Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ni^{II} Tetrahydronorcorroles: Antiaromatic Porphyrinoids with Saturated Pyrrole Units

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Table of Contents

Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. Chemical shifts were reported as the delta scale in ppm relative to $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. Mass spectra were recorded on a Bruker microTOF using ESI-TOF method for acetonitrile solutions. X-ray diffraction data of **6** was collected using synchrotron radiation (λ = 0.8000 Å) at the BL38B1 in the SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal No. 2015B1397). The oscillation angle and camera distance were 1° and 75 mm, respectively. The exposure time per frame was 1s. Two data sets consisted of 180 frames were integrated, merged, and scaled with the programs HKL2000.[1] The structure was solved with Superflip program[2] and refined by least-squares calculations on F^2 for all reflections with SHELXL[3] program on the crystallographic software packages CrystalStructure.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 612C. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Ni(II) norcorroles **1** and **5** were prepared according to the literature method.[5]

General Procedure

Hydrogenation of Ni(II) norcorrole 1

A Schlenk flask containing Ni(II) dimesitylnorcorrole **1** (50.0 mg, 86.6 μmol), *p*-tosylhydrazide (630 mg, 3.38 mmol), and zinc powder (60.0 mg, 0.918 mmol) was filled with N_2 and dry THF (21 mL) was added. The solution was stirred at 80 °C for 7 h. After cooling down, the resulting mixture was passed through a short pad of silica-gel with THF/hexane to eliminate excess *p*-tosylhydrazide and then the solution was concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane CH_2Cl_2 as eluent) to afford tetrahydronorcorrole **4** (10.1 mg, 17.3 μmol, 20%). The yields of compounds **3** (73%) and **4** (20%) were estimated on the basis of the ^{1}H NMR spectrum of the crude material after the short column chromatography.

Hydrogenation of Ni(II) cyanonorcorrole 5

A Schlenk flask containing Ni(II) dimesitylcyanonorcorrole **5** (10.8 mg, 17.9 mmol), *p*-tosylhydrazide (150 mg, 80.5 mmol), and zinc powder (20.2 mg, 0.309 mmol) was filled with N_2 and dry THF (7.0 mL) was added. The solution was stirred at 80 °C for 8 h. After cooling down, the resulting mixture was passed through a short pad of silica-gel with THF/hexane to eliminate excess *p*-tosylhydrazide and the solution concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane CH_2Cl_2 as eluent) to afford tetrahydrocyanonorcorrole **6** (7.82 mg, 12.9 μmol, 72%).

Compound Data

Ni(II) Dihydronorcorrole 3

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.58 (s, 2H, Mes), 6.56 (s, 2H, Mes), 4.05 (d, J = 3.9 Hz, 1H, β-CH), 3.92 (d, J = 5.1 Hz, 1H, β-CH), 3.85-3.84 (m, 2H, β-CH), 3.29 (d, J = 3.9 Hz, 1H, β-CH), 2.95 (d, J = 3.6 Hz, 1H, β-CH), 2.55 (s, 6H, *ortho*-Me), 2.48 (s, 6H, *ortho*-Me), 2.05 (s, 3H, *para*-Me), 2.05 (s, 3H, *para*-Me), 0.81 (m, 2H, β-CH_2), 0.54 (m, 2H, β-CH_2) ppm.

Ni(II) Tetrahydronorcorrole 4

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.77 (s, 4H, Mes), 5.49 (d, J = 4.0 Hz, 2H, β-CH), 4.39 (d, J = 4.0 Hz, 2H, β-CH), 2.32 (s, 12H, *ortho*-Me), 2.20 (s, 6H, *para*-Me), 2.00 (m, 4H, β-CH_2), 1.63 (m, 4H, β-CH_2) ppm.

^{13}C NMR (500 MHz, $CDCl_3$): δ = 175.8, 148.7, 142.7, 138.2, 136.7, 136.4, 131.9, 128.1, 120.8, 116.8, 112.9, 28.4, 27.0, 21.0, 19.3 ppm.

UV/vis (CH_2Cl_2) ε ($cm^{-1}M^{-1}$): 335(21000), 370(26000), 389(30000), 489(4900), 642(1200) nm.

