Porphyrinoids

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Singly N-Confused [26]Hexaphyrin: A Binucleating Porphyrinoid Ligand for Mixed Metals in Different Oxidation States**

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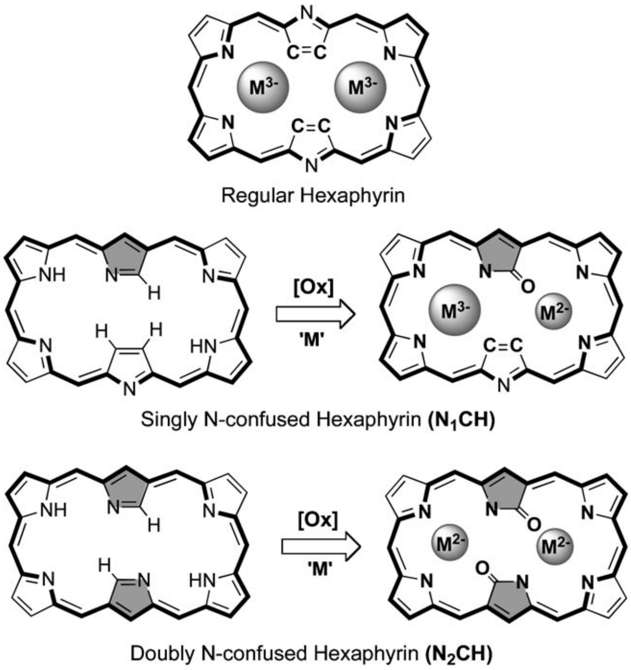
The primary goal in the search for binucleating ligands relies on creating new bimetallic species with two metal ions in close proximity—this feature leads to intriguing magnetochemistry, optical properties, catalytic activity, and functional models for metalloenzymes.[1] Binucleating ligands can be acyclic or macrocyclic in nature and depending on the donor atoms present they can be symmetric or unsymmetric.[2] Numerous nonconjugated binucleating ligands have been prepared since the first discovery of classical Schiff-base-type "Robson ligands" and many of these ligands can provide either homodinuclear or heterodinuclear complexes.[3] However, our current interest focuses on utilizing the porphyrinoids as conjugated π-donating ligands by taking advantage of conformational and geometrical factors.[4]

Porphyrins are well-known π-conjugated macrocycles that can chelate a variety of metals by the interior four nitrogen atoms (i.e. NNNN cavity). Owing to their rigidity and limited cavity size, porphyrins usually capture metals in a 1:1 fashion to afford mononuclear metal complexes.[5] For the multimetal coordination in a cavity, expanded porphyrins having larger cavities than porphyrins are promising.[6] In fact, bismetal coordination has been achieved with hexaphyrin systems. In these systems the ligand could take a rectangular conformation with multi-donor sites inside the cavities similar to porphyrin pockets.[7] For example, regular meso-aryl [26]hexaphyrin(1.1.1.1.1.1) was shown to afford bis-metal complexes with trivalent metal such as Cu^{III}, Ag^{III}, and Au^{III} by forming four metal–carbon bonds inside the twin NNCC cavities.[8] In contrast, doubly N-confused hexaphyrin (**N_2CH**; Scheme 1), which has two confused pyrrole rings in the framework, was shown to serve as a binucleating ligand for various divalent metal ions as a result of the two rigid NNNO cavities.[9] However, all those previously reported hexaphyrin(1.1.1.1.1.1) systems tend to provide a symmetric coordinating environment with NNCC or NNNO cavities for bis-metal in-plane complexes in which both the metal ions are in the same oxidation states (+2 or +3).[8,9] Thus, for coordination of two different metal ions in variable oxidation states, an unsymmetrical binucleating environment would be necessary in the macrocycles. This environment could be attained by incorporating one confused pyrrole unit into the hexaphyrin system, namely a singly N-confused hexaphyrin (**N_1CH**). We found that such a modification can offer a unique coordinating environment with NNNC and NNCO cavities to chelate metal ions in two different oxidation states. In general, our approach opens up new possibilities in the coordination chemistry for mixed-metal porphyrinoids.



Scheme 1. Conceptual representations of bis-metal complexes of various hexaphyrins.

