

Doubly N-Confused Hexaphyrin: A Novel Aromatic Expanded Porphyrin that Complexes Bis-metals in the Core

Alagar Srinivasan,[†] Tomoya Ishizuka,[†] Atsuhiko Osuka,[†] and Hiroyuki Furuta^{*,†,§,||}

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan,
Department of Applied Chemistry, Graduate School of Engineering, Kyushu University,
Fukuoka 812-8581, Japan, and PRESTO, Japan Science and Technology Corporation, Japan

Received October 19, 2002; E-mail: hfuruta@cstf.kyushu-u.ac.jp

Porphyrins are ubiquitous aromatic ligands that can chelate a variety of metals using interior four pyrrolic nitrogens (N₄) in a square-planar arrangement. Due to the limited core size, porphyrins usually serve as mononuclear ligands when they complex metals in the plane.^{1,2} Thus, for bis-metal in-plane-coordination, another class of porphyrinoids having more than four pyrrolic units in the core is contemplated.³ Among such, so-called expanded porphyrins, hexapyrrolic porphyrinoids, hexaphyrins, are promising candidates because some kinds of hexaphyrins were reported to take a planar conformation.^{4,5} For example, Sessler and co-workers have shown that [24]hexaphyrin-(1.0.0.1.0.0), "amethyrin", could coordinate two Cu(II) ions with inward-pointing six pyrrolic nitrogens and two bridging chlorides in the cavity.⁴ A more spacious hexaphyrin-(1.1.1.1.1.1) system of *meso*-aryl type, on the other hand, has been shown to have a pseudorectangular framework,⁵ but the formation of bis-metal in-plane-complex seems difficult because it accompanies the activation of inner CH of the N₂C₂ macrocyclic core.⁶ If one or more interior carbon atoms is replaced by nitrogen, the bis-metal coordination in a modified N₃C or N₄ core would become more facile. Such an idea promoted us to introduce two *confused* pyrrolic units into *normal* hexaphyrin framework to produce a doubly N-confused hexaphyrin (N₂CH).⁷ Herein, we present the syntheses and spectral and structural characterization of doubly N-confused *meso*-hexaarylhexaphyrin (**2** and **3**), the amide derivatives (**4** and **5**), and their bis-metal complexes (**6** and **7**). To the best of our knowledge, these are the first examples of doubly N-confused hexaphyrins and square-planar coordinated in-plane bis-metal complexes of aromatic porphyrinoid.

When N-confused tripyrrane (**1**) was treated with pentafluorobenzaldehyde in the presence of *p*-toluenesulfonic acid (*p*-TSA), followed by oxidation with *p*-chloranil, *meso*-hexakis(pentafluorophenyl)-substituted doubly N-confused hexaphyrins, **2** and **3**, were obtained as brown solids in 7 and 3% yields, respectively (Scheme 1a). FABMS of **2** and **3** showed the molecular ion peaks at *m/z* 1462 and 1460, suggesting the formation of the reduced and oxidized N₂CH. The ¹H NMR spectrum of **2** in CDCl₃ at -50 °C showed two different NH signals at 11.71 and 10.76 ppm and *confused* pyrrolic α-CH and β-CH signals at 7.03 and 6.40 ppm, respectively, which proved that the compound was nonaromatic [28π]. Supporting these, the electronic absorption spectra displayed three broad bands in the region from 380 to 590 nm. In contrast, the aromatic feature [26π] of compound **3** was shown in a strong Soret-like band at 591 nm and four Q-type bands from 650 to 1100 nm.⁸ However, **3** was quite unstable and gradually oxidized into amide **5** in CH₂Cl₂ solution at room temperature.

