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Porphyrinoids

Antiaromatic Hexaphyrins and Octaphyrins Stabilized by the Hydrogen-Bonding Interactions of *meso*-Imidazolyl Groups**

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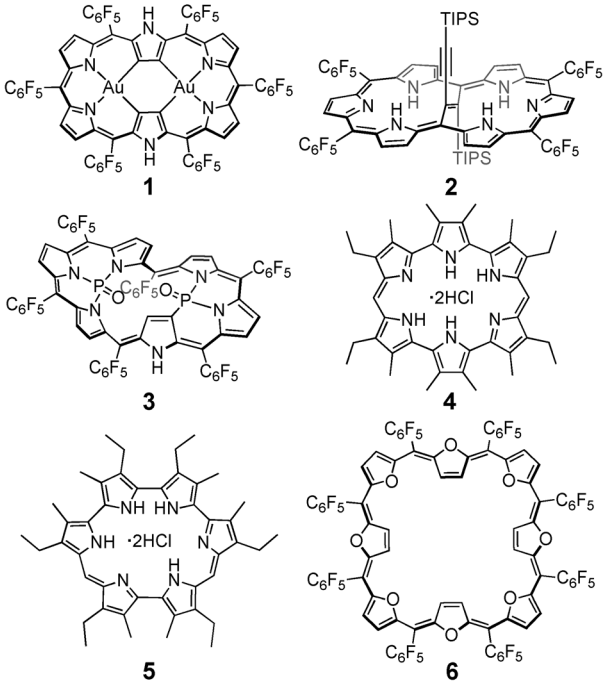
Currently, considerable attention has been focused on the exploration of antiaromatic molecules that possess characteristic electronic properties but are stable enough for standard manipulations,[1–7] since careful molecular design to stabilize antiaromatic molecules is the key to their possible application in molecular electronics, high-electron-mobility materials, and nonlinear optical materials. Among various conjugated molecular systems, expanded porphyrins that consist of more than five pyrrolic units have emerged as effective platforms for the creation of diverse electronic states, including Hückel and Möbius antiaromatic species and stable radical species.[8] However, even for expanded porphyrins, stable antiaromatic examples have been rather limited to molecules made structurally rigid by metal coordination,[9] internal bridges,[10] or protonation.[12] Representative examples are the conformationally rigid bis-Au^{III} [28]hexaphyrin complex **1**[9a,b] and the internally vinylene bridged [28]hexaphyrin **2**,[10] which display distinct Hückel antiaromatic characteristics, and the bisphosphorus [30]hexaphyrin complex **3**,[11] which shows a twisted Möbius conformation and a paratropic ring current as a Möbius antiaromatic species (Scheme 1). In the case of **3**, the two phosphoramide units are crucially important to rigidify the twisted structure and to stabilize a reduced 30 π-electronic state. Sessler and co-workers reported the [24]amethyrin **4** and [24]isoamethyrin **5**, both of which became antiaromatic upon protonation.[12] Antiaromatic expanded porphyrins without structure-rigidifying elements have remained very rare. Anand and co-workers reported that the all-oxa [40]octaphyrin(1.1.1.1.1.1.1.1) **6** exhibits a paratropic ring current.[13] Curiously, the structure of this octaphyrin has been revealed to be fairly planar in spite of its weak antiaromatic nature and lack of a structure-rigidifying element.



Scheme 1. Examples of antiaromatic expanded porphyrins. TIPS = triisopropylsilyl.

Herein we report the remarkable influence of diagonally introduced 2-imidazolyl groups on the structural and electronic properties of hexaphyrins and octaphyrins. The 5,20-(1-alkyl-2-imidazolyl)hexaphyrins **7a** and **7b** were prepared by methanesulfonic acid (MSA) catalyzed cross-condensation of the tripyrrane **10** with imidazole-2-carboxaldehydes **11a** and **11b**, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 3 and 5% yield, respectively (Scheme 2). No other isolable product was detected. In these reactions, a stoichiometric amount of MSA was necessary, since the appended imidazolyl groups effectively captured MSA and thus suppressed the condensation reactions.

