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Syntheses, Structures, and Crystal Packing of N-Confused 5,20-Diphenylporphyrin and Ag(III) Complex

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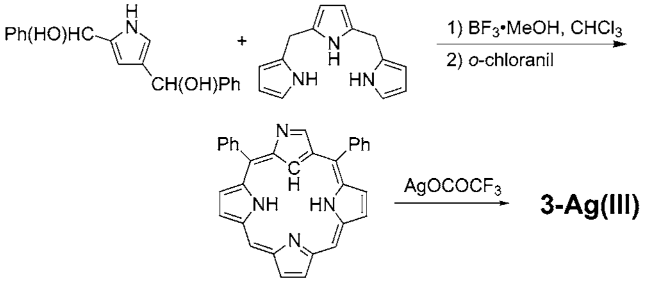
ABSTRACT



N-Confused 5,20-Diphenylporphyrin (3)

β-Unsubstituted *meso* partially free N-confused porphyrin, N-confused 5,20-diphenylporphyrin (NCDPP, 3), was synthesized in 7% yield by [3 + 1] condensation reaction followed by oxidation. The structures of the free base and its Ag(III) complex were elucidated by the single-crystal X-ray analyses. The Ag(III) complex was more planar than the free base and formed columnar structures stacking to each other with a 3.3 Å distance in the crystal.

Comparison of similarity and differences is one effective method in approaching the subject concerned. In porphyrin chemistry, a new series of porphyrin analogues such as core-modified, expanded, and contracted porphyrins has emerged and is growing progressively. Among them, porphyrin isomers are of particularly interest because they exhibit chemistry analogous to that of the parent *normal* porphyrin and reveal completely different properties in some cases. In the study of N-confused porphyrin (NCP), we and others have shown the peculiar chemistry in the structures, metal coordinations, and reactivities.[1] In this paper, we focus on the similar aspects in turn, and show the important nature of the *meso*-substituents on the molecular planarity and crystal packing. For this study, *meso*-diphenyl derivatives and Ag metal complexes of both NCP and *normal* porphyrin were newly synthesized.

Toward "N-confused porphin", a *standard* of NCP having only a basic framework, we started the syntheses of *meso*-tri-, di-, and monosubstituted NCP derivatives. Previously, *meso*-free NCPs having alkyl groups at outer α- and β-positions were synthesized.[2] Such alkyl groups may

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(1) (a) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795. (b) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767. (c) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779.

(2) (a) Liu, B. Y.; Bruckner, C.; Dolphin, D. *Chem. Commun.* **1996**, 2141. (b) Lash, T. D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076.

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be important for the syntheses and the stabilization of NCP. Here, we chose N-confused 5,20-diphenylporphyrin (NCDPP, **3**) as an initial target of outer α,β-free NCP with less than four *meso*-substituents (Figure 1).

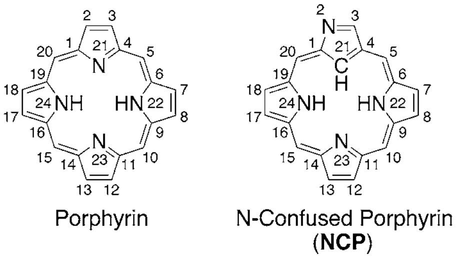
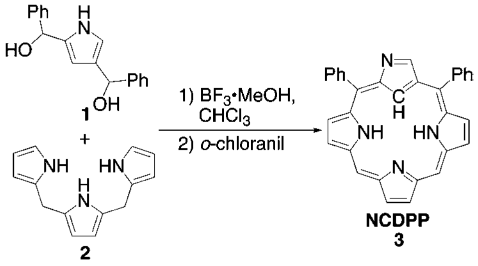


Figure 1. Framework and atom numbering system of porphyrin and N-confused porphyrin (NCP).

NCDPP (**3**) was synthesized according to the Scheme 1. In the synthesis, we have used [3 + 1] condensation reaction of 2,4-bis(phenylhydroxymethyl)pyrrole (**1**) and *meso*-unsubstituted tripyrrane (**2**) referring to the successful procedures used in the syntheses of hetero-NCP[3] and porphin.[4]At first, 2,4-dibenzoylpyrrole[5] was reduced to the corresponding dicarbinol (**1**) and the resulting diol was reacted with tripyrrane (**2**)[6] in the presence of an acid catalyst. After the oxidation with *o*-chloranil, followed by column chromatography on alumina and silica gel sequentially, the target compound **3** was isolated in 7% yield and no other NCP derivatives were obtained. Formation of *meso*-phenyl-substituted porphyrins (<1%) was only detected in a trace amount by NMR, UV/vis, and FABMS,[7] which indicates that the scrambling of phenyl groups was not significant in this NCP formation reaction. When MSA (methanesulfonic acid), a known effective acid for tetraaryl-NCP synthesis,[8] was applied instead of $BF_3 \cdot MeOH$, the yield of NCDPP decreased to 3%.

