Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Synthesis of Calix[3]dipyrrins As an Effective Trismetal-Coordinating Ligand by Modified Lindsey Protocol of Porphyrin Synthesis

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Contents

I. General Information

All reagents are commercial products without further purification. $Ni(acac)_2 \bullet xH_2O$ was purchased from Nacalai Tesque, and $Cu(OAc)_2 \bullet H_2O$ was purchased from Wako pure chemical industry. Silica gel column chromatography was performed on Wakogel C-200, C-300, and C-400. UV-visible spectra were recorded on a Shimadzu UV-3100PC spectrometer. ^{1}H and ^{19}F NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 600 MHz for ^{1}H, and 565 MHz for ^{19}F). The residual $CHCl_3$ and $CHCl_2CHCl_2$ were used as the internal reference for ^{1}H (d = 7.26 ppm for $CHCl_3$ and 6.00 ppm for $CHCl_2CHCl_2$), and hexafluorobenzene was used as external reference for ^{19}F (d = –162.9 ppm). Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF method for acetonitrile solutions. Using $CHCl_3$ as an eluent, recycling preparative GPC-HPLC was carried out on JAI LC-908 using preparative JAIGEL-2.5H, 3H, and 4H columns in series. ESR spectrum was recorded on a Bruker E500 spectrometer operating at Q band and equipped with an Oxford helium

cryostat. To determine the *g* value, the observed ESR spectrum was simulated by Bruker WIN-EPR Sim Fonia program using Lorentzian line function. The solid-state magnetic susceptibility was measured between 2 and 300 K under a magnetic field of 0.5 T with a SQUID magnetometer (Quantum Design MPMS-5 and Quantum Design MPMS-1).

II. Experimental Procedures

General Procedure for Synthesis of Calix[3]dipyrrins.

A solution of an aryl aldehyde (1.50 mmol) and pyrrole (105 μl, 1.50 mmol) in CH_2Cl_2 (150 mL) and H_2O (100 μl) was stirred for 10 min. To this solution was added TFA (120 μl, 1.50 mmol), and the resulting solution was stirred for 2 h under light shielding conditions. DDQ (1.02 g, 4.50 mmol) was added and stirring was continued for an additional 1 h. After quenching with 1 ml of triethylamine, the solvent was concentrated to ca. 10 mL under reduced pressure. The residual solution was diluted with toluene (20 ml), to which $Ni(acac)_2 \bullet xH_2O$ (0.5 g, ca. 2 mmol) was added and the resulting mixture was stirred for 2 h under reflux. After removal of the solvent, separation of products was carried out by column chromatography over silica gel, in which Ni^{II}-porphyrin product eluted as the first band and calix[3]dipyrrin Ni^{II}-complex eluted as the second band.

5,10,15,20,25,30-Hexakis(4-methoxycarbonylphenyl)calix[3]dipyrrin Ni^{II}-complex 1.

Following the general synthetic procedure, **1** was prepared from 4-methoxycarbonylbenzaldehyde (246 mg, 1.50 mmol) and pyrrole. Then the residue was purified by silica-gel chromatography using CH_2Cl_2 as an eluent, which gave Ni^{II} porphyrin product as the first red band. When the eluent was changed to a mixture of CH_2Cl_2 and acetone (40:1), and calix[3]dipyrrin product **1** eluted as a reddish purple band. Recrystallization from a mixture of CH_2Cl_2 and methanol gave **1** as red crystals (56 mg, 15%).

1: ^{1}H NMR (600 MHz, $CDCl_3$, 248 K): d = 8.24 (d, 6H, J = 8.7 Hz, Ar-H), 8.18 (d, 6H, J = 8.7 Hz, Ar-H), 8.11 (d, 3H, J = 8.3 Hz, Ar-H), 8.04 (d, 3H, J = 8.3 Hz, Ar-H), 7.54 (d, 3H, J = 8.2 Hz, Ar-H), 7.37 (d, 3H, J = 8.2 Hz, Ar-H), 6.60 (d, 6H, J = 4.1 Hz, b-pyrrole), 6.38 (d, 6H, J = 4.1 Hz, b-pyrrole), 4.00 (s, 9H, methoxycarbonyl), and 3.94 (s, 9H, methoxycarbonyl); ESI-MS: 1513.1527 $[M + Na]^+$, Calcd. for $C_{78}H_{54}N_6O_{15}Ni_3Na$: 1513.1583; UV-Vis ($CH_2Cl_2$) l_{max} nm (e x 10^{-4}): 328 (4.90), and 488(7.67).

5,10,15,20,25,30-Hexakis(4-cyanophenyl)calix[3]dipyrrin Ni^{II}-complex 4.

Following the general synthetic procedure, **4** was prepared from 4-cyanobenzaldehyde (198 mg, 1.50 mmol) and pyrrole. **4** was obtained as red crystals (42 mg, 13%).

4: ^{1}H NMR (600 MHz, $CDCl_3$, 248 K): *d* = 8.17 (d, 6H, *J* = 8.2 Hz, Ar-H), 7.81 (d, 6H, *J* = 8.3 Hz, Ar-H), 7.78 (d, 3H, *J* = 7.7 Hz, Ar-H), 7.73 (d, 3H, *J* = 7.7 Hz, Ar-H), 7.58 (d, 3H, *J* = 8.2 Hz, Ar-H), 7.43 (d, 3H, *J* = 8.2 Hz, Ar-H), 6.60 (d, 6H, *J* = 4.1 Hz, *b*-pyrrole), 6.35 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole); ESI-MS: 1315.0984 [*M* + Na]$^+$, Calcd. for $C_{72}H_{36}N_{12}O_3Ni_3Na$: 1315.0965; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 325 (4.35), and 489 (7.02).

5,10,15,20,25,30-Hexakis(4-nitrophenyl)calix[3]dipyrrin Ni^{II}-complex 5.

Following the general synthetic procedure, **5** was prepared from 4-nitrobenzaldehyde (227 mg, 1.50 mmol). **5** was obtained as red crystals (40 mg, 11%).

