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Dinuclear and Tetranuclear Copper(II) Complexes with a Ligand Bearing Phthalocyanine and Schiff-Base Coordination Sites

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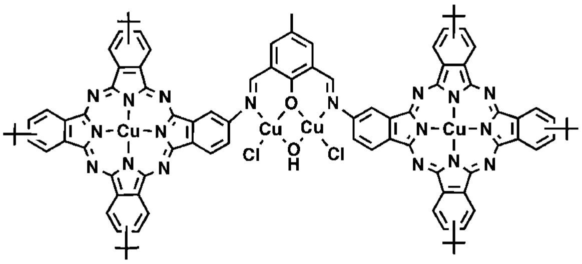
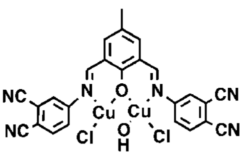
Dinuclear and tetranuclear copper(II) complexes with a ligand bearing phthalocyanine and Schiff-base coordination sites were prepared and characterized. The dinuclear complex has two copper(II) phthalocyanine units linked by 2,6-diiminomethyl-4-methylphenol. The imino nitrogen (Schiff-base) coordinates to two more copper(II) ions to give a tetranuclear copper(II) complex composed of a hydroxo- and phenoxo-bridged copper(II) dinuclear unit and two copper(II) phthalocyanine units. Magnetic, spectroscopic, and electrochemical studies showed that there is no significant interaction among the two copper(II) phthalocyanine units and the hydroxo- and phenoxo-bridged dinuclear unit.

Metallophthalocyanines ([M(pc)]) have received great interests, because of their unique properties based on the extended π system, one of which is their intensive absorptions in the visible region (ca. 680 nm ($\varepsilon \approx 10^5\,\mathrm{dm^3\,cm^{-1}\,mol^{-1}}$)).[1,2] They have been also recognized as industrially important materials and has been used in many applications, including photoconductivity agents in photocopying machines, chemical sensors, electrochromic devices, photodynamic therapy (PDT), etc.[1–3] Schiff-base complexes have also become attractive for their interesting electrochemical, catalytic, magnetic properties, etc.[4] If phthalocyanine (pc) and Schiff-base complexes are covalently combined and located closely in a complex molecule, some new interesting properties should be observed based on the pc–Schiff-base combination. To the best of our knowledge, such multinuclear complexes have not been reported, although porphyrazine complexes combined with salen-like (H_2salen = *N*,*N*′-disalicylideneethylenediamine) tetradentate compartment Schiff-base ligand units have been reported by Hoffman's group.[5] In the present study, we have prepared dinuclear and tetranuclear complexes with a ligand (H_5L^1) bearing phthalocyanine and Schiff-base coordination sites, $[Cu_2(HL^1)]\cdot 3H_2O$ (**1**) and $[Cu_4(L^1)Cl_2(\mu\text{-}OH)]\cdot C_6H_6$ (**2**). In complex **1**, two copper(II) ions are located in the pc rings. Complex **2** is made up of two outside auxiliary Cu^{II}(pc) units and an inside dinuclear unit with two copper(II) ions coordinated by Schiff-base nitrogens, chloride ions, and bridging hydroxide and phenoxide oxygens (Scheme 1a). The dinuclear copper(II) complex $[Cu_2(L^2)Cl_2(\mu\text{-}OH)]\cdot 0.5H_2O$ (**3**), of which structure is shown in Scheme 1b, was also prepared as a reference to characterize the temperature-dependent magnetic susceptibility behavior of **2**. Electrochemical properties of **1** and **2** are discussed in relation to a tetranuclear complex **4**, which is shown in Scheme 2,[6] because **4** consists of the same dinuclear core as that of **2** and two covalently bonded auxiliary mononuclear copper(II) units. Here, we mainly report on syntheses of the pc–Schiff-base fused ligand and its copper(II) complexes, **1** and **2**, and their magnetic, spectroscopic, and electrochemical properties.



(a) $[Cu_4(L^1)Cl_2(\mu\text{-}OH)]$



(b) $[Cu_2(L^2)Cl_2(\mu\text{-}OH)]$

Scheme 1.

