Supporting Information

A Quinoidal *Bis*-Phenalenyl-Fused Porphyrin with Supramolecular Organization and Broad Near-Infrared Absorption

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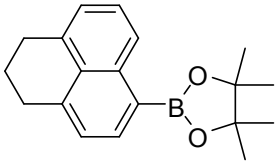
Contents

1. General.

All reagents and solvents are commercial reagent grade and were used without further purification. The starting material [5,15-*bis*-*(*3,5-di-*tert*-butylphenyl)porphyrinato(2-)]zinc(II)[1] was prepared from dipyrromethane[2] and 3,5-di-*tert*-butylbenzaldehyde[3] by known methods. [10,20-*Bis*-(3,5-di-*tert*-butylphenyl)-5,15-*bis*-bromo-porphyrinato(2-)]zinc(II) was prepared by bromination of [5,15-*bis*-(3,5-di-*tert*-butylphenyl)porphyrinato(2-)]zinc(II) with NBS in 5%-pyridine/dichloromethane according to literature.[4] The starting 6-bromo-2,3-dihydro-1*H*-phenalene[5] was obtained from 1-methyl-4-bromonaphthalene (Sigma-Aldrich) *via* bromination with NBS/CCl_4/benzoyl peroxide to give 1-bromomethyl-4-bromonaphthalene, then alkylation with dimethyl malonate/NaOMe/MeOH and alkyline hydrolysis to give 2-((4-bromonaphthalen-1-yl)methyl)malonic acid,[6] then decarboxylation to give 3-(4-bromonaphthalen-1-yl)propanoic acid,[6] then acid chloride formation (oxalyl chloride/dichloromethane) followed by Friedel-Crafts acylation ($AlCl_3$/dichloromethane) to give 6-bromo-2,3-dihydro-1H-phenalen-1-one,[7] then reduction with $NaBH_4$/MeOH followed by reduction with Et_3SiH/TFA/dichloromethane to give 6-bromo-2,3-dihydro-1*H*-phenalene.[5] Moisture or air sensitive reactions were performed under an inert atmosphere of nitrogen. Flash chromatography was carried out with silica gel (60–200 mesh) and alumina (neutral, activity grade I). ^{1}H NMR spectra were recorded on Varian 400-MR, Varian 500-MR or Varian 600-MR spectrometers, and chemical shifts were reported as the delta scale in ppm relative to the residual non-deuterated solvent $CHCl_3$ (δ 7.26 ppm) or C_6H_6 (δ 7.15 ppm). Coupling constants (J) are given in Hz. ^{13}C NMR spectra were proton wide-band decoupled and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ 77.0 ppm) or C_6D_6 (δ 128.02 ppm). MALDI-TOF mass spectra were recorded using a positive-MALDI-TOF method with/without *α*-cyano-4-hydroxycinnamic acid (CHCA) matrix. All

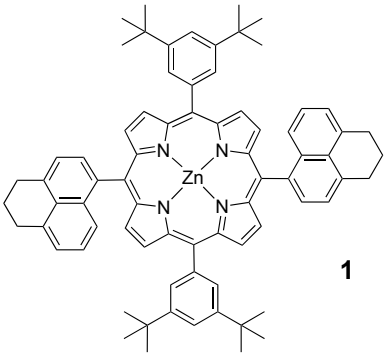
spectra were measured as solutions in the indicated solvents at room temperature using a 1 cm cell. Absorption maxima (λ_{max}) are reported in nm and extinction coefficients (ε) in $M^{-1}cm^{-1}$. Quantum efficiency measurements were carried out using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere and model C10027 photonic multichannel analyzer. Redox potentials were measured by the cyclic voltammetry method and differential pulse voltammetry method. 0.1M *n*-Bu_4NPF_6 in CH_2Cl_2 was used as the supporting electrolyte (degassed with nitrogen), a Pt wire was employed as the counter electrode, an Ag wire used as the pseudo-reference electrode and a glassy carbon electrode was used as the working electrode. Ferrocene (Fc) or decamethylferrocene (dmfc) was added as an internal reference, and the potentials were measured relative to the Fc/Fc^+ couple. CV was used to determine electrochemical reversibility, while all redox potentials were found using DPV.

2. Synthetic procedures and characterization.



4,4,5,5-tetramethyl-2-(2,3-dihydro-1*H*-phenalene-6-yl)-1,3,2-dioxaborolane. A mixture of 6-bromo-2,3-dihydro-1*H*-phenalene[5] (8.1 g, 32.8 mmol), pinacolborane (5.3 g, 6 ml, 1.26 equiv.), $Cl_2Pd(PPh_3)_2$ (150 mg, 0.23 mmol, 0.7 mol%) and triethylamine (25 ml) in toluene (200 ml) was degassed with nitrogen and refluxed overnight. Reaction mixture was quenched with water, toluene was distilled off and the residue was subjected to column chromatography on silica gel (gradient elution with hexanes:ethyl acetate mixtures from 1:0 to 1000:3) to give 4,4,5,5-tetramethyl-2-(2,3-dihydro-1*H*-phenalene-6-yl)-1,3,2-dioxaborolane (5.2 g, 17.7 mmol, 54%). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.42 (s, 12H), 2.07 (p, 2H, J = 6 Hz), 3.13 (t, 4H, J = 6 Hz),

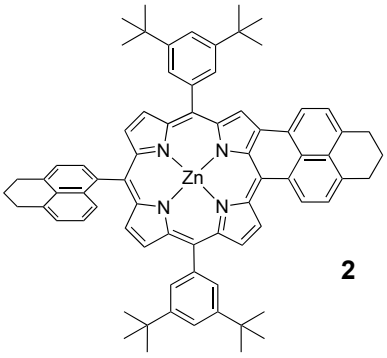
7.23 (d, 2H, J = 7 Hz), 7.42 (dd, 1H, J_1 = 7 Hz, J_2 = 9 Hz), 7.98 (d, 1H, J = 7 Hz), 8.62 (d, 1H, J = 9 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz): 23.0, 24.9, 31.7, 32.0, 83.5, 123.3, 123.7, 125.8, 126.5, 129.9, 135.3, 136.3, 137.4, 140.2. MALDI TOF: 294 (M^+), requires 294 for $C_{19}H_{23}BO_2$. Elemental analysis for $C_{19}H_{23}BO_2$: calcd: C 77.57, H 7.88; found: C 77.57, H 7.94.



1

[10,20-Bis(3,5-di-*tert*-butylphenyl)-5,15-*bis*-(2,3-dihydro-1*H*-phenalene-6-yl)porphyrinato(2$^-$)-κN^{21},κN^{22},κN^{23},κN^{24})zinc(II) 1. A mixture of [10,20-*bis*-(3,5-di-*tert*-butylphenyl)-5,15-*bis*-bromo-porphyrinato(2-)]zinc(II) (3.67 g, 4.04 mmol), cesium carbonate (13 g, 39 mmol, 10 equiv.), $Pd(PPh_3)_4$ (466 mg, 10 mol%), pyridine (5 ml) and 4,4,5,5-tetramethyl-2-(2,3-dihydro-1*H*-phenalene-6-yl)-1,3,2-dioxaborolane (2.5 g, 8.49 mmol, 2.1 equiv.) in toluene (800 ml) was degassed and refluxed under nitrogen for 12 hours. Reaction mixture was cooled and passed through a pad of silica gel washing with toluene. Toluene was distilled off in vacuum, the residue was separated by crystallization from dichloromethane by adding methanol to afford porphyrin **1** (3.98 g, 3.69 mmol, 91%). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.48 and 1.53 (s, 36H, atropoisomers), 2.36 (p, 4H, J = 6 Hz), 3.35 (t, 4H, J = 6 Hz), 3.47 (t, 4H, J = 6 Hz), 6.95-6.98 (m, 4H), 7.21 (dd, 2H, J_1 = 2 Hz, J_2 = 5 Hz), 7.61 (d, 2H, J = 7 Hz), 7.73 and 8.06 (d, 4H, J = 1.5 Hz, atropoisomers), 8.03 and 8.10 (t, 2H, J = 1.5 Hz, atropoisomers), 8.17 (dd, 2H, J1 = 5 Hz, J2 = 7), 8.69 (dd, 4H, J_1 = 2.5 Hz, J_2 = 4.5 Hz), 8.85 (d, 4H, J = 4.5 Hz). ^{13}C -NMR ($CDCl_3$, 125 MHz): 23.4, 31.7, 35.0, 118.8, 120.5, 122.1, 122.3, 123.5, 125.2, 127.22 and

127.27 (atropoisomers), 129.5, 129.7, 129.9, 130.0, 131.7, 132.0, 132.1, 132.2, 136.03 and 136.05 (atropoisomers), 136.6, 137.15 and 137.18 (atropoisomers), 138.24 and 138.26 (atropoisomers), 141.9, 148.35, 148.38 and 148.40 (atropoisomers), 150.4, 150.8. UV/VIS (CH_2Cl_2) λ, nm, (ε): 300 (23200), 425 (479300), 550 (20300), 588 (500). HRMS: 1080.5093 (M^+), calcd. 1080.5043 for $C_{74}H_{72}N_4Zn$. Elemental analysis for $C_{74}H_{72}N_4Zn*CH_3OH$: calcd: C 80.80, H 6.87, N 5.03; found: C 80.81, H 6.70, N 5.34.



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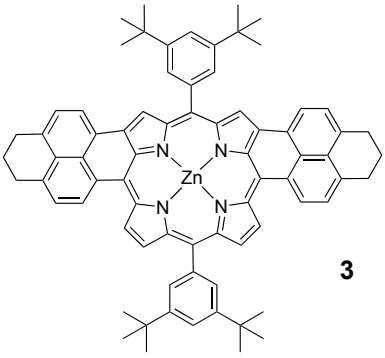
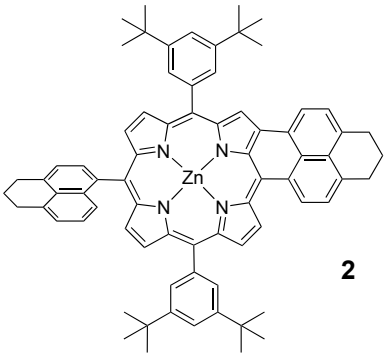


3

[10,20-*Bis*(3,5-di-*tert*-butylphenyl)-3,5-(2,3-dihydro-1*H*-phenalene-6,7-yl)-15-(2,3-dihydro-1*H*-phenalene-6-yl)porphyrinato(2-)-κN^{21},κN^{22},κN^{23},κN^{24})zinc(II) (compound **2**) and **[10,20-*Bis*(3,5-di-*tert*-butylphenyl)-3,5,13,15-*bis*-(2,3-dihydro-1*H*-phenalene-6,7-yl)-porphyrinato(2-)-κN^{21},κN^{22},κN^{23},κN^{24})zinc(II)** (compound **3**).

