Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of pyridine-fused porphyrinoid: oxopyridochlorin

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Instrumentation and Materials

^{1}H NMR (600 MHz), ^{13}CNMR (151 MHz) spectra were taken on JEOL ECA-600 spectrometer. Chemical shift were reported as delta scale in ppm relative to $CHCl_3$ ($\delta = 7.26$) for ^{1}H NMR and to $CDCl_3$ ($\delta = 77.16$) for ^{13}CNMR. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. High-resolution ESI-TOF mass spectra were taken on Bruker micro TOF. X-Ray data were taken on a Rigaku-Raxis imaging plate system. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-300). Dry toluene was distilled from CaH_2. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure and Compound data

Synthesis of 2

Dibenzoylporphyrin **2Zn** was prepared by the reported literature procedure.[1] Freebase **2H** was prepared by demetallation of **2Zn** with concentrated aqueous HCl. Nickel complex **2Ni** was obtained by treatment of **2H** with Ni(acac)$_2$.

1Zn

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 8.18$ (d, $J = 4.6$ Hz, 1H, β-H), 8.10 (d, $J = 4.6$ Hz, 1H, β-H), 8.06 (d, $J = 4.6$ Hz, 1H, β-H), 8.05 (d, $J = 4.6$ Hz, 1H, β-H), 8.00 (d, $J = 5.0$ Hz, 1H, β-H), 7.81 (d, $J =$ 1.9 Hz, 2H, Ar-*o*-H), 7.77 (d, $J = 1.9$ Hz, 2H, Ar-*o*-H), 7.75 (d, 2H, $J = 8.3$ Hz, 2H, Ph-*o*-H), 7.69 (d, J = 1.9 Hz, 2H, Ar-*o*-H), 7.67 (t, $J = 1.9$ Hz, 1H, Ar-*p*-H), 7.65 (t, $J = 1.9$ Hz, 1H, Ar-*p*-H), 7.60 (t, $J =$ 1.9 Hz, 1H, Ar-*p*-H), 7.57-7.52 (m, 3H, Ph-*m*-H & Ph-*p*-H), 7.41 (d, $J = 7.3$ Hz, 2H, Ph-*o*-H), 7.31 (s, 1H, β-H), 7.30 (d, $J = 5.0$ Hz, 1H, β-H), 7.23 (t, $J = 7.3$ Hz, 2H, Ph-*m*-H), 7.18 (d, $J = 7.3$ Hz, 1H, Ph-*p*-H), 1.49 (s, 18H, *tert*-butyl-H), 1.44 (s, 18H, *tert*-butyl-H), 1.42 (s, 18H, *tert*-butyl-H). HR-ESI-TOF MS: *m*/*z* = 1113.5701 Calcd for $C_{76}H_{81}N_4Zn$: 1113.5747 $[M]^+$.

2Zn

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.07 (d, *J* = 4.6 Hz, 1H, β-H), 8.99 (s, 3H, β-H), 8.98 (d, *J* = 4.6 Hz, 1H, β-H), 8.95 (d, *J* = 4.6 Hz, 1H, β-H), 8.91 (d, *J* = 4.6 Hz, 1H, β-H), 8.11 (d, 2H, *J* = 7.3 Hz, Ph-*o*-H), 8.07 (d, *J* = 1.8 Hz, 2H, Ar-*o*-H), 8.06 (d, *J* = 1.8 Hz, 2H, Ar-*o*-H), 8.04 (d, *J* = 1.9 Hz, 2H, Ar-*o*-H), 7.83 (bs, 2H, Ph-*o*-H), 7.80 (t, *J* = 1.8 Hz, 1H, Ar-*p*-H), 7.78 (t, *J* = 1.8 Hz, 1H, Ar-*p*-H), 7.71 (t, *J* = 1.9 Hz, 1H, Ar-*p*-H), 7.58 (t, *J* = 7.3 Hz, 1H, Ph-*p*-H), 7.42 (t, *J* = 7.8 Hz, 2H, Ph-*m*-H), 7.38 (t, *J* = 7.4 Hz, 1H, Ph-*p*-H), 7.24 (t, *J* = 7.8 Hz, 2H, Ph-*m*-H), 1.53 (s, 18H, *tert*-butyl-H), 1.51 (s, 18H, *tert*-butyl-H), 1.47 (s, 18H, *tert*-butyl-H). HR-ESI-TOF MS: *m*/*z* = 1167.5495 Calcd for $C_{76}H_{80}N_4O_2ZnNa$: 1167.5465 $[M]^+$.

2H

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 9.13 (d, *J* = 4.8 Hz, 1H, β-H), 8.93 (s, 2H, β-H), 8.88 (d, *J* = 4.8 Hz, 1H, β-H), 8.80 (d, *J* = 4.8 Hz, 1H, β-H), 8.78 (s, 1H, β-H), 8.75 (d, *J* = 4.8 Hz, 1H, β-H), 8.07-8.05 (m, 4H, Ph-*o*-H & Ar-*o*-H), 8.05 (d, *J* = 1.9 Hz, 2H, Ar-*o*-H), 8.03 (d, *J* = 1.9 Hz, 2H, Ar-*o*-H), 7.80 (t, *J* = 1.6 Hz, 1H, Ar-*p*-H), 7.79 (t, *J* = 1.6 Hz, 1H, Ar-*p*-H), 7.76 (d, *J* = 8.3 Hz, 2H, Ph-*o*-H), 7.72 (t, *J* = 1.3 Hz, 1H, Ar-*p*-H), 7.56 (t, *J* = 7.8 Hz, 1H, Ph-*p*-H), 7.41 (t, *J* = 7.8 Hz, 2H, Ph-*m*-H), 7.35 (t, *J* = 7.5 Hz, 1H, Ph-*p*-H), 7.20 (t, *J* = 7.5 Hz, 2H, Ph-*m*-H), 1.52 (s, 18H, *tert*-butyl-H), 1.51 (s, 18H, *tert*-butyl-H), 1.48 (s, 18H, *tert*-butyl-H), –2.33 (bs, 2H, NH). HR-ESI-TOF MS: *m*/*z* = 1083.6554 Calcd for $C_{76}H_{83}N_4O_2$: 1083.6511 $[M]^+$.

2Ni

^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ= 8.86 (d, J = 5.0 Hz, 1H, β-H), 8.82 (d, J = 5.0 Hz, 1H, β-H), 8.78 (d, J = 5.0 Hz, 1H, β-H), 8.78 (s, 1H, β-H), 8.76 (d, J = 5.0 Hz, 1H, β-H), 8.73 (d, J = 5.0 Hz, 1H, β-H), 8.68 (d, J = 5.0 Hz, 1H, β-H), 8.11 (d, 2H, J = 6.8 Hz, Ph-*o*-H), 7.84 (d, J = 1.8 Hz, 2H, Ar-*o*-H), 7.82 (d, J = 1.8 Hz, 2H, Ar-*o*-H), 7.80 (d, J = 1.9 Hz, 2H, Ar-*o*-H), 7.72 (t, J = 1.9 Hz, 1H, Ar-*p*-H), 7.70 (t, J = 1.8 Hz, 1H, Ar-*p*-H), 7.64 (t, J = 1.9 Hz, 1H, Ar-*p*-H), 7.54-7.52 (m, 3H, Ph-*o*-H & Ph-*p*-H), 7.38 (t, J = 7.8 Hz, 2H, Ph-*m*-H), 7.33 (t, J = 7.8 Hz, 1H, Ph-*p*-H), 7.16 (t, J = 7.4 Hz, 2H, Ph-*m*-H), 1.47 (s, 18H, *tert*-butyl-H), 1.45 (s, 18H, *tert*-butyl-H), 1.42 (s, 18H, *tert*-butyl-H). HR-ESI-TOF MS: m/z = 1139.5733 Calcd for $C_{76}H_{81}N_4O_2Ni$: 1139.5708 $[M]^+$.