HR-MS (ESI-MS): m/z = 580.2117, calcd for $(C_{36}H_{34}N_4Ni)^+$ = 580.2131 $[(M + H)^+]$.

Ni(II) Tetrahydrocyanonorcorrole 6

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.84 (s, 2H, Mes), 6.81 (s, 2H, Mes), 5.93 (s, 1H, β-CH), 5.70 (d, J = 4.0 Hz, 1H, β-CH), 4.64 (d, J = 4.0 Hz, 1H, β-CH), 2.31 (s, 6H, *ortho*-Me), 2.29 (s, 6H, *ortho*-Me), 2.24 (s, 3H, *para*-Me), 2.23 (s, 3H, *para*-Me), 2.23 (m, 4H, β-CH_2), 1.86 (m, 4H, β-CH_2) ppm.

^{13}C NMR (500 MHz, $CDCl_3$): δ = 177.9, 177.78, 148.65, 147.8, 144.9, 141.8, 138.3, 138.0, 137.7, 137.2, 137.1, 136.4, 131.4, 130.2, 128.5, 128.4, 124.8, 121.8, 120.6, 115.4, 115.0, 114.2, 93.4, 29.8, 28.6, 27.7, 27.1, 21.3, 21.2, 19.6, 19.5 ppm.

UV/vis (CH_2Cl_2) ε (cm^{-1}M^{-1}): 375(10000), 392(12000), 485(1300) nm.

HR-MS (ESI-MS): m/z = 628.1981, calcd for $(C_{37}H_{33}N_5Ni)^+$ = 628.1982 $[(M + Na)^+]$.

Single crystals were obtained by vapor diffusion of acetonitrile into a dichloromethane solution. $C_{37}H_{33}N_5Ni$, M_w = 605.21, monoclinic, $P2_1/a$, a = 7.08430(10) Å, b = 25.1223(2) Å, c = 8.23270(10) Å, β =103.8436°, V = 1422.65(3) Å^3, Z = 2, R_1 = 0.0589 ($I > 2.0\ \sigma(I)$), R_w = 0.1381 (all data), GOF = 1.146.