The above *bis*-(2,3-dihydro-1*H*-phenalene)-porphyrin **1** (3.97 g, 0.67 mmol) was dissolved in dry dichloromethane (700 ml) under nitrogen atmosphere at room temperature and to the resulting solution anhydrous $FeCl_3$ (8 g) was added at once. The reaction mixture was vigorously stirred for 10 min and after that quenched with pyridine (10 ml). The resulting brown-purple solution was passed through a short plug silica gel (prewashed with dichloromethane-pyridine = 1000:5) eluting with dichloromethane:pyridine = 1000:5. All brown-purple fractions were collected. Solution of $Zn(OAc)_2•2H_2O$ (1g) in methanol (30 ml) was added and stirred at room temperature for 1 hour. After that solvents were evaporated in vacuum and the residue passed

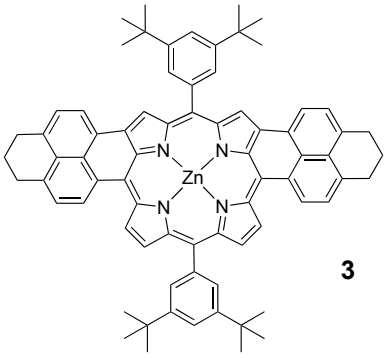
through a short plug of silica gel (prewashed with dichloromethane:pyridine = 1000:5) eluting with dichloromethane:pyridine = 1000:5. Solvents were evaporated in vacuum and the residue was crystallized from 1% pyridine:dichloromethane by layered addition of methanol to give 3.4 g of a mixture of porphyrins **2** and **3** (1:1 ratio by NMR). Separation can be done on alumina column using dichloromethane to elute porphyrin **2** and then dichloromethane:hexanes:pyridine = 300:700:5 to eluate porphyrin **3**. Porphyrin **2** was crystallized from dichloromethane and porphyrin **3** from 1% pyridine:dichloromethane by layered addition of methanol. Yields – porphyrin **2** (0.75 g) and porphyrin **3** (0.48 g).



2

[10,20-*Bis*(3,5-di-*tert*-butylphenyl)-3,5-(2,3-dihydro-1*H*-phenalene-6,7-yl)-15-(2,3-dihydro-1*H*-phenalene-6-yl)porphyrinato(2-)-κN^{21},κN^{22},κN^{23},κN^{24})zinc(II) 2. ^{1}H-NMR (5%-pyridine-d_5 in C_6D_6, 500 MHz): 1.47, 1.48 and 1.50 (s, 36H, atropoisomers), 1.95 (p, 2H, J = 5 Hz), 2.03 (p, 2H, J = 5 Hz), 2,97-3.02 (m, 4H), 3.03 (t, 2H, J = 6 Hz), 3.16 (t, 2H, J = 6 Hz), 6.76 (dd, 1H, J_1 = 7 Hz, J_2 = 9 Hz), 7.03 (d, 1H, J = 7 Hz), 7.20 (d, 1H, J = 9 Hz), 7.32 (d, 1H, J = 7.5 Hz), 7.42 (d, 1H, J = 7 Hz), 7.47 (d, 1H, J = 7.5 Hz), 7.95 (t, 1H, J = 1.5 Hz), 7.99 (t, 1H, J = 1.5 Hz), 8.28 (d, 1H, J = 7 Hz), 8.35 (t, 1H, J = 1.5 Hz), 8.37 (t, 1H, J = 1.5 Hz), 8.42 (d, 1H, J = 7.5 Hz), 8.51 (d, 2H, J = 1.5 Hz), 8.73 (d, 1H, J = 7.5 Hz), 8.78 (d, 1H, J = 4.5 Hz), 8.86 (d, 1H, J = 4.5 Hz), 9.02 (d, 1H, J = 4.5 Hz), 9.10 (d, 1H, J = 4.5 Hz), 9.19 (d, 1H, J = 4.5 Hz), 9.33 (d, 1H, J = 4.5 Hz), 9.74 (s, 1H). ^{13}C-NMR (5%-pyridine-d_5 in C_6D_6, 150 MHz): 23.7, 24.8, 31.86, 31.91,

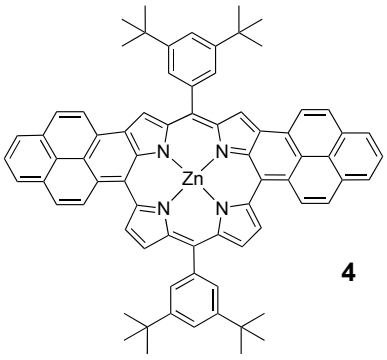
31.92, 35.16, 35.19, 35.20, 114.0, 118.7, 120.7, 120.8, 121.0, 122.7, 122.8, 122.9, 123.1, 123.3, 123.8, 124.5, 124.8, 125.6, 125.9, 125.94, 126.0, 130.1, 130.6, 130.7, 130.9, 130.94, 131.2, 131.7, 132.3, 132.4, 132.41, 132.6, 132.7, 132.9, 134.0, 136.2, 136.4, 136.9, 137.9, 138.1, 138.7, 139.4, 140.2, 143.7, 143.72, 146.1, 148.9, 149.04, 149.06, 149.8, 149.9, 150.3, 151.1, 151.7, 151.8, 152.1. UV/VIS (CH_2Cl_2) λ, nm, (ε): 299 sh (29600), 311 (31500), 385 (25800), 484 (178800), 561 (56200), 619 (12600), 650 sh (23600), 670 (42200). Emission (CH_2Cl_2): λ_{max}, 700 nm. HRMS: 1078.4895 (M^+), calcd. 1078.4886 for $C_{74}H_{70}N_4Zn$. Elemental analysis for $C_{74}H_{70}N_4Zn$: calcd: C 82.24, H 6.53, N 5.18; found: C 81.80, H 6.50, N 5.11.



3

[10,20-*Bis*(3,5-di-*tert*-butylphenyl)-3,5,13,15-*bis*-(2,3-dihydro-1*H*-phenalene-6,7-yl)-porphyrinato(2-)-κN^{21},κN^{22},κN^{23},κN^{24})zinc(II) 3. ^{1}H-NMR (5%-pyridine-d_5 in C_6D_6, 500 MHz): 1.52 (s, 18H), 1.57 (s, 18 H), 1.94 (br. s, 4H), 2.23 (br. s, 4H), 2.98 (br. s, 4H), 6.66 (d, 2H, J = 7 Hz), 6.98 (d, 2H, J = 7.5 Hz), 7.43 (d, 2H, J = 7 Hz), 7.98 (s, 1H), 8.09 (s, 1H), 8.39 (br. s, 2H), 8.52 (br. s, 2H), 8.68 (d, 2H, J = 7.5 Hz), 9.12 (d, 2H, J = 4.5 Hz), 9.24 (d, 2H, J = 4.5 Hz), 9.57 (s, 2H). ^{13}C-NMR (5%-pyridine-d_5 in C_6D_6, 125 MHz): 1.4, 23.1, 24.8, 31.9, 32.0, 35.2, 35.23, 113.2, 120.7, 123.5, 124.4, 125.8, 126.0, 126.1, 129.9, 130.6, 130.8, 132.7, 133.1, 134.1, 135.3, 136.6, 138.1, 139.2, 139.3, 143.6, 143.7, 146.5, 148.6, 149.0, 149.4, 151.4, 179.2. UV/VIS (CH_2Cl_2) λ, nm, (ε): 229 (54400), 320 (30800), 497 (152300), 535 (57100), 691 (17800), 753 (70600). Emission (CH_2Cl_2): λ_{max}, 765 nm, quantum yield – 11%. HRMS:

1076.4747 (M^+), calcd. 1076.4730 for $C_{74}H_{68}N_4Zn$. Elemental analysis for $C_{74}H_{68}N_4Zn*C_5H_5N$: calcd: C 81.95, H 6.35, N 6.05; found: C 81.30, H 6.33, N 6.13.



4

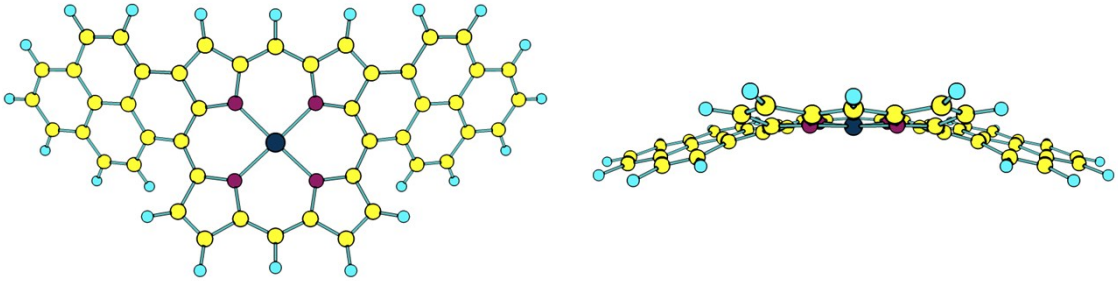
[10,20-*Bis*(3,5-di-*tert*-butylphenyl)-3,5,13,15-*bis*-(phenalene-6,7-yl)-porphyrinato(2-)-κN^{21},κN^{22},κN^{23},κN^{24})zinc(II) 4. A sample of mono-fused porphyrin **2** (255 mg, 0.237 mmol) in a glass tube was purged with nitrogen and placed into furnace preheated to 500^{0}C. The furnace temperature rose to 500^{0}C in 1-2 min and the solid sample was kept at this temperature under positive pressure of nitrogen for additional 8 min. After cooling the sample to ambient temperature under nitrogen, the crude mixture was dissolved in 1% pyridine in CH_2Cl_2 and the resulting solution was passed through a short alumina column (prewashed with 1% pyridine in CH_2Cl_2). All brown-green fractions were collected, solvents evaporated and the residue crystallized from 1% pyridine in CH_2Cl_2 by layered addition of methanol to give 60 mg (0.056 mmol, 24%) of porphyrin **4**. ^{1}H-NMR (5%-pyridine-d_5 in C_6D_6, 500 MHz): 1.43 (s, 36H), 7.37 (d, 2H, J = 4.5 Hz), 7.50 (d, 2H, J = 9 Hz), 7.55 (t, 2H, J = 7.5 Hz), 7.56 (d, 2H, J = 4.5 Hz), 7.70 (d, 2H, J = 7.5 Hz), 7.78 (d, 2H, J = 9 Hz), 7.81 (d, 2H, J = 7.5 Hz), 7.87 (t, 2H, J = 1.5 Hz), 7.99 (d, 4H, J = 1.5 Hz), 8.07 (s, 2H), 8.11 (d, 2H, J = 8.5 Hz), 8.51 (d, 2H, J = 8.5 Hz). ^{13}C-NMR (5%-pyridine-d_5 in C_6D_6, 125 MHz): 31.7, 35.1, 116.5, 119.4, 122.5, 124.5, 125.0, 125.9, 126.7, 127.17, 127.21, 128.5, 128.6, 128.7, 128.8, 129.0, 129.1, 130.2, 131.1, 131.4, 131.7, 135.6, 141.1, 145.2, 148.1, 149.5, 149.8, 150.0, 166.1. UV/VIS (CH_2Cl_2) λ, nm, (ε): 257 (42700), 296