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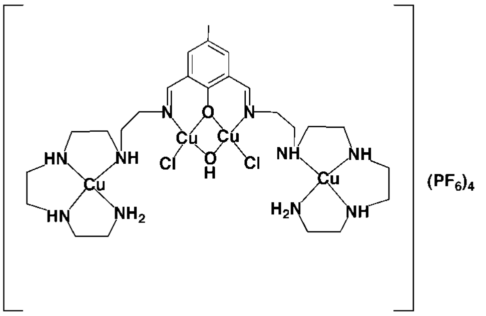


Scheme 2.

Experimental

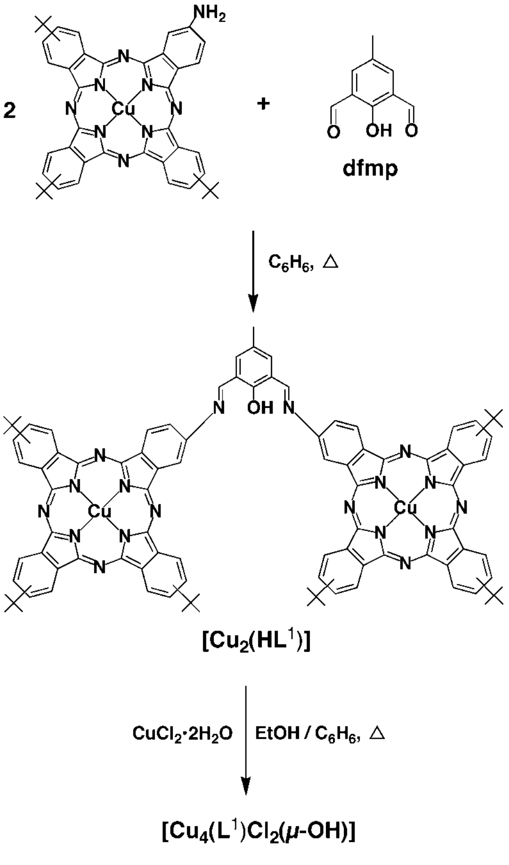
Syntheses of Complexes. Copper(II) phthalocyanine with an amino group and three *t*-butyl groups ([Cu{pc(*t*-Bu)$_3$(NH$_2$)}]) was prepared according to the method described in the literature.[7] 2,6-Diformyl-4-methylphenol (dfmp) was also prepared by the method described in the literature.[8]

[Cu$_2$(HL^1)]·3H$_2$O (1): [Cu{pc(*t*-Bu)$_3$(NH$_2$)}] (96 mg, 0.126 mmol) and dfmp (10.2 mg, 0.062 mmol) were dissolved in dry benzene (20 mL) and refluxed for 12 h. After the solvent was removed by evaporation, the resultant solid was collected, washed with methanol, and employed for gel-permeation chromatography using Bio-Beads SX-1 (Bio-rad) with benzene as an eluent. The yield was 85 mg (81%). Anal. Found C, 68.92; H, 5.42; N, 14.41%. Calcd for $C_{97}H_{92}Cu_2N_{18}O_4$: C, 68.49; H, 5.45; N, 14.82%. MALDI-TOF-MS: calcd for $C_{97}H_{86}Cu_2N_{18}O$ ([Cu$_2$(HL^1)]): 1645; found 1645.

[Cu$_4$(L^1)Cl$_2$(μ-OH)]·C$_6$H$_6$ (2): Complex **1** (50 mg, 0.029 mmol) and copper(II) chloride dihydrate (20.6 mg, 0.12 mmol) were dissolved in a small amount of ethanol–benzene (10:1) solvent mixture (ca. 10 mL) and refluxed for 3 h. The resultant solution was concentrated by evaporation, and the precipitate that deposited was collected by suction filtaration, washed with ethanol, and dried by heating under vaccum. The yield was 9.5 mg (17% based on the dinuclear complex **1**). Anal. Found C, 64.20; H, 5.03; N, 13.55%. Calcd for $C_{103}H_{92}Cl_2Cu_4N_{18}O_2$: C, 63.80; H, 4.78; N, 13.00%.