* = solvents and impurities

NMR Spectra of Compounds

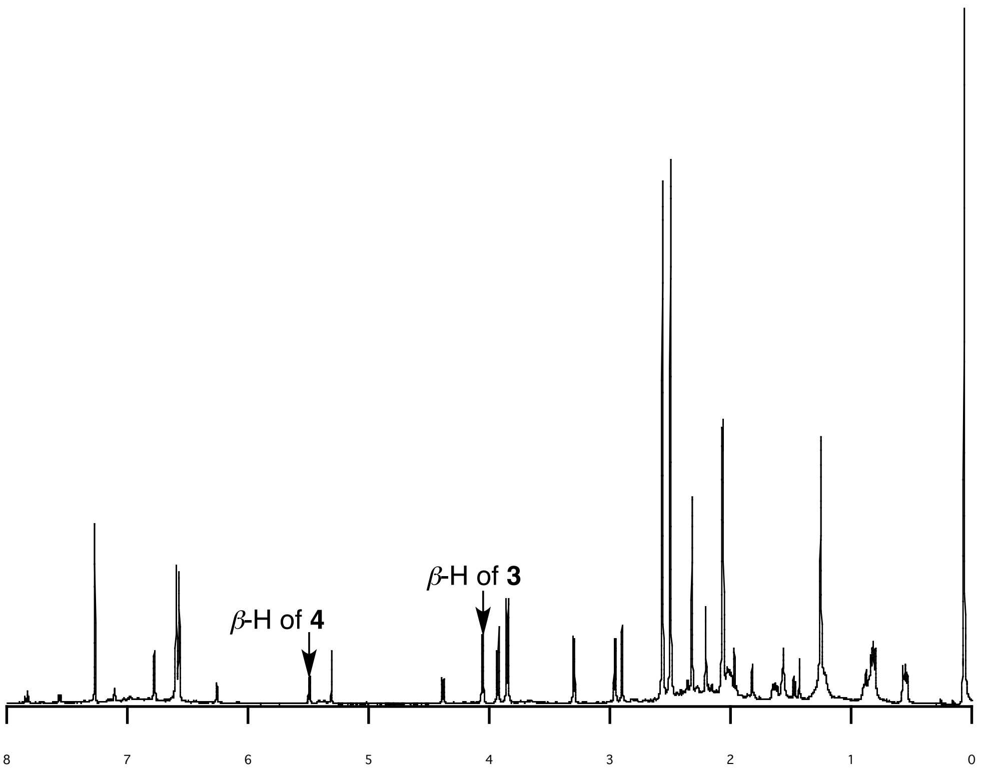


Figure S1. ^{1}H NMR spectrum of the crude product mixture containing **3** and **4** in $CDCl_3$.

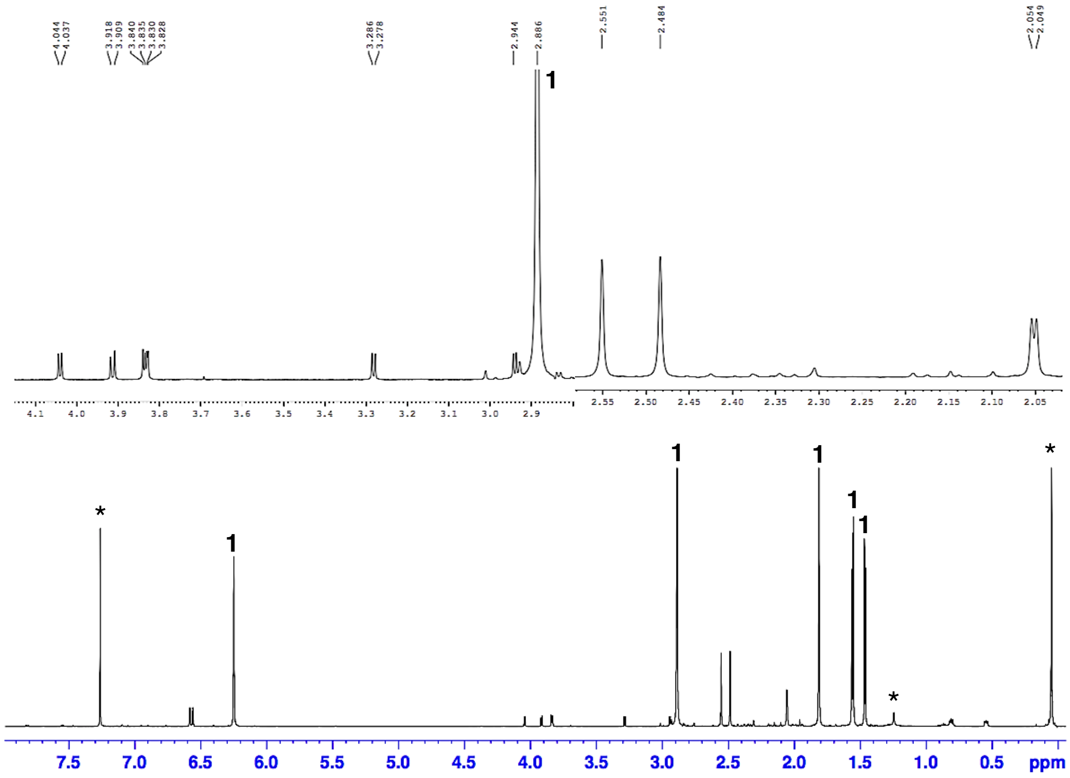


Figure S2. ^{1}H NMR spectrum of the crude product mixture containing **1** and **3** in $CDCl_3$.