Chart 1. Schematic Drawings of Bis-metal Complexes of Various Hexaphyrins



On varying the oxidizing agent from *p*-chloranil to 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in the condensation reaction, two different products **4** and **5** were obtained as greenish solids in 7 and 10% yield, respectively (Scheme 1b). FABMS of **4** and **5** showed the peaks at *m/z* 1494 and 1492, respectively, indicating the presence of N₂CH moiety as well as two oxo groups. In fact, the presence of -C=O was confirmed by the IR band at 1716 and 1683 cm⁻¹ for **4** and **5**, respectively. The difference in the frequency (33 cm⁻¹) suggested the strong hydrogen-bonding interaction in **5**. The nonaromatic [28π] characters of **4** were reflected from ¹H NMR signals in the range from 14.00 to 5.75 ppm, and the electronic absorption spectrum, where five broad bands were displayed from 325 to 755 nm. On the other hand, compound **5** [26π] showed the aromatic features and the inner hydrogen bondings as judged by ¹H NMR spectrum, in which the outer β-CH and NH signals of the *confused* ring and the NH of *normal* pyrroles resonated at 10.74, -0.73, and -0.24 ppm, respectively. The aromatic planar structure of **5** was also suggested from the absorption spectrum, displaying the intense Soret-like band at 566 nm.

The explicit structural details of **5** were revealed by the single-crystal X-ray analysis. Consistent with the above observations, two *confused* pyrrole rings in **5** were inverted and two oxo groups attached at the inner α-carbons to afford the amide groups. The two carbonyl groups were forming the intramolecular hydrogen bondings with encountered amide NH (O(1)-...N(5): 2.755 Å) and adjacent pyrrole NH (O(1)-...N(3): 2.609 Å), keeping the molecule planar. The mean deviation was only 0.054 Å to the mean plane, consisting of a core of 36 atoms (excluding the oxygen atoms). As a result of oxygenation of N₂CH, two N₃C compartments of **2** and **3** changed to two N₃O cores in **4** and **5** (Figure 1a,b).

The metal coordination chemistry was performed on stable **5** by using Cu(II) and Ni(II) salts. When it was treated with anhydrous Cu(II) acetate, in CH₂Cl₂ solution, blue-greenish solid **6** was obtained in quantitative yield (Scheme 1c). The complexation of bis-Cu(II) metal **6**, was confirmed by FABMS peak at *m/z* 1614. The electronic absorption spectrum showed the Soret-like band at 616 nm, which was 50 nm red-shifted as compared to the free base **5**. The complex was paramagnetic, and the magnetic susceptibility measurements proved that the Cu ions were present in the

[†] Kyoto University.
[§] Kyushu university.
^{||} PRESTO, JST.

