

Porphyrins

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Abstract: Di-*peri*-dinaphthoporphyrins can be regarded as a key and common substructure of fused porphyrinoids. PtCl₂-mediated cycloisomerization reaction of quinodimethane-type porphyrins provided these doubly fused porphyrins, which exhibit characteristic paratropic ring currents that presumably arise from 24 π antiaromatic circuit as a dominant resonance contributor. UV/Vis absorption spectra, cyclic voltammetry, and excited-state dynamics as well as theoretical calculation support this conclusion.

In recent years fused porphyrinoids have attracted much attention because of their promising properties as NIR-absorbing and emitting dyes, pigments of photodynamic therapy, non-linear optical materials, and electron conducting materials.^[1] Among these, *meso-meso*, β - β , β - β triply-linked porphyrin arrays (porphyrin tape **1**, Figure 1) possess a unique position in light of their remarkable bathochromic absorption shifts reaching the infrared region that arise from the effective electronic delocalization over the entire molecule.^[2] Various porphyrins fused with other aromatic segments such as anthracene-fused porphyrin **2** and BODIPY-fused porphyrin **3** have been also explored.^[3] In these examples, the aromatic characters of the porphyrin segments are mitigated due to the electron delocalization into the fused segments. As notable examples, Wu et al. reported fused quinonoidal porphyrin **4** which exhibits a nonaromatic nature intrinsic to the quinonoidal conjugation as a result of acquiring stabilization due to four Clar's sextet benzenes.^[4,5] They also synthesized phenarenyl-fused porphyrin **5** that was an open-shell biradical and was easily oxidized by air to form oxygenated derivatives.^[6] In these cases, two or more aromatic units are linked by triple C-C bonds, giving rise to formal naphthalene segments directly attached on the porphyrin peripheries (as emphasized in the structure of **1**). Thus, we naturally became interested in the common interior core, namely di-*peri*-dinaphthoporphyrin, whose nomenclature derives from analogy to hexa-*peri*-hexabenzocoronene. Intriguingly, the conjugation circuit

