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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

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Hiomitsu Maeda^a; Atsuhiko Osuka^a; Hiroyuki Furuta^b

^a Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Japan ^b Departments of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan

Online publication date: 13 May 2010

To cite this Article Maeda, Hiromitsu , Osuka, Atsuhiko and Furuta, Hiroyuki(2003) 'Hydrogen Bonding 1-D Chain Network of *cis*-Doubly N-Confused Porphyrins', *Supramolecular Chemistry*, 15: 6, 447 – 450

To link to this Article: DOI: 10.1080/1061027031000147485

URL: <http://dx.doi.org/10.1080/1061027031000147485>

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Hydrogen Bonding 1-D Chain Network of *cis*-Doubly N-Confused Porphyrins

HIROMITSU MAEDA^a, ATSUHIRO OSUKA^a and HIROYUKI FURUTA^{a,b,*}

^aDepartment of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan; ^bDepartments of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan

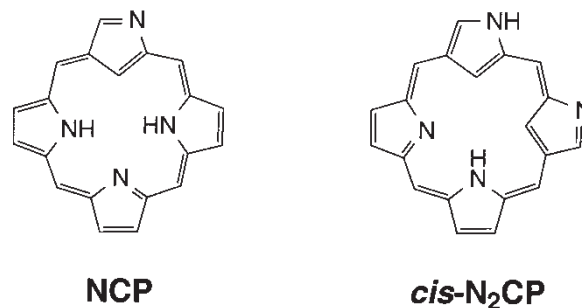
Received (in Austin, USA) 18 March 2003; Accepted 9 May 2003

The *cis*-doubly N-confused porphyrin (*cis*-N₂CP, **1) and its Cu(III) and Ag(III) complexes (1–Cu, 1–Ag) form 1-D zigzag infinite chains through hydrogen-bonding interactions between the peripheral core nitrogens (N and NH) in the solid state. Each columnar structure consists of porphyrin rings with the same chirality.**

Keywords: Porphyrin; Self-organization; Crystal structure; Hydrogen bonding

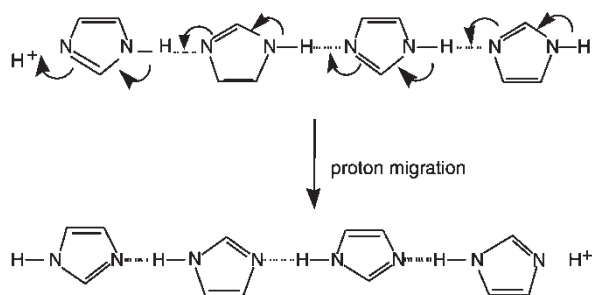
Supramolecular assemblies based on noncovalent interactions have attracted much interest as a new strategy for preparing functional materials [1–5]. One of the promising methods to fabricate molecular architectures in the solid state as well as in solution is to use hydrogen-bonding interactions that arrange each building block in a defined direction [6]. For example, a 1-D tape-like network is formed by the complementary hydrogen-bonding interactions of melamine and cyanuric acid derivatives [7]. A 2-D sheet, wherein various kinds of guest molecules can be captured, is synthesized from a resorcinol-substituted anthracene derivative by using the interactions between the hydroxyl groups [8,9]. Furthermore, a 3-D network, consisting of a mutually interpenetrating super-diamond lattice in the solid state, is synthesized from adamantane-1,3,5,7-tetracarboxylic acid bearing four hydrogen-bonding sites [10]. In the bio-related field, on the other hand, an artificial model of an ion channel in a membrane was developed by using molecular assembly of a cyclic peptide, “peptide nanotube” [11–13]. For supramolecular assembly,

pyrrole and imidazole-containing moieties are of interest because the pyrrole-like NH behaves as a hydrogen-bonding donor and the imino-type N serves as a hydrogen acceptor [14]. In fact, imidazole forms infinite hydrogen bonding chains via N–H···N in the solid state, which shows proton conductivity along the chain axis (Scheme 1) [15–18].