Scheme 1

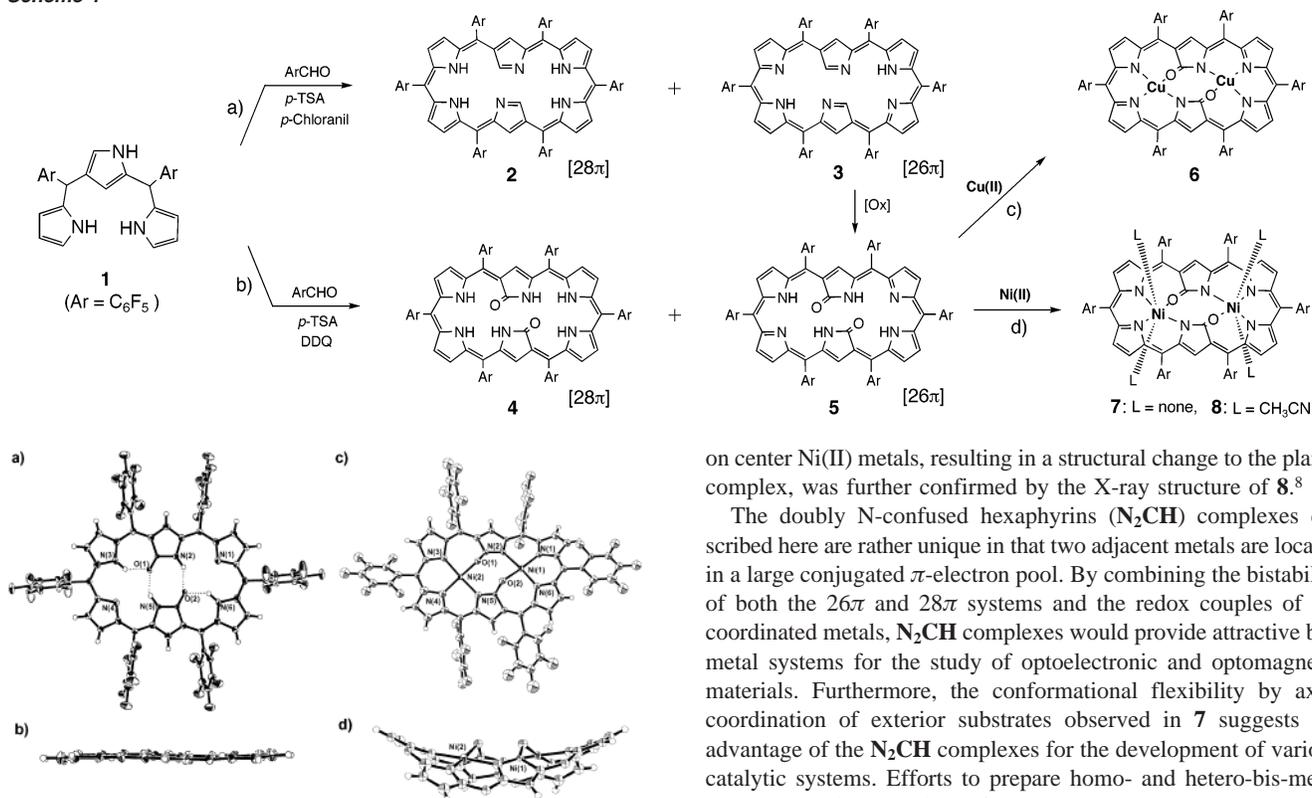


Figure 1. Molecular structures of **5** and **7** (a, c: top view, and b, d: side view). Pentafluorophenyl groups were omitted for clarity in (b) and (d). Dotted lines indicate hydrogen-bonding interactions.

paramagnetic d^8 form ($\mu_{\text{eff}} = 1.73 \mu_{\text{B}}$, at 77 K). The preliminary X-ray analysis of **6** confirmed the bis-metal coordination and the planarity of the molecule.⁸ In contrast, the bis-Ni(II) complex **7** was synthesized in a refluxing solution of **5** in toluene by using Ni(II) acetylacetonate in 95% yield (Scheme 1d). The ¹H NMR spectrum of **7** (FABMS: $m/z = 1606$) showed signals from 9.50 to 8.70 ppm, suggesting the compound was diamagnetic and both the nickel oxidation states were +2. The electronic absorption spectrum displayed the broad bands from 360 to 1210 nm indicating that the complex was distorted from planarity. The single-crystal X-ray analysis of **7** confirmed that each Ni metal was coordinated by three nitrogens and an oxygen atom in a square-planar fashion at the distance of 4.689(5) Å. The molecule was completely distorted from the mean macrocyclic plane, and the mean deviation of core 36 atoms was 0.6632 Å (Figure 1c,d).

Interestingly, when the absorption spectrum of **7** was measured in CH₃CN, the broad bands in **7** became sharper to give a more porphyrin-like spectrum, suggesting the large structural change from distorted to planar due to the solvent coordination. Such a change was also reflected in the ¹H NMR spectrum where paramagnetic downfield shifting ($\Delta\delta = 5\text{--}6$ ppm) was observed, probably due to Ni(II) hexacoordination. The solvent coordination

on center Ni(II) metals, resulting in a structural change to the planar complex, was further confirmed by the X-ray structure of **8**.⁸

The doubly N-confused hexaphyrins (**N₂CH**) complexes described here are rather unique in that two adjacent metals are located in a large conjugated π -electron pool. By combining the bistability of both the 26 π and 28 π systems and the redox couples of the coordinated metals, **N₂CH** complexes would provide attractive bis-metal systems for the study of optoelectronic and optomagnetic materials. Furthermore, the conformational flexibility by axial coordination of exterior substrates observed in **7** suggests the advantage of the **N₂CH** complexes for the development of various catalytic systems. Efforts to prepare homo- and hetero-bis-metal complexes using a variety of metals are currently underway.

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Supporting Information Available: Synthetic details and absorption spectra (**2–8**), crystallographic data of **5** and **7**, crystal figures of **6** and **8** (PDF/CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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