[Cu$_2$(L^2)Cl$_2$(μ-OH)]·0.5H$_2$O (3): Copper(II) chloride dihydrate (0.34 g, 2.0 mmol), dfmp (0.146 g, 0.89 mmol), and 4-aminophthalonitrile (0.286 g, 2.0 mmol) were dissolved in ethanol (20 mL) and refluxed for 1 h. The resultant precipitate was collected by filtration, washed with ethanol, and dried over P_2O_5 under vacuum. The yield was 0.13 g (23% based on dfmp). Anal. Found C, 47.06; H, 2.17; N, 12.91; Cu, 19.3%. Calcd for $C_{25}H_{15}Cl_2Cu_2N_6O_{2.5}$: C, 47.11; H, 2.37; N, 13.18; Cu, 19.9%.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanaco CHN CORDER MT-5. Analysis of copper ion was carried out with a Hitachi Z-5000 Polarized Zeeman Atomic Absorption Spectrophotometer. Magnetic susceptibilities were measured by using the Faraday method over the temperature range of 5–300 K with a magnetic field of 0.5 T. The susceptibilities were corrected for diamagnetism of constituent atoms using Pascal's constant.[9] EPR and electronic spectra were measured on JEOL-1X and Shimadzu UV-3100 spectrometers, respectively. Cyclic voltammograms were measured in dichloromethane containing tetrabutylammonium perchlorate (TBAP) on a BAS 100BW Electrochemical Workstation. A glassy carbon disk (1.5 mm radius), a platinum wire, and an Ag/Ag$^+$ (TBAP/CH$_3$CN) electrode were used as working, counter, and reference electrodes, respectively. Ferrocene (Fc) was used as an internal standard, and all of the potentials are quoted relative to Fc$^+$/Fc couple. The TOF mass spectrum was recorded on a Bruker Daltonics autoflex-T1 mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix.



Scheme 3.

Results and Discussion

The synthetic procedure to prepare the tetranuclear copper(II) complex **2** through dinuclear complex **1** is illustrated in Scheme 3. The peripheral amino group on the pc ring reacts with carbonyl group of 2,6-diformyl-4-methylphenol (dfmp) to give the Schiff-base coordination site. The formation of **1** was confirmed by the MALDI-TOF mass spectrum and elemental analysis in addition to the absorption spectrum showing a Q band peak around 680 nm (vide infra). The reaction of **1** with copper(II) chloride dihydrate in an ethanol–benzene solvent mixture gave the tetranuclear complex **2**, in which two copper(II) ions coordinated by Schiff-base imine nitrogens and chloride ions are bridged by hydroxide oxygen as well as phenoxide one from the tetranucleating ligand itself. The hydroxide bridge is known to be occasionally introduced in the formation of copper(II) dinuclear complexes upon reacting copper(II) salts and multidentate ligands.[6,10,11] Tetranuclear copper(II) complex **4** (Scheme 2), which has the same copper(II) dinulear core with phenoxide and hydroxide bridges as that of **2** and two copper(II) mononuclear auxiliary units, has been prepared by the reaction of μ-chloro-μ-(2,6-diformyl-4-methylphenolato)dichlorodicopper(II) and 1,4,7,10,13-pentaazatridecanecopper(II) ion.[6]

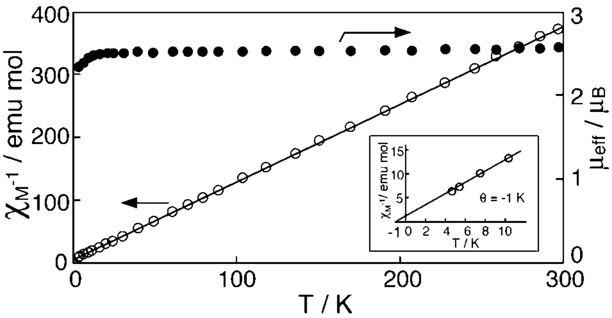


Fig. 1. Temperature dependences of magnetic moment and reciprocal χ_M values per the dinuclear molecule for **1**. Reciprocal χ_M values in the temperature range close to 0 K are displayed in the inset.