In the course of our study on N-confused porphyrin (NCP), a porphyrin isomer wherein one of the pyrrole rings is connected to *meso*-carbons at the α - and β' -positions [19–25], we and others have found that the peripheral nitrogen can bind a hydrogen atom derived from an acid added or transferred from inner core by NH tautomerism [19,25]. To this outer NH, association of a solvent molecule such as dimethylformamide (DMF) or anion through hydrogen bonding is observed [25–28]. In this context, the multiply NCP, wherein more than one of the pyrrole rings are confused [29], are considered as possible building blocks for supramolecular assemblies because these compounds have both the hydrogen-bonding

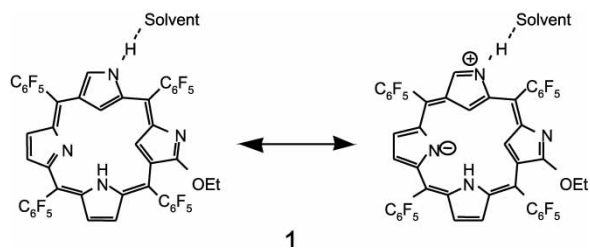
*Corresponding author. Tel.: +81-92-642-3548. Fax: +81-92-651-5606. E-mail: hfuruta@cstf.kyushu-u.ac.jp



SCHEME 1 Proton transfer cascade in imidazole network system.

donor (NH) and acceptor (N) sites for self-association. Herein, we report the formation of 1-D chain networks of *cis*-doubly N-confused porphyrin [*cis*-N₂CP (**1**)] [30–34] and its metal complexes (**1**-Cu, **1**-Ag) in the solid state. The hydrogen-bonding interaction in solution is also described.

The syntheses and X-ray structures of the title compounds have been previously reported [30]. The free base and Ag(III) complex of **1** show only one outer NH signal, indicating that the other outer nitrogen of the confused pyrrole ring exists as an amino form (N). The nature of hydrogen bonding donor of the outer NH can be evaluated from the relative ¹H NMR chemical shifts of the NH signal in various solvents. When the solvent molecules associate tightly with the peripheral nitrogen, the electronic states and the conformation of N₂CP may change greatly. In fact, the ¹H NMR spectra of **1** showed large resonance shifts according to the solvent polarity and basicity. (Table I) For example, the outer NH signal appeared at 14.71 ppm in pyridine-*d*₅ which is shifted +5.76 ppm downfield compared with the corresponding signal in CDCl₃. By increasing the polarity of the solvents, the inner



SCHEME 2 Resonance forms of *cis*-N₂CP, **1**.

NH and CH protons are shifted to higher field, probably due to the contribution of the aromatic zwitterionic resonance form (Scheme 2) [35].[†]

In the single crystals of **1** and **1**-M (M = Cu, Ag),[‡] 1-D chain networks are formed, in which the peripheral N and NH connect to each other through hydrogen-bonding interactions (Scheme 3). The N...H–N distances and angles (∠N–H...N) are 2.915, 2.924 and 2.903 Å and 152.0, 159.4 and 159.6°, respectively (Fig. 1). Furthermore, the dihedral angles (Fig. 2(a)) between the two neighboring porphyrins, which are defined by using the mean planes of core 24 (**1**) or 25 atoms (**1**-Cu, **1**-Ag), are 62.05, 67.71 and 68.31°, respectively. On the other hand, the distances between two parallel planes (Fig. 2(b)) are 7.15, 6.89 and 6.93 Å in **1**, **1**-Cu and **1**-Ag, respectively, and the metal–metal distances for Cu(III) and Ag(III) complexes (Fig. 2(c)) are 8.395 and 8.329 Å. To the best of our knowledge, the 1-D chains observed in N₂CP (**1**, **1**-Cu, **1**-Ag) are the first examples of direct hydrogen-bonding interactions between the periphery of two porphyrinoid molecules.

In *cis*-N₂CP (**1**), the confused pyrrole ring is canted, and thus, two enantiomers could exist according to the direction of the confused pyrrole rings, “up or down”, with respect to the plane of the asymmetric macrocycle. In solution, however, the “flip-flop” motion of the confused pyrrole ring is

TABLE I Selective ¹H NMR chemical shifts (ppm) of **1** at rt

	CDCl ₃ [*]	CD ₂ Cl ₂	Acetone- <i>d</i> ₆	DMSO- <i>d</i> ₆	DMF- <i>d</i> ₇	Pyridine- <i>d</i> ₅
Outer NH	8.95	9.15	12.10	12.96	13.30	14.71
βH	7.36	7.43	7.82	7.90	8.06	8.18
βH	7.28	7.35	7.79	7.90	8.06	8.12
βH	7.06	7.14	7.60	7.70	7.87	7.93
βH	6.98	7.05	7.42	7.50	7.66	7.78
αH	6.94	7.05	7.76	7.90	8.15	8.24
Inner NH	6.38	6.20	5.58	4.86	5.14	5.52
Inner CH	3.50	3.32	2.73	2.06	2.30	2.63
Inner CH	3.20	3.04	2.52	1.83	2.11	2.58

^{*}Ref. [30].

