Supporting Information

β-Functionalized Trans-A2B2 Push-Pull Tetrabenzoporphyrins

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Contents

General Information

All the chemicals used in synthesis were obtained either from Sigma-Aldrich or Fischer. Solvents used in reactions were ACS grade obtained from Fischer or ACROS and were run though a commercially available solvent purification system. NMR data of compounds were either obtained on a Bruker 500 at Miami University, Ohio / Varian 500 NMR at UNT. For ^{1}H and ^{13}C NMR the chemical shift for the chloroform peaks were referenced to 7.26 ppm and 77.16 ppm respectively. Mass data was obtained on the Thermo Scientific MALDI-TOF mass spectrometer fitted with an LTQ orbitrap. All UV/ Vis data were obtained on a CARY 5000 spectrometer and fluorescence data were obtained using a CARY/Perkin-Elmer fluorimeter. All reactions unless otherwise stated were carried out under argon. The starting porphyrins **10** and **5** were synthesized per literature procedures[1,2].

Synthetic Schemes

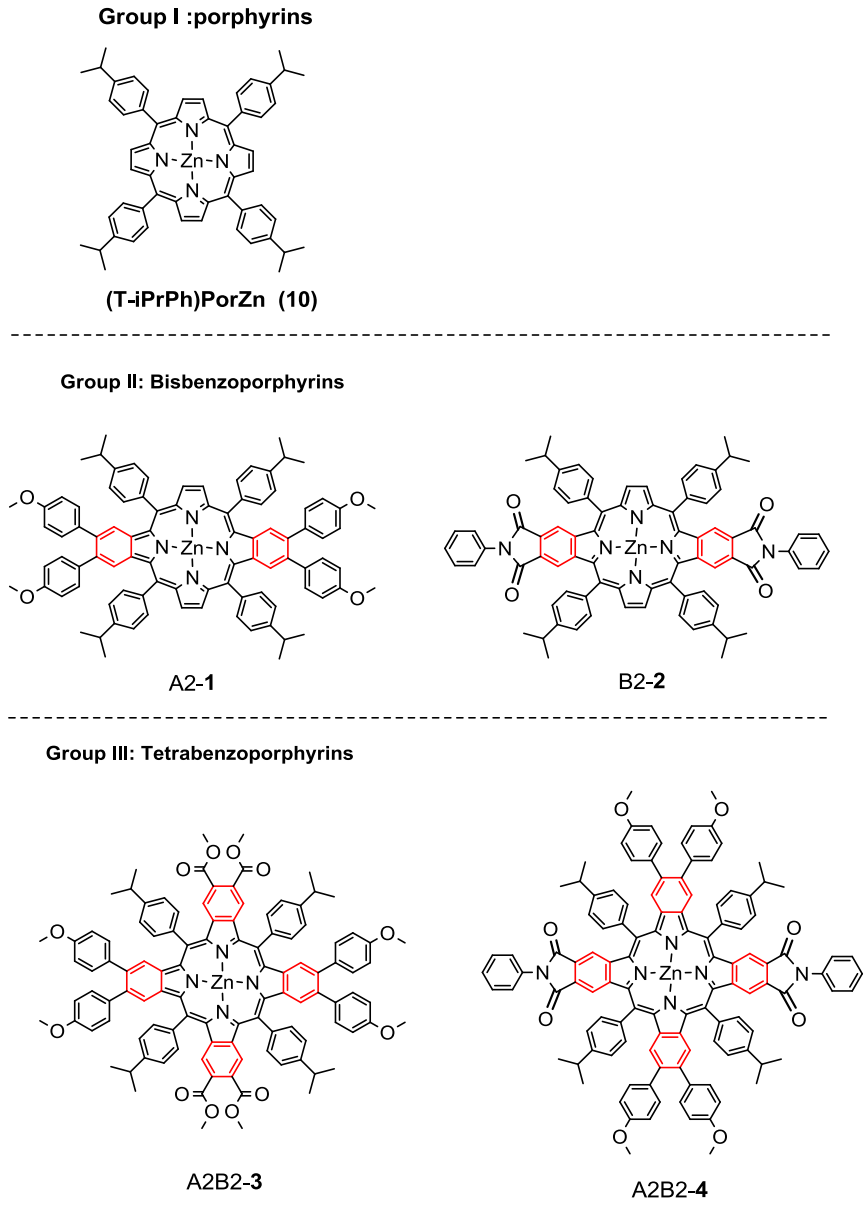
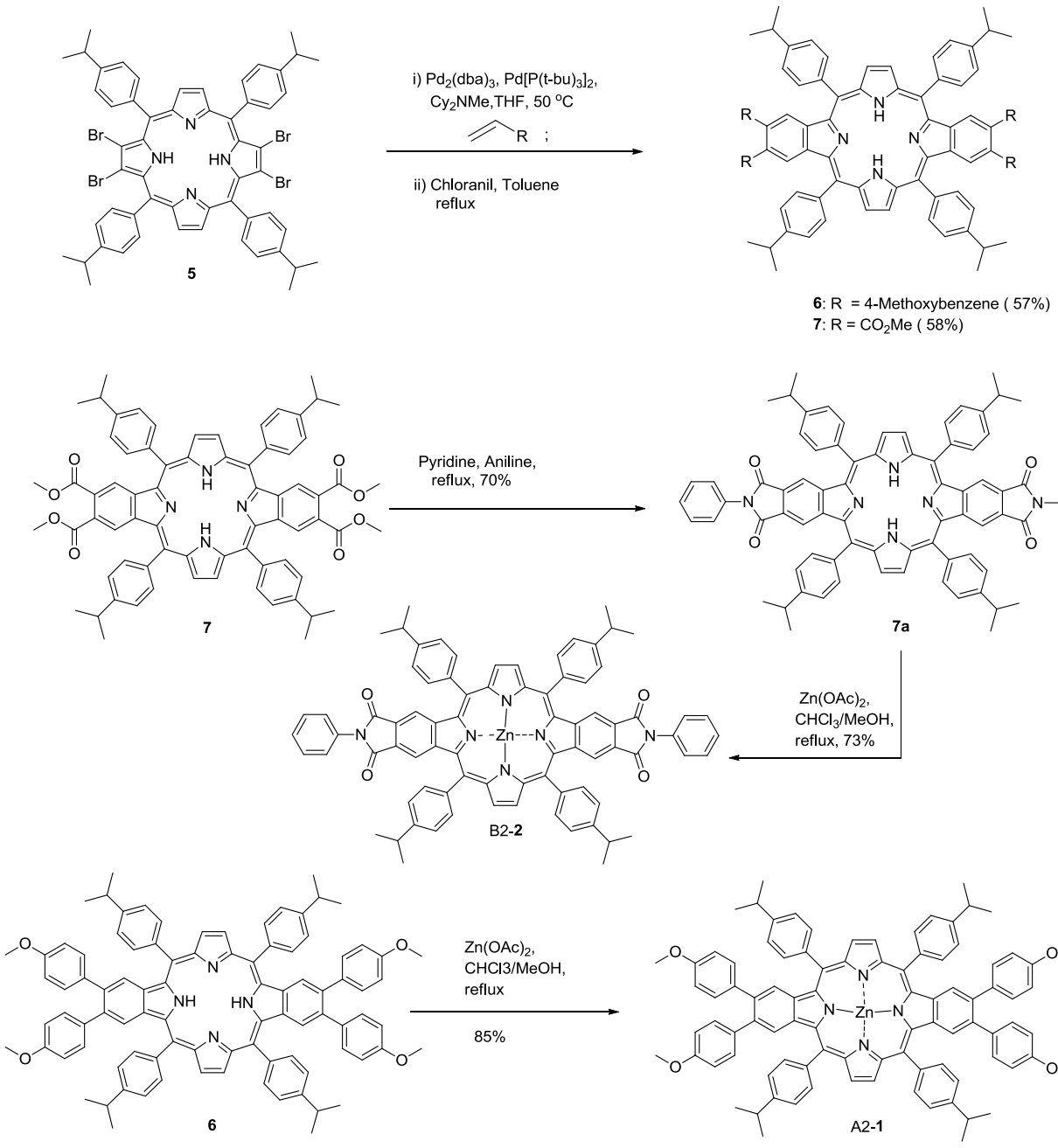
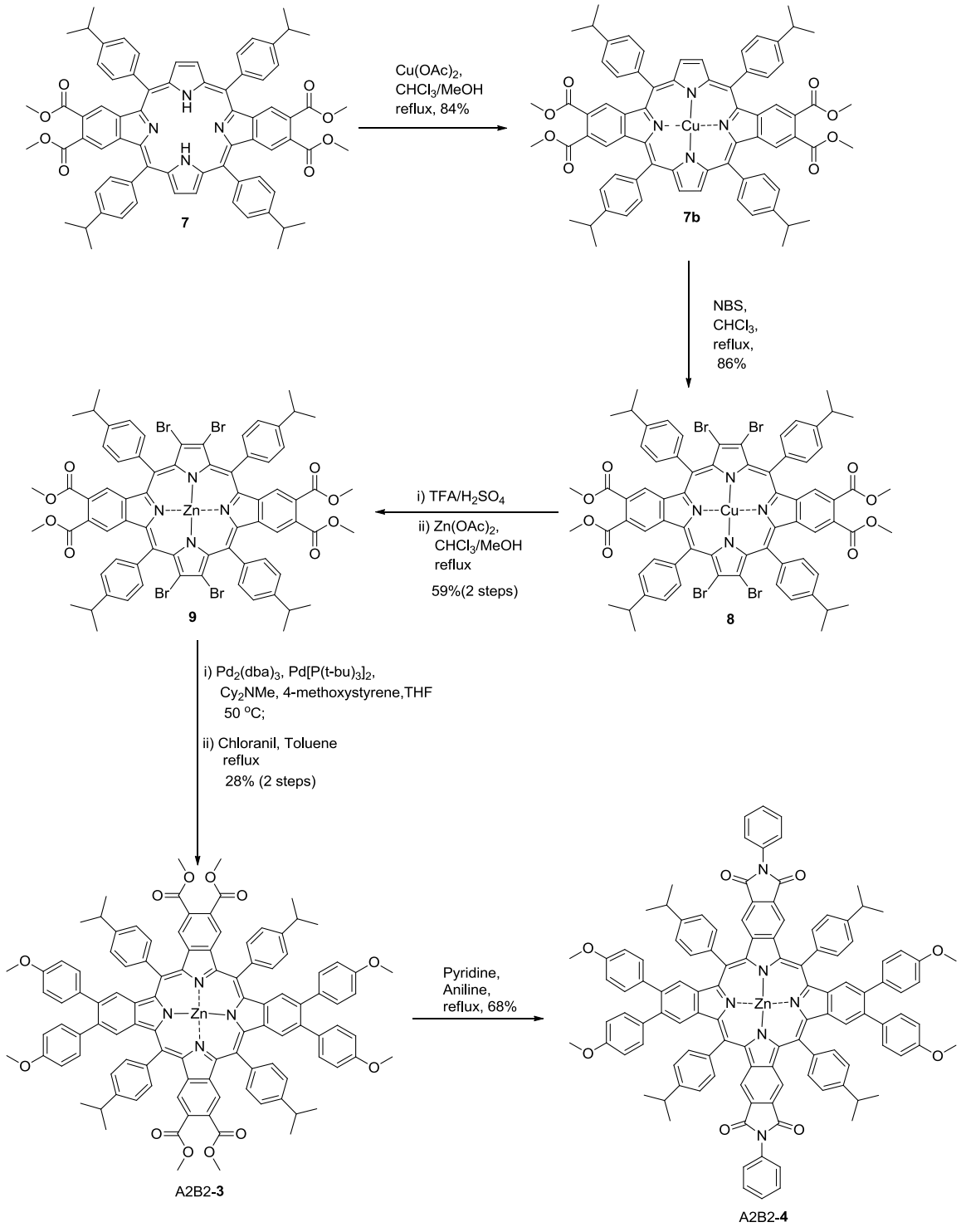


Chart S1. Structures of investigated benzoporphyrins.

Scheme S1. Synthesis of A2 Porphyrins

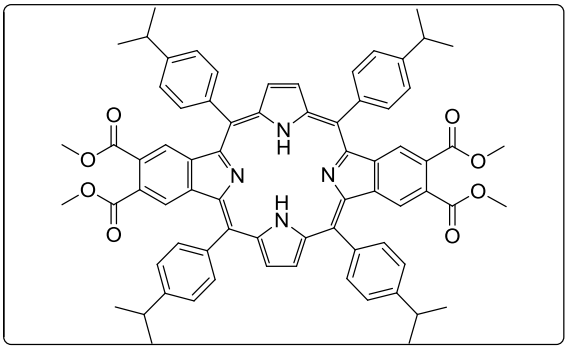


Scheme S2. Synthesis of A2B2 Porphyrins



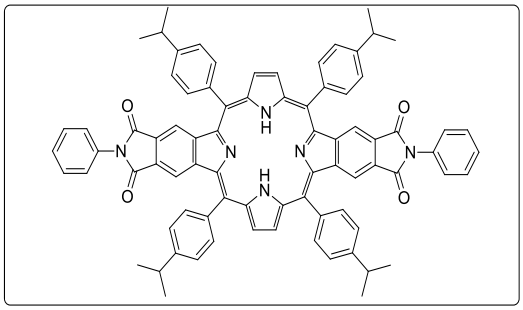
Synthetic Procedures

Synthesis of tetraester **7**



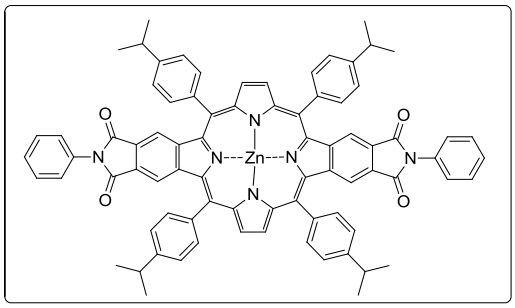
195mg (0.177 mmol) of **5** was taken in a schlenk flask and to this was added 167 µl of Cy_2NMe (0.779 mmol) and 15 ml of THF after which the solution was degassed twice via freeze-pump-thaw cycles. To this solution 25 mg (0.027 mmol) of $Pd_2(dba)_3$ and 27 mg (0.053 mmol) of $Pd[P(t\text{-}Bu)_3]_2$ were added and the solution was degassed again two times. Finally, 319 µl (3.54 mmol) of methylacrylate was added to the reaction mixture and the solution was then heated at 50 ^oC for 48 hrs. The reaction was then cooled down and the solution was passed through a short silica plug using THF as the eluent. After THF was rotavaped off, the solid obtained was recrystallized from DCM/methanol, giving a brown solid. This brown solid was dried overnight in vacuum and to this was added 100 mg (0.408 mmol) of *p*-chloranil in 15 ml of toluene and refluxed overnight to cyclize and oxidize the intermediates. The reaction mixture was diluted with ethyl acetate and subjected to an aqueous NaOH workup to remove the phenolic impurities; the organic solvents were rotavaped off and the product was recrystallized from chloroform/methanol to obtain 160 mg of crude product which after purification by chromatography with 0.2% methanol in chloroform, yielded 114 mg of pure **7**. **Yield**: 58%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (s, 4H), 8.11 (d, *J* = 7.8 Hz, 8H), 7.69 (d, *J* = 7.7 Hz, 8H), 7.40 (s, 4H), 3.86 (s, 12H), 3.36 – 3.29 (m, 4H), 1.59 (d, *J* = 6.9 Hz, 24H), -2.60 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.72, 149.97, 148.83, 142.65, 139.35, 139.05, 134.02, 129.19, 128.07, 126.10, 125.46, 119.15, 52.64, 34.48, 24.58; **HRMS MALDI-TOF**: *m/z* calculated for $C_{72}H_{66}N_4O_8$ (M^+) 1114.4881, found 1114.4937. (The analytical data matches our previously reported[2] synthesis of **7**.)

Synthesis of diimide **7a**



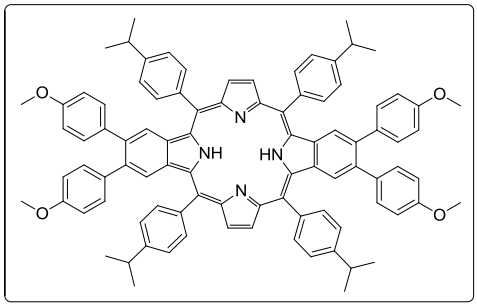
Diimide **7a** was synthesized by refluxing the corresponding tetraester **7** (100mg, 0.09 mmol) in 10 ml of 1: 1 mixture of pyridine and aniline for 5 days. After evaporating the solvent and recrystallizing the crude product from a mixture of chloroform and methanol, 73 mg of **7a** was obtained as a purple solid. **Yield**: 70%; **UV-Vis in $CHCl_3$** λ in nm (ε): 462 (219100), 547 (9300), 586 (13900), 620 (6800); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.95 (s, 4H), 8.15 (d, *J* = 7.7 Hz, 8H), 7.74 (d, *J* = 7.7 Hz, 8H), 7.54 – 7.46 (m, 4H), 7.45 – 7.35 (m, 10H), 3.43 – 3.28 (m, 4H), 1.62 (d, *J* = 6.9 Hz, 24H), -2.53 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) 167.56, 150.76, 149.01, 145.57, 139.71, 138.86, 133.96, 132.33, 129.24, 128.83, 128.68, 128.10, 126.98, 126.39, 120.46, 119.80, 77.41, 77.16, 76.91, 34.66, 24.63; **HRMS MALDI-TOF**: *m/z* calculated for $C_{80}H_{64}N_6O_4$(M^+) 1172.4989, found 1172.4988.

Synthesis of Zn-diimide B2-**2**



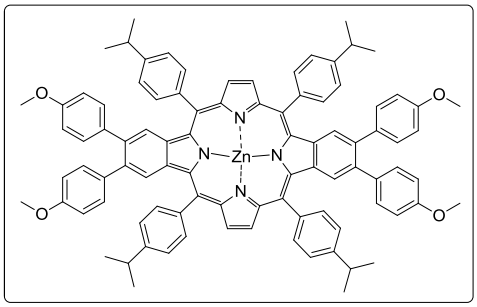
Zn-b2-diimide B2-**2** was synthesized by refluxing the corresponding imide **7a** (30 mg, 0.025 mmol) with 30 mg (0.137 mmol) of $Zn(OAc)_2$.$2H_2O$in 10 ml of 3: 1 mixture of $CHCl_3$ and methanol overnight. After rotavaping off the solvent, the crude product was dissolved in $CHCl_3$ and subjected to aqueous workup to remove any inorganic impurities. Recrystallization of the crude product from a mixture of chloroform and methanol yielded 23 mg of B2-**2** as a green solid. **Yield**: 73%; **UV-Vis in $CHCl_3$** λ in nm (ε): 477 (250300), 596 (18200), 631 (20300); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.93 (s, 4H), 8.06 (d, *J* = 7.8 Hz, 8H), 7.69 (d, *J* = 7.8 Hz, 8H), 7.55 (s, 4H), 7.51 – 7.34 (m, 10H), 3.37 – 3.27 (m, 4H), 1.62 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.74, 151.27, 150.13, 144.29, 143.73, 140.27, 133.41, 132.40, 132.23, 129.19, 128.04, 127.84, 127.04, 125.90, 120.95, 120.33, 77.41, 77.16, 76.91, 34.62, 24.66 ; **HRMS MALDI-TOF**: *m/z* calculated for $C_{80}H_{62}N_6O_4Zn(M^+)$ 1234.4124, found 1234.4124.

Synthesis of tetramethoxyporphyrin **6**



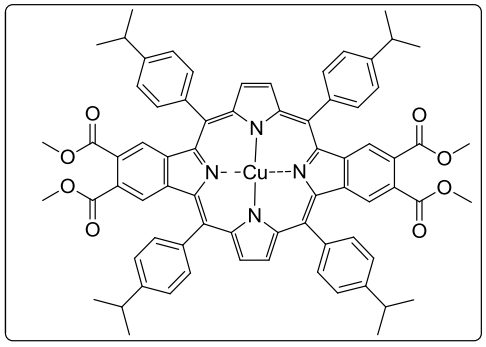
100 mg (0.091 mmol) of the **5** was taken in a schlenk flask and to this was added 86 µl of Cy_2NMe (0.40 mmol) and 10 ml of THF after which the solution was degassed twice via freeze-pump-thaw cycles. To this solution 12.5 mg (0.014 mmol) of $Pd_2(dba)_3$ and 14.0 mg (0.027 mmol) of $Pd[P(t\text{-}Bu)_3]_2$ were added and the solution was degassed again two times; finally, 183 µl (1.365 mmol) of 4-methoxystyrene was added and the solution was degassed again and then heated at 50 ^{o}C for 48 hrs. The reaction was then cooled down and the solution was passed through a short silica plug using THF as the eluent; THF was rotavaped off and the solid thus obtained was recrystallized from DCM/Methanol to obtain a brown solid. This brown solid was dried overnight in vacuum and to this was added 50 mg (0.20 mmol) of *p*-chloranil in 15 ml of toluene and refluxed for 20 hrs to cyclize and oxidize the intermediates. The reaction mixture was diluted with ethyl acetate and subjected to an aqueous NaOH workup to remove the phenolic impurities and the organic solvents were rotavaped off and the product was recrystallized from chloroform/methanol to obtain 69 mg of **6**. **Yield**: 57%; **UV-Vis in $CHCl_3$** λ in nm (ε): 447 (324500), 528 (22778), 557 (11214), 615 (5606), 672(2803) ; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.4 Hz, 4H), 8.14 (d, *J* = 8.0 Hz, 8H), 7.62 (d, *J* = 8.0 Hz, 8H), 7.18 (s, 4H), 6.97 (d, *J* = 8.7 Hz, 8H), 6.73 (d, *J* = 8.7 Hz, 8H), 3.80 (s, 12H), 3.23 (dt, *J* = 13.6, 6.9 Hz, 4H), 1.47 (d, *J* = 7.0 Hz, 24H), -2.49 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.13, 149.93, 149.24, 138.89, 135.02, 133.84, 131.27, 127.06, 126.85, 125.95, 113.40, 77.56, 77.41, 77.16, 76.91, 55.34, 34.36, 24.47; **HRMS MALDI-TOF**: *m/z* calculated for $C_{92}H_{82}N_4O_4$ (M^+) 1306.6336, found 1306.6395.