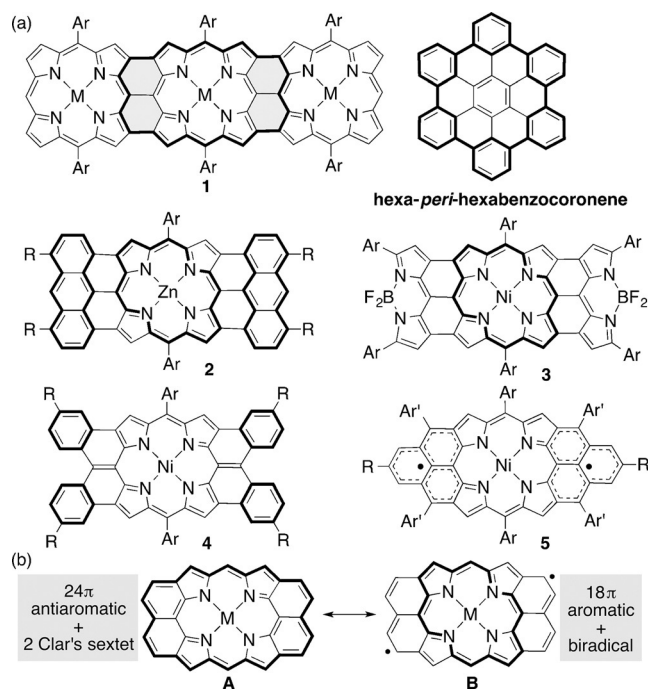


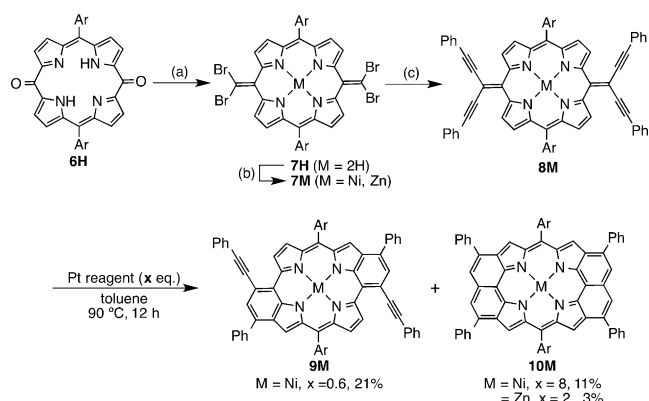
Figure 1. a) Porphyrin tape **1**, hexa-*peri*-hexabenzocoronene, and precedent fused porphyrinoids **2–5**. b) Resonance structures of di-*peri*-dinaphthoporphyrin between **A** (closed-shell: 24 π antiaromatic circuit with two Clar's sextets) and **B** (biradical: 18 π aromatic circuit).

of this unique fused porphyrin cannot be simply delineated as the usual porphyrin 18 π circuit. As shown in Figure 1b, resonance form **A** represents a closed-shell 24 π -antiaromatic circuit together with two Clar's sextet benzenes and resonance form **B** is delineated as a biradical with a 18 π -aromatic porphyrin network. These two forms may be competitive to determine the actual electronic state. Herein we report the synthesis of *peri*-naphtho-fused porphyrin **10** and its electronic properties.

First, 5,15-dioxoporphodimethene **6H**^[4,7] was transformed to tetrabromide **7H** by Corey–Fuchs reaction with tetrabromomethane in the presence of triphenylphosphine, which was then metalated with Ni^{II}(acac)₂ to give Ni^{II} complex **7Ni** (Scheme 1). Quinodimethane-type porphyrin **8Ni** was synthesized by Stille coupling of **7Ni** with 8 equiv of tributyl(phenylethynyl)tin in 59 % yield. Reaction of **8Ni** with 0.6 equiv of PtCl₂ afforded a 2-fold cyclization product **9Ni** in 21 % yield.^[8,9] When the reaction was conducted with 2 equiv of PtCl₂ in toluene at 90 °C, the formation of a 4-fold cyclization product **10Ni** was observed in a small amount along with many side products. We could not isolate **10Ni** in

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Scheme 1. Synthesis of di-*peri*-dinaphthoporphyrins **10M**. Reagents and conditions: a) CBr_4 , PPh_3 , toluene, 80°C , 12 h, 75%; b) $\text{M} = \text{Ni}$: $\text{Ni}(\text{acac})_2$, toluene, reflux, 3 h, 91%, $\text{M} = \text{Zn}$: $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, CH_2Cl_2 , MeOH , RT, 1 h, 91%; c) tributyl(phenylethynyl)tin, $\text{Pd}_2(\text{dba})_3$, $\text{P}(2\text{-furyl})_3$, toluene, 80°C , 1 h, 59% ($\text{M} = \text{Ni}$), 38% ($\text{M} = \text{Zn}$). $\text{Ar} = 3,5\text{-di-tert-butylphenyl}$.

a pure form from this reaction mixture. After screening of various platinum salts, we found that use of 8 equiv of $\text{Pt}(\text{MeCN})_2\text{Cl}_2$ resulted in a cleaner reaction that allowed for the isolation of **10Ni** in 11% yield. The structures of **8Ni**, **9Ni**, and **10Ni** were confirmed by X-ray diffraction analysis (Figure 2).^[10] Compounds **8Ni** and **9Ni** show gable-like bent structures with mean-plane deviation (MPD) values of 0.49 and 0.32 Å, respectively.^[11] These bent structures are consid-

ered to arise from the steric repulsion between the β -protons and phenylethynyl groups. In contrast, the structure of **10Ni** has been shown to be quite planar with an MPD value of only 0.050 Å. The $\text{C}=\text{C}$ double bond length of the *exo* methylene group is 1.38 Å in **8Ni**, indicating its typical double bond character, while those of **9Ni** and **10Ni** are both 1.41 Å, respectively. The newly formed benzene rings of **9Ni** and **10Ni** do not display significant bond-length alterations and the HOMA values of these benzene rings are calculated to be 0.71 and 0.83, respectively.^[12] Interestingly, among several possible 2-fold cyclized products, only **9Ni** was selectively formed probably due to structural restriction or electronic reason in the preformed 1-fold cyclized product (See Figure S8-3 in the Supporting Information, SI).

