

A Doubly *meso-α* Linked N-Confused Porphyrin Tape Silver(III) Complex Comprising an Antiaromatic Pyrrolo[2,3-*f*]indole Segment

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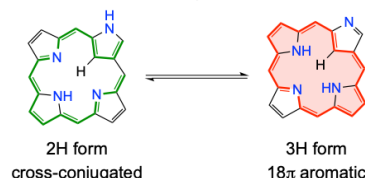
Abstract: The free base form of doubly *meso-α* linked N-confused porphyrin (NCP) tape **3** was successfully synthesized via Ir(I) mediated intramolecular coupling. The following silver complexation afforded the Ag(III) complex of doubly *meso-α* linked NCP tape **4**. While **3** exhibited 38π aromatic characters, **4** exhibited not only 18π aromatic NCP-type characteristics but also a decent antiaromatic contribution of 12π pyrrolo[2,3-*f*]indole segment, as probed by NMR spectra, absorption spectra, and DFT calculations.

Introduction

N-Confused porphyrin (NCP) is a kind of porphyrin isomers bearing a so-called "confused" pyrrole subunit.^[1] NCPs display structurally and electronically different features from those of porphyrins such as solvent-dependent NH-tautomerism, high reactivity at the confused pyrrole moiety, and versatile coordination mode including carbon-metal bond.^[2] Among them, the tautomerism of NCPs involves not only the inner pyrrolic protons but also the outer pyrrolic proton, thereby causing a switching of the electron circuit between a cross-conjugated 2H form and an 18π aromatic 3H form (Figure 1a). Such a tautomerism has been applied for stimuli-responsive materials that can control the proton transfer and anion sensing. Several NCP oligomers have also been used for the same purpose. As such, various NCP oligomers have been explored but fully conjugated fused NCP oligomers are quite limited.^[3] Recently, we have reported the first example of doubly *meso-α* linked NCP dimer **2**, which was obtained by Ni(II) metalation-induced transannular bond formation of *meso*-free tetrabromo[36]octaphyrin **1** (Scheme 1).^[4] Notably, the electron conjugation mode in **2** is represented as type C (each inner 2H form) that possesses a global 36π antiaromatic conjugation circuit (Figure 1b). Despite its formally fused dimer type structure, the dominant contribution is derived from the octapyrrolic network. Indeed, **2** was oxidized to afford a type D structure exhibiting global 34π aromaticity. The inner 3H form represented as type B can be created via tautomerization of type C form, which may exhibit a genuine fused NCP dimer-like electronic state (18π+18π), switchable with a 38π aromatic type A structure via

redox interconversion. In light of the prominent attributes of porphyrin tapes,^[5] further investigation on the fused NCP dimer is indispensable in the chemistry of NCP. Herein, we report the synthesis of doubly *meso-α* linked NCP tape with a type B electronic state exhibiting an 18π+18π electron conjugated system via fixation of the inner 3H-type coordination sphere by Ag(III) complexation. Interestingly, along with its 18π aromatic conjugation, a decent contribution of 12π antiaromatic pyrrolo[2,3-*f*]indole segment is probed. This system thus demonstrates a novel hybrid aromatic/antiaromatic conjugation system in one chromophore.

a) N-confused porphyrin



b) doubly-linked N-confused porphyrin tapes

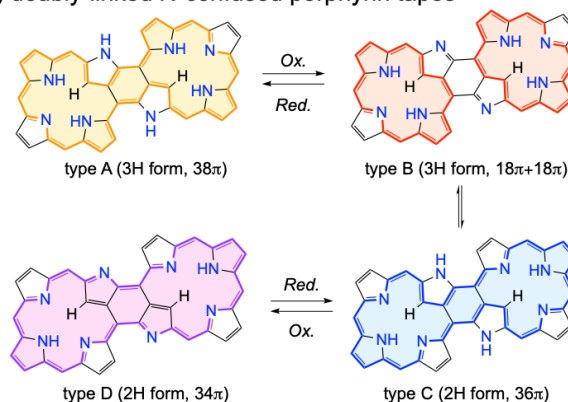
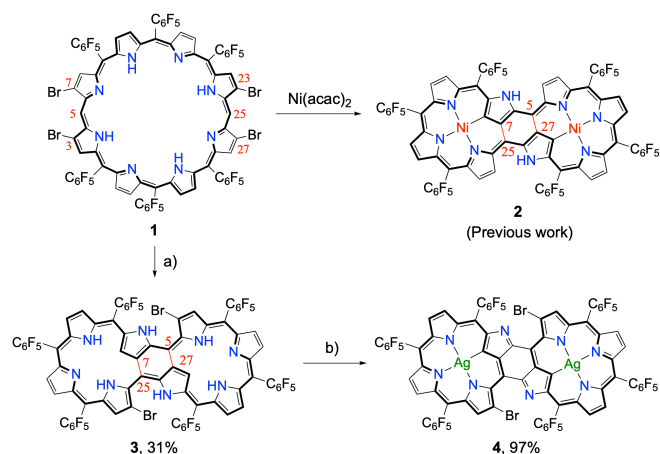


