Supporting Information

N-Heterocycle-fused Ni(II) porphyrin dimers upon heating of *meso*-amino Ni(II) porphyrins in nitrobenzene

Qingjie Pan, Li Liu, Ying Pan, Mingbo Zhou,* Ling Xu, Yutao Rao, Bangshao Yin, Jianxin Song,* and Atsuhiro Osuka

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), and Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, P. R. China

E-mail: zhoumingbo@hunnu.edu.cn to M. Z. and jxsong@hunnu.edu.cn to J. S.

Table of Contents

1. Materials and instrumentation

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were taken on a Bruker AVANCE-500 spectrometer. Chemical shifts were reported as the delta scale in ppm. The residual peak of $CDCl_3$ was used as internal reference for ^{1}H NMR (δ = 7.26 ppm) and ^{13}C NMR (δ = 77.0 ppm); toluene-d_8 was used as internal reference for ^{1}H NMR (δ = 7.01 ppm). UV/Vis/NIR absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. MALDI-TOF mass spectra were obtained with a Bruker ultrafle Xtreme MALDI-TOF/TOF spectrometer with matrix. All solvents and reagents were commercially available and used without further purification. Column chromatography was carried out on silica gel (100-200 mesh). Amino Ni(II) porphyrins **5** and **6** were synthesized according to the reported procedures.[S1]

2. Data of fused porphyrin dimers 9-13

Data of **9**: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 10.85 (s, 1H, *N*-H), 10.75 (s, 1H, *meso*-H), 9.92 (s, 1H, *β*-H), 9.25 (d, *J* = 5.0 Hz, 1H, *β*-H), 9.06 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.96 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.92 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.86 (br, 2H, Ar-H), 8.77 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.67 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.63 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.60 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.52 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.39 (t, *J* = 2.0 Hz, 1H, Ar-H), 8.31 (d, *J* = 2.0 Hz, 2H, Ar-H), 8.27 (d, *J* = 2.0 Hz, 2H, Ar-H), 8.19 (d, *J* = 5.0 Hz, 1H, *β*-H), 7.97 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.96 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.94 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.92 (t, *J* = 2.0 Hz, 1H Ar-H), 7.86 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.79 (d, *J* = 5.0 Hz, 1H, *β*-H), 7.78 (d, *J* = 5.0 Hz, 1 H, *β*-H) 7.76 (t, *J* = 2.0 Hz, 1H, Ar-H), 7.68 (t, *J* = 2.0 Hz, 1H, Ar-H), 1.71 (br, 18H, *t*-Bu-H), 1.57 (br,

36H, *t*-Bu-H), 1.54 (br, 18H, *t*-Bu-H), 1.50 (br, 18H, *t*-Bu-H), and 1.49 (br, 18H, *t*-Bu-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 152.5, 149.7, 149.1, 148.99, 148.97, 148.9, 146.5, 144.8, 143.8, 143.5, 143.1, 142.3, 141.8, 141.3, 141.0, 140.5, 140.4, 140.0, 139.9, 139.79, 139.77, 138.9, 136.8, 134.0, 133.5, 132.9, 132.8, 132.6, 132.4, 132.1, 132.0, 131.9, 131.8, 130.9, 130.4, 130.1, 129.3, 129.13, 129.06, 128.72, 128.65, 128.5, 127.7, 124.2, 122.8, 122.3, 121.28, 121.26, 121.0, 120.8, 120.6, 120.5, 120.1, 119.2, 117.4, 116.2, 114.7, 110.6, 101.3, 35.6, 35.3, 35.08, 35.06, 35.03, and 34.99 ppm. MALDI-TOF-MS: *m/z* = 1872.0097, calcd for $C_{124}H_{141}N_9Ni_2^+$ $[M]^+$: 1872.0011. UV-vis (CH_2Cl_2) λ_{max} ($[M^{-1}cm^{-1}]$) = 415 nm (120000), 457 nm (193000), 529 nm (38000), and 637 nm (45000).

Data of **10**: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 11.55 (s, 1H, *meso*-H), 9.15 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.93 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.88 (d, *J* = 5.0Hz, 1H, *β*-H), 8.83 (d, *J* = 5.00 Hz, 1H, *β*-H), 8.75 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.71 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.26 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.06 (d, *J* = 5.0 Hz, 1H, *β*-H), 8.00 (d, *J* = 5.0 Hz, 1H, *β*-H), 7.96 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.95 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.90 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.89 (br, 1H, *β*-H), 7.88 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.80 (d, *J* = 5.0 Hz, 1H, *β*-H), 7.75 (t, *J* = 2.0 Hz, 4H, Ar-H), 7.73 (t, *J* = 2.0 Hz, 2H, Ar-H), 7.69 (d, *J* = 5.0 Hz, 1H, *β*-H), 7.66 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.64 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.62 (d, *J* = 2.0 Hz, 2H, Ar-H), 1.57 (br, 18H, *t*-Bu-H) 1.52 (br, 36H, *t*-Bu-H) 1.48 (br, 18H, *t*-Bu-H), and 1.45 (br, 36H, *t*-Bu-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 192.1, 154.4, 152.9, 150.7, 149.9, 149.63, 149.57, 149.12, 149.11, 149.0, 145.2, 144.6, 143.8, 142.9, 142.2, 142.1, 141.5, 141.3, 140.9, 140.73, 140.69, 140.1,

139.6, 139.5, 138.4, 138.3, 138.2, 137.0, 136.8, 135.2, 133.8, 133.4, 133.1, 132.9, 132.7, 132.1, 131.7, 131.6, 131.5, 130.7, 130.0, 129.3, 129.2, 128.9, 128.4, 128.33, 128.26, 128.2, 127.6, 126.9, 126.8, 126.1, 123.0, 121.9, 121.8, 121.7, 121.5, 121.3, 121.2, 120.1, 119.4, 116.0, 104.2, 35.2, 35.1, 35.04, 35.01, 34.98, and 34.96 ppm. MALDI-TOF-MS: *m/z* = 1885.9819, calcd for $C_{124}H_{139}N_9Ni_2O^+$ $[M]^+$: 1885.9804. UV-vis (CH_2Cl_2) λ_{max} ($[M^{-1}cm^{-1}]$) = 420 nm (148000), 537 nm (72000), 711 nm (29000), and 796 nm (22000).

Data of **11**: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.09 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.59 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.58 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.50 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.37 (br, 4H, *β*-H), 8.11 (d, *J* = 1.5 Hz, 4H, Ar-H), 8.07 (d, *J* = 1.5 Hz, 2H, Ar-H), 7.86 (d, *J* = 2.0 Hz, 4H, Ar-H), 7.84 (d, *J* = 1.5 Hz, 4H, Ar-H), 7.76 (t, *J* = 2.0 Hz, 2H, Ar-H), 7.72 (t, *J* = 2.0 Hz, 2H, Ar-H), 1.55 (br, 36H, *t*-Bu-H), 1.52 (br, 36H, *t*-Bu-H), and 1.49 (br, 36H, *t*-Bu-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 161.3, 150.3, 149.20, 149.15, 149.1, 143.5, 143.2, 141.6, 141.4, 139.7, 139.4, 138.2, 135.4, 134.3, 133.4, 131.4, 131.0, 130.6, 130.4, 128.7, 128.3, 128.0, 127.6, 127.0, 125.6, 121.7, 121.4, 121.39, 118.5, 35.2, 35.1, and 35.0 ppm; HR-MS (MALDI-TOF-MS) *m/z* = 1882.9773, calcd for $C_{124}H_{138}N_{10}Ni_2^+$ $[M]^+$: 1882.9807. UV-vis (CH_2Cl_2) λ_{max} ($[M^{-1}cm^{-1}]$) = 404 nm (75000), 516 nm (93000), 555 nm (92000), 745 nm (27000), and 896 nm (58000).

Data of **12**: ^{1}H NMR (500 MHz, toluene-d_8, 353 K) *δ* = 9.44 (d, *J* = 4.5 Hz, 2H, *β*-H), 8.78 (d, *J* = 4.5 Hz, 2H, *β*-H), 8.56 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.49 (d, *J* = 2.0 Hz, 4H, Ar-H), 8.45 (d, *J* = 4.5 Hz, 2H, *β*-H), 8.35 (d, *J* = 4.5 Hz, 2H, *β*-H), 8.31-8.30 (m,

4H, containing 2 *β*-H), 8.10 (d, *J* = 2.0 Hz, 4H, Ar-H), 8.06 (d, *J* = 2.0 Hz, 4H, Ar-H), 7.89 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.87 (d, *J* = 2.0 Hz, 2H, Ar-H), 3.20 (s, 1H, *N*-H), 2.40 (s, 1H, *N*-H), 1.66 (br, 36H, *t*-Bu-H), 1.48 (br, 36H, *t*-Bu-H), and 1.46 (br, 36H, *t*-Bu-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 150.3, 149.1, 148.9, 140.9, 139.1, 138.6, 130.4, 128.8, 128.4, 128.3, 121.8, 121.5, 121.3, 35.3, 35.1, and 35.0 ppm. HR-MS (MALDI-TOF-MS) *m/z* = 1771.1479, calcd for $C_{124}H_{142}N_{10}^+$ $[M]^+$: 1771.1413. UV-vis (CH_2Cl_2) λ_{max} ($[M^{-1}cm^{-1}]$) = 398 nm (100000), 517 nm (109000), 811 nm (30000), and 899 nm (62000).

Data of **13**: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.24 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.67 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.66 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.53 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.43 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.42 (d, *J* = 5.0 Hz, 2H, *β*-H), 8.34 (br, 4H, Ar -H), 8.17 (t, *J* = 1.5 Hz, 2H, Ar-H), 8.00 (d, *J* = 1.5 Hz, 4H, Ar-H), 7.94 (d, *J* = 2.0 Hz, 4H, Ar-H), 7.80 (t, *J* = 1.5 Hz, 2H, Ar-H), 7.73 (t, *J* = 2.0 Hz, 2H, Ar-H), 1.62 (br, 36H, *t*-Bu-H), 1.55 (br, 36H, *t*-Bu-H), and 1.50 (br, 36H, *t*-Bu-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ = 159.2, 158.7, 156.4, 150.2, 150.0, 149.6, 149.3, 148.9, 148.8, 148.1, 142.0, 141.2, 141.0, 140.1, 134.6, 133.6, 131.6, 131.2, 130.8, 130.4, 129.9, 128.7, 128.5, 127.4, 125.6, 121.4, 121.4, 121.1, 120.8, 35.3, 35.1, and 35.0 ppm. MALDI-TOF-MS: *m/z* = 1894.9683, calcd for $C_{124}H_{138}N_{10}Zn_2^+$ $[M]^+$: 1894.9633. UV-vis (CH_2Cl_2) λ_{max} ($[M^{-1}cm^{-1}]$) =402 nm (116000), 520 nm (148000), 568 nm (74000), 827 nm (36000), and 927 nm (100000).