(35600), 341 (26300), 392 (20400), 477 (63800), 530 (23800), 654 sh (20900), 728 sh (44500), 796 (69900). Emission (CH_2Cl_2): λ_{max}, 835 nm, quantum yield – 0.3%. HRMS: 1070.4270 (M^+), calcd. 1070.4260 for $C_{74}H_{62}N_4Zn$. Elemental analysis for $C_{74}H_{62}N_4Zn*C_5H_5N*CH_2Cl_2$: calcd: C 77.69, H 5.62, N 5.66; found: C 78.05, H 5.40, N 5.68.

3. Theoretical calculation data for **4'** and **4''**

Calculations on **4'** (*tert*-butyl groups replaced with H) were performed using Jaguar 8.9 in the Material Science package, release 2014-3 (Schrödinger, LLC, New York, NY, 2014) for TDDFT results (B3LYP/LACVP**).[8] Calculations on **3''** and **4''** (*meso*-3,5-di-*tert*-butyl phenyl groups replaced with H) were performed using Gaussian '03 (Gaussian, Inc., Pittsburgh PA, 2003).[9] Broken symmetry calculations were performed by applying the keyword guess=mix to the unrestricted B3LYP method.

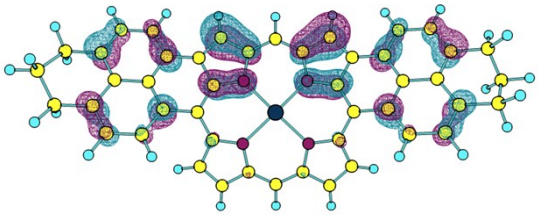
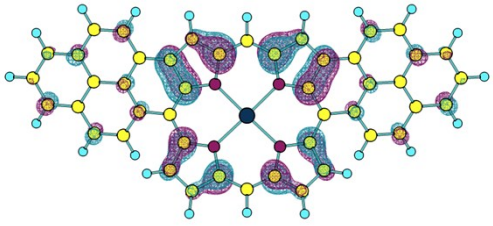
Figure S1. Optimized structure of **4''** by B3LYP/6-31G*/LANL2DZ:

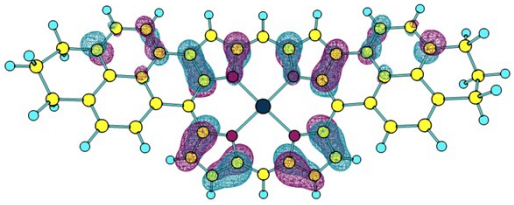


front view side view

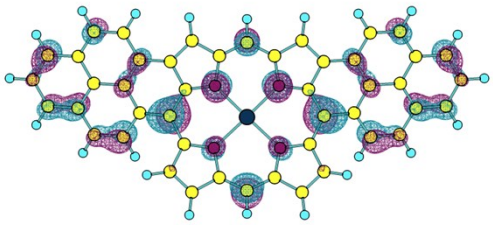
E^0= -2050.6095516 a.u. (B3LYP/6-31G*/LANL2DZ)

Figure S2. Frontier molecular orbitals of **3''** and **4''**

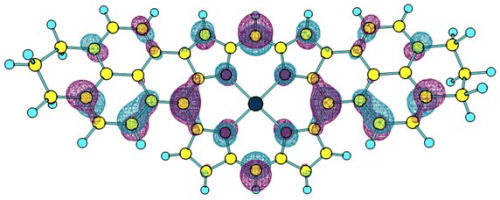
doubly-fused 3''	**quinoidal-4''**
HOMO-2, ε_{HOMO} = -5.77 eV	HOMO-2, ε = -5.56 eV
	
HOMO-1, ε_{HOMO} = -5.16 eV	HOMO-1, ε = -5.51 eV



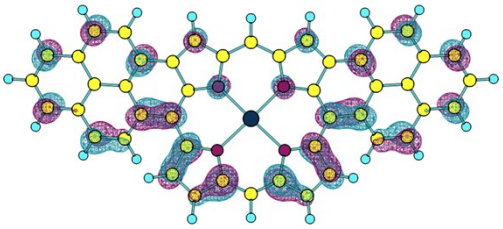
HOMO, ε_{HOMO} = -4.68 eV



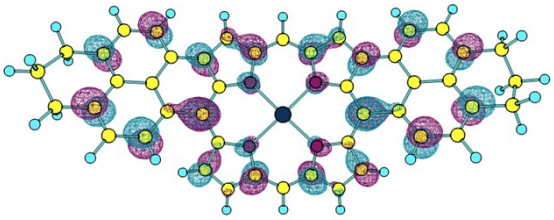
HOMO, ε = -4.66 eV



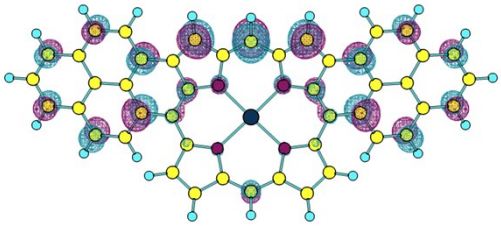
LUMO, ε_{HOMO} = -2.71 eV



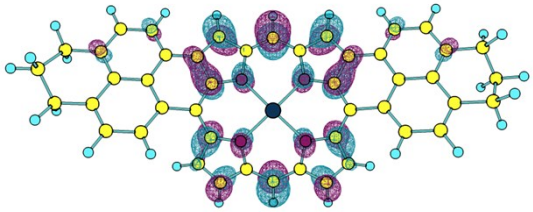
LUMO, ε = -3.40 eV



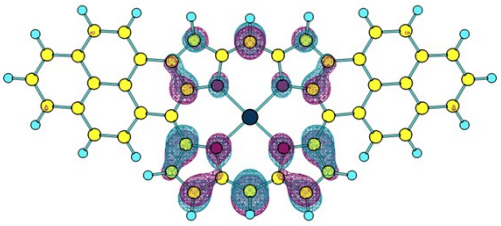
LUMO+1, ε_{HOMO} = -2.29 eV



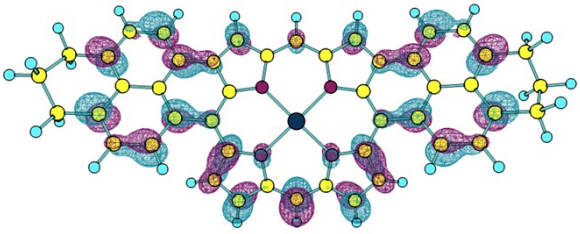
LUMO+1, ε = -2.37 eV



LUMO+2, ε_{HOMO} = -1.78 eV



LUMO+2, ε = -1.87 eV



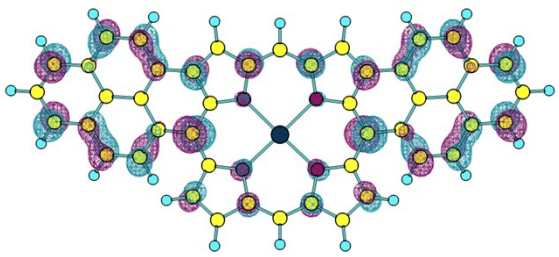


Table S1. Cartesian coordinates for the optimized structure of **4'**

Atom	x	y	z
C1	6.5189777938	5.7405280692	1.9089208035
C2	6.8550652829	4.6543560881	1.0360853635
H3	7.2264342435	4.7426383849	0.0269767092
C4	6.5565487885	3.4913170701	1.7029942153
H5	6.6907350383	2.4819501608	1.3433738633
C6	6.0111591831	3.8620312041	2.9721513124
C7	5.5699618543	2.9737600931	3.9751390631
C8	5.0043285240	3.3068548038	5.2238853195
C9	4.4783745024	2.3722584695	6.1702094796
H10	4.4602739827	1.2989128218	6.0514408861
C11	3.9701126738	3.0981593267	7.2183694067
H12	3.4386317721	2.7090210326	8.0731051795
C13	4.1858652259	4.4844932632	6.9157846921
C14	3.7007593918	5.6208308621	7.6940592206
C15	3.3919458128	5.5147773344	9.0818942261
C16	3.9250117965	4.4583141422	9.8992028377
H17	4.6602858526	3.7940795605	9.4647828990
C18	3.5824724993	4.2990461787	11.2078582278
H19	4.0292514158	3.4969559422	11.7905423013
C20	2.6604531290	5.1845630358	11.8575520139
C21	2.2638510472	5.0084690232	13.1896715715
H22	2.6470181973	4.1569561424	13.7464803726
C23	1.3898219993	5.9118092463	13.8019182378
H24	1.0881749891	5.7565572559	14.8340085853
C25	0.9125962489	7.0076921691	13.0978362608
H26	0.2369620583	7.7135918205	13.5745316725
C27	1.2952999834	7.2309781306	11.7565089847
C28	2.1725464795	6.3015857823	11.1155311440
C29	0.8351454974	8.3619878093	11.0199915603
H30	0.1645444897	9.0656175294	11.5070024190
C31	1.2373388684	8.5682442539	9.7279429281
H32	0.8897802950	9.4412052311	9.1840161875
C33	2.1085827482	7.6548024777	9.0741215415
C34	2.5611384391	6.4966231534	9.7531390842
C35	2.5959599277	7.8655248487	7.7505592709
C36	3.4047939227	6.8752781779	7.0828031074
C37	2.4793439084	8.9323034500	6.8673705197
H38	1.9358747213	9.8529966741	7.0153094373
C39	3.2523246599	8.6004717052	5.7192097675
C40	3.5009470732	9.4636046690	4.6277155599
C41	4.3377494371	9.1709721784	3.5254364630
C42	4.7700242441	10.1241173223	2.5596605552
H43	4.4672250417	11.1592198059	2.5222606928
C44	5.6956279085	9.4794977857	1.7464341206
C45	6.5080917052	9.9288772045	0.6628007402
C46	6.3981027740	11.2336349739	0.1079542533
H47	5.6370181710	11.9048196481	0.4936127524
C48	7.2320421366	11.6467040966	-0.8956863092
H49	7.1361063831	12.6450159357	-1.3143092038
C50	8.2502448975	10.7866236606	-1.4034660150
C51	9.1366739157	11.2034223099	-2.4212951050
H52	9.0259959206	12.2024217723	-2.8355893649
C53	10.1361138461	10.3605052998	-2.8838333259