5: ^{1}H NMR (600 MHz, $CDCl_3$, 248 K): *d* = 8.17 (d, 6H, *J* = 8.8 Hz, Ar-H), 7.81 (d, 6H, *J* = 8.3 Hz, Ar-H), 7.78 (d, 3H, *J* = 7.8 Hz, Ar-H), 7.73 (d, 3H, *J* = 8.2 Hz, Ar-H), 7.58 (d, 3H, *J* = 7.8 Hz, Ar-H), 7.43 (d, 3H, *J* = 6.9 Hz, Ar-H), 6.60 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole), and 6.35 (d, 6H, *J* = 4.9 Hz, *b*-pyrrole); ESI-MS: 1435.0351 [*M* + Na]$^+$, Calcd. for $C_{66}H_{36}N_{12}O_{15}Ni_3Na$: 1435.0353; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 326 (5.16), and 496(6.37).

5,10,15,20,25,30-Hexakis(4-trifluoromethylphenyl)calix[3]dipyrrin Ni^{II}-complex 6.

Following the general synthetic procedure, **6** was prepared from 4-trifluoromethylbenzaldehyde (262 mg, 1.50 mmol). The reaction mixture was concentrated and dissolved in a small amount of CH_2Cl_2 and passed through a pad of basic alumina. The solvent was evaporated under reduced pressure and the residue was purified by silica-gel chromatography using a mixture of CH_2Cl_2 and hexane (1:2) as an eluent. **6** was eluted with Ni^{II}-porphyrin and unidentified byproducts. After evaporation under reduced pressure, purification by recycling preparative GPC-HPLC gave **6** as red crystals (29 mg, 7.5%).

6: ^{1}H NMR (600 MHz, $CDCl_3$, 248 K): *d* = 8.25 (d, 6H, *J* = 8.3 Hz, Ar-H), 7.77 (d, 6H, *J* = 8.3 Hz, Ar-H), 7.73 (d, 3H, *J* = 7.8 Hz, Ar-H), 7.66 (d, 3H, *J* = 7.7 Hz, Ar-H), 7.58 (d, 3H, *J* = 8.2 Hz, Ar-H), 7.41 (d, 3H, *J* = 7.8 Hz, Ar-H), 6.61 (d, 6H, *J* = 4. 6 Hz, *b*-pyrrole), and 6.38 (d, 6H, *J* = 4. 6 Hz, *b*-pyrrole); ^{19}F NMR (600 MHz, $CDCl_3$, 298 K): *d* = –63.4 (s, 9F, CF_3), –63.7 (s, 9F, CF_3); ESI-MS: 1573.0518 [*M* + Na]$^+$, Calcd. for $C_{72}H_{36}F_{18}N_6O_3Ni_3Na$: 1573.0493; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 324 (3.31), and 484 (6.98).

5,10,15,20,25,30-Hexakis(4-fluorophenyl)calix[3]dipyrrin Ni^{II}-complex 7.

Following the general synthetic procedure, **7** was prepared from 4-fluorobenzaldehyde (186 mg, 1.50 mmol). Recrystallization from CH_2Cl_2 and hexane gave **7** as red crystals (4.4 mg, 1.4%).

7: ^{1}H NMR (600 MHz, $CDCl_3$, 248 K): *d* = 8.07 (m, 6H, Ar-H), 7.45 (m, 3H, Ar-H), 7.31 (m, 3H, Ar-H), 7.17 to 7.14 (m, 9H, Ar-H), 7.09 (m, 3H, Ar-H), 6.64 (d, 6H, *J* = 4.1 Hz, *b*-pyrrole), and 6.33 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole); ^{19}F NMR (600 MHz, $CDCl_3$, 298 K): *d* = –112 (m, 3F, *p*-F), –116 (m, 3F, *p*-F); ESI-MS: 1273.0676 [*M* + Na]$^+$, Calcd. for $C_{66}F_6H_{36}N_6O_3Ni_3Na$: 1273.0681; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 336 (2.88), and 481 (5.60).

5,10,15,20,25,30-Hexakis(4-chlorophenyl)calix[3]dipyrrin Ni^{II}-complex 8.

Following the general synthetic procedure, **8** was prepared from 4-chlorobenzaldehyde (211 mg, 1.50 mmol). Recrystallization from CH_2Cl_2 and methanol gave **8** as red crystals (18 mg, 5.5%).

8: ^{1}H NMR (600 MHz, $CDCl_3$, 248 K): *d* = 8.03 (d, 6H, *J* = 8.3 Hz, Ar-H), 7.45 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.42 to 7.36 (m, 9H, Ar-H), 7.26 (d, 3H, *J* = 8.7 Hz, Ar-H), 7.58 (d, 3H, *J* = 8.2 Hz, Ar-H), 7.41 (d, 3H, *J* = 7.8 Hz, Ar-H), 6.62 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole), 6.32 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole); ESI-MS: 1370.8868 [*M* + Na]$^+$, Calcd. for $C_{66}H_{36}Cl_6N_6O_3Ni_3Na$: 1370.8879; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 339 (3.78), and 484 (6.78).

5,10,15,20,25,30-Hexakis(4-bromophenyl)calix[3]dipyrrin Ni^{II}-complex 9.

Following the general synthetic procedure, **9** was prepared from 4-bromobenzaldehyde (278 mg, 1.50 mmol). Recrystallization from CH_2Cl_2 and methanol gave **9** as red crystals (8.5 mg, 2.1%).

9: ^{1}H NMR (600 MHz, $CDCl_3$, 248 K): *d* = 7.96 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.60 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.58 (d, 3H, *J* = 8.3 Hz, Ar-H), 7.53 (d, 3H, *J* = 8.3 Hz, Ar-H), 7.32 (d, 3H, *J* = 8.3 Hz, Ar-H), 7.19 (d, 3H, *J* = 7.7 Hz, Ar-H), 6.61 (d, 6H, *J* = 4. 6 Hz, *b*-pyrrole), and 6.31 (d, 6H, *J* = 4. 6 Hz, *b*-pyrrole); ESI-MS: 1616.5952 [*M* + H]$^+$, Calcd. For $C_{66}H_{37}Br_6N_6O_3Ni_3$: 1616.5997; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 341 (4.90), and 486 (8.31).

5,10,15,20,25,30-Hexakis(3-nitrophenyl)calix[3]dipyrrin Ni^{II}-complex 10.

Following the general synthetic procedure, **10** was prepared from 3-nitrobenzaldehyde (227 mg, 1.50 mmol). Recrystallization from CH_2Cl_2 and methanol gave **10** as red crystals (14 mg, 4.0%).

