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SYNTHESIS AND PROPERTIES OF BENZENE-FUSED DIPORPHYRINS WITH VARIOUS METALS

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Dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday

Abstract – Various metalloporphyrins bearing a dihydroethanoisoindole unit were prepared by the inverse-type [3+1] porphyrin synthesis of a bicyclo[2.2.2]octadiene[BCOD]-connected dipyrrole with tetrahydrotripyrrin-dicarbaldehyde followed by metallation. Another [3+1] porphyrin synthesis of the pyrrole-connected porphyrins followed by the second metallation afforded BCOD-connected diporphyrins with different metals. Thermal conversion of the BCOD skeleton into benzene moiety gave π-system-fused diporphyrin with the different metals in a highly pure form.

INTRODUCTION

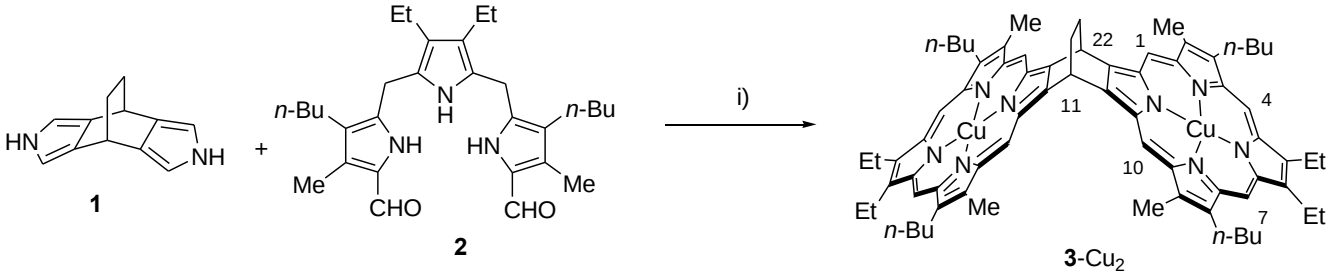
Recently, porphyrinoid compounds with a highly conjugated π-system have been attracted much attention due to not only the potential applicability for optical and opto-electronic materials[1] but also the fundamental interest in their aromaticity.[2] The electronic properties of the porphyrinoids were greatly affected by the center metals. However, in the preparation of such metallated compounds, a severe problem was encountered. Once the targeted large planar π-systems were built, further modification, derivatization, and purification became quite difficult due to their poor solubility in common solvents. For an example, complete introduction or exchange of the center metals of tetrabenzoporphyrin (TBP) was quite difficult after the TBP skeleton was formed.[3] In order to overcome this difficulty, soluble substituents such as bulky alkyl and/or aryl groups were often installed for prevention of the π-π stacking.[4] Introduction of such bulky groups, however, affected not only the stabilities, reactivities, and

structures of the targeted compounds but also the electronic properties of their π-systems, because the π-systems were inevitably distorted by the steric interactions.[5] Long alkyl chains were also employed for this purpose. In this case, other properties such as a mesogenic property were sometimes given by nature of the long alkyl chains.[6] In order to prepare the highly conjugated porphyrinoid π-systems without the effects of solubilizing substituents, we have developed a new synthesis of highly pure π-expanded porphyrins,[7] porphyrinoids,[8] and π-fused diporphyrins[9] based on the final retro-Diels-Alder conversion of precursors bearing bicyclo[2.2.2]octadiene [BCOD] moieties. In this paper, we demonstrate this method for preparation of π-system-fused diporphyrins with paramagnetic center metals and discuss their electronic properties.

