

# Confusion Approach to Porphyrinoid Chemistry

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## ABSTRACT

N-confused porphyrin (NCP) is a porphyrin isomer that is different largely from the parent porphyrin, particularly in the physical, chemical, structural, and coordination properties. Introduction of the *confused* pyrrole into the *normal* and *expanded* porphyrins leads to generation of the *confused* porphyrinoids having rich structural diversity. In this Account, we introduce a series of N-confused porphyrinoids recently synthesized and highlight their properties such as *fusion*, peripheral N coordination, supramolecular assemblies, anion binding, and singlet-oxygen sensitization.

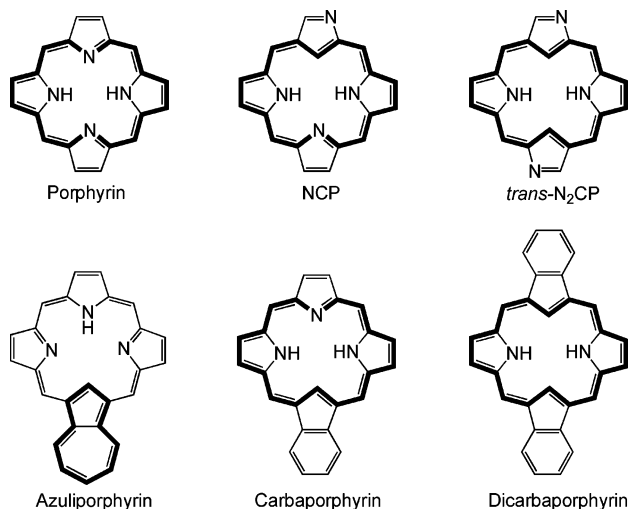
## Introduction

Porphyrin, a representative of conjugated tetrapyrrolic macrocycles, has been a potent candidate for diverse applications in the areas of biology, medicine, material science and catalysis.<sup>1</sup> Recently, syntheses of new porphyrin isomers continue to attract the attention of chemists because of their spectral, structural, chemical, and physical properties, in comparison with the parent porphyrin system. So far, two kinds of porphyrin isomers have been discovered. Both the isomers have a formula of C<sub>20</sub>H<sub>14</sub>N<sub>4</sub> in their macrocyclic core with an 18  $\pi$ -electron-conjugated pathway. In the first category, all of the pyrrole nitrogens (N<sub>4</sub>) are inside the core that differs from the arrangement of the pyrrole-linking carbon atoms from that of *normal* porphyrin. The first isomer of such kind, *porphycene*, was synthesized by Vogel et al. in 1986.<sup>2</sup> Since then, *corrphycene*,<sup>3</sup> *hemiporphycene*,<sup>4</sup> and *isoporphycene*<sup>5</sup> have been reported. In the second category, one of the pyrrole rings is *confused* or *inverted* to form an N<sub>3</sub>C core, which is considered a “true porphyrin isomer,” because it contains four *meso*-carbon atoms as the same as the *normal* one. The first isomer of such kind, *N-confused porphyrin* (NCP), was independently reported in 1994 by us and Latos-Grażyński's group.<sup>6</sup> Recently, second genera-

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Chart 1



tion of the *confused* isomers, *doubly N-confused porphyrins* (N<sub>2</sub>CP), was also synthesized.<sup>7,8</sup> Apart from the isomers, various carbaporphyrinoids such as azuliporphyrin,<sup>9a</sup> carbaporphyrins,<sup>9b</sup> and dicarbaporphyrins<sup>9c</sup> were synthesized by Lash et al. (Chart 1). Because of the similar inner framework to NCPs, the coordination chemistry of these ligands is closely related but in no way parallel to the NCPs.<sup>9</sup> Furthermore, heteroatom-containing porphyrins, in which one or more pyrrolic nitrogen atoms are replaced by O, S, Se, or Te, were reported first by Ulman and co-workers,<sup>10a</sup> and later by Latos-Grażyński et al.<sup>10b</sup>

Research on the expanded analogues has also received considerable attention. The first expanded porphyrin, *sapphyrin*, wherein five pyrrole rings are connected through four *meso*-carbon atoms, was reported by Woodward in 1966.<sup>11</sup> In series, the first carbaporphyrin was introduced by Lash et al.,<sup>12</sup> and the core-modified N-confused sapphyrin was synthesized by us along with Chandrashekar et al.<sup>13</sup> The next higher homologues, *pentaphyrin* and *hexaphyrin*, were reported by Gossauer in 1983 (Chart 2).<sup>14</sup> Since then, a series of expanded porphyrins have been reported.<sup>15</sup> These macrocycles are widely used as receptors for anions,<sup>15</sup> sensitizers for photodynamic therapy (PDT),<sup>16</sup> and magnetic resonance imaging (MRI) contrasting agents.<sup>17</sup>

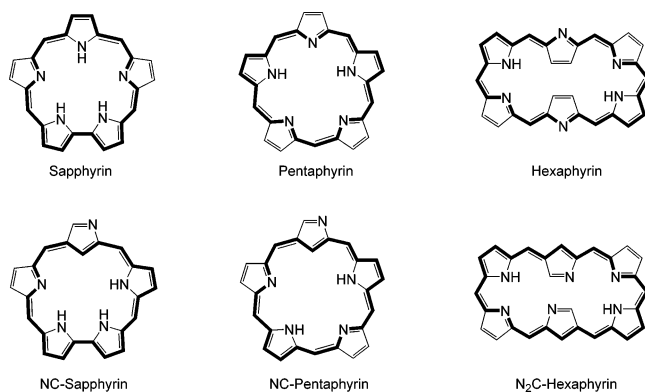
In this Account, we emphasized our recent results, especially focusing on the *confused* analogues. At first, we described the synthesis of *meso*-aryl N-confused porphyrin (NCP, **1**) and one of its characteristic properties, NH tautomerism. Second, we focused on the second generation of NCP, such as *cis*- and *trans*-N<sub>2</sub>CP and their metal complexes. Third, we discussed the transformation of the *confused* unit into a *fused* one in NCP and N-confused pentaphyrin. Next, we described the doubly N-confused derivatives of pentaphyrin and hexaphyrin, particularly, their *oxo* derivatives and metal complexes. Finally, we

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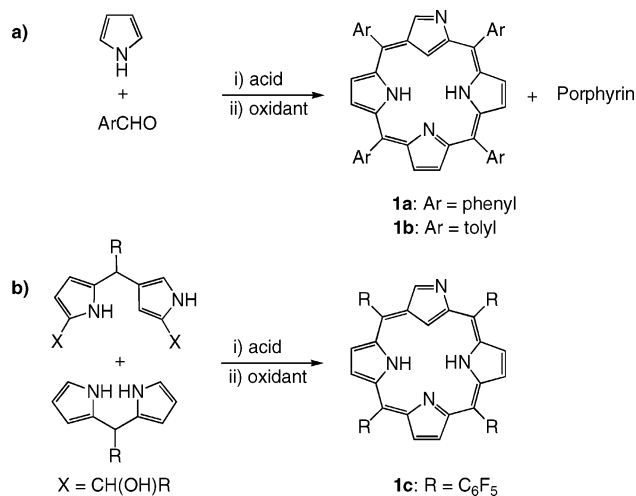
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Chart 2



