DOI: 10.1002/anie.200705568

Möbius Porphyrins

The Porphyrin Twist: Hückel and Möbius Aromaticity

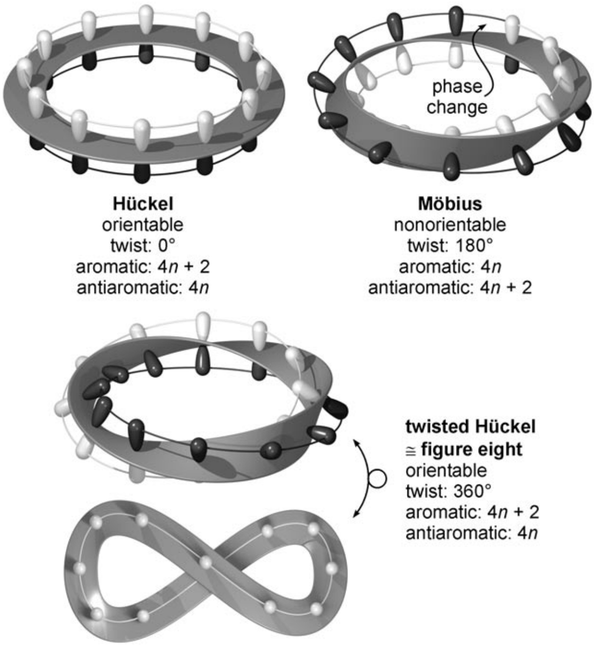
*Norbert Jux**

Dedicated to Professor Emanuel Vogel on the occasion of his 80th birthday

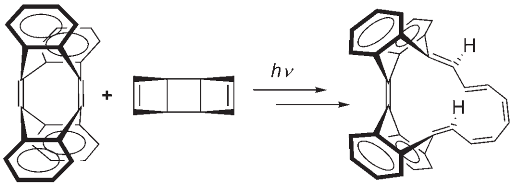
aromaticity · expanded porphyrins · Möbius aromaticity · porphyrinoids

The Möbius strip is the classic example of a single-sided nonorientable surface. It can be constructed by taking a strip of paper, twisting it by 180°, and joining its ends to form a single strip. An excellent visualization of a Möbius strip is the famous ant walk in "Möbius Strip II" by the Dutch artist M. C. Escher. The intriguing concept of Möbius aromaticity was proposed more than 40 years ago by Heilbronner,[1] who predicted that Möbius strip-like twisted annulenes with 4*n* π electrons should be closed-shell species and aromatic (Scheme 1).

Despite the high number of papers in which the properties of such compounds were calculated,[3] the synthesis of a Möbius aromatic annulene was reported only recently by Herges and co-workers.[4] The clever conceptual combination of a flexible polyene chain containing one *E* double bond with a rigid bianthraquinodimethane moiety resulted in Möbius-stabilized [16]annulene **3** (Scheme 2). Its synthesis was realized through stepwise irradiation starting from tetradehydrodianthracene **1** and *syn*-tricyclooctadiene **2**. High-level calculations by the same group have shown that Heilbronner's assessment is only valid on the level of Hückel molecular orbital theory, which does not take the twist-induced strain into account—this strain overcomes any Möbius aromatic stabilization. Together with their synthetic work, these calculations helped Herges and co-workers to decouple the energetic contributions from strain and Möbius aromaticity. Thus, benzoannelation in these systems helps to stabilize the twist but does not diminish the aromatic character significantly,[5] which contradicts other purely theoretical work.[6]



Scheme 1. Topologies of conjugated π-electron systems with different numbers of half twists; the number of π electrons in the aromatic and antiaromatic systems is given in each case (from reference [2]).



1 **2** **3**

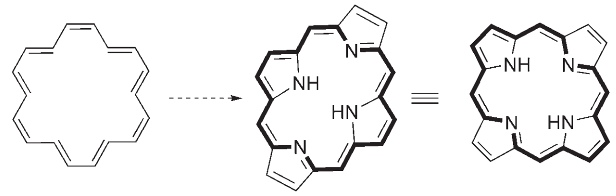
Scheme 2. Synthesis of Möbius-stabilized [16]annulene **3**.