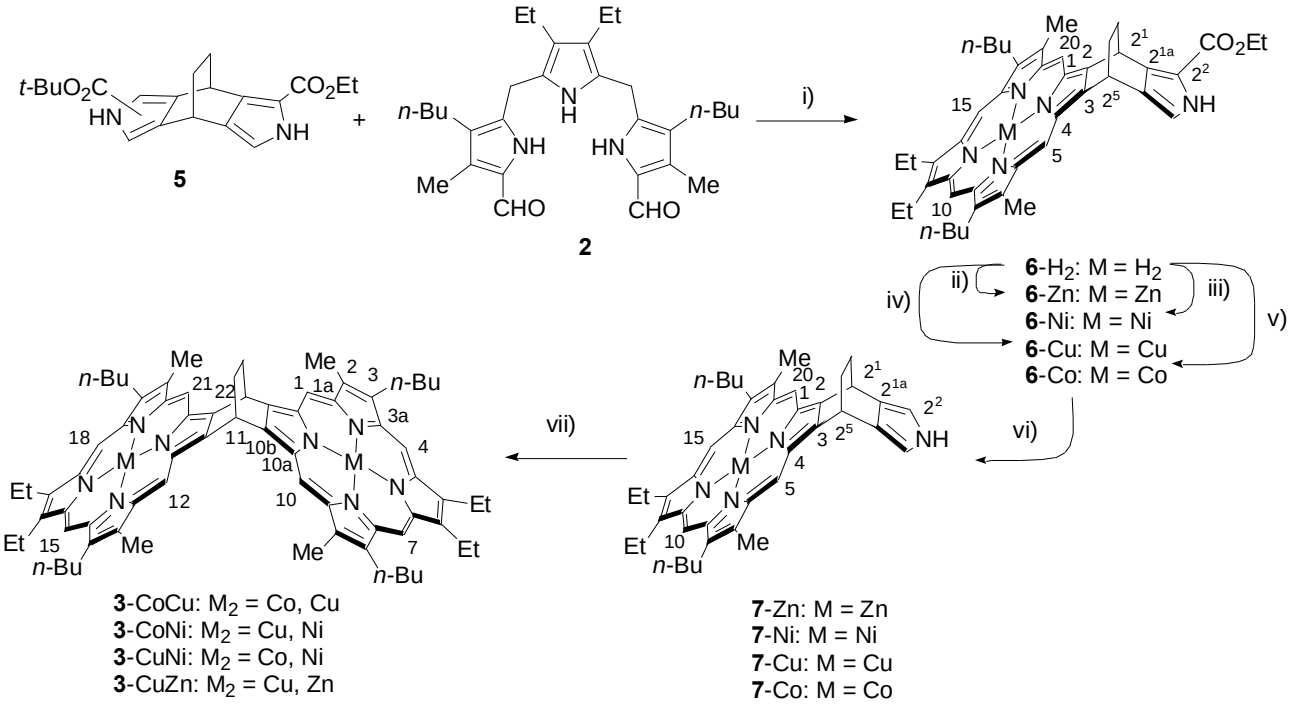
RESULTS AND DISCUSSION

The diporphyrin synthesis was based on the reported procedures illustrated in Schemes and equation.[9] The double inverse [3+1] porphyrin synthesis of α-free BCOD-connected dipyrrole **1**[10] with tetrahydrotripyrrindicarbaldehyde **2**[11] was conducted by successive treatment with TFA, Et_3N, and DDQ. The crude free-base BCOD-connected diporphyrin was metallated with $Cu(OAc)_2·H_2O$ to give BCOD-connected diporphyrinato dicopper **3**-Cu_2 in a 6% yield (Scheme 1).

For the preparation of BCOD-connected diporphyrins with different metals, free-base pyrrole-connected porphyrin **6**-H_2 were prepared by the inverse [3+1] porphyrin synthesis of BCOD-connected *tert*-butyl ethyl dipyrroledicarboxylate **5** (Scheme 2).[9] Metallation of free-base porphyrin **6**-H_2 with $Zn(OAc)_2·2H_2O$, $Ni(OAc)_2·4H_2O$, $Cu(OAc)_2·H_2O$, and $Co(OAc)_2·4H_2O$ gave metalloporphyrins **6**-Zn,[9] **6**-Ni,[9] **6**-Cu, and **6**-Co, in respective yields of 27%, 37%, 37%, and 27% from **5**. The ethyl ester group of **6** was removed by treatment of KOH in ethylene glycol at 180 °C to afford **7** in good yields. Another porphyrin ring formation was achieved at the pyrrole moiety of metalloporphyrins **7** by the inverse [3+1] porphyrin synthesis. In the cases of **7**-Zn and **7**-Co, partial demetallation occurred under the acidic conditions of the porphyrin synthesis, and the second metallation gave inseparable mixtures. On the



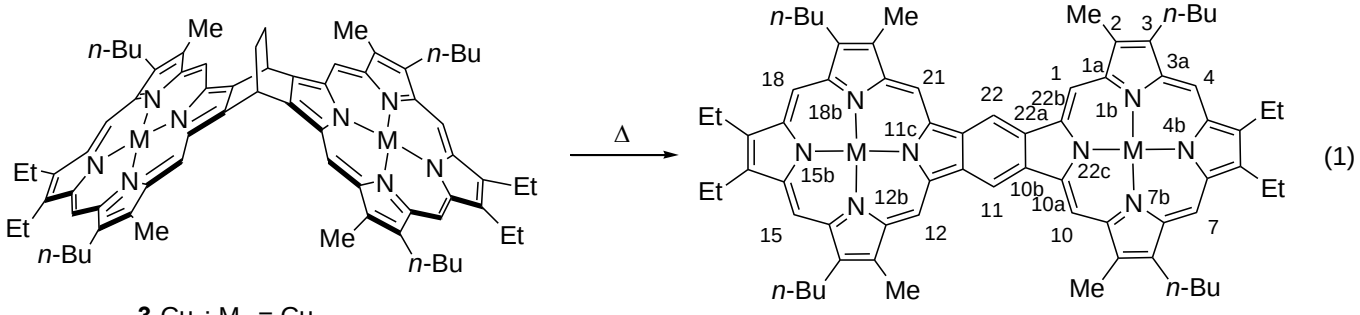
Scheme 1. Preparation of BCOD-connected diporphyrinato copper **3**-Cu_2.
Reagents, condition, and yield: TFA, $CHCl_3$, rt; Et_3N; DDQ; $Cu(OAc)_2$, $CHCl_3$, rt; 6%.



Scheme 2. Preparation of BCOD-connected diporphyrins with different metals. *Reagents, conditions, and yields*: i) TFA, CH_2Cl_2, rt; Et_3N; DDQ. ii) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$, rt; 27% (2 steps); iii) $Ni(OAc)_2 \cdot 4H_2O$, $CHCl_3$/MeOH, rt; 37%; iv) $Cu(OAc)_2 \cdot H_2O$, $CHCl_3$, rt; 37%; v) $Co(OAc)_2 \cdot 4H_2O$, $CHCl_3$/MeOH, refl.; 27%; vi) KOH, $HOCH_2CH_2OH$, 180 °C; **7**-Zn: 74%; **7**-Ni: 64%; **7**-Cu: 90%; **7**-Co: 47%; vii) **2**, TFA, CH_2Cl_2, rt; Et_3N; DDQ; $M(OAc)_2 \cdot xH_2O$, $CHCl_3$; **3**-CoCu: 26%; **3**-CoNi: 33%; **3**-CuNi: 27%; **3**-CuZn: 12%.

other hand, the targeted metal-mixed diporphyrins **3**-CoCu, **3**-CuNi, and **3**-CuZn were successfully obtained in respective yields of 26%, 27%, and 12% by using copper porphyrin **7**-Cu as the starting substrate. This result is easily understood by the stability of metalloporphyrins.[12] Nickel porphyrin **7**-Ni was also used as the substrate and **3**-CoNi was obtained in the similar yield.

Thermal cycloreversion of the BCOD moiety into the benzene unit was examined by thermogravimetric (TG) analysis. In all metallodiporphyrins, the weight loss started at around 135 °C and subsided at 175°C. The half points of weight losses were between 163 and 169 °C.