Synthesis of A2-**1**



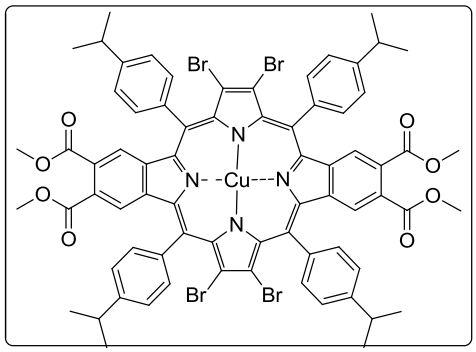
20 mg of **6** was dissolved in 20 ml of 1:3 methanol in chloroform and 20 mg of zinc acetate was added and refluxed overnight. The reaction mixture was then rotavaped off and subjected to an aqueous workup followed by recrystallization from a mixture of chloroform and methanol to obtain 17 mg of the product as a purple solid. **Yield**: 85%; **UV-Vis in $CHCl_3$** λ in nm (ε): 456 (419900), 588 (33000), 637 (22900); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.85 (s, 4H), 8.11 (d, *J* = 7.8 Hz, 8H), 7.62 (d, *J* = 7.8 Hz, 8H), 7.40 (s, 4H), 7.01 (d, *J* = 8.4 Hz, 8H), 6.76 (d, *J* = 8.4 Hz, 8H), 3.82 (s, 12H), 3.29 – 3.19 (m, 4H), 1.49 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.05, 150.15, 148.62, 144.81, 141.56, 139.50, 137.43, 133.38, 131.36, 130.60, 126.92, 125.44, 118.74, 114.26, 113.39, 55.29, 34.28, 24.49. **HRMS MALDI-TOF**: *m/z* calculated for $C_{92}H_{80}N_4O_4Zn(M^+)$ 1368.5471, found 1368.5473.

Synthesis of copper-tetraester **7b**



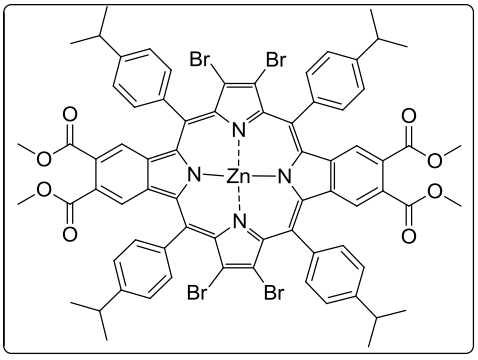
120mg (0.102 mmol) of tetraester **7** and 122 mg (0.61 mmol) of copper acetate was added to round bottom flask and to this was added 30 ml of 1:3 mixture of methanol in chloroform was added and the reaction mixture was refluxed overnight. After completion of the reaction, the solvent was rotavaped off and the crude product was dissolved in chloroform and subjected to an aqueous workup. The solvent was then removed and the crude material was recrystallized from chloroform/methanol to obtain 109 mg of the copper inserted porphyrin **7b** as a green solid. **Yield**: 84%; **UV-Vis in $CHCl_3$** λ in nm (ε): 450 (195800), 575 (13100), 597 (9000); **HRMS MALDI**: *m/z* Calculated for $C_{72}H_{64}CuN_4O_8(M^+)$ 1175.4020, found 1175.4023.

Synthesis of copper-tetrabromo porphyrin **8**



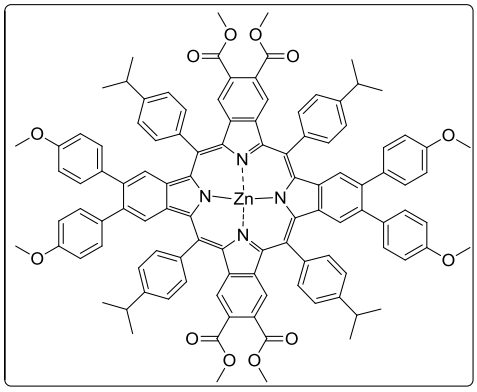
106mg (0.09 mmol) of the **7b** was dissolved in 30ml of dry $CHCl_3$ and to this was added 96 mg (0.54 mmol) of NBS and refluxed for 16 hrs. On completion of the reaction the reaction was worked up with aqueous NaOH solution. The organic layers were rotavaped off and the crude product was recrystallized from $CHCl_3$/MeOH to obtain 116 mg of the tetrabrominated copper inserted porphyrin **8** as a green solid. **Yield**: 86%; **UV-Vis in $CHCl_3$** λ in nm (ε): 469 (116100), 597 (6500), 652 (6600); **HRMS MALDI**: *m/z* calculated for $C_{72}H_{60}Br_4CuN_4O_8(M^+)$ 1491.0400, found 1491.0407.

Synthesis of Zinc -tetrabromo porphyrin **9**



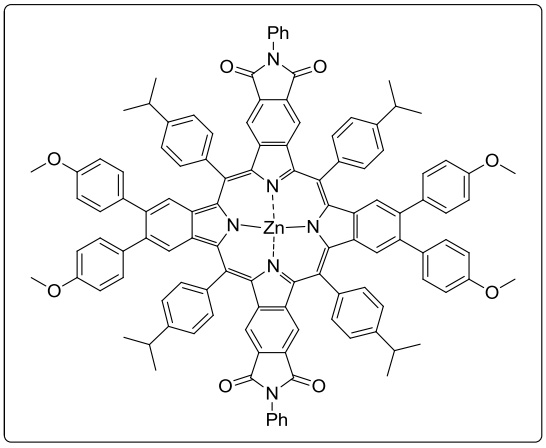
126mg (0.84 mmol) of the **8** was taken in a round bottomed flask and to this was added 9ml of 2/1 TFA/sulfuric acid mixture at 0 ^{o}C. The ice bath was removed after the addition of acid and stirred at room temperature for 30 minutes. The reaction mixture was then poured slowly into a cold $NaHCO_3$ solution and this mixture was then extracted with chloroform. The organic layers were finally washed with dilute NaOH solution. The organic extract was then rotavaped off and dried under vacuum. To this crude material, 199mg (0.9 mmol) of zinc acetate dihydrate and 30 ml of 3/1 mixture of chloroform and methanol was added and refluxed overnight. The solution was then rotavaped off. The crude product was then dissolved in chloroform and an aqueous workup was done to remove any inorganic salts. The crude material thus obtained was subjected to a short silica plug using 2% methanol in chloroform to remove any baseline impurities. 74 mg of the final product was obtained as a green solid. **Yield**: 59% (2 Steps); **UV-Vis in $CHCl_3$** λ in nm (ε): 483 (215600), 615 (9900), 664 (7300); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 8H), 7.63 (d, *J* = 7.9 Hz, 8H), 7.23 (s, 4H), 3.79 (s, 12H), 3.33 – 3.18 (m, 4H), 1.53 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.48, 150.67, 145.64, 144.11, 140.31, 138.18, 135.34, 128.70, 126.39, 125.75, 123.38, 119.64, 52.58, 34.42, 24.60; **HRMS MALDI** : *m/z* calculated for $C_{72}H_{60}Br_4N_4O_8Zn(M^+)$ 1492.0395, found 1492.0397.

Synthesis of A2B2-**3**



69 mg (0.046 mmol) of the **9** was taken in a schlenk flask and to this was added 44 µl of Cy_2NMe (0.203 mmol) and 10 ml of THF was and the solution was degassed twice via freeze-pump-thaw cycles. To this solution, 6.3 mg (0.007 mmol) of $Pd_2(dba)_3$ and 7.08 mg (0.0138 mmol) of $Pd[P(t\text{-}Bu)_3]_2$ were added and the solution was degassed again two times. Finally 93 µl (0.693 mmol) of 4-methoxystrene was added and the solution was degassed again and then heated at 50 ^{o}C for 48 hrs. TLC showed the the presence of some starting material so another portion of the catalysts, 6.3 mg (0.007 mmol) of $Pd_2(dba)_3$, 7.08 mg (0.0138 mmol) of $Pd[P(t\text{-}Bu)_3]_2$, 44 µl (0.203 mmol) of the base and 93 µl (0.693 mmol) of 4-methoxystyrene was added and the reaction was kept at 60 ^{o}C for another 24 hrs. The reaction was then cooled and the solution was passed through a short silica plug using THF as eluent and the solution was rotavaped off. The solid obtained was then recrystallized from a mixture of DCM and methanol. 55 mg of a green solid with a λ(max) of 480 nm in DCM was obtained. This green solid was dried overnight in vacuum and to this was added 32 mg (0.13 mmol) of *p*-chloranil in 15 ml of toluene and refluxed for 20 hrs to cyclize and oxidize the intermediates. The reaction mixture was diluted with ethyl acetate and subjected to an aqueous NaOH workup to remove the phenolic impurities. The organic solvents were rotavaped off and the product was recrystallized from chloroform/methanol to obtain 22mg of A2B2-**3**. **Yield**: 28%; **UV-Vis in DCM** λ in nm (ε): 480 (182700), 653 (21100), 685 (21000); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 8H), 7.69 (d, *J* = 7.8 Hz, 8H), 7.54 (s, 4H), 7.28 (s, 4H), 6.93 (d, *J* = 8.5 Hz, 8H), 6.72 (d, *J* = 8.6 Hz, 8H), 3.83 (s, 12H), 3.78 (s, 12H), 3.30 – 3.20 (m, 4H), 1.49 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.88, 158.11, 150.33, 145.21, 143.15, 140.55, 139.62, 138.39, 137.56, 134.88, 134.08, 131.17, 127.67, 126.97, 125.95, 123.54, 117.69, 113.35, 77.41, 77.16, 76.91, 55.25, 52.45, 34.46, 24.53; **HRMS MALDI** : Exact mass calculated for $C_{108}H_{92}N_4O_{12}Zn(M^+)$ 1700.6003, found 1700.6007.

Synthesis of A2B2-**4**



23 mg (0.013 mmol) of the A2B2-**3** was refluxed in 10 ml of 1:1 solution of pyridine and aniline for 5 days. The solution was then rotavaped off and the crude product was dissolved in chloroform and worked up with very dilute HCl. The organic layer was collected and rotavaped off. After recrystallization of the crude product from a mixture of chloroform and methanol, 16 mg of the product was obtained as a green solid. **Yield**: 68 %; **UV-Vis in $CHCl_3$** λ in nm, (ε): 507 (145400), 649 (9200), 721 (35800); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (s, 8H), 7.74 (s, 8H), 7.45 (dd, *J* = 24.1, 16.6 Hz, 18H), 6.96 (d, *J* = 7.6 Hz, 8H), 6.74 (d, *J* = 8.3 Hz, 8H), 3.79 (s, 12H), 3.33 – 3.22 (m, 4H), 1.54 (d, *J* = 6.7 Hz, 24H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.41, 158.22, 150.98, 145.65, 143.67, 141.71, 140.18, 138.61, 137.82, 134.65, 133.89, 132.49, 131.17, 129.07, 127.80, 127.12, 126.91, 120.93, 118.29, 113.39, 55.24, 34.66, 24.61; **HRMS MALDI** : Exact mass calculated for $C_{116}H_{90}N_6O_8Zn(M^+)$ 1758.6112, found 1758.6121.

Characterization data for all synthesized compounds

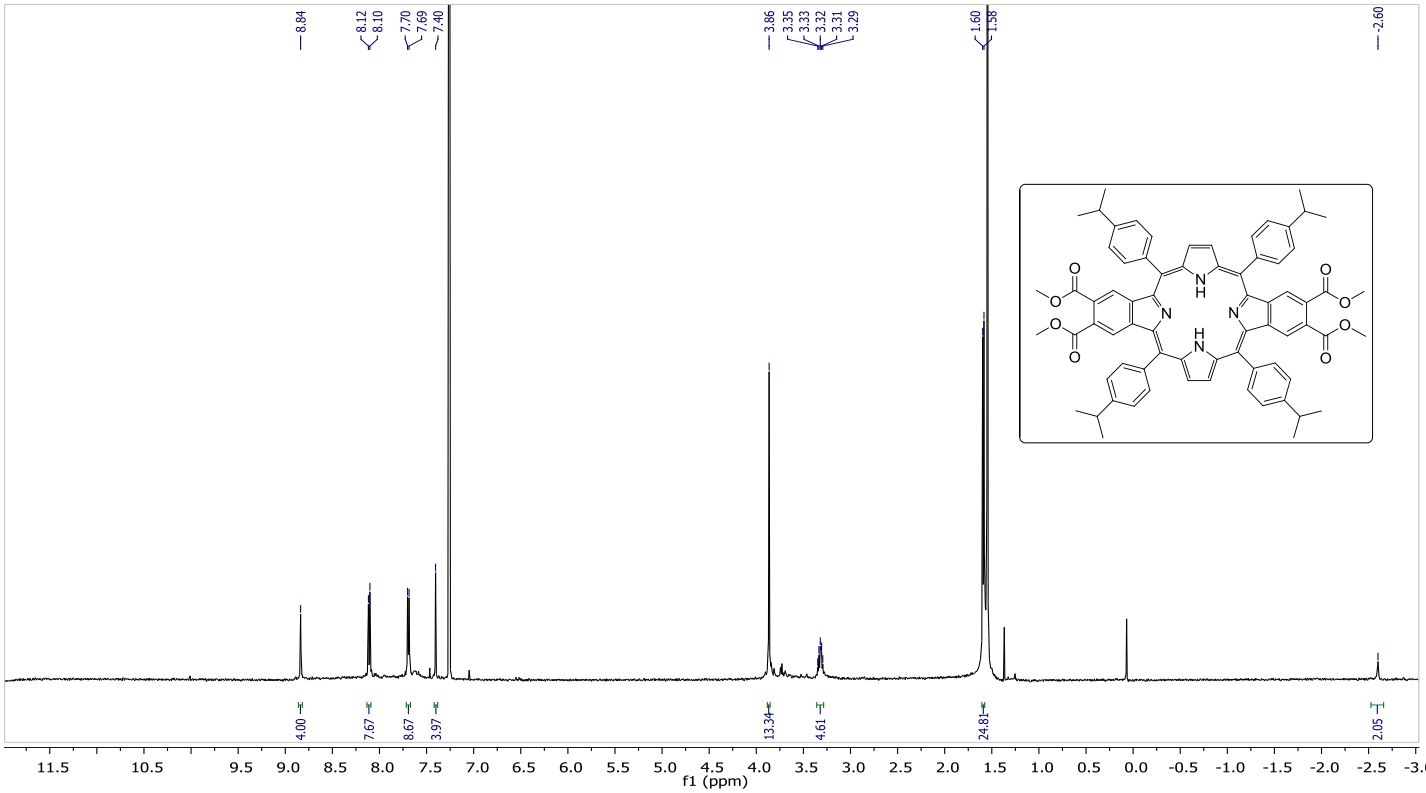


Figure S1. ^{1}H NMR of **7** in $CDCl_3$ at 500 MHz.

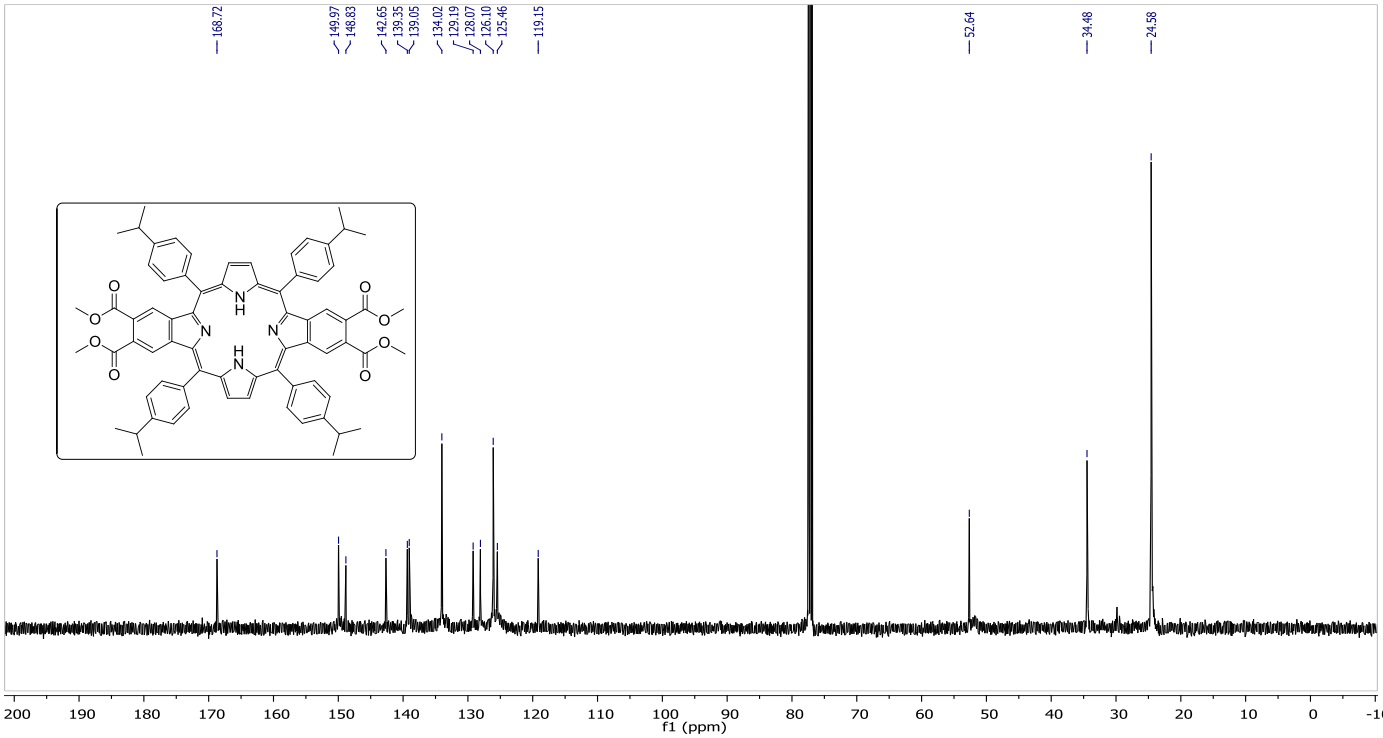


Figure S2. ^{13}C NMR of **7** in $CDCl_3$ at 126 MHz.

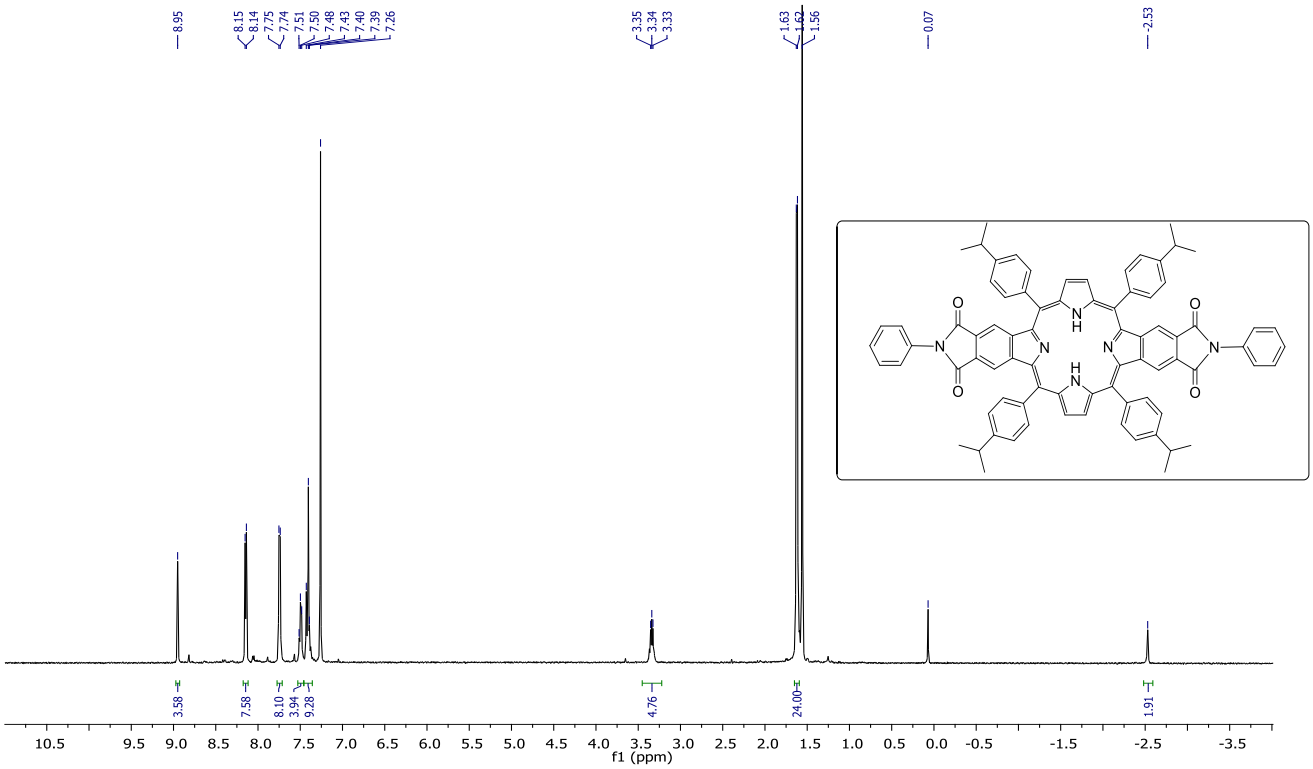


Figure S3. ^{1}H NMR of **7a** in $CDCl_3$ at 500 MHz.