Scheme 1. Synthesis of 5,20-Diphenyl-NCP (NCDPP, **3**)



In the ^1H NMR spectrum of **3** in $CDCl_3$, the inner $C_{21}-H$ signal was observed at −5.9 ppm, which was shifted upfield compared to that of N-confused tetraphenylporphyrin, NCTPP, at −5.1 ppm. Such a substituent effect is known in the *normal* porphyrin systems and is attributable to the enhancement of the ring current as the result of the removal of the electron-withdrawing *meso*-phenyl groups.[9] The outer α-proton of the *confused* ring (C_3-H) and β-protons are shifted slightly downfield (8.8−9.1 ppm) compared to NCTPP (8.5−9.0 ppm). In addition, two new singlet signals at 9.4 and 9.5 ppm assignable to *meso*-protons ($C_{10}-H$ and $C_{15}-H$) were observed.

The UV/vis spectrum of **3** showed the absorption maxima at 430 (Soret), 527, 566, and 705 nm (Q-bands) in CH_2Cl_2. The spectrum was similar to that of NCTPP with respect to the shape but showed hypsochromic shifts compared to NCTPP.[10] On the other hand, in DMF, the Soret band was bathochromic shifted (434 nm) and the appearance of characteristic Q-bands (579, 626, 679 nm) indicates the formation of another tautomer of the inner-2H-type as demonstrated in NCTPP (Figure 2).[11]

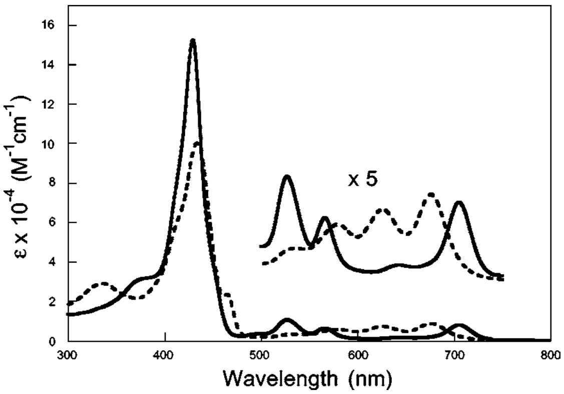


Figure 2. Absorption spectra of **3** in CH_2Cl_2 (solid line) and in DMF (broken line).

In a single crystal of **3**, the two independent NCDPP molecules form a pair with stacking to each other in the same direction. The intermolecular distances between the porphyrin rings are 3.55 Å in the pair (r_1) and 3.69 Å between the

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[3] (a) Heo, P.-Y.; Shin, K.; Lee, C.-H. *Tetrahedron Lett.* **1996**, *37*, 197. (b) Heo, P.-Y.; Shin, K.; Lee, C.-H. *Tetrahedron Lett.* **1996**, *37*, 1521.

[4] Taniguchi, S.; Hasegawa, H.; Nishimura, M.; Takahashi, M. *Synlett* **1999**, 73.

[5] Cadamuro, S.; Degani, I.; Dughera, S.; Fochi, R.; Gatti, A.; Piscopo, L. *J. Chem. Soc., Perkin Trans. 1* **1993**, 273.

[6] High-yield and stepwise synthesis of **2**: Taniguchi, S.; Hasegawa, H.; Yanagiya, S.; Tabeta, Y.; Nakano, Y.; Takahashi, M. *Tetrahedron* **2001**, *57*, 2103. Another one-pot synthesis: Ka, J.-W.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 4609.

[7] Formation of a trace amount of porphine, mono-, di-, and triphenylporphyrins was detected by NMR and FABMS. *meso*-Diphenyl-β-benzylporphyrin was also produced according to the quenching procedure in the reduction step.

[8] Geier, G. R., III; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **1999**, *1*, 1455.

[9] Chemical shifts of the inner NH signal of TPP, 5,10-DPP, and porphin were reported −2.76, −3.34, and −3.76 ppm, respectively. See, ref 17b and: Medforth, C. J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 5, Chapter 35.

[10] Such shifts were also observed in *normal* porphyrins. For example, the Soret bands of TPP and 5,10-DPP were observed at 419 and 405 nm in CH_2Cl_2, respectively.