The ^1H NMR spectrum of **8Ni** showed two doublets at 7.35 and 6.67 ppm due to the β -protons, and that of **9Ni** exhibited three signals due to the β -protons at 8.16, 7.34, and 7.20 ppm and a singlet at 6.92 ppm due to the *peri*-benzene protons (SI). These chemical shifts are consistent with their nonaromatic characters as confirmed by comparison with the ^1H NMR spectrum of aromatic **11Ni**. On the other hand, ^1H NMR spectrum of **10Ni** showed two singlets at 5.64 and 5.23 ppm due to the β -protons and naphthalene protons, respectively, which are certainly upfield shifted as compared with those of **8Ni** and **9Ni**, indicating a distinct paratropic ring current.

In the next step, we attempted to obtain freebase **10H** by demetalation of **10Ni** under various conditions, but failed to find suitable reaction conditions. We thus decided to synthesize **10Zn** as a precursor of **10H**. Zn^{II} complex **7Zn** was prepared by zincation of **7H** and was converted to **8Zn** by Stille coupling. Cyclization of **8Zn** was conducted under similar conditions used for the synthesis of **10Ni**, giving **10Zn** in 3% yield.^[13] Treatment of **10Zn** with aqueous HCl gave **10H** in good yield. The ^1H NMR spectrum of **10H** showed a signal at 18.42 ppm due to the inner NH protons, and two singlets at 6.05 and 5.94 ppm due to the β -protons and naphthalene protons, respectively, indicating its distinct paratropic ring-current effect. Fortunately, single crystals were obtained from a solution of **10H** in THF and methanol (Figure 3a).^[10] Similarly to **10Ni**, freebase **10H** displays a planar structure with an MPD value of 0.050 Å. The HOMA values of four benzene rings fused on the *peri*-region are 0.76 and 0.63, indicating slightly clearer bond-length alternation. The ^1H NMR signals of its outer-protons (6.05 and 5.94 ppm) are slightly downfield shifted as compared with those of **10Ni** and **10Zn** probably due to a weaker paratropic ring-current effect. The antiaromatic natures of **10H**, **10Zn** and **10Ni** are evaluated by nucleus-independent chemical shift (NICS) and anisotropy of induced current density (AICD) calculations (Figures 2 and S8-4–6 in SI).^[14,15] The calculated NICS values of **10H**, **10Zn**, and **10Ni** are all positive inside the tetrapyrrole macrocycles, and the NICS value at the center of **10H** is +7.75 ppm. These positive NICS values indicate the antiaromatic characters of **10H**, **10Zn** and **10Ni**. The AICD plot of **10H** shows a counter-clockwise current flow that involves *peri*-benzene regions. Thus, the observed paratropic ring current can be ascribed to 24π antiaromatic circuit with the aid of the Clar's sextet effect.^[16]