Figure 1. (a) Tautomerization of NCP. (b) Possible tautomerization and electronic conjugation in doubly-linked NCP tape.



Scheme 1. Synthesis of **3** and **4**. a) $[\text{Ir}(\text{cod})\text{Cl}]_2$, Cs_2CO_3 , THF, reflux, b) AgOTf , NaOAc , CHCl_3 / MeOH , RT.

Results and Discussion

As an initial attempt, demetalation of **2** to obtain its free base form was examined with $\text{H}_2\text{SO}_4/\text{TFA}$, which, however, ended in failure. Meanwhile, we found that treatment of *meso*-free tetrabromooctaphyrin **1** with $[\text{Ir}(\text{cod})\text{Cl}]_2$ in the presence of Cs_2CO_3 in refluxing THF afforded N-confused porphyrin dimer **3** in 31% yield. High-resolution atmospheric-pressure-chemical-ionization time-of-flight (HR-APCI-TOF) mass spectrometry indicated the molecular ion peak of **3** at $m/z = 1770.9562$ (calcd for $\text{C}_{76}\text{H}_{19}\text{N}_8\text{F}_{30}\text{Br}_2$ $[M+\text{H}]^+$: 1770.9615), confirming the loss of only two bromine atoms from **1**. The structure has been assigned by X-ray crystallographic analysis (Figure 2a).^[6] It is inferred that Ir(I) mediated intramolecular C–H/C–Br heterolytic coupling led to the fused structure followed by two-electron reduction of the resulting macrocycle by excessive Ir(I) reagent (See the Supporting Information, SI). As a result, 5,27- and 7,25-positions are connected in **3**, giving rise to the same molecular framework as that of **2**. Importantly, however, **3** was revealed to be classified as type A as indicated by the angles of $\angle\text{C6-N1-C9}$, $\angle\text{C11-N2-C14}$, $\angle\text{C16-N3-C19}$, and $\angle\text{C21-N4-C24}$ to be $109.4(4)^\circ$, $110.7(4)^\circ$, $104.9(4)^\circ$, $111.6(4)^\circ$, respectively (Figure 2b). Notably, steric repulsion between the bromide and the outer-pointing NH results in deformation as depicted by the mean-plane deviation (MPD) value^[7] of 0.50 Å. In the ^1H NMR spectrum of **3**, the signals due to the outer β -protons are observed in the range of 7.74–7.23 ppm and the inner β -proton signal is observed at 2.75 ppm, indicating the diatropic ring current effect. The aromatic nature of **3** was also supported by the negative NICS(0) values^[8,9] in the NCP-segment as well as in the fused site (ring I) (Figure 2c). The ACID calculation showed clockwise ring-current flow mainly along the whole macrocycle, indicating the dominant contribution of global 38π aromaticity (Figure 2d).^[9,10]