[11] Furuta, H.; Ishizuka, T.; Osuka, A.; Dejima, H.; Nakagawa, H.; Ishikawa, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6207.

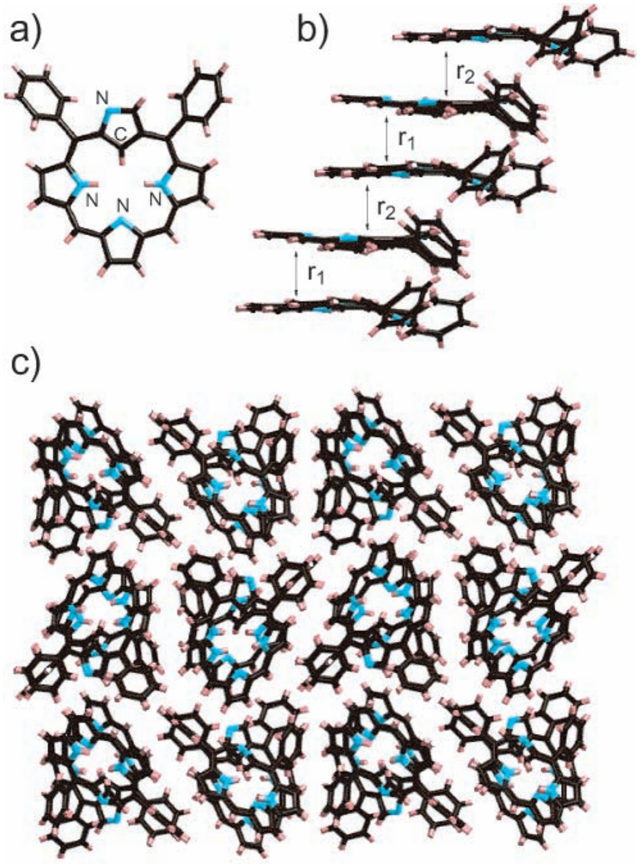

Figure 3. Molecular structure of **3**: (a) top view, (b) side view, and (c) packing diagram from the *c*-axis. r_1 and r_2 denote the interplane distances between the paired and unpaired porphyrins (see text). Solvent molecules are omitted for clarity.

nearest unpaired porphyrins (r_2), respectively (Figure 3).[12] The *confused* pyrrole ring of **3** is tilted by 21.6° from the mean plane consisting of 24 atoms of NCP skeleton, and the other pyrroles are canted by 5.7, 3.5, and 8.4°, respectively. The *confused* ring of the opposite NCP is tilted by 16.4° from the plane, and the remaining pyrroles by 10.6, 2.0, and 11.4°, respectively. Such tilting of the *confused* pyrrole rings is commonly observed in the inner-3H-type of the NCP tautomer, which is not the case in the *normal* porphyrin.

Next, NCDPP was complexed with Ag(III) ions using excess Ag(I) trifluoroacetate in CH_2Cl_2/MeOH. As reported previously, NCP ligand can form a neutral square-planar complex with Ag(III) ion,[13,1a] which is in marked contrast to *normal* porphyrin, which forms a neutral square-planar complex with Ag(II).[14] The X-ray structure of NCDPP-Ag(III) complex (**3-Ag(III)**) is shown in Figure 4.[15] The complex shows the planar structure with the mean deviation of 0.02 Å, which is rather smaller than that of NCTPP-Ag(III) complex (0.19 Å). Interestingly, the crystal packing is dramatically different from the free base (**3**). In a columnar packing of **3-Ag(III)**, NCP skeletons are almost parallel to each other (dihedral angle < 1°) and perpendicular to the *b*-axis of the column.[16] The NCP molecules stack in an opposite direction to each other with the distances of 3.30 and 3.31 Å (r_1 and r_2, see Figure 4), and the Ag(III) metals are located along a zigzag line with a distance of 3.73 Å. In the case of the NCTPP-Ag(III) complex, the distances between the two molecular planes are 3.90 and 3.83 Å, and the Ag(III) metals are arranged along a zigzag line with alternate distances of 5.10 and 5.13 Å.