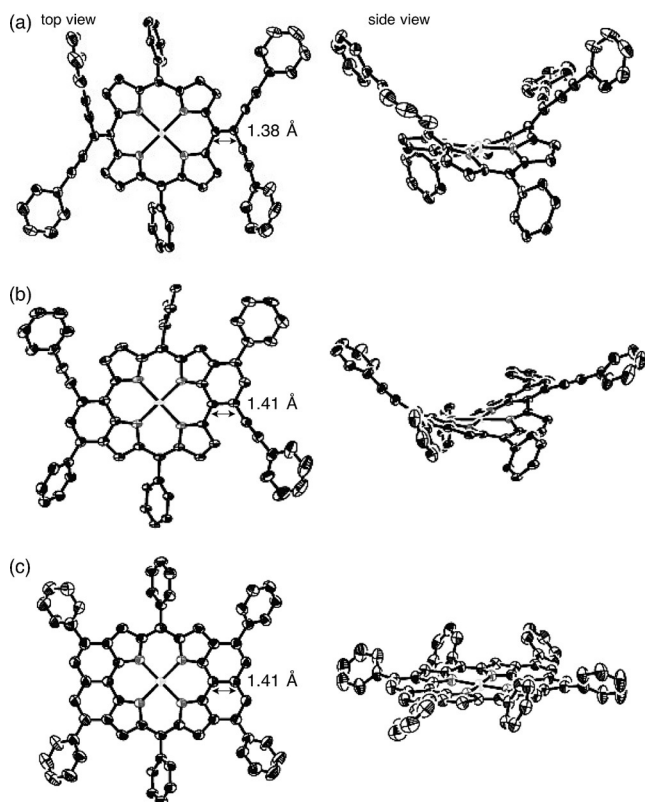


Figure 2. X-ray crystal structures of a) **8Ni**, b) **9Ni**, and c) **10Ni**. *tert*-Butyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to the 50% probability.

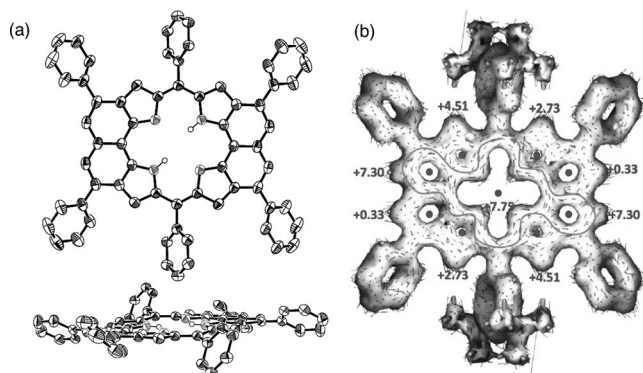


Figure 3. a) X-ray crystal structure of **10H**. *tert*-Butyl groups, solvent molecules, and hydrogen atoms except for NHs are omitted for clarity. The thermal ellipsoids are scaled to the 50% probability. b) AICD plot for **10H** (isosurface value: 0.03). The NICS(0) values at the central points of constitutional rings are also shown.

Despite the antiaromatic characters, **10Ni** and **10Zn** are stable compounds and can be stored as solids without deterioration under ambient conditions over several months.

The UV/Vis absorption spectra of **8Ni**, **9Ni**, **10Ni**, and **11Ni** in CH_2Cl_2 are shown in Figure 4a. **Ni^{II}** porphyrin **11Ni** exhibits a sharp Soret band at 401 nm and a weak Q band at 516 nm. Compared to **11Ni**, compounds **8Ni** and **9Ni** display

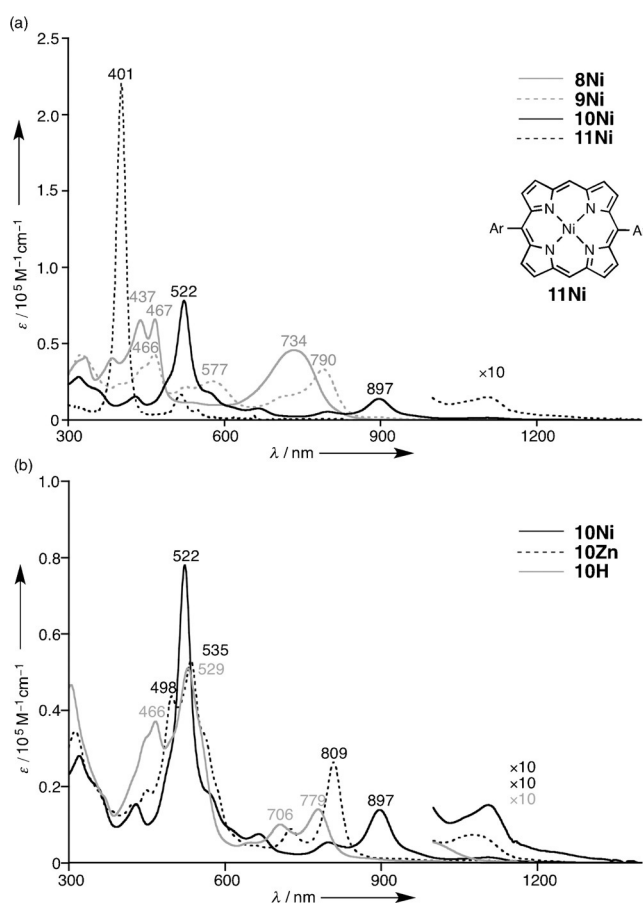


Figure 4. UV/Vis/NIR absorption spectra of a) **8Ni**, **9Ni**, **10Ni**, and **11Ni**, b) **10Ni**, **10Zn**, and **10H** in CH_2Cl_2 .

