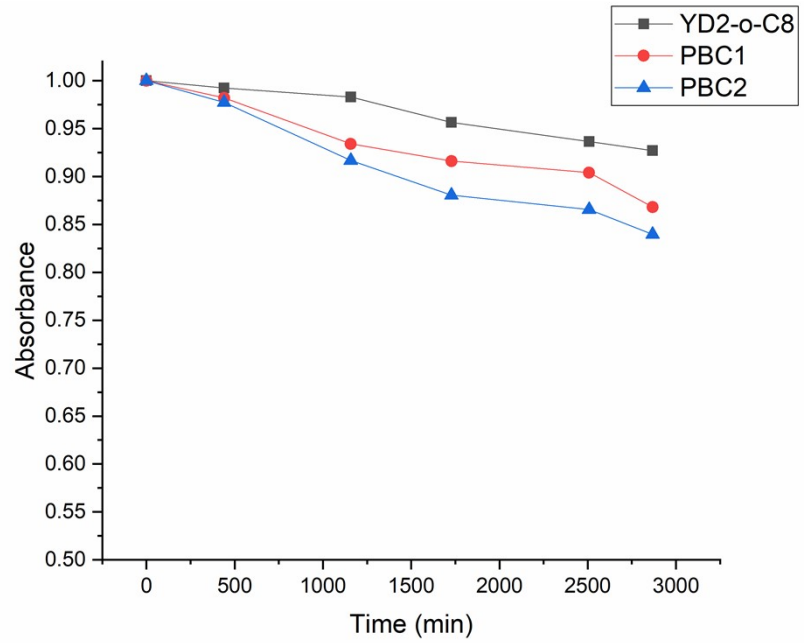


Figure S40. Photostability of **PBC1, PBC2** and **YD2-*o*-C8** in toluene, monitored by observing changes in absorbance at the λ_{max} at different time interval upon exposing the sample solution to UV radiation (8 watt, 365 nm).

9. REFERENCES:

S1. S. Paul, T. Ahmed, S. Das and A. Samanta, Effect of Lead: Halide Precursor Ratio on the Photoluminescence and Carrier Dynamics of Violet- and Blue-Emitting Lead Halide Perovskite. Nanocrystals. *J. Phys. Chem. C*., 2021, **125**, 23539−23547.

S2. A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, W.-G. Diau, E. C.-Y. Yeh and M. Grätzel, Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science*., 2011, **334**, 629-634.

S3 S. H. Kang, I, T. Choi, M. S. Kang, Y. K. Eom, M. J. Ju, J. Y. Hong, H. S. Kang and H. K. Kim, Novel D–π–A structured porphyrin dyes with diphenylamine derived electron-donating substituents for highly efficient dye-sensitized solar cells *J. Mater. Chem. A*, 2013, **1**, 3977-3982.

S4. T. Sarma, P. K. Panda, P. T. Anusha, S. V. Rao, Dinaphthoporphycenes: Synthesis and Nonlinear Optical Studies. *Org. Lett*. 2011, **13**, 188-191.

S5. Gaussian 09, (Revision C.01), Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2010.

S6. N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, cclib: A library for package-independent computational chemistry algorithms. *J. Comp. Chem.,* 2008, **29**, 839-845.

S7. a) M. Taniguchi, J. S. Lindsey, D. F. Bocian and D. Holten. Comprehensive review of photophysical parameters (ε, ϕ_f, τ_s) of tetraphenylporphyrin (H2TPP) and zinc tetraphenylporphyrin (ZnTPP) – Critical benchmark molecules in photochemistry and photosynthesis *J. Photochem. Photobiol. C: Photochem. Rev*., 2021, **46**, 100401; b) P. G. Seybold, M. Gouterman, *J. Mol. Spectrosc*.1969, **31**, 1-13.