Herein, we report the syntheses as well as structural and redox properties of singly N-confused meso-aryl hexaphyrins **3** and **4**, mono-Au^{III} complex **5**, and bis-(Au^{III},Pt^{II}) complex **6**. The 26π and 28π hexaphyrin ligands, **3** and **4**, were prepared in 23% and 11% yields, respectively, by an acid-catalyzed

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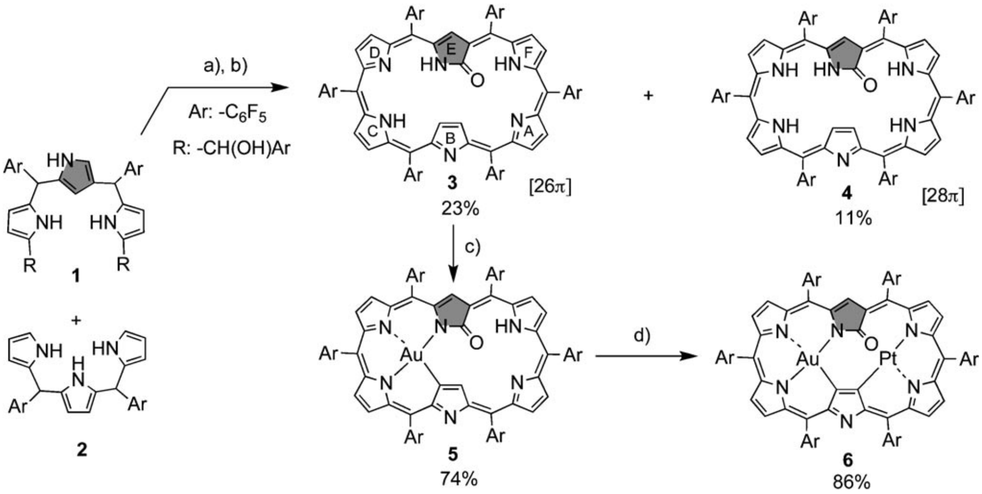
[3+3] condensation of N-confused tripyrrane dicarbinol **1** and tripyrrane **2** (Scheme 2).[10] Interestingly, the conformational flexibility of **3** is evident at room temperature and results in very broad ^{1}H NMR signals in $CDCl_3$, and such conformational dynamics was frozen at low temperature.[11a] The ^{1}H NMR spectrum at −60 °C exhibits well resolved signals and reveals a strong diatropic ring current arising from its 26π aromatic circuit. A signal at $\delta = 9.46$ ppm for the β proton of the N-confused pyrrole rings and six sets of multiplet signals appear between $\delta = 8.35$–9.25 ppm for the remaining outer β protons. In addition, three signals appear at $\delta = 1.22$, 0.61, and 0.06 ppm for inner NH protons and a pair of multiplet signals around $\delta = 0.84$ and −0.72 ppm correspond to the inner β protons of ring **B**. These data unambiguously indicate the inversion of the regular pyrrole ring away from the macrocyclic cavity, while the confused pyrrole ring points towards the macrocyclic cavity—this is in sharp contrast to the structure of **N_2CH** with two confused pyrrole rings that are inverted.[9] In contrast, the reduced isomer **4** with a 28π conjugated circuit exhibits a well resolved spectrum at room temperature featuring three signals at $\delta = 6.91$, 10.41, and 12.03 ppm resulting from NH protons, nine different signals in the range $\delta = 5.43$–7.54 ppm ascribed to the pyrrolic β protons, and a signal at $\delta = 6.74$ ppm for the β proton of the confused pyrrole rings, therefore suggesting that the structure of **4** is nonsymmetric and nonaromatic.



Scheme 2. Preparation of N-confused hexaphyrin (**3** and **4**) and metal complexes (**5** and **6**). Reaction conditions. a) $BF_3{\cdot}Et_2O$ (0.5 equiv), 1 h, RT; b) DDQ (3.5 equiv), 14 h, RT; c) $AuCl{\cdot}SMe_2$ (4 equiv), 1 h, RT; d) $[PtCl_2(PhCN)_2]$ (4 equiv), 6 h, RT. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

The UV/Vis absorption spectrum of **3** displays an intense Soret-like band at 570 nm, which is a characteristic band for hexaphyrin systems, and Q-bands between 700 and 980 nm, in line with its aromaticity. On the other hand, **4** features two broad bands in the region from 400 to 600 nm arising from its 28π nonaromatic conjugated circuit (Figure 1).[12] Notably, [26]hexaphyrin **3** and [28]hexaphyrin **4** undergo reversible redox interconversion with the aid of simple redox reagents such as DDQ and $NaBH_4$.[13] Several attempts to obtain the X-ray-quality crystals of **3** in the neutral form were unsuccessful, but fortunately crystals suitable for X-ray analysis were obtained from slow diffusion of *n*-hexane into a solution of **3** in CH_2Cl_2/trifluoroacetic acid (TFA; 5:1). The X-ray structure revealed the monoprotonated structure of **3** with a twisted hexapyrrolic framework (Figure 2a).[11b] Interestingly, effective hydrogen-bonding interactions are found for pyrrole ring **B**···TFA···ring **E**, thus forcing the pyrrole subunits to be tilted or fully inverted to maintain a twisted conformation.[11a]