weak, broad and ill-defined absorption spectra with low-energy absorption bands at 734 and 790 nm, respectively, indicating that their porphyrinic π -electron systems are largely perturbed by peripheral groups. On the other hand, **10Ni** exhibits a sharp Soret-like band at 522 nm and a red-shifted band at 897 nm with very weak absorption tail reaching to around 1300 nm. The similar spectral features were observed for **10Zn** and **10H** (Figure 4b). These weak absorption tails refer to the presence of NIR dark states, which is a characteristic feature of antiaromatic porphyrinoids.^[17,18]

Femtosecond transient absorption (TA) measurements were carried out for **8Ni** and **10Ni**. (Figure S10). **8Ni** exhibits a double exponential decay profile (12 and 800 ps) without fluorescence emission. This excited state dynamics of **8Ni** can be explained by Ni^{II} -centered (d,d) state of typical Ni^{II} porphyrinoids, where the excited population undergoes a rapid internal conversion (IC) process to the (d,d) state and subsequent deactivation process to the ground state on the order of hundreds ps.^[19] On the other hand, the TA absorbance of **10Ni** decays rapidly with two time constants of 1.2 and 12 ps. The ultrafast relaxation dynamics can be comprehended by the optically dark state, characteristic of antiaromatic porphyrinoids.^[16] Since the dark state acts as a ladder in the deactivation process to the ground state, **10Ni** shows fast IC process to the dark state with $\tau = 1.2$ ps and subsequent relaxation to the ground state with $\tau = 12$ ps. Two-photon absorption (TPA) measurements were carried out for **8Ni** and **10Ni** by using an open-aperture Z-scan method in the range of 1200–1900 nm, whereby one-photon absorption is negligible. The TPA cross-section values are 190 GM for **8Ni** at 1400 nm, and 380 GM for **10Ni** at 1800 nm, respectively (Figures S11-1, S11-2). The observed larger TPA value of **10Ni** can be ascribed to the reduced HOMO–LUMO gap arising from extended π -conjugation.^[20]

Cyclic voltammetry and differential-pulse voltammetry (DPV) experiments have been conducted in CH_2Cl_2 against ferrocene/ferrocenium ion couple (Table 1). These experiments exhibited two reduction potentials at –1.10 and –1.49 V for **8Ni** and at –1.13 and –1.58 V for **9Ni**, and one oxidation potential at 0.32 V for **8Ni** and at 0.34 V for **9Ni**. The electrochemical HOMO–LUMO gaps (ΔE_{HL}) are determined to be 1.42 and 1.47 eV for **8Ni** and **9Ni**, respectively. **10Ni** exhibited two reversible reduction waves at –0.92 and –1.48 V and three reversible oxidation waves at 0.31, 0.38, and

Table 1: Electrochemical properties of **8Ni**, **9Ni**, **10Ni**, **10Zn**, and **10H** measured in CH_2Cl_2 .^[a]

Compd.	$E_{\text{ox},3}$	$E_{\text{ox},2}$	$E_{\text{ox},1}$	$E_{\text{red},1}$	$E_{\text{red},2}$	$\Delta E_{\text{HL}}^{[c]}$
8Ni	–	–	0.32 ^[b]	–1.10	–1.49	1.42
9Ni	–	–	0.34 ^[b]	–1.13	–1.58	1.47
10Ni	0.80	0.38	0.31	–0.92	–1.48	1.23
10Zn	–	0.70	0.29	–1.01	–1.53	1.30
10H	–	–	0.45	–0.95	–1.43	1.40