10: ^{1}H NMR (600 MHz, $CDCl_2CDCl_2$, 418 K): *d* = 9.03 (s, 3H, *o*-H), 8.72 (d, 3H, *J* = 7.8 Hz, *o*-H), 8.36 (d, 3H, *J* = 8.2 Hz, *o*-H), 8.31 (s, 3H, *o*-H), 8.30 (d, 3H, *J* = 8.3 Hz, *p*-H), 7,85 (dd, 3H, *J* = 7.8 and 8.3 Hz, *m*-H), 7.80 (d, 3H, *J* = 7.8 Hz, *p*-H), 7.67 (dd, 3H, *J* = 8.3 and 7.8 Hz, *m*-H), 6.67 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole), and 6.52 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole); ESI-MS: 1435.0344 $[M + Na]^+$, Calcd. for $C_{66}H_{36}N_{12}O_{15}Ni_3Na$: 1435.0353; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 323 (4.17), and 487 (6.92).

5,10,15,20,25,30-Hexakis(3-trifluoromethylphenyl)calix[3]dipyrrin Ni^{II}-complex 11.

Following the general synthetic procedure, **11** was prepared from 3-trifluoromethylbenzaldehyde (262 mg, 1.50 mmol). The reaction mixture was concentrated and dissolved in a small amount of CH_2Cl_2 and passed through a pad of basic alumina. The solvent was evaporated under reduced pressure and the residue was purified by silica-gel chromatography using a mixture of CH_2Cl_2 and hexane (1:2) as an eluent. **11** was eluted a Ni^{II}-porphyrin product and unidentified byproducts. After evaporation under reduced pressure, purification by recycling preparative GPC-HPLC gave **11** as red crystals (15 mg, 4.0%).

11: ^{1}H NMR (600 MHz, $CDCl_2CDCl_2$, 418 K): *d* = 8.55 (d, 3H, *J* = 6.9 Hz, *o*-H), 8.38 (s, 3H, *o*-H), 7.80 (d, 3H, *J* = 7.8 Hz *o*-H), 7.77 (s, 3H, *o*-H), 7.74 to 7.72 (m, 6H, *m*-H and *p*-H), 7.69 (d, 3H, *J* = 7.8 Hz, *p*-H), 7.61 (dd, 3H, *J* = 7.8 and 7.8 Hz, *m*-H), 6.65 (d, 6H, *J* = 4. 6 Hz, *b*-pyrrole), and 6.45 (d, 6H, *J* = 4.6 Hz, *b*-pyrrole); ESI-MS: 1573.0480 $[M + Na]^+$, Calcd. for $C_{72}H_{36}F_{18}N_6O_3Ni_3Na$: 1573.0493; UV-Vis ($CH_2Cl_2$) l_{max} nm (*e* x 10^{-4}): 325 (3.64), and 483 (7.45).

5,10,15,20,25,30-Hexakis(4-methoxycarbonylphenyl)calix[3]dipyrrin 2.

TFA (ca. 2 ml) was added to a solution of **1** (74.6 mg, 0.05 mmol) in $CHCl_3$. Immediately the reaction was quenched with aqueous NaOH solution. After the reaction mixture was neutralized with aqueous $NaHCO_3$ solution, the organic layer was separated and passed through a pad of silica-gel and Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by silica-gel chromatography using a mixture of CH_2Cl_2 and acetone (40:1) as an eluent. Recrystallization from CH_2Cl_2 and hexane gave **2** as orange crystals (62 mg, 94%).

2: ^{1}H NMR (600MHz, $CDCl_3$, 248K): *d* = 13.2 (br s, 3H, NH or OH), 8.11 (d, 3H, *J* = 7.8 Hz, Ar-H), 8.07 (d, 3H, *J* = 7.8 Hz, Ar-H), 8.00 (d, 6H, *J* = 8.2 Hz, Ar-H), 7.62 (d, 3H, *J* = 8.2 Hz, Ar-H), 7.59 (d, 6H, *J* = 8.2 Hz, Ar-H), 7.50 (d, 3H, *J* = 8.2 Hz, Ar-H), 6.55 (d, 6H, *J* = 4.1 Hz, *b*-pyrrole), 6.42 (br s, 3H, OH or NH), 6.31 (d,

6H, J = 4.1 Hz, *b*-pyrrole), 3.95 (s, 9H, methoxycarbonyl), 3.90 (s, 9H, methoxycarbonyl); ESI-MS: 1343.3963 $[M + Na]^+$, Calcd. *F*or $C_{78}H_{60}N_6O_{15}Na$: 1343.4009; UV-Vis (CH_2Cl_2) l_{max} nm (e x 10^{-4}): 311 (3.19), and 451 (12.4).

5,10,15,20,25,30-Hexakis(4-methoxycarbonylphenyl)calix[3]dipyrrin Cu(II)-complex 3.

An excess amount of $Cu(OAc)_2 \bullet H_2O$ was added to a solution of **2** (62 mg, 0.047 mmol) in $CHCl_3$ at 50 ^{O}C until the color of the solution changed from dark orange to red. Metallation was monitored by ESI-TOF mass measurement. The solvent was evaporated under reduced pressure and the residue was purified by silica-gel chromatography using a mixture of CH_2Cl_2 and acetone (40:1) as an eluent. Recrystallization from a mixture of CH_2Cl_2 and methanol gave **3** as red crystals (71 mg, 100%).

3: ESI-MS: 1506.1592 $[M + H]^+$, Calcd. For $C_{78}H_{55}N_6O_{15}Cu_3$: 1506.1609; UV-Vis ($CH_2Cl_2$) l_{max} nm (e x 10^{-4}): 328 (5.16), and 501 (15.5).