Reaction of dibenzoylporphyrins 2 with ammonium acetate

A mixture of **2** (20 µmol) and an excess amount of ammonium acetate in toluene (15 mL) and AcOH (20 mL) was heated at 120 °C for 2 days. The reaction mixture was cooled down to room temperature, washed with saturated aqueous $NaHCO_3$ and brine, and extracted with AcOEt. The extract was dried over Na_2SO_4. After removal of solvent in vacuo, the residue was purified by silica gel chromatography eluting with CH_2Cl_2/hexane and was recrystallized from CH_2Cl_2/MeOH to afford the target compounds in their respective yields as described.

3Zn

^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 8.42 (dd, 2H, *J* = 7.8, 2.1 Hz, Ph-*o*-H), 7.99 (d, *J* = 4.6 Hz, 1H, β-H), 7.88 (d, *J* = 4.4 Hz, 1H, β-H), 7.85 (d, *J* = 4.4 Hz, 1H, β-H), 7.79 (d, *J* = 4.6 Hz, 1H, β-H), 7.77 (d, 2H, *J* = 7.2 Hz, Ph-*o*-H), 7.71 (d, *J* = 1.8 Hz, 2H, Ar-*o*-H), 7.69 (d, *J* = 1.8 Hz, 2H, Ar-*o*-H), 7.65 (d, *J* = 4.6 Hz, 1H, β-H), 7.65 (t, *J* = 1.8 Hz, 1H, Ar-*p*-H), 7.65 (t, *J* = 1.8 Hz, 1H, Ar-*p*-H), 7.57 (t, *J* = 1.8 Hz, 1H, Ar-*p*-H), 7.54 (d, *J* = 1.8 Hz, 2H, Ar-*o*-H), 7.55-7.49 (m, 6H, Ph-*m*-H & Ph-*p*-H), 7.47 (d, *J* = 4.6 Hz, 1H, β-H), 1.45 (s, 18H, *tert*-butyl-H), 1.44 (s, 18H, *tert*-butyl-H), 1.43 (s, 18H, *tert*-butyl-H). ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 191.17, 167.10, 161.28, 160.69, 157.65, 154.16, 150.04, 149.56, 149.32, 149.29, 148.95, 147.06, 145.72, 145.40, 144.79, 139.97, 139.95, 138.83, 137.41, 135.12, 134.47, 132,16, 131.72, 130.28, 130.02, 129.61, 129.44, 128.24, 128.19, 127.76, 127.62, 127.53, 126.74, 123.90, 121.75, 121.67, 120.49, 118.11, 115.63, 105.99, 35.11, 31.83, 31.76. UV (CH$_2$Cl$_2$): $\lambda_{\max}$ [ε (M^{-1}cm^{-1})] = 753 (2.42 x 10^4), 691 (1.65 x 10^4), 477 (5.93 x 10^4), 403 (7.84 x 10^4), 345 (3.17 x 10^4) nm. HR-ESI-TOF MS: *m/z* = 1142.5619. Calcd for $C_{76}H_{82}N_5O$: 1142.5649 [M]$^+$.

3H

^{1}H NMR (600 MHz, CDCl$_3$, 60 °C): δ = 8.38 (dd, 2H, *J* = 7.8, 2.8 Hz, Ph-*o*-H), 7.80 (d, 2H, *J* = 6.9, Ph-*o*-H), 7.33 (bs, 1H, NH), 7.08 (bs, 1H, NH), 1.43 (d, 54H, *tert*-butyl-H). UV (CH$_2$Cl$_2$): $\lambda_{\max}$ [ε (M^{-1}cm^{-1})] = 785 (6.44 x 10^3), 690 (1.80 x 10^4), 448 (6.39 x 10^4), 414 (6.46 x10^4), 330 (3.41 x 10^4) nm. HR-ESI-TOF MS: *m/z* = 1080.6554. Calcd for $C_{76}H_{80}N_5OZn$: 1080.6514 [M]$^+$

3Ni

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.44 (dd, 2H, J = 7.8, 1.8 Hz, Ph-*o*-H), 8.02 (d, J = 4.8 Hz, 1H, β-H), 7.84 (d, J = 4.6 Hz, 1H, β-H), 7.79 (d, J = 4.6 Hz, 1H, β-H), 7.74 (d, J = 4.6 Hz, 1H, β-H), 7.42 (d, 2H, J = 6.6 Hz, Ph-*o*-H), 7.64 (d, J = 4.8 Hz, 1H, β-H), 7.63 (t, J = 1.8 Hz, 1H, Ar-*p*-H), 7.60-7.57 (m, 5H, Ar-*o*-H & Ar-*p*-H), 7.53–7.49 (m, 5H, Ar-*p*-H & Ph-*o*-H & Ph-*m*-H), 7.46 (t, 2H, J = 7.5 Hz, Ph-*m*-H), 7.44 (d, J = 4.6 Hz, 1H, β-H), 7.37 (d, J = 1.2 Hz, 2H, Ar-*o*-H), 1.41 (s, 18H, *tert*-butyl-H), 1.40 (s, 18H, *tert*-butyl-H), 1.39 (s, 18H, *tert*-butyl-H). UV (CH_2Cl_2): λ_{max} [ε ($M^{-1}cm^{-1}$)] = 767 (1.87 x 10^4), 700 (1.18 x 10^4), 664 (1.04 x 10^4), 480 (5.17 x 10^4), 405 (6.69 x 10^4) nm. HR-ESI-TOF MS: m/z = 1136.5706. Calcd for $C_{76}H_{82}N_5O$: 1136.5711 $[M]^+$.