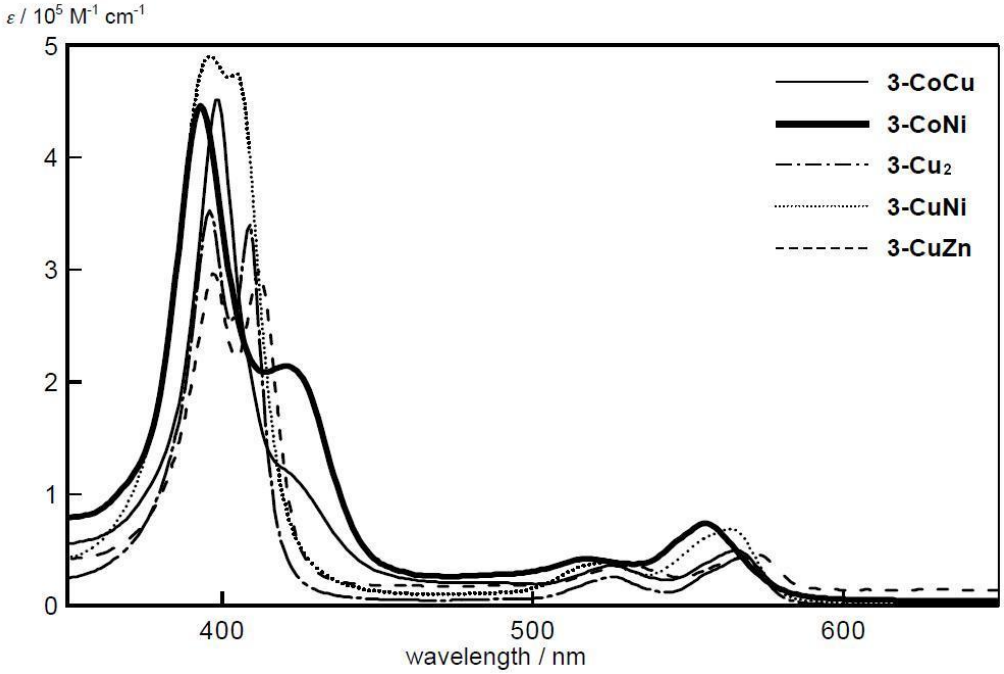


Figure 1. UV-vis spectra of BCOD-connected dimetallodiporphyrins **3**-Cu_2 (dotted broken line), **3**-CoCu (solid line), **3**-CoNi (bold line), **3**-CuNi (dotted line), **3**-CuZn (broken line) in $CHCl_3$.

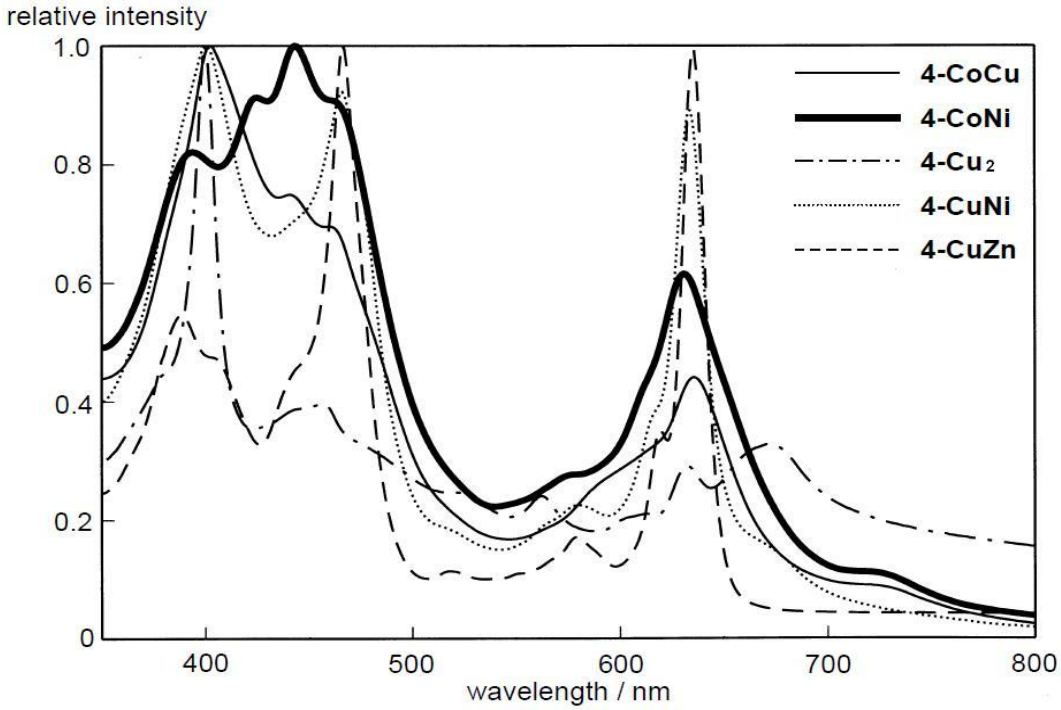


Figure 2. UV-vis spectra of benzene-connected diporphyrins **4**-Cu_2 (dotted broken line, PhCl), **4**-CoCu (solid line, pyridine), **4**-CoNi (bold line, pyridine), **4**-CuNi (dotted line, pyridine), **4**-CuZn (broken line, pyridine).

Absorption spectra of BCOD- and benzene-connected diporphyrins

UV-vis spectra of BCOD-connected diporphyrin **3** are shown in Figure 1. Soret bands of the ethanoisoindoloporphyrins **6**-Zn,[9] **6**-Ni,[9] **6**-Cu, and **6**-Co were observed at 403 (log ε = 5.49), 394 (5.28),

