Unusual Conformational Preference of an Aromatic Secondary Urea: Solvent-dependent Open-Closed Conformational Switching of *N,N'*-Bis(porphyrinyl)urea

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Supporting Information **page**

1. Experimental

1.1. General

All reagents were purchased from Sigma-Aldrich Chemical Co., Wako pure Chemical Industries, Tokyo Kasei Kogyo Co., or Kanto Kagaku Co., Inc. Silica Gel 60 N (spherical, neutral) for column chromatography was purchased from Kanto Kagaku Co., Inc.

^{1}H NMR spectra were recorded on JEOL JNM-AL 400 spectrometer or Bruker Avance 600 spectrometer. The chemical shifts of ^{1}H are reported in ppm relative to the solvent residual peak in $CDCl_3$ (δ 7.26) or THF-d_8 (1.73) for ^{1}H NMR. For the ^{13}C NMR spectra, the solvent signals of $CDCl_3$ (δ 77.0) were used as the internal standards. Mass spectra were recorded on Bruker Daltonics microTOF-2focus spectrometer or APEX III spectrometer in the positive and negative ion detection modes.

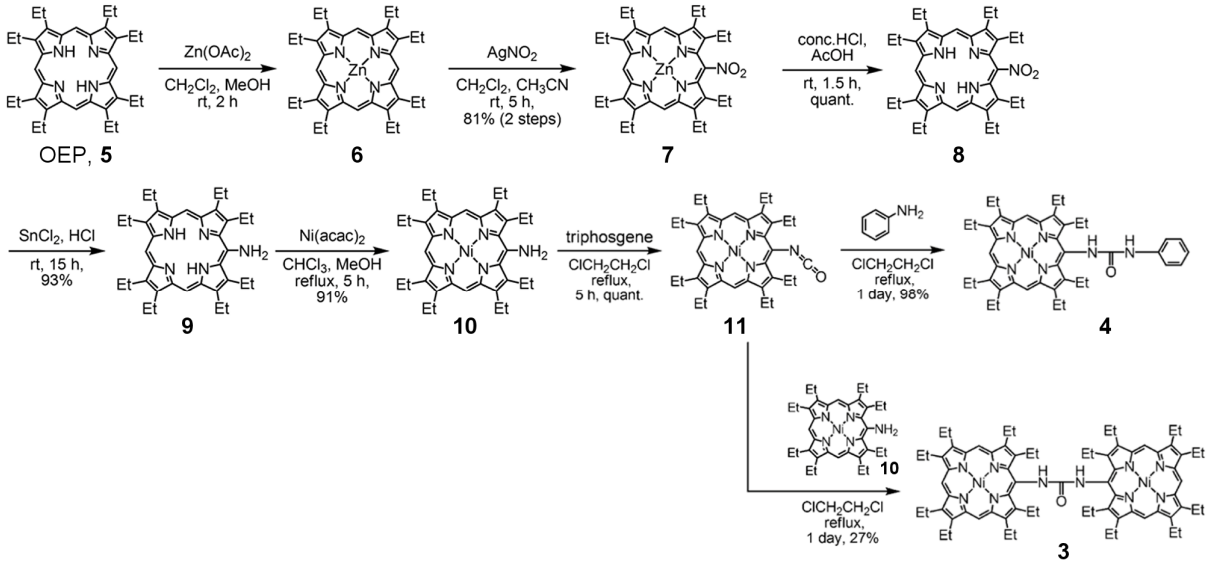
Crystallographic data were collected on a CCD detector with monocromated Mo Kα (λ = 0.71073 Å). The crystal structures were solved by direct methods SHELXS-97 or SIR2004 and refined by full-matrix least-squares SHELXL-97*. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included as their calculated positions.

The electronic absorption spectra were recorded with a JASCO V650 spectrometer. Cyclic voltammetry measurements were carried out with Hokuto Denko HZ-3000 voltammetric analyzer. A glassy carbon disc, a platinum wire, and Ag/AgCl electrodes were used as the working, counter, and reference electrodes, respectively. A 0.1 M solution of n-Bu_4NClO_4 (TBAP) in CH_2Cl_2 containing 0.2 mM sample was purged with Ar for a few minutes, and then voltammograms were recorded at ambient temperature.

* A short history of SHELX. Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.

1.2. Synthesis of porphyrinylureas

Scheme S1 Synthetic scheme for compounds 3 and 4



Synthesis of zinc (II) 2,3,7,8,12,13,17,18-octaethylporphyrin (6)

A solution of zinc(II) acetate (366 mg, 2.65 mmol) in methanol (10 ml) was added to a solution of 2,3,7,8,12,13,17,18-octaethylporphyrin (**5**, 403 mg, 0.753 mmol) in methylene chloride (400 ml), and .the mixture was stirred at room temperature for 1 h. After concentration, the residue was used for the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 4 H), 4.13 (q, 16 H, J = 7.8 Hz), 1.94 (t, 24 H, J = 7.8 Hz).

Synthesis of zinc (II) 2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrin (7)

This compound was synthesized according to the procedure reported by Crossley *et al.*[S1] A solution of silver nitrite (146 mg, 0.956 mmol) in acetonitrile (45 ml) was added slowly to a suspension of the zinc (II) 2,3,7,8,12,13,17,18-octaethylporphyrin (**6**, 636 mg) and iodine (136 mg) in dichloromethane (620 ml) and acetonitrile (280 ml) under Ar atmosphere was over 5 h. The mixture was filtered over celite, and the filterate was concentrated. The residue was purified by silica gel column chromatography (50% chloroform/*n*-hexane) to give zinc (II) 2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrin (**7**, 393 mg, 81%) as red purple solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 2 H), 9.40 (s, 1 H), 4.01 (q, 4 H, J = 7.8 Hz), 3.96 (m,

8 H), 3.78 (q, 4 H, J = 7.3 Hz), 1.93 (t, 6 H, J = 7.8 Hz), 1.85 (m, 12 H), 1.73 (t, 6H, J = 7.3 Hz).

Synthesis of 2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrin (8)

Concentrated hydrochloric acid (110 ml) was added to a solution of zinc(II) 2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrin (**7**, 393 mg, 0.611 mmol) in acetic acid (200 ml) at room temperature. After 3 h, water was added, and extracted with chloroform. The organic layer was washed successively with water, saturated sodium bicarbonate, and water. The organic layer was dried over sodium sulfate, and concentrated. This residue was used for the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 2 H), 10.06 (s, 1 H), 4.04-4.13 (m, 12 H), 3.73 (q, 4 H, J = 7.3 Hz), 1.90-1.95 (m, 18 H), 1.70 (t, 6 H, J = 7.3 Hz), -3.59 (br, 1 H), -3.81 (br, 1 H).

Synthesis of 5-amino-2,3,7,8,12,13,17,18-octaethylporphyrin (9)

Tin chloride (679 mg, 3.58 mmol) was added to as solution of 2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrin (**8**, 358 mg) in concentrated hydrochloric acid (220 ml), and the mixture was stirred for 16 h. The mixture was poured into water, and extracted with chloroform. The organic layer was washed with brine, dried over sodium bicarbonate, and concentrated. The residue was purified by silica gel column chromatography (70% chloroform/*n*-hexane to 5% methanol/ chloroform) to give 5-amino-2,3,7,8,12,13,17,18-octaethylporphyrin (**9**, 316 mg, 91%) as purple solid. ^{1}H NMR (400 MHz $CDCl_3$) δ 9.53 (s, 2 H), 9.17 (s, 1 H), 6.53 (s, 2 H), 3.75-3.94 (m, 16 H), 1.73-1.85 (m, 24 H), -1.15 (br, 2 H).

