Porphyrinoids

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# Triply N-Confused Hexaphyrins: Near-Infrared Luminescent Dyes with a Triangular Shape**

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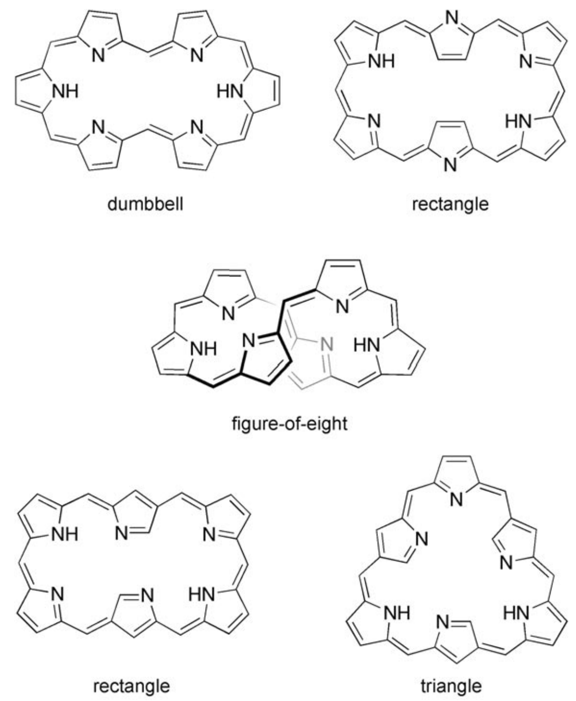
Molecular shape confines the spatial distribution of electrons that govern the properties of a molecule.[1] In general, the larger the size, the more flexibility the molecule can have. In the field of expanded porphyrins, understanding the shape-property relationship is becoming more important because of their potential applications as functional dyes that absorb and emit light in the near-infrared (NIR) region.[2] However, the large flexibility of the molecules results in them displaying a variety of structures with many conformers and tautomers, and this frequently makes analysis of their shape–property relationship difficult. Thus, it is desirable to fix the molecular shape by controlling, for example, the linker, position of the substituents, number of π electrons, protonation, metalation, and components of the rings. In the case of hexaphyrin(1.1.1.1.1.1), where six pyrrole rings and meso carbon atoms are connected alternately, the compound has been shown to display various conformations, such as a dumbbell,[3] rectangle,[4] and figure-of-eight,[5] depending on the substituents on the framework. Structural flexibility of hexaphyrins, or more generally, expanded porphyrins, is usually accompanied by inversion or rotation of the constituent pyrrole rings. Thus, regulation of pyrrole ring inversion is a way to force the molecule into a stable shape.



During the course of our studies on porphyrin analogues we have been interested in synthesizing a series of N-confused porphyrinoids by introducing one or more α,β′-linked pyrrolic ring(s) into the skeletons to assess if they have properties that are different from those of regular porphyrinoids.[6] The facile inversion (and fusion) of the confused pyrrole rings and their participation in a hydrogen-bonding network inside the cavity means that the shape and properties of confused porphyrinoids are likely to be controlled by changing the number and position of the confused pyrrole rings in the macrocycles. For example, a singly N-confused pentaphyrin has two fused rings,[7a] while a doubly N-confused pentaphyrin possesses two inverted pyrrole rings.[7b] In regard to the hexapyrrolic system, a doubly N-confused hexaphyrin having $C_2$ symmetry has already been shown to take a rectangular form, wherein a pair of confused pyrrole rings are inverted and face each other while the remaining four pyrrolic rings are regularly arranged with their N atoms pointed inwards.[8] Here we are interested in the triply N-confused hexaphyrin system which possesses the same number of alternately linked confused and normal pyrrole rings, since a triangular shape is inferred from its $C_3$-symmetric structure in two-dimensional diagrams.[9] If several different shapes were available, then analysis of the shape–property relationship of hexaphyrins would become possible.