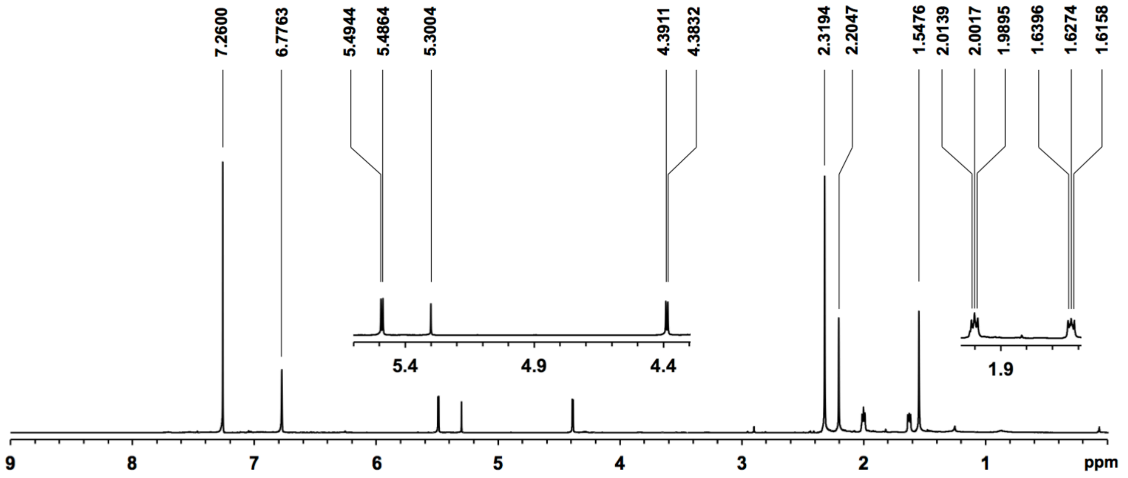


Figure S3. ^{1}H NMR spectrum of **4** in CDCl$_3$.

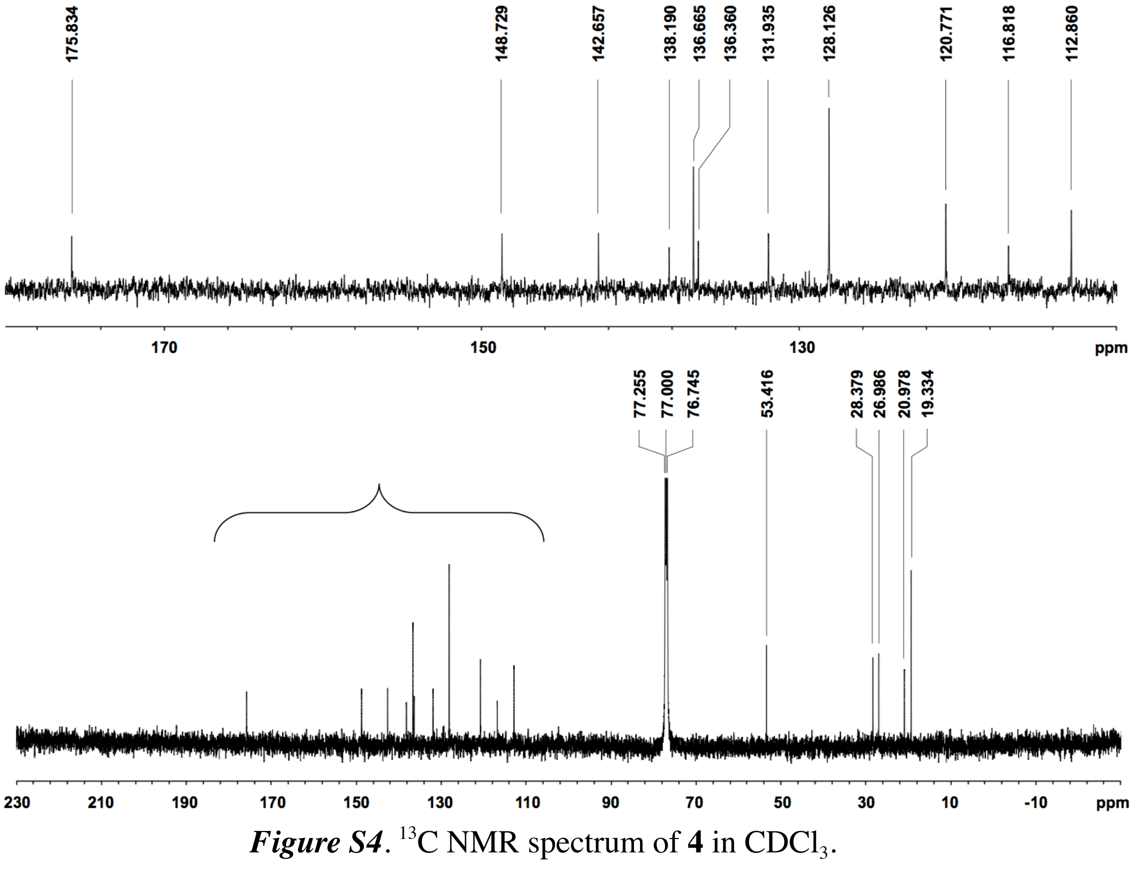


Figure S4. ^{13}C NMR spectrum of **4** in CDCl$_3$.