3. NMR spectra

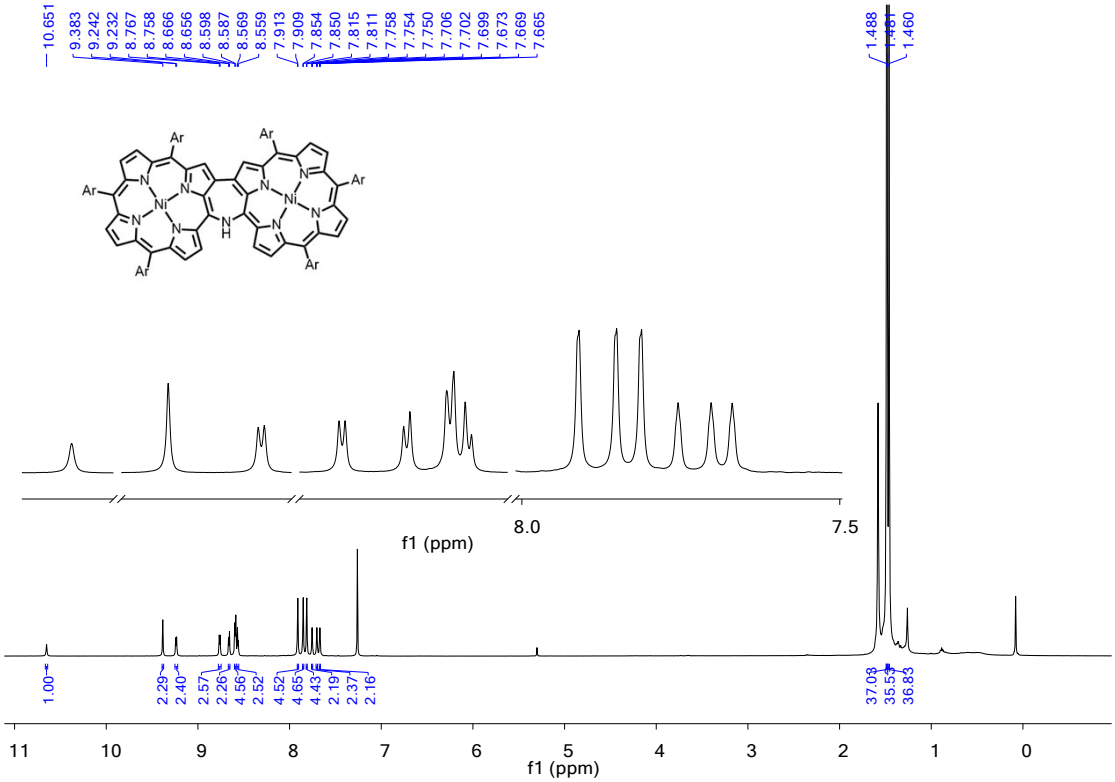


Figure S1. ^{1}H NMR spectrum of **7** (known compound) in $CDCl_3$ at 298 K

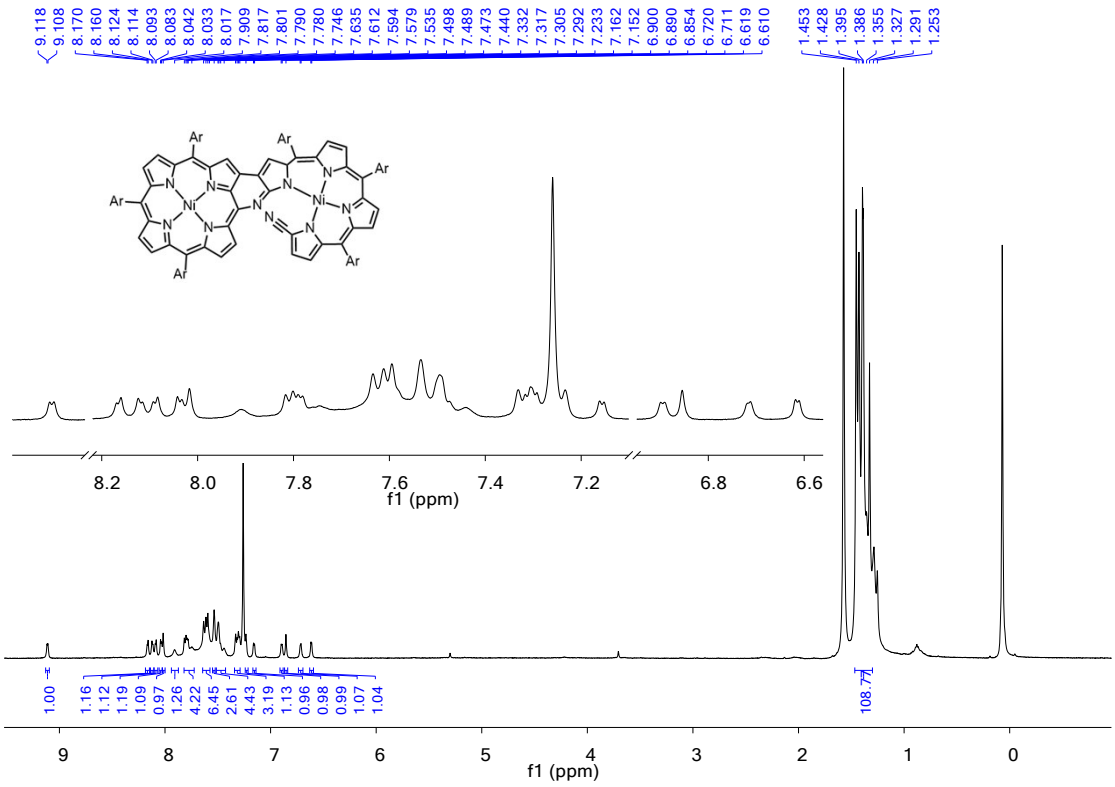


Figure S2. ^{1}H NMR spectrum of **8** (known compound) in $CDCl_3$ at 298 K

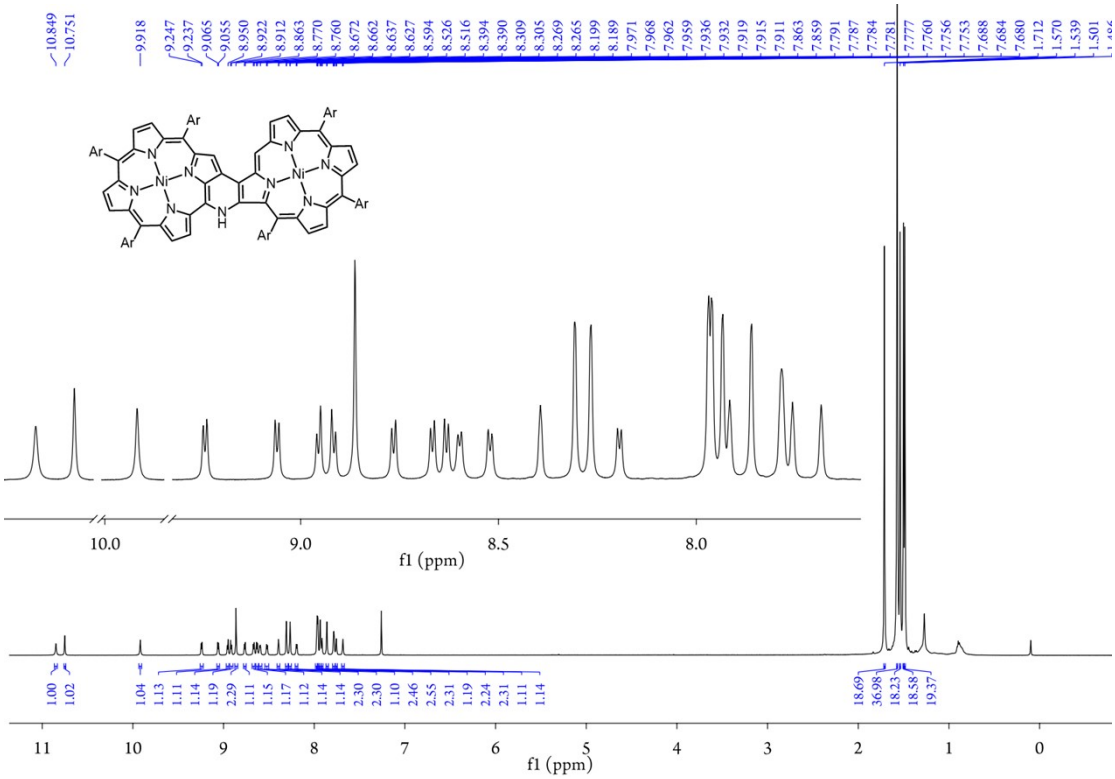


Figure S3. ^{1}H NMR spectrum of **9** in $CDCl_3$ at 298 K

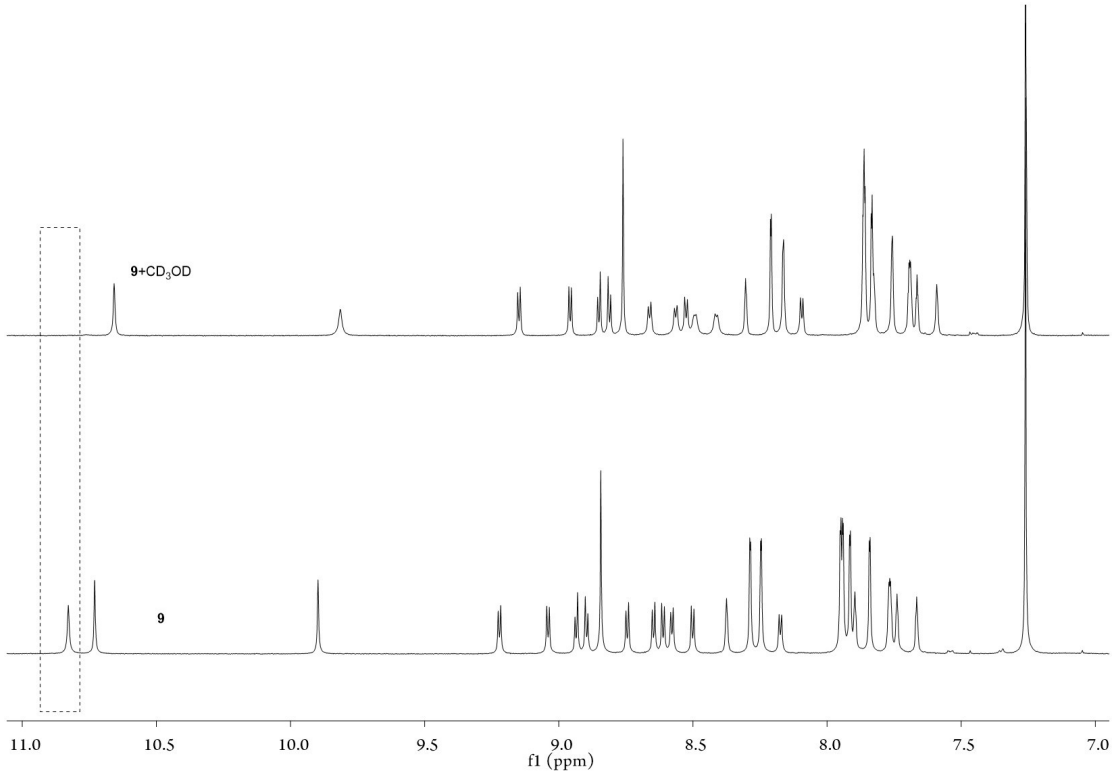


Figure S4. ^{1}H NMR spectra of **9** and **9** with CD_3OD in $CDCl_3$ at 298 K

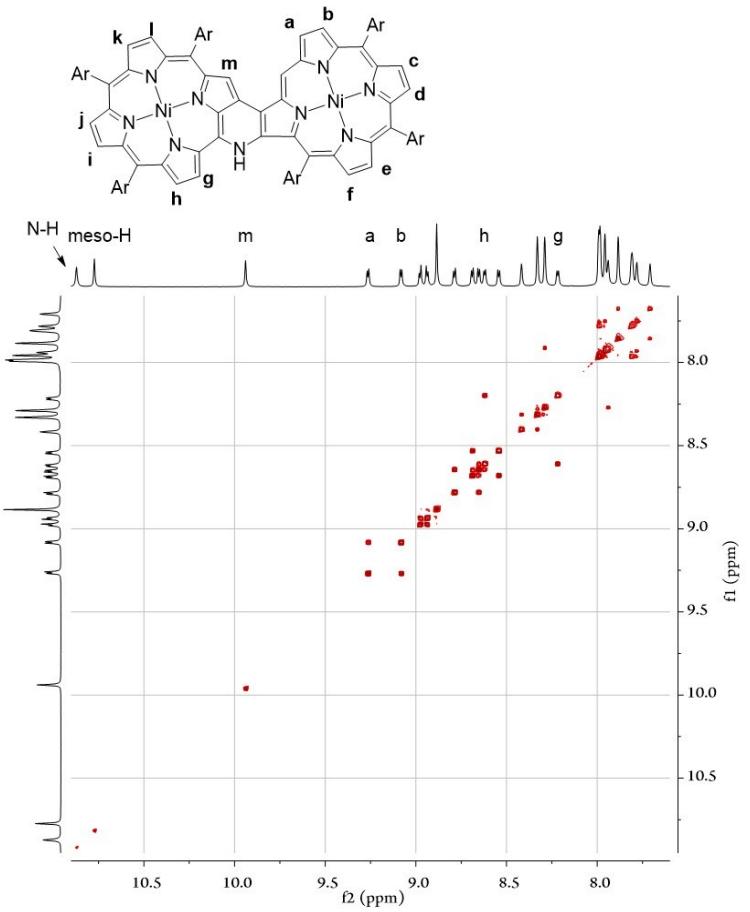


Figure S5. ^{1}H-^{1}H COSY spectrum of **9** (10.85-7.60 ppm) in $CDCl_3$ at 298 K

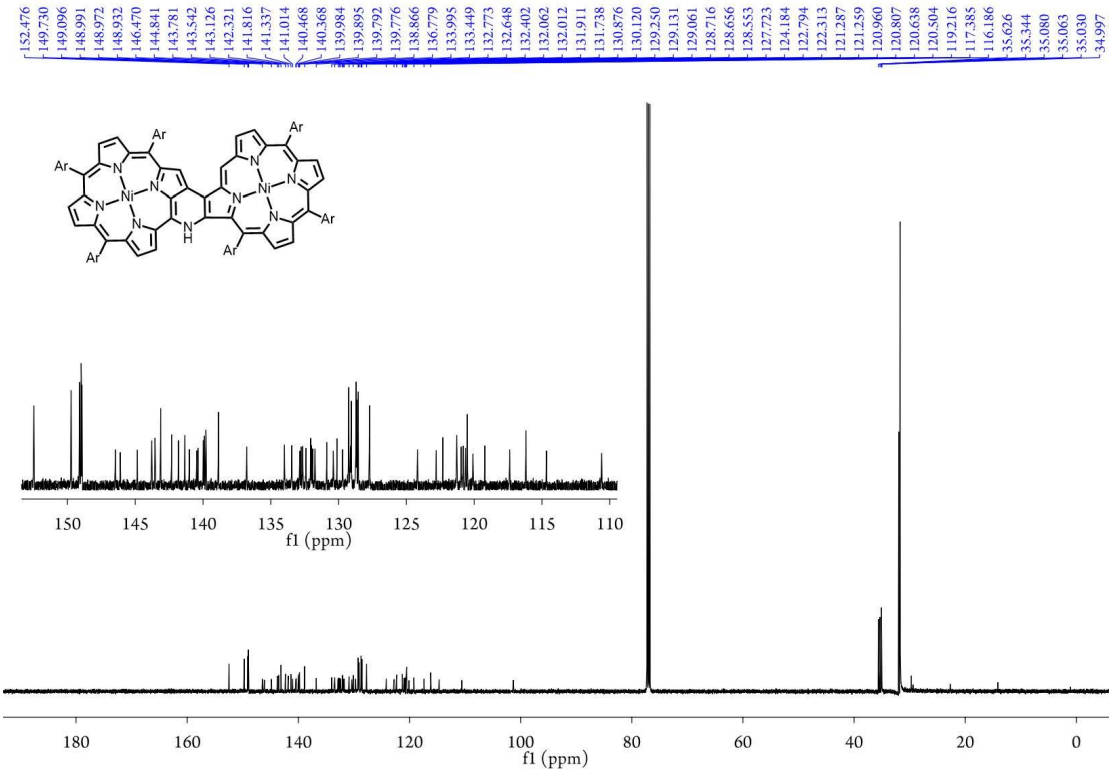


Figure S6. ^{13}C NMR spectrum of **9** in $CDCl_3$ at 298 K

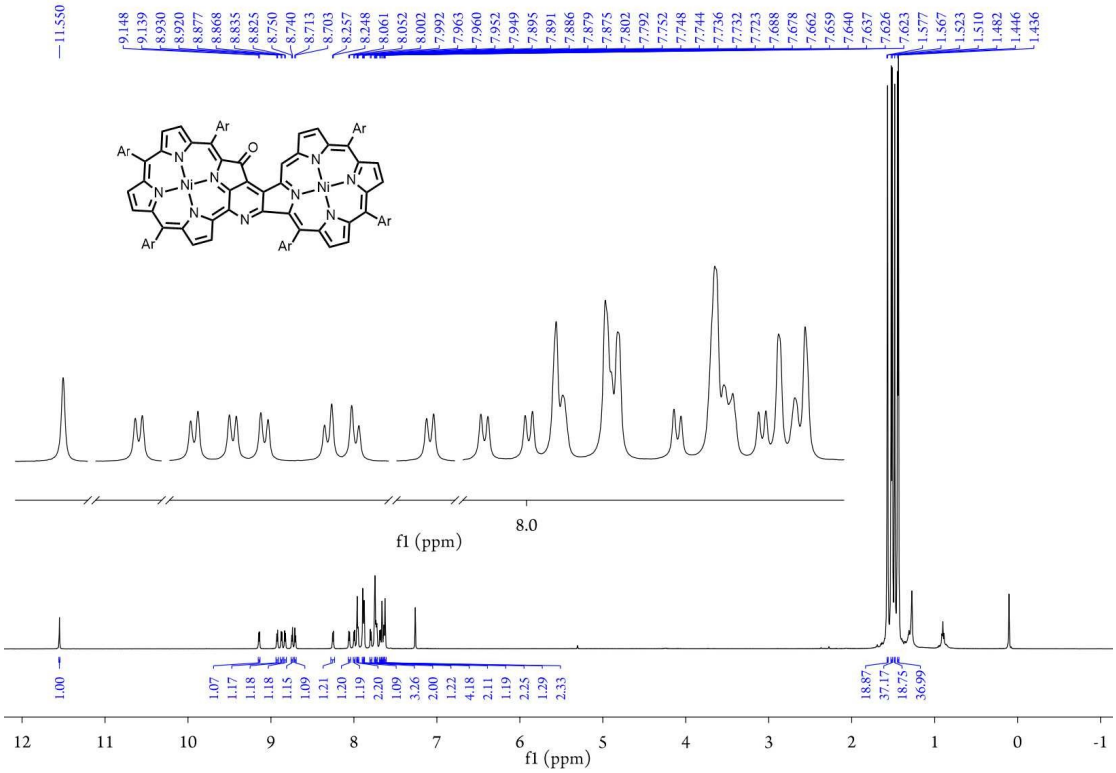


Figure S7. ^{1}H NMR spectrum of **10** in $CDCl_3$ at 298 K

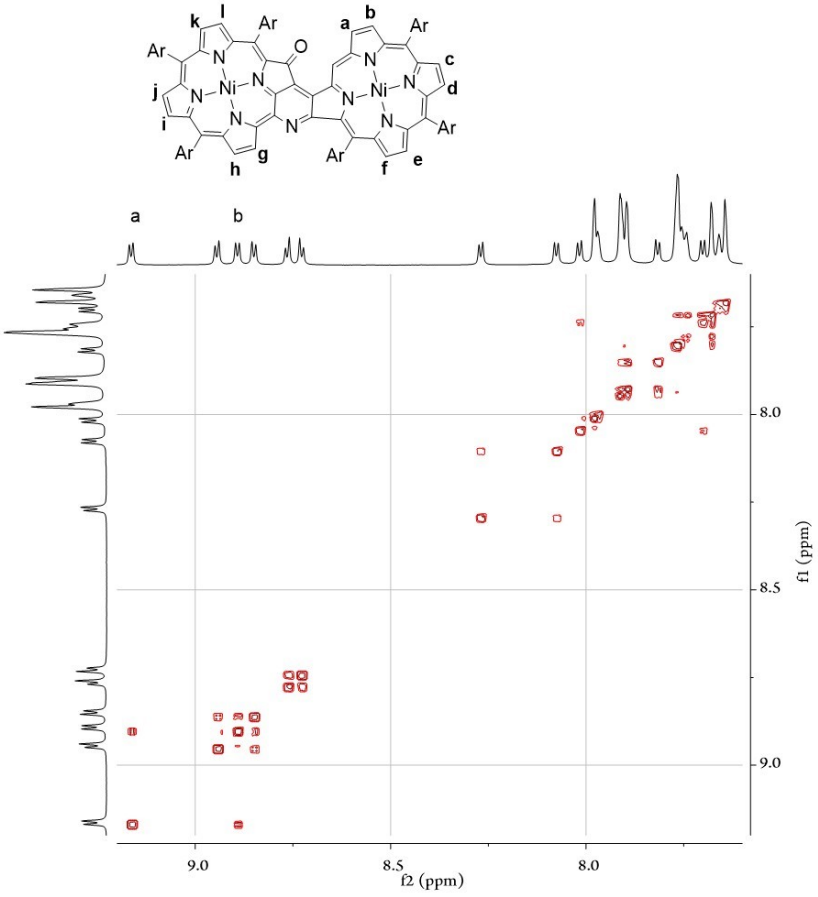


Figure S8. ^{1}H-^{1}H COSY spectrum of **10** (9.20-7.60 ppm) in $CDCl_3$ at 298 K

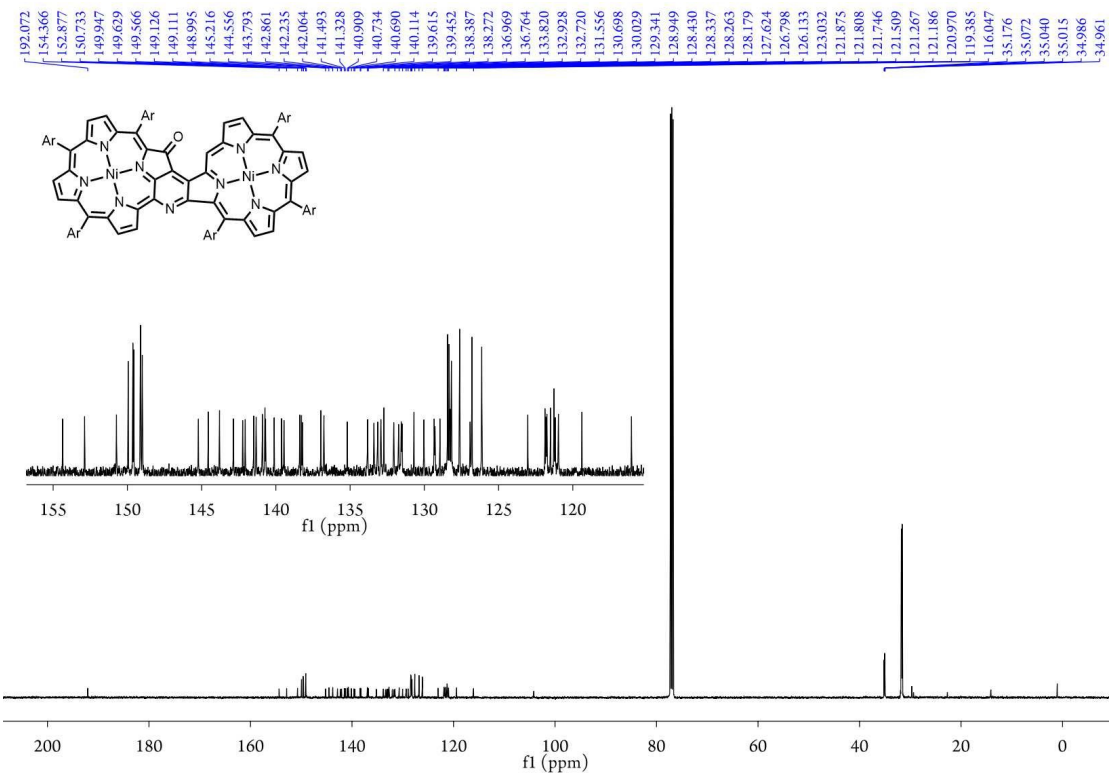


Figure S9. ^{13}C NMR spectrum of **10** in $CDCl_3$ at 298 K

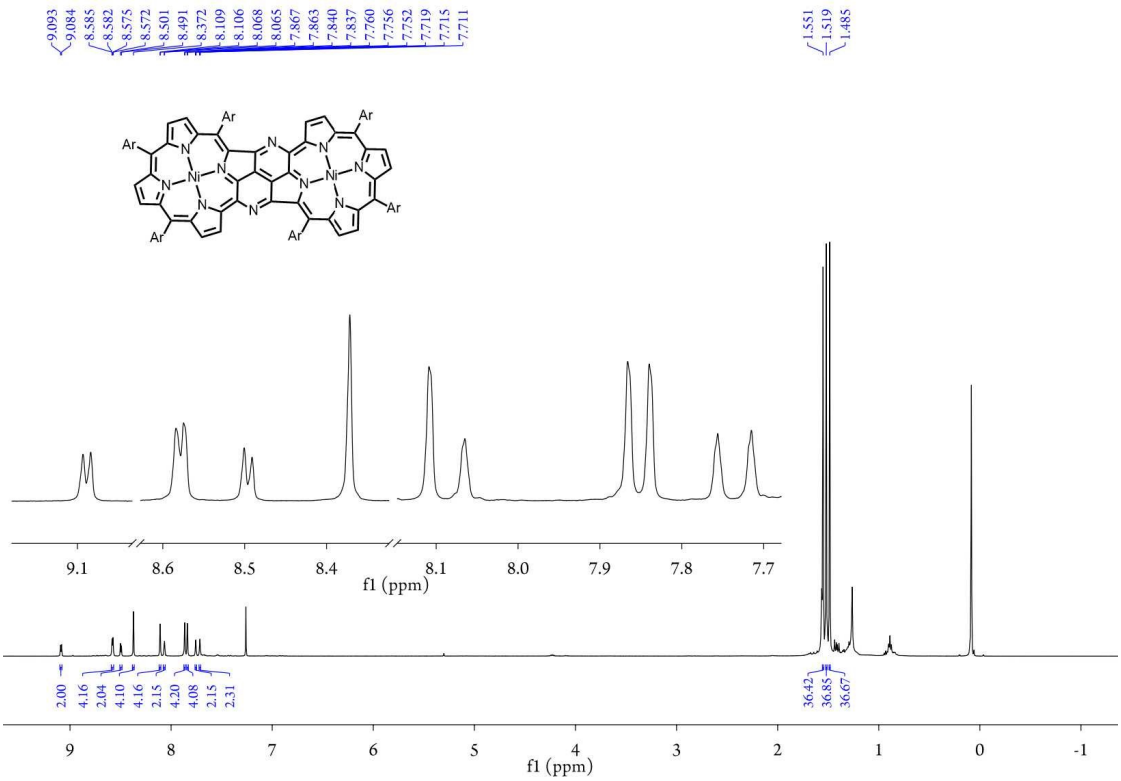


Figure S10. ^{1}H NMR spectrum of **11** in $CDCl_3$ at 298 K

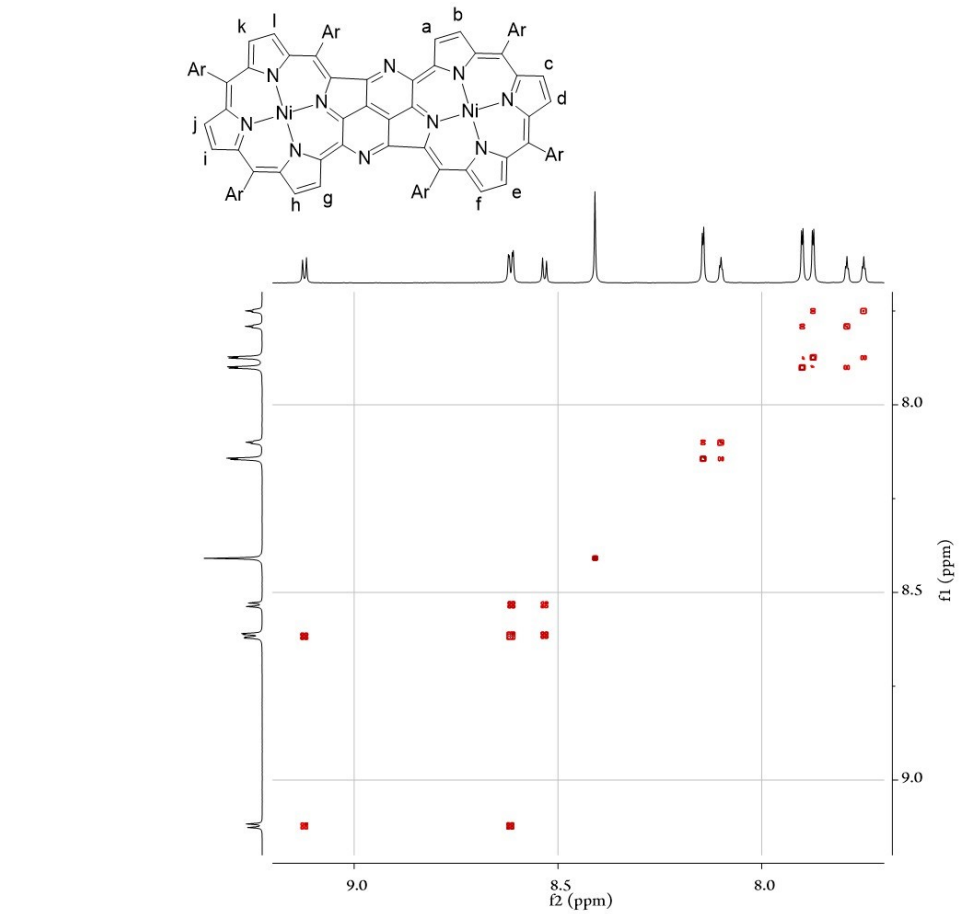


Figure S11. ^{1}H-^{1}H COSY spectrum of **11** (9.30-7.70 ppm) in $CDCl_3$ at 298 K

