

Control of Cu(II) and Cu(III) States in N-Confused Porphyrin by Protonation/Deprotonation at the Peripheral Nitrogen

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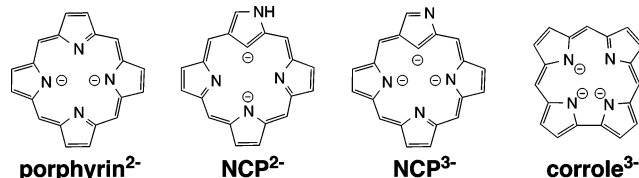
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Porphyrin and corrole are well-known aromatic macrocyclic ligands that form neutral square-planar complexes with a variety of divalent and trivalent metals, respectively.^{1,2} The difference in the metal valency results from the number of protons inside the macrocyclic cores, in principle (Chart 1). When the metal oxidation state rises from 2+ to 3+ in the porphyrin complex, the coordination of a counteranion to the axial position on the metal usually takes place. To maintain square-planarity for the complexes having a different oxidation state of metal, ion transfer from or to the porphyrinoid ring needs to occur. For such purpose, N-confused porphyrin (NCP)³ is a promising ligand because NCP is known to complex with the tri- and divalent metals according to the metal species in a neutral square-planar fashion by using two different tautomeric forms.⁴ To date, however, attempts to isolate the complexes with different oxidation states of the same metal have not been successful due to the presence of a counteranion or the high reactivity of the inner carbon.⁵ In this Communication, we show the first X-ray structure of a Cu(III)–NCP complex that proved to have square-planarity similar to that of a Cu(II) complex. The interconversion between the Cu(II) and Cu(III) complexes by chemical oxidation and reduction is also reported. To the best of our knowledge, this is the first example of porphyrinoid complexes in which the metal ion exists in two different oxidation states with the same neutral square-planar coordination environment.

The Cu(II) complex of NCP was synthesized by using *meso*-pentafluorophenyl-substituted NCP, whose square-planar structure was elucidated by X-ray crystallography.⁶ When the Cu(II) complex (**1**) was treated with 1.5 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CHCl₃, the solution changed from yellowish-brown to red immediately. After silica gel column chromatography, a new complex (**2**) was isolated quantitatively (Scheme 1). The first clue for the diamagnetic Cu(III)–NCP complex came from the ¹H NMR spectrum of **2** in CDCl₃, which showed a singlet at 9.41 ppm, ascribable to the outer α -CH of the confused pyrrole ring, and the remaining β -CH signals appeared at 8.88 (doublet) and 8.72–8.67 ppm (multiplet). In accordance with this result, the ESR signals of the paramagnetic Cu(II) complex **1** ($g_{\text{iso}} = 2.09$, $g_{\parallel} = 2.12$, $[A_{\parallel}] = 168$ G in toluene (4 mM) at 77 K)⁷ disappeared upon the addition of quantitative amounts of DDQ. The obtained Cu(III) complex was easily reduced by *p*-toluenesulfonylhydrazide to afford the Cu(II) complex (**1**) (see Supporting Information).

The UV/vis absorption spectra of the Cu(II) and Cu(III) complexes (**1**, **2**) and the colors in solutions are shown in Figure 1. The absorption spectrum of **2** showed a split Soret band at 453.0 nm, 11 nm red-shifted as compared to that of **1** (441.5 nm); in contrast, the Q-bands are blue-shifted and appeared in the region

Chart 1. Anionic Forms of Porphyrin and Its Analogues



Scheme 1. Interconversion between Cu(II) Complex (**1**) and Cu(III) Complex (**2**) by Detachment and Attachment of the Peripheral NH

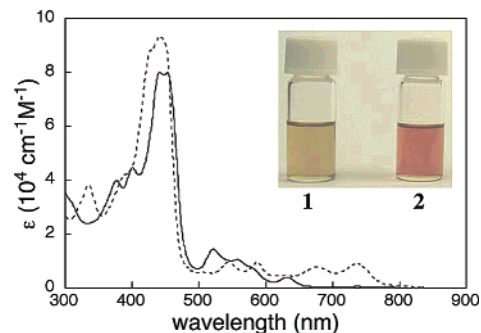
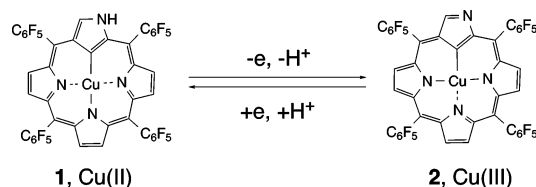


Figure 1. UV/vis absorption spectra and the naked colors of the solutions (inset) of **1** (dotted line, left) and **2** (solid line, right) in CH₂Cl₂.