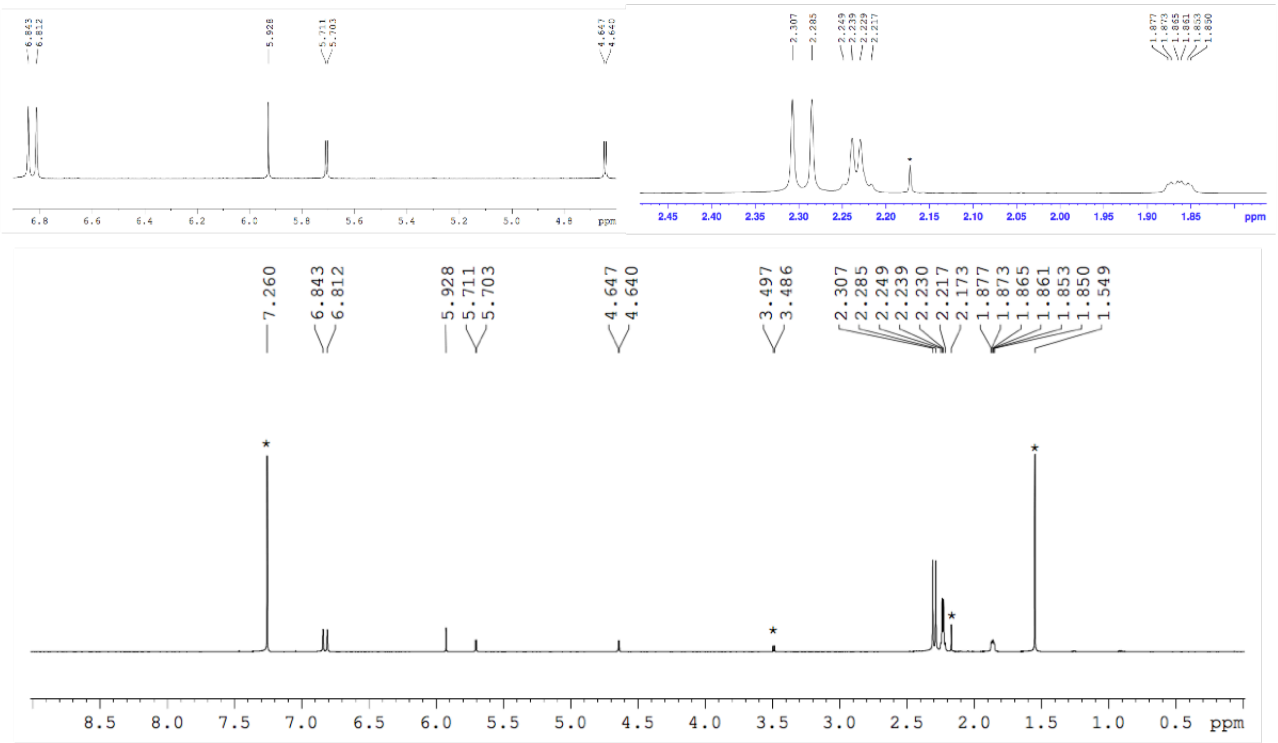


Figure S5. ^{1}H NMR spectrum of **6** in $CDCl_3$.