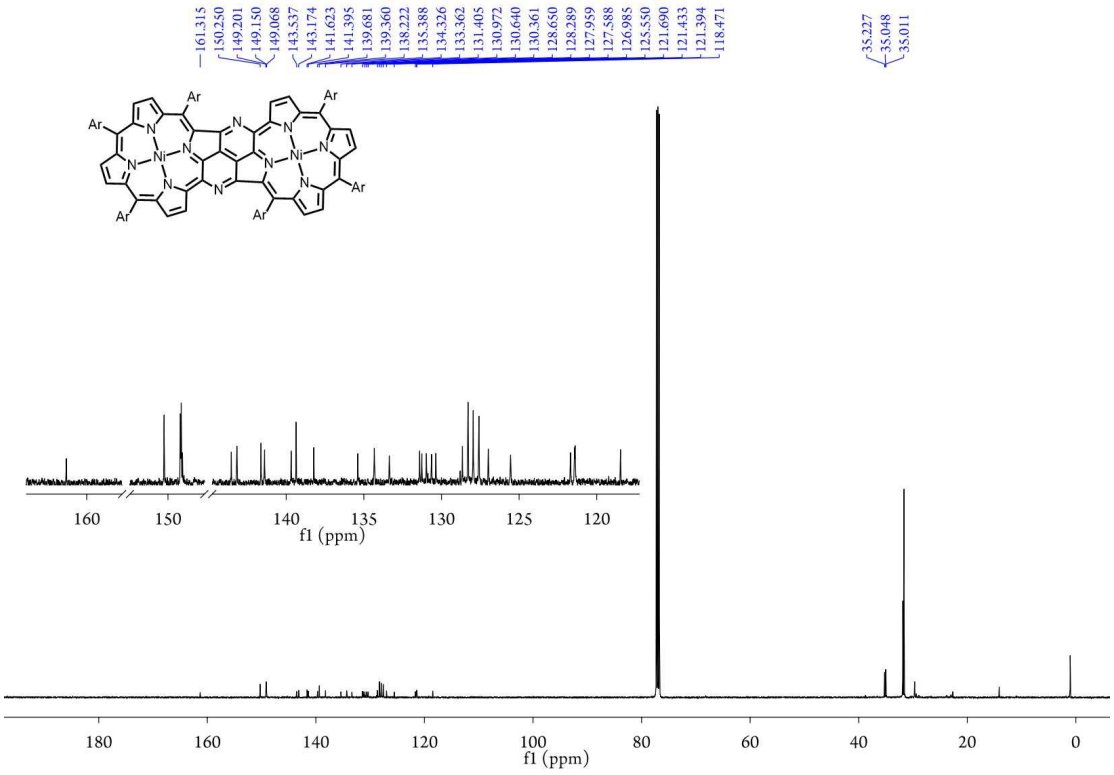


Figure S12. ^{13}C NMR spectrum of **11** in $CDCl_3$ at 298 K

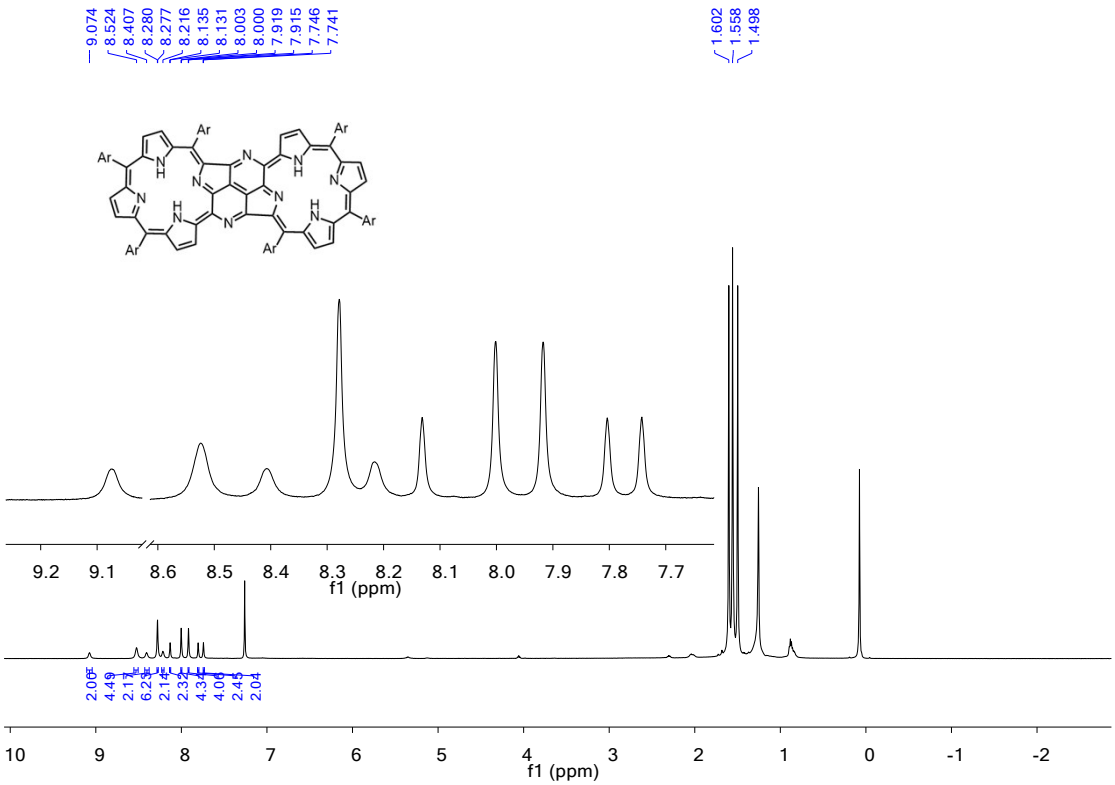


Figure S13. ^{1}H NMR spectrum of **12** in $CDCl_3$ at 298 K

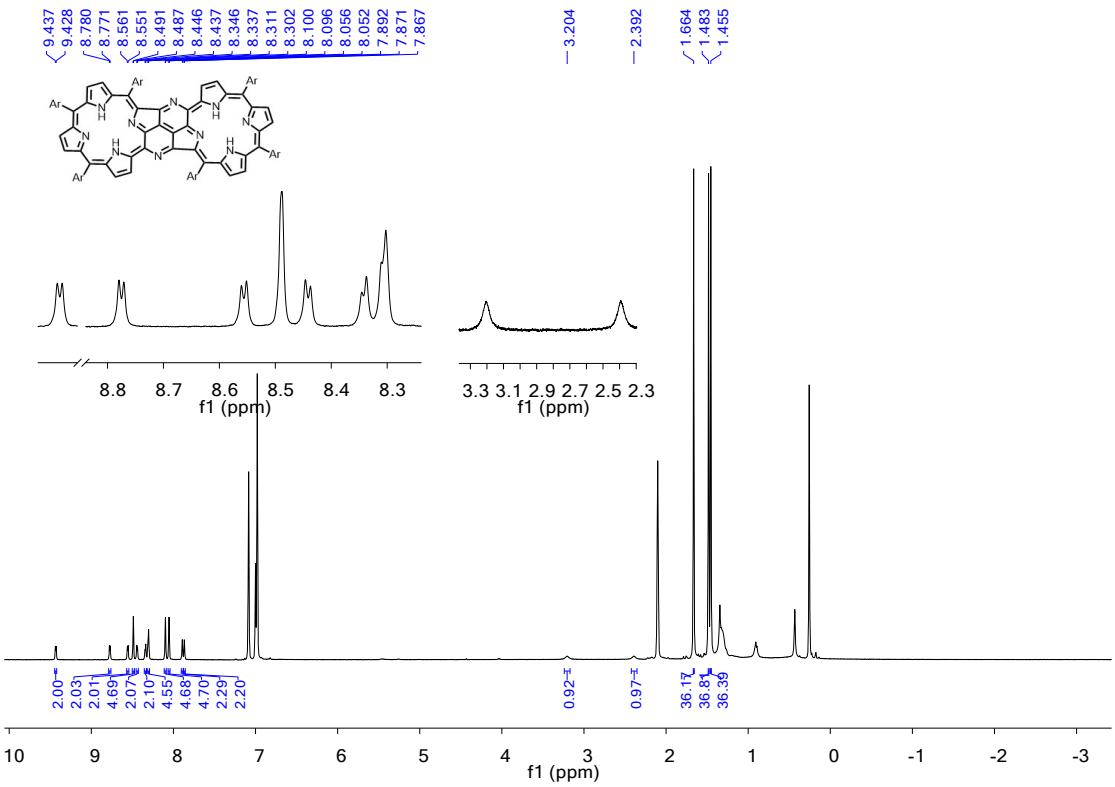


Figure S14. ^{1}H NMR spectrum of **12** in toluene-d_8 at 353 K

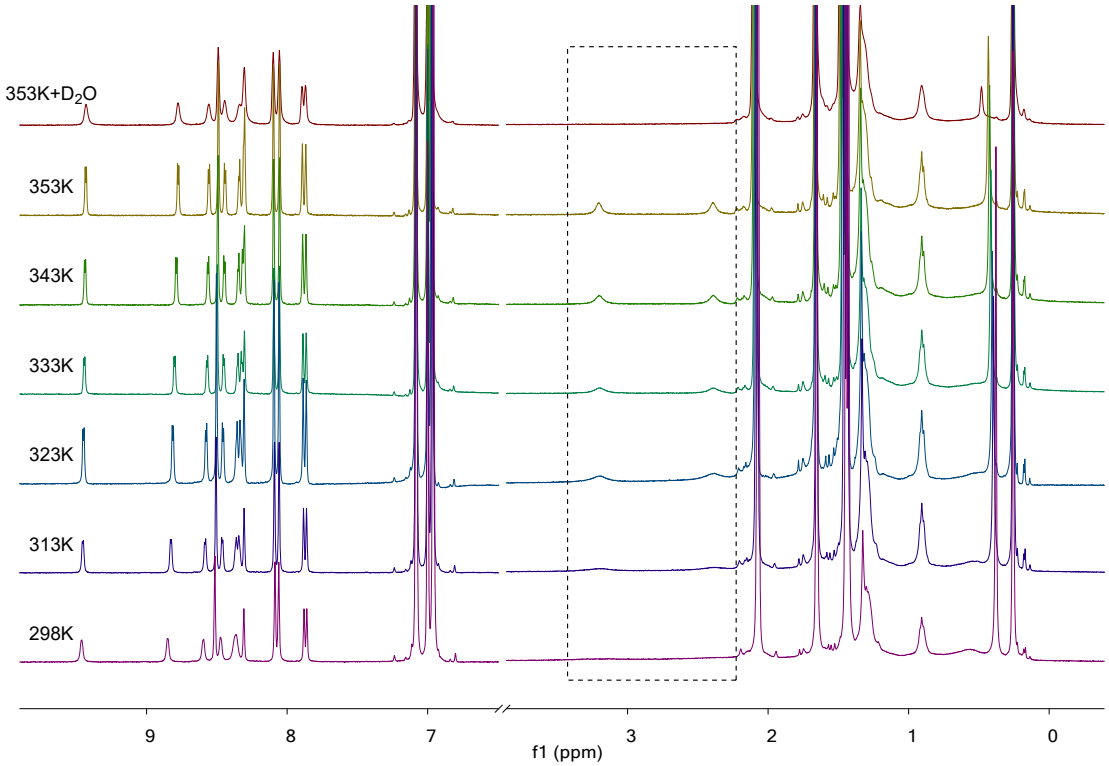


Figure S15. VT-^{1}H NMR spectra of **12** in toluene-d_8 from 298 to 353 K and **12** with D_2O at 353 K

