Möbius Aromaticity

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meso-Aryl [20]π Homoporphyrin: The Simplest Expanded Porphyrin with the Smallest Möbius Topology

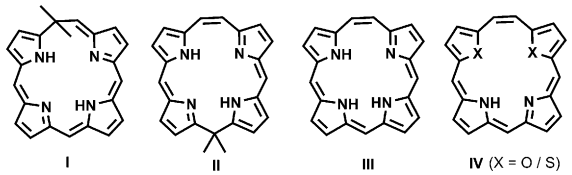
K. S. Anju[+], Mainak Das[+], B. Adinarayana, Cherumuttathu H. Suresh, and A. Srinivasan**

Dedicated to Prof. Atsuhiro Osuka

Abstract: *An unstable conjugated homoporphyrin was successfully stabilized by introducing meso-aryl substitutents. It was evident from the moderate diatropic ring current found by NMR analysis that the newly formed 20π conjugated free base and its protonated form exhibited Möbius aromatic character. Furthermore, complexation as a ligand with an Rh^{I} ion afforded a unique binding mode and retained the Möbius aromaticity. Overall, these compounds are the smallest Möbius aromatic molecules, as confirmed by spectral and crystal-structure analysis and supported by theoretical studies.*

Porphyrins, 18π macrocycles termed "pigments of life," play diverse and critical roles in nature. Numerous analogues of porphyrins, such as contracted, expanded, and isomeric porphyrins,[1] have been reported. Expanded porphyrins in particular have attracted much attention owing to their diverse applications. They have more than 18π electrons in their conjugated pathway owing to either an increased number of heterocyclic rings or *meso* carbon bridges. Since the serendipitous discovery of 22π sapphyrins by Woodward and co-workers in 1966,[2] there has been intense study in this area up to 96π tetracosapphyrin.[3] In particular, the simplest expanded porphyrins, homoporphyrins, have been studied much less. This class of porphyrins contains an extra atom between a *meso* and an α-pyrrolic carbon atom and has 17 atoms in its smallest macrocyclic ring (Scheme 1).[4] Type **I** and **II** systems contain an sp^3-hybridized centre that breaks the π-electron conjugation pathway, whereas type **III** compounds are fully conjugated 20π systems.

In 1971, Grigg reported the first homoporphyrin, *meso*-homoazaoctaethylporphyrin, a type **I** system, which was found to be unstable and also unable to afford stable metal complexes.[5] Subsequently, Callot and co-workers reported the corresponding carbon analogue,[6] which led to the formation of a type **III** homoporphyrin under acidic conditions.[7] However, the system (type **III** homoporphyrin) was reported to be very unstable, decomposed even at 0 °C in the solid state, and one of the substituents at the vinylene bridge was confined to an ester group only. Furthermore, metallation turned out to be very complex and led to species with interrupted conjugation (types **I** and **II**) and in some cases converted into metalloporphyrins. Recently, a stable core-modified non-aromatic homoporphyrin (type **IV**) was reported by Ravikanth and co-workers.[8] However, to the best of our knowledge, even after four decades since the discovery of homoporphyrins, a completely conjugated stable free-base homoporphyrin system and its corresponding metal complexes remain elusive. Thus, the development of a reliable synthetic route is highly desirable and remains a fascinating area in the chemistry of expanded porphyrins.



Scheme 1. Classes of homoporphyrins.

In 1964, Heilbronner suggested the concept of Möbius aromaticity and predicted the aromatic character of [4*n*]π annulenes lying on a single-sided, non-orientable Möbius strip.[9] However, the first experimental evidence, reported by Herges and co-workers, came into the limelight only in 2003.[10] The concept of Möbius aromaticity in expanded porphyrins was introduced by Latos-Grażyński and co-workers[11] and further extensively studied by the research groups of Osuka and Kim.[12a–d] So far, a series of Möbius expanded porphyrins have been reported, in which aromaticity was induced by i) varying temperature,[13] ii) coordination,[14] iii) thermal fusion,[15] iv) protonation,[16] v) oxidation/reduction,[17] and vi) changing the solvent.[11a,18] Despite these extensive reports, N-fused 24π pentaphyrin with a Rh^{I} salt is the smallest Möbius aromatic expanded porphyrin confirmed structurally to date.[14j] Recently, Mallick and Haraprivya synthesized a core-modified heterocyclic [20]π tripyrrane derivative and demonstrated that it was a Möbius aromatic system by spectral and theoretical studies.[19] However, it remains a challenge for the tetrapyrrolic skeleton to achieve a Möbius twisted topology within itself, as the cavity is not large enough to mitigate the distortion associated with molecular twist. Herein, we report the first facile synthesis and structural characterization of stable *meso*-aryl [20]π