Interestingly, a detailed analysis of figure-eight-shaped expanded porphyrins was presented in a recent review by Herges dealing with the design of Möbius molecules.[3b] Given the degree of flexibility and accessibility of various redox states that expanded porphyrins provide, it comes with no surprise that these porphyrins also contribute to the field of Möbius aromaticity.

With regard to aromaticity in general, porphyrins have been given major attention ever since Hückel's rule was established. Porphyrin **5** is frequently described as bridged [18]annulene **4** with a main conjugation pathway that follows Hückel's rule (Scheme 3).[7] Although the rule is defined for monocycles, the concept of a main conjugation pathway helps in getting a fast and reliable estimation of a porphyrin's electronic nature. This also holds true for expanded porphyrins such as [22]porphyrin(1.3.1.3) **6**[8] and [26]porphyrin(3.3.3.3) dication **7**,[9] which show extraordinary aromatic properties (Scheme 4). These compounds were aptly described as "superarenes". As ^{1}H NMR spectroscopy provides

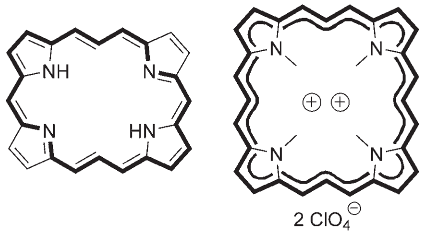
---

[*] Priv.-Doz. Dr. N. Jux
Department of Chemistry and Pharmacy
Friedrich-Alexander-Universität Erlangen-Nürnberg
Henkestrasse 42, 91054 Erlangen (Germany)
Fax: (+49) 9131-852-6864
E-mail: norbert.jux@chemie.uni-erlangen.de
Homepage: http://www.chemie.uni-erlangen.de/oc/jux



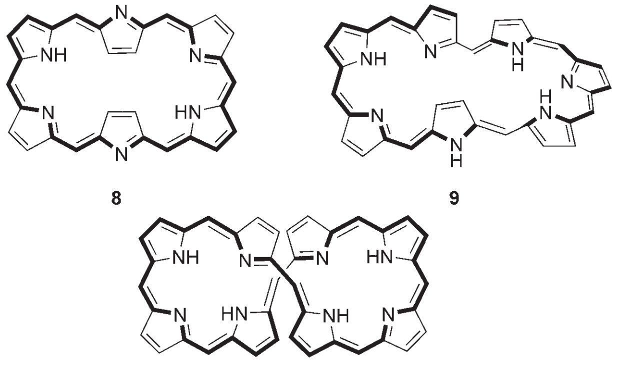
4 5

Scheme 3. Conceptual transformation of [18]annulene **4** into [18]porphyrin(1.1.1.1) (**5**); the main conjugation pathway is shown in bold.



6 7

Scheme 4. Expanded porphyrins: [22]porphyrin(1.3.1.3) (**6**), tetrakis-*N*-methyl[26]porphyrin(3.3.3.3) dication (**7**) as bisperchlorate; substituents not shown.



8 9 10

Scheme 5. Examples of expanded porphyrins with more than four heterocycles and one-carbon-atom bridges; substituents not shown.

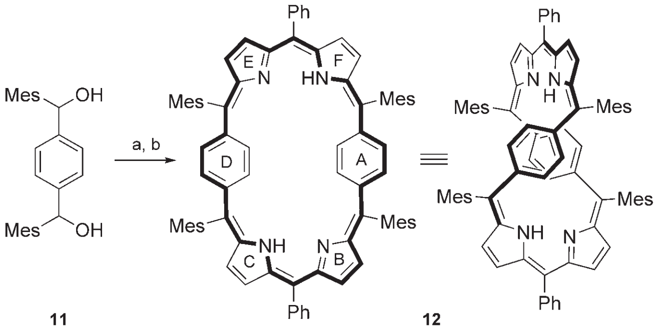
an easy tool to verify aromaticity experimentally through ring current effects, it is the method of choice for porphyrin chemists.[10]