from 521 to 632 nm. A similar blue-shift of the Q-bands is observed in Ag(III)–NCP complexes.^{6,7}

The structure of the Cu(III) complex **2** was explicitly determined by single-crystal X-ray analysis (Figure 2).⁸ The crystal parameters of **2** are quite similar to those of **1**, but the average bond lengths of Cu–C and Cu–N, 1.961(7) and 1.975(8) Å, are shorter than those of **1** (1.980(9) and 2.018(9) Å)⁶ and comparable to the Cu(III) complex of *cis*-doubly N-confused porphyrin, *cis*-N₂CP (Cu–C, 1.939(3), 1.934(4) Å; Cu–N, 1.969(3), 1.954(4) Å).⁹ The absence of counteranions in the crystal indicates that the complex is neutral. The absorption spectrum of the crystal after the X-ray measurements was intact, which excluded the possibility of contamination of Cu(II) complex **1** or reduction to **1** during the X-ray irradiation.

Interestingly, the electrochemical interconversion between the two NCP complexes, **1** and **2**, was controlled by the addition of anions. The redox potentials for the Cu³⁺/Cu²⁺ couple of **1** in the presence of 0.1 M tetrabutylammonium salts (TBAX, X = Cl[−],

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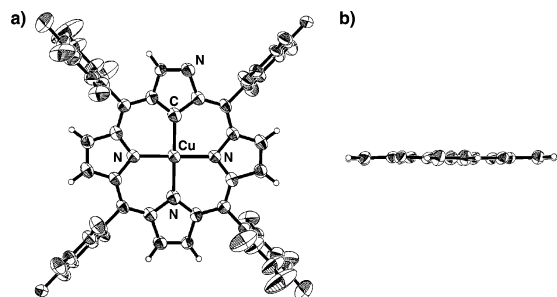


Figure 2. X-ray single-crystal structure of **2**: (a) top and (b) side views. Meso substituents are omitted for clarity in the side view. The thermal ellipsoids were scaled to the 30% probability levels. Due to the disorder of the nitrogen at a confused pyrrole ring, one of the eight possible forms is shown.

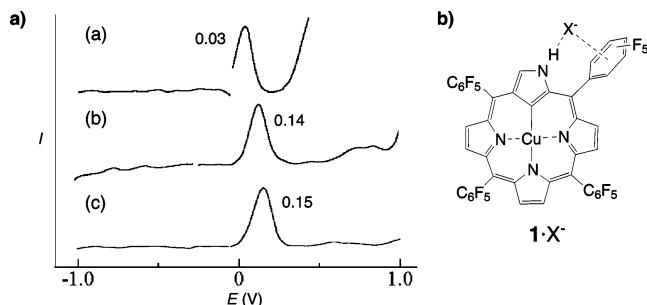


Figure 3. (a) Shifts of the redox potential (vs Fc^+/Fc) coupled with $\text{Cu}^{3+}/\text{Cu}^{2+}$ in the differential pulse voltammetry (DPV) of **1** (1 mM) in CH_2Cl_2 upon addition of (a) Cl^- , (b) ClO_4^- , and (c) PF_6^- as tetrabutylammonium salts (0.1 M), and (b) a possible anion-binding mode of **1**.

ClO_4^- , and PF_6^- were 0.03, 0.14, and 0.15 V (vs Fc^+/Fc , 1 mM in CH_2Cl_2), respectively, which were well correlated to the anion binding affinity of the complex **1** (Figure 3).^{10,11} The finding that the ESR spectrum of the Cu(II) complex **1** in CH_2Cl_2 did not change in the presence of Cl^- ruled out the possibility of anion coordination to the center Cu(II) metal in this system. The large negative potential shift observed for Cl^- might be attributable to a hydrogen-bonding interaction with the outer NH of the confused pyrrole ring.¹² Transmission of the partial negative charge from the peripheral hydrogen-bonded anion, $\text{N}-\text{H}\cdots\text{X}^-$, to the Cu cation through the inner carbon of the confused pyrrole ring might be occurring. Similar tuning of the electronic state of the center metal by proton stimuli was demonstrated in the Sb(V)–NCP complex.¹³ It is noteworthy that the estimated Cl^- binding affinity, $4.9 \times 10^4 \text{ M}^{-1}$, is unusually high for a single hydrogen-bonding system; thus, we believe that the contribution of a zwitterionic resonance form¹⁴ and additional interaction between Cl^- and the electron-deficient C_6F_5 group nearest to the outer NH also participate in this anion-binding system.¹⁵