III. Selected Bond Distances and Bond Angles of X-Ray Structures of 1 and 3

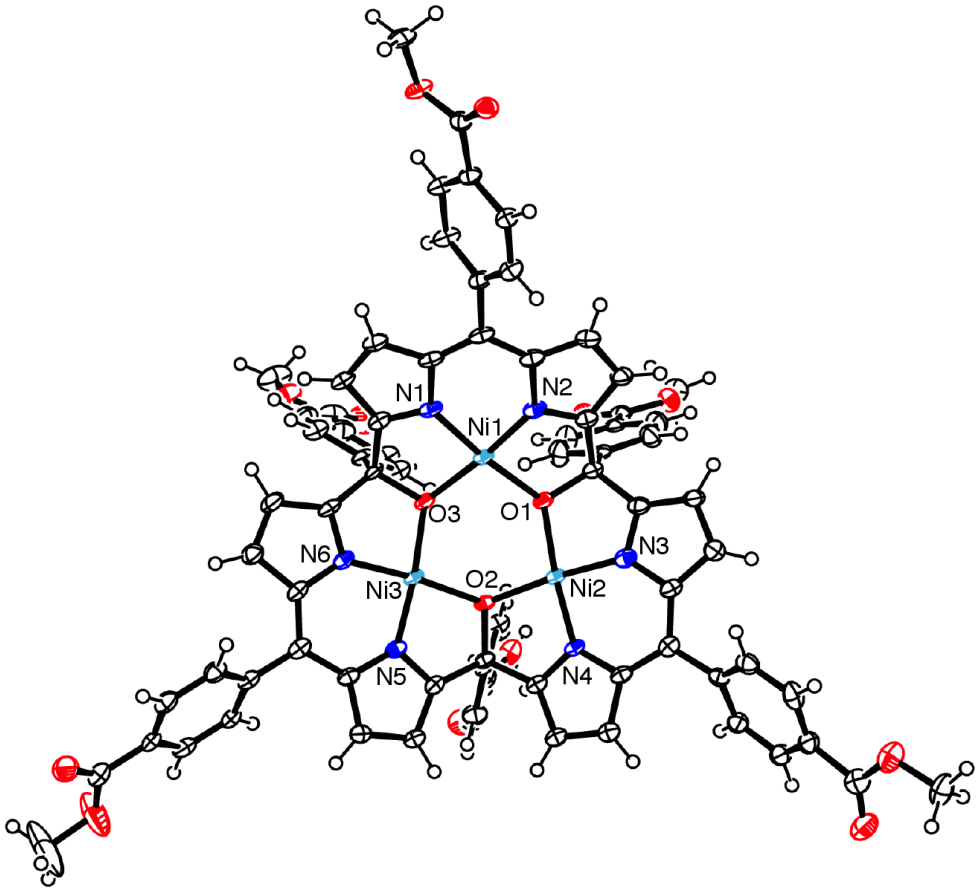

***Figure S1*. 1**: selected bond distances (Å): N1-Ni1, 1.811(4); N2-Ni1, 1.812(4); N3-Ni2, 1.813(4); N4-Ni2, 1.810(4); N5-Ni3, 1.803(4); N6-Ni3, 1.805(4); Ni1-O3, 1.900(3); Ni1-O1, 1.908(3); Ni2-O2, 1.901(3); Ni2-O1, 1.906(3); Ni3-O3, 1.898(3); Ni3-O2, 1.904(4). Selected bond angles (deg): N1-Ni1-N2, 89.14(19); N1-Ni1-O3, 84.66(17); N2-Ni1-O3, 173.80(17); N1-Ni1-O1, 174.36(16); N2-Ni1-O1, 85.22(17); O3-Ni1-O1, 100.98(15); N4-Ni2-N3, 89.23(19); N4-Ni2-O2, 84.97(17); N3-Ni2-O2, 173.93(17); N4-Ni2-O1, 174.26(17); N3-Ni2-O1, 85.04(16); O2-Ni2-O1, 100.77(15); N5-Ni3-N6, 89.02(19); N5-Ni3-O3, 173.66(18); N6-Ni3-O3, 85.16(17); N5-Ni3-O2, 85.47(17); N6-Ni3-O2, 174.38(16); O3-Ni3-O2, 100.29(15); Ni2-O1-Ni1, 131.78(17); Ni2-O2-Ni3, 130.15(18); Ni3-O3-Ni1, 131.34(19).