Even if more rings are part of the system, Hückel's rule still works. Interestingly, as the number of heterocycles—typically, but not necessarily,[11] pyrroles[12]—increases, more redox states become accessible, and, thus, aromatic and antiaromatic systems can be observed within the same framework. Conformational flexibility and the number and the nature of substituents on the pyrrolic and meso positions must also be taken into account for larger porphyrins, as these can have a profound influence on the shape of the molecule. The number of carbon atoms bridging the heterocycles may also vary greatly, even within the same molecule.[12]

[26]Hexaphyrin(1.1.1.1.1.1) **8**[13] can adopt planar conformations though inversion of pyrrolic subunits, whereas higher expanded porphyrins, such as heptaphyrin **9**[14] (shown with a 32 π electron main conjugation pathway in Scheme 5) and octaphyrin **10**,[12] possess twisted structures and are rather flexible. Often, conformers of larger expanded porphyrins are stable at room temperature and in some cases were resolved into the enantiomers.[15] In particular, octaphyrins such as **10** form figure-eight topologies that do not invert.[14a,16] Substituents play an important role as they influence the overall topology of expanded porphyrins.

Very recently, two novel porphyrin systems that introduced Möbius aromaticity to the porphyrin field were presented by the groups of Latos-Grażyński and Osuka. Latos-Grażyński and co-workers prepared A,D-di-*para*-benzi[28]hexaphyrin(1.1.1.1.1.1) (**12**; A and D denote the positions of the phenyl rings in the macrocycle) from dicarbinol **11**, pyrrole, and benzaldehyde by acid-catalyzed condensation, followed by DDQ oxidation (Scheme 6). The crystal structure of **12** showed that the molecule possesses a C_2 axis with two nonequivalent phenylene rings. These rings are perpendicular and parallel, respectively, to the symmetry axis, forming an "edge to face" orientation (Figure 1).[2]

Interestingly, the Möbius conformation of **12** in the crystal is lost in solution as evidenced by ^{1}H NMR spectroscopy. In particular, the phenylene rings are equivalent on the NMR timescale and rotate freely, leading to a coalescence of their signals. Nevertheless, the whole structure maintains its integrity and the enantiomers are stable at room temperature. Analysis of NMR spectra recorded over a temperature range of 203–343 K supports the existence of two species in equilibrium, one of which is the twisted Hückel-type porphyrin that shows significant paratropic ring current. In this case, both phenylene rings are parallel. The other species displays chemical shifts that correspond to porphyrins devoid of macrocyclic aromaticity. This behavior can be explained by assuming a Möbius-type system in which the aromatic stabilization does not overcome the twist-induced strain energy. The NMR data of this species correspond to the conformation found in the crystal in which the phenylene rings are perpendicular. It should be pointed out that the equilibrium of this dynamic Hückel–Möbius system is also solvent-dependent. The Möbius conformer becomes the



11 12

Scheme 6. Synthesis of Hückel–Möbius-switchable dibenzihexaphyrin **12**; a) pyrrole, benzaldehyde, cat. $BF_3\cdot OEt_2$; b) DDQ. Mes = 2,4,6-trimethylphenyl.

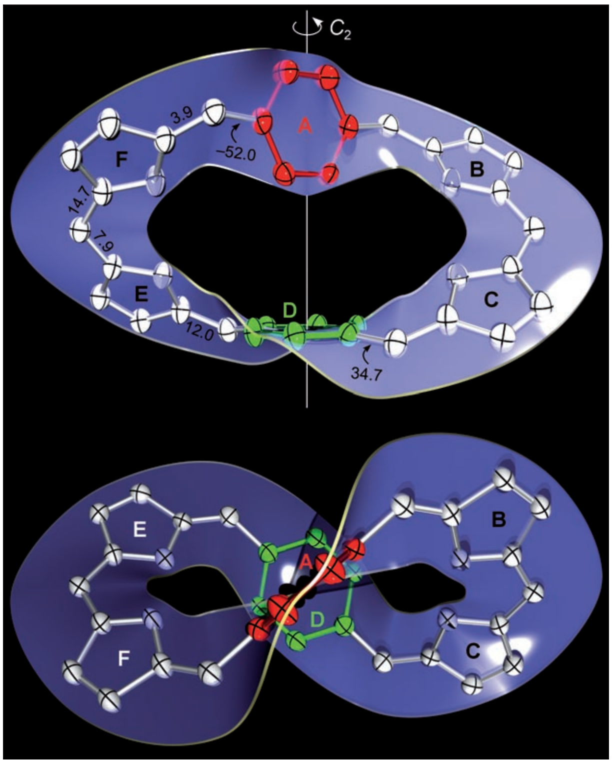
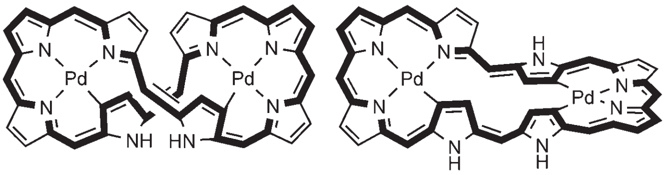