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Thus, we have attempted and succeeded in synthesizing a triply N-confused hexaphyrin and its tri-oxo derivatives, all of which contain three confused pyrrole rings arranged in an alternate fashion with normal pyrrole rings, and demonstrated that they have a triangular shape. Remarkably, the triangular triply N-confused hexaphyrin has been found to exhibit an intensified NIR emission in its completely $C_3$-symmetric protonated form.

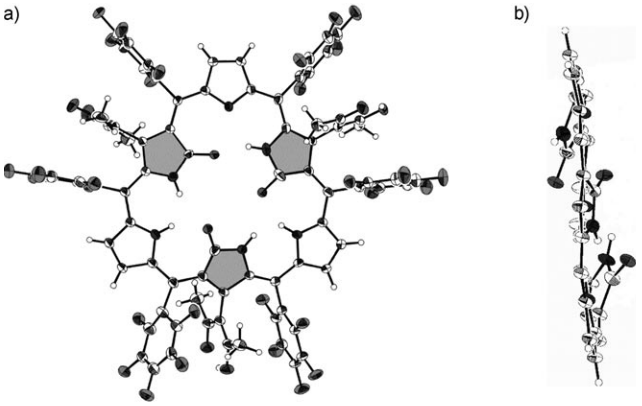
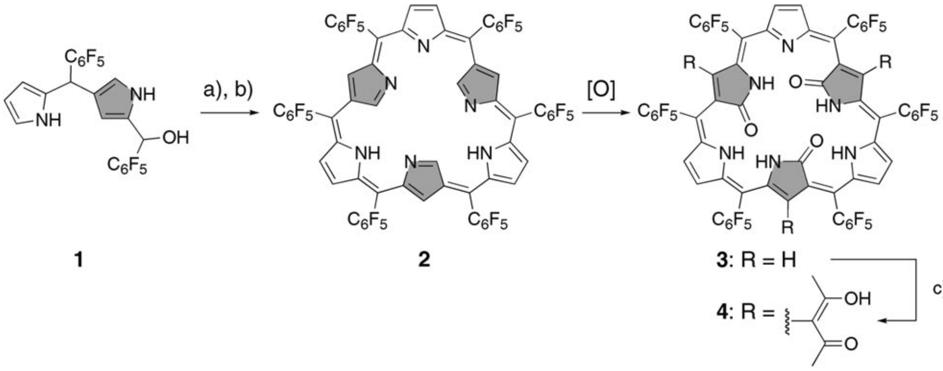


***Figure 1.*** ORTEP structure of **4**: a) top view, b) side view. Pentafluorophenyl groups are omitted for clarity in (b). Thermal ellipsoids are shown at the 30% probability level.

Triply N-confused meso-pentafluorophenylhexaphyrin **3** was synthesized by an acid-catalyzed [2+2+2] self-condensation of N-confused dipyrromethane carbinol **1**[10] in $CH_2Cl_2$ (Scheme 1). Oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) followed by chromatography on silica gel led to isolation of **3** in 13% yield. A signal at $m/z = 1509.07$ in the MALDI-TOF spectrum indicated the presence of trioxo-substituted hexaphyrin **3**. A signal corresponding to the target hexaphyrin (**2**) was also observed in the early stages of the DDQ oxidation, but this soon changed to signals for the mono-, di-, and tri-oxo species during the oxidation. Intact **2** was also isolated from the chromatographic separation when *p*-chloranil was used as the oxidant instead of DDQ, but **2** was unstable and gradually oxidized to **3** in solution. For crystallographic purposes, **3** was converted into acetylacetonate derivative **4** by treating it with manganese(III) acetylacetonate.[11]



***Scheme 1.*** Preparation of triply N-confused hexaphyrins (**2**–**4**). a) $BF_3{\cdot}OEt_2$ (0.33 equiv), $Bu_4NI$ (0.33 equiv), b) DDQ (3.0 equiv), c) $[Mn^{III}(acac)_3]$ (10 equiv), toluene. acac = acetylacetonate.