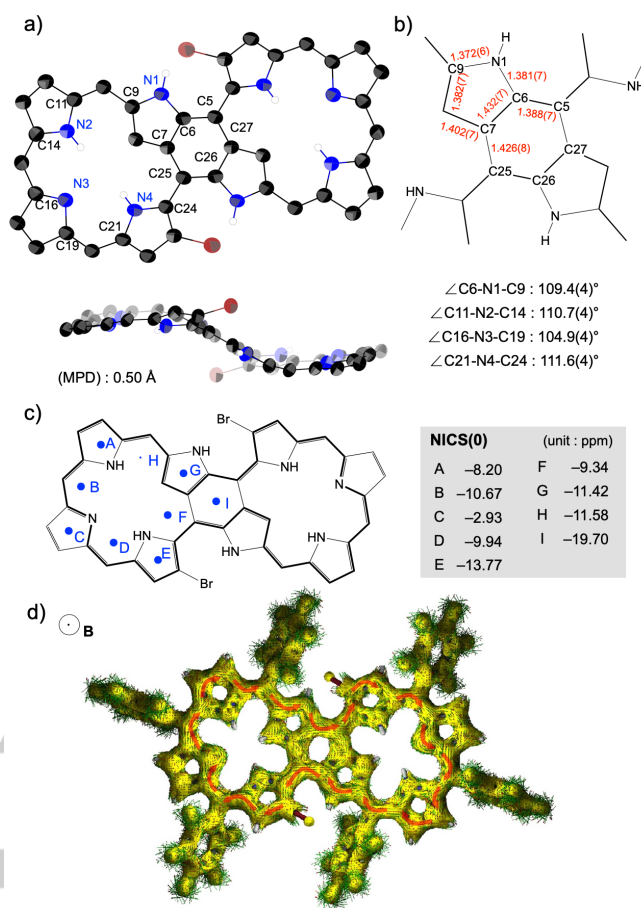


Figure 2. a) X-Ray crystal structure of **3**.^[6] Top: perspective view, bottom: side view. Solvent molecules, pentafluorophenyl groups, and hydrogen atoms except for NHs are omitted for clarity. The thermal ellipsoids are scaled to 50% probability. b) Selected bond lengths and angles. c) Selected NICS(0) values. d) ACID plot for **3** (isosurface value: 0.05).

The cyclic voltammetry experiment of **3** revealed its first oxidation potential at 0.24 V relative to ferrocene (Fc)-ferrocenium ion (Fc^+) couple as a pseudo-reversible peak (Figure S5). The reduction waves were observed as reversible peaks at -1.29 and -1.68 V. The results indicate **3** is easily oxidizable, likely accompanied with proton dissociation.^[11] Thus, oxidation of **3** was examined by using MnO_2 , PbO_2 , or DDQ. However, these attempts resulted in an observation of multiple spots in TLC analyses. Then, we examined Ag(III) complexation to fix the 3H-form of the NCP segments.^[12] Treatment of **3** with AgOTf in the presence of NaOAc indeed afforded bis-Ag(III) complex **4** in 97% yield. HR-APCI-TOF mass spectrometry indicated the molecular ion peak of **4** at $m/z = 1975.7949$ (calcd for $\text{C}_{76}\text{H}_{10}\text{N}_8\text{F}_{30}\text{Ag}_2\text{Br}_2$ $[M]^+$: 1975.7024), suggesting two silver ions were incorporated accompanied with the loss of two hydrogen atoms. The structure has been assigned by X-ray crystallographic analysis (Figure 3a).^[13] The angles of $\angle\text{C6-N1-C9}$ and $\angle\text{C26-N5-C29}$ were $105.7(4)^\circ$ and $105.7(4)^\circ$, respectively, indicating that the outer pointing pyrroles (N1 and N5) were converted to imine-type nitrogen during the metalation (Figure 3b). The X-ray structure also showed the core deformation due to the steric repulsion between the bromide and the lone pair of nitrogen atom with its MPD value of 0.68 Å.^[14] Nevertheless, each NCP unit was relatively planar (its MPD value^[15] of 0.18 Å). In the ^1H NMR

spectrum of **4**, the signals due to the outer β -protons are observed in the range of 8.04–7.71 ppm, indicating aromatic character, although these peaks are upfield-shifted when compared with *meso*-pentafluorophenyl-substituted N-confused porphyrin Ag(III) complex (8.94–8.71 ppm for outer β -H).^[12] The shifts are partially attributable to the decreased aromatic ring current effect associated with enhanced electronic conjugation over the array.^[16,17] Notably, ACID calculation^[9,10] showed not only clockwise ring-current flow along the NCP segment but also counter-clockwise antiaromatic ring-current flow along the central pyrrolo[2,3-*f*]indole segment (Figure 3d). NICS(0) calculation supports these assignments;^[8,9] the NICS(0) values at the center of ring G and ring I showed positive values (+21.69 and +23.98 ppm, respectively), while the values in the NCP segments are negative (Figure 3c). To visualize the hybridized nature of 18π aromatic and 12π antiaromatic segments, 2D isochemical

shielding surface (ICSS) map calculation was conducted at 1 Å above the mean plane of **4**, which obviously illuminated both contributions (Figure 3e,f).^[17] Previously reported doubly *meso*- β linked porphyrin dimer exhibited negligible contributions of such dual aromatic characteristics.^[18]