At present, the correlation between the redox potentials for the M(III)/M(II) couple and the preferential M(II) or M(III) coordination of NCP is not clearly understood. Similar DDQ treatment of Ni(II)– and Pd(II)–NCP complexes only resulted in the recovery of the starting M(II) materials. The electron-withdrawing C_6F_5 group at the meso position raises both the acidity of the outer NH and the oxidation potential of the π -ring system. The former may increase the electronic density of inner carbon that is directly

transferred to the central metal, consequently stabilizing the M(III) oxidation state, and the latter may widen the potential window for the metal oxidation. Compared with the Cu(III) complex of *cis*- N_2CP ,⁹ the complex **2** was less stable and gradually transformed to the Cu(II) complex in CHCl_3 or CH_2Cl_2 solution, suggesting that the Cu(III)/Cu(II) redox couple lies near or on the border of M(II) and M(III) complexation in this C_6F_5 -substituted N-confused porphyrin ligand. As the control of the metal valencies by outer stimuli may offer a variety of applications, including molecular switches¹⁶ and anion sensors,¹⁷ we think the present NCP ligand system is promising for such use.

Acknowledgment. The authors thank Prof. Yoshio Hisaeda and Mr. Isao Aritome at Kyushu University for X-ray measurement. H.M. thanks JSPS for a Research Fellowship for Young Scientists.

Supporting Information Available: Synthetic procedures and spectral data of the Cu(III) complex (**2**); ^1H NMR, ESR, and absorption spectra; anion binding details (DPV, titration curve, ESR) (PDF); and X-ray crystallographic data for **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, 2000; Vol. 3, Chapter 16.
- (2) Erben, C.; Will, S.; Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, Chapter 12.
- (3) (a) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767–768. (b) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779–781. (c) Latos-Grażyński, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, Chapter 14. (d) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795–1804.
- (4) Furuta, H.; Ishizuka, T.; Osuka, A.; Dejjima, H.; Nakagawa, H.; Ishikawa, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6207–6208.
- (5) (a) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **1997**, *36*, 840–845. (b) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **2000**, *40*, 5475–5482. (c) Bohle, D. S.; Chen, W.-C.; Hung, C.-H. *Inorg. Chem.* **2002**, *41*, 3334–3336.
- (6) Maeda, H.; Osuka, A.; Ishikawa, Y.; Aritome, I.; Hisaeda, Y.; Furuta, H. *Org. Lett.* **2003**, *5*, 1293–1296.
- (7) Interestingly, the profile of the spectrum of **1** in CHCl_3 (ref 6) differs largely from that in CH_2Cl_2 . Currently, we are investigating this solvent effect.
- (8) Crystal data for **2**: $\text{C}_{44}\text{H}_7\text{N}_4\text{F}_{20}\text{Cu}$, $M_w = 1035.09$, trigonal $R\bar{3}(h)$ (No. 148), $a = b = 20.0878(10) \text{ \AA}$, $c = 23.882(3) \text{ \AA}$, $V = 8430.4(9) \text{ \AA}^3$, $D_c = 1.835 \text{ g/cm}^3$, $Z = 9$, $R = 0.0681$, $wR = 0.17578$, $\text{GOF} = 1.038$ ($I > 2.0\sigma(I)$).
- (9) Furuta, H.; Maeda, H.; Osuka, A. *J. Am. Chem. Soc.* **2000**, *122*, 803–807.
- (10) The association constants of **1** with Cl^- , Br^- , ClO_4^- , and PF_6^- in CH_2Cl_2 were determined as 4.9×10^4 , 6.9×10^3 , 360, and 50 M^{-1} , respectively, from the absorption spectral changes (see Supporting Information).
- (11) The oxidation potential using TBABr salt cannot be determined due to the overlap with the oxidation wave of Br^- .
- (12) In the ^1H NMR spectra of diamagnetic Ni(II) complex⁶ ($2.0 \times 10^3 \text{ M}$) in CDCl_3 , the outer NH signal shifted to the low field from 10.05 to 14.65 ppm upon the addition of 1 equiv of TBACl.
- (13) In the Sb(V) complexes, the bond lengths between the center Sb and axial ligands are changed according to the protonation/deprotonation at the peripheral nitrogen. Liu, J.-C.; Ishizuka, T.; Osuka, A.; Furuta, H. *Chem. Commun.* **2003**, 1908–1909.
- (14) Xiao, Z.; Patrick, B. O.; Dolphin, D. *Chem. Commun.* **2002**, 1816–1817.
- (15) Alkorta, I.; Rozas, I.; Elguero, J. *J. Am. Chem. Soc.* **2002**, *124*, 8593–8598.
- (16) Fabbrizzi, L.; Licchelli, M.; Mascheroni, S.; Poggi, A.; Sacchi, D.; Zema, M. *Inorg. Chem.* **2002**, *41*, 6129–6136.
- (17) (a) Mizuno, T.; Wei, W.-H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1134–1135. (b) Nielsen, K. A.; Jeppesen, J. O.; Levillain, E.; Becher, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 187–191.

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