The properties of hexaphyrins **7a** and **7b** are similar. Herein we describe the characterization of **7b**, mainly because of its better solubility (for the properties of **7a**, see the Supporting Information). The high-resolution electrospray ionization time-of-flight (HR ESI-TOF) mass spectrum of **7b** exhibited a parent ion at *m*/*z* 1441.2513 ($[M-H]^-$; calcd for $C_{74}H_{33}N_{10}F_{20}$: 1441.2565). The ^{1}H NMR spectrum of **7b** at −60 °C indicated a C_2-symmetric structure. It featured six

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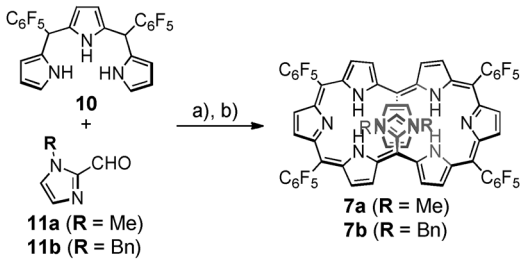


Scheme 2. Synthesis of **7a** and **7b**: a) MSA (1.2 equiv); b) DDQ (4.0 equiv), CH_2Cl_2, 0 °C. Bn = benzyl.

signals due to the outer β-H atoms in the range $\delta = 5.83$–4.23 ppm, five signals due to the *N*-benzyl group protons in the range $\delta = 8.59$–7.40 ppm, two signals due to the imidazolyl H atoms at $\delta = 9.64$ and 8.95 ppm, and two signals due to the pyrrolic NH atoms at $\delta = 21.71$ and 20.41 ppm. Overall, these data indicate a strong paratropic ring current and aid the assignment of **7b** as a Hückel antiaromatic [28]hexaphyrin.

The UV/Vis spectrum of **7b** exhibits ill-defined Soret-like bands at $\lambda_{max} = 495$ and 629 nm and a broad band ranging from 800 to 1600 nm (Figure 1), which are characteristic of

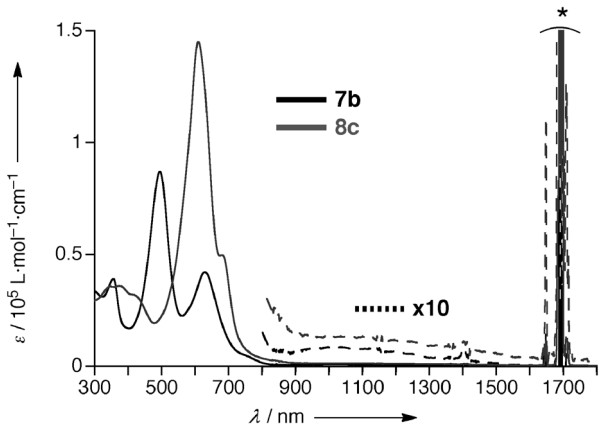


Figure 1. UV/Vis absorption spectra of **7b** and **8c** in CH_2Cl_2. * indicates solvent peaks.

antiaromatic porphyrinoids.[8g,h,14] Finally, the structure of **7b** was determined by X-ray diffraction analysis, which revealed a C_2-symmetric roughly planar conformation fixed by two effective hydrogen-bond networks involving three pyrrolic units and an imidazolyl group in each case (N1*H–N3–N2H–N4 and N1H–N3*–N2*H–N4*; Figure 2).[15]

In line with the assignment of **7b** as an antiaromatic molecule with 28 π electrons, the harmonic oscillator model of aromaticity (HOMA) value[16] was calculated to be 0.373, and the nucleus-independent chemical shift (NICS) values[17] were calculated to be +16.00 and +12.68 ppm at points A and B (Figure 2), respectively. Cyclic voltammetry in CH_2Cl_2 revealed two reversible oxidation waves at −0.146 and 0.157 V and two reversible reduction waves at −1.430 and −1.267 V (see the Supporting Information), which indicated an electrochemical HOMO–LUMO gap of 1.12 eV. This