399 (5.52), and 393 (5.26) nm, which were almost the same as those of the octaalkyl-substituted metalloporphyrins. In the case of dicopper diporphyrin **3**-Cu_2, two separated Soret bands were observed at 396 and 409 nm with the similar intensities (log ε = 5.55 and 5.53, respectively). Therefore, one absorption peak shifted 3-nm shorter and another shifted 10-nm longer. The splitting width of 13 nm is similar to that of the corresponding dizinc diporphyrin (15 nm).[9] This is due to the exciton coupling between the porphyrin rings through the BCOD skeleton by homo conjugation.[13] In the cases of metal-mixed BCOD-connected diporphyrins, interesting phenomena were observed in the splitting Soret absorption bands. In the case of copper zinc diporphyrin **3**-CuZn, the similar behavior was observed as the corresponding nickel zinc diporphyrin.[9] The higher-energy Soret-band absorption appeared at slightly shorter wavelength region (397 nm) compared with copper porphyrin **6**-Cu, and the lower-energy Soret band appeared at 412 nm, which was 9-nm longer compared with that of zinc porphyrin **6**-Zn (403 nm).[9] These two intensities are almost the same (log ε = 5.47 and 5.48, respectively). Almost the similar behavior in the UV spectra was reported for the corresponding nickel zinc diporphyrin.[9] The Soret-band absorptions of copper nickel diporphyrin **3**-CuNi appeared at 396 and 404 nm with the similar intensities (log ε = 5.69 and 5.67, respectively). However, both wavelengths were longer than those of the corresponding monometallic porphyrins **6**-Ni (394 nm) and **6**-Cu (399 nm). In the cases of metallodiporphyrins containing cobalt **3**-CoNi and **3**-CoCu, the Soret-band absorptions were quite different from others. The higher-energy absorption bands of **3**-CoNi and **3**-CoCu appeared at the same wavelengths (393 and 399 nm) as the monomeric metalloporphyrins **6**-Ni and **6**-Cu, respectively, and the lower-energy absorptions appeared at 420 and ca. 420 (shoulder) nm with low intensities (log ε = 5.55 and *ca*. 5.1). These phenomena must correlate with the coefficients of β positions which were fused in the BCOD ring and remain to be explained.

UV-vis spectra of benzene-connected diporphyrins **4** are shown in Figure 2. In the cases of **4**-CuNi and **4**-CuZn, strong Soret-like bands appeared at the longer wavelength (466 nm), and modestly strong absorption bands were also observed at the Soret-band region of the monomeric porphyrins (400 nm for **4**-CuNi and 389 and 404 (shoulder) nm for **4**-CuZn). The most distinctive features of these spectra were the sharp longest-wavelength absorptions with very large intensities in the Q-band region (634 nm for **4**-CuNi and 635 nm for **4**-CuZn). Contrarily, the Q-band absorptions of cobalt-containing diporphyrins **4**-CoNi and **4**-CoCu were broad and, therefore, the intensities were lower than others. Moreover, new weak absorptions around 730 nm and several absorption bands in the Soret-band-like region were observed. When red and green laser lights were irradiated to these **4**-Cu_2, **4**-CoNi, **4**-CoCu, and **4**-CuNi solutions, light scattering was observed by Tyndall effect. Therefore, diporphyrins **4**-Cu_2, **4**-CoNi, **4**-CoCu, and **4**-CuNi aggregated even in these highly diluted solutions. In the case of **4**-CuZn, red light emission was observed even by green light irradiation.

In conclusion, BCOD-connected diporphyrins with different metals were prepared by the sequential construction of two porphyrin rings. Zinc and cobalt metals were not suitable for the first metallation, because these metalloporphyrins underwent partial demetallation during the second porphyrin synthesis and/or metallation steps. The nickel and copper derivatives were stable enough. Therefore, metal-mixed diporphyrins containing either one copper or one nickel metal were successfully prepared. Thermal decomposition of the BCOD into benzene gave π-system-fused diporphyrin with the different metals in a highly pure form. The UV-vis spectra of BCOD-connected diporphyrins **3** revealed interesting splitting behaviors in their Soret band absorptions. The benzene-connected diporphyrins **4**-CoCu and **4**-CoNi formed aggregates even in diluted solutions.

EXPERIMENTAL

General: Nomenclature and numbering of the pyrrole-fused porphyrins were done according to recommendations by Moss.[14] However, the IUPAC general rule was applied for the numbering of the BCOD- and benzene-connected diporphyrins due to the lack of a proper rule for such fused systems in the recommendations. Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were obtained with a JEOL AL-400 or EX-400 spectrometer at the ambient temperature by using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard for ^1H and ^{13}C. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. Mass spectra were measured with a JEOL JMS-700 (EI, 70 eV; FAB, glycerin) or Voyager DE Pro (MALDI-TOF). Elemental analyses were performed with a Yanaco MT-5 elemental analyzer. Dehydrated tetrahydrofuran and dichloromethane were purchased from Kanto Chemical Co. and used without further purification. Potassium *tert*-butoxide was sublimed at 200 °C under a reduced pressure (*ca.* 13 Pa) and dissolved in dry THF (1.0 mol L^{-1}). Triethylamine was distilled from CaH_2 under nitrogen and stored on molecular sieves 4A. DBU was distilled under reduced pressure (ca. 2000 Pa) and then stored over molecular sieves 13A. Other commercially available materials were used without further purification. 2,4,6,8-Tetrahydro-4,8-ethanobenzo[1,2-*c*:4,5-*c'*]dipyrrole (**1**),[10] a mixture of *t*-butyl ethyl 2,4,6,8-tetrahydro-4,8-ethano-benzo[1,2-*c*:4,5-*c'*]dipyrro-1,7-dicarboxylate and 1,5-dicarboxylate (**5**),[9] 3,12-dibutyl-7,8-diethyl-2,13-dimethyl-5,10,15,17-tetrahydrotripyrrin-1,14-dicarbaldehyde (**2**),[9] 8,17-dibutyl-2^2-ethoxycarbonyl-12,13-diethyl-7,18-dimethyl-2^1,2^5-ethanoisoindolo[5,6-*b*]porphyrins (**6**-H_2, **6**-Zn, and **6**-Ni)[9] were prepared according to the literature procedures. All porphyrin synthesis reactions were performed in the dark by rapping the reaction vessels with aluminum foil.