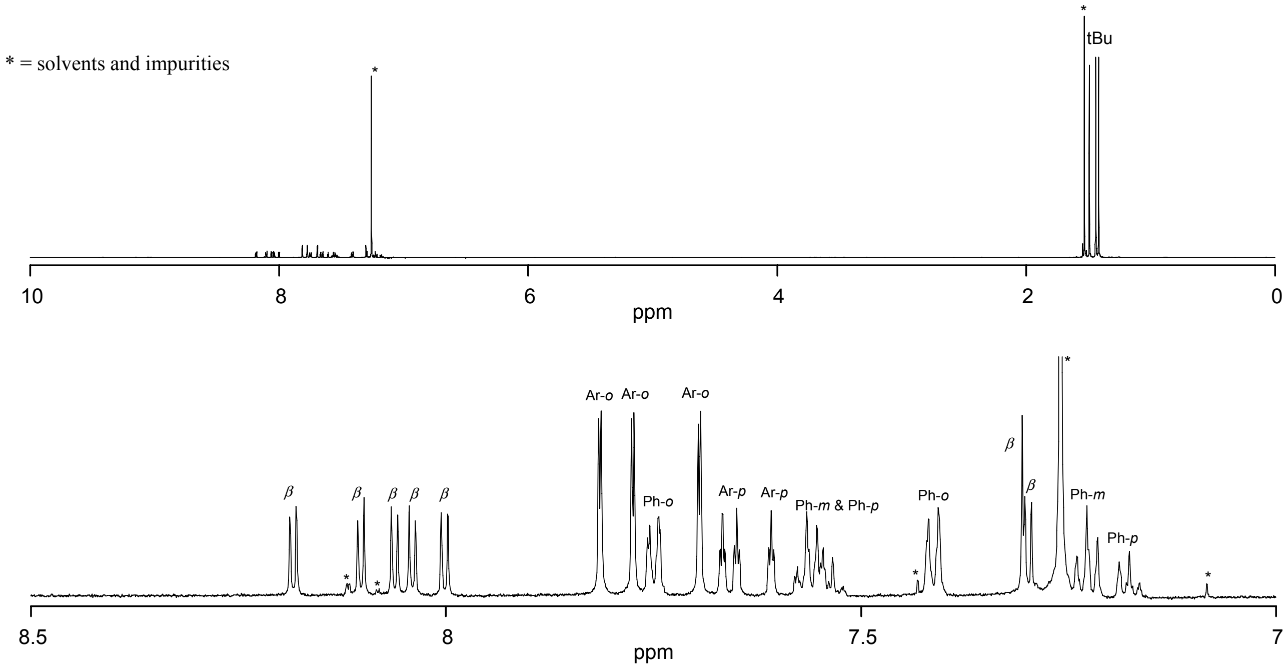


Figure S1. ^{1}H NMR spectrum of **1Zn** in CDCl$_3$.

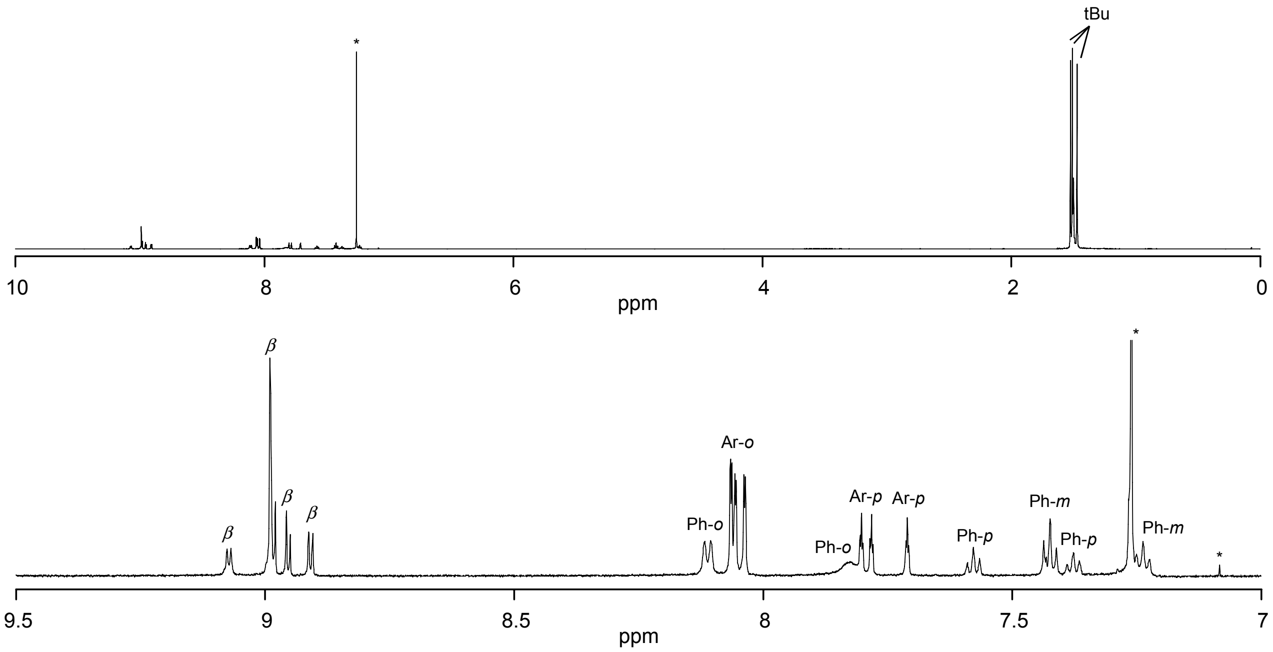


Figure S2. ^{1}H NMR spectrum of **2Zn** in CDCl$_3$.

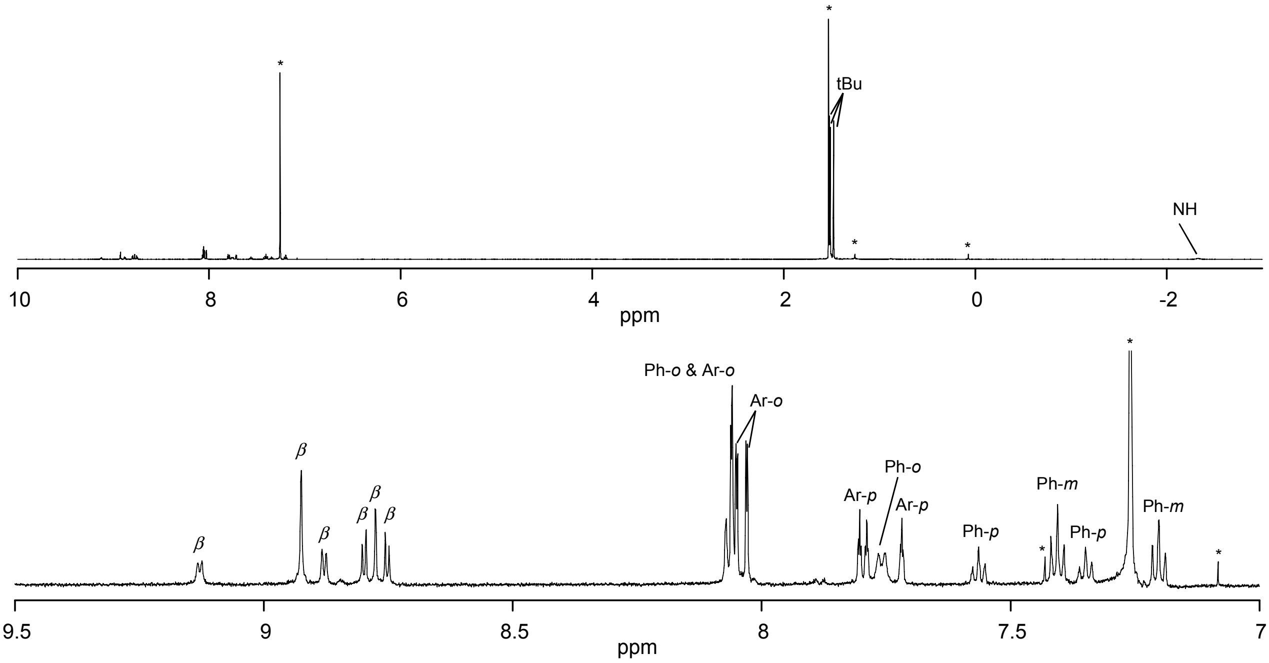


Figure S3. ^{1}H NMR spectrum of **2H** in $CDCl_3$.