H54	10.8125033450	10.6974502378	-3.6643477494
C55	10.2818083432	9.0796946279	-2.3423547217
H56	11.0747707760	8.4249381832	-2.6951350415
C57	9.4181898275	8.6219862864	-1.3391118226
C58	8.3771659807	9.4723381915	-0.8584203999
C59	9.5643510708	7.3323147808	-0.7303222536
H60	10.4078572899	6.7121053159	-1.0241154747
C61	8.6952208268	6.8890873881	0.2193742976
H62	8.8759796800	5.9313089937	0.6879782410
C63	7.5747858144	7.6705362304	0.6708382589
C64	7.4812893733	9.0263073688	0.1632668203
C65	6.6365914695	7.1645151800	1.6155615829
C66	5.7771009195	8.1225926076	2.2280741075
C67	5.7045216453	1.5121288657	3.6770595427
C68	4.9159016423	0.9076374551	2.6871178213
H69	4.1984334668	1.5105317231	2.1378848477
C70	5.0400511892	-0.4546293801	2.4146974396
C71	5.9593753848	-1.2306564364	3.1221940427
H72	6.0579943366	-2.2913195528	2.9074374428
C73	6.7503771990	-0.6380843737	4.1075032527
C74	6.6208519729	0.7224246473	4.3865179885
H75	7.2365836204	1.1834904228	5.1534130247
C76	2.8724444881	10.8179610437	4.6614647173
C77	3.2192362026	11.7490476713	5.6533842959
H78	3.9606667607	11.4791855990	6.3995326327
C79	2.6345163943	13.0146752252	5.6729912741
C80	1.6877489983	13.3653089113	4.7092422011
H81	1.2288099816	14.3500274125	4.7284078308
C82	1.3351458442	12.4469139944	3.7194042530
C83	1.9282980729	11.1850358289	3.6900172933
H84	1.6531936372	10.4703283487	2.9198847188
N95	5.9895380445	5.2493838927	3.0601553354
N96	4.7979149003	4.5956943447	5.7066486243
N97	3.7873879707	7.3250391689	5.8620584957
N98	4.9548616996	7.9484865755	3.2938490689
Zn100	4.9472314442	6.2839768205	4.5150532343
H101	2.9214342385	13.7278467561	6.4409968961
H102	0.5965547754	12.7120377351	2.9678252533
H103	7.4704546018	-1.2350396224	4.6607781913
H104	4.4163949674	-0.9097814574	1.6499086054

Table S2. Cartesian coordinates for the optimized structure of **4''**

Atom	x	y	z
C	3.502815000	-1.809239000	-0.410116000
C	2.514604000	-2.767688000	-0.679394000
C	1.259324000	-2.074788000	-0.688854000
N	1.462912000	-0.701827000	-0.467556000
C	2.816906000	-0.530019000	-0.299648000
C	2.522350000	4.186716000	-0.734914000
C	3.523020000	3.241856000	-0.562291000
C	2.879260000	1.982739000	-0.240999000
N	1.511067000	2.158563000	-0.250290000
C	1.266409000	3.514209000	-0.534993000
C	3.529374000	0.685606000	-0.049517000
C	-3.523024000	3.241844000	-0.562349000
C	-2.522355000	4.186710000	-0.734950000
C	-1.266414000	3.514209000	-0.535005000
N	-1.511071000	2.158564000	-0.250306000
C	-2.879264000	1.982739000	-0.241017000
C	-0.000002000	4.106346000	-0.649235000
C	-2.514613000	-2.767682000	-0.679436000
C	-3.502824000	-1.809232000	-0.410159000
C	-2.816909000	-0.530017000	-0.299667000
N	-1.462916000	-0.701827000	-0.467573000
C	-1.259329000	-2.074787000	-0.688871000
C	-0.000002000	-2.685612000	-0.814245000
C	-3.529374000	0.685607000	-0.049527000
C	4.909559000	0.549480000	0.317385000
C	-4.909553000	0.549479000	0.317389000
C	5.660937000	1.646989000	0.889317000
C	6.997841000	1.549521000	1.190291000
C	7.738885000	0.334821000	0.950698000
C	7.018947000	-0.808433000	0.466180000
C	5.609986000	-0.724392000	0.186060000
H	5.133054000	2.558748000	1.137244000
C	7.725760000	-2.045720000	0.277009000
C	6.999491000	-3.197755000	-0.177414000
C	5.640841000	-3.127220000	-0.411983000
C	4.922061000	-1.903265000	-0.228405000
C	-5.660902000	1.646963000	0.889406000
C	-6.997802000	1.549493000	1.190402000
C	-7.738863000	0.334814000	0.950756000
C	-7.018944000	-0.808426000	0.466174000
C	-5.609989000	-0.724383000	0.186031000
C	-7.725767000	-2.045701000	0.276969000
C	-6.999512000	-3.197725000	-0.177503000
C	-5.640861000	-3.127195000	-0.412074000
C	-4.922072000	-1.903250000	-0.228465000
H	-5.133000000	2.558699000	1.137383000
C	-9.120959000	-2.104437000	0.546751000
H	-9.649191000	-3.042614000	0.391750000
H	-7.537761000	-4.131447000	-0.324708000
C	-9.120764000	0.235250000	1.217622000
C	-9.809113000	-0.977385000	1.009447000
C	9.120790000	0.235260000	1.217541000
C	9.809127000	-0.977389000	1.009405000

C	9.120955000	-2.104455000	0.546769000
H	9.649179000	-3.042641000	0.391793000
H	7.537734000	-4.131484000	-0.324599000
H	2.639703000	-3.833244000	-0.818287000
H	2.639802000	5.229822000	-0.999061000
H	4.580606000	3.391621000	-0.713483000
H	-2.639805000	5.229813000	-0.999113000
H	0.000000000	5.172102000	-0.872808000
H	-2.639715000	-3.833236000	-0.818342000
H	-0.000001000	-3.760981000	-0.982755000
H	7.516422000	2.393870000	1.639629000
H	5.099413000	-4.009253000	-0.742511000
H	-7.516364000	2.393822000	1.639798000
H	-5.099440000	-4.009224000	-0.742623000
H	-9.654362000	1.106926000	1.590192000
H	-10.874792000	-1.036771000	1.214568000
H	9.654402000	1.106948000	1.590062000
H	10.874810000	-1.036774000	1.214506000
Zn	-0.000007000	0.737756000	-0.281614000
H	-4.580607000	3.391598000	-0.713580000

Table S3. Total atomic spin densities of **4''** obtained by BS-UB3LYP/6-31G*/LANL2DZ.

Mulliken atomic spin densities:

1 C 0.012704	21 N -0.011215	41 C -0.013776	61 H 0.000000
2 C -0.029913	22 C -0.001289	42 C -0.010633	62 H -0.002032
3 C 0.001291	23 C -0.000002	43 C 0.021117	63 H 0.000000
4 N 0.011215	24 C -0.026336	44 C -0.013623	64 H 0.001713
5 C -0.010855	25 C -0.031684	45 C 0.026988	65 H -0.000733
6 C -0.006927	26 C 0.031684	46 H 0.001039	66 H -0.001713
7 C 0.004252	27 C 0.018259	47 C 0.021581	67 H 0.000733
8 C -0.014245	28 C -0.025927	48 H -0.001423	68 H -0.001464
9 N 0.006117	29 C 0.012751	49 H -0.001383	69 H 0.000654
10 C -0.000837	30 C -0.006311	50 C 0.022302	70 H 0.001464
11 C 0.026336	31 C 0.013776	51 C -0.012421	71 H -0.000654
12 C -0.004252	32 H -0.001039	52 C -0.022301	72 Zn 0.000000
13 C 0.006927	33 C 0.010632	53 C 0.012420	73 H 0.000234
14 C 0.000838	34 C -0.021117	54 C -0.021581	
15 N -0.006117	35 C 0.013623	55 H 0.001423	
16 C 0.014246	36 C -0.026988	56 H 0.001383	
17 C -0.000001	37 C -0.018259	57 H 0.002032	
18 C 0.029913	38 C 0.025928	58 H 0.000489	
19 C -0.012704	39 C -0.012751	59 H -0.000234	
20 C 0.010855	40 C 0.006312	60 H -0.000489	

S4. Cyclic voltammetry data of porphyrins **1–4**.