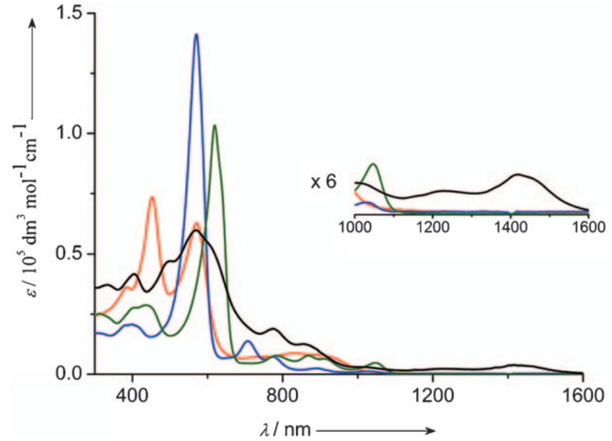


Figure 1. UV/Vis/NIR absorption spectra of **3** (blue), **4** (red), **5** (green), and **6** (black) in CH_2Cl_2.

First, a monometalation reaction was performed on the aromatic [26]hexaphyrin **3** by treatment with $AuCl{\cdot}S(CH_3)_2$ in a mixture of CH_2Cl_2 and methanol (5:1) for 1 hour at room temperature. Purification by using a short column of silica gel afforded mono-Au^{III} complex **5** in 74% yield. The X-ray structure shows a rectangular and a fairly planar framework with a mean plane deviation of 0.697 Å from the plane defined by 36 atoms on pyrrole rings and methine carbon atoms (excluding the oxygen atom; Figure 2b).[11b] The Au atom is located within the NNNC cavity in a square-planar fashion, in which three Au–N and one Au–C bond lengths are 2.033(6), 2.028(6), 2.073(4), and 2.027(5) Å, respectively. This square-planar arrangement is similar to that observed for a previously reported N-confused porphyrin to Au^{III} complex.[14] The NH proton (at N4) forms two intramolecular hydrogen bonds with neighboring atoms (N4-H···N3 and N4–H···O1 with distances of 2.245(5) Å for N4···N3 and 2.404(4) Å for N4···O1). The

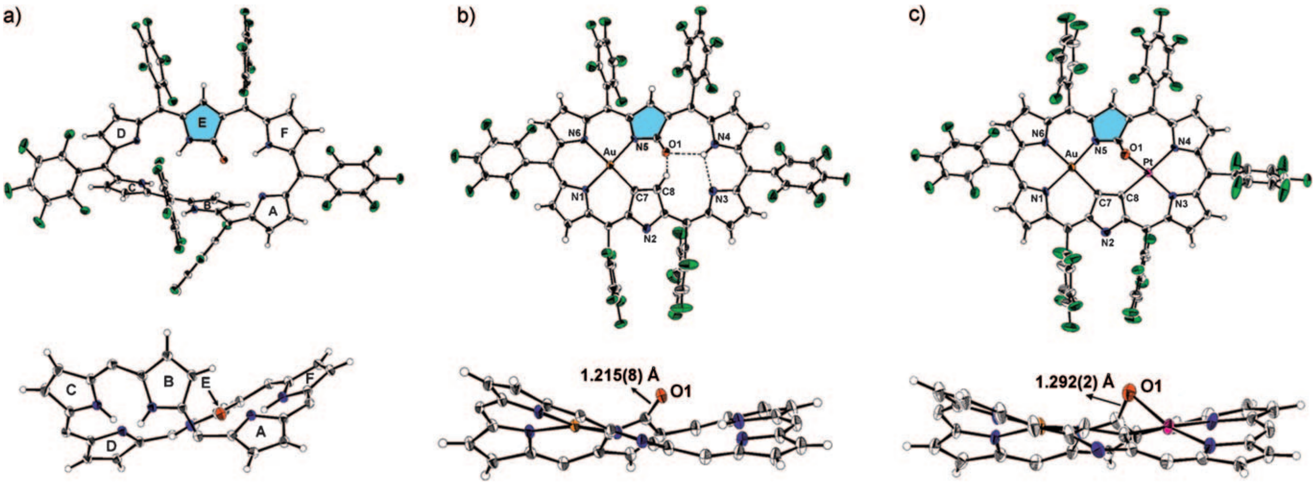


Figure 2. ORTEP drawings of a) monoprotonated **3**, b) **5**, and c) **6**; top views (upper) and side views (lower). A TFA counter anion in **3** and meso-aryl groups in side views were omitted for clarity. Hydrogen-bonding interactions in **5** are indicated by broken lines. Thermal ellipsoids are drawn at the 30% probability level.