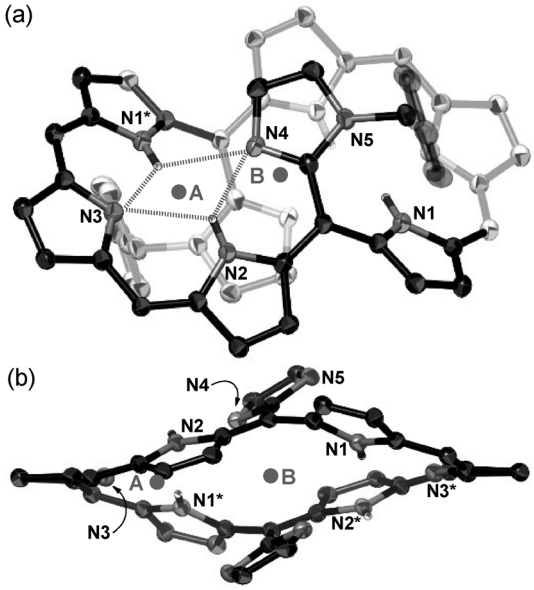


Figure 2. X-ray crystal structure of **7b**: a) perspective view; b) side view. The *meso* pentafluorophenyl groups, hydrogen atoms (except for the inner NH protons), and the *N*-benzyl groups in (b) are omitted for clarity. The thermal ellipsoids are scaled to 50% probability.

value is considerably smaller than that (1.47 eV) of the parent aromatic hexakis(pentafluorophenyl) [26]hexaphyrin. Importantly, despite its distinct antiaromatic character, the oxidation of **7b** was rather difficult with an equimolar amount of DDQ or MnO_2, and the use of a large excess of the oxidants led to the decomposition of **7b**. The treatment of **7b** with $NaBH_4$ caused a smooth color change from dark green to light yellow-green, which suggested its reduction; however, **7b** was recovered (with partial decomposition) after a standard aqueous workup. These experiments indicate that the [28]hexaphyrin **7b** is the most stable oxidation state of this hexaphyrin system.

Previous studies of the photophysical properties of antiaromatic compounds revealed that antiaromatic compounds commonly exhibit relatively short excited-state lifetimes owing to the existence of an optically dark state in the near-IR region and to their smaller two-photon-absorption cross-section values relative to those of aromatic compounds.[10b,18,19] We therefore measured the excited-state lifetimes and two-photon-absorption cross-section values of **7b**. In accordance with the previous studies,[10b,18,19] the excited-state lifetime of **7b** was estimated by femtosecond transient absorption (TA) measurements to have two fast-decay components with time constants of 400 fs and 8 ps (Figure 3). Furthermore, the two-photon-absorption (TPA) cross-section value of **7b** was determined to be 520 GM by photoexcitation at 2000 nm (see the Supporting Information). This value is smaller than that of aromatic [26]hexaphyrins (ca. 1000 GM at 1200 nm). From these results, we could conclude that **7b** shows antiaromatic behavior, which is consistent with the NMR spectroscopic data, quantum-mechanical calculations, and X-ray crystal data for **7b**.

The imidazolyl-appended octaphyrins **8a–c** were prepared by similar [4+4] condensation reactions of tetrapyrrane