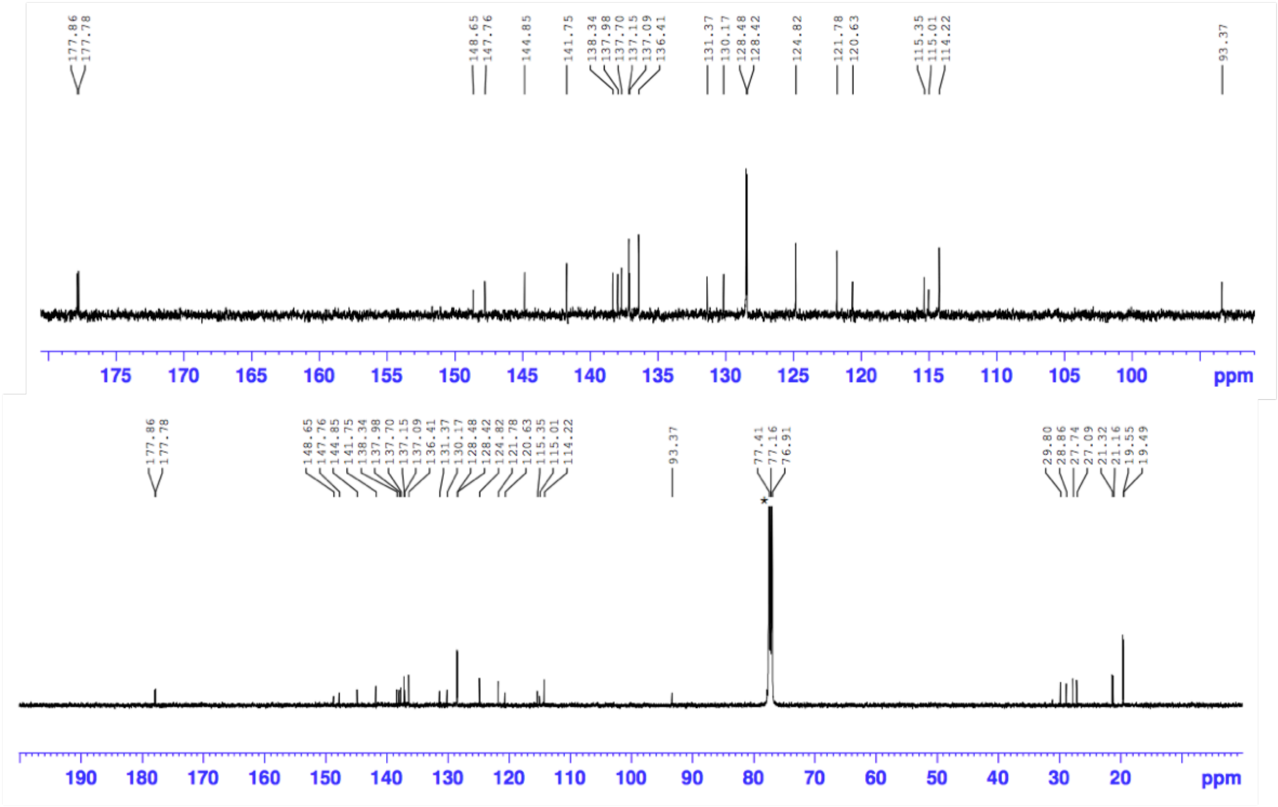


Figure S6. ^{13}C NMR spectrum of **6** in $CDCl_3$.