Synthesis of nickel (II) 5-amino-2,3,7,8,12,13,17,18-octaethylporphyrin (10)

A solution of nickel(II) acetylacetonate (536 mg, 2.09 mmol) in methanol (50 ml) was added to a solution of 5-amino-2,3,7,8,12,13,17,18-octaethylporphyrin (**9**, 316 mg, 0.575 mmol) in chloroform (600 ml), and the mixture was refluxed for 100 min. After evaporation, the residue was dissolved in chloroform, washed with water and brine, dried over sodium sulfonate, and concentrated. The residue was purified by silica gel column chromatography

(50% chloroform/*n*-hexane to 100% chloroform) to give nickel (II) 5-amino-2,3,7,8,12,13,17,18-octaethylporphyrin (**10**, 320 mg, 91%) as purple solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 2 H), 8.94 (s, 1 H), 5.43 (br, 2 H), 3.80 (q, 4 H, J = 7.3), 3.65-3.74 (m, 12 H), 1.66-1.72 (m, 24 H).

Synthesis of nickel (II) 2,3,7,8,12,13,17,18-octaethyl-5-isocyanatoporphyrin (11)

A solution of triphosgene in 1,2-dichloroethane (0.0562 mM, 1 ml, 0.0562 mmol) was added to a solution of nickel (II) 5-amino-2,3,7,8,12,13,17,18-octaethylporphyrin (**10**, 50 mg, 0.0827 mmol) in 1,2-dichloroethane (12 ml) at room temperature. The reaction mixture was refluxed at 80ºC for 5 h. After concentration, the residue was used for the next reaction without further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.50 (s, 2 H), 9.46 (s, 1 H), 3.94-3.96 (q, 4 H, J = 7.3 Hz), 3.80-3.92 (m, 12 H), 1.74-1.81 (m, 24 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 143.5, 143.4, 142.8, 141.1, 139.9, 138.3, 135.8, 123.4, 105.9, 97.1, 96.1, 77.2, 77.0, 76.8, 22.1, 19.6, 19.5, 19.4, 18.2, 18.1, 18.1, 17.0.

Synthesis of *N,N'*-Bis[Ni (II) 2,3,7,8,12,13,17,18-octaethylporphyrin-5-yl]urea (3)

A solution of nickel (II) 2,3,7,8,12,13,17,18-octaethyl-5-isocyanatoporphyrin (**11**, 77 mg, 0.123 mmol) in 1,2-dichloroethane (5 ml) was added to a solution of nickel (II) 5-amino-2,3,7,8,12,13,17,18-octaethylporphyrin (**10**, 76 mg, 0.122 mmol) in 1,2-dichloroethane (20 ml) at room temperature. The reaction mixture was refluxed at 85ºC for 19 h. After concentration, the residue was purified by silica gel column chromatography (85% chloroform/*n*-hexane to 100% chloroform) and preparative TLC (chloroform) to give *N,N'*-Bis[Ni (II) 2,3,7,8,12,13,17,18-octaethylporphyrin-5-yl]urea (**3**, 41 mg, 27%) as purple solid. ^{1}H NMR (600 MHz, $CDCl_3$, 223 K, major : minor = 0.92 : 0.08) δ 9.77 (major, s, 1.84 H), 9.71 (major, s, 0.92 H), 9.31 (major, s, 0.92 H), 9.16 (major, s, 0.92×2 H), 8.03 (major, s, 0.92 H), 8.25 (minor, s, 0.08×2 H), 8.24 (minor, 0.08×4 H), 8.03 (minor, s, 0.08×2 H), 5.92 (major, s, 0.92 H), 3.31-4.28 (major and minor, m, 0.92×28 H and 0.08×32 H), 2.49-2.67 (major, 0.92×4 H), 1.94 (major, t, 0.92×6 H, J = 7.6 Hz), 1.90 (major, t, 0.92×6 H, J = 7.6 Hz), 1.80 (major, t, 0.92×6 H, J = 7.6 Hz), 1.70 (major, t, 0.92×6 H, J = 7.6 Hz), 1.68 (major, t, 0.92×6

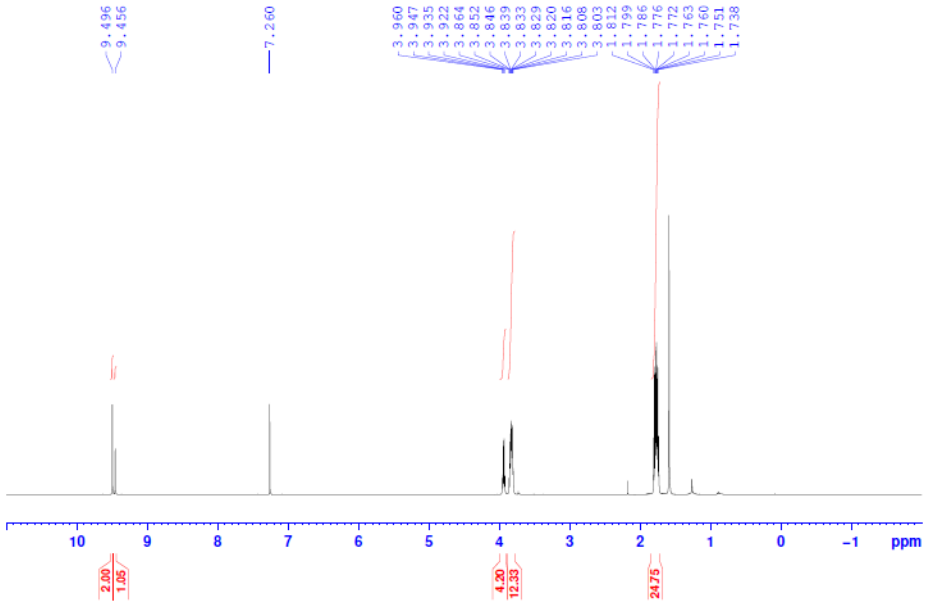
H, *J* = 7.6 Hz), 1.57-1.62 (major and minor, m, 0.92×6 H and 0.08×12 H), 1.46 (minor, t, 0.08×12 H, *J* = 7.6 Hz), 1.33 (minor, t, 0.08×12 H, *J* = 7.6 Hz), 1.27-1.30 (major and minor, m, 0.92×6 H and 0.08×12 H), -1.14 (major, t, 0.92×6 H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, 223 K) δ 158.2, 145.7, 144.4, 143.6, 143.5, 143.2, 142.9, 142.6, 140.3, 140.1, 139.0, 138.9, 138.8, 138.5, 137.3, 136.5, 106.9, 104.9, 97.4, 97.3, 96.3, 95.8, 31.6, 22.7, 22.1, 20.4, 19.7, 19.5, 19.4, 19.4, 19.2, 18.9, 18.88, 18.81, 18.76, 18.5, 18.1, 16.2, 14.4; HRMS (ESI^+), Calcd for $C_{73}H_{89}N_{10}Ni_2O_2$ $[M+H]^+$: 1237.5922, Found : 1237.5914.