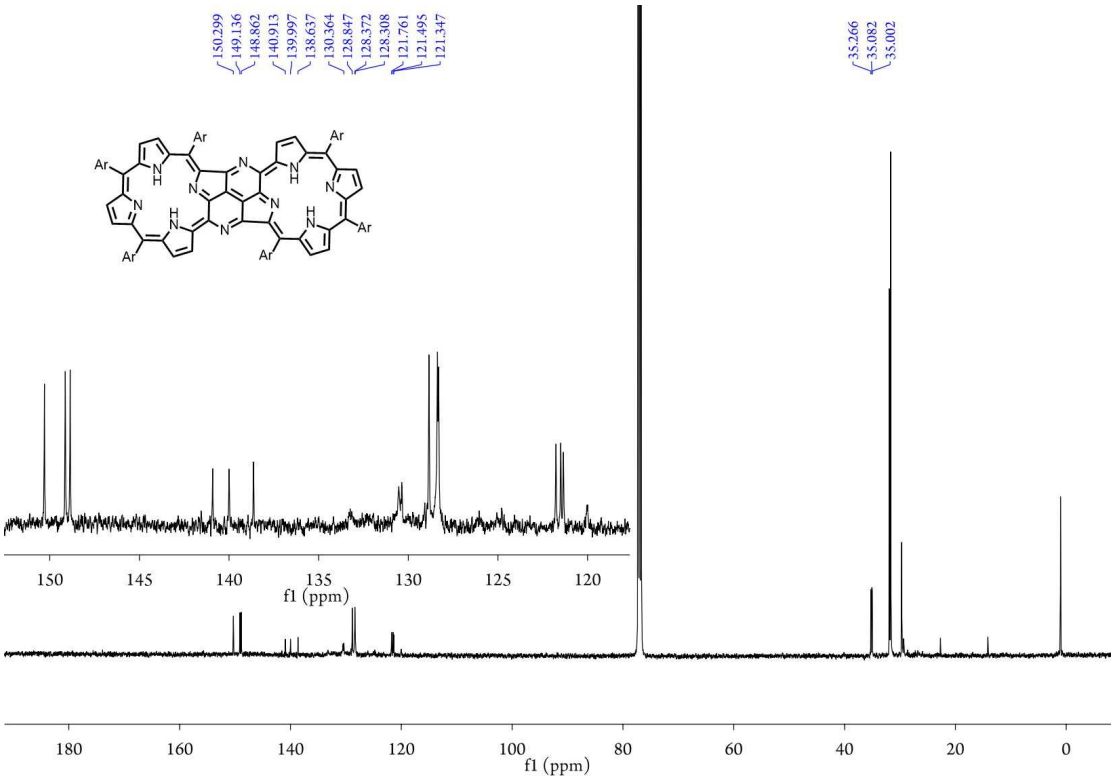


Figure S16. ^{13}C NMR spectrum of **12** in $CDCl_3$ at 298 K

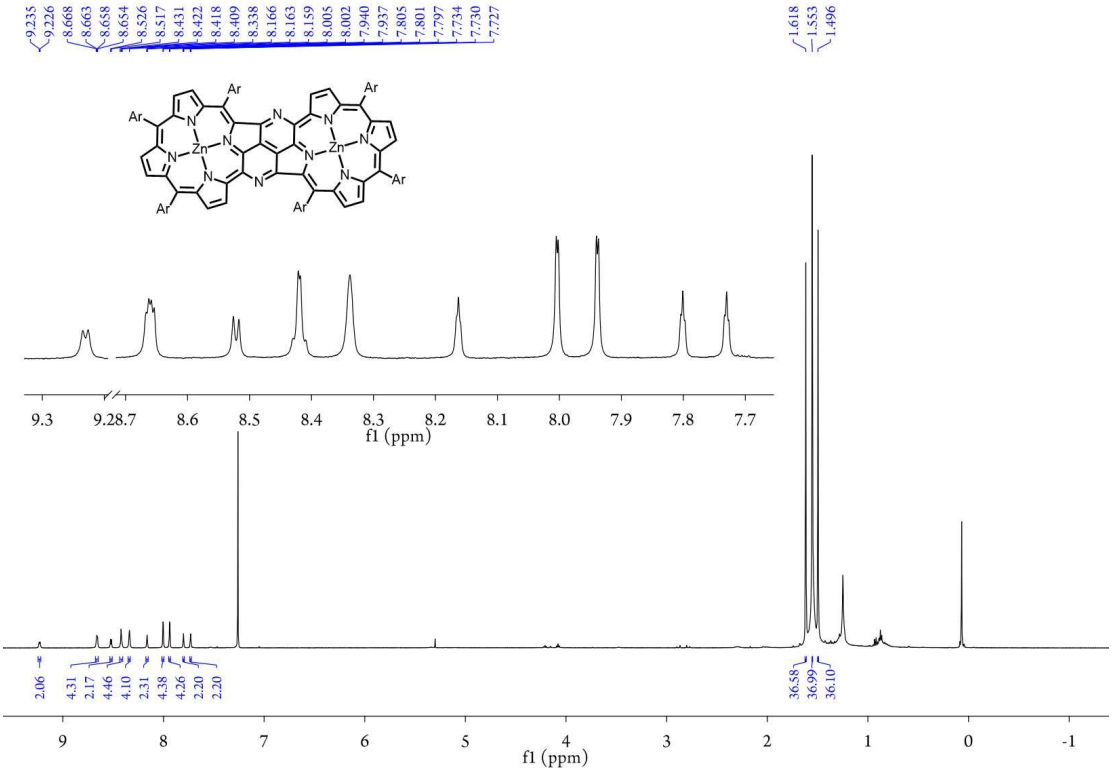


Figure S17. ^{1}H NMR spectrum of **13** in $CDCl_3$ at 298 K

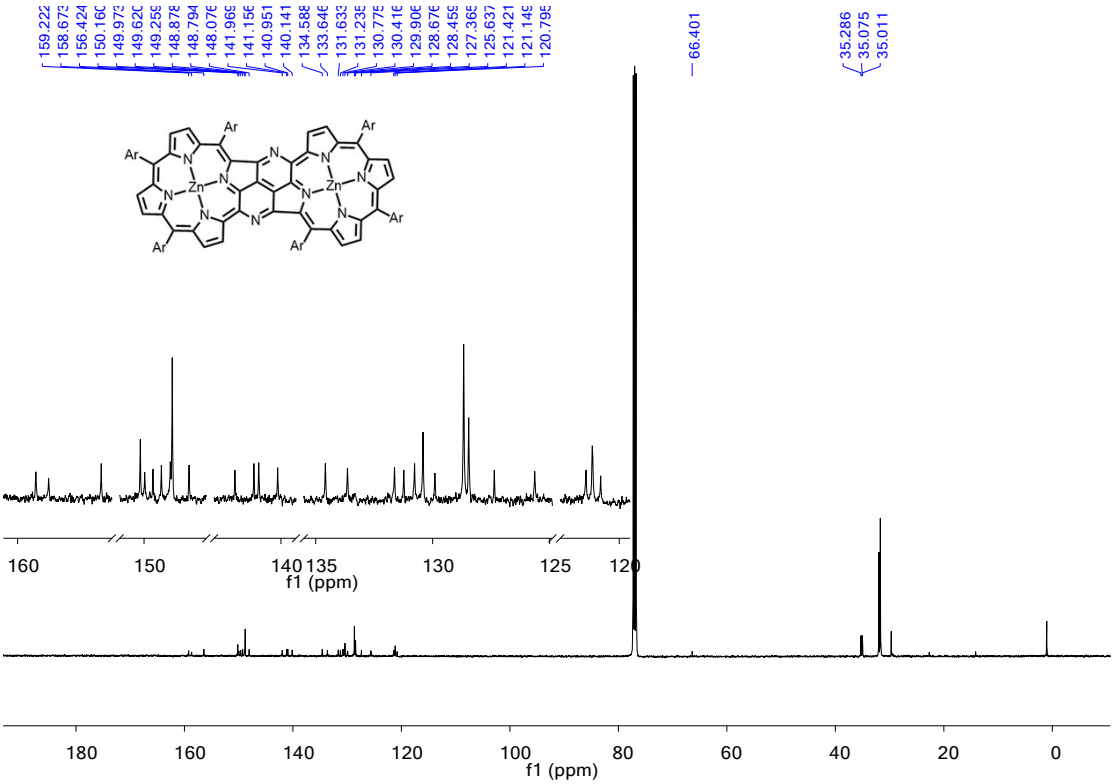


Figure S18. ^{13}C NMR spectrum of **13** in $CDCl_3$ at 298 K

4. MALDI-TOF mass spectra

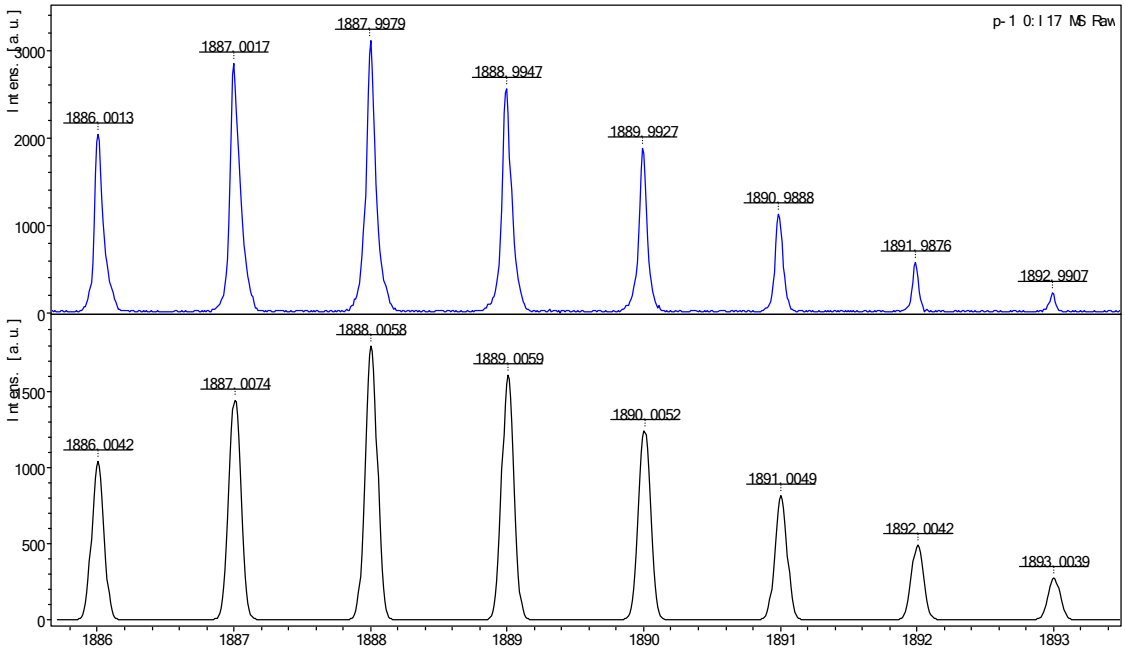


Figure S19. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **8**

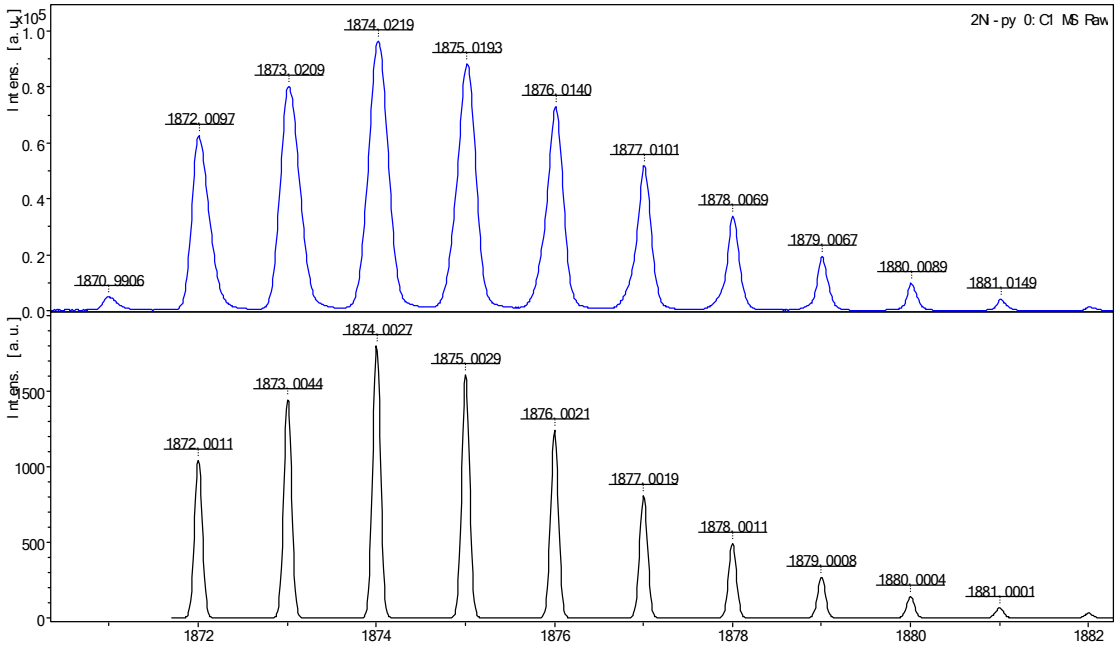


Figure S20. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **9**

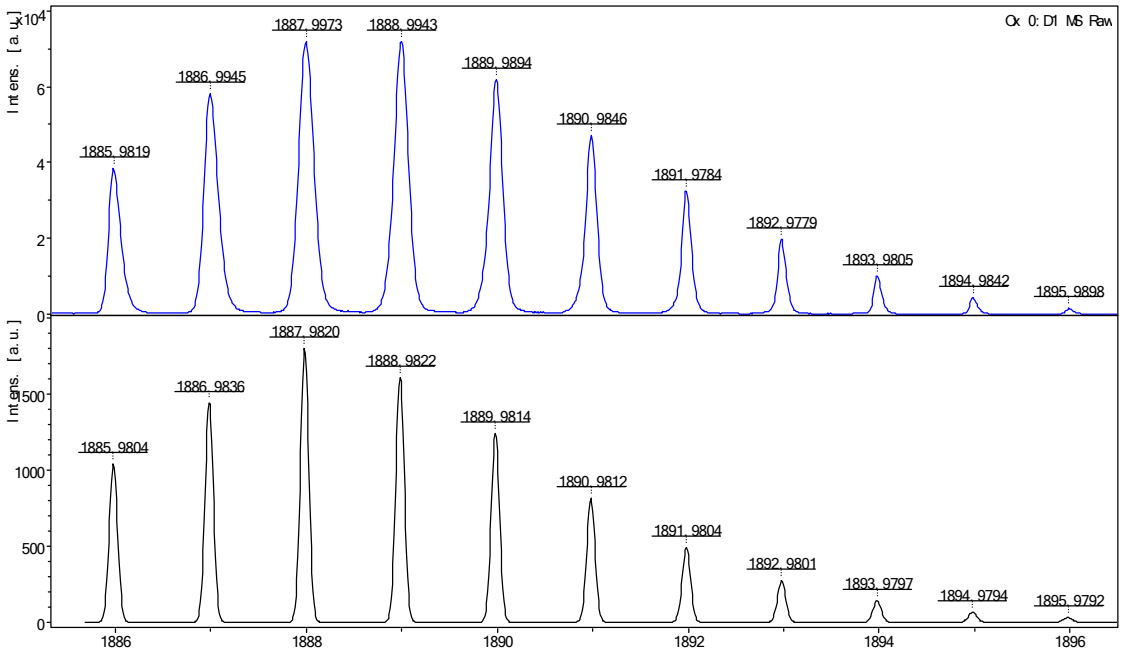


Figure S21. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **10**

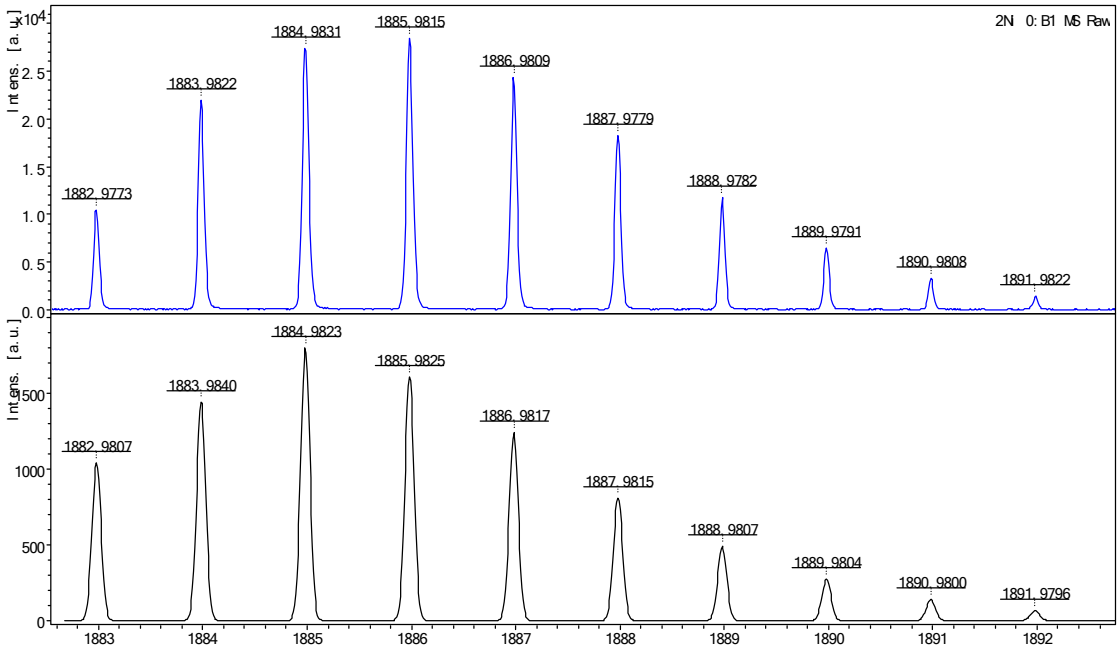


Figure S22. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **11**

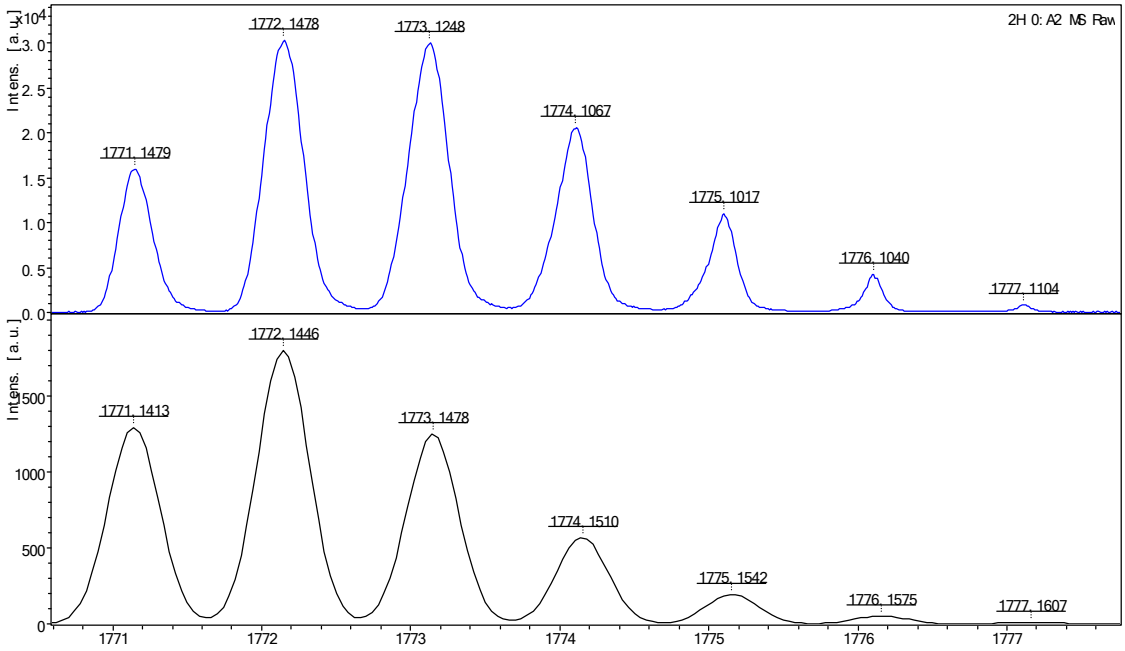


Figure S23. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **12**

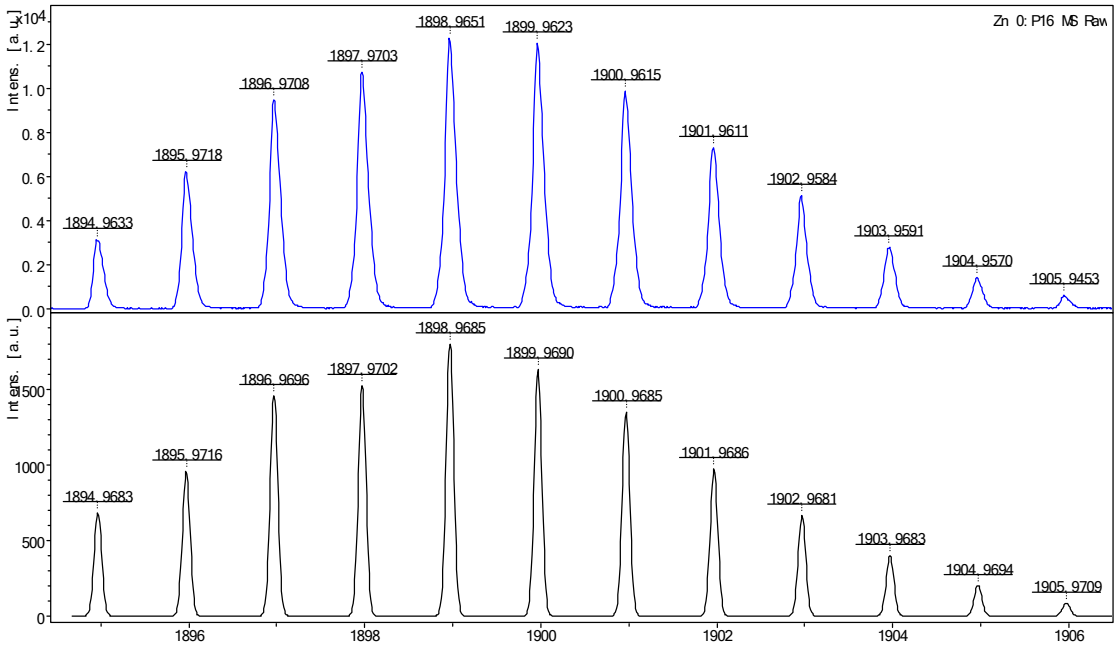


Figure S24. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **13**

5. UV/Vis/NIR absorption spectra and data

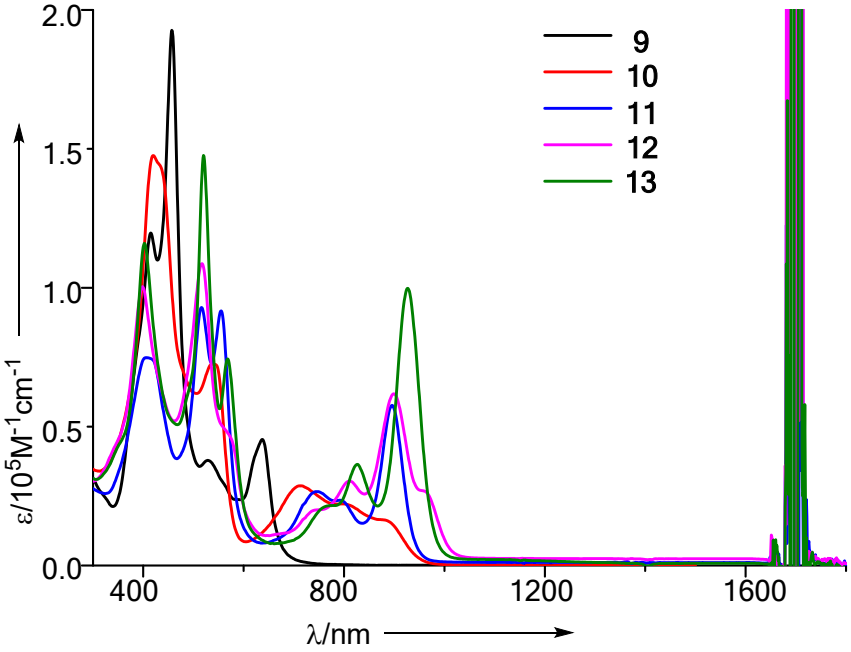


Figure S25. Absorption spectra of fused porphyrin dimers **9**-**13** in CH_2Cl_2

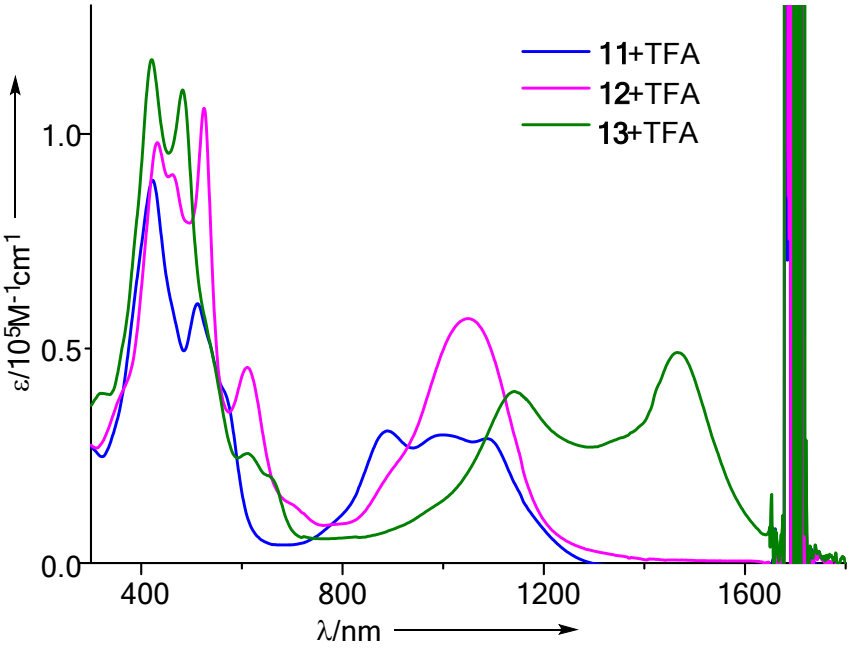


Figure S26. Absorption spectra of **11**+TFA, **12**+TFA, and **13**+TFA in CH_2Cl_2