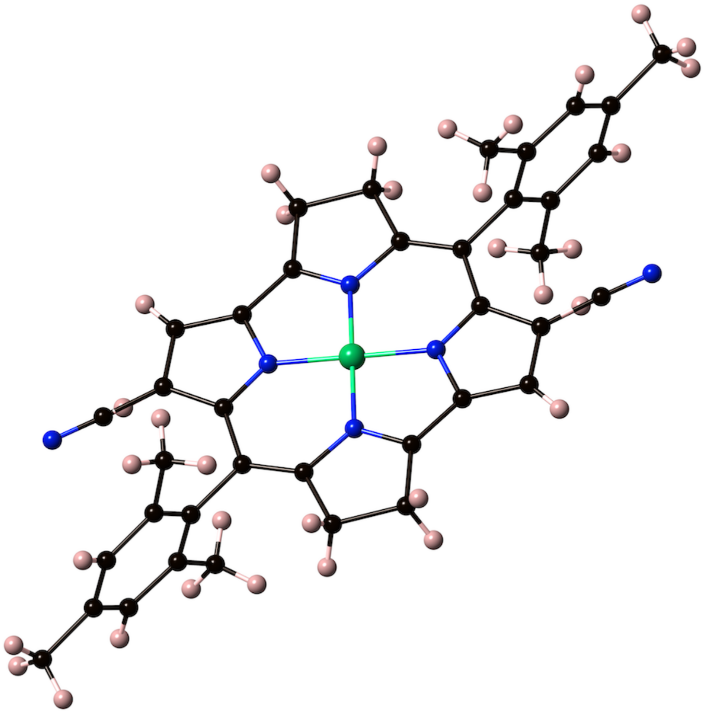


Figure S7. X-ray crystal structure of **6**. The cyano group is disordered in the two orientations (50:50). The central Ni site is lying on a crystallographic inversion center.

Cyclic Voltammetry

Cyclic voltammograms of **1**, **4**, **5** and **6** were recorded on ALS electrochemical analyzer 612C. Measurements were performed in freshly distilled dichloromethane with tetrabutylammonium hexafluorophosphate as electrolyte. A three-electrode system was used and consisted of a grassy carbon working electrode, a platinum wire and Ag/$AgClO_4$ as the reference electrode. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

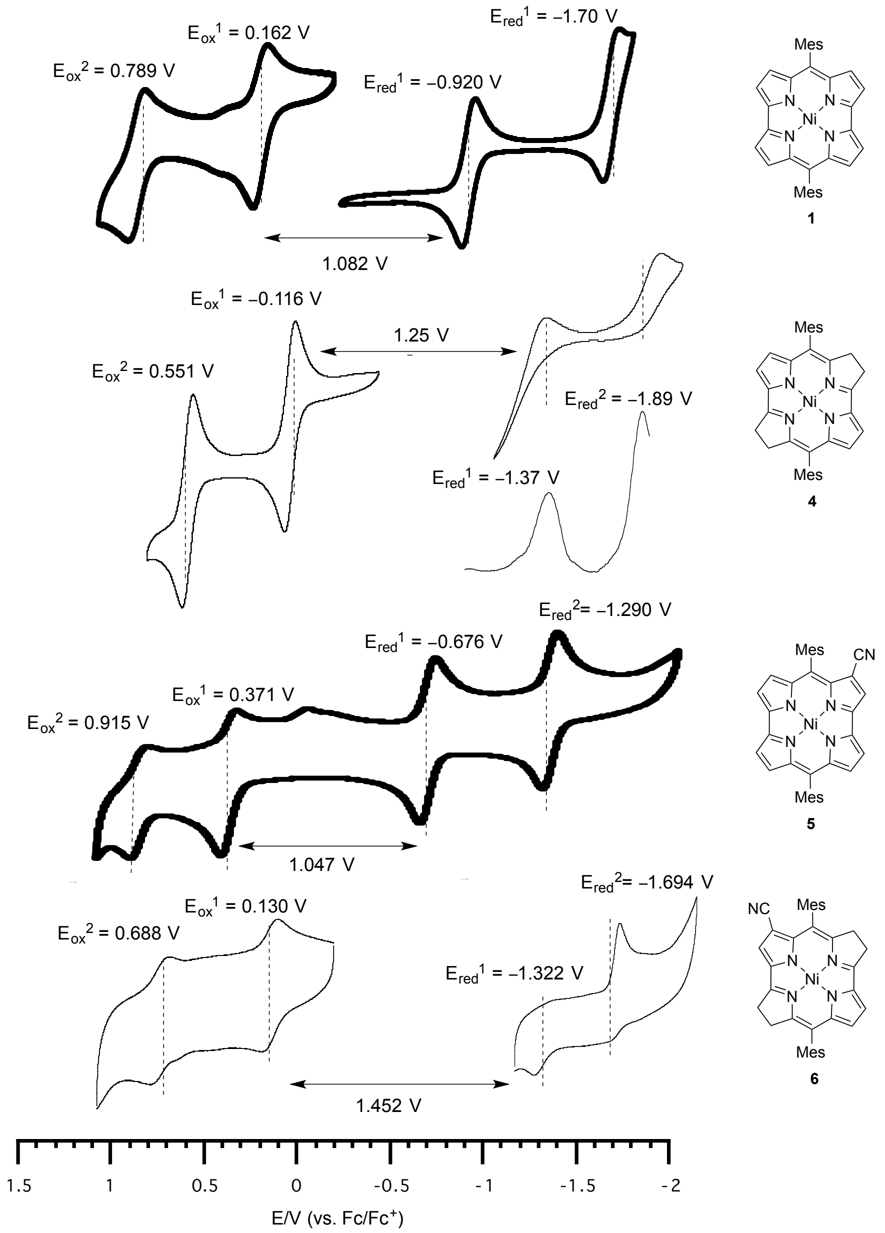
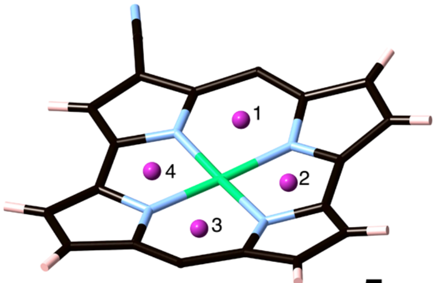