[†]In a CH₂Cl₂ solution containing a small amount of water, association of H₂O molecules at the peripheral nitrogens was suggested from the electrochemical study of *cis*-N₂CP (**1**, **1**-Cu, **1**-Ag) [33].

[‡]CCDC Ref code: **1** (KAXNEC), **1**-Cu (KAXPAA), **1**-Ag (KAXNOM).

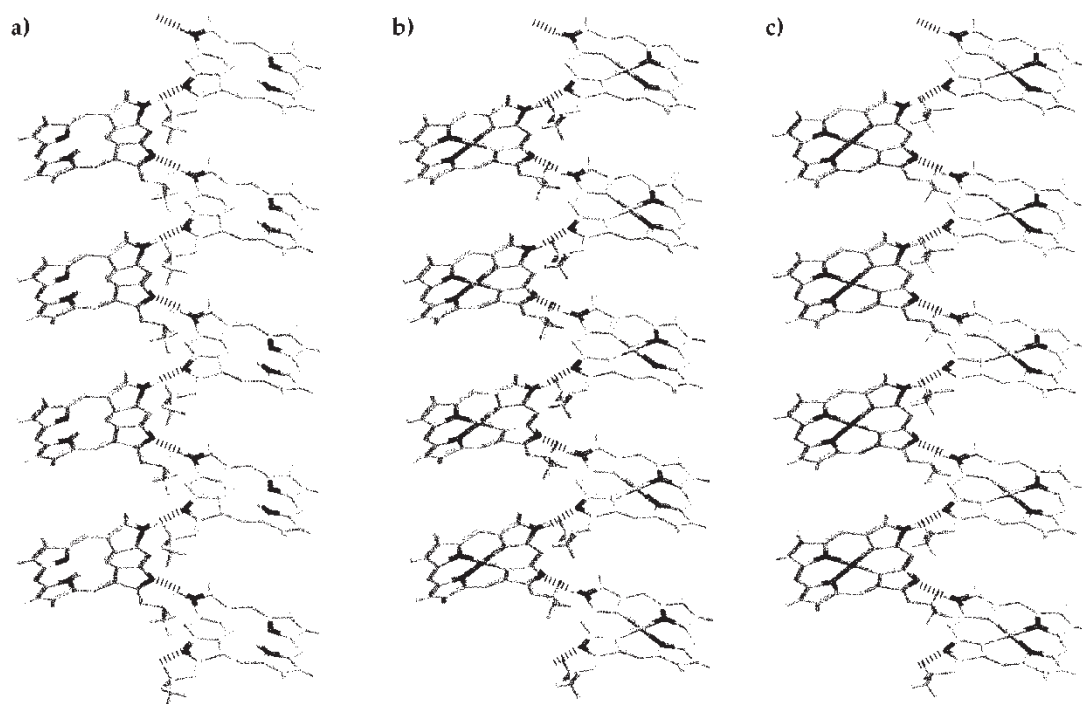
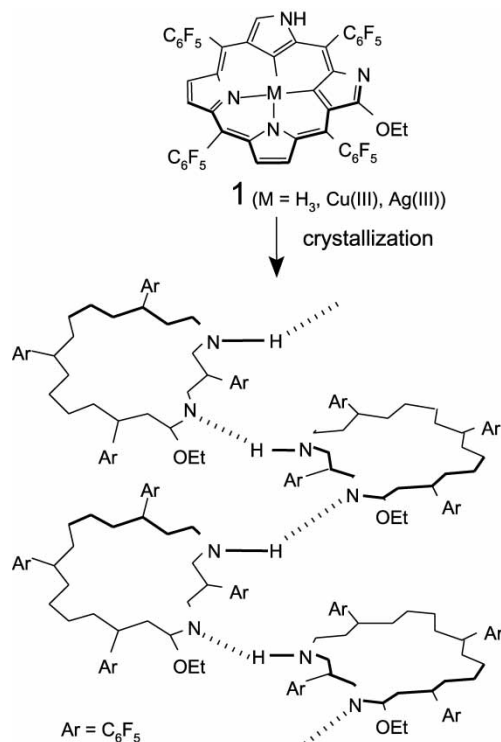


