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N-Confused Porphyrin-Bearing *meso*-Perfluorophenyl Groups: A Potential Agent That Forms Stable Square-Planar Complexes with Cu(II) and Ag(III)

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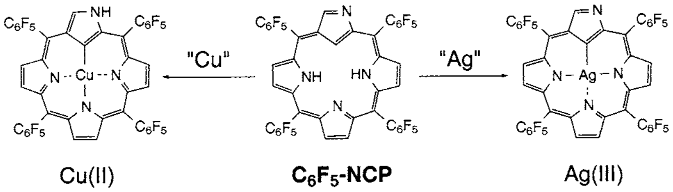
ABSTRACT



N-Confused porphyrin (NCP) bearing pentafluorophenyl groups at *meso*-positions, which were obtained from N-confused dipyrromethane in ca. 20% yield, can form Cu(II) complex as well as Ag(III), Ni(II), and Pd(II) complexes. The square-planar structures of all these metal complexes were elucidated by X-ray single-crystal analyses.

In recent years, there has been much attention on the syntheses of porphyrinoids bearing electron-withdrawing groups because of the catalytic reactivity of the metal complexes. For example, pentafluorophenyl (C_6F_5)-substituted corrole was synthesized in good yield by solvent-free acid-catalyzed pyrrole-aldehyde condensation, and the Fe(IV) and Rh(III) complexes were shown to catalyze the cyclopropanation reaction effectively.[1] Similarly, the Rh(II) complex of perfluorinated *meso*-tetraarylporphyrin was used for C−H activation of methane.[2] Furthermore, the efficient one-pot syntheses of a series of *meso*-C_6F_5 substituted expanded porphyrins were recently reported.[3] Such examples prompted us to synthesize *meso*-C_6F_5-substituted N-confused porphyrin (C_6F_5-NCP), because we hope that the C_6F_5 substituent may stabilize the metal complexes which are

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difficult to prepare from the standard *meso*-phenyl derivative.[4−9] In addition, C_6F_5-NCP may serve as an appropriate reference to the existing *cis*-doubly N-confused porphyrin (*cis*-N_2CP, Figure 1) that can stabilize the unusual higher oxidation states of metals such as Cu(III).[10] Herein, we report the synthesis of C_6F_5-NCP (**4**) and the X-ray structures of Ag(III), Ni(II), Pd(II), and Cu(II) complexes. To the best of our knowledge, the Cu(II) complex is the first example of an organocopper(II) complex of aromatic porphyrinoid to be characterized by X-ray crystallography.[11]

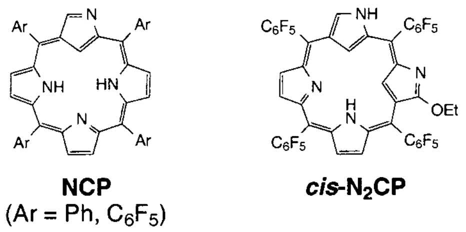
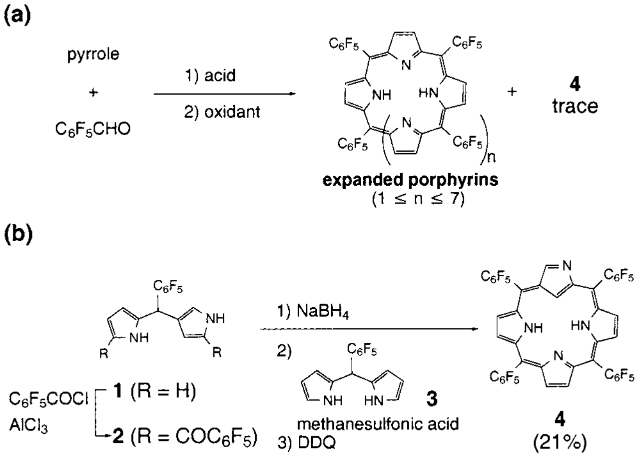


Figure 1. The structures of N-confused porphyrin (NCP) and *cis*-doubly N-confused porphyrin (*cis*-N_2CP).

The initial attempt to obtain C_6F_5-NCP from the Rothemund-type condensation reaction between pyrrole and pentafluorobenzaldehyde was hampered by the preferential formation of a series of expanded porphyrins (Scheme 1(a)).[3a−d]

Scheme 1. Synthesis of C_6F_5-NCP (**4**): (a) One-Pot Route[3b] and (b) [2+2] Stepwise Route



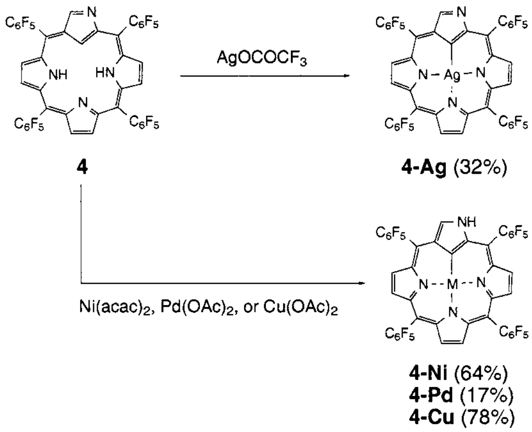
The isolated yield of C_6F_5-NCP was quite low (<0.1%), therefore we decided to synthesize C_6F_5-NCP by a stepwise [2+2] condensation route (Scheme 1b).