Synthesis of *N*-[Ni (II) 2,3,7,8,12,13,17,18-octaethylporphyrin-5-yl]-*N'*-phenylurea (4)

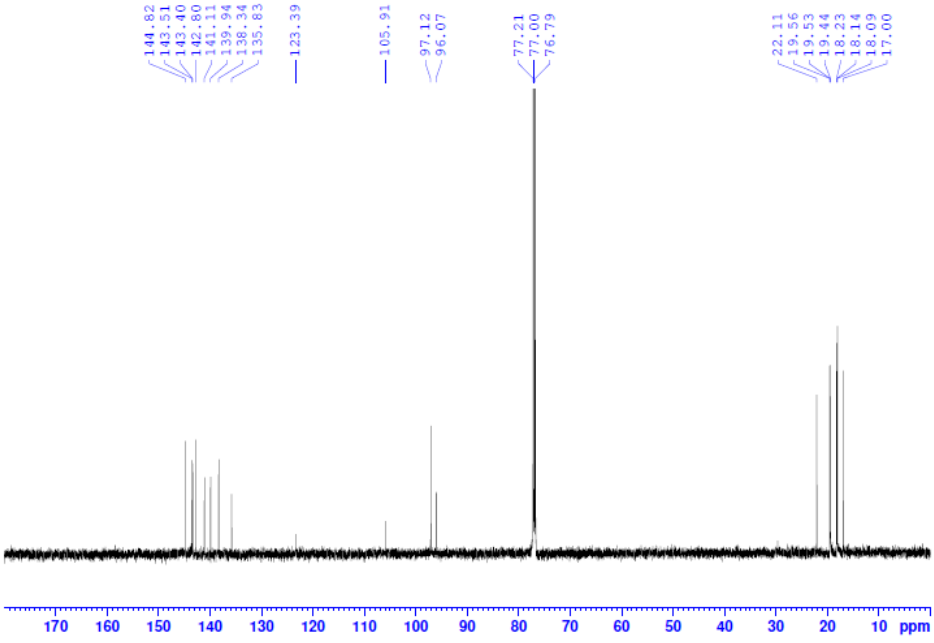
A solution of aniline in 1,2-dichloroethane (27.5 mM, 1 ml, 0.0275 mmol) was added to a solution of nickel (II) 2,3,7,8,12,13,17,18-octaethyl-5-isocyanatoporphyrin (**11**, 17.5 mg, 0.0277 mmol) in 1,2-dichloroethane (3 ml) at room temperature. The reaction mixture was refluxed at 80 ºC for 1 d. After concentration, the residue was purified by silica gel column chromatography (60% chloroform/*n*-hexane to 100% chloroform) to give *N*-[Ni (II) 2,3,7,8,12,13,17,18-octaethylporphyrin-5-yl]-*N'*-phenylurea (**4**, 20 mg, 98%) as purple solid. ^{1}H NMR (600 MHz, $CDCl_3$, 223 K) δ 9.57 (s, 1 H), 9.56 (s, 2 H), 8.12 (s, 1 H), 6.90 (d, 2 H, *J* = 7.4 Hz, 8.1 Hz), 6.74 (t, 1 H, *J* = 7.4 Hz) 6.69 (d, 2 H, *J* = 8.1 Hz), 3.78-4.66 (m, 16 H), 1.79-1.66 (m, 24 H); ^{13}C NMR (150 MHz, $CDCl_3$, 223 K) δ 156.1, 146.0, 144.0, 143.6, 143.4, 140.0, 139.5, 138.6, 138.2, 136.8, 128.3, 122.9, 119.2, 105.9, 97.5, 96.94, 96.87, 22.3, 19.4, 19.4, 19.3, 18.64, 18.59, 17.6; HRMS (ESI^+), Calcd for $C_{43}H_{51}N_6NiO_1$ $[M+H]^+$: 725.3472, Found: 725.3490.

2. NMR spectra of compounds 11, 3 and 4

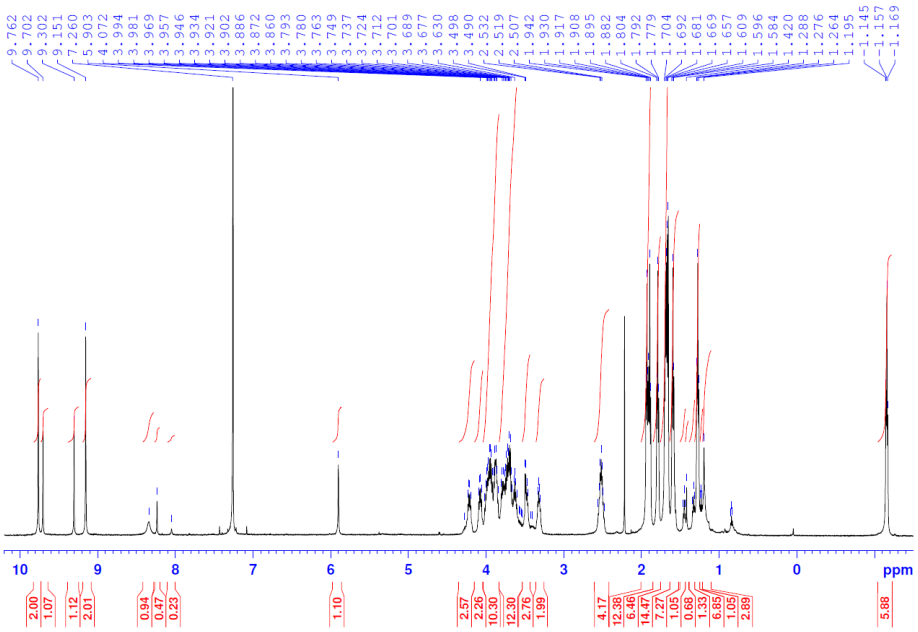
Fig. S1 (a) ^{1}H NMR of Compound 11 in $CDCl_3$ at 298 K



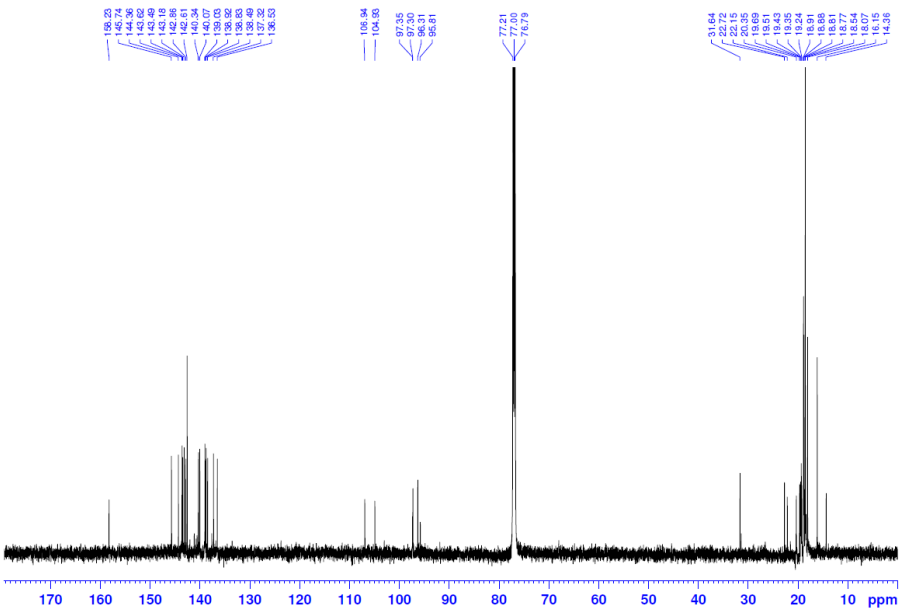
(b) ^{13}C NMR of Compound 11 in $CDCl_3$ at 298 K