Figure 1. X-ray crystal structure of **12**; *meso* substituents, hydrogen atoms, and solvent molecules are omitted for clarity. The nonequivalent phenylene units are shown in green and red. The blue ribbon follows the surface of the π system; side and top view. Graphics taken from reference [2].

dominant species in DMF and chloroform, whereas in solvents such as hexane or ethanol it is not observed at all.

Combining both temperature and solvent dependence allowed the measurement of UV/Vis spectra of both species. The spectrum of the blue Möbius aromatic compound resembles more that of a porphyrin spectrum expected for a compound with 28 π electrons (Soret band at around 580 nm and Q bands at around 660–750 nm). The spectrum of the green Hückel antiaromatic species appears to be more like that of a polyene. The general features of the equilibrium are also corroborated by DFT calculations at the B3LYP/6-31G** level. A drawback of this work with regard to aromaticity itself is that the Möbius-stabilized system is only available under certain conditions. This situation may very well be seen as an advantage for the design of functional receptor materials as phenylene-bridged expanded porphyrins are capable of both metal coordination and anion binding.

Osuka and co-workers have now made the next step towards truly stable Möbius aromatic systems by metalation of expanded porphyrins.[17] By taking advantage of the fact that Group 10 metals are known to form complexes not only with the N_4 coordination set of parent porphyrins, but also with the N_3C donor set of so-called inverted porphyrins,[18] they metalated [36]octaphyrin(1.1.1.1.1.1.1.1) (**10**; Scheme 3)[14a] with palladium(II) ions to yield two distinctively different species (Scheme 7).[17] Both complexes were fully characterized and their structures in the crystal elucidated.



13 **14**

Scheme 7. Twisted Hückel-type bispalladium octaphyrin **13** and Möbius-type bispalladium octaphyrin **14**.

The major product of the metalation is the C_2-symmetric, figure-eight-type porphyrinoid **13** with two inverted pyrroles that coordinate to the palladium(II) ions through one carbon atom each (Figure 2A). Compound **13** shows a significant paratropic ring current and is, in accord with its 36 π electron main conjugation pathway, a twisted Hückel-type, largely antiaromatic system.