[a] Potentials [V] vs. ferrocene/ferrocenium ion. Scan rate 0.05 Vs^{-1} ; working electrode, glassy carbon; counter electrode, Pt wire; supporting electrolyte, 0.1 M $n\text{Bu}_4\text{NPF}_6$; reference electrode, Ag/AgClO_4 . [b] Irreversible peaks. [c] Electrochemical HOMO–LUMO gaps ($\Delta E_{\text{HL}} = E_{\text{ox},1} - E_{\text{red},1}$ [eV]).

and 0.80 V. The first reduction potential of **10Ni** is anodically shifted from those of **8Ni** and **9Ni** and thus the electrochemical HOMO–LUMO gap of **10Ni** is decreased ($\Delta E_{\text{HL}} = 1.23$ eV). The first oxidation potential of **10H** is higher than that of **10Ni**, which leads to a larger ΔE_{HL} value (1.40 eV). These results are roughly consistent with those obtained by DFT calculations (Figure S8-1). It is worthy to note that the LUMO energy levels of **10M** are lower than those of dimeric porphyrin tapes,^[2a–d] while the HOMO levels remain intact. Indeed, addition of an equimolar amount of cobaltocene to a solution of **10Ni** in THF caused a clean change to its radical anion with NIR absorption bands at 1137, 1194, and 1402 nm via clear isosbestic points (Figure S9-2). The reduced species was ESR active, displaying a sharp signal with $g = 2.0026$ (Figure S9-3). In addition, chemical oxidation of **10Ni** proceeded in a stepwise manner upon treatment with tris(*p*-bromophenyl)aminium hexachloroantimonate (Figure S9-1). Such an ambipolar character of di-*peri*-dinaphthoporphyrin is promising an application for multi-charge storage materials^[2c] and organic rechargeable batteries.^[21]

In summary, we have synthesized di-*peri*-dinaphthoporphyrin **10M** via PtCl₂-mediated cycloisomerization reaction of quinodimethane-type porphyrins. The ¹H NMR, UV/Vis absorption spectra, cyclic voltammetry, and theoretical calculation of **10M** supported the presence of 24 π antiaromatic contribution. The freebase **10H** displayed a weak paratropic ring-current effect. The observed smaller HOMO–LUMO gaps of **10M** arise from stabilized LUMO levels. These characteristic properties provide an important clue to understand the intrinsic physical properties of the fused porphyrinoids.

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Keywords: antiaromaticity · cyclic voltammetry · cycloisomerization · porphyrin · porphyrin tape

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- [1] a) J. R. Reimers, N. S. Hush, M. J. Crossley, *J. Porphyrins Phthalocyanines* **2002**, *6*, 795; b) S. Fox, R. W. Boyle, *Tetrahedron* **2006**, *62*, 10039; c) N. Aratani, D. Kim, A. Osuka, *Chem. Asian J.* **2009**, *4*, 1172; d) C. Jiao, J. Wu, *Synlett* **2012**, 171; e) J. P. Lewtak, D. T. Gryko, *Chem. Commun.* **2012**, 48, 10069; f) A. M. V. M. Pereira, S. Richetera, C. Jeandona, J.-P. Gisselbrecht, J. Wytka, R. Ruppert, *J. Porphyrins Phthalocyanines* **2012**, *16*, 464; g) H. Mori, T. Tanaka, A. Osuka, *J. Mater. Chem.*