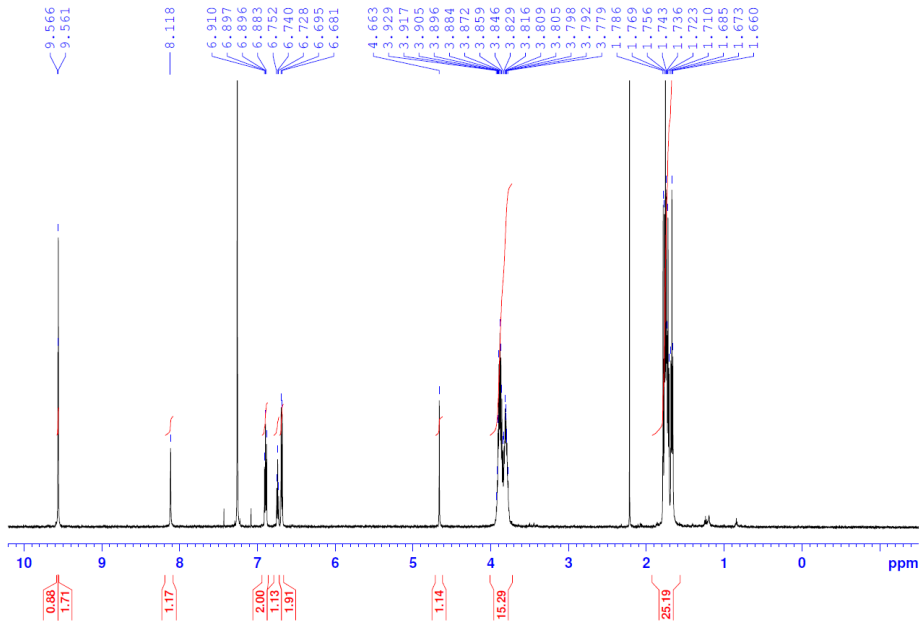
(c) ^{1}H NMR of Compound 3 in $CDCl_3$ at 223 K



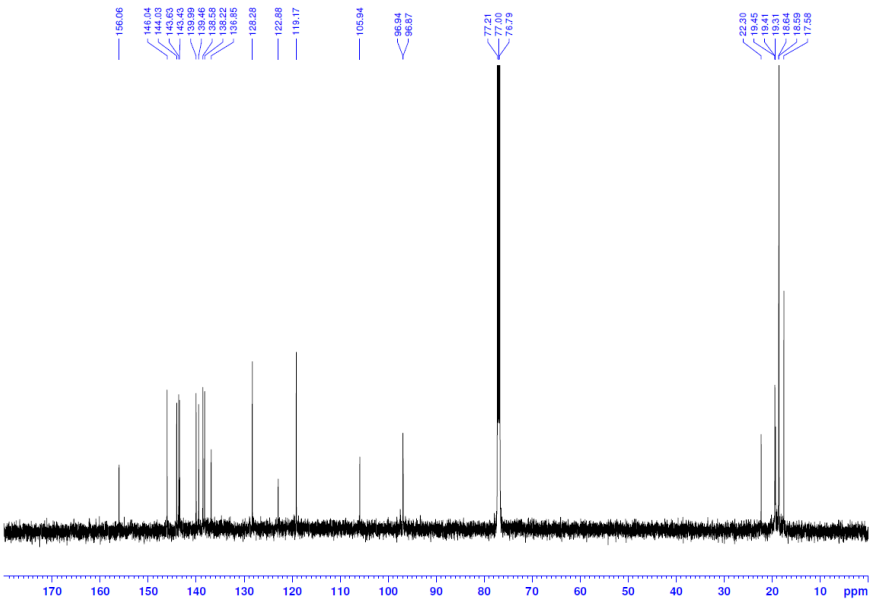
(d) ^{13}C NMR of Compound 3 in $CDCl_3$ at 223 K