Table S4. Redox potentials in dichloromethane (volts versus ferrocene/ferrocenium)

compound	$E_{1/2}^{ox,1}$	$E_{1/2}^{red,1}$	$E_{1/2}^{red,2}$	$\Delta E^{ox\text{-}red}$
1	+0.25	-1.98	-2.34	2.23
2	+0.17	-1.66	-1.87	1.83
3	-0.08	-1.66		1.58
4	+0.04	-1.32	-1.70	1.36

Figure S3. Porphyrin **1** CV and DPV (decamethylferrocene as standard):

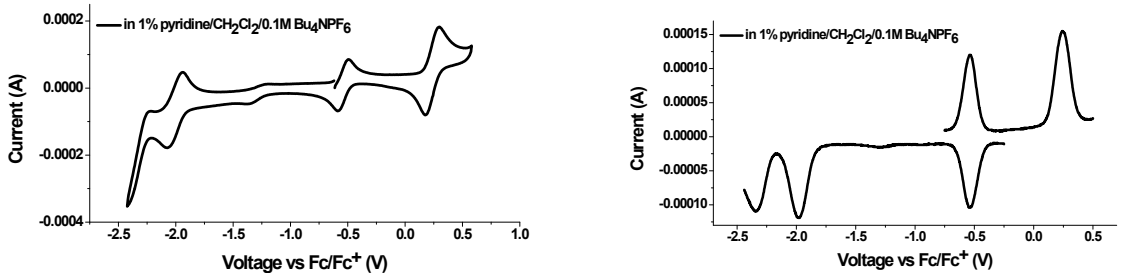


Figure S4. Porphyrin **2** CV and DPV (decamethylferrocene as standard):

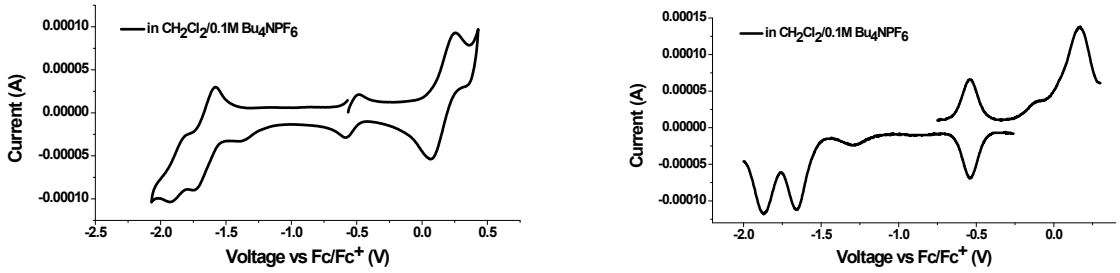


Figure S5. Porphyrin **3** CV and DPV (decamethylferrocene as standard):

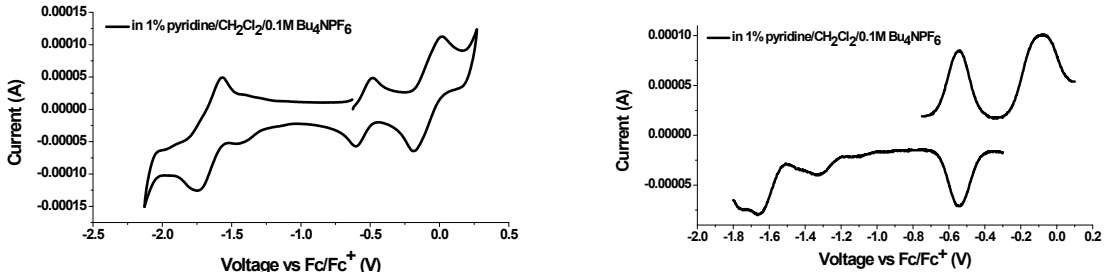
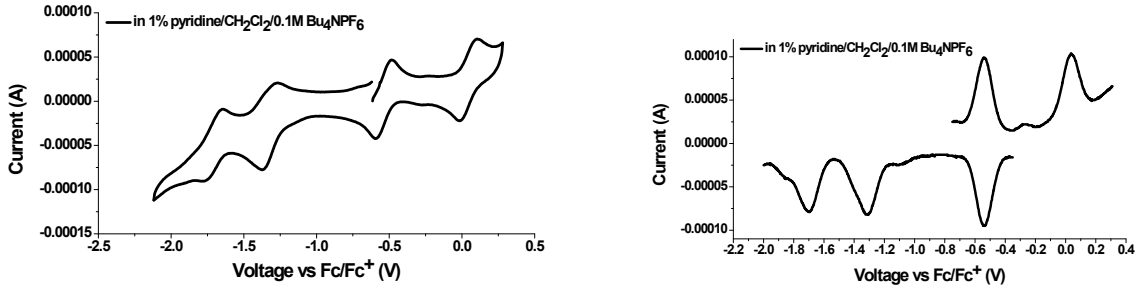


Figure S6. Porphyrin **4** CV and DPV (decamethylferrocene as standard):



5. UV-visible spectra of free-base **2H-4** and thin films of quinoidal porphyrins **3** and **4**.

Figure S7. UV-visible spectra of free-base **2H-4** and **4**.

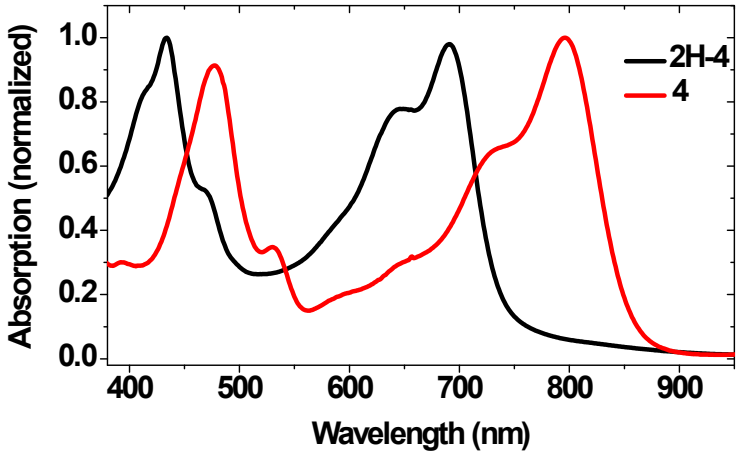
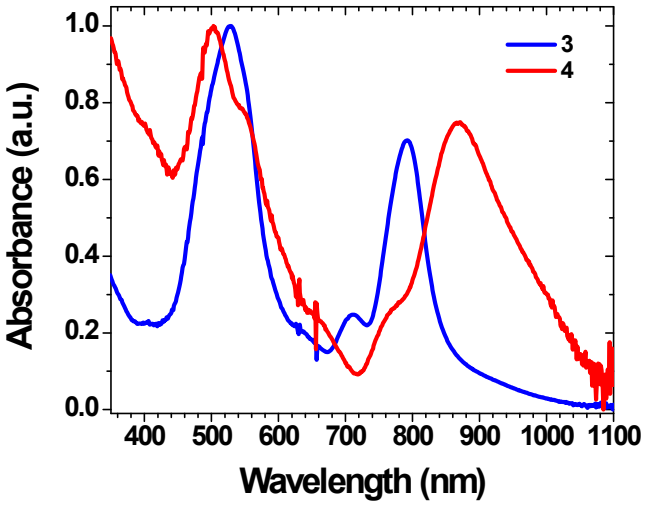
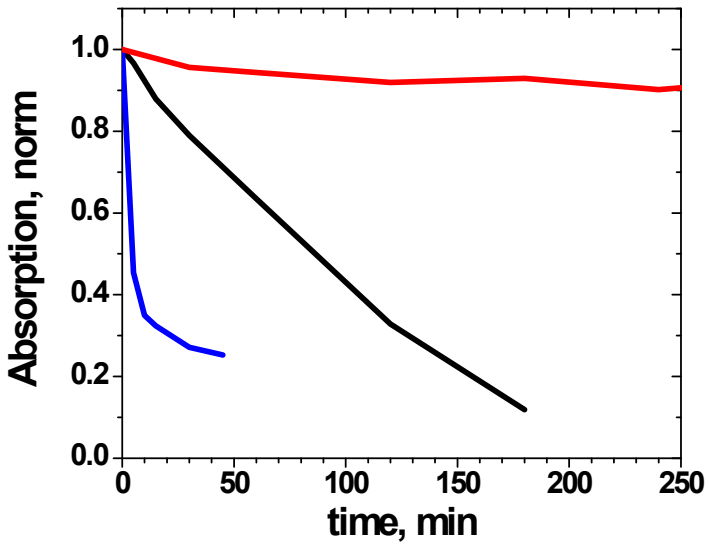


Figure S8. UV-visible absorption spectra of porphyrins **3** and **4** as thin films cast from CH_2Cl_2 solution.



6. Photooxidation of porphyrins **1**, **3** and **4**.

Figure S9. Photooxidation of porphyrins **1**, **3** and **4**.



Relative rates of photooxidation of porphyrins **1** (black curve), **3** (blue curve) and **4** (red curve) as determined by normalized changes of absorption max of the lowest energy absorption peak upon irradiation under standardized conditions (300 W white light lamp, quartz cell in air).

7. ^{1}H NMR and ^{13}C NMR spectra of **1–4**.

Figure S10. ^{1}H-NMR and ^{13}C NMR spectra of porphyrin **1** in $CDCl_3$ at 25^0C