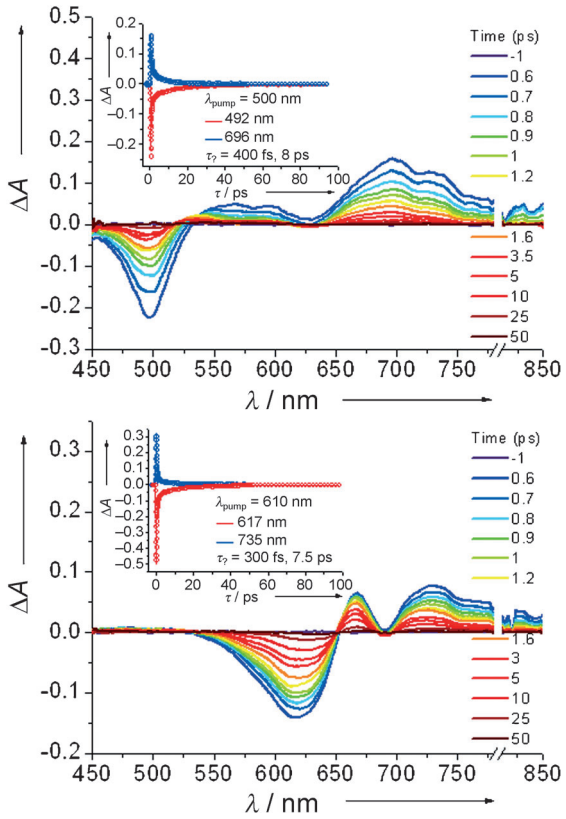
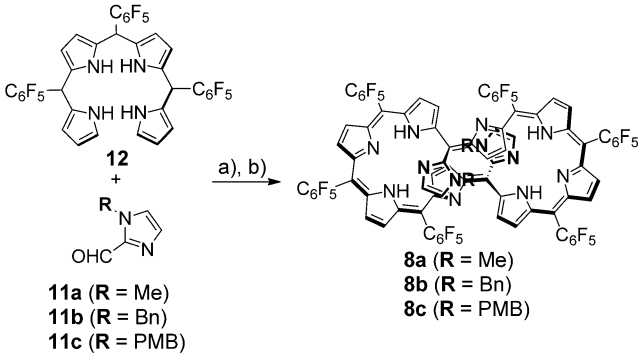
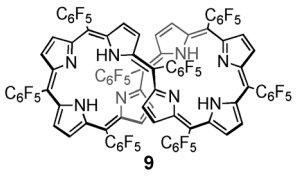


Figure 3. TA spectra of **7b** (top) and **8c** (bottom), and TA decay profiles of **7b** (inset, top) and **8c** (inset, bottom).

12[20] with imidazolecarboxaldehydes **11a–c**, followed by oxidation with DDQ in 5, 6, and 7% yield, respectively (Scheme 3). As in the case of **7a**,**b**, the absence of other products facilitated the isolation of **8a–c**. Again, we focus herein on the characterization of **8c** because of its better solubility (for the characterization of **8a** and **8b**, see the Supporting Information). The HR ESI-TOF mass spectrum of **8c** showed a parent-ion peak at *m*/*z* 1988.3013 ($[M-H]^-$; calcd for $C_{98}H_{41}N_{12}O_2F_{30}$: 1988.3022), which identified **8c** as a [36]octaphyrin. The solid-state structure of **8c** was revealed by X-ray diffraction analysis not to be a doubly twisted figure eight as adopted by the parent octakis(pentafluorophenyl) [36]octaphyrin **9** but rather a nontwisted planar conformation



Scheme 3. Synthesis of **8a–c**: a) MSA (1.5 equiv); b) DDQ (6.0 equiv), CH_2Cl_2, 0°C. PMB = *p*-methoxybenzyl.



(Figure 4). This structure is apparently stabilized by two porphyrin-like hydrogen-bonding networks (N2H–N3–N4H–N5),[15] similar to those in **7b**. The remaining two pyrrolic

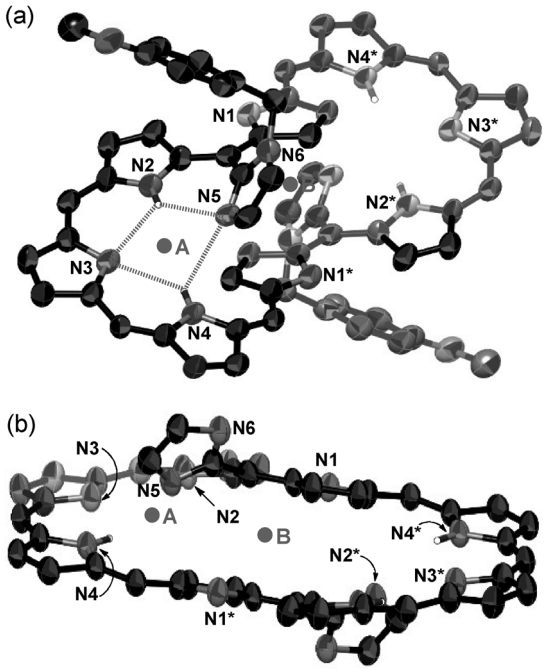


Figure 4. X-ray crystal structure of **8c**: a) perspective view; b) side view. The *meso* pentafluorophenyl groups, hydrogen atoms, and the *N*-*p*-methoxybenzyl groups in (b) are omitted for clarity. The thermal ellipsoids are scaled to 50% probability.