Direct evidence of the triangular shape of triply N-confused hexaphyrin came from the crystal structure of **4**, and is in marked contrast to the previously reported rectangular form of meso-aryl hexaphyrins (Figure 1).[8a,b,12] In the crystal, the confused and normal pyrrolic rings are arranged alternately to form a triangular shape. The molecule is slightly distorted, with a standard deviation of 0.285 Å from the mean plane of the macrocycle consisting of 36 atoms. The confused pyrrole rings are oxo-substituted and inverted, with tilting angles of 20.0, 27.4, and −13.0°. In the cavity, the amide-like CO and NH moieties of the confused pyrrole rings and the N and NH groups of the normal pyrrole rings are located within hydrogen-bonding distances (O···N: 2.546–3.136 Å, N···N: 2.809–2.956 Å). The substituted acetylacetonate substituents are perpendicular to the confused pyrrole rings and sandwiched by the neighboring meso-pentafluorophenyl groups.

In the $^1H$ NMR spectrum of **3** recorded in $CDCl_3$, the β-proton signals of the confused rings appear at $\delta = 10.11$, 9.52, and 9.17 ppm, while those of the normal pyrrole rings appear at around $\delta = 8.60$ ppm. The signals for the amide-like protons of the confused rings appear at $\delta = 4.49$, 3.98, and 3.20 ppm, while the signals for the pyrrolic NH protons of the normal rings appear at $\delta = -0.29$ and $-0.36$ ppm. These features indicate the molecule is 26π aromatic. Interestingly, the spectrum changed completely on addition of trifluoroacetic acid (TFA): the three β-proton signals of the confused pyrrole rings were shifted downfield and coalesced at $\delta = 11.55$ ppm, while the signals for the inner amide-like and pyrrolic NH protons were shifted upfield and coalesced at $\delta = -1.42$ and $-2.66$ ppm, respectively. The aromaticity of **3** is enhanced upon protonation, as evident from the difference in the chemical shifts of the outside and inside protons of the macrocycle: $\Delta\delta_{\text{out-in}} = 10.47$ ppm for **3** and $\Delta\delta_{\text{out-in}} = 14.21$ ppm for protonated **3**. Protonation results in all the normal pyrrole rings in **3** becoming equivalent and affords a $C_3$-symmetric triangular structure, which could be the origin of the enhanced aromaticity in **3**.

The triangular structure of **3** in solution is supported by the resemblance of its $^1H$ NMR spectrum to that of **4**. For **4**, the signals for the six β protons of the normal pyrrole rings appear at $\delta = 7.53$–7.92 ppm and those of the NH protons at $\delta = 3.24$ and 3.03 ppm, thus indicating the regular arrangement of these pyrrole rings. On the other hand, the signals for the three amide-like NH protons appear at $\delta = 8.38$, 6.69, and 6.30 ppm while the signals for the methyl groups of the acetylacetonate groups appear at $\delta = 1.88$, 1.71, and 1.60 ppm. This finding is consistent with the inverted arrangement of the confused pyrrole rings revealed by the X-ray structure. These data strongly indicate that the triangular structure of **4** is preserved even in $CDCl_3$ solution. The lower aromaticity of **4** ($\Delta\delta_{\text{out-in}} = 4.89$ ppm) might be due to steric effects introduced by the acetylacetonate groups, which greatly distort the molecule. The $^1$H NMR spectrum of hexaphyrin **2** shows signals for the six β protons of normal pyrrole rings at $\delta =$ 8.12–8.39 ppm and signals for the three β protons of the confused pyrrole rings at $\delta = 9.25$, 8.74, and 8.67 ppm, as well as signals for the inner CH proton at $\delta = -0.48$ (2H) and $-0.54$ ppm; these data are also compatible with **2** having a triangular structure.