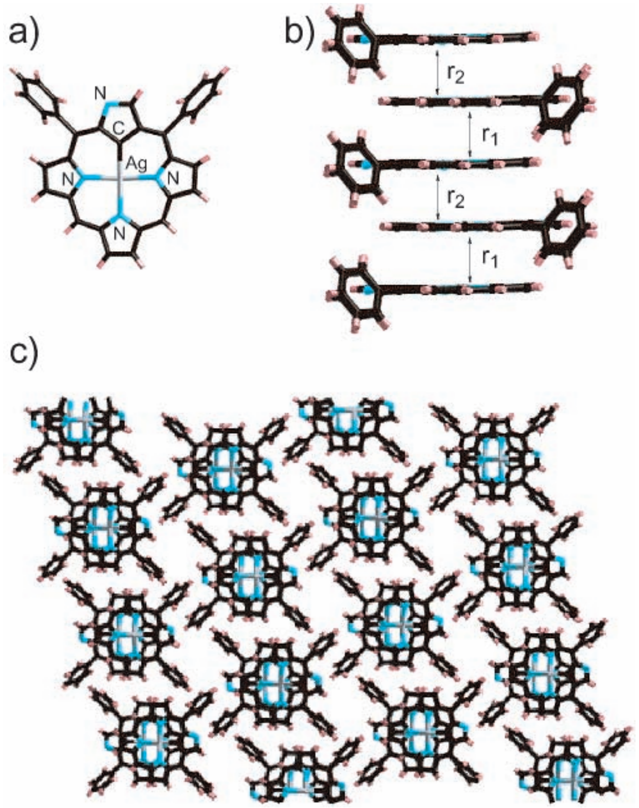

Figure 4. Molecular structure of **3-Ag(III)**: (a) top view, (b) side view, and (c) packing diagram from the *b*-axis. r_1 and r_2 denote the interplane distances between the paired and unpaired porphyrins (see text). Solvent molecules are omitted for clarity.

To clarify the factors for the change of the crystal packing of NCDPP, we synthesized the Ag(II) complex of *normal* 5,10-diphenylporphyrin (**4-Ag(II)**) as a control.[17] If the

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[12] (12) Crystal data for NCDPP (**3**): $C_{32}H_{22}N_4$, $M_w = 462.55$, orthorhombic, space group $P2_12_12$ (no. 18), $a = 21.176(2)$, $b = 22.188(2)$, $c = 9.8918(8)$ Å, $V = 4647.5(7)$ Å^3, $Z = 8$, $D_{calcd} = 1.322$ g/cm^3, $T = -150$ °C, $R = 0.078$, $R_w = 0.097$, GOF $= 0.918$.

[13] (13) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676.

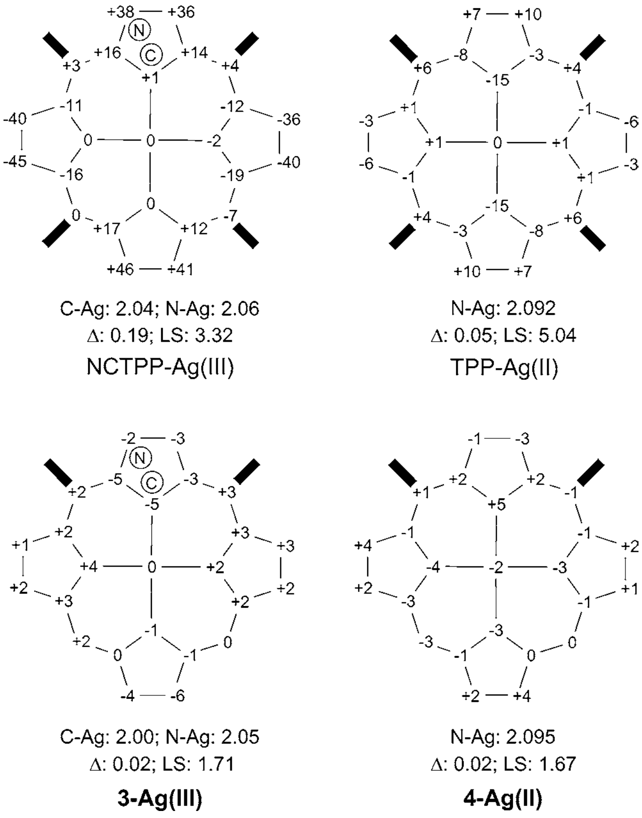
[14] (14) Scheidt, W. R.; Mondal, J. U.; Eigenbrot, C. W.; Adler, A.; Radonovich, L. J.; Hoard, J. L. *Inorg. Chem.* **1986**, *25*, 795.

[15] (15) Crystal data for **3-Ag(III)**: $C_{32}H_{17}N_4 \cdot H_2O$, $M_w = 583.40$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.224(2)$, $b = 6.6255(7)$, $c = 24.759(3)$ Å, $\beta = 102.717°$, $V = 2436.2(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.590$ g/cm^3, $T = -150$ °C, $R = 0.076$, $R_w = 0.125$, GOF $= 1.919$.