A key starting unit, bis(pentafluorobenzoyl) N-confused dipyrromethane **2**, was synthesized by Friedel−Crafts reaction of corresponding dipyrromethane **1**.[10a,12] N-Confused tetrakis(pentafluorophenyl)porphyrin (C_6F_5−NCP, **4**) was obtained in 21% yield by the acid-catalyzed condensation between normal dipyrromethane **3** and the carbinol derivative of **2**, and the subsequent oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Scheme 1b). The advantage of using dibenzoyl-substituted dipyrromethane is well documented in the syntheses of porphyrins bearing different *meso*-substituents.[13,14] This type of [2+2] condensation was previously reported for the syntheses of β-alkyl-substituted NCP,[15] but not applied for *meso*-aryl-type NCP synthesis.

The ^{1}H NMR spectrum of C_6F_5-NCP in $CDCl_3$ showed an aromatic feature, in which the signals of two inner NH and CH are observed at −2.57 and −5.26 ppm, and those of the peripheral CH appeared around 8.96−8.55 ppm, respectively. Interestingly, the electron-deficient π-system was reflected from the absorption spectrum of C_6F_5-NCP in methanol, where the weak aromatic inner 2H-tautomer is predominant. In the case of NCTPP, aromatic inner 3H-tautomer was favored by using the same solvent.[16]

NCP is known to behave as either trianionic or dianionic ligands according to the center metals (e.g. Ag(III),[5] Ni(II),[4b,6] and Pd(II)[7]) affording square-planar complexes. As expected, C_6F_5-NCP complexed with Ag(III), Ni(II), Pd(II), and Cu(II)[9] was obtained in modest yields compared to NCTPP (Scheme 2). The complexes **4-Ag**, **4-Ni**, and **4-Pd** showed the diamagnetic features of the d^8 configuration as judged by the resonance of ^{1}H NMR spectra in the normal region (10.0−7.4 ppm for the peripheral protons). Among them, outer NH and the neighboring α-CH signals were observed

Scheme 2. Metal Complexation of C_6F_5-NCP (**4**)



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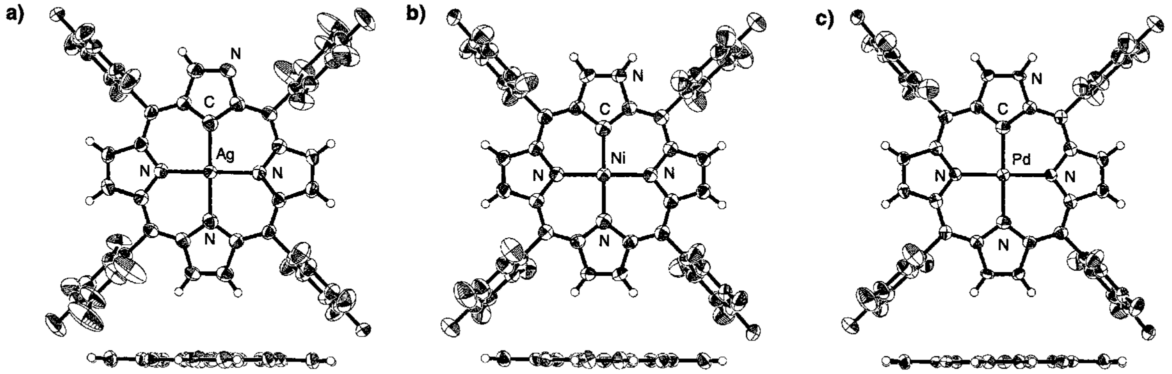

Figure 2. X-ray single-crystal structures of (a) **4-Ag**, (b) **4-Ni**, and (c) **4-Pd** (top and side view). *Meso*-substituents are omitted for clarity in the side view. The thermal ellipsoids were scaled to the 50% probability levels. Due to the disorder of the nitrogen atom at the *confused* pyrrole ring, one of the eight possible structures is shown in each complex.

in **4-Ni** (9.94 and 8.45 ppm, $J = 2.7$ Hz) and **4-Pd** (9.87 and 8.38 ppm, $J = 2.7$ Hz), but only the α-CH signal was resonated at 9.38 ppm in **4-Ag** as expected from the structures. On the other hand, the signals of **4-Cu** were not detected in the region from −30 to +40 ppm, which proved that the complex was paramagnetic and the Cu(II) was in the d^9 configuration. FAB-MS of each complex was also consistent with the formulation above.