The cyclic voltammetry experiment revealed the oxidation potentials of **4** at 0.61 and 0.88 V and reduction potentials at –0.31 and –0.70 V relative to Fc/Fc⁺ couple (Figure S5b). Compared with **2**,^[5] the reduction potential of **4** was almost the same, while the oxidation potential of **4** was positively shifted, giving rise to the wider HOMO–LUMO gap (0.92 eV). Reduction of **4** was attempted to obtain Ag(III) complex of **3** with maintenance of the type A conjugation system. However, treatment of **4** with NaBH₄ or hydrazine monohydrate only promoted demetalation to give freebase **3**.

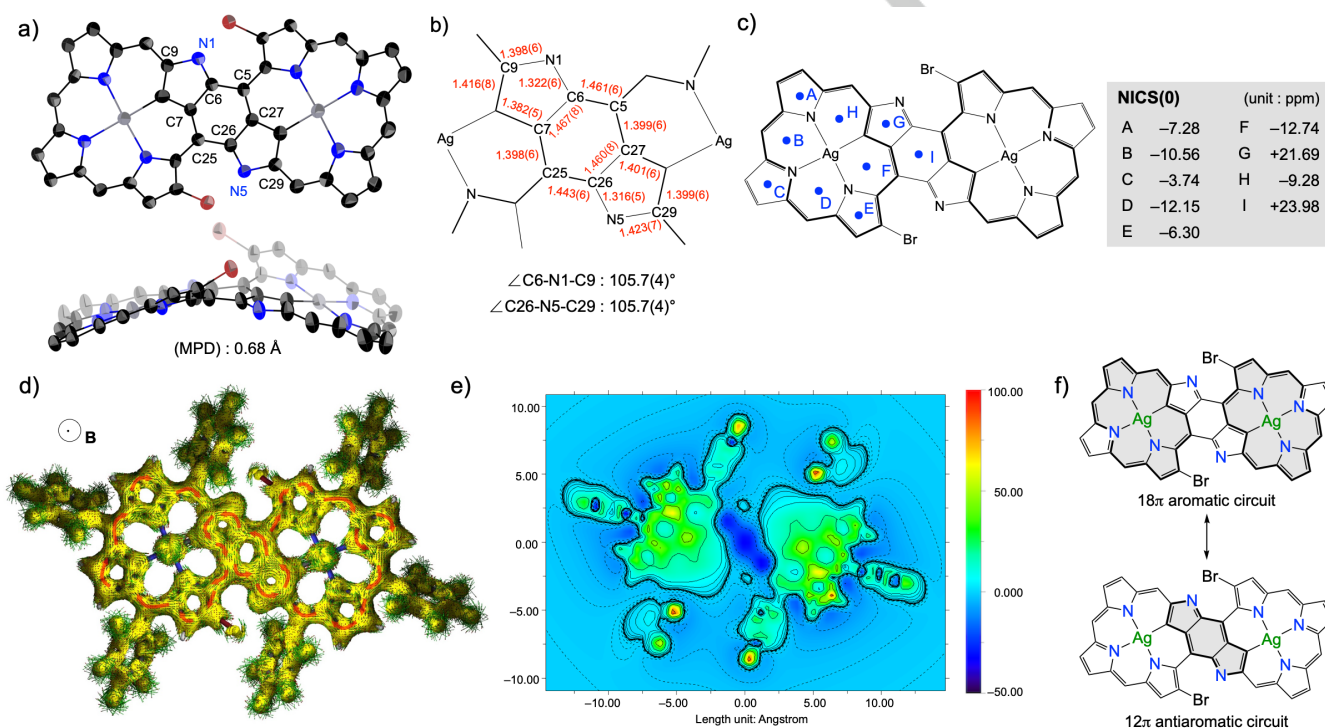


Figure 3. a) X-Ray crystal structure of **4**.^[13] Top: perspective view, bottom: side view. Solvent molecules, pentafluorophenyl groups, and hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 50% probability. b) Selected bond lengths and angles. c) Selected NICS(0) values. d) ACID plot for **4** (isosurface value: 0.05). e) Calculated 2D ICSS(1)_{zz} map for **4**. f) Schematic drawing of the possible resonance structures in **4**.