Scheme 1

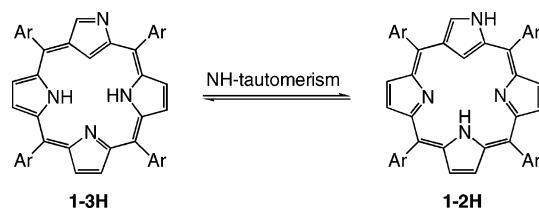


focused on the supramolecular chemistry of NCP, mainly the role of unique *confused* pyrrole in the coordination chemistry, its anion-binding ability, and the attempt of using as sensitizers for the singlet-oxygen generation. For nomenclature, we used the same terms (*normal*, *confused*, *inverted*, and *fused*) here as we mentioned in our earlier article.<sup>18</sup>

## N-Confused Porphyrins (NCP)

The first NCP (**1**) was synthesized through the Rothmund-type reaction, namely, the acid-catalyzed condensation of pyrrole and benzaldehyde, with concurrent formation of *normal* porphyrin. The reported yields were low [N-confused tetraphenylporphyrin (NCTPP, **1a**), 5–7%, and N-confused tetratolylporphyrin (NCTTP, **1b**), 4%] (Scheme 1a).<sup>6</sup> In 1999, Lindsey and co-workers reported an improved synthesis of **1a** by using methanesulfonic acid as a catalyst, and the yield was increased to 39%.<sup>19</sup> Perusal of the literature also revealed the *meso*-free type of NCP synthesis, which was obtained through the [2+2] and [3+1] acid-catalyzed condensation of the respective precursors followed by oxidation.<sup>20,21</sup> For the synthesis of pentafluorophenyl-substituted NCP (**1c**), Lindsey's modified procedure was not efficiently helpful; thus, we

Scheme 2



adopted a [2+2] acid-catalyzed condensation reaction (Scheme 1b).<sup>22</sup>

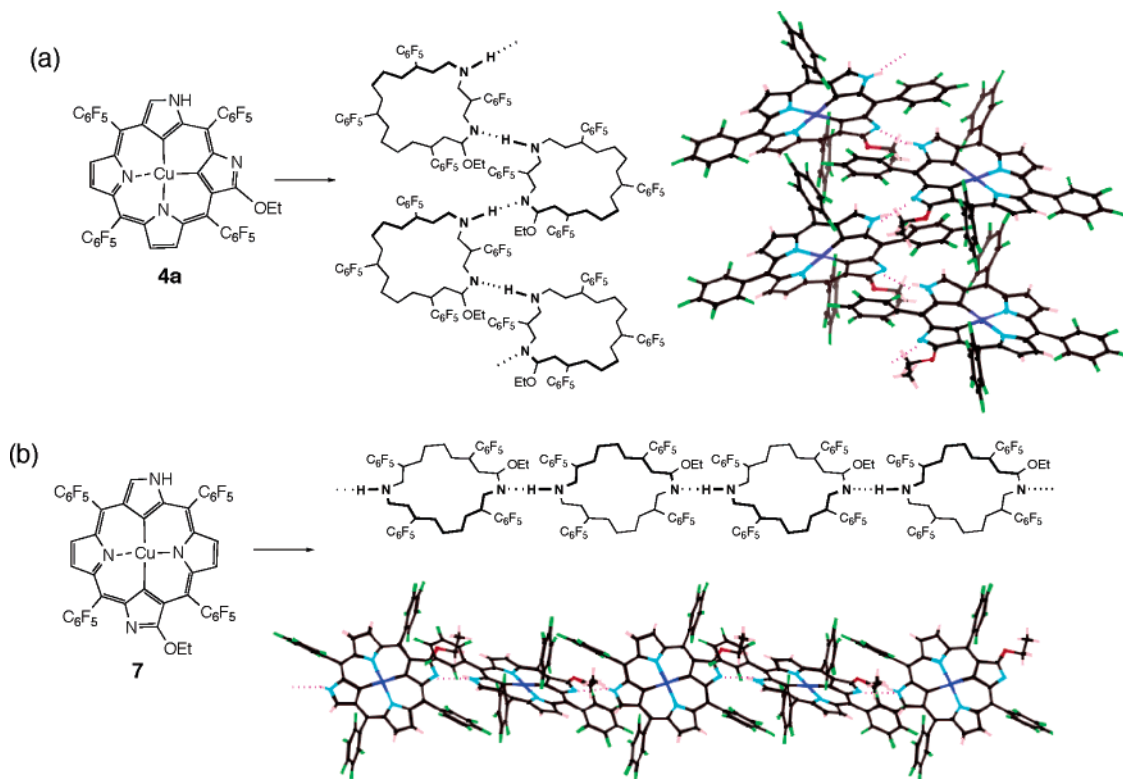
The <sup>1</sup>H NMR signals of inner CH and NH protons in **1a** were resonated at –4.99 and –2.41 ppm in CDCl<sub>3</sub>, respectively, which indicates the formation of inner 3H (**1–3H**) tautomer.<sup>6a</sup> While, in deuterated dimethylformamide (DMF-*d*<sub>7</sub>), new tautomeric species [inner 2H tautomer (**1–2H**)] was formed and the corresponding signals were resonated at 0.76 and 2.27 ppm, respectively, along with the outer NH signal at 13.54 ppm (Scheme 2).<sup>23</sup> In less polar solvents such as CHCl<sub>3</sub>, the electronic absorption spectrum displayed a strong Soret-like band at 439 nm and the last Q band at 725 nm. In polar solvents such as DMF, the color of NCTPP changed from red to green and the Soret band was bathochromic-shifted, while the Q bands were hypsochromic-shifted as compared with the CHCl<sub>3</sub> solution. Both the tautomers were further confirmed by X-ray single-crystal analyses.<sup>23</sup>

## Cis- and Trans-Doubly N-Confused Porphyrin (N<sub>2</sub>CP)

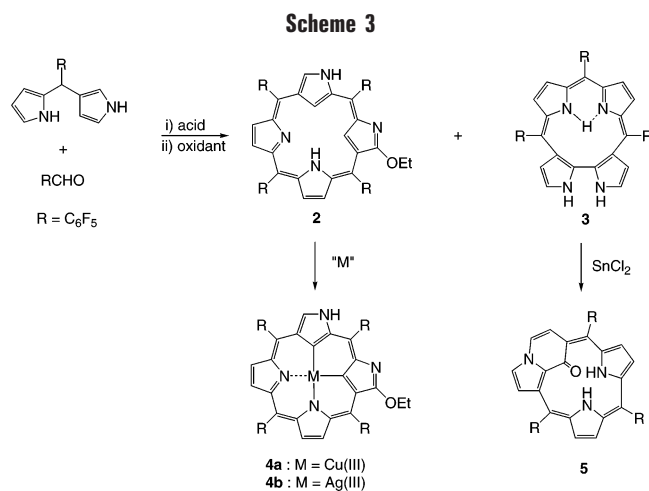
One of the special features of NCP chemistry that differs from *normal* porphyrins is its multivalent nature as a metal ligand. If such effects were observed for other NCPs, especially, for the porphyrin-like macrocycles with more than one *confused* pyrrole ring, it could provide a potent strategy for stabilizing higher oxidation states of metals. In this section, we presented the cis- and trans-doubly N-confused porphyrins (*cis*-N<sub>2</sub>CP<sup>7</sup> and *trans*-N<sub>2</sub>CP<sup>8</sup>) and their metal complexes.