The explicit evidence of the square-planar coordination in the N_3C cores of **4-Ag**, **4-Ni**, and **4-Pd** was afforded by X-ray single-crystal analyses (Figure 2).[17−19] In **4-Ag**, the average bond lengths of Ag(III) and coordinating atoms (C and N) are 2.033(4) and 2.039(4) Å, which are comparable to those of the Ag(III) complex of NCTPP (2.03−2.08 Å).[5] The corresponding values are 1.933(3) and 1.955(3) Å in **4-Ni** and 2.004(4) and 2.026(4) Å in **4-Pd**, which are similar to those of the N-confused tetra(*p*-tolyl)porphyrin (NCTTP) Ni(II) complex (1.955(3) and 1.963(3) Å)[4b] and Pd(II)NCTTP (2.016(4) and 2.023(5) Å).[7]

The coordination mode of the Cu(II) complex of NCP (**4-Cu**) was also elucidated by X-ray analysis (Figure 3).[20] The center Cu(II) is coordinated in a square-planar fashion as expected.[9] The average bond lengths between Cu(II) and ligand atoms are 1.980(9) and 2.018(9) Å, which are longer

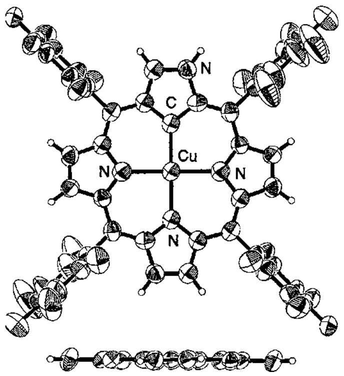

Figure 3. X-ray single-crystal structure of **4-Cu** (top and side view). *Meso*-substituents are omitted for clarity in the side view. The thermal ellipsoids were scaled to the 30% probability levels. The position of the nitrogen at *confused* pyrrole is disordered, so one of the eight possible forms is shown.

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(14) Acid-catalyzed condensation of NC-dipyrromethane **1**, normal dipyrromethane **3**, and pentafluorobenzaldehyde affords the complicated mixture of expanded porphyrins and a trace of **4**.

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(17) Crystal data for **4-Ag**: $C_{44}H_7N_4F_{20}Ag{\cdot}0.5H_2O$, $M_w = 1088.42$, trigonal $R\bar{3}(h)$ (no. 148), $a = b = 20.29(1)$ Å, $c = 24.25(3)$ Å, $V = 8647.4(1)$ Å^3, $D_c = 1.881$ g/cm^3, $Z = 9$, $R = 0.057$, $wR = 0.081$, $GOF = 0.998$ ($I > 3.0\sigma(I)$). Hydrogen atoms of water molecules incorporated in the crystal were omitted for the refinement due to the significant disorder of the solvent.

(18) Crystal data for **4-Ni**: $C_{44}H_8N_4F_{20}Ni$, $M_w = 1031.25$, trigonal $R\bar{3}(h)$ (no. 148), $a = b = 19.6856(10)$ Å, $c = 24.831(3)$ Å, $V = 8333.5(11)$ Å^3, $D_c = 1.849$ g/cm^3, $Z = 9$, $R = 0.0489$, $wR = 0.1207$, $GOF = 1.046$ ($I > 2.0\sigma(I)$).

(19) Crystal data for **4-Pd**: $C_{44}H_8N_4F_{20}Pd$, $M_w = 1078.94$, trigonal $R\bar{3}(h)$ (no. 148), $a = b = 19.6798(10)$ Å, $c = 25.097(3)$ Å, $V = 8417.6(11)$ Å^3, $D_c = 1.916$ g/cm^3, $Z = 9$, $R = 0.0478$, $wR = 0.1148$, $GOF = 0.997$ ($I > 2.0\sigma(I)$).

than those of the *cis*-N_2CP-Cu(III) complex (1.934−1.969 Å)[10a] reflecting the larger Cu(II) radius than that of Cu(III). The ESR parameters of **4-Cu** (g_{iso} = 2.09, $g_{||}$ = 2.12, [$A_{||}$] =168 G in toluene (4 mM) at 77 K) are also consistent with the square-planar structure.[21]

The absorption spectra of the free base form of C_6F_5-NCP and the Ag(III) and Cu(II) complexes in $CHCl_3$ are shown in Figure 4. The Soret band of **4-Cu** shows the peak at 428.0 nm and a characteristic shoulder around 440 nm. The last Q-band reaches to 739.0 nm, which is 27 and 103 nm red-shifted compared to those of **4** and **4-Ag**, respectively, but is more blue-shifted than other divalent metal complexes (**4-Ni**, 810.0 nm; **4-Pd**, 762.0 nm; see Supporting Information).