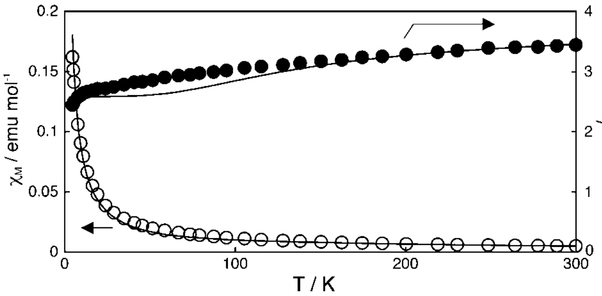
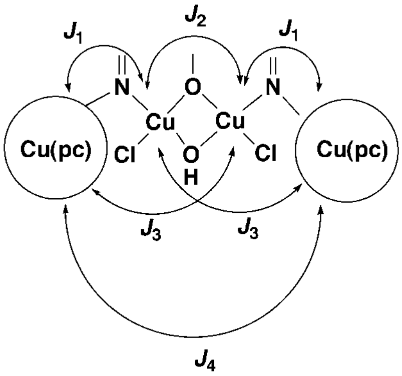


Fig. 2. Temperature dependences of magnetic susceptibility and moment per the tetranuclear molecule for **2**. The solid lines were calculated with the parameters described in the text.



Scheme 4.

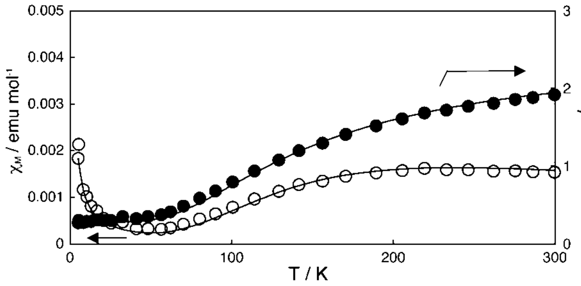


Fig. 3. Temperature dependences of magnetic susceptibility and moment per the dinuclear molecule for **3**. The solid lines were calculated with the parameters described in the text.