*Cis*-N<sub>2</sub>CP (**2**) was synthesized via the acid-catalyzed condensation of pentafluorobenzaldehyde with N-confused dipyrromethane in CHCl<sub>3</sub> containing a trace of EtOH. After oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a greenish product **2** was obtained in 2% yield along with the major product corrorin (**3**), a corrole isomer, in 13% yield (Scheme 3).<sup>7a</sup> The β-CH protons of two *confused* pyrrole rings in **2** were observed at 3.50 and 3.20 ppm in the <sup>1</sup>H NMR spectrum, while the outer NH proton was resonated at 8.95 ppm, suggesting the weak aromatic nature of the compound. Interestingly, by treating with SnCl<sub>2</sub>, **3** was transformed into a new aromatic macrocycle oxyindolophyrin **5** that showed the high affinity for fluoride anion (Scheme 3).<sup>24</sup>

On treating with Cu<sup>II</sup> and Ag<sup>I</sup> acetate, corresponding metal complexes **4a** and **4b** were obtained in quantitative yield.<sup>7a</sup> The <sup>1</sup>H NMR analyses suggested that both are diamagnetic with +3 metal oxidation states. In the single crystal of **4a** and **4b**, the geometry around the metal center is nearly square-planar and 1D chain networks, in which



**FIGURE 1.** One-dimensional networks of Cu<sup>III</sup> complexes of (a) *cis*-N<sub>2</sub>CP (**4a**) and (b) *trans*-N<sub>2</sub>CP (**7**).

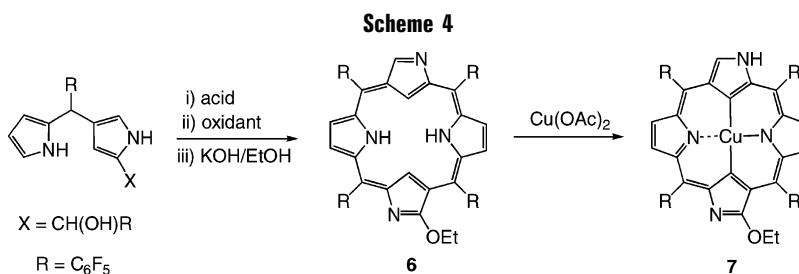


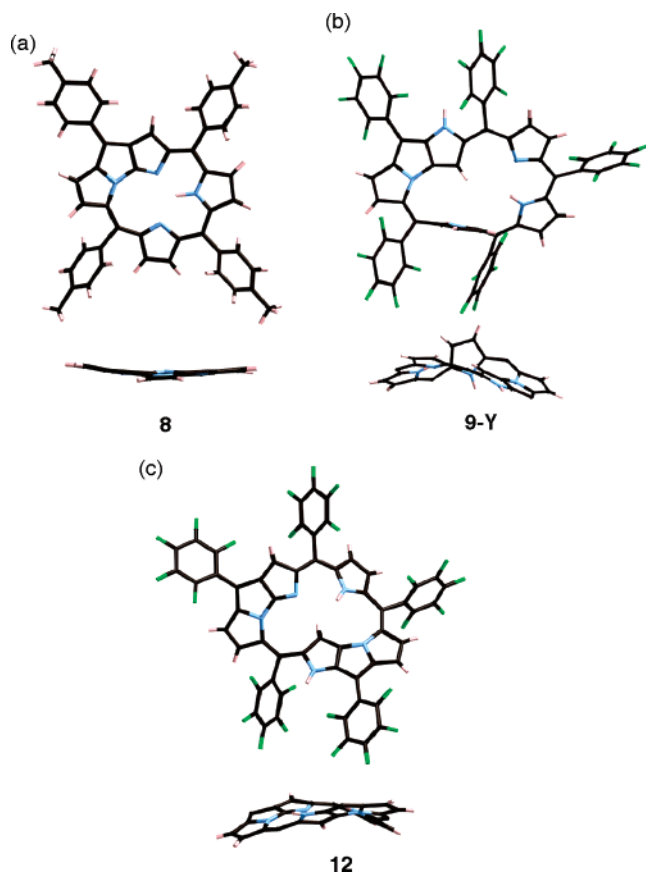
the peripheral N and NH are connected to each other through the hydrogen-bonding interactions, are formed. The distances between the two parallel planes are 6.89 and 6.39 Å, and the metal–metal distances are 8.395 and 8.329 Å for **4a** and **4b**, respectively (Figure 1a).<sup>7b</sup>

The other doubly N-confused porphyrin, *trans*-N<sub>2</sub>CP (**6**), was obtained in 53% yield from the [2+2] acid-

catalyzed condensation reaction of pentafluorophenyl-substituted N-confused dipyrromethane monocarbinol, followed by oxidation and base treatment (Scheme 4). The ethoxy group was derived from the alcoholic KOH.<sup>8</sup> In contrast to the weak aromatic character of **2**, the two inner NH and two β-CH protons were observed at −2.73, −3.21 ppm and −4.34, −4.36 ppm, respectively, indicating an 18π aromatic character of **6**. Supporting this, the absorption spectrum exhibited a sharp Soret-like band at 449 nm.

Using Cu(OAc)<sub>2</sub>, the corresponding metal complex **7** was formed in 59% yield (Scheme 4).<sup>8</sup> Absence of inner CH and NH signals suggests that the obtained complex contains a diamagnetic Cu<sup>III</sup> in the core. The X-ray structure reveals that the square-planar complex is rather planar with a small deviation (0.06 Å) from a mean plane consisting of 25 core atoms compared with the distorted free base (0.30 Å). The complex **7** forms intermolecular hydrogen-bonding rodlike chains as comparable with the zigzag chains of **4a**. Reflecting the linear structure, the nearest Cu<sup>III</sup>–Cu<sup>III</sup> distance of **7**, 10.83 Å, is longer than **4a** (Figure 1b).





**FIGURE 2.** X-ray structures of (a) N-fused porphyrin (**8**), (b) N-fused pentaphyrin (**9-Y**), and (c) doubly N-fused pentaphyrin (**12**). *Meso*-aryl groups are omitted for clarity in the side views (bottom).

## N-Fused Porphyrin and Doubly N-Fused Pentaphyrin

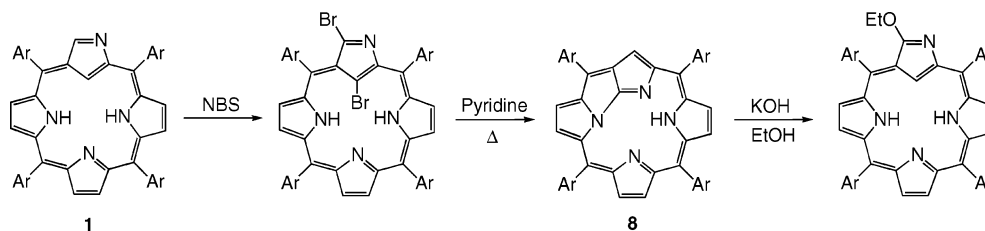
Our earlier observation that the *confused* pyrrole ring in **1** is tilted largely from the porphyrin plane, e.g.,  $26.9^\circ$  in **1a**<sup>6a</sup> and  $42.4^\circ$  in the inner  $\text{NO}_2$ -substituted NCP,<sup>25a</sup> drove us to a further study on core modification with the expectation of more flipping of the *confused* ring. Interestingly, during the halogenation, we obtained a new type of aromatic porphyrinoid with a *fused* pyrrole tripen-

cyclic ring in the macrocyclic core, N-fused porphyrin (NFP, **8**),<sup>25b</sup> which was derived by the *inversion* of the *confused* pyrrole. The X-ray structure of **8** revealed the existence of a *fused* tripentacyclic ring in the porphyrin skeleton, where all of the nitrogens are inside the core (Figure 2a). Moreover, on treatment with nucleophilic base, **8** was returned to alkoxy-substituted NCP by reinversion of the pyrrole ring (Scheme 5).<sup>25c</sup> An NCP dimer connecting each other at both the inner carbon atoms was synthesized from an NFP dimer by this ring-opening reaction.<sup>26</sup>

