Regioselective Metallation of Octaphyrin(1.0.1.0.1.0.1.0) with Mixed Bipyrrole Units by Using $\mathrm{Cu^{II}}$ or $\mathrm{Cu^{I}}$

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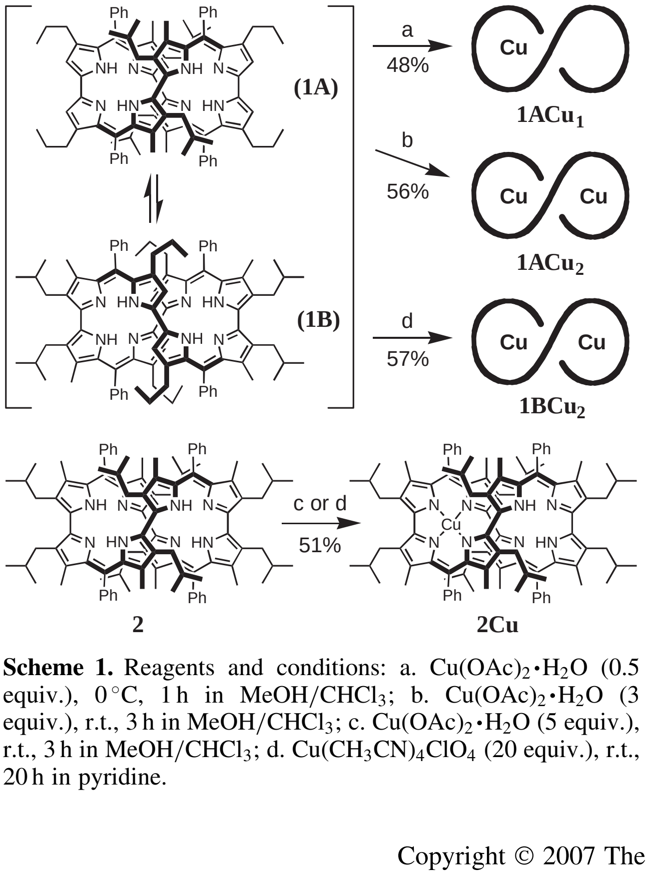
Metallation of *meso*-tetraphenyloctaphyrin(1.0.1.0.1.0.1.0) with mixed bipyrrole units with $\mathrm{Cu^{II}}$ or $\mathrm{Cu^{I}}$ resulted in the selective formation of $\mathrm{Cu^{II}}$ octaphyrins in two different figure eight loop conformations.

Octaphyrin is a member of porphyrinoids containing eight pyrroles.[1] These octaphyrins and their metal complexes have been drawing great attention due to their interesting chemistry such as anion binding,[2] novel skeletal rearrangement,[3] optical resolution,[4] supramolecular chirogenesis,[5] and multi-step redox.[6] In an attempt to explore axial coordination chemistry of octaphyrin metal complexes, we have recently synthesized octaphyrin(1.0.1.0.1.0.1.0) **1** and its cobalt(II) complex with the unique figure eight structures composed of two pairs of different bipyrroles.[7] Although bulky substituents at the pyrrole β-position help increase the yield of octaphyrins, they interfere with complexation of ligand substrates at the metal sites. These conflicting requirements were balanced in the free base **1**, which is able to take two figure eight loop conformations, (**1A**) and (**1B**), as shown in Scheme 1. The latter is of great interest because the propyl-substituted bipyrrole at the crossing point of the figure eight loop does not interfere with the metal site. We describe in this paper that each conformation (**1A**) or (**1B**) could be fixed selectively as a $\mathrm{Cu^{II}}$ complex using $\mathrm{Cu^{II}}$ or $\mathrm{Cu^{I}}$ salt as a metal source.