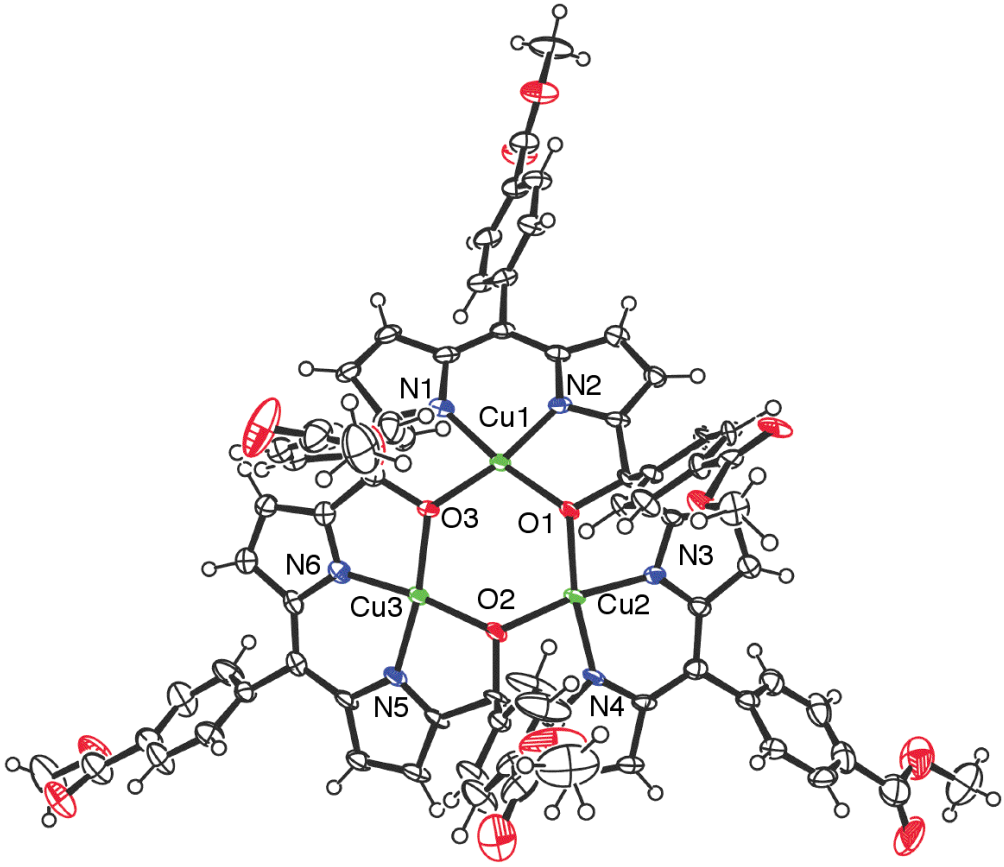

Figure S2. **3**: selected bond distances (Å): Cu1-N6, 1.891(6); Cu1-N5, 1.899(6); Cu2-N1, 1.897(6); Cu2-N2, 1.901(6); Cu3-N3, 1.883(6); Cu3-N4, 1.908(6); Cu1-O3, 1.937(5); Cu1-O1, 1.960(5); Cu2-O2, 1.936(5); Cu2-O1, 1.947(5); Cu3-O3, 1.956(5); Cu3-O2, 1.963(5). Selected bond angles (deg): N6-Cu1-N5, 88.7(3); N6-Cu1-O3, 172.0(2); N5-Cu1-O3, 83.4(2); N6-Cu1-O1, 82.4(2); N5-Cu1-O1, 169.2(2); O3-Cu1-O1, 105.4(2); N1-Cu2-N2, 88.1(3); N1-Cu2-O2, 171.6(2); N2-Cu2-O2, 83.7(2); N1-Cu2-O1, 82.8(2); N2-Cu2-O1, 170.9(2); O2-Cu2-O1, 105.4(2); N3-Cu3-N4, 88.1(3); N3-Cu3-O3, 169.8(2); N4-Cu3-O3, 83.1(2); N3-Cu3-O2, 83.0(2); N4-Cu3-O2, 170.8(2); O3-Cu3-O2, 105.6(2); Cu2-O1-Cu1, 125.2(3); Cu2-O2-Cu3, 125.0(3); Cu1-O3-Cu3, 121.2(2).

IV. ^{1}H NMR Spectra of 1 and 2

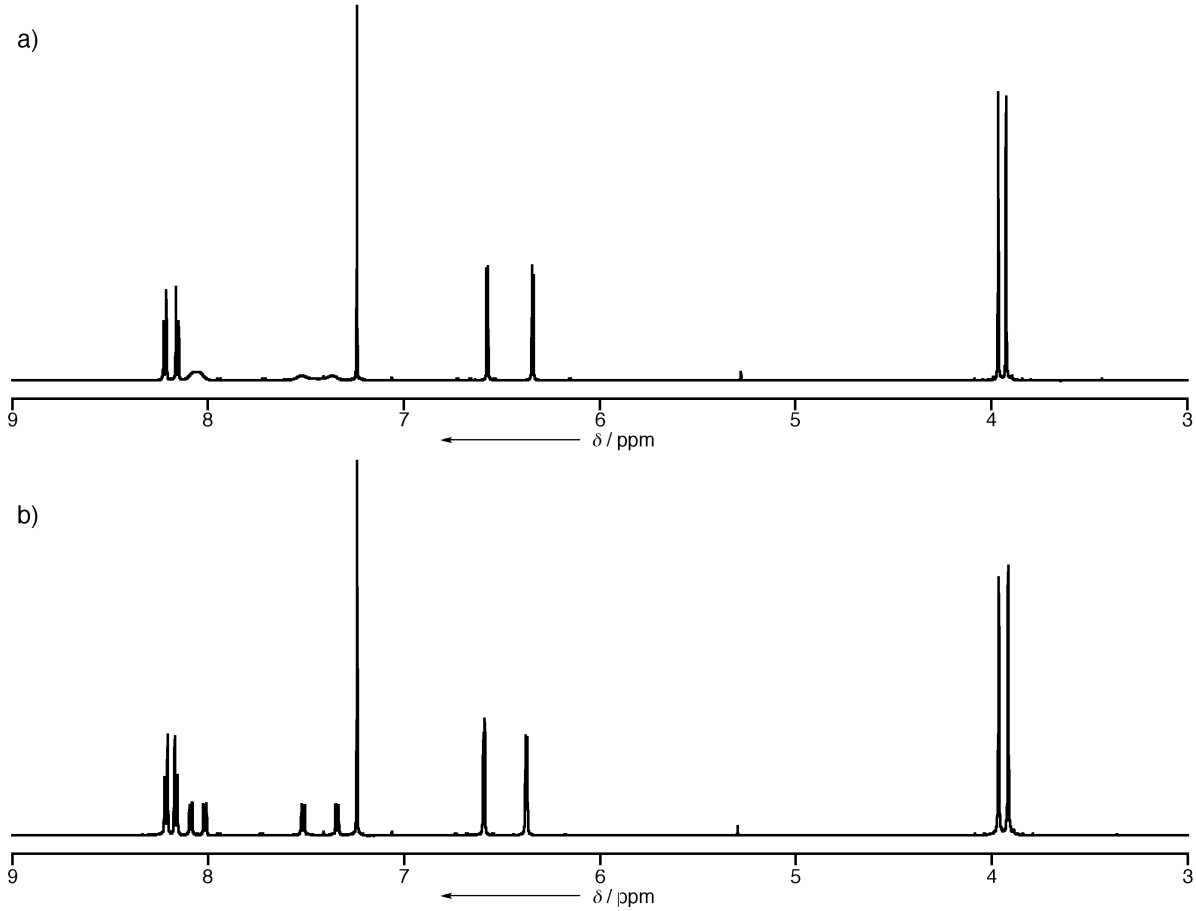

Figure S3. ^{1}H NMR spectra of **1** in $CDCl_3$: a) at 293 K and b) at 248 K.