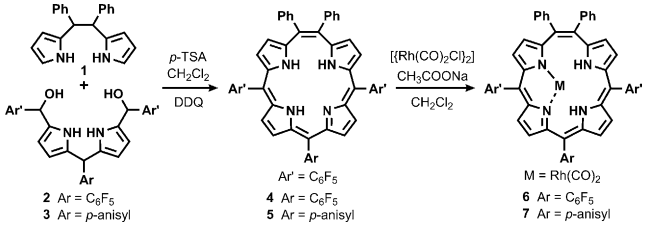
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tetraphyrin(2.1.1.1) and its Rh^{I} complex. The hitherto unknown homoporphyrin is the smallest molecule to show Möbius topology in three different forms: as the free base, when protonated, and with a coordinated metal ion.

The target macrocycles were synthesized by a [2+2] MacDonald-type condensation between *meso*-5,6-diphenyldipyrroethane (**1**)[20] and 1,9-bis(pentafluorophenylhydroxymethyl)-5-(aryl)dipyrromethanes **2** and **3** in dry CH_2Cl_2 under the catalysis of *p*-toluenesulphonic acid (*p*-TSA), followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ; Scheme 2). The crude mixture was purified by column



Scheme 2. Synthesis of **4** and **5** and their Rh^{I} complexes **6** and **7**.

chromatography on silica gel with CH_2Cl_2/*n*-hexane as the eluent. The desired products **4** and **5** were obtained as green compounds in 15% yield and were found to be highly stable. Mass spectrometric analysis of **4** and **5** confirmed the exact composition with a molecular-ion signal at *m*/*z* 975.1156 and 915.1786 ($M+1$), respectively (see Figures S1 and S2 in the Supporting Information).

The ^{1}H NMR spectrum of **4** in CD_2Cl_2 is shown in Figure 1a. At room temperature, the macrocycle **4** exhibits three sets of doublets at $\delta = 6.43$, 6.51, and 6.97 ppm, corresponding to six pyrrolic β-CH hydrogen atoms. The remaining pyrrolic β-CH protons as well as the *meso*-aryl protons resonated between 7.05 and 7.16 ppm. These assignments were further confirmed by ^{1}H–^{1}H COSY spectral analysis (see Figure S6). The correlation between the signals at 6.43 and 6.51 ppm revealed that these pyrrole units were linked by a dipyrroethene bridge, and the correlation between the signals at 6.97 and 7.14 ppm revealed that these pyrrole units were linked by a dipyrromethene unit. Owing to rapid tautomerism, one broad signal was observed at 6.25 ppm for the NH hydrogen atoms. To reveal the NH signals, we further performed variable-temperature (VT) ^{1}H NMR spectroscopy (see Figure S7). At −20 °C, well-resolved NH signals were observed at 6.01 and 6.07 ppm (see Figure S9a). The pyrrolic β-CH proton signal initially merged with the phenyl proton peaks were separated out and resonated as doublets at 7.16 ppm. The upfield shift of the inner NH signals as compared to those of reported core-modified homoporphyrins (**IV**)[8] clearly suggests that the [20]π homoporphyrin experiences a moderate aromatic character.