- C* **2013**, *1*, 2500; h) T. Tanaka, A. Osuka, *Chem. Soc. Rev.* **2015**, *44*, 943.
- [2] a) A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem. Int. Ed.* **2000**, *39*, 2549; *Angew. Chem.* **2000**, *112*, 2649; b) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79; c) D. Bonifazi, M. Scholl, F. Song, L. Echegoyen, G. Accorsi, N. Armaroli, F. Diederich, *Angew. Chem. Int. Ed.* **2003**, *42*, 4966; *Angew. Chem.* **2003**, *115*, 5116; d) T. Ikeda, N. Aratani, A. Osuka, *Chem. Asian J.* **2009**, *4*, 1248.
- [3] a) N. K. S. Davis, A. L. Thompson, H. L. Anderson, *Org. Lett.* **2010**, *12*, 2124; b) N. K. S. Davis, A. L. Thompson, H. L. Anderson, *J. Am. Chem. Soc.* **2011**, *133*, 30; c) C. Jiao, L. Zhu, J. Wu, *Chem. Eur. J.* **2011**, *17*, 6610.
- [4] W. Zeng, B. S. Lee, Y. M. Sung, K.-W. Huang, Y. Li, D. Kim, J. Wu, *Chem. Commun.* **2012**, 48, 7684.
- [5] a) E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London, **1964**; b) M. Randic, *Chem. Rev.* **2003**, *103*, 3449.
- [6] W. Zeng, S. Lee, M. Son, M. Ishida, K. Furukawa, P. Hu, Z. Sun, D. Kim, J. Wu, *Chem. Sci.* **2015**, *6*, 2427.
- [7] a) D. Lahaye, K. Muthukumar, C.-H. Hung, D. Gryko, J. S. Rebouças, I. Spasojević, I. Batinić-Haberle, J. S. Lindsey, *Bioorg. Med. Chem.* **2007**, *15*, 7066; b) N. L. Bill, M. Ishida, S. Bähring, J. M. Lim, S. Lee, C. M. Davis, V. M. Lynch, K. A. Nielsen, J. O. Jeppesen, K. Ohkubo, S. Fukuzumi, D. Kim, J. L. Sessler, *J. Am. Chem. Soc.* **2013**, *135*, 10852.
- [8] a) D. P. Arnold, R. G. Holmes, A. W. Johnson, A. R. P. Smith, G. A. Williams, *J. Chem. Soc. Perkin Trans. 1* **1978**, 1660; b) M. G. H. Vicente, I. N. Rezzano, K. M. Smith, *Tetrahedron Lett.* **1990**, *31*, 1365; c) M. G. H. Vicente, K. M. Smith, *J. Org. Chem.* **1991**, *56*, 4407; d) A. R. Morgan, S. Gupta, *Tetrahedron Lett.* **1994**, *35*, 5347.
- [9] L. J. K. Boerner, D. F. Dye, T. Köpke, J. M. Zaleski, *Coord. Chem. Rev.* **2013**, *257*, 599.
- [10] Crystallographic data for **8Ni**; C₈₂H₇₀N₄Ni, 0.53 (CH₂Cl₂); $M_w = 1215.13$ g mol⁻¹; monoclinic; *P* 2₁/n (No.13); $a = 21.287(5)$, $b = 11.687(2)$, $c = 28.514(6)$ Å; $\beta = 111.753(5)^\circ$; $V = 6589(2)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.225$ g cm⁻³; $RI = 0.1086$ [$I > 2\sigma(I)$]; $wR2 = 0.3151$ (all data); GOF = 1.073; Crystallographic data for **9Ni**; C₈₂H₇₀N₄Ni, 2(C₆H₅Cl); $M_w = 1395.21$ g mol⁻¹; triclinic; *P* $\bar{1}$ (No. 2); $a = 14.9249(11)$, $b = 15.6008(10)$, $c = 16.9809(14)$ Å; $\alpha = 73.799(18)$, $\beta = 75.88(2)$, $\gamma = 72.151(18)^\circ$; $V = 3559.4(7)$ Å³; $Z = 2$; $\rho_{\text{calcd}} = 1.302$ g cm⁻³; $RI = 0.0704$ [$I > 2\sigma(I)$]; $wR2 = 0.2153$ (all data); GOF = 1.011; Crystallographic data for **10Ni**; C₈₂H_{68.57}N₄Ni, 2(C₇H₈), 0.35(CO); $M_w = 1362.74$ g mol⁻¹; monoclinic; *P*2₁/c (No.14); $a = 20.126(6)$, $b = 18.285(5)$, $c = 20.711(6)$ Å; $\beta = 101.835(9)^\circ$; $V = 7460(4)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.213$ g cm⁻³; $RI = 0.0860$ [$I > 2\sigma(I)$]; $wR2 = 0.2825$ (all data); GOF = 1.004; Crystallographic data for **10H**; C₈₂H₇₂N₄Ni, (C₄O); $M_w = 1177.48$ g mol⁻¹; monoclinic; *C*2/c (No.15); $a = 25.625(7)$, $b = 18.524(5)$, $c = 14.530(4)$ Å; $\beta = 111.845(7)^\circ$; $V = 6402(3)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.222$ g cm⁻³; $RI = 0.0516$ [$I > 2\sigma(I)$]; $wR2 = 0.1655$ (all data); GOF = 1.040; CCDC 1451282, 1451281, and 1451280 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [11] The mean-plane deviations of **8Ni**, **9Ni** and **10Ni** were defined by core 24 atoms of porphyrin unit.
- [12] a) T. M. Krygowski, T. M. Cryański, *Tetrahedron* **1996**, *52*, 1713; b) T. M. Krygowski, T. M. Cryański, *Tetrahedron* **1996**, *52*, 10255.
- [13] We thought that particular instabilities of **8Ni** and **8Zn** are a main reason for the low yields of **10Ni** and **10Zn**. We did not observe the formation of meaningful side products in the cyclization reactions of **8Ni** and **8Zn**.
- [14] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