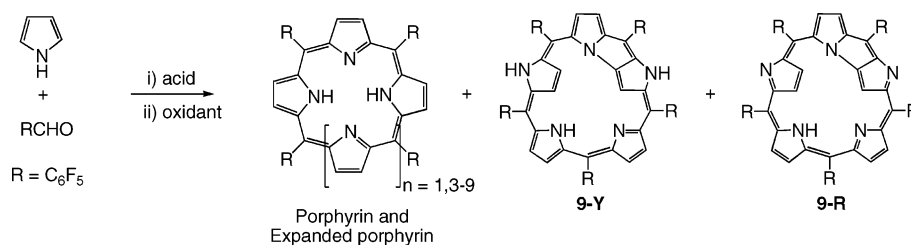
The above successful transformation encouraged us to apply similar strategies to higher homologues in the expanded porphyrins. As the first target, we chose a pentapyrrolic porphyrin, pentaphyrin, because the *meso*-aryl pentaphyrin is shown to exist in the form of N-fused pentaphyrin.<sup>27a</sup> The first N-fused pentaphyrin was obtained from the Rothmund-type condensation reactions in 15% yield, by using pentafluorobenzaldehyde and pyrrole, followed by oxidation with DDQ (Scheme 6).<sup>27a</sup> Two products (**9-Y** and **9-R**) were formed, and the yield changed greatly according to the amount of oxidants used. From  $^1\text{H}$  NMR analyses, formation of a *fused* tripentacyclic ring was suggested by the absence of one of the  $\beta$ -CH protons. It was further confirmed by the X-ray structural analysis of **9-Y**, where the inward- and outward-pointing nitrogen atoms were present in the *fused* tripentacyclic ring (Figure 2b), which is in contrast with the inward-pointing nitrogen atoms of **8**. Therefore, the N-fused porphyrinoids can be classified as *normal*-type (**9-Y**) and *confused*-type (**8**) based on the linkage of the pyrrole rings.

At this point, it was really a question whether the introduction of a *confused* pyrrole ring into such a macrocyclic system lead to a similar *fused* one or hitherto unknown N-confused pentaphyrin. To answer this question, we tried a [3+2] acid-catalyzed condensation reaction of N-confused tripyrrane and dipyrromethane dicarbinol, followed by oxidation, which afforded **10** in 40% yield.<sup>27b</sup>  $^1\text{H}$  NMR analysis suggested the presence of a *fused* tripentacyclic ring in the nonaromatic pentaphyrin **10**.

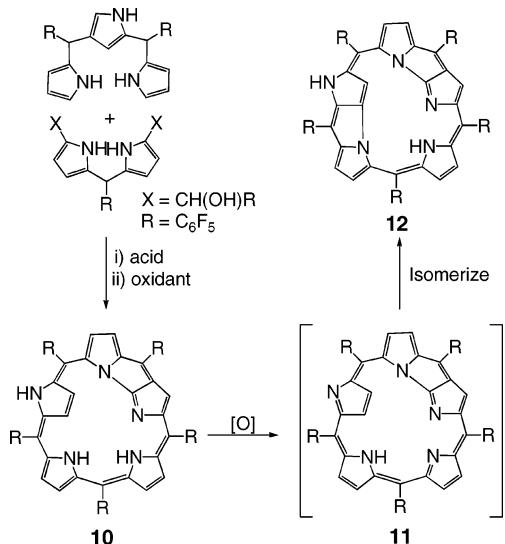
**Scheme 5**



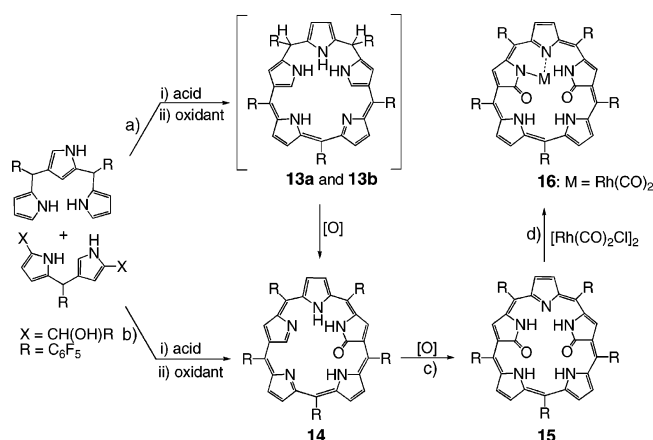
**Scheme 6**



Scheme 7



Scheme 8



Further oxidation led to the quantitative formation of aromatic compound **11**. However, **11** was unstable in  $\text{CH}_2\text{Cl}_2$  and gradually isomerized into doubly N-fused pentaphyrins **12** (Scheme 7).<sup>27b</sup> The isomerization took place with the loss of aromatic stabilization of the pentaphyrin core and turned into nonaromatic. This was reflected from the  $^1\text{H}$  NMR and the electronic spectral analyses.

The explicit structure of **12** was revealed by X-ray single-crystal analysis (Figure 2c). There are two tripentacyclic rings and a pyrrole ring in the macrocycle. Both the nitrogen atoms in one of the *fused* rings are inside the core (like **8**), while in the other, the outward- and inward-pointing nitrogen atoms are found in the macrocyclic core (like **9-Y**). The core plane is highly distorted from the least-squares plane, with a mean deviation of 0.413 Å. Each asymmetric unit of the crystal data contains one pentaphyrin with a cocrystallized acetonitrile solvent molecule. Similar to **8** and **9-Y**, the inner proton shows an intramolecular hydrogen-bonding interaction with an adjacent pyrrolic nitrogen atom.

## Doubly N-Confused Pentaphyrin and Hexaphyrin

In the N-confused pentaphyrin chemistry, we already observed the N-confused, doubly N-fused pentaphyrin

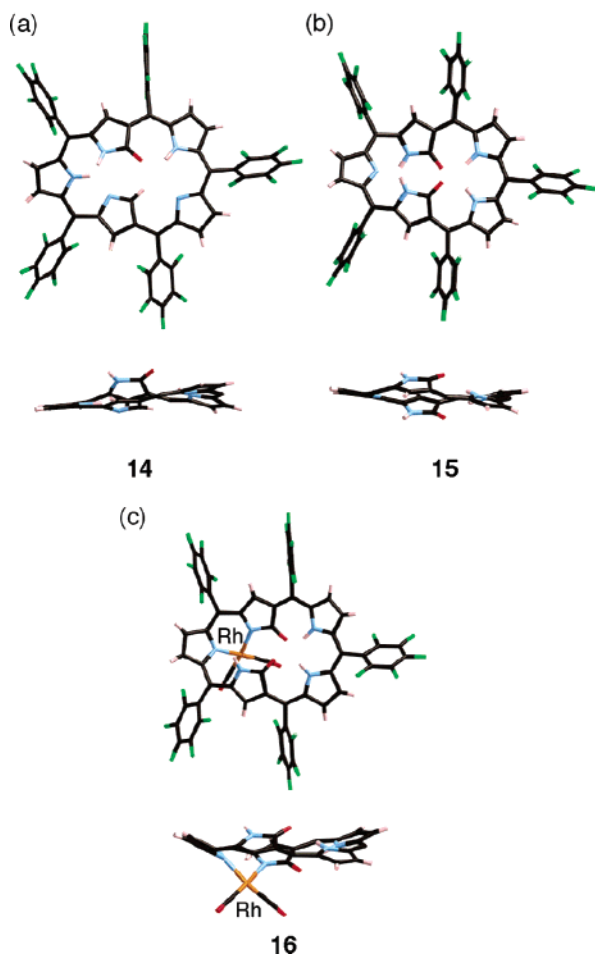
**(12)**.<sup>27b</sup> If we introduce one more *confused* pyrrole to such a macrocycle, which we call the *doubly confusion approach*, we do expect the hitherto unknown doubly N-confused pentaphyrin. Interestingly, the obtained pentaphyrin was not *fused* but *oxo*-substituted at the  $\alpha$  position of the *confused* pyrrole rings. In this section, we described such pentaphyrins and their metal complexes.