The change in aromaticity observed upon protonation is also reflected in both the absorption and emission spectra. In $CH_2Cl_2$, **3** exhibits a broad Soret-like band split at 475 and 591 nm and Q-like bands at 835, 947, and 1087 nm (Figure 2). The longest wavelength transition is bathochromically shifted by about 40 nm compared to that of the corresponding rectangular doubly N-confused dioxohexaphyrin.[8a] The solution showed a vivid color change from blue to green when TFA was added. Protonated **3** displays a sharpened Soret-like band at 638 nm and Q-like bands at 809, 888, and 1016 nm. The transition at 1016 nm, in particular, is considerably enhanced. In the fluorescence spectra of **3** in $CH_2Cl_2$, an intense emission is observed at 1094 nm ($\Phi_F = 0.001$), which is about 50 nm longer and is more intense than that of the doubly N-confused hexaphyrin (Figure 2b).[8c] When **3** was protonated, the emission band was even more enhanced ($\Phi_F = 0.0055$), with a hypsochromic shift to 1044 nm.[13] Thus, the $C_3$-symmetric structure induced by protonation might be effective in increasing the molecular rigidity, which should be relevant to the enhanced aromaticity as well as the more intense absorption and emission spectra.

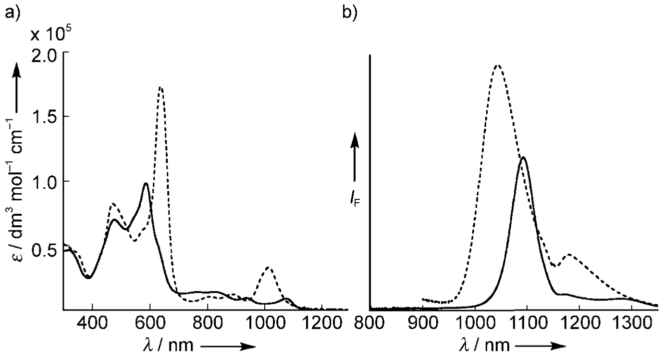


*Figure 2.* The optical spectra of free-base (——) and protonated (-----) forms of **3** in $CH_2Cl_2$: a) absorption and b) emission (excitation at 600 nm).

From a symmetry viewpoint, the asymmetric nature of the confused pyrrole ring means that the allowed symmetry is only $C_2$ for doubly N-confused hexaphyrin and $C_3$ for triply N-confused hexaphyrin, which lead to the rectangular and triangular shapes, respectively. To gain insight into the relative stability of the rectangular and triangular forms of the two confused hexaphyrins, density functional theory (DFT) calculations were performed at the B3LYP/6-31G** level on both the free-base and monoprotonated species.[14] Consistent with the experimental results, the triangular structures of the triply N-confused hexaphyrin (**2**), both in free-base and protonated forms, are found to be more stable than the rectangular structure by 11.7 and 25.2 kcal mol$^{-1}$, respectively (Figure 3). A set of intramolecular hydrogen bonds in the dipyrromethene substructures—two in the neutral and three in the protonated forms—are seen in the optimized structure of **2** and protonated **2**, respectively, which could be the origin of the high stability of the triangular form. On the other hand, in the case of doubly N-confused hexaphyrin, two intramolecular hydrogen bonds are possible in the rectangular form but only one in the triangular form, and the neutral and monoprotonated species show an energy difference of 7.3 and 4.8 kcal mol$^{-1}$, respectively, over the triangular form. As the energy difference is so large, we can qualitatively deduce the relative stability of N-confused hexaphyrins from the number of possible hydrogen bonds, although the steric repulsion cannot be totally neglected.