Temperature dependences of effective magnetic moment (μ_{eff}) and reciprocal susceptibility ($1/\chi_M$) and magnetic moment and susceptibility (χ_M) are shown for **1** and **2** in Figs. 1 and 2, respectively. The moment for **1** is 2.53 μ_B at room temperature (298 K), which is for two magnetically independent $S = 1/2$ spins of copper(II) ions residing in the pc ring. The temperature variation of $1/\chi_M$ could be fully explained with Curie–Weiss equation[12] with a small minus θ ($= -1$ K) value (see the inset of Fig. 1), indicating that the interaction between copper(II) ions in pc rings is very weak. The magnetic moment of **2** is 3.44 μ_B at room temperature (300 K), which is slightly lower than the spin-only value (3.46 μ_B) for four $S = 1/2$ spins, and it decreases steadily with a decrease in the temperature, falling down to 2.44 μ_B at 4.6 K. This behavior implies that antiferromagnetic interaction operates in **2**. As shown by the model illustrated in Scheme 4, four exchange parameters, J_1, J_2, J_3, and J_4, should be take into account to simulate the magnetic susceptibility behavior for the tetranuclear system, of which the spin Hamiltonian is described by $\boldsymbol{H} = -2J_1(\boldsymbol{S}_1 \cdot \boldsymbol{S}_3 + \boldsymbol{S}_2 \cdot \boldsymbol{S}_4) - 2J_2\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 - 2J_3(\boldsymbol{S}_1 \cdot \boldsymbol{S}_4 + \boldsymbol{S}_2 \cdot \boldsymbol{S}_3) - 2J_4\boldsymbol{S}_3 \cdot \boldsymbol{S}_4$. By using the van Vleck equation, the theoretical expression is introduced for the tetranuclear system.[13] In the present case, the parameters J_3 and J_4 were fixed at zero, because the distances between the magnetic centers for the interactions corresponding to the parameters J_3 and J_4 are both too long to affect the magnetic behavior of **2**.[14] In Fig. 2, the fitting curve is drawn using $J_2 = -100\,\text{cm}^{-1}$, $J_1 = J_3 = J_4 = 0\,\text{cm}^{-1}$, $g = 2.1$, $N\alpha = 60 \times 10^{-6}$ emu mol^{-1}, and $p = 0$, where g is the Landé g factor, p the fraction of mononuclear impurity, and $N\alpha$ the temperature-independent paramagnetic term. The fit indicates that a fairly large interaction ($J_2 = -100\,\text{cm}^{-1}$) operates between copper(II) ions within the inner dinuclear unit, but the interaction between copper(II) ions in the pc ring and the dinuclear core is negligible ($J_1 = 0\,\text{cm}^{-1}$). The magnetic behavior could not be reproduced completely in the temperature range of ca. 20–120 K, even when other parameter values were employed in the magnetic simulation. It is difficult to find the reason, because there is no crystal structural data available for **2**; the existence of isomers due to *t*-butyl groups introduced on different peripheral positions of the pc rings makes isolation of the single crystals impossible. In order to undersatnd the strong interaction $J_2 = -100$ cm^{-1} of **2**, we prepared dinuclear complex **3**, which has basically the same dinuclear core structure as that of **2**, and measured its temperature-dependent magnetic susceptibility. The temperature-dependent magnetic behavior, which is shown in Fig. 3, was simulated using the Bleaney–Bowers equation[15] for the dinuclear copper(II) system based on the spin Hamiltonian $\boldsymbol{H} = -2J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$, where J describes the interaction between copper(II) magnetic centers in **3**. The obtained parameters were as follows: $J = -135\,\text{cm}^{-1}$, $g = 2.02$, $N\alpha = 15 \times 10^{-6}$ emu mol^{-1}, and p (fraction of mononuclear impurity) $= 0.012$. The J value ($-135\,\text{cm}^{-1}$) is similar to that ($J_2 = -100\,\text{cm}^{-1}$) for **2**. This result supports the existence of a fairly large magnetic interaction within the dinuclear core in **2** ($J_2 = -100\,\text{cm}^{-1}$). Such strong interactions have been reported for the μ-hydroxo-μ-phenoxodicopper(II) complexes of Schiff-base ligands ($J =$ ca. $-$ 80–$-$220 cm^{-1}).[10,11] The

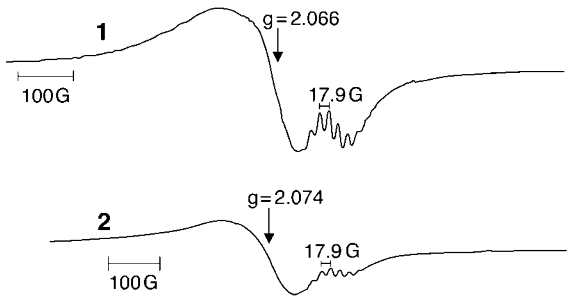
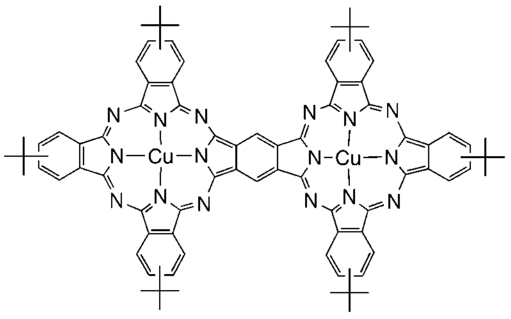


Fig. 4. EPR spectra of **1** and **2** in benzene at room temperature.