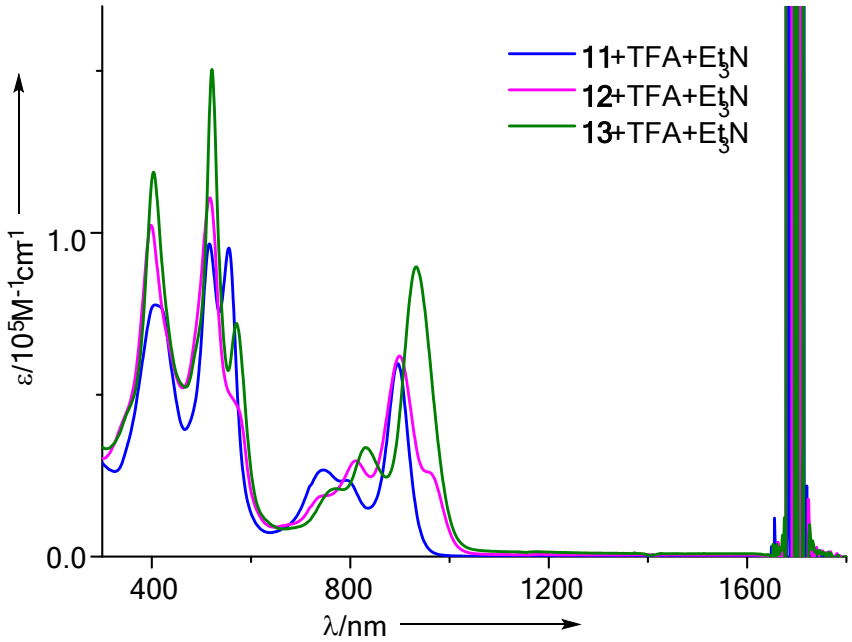


Figure S27. Absorption spectra of **11**+TFA+Et_3N, **12**+TFA+ Et_3N, and **13**+TFA+ Et_3N in CH_2Cl_2

Table S1. UV/Vis/NIR absorption spectra data

Compounds	λ_{abs}/nm ($\varepsilon/10^5$ M^{-1} cm^{-1})
9	415 (1.20), 457 (1.93), 529 (0.38), 637 (0.45)
10	420 (1.48), 537 (0.72), 711 (0.29), 796 (0.22)
11	404 (0.75), 516 (0.93), 555 (0.92), 745 (0.27), 896 (0.58)
12	398 (1.00), 517 (1.09), 811 (0.30), 899 (0.62)
13	402 (1.16), 520 (1.48), 568 (0.74), 827 (0.36), 927 (1.00)
11+TFA	423 (0.89), 512 (0.60), 890 (0.31), 996 (0.30), 1087 (0.29)
12+TFA	432 (0.98), 462 (0.91), 525 (1.06), 611 (0.46), 1050 (0.57)
13+TFA	321 (0.40), 421 (1.17), 482 (1.10), 612 (0.26), 1142 (0.40), 1465 (0.49)
11+TFA+Et_3N	406 (0.78), 516 (0.97), 555 (0.95), 746 (0.27), 896 (0.60)
12+TFA+ Et_3N	398 (1.02), 517 (1.11), 811 (0.30), 899 (0.62)
13+TFA+ Et_3N	403 (1.19), 521 (1.50), 570 (0.72), 831 (0.34), 933 (0.89)

6. Electrochemical properties

Cyclic voltammetry was performed in a three-electrode cell using the Chi-610E electrochemistry station. A three-electrode cell was used for cyclic voltammetric measurements, consisting of a platinum or glassy carbon working electrode, a Pt wire counter electrode and a $Ag/AgNO_3$ supporting electrolyte reference electrode. 0.1 M *n*-Bu_4NPF_6 in dichloromethane was used as supporting electrolyte.

Table S2. Electrochemical data.[a]

Compounds	$E_{ox.2}$ (V)	$E_{ox.1}$ (V)	$E_{red.1}$ (V)	$E_{red.2}$ (V)	$\triangle E_{HL}$ (eV)[b]
9	-	0.09	-1.69	-	1.78
10	0.73	0.45	-0.97	-1.42	1.42
11	0.64	0.33	-1.07	-1.34	1.40

[a]Potentials were determined vs ferrocene/ferrocenium ion by differential pulse voltammograms; Scan rate: 0.05 V/s; working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: $Ag/AgNO_3$ supporting electrolyte: 0.1 M *n*-Bu_4NPF_6 in CH_2Cl_2. [b]Electrochemical HOMO-LUMO gaps (ΔE_{HL} = e ($E_{ox.1} - E_{red.1}$) [eV]).

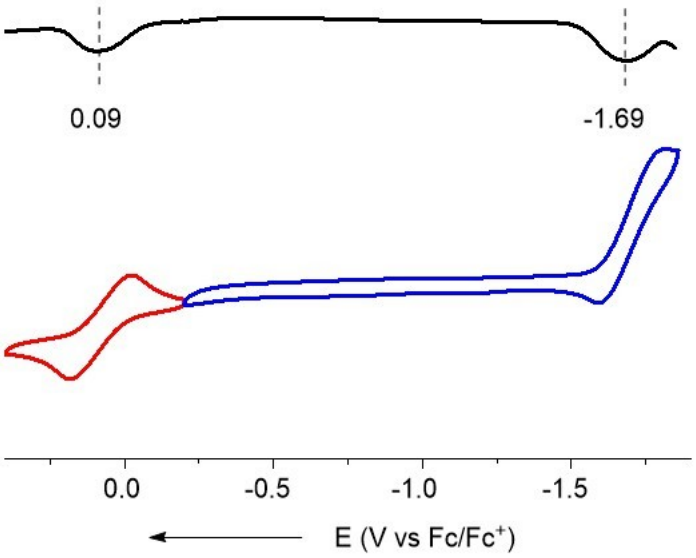


Figure S28. Cyclic voltammograms and differential pulse voltammograms of **9**

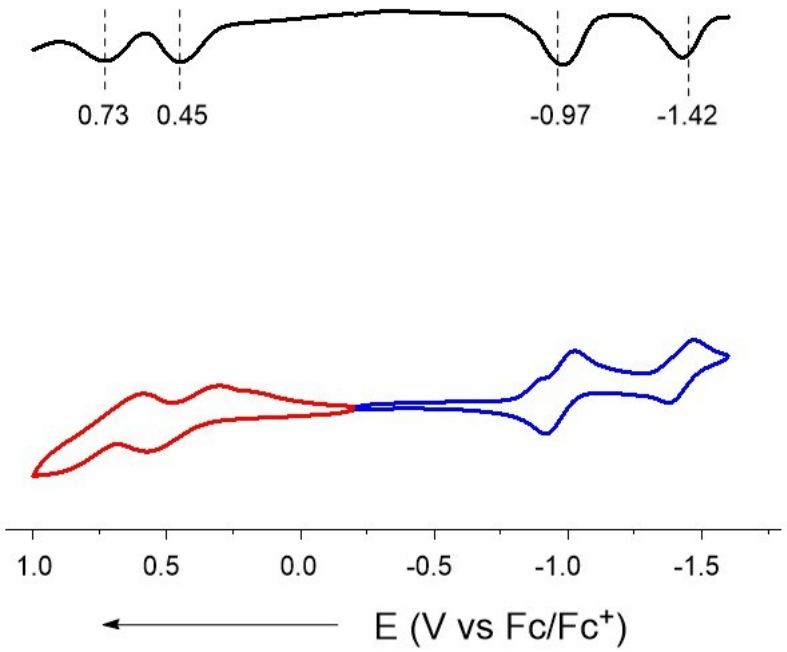


Figure S29. Cyclic voltammograms and differential pulse voltammograms of **10**

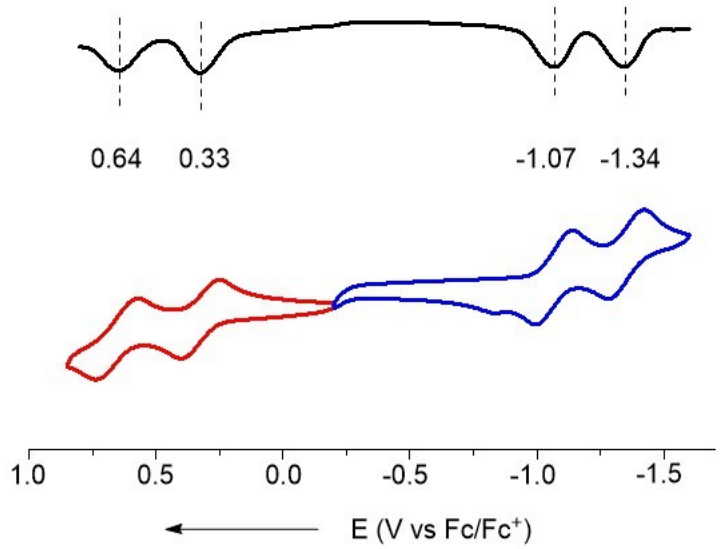


Figure S30. Cyclic voltammograms and differential pulse voltammograms of **11**

7. DFT calculations

All calculations were carried out using the Gaussian 09 program. Initial geometries of **9**, **10**, and **13** were from the corresponding X-ray structures. The structure was optimized without any symmetry restriction. Geometry optimization in the ground state were performed by the density functional theory (DFT) with B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level employing a basis set of 6-31G(d) for all of the atoms.[S2]

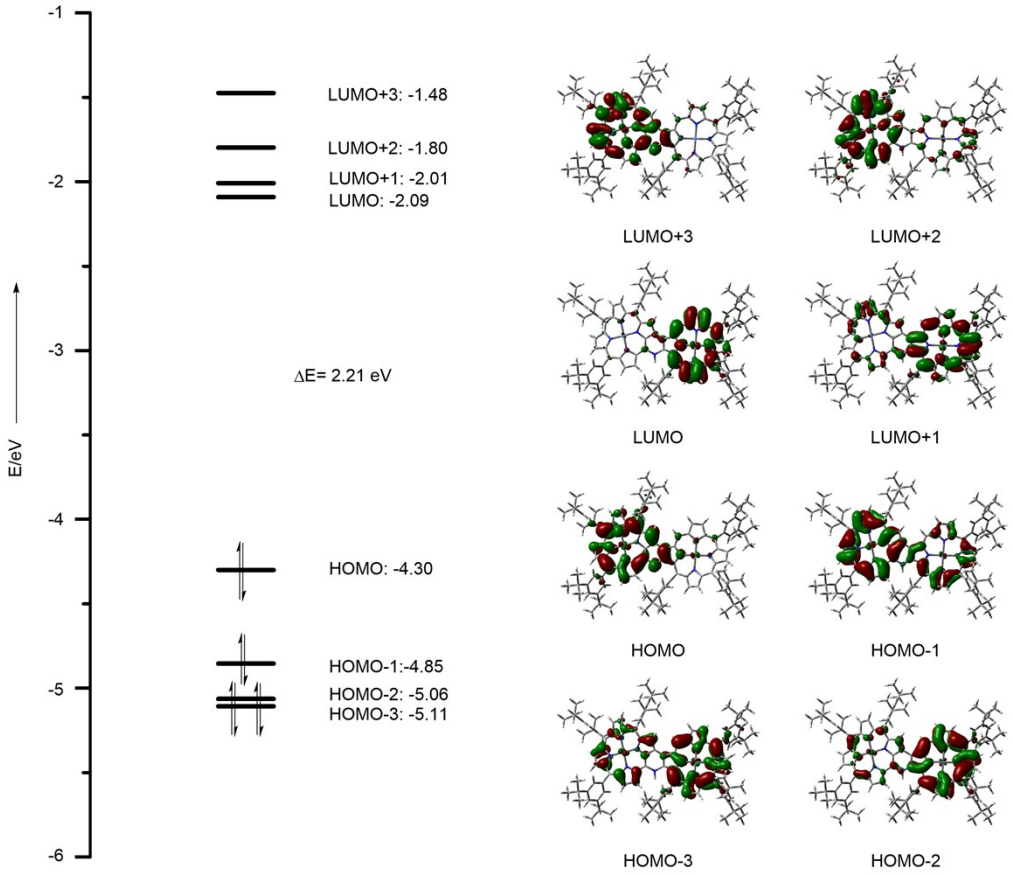


Figure S31. Frontier molecular orbitals and orbital energies of **9**

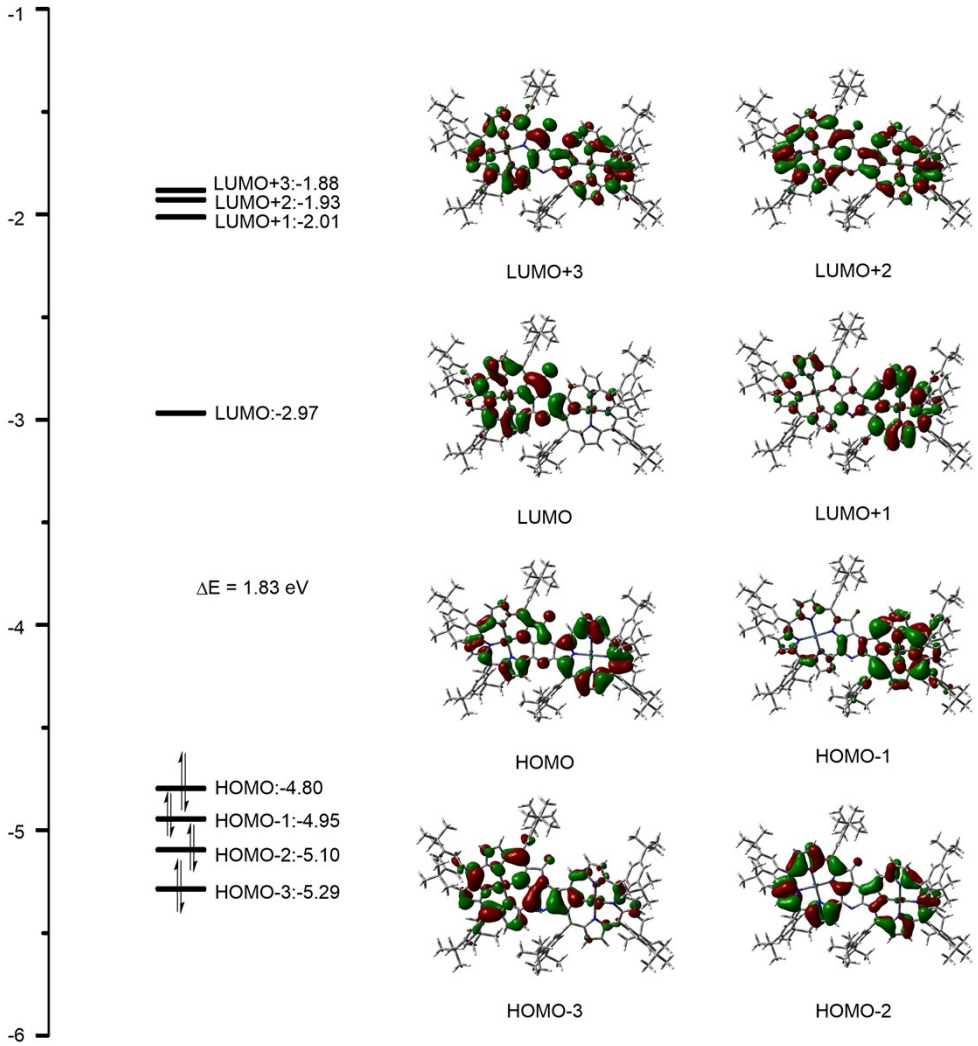


Figure S32. Frontier molecular orbitals and orbital energies of **10**

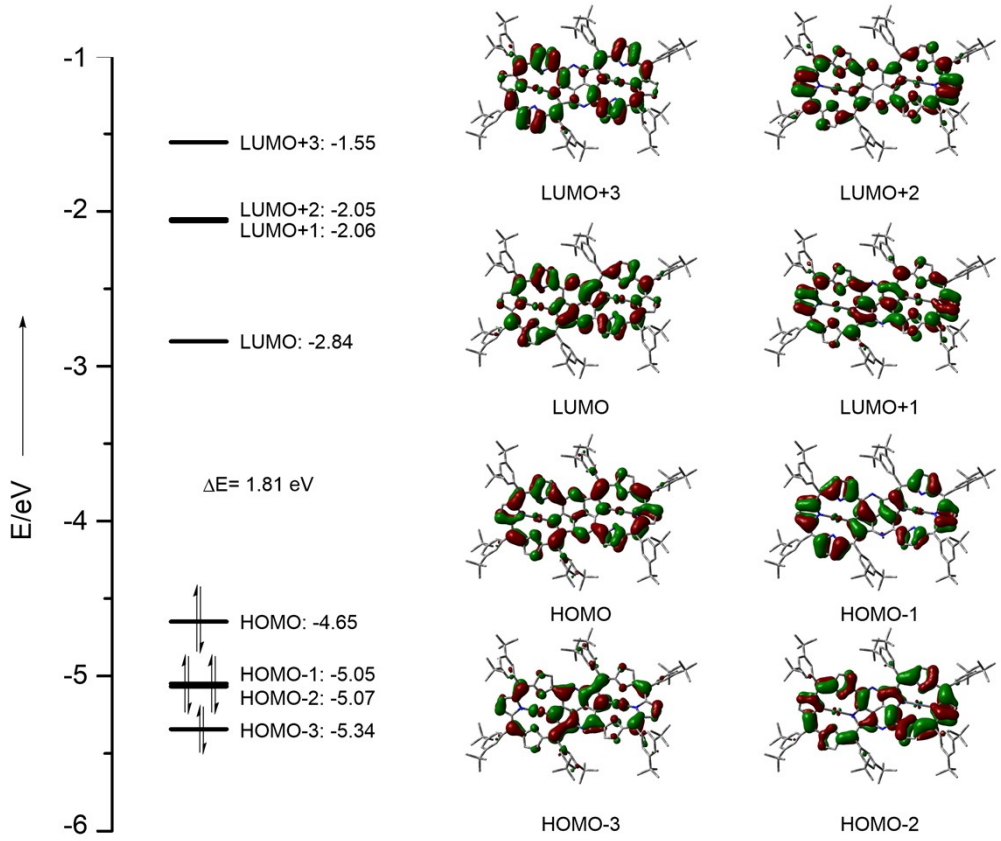


Figure S33. Frontier molecular orbitals and orbital energies of **11**

8. X-ray crystal structures and data

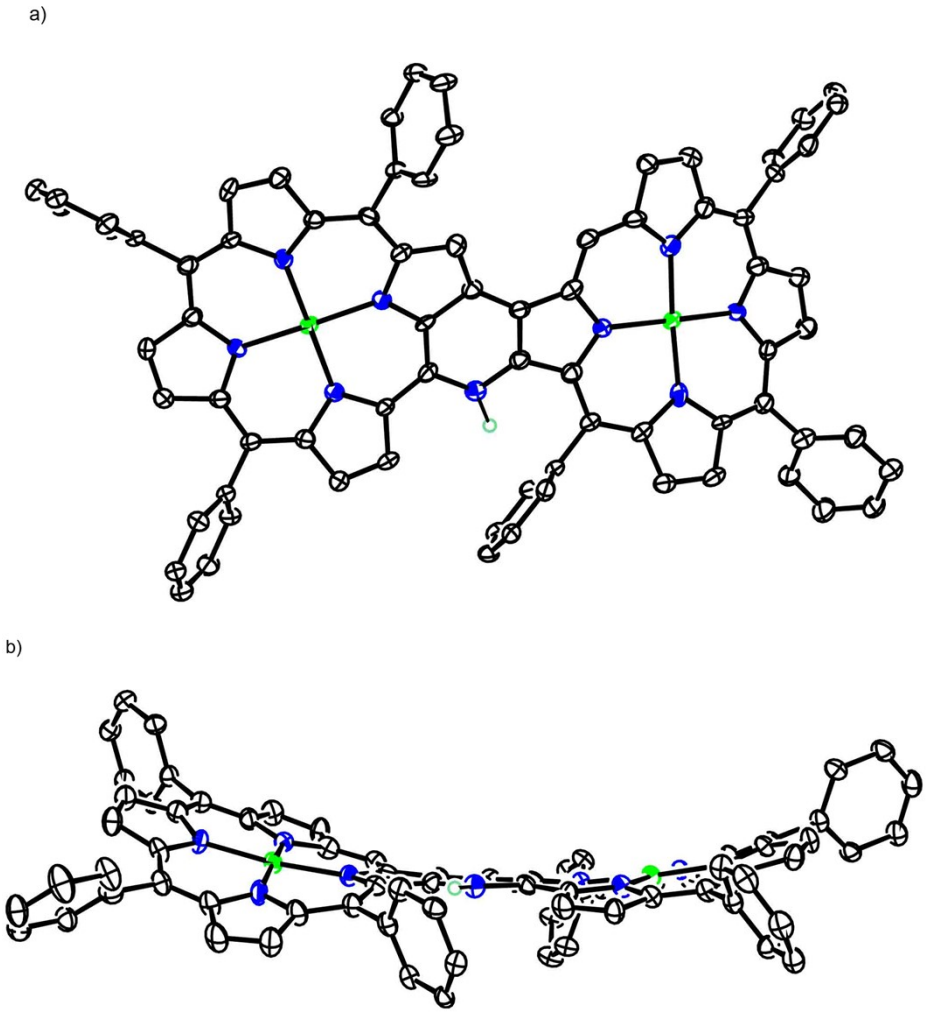


Figure S34. X-ray crystal structure of **9**: a) top view, b) side view. The thermal ellipsoids are 50% probability level. H atoms except for the N-H, alkyl groups and solvent molecules are omitted for clarity