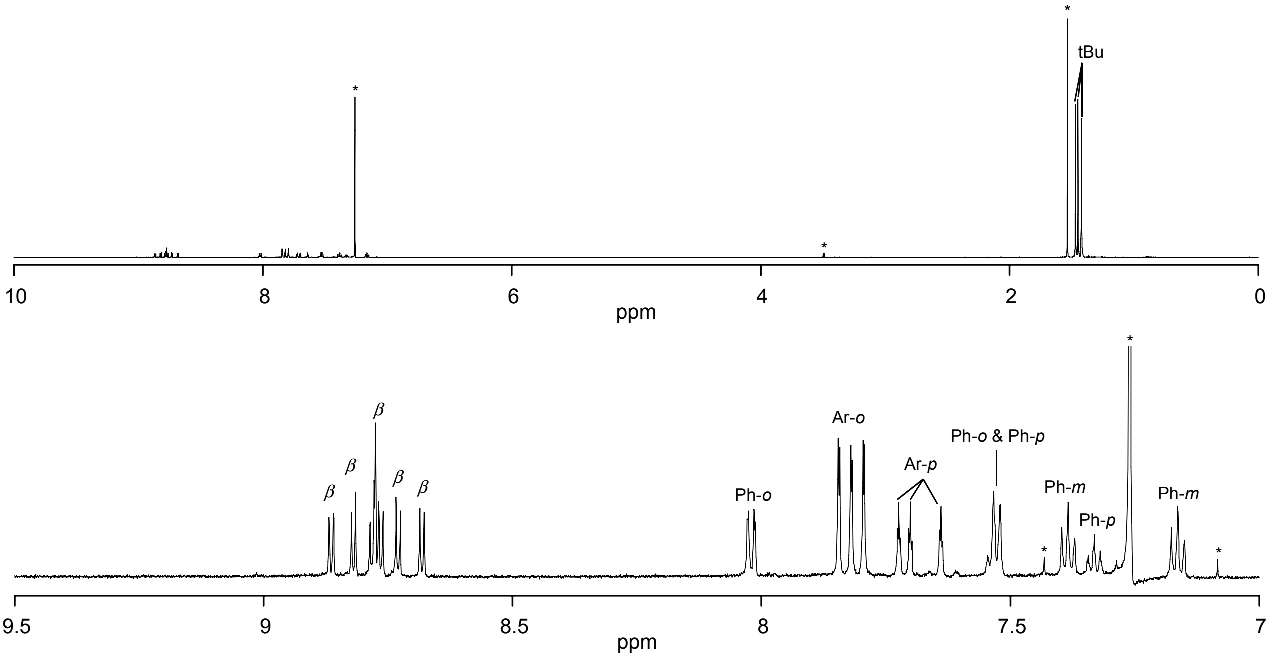


Figure S4. ^{1}H NMR spectrum of **2Ni** in $CDCl_3$.

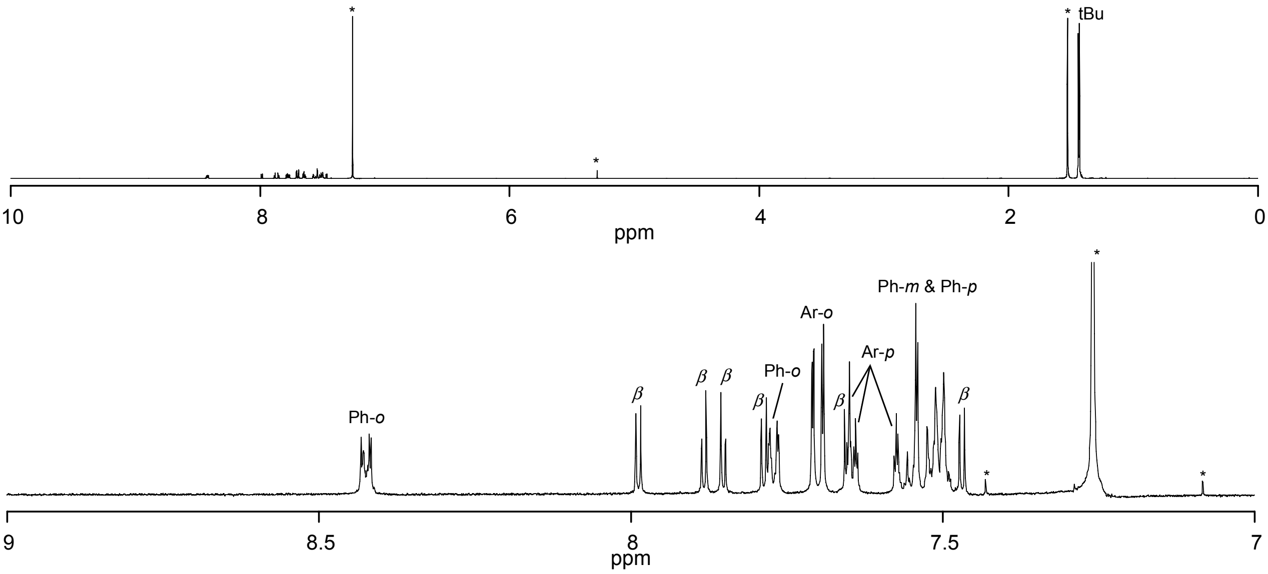


Figure S5. ^{1}H NMR spectrum of **3Zn** in $CDCl_3$.

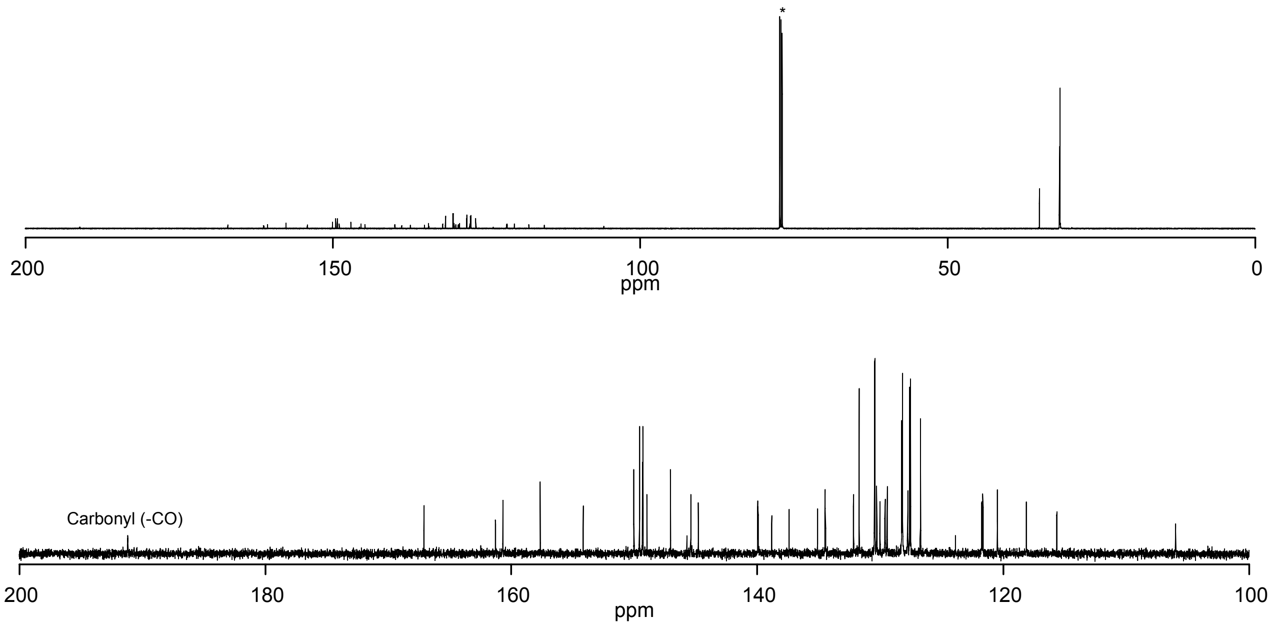


Figure S6. ^{13}C NMR spectrum of **3Zn** in $CDCl_3$.