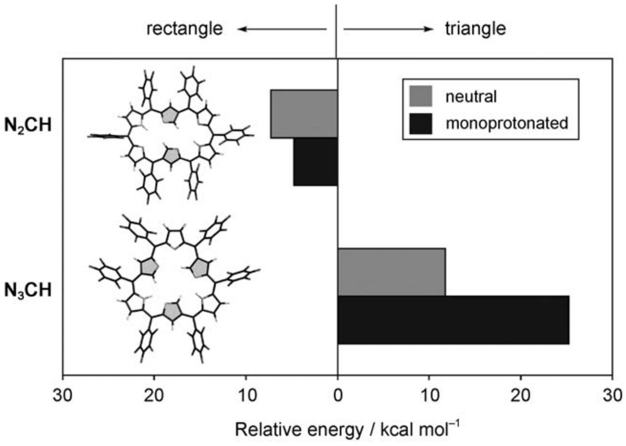


*Figure 3.* Relative energy of doubly and triply N-confused hexaphyrins (**$N_2CH$** and **$N_3CH$**).

Although the above symmetry-based discussion should be limited to the N-confused hexaphyrin system, it would be of interest to check the possibility of a triangular shape for regular hexaphyrins, because the $C_3$-symmetric shape can also be drawn. Interestingly, the calculation suggested a possibility of stabilizing the $C_3$-symmetric triangular structure even in regular meso-aryl hexaphyrins by protonation.[14] We checked several crystal structures of protonated hexaphyrins at hand and we were very pleased to find such an example. Figure 4 shows the X-ray structure of an ion-pair complex of meso-hexaphenylhexaphyrin (**5**) and methanesulfonic acid (MSA).[12] The molecule consists of the same number of amino and imino pyrrole rings and displays a triangular structure. The molecule is rather distorted to a bowl-shape because of the hydrogen-bonding interactions between inward-pointing amino-pyrrole NH atoms and the oxygen atoms of the methanesulfonate anion. The free-base form of **5** was reported to be unstable in solution,[15] but we found the stability of **5** was remarkably increased in the protonated form, especially in the presence of the MSA anion.[14] Thus, it

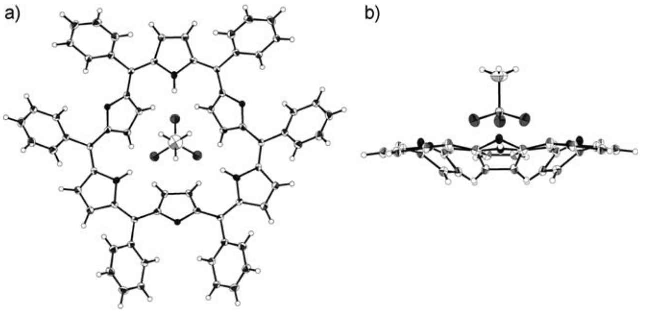


***Figure 4.*** ORTEP structure of ion-pair complex of **5** and MSA: a) top view, b) side view. Phenyl groups are omitted for clarity in (b). Thermal ellipsoids are shown at the 30% probability level.

is likely that the $C_3$-symmetric structure of protonated **5** is significantly stabilized by the MSA anion in a form that is favorable for $C_3$-symmetric hydrogen bonds. Partially supporting this, a $C_3$-symmetric type of signal pattern was observed in the $^1$H NMR spectrum of **5** with five equivalents of MSA in $CD_2Cl_2$ at −30 °C.[14]

In summary, we have synthesized a new class of N-confused expanded porphyrins, triply N-confused hexaphyrins (**2**–**4**), with triangular shapes and NIR emission. We have also identified the triangular conformation of the protonated regular hexaphenyl [26]hexaphyrin. It is concluded that the triangular conformation of meso-aryl N-confused hexaphyrin can be obtained by making the molecule $C_3$-symmetric, which is achieved by the introduction of three alternate confused pyrrole rings. The results are a good indication of the ability of confused pyrrole rings to readily change the shape and properties of the macrocycles as a result of hydrogen-bonding interactions inside the cavity. More importantly, the study suggests that the shape and properties of N-confused expanded porphyrinoids could be controlled at the stage of molecular design just by changing the number and arrangement of the normal and confused pyrrole rings in the macrocycle. For an intrinsic understanding of the shape–property relationship, it would be necessary to compare species that differ only in their geometry. Further investigation of a series of N-confused hexaphyrins and other porphyrinoids with various shapes could be one of the ways to address this issue.

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