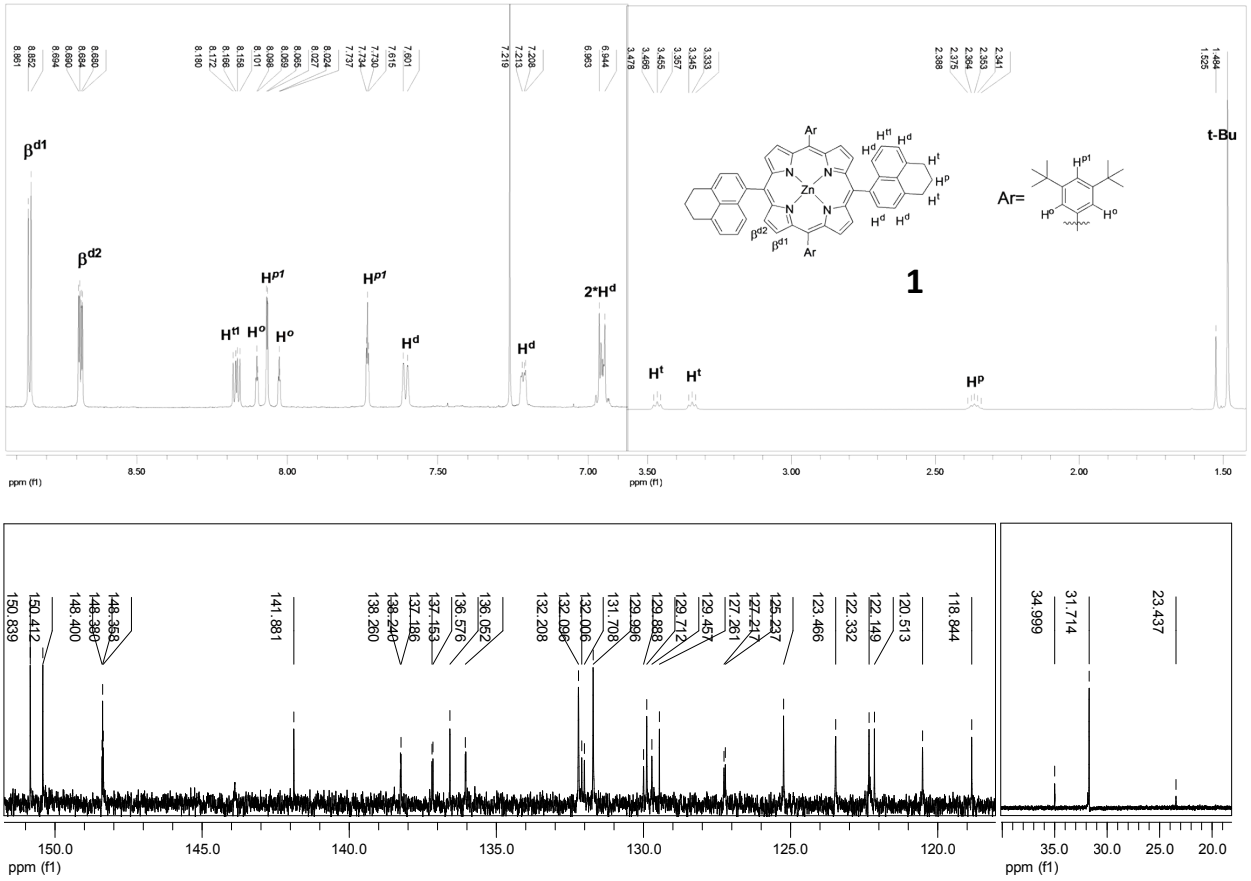
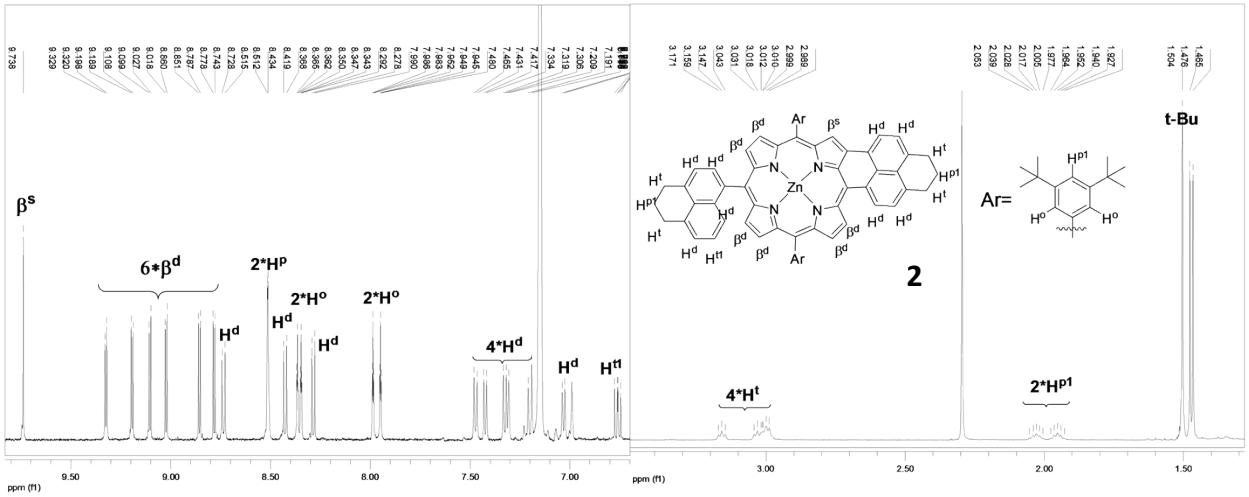


Figure S11. ^{1}H-NMR and ^{13}C NMR spectra of porphyrin **2** in 1% C_5D_5N - C_6D_6 at 25^{0}C



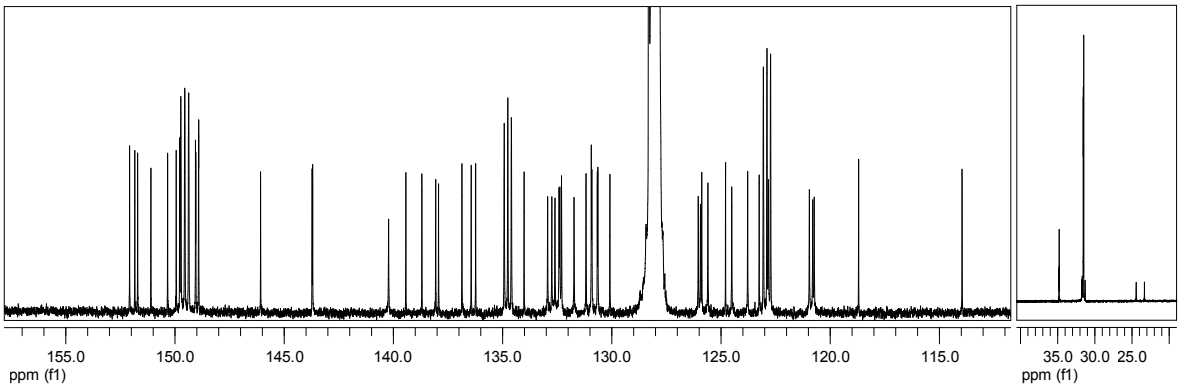
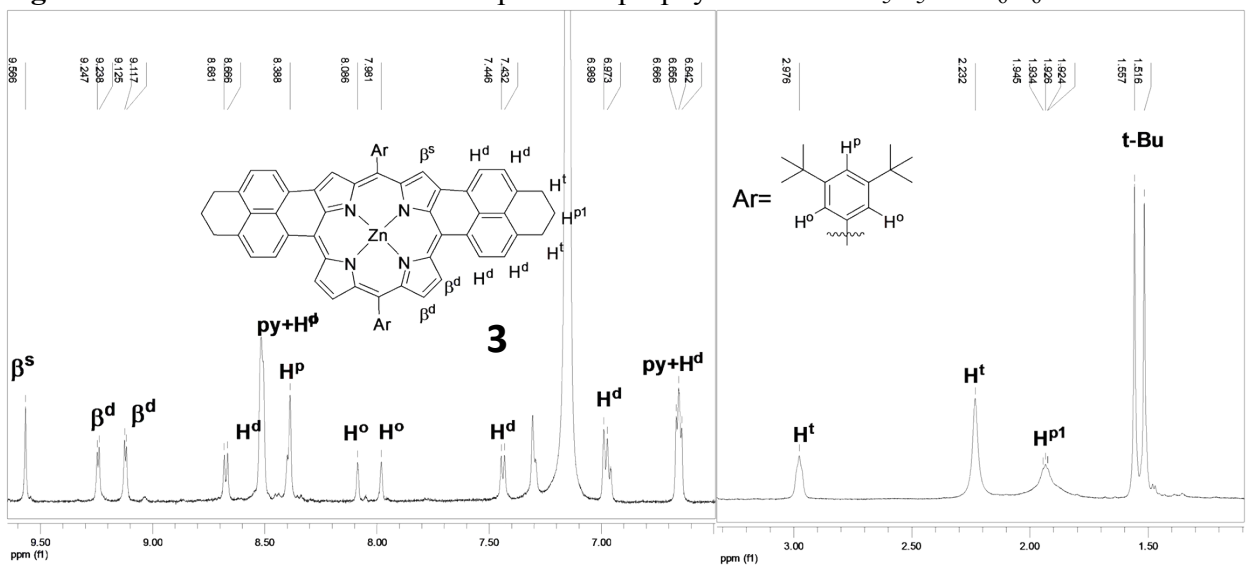


Figure S12. ^{1}H-NMR and ^{13}C NMR spectra of porphyrin **3** in 1% C_5D_5N - C_6D_6 at 25^{0}C