Stirring a mixture solution of N-confused tripyrrane and N-confused dipyrromethane dicarbinol through a [3+2] acid-catalyzed condensation, followed by *p*-chloranil oxidation, afforded two isomeric, partially oxidized products **13a** and **13b** in 23 and 12% yields, respectively, along with a trace amount of **14** (path a of Scheme 8).<sup>27c</sup> The observed  $^1\text{H}$  NMR spectra suggested that both isomers were symmetrical pentaphyrinogen intermediates, which were rather unstable and easily oxidized into aromatic **14**.

By changing the oxidizing agent from *p*-chloranil to DDQ, the doubly N-confused *oxo*-pentaphyrin (**14**) was obtained as a green solid in 32% yield (path b of Scheme 8).<sup>27c</sup> However, the compound was relatively unstable and gradually oxidized into doubly N-confused di-*oxo*-pentaphyrin (**15**) in  $\text{CH}_2\text{Cl}_2$  at room temperature over 7 days in 45% yield (path c of Scheme 8). The presence of mono- and di-*oxo* groups was confirmed by fast atom bombardment mass spectrometry (FABMS) and IR measurements. The  $^1\text{H}$  NMR spectra of unsymmetrical **14** and symmetrical **15** were proved as  $22\pi$  aromatic. Supporting this, the electronic absorption spectra of **14** displayed a Soret-like band at 544 nm, while in **15**, the band was observed split at 542 and 585 nm.

The X-ray crystal analyses of **14** and **15** confirm that the *confused* pyrroles are *inverted* and one oxygen atom is attached at an inner  $\alpha$  carbon in **14** (Figure 3a), while two oxygen atoms are present in **15** (Figure 3b). The mono-*oxo*-pentaphyrin (**14**) plane consisting of 30 core atoms is highly distorted from the least-squares plane with a mean deviation of 0.32(1) Å. There are three inner NH protons: two of them are forming intramolecular hydrogen bonding with the neighbors, while the remaining NH proton interacts with its countered moiety to form a dimer through the intermolecular hydrogen bondings. In contrast, the two CONH units in **15** interact intramolecularly with its neighbor. Because of such hydrogen bondings, the pentaphyrin core is less distorted [mean deviation = 0.270(7) Å] as compared with **14**. These are the first examples of stable non-*fused* pentaphyrins of *meso*-aryl type. Here, it is clear that the introduction of one more *confused* pyrrole brings the remarkable structural diversity.<sup>14,27</sup>

The metal coordination chemistry was examined on stable **15** by using  $\text{Rh}^{\text{I}}$  salt. By treatment of **15** with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in refluxing  $\text{CH}_2\text{Cl}_2$ , the  $\text{Rh}^{\text{I}}$  complex (**16**) was obtained in quantitative yield (path d of Scheme 8).<sup>27c</sup> An unsymmetrical structure of **16** was suggested by  $^1\text{H}$  NMR analysis, and the electronic absorption spectrum displayed the bathochromic shift of the Soret and Q bands (40 and 46 nm) as compared with **15**. The X-ray analysis of **16** confirmed the presence of the Rh atom in the pentaphyrin core, which is located above the mean plane, and the



**FIGURE 3.** X-ray structures of (a) doubly N-confused mono-oxo-pentaphyrin (**14**), (b) doubly N-confused di-oxo-pentaphyrin (**15**), and (c) the Rh<sup>I</sup> complex (**16**). *Meso*-aryl groups are omitted for clarity in the side views (bottom).

geometry around the metal center is close to square-planar [N–Rh–N, 80.2(2)°] (Figure 3c).

To introduce one more metal ion or heavier metal ions in the core, the higher homologue, hexaphyrin, is attractive, because of its bigger core size. The first *meso*-aryl hexaphyrin of *normal* type was reported by Dolphin et al.<sup>28a</sup> But the poor stability of the compound hampered further spectroscopic characterization. The stable hexaphyrins (**17a** and **17b**) were synthesized by Cavaleiro and co-workers through the modified Rothmund reaction in 1% yield.<sup>28b</sup> Using the oligopyrrole precursors, the yields

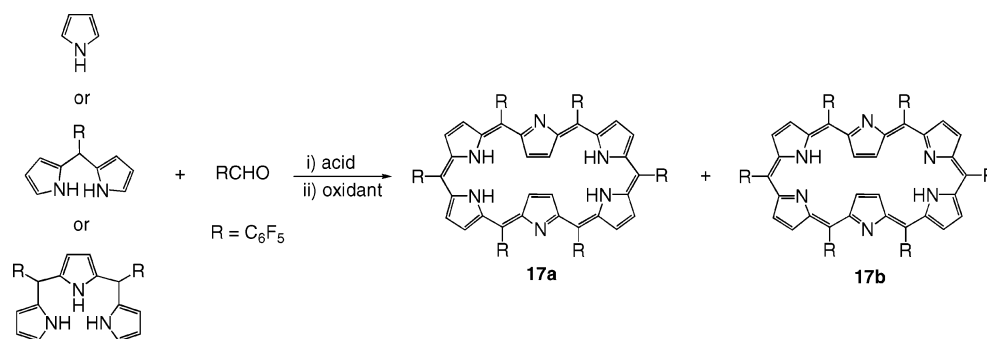
of **17a** and **17b** were largely improved (Scheme 9).<sup>28c,d</sup> The structure of **17b** was confirmed by X-ray analysis, where two pyrrole rings were inverted and distorted above and below the macrocyclic plane with a mean deviation of 0.536(8) Å.

The *confused* derivatives of hexaphyrin were recently synthesized.<sup>29</sup> When N-confused tripyrrane was treated with pentafluorobenzaldehyde in the presence of acid catalyst, followed by oxidation with *p*-chloranil, doubly N-confused hexaphyrins (**18a** and **18b**) were obtained as a brown solid in 7 and 3% yields, respectively (path a of Scheme 10). Both nonaromatic 28 $\pi$  and aromatic 26 $\pi$  compounds were identified by <sup>1</sup>H NMR and electronic spectral analyses. However, the aromatic **18b** was unstable and gradually oxidized into the di-*oxo* derivative (**19b**) in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature.