FIGURE 1 The columnar packing diagrams of (a) **1**, (b) **1-Cu** and (c) **1-Ag**.



SCHEME 3 Schematic drawings of 1-D chain networks of *cis*-N₂CP, **1**.

so fast as to cause spontaneous racemization. In the solid state, on the other hand, the motions of the pyrrole rings and also the pentafluorophenyl rings are rather suppressed, as a result, the two enantiomers become distinguishable in the free base as well as the metal complexes, **1-Cu** and **1-Ag**. As seen in the columnar structures of **1**, **1-Cu** and **1-Ag**, each hydrogen-bonding chain includes enantiomers of the *same* chirality. The zigzag spiral, thus, has its own chirality and the direction of N-H...N pathway is opposite in the neighboring columns.

In summary, in the solid state, *cis*-N₂CP (**1**) and the metal complexes (**1-Cu**, **1-Ag**) form 1-D zigzag infinite chains by means of hydrogen-bonding interactions between nitrogens (N and NH) of the macrocyclic periphery. Each columnar structure consists of macrocycles of the same chirality. The hydrogen-bonding interaction at the peripheral nitrogens in *cis*-N₂CP is also suggested from the ¹H NMR spectra in solution, especially in polar or basic solvents, where the NH signal is shifted to the lower field.[¶] At present, only alkoxy-substituted *cis*-N₂CP (**1**) has been synthesized, in which the peripheral nitrogens are distinguishable, namely, N in the alkoxy-substituted ring and NH in the remaining confused pyrrole ring.[§]

[¶]The dimerization constant for **1** was determined to be less than 20 M⁻¹ from the concentration-dependent ¹H NMR spectral changes in CDCl₃ at rt. Moreover, the "molecular weight" of **1** measured by vapor pressure osmometry (VPO) in CHCl₃ was 1178 g mol⁻¹, which is nearly equal to that of monomer **1** (*m/z* = 1018). These data suggest that the degree of the self-association of **1** in CHCl₃ is relatively small.

[§]Alkoxy-free *cis*-N₂CP was also obtained in low yields by using alcohol-free solvent in the final [2 + 2] coupling reaction of **1** (unpublished data).

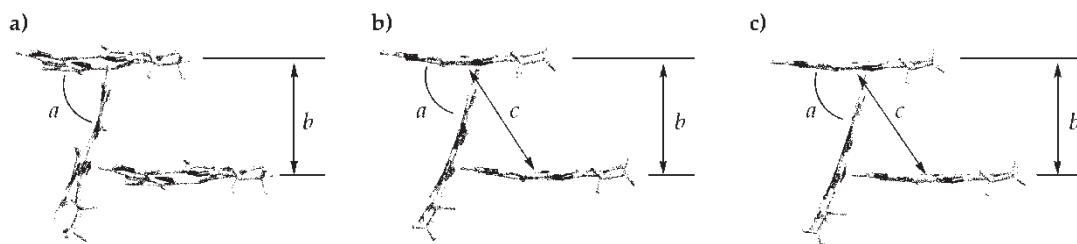


FIGURE 2 Arrangements of the neighboring three molecules of (a) **1**, (b) **1-Cu** and (c) **1-Ag**.

When the alkoxy-free *cis*-N₂CP is available, whose two outer nitrogens are equivalent just like in imidazole, a supramolecular proton transfer system could be contemplated [15–18]. Moreover, the *trans*-type of N₂CP [36,37], wherein two confused pyrroles are encountered, may form a different network from that of *cis*-N₂CP in the solid state. The design and fabrication of additional solid-state architectures using multiply N-confused porphyrins are currently underway.

Acknowledgements

M. H. thanks JSPS for a Research Fellowship for Young Scientists.

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