(e) ^{1}H NMR of Compound 4 in $CDCl_3$ at 223 K

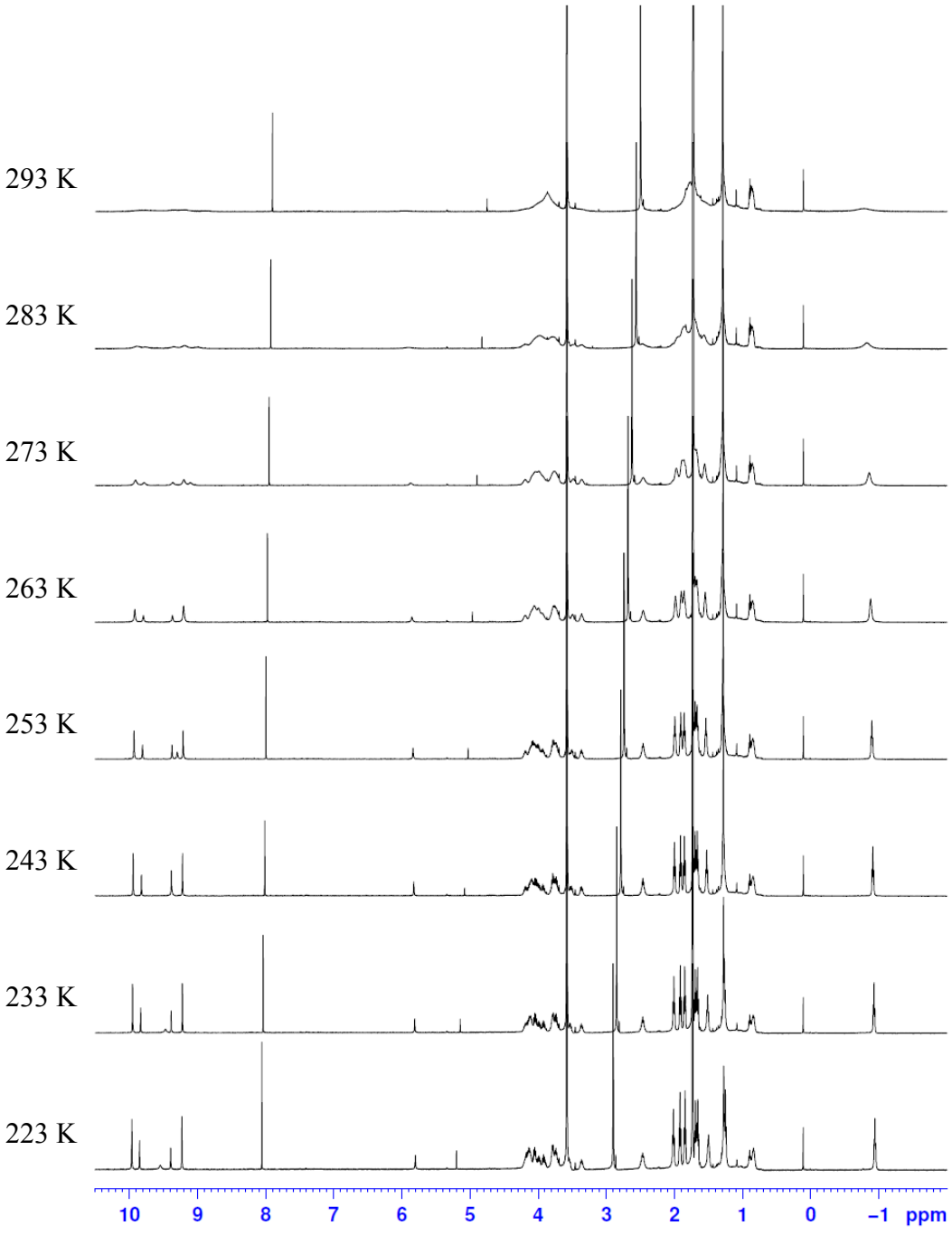


(f) ^{13}C NMR of Compound 4 in $CDCl_3$ at 223 K

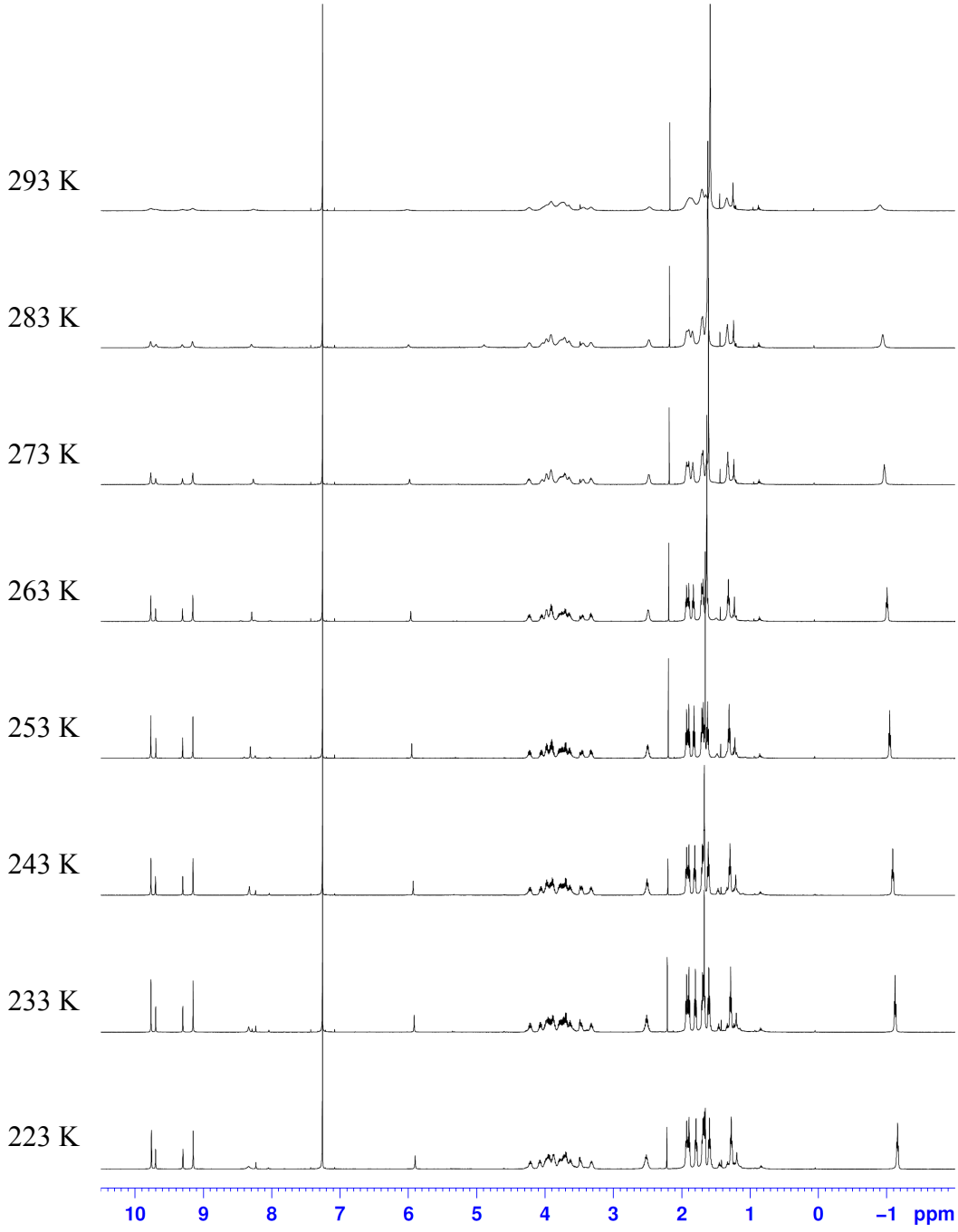


3. Valuable temperature ^{1}H NMR of compounds 3 and 4

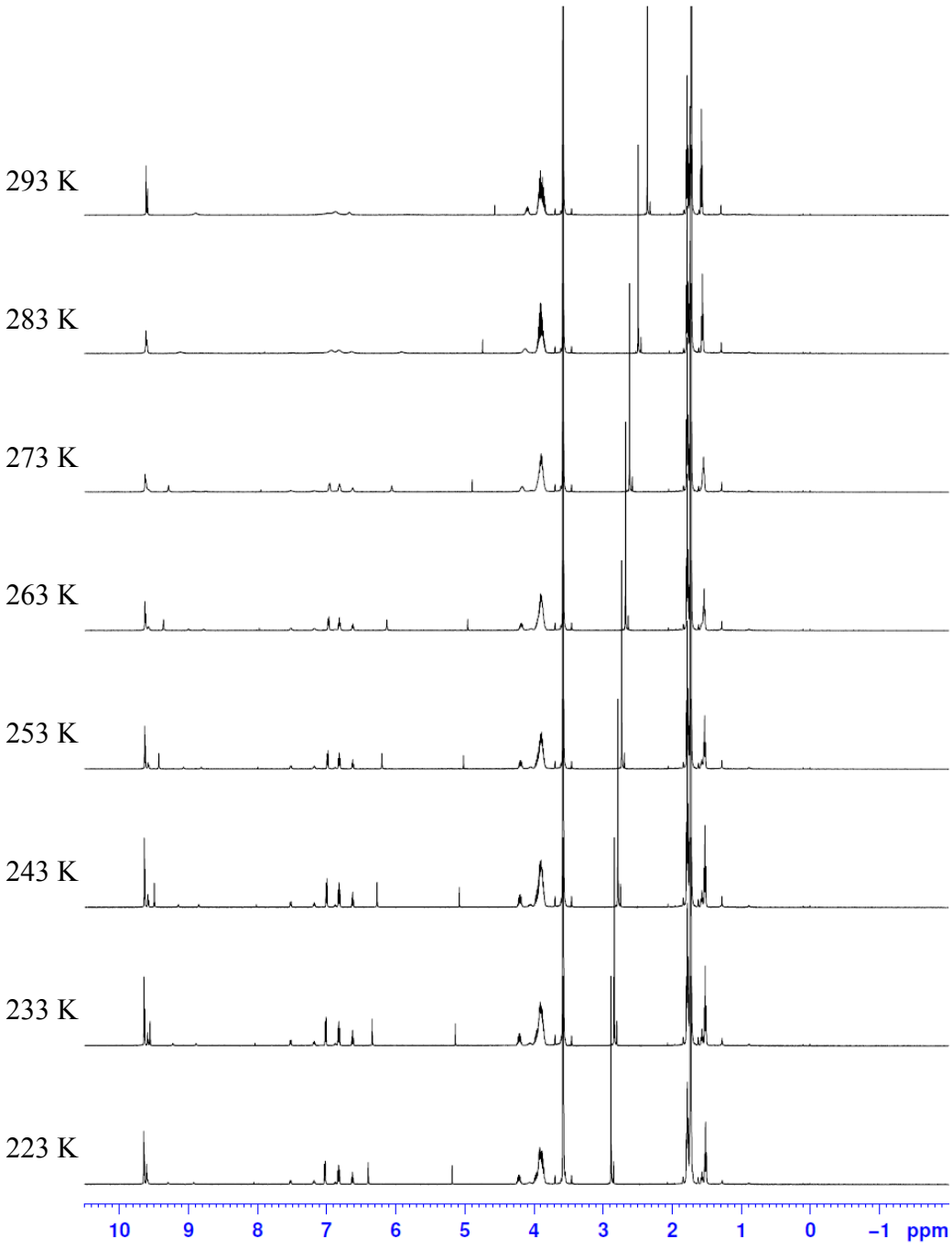
Fig. S2 (a) Compound 3 in THF-d_8



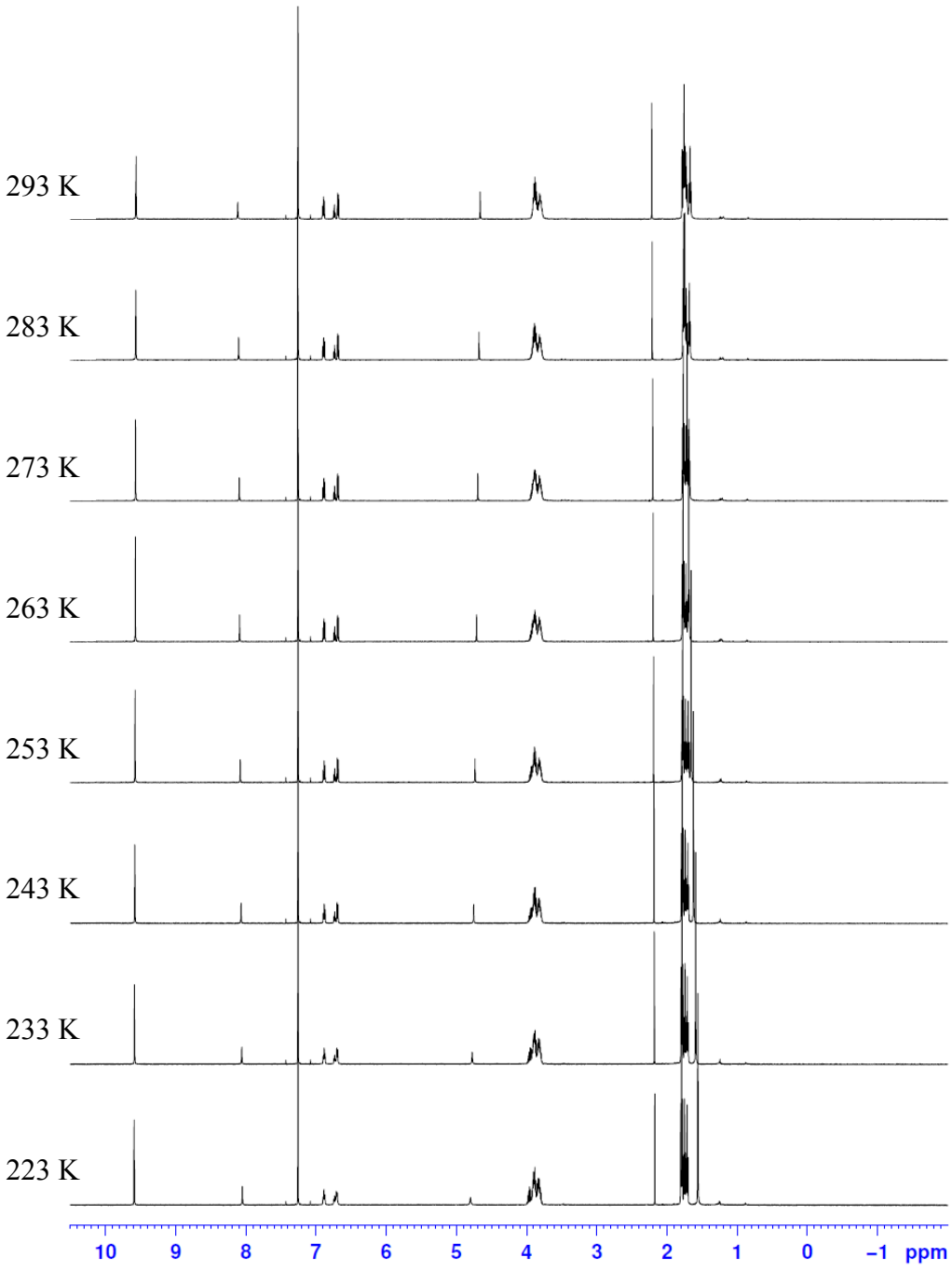
(b) Compound 3 in $CDCl_3$



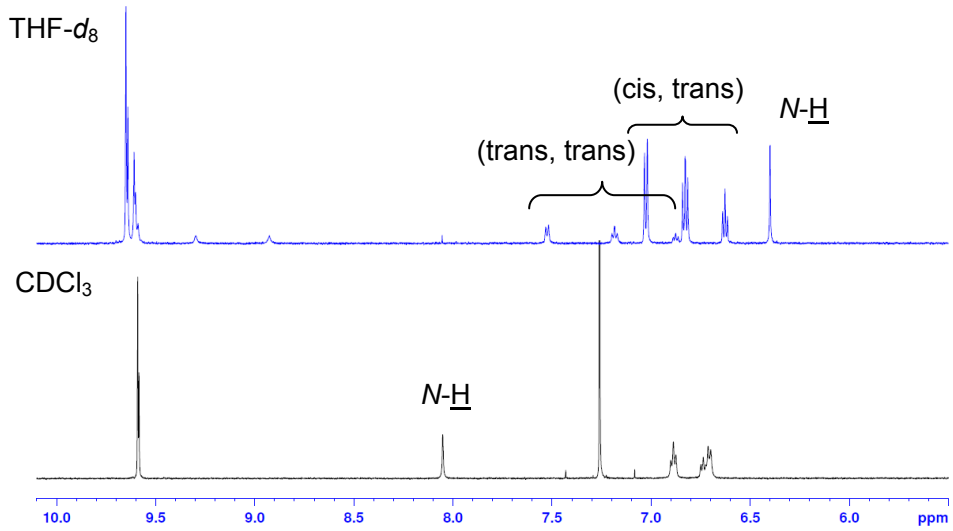
(c) Compound 4 in THF-d_8



(d) Compound 4 in $CDCl_3$



(e) Aromatic region of Compound 4 in THF-d_8 and $CDCl_3$ at 223 K



4. X-ray Crystallographic Analysis

Crystal data of compound 3 (crystal A recrystallized from THF/*n*-hexane). $C_{73}H_{88}N_{10}Ni_2O$, M = 1238.95, monoclinic, a = 29.4464(3), b = 17.6777(2), c = 25.0277(9) Å, β = 100.1173(9)°, V = 12825.5(2) Å^3, T = 90 K, space group $P2_1/c$ (no. 14), Z = 8, D_{calc} = 1.283 Mg m^{-3}, $2\theta_{max}$ = 60.24°, 339391 reflections measured, 37687 unique (R_{int} = 0.0608). μ(Mo Kα) = 0.460 mm^{-1}. The final R_1 and wR_2 were 0.0475 and 0.1236 ($I > 2\sigma(I)$), 0.0751 and 0.1393 (all data) for 1682 parameters and 55 restraints. The residual electron densities (peak and hole) were 1.151 and –1.395 e.Å^{-3}. CCDC-897914.

Two molecules of **3** are included in the asymmetric unit of the crystal. Some ethyl groups are disordered (Fig. S4). The occupancies of the disordered atoms were refined.

Fig. S3 Crystal shape of crystal A.