Table S3. Crystal data and structure refinement for **9**

Identification code	exp_2089_sq	
Empirical formula	$C_{124}H_{141}N_9Ni_2$	
Formula weight	1872.00	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 15.0711(8) Å	α = 90°.

	b = 17.7558(9) Å	β = 97.378(6)°.
	c = 47.125(4) Å	γ = 90°.
Volume	12506.3(14) Å^3	
Z	4	
Density (calculated)	0.996 Mg/m^3	
Absorption coefficient	0.714 mm^{-1}	
F(000)	4016	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	2.662 to 66.600°.	
Index ranges	-17<=h<=16, -21<=k<=14, -52<=l<=56	
Reflections collected	43654	
Independent reflections	22054 [R(int) = 0.1052]	
Completeness to theta = 66.600°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.31241	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22055 / 0 / 1256	
Goodness-of-fit on F^2	0.967	
Final R indices [I>2sigma(I)]	R1 = 0.0843, wR2 = 0.1898	
R indices (all data)	R1 = 0.1581, wR2 = 0.2468	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.580 and -0.483 e.Å^{-3}	

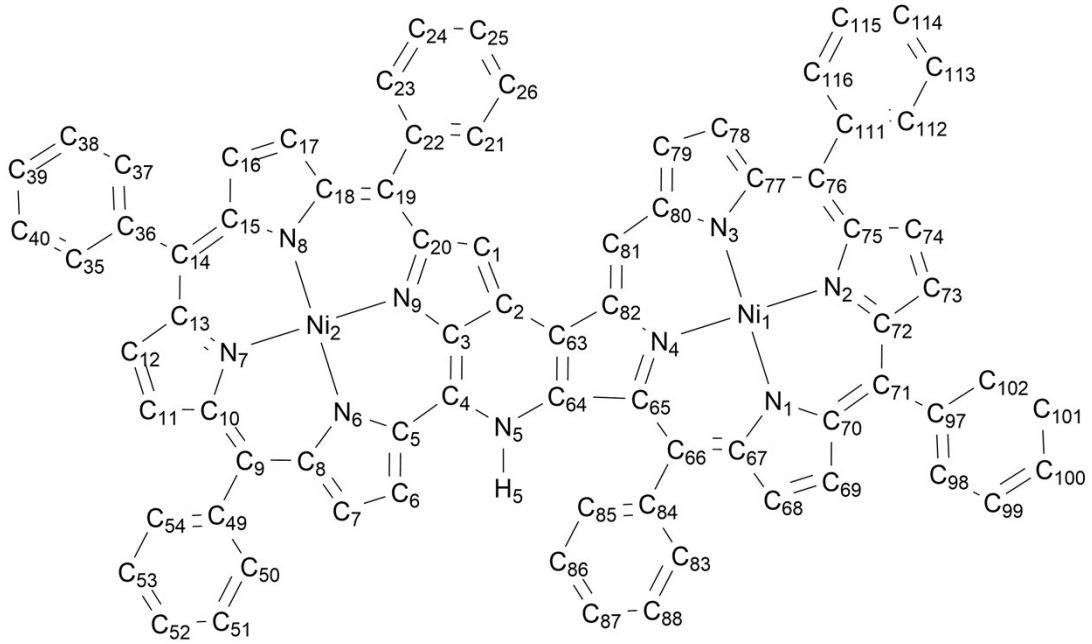


Table S4. bond lengths (Å) and angles (°) for **9**

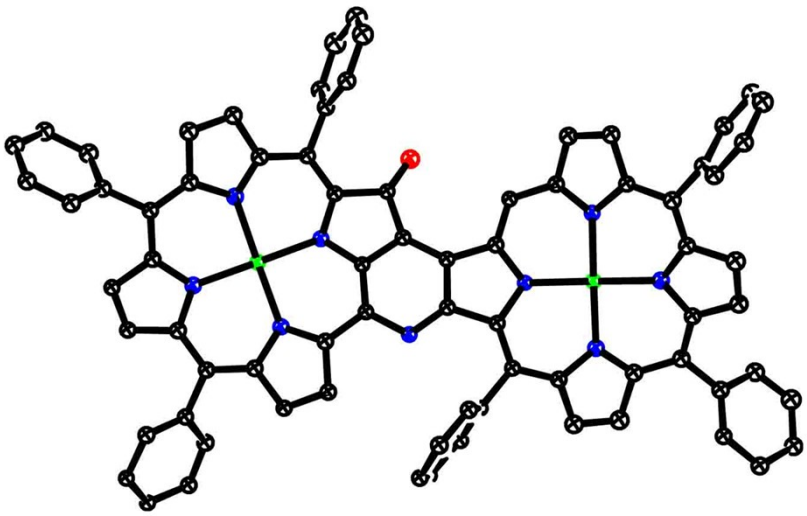
Ni(1)-N(1)	1.933(5)	C(10)-C(11)	1.434(8)
Ni(1)-N(2)	1.939(4)	C(11)-C(12)	1.338(8)
Ni(1)-N(3)	1.935(4)	C(12)-C(13)	1.449(7)
Ni(1)-N(4)	1.960(4)	C(13)-C(14)	1.388(7)
Ni(2)-N(6)	1.939(4)	C(14)-C(15)	1.370(7)
Ni(2)-N(7)	1.932(4)	C(14)-C(36)	1.483(7)
Ni(2)-N(8)	1.925(4)	C(15)-C(16)	1.434(7)
Ni(2)-N(9)	1.945(4)	C(16)-C(17)	1.359(8)
N(1)-C(67)	1.389(7)	C(17)-C(18)	1.434(7)
N(1)-C(70)	1.372(7)	C(18)-C(19)	1.363(8)
N(2)-C(72)	1.379(7)	C(19)-C(20)	1.405(7)
N(2)-C(75)	1.394(7)	C(19)-C(22)	1.502(6)
N(3)-C(77)	1.396(7)	C(21)-C(22)	1.387(7)
N(3)-C(80)	1.364(7)	C(21)-C(26)	1.407(7)
N(4)-C(65)	1.397(7)	C(22)-C(23)	1.409(7)
N(4)-C(82)	1.362(7)	C(23)-C(24)	1.408(7)
N(5)-H(5)	1.08(7)	C(24)-C(25)	1.385(7)
N(6)-C(5)	1.379(7)	C(25)-C(26)	1.397(7)
N(6)-C(8)	1.412(6)	C(35)-C(36)	1.389(7)
N(7)-C(10)	1.397(6)	C(35)-C(40)	1.401(8)
N(7)-C(13)	1.372(7)	C(36)-C(37)	1.408(7)
N(8)-C(15)	1.395(7)	C(37)-C(38)	1.391(8)
N(8)-C(18)	1.405(6)	C(38)-C(39)	1.390(8)
N(9)-C(3)	1.376(7)	C(39)-C(40)	1.377(8)
N(9)-C(20)	1.389(6)	C(49)-C(50)	1.391(7)
C(1)-C(2)	1.380(7)	C(49)-C(54)	1.397(7)
C(1)-C(20)	1.415(8)	C(50)-C(51)	1.402(7)
C(2)-C(3)	1.464(7)	C(51)-C(52)	1.381(8)
C(2)-C(63)	1.441(7)	C(52)-C(53)	1.385(8)
C(3)-C(4)	1.364(7)	C(53)-C(54)	1.401(7)
C(4)-C(5)	1.396(7)	C(63)-C(64)	1.366(7)
C(5)-C(6)	1.410(7)	C(63)-C(82)	1.445(8)
C(6)-C(7)	1.358(8)	C(64)-C(65)	1.433(8)
C(7)-C(8)	1.418(7)	C(65)-C(66)	1.364(7)
C(8)-C(9)	1.379(8)	C(66)-C(67)	1.386(8)
C(9)-C(10)	1.357(7)	C(66)-C(84)	1.507(7)
C(9)-C(49)	1.503(7)	C(67)-C(68)	1.444(7)

C(68)-C(69)	1.350(8)	C(4)-N(5)-H(5)	137(4)
C(69)-C(70)	1.436(7)	C(64)-N(5)-H(5)	102(4)
C(70)-C(71)	1.378(8)	N(6)-Ni(2)-N(9)	90.10(18)
C(71)-C(72)	1.403(8)	N(7)-Ni(2)-N(6)	90.18(18)
C(71)-C(97)	1.493(8)	N(7)-Ni(2)-N(9)	177.17(18)
C(72)-C(73)	1.446(8)	N(8)-Ni(2)-N(6)	176.89(19)
C(73)-C(74)	1.347(8)	N(8)-Ni(2)-N(7)	89.71(18)
C(76)-C(77)	1.369(8)	N(8)-Ni(2)-N(9)	90.15(18)
C(76)-C(111)	1.504(7)	C(67)-N(1)-Ni(1)	126.5(4)
C(77)-C(78)	1.438(8)	C(70)-N(1)-Ni(1)	128.1(4)
C(78)-C(79)	1.345(8)	C(70)-N(1)-C(67)	105.1(5)
C(79)-C(80)	1.437(7)	C(72)-N(2)-Ni(1)	127.8(4)
C(80)-C(81)	1.385(8)	C(77)-N(3)-Ni(1)	128.6(4)
C(81)-C(82)	1.380(7)	C(80)-N(3)-Ni(1)	126.9(4)
C(83)-C(84)	1.394(7)	C(80)-N(3)-C(77)	104.5(4)
C(83)-C(88)	1.410(8)	C(65)-N(4)-Ni(1)	125.3(3)
C(84)-C(85)	1.401(8)	C(82)-N(4)-Ni(1)	127.4(4)
C(85)-C(86)	1.404(7)	C(82)-N(4)-C(65)	106.9(5)
C(86)-C(87)	1.372(7)	C(5)-N(6)-Ni(2)	128.6(4)
C(87)-C(88)	1.420(7)	C(5)-N(6)-C(8)	103.8(4)
C(97)-C(98)	1.394(8)	C(8)-N(6)-Ni(2)	127.1(4)
C(97)-C(102)	1.391(8)	C(10)-N(7)-Ni(2)	127.2(4)
C(98)-C(99)	1.399(9)	C(13)-N(7)-Ni(2)	126.6(3)
C(99)-C(100)	1.388(9)	C(13)-N(7)-C(10)	106.1(4)
C(100)-C(101)	1.395(8)	C(15)-N(8)-Ni(2)	128.7(3)
C(101)-C(102)	1.377(8)	C(15)-N(8)-C(18)	104.7(4)
C(111)-C(112)	1.394(7)	C(18)-N(8)-Ni(2)	126.6(4)
C(111)-C(116)	1.398(7)	C(3)-N(9)-Ni(2)	126.2(3)
C(112)-C(113)	1.405(8)	C(3)-N(9)-C(20)	103.9(4)
C(113)-C(114)	1.396(8)	C(20)-N(9)-Ni(2)	129.5(4)
C(114)-C(115)	1.393(7)	C(2)-C(1)-C(20)	106.6(5)
C(115)-C(116)	1.379(8)	C(1)-C(2)-C(3)	105.5(5)
N(1)-Ni(1)-N(2)	89.28(19)	C(1)-C(2)-C(63)	138.2(5)
N(1)-Ni(1)-N(3)	173.12(19)	C(63)-C(2)-C(3)	116.2(4)
N(1)-Ni(1)-N(4)	90.88(19)	N(9)-C(3)-C(2)	111.2(4)
N(2)-Ni(1)-N(4)	173.17(18)	C(4)-C(3)-N(9)	126.2(5)
N(3)-Ni(1)-N(2)	90.19(19)	C(4)-C(3)-C(2)	122.2(5)
N(3)-Ni(1)-N(4)	90.47(19)	N(5)-C(4)-C(5)	118.1(5)

C(3)-C(4)-N(5)	118.8(5)	C(21)-C(22)-C(23)	120.3(5)
C(3)-C(4)-C(5)	122.9(5)	C(23)-C(22)-C(19)	120.5(5)
N(6)-C(5)-C(4)	123.6(4)	C(24)-C(23)-C(22)	120.2(5)
N(6)-C(5)-C(6)	111.7(5)	C(25)-C(24)-C(23)	117.8(5)
C(4)-C(5)-C(6)	124.8(5)	C(24)-C(25)-C(26)	123.4(5)
C(7)-C(6)-C(5)	107.0(5)	C(25)-C(26)-C(21)	117.8(5)
C(6)-C(7)-C(8)	107.5(5)	C(36)-C(35)-C(40)	121.6(5)
N(6)-C(8)-C(7)	109.9(5)	C(35)-C(36)-C(14)	121.7(5)
C(9)-C(8)-N(6)	124.2(5)	C(35)-C(36)-C(37)	118.7(5)
C(9)-C(8)-C(7)	125.7(5)	C(37)-C(36)-C(14)	119.6(5)
C(8)-C(9)-C(49)	117.5(5)	C(38)-C(37)-C(36)	120.8(5)
C(10)-C(9)-C(8)	122.9(5)	C(39)-C(38)-C(37)	118.1(5)
C(10)-C(9)-C(49)	119.5(5)	C(40)-C(39)-C(38)	123.1(6)
N(7)-C(10)-C(11)	109.3(4)	C(39)-C(40)-C(35)	117.7(6)
C(9)-C(10)-N(7)	126.2(5)	C(50)-C(49)-C(9)	121.0(5)
C(9)-C(10)-C(11)	124.4(5)	C(50)-C(49)-C(54)	119.9(5)
N(7)-C(13)-C(12)	109.2(4)	C(54)-C(49)-C(9)	119.0(5)
N(7)-C(13)-C(14)	127.2(5)	C(49)-C(50)-C(51)	120.6(5)
C(14)-C(13)-C(12)	123.0(5)	C(52)-C(51)-C(50)	117.9(5)
C(13)-C(14)-C(36)	119.0(5)	C(51)-C(52)-C(53)	123.4(5)
C(15)-C(14)-C(13)	120.7(5)	C(52)-C(53)-C(54)	117.9(6)
C(15)-C(14)-C(36)	120.2(5)	C(49)-C(54)-C(53)	120.4(5)
N(8)-C(15)-C(16)	110.3(4)	C(2)-C(63)-C(82)	135.9(5)
C(14)-C(15)-N(8)	124.9(5)	C(64)-C(63)-C(2)	118.9(5)
C(14)-C(15)-C(16)	124.8(5)	C(64)-C(63)-C(82)	105.3(5)
C(17)-C(16)-C(15)	107.5(5)	N(5)-C(64)-C(65)	128.3(5)
C(16)-C(17)-C(18)	107.2(5)	C(63)-C(64)-N(5)	122.7(5)
N(8)-C(18)-C(17)	110.1(5)	C(63)-C(64)-C(65)	108.9(5)
C(19)-C(18)-N(8)	126.0(5)	N(4)-C(65)-C(64)	107.8(4)
C(19)-C(18)-C(17)	123.3(5)	C(66)-C(65)-N(4)	124.9(5)
C(18)-C(19)-C(20)	123.4(5)	C(66)-C(65)-C(64)	126.0(5)
C(18)-C(19)-C(22)	118.7(5)	C(65)-C(66)-C(67)	122.6(5)
C(20)-C(19)-C(22)	117.9(5)	C(65)-C(66)-C(84)	120.2(5)
N(9)-C(20)-C(1)	112.6(5)	C(67)-C(66)-C(84)	117.0(5)
N(9)-C(20)-C(19)	122.4(5)	N(1)-C(67)-C(68)	110.3(5)
C(19)-C(20)-C(1)	124.9(5)	C(66)-C(67)-N(1)	125.7(5)
C(22)-C(21)-C(26)	120.5(5)	C(66)-C(67)-C(68)	124.0(6)
C(21)-C(22)-C(19)	119.3(5)	C(69)-C(68)-C(67)	106.3(5)

C(68)-C(69)-C(70)	107.7(5)	N(4)-C(82)-C(63)	110.7(5)
N(1)-C(70)-C(69)	110.3(5)	N(4)-C(82)-C(81)	125.1(5)
N(1)-C(70)-C(71)	125.8(5)	C(81)-C(82)-C(63)	124.2(5)
C(71)-C(70)-C(69)	123.3(5)	C(84)-C(83)-C(88)	120.7(5)
C(70)-C(71)-C(72)	119.9(5)	C(83)-C(84)-C(66)	121.6(5)
C(70)-C(71)-C(97)	120.3(5)	C(83)-C(84)-C(85)	120.4(5)
C(72)-C(71)-C(97)	119.7(5)	C(85)-C(84)-C(66)	118.0(5)
N(2)-C(72)-C(71)	126.4(5)	C(84)-C(85)-C(86)	120.1(5)
N(2)-C(72)-C(73)	110.0(5)	C(87)-C(86)-C(85)	118.8(5)
C(71)-C(72)-C(73)	123.6(5)	C(86)-C(87)-C(88)	123.1(5)
C(74)-C(73)-C(72)	106.3(5)	C(83)-C(88)-C(87)	117.0(5)
C(73)-C(74)-C(75)	108.5(5)	C(98)-C(97)-C(71)	119.0(5)
N(2)-C(75)-C(74)	109.9(5)	C(102)-C(97)-C(71)	122.4(5)
C(76)-C(75)-N(2)	124.4(5)	C(102)-C(97)-C(98)	118.6(6)
C(76)-C(75)-C(74)	125.4(5)	C(97)-C(98)-C(99)	121.6(6)
C(75)-C(76)-C(111)	117.5(5)	C(100)-C(99)-C(98)	117.2(6)
C(77)-C(76)-C(75)	124.0(5)	C(99)-C(100)-C(101)	122.9(6)
C(77)-C(76)-C(111)	118.3(5)	C(102)-C(101)-C(100)	117.9(6)
N(3)-C(77)-C(78)	110.1(5)	C(101)-C(102)-C(97)	121.8(5)
C(76)-C(77)-N(3)	123.8(5)	C(112)-C(111)-C(76)	120.5(5)
C(76)-C(77)-C(78)	126.0(5)	C(112)-C(111)-C(116)	118.4(5)
C(79)-C(78)-C(77)	107.2(5)	C(116)-C(111)-C(76)	121.1(5)
C(78)-C(79)-C(80)	106.7(5)	C(111)-C(112)-C(113)	121.0(5)
N(3)-C(80)-C(79)	111.4(5)	C(114)-C(113)-C(112)	118.5(5)
N(3)-C(80)-C(81)	126.1(5)	C(115)-C(114)-C(113)	121.5(5)
C(81)-C(80)-C(79)	122.1(5)	C(116)-C(115)-C(114)	118.6(5)
C(82)-C(81)-C(80)	122.5(5)	C(115)-C(116)-C(111)	122.1(5)

a)



b)