8,17-Dibutyl-2^2-ethoxycarbonyl-12,13-diethyl-7,18-dimethyl-2^1,2^5-ethanoisoindolo[5,6-*b*]porphyrinato copper (6-Cu**):** To a mixture of *t*-butyl ethyl 2,4,6,8-tetrahydro-4,8-ethano-benzo[1,2-*c*:4,5-*c'*]dipyrro-1,7-dicarboxylate and 1,5-dicarboxylate (**5**; 0.356 g, 1.00 mmol) was added

TFA (2.0 mL) at rt in the dark, and the solution was stirred for 10 min. After the mixture was diluted with dry-CH_2Cl_2 (64 mL), 3,12-dibutyl-7,8-diethyl-2,13-dimethyl-5,10,15,17- tetrahydrotripyrrin-1,14-dicarbaldehyde (**2**; 0.477 g, 1.00 mmol) was added and the mixture was stirred overnight at rt. Triethylamine (2 mL) and then DDQ (146 mg, 0.64 mmol) were added and the mixture was additionally stirred overnight at rt. The mixture was successively washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated to give crude free-base porphyrin (**6**-H_2). To the residue were added $CHCl_3$ (50 mL) and a saturated solution of $Cu(OAc)_2 \cdot H_2O$ in MeOH (20 mL) and the mixture was stirred for 3 h at rt. The mixture was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel ($CHCl_3$) to give a red powdery solid, which was triturated with MeOH to give 0.280 g (37%) of the title compound as red crystals: mp >246 °C (decomp.); Rf = 0.55 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max} (logε) = 399 (5.52), 524 (4.14), and 562 (4.31). IR (KBr) ν/cm^{-1} = 3292, 2956, 2929, 2860, 1684, and 1144; MS (FAB$^+$) *m/z* = 757 (M^++1); HRMS (FAB$^+$) Calcd for $C_{45}H_{51}CuN_5O_2$+H^+: 757.3417. Found: 757.3420.

8,17-Dibutyl-12,13-diethyl-7,18-dimethyl-2^1,2^5-ethanoisoindolo[5,6-*b*]porphyrinato copper (7-Cu**)**: Porphyrinato copper (**6**-Cu; 75.7 mg, 0.10 mmol) and KOH (3.4 g) were dissolved with ethylene glycol (70 mL) under a nitrogen atmosphere in the dark and the mixture was heated with stirring at 180 °C for 2 h. The mixture was diluted with water at rt and then extracted with EtOAc. The organic extract was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel ($CHCl_3$) to give 63 mg (90%) of the title compound as purple crystals: mp >242 °C (decomp.); Rf = 0.75 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max} (logε) = 399 (5.48), 524 (4.10), and 562 (4.27); MS (FAB$^+$) *m/z* = 685 (M^++1); IR (KBr) ν/cm^{-1} = 2956, 2929, 2860, 1551, 1508, and 1458; HRMS (FAB$^+$) Calcd for $C_{42}H_{47}CuN_5$+H^+: 685.3206. Found: 685.3217.

8,17-Dibutyl-2^2-ethoxycarbonyl-12,13-diethyl-7,18-dimethyl-2^1,2^5-ethanoisoindolo[5,6-*b*]porphyrinato cobalt (6-Co**)**: The crude free-base porphyrin (**6**-H_2; 0.65 g, 0.934 mmol) was dissolved in $CHCl_3$ (100 mL) and a saturated solution of $Co(OAc)_2 \cdot 4H_2O$ in MeOH (14 mL) was added in the dark. The mixture was refluxed for 5 h and then cooled to rt. A 4% aqueous $NaHCO_3$ solution was added and the mixture was stirred for 20 min. The mixture was filtered through a Celite pad, which was washed with $CHCl_3$. The organic phase was separated, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel ($CHCl_3$) to give 0.18 g (27%) of the title compound as red crystals: mp >246 °C (decomp.); Rf = 0.55 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max} (logε) = 393 (5.26), 517 (3.93), and 551(4.15); ^{1}H-NMR (400 MHz): δ = 2.75 (m, 6H), 2.82 (m, 2H), 4.29 (m, 2H), 3.11 (m, 3H), 5.20-5.32 (m, 10H), 5.60 (m, 2H), 7.51 (m, 4H), 7.68 (m, 2H), 7.89 (m, 2H), 8.70 (s, 1H), 9.05 (s, 1H), 9.42 (s, 6H), 9.89 (m, 4H), 12.21 (s, 1H), 12.80 (br, NH), 29.47 (br, 2H), 29.82 (br, 1H), and 30.00 (br, 1H); ^{13}C-NMR (100 MHz) δ = 14.37, 16.10, 20.57, 23.30, 26.20, 26.89, 27.02, 28.08, 29.80,

35.59, 35.62, 35.84, 37.26, 38.38, 61.53, 90.29, 93.76, 97.57, 97.90, 111.57, 113.20, 115.31, 115.59, 115.71, 116.42, 121.66, 132.53, 134.82, 137.74, 150.91, 152.46, 171.62, 180.73, and 184.80; MS (FAB^+) *m/z* = 753 (M^++1); IR (KBr) ν/cm^{-1} = 3298, 2956, 2929, 2860, 1684, 1144, and 837; HRMS (FAB^+) Calcd for $C_{45}H_{51}CoN_5O_2$+H^+: 753.3453. Found: 753.3449.