bond length between the carbon and oxygen atoms are in the range of a C−O double bond, that is, 1.215(8) Å.[15]

A diatropic ring current in **5** are evident from its ^{1}H NMR spectrum, in which a sharp singlet at $\delta = 9.56$ ppm is observed for the β proton of the confused pyrrole rings, as well as a multiplet at $\delta = 8.52$ ppm and three doublets at $\delta = 8.31$, 8.23, and 8.14 ppm are observed for the remaining outer β protons. The presence of inner NH and β protons is confirmed by the singlet signals in the upfield region at $\delta = 1.78$ and 0.21 ppm, respectively.

Next, a solution of **5** in *o*-$Cl_2C_6H_4$ was heated at reflux with $[PtCl_2(PhCN)_2]$ in the presence of NaOAc under anaerobic conditions, and provided bis-(Au^{III},Pt^{II}) complex **6** in 86% yield. The structure of **6** was determined by X-ray analysis and is quite similar to that of mono-Au^{III} complex **5** with a mean plane deviation of 0.648 Å (Figure 2c).[11b] As expected, the Pt^{II} ion is coordinated to the NNCO cavity in a square-planar geometry and the basic skeleton keeps the original structure as that of **5**. In particular, two Pt−N bonds with pyrrolic nitrogen atoms and a Pt−O bond with an oxygen atom of the confused pyrrole ring were formed. The bond lengths between Pt−O, Pt−C, and the two Pt−N bonds are 2.047(8), 2.002(1), 2.056(8), and 2.028(9) Å, respectively. Interestingly, lone pair electrons on the oxygen atom participated in Pt^{II} coordination and resulted in the alteration of the C−O bond length with a distance of 1.292(2) Å, which is longer than was observed for **5**. This bond length is between that of a C−O single bond and a C−O double bond.[16] Importantly, this structure leads to the assignment of a $Au^{III}\cdots Pt^{II}$ system without involvement of axial or bridging ligands. Also, the distance between two metal centers is long (4.362 Å), hence no direct metal–metal interactions are found in the solid state.[11a]

From the well-resolved ^{1}H NMR spectrum, complex **6** was further assigned as being diamagnetic. Specifically, complex **6** showed a multiplet signal at $\delta = 9.10$ ppm for the outer β proton and six set of multiplet signals between $\delta = 9.52$–8.51 ppm for the remaining outer β protons, thus revealing a diatropic ring current. The electronic absorption spectrum of **5** features an intense Soret-like band at 619 nm and Q-like bands at 785, 868, 919, and 1046 nm, whereas **6** exhibits ill-defined bands between 403 and 774 nm (Figure 1). Interestingly, the absorption at approximately 1400 nm in **6** reaches deep into the near infrared region, and is significantly red-shifted relative to **5**.

The electrochemical characteristics of **5** and **6** were studied by cyclic voltammetry in CH_2Cl_2 using tetrabutylammonium perchlorate as an electrolyte (Figure 3). The mono-Au^{III} complex **5** undergoes two reversible one-electron oxidations at 0.07 and 0.41 V, and one irreversible (state a) and one reversible reduction at −1.12 and −0.84 V, respectively. Meanwhile, complex **6** displays two reversible one-electron oxidations at 0.49 and 0.85 V and two reversible one-electron reductions at −0.28 and −0.77 V. The difference in the first oxidation (E_{ox1}) and first reduction (E_{red1}) is found to be 0.77 V, and therefore indicates a narrowing of the HOMO–LUMO gap with respect to **5** (0.91 V) that is consistent with the observed red-shift in the absorption spectra. In the absorption spectra, only a slight red shift is observed for