After the addition of trifluoroacetic acid (TFA), all the signals for pyrrolic β-CH hydrogen atoms were shifted downfield as compared to the free base and resonated between 6.76 and 7.87 ppm (see Figure S8b). At room temperature, of four NH protons, only two were observed as a broad singlet at 6.45 ppm. The other two NH signals were observed by variable-temperature analysis. Specifically, at −20 °C, the protonated form showed a sharp singlet at 5.85 ppm corresponding to two NH protons, and the other two NH protons resonated as a broad singlet at 6.45 ppm (see Figure S9b). Overall, as observed in the free base, the moderate diatropic ring current was further retained in the protonated state, which suggests the existence of Möbius aromaticity even after protonation.

The explicit structure of homoporphyrin **5** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 2; see also Table S2). As observed by NMR analysis, the dipyrroethene and dipyrromethene units are linked by *meso*-aryl bridges, and all pyrrolic nitrogen atoms point inward. Of the four pyrrolic units, three are amino (N1, N3, and N4) and one is imino (N2) in nature. Two amine-like pyrrole units (N1 and N4) are connected through a *meso*-phenyl-substituted vinylene and/or ethylene C20–C21 bridge. The structure is substantially distorted from planarity and was found to have a Möbius topology with a 20π electron circuit. The tilt angles of the pyrrole units N1–N4 with respect to the mean plane defined by the 25 inner-core atoms are 42.70(6)° [N1], 17.78(5)° [N2], 21.12(5)° [N3] and 63.69(7)° [N4]. The remarkable tilting of the pyrrole rings N1 and N4 is caused by the steric congestion imposed by the *meso*-phenyl-substituted vinylene bridge, which leads to the Möbius conformation with overall π-electron conjugation. Furthermore, the torsion

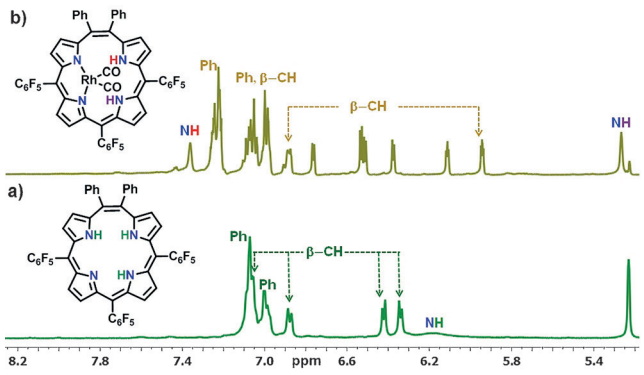


Figure 1. ^{1}H NMR spectra of a) **4** and b) **6** in CD_2Cl_2.

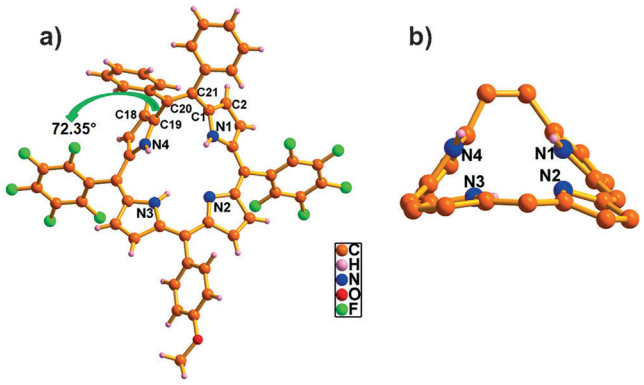


Figure 2. Single-crystal X-ray structure of **5**. a) Top view; b) side view. The *meso*-aryl groups are omitted for clarity in the side view.

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angle at the twisted position (C18–C19–C20–C21) is 72.35°, which is higher than that of Möbius systems reported to date,[11b,12] thus revealing the moderate aromatic behaviour of the [20]π system (see Table S1 and Figure S27).