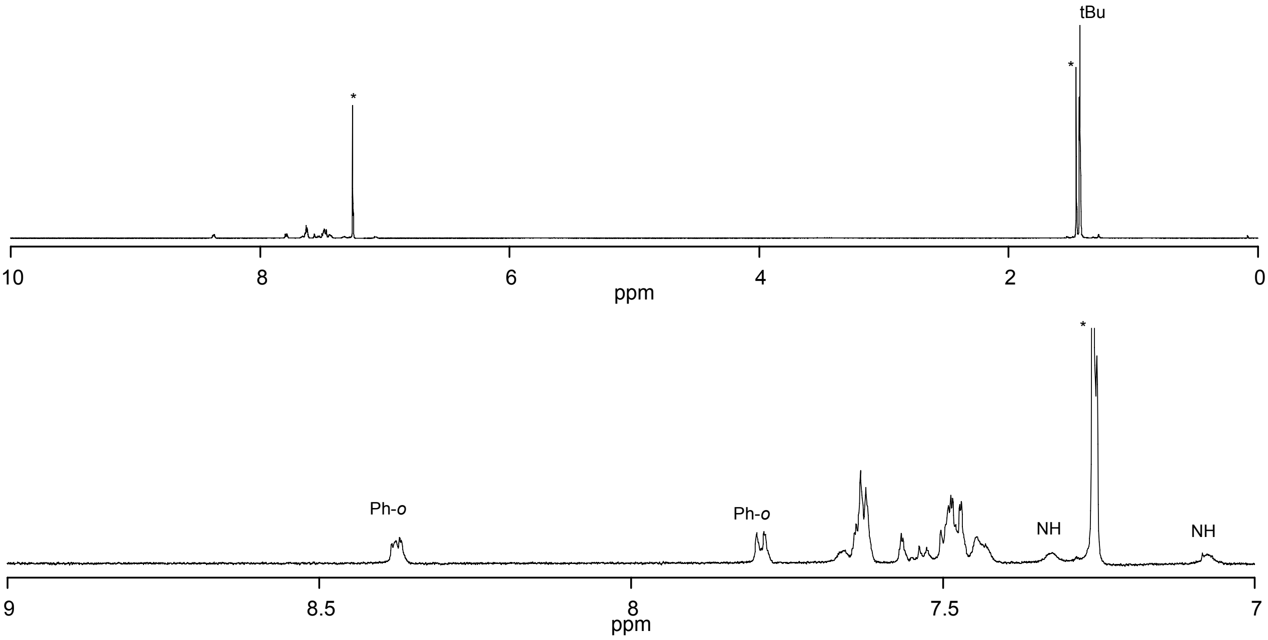


Figure S7. ^{1}H NMR spectrum of **3H** in CDCl$_3$.

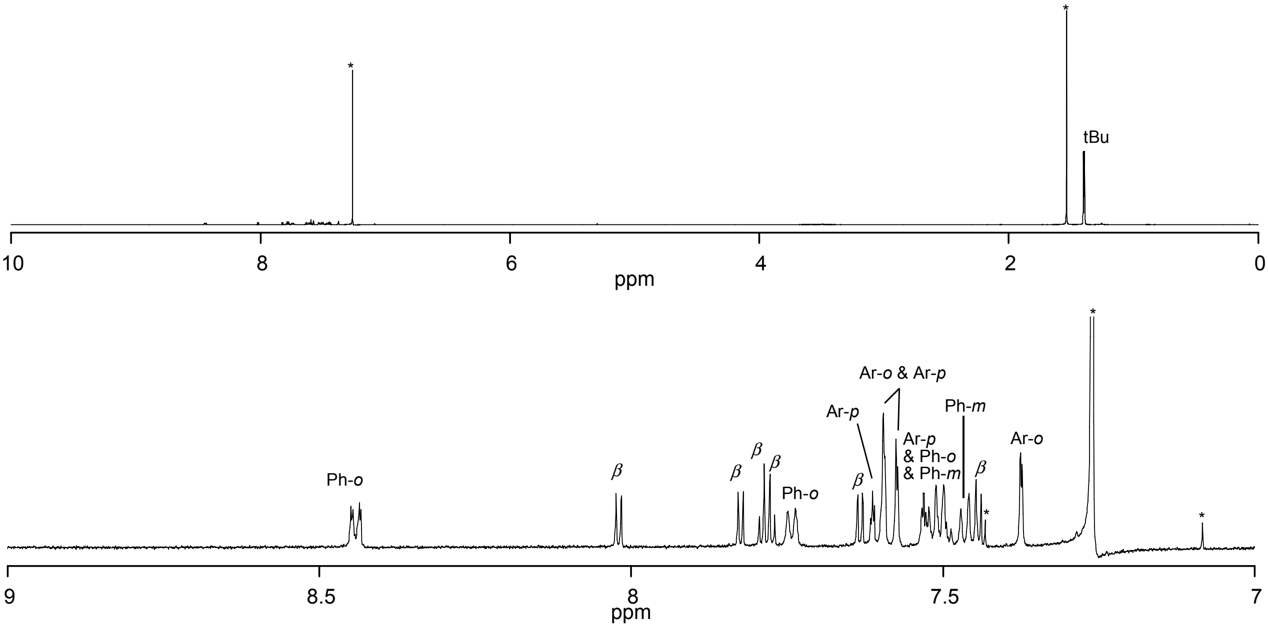


Figure S8. ^{1}H NMR spectrum of **3Ni** in CDCl$_3$.

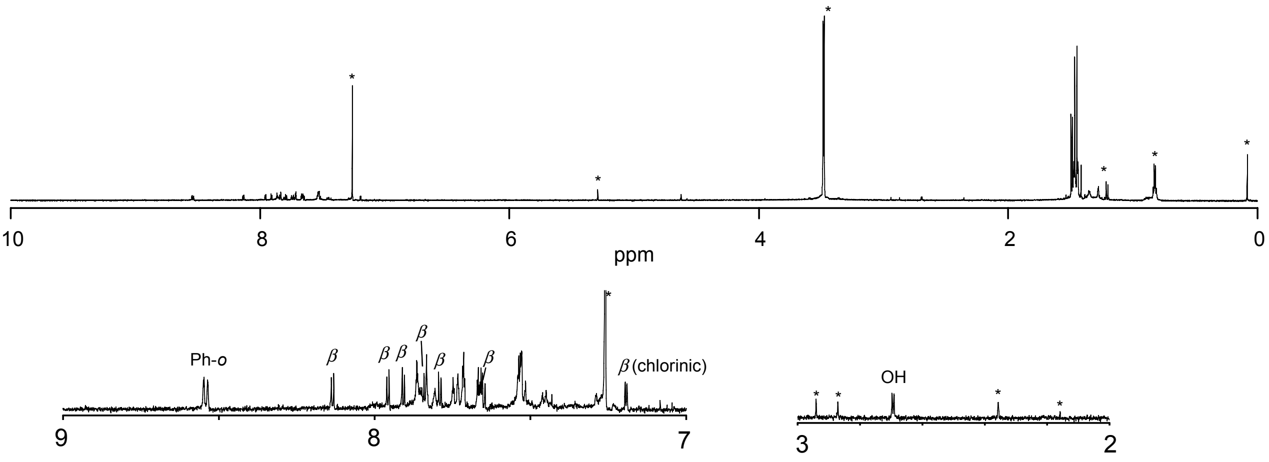


Figure S9. ^{1}H NMR spectrum of **4Zn** in CDCl$_3$.