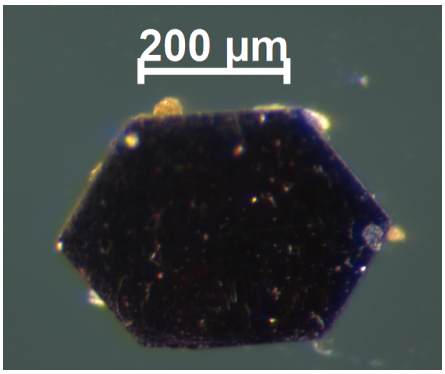
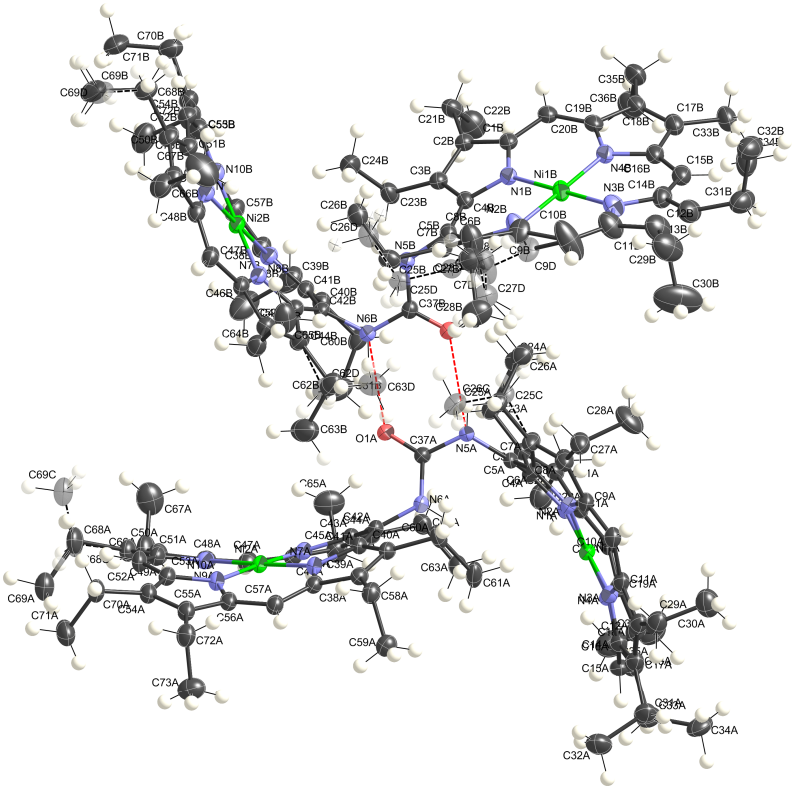


Fig. S4 Thermal ellipsoid model of compound **3** (crystal A). The ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels of hydrogen atoms are omitted for clarity. Disordered atoms are colored transparently. Hydrogen bonds are indicated with red dotted lines.



Crystal data of compound 3 (crystal B recrystallized from $CHCl_3$/*n*-hexane). $C_{73}H_{88}N_{10}Ni_2O$•$2CHCl_3$, M = 1477.69, orthorhombic, a = 16.8849(4), b = 14.7428(3), c = 28.8660(7) Å, V = 7185.6(3) Å^3, T = 90 K, space group *Pbcn* (no. 60), Z = 4, D_{calc} = 1.366 Mg m^{-3}, $2\theta_{max}$ = 60.18°, 167863 reflections measured, 10416 unique (R_{int} = 0.0897). μ(Mo Kα) = 0.799 mm^{-1}. The final R_1 and wR_2 were 0.0721 and 0.1887 ($I > 2\sigma(I)$), 0.0900 and 0.1990 (all data) for 498 parameters and 12 restraints. The residual electron densities (peak and hole) were 0.826 and –0.931 e.Å^{-3}. CCDC-897915.

An urea group (C35, N5, N6, and O1) is disordered to two positions with 0.5 of occupancies respectively. An included chloroform molecule is also disordered (Fig. S6).

Fig. S5 Crystal Shape of crystal B.

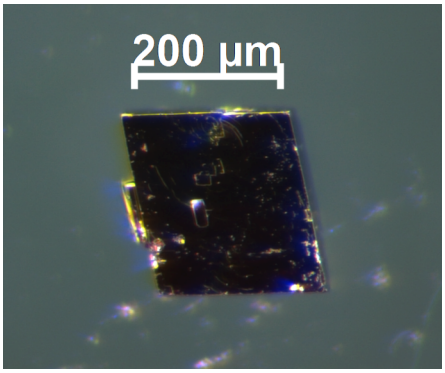
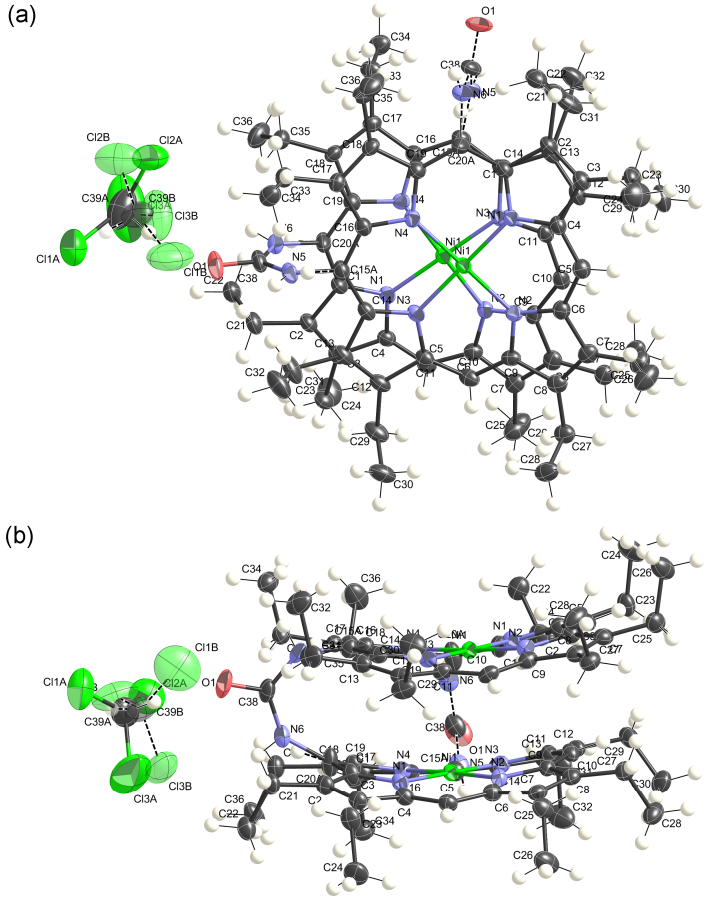


Fig. S6 Thermal ellipsoid model of compound **3** (crystal B). Top view (a) and side view (b). The ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels of hydrogen atoms are omitted for clarity. Disordered atoms are colored transparently or shown with dotted lines.