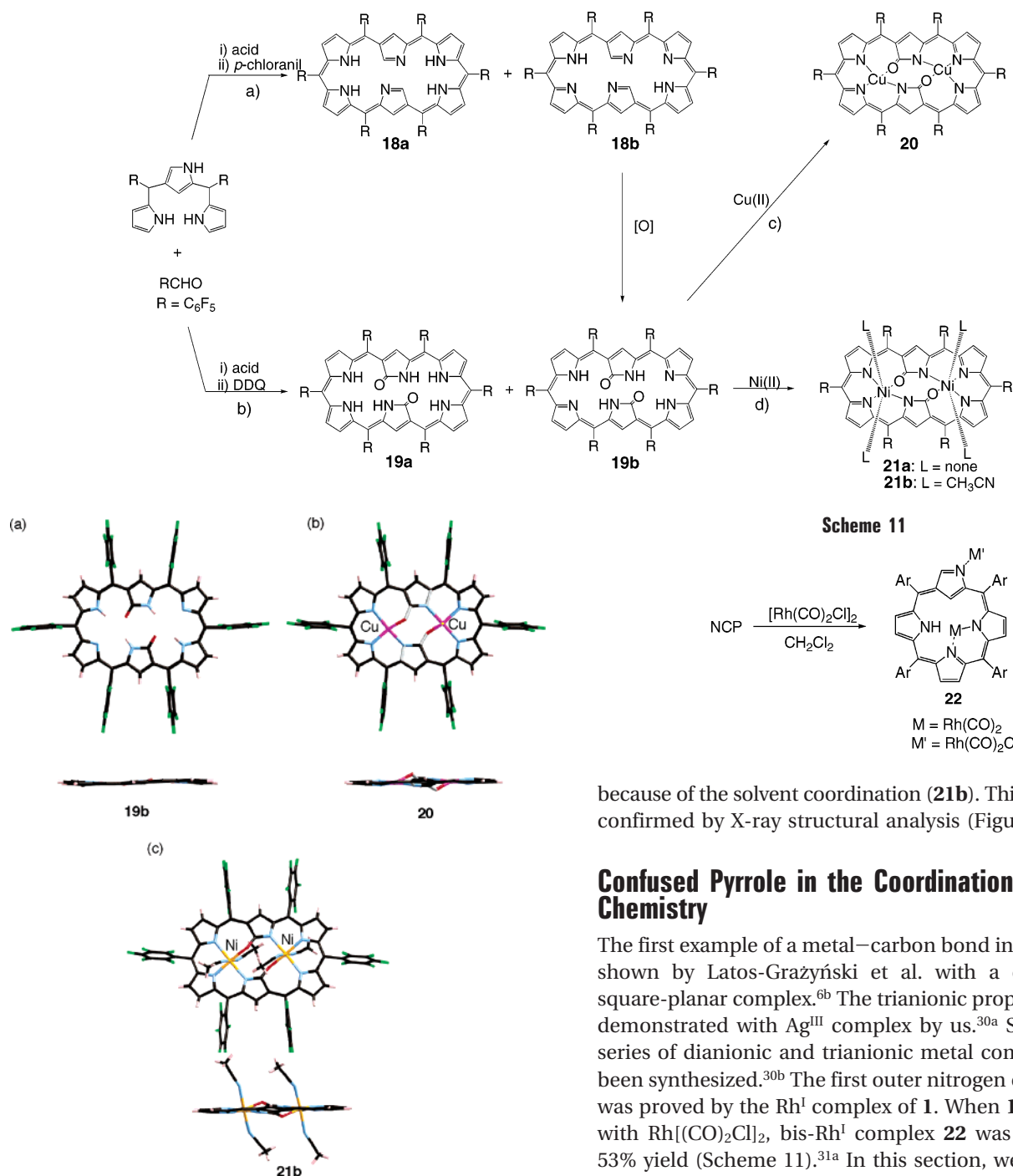
On varying the oxidizing agent from *p*-chloranil to DDQ in the condensation reaction, two different products (**19a** and **19b**) were obtained as greenish solid in 7 and 10% yields (path b of Scheme 10).<sup>29</sup> FABMS and IR analyses indicated the presence of two *oxo* groups. The outer  $\beta$ -CH and NH signals of *confused* pyrrole and the NH signals of *normal* pyrrole in **19b** were resonated at 10.74, –0.73, and –0.24 ppm, suggesting the symmetrical structures with aromatic nature. Supporting this, the absorption spectrum displayed an intense Soret-like band at 566 nm. The X-ray analysis of **19b** revealed that the *confused* pyrrole rings are inverted and the two *oxo* groups are attached at the inner  $\alpha$ -carbon atoms affording the CONH groups (Figure 4a). Both the carbonyl groups are forming the intramolecular hydrogen bonding with adjacent pyrroles, keeping the molecule planar. The mean deviation is only 0.054 Å to a mean plane consisting of 36 core atoms.

The doubly N-confused porphyrin **18** (and **19**) contains the two N<sub>3</sub>C (N<sub>3</sub>O) compartments that facilitate the formation of bismetal complexes when it binds metals inside the core. Actually, the stable bis-Cu<sup>II</sup> complex **20** was obtained by treating **19b** with Cu<sup>II</sup> acetate in CH<sub>2</sub>Cl<sub>2</sub> solution in quantitative yield (path c of Scheme 10).<sup>29</sup> The complex was paramagnetic, and the magnetic susceptibility measurements proved that the Cu ions were present in the paramagnetic d<sup>8</sup> form ( $\mu_{\text{eff}} = 1.73 \mu_{\text{B}}$ , at 77 K). The X-ray analysis of **20** confirmed the bismetal coordination and planarity of the molecule (Figure 4b). In contrast, the bis-Ni complex **21a** was synthesized by a refluxing solution

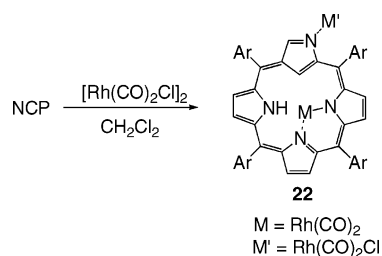
**Scheme 9**



Scheme 10



Scheme 11



because of the solvent coordination (**21b**). This was further confirmed by X-ray structural analysis (Figure 4c).<sup>29</sup>

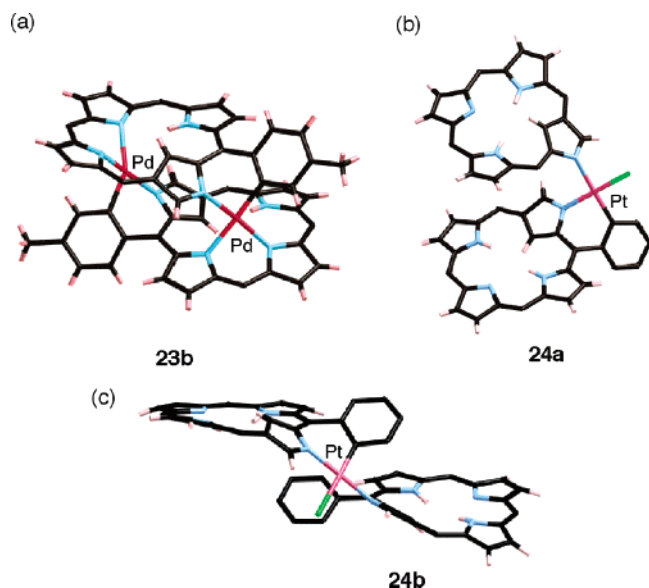
### Confused Pyrrole in the Coordination Chemistry

The first example of a metal–carbon bond in NCP (**1**) was shown by Latos-Grażyński et al. with a divalent  $Ni^{II}$  square-planar complex.<sup>6b</sup> The trianionic property of **1** was demonstrated with  $Ag^{III}$  complex by us.<sup>30a</sup> Since then, a series of dianionic and trianionic metal complexes have been synthesized.<sup>30b</sup> The first outer nitrogen coordination was proved by the  $Rh^I$  complex of **1**. When **1** was treated with  $Rh[(CO)_2Cl]_2$ , bis- $Rh^I$  complex **22** was obtained in 53% yield (Scheme 11).<sup>31a</sup> In this section, we focused on the role of *confused* pyrrole in the outer coordination and anion-binding chemistry.