The coordination chemistry of **4** was performed with $[\{Rh(CO)_2Cl\}_2]$ in the presence of sodium acetate in CH_2Cl_2 at reflux resulted in the formation of Rh^I complex **6** in quantitative yield (Scheme 2). The complexation was confirmed by mass spectrometric analysis with a molecular-ion signal at *m*/*z* 1132.98 (see Figure S3). The insertion of Rh^I resulted in major changes in the ^1H NMR spectral pattern (Figure 1 b). Upon coordination, the appearance of two NH signals at 7.43 and 5.34 ppm suggested that the Rh^I center coordinated with the ligand in a BODIPY bonding mode, and the β-CH signals of each pyrrole ring resonated as individual peaks between 6.02 and 7.06 ppm, thus reflecting the unsymmetrical nature of the complex. These signals were confirmed by ^1H–^1H COSY spectral analysis (see Figure S13). There was a correlation found between one of the uncoordinated [N1] pyrrolic β-CH protons and the NH proton, and the two β-CH protons resonated as triplets at 6.02 and 6.19 ppm, whereas the [N2] pyrrolic β-CH protons correlated with the NH proton and appeared at 6.96 and 7.06 ppm. The Rh^I-coordinated [N3 and N4] pyrrolic β-CH protons were shifted slightly upfield as compared to the free base and appeared between 6.44 and 6.84 ppm. Furthermore, the signal for one of the pyrrolic NH atoms observed at 5.34 ppm at room temperature was shifted upfield upon lowering of the temperature and observed at 4.8 ppm at 193 K (see Figure S14), thus clearly indicating the Möbius aromatic character of the system even after complexation of the ligand with the Rh^I ion.

The insertion of Rh^I (in **7**) was confirmed by single-crystal X-ray analysis (Figure 3; see also Table S2). The metal ion was coordinated to two of the four pyrrole rings, one from the dipyrroethene unit and another from the dipyrromethene unit. In the twisted Möbius topology of **7** with moderate aromatic character, the pyrrole rings connected to the ethylene bridge (N1 and N4) deviate strongly from the mean plane with tilt angles of 79.48(2)° [N1] and 41.18(2)° [N4] to release the steric strain of the macrocycle, and the torsion angle at C20-C21-C1-C2, found to be 67.32°, is less than in **5**, thus maintaining the moderate aromatic character of the [20]π system (see Table S1 and Figure S27).[11–18] Furthermore, the upfield shift of the NMR signal for one of the inner NH atomswas confirmed by the close proximity of the hydrogen atom to the metal center, with a N2-H2···Rh bond distance and angle of 2.848(1) Å and 128.89(4)° (see Figure S22). Overall, the variable-temperature NMR studies and single-crystal analysis proves that both the free bases and the Rh complexes exhibit moderate 20π Möbius aromatic character rather than 20π Hückel antiaromatic character.

The electronic absorption spectra of **4** and **5**, their protonated derivatives **4.H**$^+$ and **5.H**$^+$, and Rh^I complexes **6** and **7** were recorded in CH_2Cl_2 (see Figures S29–S32). For example, the macrocycle **4** showed broad absorption bands from 366 to 442 nm and a prominent Q-like band at 683 nm. Upon protonation of **4** with TFA, the broad bands were split into two well-defined bands at 407 and 499 nm, whereas the Q-like band was red-shifted by 84 nm and observed at 767 nm (see Figure S29). On the other hand, the Rh^I complex **6** displayed a Soret-like band at 416 nm along with a shoulder at 470 nm, and the lower-energy band was red-shifted by 59 nm in comparison to **4** and appeared at 742 nm. The molar extinction coefficients of these molecules were found to be in the order of 10^5, thus suggesting their aromatic behaviour and Möbius aromaticity instead of Hückel antiaromatic character.

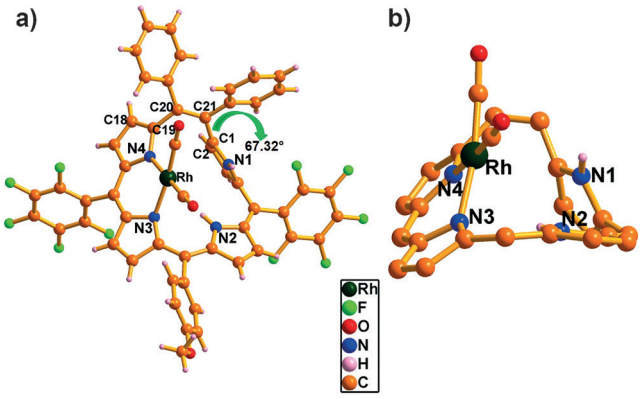


Figure 3. Single-crystal X-ray structure of **7**. a) Top view; b) side view. The *meso*-aryl groups are omitted for clarity in the side view.