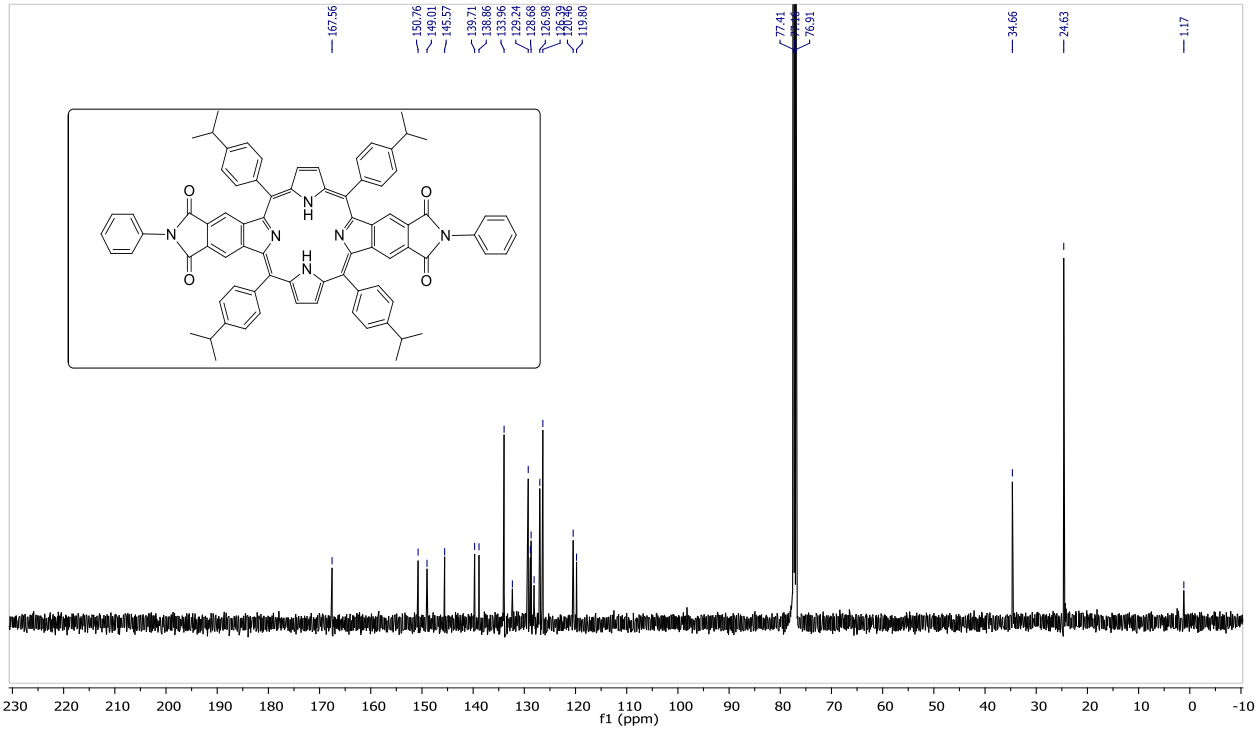


Figure S4. ^{13}C NMR of **7a** in $CDCl_3$ at 126 MHz.

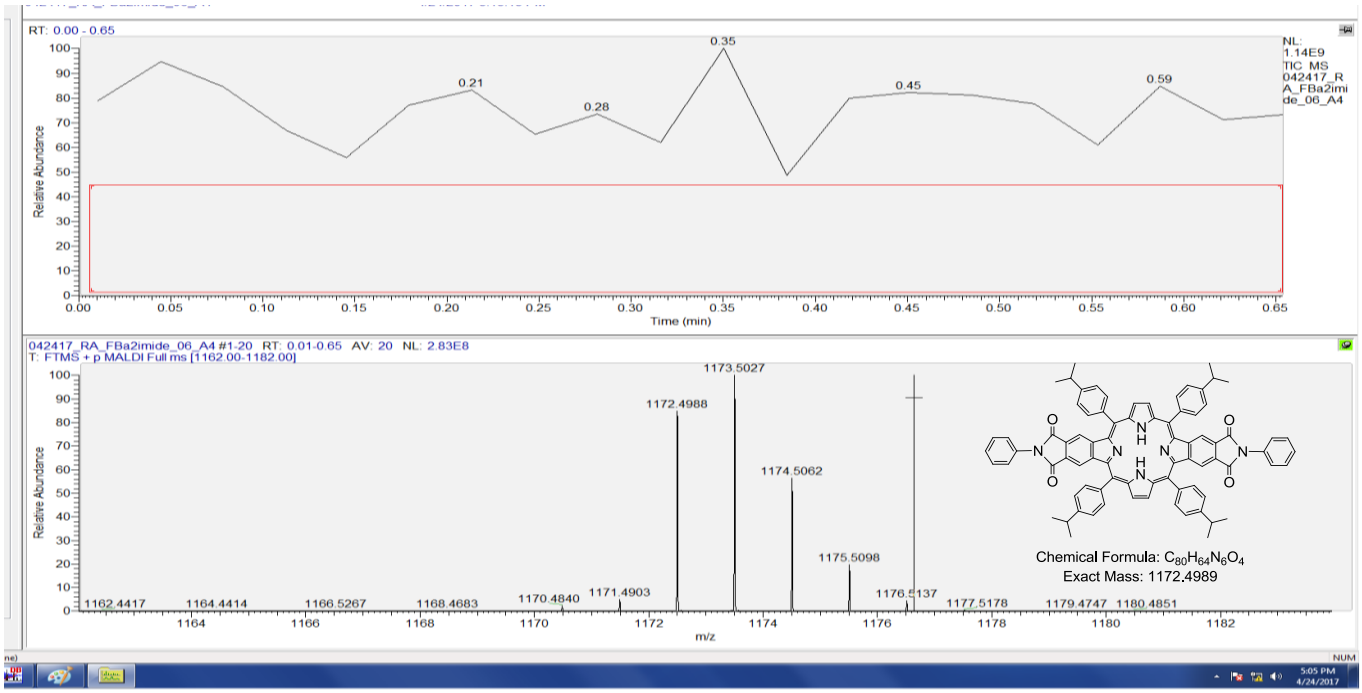


Figure S5. HRMS-MALDI of **7a.**

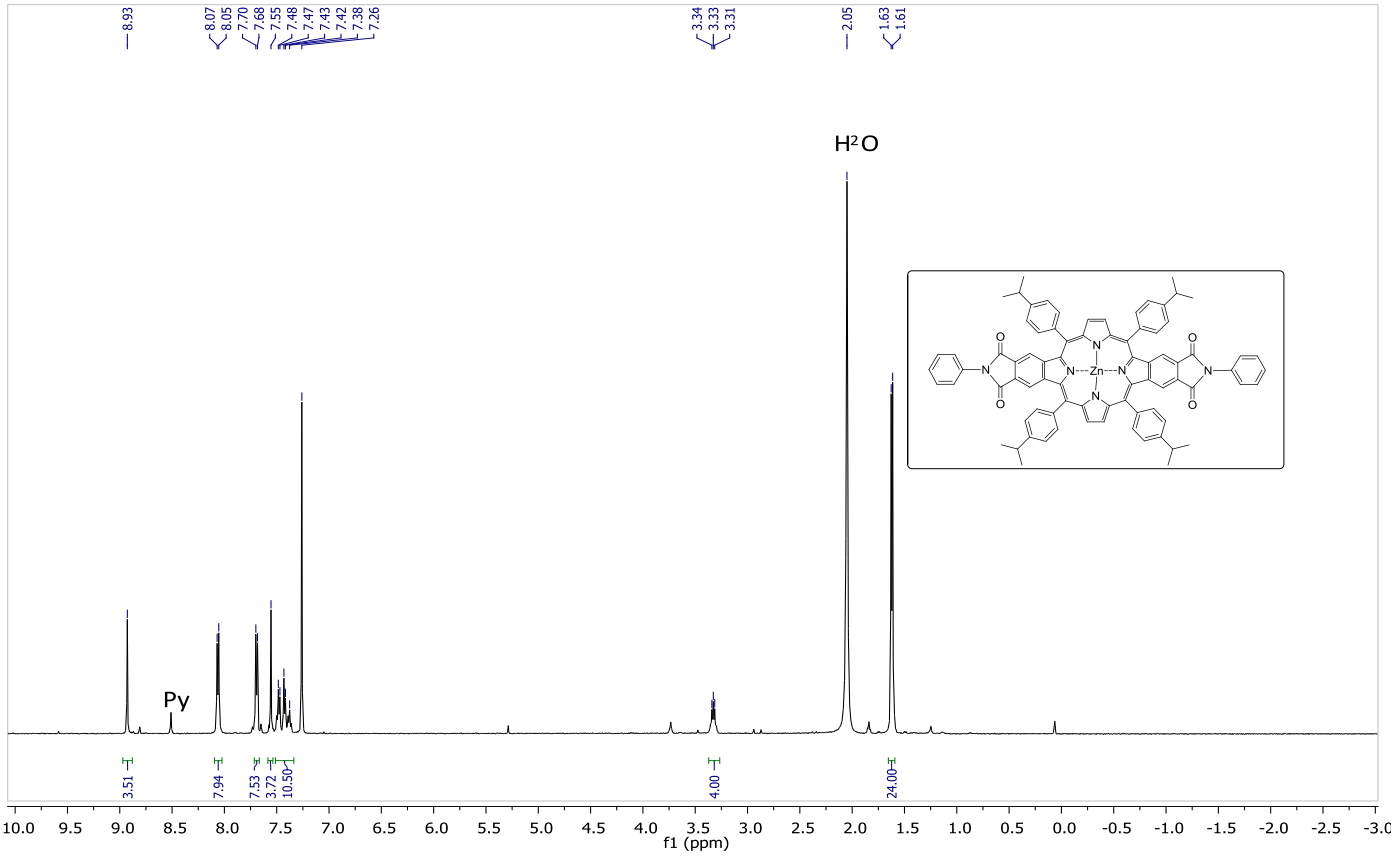


Figure S6. ^{1}H NMR of B2-**2** in $CDCl_3$(added one drop of d5-pyridine) at 500 MHz.

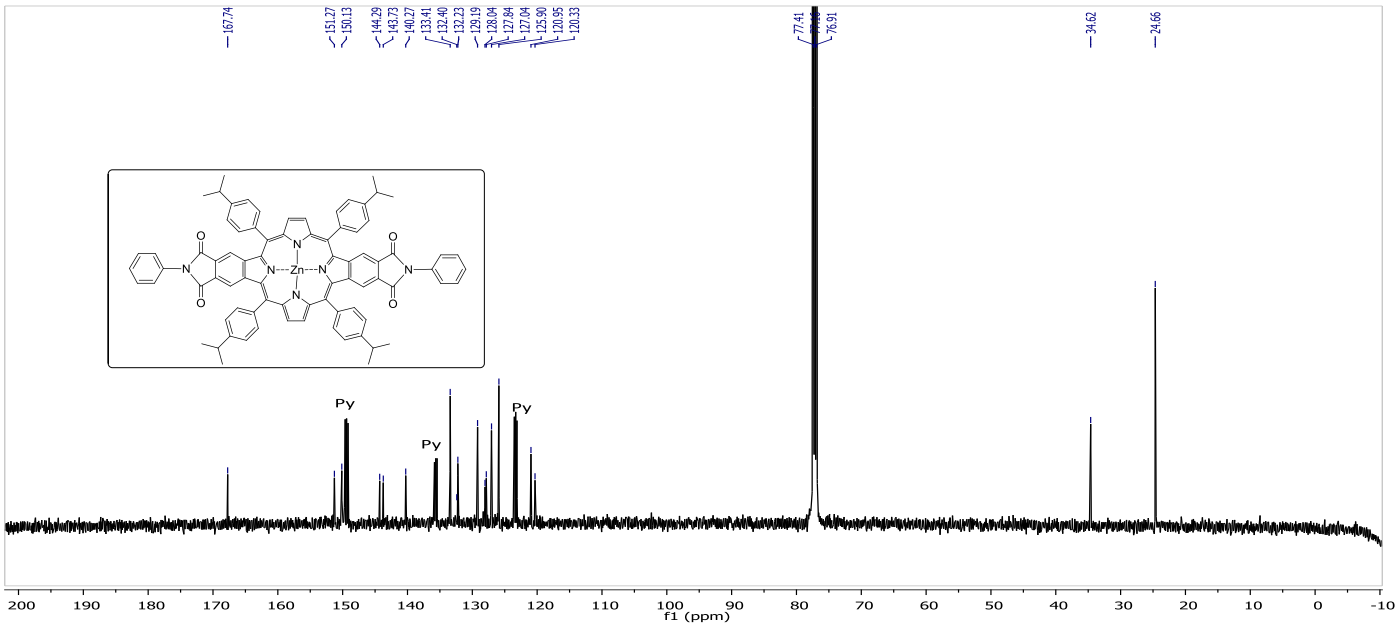


Figure S7. ^{13}C NMR of B2-**2** in $CDCl_3$(added one drop of d5-pyridine) at 126 MHz.

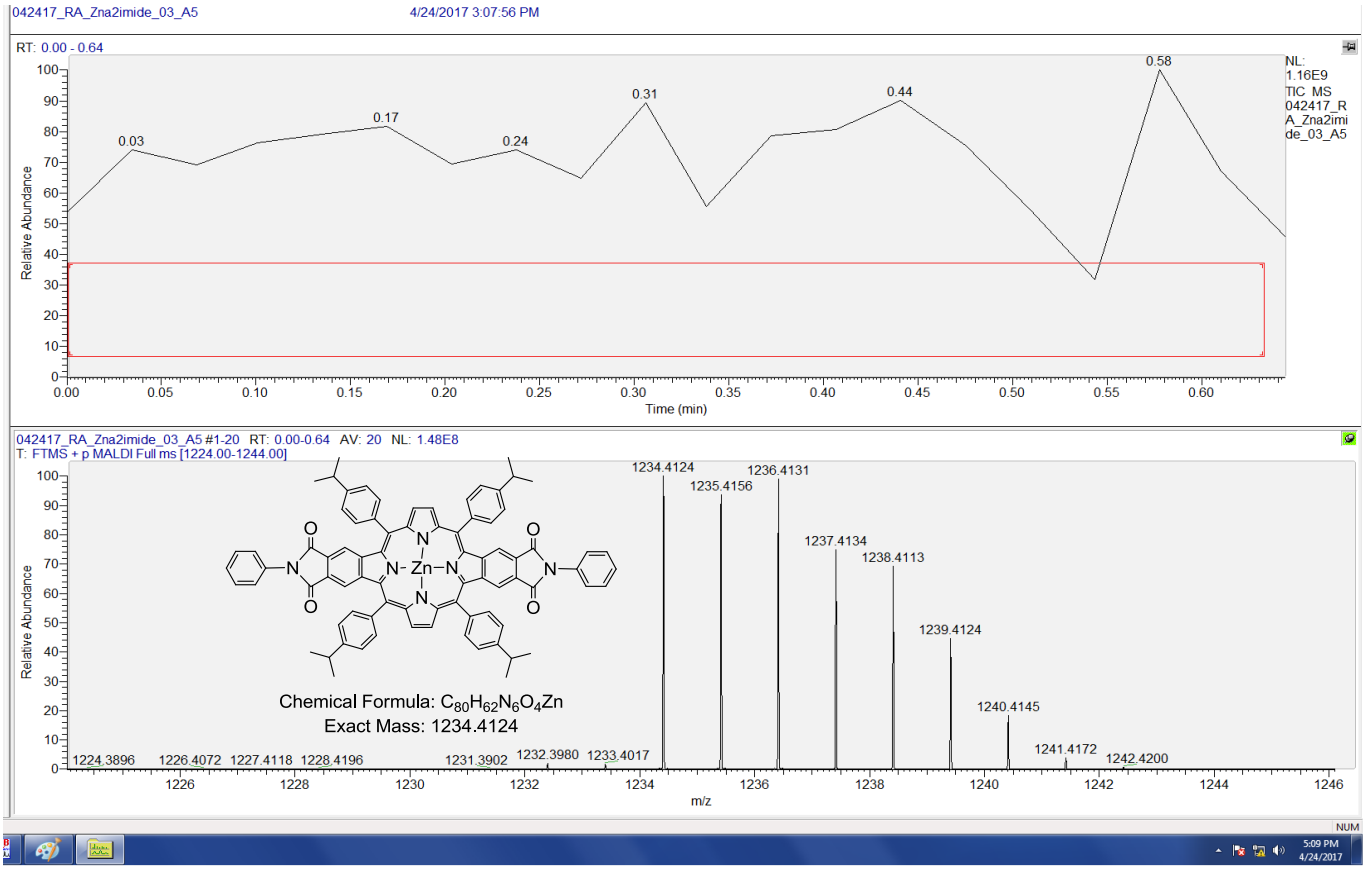


Figure S8. HRMS-MALDI data for B2-**2.**

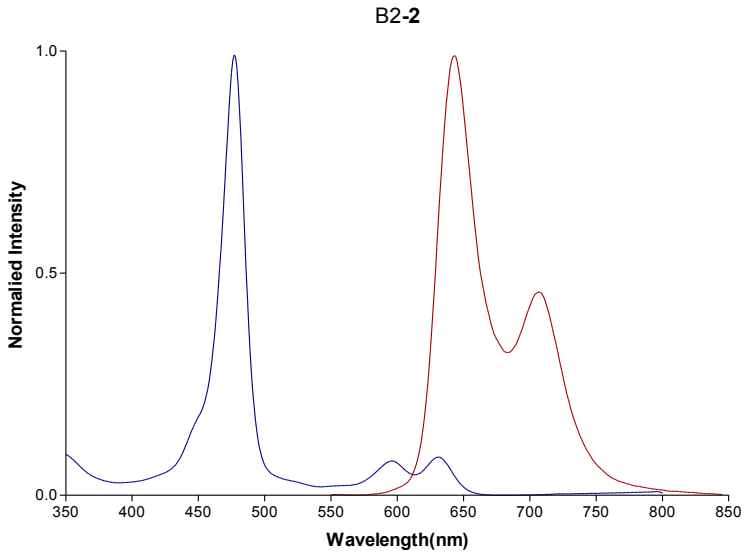


Figure S9. Normalized overlap of UV and Fluorescence of B2-**2** in $CHCl_3$ (Conc. 10^{-6}M).

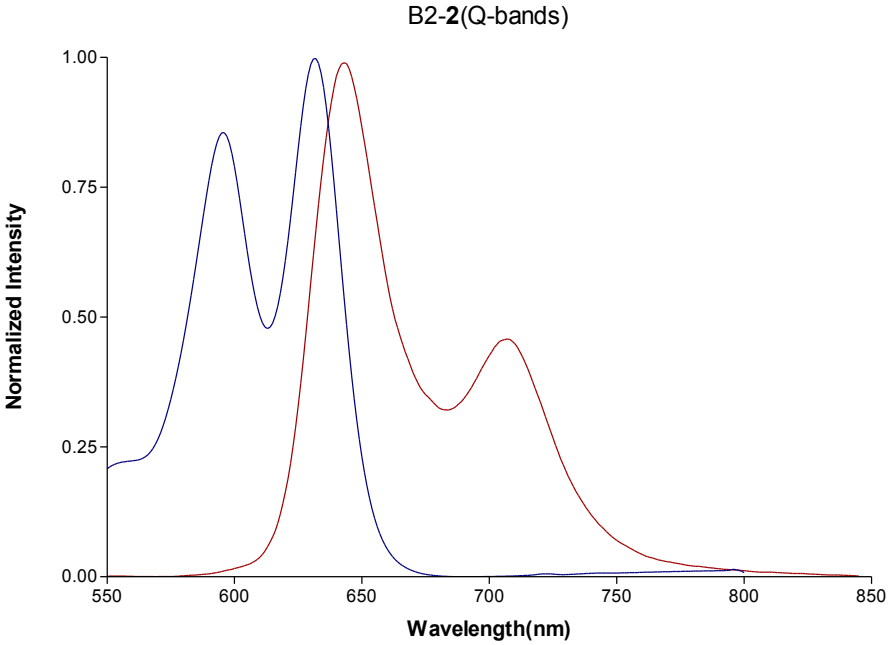


Figure S10. Normalized overlap of UV and Fluorescence of B2-**2** in $CHCl_3$ (Q-bands).