Using  $Pd(OAc)_2$ , in the presence of **1** in toluene, along with the inner-coordinated monomer  $Pd^{II}$  complex, two more new dimer complexes (**23a** and **23b**) were also obtained in 27 and 36% yield, respectively (path a of Scheme 12).<sup>31b</sup> In both complexes, two NCP units coordinated to two  $Pd$  atoms forming cyclic dimers. The geometry around one of the  $Pd$  metal centers is square-planar, while the other is distorted to tetrahedral (Figure 5a). The difference between the dimer complexes is the orientation of two NCP units, which is revealed by X-ray analyses.

**FIGURE 4.** X-ray structures of (a) doubly N-confused di-oxo-hexaphyrin (**19b**), (b) bis- $Cu^{II}$  complex (**20**), and (c) bis- $Ni^{II}$  complex (**21b**). *Meso*-aryl groups are omitted for clarity in the side view (bottom).

of **19b** in toluene by using  $Ni^{II}$  salt in 95% yield (path d of Scheme 10). The  $^1H$  NMR spectrum suggested that the compound was diamagnetic and the absorption spectrum displayed the broad bands, indicating that the complex was distorted largely from planarity. Interestingly, the observed broad bands were turned into sharper bands to afford a more porphyrin-like spectrum in  $CH_3CN$ , suggesting the large structural change from distorted to planar



**FIGURE 5.** X-ray structures of NCP dimer complexes of (a) bis-Pd<sup>II</sup> (**23b**), (b) *cis*-Pt<sup>II</sup> (**24a**), and (c) *trans*-Pt<sup>II</sup> (**24b**). *Meso*-aryl groups are omitted for clarity.

In continuation of the Pd<sup>II</sup> complexes, we applied the similar strategies to the Pt<sup>II</sup> complexes. When N-confused tetra(*p*-*tert*-butylphenyl)porphyrin (**1**-*t*Bu) was treated with 0.5 equiv of PtCl<sub>2</sub> in refluxing toluene for 1 h, greenish dimer complexes **24a** and **24b** were obtained in 69 and 5% yield, respectively, along with a trace amount of the monomer complex (path b of Scheme 12).<sup>31c</sup> The X-ray structures revealed that the Pt atom is connected in a square-planar fashion with two outer nitrogen atoms of NCP molecules, an *ortho*-carbon of the *meso*-aryl group and a chloride atom. Two *confused* pyrrole rings are arranged in *cis* (**24a**) and *trans* (**24b**) configurations and tilted 20.94° for **24a** and 28.72° for **24b** to the mean planes consisting of 24 core atoms (parts b and c of Figure 5).

When **1** was treated with 2 equiv of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, green color crystals of tetra-Zn<sup>II</sup>-coordinated dimer (**25**) were obtained quantitatively (path a of Scheme 13). Subsequent treatment with 1%

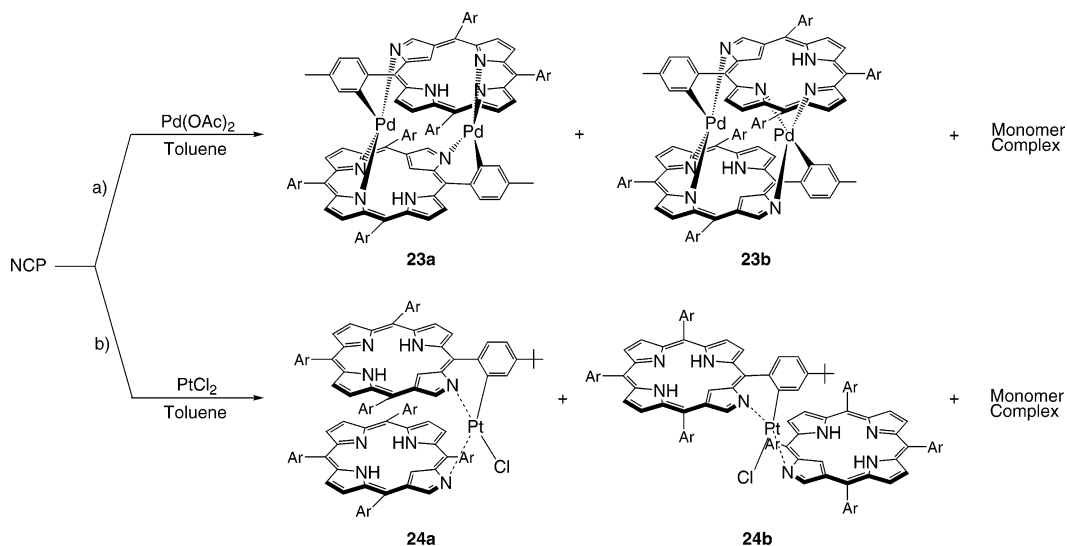
aqueous Et<sub>4</sub>NOH solution led to the formation of a brownish dinuclear dimer (**26a**).<sup>32a</sup> Like **26a**, Cd<sup>II</sup> (**26b**) and Hg<sup>II</sup> (**26c**) complexes were synthesized under similar conditions (path b of Scheme 13). In **26a**, two Zn<sup>II</sup> metals were coordinated with the inner N<sub>3</sub>C atoms and an outer nitrogen of the other NCP paired.<sup>32b</sup> Interestingly, the structures are similar to the reported Mn<sup>II</sup><sup>32c</sup> and Fe<sup>II</sup><sup>32d</sup> dimer complexes except for the relative orientation of the *confused* pyrrole rings. In the crystals, two *confused* pyrrole rings in **26a** (and **26b**) are tilted by 47.5(3) and 49.9(3)° [41.3(5) and 42.9(5)°] from the corresponding N3 mean plane comprising three inner nitrogen atoms. The distances between the two metal centers are 5.217(2) Å for **26a** and 5.230(2) Å for **26b** (parts a and b of Figure 6).

## Confused Pyrrole in Anion-Binding Chemistry

Aside from the outer metal coordination chemistry, the peripheral nitrogen is also essential for binding anions. The first such example was demonstrated with a Sb<sup>V</sup> complex. When **1** was treated with 10 equiv of SbBr<sub>3</sub>, anion-bound crystals (**27a**) were obtained in 42% yield. When a slight excess of pyridine was added to **27a**, neutral complex **27b** was obtained in quantitative yield. Similarly, by adding HBr to **27b**, **27a** was retained (Scheme 14a).<sup>33a</sup> The X-ray crystal analysis of **27a** confirmed that a bromide ion is bound at the outer nitrogen with a distance of 3.771(9) Å, which is within a range of the hydrogen-bonding interaction (Figure 7).