[16] (16) In CH_2Cl_2 and DMF solutions, compound **3** and **3-Ag(III)** exist as monomers and do not form dimers or aggregates, as judged by UV/vis spectra at various concentrations.

[17] (17) (a) Hatscher, S.; Senge, M. O. *Tetrahedron Lett.* **2003**, *44*, 157. (b) Brinas, R. P.; Bruckner, C. *Tetrahedron* **2002**, *58*, 4375. (c) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

Table 1. Deviations of Core Atoms from the Mean Plane ($\times 10^{-2}$ Å), Ag−C and Averaged Ag−N Bond Lengths (Å), Mean Plane Deviation (Δ, Å), and Lateral Shifts (LS, Å) in NCTPP-Ag(III), **3-Ag(III)**, TPP-Ag(II), and **4-Ag(II)** Complexes



packing structure of **4-Ag(II)** is the same as that of **3-Ag(III)**, the structural similarity of having only two phenyl groups is the likely main reason. If the packing structure differs largely, then the unusual electronic states of metals, Ag(II) vs Ag(III), need to be taken into account.

Interestingly, the observed crystal packing of **4-Ag(II)** is almost same as that of **3-Ag(III)**.[18] Moreover, the molecular planarity of **4-Ag(II)** was much enhanced compared with TPP-Ag(II) as judged by the mean deviation values, 0.02 and 0.05 Å, respectively. In the complexation of Ag(III) with a smaller ionic size, the NCTPP core was slightly distorted from planarity with a deviation of 0.19 Å; on the other hand, complex **3-Ag(III)** was almost planar with a deviation of 0.02 Å. Although it is not simple to interpret the relation between the substituent effects and the planarity of the porphyrin rings in general, it is likely that the complementary molecular structures favorable for the stacking could induce the planarity of the ring, at least in the present diphenyl derivative of NCP and *normal* porphyrin cases (**3** and **4**). The additional characteristic for both the crystal packing of **3-Ag(III)** and **4-Ag(II)** was short a lateral shift (LS)[19] between the porphyrin rings, 1.71 and 1.67 Å, respectively. These values were much smaller than those of NCTPP-Ag(III) and TPP-Ag(II), 3.32 and 5.04 Å, respectively, supporting the complementary packing of the silver complex of diphenyl derivatives. Deviation of the core atoms (Δ), C−Ag and averaged N−Ag bond lengths, and LS are summarized in Table 1.

In conclusion, N-confused 5,20-diphenylporphyrin (NCDPP) was synthesized by [3 + 1] condensation reaction, and the structure was determined by single-crystal X-ray analysis. The Ag(III) complex was found to stack regularly in the crystal, in which the packing mode was rather different from the free base form and NCTPP-Ag(III) but the same as that of the corresponding Ag(II) complex of the diphenyl derivative. Because of the resemblance to the *normal* porphyrin and the facile modification at *meso*-positions, we believe that this unsubstituted type of NCP will be useful for introducing *local perturbation* into the porphyrin-based molecular architecture.[20] Furthermore, the potential alignment of the coordinated metals in close proximity in the crystals might be of interest in applying these diphenyl-substituted porphyrin and NCP ligands for the development of conductive materials[21] or one-dimensional magnetic systems.[22]

Acknowledgment. We thank Prof. Shozo Taniguchi at Ibaraki National College of Technology for the valuable suggestion for the synthesis of **3**.

Supporting Information Available: Experimental procedures, spectral data of NCDPP (**3**), **3-Ag(III)**, and **4-Ag(II)**, a crystal packing diagram of **4-Ag(II)**, and crystallographic data (CIF) for **3**, **3-Ag(III)**, and **4-Ag(II)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Crystal data for **4-Ag(II)**: $C_{32}H_{20}N_4Ag{\cdot}0.42CH_2Cl_2$, $M_w = 604.08$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.635(6)$, $b = 6.623(2)$, $c = 24.964(9)$ Å, $\beta = 104.14(3)°$, $V = 2506.8(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.600$ g/cm^3, $T = -150$ °C, $R = 0.045$, $R_w = 0.052$, GOF = 0.907. The crystal packing diagram is shown in Supporting Information.

(19) Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 3, Chapter 16.

(20) (a) Aratani, N.; Osuka, A. *Org. Lett.* **2001**, *3*, 4213. (b) Sugiura, K.; Fujimoto, Y.; Sakata, Y. *Chem. Commun.* **2000**, 1105. (c) Liu, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.

(21) Miller, D. C.; Bollinger, J. C.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1994**, *33*, 3354.

(22) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760.