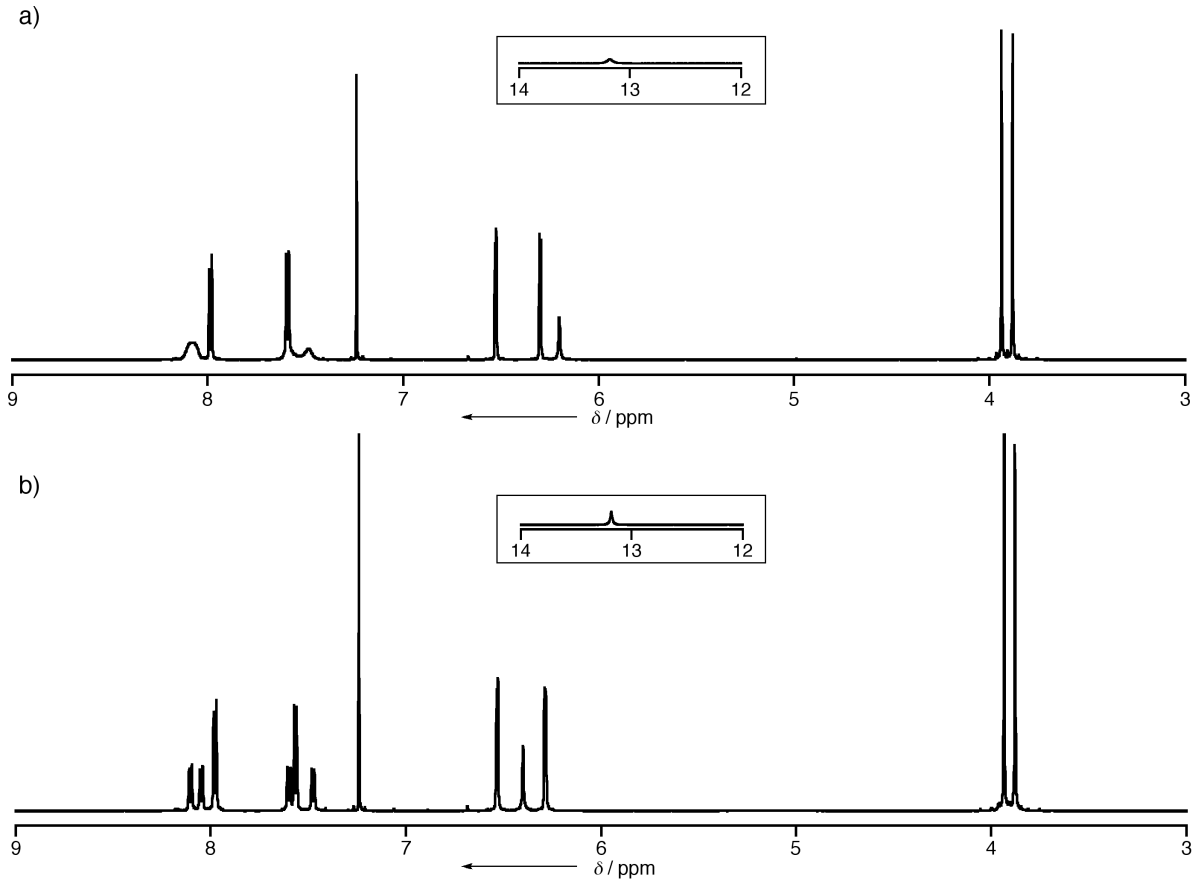

Figure S4. ^{1}H NMR spectra of **2** in $CDCl_3$: a) at 293 K and b) at 248 K.

V. Estimation of Rotational Barrier of *meso*-Aryl Group of 1 and 2

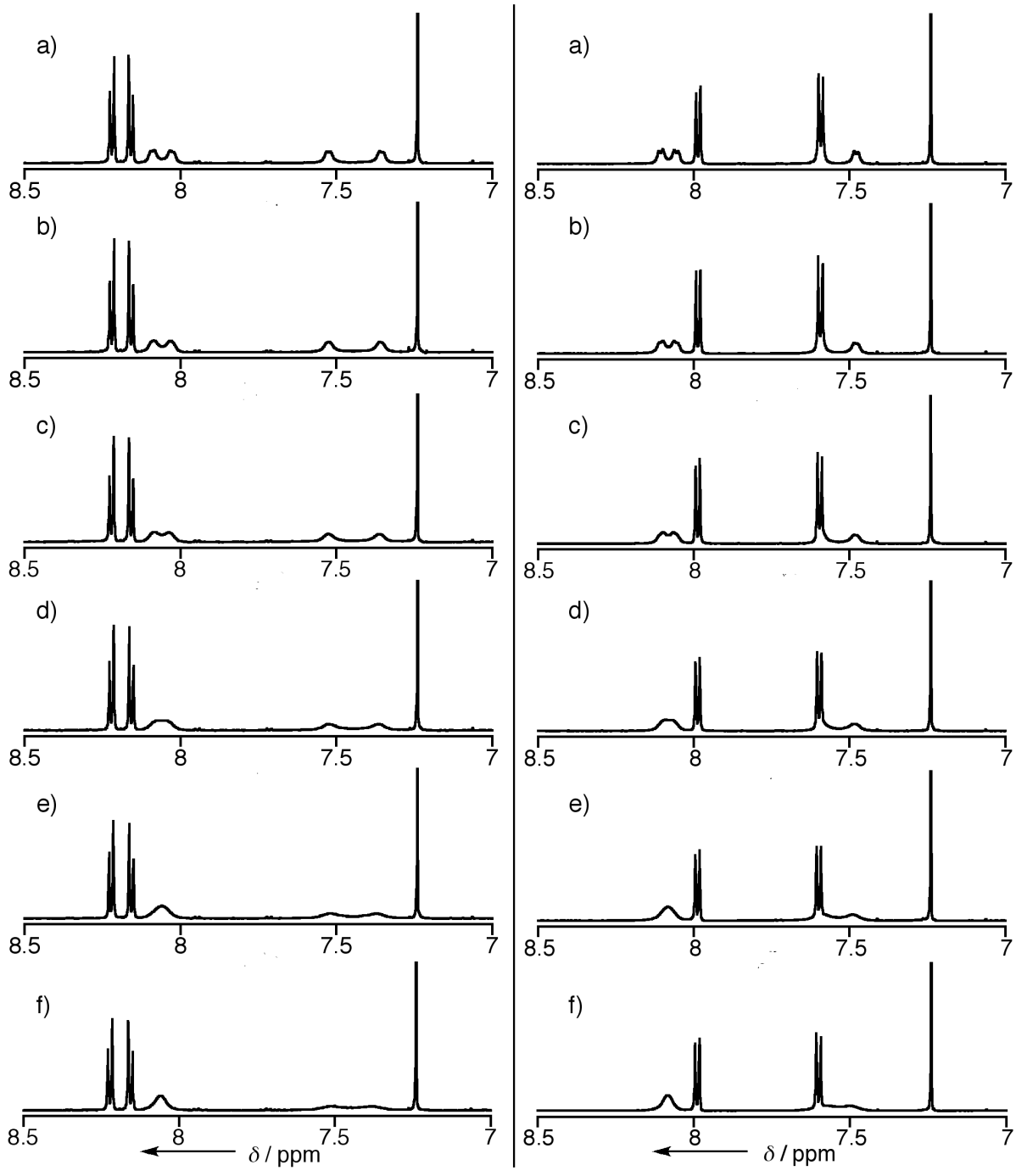

Figure S5. Temperature dependent transition of ^{1}H NMR spectra of **1** and **2** in $CDCl_3$: a) at 283 K, b) at 288 K, c) at 293 K, d) at 298 K, e) at 303 K, and f) at 308K. **1**; left column and **2**; right column.