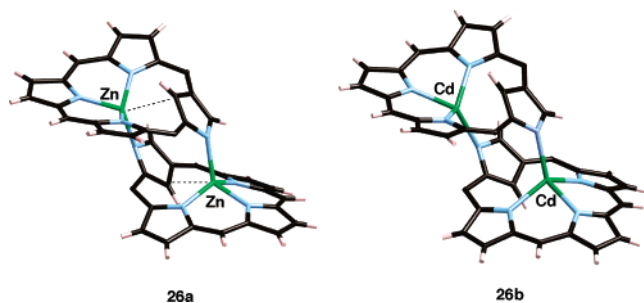
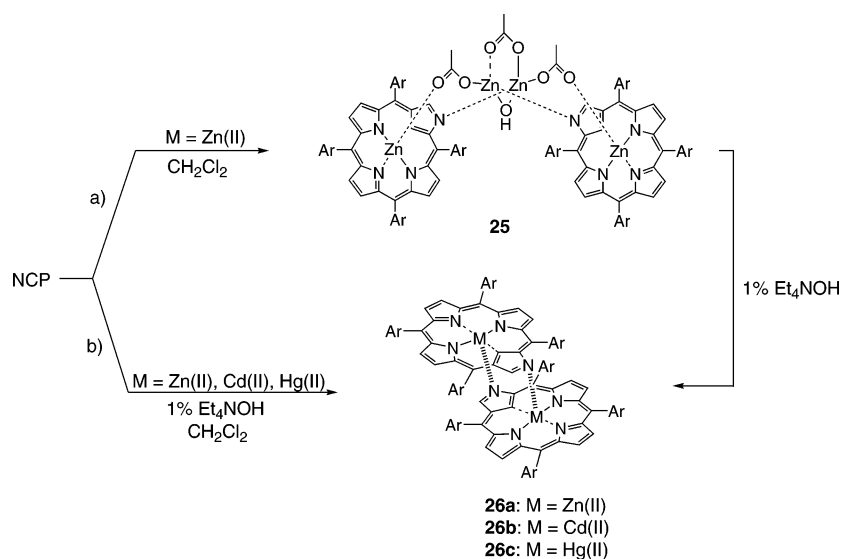
These results encouraged us to investigate the anion binding at the peripheral nitrogen of other NCP metal complexes. Recently, we synthesized the Cu<sup>I</sup> (**28a**) and Cu<sup>III</sup> (**28b**) NCP complexes (Scheme 14b).<sup>33b</sup> Interestingly, electrochemical interconversion between these two complexes was controlled by the addition of anions. The large negative potential shift observed for Cl<sup>-</sup> [0.03 V as compared to ClO<sub>4</sub><sup>-</sup> (0.14 V) and PF<sub>6</sub><sup>-</sup> (0.15 V)] might be attributable to a hydrogen-bonding interaction with the outer NH of the *confused* pyrrole ring. Transmission of the partial negative charge from the peripheral hydrogen-

## Scheme 12

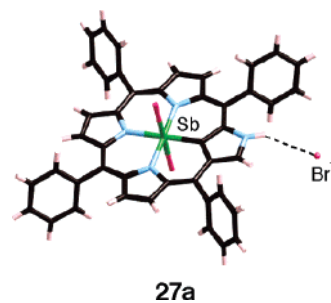




Scheme 13

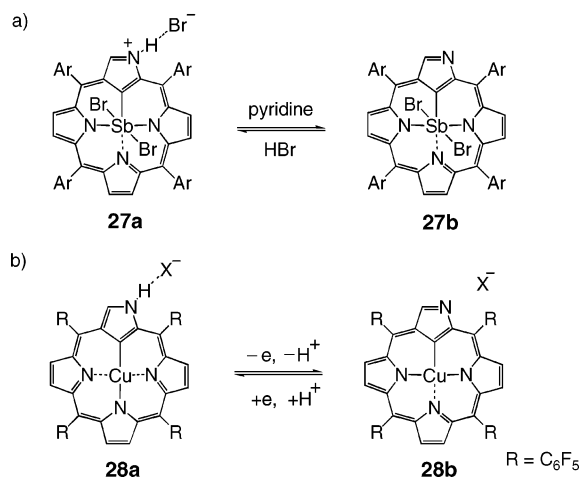


**FIGURE 6.** X-ray structures of NCP dimer complexes of (a) bis-Zn<sup>II</sup> (**26a**) and (b) bis-Cd<sup>II</sup> (**26b**).



**FIGURE 7.** X-ray structure of HBr salt of antimony(V) NCP complex (**27a**). A broken line indicates the hydrogen-bonding interaction.

Scheme 14



bonding anion,  $\text{N}-\text{H}\cdots\text{X}^-$ , to the Cu cation through the inner carbon of the *confused* pyrrole ring might be occurring. It is noteworthy that the estimated  $\text{Cl}^-$ -binding affinity,  $4.9 \times 10^4 \text{ M}^{-1}$  is unusually high for a single hydrogen-bonding system ( $\text{Br}^-$ ,  $\text{ClO}_4^-$ , and  $\text{PF}_6^-$  in  $\text{CH}_2\text{-Cl}_2$  were determined as  $6.9 \times 10^3$ , 360, and  $50 \text{ M}^{-1}$ , respectively, from the absorption spectral changes); thus, the contribution of a zwitterionic resonance form of **28a** and an additional interaction between  $\text{Cl}^-$  and the electron-deficient  $\text{C}_6\text{F}_5$  group nearest to the outer NH were suggested in this anion-binding system.<sup>33b,c</sup>

## Efficient Sensitizers for Singlet-Oxygen Generation

Nowadays, there is a great interest in finding new molecules that can be used as sensitizers in PDT.<sup>16</sup> Porphyrins and their analogues are being extensively studied; however, the majority of the porphyrins have low absorptivities in the phototherapeutic window (about 600–1000 nm), where light can be more effectively used, because it can penetrate deeper in the tissues.<sup>16</sup> The *cis*- $\text{N}_2\text{CP}$  (**2**) and its Cu (**4a**) and Ag (**4b**) complexes exhibit relatively intense absorption bands around 660 nm, and a remarkable discovery is that the complex **4b** is a very efficient singlet-oxygen sensitizer in  $\text{CH}_3\text{CN}$  solution.<sup>34</sup>

The photophysical properties of **2**, **4a**, and **4b** were examined by means of electronic and time-resolved spectroscopy, inferring that the fluorescence of the metal complexes is being suppressed by the enhancement of the intersystem crossing, induced by the heavy-atom effects. The singlet-oxygen quantum yield of **4b** ( $\phi_\Delta = 0.92$ ) was higher than **2**, **4a**, TPP, and monoacidic benzoporphyrins (0.2, 0.66, 0.73, and 0.76). Because of the relatively red-shifted absorption bands (613 and 665 nm), molar absorptivities ( $\log \epsilon = 4.2, 3.9$ ), and good thermal and photochemical stability, **4b** becomes the first unusual valence metal complex with suitable features as a PDT photosensitizer. Aside from *cis*- $\text{N}_2\text{CP}$ , singlet-oxygen gen-

eration upon irradiation above 700 nm was demonstrated with *N,N'*-dimethylated NCP by Dolphin and co-worker.<sup>35</sup>

## Summary and Outlook

The serendipitous discovery of N-confused porphyrin disclosed some new aspects apart from *confusion*. By the "single confusion approach", we found *inversion* followed by *fusion*. The unique *confused* pyrrole in NCP exploited a series of outer nitrogen coordination, particularly bound with the second and third row transition metals as well as various anions. The metal valencies are controlled by outer stimuli, which may offer a variety of applications, including molecular switches and anion sensors. The long wavelength absorption of *fused* derivatives might be potentially useful as NIR materials.

By the "double confusion approach", we synthesized the second generation of NCPs called *cis*- and *trans*-N<sub>2</sub>-CP. These ligands can stabilize the higher oxidation states of metals by forming two metal-carbon bonds, which would be useful in employing as organometallic reagents. The presence of acid (protonated nitrogen) and base (deprotonated nitrogen) moieties at the periphery would make these "imidazole porphyrinoids" attractive for the use as acid catalysts and anion/cation sensors. Formation of supramolecular assemblies in the solid state is of much interest for preparing functional materials. The efficient singlet-oxygen sensitization of such macrocycles is appealing in using as PDT agents. In the expanded porphyrin area, besides the structural diversity, we found one more important *confused* ring of *oxo* type. The availability of bigger cavities would provide attractive bismetall complexes for the study of optoelectronic and optomagnetic materials.

Introduction of further *confusion* in oligopyrrolic macrocycles, therefore, can be interpreted, in some sense, to *activate macrocycles for further mutation*. The future of the "confusion approach" toward novel porphyrinoids thus looks especially bright particularly in the areas of 2D and 3D supramolecular architectures.

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