- [15] a) D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758; b) R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214; c) R. Herges, *Chem. Rev.* **2006**, *106*, 4820.
- [16] As described in the introduction part in the text, compounds **1**, **2**, and **3** are all aromatic but their aromatic characters are mitigated due to the fused structures. Consistent with the relatively small electronic perturbations, the porphyrin electronic networks of **1**, **2**, and **3** can be delineated as shown in Figure 1. But such delineation is difficult for porphyrins **4**, **5**, and **10M**. The four peripheral benzene rings in **4** maintain the local aromaticity, hence decreasing the contribution of the peripheral antiaromatic macrocyclic network. The fusion of the phenalenyl segments (a typical radical segment) leads to an open shell molecule **5**. Porphyrins **10M** possess the bare di-*peri*-naphthoporphyrin chromophore, in which the outside peripheral electronic network is effective, allowing the antiaromatic character.
- [17] a) M.-C. Yoon, S. Cho, M. Suzuki, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 7360; b) J. M. Lim, Z. S. Yoon, J.-Y. Shin, K. S. Kim, M.-C. Yoon, D. Kim, *Chem. Commun.* **2009**, 261; c) S. Cho, Z. S. Yoon, K. S. Kim, M. C. Yoon, D. G. Cho, J. L. Sessler, D. Kim, *J. Phys. Chem. Lett.* **2010**, *1*, 895.
- [18] Phenanthriporphyrin has been recently reported by L. Latos-Grażyński et al., which displays an antiaromatic character; B. Szyszko, A. Białońska, L. Szterenber, L. Latos-Grażyński, *Angew. Chem. Int. Ed.* **2015**, *54*, 4932; *Angew. Chem.* **2015**, *127*, 5014.
- [19] a) T. C. Gunaratne, A. V. Gusev, X. Peng, A. Rosa, G. Ricciardi, E. J. Baerends, C. Rizzoli, M. E. Kenney, M. A. J. Rodgers, *J. Phys. Chem. A* **2005**, *109*, 2078; b) D. Rais, P. Toman, J. Černý, M. Menšík, J. Pflieger, *J. Phys. Chem. A* **2014**, *118*, 5419; c) X. Zhang, E. C. Wasinger, A. Z. Muresan, K. Attenkofer, G. Jennings, J. S. Lindsey, L. X. Chen, *J. Phys. Chem. A* **2007**, *111*, 11736; d) J. Oh, H. Yoon, Y. M. Sung, P. Kang, M.-G. Choi, W.-D. Jang, D. Kim, *J. Phys. Chem. B* **2015**, *119*, 7053.
- [20] a) K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2006**, *45*, 3944; *Angew. Chem.* **2006**, *118*, 4048; b) P. Kim, S. Ham, J. Oh, H. Uoyama, H. Watanabe, K. Tagawa, H. Uno, D. Kim, *Phys. Chem. Chem. Phys.* **2013**, *15*, 10612.
- [21] J.-Y. Shin, T. Yamada, H. Yoshikawa, K. Awaga, H. Shinokubo, *Angew. Chem. Int. Ed.* **2014**, *53*, 3096; *Angew. Chem.* **2014**, *126*, 3160.

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