

Trans Doubly N-Confused Porphyrins: Cu(III) Complexation and Formation of Rodlike Hydrogen-Bonding Networks

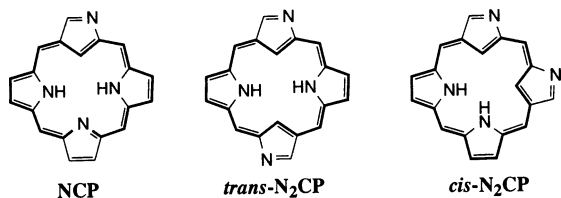
Hiromitsu Maeda,^{†,‡} Atsuhiko Osuka,[‡] and Hiroyuki Furuta^{*,†}

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan, and Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

Received September 15, 2003; E-mail: hfuruta@cstf.kyushu-u.ac.jp

Since the serendipitous discovery of N-confused porphyrin (NCP),¹ a number of unusual properties that are different from normal porphyrins have been disclosed in a variety of *confused* porphyrinoids.² Among such *confused* analogues, doubly N-confused porphyrin (N₂CP) is of particular interest because there exist two inner core carbon and two nitrogen atoms that can be used for metal coordination and two outer peripheral nitrogen atoms for the interaction to the external ions or molecules. Previously, we reported the synthesis of *cis*-type N₂CP, in which two neighboring pyrroles are *confused*, and showed the formation of complexes with rare Cu(III) and Ag(III) metals^{3a,b} and 1-D hydrogen-bonding zigzag chains in the solid state.^{3c} Theoretically, N₂CP consists of five regioisomers with different stabilities and aromaticities.⁴ Thus, it has been an open question whether such properties are limited only to a *cis*-isomer or even applicable to another possible *trans*-isomer whose two *confused* pyrroles are located at the counterposed sides (Chart 1).⁴ In this communication, synthesis, characterization, and metal coordination of the first *trans*-N₂CP are reported.

Chart 1. Basic Framework of NCP and *trans*-, *cis*-N₂CP



The synthesis of *trans*-N₂CP was performed by using [2 + 2] self-cyclization of carbinol derivative of pentafluorobenzoyl-substituted N-confused dipyrromethane **2**. Surprisingly, the isolated main product after 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation was not an expected *trans*-N₂CP, but its isomer of N-fused type (N-confused, N-fused porphyrin, NcFP, **3**) (Scheme 1a).^{5–7} This is contrasted to the straightforward synthesis of *cis*-N₂CP (**6**) from N-confused dipyrromethane (**1**) and pentafluorobenzaldehyde.^{3a}

The structure of **3** was determined from the ¹H NMR spectrum in CDCl₃, where the peripheral and inner CH protons are seen at 8.62–7.67 and 1.48 ppm, respectively, reflecting the aromatic nature of **3**. The lower field shift of the inner NH at 8.37 ppm is due to the intramolecular hydrogen bonding. The absorption spectrum of **3** in CH₂Cl₂ exhibits a sharp Soret-like band at 486.0 nm, and the edge of Q-bands in the long wavelength region reaches around 1000 nm. As demonstrated in N-fused porphyrin (NFP),⁵ the treatment of NcFP (**3**) with KOH/EtOH or KOH/MeOH afforded ring-opened product, alkoxy-substituted *trans*-N₂CP (**4a,b**), in 53 and 31% yields, respectively (Scheme 1a).

The explicit structure of **4b** was determined by X-ray diffraction analysis (Figure 1a).⁸ In the crystal, the two *confused* pyrrole rings, unsubstituted and a methoxy attached, bent to the same side at 21.2 and 21.9° to the macrocyclic mean plane consisting of a core of 24 atoms, respectively. The remaining *normal* pyrroles cant 6.8 and 9.3° to the opposite side. The macrocycle exhibits a saddle conformation, wherein a solvent toluene molecule is captured by the two *trans*-N₂CP with a distance of 3.16 Å. In the case of toluene-free crystals of **4a**, a π -stacked columnar structure is observed,⁹ which is different from the zigzag chain of *cis*-isomer **6**.^{3c}

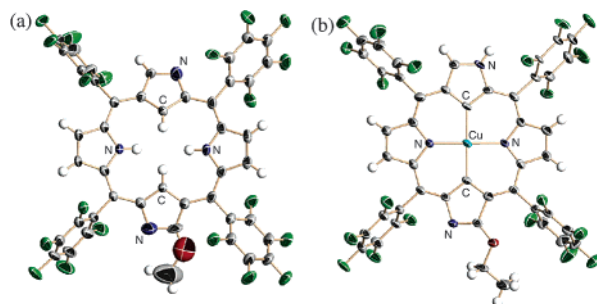


Figure 1. X-ray single-crystal structures of (a) **4b** and (b) Cu(III) complex **5a**. The thermal ellipsoids were scaled to the 50% probability level. In both cases, solvent molecules are omitted for clarity.