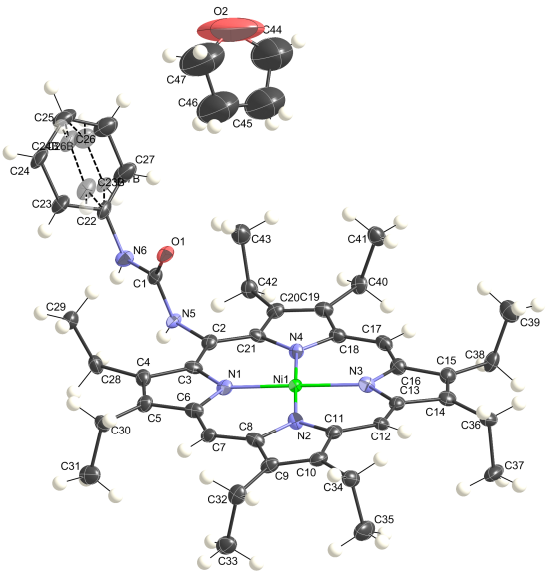


Crystal data of compound 4. $C_{43}H_{50}N_6NiO•2C_4H_8O$, M = 797.70, triclinic, a = 4.808(2), b = 13.525(7), c = 31.228(16) Å, α = 81.982(7), β = 89.135(6), γ = 86.992(7)°, V = 2008.0(17) Å^3, T = 120 K, space group P-1 (no. 2), Z = 2, D_{calc} = 1.319 Mg m^{-3}, $2\theta_{max}$ = 52.74°, 11199 reflections measured, 7346 unique (R_{int} = 0.0503). μ(Mo Kα) = 0.531 mm^{-1}. The final R_1 and wR_2 were 0.0881 and 0.2435 ($I > 2\sigma(I)$), 0.1076 and 0.2546 (all data) for 551 parameters and 59 restraints. The residual electron densities (peak and hole) were 0.809 and –1.063 e.Å^{-3}. CCDC-900116.

An phenyl group of compound **4** is disordered to two positions (Fig. S7). The occupancies of the disordered atoms were refined.

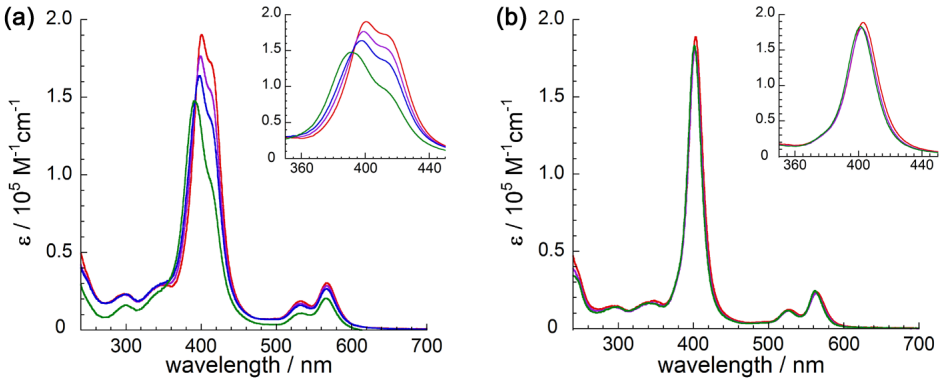
The low data completeness of the crystals was caused by deficiency of the diffraction data at high-angle θ range. Large disorders of included solvent molecules (tetrahydrofuran) reduced the diffractions at that range.

Fig. S7 Thermal ellipsoid model of compound **4**. The ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels of hydrogen atoms are omitted for clarity. Disordered atoms are colored transparently.



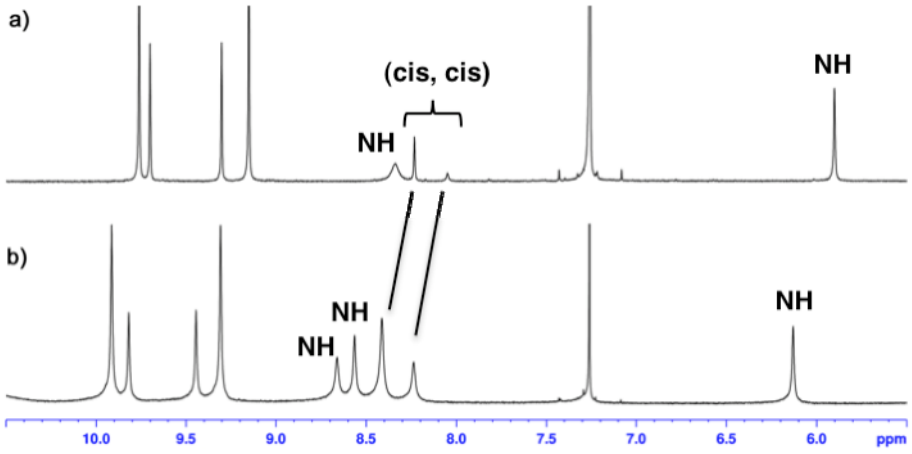
5. UV/vis specta of compounds 3 and 4 in $CHCl_3$/*n*-hexane.

Fig. S8 UV/vis spectra of (a) **3** (5.9×10^{-6} M) in $CHCl_3$/*n*-hexane, and (b) **4** (6.3×10^{-6} M) in $CHCl_3$/*n*-hexane. The ratio of $CHCl_3$ is 100 (red), 50 (purple), 30 (blue), 10 (green) and 100% (yellow).



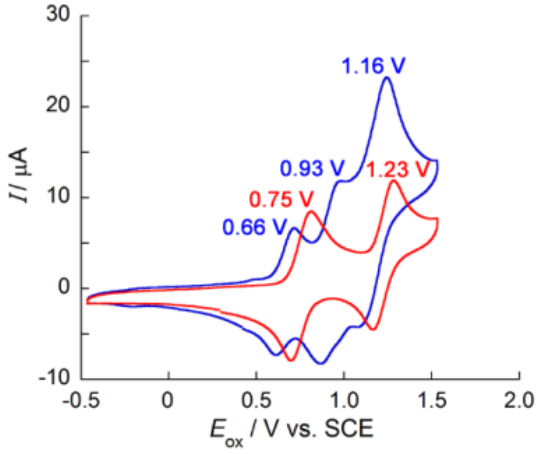
6. ^{1}H NMR of 3 in $CDCl_3$-*n*-C_6D_{14}

Fig. S9 ^{1}H NMR (aromatic region) of **3** in (a) $CDCl_3$ at 223 K, and (b) $CDCl_3$-*n*-C_6D_{14} (7:3) at 263 K. The ratio (cis, cis) conformer is 30% in $CDCl_3$-*n*-C_6D_{14}.



7. Cyclic voltammograms

Fig. S10 Cyclic voltammograms (scan rate, 100 mV/s) of compound **3** (0.2 mM, blue line) in CH_2Cl_2 containing 0.1 M TBAP and Ni (II) 2,3,7,8,12,13,17,18-octaethylporphyrin (1.6 mM, red line) in CH_2Cl_2 using 0.1 M TBAP.



Nickel octaethylporphyrin undergoes two one-electron oxidations (0.75 and 1.23 V vs SCE),[S2] while the bisporphyrin (**3**) exhibited three oxidation waves (0.66, 0.93 and 1.16 V vs SCE, Fig. S10). The first oxidation of the monomer was split into two processes for the dimer, indicating that the monocation species of the urea-bridged bisporphyrin is more stabilized than that of the monomer as a result of the $\pi-\pi$ interactions between the porphyrin rings. The separation of the first and second oxidation potentials (0.27 V) of **3** is much larger than that of *cis*- and *trans*-ethene-bridged bis(nickel octaethylporphyrin) (0.19 and 0.08 V for the cis and trans forms, respectively[14b]). The large separation can be attributed to the geometrical change upon oxidation. Thus, the bisporphyrin (**3**) adopts (cis, cis) conformation upon the first oxidation to form a porphyrin mixed-valence π-cation radical.[S3] Due to the presence of the strong interporphyrin interactions, the second oxidation wave is observed at a significantly higher potential.[S4] The third oxidation potential of **3** (1.16 V) was lower than the second oxidation potential of the monomer (1.23 V). Similar shifts were also observed for *cis*- and *trans*-ethene-bridged bis(nickel octaethylporphyrin).[14b]

8. References for Supporting Information

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