The molecular systems **4**, **5**, **4.H**$^+$, **5.H**$^+$, **6**, and **7** were optimized at the B3LYP/DGDZVP level of density functional theory.[22] For evaluation of the degree of aromaticity, NICS-(0), HOMA, and BLA calculations and AICD plots were considered as the best index.[23] The NICS(0) and HOMA values of **5** and **7** are shown in Figure 4, and the NICS(0), HOMA, and BLA values of **4**–**7** are listed in Table 1. The NICS(0) values found are between −6.30 and −9.16 ppm (see Tables S4 and S6); the HOMA values are 0.53 and 0.68 (see Tables S5 and S6), and the BLA values are between 0.081 and 0.104 Å (see Figures S33–S38). All these values are comparable with those previously reported for 4nπ molecules with

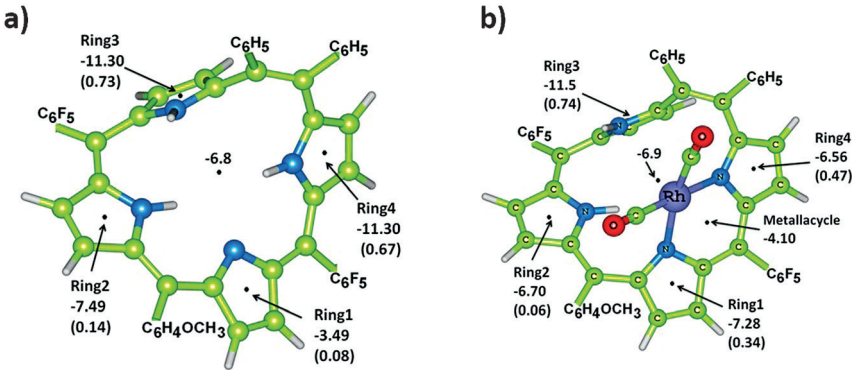


Figure 4. Optimized geometry (B3LYP/DGDZVP level) of a) **5** and b) **7** with NICS(0) and HOMA values (in parentheses).

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Table 1: NICS(0) [ppm], HOMA, and BLA [Å] values of **4**, **5**, **4.H**$^+$, **5.H**$^+$, **6**, and **7**.

Calculation	**4**	**5**	**4.H**$^+$	**5.H**$^+$	**6**	**7**
NICS(0)	−6.30	−6.80	−9.16	−9.08	−6.53	−6.90
HOMA	0.62	0.63	0.68	0.65	0.58	0.53
BLA	0.102	0.099	0.084	0.081	0.104	0.102

Möbius aromatic character.[11–18] The clockwise current density from the AICD plots further supports the diatropic ring current and aromaticity (see Table S7). In particular, a higher degree of aromaticity in **4.H**$^+$ as compared to **4** and **6** was reflected by the moderate increase in diatropic ring current indicated by NMR analysis, the lower torsion angles of the optimized geometry (see Table S8 and Figure S39), and high negative NICS(0) values. Overall, the Möbius aromatic character was further corroborated by the theoretical studies.

In summary, we have successfully isolated a stable *meso*-aryl [20]π tetraphyrin(2.1.1.1): a system reported to be unstable until now. Thus, we have described the simplest expanded porphyrin, a missing link in the rich area of expanded porphyrinoids, for the first time. The present study demonstrated the smallest Möbius aromatic character of [20]π homoporphyrins in three different forms: neutral, protonated, and as Rh^I ion complexes. The Möbius aromaticity was unambiguously supported by spectral studies and theoretical calculations and finally confirmed by crystal analysis. The newly formed trianionic homoporphyrin system could be an ideal platform to stabilize metal ions in their higher oxidation states and also for exploration of the aromatic character of such systems, research on which is currently in progress in our group.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: conjugation · coordination chemistry · homoporphyrins · Möbius aromaticity · porphyrinoids

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