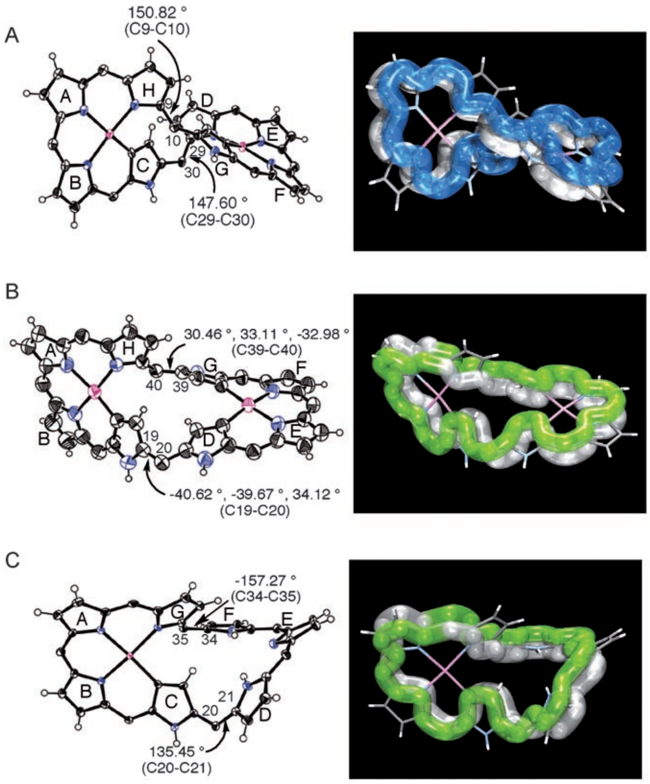


Figure 2. Crystal structures of A) twisted Hückel-type bispalladium octaphyrin **13**, B) Möbius-type bispalladium octaphyrin **14**, and C) Möbius-type monopalladium heptaphyrin **15**. Reproduced from reference [17].

Most interestingly, the second metal complex **14** shows a twisted single-sided Möbius topology with three inverted pyrrolic rings. Compound **14** is not symmetrical: one Pd^{II} ion is in an N_3C and the other in an N_2C_2 coordination environment (Figure 2B). The distinct diatropic ring current of **14** is aptly demonstrated by resonances of the inner protons between $\delta = 0.24$ and -1.77 ppm, whereas the outer proton signals appear in the deshielded region at around $\delta = 8$–7 ppm. As was observed for dibenzihexaphyrin **12**, the porphyrin-like—and thus aromatic—character of **14** is also supported by its UV/Vis spectrum, which shows an intense Soret-like band at 735 nm and Q-like bands at 822, 1020, and 1143 nm. In contrast to its precursor **10** and, most importantly, in contrast to **12**, the ^{1}H NMR spectra of **14** are independent of changes in either temperature or solvent. Thus, **14** is a stable Möbius aromatic porphyrin!

Osuka and co-workers also prepared palladium(II) complexes of [32]heptaphyrin-(1.1.1.1.1.1.1) (**9**; Figure 2C) and reexamined the Group 10 metal complexes formed upon metalation of [26]hexaphyrin(1.1.1.1.1.1) (**8**). Although in both cases only one metal ion is bound, the spectral characteristics again indicate the presence of twisted Möbius strip structures.[17] Metal complexes of **8** of this type, which are actually derivatives of [28]porphyrin(1.1.1.1.1.1), were already prepared in 2005,[19] but only now have the authors recognized their true nature as Möbius aromatic compounds. Further proof for the correct assessment of the electronic and structural properties of the above-mentioned compounds comes from calculated NICS values (NICS = nucleus-independent chemical shift) as well as the examination of the two-photon absorption cross section $(\sigma^{(2)})$.[17]

Latos-Grażyński and co-workers have shown that Möbius aromaticity is accessible by conformational changes of a dibenzihexaphyrin, thus experimentally supporting calculations[20] which indicate that Möbius-type conformers stabilize [4*n*]annulenes. In an approach that excludes conformational freedom, Osuka and co-workers used Group 10 metals as clamps to stabilize Möbius twists and generate aromatic Möbius systems, thus fully validating Heilbronner's prediction.[21]

[1] E. Heilbronner, *Tetrahedron Lett.* **1964**, *5*, 1923 – 1928.

[2] M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg, *Angew. Chem.* **2007**, *119*, 8015 – 8019; *Angew. Chem. Int. Ed.* **2007**, *46*, 7869 – 7873.

[3] See two excellent reviews on the topic of Möbius aromaticity: a) H. S. Rzepa, *Chem. Rev.* **2005**, *105*, 3697 – 3715; b) R. Herges, *Chem. Rev.* **2006**, *106*, 4820 – 4842, and references therein.

[4] D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature* **2003**, *426*, 819 – 821.

[5] D. Ajami, K. Hess, F. Köhler, C. Näther, O. Oeckler, A. Simon, C. Yamamoto, Y. Okamoto, R. Herges, *Chem. Eur. J.* **2006**, *12*, 5434 – 5445.

[6] C. Castro, Z. Chen, C. S. Wannere, H. Jiao, W. L. Karney, M. Mauksch, R. Puchta, N. J. R. van Eikema Hommes, P. von R. Schleyer, *J. Am. Chem. Soc.* **2005**, *127*, 2425 – 2432.