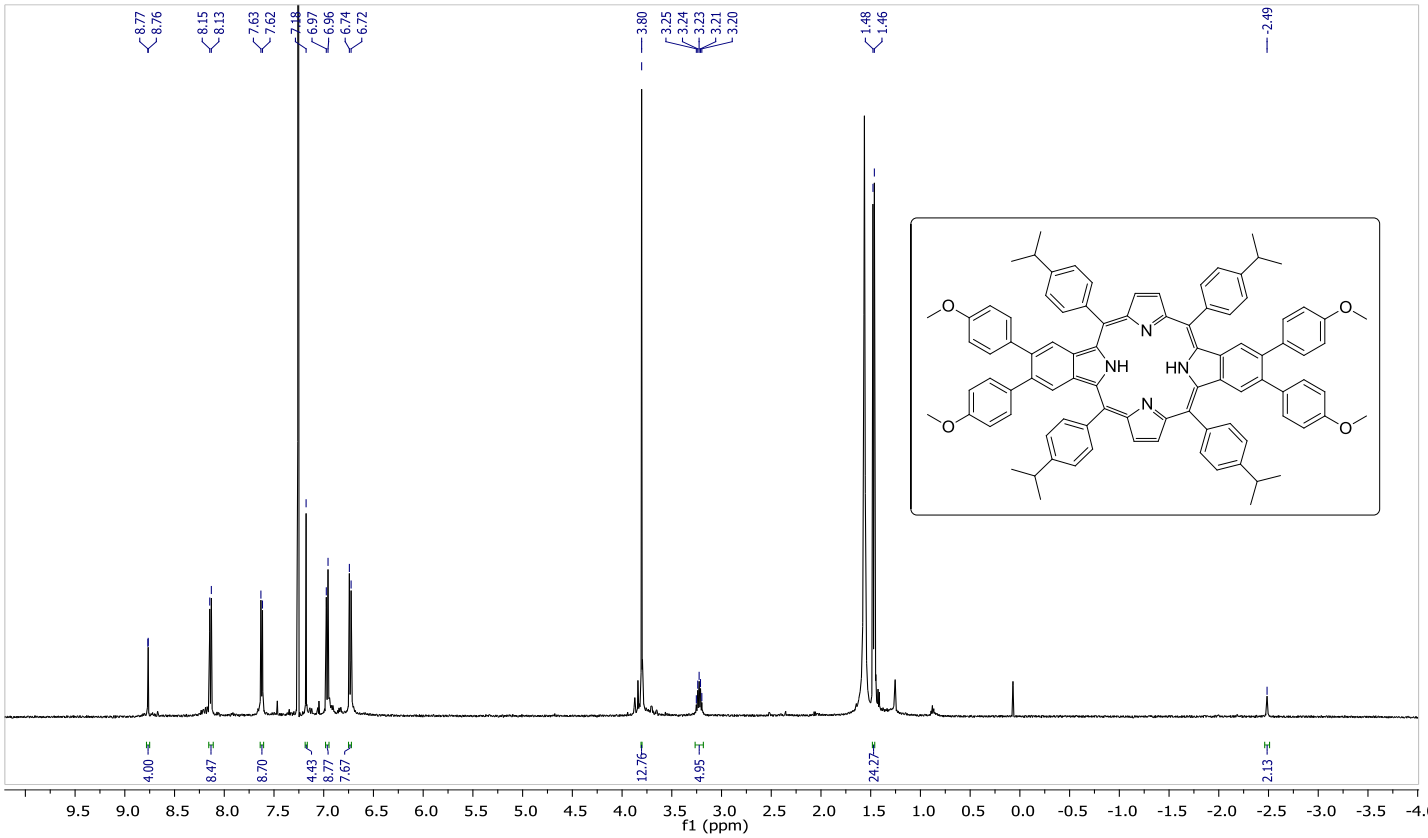


Figure S11. ^{1}H NMR of **6** in $CDCl_3$ at 500 MHz.

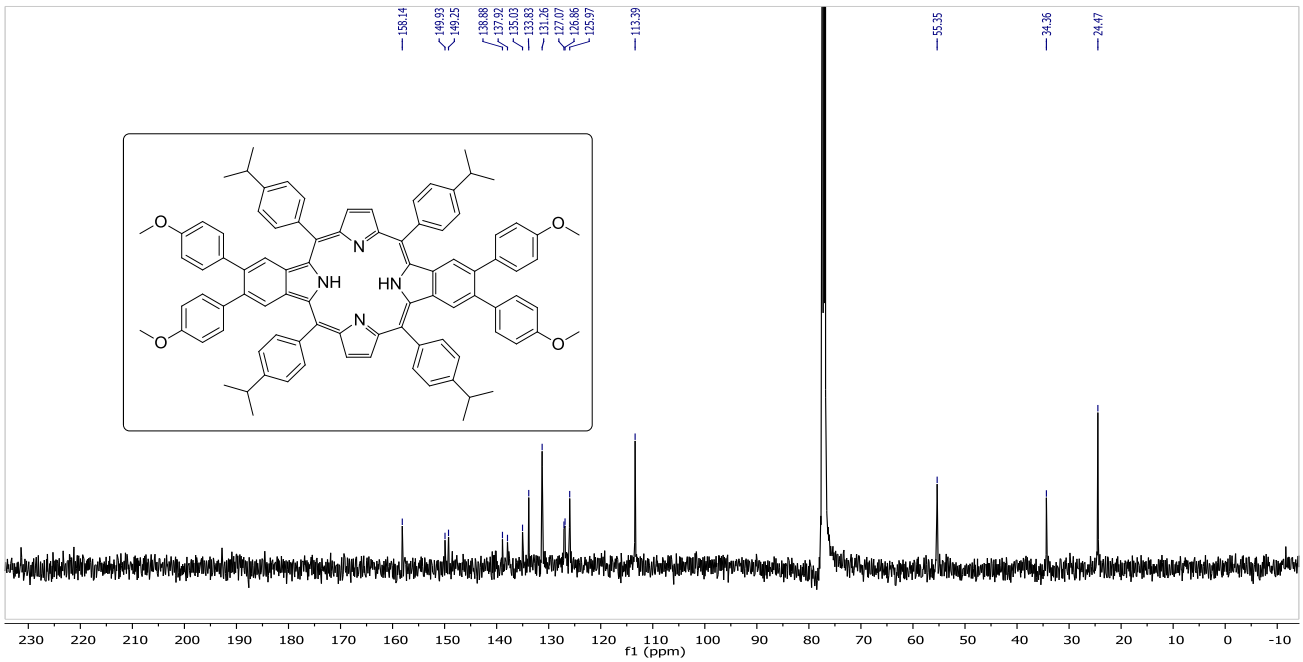


Figure S12. ^{13}C NMR of **6** in $CDCl_3$ at 126 MHz.

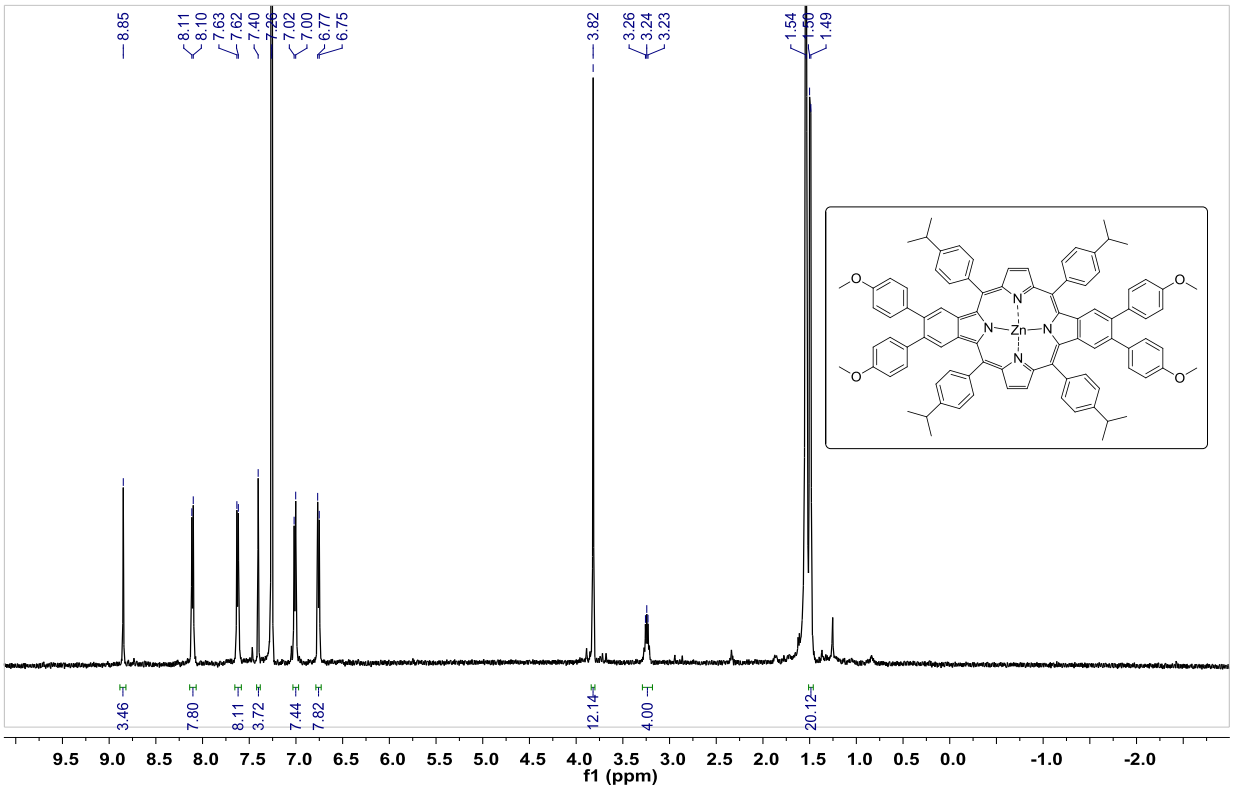


Figure S13. ^{1}H NMR of A2-**1** in $CDCl_3$ at 500 MHz.

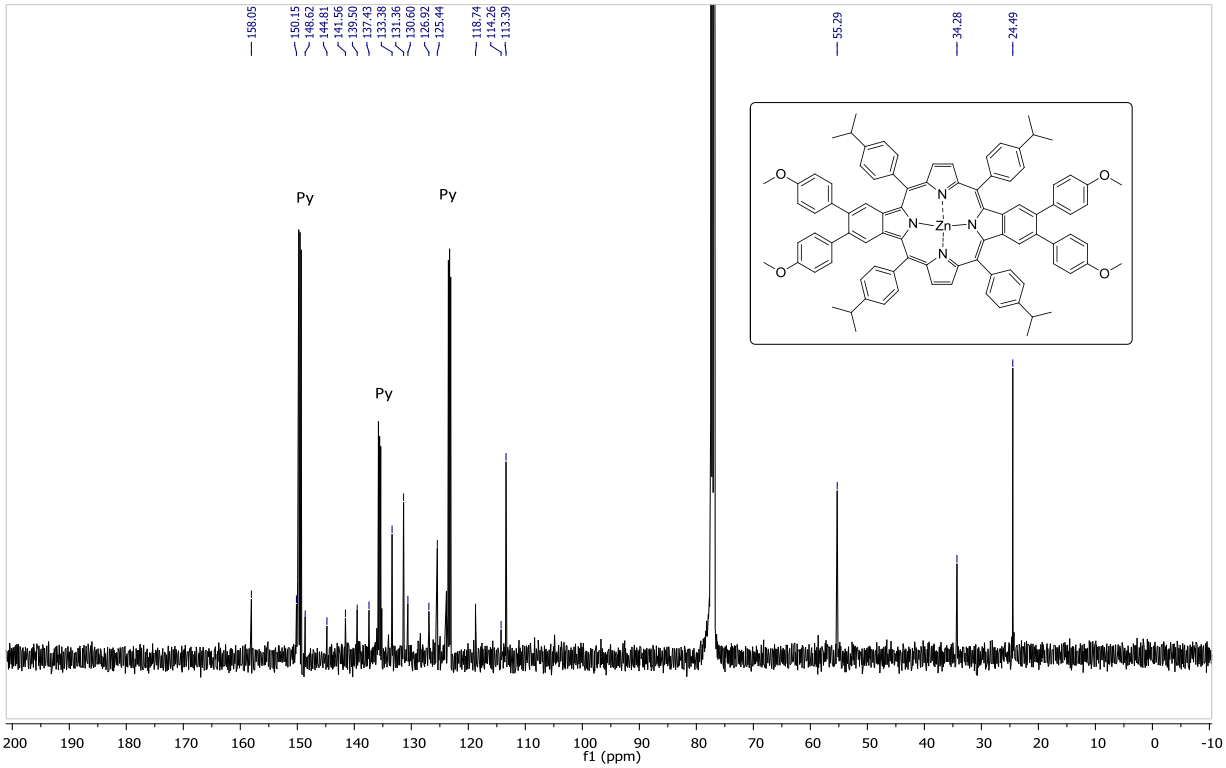


Figure S14. ^{13}C NMR of A2-**1** in $CDCl_3$(added one drop of d5-pyridine) at 500 MHz.

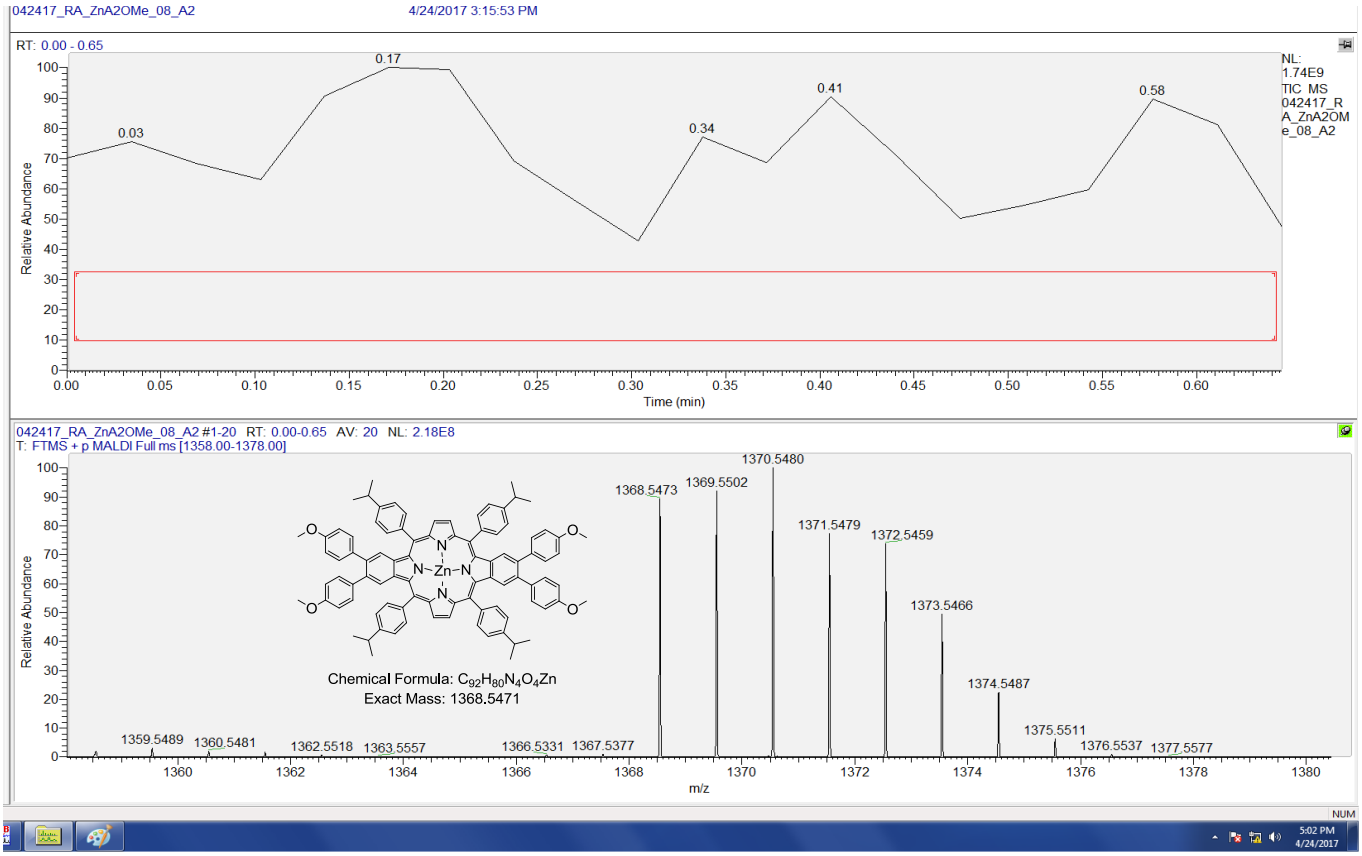


Figure S15. HRMS MALDI of A2-**1.**

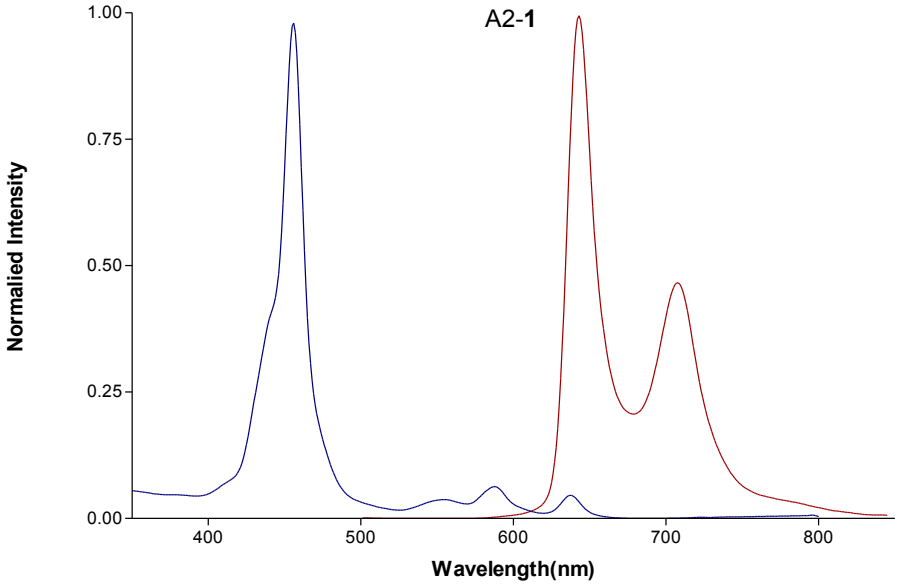


Figure S16. Normalized overlap of UV and Fluorescence of A2-**1** in $CHCl_3$ (Conc. 10^{-6}M).

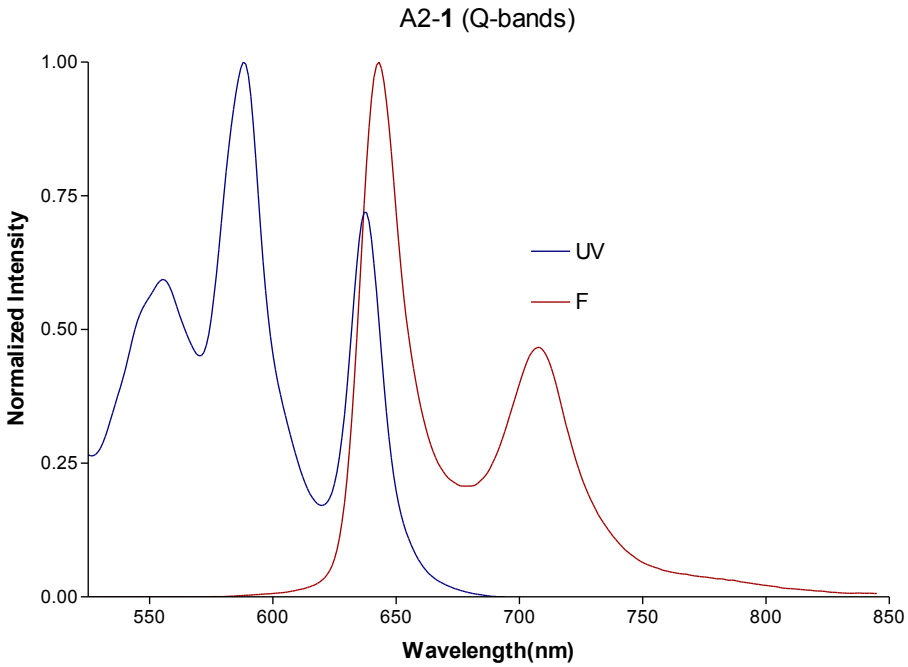


Figure S17. Normalized overlap of UV and Fluorescence of A2-**1** in $CHCl_3$ (Q-bands).

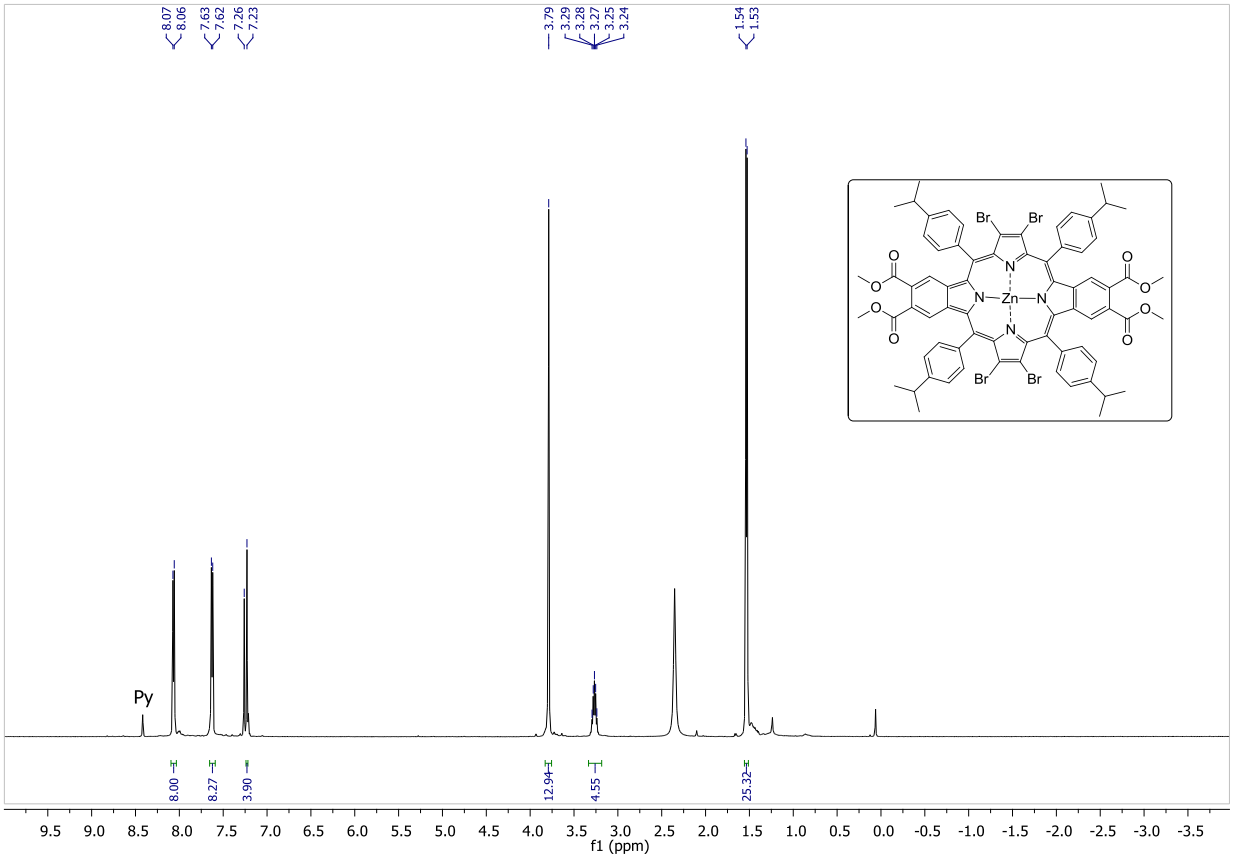


Figure S18. ^1H NMR of **9** in $CDCl_3$(added 1 drop of d5-pyridine) at 500 MHz.