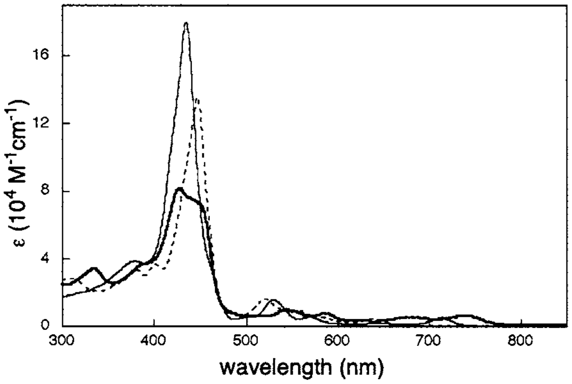

Figure 4. UV/vis absorption spectra of C_6F_5-NCP (**4**) (solid line), **4-Ag** (broken line), and **4-Cu** (bold line) in $CHCl_3$.

Interestingly, the oxidation state of the copper ion changes in NCP (Cu(II)) and N_2CP (Cu(III)), whereas that of silver is kept in the same (Ag(III)) state, despite the same group 11 elements. As *meso*-substituents are identical in both NCP and N_2CP, we can clearly state that the introduction of a second *confused* ring in the NCP core facilitates to stabilize the higher oxidation state of metals, just as the first *confusion* does in the NCP-Ag(III) complex. The effect of the C_6F_5 unit in NCP is reflected in the Cu(II/III) redox couple at +0.14 V (vs Fc/Fc^+), which is shifted to higher potential compared with that of NCTPP at −0.11 V.[9] In other words, the electron-withdrawing C_6F_5 groups decrease the electron density of the π system, including the center metal, as a result, the reactivity of the inner carbon bound to Cu(II) decreases to afford sufficient stability to grow single crystals. In the case of the NCTPP-Cu(II) complex, the core framework is easily cleaved and fragmented to transform into the tripyrrinone-Cu(II) complex under aerobic conditions.[22] In the case of **4-Cu**, however, the complex retains its framework under similar aerobic conditions.[23]

In summary, we have succeeded in synthesizing the *meso*-pentafluorophenyl-substituted NCP (C_6F_5-NCP, **4**) in good yield. C_6F_5-NCP can form square-planar complexes with a variety of metals such as Ag(III), Ni(II), Pd(II), and Cu(II). The stabilizing effect of the electron-withdrawing C_6F_5 substituents was demonstrated explicitly by the preparation of single crystals of the Cu(II) complex, which are not available from the *meso*-phenyl derivative due to the instability of the complex.[24] C_6F_5-NCP is, thus, attractive as a potential ligand in complexing various metals that can exhibit the catalytic activity as shown in the corrole complexes.[1c] Furthermore, the stepwise synthesis used for C_6F_5-NCP would be applicable for the preparation of NCP derivatives with various functional group at *meso*-positions.

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Supporting Information Available: Synthetic procedures and spectral data of dipyrromethane (**2**), free base (**4**), and the metal complexes, UV/vis absorption spectra of **4-Ni** and **4-Pd**, and CIF files for the X-ray structural data of **4-Ag**, **4-Ni**, **4-Pd**, and **4-Cu**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Crystal data for **4-Cu**: $C_{44}H_8N_4F_{20}Cu$, M_w = 1036.09, trigonal $R\bar{3}(h)$ (no. 148), $a = b$ = 20.1647(9) Å, c = 23.941(2) Å, V = 8430.4(9) $Å^3$, D_c = 1.837 g/cm^3, Z = 9, R = 0.0707, wR = 0.1996, GOF = 1.017 ($I > 2.0\sigma(I)$).

(21) The obtained values are slightly different from the reported Cu(II)-NCTPP complex, g_{iso} = 2.070, $g_{||}$ = 2.139, [$A_{||}$] =143 G in toluene/CH_2Cl_2 (80/20, v/v) at 77 K. See ref 9.

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(23) The details of the oxidation of **4-Cu** are under investigation. The complexation of Cu(II) under toluene reflux conditions yielded the unidentified product different from tripyrrinone-Cu(II) complex,[22] quantitatively.

(24) Introduction of electron-withdrawing groups directly at the NCP core may also be helpful to stabilize the metal complexes. In fact, an air-stable Cu(II) complex was also obtained from CN-substituted NCTPP at the confused pyrrole ring. Ishikawa, Y.; Dejima, H.; Furuta, H. Manuscript in preparation.