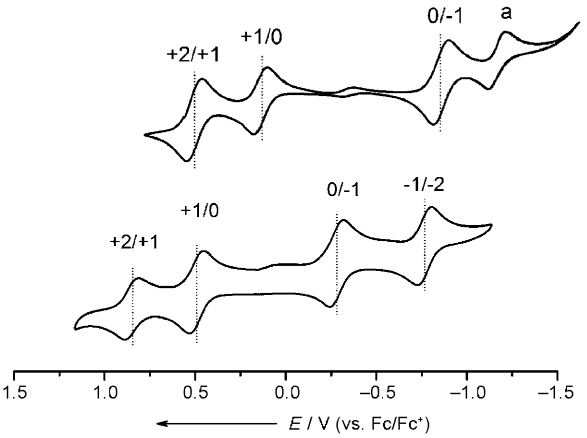


Figure 3. Cyclic voltammogram traces of **5** (top) and **6** (bottom) in anhydrous CH_2Cl_2 containing 0.1 M of $TBAClO_4$. Scan rate = $0.1\,V\,s^{-1}$. State a denotes an irreversible process. TBA = tetra-*n*-butylammonium.

mono-Au$^{\mathrm{III}}$ complex **5** (**3**: 1028 nm, **5**: 1048 nm), and subsequent Pt$^{\mathrm{II}}$ metalation results in the significant red-shift (**6**: 1400 nm; see inset of Figure 1). Taken together, the first Au$^{\mathrm{III}}$ metalation gives only small perturbation on the HOMO–LUMO energy gap, while the second Pt$^{\mathrm{II}}$ metalation causes significant change. The HOMO–LUMO energy gaps as well as observed absorption spectra are in good agreement with theoretical estimation.[11a]

The unique electrochemical features of **6** could be rationalized by a metal-assisted endocyclic extension of the porphyrin π-system. The HOMO and LUMO of **5** are quite similar to those of **3**. The contribution from metal d-orbitals is rather small in **5**, whereas a marked difference is observed for **6**. Thus, a contribution from the metal d-orbitals is observed both in the HOMO and LUMO of **6**. More importantly, contribution from the C=C π-orbital at the inverted normal pyrrole ring is clearly observed in the HOMO (Figure 4). Such participation of the π-orbital inside the aromatic annulenic substructure causes an unusually narrow HOMO–LUMO energy gap as observed in a series of ring-fused porphyrinoids.[17] This result would constitute the first explicit example of metal-assisted endocyclic extension of porphyrin π-system. From the viewpoint of metal electronic states, metal–metal interaction through the C=C π-orbital could be expected, although no clear experimental evidence has been obtained so far. Because the molecular shapes are essentially same in **5** and **6**, conformational factors would not account for the large red-shift. The contribution of charge transfer cannot be ruled out, but it seems to be rather small or negligible judging from the modest shift of the absorption maxima in polar solvents.[18]

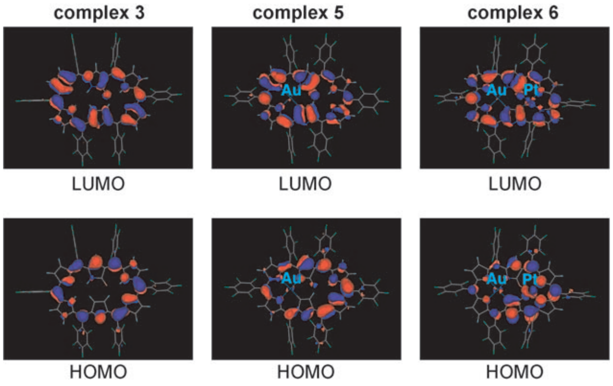


Figure 4. HOMO and LUMO for singly N-confused hexaphyrin **3**, its mono-Au$^{\mathrm{III}}$ complex **5**, and bis-(Au$^{\mathrm{III}}$,Pt$^{\mathrm{II}}$) complex **6**.

In summary, we have synthesized new isomers of singly N-confused hexaphyrin (**3** and **4**), and demonstrated the unique coordination chemistry of **3** by stepwise metal complexation in a facile manner that led to the formation of mono-Au$^{\mathrm{III}}$ complex **5** and bis-(Au$^{\mathrm{III}}$,Pt$^{\mathrm{II}}$) complex **6**. Retention of the rectangular structures for both **5** and **6** was clearly shown from their X-ray structures. From the ground and excited state properties, the introduction of the Au ion caused moderate changes to the porphyrin framework, whereas the second metal insertion led to significant perturbation on the hexaphyrin π-system. These results indicate large electronic changes in [26]hexaphyrin can be caused by the incorporation of two dissimilar metals in different oxidation states. Furthermore, tuning the properties of these functional systems may be useful for various applications such as molecular sensors, magneto devices, and organic functional dyes.[19] Further extension of this unique coordination chemistry and study of their photophysical properties by incorporating various 3d metal ions into this versatile porphyrinoid ligand is in progress.

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