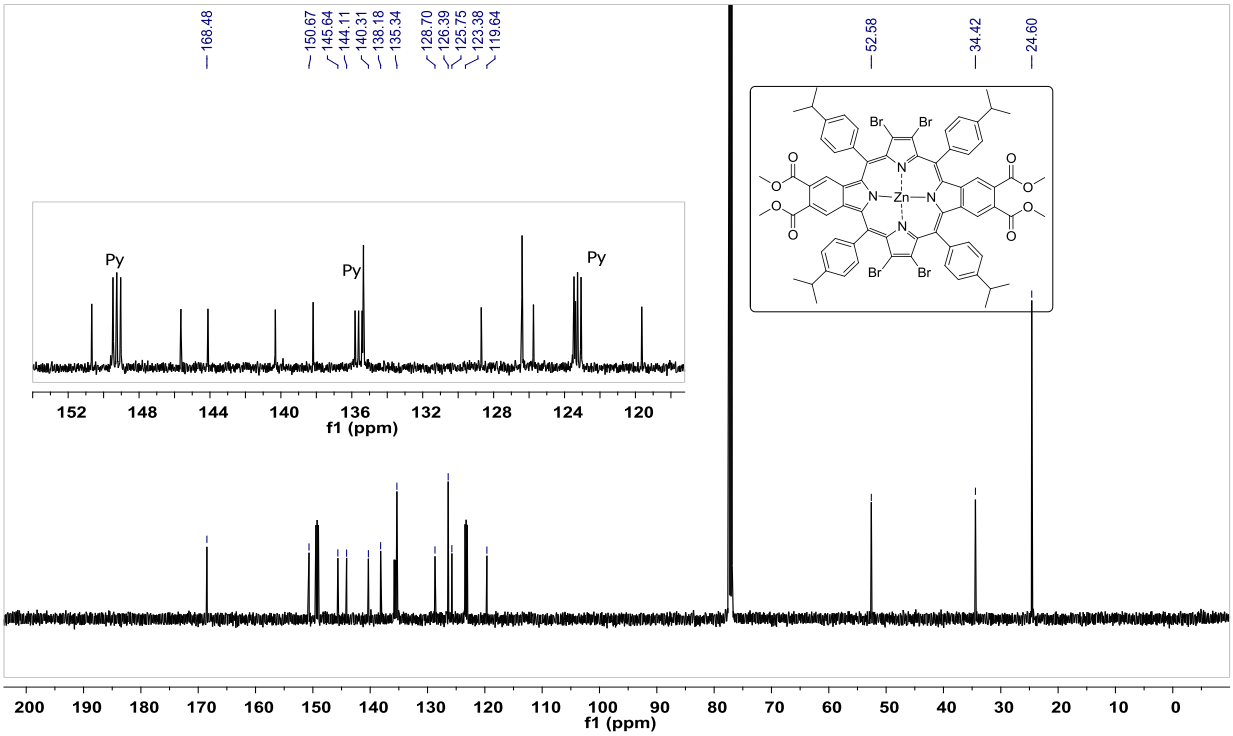


Figure S19. ^{13}C NMR of **9** in $CDCl_3$(added 1 drop of d5-pyridine) at 126 MHz.

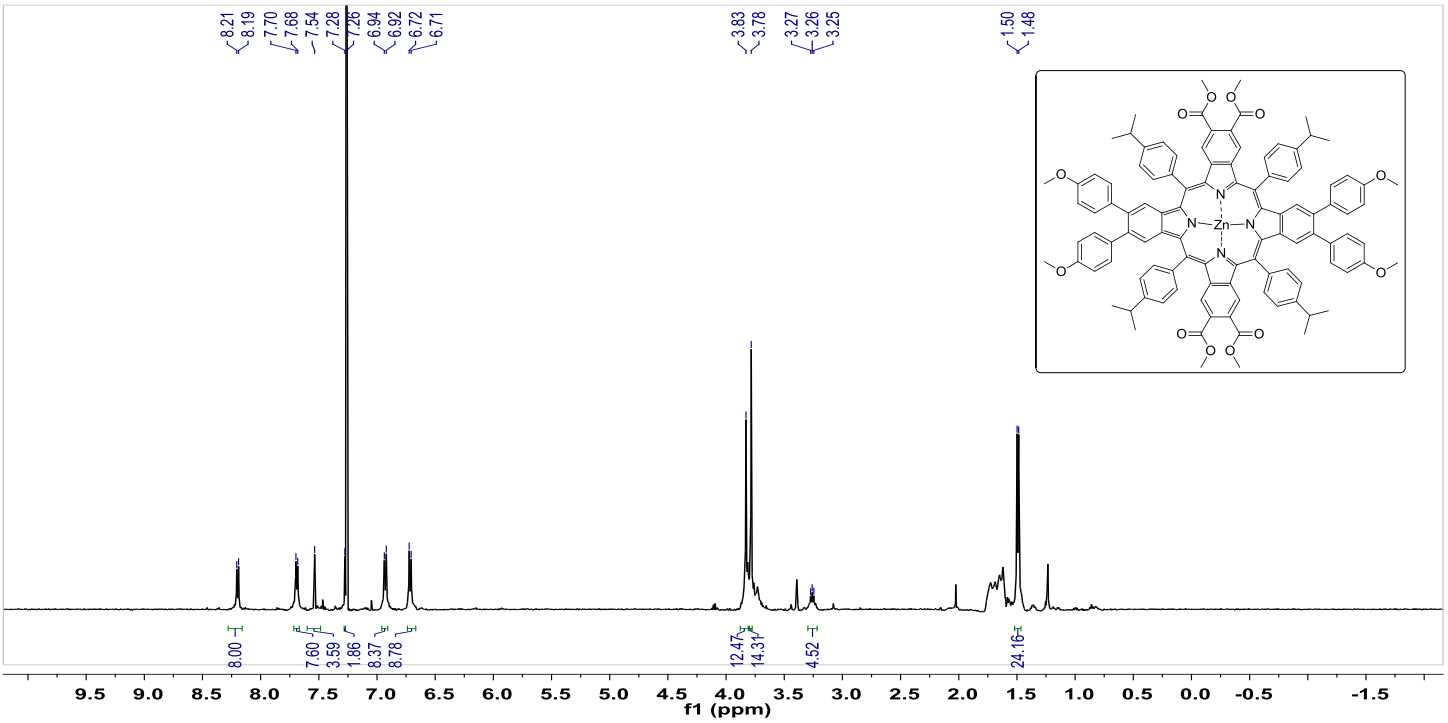


Figure S20. ^{1}H NMR of A2B2-**3** in $CDCl_3$ at 500 MHz.

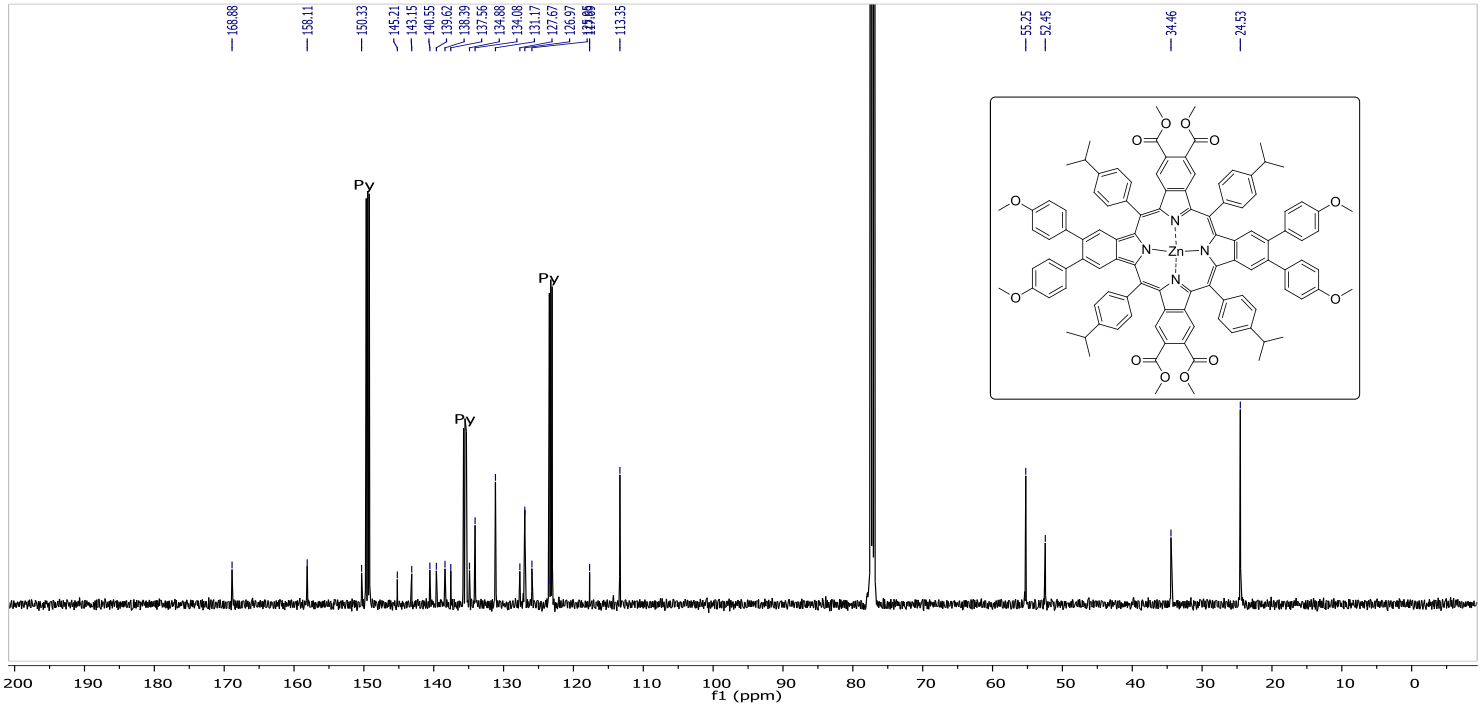


Figure S21. ^{13}C NMR of A2B2-**3** in $CDCl_3$(added one drop of d5-pyridine) at 126 MHz.

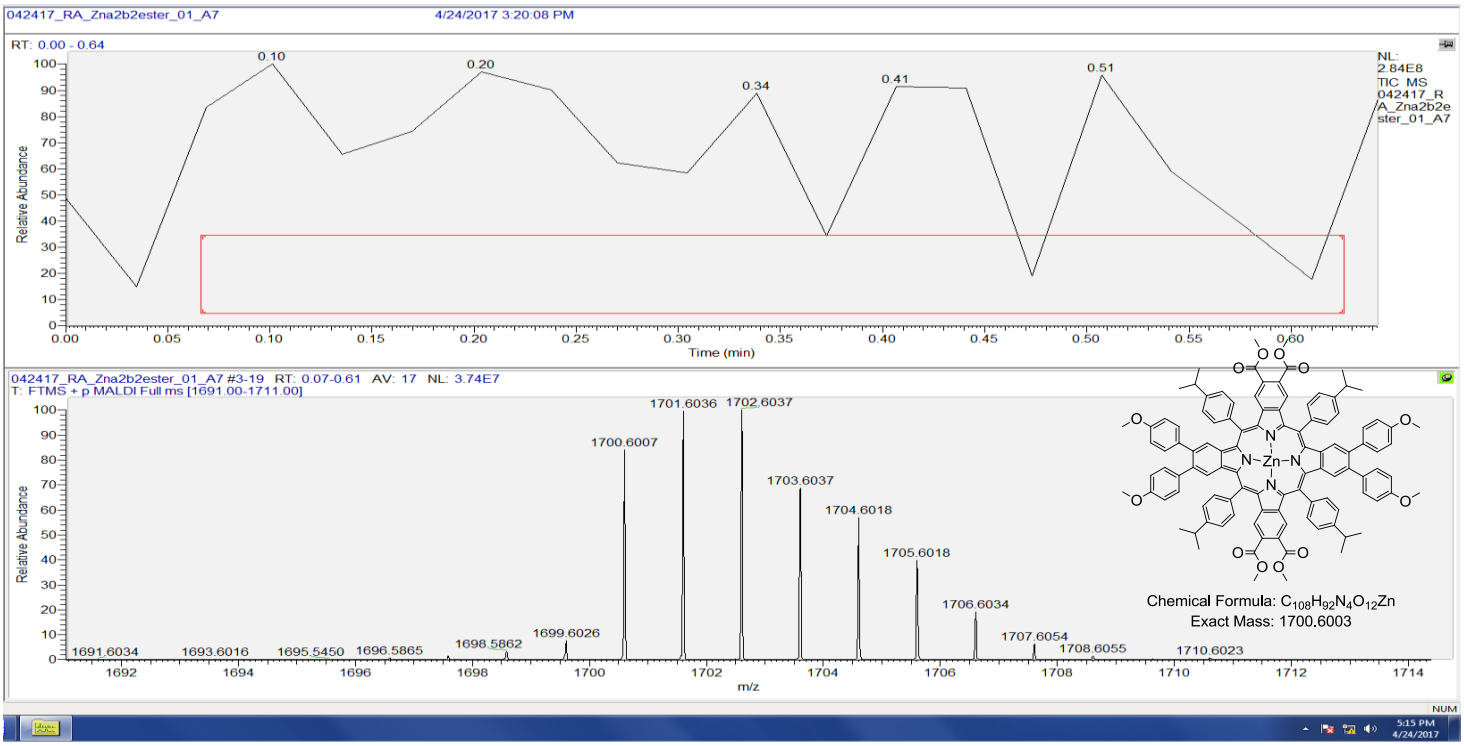


Figure S22. HRMS-MALDI of A2B2-**3.**

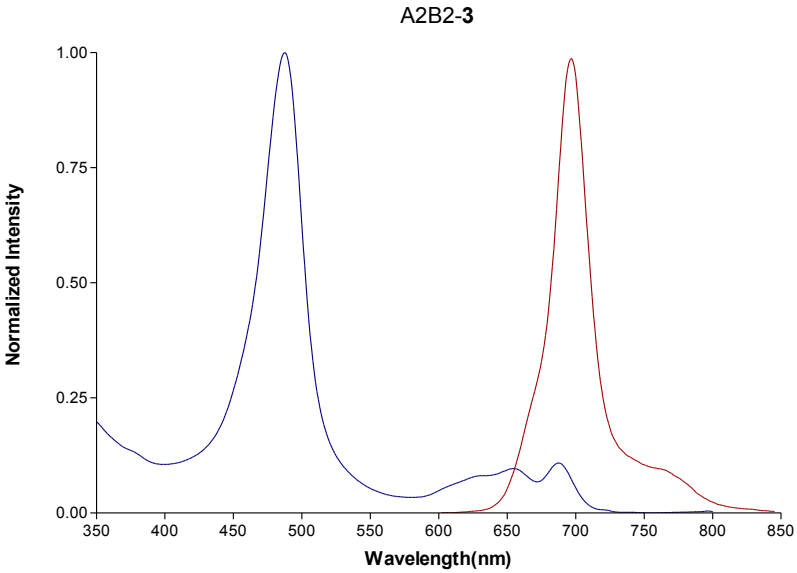


Figure S23. Normalized overlap of UV and Fluorescence of A2B2-**3** in CHCl3 (Conc. 10-6M).

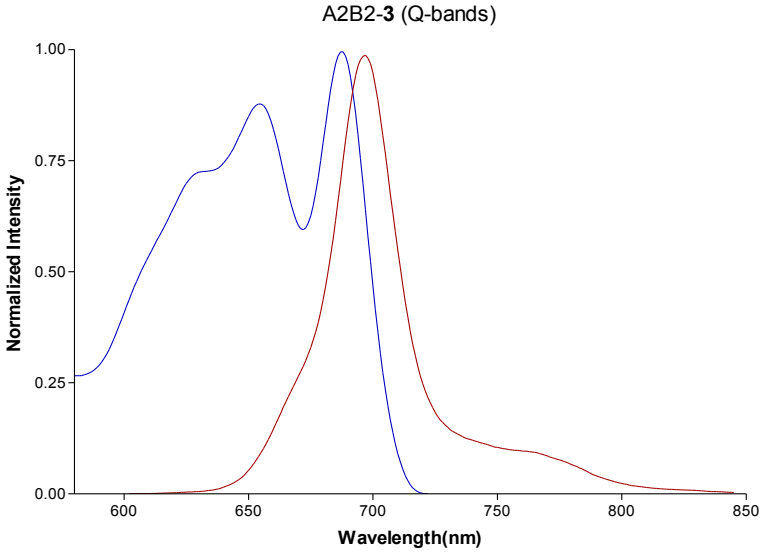


Figure S24. Normalized overlap of UV and Fluorescence of A2B2-**3** in $CHCl_3$ (Q-bands).

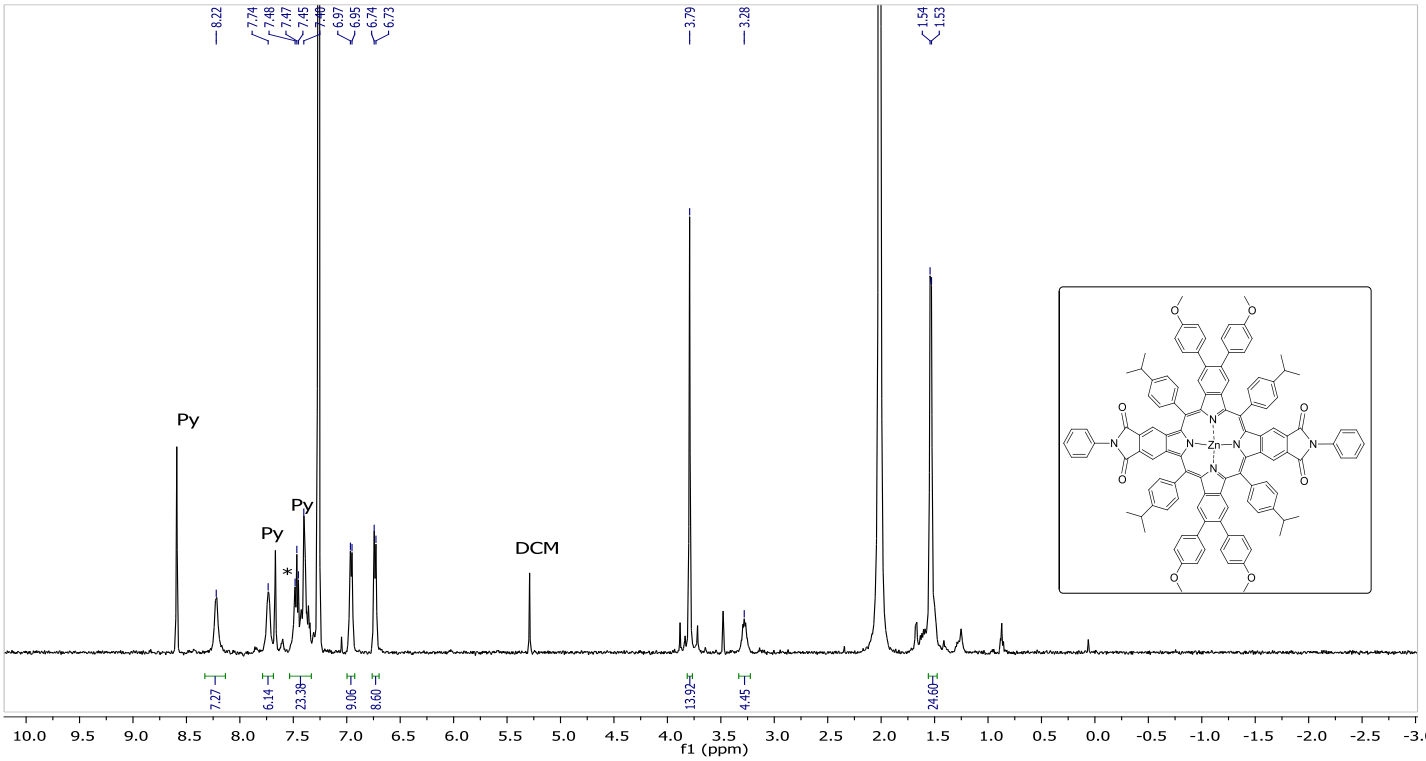


Figure S25. ^{1}H NMR of A2B2-**4** in $CDCl_3$(added one drop of d5-Py) at 500 MHz.