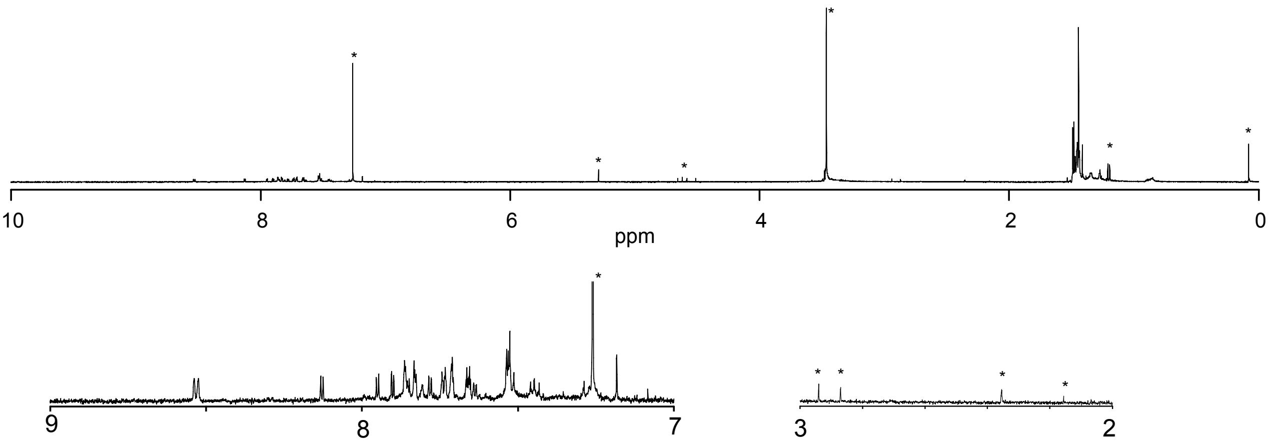


Figure S10. ^{1}H NMR spectrum of **4Zn** in CDCl$_3$ after addition of D$_2$O.

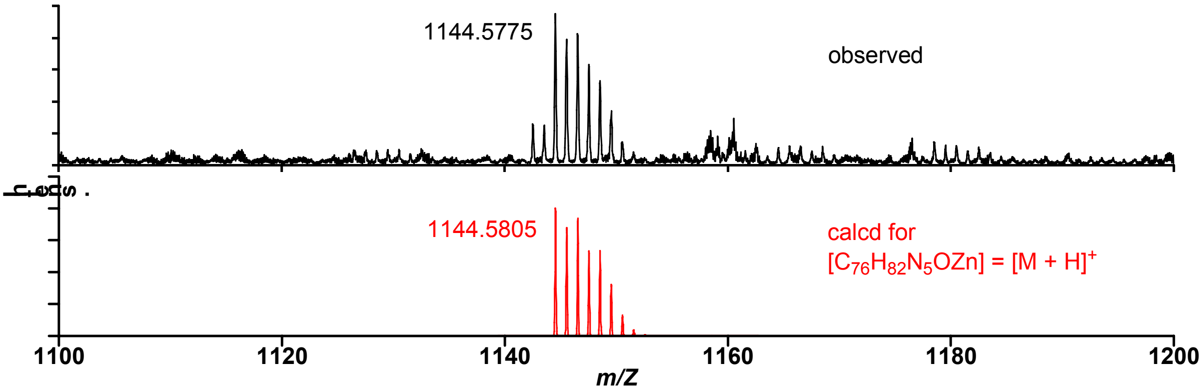


Figure S11. HR-ESI-TOF mass spectra of **4Zn** (positive mode).

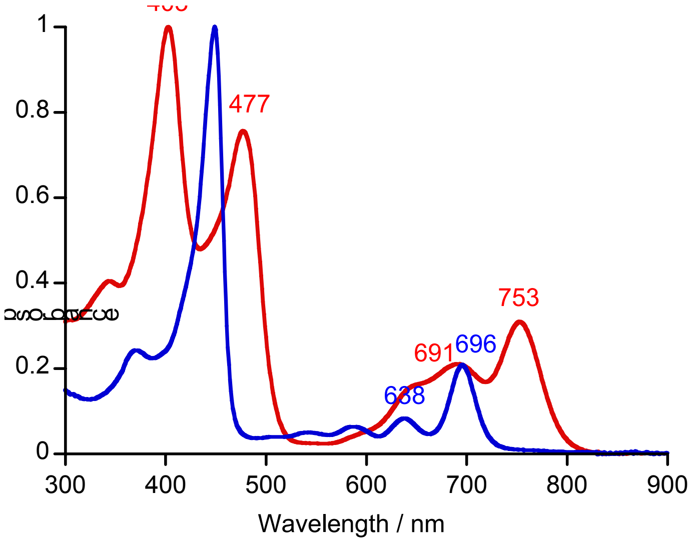
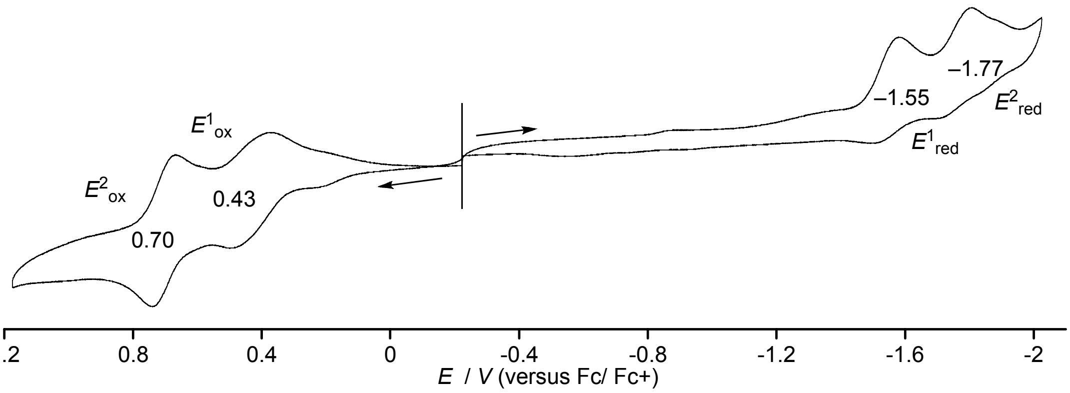
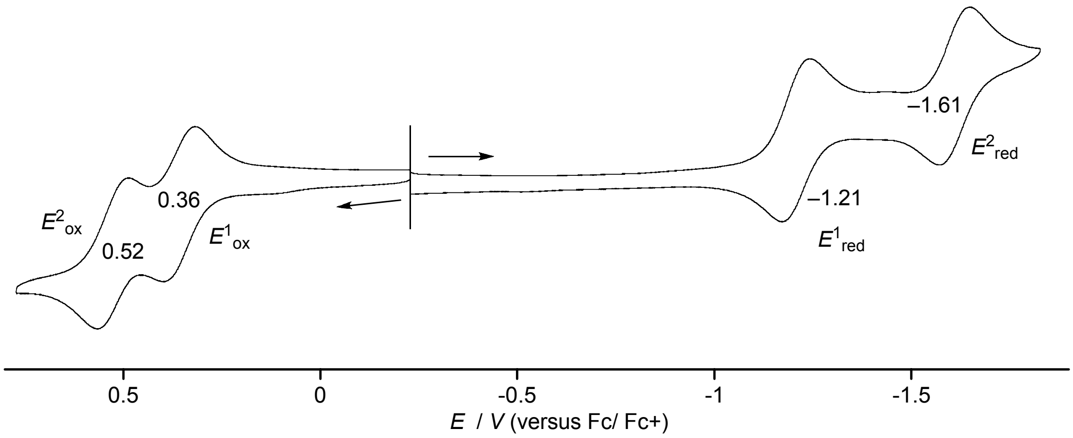


Figure S12. UV-vis absorption spectra of **3Zn** (red) and **4Zn** (blue) in $CDCl_3$.