Figure S8. Cyclicvoltammograms (0.1 V•s^{-1}) of **1**, **4**, **5** and **6** in CH_2Cl_2 (0.1 M $TBAPF_6$). Working electrode: grass carbon, counter electrode: Pt, reference electrode: Ag/$AgClO_4$.

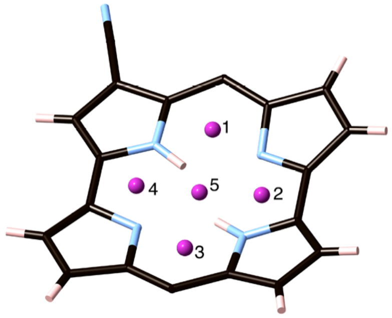
Theoretical calculations

All calculations were carried out using the *Gaussian 09* program.[6] Geometries of **5** and **6** for NICS and ACID calculations were obtained from their X-ray structures. All calculations were performed with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)[7] and a basis set consisting of SDD[8] for Ni and 6-31G(d) for the rest (denoted as 631SDD).



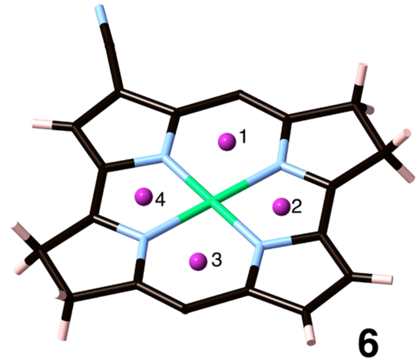
5

1	NICS(0)	+35.6 ppm
2	NICS(0)	+38.5 ppm
3	NICS(0)	+37.3 ppm
4	NICS(0)	+35.3 ppm



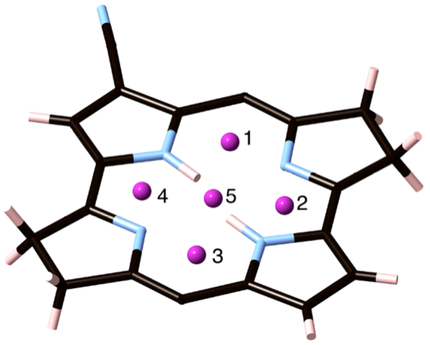
1	NICS(0)	+27.9 ppm
2	NICS(0)	+28.5 ppm
3	NICS(0)	+28.3 ppm
4	NICS(0)	+27.3 ppm
5	NICS(0)	+22.4 ppm

Figure S9. NICS values of Ni(II) cyanonorcorrole **5** and its free-base.



6

1	NICS(0)	+11.0 ppm
2	NICS(0)	+13.3 ppm
3	NICS(0)	+11.5 ppm
4	NICS(0)	+11.9 ppm



1	NICS(0)	+15.1 ppm
2	NICS(0)	+15.9 ppm
3	NICS(0)	+15.6 ppm
4	NICS(0)	+15.8 ppm
5	NICS(0)	+12.0 ppm

Figure S10. NICS values of Ni(II) cyanotetrahydronorcorrole **6** and its free-base.

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