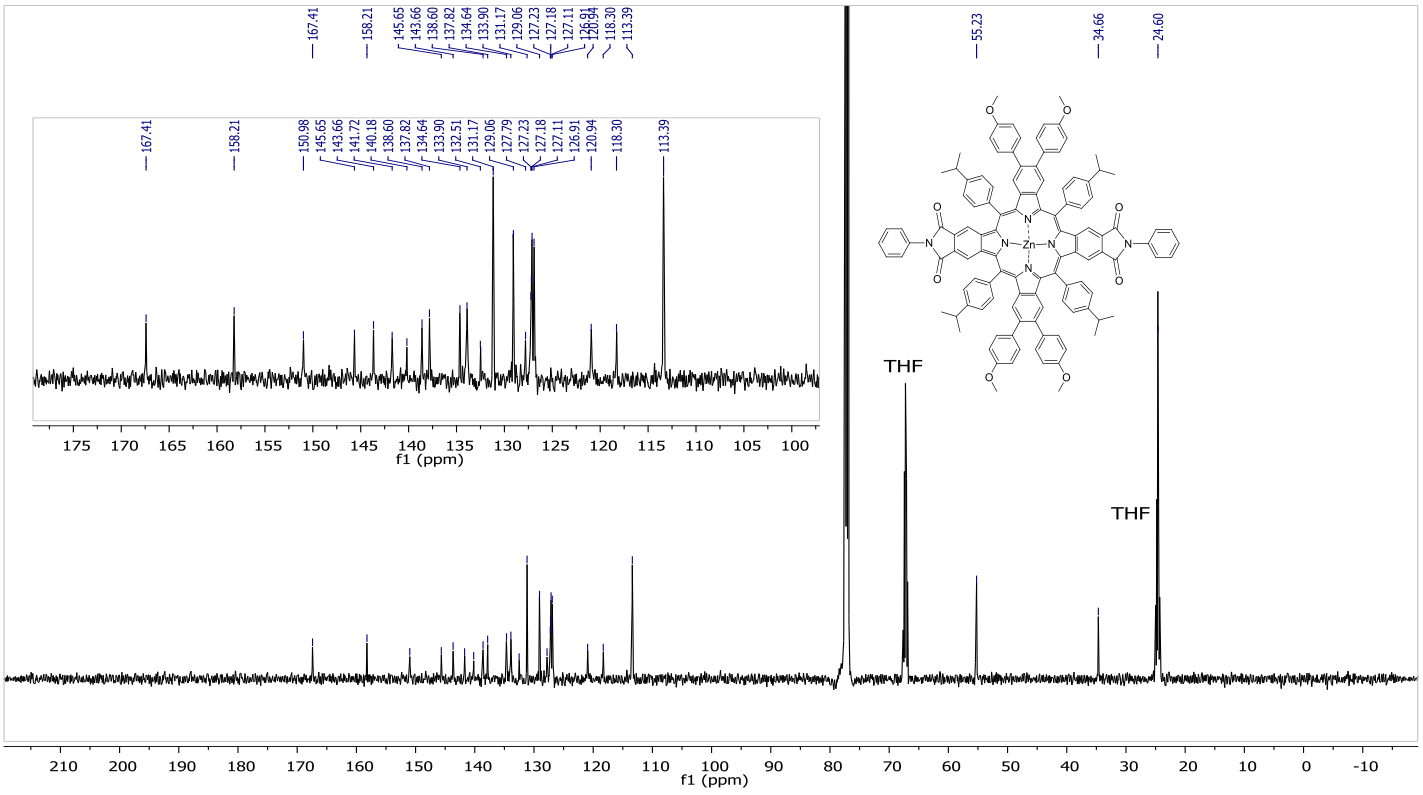


Figure S26. ^{13}C NMR of A2B2-**4** in $CDCl_3$(added one drop of d8-THF) at 126 MHz.

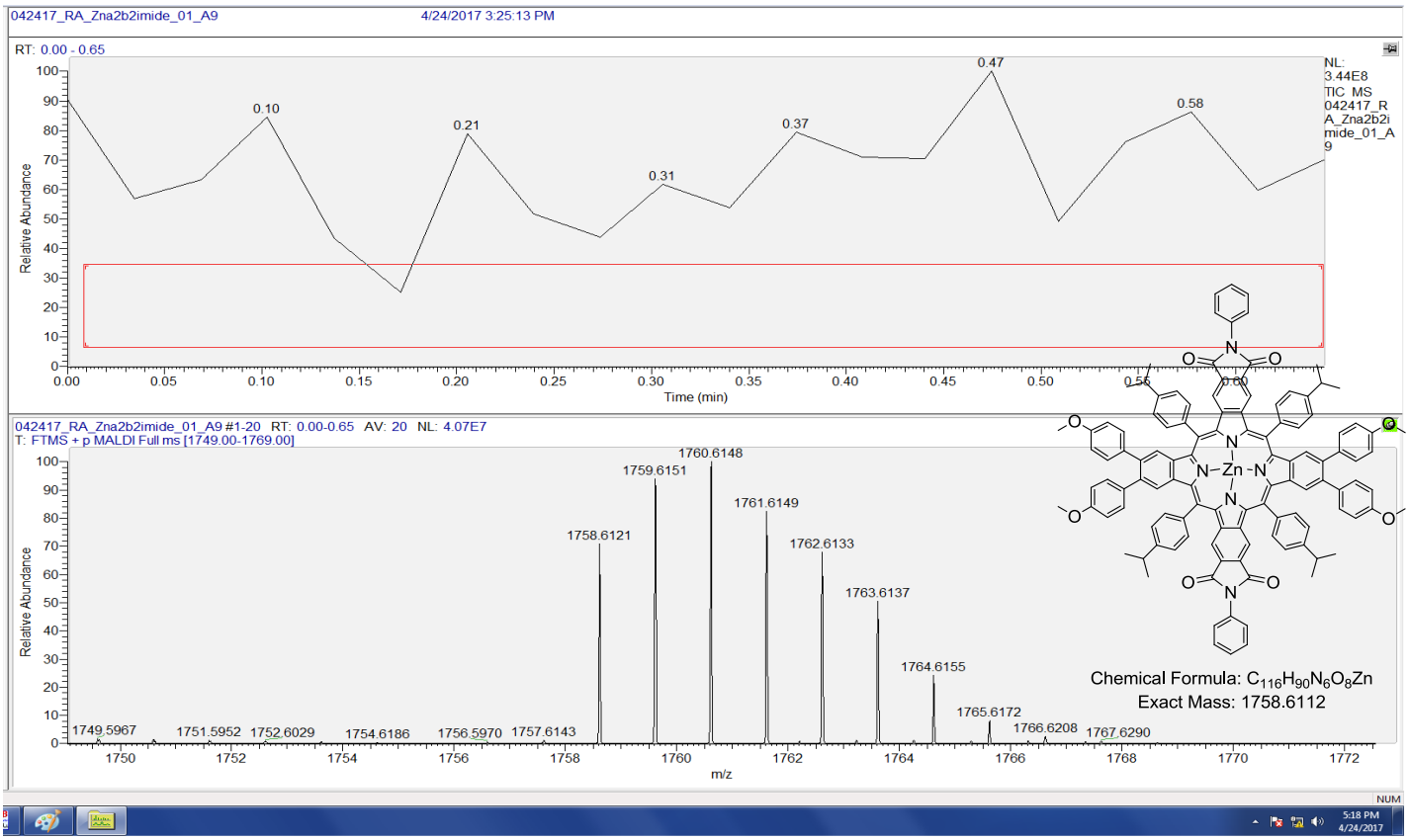


Figure S27. HRMS MALDI of A2B2-**4.**

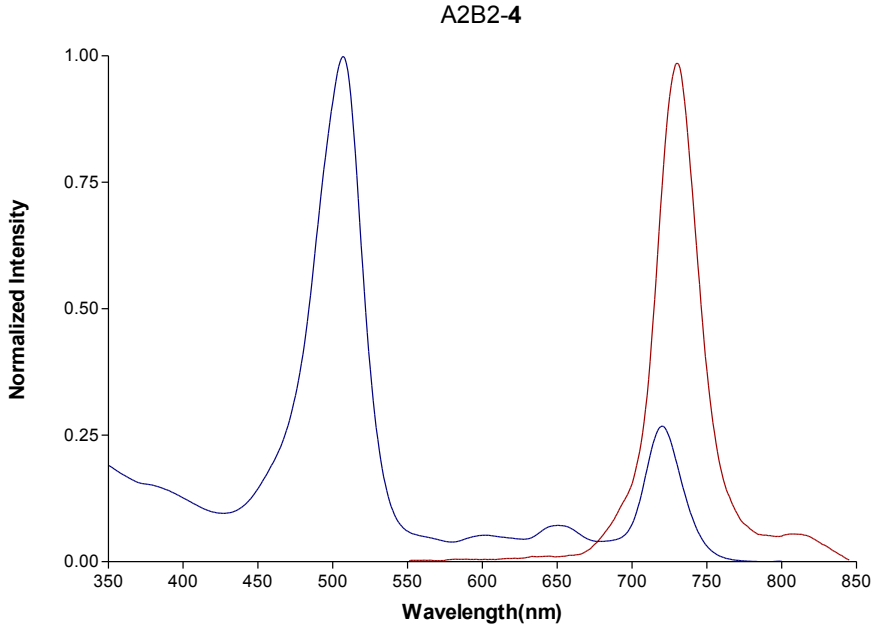


Figure S28. Normalized overlap of UV and Fluorescence of A2B2-**4** in $CHCl_3$ (Conc. 10^{-6}M).

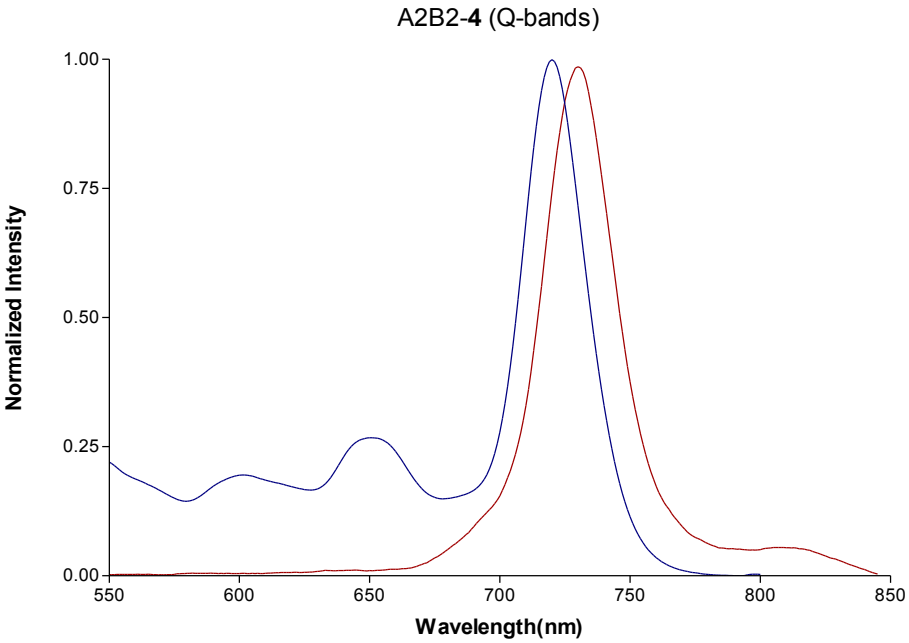


Figure S29. Normalized overlap of UV and Fluorescence of A2B2-**4** in $CHCl_3$ (Q-bands).

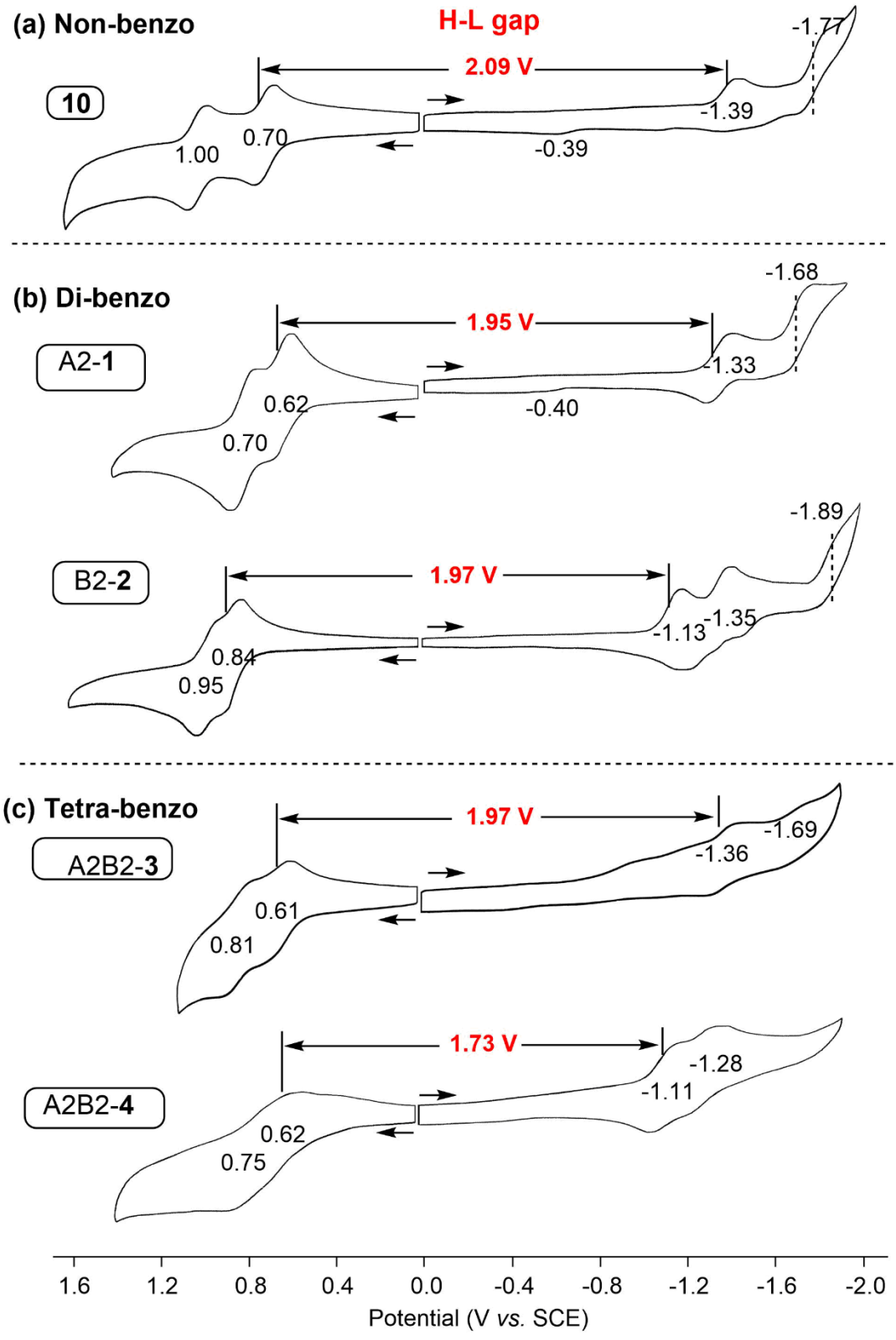


Figure S30. Cyclic voltammograms of investigated compounds in CH_2Cl_2 containing 0.1 M TBAP.

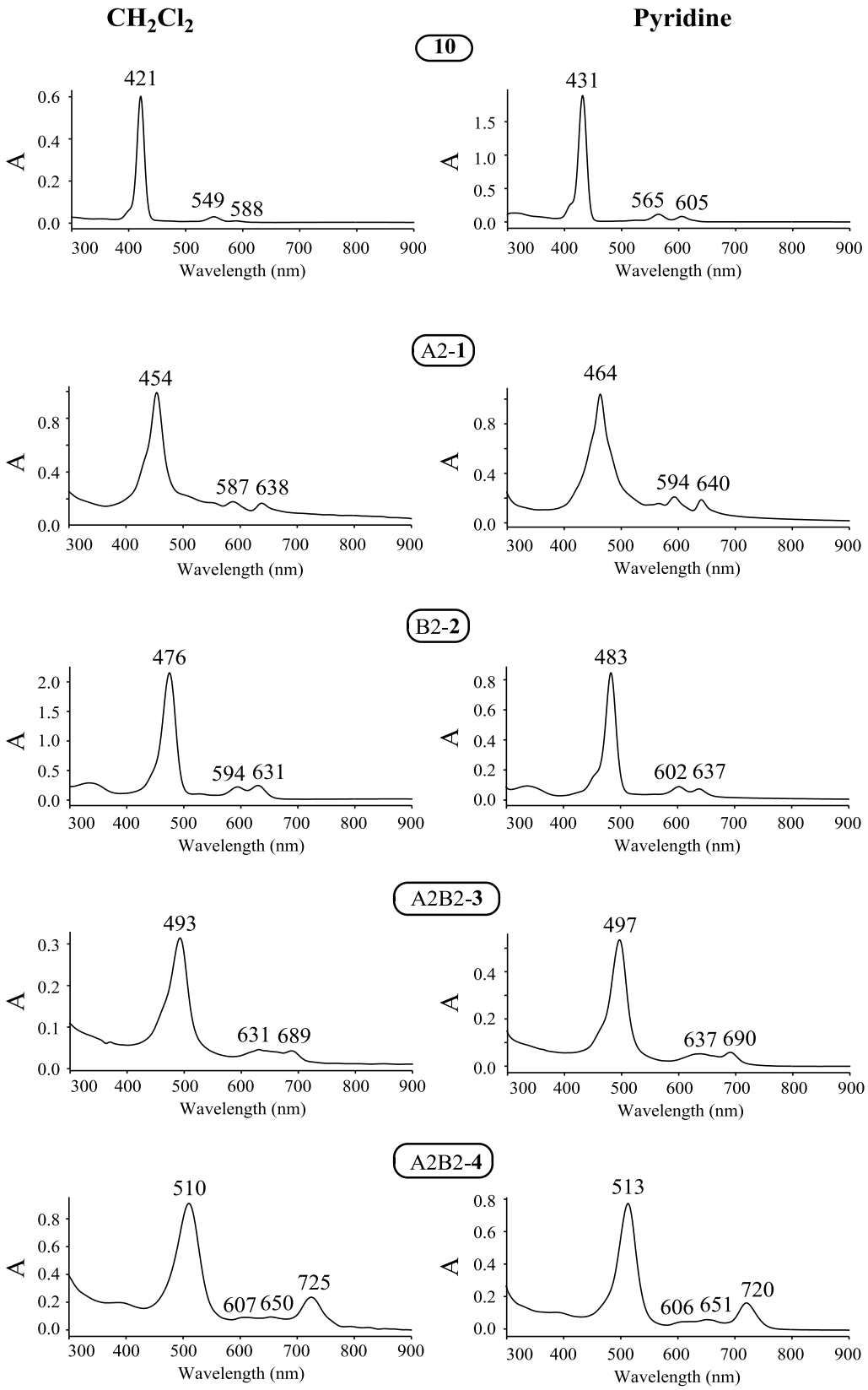


Figure S31. UV-vis spectra of investigated compounds in CH_2Cl_2 and Py containing 0.1 M TBAP.

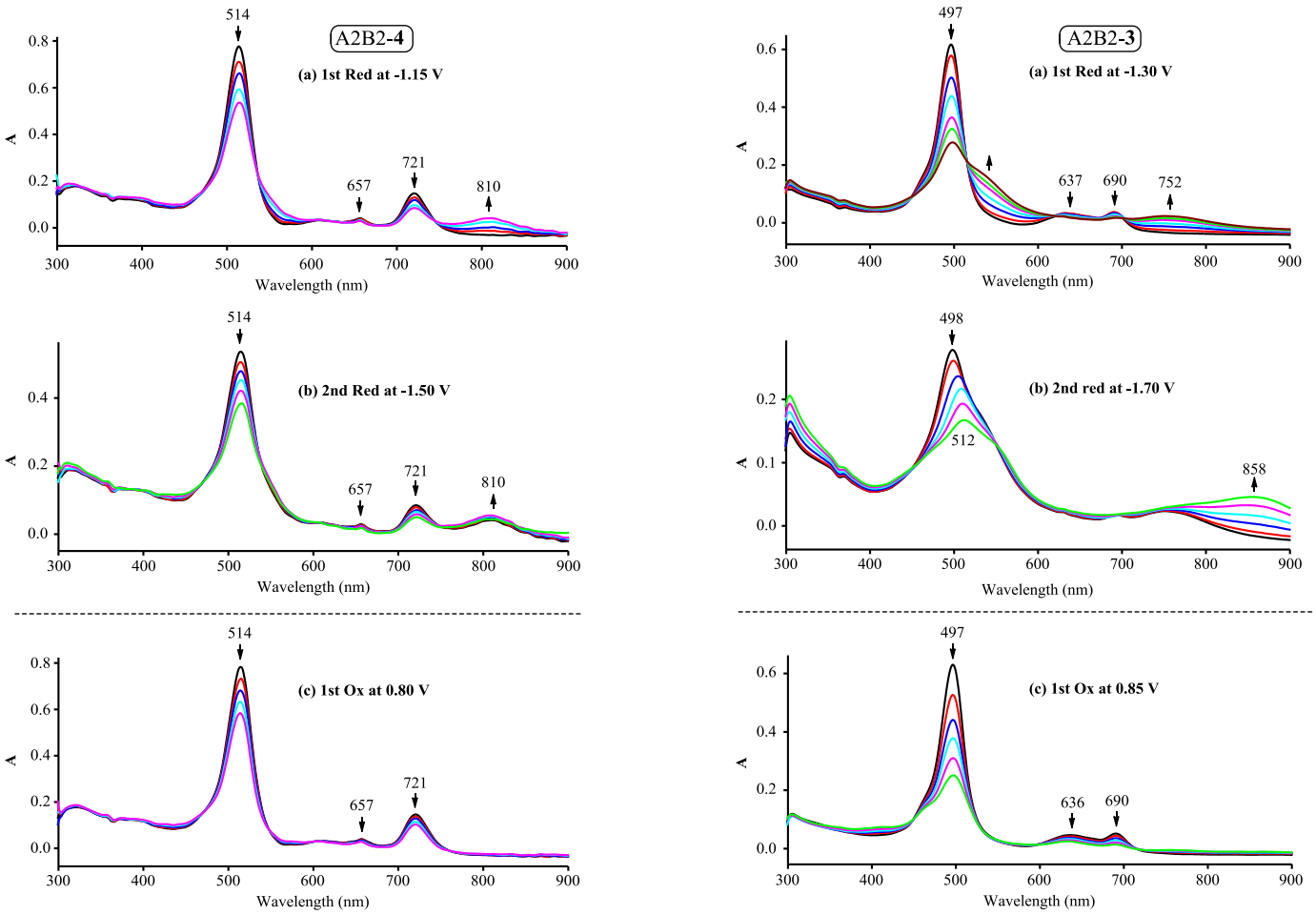


Figure S32. Spectral changes during first two reductions and the first oxidation of A2B2-**4** and A2B2-**3** in pyridine containing 0.1 M TBAP.