[Cu$_2${(pc)$_2$(*t*-Bu)$_6$}]

Scheme 5.

antiferromagnetic interaction within the dinuclear core was also found in the EPR spectra obtained in benzene solutions at room temperature. Complexes **1** and **2** have quite similar spectral features with the same A_N value (17.9 G) (Fig. 4), which indicates that the observed signals for **2** are due to the auxiliary Cu^{II}(pc) units. It is considered that the signal for the inner dinuclear unit is washed out, because of the strong antiferromagnetic interaction through the hydroxo- and phenoxo-bridges since there is no significant interaction between Cu^{II}(pc) and the dinuclear core units, which is consistent with $J_1 = 0\,\mathrm{cm}^{-1}$ in the magnetic simulation of **2**. Complexes **1** and **2** did not show the isotropic four line pattern based on electron–nuclear–spin hyperfine interactions, which is characteristic for the spectra of copper(II) species in solution at room temperature.[16,17] A similar spectral pattern has been obtained for a planar dinuclear copper(II) phthalocyanine with six peripheral *t*-butyl groups [Cu$_2${(pc)$_2$(*t*-Bu)$_6$}]$_2$ (Scheme 5), in which two Cu^{II}(pc) units are linked by a common benzene ring within the molecule. In the study, we concluded that the broadened spectral feature comes from the aggregation of the dimer in the solution, because the spectral feautre became more broadened at higher concentrations.[17]

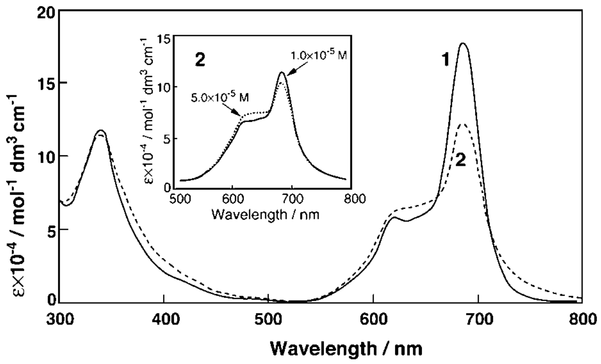


Fig. 5. Absorption spectra of **1** and **2**, measured in chloroform, the concentrations being 1.0×10^{-6} M. The spectra of **2** at the concentrations of 1.0×10^{-5} and 5.0×10^{-5} M are displayed in the inset.

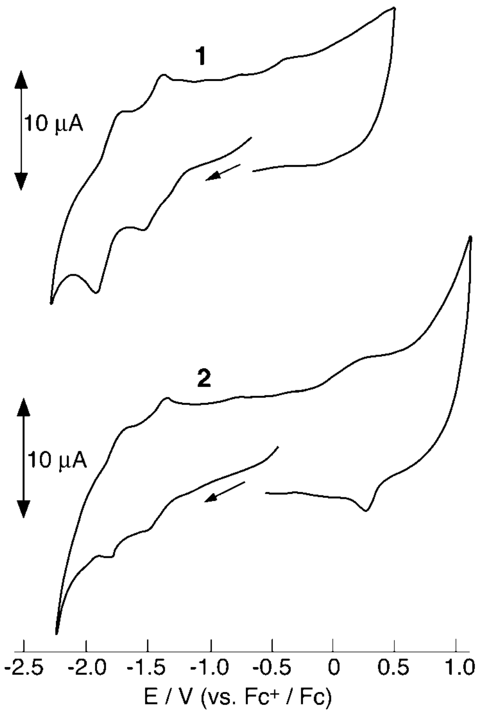


Fig. 6. Cyclic voltammograms of **1** and **2** in dichloromethane ([complex] = 1×10^{-4} M; [TBAP] = 0.1 M (TBAP = tetrabutylammonium perchlorate); scan rate = 100 mV s^{-1}).

Absorption spectra of **1** and **2** obtained in chloroform are displayed in Fig. 5. The Q bands are located at 686 nm for **1** and 681 nm for **2**. It is well known that the Q band is blue-shifted and appears as a broad band when the phthalocyanine molecules aggregate in a face to face mode.[18] The aggregating nature seems to be stronger in **2**, because the shoulder band at the shorter wavelength region is stronger compared to that of **1**. The shoulder band of **2** became relatively stronger when the concentration was increased, as shown in the inset of Fig. 5; the increase in the concentration made the shoulder band absorption stronger and the Q band weaker, which supports the assignment of the shoulder band as that originated from the aggregated species. The concentration dependence has been also observed for the planar dinuclear copper(II) phthalocyanine complex [Cu$_2${(pc)$_2$(*t*-Bu)$_6$}].[17] The larger molecular size of the two Cu^{II}(pc) units bound by the aldehyde dfmp or a common benzene ring may increase the aggregating nature. A mononuclear copper(II) phthalocyanine with four peripheral *t*-butyl groups [Cu{pc(*t*-Bu)$_4$}] does not show the concentration dependence in the concentration region measured for **2** and [Cu$_2${(pc)$_2$(*t*-Bu)$_6$}].[17]