The absorption spectra of **3** and **4** are shown in Figure 4. NCP tape **3** shows split Soret-like bands at 455 and 517 nm, and Q-like bands at 600–900 nm, which is characteristic of fused porphyrinoids.^[19] On the other hand, Ag(III) complex **4** shows Soret-like bands at 621 nm and Q-like bands at 820 nm with a weak absorption tail up to 1700 nm. This forbidden absorption band in the NIR region is characteristic of antiaromatic porphyrinoid species^[19] and is attributed to the HOMO-to-LUMO transition. TD-DFT calculation indeed shows the lowest-energy transition at 1126 nm (Figure S13). Therefore, it is conceivable that **4** possesses both aromatic and antiaromatic nature. Notably, such weak NIR absorption was not observed for *meso*- β , *meso*- β doubly linked porphyrin dimers.^[18] Nevertheless, **4** represents the

first example of NCP tapes featuring effective $18\pi+18\pi$ conjugation throughout the chromophores as indicated by its MO profile (Figure S8).

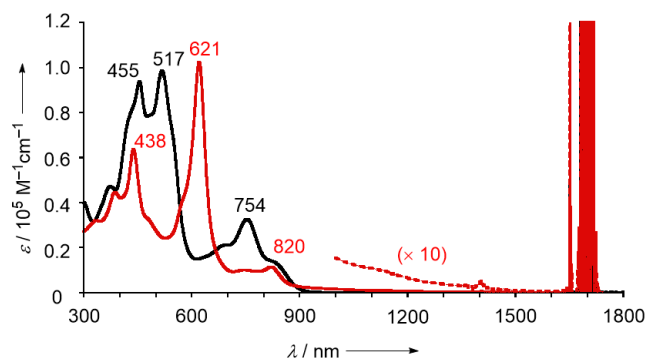


Figure 4. UV/Vis/NIR absorption spectra of **3** (black) and **4** (red) in CH_2Cl_2 .

Conclusion

In summary, the free base form of doubly *meso-α* linked NCP tape **3** was obtained via iridium-mediated intramolecular coupling. Although **3** exhibited 38π aromatic characters, Ag(III) complexation afforded the “genuine” doubly *meso-α* linked NCP tape Ag(III) complex **4** which featured type B ($18\pi+18\pi$) electronic conjugation. Besides, **4** exhibited a hybridized character of 18π aromatic and 12π antiaromatic conjugation systems, the latter derived from the central pyrrolo[2,3-*f*]indole segment. This study links the chemistry of expanded porphyrins with that of NCPs and further exploration along this strategy will lead to give novel electronic systems.

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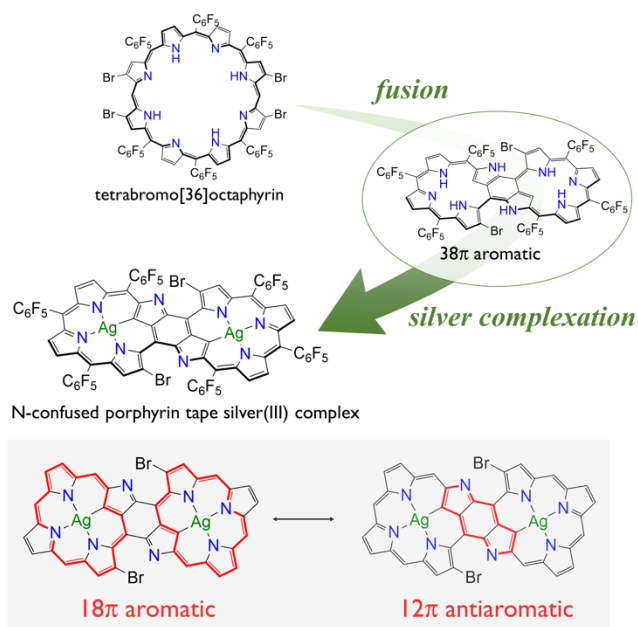
Keywords: aromaticity • expanded porphyrin • N-confused porphyrin • porphyrin tape • metal complex

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A free base form of *meso- α* linked N-confused porphyrin dimer was obtained via Ir(I)-mediated intramolecular fusion reaction. Its Ag(III) complex was obtained and characterized to have a hybrid character of 18 π aromatic N-confused porphyrin and 12 π antiaromatic pyrrolo[2,3-*f*]indole segments.