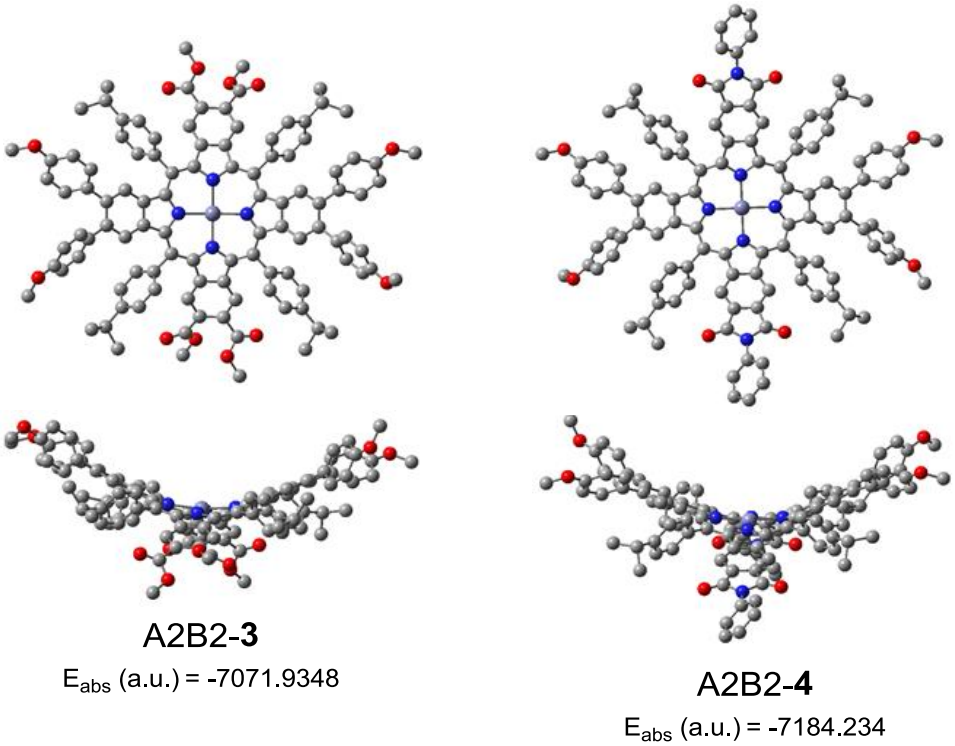


Figure S33. Geometry-optimized molecule structures of A2B2-**3** and A2B2-**4**; (Top) front view (bottom) side view.

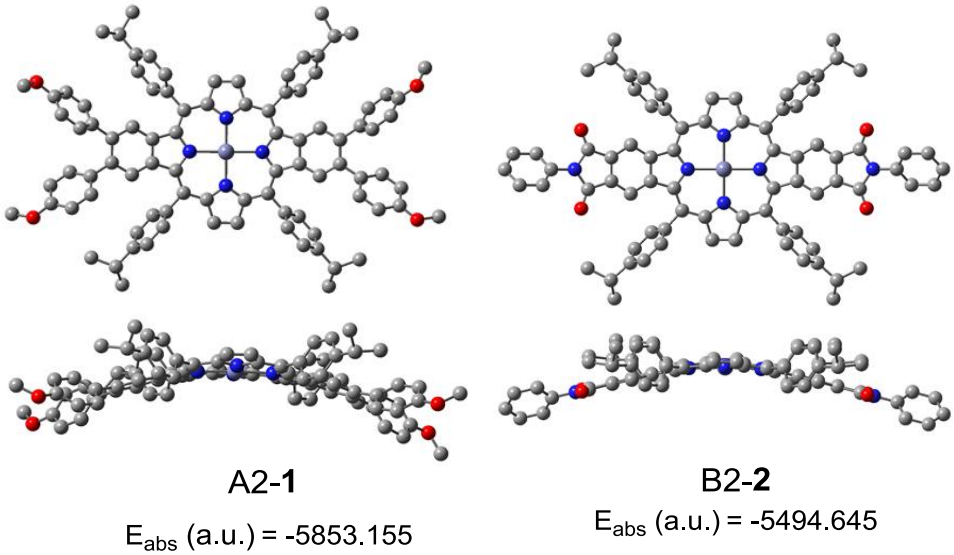


Figure S34. Geometry-optimized molecule structures of A2-**1** and B2-**2**; (Top) front view (bottom) side view.

Table S1. Half-wave potentials ($E_{1/2}$, V vs. SCE) of investigated compounds in CH_2Cl_2 and pyridine containing 0.1M TBAP.

Solvent	Compounds	Ox		Red			H-L gap
		2nd	1st	1st	2nd	3rd	
CH_2Cl_2	(T-iPrPh)PorZn (**10**)	1.00	0.70	-1.39	-1.77		2.09
	A2-**1**	0.70	0.62	-1.33	-1.68		1.95
	B2-**2**	0.95	0.84	-1.13	-1.35	-1.89	1.97
	A2B2-**4**	0.75	0.62	-1.11	-1.28		1.73
	A2B2-**3**	0.81	0.61	-1.36	-1.69		1.97
Pyridine	(T-iPrPh)PorZn (**10**)		0.77	-1.38	-1.86		2.15
	A2-**1**	0.86	0.68	-1.34	-1.83		2.02
	B2-**2**		0.90	-1.09	-1.34	-1.94	1.99
	A2B2-**4**		0.75	-1.00	-1.26		1.75
	A2B2-**3**		0.72	-1.17	-1.47		1.89

Table S2. UV-Vis spectral data of investigated compounds in CH_2Cl_2 and pyridine containing 0.1 M TBAP.

Solvent	Compounds	λ_{max}, nm			
		Soret region	Visible region		
CH_2Cl_2	(T-iPrPh)PorZn (**10**)	421	549	588	
	A2-**1**	454	587	638	
	B2-**2**	476	594	631	
	A2B2-**3**	493		631	689
	A2B2-**4**	510	607	650	725
Pyridine	(T-iPrPh)PorZn (**10**)	431	565	605	
	A2-**1**	464	594	640	
	B2-**2**	483	602	637	
	A2B2-**3**	497		637	690
	A2B2-**4**	513	606	651	720

Table S3: Comparison of UV and Fluorescence spectral data in CHCl3 (conc. 10-6 M).

Solvent	Compounds	λ_{max}, nm			
		Soret bands	Q-bands		Fl Bands
$CHCl_3$	A2-**1**	456	588	637	643, 706
	B2-**2**	477	596	631	643, 706
	A2B2-**3**	488	653	688	697
	A2B2-**4**	507	649	721	730

Table S4. Fluorescence quantum yields of A2 and A2B2 porphyrins in toluene.

Compound	Excitation(nm)	Emission(nm)	Quantum Yields {Φ(F)}
A2-**1**	455	638, 702	0.098
B2-**2**	470	627, 693	0.201
A2B2-**3**	483	688	0.046
A2B2-**4**	500	714	0.047

NOTE: The quantum yields were standardized against the known quantum yield of the freebase *meso*-tetraphenyl porphyrin [Φ(F)= 0.11].[3] The measurements were taken in solutions with absorbance ranging from 0.01-0.05.

Table S5. Atom coordinates for the optimized structure B2-**2**.

E_{abs} (a.u.) = -5494.645

Number of imaginary frequencies = 0

Atom	**X**	**Y**	**Z**
Zn	0.00001	0.00005	-0.37009
N	0.00042	-1.98568	-0.43817
N	-0.00041	1.98570	-0.43829
C	-1.10483	-2.80535	-0.54579
C	1.10664	-2.80512	-0.53630
N	2.12150	0.00065	-0.30103
N	-2.12149	-0.00077	-0.30093
C	1.10484	2.80533	-0.54592
C	-1.10664	2.80510	-0.53639
C	-2.45268	-2.43247	-0.40304
C	-0.67772	-4.16454	-0.77385
C	2.45341	-2.43146	-0.38559
C	0.68184	-4.16451	-0.76712
C	2.91484	1.11802	-0.20561
C	2.91473	-1.11593	-0.19502

C	-2.91485	-1.11811	-0.20556
C	-2.91470	1.11584	-0.19495
C	2.45267	2.43238	-0.40314
C	0.67773	4.16451	-0.77402
C	-2.45337	2.43139	-0.38560
C	-0.68185	4.16448	-0.76726
C	-3.46030	-3.53898	-0.48604
C	3.46104	-3.53900	-0.45462
C	4.29187	0.71348	0.08023
C	4.29148	-0.70891	0.08841
C	-4.29189	-0.71356	0.08020
C	-4.29146	0.70883	0.08847
C	3.46030	3.53889	-0.48617
C	-3.46102	3.53893	-0.45461
C	-4.23316	-3.71240	-1.64344
C	-3.68173	-4.40142	0.59505
C	4.23714	-3.72468	-1.60793
C	3.67888	-4.39027	0.63595
C	5.46453	1.44152	0.37256
C	5.46357	-1.43430	0.38944
C	-5.46461	-1.44157	0.37238
C	-5.46351	1.43425	0.38956
C	4.23343	3.71206	-1.64343
C	3.68143	4.40161	0.59476
C	-4.23722	3.72457	-1.60785
C	-3.67869	4.39029	0.63592
C	-5.22654	-4.68730	-1.69836
C	-4.68438	-5.37066	0.53692
C	5.23026	-4.70049	-1.64977
C	4.68141	-5.36034	0.59098
C	6.59895	0.70564	0.64933
C	6.59868	-0.69602	0.65688
C	-6.59901	-0.70567	0.64917
C	-6.59866	0.69600	0.65690
C	5.22677	4.68699	-1.69836
C	4.68405	5.37089	0.53662
C	-5.23029	4.70042	-1.64966
C	-4.68119	5.36040	0.59098
C	-5.48774	-5.52148	-0.60041
C	5.48794	-5.52325	-0.54240
C	7.96476	1.17989	0.98945
C	7.96455	-1.16710	1.00116
C	-7.96484	-1.17989	0.98921
C	-7.96452	1.16710	1.00120
C	5.48766	5.52146	-0.60055

C	-5.48784	5.52326	-0.54232
C	-6.62320	-6.53458	-0.62381
C	6.62319	-6.53688	-0.55183
N	8.74294	0.00732	1.19000
O	8.36832	2.32177	1.08529
O	8.36837	-2.30803	1.10655
N	-8.74296	-0.00730	1.18989
O	-8.36846	-2.32176	1.08493
O	-8.36829	2.30804	1.10671
C	6.62304	6.53467	-0.62397
C	-6.62303	6.53695	-0.55170
C	-6.41631	-7.61309	-1.70339
C	-7.98913	-5.83797	-0.78440
C	6.42033	-7.62541	-1.62200
C	7.98980	-5.84185	-0.71365
C	10.12779	0.00917	1.53230
C	-10.12782	-0.00912	1.53218
C	6.41617	7.61298	-1.70376
C	7.98906	5.83817	-0.78428
C	-6.42019	7.62544	-1.62190
C	-7.98969	5.84199	-0.71343
C	10.61746	0.93765	2.45893
C	10.99545	-0.91728	0.94123
C	-10.61754	-0.93764	2.45875
C	-10.99544	0.91740	0.94116
C	11.97325	0.93903	2.78313
C	12.34624	-0.91413	1.28561
C	-11.97333	-0.93898	2.78295
C	-12.34623	0.91428	1.28553
C	12.84194	0.01365	2.20283
C	-12.84197	-0.01354	2.20270
H	-1.33775	-5.00730	-0.91463
H	1.34332	-5.00721	-0.90145
H	1.33775	5.00726	-0.91482
H	-1.34333	5.00718	-0.90157
H	-4.06709	-3.06058	-2.49709
H	-3.08758	-4.28963	1.49817
H	4.07376	-3.08169	-2.46877
H	3.08213	-4.26897	1.53612
H	5.50021	2.52034	0.40075
H	5.49861	-2.51277	0.42976
H	-5.50035	-2.52039	0.40043
H	-5.49850	2.51271	0.43000
H	4.06759	3.06001	-2.49695
H	3.08706	4.29002	1.49776

H	-4.07394	3.08154	-2.46868
H	-3.08182	4.26904	1.53601
H	-5.81982	-4.78508	-2.60399
H	-4.85783	-6.00962	1.39997
H	5.82587	-4.80811	-2.55279
H	4.85223	-5.99009	1.46125
H	5.82027	4.78458	-2.60387
H	4.85726	6.01007	1.39955
H	-5.82599	4.80801	-2.55263
H	-4.85188	5.99023	1.46123
H	-6.62221	-7.03946	0.35182
H	6.61859	-7.03229	0.42856
H	6.62187	7.03970	0.35157
H	-6.61836	7.03237	0.42868
H	-6.41862	-7.17549	-2.70888
H	-7.22169	-8.35589	-1.66366
H	-5.46289	-8.13583	-1.56808
H	-8.07969	-5.37038	-1.77243
H	-8.13067	-5.05351	-0.03356
H	-8.80417	-6.56494	-0.68678
H	6.42610	-7.19715	-2.63150
H	5.46643	-8.14684	-1.48522
H	7.22548	-8.36789	-1.57254
H	8.08370	-5.38364	-1.70584
H	8.80442	-6.56791	-0.60604
H	8.12792	-5.05072	0.03086
H	6.41866	7.17521	-2.70918
H	7.22147	8.35587	-1.66404
H	5.46269	8.13564	-1.56866
H	8.07976	5.37035	-1.77218
H	8.13060	5.05390	-0.03323
H	8.80401	6.56524	-0.68673
H	-6.42602	7.19716	-2.63139
H	-5.46626	8.14684	-1.48518
H	-7.22531	8.36796	-1.57242
H	-8.08367	5.38375	-1.70560
H	-8.80427	6.56809	-0.60579
H	-8.12782	5.05087	0.03111
H	9.94503	1.65743	2.90851
H	10.61182	-1.63909	0.23122
H	-9.94513	-1.65748	2.90829
H	-10.61177	1.63923	0.23120
H	12.34793	1.66596	3.49857
H	13.01317	-1.63956	0.82774
H	-12.34803	-1.66595	3.49834

H	-13.01313	1.63976	0.82770
H	13.89673	0.01536	2.46345
H	-13.89676	-0.01521	2.46331

Table S6. Atom coordinates for the optimized structure A2B2-**3.**

E_{abs} (a.u.) = -7071.9348

Number of imaginary frequencies = 0

Atom	**X**	**Y**	**Z**
C	0.86143	4.06158	-0.54689
C	2.17020	3.53246	-0.56564
C	2.07840	2.18239	-0.01150
N	0.75258	1.88176	0.20622
C	0.00000	3.01686	0.00700
C	-4.05239	0.85279	1.34111
C	-3.53023	2.16867	1.33875
C	-2.18056	2.07720	0.78582
N	-1.88381	0.75162	0.57229
C	-3.01205	-0.00624	0.78100
C	-1.34574	3.14602	0.39871
C	-0.86143	-4.06158	-0.54689
C	-2.17020	-3.53246	-0.56564
C	-2.07840	-2.18239	-0.01150
N	-0.75258	-1.88176	0.20622
C	0.00000	-3.01686	0.00700
C	-3.14552	-1.35295	0.38083
C	4.05239	-0.85279	1.34111
C	3.53023	-2.16867	1.33875
C	2.18056	-2.07720	0.78582
N	1.88381	-0.75162	0.57229
C	3.01205	0.00624	0.78100
C	3.14552	1.35295	0.38083
C	1.34574	-3.14602	0.39871
C	-1.94428	4.51756	0.40922
C	-4.52668	-1.92947	0.38865
C	1.94428	-4.51756	0.40922
C	4.52668	1.92947	0.38865
C	-1.59695	5.44522	1.40207
C	-2.19667	6.70157	1.44536
C	-3.15855	7.08033	0.49643
C	-3.48231	6.15876	-0.50748
C	-2.88994	4.89643	-0.55169
C	5.49179	1.49580	-0.52961

C	6.80020	1.97439	-0.46845
C	7.19491	2.89258	0.51231
C	6.21722	3.34729	1.41146
C	4.90590	2.87911	1.34935
C	2.88994	-4.89643	-0.55169
C	3.48231	-6.15876	-0.50748
C	3.15855	-7.08033	0.49643
C	2.19667	-6.70157	1.44536
C	1.59695	-5.44522	1.40207
C	-4.90590	-2.87911	1.34935
C	-6.21722	-3.34729	1.41146
C	-7.19491	-2.89258	0.51231
C	-6.80020	-1.97439	-0.46845
C	-5.49179	-1.49580	-0.52961
C	-0.62387	-5.34101	-1.06458
C	-1.66284	-6.09662	-1.61647
C	-2.97768	-5.54193	-1.67752
C	-3.21246	-4.27272	-1.13920
C	3.84445	-8.43722	0.55942
C	4.61357	-8.62149	1.88233
C	2.85211	-9.59240	0.32555
C	8.64306	3.35116	0.60874
C	8.79210	4.85838	0.33003
C	9.26806	2.96770	1.96406
C	-3.84445	8.43722	0.55942
C	-4.61357	8.62149	1.88233
C	-2.85211	9.59240	0.32555
C	-8.64306	-3.35116	0.60874
C	-8.79210	-4.85838	0.33003
C	-9.26806	-2.96770	1.96406
H	-0.86232	5.16981	2.15375
H	-1.92035	7.39154	2.23821
H	-4.22092	6.42829	-1.25950
H	-3.17051	4.19196	-1.33020
H	5.21817	0.76444	-1.28518
H	7.53478	1.61031	-1.18304
H	6.48616	4.06083	2.18654
H	4.17004	3.23282	2.06645
H	3.17051	-4.19196	-1.33020
H	4.22092	-6.42829	-1.25950
H	1.92035	-7.39154	2.23821
H	0.86232	-5.16981	2.15375
H	-4.17004	-3.23282	2.06645
H	-6.48616	-4.06083	2.18654
H	-7.53478	-1.61031	-1.18304

H	-5.21817	-0.76444	-1.28518
H	0.36276	-5.78036	-1.03029
H	-4.20603	-3.85378	-1.22738
H	4.57923	-8.46285	-0.25727
H	5.19437	-9.55166	1.86171
H	5.29523	-7.78540	2.07062
H	3.92619	-8.68036	2.73458
H	3.37659	-10.55563	0.32086
H	2.32626	-9.48122	-0.62915
H	2.09501	-9.63062	1.11775
H	9.19931	2.81640	-0.17300
H	9.84834	5.15242	0.35588
H	8.38656	5.11912	-0.65390
H	8.26300	5.45632	1.08223
H	10.33733	3.21213	1.97458
H	9.14941	1.89885	2.16613
H	8.79583	3.51882	2.78669
H	-4.57923	8.46285	-0.25727
H	-5.19437	9.55166	1.86171
H	-5.29523	7.78540	2.07062
H	-3.92619	8.68036	2.73458
H	-3.37659	10.55563	0.32086
H	-2.32626	9.48122	-0.62915
H	-2.09501	9.63062	1.11775
H	-9.19931	-2.81640	-0.17300
H	-9.84834	-5.15242	0.35588
H	-8.38656	-5.11912	-0.65390
H	-8.26300	-5.45632	1.08223
H	-10.33733	-3.21213	1.97458
H	-9.14941	-1.89885	2.16613
H	-8.79583	-3.51882	2.78669
Zn	0.00000	0.00000	0.38271
C	3.21246	4.27272	-1.13920
C	2.97768	5.54193	-1.67752
C	1.66284	6.09662	-1.61647
C	0.62387	5.34101	-1.06458
C	1.33694	7.47471	-2.08289
C	2.09187	8.59215	-1.67589
C	0.21688	7.71202	-2.88933
C	1.74224	9.87830	-2.05874
C	0.61977	10.09505	-2.87230
C	-0.14685	9.00165	-3.28877
C	4.11717	6.23732	-2.34087
C	5.35334	6.36210	-1.69532
C	4.01228	6.74480	-3.65050