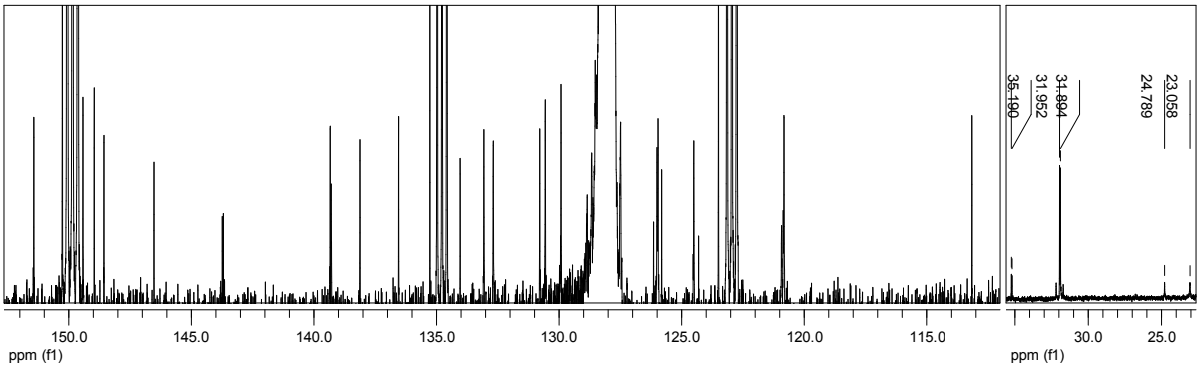
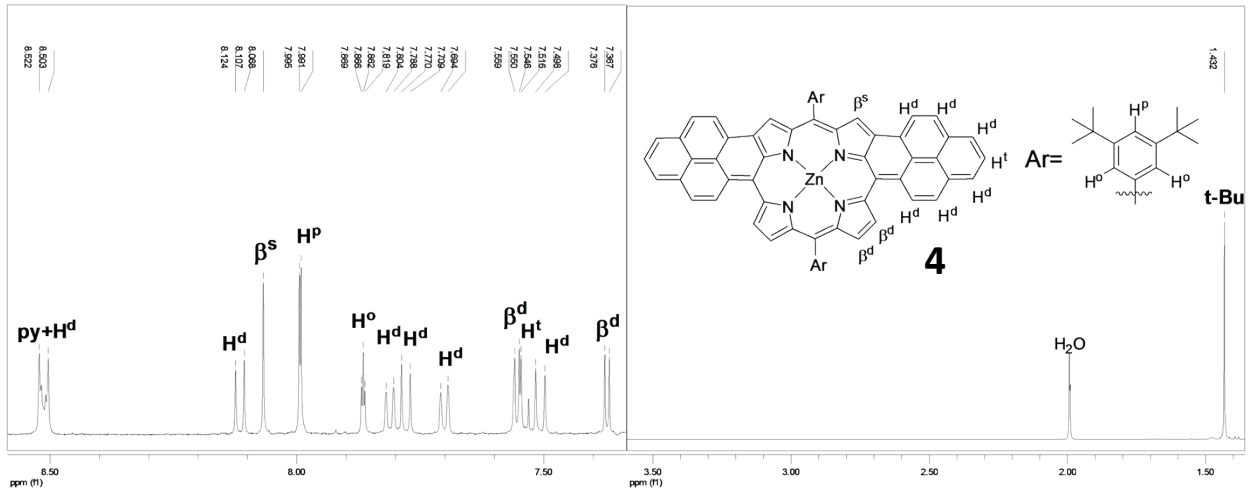
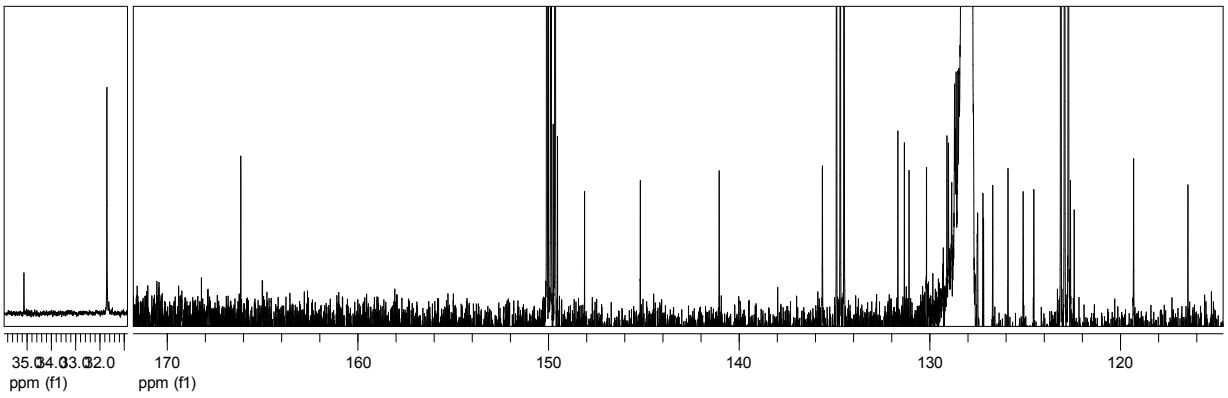


Figure S13. ^{1}H-NMR and ^{13}C NMR spectra of porphyrin **4** in 1% C_5D_5N - C_6D_6 at 25^{0}C

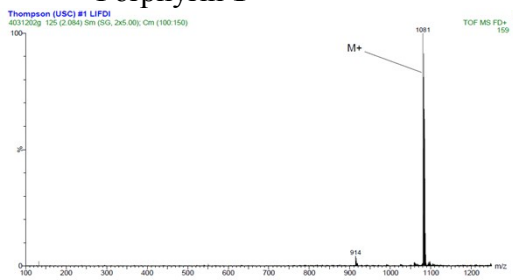


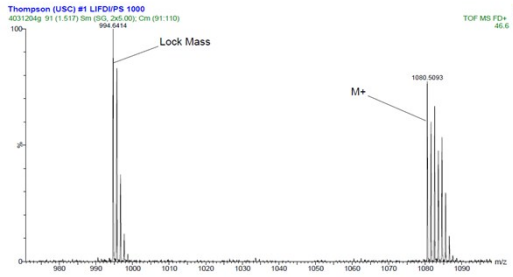


8. HRMS and MALDI-TOF spectra of **1**–**4**.

Figure S14. HRMS and MALDI-TOF spectra of **1**–**4**.

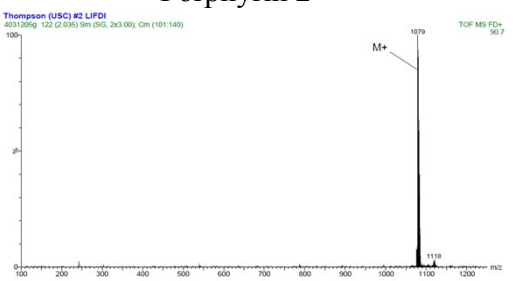
Porphyrin **1**

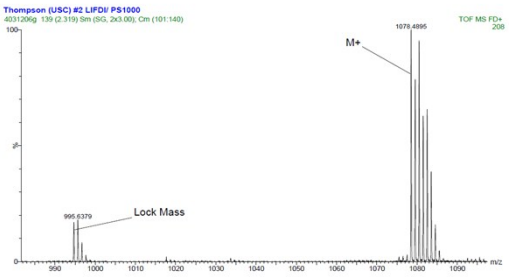




Measured Mass	1080.5093				
Element	Low Limit	High Limit			
C	70	80			
H	55	80			
N	2	6			
Zn	0	1			
Formula	Calculated Mass	mDaError	ppmError	RDB	
C80 H64 N4	1080.5126	-3.3	-3.0	51	
C74 H72 N4 Zn	1080.5043	5.0	4.6	41	

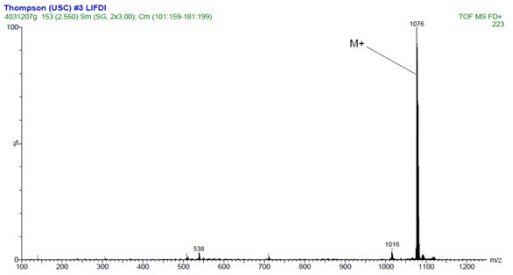
Porphyrin **2**

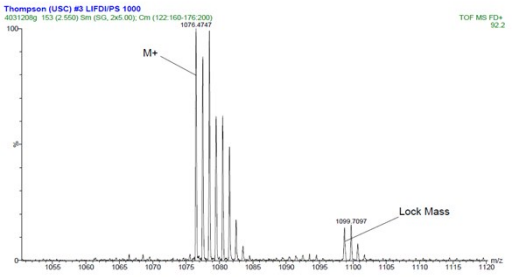




Measured Mass	1078.4895				
Element	Low Limit	High Limit			
C	70	80			
H	55	80			
N	2	6			
Zn	0	1			
Formula	Calculated Mass	mDaError	ppmError	RDB	
C74 H70 N4 Zn	1078.4886	0.9	0.8	42	
C79 H60 N5	1078.4843	5.2	4.8	52.5	

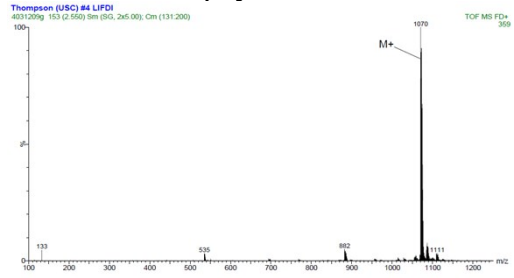
Porphyrin **3**

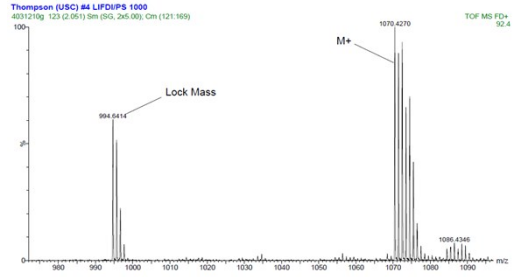




Measured Mass	1076.4747				
Element	Low Limit	High Limit			
C	70	80			
H	55	80			
N	2	6			
Zn	0	1			
Formula	Calculated Mass	mDaError	ppmError	RDB	
C74 H68 N4 Zn	1076.4730	1.7	1.6	43	

Porphyrin **4**





Measured Mass	1070.427				
Element	Low Limit	High Limit			
C	70	80			
H	55	80			
N	2	6			
Zn	0	1			
Formula	Calculated Mass	mDaError	ppmError	RDB	
C74 H62 N4 Zn	1070.4260	1.0	0.9	46	

9. Crystallographic data for **4**.

The single crystal X-ray diffraction data for $C_{97}H_{85}N_5Zn$ (**4**•pyridine) were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD detector with the χ-axis fixed at 54.74°, and using Cu $K_{\square}$ radiation (multi-layer optics monochromator) from an IμS microsource. The diffractometer was equipped with an Oxford Cryostream 700 apparatus for low-temperature data collection. A complete hemisphere of data was scanned on omega and phi (2° width) with a run time of 30 to 120 seconds per frame at a detector resolution of 512 x 512 pixels using the BIS software package.[10] A total of 2064 frames were collected with a total exposure time of 43.43 hours. The frames were then integrated using the SAINT algorithm[11] to give the hkl files corrected for Lp/decay. The absorption correction was performed using the SADABS program.[12] The structures were solved by the Direct Method and refined on F^2 using the Bruker SHELXTL Software Package.[13] All non-hydrogen atoms were refined anisotropically. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 1434349).

Table S5. Sample and crystal data for $C_{97}H_{85}N_5Zn$ (**4**•pyridine).

Chemical formula	$C_{97}H_{85}N_5Zn$	
Formula weight	1386.06 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.069 x 0.118 x 0.270 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.8075(4) Å	α = 81.213(3)°
	b = 20.3411(7) Å	β = 86.010(3)°
	c = 27.8465(9) Å	γ = 75.367(3)°
Volume	7474.5(4) Å^3	
Z	4	
Density (calculated)	1.232 g/cm^3	
Absorption coefficient	0.853 mm^{-1}	
F(000)	2928	
Theta range	2.27 to 69.36°	
Index ranges	$-16 \leq h \geq 16$	
	$-24 \leq k \geq 24$	
	$-30 \leq k \geq 33$	
Reflections collected	80677	
Independent reflections	24937 [R(int) = 0.1733]	
Data / restraints / parameters	24937 / 282 / 1919	
Final R indices	10989 data; I>2σ(I)	R1 = 0.0843, wR2 = 0.1683
	all data	R1 = 0.2037, wR2 = 0.2144
Goodness-of-fit	1.008	
Largest diff. peak and hole	0.764 and -0.543 eÅ^{-3}	

Figure S15. Unit cell of $C_{97}H_{85}N_5Zn$ (**4**•pyridine). View along a.