Scheme 1. Reagents and conditions: a. $\mathrm{Cu(OAc)_2{\cdot}H_2O}$ (0.5 equiv.), 0 °C, 1 h in $\mathrm{MeOH/CHCl_3}$; b. $\mathrm{Cu(OAc)_2{\cdot}H_2O}$ (3 equiv.), r.t., 3 h in $\mathrm{MeOH/CHCl_3}$; c. $\mathrm{Cu(OAc)_2{\cdot}H_2O}$ (5 equiv.), r.t., 3 h in $\mathrm{MeOH/CHCl_3}$; d. $\mathrm{Cu(CH_3CN)_4ClO_4}$ (20 equiv.), r.t., 20 h in pyridine.

2,7,20,25-Tetrapropyl-11,16,29,34-tetramethyl-12,15,30,33-tetraisobutyl-9,18,27,36-*meso*-tetraphenyloctaphyrin (**1**) reacted with $\mathrm{Cu^{II}}$ acetate (0.5 equiv.) in $\mathrm{MeOH/CHCl_3}$ (1/3) at 0 °C for 1 h under argon to give a mononuclear copper(II) complex **1ACu$_1$** in 48% yield. A dicopper(II) complex **1ACu$_2$** was obtained in 56% yield when **1** was reacted with $\mathrm{Cu^{II}}$ acetate (3 equiv.) at room temperature for 3 h (Scheme 1). 2,7,11,16,20,25,29,34-Octamethyl-3,6,12,15,21,24,30,33-octaisobutyl-9,18,27,36-*meso*-tetraphenyloctaphyrin (**2**) gave a mononuclear copper(II) complex **2Cu** in 51% yield as a major product even if 5 equiv. of $\mathrm{Cu^{II}}$ acetate was used. It was difficult to give a dicopper(II) complex of **2** probably because of the steric hindrance of the isobutyl substituents at the second coordination site in the figure eight loop.

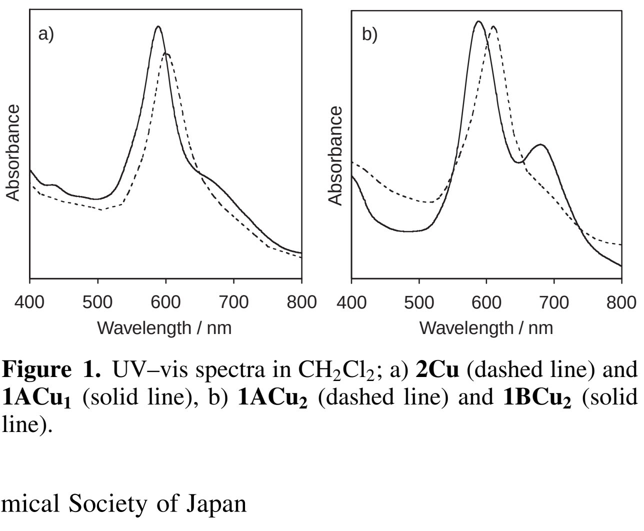


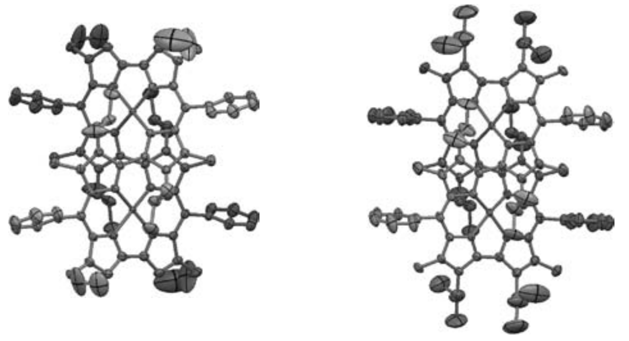
Figure 1. UV–vis spectra in $\mathrm{CH_2Cl_2}$; a) **2Cu** (dashed line) and **1ACu$_1$** (solid line), b) **1ACu$_2$** (dashed line) and **1BCu$_2$** (solid line).