[7] a) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, A. A. Bothner-By, *J. Am. Chem. Soc.* **1962**, *84*, 4307 – 4312; b) E. Vogel, W. Pretzer, W. A. Böll, *Tetrahedron Lett.* **1965**, *6*, 3613 – 3617; c) E. Vogel, *Pure Appl. Chem.* **1993**, *65* 143 – 152.

[8] a) H. König, C. Eickmeier, M. Möller, U. Rodewald, B. Franck, *Angew. Chem.* **1990**, *102*, 1437 – 1439; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1393 – 1395; b) S. Beckmann, T. Wessel, B. Franck, W. Hönle, H. Borrmann, H. G. von Schnering, *Angew. Chem.* **1990**, *102*, 1439 – 1441; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1395 – 1397; the nomenclature of expanded porphyrin was suggested by Franck and Nonn (B. Franck, A. Nonn, *Angew. Chem.* **1995**, *107*, 1941 – 1957; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1795 – 1811) and is given as: 1) a number in square brackets corresponding to the number of π electrons in the shortest main conjugation pathway, 2) a core name representing the number of pyrroles or other (hetero)cycles in the overall system, and 3) numbers in round brackets following the main name that specify the number of bridging carbon atoms between each pyrrole subunit, starting with the largest bridge.

[9] a) M. Gosmann, B. Franck, *Angew. Chem.* **1986**, *98*, 1107 – 1108; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1100 – 1101; b) G. Knübel, B. Franck, *Angew. Chem.* **1988**, *100*, 1203 – 1211; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1170 – 1172; c) M. Bröring, H.-J. Dietrich, J. Dörr, G. Hohlneicher, J. Lex, N. Jux, C. Pütz, M. Roeb, H. Schmickler, E. Vogel, *Angew. Chem.* **2000**, *112*, 1147 – 1150; *Angew. Chem. Int. Ed.* **2000**, *39*, 1105 – 1108.

[10] a) C. J. Medforth in *The Porphyrin Handbook*, *Vol. 5* (Eds: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 1 – 80; b) F. A. Walker in *The Porphyrin Handbook*, *Vol. 5* (Eds: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 81 – 174.

[11] T. K. Chandrashekar, S. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676 – 691.

[12] J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, *115*, 5292 – 5333; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134 – 5175, and references therein.

[13] a) R. Charriere, T. A. Jenny, H. Rexhausen, A. Gossauer, *Heterocycles* **1993**, *36*, 1561 – 1575; b) M. Suzuki, A. Osuka, *Org. Lett.* **2003**, *5*, 3943 – 3946.

[14] a) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190 – 7191; b) S. Saito, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 1923 – 1928.

[15] A. Werner, M. Michels, L. Zander, J. Lex, E. Vogel, *Angew. Chem.* **1999**, *111*, 3866 – 3870; *Angew. Chem. Int. Ed.* **1999**, *38*, 3650 – 3653.

[16] R. Taniguchi, S. Shimizu, M. Suzuki, J.-Y. Shin, H. Furuta, A. Osuka, *Tetrahedron Lett.* **2003**, *44*, 2505 – 2507.

[17] Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem.* **2008**, 120, 693 – 696; *Angew. Chem. Int. Ed.* **2008**, *47*, 681 – 684.

[18] a) J. D. Harvey, C. J. Ziegler, *J. Inorg. Biochem.* **2006**, *100*, 869 – 880; b) P. J. Chmielewski, L. Latos-Grażyński, *Coord. Chem. Rev.* **2005**, *249*, 2510 – 2533.

[19] S. Mori, S. Schimizu, R. Taniguchi, A. Osuka, *Inorg. Chem.* **2005**, *44*, 4127 – 4129.

[20] C. Castro, C. M. Isborn, W. L. Karney, M. Mauksch, P. von R. Schleyer, *Org. Lett.* **2002**, *4*, 3431 – 3434.

[21] And the story continues: In a recent publication Möbius-aromatic metal complexes of so-called N-confused porphyrins were reported; see J. K. Park, Z. S. Yoon, M.-C. Yoon, K. S. Kim, S. Mori, J.-Y. Shin, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2008**, *130*, 1824 – 1825.