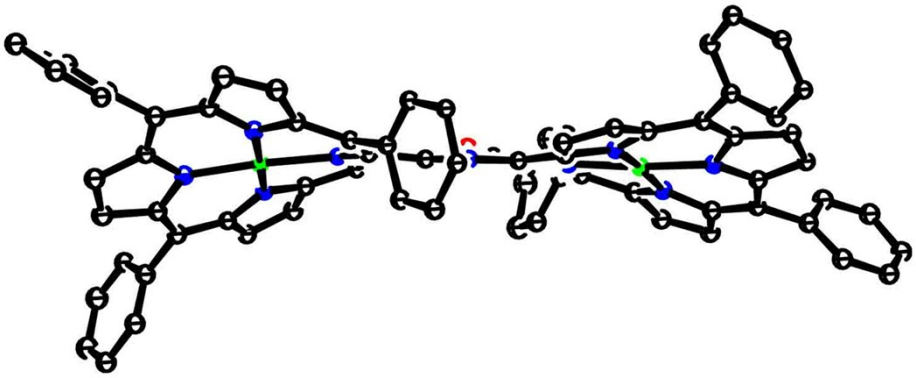


Figure S35. X-ray crystal structure of **10**: a) top view, b) side view. The thermal ellipsoids are 50% probability level. H atoms, alkyl groups and solvent molecules are omitted for clarity

Table S5. Crystal data and structure refinement for **10**

Identification code	exp_2672_sq	
Empirical formula	$C_{124}H_{139}N_9Ni_2O$	
Formula weight	1885.98	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.6749(3) Å	α = 80.6240(10)°.
	b = 28.8378(6) Å	β= 80.4790(10)°.
	c = 35.2694(5) Å	γ = 85.127(2)°.
Volume	13509.7(5) $Å^3$	

Z	4
Density (calculated)	0.929 Mg/m^3
Absorption coefficient	0.670 mm^{-1}
F(000)	4040
Crystal size	0.1 x 0.1 x 0.05 mm^3
Theta range for data collection	2.570 to 66.600°.
Index ranges	-16<=h<=16, -32<=k<=34, -31<=l<=41
Reflections collected	86471
Independent reflections	47486 [R(int) = 0.0770]
Completeness to theta = 66.600°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.58358
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	47486 / 1192 / 2641
Goodness-of-fit on F^2	0.993
Final R indices [I>2sigma(I)]	R1 = 0.0895, wR2 = 0.2400
R indices (all data)	R1 = 0.1427, wR2 = 0.2874
Extinction coefficient	n/a
Largest diff. peak and hole	0.744 and -0.500 $e.Å^{-3}$

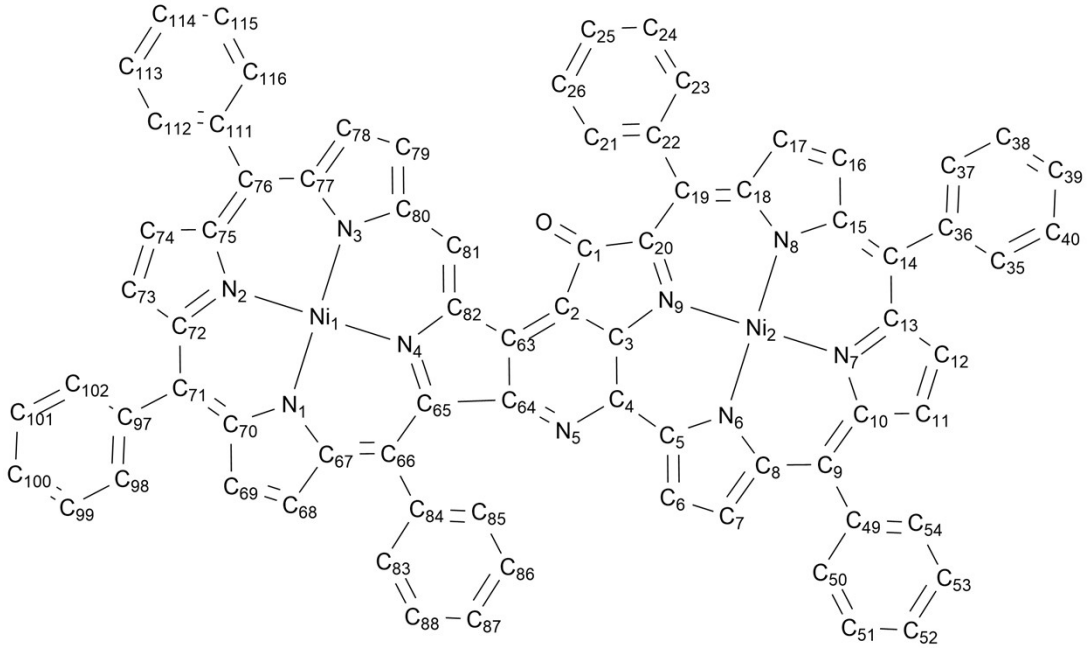


Table S6. bond lengths (Å) and angles (°) for **10**

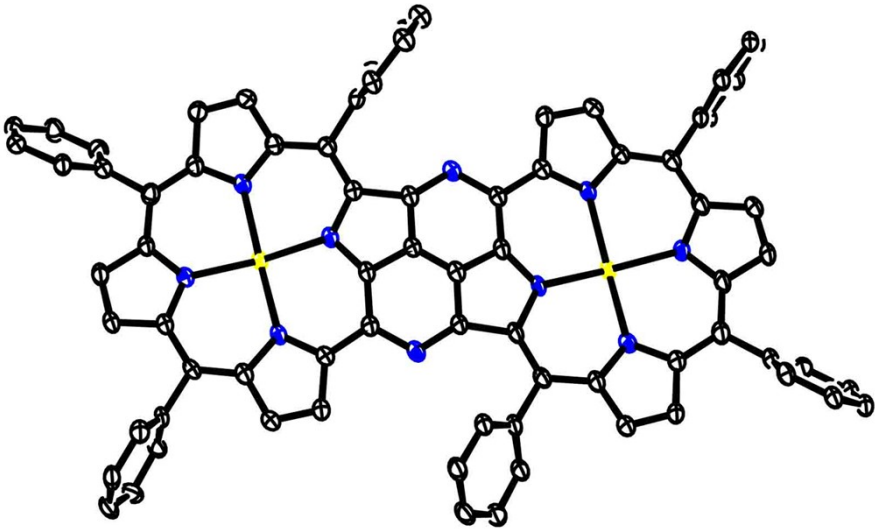
Ni(1)-N(4)	1.932(11)	C(84)-C(83)	1.41(2)
Ni(1)-N(1)	1.948(11)	C(85)-C(86)	1.410(18)
Ni(1)-N(2)	1.920(11)	C(12)-C(11)	1.352(19)
Ni(1)-N(3)	1.954(11)	C(12)-C(13)	1.439(18)
Ni(2)-N(6)	1.909(11)	C(6)-C(5)	1.438(18)
Ni(2)-N(9)	1.925(10)	C(6)-C(7)	1.339(18)
Ni(2)-N(8)	1.932(11)	C(82)-C(81)	1.372(18)
Ni(2)-N(7)	1.908(10)	C(53)-C(54)	1.409(18)
O(1)-C(1)	1.218(16)	C(53)-C(52)	1.38(2)
N(5)-C(4)	1.401(16)	C(64)-C(65)	1.473(17)
N(5)-C(64)	1.349(16)	C(11)-C(10)	1.418(18)
N(6)-C(67)	1.365(16)	C(54)-C(49)	1.377(19)
N(6)-C(70)	1.375(18)	C(67)-C(66)	1.403(18)
N(4)-C(3)	1.373(16)	C(67)-C(68)	1.465(19)
N(4)-C(20)	1.367(17)	C(65)-C(66)	1.354(18)
N(9)-C(82)	1.385(16)	C(86)-C(87)	1.36(2)
N(9)-C(65)	1.415(16)	C(49)-C(9)	1.515(17)
NI(1)-C(5)	1.354(17)	C(70)-C(71)	1.369(19)
NI(1)-C(8)	1.386(16)	C(70)-C(69)	1.486(18)
N(2)-C(10)	1.429(16)	C(80)-C(81)	1.377(18)
N(2)-C(13)	1.357(17)	C(80)-C(79)	1.465(17)
N(3)-C(15)	1.403(17)	C(88)-C(83)	1.369(19)
N(3)-C(18)	1.364(17)	C(88)-C(87)	1.447(18)
N(8)-C(80)	1.376(17)	C(36)-C(35)	1.39(2)
N(8)-C(77)	1.349(17)	C(36)-C(14)	1.495(18)
N(7)-C(72)	1.380(18)	C(52)-C(51)	1.43(2)
N(7)-C(75)	1.406(17)	C(22)-C(19)	1.533(18)
C(63)-C(2)	1.400(18)	C(22)-C(21)	1.40(2)
C(63)-C(82)	1.428(17)	C(22)-C(23)	1.36(2)
C(63)-C(64)	1.396(18)	C(17)-C(16)	1.38(2)
C(4)-C(3)	1.399(18)	C(17)-C(18)	1.417(19)
C(4)-C(5)	1.402(17)	C(10)-C(9)	1.377(19)
C(2)-C(1)	1.464(18)	C(15)-C(16)	1.456(19)
C(2)-C(3)	1.400(17)	C(15)-C(14)	1.350(19)
C(1)-C(20)	1.510(18)	C(20)-C(19)	1.333(19)
C(84)-C(85)	1.374(19)	C(7)-C(8)	1.401(18)
C(84)-C(66)	1.495(17)	C(18)-C(19)	1.385(19)

C(102)-C(97)	1.41(2)	N(6)-Ni(2)-N(9)	90.6(4)
C(102)-C(101)	1.36(2)	N(6)-Ni(2)-N(8)	176.4(5)
C(76)-C(111)	1.516(19)	N(8)-Ni(2)-N(9)	90.7(4)
C(76)-C(77)	1.420(18)	N(7)-Ni(2)-N(6)	89.5(5)
C(76)-C(75)	1.36(2)	N(7)-Ni(2)-N(9)	175.1(5)
C(78)-C(79)	1.35(2)	N(7)-Ni(2)-N(8)	89.4(5)
C(78)-C(77)	1.457(19)	C(64)-N(5)-C(4)	115.0(10)
C(71)-C(72)	1.40(2)	C(67)-N(6)-Ni(2)	127.0(9)
C(71)-C(97)	1.513(19)	C(67)-N(6)-C(70)	106.6(11)
C(21)-C(26)	1.44(2)	C(70)-N(6)-Ni(2)	126.3(9)
C(112)-C(113)	1.43(2)	C(3)-N(4)-Ni(1)	126.3(9)
C(112)-C(111)	1.41(2)	C(20)-N(4)-Ni(1)	127.5(9)
C(72)-C(73)	1.448(17)	C(20)-N(4)-C(3)	106.1(10)
C(13)-C(14)	1.409(18)	C(82)-N(9)-Ni(2)	127.7(8)
C(8)-C(9)	1.406(18)	C(65)-N(9)-Ni(2)	124.6(8)
C(113)-C(114)	1.41(2)	C(65)-N(9)-C(82)	107.6(10)
C(97)-C(98)	1.37(2)	C(5)-N(1)-Ni(1)	126.6(9)
C(69)-C(68)	1.37(2)	C(5)-N(1)-C(8)	105.1(11)
C(35)-C(40)	1.39(2)	C(8)-N(1)-Ni(1)	128.2(9)
C(40)-C(39)	1.37(2)	C(10)-N(2)-Ni(1)	125.9(9)
C(100)-C(99)	1.41(2)	C(13)-N(2)-Ni(1)	128.4(9)
C(100)-C(101)	1.41(2)	C(13)-N(2)-C(10)	104.7(10)
C(111)-C(116)	1.41(2)	C(15)-N(3)-Ni(1)	125.3(9)
C(23)-C(24)	1.50(2)	C(18)-N(3)-Ni(1)	128.2(9)
C(75)-C(74)	1.407(19)	C(18)-N(3)-C(15)	106.5(11)
C(39)-C(38)	1.40(2)	C(80)-N(8)-Ni(2)	124.5(9)
C(116)-C(115)	1.35(2)	C(80)-N(8)-C(77)	106.6(11)
C(99)-C(98)	1.448(19)	C(77)-N(8)-Ni(2)	128.9(9)
C(115)-C(114)	1.43(3)	C(72)-N(7)-Ni(2)	128.1(9)
C(73)-C(74)	1.36(2)	C(75)-N(7)-Ni(2)	126.4(9)
C(26)-C(25)	1.41(3)	C(75)-N(7)-C(72)	105.3(10)
C(24)-C(25)	1.33(3)	C(2)-C(63)-C(82)	135.4(12)
N(4)-Ni(1)-N(1)	90.7(5)	C(2)-C(63)-C(64)	117.4(11)
N(4)-Ni(1)-N(2)	174.9(5)	C(82)-C(63)-C(64)	107.0(11)
N(4)-Ni(1)-N(3)	89.1(5)	N(5)-C(4)-C(3)	122.3(11)
N (1)-Ni(1)-N(3)	175.6(5)	N(5)-C(4)-C(5)	115.7(11)
N(2)-Ni(1)-N(1)	90.2(5)	C(3)-C(4)-C(5)	121.6(11)
N(2)-Ni(1)-N(3)	90.4(5)	C(63)-C(2)-C(1)	134.8(12)

C(63)-C(2)-C(3)	118.9(12)	N(8)-C(80)-C(79)	108.7(11)
C(3)-C(2)-C(1)	106.2(11)	C(81)-C(80)-C(79)	123.0(12)
O(1)-C(1)-C(2)	129.9(12)	C(83)-C(88)-C(87)	116.9(13)
O(1)-C(1)-C(20)	127.6(12)	C(35)-C(36)-C(14)	122.5(13)
C(2)-C(1)-C(20)	102.5(11)	C(80)-C(81)-C(82)	122.6(12)
C(85)-C(84)-C(66)	124.4(13)	C(53)-C(52)-C(51)	121.1(12)
C(83)-C(84)-C(85)	119.9(12)	N(1)-C(5)-C(4)	125.2(12)
C(83)-C(84)-C(66)	115.6(12)	N(1)-C(5)-C(6)	110.6(11)
C(84)-C(85)-C(86)	120.6(13)	C(4)-C(5)-C(6)	123.4(12)
C(11)-C(12)-C(13)	106.3(11)	C(21)-C(22)-C(19)	116.7(13)
N(4)-C(3)-C(4)	126.2(11)	C(23)-C(22)-C(19)	118.9(13)
N(4)-C(3)-C(2)	113.8(11)	C(23)-C(22)-C(21)	124.4(14)
C(2)-C(3)-C(4)	119.8(12)	C(84)-C(83)-C(88)	121.5(13)
C(7)-C(6)-C(5)	105.9(12)	C(16)-C(17)-C(18)	108.3(12)
N(9)-C(82)-C(63)	110.4(11)	N(2)-C(10)-C(11)	108.9(12)
C(81)-C(82)-N(9)	123.9(11)	N(2)-C(10)-C(9)	124.5(11)
C(81)-C(82)-C(63)	125.2(12)	C(9)-C(10)-C(11)	125.9(12)
C(52)-C(53)-C(54)	118.9(12)	N(3)-C(15)-C(16)	108.6(12)
N(5)-C(64)-C(63)	126.4(12)	C(14)-C(15)-N(3)	125.7(12)
N(5)-C(64)-C(65)	125.9(12)	C(14)-C(15)-C(16)	125.5(12)
C(63)-C(64)-C(65)	107.3(11)	N(4)-C(20)-C(1)	110.6(11)
C(12)-C(11)-C(10)	108.5(12)	C(19)-C(20)-N(4)	125.9(12)
C(49)-C(54)-C(53)	119.9(13)	C(19)-C(20)-C(1)	123.1(12)
N(6)-C(67)-C(66)	125.9(12)	C(86)-C(87)-C(88)	122.3(13)
N(6)-C(67)-C(68)	110.9(12)	C(17)-C(16)-C(15)	105.6(13)
C(66)-C(67)-C(68)	123.1(12)	C(6)-C(7)-C(8)	108.3(11)
N(9)-C(65)-C(64)	107.0(11)	N(3)-C(18)-C(17)	110.2(12)
C(66)-C(65)-N(9)	126.0(11)	N(3)-C(18)-C(19)	123.8(12)
C(66)-C(65)-C(64)	126.6(11)	C(19)-C(18)-C(17)	125.5(12)
C(67)-C(66)-C(84)	119.9(12)	C(97)-C(102)-C(101)	122.4(14)
C(65)-C(66)-C(84)	120.1(12)	C(77)-C(76)-C(111)	117.2(13)
C(65)-C(66)-C(67)	119.9(12)	C(75)-C(76)-C(111)	120.8(12)
C(87)-C(86)-C(85)	118.6(12)	C(75)-C(76)-C(77)	121.9(13)
C(54)-C(49)-C(9)	120.1(13)	C(79)-C(78)-C(77)	105.2(11)
N(6)-C(70)-C(71)	126.2(13)	C(20)-C(19)-C(22)	122.7(12)
N(6)-C(70)-C(69)	109.3(11)	C(20)-C(19)-C(18)	123.5(13)
C(71)-C(70)-C(69)	123.8(13)	C(18)-C(19)-C(22)	113.4(12)
N(8)-C(80)-C(81)	126.9(12)	C(70)-C(71)-C(72)	120.1(13)

C(70)-C(71)-C(97)	122.4(13)	C(116)-C(111)-C(76)	121.5(15)
C(72)-C(71)-C(97)	116.9(12)	C(69)-C(68)-C(67)	106.1(12)
C(78)-C(79)-C(80)	107.7(12)	N(8)-C(77)-C(76)	123.9(13)
C(26)-C(21)-C(22)	118.2(16)	N(8)-C(77)-C(78)	111.5(11)
C(111)-C(112)-C(113)	119.5(14)	C(76)-C(77)-C(78)	124.6(12)
N(7)-C(72)-C(71)	124.7(11)	C(22)-C(23)-C(24)	117.7(16)
N(7)-C(72)-C(73)	109.9(12)	N(7)-C(75)-C(74)	110.0(12)
C(71)-C(72)-C(73)	125.1(13)	C(76)-C(75)-N(7)	124.8(12)
N(2)-C(13)-C(12)	111.5(11)	C(76)-C(75)-C(74)	124.2(13)
N(2)-C(13)-C(14)	124.8(12)	C(38)-C(39)-C(40)	122.8(14)
C(14)-C(13)-C(12)	123.5(12)	C(115)-C(116)-C(111)	122.1(17)
NI(1)-C(8)-C(7)	110.0(11)	C(100)-C(99)-C(98)	117.4(14)
C(9)-C(8)-NI(1)	124.1(12)	C(116)-C(115)-C(114)	118.1(15)
C(9)-C(8)-C(7)	125.8(12)	C(97)-C(98)-C(99)	119.1(14)
C(112)-C(113)-C(114)	117.2(16)	C(74)-C(73)-C(72)	106.5(12)
C(102)-C(97)-C(71)	119.5(13)	C(115)-C(114)-C(113)	122.6(15)
C(102)-C(97)-C(98)	120.6(14)	C(73)-C(74)-C(75)	108.2(12)
C(98)-C(97)-C(71)	119.8(13)	C(21)-C(26)-C(25)	116.4(17)
C(68)-C(69)-C(70)	106.2(12)	C(25)-C(24)-C(23)	117.0(18)
C(10)-C(9)-C(49)	120.1(11)	C(102)-C(101)-C(100)	117.5(13)
C(8)-C(9)-C(49)	117.2(12)	C(24)-C(25)-C(26)	126.3(16)
C(8)-C(9)-C(10)	122.7(12)		
C(36)-C(35)-C(40)	119.9(15)		
C(15)-C(14)-C(36)	119.3(12)		
C(15)-C(14)-C(13)	122.2(12)		
C(13)-C(14)-C(36)	117.7(11)		
C(39)-C(40)-C(35)	119.5(15)		
C(99)-C(100)-C(101)	122.4(14)		
C(112)-C(111)-C(76)	118.0(13)		
C(112)-C(111)-C(116)	120.3(14)		

a)



b)