The UV–vis absorption bands of the mononuclear complexes **1ACu$_1$** and **2Cu** at 589.0 and 598.5 nm, respectively, are blue-shifted relative to that of the dinuclear complex **1ACu$_2$** at 609 nm as shown in Figure 1. The X-ray crystallographic analysis showed that both **1ACu$_1$**[8] and **1ACu$_2$**[8] are in the type-(**1A**) conformation with the isobutyl-substituted bipyrrole at the crossing point and there is little difference in their structural features (see Table 1 and Figure 2). In the X-ray structure of **2Cu**,[8] the copper atom is disordered equally between the two coordination sites in the same way as **1ACu$_1$**. The *cis*-N–C_α–C_α–N torsion angles (6.0 and 6.5°) of **1ACu$_1$** and **1ACu$_2$** are smaller and their *trans*-N–C_α–C_α–N torsion angles (159.9 and 155.7°) are larger than the corresponding angles (17.0 and 151.8°) of **2Cu**, while the N–C_α–C_{meso}–C_α (or C_α–C_{meso}–C_α–N) torsion angles (24.0 and 23.1°) of **1ACu$_1$** and **1ACu$_2$** are larger than that (9.8°) of **2Cu**. Thus, the steric constraint at the bipyrrole 3,3′-position in-

Table 1. Distances (Å) and angles (°) in the X-ray structures of **$1ACu_2$**, **$1ACu_1$**, and **2Cu**[a]

	$1ACu_2$	**$1ACu_1$**	**2Cu**
Cu–N	1.93	1.96	1.96
N–Cu–N	91.2	91.3	90.9
N–C_α–C_α–N	6.5 155.7	6.0 159.9	17.0 151.8
N–C_α–C_{meso}–C_α	23.1	24.0	9.8

[a]All data are averaged values.



$1ACu_1$ **2Cu**

Figure 2. 50% Level ORTEP drawings of **$1ACu_1$** and **2Cu**. The Cu atom is disordered between two coordination sites.

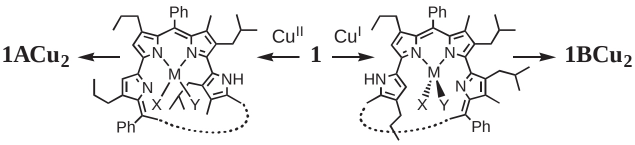
duces twisting in the bipyrrole unit with keeping the planarity of the dipyrrolylmethene unit.

2Cu was obtained in a moderate yield alternatively by reacting **2** with $Cu(CH_3CN)_4ClO_4$ as a metal source. Therefore, the Cu^I is also useful for synthesizing octaphyrin copper(II) complexes. The reaction of **1** with the Cu^I salt gave a dicopper(II) complex **$1BCu_2$** in 57% yield (Scheme 1). The observed MS signal of **$1BCu_2$** at 1444.76 is substantially the same as that of **$1ACu_2$** (1444.34 obs.; 1444.67 calcd for $C_{92}H_{100}N_8Cu_2$). However, the UV–vis main band at 588.5 nm of **$1BCu_2$** is blue-shifted relative to the band at 609 nm for **$1ACu_2$** and the intensity of the shoulder band of **$1BCu_2$** at 682.5 nm was remarkably increased (see Figure 1b). An ESR signal was observed both for **$1ACu_2$** and **$1BCu_2$** with slightly different g-values at 2.07 and 2.08, respectively. But, the signal of **$1BCu_2$** with 250.5 gauss linewidth is weaker and broader than that of **$1ACu_2$** with 222.0 gauss linewidth. Vogel and co-workers observed the π-electron-based redox processes at −2.10, −1.36, −0.45, 0.01, and 1.08 V relative to Ag/AgCl in the CV study of dicopper(II) complex of 2,3,6,7,11,12,15,16,20,21,24,25,29,30,33,34-hexadecaethyloctaphyrin(1.0.1.0.1.0.1.0) (**$3Cu_2$**).[6] **$1ACu_2$** and **$1BCu_2$** showed similar CV profiles to that of **$3Cu_2$** as shown in Table 2. But, the first oxidation potential of **$1BCu_2$** at −0.53 V was shifted to more negative region by 60 mV than that of **$1ACu_2$** at −0.47 V and the first reduction potential of **$1BCu_2$** at −1.25 V was shifted to more positive region by 220 mV than that of **$1ACu_2$** at −1.47 V. Thus, the remarkable differences in the UV–vis, ESR, and CV between **$1ACu_2$** and **$1BCu_2$** strongly suggest that **$1BCu_2$** is isomeric with **$1ACu_2$** and possesses type-(**1B**) conformation with the propyl-substituted bipyrrole at the crossing point.