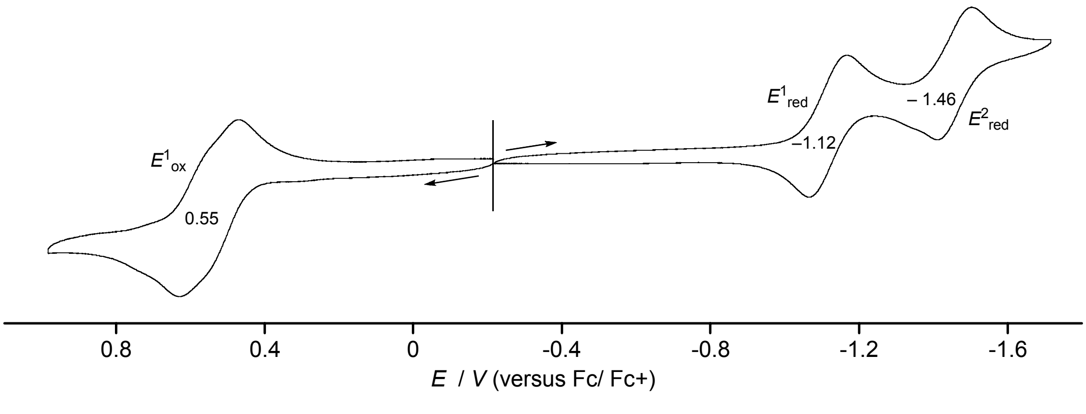
(a)


E^1_{ox}
E^2_{ox}
0.43
0.70
−1.77
−1.55
E^2_{red}
E^1_{red}
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
-2
E / V (versus Fc/ Fc+)

(b)


−1.61
E^2_{red}
0.36
E^2_{ox}
E^1_{ox}
0.52
−1.21
E^1_{red}
0.5
0
-0.5
-1
-1.5
E / V (versus Fc/ Fc+)

(c)


E^1_{red}
− 1.46
E^2_{red}
E^1_{ox}
−1.12
0.55
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
E / V (versus Fc/ Fc+)

(d)

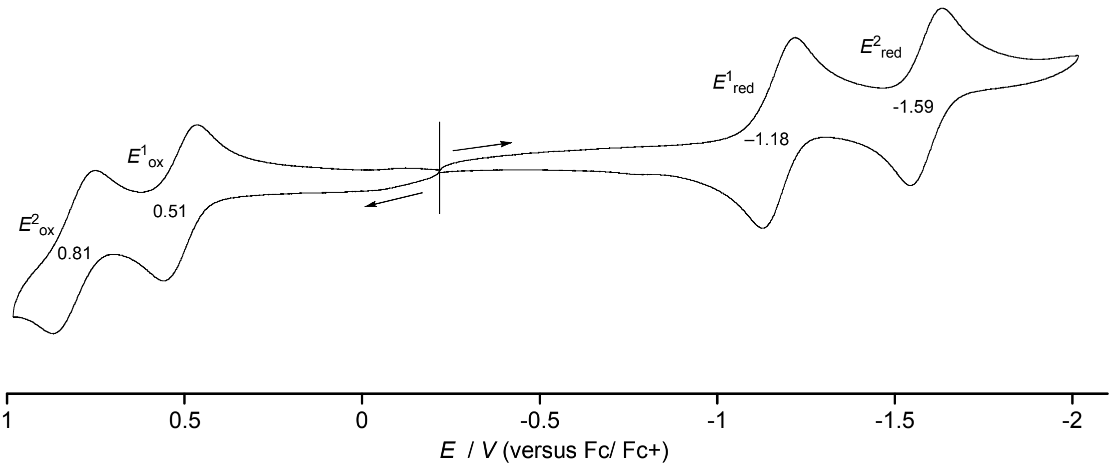


Figure S13. Cyclic voltammograms of (a) **2Zn**, (b) **3Zn**, (c) **3H**, (d) **3Ni**. All spectra were measured in CH_2Cl_2 solution with Bu_4NPF_6 as an electrolyte.

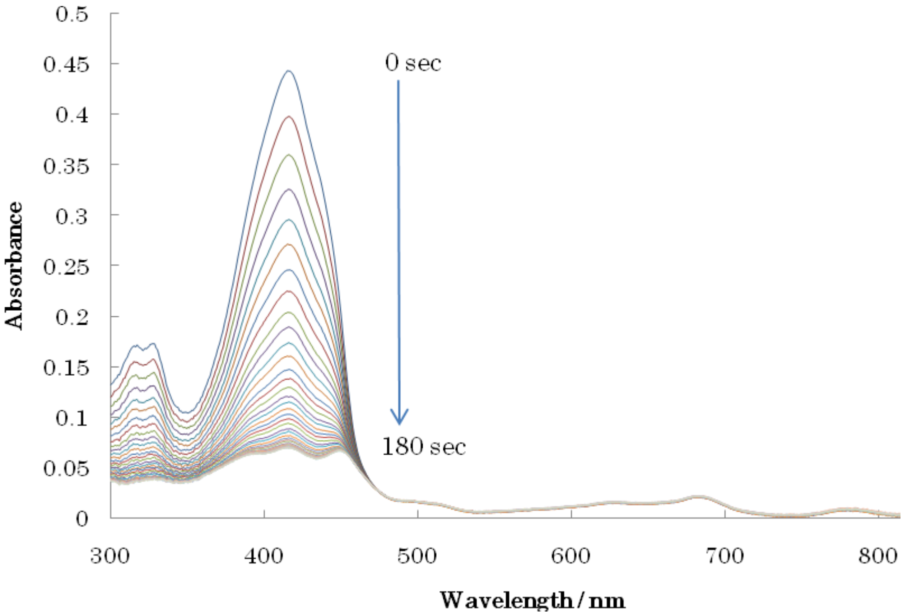


Figure S14. Time evolution of the UV-Vis spectrum of a DPBF (20 μM) and **3H** (1 μM) toluene solution.

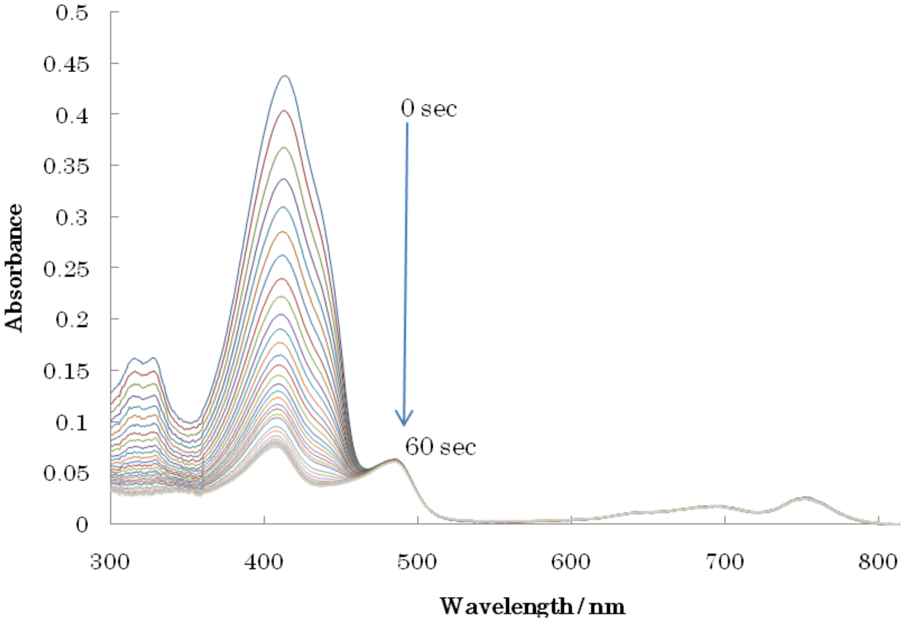


Figure S15. Time evolution of the UV-Vis spectrum of a DPBF (20 μM) and **3Zn** (1 μM) toluene solution.