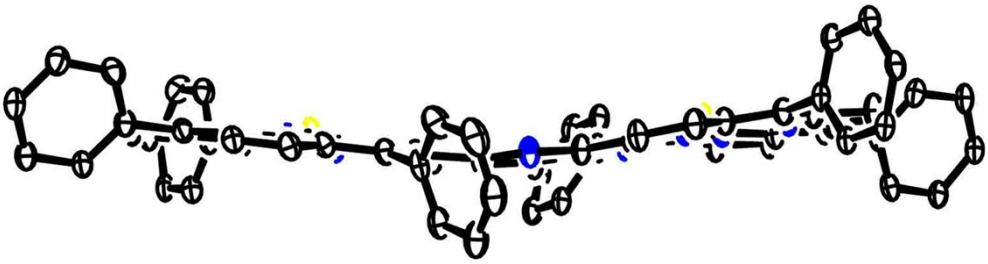


Figure S36. X-ray crystal structure of **13**: a) top view, b) side view. The thermal ellipsoids are 50% probability level. H atoms, alkyl groups and solvent molecules are omitted for clarity

Table S7. Crystal data and structure refinement for**13**

Identification code	exp_2084_sq	
Empirical formula	$C_{124}H_{138}N_{10}Zn_2$	
Formula weight	1894.96	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 18.3265(6) Å	α= 75.814(3)°.
	b = 19.8075(7) Å	β = 86.784(3)°.
	c = 20.8248(7) Å	γ = 70.175(3)°.
Volume	6891.5(4) $Å^3$	

Z	2
Density (calculated)	0.991 Mg/m^3
Absorption coefficient	0.778 mm^{-1}
F(000)	2192
Crystal size	0.2 x 0.2 x 0.1 mm^3
Theta range for data collection	2.189 to 66.596°.
Index ranges	-19<=h<=21, -19<=k<=23, -24<=l<=24
Reflections collected	47079
Independent reflections	24343 [R(int) = 0.0458]
Completeness to theta = 66.596°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.77866
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	24343 / 0 / 1369
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0679, wR2 = 0.1800
R indices (all data)	R1 = 0.0915, wR2 = 0.1974
Extinction coefficient	n/a
Largest diff. peak and hole	1.014 and -0.640 $e.Å^{-3}$

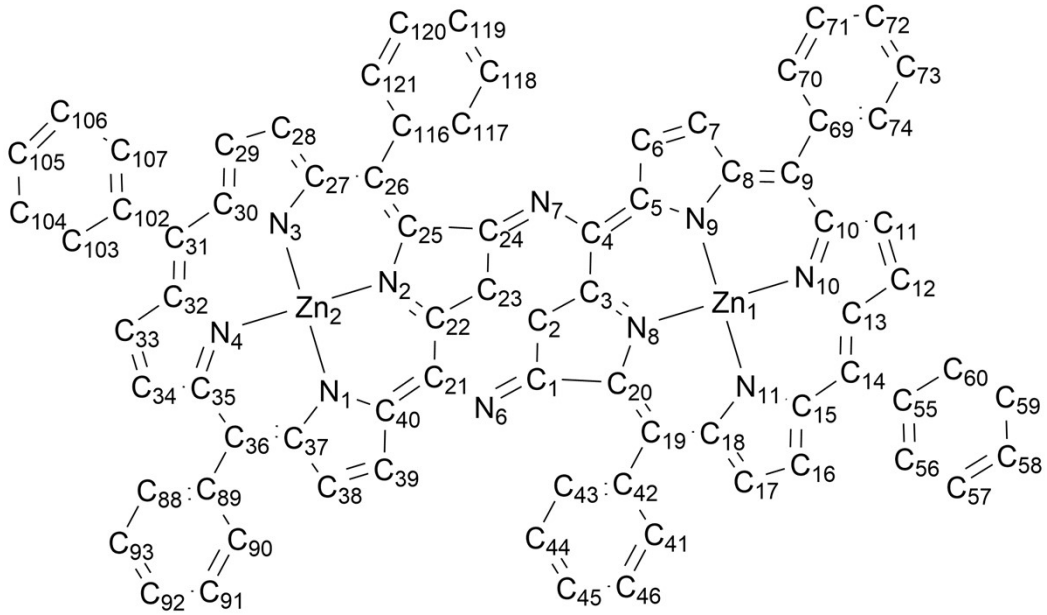


Table S8. bond lengths (Å) and angles (°) for **13**

Zn(1)-N(10)	2.025(3)	C(59)-C(60)	1.404(5)
Zn(1)-N(11)	2.094(3)	C(107)-C(102)	1.390(5)
Zn(1)-N(8)	2.028(3)	C(13)-C(12)	1.434(5)
Zn(1)-N(9)	2.154(3)	C(13)-C(14)	1.419(5)
Zn(2)-N(2)	2.024(3)	C(18)-C(19)	1.419(5)
Zn(2)-N(4)	2.024(3)	C(18)-C(17)	1.440(5)
Zn(2)-N(1)	2.157(3)	C(57)-C(56)	1.395(5)
Zn(2)-N(3)	2.103(3)	C(12)-C(11)	1.350(5)
N(10)-C(10)	1.374(4)	C(16)-C(15)	1.445(5)
N(10)-C(13)	1.374(4)	C(16)-C(17)	1.350(5)
N(2)-C(22)	1.379(5)	C(22)-C(21)	1.438(5)
N(2)-C(25)	1.410(4)	C(22)-C(23)	1.370(5)
N(11)-C(18)	1.360(4)	C(32)-C(33)	1.437(5)
N(11)-C(15)	1.376(4)	C(32)-C(31)	1.411(5)
N(4)-C(32)	1.369(5)	C(69)-C(9)	1.496(4)
N(4)-C(35)	1.383(4)	C(69)-C(70)	1.385(5)
N(1)-C(37)	1.394(4)	C(69)-C(74)	1.380(5)
N(1)-C(40)	1.357(5)	C(19)-C(42)	1.502(5)
N(8)-C(3)	1.372(5)	C(19)-C(20)	1.388(5)
N(8)-C(20)	1.392(4)	C(15)-C(14)	1.403(5)
N(9)-C(8)	1.384(4)	C(89)-C(88)	1.392(5)
N(9)-C(5)	1.365(5)	C(89)-C(36)	1.508(4)
N(3)-C(30)	1.382(5)	C(42)-C(43)	1.390(6)
N(3)-C(27)	1.362(4)	C(42)-C(41)	1.382(5)
N(6)-C(21)	1.393(5)	C(56)-C(55)	1.397(5)
N(6)-C(1)	1.329(5)	C(3)-C(2)	1.374(5)
N(7)-C(4)	1.390(5)	C(3)-C(4)	1.427(5)
N(7)-C(24)	1.341(4)	C(9)-C(8)	1.392(5)
C(90)-C(89)	1.389(5)	C(71)-C(72)	1.383(6)
C(90)-C(91)	1.398(5)	C(71)-C(70)	1.404(5)
C(106)-C(105)	1.400(5)	C(21)-C(40)	1.429(5)
C(106)-C(107)	1.387(5)	C(55)-C(60)	1.373(5)
C(58)-C(59)	1.387(5)	C(55)-C(14)	1.502(5)
C(58)-C(57)	1.393(5)	C(91)-C(92)	1.399(5)
C(105)-C(104)	1.394(5)	C(117)-C(116)	1.383(5)
C(10)-C(11)	1.430(5)	C(117)-C(118)	1.404(5)
C(10)-C(9)	1.414(5)	C(120)-C(121)	1.392(5)

C(120)-C(119)	1.396(6)	N(10)-Zn(1)-N(11)	90.40(11)
C(72)-C(73)	1.395(5)	N(10)-Zn(1)-N(8)	159.20(13)
C(37)-C(38)	1.439(5)	N(10)-Zn(1)-N(9)	89.75(11)
C(37)-C(36)	1.389(5)	N(11)-Zn(1)-N(9)	165.73(12)
C(38)-C(39)	1.354(5)	N(8)-Zn(1)-N(11)	86.43(11)
C(23)-C(2)	1.332(5)	N(8)-Zn(1)-N(9)	88.38(11)
C(23)-C(24)	1.387(5)	N(2)-Zn(2)-N(1)	88.99(11)
C(25)-C(26)	1.381(5)	N(2)-Zn(2)-N(3)	85.35(11)
C(25)-C(24)	1.511(5)	N(4)-Zn(2)-N(2)	159.44(13)
C(28)-C(27)	1.437(5)	N(4)-Zn(2)-N(1)	89.39(11)
C(28)-C(29)	1.354(5)	N(4)-Zn(2)-N(3)	90.12(11)
C(30)-C(31)	1.400(5)	N(3)-Zn(2)-N(1)	162.48(12)
C(30)-C(29)	1.438(5)	C(10)-N(10)-Zn(1)	126.4(2)
C(104)-C(103)	1.390(5)	C(10)-N(10)-C(13)	106.5(3)
C(26)-C(27)	1.437(5)	C(13)-N(10)-Zn(1)	125.9(2)
C(26)-C(116)	1.507(5)	C(22)-N(2)-Zn(2)	120.6(2)
C(1)-C(20)	1.518(5)	C(22)-N(2)-C(25)	108.2(3)
C(1)-C(2)	1.399(5)	C(25)-N(2)-Zn(2)	130.2(2)
C(92)-C(93)	1.397(5)	C(18)-N(11)-Zn(1)	127.9(2)
C(88)-C(93)	1.393(5)	C(18)-N(11)-C(15)	107.3(3)
C(8)-C(7)	1.436(5)	C(15)-N(11)-Zn(1)	124.7(2)
C(121)-C(116)	1.392(5)	C(32)-N(4)-Zn(2)	126.8(2)
C(40)-C(39)	1.438(5)	C(32)-N(4)-C(35)	106.7(3)
C(102)-C(103)	1.380(5)	C(35)-N(4)-Zn(2)	126.1(2)
C(102)-C(31)	1.499(5)	C(37)-N(1)-Zn(2)	123.2(2)
C(33)-C(34)	1.348(5)	C(40)-N(1)-Zn(2)	129.9(2)
C(36)-C(35)	1.419(5)	C(40)-N(1)-C(37)	105.8(3)
C(35)-C(34)	1.423(5)	C(3)-N(8)-Zn(1)	120.2(2)
C(73)-C(74)	1.394(5)	C(3)-N(8)-C(20)	108.5(3)
C(5)-C(4)	1.425(5)	C(20)-N(8)-Zn(1)	130.1(2)
C(5)-C(6)	1.428(5)	C(8)-N(9)-Zn(1)	123.3(2)
C(6)-C(7)	1.356(5)	C(5)-N(9)-Zn(1)	129.5(2)
C(118)-C(119)	1.380(6)	C(5)-N(9)-C(8)	105.7(3)
C(43)-C(44)	1.394(5)	C(30)-N(3)-Zn(2)	125.0(2)
C(41)-C(46)	1.420(6)	C(27)-N(3)-Zn(2)	128.2(2)
C(44)-C(45)	1.368(6)	C(27)-N(3)-C(30)	106.9(3)
C(46)-C(45)	1.374(7)	C(1)-N(6)-C(21)	118.3(3)
		C(24)-N(7)-C(4)	118.8(3)

C(89)-C(90)-C(91)	121.3(3)	C(41)-C(42)-C(43)	119.7(4)
C(107)-C(106)-C(105)	118.1(3)	C(57)-C(56)-C(55)	120.6(3)
C(59)-C(58)-C(57)	122.6(3)	C(12)-C(11)-C(10)	107.1(3)
C(104)-C(105)-C(106)	121.8(3)	N(8)-C(3)-C(2)	107.9(3)
N(10)-C(10)-C(11)	109.7(3)	N(8)-C(3)-C(4)	136.9(3)
N(10)-C(10)-C(9)	126.2(3)	C(2)-C(3)-C(4)	114.8(3)
C(9)-C(10)-C(11)	124.1(3)	C(10)-C(9)-C(69)	117.1(3)
C(58)-C(59)-C(60)	117.7(3)	C(8)-C(9)-C(10)	126.9(3)
C(106)-C(107)-C(102)	121.7(3)	C(8)-C(9)-C(69)	116.0(3)
N(10)-C(13)-C(12)	109.2(3)	C(72)-C(71)-C(70)	118.5(3)
N(10)-C(13)-C(14)	125.5(3)	N(6)-C(21)-C(22)	122.9(3)
C(14)-C(13)-C(12)	125.3(3)	N(6)-C(21)-C(40)	117.1(3)
N(11)-C(18)-C(19)	125.7(3)	C(40)-C(21)-C(22)	119.9(3)
N(11)-C(18)-C(17)	109.2(3)	C(56)-C(55)-C(14)	119.3(3)
C(19)-C(18)-C(17)	125.2(3)	C(60)-C(55)-C(56)	119.8(3)
C(58)-C(57)-C(56)	118.1(3)	C(60)-C(55)-C(14)	120.8(3)
C(11)-C(12)-C(13)	107.5(3)	C(90)-C(91)-C(92)	117.5(3)
C(17)-C(16)-C(15)	106.7(3)	C(116)-C(117)-C(118)	120.6(4)
N(2)-C(22)-C(21)	136.6(3)	C(121)-C(120)-C(119)	117.6(4)
C(23)-C(22)-N(2)	108.0(3)	C(71)-C(72)-C(73)	122.4(3)
C(23)-C(22)-C(21)	114.8(3)	C(16)-C(17)-C(18)	107.7(3)
N(4)-C(32)-C(33)	109.1(3)	N(1)-C(37)-C(38)	108.9(3)
N(4)-C(32)-C(31)	126.2(3)	C(36)-C(37)-N(1)	124.8(3)
C(31)-C(32)-C(33)	124.7(3)	C(36)-C(37)-C(38)	126.2(3)
C(70)-C(69)-C(9)	120.1(3)	C(39)-C(38)-C(37)	107.8(3)
C(74)-C(69)-C(9)	119.5(3)	C(55)-C(60)-C(59)	121.3(3)
C(74)-C(69)-C(70)	120.4(3)	C(22)-C(23)-C(24)	114.2(3)
C(18)-C(19)-C(42)	119.4(3)	C(2)-C(23)-C(22)	121.9(4)
C(20)-C(19)-C(18)	124.4(3)	C(2)-C(23)-C(24)	122.4(4)
C(20)-C(19)-C(42)	115.7(3)	N(2)-C(25)-C(24)	108.1(3)
N(11)-C(15)-C(16)	109.0(3)	C(26)-C(25)-N(2)	123.8(3)
N(11)-C(15)-C(14)	125.3(3)	C(26)-C(25)-C(24)	128.1(3)
C(14)-C(15)-C(16)	125.5(3)	C(29)-C(28)-C(27)	107.4(3)
C(90)-C(89)-C(88)	119.7(3)	N(3)-C(30)-C(31)	125.6(3)
C(90)-C(89)-C(36)	121.8(3)	N(3)-C(30)-C(29)	109.1(3)
C(88)-C(89)-C(36)	118.4(3)	C(31)-C(30)-C(29)	125.2(3)
C(43)-C(42)-C(19)	117.3(3)	C(103)-C(104)-C(105)	117.6(3)
C(41)-C(42)-C(19)	122.8(4)	C(25)-C(26)-C(27)	123.7(3)

C(25)-C(26)-C(116)	119.2(3)	N(4)-C(35)-C(34)	109.2(3)
C(27)-C(26)-C(116)	116.8(3)	C(36)-C(35)-C(34)	125.0(3)
N(6)-C(1)-C(20)	139.5(3)	C(74)-C(73)-C(72)	117.8(4)
N(6)-C(1)-C(2)	119.8(3)	N(9)-C(5)-C(4)	121.2(3)
C(2)-C(1)-C(20)	100.1(3)	N(9)-C(5)-C(6)	111.2(3)
C(93)-C(92)-C(91)	122.6(3)	C(4)-C(5)-C(6)	127.6(3)
C(89)-C(88)-C(93)	121.0(3)	C(38)-C(39)-C(40)	106.2(3)
N(3)-C(27)-C(28)	109.6(3)	C(3)-C(2)-C(1)	114.1(3)
N(3)-C(27)-C(26)	125.4(3)	C(23)-C(2)-C(3)	122.1(4)
C(28)-C(27)-C(26)	124.9(3)	C(23)-C(2)-C(1)	122.3(3)
N(9)-C(8)-C(9)	125.2(3)	N(7)-C(4)-C(3)	122.6(3)
N(9)-C(8)-C(7)	109.1(3)	N(7)-C(4)-C(5)	117.1(3)
C(9)-C(8)-C(7)	125.6(3)	C(5)-C(4)-C(3)	120.3(3)
N(8)-C(20)-C(1)	109.1(3)	C(7)-C(6)-C(5)	106.1(3)
C(19)-C(20)-N(8)	123.9(3)	C(88)-C(93)-C(92)	117.9(3)
C(19)-C(20)-C(1)	127.0(3)	C(102)-C(103)-C(104)	122.4(3)
C(120)-C(121)-C(116)	120.9(4)	C(119)-C(118)-C(117)	117.9(3)
N(1)-C(40)-C(21)	122.1(3)	C(118)-C(119)-C(120)	123.1(3)
N(1)-C(40)-C(39)	111.2(3)	C(42)-C(43)-C(44)	121.5(4)
C(21)-C(40)-C(39)	126.7(3)	C(32)-C(31)-C(102)	116.9(3)
C(107)-C(102)-C(31)	119.7(3)	C(30)-C(31)-C(32)	125.8(3)
C(103)-C(102)-C(107)	118.4(3)	C(30)-C(31)-C(102)	117.3(3)
C(103)-C(102)-C(31)	121.9(3)	C(28)-C(29)-C(30)	107.0(3)
C(117)-C(116)-C(26)	119.2(3)	C(69)-C(74)-C(73)	121.0(3)
C(117)-C(116)-C(121)	120.0(3)	N(7)-C(24)-C(23)	119.1(3)
C(121)-C(116)-C(26)	120.7(3)	N(7)-C(24)-C(25)	139.0(3)
C(34)-C(33)-C(32)	107.4(3)	C(23)-C(24)-C(25)	101.3(3)
C(69)-C(70)-C(71)	120.0(4)	C(33)-C(34)-C(35)	107.6(3)
C(13)-C(14)-C(55)	116.0(3)	C(6)-C(7)-C(8)	107.8(3)
C(15)-C(14)-C(13)	126.2(3)	C(42)-C(41)-C(46)	119.7(4)
C(15)-C(14)-C(55)	117.8(3)	C(45)-C(44)-C(43)	117.4(4)
C(37)-C(36)-C(89)	117.7(3)	C(45)-C(46)-C(41)	118.0(4)
C(37)-C(36)-C(35)	127.0(3)	C(44)-C(45)-C(46)	123.7(4)
C(35)-C(36)-C(89)	115.3(3)	C(85)-C(86)-C(87)	119.0(5)
N(4)-C(35)-C(36)	125.7(3)		

9. References

[S1] (*a*) K. Fujimoto, D. Shimizu and A. Osuka, Porphyrin-stabilized nitrenium dication, *Chem.-Eur. J.,* 2019, **25**, 521-525; (*b*) K. Fujimoto, D. Shimizu, T. Mori, Y. Li, M. Zhou, J. Song and A. Osuka, Selective formation of helical tetrapyrrin-fused porphyrins by oxidation of β-to-β linked meso-aminoporphyrin dimers, *Chem.-Eur. J.,* 2019, **25**, 1711-715.

[S2] (*a*) W. J. Hehre, R. Ditchfield and J. A. Pople, Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules, *J. Chem. Phys.*, 1972, **56**, 2257-2261; (*b*) T. Yanai, D. P. Tew and N. C. Handy, A new hybrid exchange-correlation functional using the coulomb-attenuating method (CAM-B3LYP), *Chem. Phys. Lett.*, 2004, **393**, 51-57; (*c*) M. J. Frisch, G. W. Trucks, H.B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, *et al.* J gaussian 09 revision D 01. Wallingford CT: Gaussian Inc; 2009.