8,17-Dibutyl-12,13-diethyl-7,18-dimethyl-2^1,2^5-ethanoisoindolo[5,6-*b*]porphyrinato cobalt (7-Co**)**: Porphyrinato cobalt (**6**-Co; 75.3 mg, 0.10 mmol) and KOH (3.4 g) were dissolved with ethylene glycol (70 mL) under a nitrogen atmosphere in the dark and the mixture was heated with stirring at 180 °C for 2 h. After being cooled at rt, the mixture was diluted with water and then extracted with EtOAc. The organic extract was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel ($CHCl_3$) to give 31.8 mg (47%) of the title compound as purple crystals: mp >261 °C (decomp.); Rf = 0.80 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max} (logε): 392 (5.28), 517 (3.96), and 551(4.19); ^{1}H-NMR (400 MHz): δ = 2.72 (m, 6H), 4.21 (m, 2H), 5.16 (m, 12H), 7.21-7.78 (m, 8H), 8.13 (s, 1H), 8.49 (s, 2H), 9.56 (s, 6H), 9.9-10.1 (m, 4H), 12.12 (s, 2H), 29.59 (br, 2H), and 30.07 (br, 2H); MS (FAB^+) *m/z* 681 (M^++1); IR (KBr) ν/cm^{-1}: 3056, 2958, 2929, 2859, 1457, 1261, 1097,n1018, and 802. HRMS (FAB^+): Calcd for $C_{42}H_{47}CoN_5$+H^+, 681.3242. Found: 681.3238.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethyl-11,22-dihydro-11,22-ethanobenzo-[1,2-*b*;4,5-*b*']diporphyrinato dicopper (**3**-Cu_2): To a stirred solution of dipyrrole **1** (46 mg, 0.25 mmol) and tetrahydrotripyrrin-1,14-dicarbaldehyde (**2**; 242 mg, 0.51 mmol) in CH_2Cl_2 (55 mL) was added trifluoroacetic acid (3.05 mL) in the dark under a nitrogen atmosphere. After the mixture was stirred at 50 °C for 24 h, triethylamine (5.4 mL) was slowly added at rt. The mixture was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. Chromatographic separation followed by rinse with MeOH gave 26.6 mg (10%) of the free-base diporphyrin.[9] The free-base porphyrin (19.9 mg, 0.019 mmol) was dissolved in CH_2Cl_2 (150 mL) and a saturated solution of $Cu(OAc)_2 \cdot H_2O$ in MeOH (8 mL) was added. The mixture was stirred overnight at rt. The mixture was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (50% $CHCl_3$/hexane) to give 14 mg (6%) of the title compound as a red powdery solid: mp >169 °C (decomp.); UV-vis ($CHCl_3$) λ_{max} (log ε) = 396 (5.55), 409 (5.53), 525 (4.42), and 568 (4.64); IR (KBr) ν/cm^{-1} 3048, 2958, 2929, 2860, 1458, 1146, and 837; MS (MALDI-TOF^+): *m/z* = 1157.48 (M^+-C_2H_4). Anal. Calcd for $C_{72}H_{82}Cu_2N_8 \cdot 0.5CHCl_3$: C, 69.87; H, 6.67; N, 8.99%. Found: C, 70.16; H, 6.89; N, 8.70%. HRMS (FAB^+) Calcd for $C_{72}H_{82}Cu_2N_8$+H^+: 1185.5333. Found: 1185.5325.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethyl-11,22-dihydro-11,22-ethanobenzo-[1,2-*b*:4,5-*b*']diporphyrinato cobalt copper (3-CoCu**)**: To a solution of isoindoloporphyrinato copper

7-Cu (25.0 mg, 0.0365 mmol) and tetrahydrotripyrrin-1,14-dicarbaldehyde **2** (17.4 mg, 0.0365 mmol) in dry CH_2Cl_2 (11 mL) was added TFA (0.23 mL) at rt in the dark. The mixture was stirred overnight at rt. After the condensation was stopped by addition of triethylamine (0.23 mL) at 0 °C, DDQ (16.6 mg) was added and the mixture was further stirred overnight. The mixture was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was dissolved in $CHCl_3$ (15 mL) and a solution of $Co(OAc)_2 \cdot 4H_2O$ (90.9 mg, 0.365 mmol) in a minimum amount of methanol was added. The mixture was refluxed for 5 h. After being cooled at rt, the mixture was stirred with a 4% aqueous $NaHCO_3$ solution for 20 min. The mixture was filtered through a Celite pad, which was washed with $CHCl_3$. The organic phase was separated, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel to give a crude material, which was recrystallized from $CHCl_3$/MeOH to give 11.3 mg (26%) of the title compound as red crystals: mp >168 °C (decomp.). Rf = 0.92 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max} (log ε) = 399 (5.65), 420 (shoulder, ca. 5.1), 525 (4.56), and 565 (4.70); MS (MALDI-TOF$^+$) *m/z* = 1153.41 (M^+-C_2H_4). Anal. Calcd for $C_{72}H_{82}CoCuN_8 \cdot CHCl_3 \cdot H_2O$: C, 66.46; H, 6.49; N, 8.49%. Found: C, 66.81; H, 6.43; N, 8.60%. HRMS (FAB$^+$) Calcd for $C_{72}H_{82}CoCuN_8$+H^+: 1181.5369. Found: 1181.5361.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethyl-11,22-dihydro-11,22-ethanobenzo-[1,2-*b*:4,5-*b'*]diporphyrinato cobalt nickel (3-CoNi**)**: To a solution of isoindoloporphyrinato nickel **7**-Ni (30.0 mg, 0.0441 mmol) and tetrahydrotripyrrin-1,14-dicarbaldehyde **2** (21.1 mg, 0.0441 mmol) in dry CH_2Cl_2 (13 mL) was added TFA (0.28 mL) at rt in the dark. The mixture was stirred overnight at rt. After the condensation was stopped by addition of triethylamine (0.28 mL) at 0 °C, DDQ (20.1 mg) was added and the mixture was further stirred overnight. The mixture was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was dissolved in $CHCl_3$ (15 mL) and a solution of $Co(OAc)_2 \cdot 4H_2O$ (110 mg, 0.44 mmol) in a minimum amount of MeOH was added. The mixture was refluxed for 5 h. After being cooled at rt, the mixture was stirred with a 4% aqueous $NaHCO_3$ solution for 20 min. The mixture was filtered through a Celite pad, which was washed with $CHCl_3$. The organic phase was separated, washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel to give a crude material, which was recrystallized from $CHCl_3$/MeOH to give 16.6 mg (33%) of the title compound as red crystals: mp >165 °C (decomp.); Rf = 0.92 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max} (log ε) = 393 (5.65), 420 (5.55), 519 (4.62), and 556 (4.86); MS (MALDI-TOF$^+$) *m/z* 1148.52 (M^+-C_2H_4). Anal. Calcd for $C_{72}H_{82}CoN_8Ni$+MeOH: C, 72.51; H, 7.17; N, 9.27%. Found: C, 72.35; H, 6.92; N, 9.38%. HRMS (FAB$^+$) Calcd for $C_{72}H_{82}CoN_8Ni$+H^+: 1176.5426. Found: 1176.5430.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethyl-11,22-dihydro-11,22-ethanobenzo-[1,2-*b*:4,5-*b'*]diporphyrinato copper nickel (3-CuNi**)**: To a solution of isoindoloporphyrinato copper