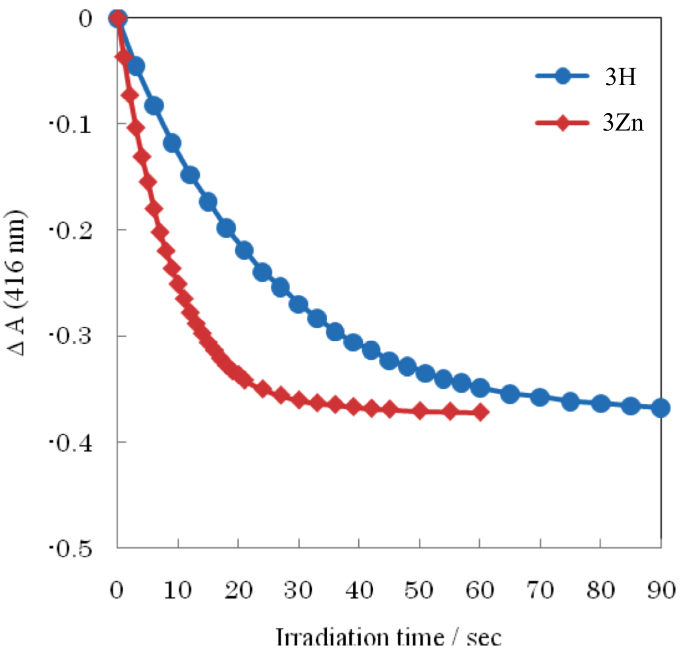


Figure S16. Plots of the absorbance changes at 416 nm against photoirradiation time.

X-ray Crystallographic Data for 3

Method for X-ray analysis: Crystallographic data for **3** are summarized in the footnote in the manuscript. All single crystals of **3** were obtained by vapor diffusion of methanol into a dichloroethane solution. All data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71075 Å), and structures were solved by direct method(SHELXS-97). For crystal structure **3Zn**: the 3,5-di-*tert*-butylphenyl groups were dynamically disordered. In order to solve these problems, some bonds dealing with this moiety were restrained by means of the DFIX instruction and the anisotropic refinement of the disordered parts restrained by means of ISOR and SIMU instructions. Disorder features of one phenyl group were solved by a split model and employing ISOR and SIMU instructions. Dynamic disorder behavior was found for two methanol molecules and then solved by using ISOR instructions. These restraints do not affect GOF value so much. For crystal structure **3H**: though some electron density was properly assigned as a molecule of methanol, other electron density due to severely disordered solvents still remained. All attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to this solvent molecule were removed by use of the utility SQUEEZE in PLATON software packate, SQUEEZE-PLATON.[2] For crystal structure **3Ni**: dynamic disorder problems in two 3,5-di-*tert*-butyl groups and a solvent molecule of dichloroethane were fixed by means of DFIX, SIMU and ISOR instructions. Dynamic disorder problems have been also found in the two phenyl groups and solved by means of SIMU and ISOR instructions.

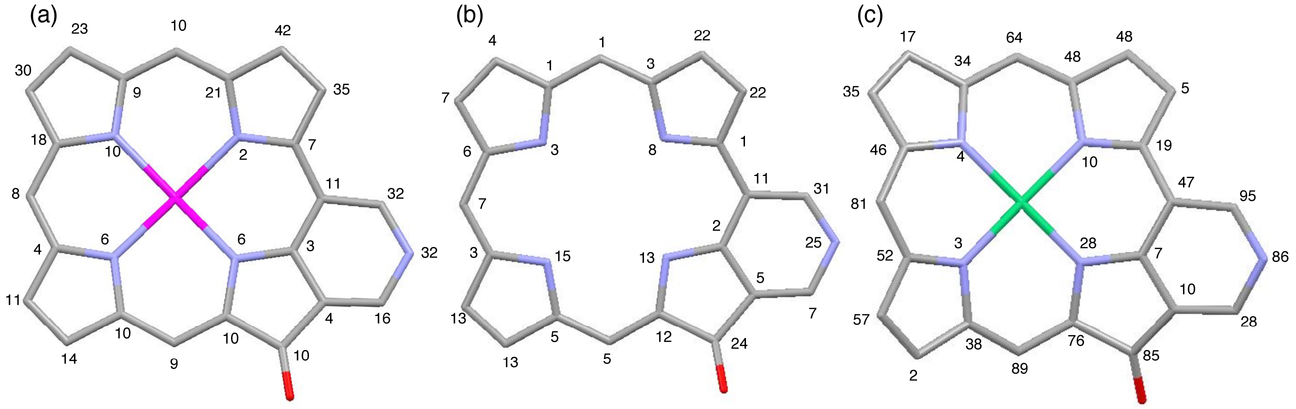


Figure S17. Deviations in units of 0.01 Å from the plane defined by the 27 core atoms in a) **3Zn**, b) **3H** and c) **3Ni**.

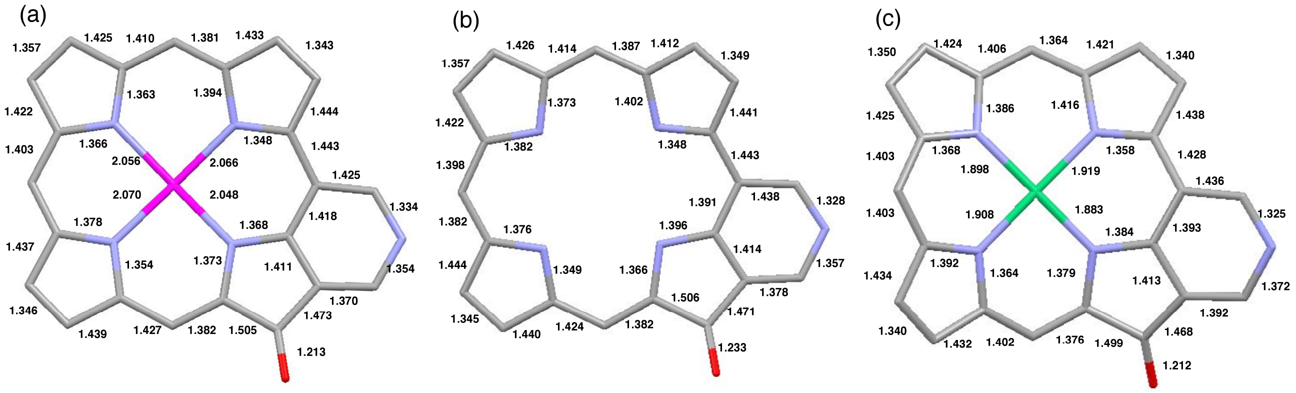


Figure S18. Bond-length alternation (in Å) in the porphyrin cores and pyridine moieties of a) **3Zn**, b) **3H** and c) **3Ni**.

References

1 A. K. Sahoo, S. Mori, H. Shinokubo and A. Osuka, *Angew. Chem. Int. Ed.*, 2006, **45**, 7972.

2 (a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2005. (b) P. V. D. Sluis, A. L. Spek, *Acta Crystallogr. A,* 1990, **46**, 194.