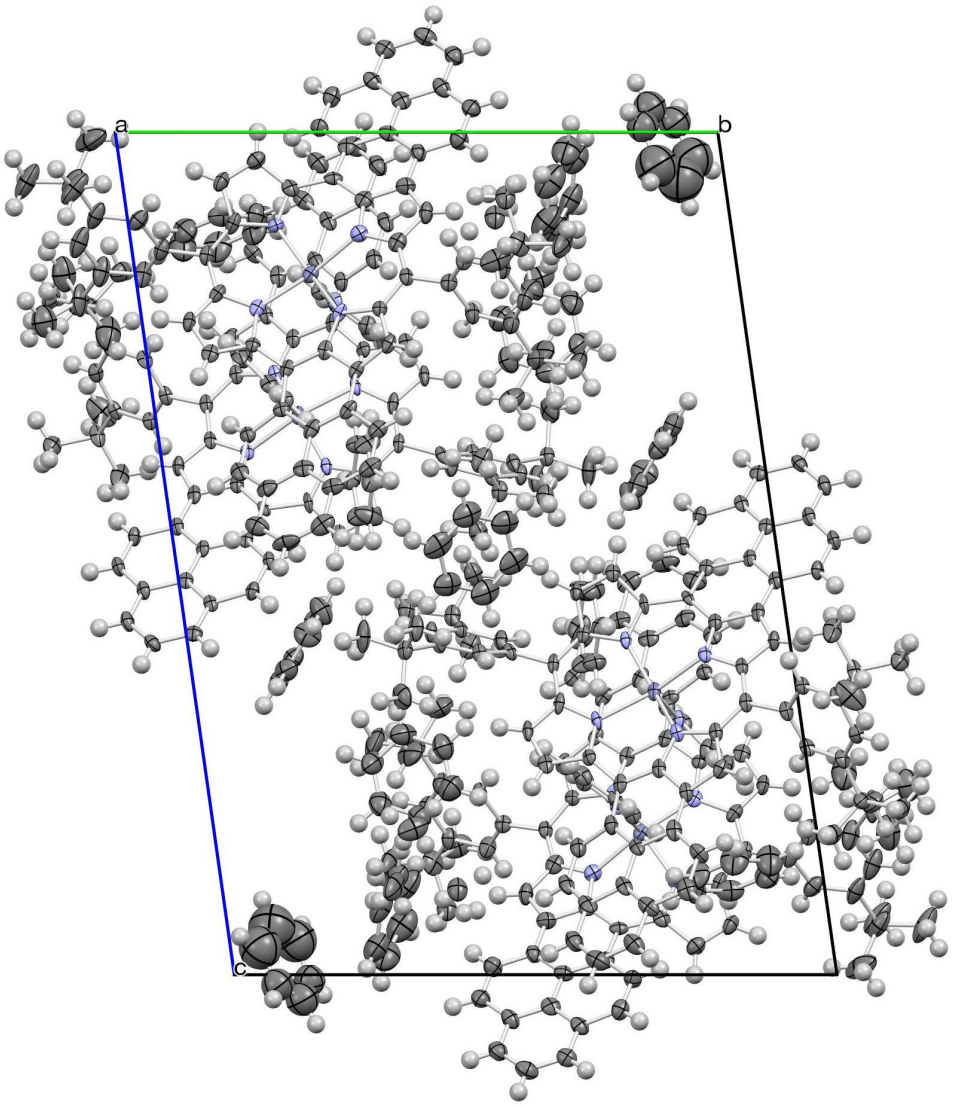


Figure S14. Unit cell of $C_{97}H_{85}N_5Zn$ (**4**•pyridine). View along b.

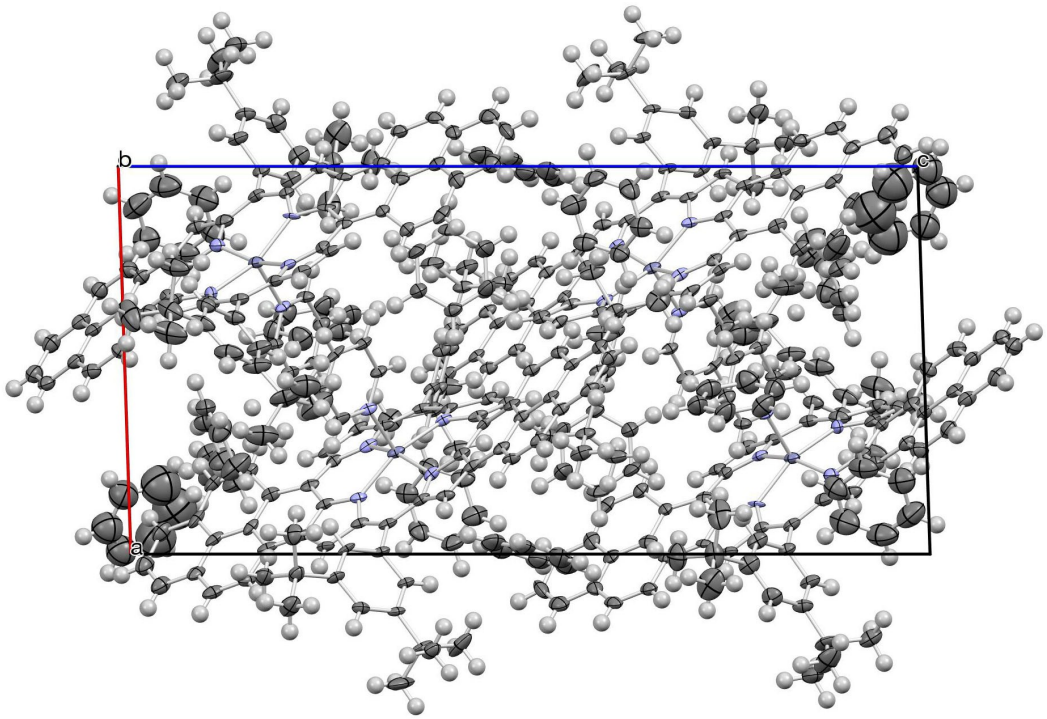
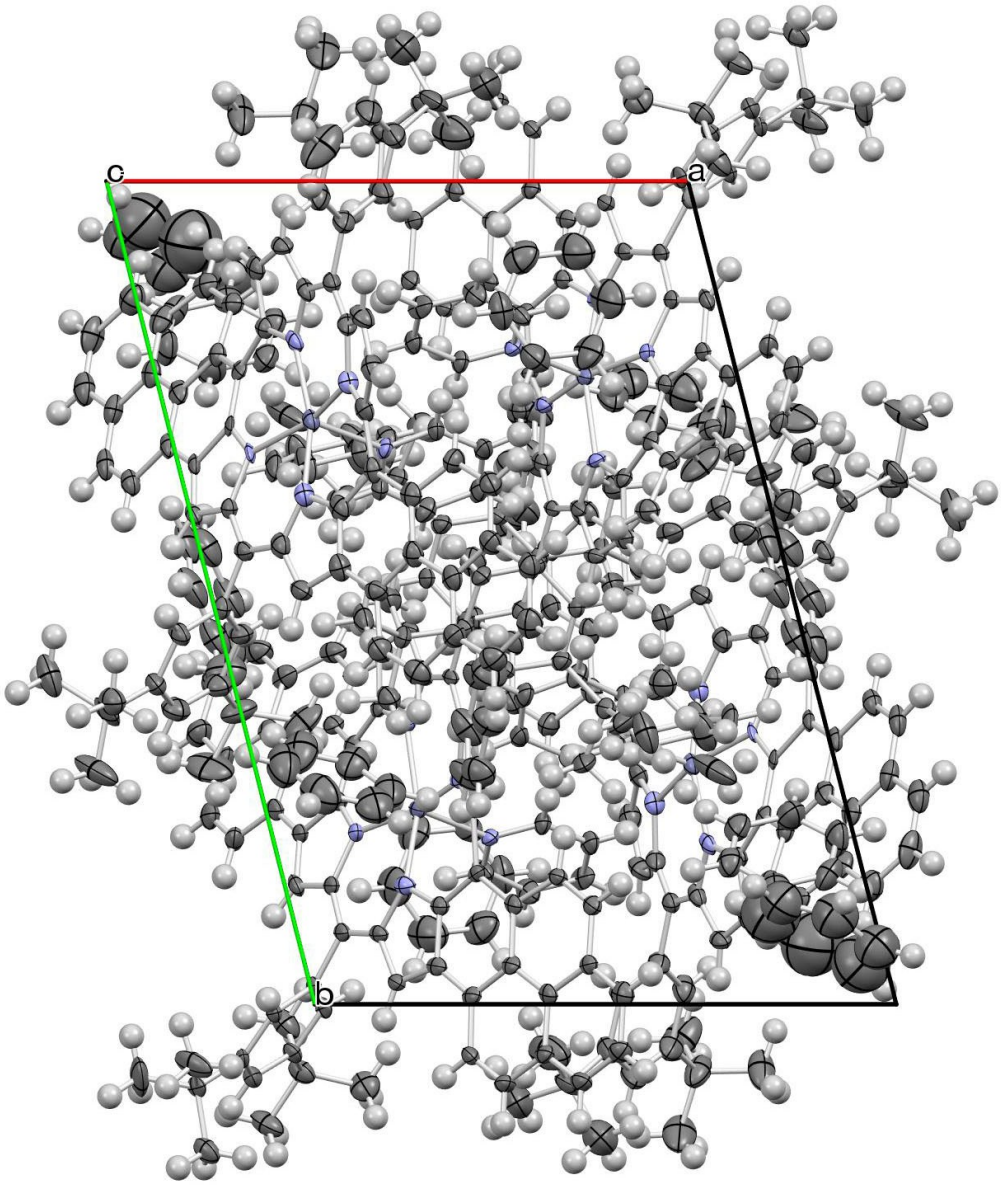


Figure S16. Unit cell of $C_{97}H_{85}N_5Zn$ (**4**•pyridine). View along c.



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