7-Cu (30.0 mg, 0.0438 mmol) and tetrahydrotripyrrin-1,14-dicarbaldehyde **2** (20.9 mg, 0.0438 mmol) in dry CH_2Cl_2 (13 mL) was added TFA (0.28 mL) at rt in the dark. The mixture was stirred overnight at rt. After the condensation was stopped by addition of triethylamine (0.28 ml) at 0 °C, DDQ (19.9 mg) was added and the mixture was further stirred overnight. The mixture was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was dissolved in $CHCl_3$ (15 mL) and $Ni(OAc)_2 \cdot 4H_2O$ (0.16 g, 0. 65 mmol) was added. The mixture was refluxed overnight. The mixture was filtered through a Celite pad, which was washed with $CHCl_3$. The organic phase washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel to give a crude material, which was recrystallized from $CHCl_3$/MeOH to give 13.5 mg (27%) of the title compound as red crystals: mp >163 °C (decomp.); Rf = 0.92 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max} (log ε) = 396 (5.69), 404 (5.67), 523 (4.59), and 564 (4.84); MS (MALDI-TOF$^+$) *m/z* = 1154.53 (M^+-C_2H_4). Anal. Calcd for $C_{72}H_{82}CuN_8Ni \cdot MeOH$: C, 72.24; H, 7.14; N, 9.23%. Found: C, 72.07; H, 6.98; N, 9.42%. HRMS (FAB$^+$): Calcd for $C_{72}H_{82}CuN_8Ni+H^+$: 1180.5390. Found: 1180.5397.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethyl-11,22-dihydro-11,22-ethanobenzo-[1,2-*b*:4,5-*b'*]diporphyrinato copper zinc (3-**CuZn)**: To a solution of isoindoloporphyrinato copper **7**-Cu (25.3 mg, 0.0369 mmol) and tetrahydrotripyrrin-1,14-dicarbaldehyde **2** (18.3 mg, 0.0383 mmol) in dry CH_2Cl_2 (10 mL) was added TFA (0.24 mL) at rt in the dark. The mixture was stirred overnight at rt. After the condensation was stopped by addition of triethylamine (0.24 mL) at 0 °C, DDQ (17 mg) was added and the mixture was further stirred for 1 h. To the mixture was added $Zn(OAc)_2 \cdot H_2O$ (0.11 g, 0.51 mmol). The mixture was stirred overnight. The mixture was washed with a saturated aqueous $NaHCO_3$ solution, water, and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel to give a crude material, which was triturated with MeOH to give 5.1 mg (12%) of the title compound as a red powder: mp >164 °C (decomp.); Rf = 0.31 (40% $CHCl_3$/hexane); UV-vis ($CHCl_3$) λ_{max} (log ε) = 397 (5.47), 412 (5.48), 531 (4.56), and 572 (4.66); IR (KBr) ν/cm^{-1} = 2958, 2929, 2859, 1457, 1085, 1010, and 800; MS (MALDI-TOF$^+$) *m/z* = 1158.15 (M^+-C_2H_4). Anal. Calcd for $C_{72}H_{82}CuN_8Zn \cdot CHCl_3$: C, 67.04; H, 6.40; N, 8.57%. Found: C, 66.61; H, 6.34; N, 8.59%. HRMS (FAB$^+$): Calcd for $C_{72}H_{82}CuN_8Zn+H^+$: 1186.5328. Found: 1186.5326.

General procedure for retro Diels-Alder reaction of the BCOD-fused diporphyrins: The BCOD-fused diporphyrin (**3**; *ca*. 1 mg) in a glass sample tube was placed in a glass vessel. The vessel was evacuated with an oil rotary pomp and then placed in a glass tube oven, which was pre-heated at 200 °C. After 1 h, the vessel was taken out. The sample was pure enough.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethylbenzo[1,2-*b*:4,5-*b'*]diporphyrinato dicopper (4-**Cu_2)**: green powder; UV-vis (PhCl) λ_{max} (relative intensity) = 400 (1.00), 457 (0.4), 562 (0.24), 632 (0.30), and 672 (0.33); MS (MALDI-TOF$^+$) *m/z* = 1157.29 (M^++1). HRMS (FAB$^+$) Calcd for

$C_{70}H_{78}Cu_2N_8+H^+$:1157.5020. Found: 1157.5027.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethylbenzo[1,2-*b*:4,5-*b'*]diporphyrinato cobalt copper (4-CoCu**)**: green powder; UV-vis (pyridine) λ_{max} (relative intensity) = 402 (1.00), 428 (0.77), 441 (0.75), and 636 (0.44); MS (MALDI-TOF$^+$) *m/z* = 1153.47 (M^++1); HRMS (FAB$^+$) Calcd for $C_{70}H_{78}CoCuN_8+H^+$: 1153.5057. Found: 1153.5055.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethylbenzo[1,2-*b*:4,5-*b'*]diporphyrinato cobalt nickel (4-CoNi**)**: green powder; UV-vis (pyridine) λ_{max} (relative intensity) = 394 (0.82), 425 (0.91), 443 (1.00), and 631 (0.35); MS (MALDI-TOF$^+$) *m/z* = 1148.52 (M^++1). HRMS (FAB$^+$) Calcd for $C_{70}H_{78}CoN_8Ni+H^+$:1148.5115. Found: 1148.5116.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethylbenzo[1,2-*b*:4,5-*b'*]diporphyrinato copper nickel (4-CuNi**)**: green powder; UV-vis (pyridine) λ_{max} (relative intensity) = 400 (1.00), 466 (0.92), 580 (0.22), and 634 (0.89); MS (MALDI-TOF$^+$) *m/z* = 1154.53 (M^++3). HRMS (FAB$^+$) Calcd for $C_{70}H_{78}CuN_8Ni+H^+$: 1152.5079. Found: 1152.5070.