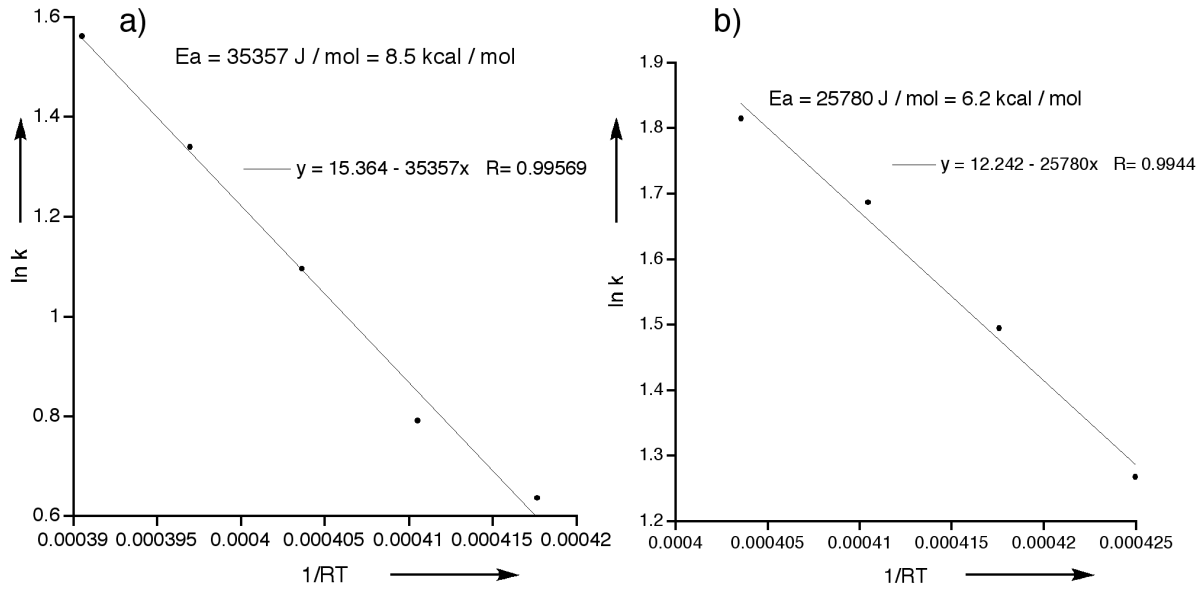

Figure S6. Arrhenius plots of rotational rates of **1** and **2**: a) **1** and b) **2**. Activation barriers (*Ea*) were estimated from the respective slopes on the basis of Arrhenius equation ($k = A\exp(-Ea/RT)$).

VI. ESI-MS Spectrum of ^{18}O Enriched 1

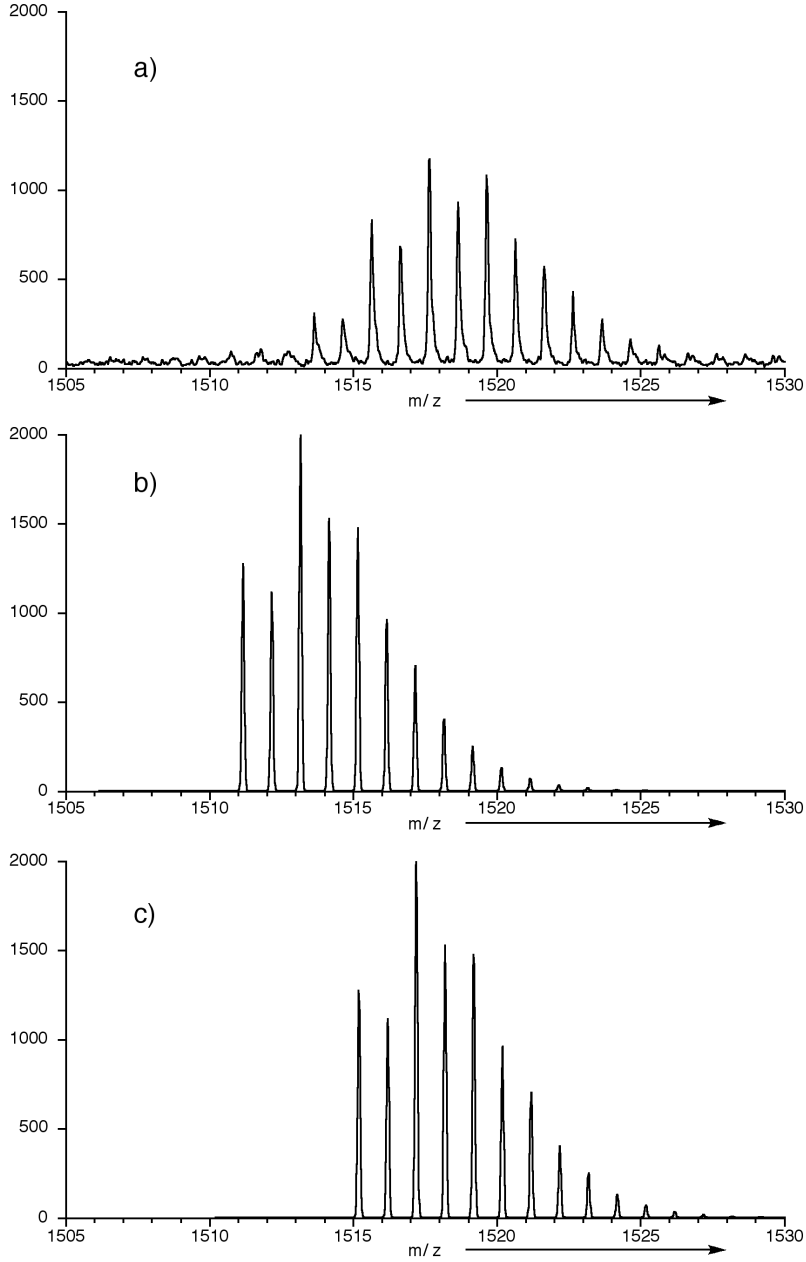

Figure S7. ESI-MS spectrum of ^{18}O enriched **1**: a) Observed spectrum, b) calculated spectrum for $C_{78}H_{54}N_6O_{15}Ni_3Na$, and c) calculated spectrum for $C_{78}H_{54}N_6O_{15}Ni_3Na$ + 4 mass units.