C	6.44704	6.97829	-2.31092
C	5.09064	7.34928	-4.27885
C	6.31844	7.47562	-3.61158
H	5.46627	5.97995	-0.68423
H	7.37957	7.06878	-1.76549
H	5.00874	7.73229	-5.29138
H	3.07076	6.65616	-4.18334
H	2.32284	10.73738	-1.73700
H	2.96081	8.44697	-1.04205
H	-1.01495	9.13508	-3.92465
H	-0.38267	6.87096	-3.22728
H	-0.36276	5.78036	-1.03029
H	4.20603	3.85378	-1.22738
O	7.31481	8.09371	-4.31247
O	0.36573	11.39651	-3.20023
C	8.57756	8.24587	-3.68629
C	-0.76025	11.67281	-4.01593
H	9.02225	7.27471	-3.43066
H	9.21414	8.75334	-4.41362
H	8.50717	8.85820	-2.77726
H	-1.69533	11.35454	-3.53553
H	-0.77507	12.75604	-4.15055
H	-0.67800	11.18706	-4.99751
C	-4.11717	-6.23732	-2.34087
C	-5.35334	-6.36210	-1.69532
C	-6.44704	-6.97829	-2.31092
C	-4.01228	-6.74480	-3.65050
C	-5.09064	-7.34928	-4.27885
C	-6.31844	-7.47562	-3.61158
C	-1.33694	-7.47471	-2.08289
C	-2.09187	-8.59215	-1.67589
C	-0.21688	-7.71202	-2.88933
C	0.14685	-9.00165	-3.28877
C	-1.74224	-9.87830	-2.05874
C	-0.61977	-10.09505	-2.87230
O	-0.36573	-11.39651	-3.20023
O	-7.31481	-8.09371	-4.31247
C	0.76025	-11.67281	-4.01593
C	-8.57756	-8.24587	-3.68629
H	-5.46627	-5.97995	-0.68423
H	-7.37957	-7.06878	-1.76549
H	-3.07076	-6.65616	-4.18334
H	-5.00874	-7.73229	-5.29138
H	-2.96081	-8.44697	-1.04205
H	0.38267	-6.87096	-3.22728

H	1.01495	-9.13508	-3.92465
H	-2.32284	-10.73738	-1.73700
H	0.77507	-12.75604	-4.15055
H	1.69533	-11.35454	-3.53553
H	0.67800	-11.18706	-4.99751
H	-9.21414	-8.75334	-4.41362
H	-9.02225	-7.27471	-3.43066
H	-8.50717	-8.85820	-2.77726
C	-4.29331	3.22452	1.86040
C	-5.31333	0.60030	1.90488
C	-5.55964	2.97640	2.38160
C	-6.05848	1.64744	2.43766
C	4.29331	-3.22452	1.86040
C	5.31333	-0.60030	1.90488
C	6.05848	-1.64744	2.43766
C	5.55964	-2.97640	2.38160
C	6.34936	-4.18550	2.76555
C	7.32147	-1.26196	3.13900
C	-6.34936	4.18550	2.76555
C	-7.32147	1.26196	3.13900
O	-5.87275	5.21064	3.21122
O	-7.66273	4.04919	2.46981
O	-7.47717	1.93128	4.30335
O	-8.08487	0.39477	2.76351
O	7.66273	-4.04919	2.46981
O	5.87275	-5.21064	3.21122
O	7.47717	-1.93128	4.30335
O	8.08487	-0.39477	2.76351
C	8.66868	-1.61327	5.03649
C	8.48441	-5.17748	2.80078
C	-8.66868	1.61327	5.03649
C	-8.48441	5.17748	2.80078
H	-3.93635	4.24371	1.87008
H	-5.71661	-0.39972	1.97625
H	3.93635	-4.24371	1.87008
H	5.71661	0.39972	1.97625
H	8.62611	-2.22146	5.94065
H	8.69299	-0.54994	5.28905
H	9.55810	-1.85825	4.44899
H	8.43799	-5.38667	3.87311
H	9.49660	-4.89783	2.50647
H	8.15741	-6.06540	2.25296
H	-8.62611	2.22146	5.94065
H	-8.69299	0.54994	5.28905
H	-9.55810	1.85825	4.44899

H	-8.15741	6.06540	2.25296
H	-8.43799	5.38667	3.87311
H	-9.49660	4.89783	2.50647

Table S7. Atom coordinates for the optimized structure A2B2-**4.**

E_{abs} (a.u.) = -7184.234

Number of imaginary frequencies = 0

Atom	**X**	**Y**	**Z**
Zn	0.00000	0.00000	0.21375
N	0.00000	2.02827	0.04324
N	0.00000	-2.02827	0.04324
C	1.12087	2.80745	-0.13328
C	-1.11817	2.80024	-0.18014
N	-2.02719	0.00123	0.41099
N	2.02719	-0.00123	0.41099
C	-1.12087	-2.80745	-0.13328
C	1.11817	-2.80024	-0.18014
C	2.41446	2.42501	0.26600
C	0.71331	4.10548	-0.67266
C	-2.42052	2.42097	0.19034
C	-0.69768	4.09812	-0.70829
C	-2.79141	-1.11793	0.64265
C	-2.79797	1.12318	0.60076
C	2.79141	1.11793	0.64265
C	2.79797	-1.12318	0.60076
C	-2.41446	-2.42501	0.26600
C	-0.71331	-4.10548	-0.67266
C	2.42052	-2.42097	0.19034
C	0.69768	-4.09812	-0.70829
C	3.48321	3.47173	0.29428
C	1.41328	5.21706	-1.15810
C	-3.50031	3.45659	0.15845
C	-1.38488	5.18771	-1.25811
C	-4.07835	-0.70328	1.19407
C	-4.08422	0.72137	1.16391
C	4.07835	0.70328	1.19407
C	4.08422	-0.72137	1.16391
C	-3.48321	-3.47173	0.29428
C	-1.41328	-5.21706	-1.15810
C	3.50031	-3.45659	0.15845
C	1.38488	-5.18771	-1.25811
C	4.51624	3.46732	-0.65458

C	3.50689	4.44920	1.29697
C	0.73384	6.32057	-1.68437
H	2.49231	5.25668	-1.11434
C	-4.51576	3.39674	-0.80746
C	-3.56331	4.46885	1.12463
C	-0.69205	6.29654	-1.75508
H	-2.46172	5.17185	-1.35659
C	-5.15576	-1.42256	1.75444
C	-5.17011	1.45365	1.69021
C	5.15576	1.42256	1.75444
C	5.17011	-1.45365	1.69021
C	-4.51624	-3.46732	-0.65458
C	-3.50689	-4.44920	1.29697
C	-0.73384	-6.32057	-1.68437
H	-2.49231	-5.25668	-1.11434
C	4.51576	-3.39674	-0.80746
C	3.56331	-4.46885	1.12463
C	0.69205	-6.29654	-1.75508
H	2.46172	-5.17185	-1.35659
C	5.55219	4.39614	-0.58616
H	4.51111	2.71869	-1.44240
C	4.55230	5.37018	1.36651
H	2.71219	4.47369	2.03770
C	1.55411	7.48878	-2.11511
C	-5.57617	4.29970	-0.78689
H	-4.47929	2.62284	-1.56951
C	-4.63411	5.36362	1.14736
H	-2.78404	4.53629	1.87892
C	-1.49483	7.38826	-2.37659
C	-6.20719	-0.67988	2.25063
H	-5.17340	-2.50073	1.82353
C	-6.21499	0.72321	2.21756
H	-5.20014	2.53353	1.70966
C	6.20719	0.67988	2.25063
H	5.17340	2.50073	1.82353
C	6.21499	-0.72321	2.21756
H	5.20014	-2.53353	1.70966
C	-5.55219	-4.39614	-0.58616
H	-4.51111	-2.71869	-1.44240
C	-4.55230	-5.37018	1.36651
H	-2.71219	-4.47369	2.03770
C	-1.55411	-7.48878	-2.11511
C	5.57617	-4.29970	-0.78689
H	4.47929	-2.62284	-1.56951
C	4.63411	-5.36362	1.14736

H	2.78404	-4.53629	1.87892
C	1.49483	-7.38826	-2.37659
C	5.60003	5.35599	0.43641
H	6.34374	4.36118	-1.33031
H	4.56142	6.10669	2.16680
C	1.27811	8.79001	-1.67414
C	2.68633	7.30668	-2.93103
C	-5.66838	5.28850	0.20427
H	-6.35348	4.21886	-1.54227
H	-4.67899	6.12084	1.92714
C	-2.60641	7.92769	-1.70261
C	-1.21512	7.87733	-3.65947
C	-7.46062	-1.14421	2.89590
C	-7.47472	1.20309	2.83885
C	7.46062	1.14421	2.89590
C	7.47472	-1.20309	2.83885
C	-5.60003	-5.35599	0.43641
H	-6.34374	-4.36118	-1.33031
H	-4.56142	-6.10669	2.16680
C	-1.27811	-8.79001	-1.67414
C	-2.68633	-7.30668	-2.93103
C	5.66838	-5.28850	0.20427
H	6.35348	-4.21886	-1.54227
H	4.67899	-6.12084	1.92714
C	2.60641	-7.92769	-1.70261
C	1.21512	-7.87733	-3.65947
C	6.76258	6.33006	0.55747
C	2.08620	9.87212	-2.02597
H	0.41888	8.96606	-1.03465
C	3.49836	8.37345	-3.29472
H	2.92484	6.31119	-3.29570
C	-6.86895	6.21978	0.28708
C	-3.39174	8.91846	-2.27834
H	-2.84969	7.56813	-0.70646
C	-2.00045	8.86480	-4.25614
H	-0.37046	7.47679	-4.21135
N	-8.18372	0.03424	3.22924
O	-7.82713	-2.28275	3.11038
O	-7.85574	2.34640	2.99624
N	8.18372	-0.03424	3.22924
O	7.82713	2.28275	3.11038
O	7.85574	-2.34640	2.99624
C	-6.76258	-6.33006	0.55747
C	-2.08620	-9.87212	-2.02597
H	-0.41888	-8.96606	-1.03465

C	-3.49836	-8.37345	-3.29472
H	-2.92484	-6.31119	-3.29570
C	6.86895	-6.21978	0.28708
C	3.39174	-8.91846	-2.27834
H	2.84969	-7.56813	-0.70646
C	2.00045	-8.86480	-4.25614
H	0.37046	-7.47679	-4.21135
C	6.88843	7.23921	-0.67934
C	8.08367	5.58745	0.84155
H	6.55169	6.97421	1.42188
C	3.20399	9.66781	-2.84377
H	1.83789	10.85994	-1.65468
H	4.36445	8.22984	-3.93337
C	-7.05234	7.05400	-0.99407
C	-8.15279	5.43623	0.62817
H	-6.67765	6.91802	1.11333
C	-3.09517	9.39493	-3.56291
H	-4.23917	9.34399	-1.74946
H	-1.75145	9.20724	-5.25409
C	-9.45879	0.04178	3.86812
C	9.45879	-0.04178	3.86812
C	-6.88843	-7.23921	-0.67934
C	-8.08367	-5.58745	0.84155
H	-6.55169	-6.97421	1.42188
C	-3.20399	-9.66781	-2.84377
H	-1.83789	-10.85994	-1.65468
H	-4.36445	-8.22984	-3.93337
C	7.05234	-7.05400	-0.99407
C	8.15279	-5.43623	0.62817
H	6.67765	-6.91802	1.11333
C	3.09517	-9.39493	-3.56291
H	4.23917	-9.34399	-1.74946
H	1.75145	-9.20724	-5.25409
H	7.13235	6.65742	-1.57650
H	7.68929	7.97420	-0.53560
H	5.95686	7.78058	-0.87701
H	8.89193	6.30248	1.03629
H	8.38315	4.97539	-0.01802
H	7.99344	4.92077	1.70569
O	4.05892	10.65022	-3.25536
H	-7.88171	7.76119	-0.87579
H	-7.28332	6.41624	-1.85566
H	-6.14804	7.62259	-1.23672
H	-8.99059	6.12481	0.79119
H	-8.43018	4.76419	-0.19326

H	-8.02497	4.82407	1.52705
O	-3.92530	10.36751	-4.04285
C	-9.72461	-0.85770	4.90777
C	-10.44300	0.94810	3.45505
C	9.72461	0.85770	4.90777
C	10.44300	-0.94810	3.45505
H	-7.13235	-6.65742	-1.57650
H	-7.68929	-7.97420	-0.53560
H	-5.95686	-7.78058	-0.87701
H	-8.89193	-6.30248	1.03629
H	-8.38315	-4.97539	-0.01802
H	-7.99344	-4.92077	1.70569
O	-4.05892	-10.65022	-3.25536
H	7.88171	-7.76119	-0.87579
H	7.28332	-6.41624	-1.85566
H	6.14804	-7.62259	-1.23672
H	8.99059	-6.12481	0.79119
H	8.43018	-4.76419	-0.19326
H	8.02497	-4.82407	1.52705
O	3.92530	-10.36751	-4.04285
C	3.81062	11.97873	-2.82564
C	-3.67728	10.88027	-5.34161
C	-10.97528	-0.85019	5.52344
H	-8.96357	-1.56232	5.21855
C	-11.68453	0.95421	4.08897
H	-10.23075	1.64768	2.65642
C	10.97528	0.85019	5.52344
H	8.96357	1.56232	5.21855
C	11.68453	-0.95421	4.08897
H	10.23075	-1.64768	2.65642
C	-3.81062	-11.97873	-2.82564
C	3.67728	-10.88027	-5.34161
H	3.85482	12.06547	-1.73176
H	2.83483	12.34172	-3.17517
H	4.60092	12.58895	-3.26696
H	-3.75192	10.09634	-6.10699
H	-2.68853	11.35370	-5.40804
H	-4.44894	11.63165	-5.51958
C	-11.95798	0.05547	5.12110
H	-11.17708	-1.55438	6.32599
H	-12.44200	1.66405	3.76788
C	11.95798	-0.05547	5.12110
H	11.17708	1.55438	6.32599
H	12.44200	-1.66405	3.76788
H	-3.85482	-12.06547	-1.73176

H	-2.83483	-12.34172	-3.17517
H	-4.60092	-12.58895	-3.26696
H	3.75192	-10.09634	-6.10699
H	2.68853	-11.35370	-5.40804
H	4.44894	-11.63165	-5.51958
H	-12.92919	0.06104	5.60825
H	12.92919	-0.06104	5.60825

Table S8. Atom coordinates for the optimized structure A2-**1.**

E = -5853.155 a.u

Number of imaginary frequencies = 0

Symbol	X	Y	Z
C	4.27871	-0.77579	-0.01156
C	4.28902	0.63360	-0.06611
C	2.92410	1.04213	-0.40471
N	2.12189	-0.07272	-0.47756
C	2.90765	-1.19001	-0.31777
C	-0.69961	-4.22456	-0.88376
C	0.66114	-4.23412	-0.86466
C	1.09403	-2.87619	-0.64758
N	-0.00807	-2.04877	-0.57421
C	-1.11934	-2.86086	-0.67704
C	2.44216	-2.50531	-0.48162
C	-4.27273	0.68918	-0.11316
C	-4.28536	-0.72101	-0.08418
C	-2.91602	-1.15141	-0.37565
N	-2.11175	-0.04402	-0.50888
C	-2.89828	1.08172	-0.43084
C	-2.46575	-2.47180	-0.54228
C	0.71707	4.06218	-1.19564
C	-0.64405	4.07242	-1.19598
C	-1.08080	2.73888	-0.86689
N	0.02025	1.92153	-0.70909
C	1.13361	2.72253	-0.86457
C	2.47836	2.34644	-0.67514
C	-2.43173	2.38190	-0.68505
C	3.43353	-3.63046	-0.51384
C	-3.47239	-3.58177	-0.60736
C	-3.41954	3.50294	-0.81518
C	3.48353	3.45112	-0.81214

C	4.22251	-3.85483	-1.65156
C	5.14129	-4.90129	-1.69046
C	5.30905	-5.76323	-0.59599
C	4.51046	-5.54246	0.53293
C	3.58441	-4.49869	0.57487
C	3.60928	4.44586	0.16908
C	4.51955	5.49095	0.01930
C	5.33525	5.58590	-1.11784
C	5.20420	4.59175	-2.09644
C	4.29607	3.54261	-1.94973
C	-3.53501	4.48811	0.17687
C	-4.43082	5.54691	0.03627
C	-5.24128	5.66619	-1.10237
C	-5.11912	4.68222	-2.09248
C	-4.22593	3.61910	-1.95489
C	-4.23899	-3.78336	-1.76446
C	-5.17183	-4.81576	-1.83436
C	-5.37663	-5.68563	-0.75253
C	-4.60065	-5.48733	0.39618
C	-3.66065	-4.45795	0.46923
C	-5.43409	1.40171	0.21280
C	-6.61600	0.73299	0.54765
C	-6.63878	-0.69388	0.54026
C	-5.46861	-1.39748	0.23809
C	-6.19936	6.83614	-1.28203
C	-7.16869	6.99373	-0.09634
C	-5.43422	8.14829	-1.54541
C	6.30872	6.74132	-1.30837
C	5.56239	8.06221	-1.58125
C	7.28120	6.89465	-0.12452
C	6.31951	-6.90191	-0.62597
C	5.96812	-7.94972	-1.69957
C	7.75974	-6.38571	-0.80514
C	-6.40133	-6.80996	-0.81680
C	-7.82915	-6.27372	-1.03229
C	-6.03444	-7.85626	-1.88677
H	4.11655	-3.19576	-2.50907
H	5.73865	-5.04495	-2.58747
H	4.61512	-6.19698	1.39582
H	2.97819	-4.34767	1.46413
H	2.98678	4.39459	1.05826
H	4.59017	6.24304	0.80124
H	5.81766	4.64382	-2.99384
H	4.21308	2.78613	-2.72539

H	-2.91641	4.41805	1.06755
H	-4.49484	6.29068	0.82662
H	-5.72858	4.75300	-2.99129
H	-4.15054	2.87059	-2.73902
H	-4.10425	-3.11774	-2.61283
H	-5.75088	-4.94209	-2.74592
H	-4.73416	-6.14839	1.25006
H	-3.07267	-4.32423	1.37338
H	-5.42717	2.48185	0.26193
H	-5.51029	-2.47715	0.23780
H	-6.80266	6.62253	-2.17521
H	-7.89737	7.78716	-0.30058
H	-7.71617	6.06579	0.09950
H	-6.63682	7.26549	0.82314
H	-6.13219	8.97502	-1.72462
H	-4.77938	8.05813	-2.41905
H	-4.80886	8.41783	-0.68573
H	6.90823	6.51218	-2.20032
H	6.27161	8.87751	-1.76879
H	4.90489	7.97385	-2.45298
H	4.94239	8.34786	-0.72297
H	8.02166	7.67552	-0.33613
H	7.81255	5.95875	0.07914
H	6.75427	7.18225	0.79285
H	6.26824	-7.40278	0.35060
H	6.67360	-8.78861	-1.66587
H	4.95783	-8.34697	-1.55184
H	6.01302	-7.51783	-2.70657
H	8.47483	-7.21577	-0.75648
H	8.02211	-5.65992	-0.02823
H	7.88721	-5.89403	-1.77697
H	-6.38360	-7.31706	0.15776
H	-8.55618	-7.09437	-1.00673
H	-8.10269	-5.54790	-0.25925
H	-7.92400	-5.77640	-2.00500
H	-6.75142	-8.68599	-1.87755
H	-5.03379	-8.26753	-1.71395
H	-6.04612	-7.41791	-2.89192
Zn	0.00548	-0.06096	-0.56153
C	5.45910	1.33285	0.25731
C	6.62679	0.65156	0.61652
C	6.62407	-0.77519	0.64392
C	5.44557	-1.46495	0.34186
C	7.83500	-1.58794	0.95531

C	9.05694	-1.38092	0.30154
C	7.76766	-2.64275	1.88453
C	10.17290	-2.17919	0.55789
C	10.08495	-3.21680	1.49322
C	8.87016	-3.44403	2.15525
C	7.81549	1.46761	0.99714
C	8.26201	2.50481	0.16937
C	8.49872	1.26563	2.21203
C	9.35273	3.30863	0.51648
C	9.57581	2.06030	2.57587
C	10.01563	3.08793	1.72797
H	7.75528	2.68605	-0.77471
H	9.67476	4.08817	-0.16497
H	10.09429	1.90714	3.51738
H	8.17263	0.47696	2.88274
H	11.09624	-1.98469	0.02414
H	9.14195	-0.58300	-0.42951
H	8.81741	-4.24715	2.88406
H	6.83562	-2.82726	2.41177
H	5.46812	-2.54492	0.36677
H	5.47064	2.41366	0.28402
O	11.08890	3.80793	2.17245
O	11.11214	-4.05306	1.82953
C	11.55935	4.87338	1.36477
C	12.36460	-3.86431	1.19235
H	10.78580	5.63829	1.21345
H	12.39940	5.31264	1.90631
H	11.90721	4.51723	0.38557
H	12.77836	-2.86835	1.39957
H	13.02978	-4.62403	1.60741
H	12.29066	-4.00306	0.10536
C	-7.86865	-1.49200	0.81358
C	-9.07506	-1.24811	0.14383
C	-10.20841	-2.03361	0.36011
C	-7.83575	-2.56986	1.71763
C	-8.95617	-3.35890	1.94882
C	-10.15445	-3.09560	1.27046
C	-7.79186	1.55943	0.94494
C	-8.21918	2.63266	0.14140
C	-8.48075	1.33575	2.14435
C	-9.55547	2.13547	2.53574
C	-9.29397	3.43243	0.51171
C	-9.97170	3.18968	1.71447
O	-11.01521	4.02797	1.99108

O	-11.20116	-3.92319	1.56684
C	-11.73523	3.82426	3.19534
C	-12.43435	-3.70640	0.90183
H	-9.13362	-0.43116	-0.56861
H	-11.11817	-1.81084	-0.18584
H	-6.91624	-2.78341	2.25583
H	-8.92953	-4.18094	2.65769
H	-7.70456	2.83368	-0.79432
H	-8.17053	0.52296	2.79365
H	-10.05297	1.92839	3.47646
H	-9.63299	4.24800	-0.11993
H	-12.51345	4.58978	3.21270
H	-11.09181	3.94273	4.07745
H	-12.20335	2.83114	3.22424
H	-13.11783	-4.46865	1.28097
H	-12.33300	-3.81978	-0.18585
H	-12.84393	-2.71130	1.12163
H	-1.36189	-5.06620	-1.02048
H	1.31521	-5.08489	-0.98325
H	1.37996	4.88940	-1.39967
H	-1.29471	4.90928	-1.40033

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