Table 2. CV data of **$1ACu_2$**, **$1BCu_2$**, and **$3Cu_2$** in CH_2Cl_2 (Volt)[a]

Compound	Eox$_3$	Eox$_2$ ($L^{+\bullet}/L^{2+}$)	Eox$_1$ ($L/L^{+\bullet}$)	Ered$_1$ ($L/L^{-\bullet}$)	Ered$_2$ ($L^{-\bullet}/L^{2-}$)	HL gap
$1ACu_2$	0.95	0.06	−0.47	−1.47		1.00
$1BCu_2$	0.75	−0.08	−0.53	−1.25	−1.97	0.72
$3Cu_2$	1.08	0.01	−0.45	−1.36	−2.10	0.91

[a]Scan rate: 0.1 V/s; 0.1 M Bu_4NPF_6; $E = (E_{pc} + E_{pa})/2$; potential vs ferrocene (0.01 V); WE: Glassy Carbon; CE: Pt wire; RE: Ag/AgCl.



Scheme 2. Plausible intermediates in the metal insertion to octaphyrin **1** by using Cu^{II} and Cu^I.

We assume that one of the four dipyrrolylmethene units coordinates to the metal as a bidentate ligand in the first step of metal insertion to octaphyrin as shown in Scheme 2. A tetrahedral Cu^I prefers type-(**1B**) conformation to type-(**1A**) conformation because of the steric hindrance of the isobutyl group inside the cavity of the latter. Although a square planar Cu^{II} can keep away from the isobutyl group in both conformations, the nitrogen atom of the highly planar *cis*-propylbipyrrole unit can coordinate more easily to Cu^{II} to lead to type-(**1A**) complex.

In summary, selective synthesis of Cu^{II} complexes of octaphyrin **1** in two different figure eight loop conformations was achieved by changing the metal source, Cu^I or Cu^{II}. The substitution pattern of peripheral alkyl groups of octaphyrin **1** has a great influence on the figure eight loop structure, thus affecting cyclic voltammograph and UV–vis and ESR spectra.

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8 Crystal data for a) **$1ACu_1$** $C_{92}H_{102}N_8Cu$, M_r 1383.36, monoclinic, space group $C2/c$, $a = 27.287(2)$, $b = 17.463(2)$, $c = 21.478(2)$ Å, $\beta = 120.975(2)°$, $Z = 4$, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0915$, $wR2 = 0.2743$, $GOF = 1.072$, CCDC 629150; b) **$1ACu_2$** $C_{92}H_{100}N_8Cu_2 \cdot C_6H_{14}$, M_r 1531.05, monoclinic, space group $I2/a$, $a = 21.307(3)$, $b = 17.384(2)$, $c = 24.820(3)$ Å, $\beta = 107.721(2)°$, $Z = 4$, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0820$, $wR2 = 0.2104$, $GOF = 1.032$, CCDC 629149; c) **2Cu** $C_{100}H_{118}N_8Cu$, M_r 1495.65, monoclinic, space group $C2/c$, $a = 26.115(4)$, $b = 17.508(4)$, $c = 20.856(4)$ Å, $\beta = 106.306(5)°$, $Z = 4$, final R indices [$I > 2\sigma(I)$]: $R1 = 0.1071$, $wR2 = 0.2948$, $GOF = 1.042$, CCDC 629151.

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