In the ¹H NMR spectrum of **4a** in CDCl₃, the peripheral protons resonate at 8.85–8.44 ppm, and the two inner NH and two inner CH protons are observed at –2.73, –3.21 and –4.34, –4.36 ppm, respectively, indicating the 18 π aromatic character of *trans*-N₂CP. This is a marked contrast to the *cis*-isomer **6**, which possesses only three protons in the core (6.40, 3.52, and 3.22 ppm for inner NH and two inner CH, respectively), displaying the weak aromatic character.^{3a} Supporting this, the absorption spectrum of *trans*-N₂CP (**4a**) in CH₂Cl₂ exhibits a sharp normal, porphyrin-like Soret band at 449.0 nm, which is quite different from the broad one at 424.0 nm of *cis*-N₂CP (**6**) (Figure 2a).

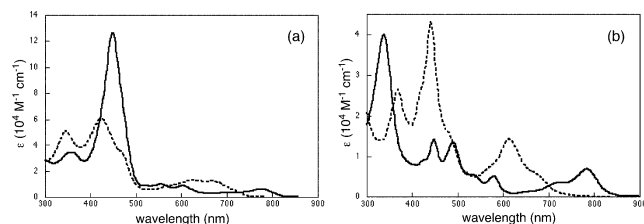
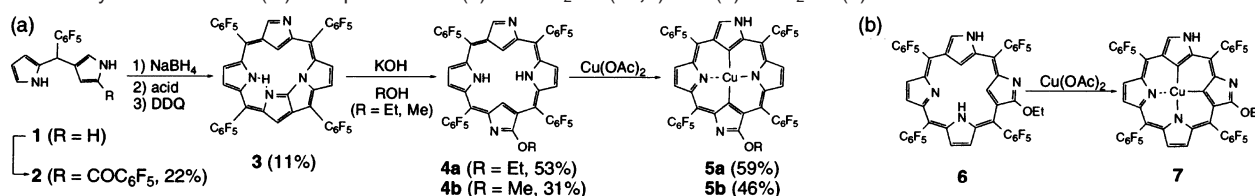


Figure 2. UV/vis absorption spectra of (a) *trans*-N₂CP (**4a**, solid line) and *cis*-N₂CP (**6**, dotted line)^{3b} and (b) Cu(III) complexes of *trans*-N₂CP (**5a**, solid line) and *cis*-N₂CP (**7**, dotted line)^{3b} in CH₂Cl₂.

The preferential formation of an aromatic tautomer observed in **4** is well consistent with the results of DFT calculations,⁴ where

[†] Kyushu University.
[‡] Kyoto University.

Scheme 1. Syntheses and Cu(III) Complexation of (a) *trans*-N₂CP (**4a,b**) and (b) *cis*-N₂CP (**6**)^{3a}

the most stable form of *trans*-N₂CP favors the fully conjugated aromatic inner 4H-type, while the *cis*-N₂CP **6** prefers the weak aromatic inner 3H-type tautomer.¹⁰

The metal coordination of **4a,b** was examined by using Cu(OAc)₂ as performed in the *cis*-isomer **6** (Scheme 1a,b). After stirring the reaction mixture in CH₂Cl₂ for 5 h at room temperature, red-colored copper complexes (**5a,b**) were formed in 59 and 46% yield, respectively. The ¹H NMR of **5a** shows distinct signals at 8.50–7.52 ppm assignable to peripheral CH, while the outer NH appears at 10.22 ppm. The absence of the inner CH and NH signals suggests that the obtained copper complex contains the diamagnetic center metal cation, Cu(III) in the core. The UV/vis absorption spectrum of **5a** in CH₂Cl₂ exhibits strong transition at 337 nm and broad bands from 400 to 800 nm, which is contrasted to the Cu(III) complex of *cis*-isomer (**7**) (Figure 2b).