VII. Absorption Spectra of 1, 2, and 3

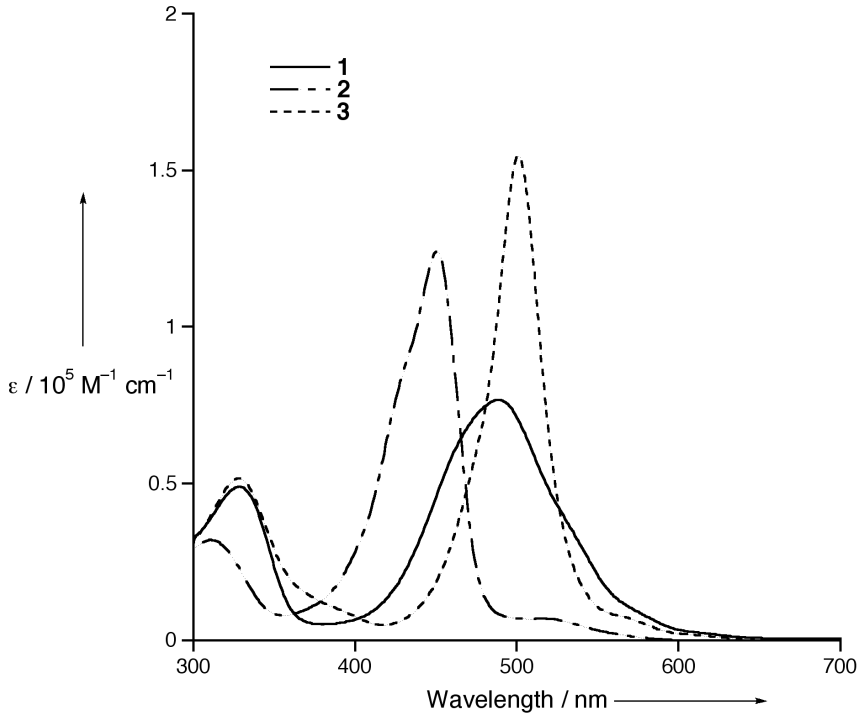

Figure S8. Absorption spectra **1**, **2**, and **3** in ///.

VIII. Dependence of Yields of 1 upon the Amount of Water.

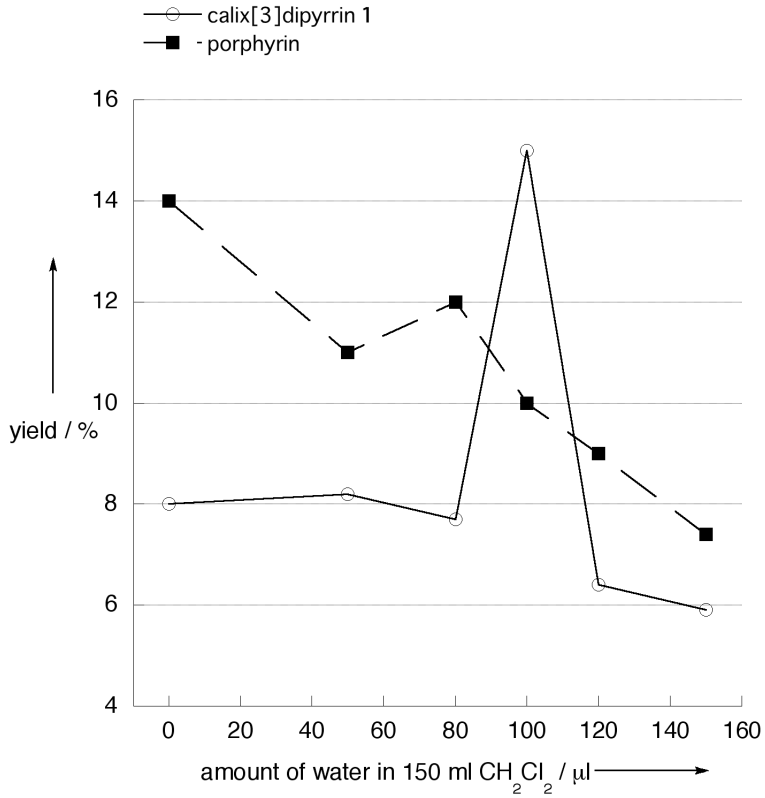

Figure S9. Dependence of yield of **1** upon the amount of water in CH_2Cl_2 (150 ml).

IX. ESR Spectrum of 3

The observed Q-band ESR spectrum (34 GHz) at 20 K was shown in figure S10. No forbidden transition at half field was observed. Then, the observed ESR signals are attributed to the doublet (S = 1/2) state. The ESR signal for the quartet (S = 3/2) state could not be obtained in the temperature range 4 K to 300 K probably due to the broadening of the ESR lines. The spin Hamiltonian was expressed by the summation of the electron Zeeman, nuclear Zeeman, and hyperfine interactions between the electron spin and the nuclear spin of the Cu^{II} ions. The spectrum simulation was performed based on the perturbation theory. The simulated spectrum was given in figure S8. The fitted parameters are shown as follows; S = 1/2, $\mathbf{g}$ = (2.037, 2.050, 2.204), I = 3/2, and $\mathbf{A}_{Cu}$ = (0.90, 0.90, 20.0) mT. The ESR spectrum was characterized by the doublet state (S =1/2). This result is valid for the frustration system.

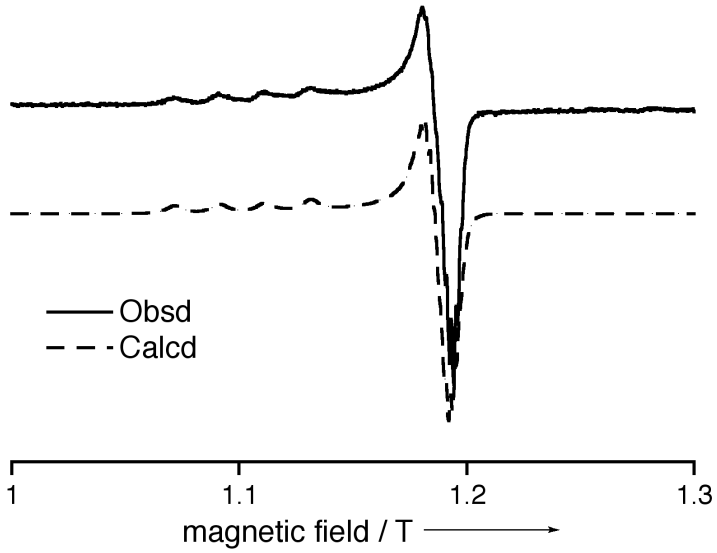

Figure S10. Q-band ESR spectrum of **3** taken at 20 K in toulene.