Figure 6 shows cyclic voltammograms (CV) measured in CH$_2$Cl$_2$ containing tetrabutylammonium perchlorate (0.1 M) for **1** and **2**. There are two redox couples ($E_{1/2} = -1.44$ and -1.83 V vs. Fc^+/Fc for **1** and -1.41 and -1.75 V vs. Fc^+/Fc for **2**)[19] on the reduction side, which were assigned to reduction at the pc rings based on the corresponding redox potentials ($E_{1/2} = -1.42$ and -1.78 V vs. Fc^+/Fc in CH_2Cl_2)[20] for the copper(II) phthalocyanine with four *t*-butyl groups [Cu{pc(*t*-Bu)$_4$}].[21] The first and second reductions occur simultaneously for both of the two Cu^{II}(pc) units for **1** and **2**, respectively, indicating that there is no significant electrochemical interaction between the pc units. The broad wave in the oxidation side (ca. 0.3 V vs. Fc^+/Fc) was attributed to the oxidation of the aggregated pc rings.[21,22] The redox waves for the hydroxo- and phenoxo-bridged dinuclear unit in **2** were not clearly observed on the oxidation and reduction sides,[23] probably because of the superposition by the pc oxidation waves and/or the aggregation of the complex molecules. It has been reported that complex **4** has an interesting redox behavior concerning an electron-transfer from the reduced auxiliary copper(I) units ($E^{red} = -0.65$ V vs. SCE) to dinuclear copper(II) core.[6] The dinuclear copper(II) core has been considered to be impossible to be reduced before the reduction of the auxiliary copper(II) unit on the potential sweep in the CV, because the reduction potential for the corresponding component dinuclear compound μ-hydroxo-μ-[2,6-di(*N*-alkyliminomethyl)-4-methylphenolato]dichlorodicopper(II) is more negative than that of the auxiliary component complex, triethylenetetraminecopper(II) hexafluorophosphate. Hence, an intramolecular electron-transfer Cu^I–Cu^{II}–Cu^{II}–Cu^I → Cu^{II}–Cu^I–Cu^I–Cu^{II} must occurr in **4**. Similar redox behaviors have also been reported for the other related complexes composed of the covalently bound units, copper(II) dinuclear core and two auxiliary copper(II) mononuclear units.[24] In the CV for **2**, such an intramolecular electron-transfer was not observed, in spite of the fact that **2** has the dinuclear copper(II) core structure with two mononuclear Cu^{II}(pc) auxiliary units; **2** showed only two reversible or quasireversible redox couples on the reduction side as in the case of **1**. There is an important point to be noted for the difference between **2** and **4**, that is, the reduced outside units of **2**, where the reduction occurs at the organic π-conjugated system of the pc ring, may be stable compared to those of **4**. However, it is difficult to make the conclusion for the different electrochemical behavior between **2** and **4** at the present stage. Hence, further study is now in progress by changing the metal ions inserted in the pc ring centers, because the redox potential can be changed for the pc ring of the auxiliary units.[21]

In this study, we prepared a tetranuclear copper(II) complex having a hydroxo- and phenoxo-bridged copper(II) dinuclear unit covalently linked with two Cu^{II}(pc) auxiliary units as well as its precursor of the dinuclear complex composed of the Cu^{II}(pc) units. They were spectroscopically, electrochemically and magnetically investigated. Unfortunately, we could not observe any significant interaction between the inside copper(II) dinuclear core and the outside Cu^{II}(pc) auxiliary units. Different metal ions accommodated in the tetranucleating ligand and modification of the ligand itself may give rise to an interaction between the phthalocyanine and Schiff-base units and produce new important properties based on the pc–Schiff-base combination.

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