3,8,14,19-Tetrabutyl-5,6,16,17-tetraethyl-2,9,13,20-tetramethylbenzo[1,2-*b*:4,5-*b'*]diporphyrinato copper zinc (4-CuZn**)**: green powder; UV-vis (pyridine) λ_{max} (relative intensity) = 389 (0.55), 404 (shoulder, *ca.* 0.47), 466 (1.00), 579 (0.17), and 635 (0.99); MS (MALDI-TOF$^+$) *m/z* = 1158.25 (M^+). HRMS (FAB$^+$) Calcd for $C_{70}H_{78}CuN_8Zn+H^+$:1158.5015. Found: 1158.5017.

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REFERENCES

1. For examples: M.-H. Qi and G.-F. Liu, *J. Mater. Chem.*, 2003, **13**, 2479; P. Bonifassi, P. C. Ray, and J. Leszczynski, *Chem. Phys. Lett.*, 2006, **431**, 321; P. B. Shea, L. R. Pattison, M. Kawano, C. Chen, J. Chen, P. Petroff, D. C. Martin, H. Yamada, N. Ono, and J. Kanichi, *Synth. Met.*, 2007, **157**, 190; M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos, and E. M. Ni Mhuircheartaigh, *Adv. Mater.*, 2007, **19**, 2737.
2. M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, and L. Szterenberg, *Angew. Chem. Int. Ed.*, 2007, **46**, 7869; Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, and A. Osuka, *Angew. Chem. Int. Ed.*, 2008, **47**, 681; N. Jux, *Angew. Chem. Int. Ed.*, 2008, **47**, 2543.
3. R. P. Linstead and E. G. Noble, *J. Chem. Soc.*, 1937, 933; P. A. Barrett, R. P. Linstead, F. G. Rundall, and G. A. P. Tuey, *J. Chem. Soc.*, 1940, 1079; M. G. H. Vicente, A. C. Walter, and J. A. S.

Cavaleiro, *Tetrahedron Lett.*, 1997, **38**, 3639.

4. H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda, and A. Osuka, *J. Am. Chem. Soc.*, 2002, **124**, 14642; O. Fikikova, A. Galkin, V. Rozhkov, M. Cordero, C. Hägerhäll, and S. Vinogradov, *J. Am. Chem. Soc.*, 2003, **125**, 4882; O. S. Finikova, A. V. Chepracov, I. P. Beletskaya, P. J. Carroll, and S. A. Vinogradov, *J. Org. Chem.*, 2004, **69**, 522; O. S. Finikova, A. V. Cheprakov, and S. A. Vinogradov, *J. Org. Chem.*, 2005, **70**, 9562; O. Ongayi, V. Gottumukkala, F. R. Fronczek, and M. Graça H. Vicente, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 1665.
5. M. O. Senge, '*Highly Substituted Porphyrins*,' in '*The Porphyrin Handbook,' Vol.1* (Eds.: K. M. Kadish, K. M. Smith, and R. Guilard), Academic Press, San Diego, 2000, chapter 6, pp.239-347.
6. M.-H. Qi and G.-F. Liu, *J. Mater. Chem.*, 2003, **13**, 2479; A. Segade, F. Lopez-Calahorra, and D. Velasco, *J. Phys. Chem. B*, 2008, **112**, 7395.
7. T. Okujima, Y. Hashimoto, G. Jin, H. Yamada, H. Uno, and N. Ono, *Tetrahedron*, 2008, **64**, 2405; H. Yamada, K. Kusibe, T. Okujima, H. Uno, and N. Ono, *Chem. Commun.*, 2006, 383; H. Uno, T. Ishikawa, T. Hoshi, and N. Ono, *Tetrahedron Lett.*, 2003, **44**, 5163; S. Ito, N. Ochi, H. Uno, T. Murashima, and N. Ono, *Chem. Commun*. 2000, 893; S. Ito, N. Ochi, T. Murashima, H. Uno, and N. Ono, *Heterocycles*, 2000, **52**, 399; S. Itoh, T. Murashima, H. Uno, and N. Ono, *J. Chem. Soc., Chem. Commun.*, 1998, 1661.
8. J. Mack, M. Bunya, Y. Shimizu, H. Uoyama, N. Komobuchi, T. Okujima, H. Uno, S. Ito, M. J. Stillman, N. Ono, and N. Kobayashi, *Chem. Eur. J.* 2008, **14**, 5001; H. Uno, Y. Shimizu, H. Uoyama, Y. Tanaka, T. Okujima, and N. Ono, *Eur. J. Org. Chem.*, 2008, 87; Y. Inokuma, T. Matsunari, N. Ono, H. Uno, and A, Osuka, *Angew. Chem. Int. Ed.*, 2005, **44**, 1856; T. Okujima, N. Komobuchi, Y. Shimizu, H. Uno, and N. Ono, *Tetrahedron Lett*, 2004, **45**, 5461; Y. Shimizu, Z. Shen, T. Okujima, H. Uno, and N. Ono, *Chem. Commun*., 2004, 374; N. Ono, K. Kuroki, E. Watanabe, N. Ochi, and H. Uno, *Heterocycles*, 2004, **62**, 365.
9. H. Uno, K. Nakamoto, K. Kuroki, A. Fujimoto, and N. Ono, *Chem. Eur. J.*, 2007, **13**, 5773; S. Ito, K. Nakamoto, H. Uno, T. Murashima, and N. Ono, *Chem. Commun.*, 2001, 2696.
10. H. Uno, S. Ito, M. Wada, H. Watanabe, M. Nagai, A. Hayashi, T. Murashima, and N. Ono, *J. Chem. Soc., Perkin Trans. 1*, 2000, 4347.
11. J. L. Sessler, M. R. Johnson, and V. Lynch, *J. Org. Chem.*, 1987, **52**, 4394; S. V. Shevchuk, J. M. Davis, and J. L. Sessler, *Tetrahedron Lett.*, 2001, **42**, 2447.
12. J. W. Buchler, '*Static Coordination Chemistry of Metalloporphyrins*,' in *Porphyrin and Metalloporphyrins* (Ed: K. M. Smith), Elsevier, Amsterdam, 1975, chapter 5, pp.157-231.
13. J. B. Paine, III, D. Dolphin, and M. Gouterman, *Can. J. Chem.*, 1978, **56**, 1712.
14. G. P. Moss, *Pure & Appl. Chem.*, 1987, **59**, 779.