The X-ray structure of Cu(III) complex **5a** exhibits square-planar complex (Figure 1b).¹¹ The distances between Cu–C are 1.940(7) and 1.944(7) Å, and Cu–N are 1.965(6) and 1.967(6) Å, respectively, which are comparable to that of Cu(III) complex of *cis*-N₂CP, Cu–C: 1.939(3) and 1.934(4) Å, Cu–N: 1.969(3) and 1.954(4) Å.^{3a} The molecule is rather planar with small deviation (0.06 Å) from a mean plane consisting of 25 core atoms compared to the distorted free base **4b** (0.30 Å). Cu(III) complex **5a** forms intermolecular hydrogen-bonding linear chains as comparable with zigzag chains of *cis*-N₂CP (Figure 3).^{3c} The dihedral angle between neighboring planes and the distance of N–H···N are 83.74° and 2.980 Å, respectively.¹² The nearest Cu(III)–Cu(III) distance is 10.83 Å which is longer than that of *cis*-isomer (**7**), 8.40 Å, reflecting the linear structure of **5a**.

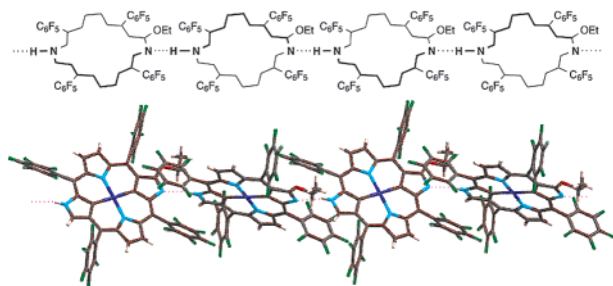


Figure 3. Hydrogen bonding 1-D chain in the solid state of Cu(III) complex (**5a**). Dotted lines indicate hydrogen bondings. Solvent molecules are omitted for clarity.

In the Cu(III) complexes, both *cis*- and *trans*-N₂CP serve as trianionic ligands despite the difference of preferential tautomeric form (inner 3H or 4H) in the free base. As the result, just like an imidazole, one of the nitrogen atoms at the periphery is protonated (NH), and the other is deprotonated (N). The relative arrangement of such an acid–base pair in the Cu(III)N₂CP determines the structures of the hydrogen-bonding assemblies.¹³ As the N₂CP is a potent tetraanionic ligand, the redox change Cu(II)/Cu(III) or Cu(III)/Cu(IV), similar to the Cu(II)/Cu(III) change in the NCP complex,¹⁴ would cause the large perturbation in the structures of

supramolecular architecture. In addition, the combination of acid and base moieties at the periphery of multiply *N-confused* isomers would make these “imidazole porphyrinoids” attractive for the use as catalysts¹⁵ and anion/cation sensors.^{14,16}

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Supporting Information Available: Synthetic procedures and spectral data of **2–5**, DFT calculations for NcFP structures, crystal packing of **4a**, **5a**, and **7** (PDF). CIF files for the X-ray structural analyses of **4b** and **5a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) The most possible tautomeric form estimated by DFT calculations of **3** is shown in Scheme 1. See Supporting Information.
- (7) Less amount of oxidant (0.5 equiv of DDQ) gave the nonconjugated “reduced” type of NcFP (**3'**) in 10% yield instead of NcFP (**3**), which suggests NcFP (**3**) was derived from the nonconjugated fused porphyrinoid NcFP (**3'**) by oxidation. This is similar to the *meso*-aryl *N*-fused pentaphyrin (NFP₅). Shin, J.-Y.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 619–621.
- (8) Crystal data for **4b** (from CHCl₃/heptane/toluene): C₄₅H₁₁N₄F₂₀O·0.5C₇H₈·0.5C₂H₄O, *M_w* = 1073.70, *P2₁/n* (no. 14), *a* = 10.6400(7) Å, *b* = 27.0071(18) Å, *c* = 14.7614(10) Å, β = 98.643(2)°, *V* = 4193.6(5) Å³, *Z* = 4, *D_c* = 1.701 g/cm³, *R* = 0.0985, *wR* (all data) = 0.3362, GOF = 1.271 (*I* > 2σ(*I*)).
- (9) Crystal packing structure of **4a** is shown in Supporting Information.
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- (11) Crystal data for **5a**: C₄₆H₁₄N₄F₂₀OCu·CHCl₃·C₇H₁₆, *M_w* = 1298.69, *P2₁/n* (no. 14), *a* = 12.9802(10) Å, *b* = 22.8224(17) Å, *c* = 17.0361(13) Å, β = 91.195(2)°, *V* = 5045.7(7) Å³, *D_c* = 1.710 g/cm³, *Z* = 4, *R* = 0.0792, *wR* (all data) = 0.2433, GOF = 0.968 (*I* > 2σ(*I*)).
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