units at the hinge position point outward and are thus outside of the hydrogen-bonding networks. The solid-state structure of **8b** was determined to be similar to that of **8c** (see the Supporting Information). The ^{1}H NMR spectrum of **8c** in $CDCl_3$ showed two sets of C_2-symmetric signals in a 7:1 ratio. The major set was assigned to the crystal structure (for details, see the Supporting Information). Characteristically, the signals of the outer β-H atoms were observed in the range $\delta = 5.74$–4.90 ppm, those of the inner β-H atoms were observed at $\delta = 13.00$ and 9.86 ppm, and those of the inner pyrrolic NH atoms appeared at $\delta = 19.81$ and 19.43 ppm; these values indicate a paratropic ring current for this conformer. The similarity of the ^{1}H NMR spectral pattern of the minor set of C_2-symmetric signals to that of the nonaromatic parent compound **9** (for detailed assignments, see the Supporting Information) suggests a figure-eight conformation.

The UV/Vis spectrum of **8c** exhibited an ill-defined Soret-like band at $\lambda_{max} = 609$ nm and a very broad forbidden band ranging from 800 to 1800 nm (Figure 1). These bands are characteristic of antiaromatic porphyrinoids. The antiaromaticity of **8c** is supported by its HOMA (0.137) and NICS values (+15.85 ppm at A and +8.33 ppm at B in Figure 4). The electrochemical HOMO–LUMO gap of **8c** as determined by cyclic voltammetry was 0.943 eV: slightly smaller than that of **9** (0.971 eV). As found for **7b**, the oxidation and reduction of octaphyrins **8a–c** were difficult (see the Supporting Information). These compounds thus show considerable chemical stability.

The excited-state dynamics of **8c** were similar to those observed for **7b**: two fast-decay components were found with time constants of 300 fs and 7.5 ps (Figure 3). Furthermore, the TPA cross-section value of **8c** was determined to be 600 GM by photoexcitation at 2000 nm (see the Supporting Information). From these photophysical properties of **8c**, we also assume that **8c** exhibits antiaromatic behavior, as expected on the basis of NMR spectroscopic data, quantum-mechanical calculations, and its X-ray crystal structure.

In summary, the [28]hexaphyrins **7a**,**b** and [36]octaphyrins **8a–c** containing *meso*-imidazolyl groups were prepared and shown to be stable antiaromatic porphyrinoids on the grounds of their paratropic ring currents, absorption characteristics, forbidden low-energy bands in the near-IR region, short excited-state lifetimes, and small TPA values. The introduced *meso*-imidazolyl groups stabilize the respective 28π and 36π antiaromatic electronic networks through effective hydrogen-bonding interactions in their roughly planar Hückel conformations, probably because the resulting stabilization is larger than the antiaromatic destabilization. This hydrogen-bonding strategy may be effective for the construction of other Hückel antiaromatic expanded porphyrins. Further studies based on this strategy are underway in our laboratory.

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[15] Crystal data for **7b**: $C_{74}H_{34}N_{10}F_{20}$, $M_r = 1443.11$, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.3787(2)$, $b = 12.5111(2)$, $c = 18.1373(3)$ Å, $\beta = 104.0018(11)°$, $V = 2945.66(8)$ Å^3, $Z = 2$, $T = 93$ K, $D_{calcd} = 1.627$ g cm^{-3}, $R_1 = 0.0743$ ($I > 2\sigma(I)$), $R_w = 0.2362$ (all data), GOF = 1.066; **8c**: $C_{98}H_{42}N_{12}F_{30}\cdot(C_6H_{14})_{3.47}\cdot(CH_2Cl_2)_{1.06}$, $M_r = 2377.95$, triclinic, space group $P\bar{1}$ (No. 2), $a =$

10.3148(9), $b = 14.5506(14)$, $c = 19.2425(4)$ Å, $\alpha = 86.188(4)$, $\beta = 89.206(4)$, $\gamma = 73.911(4)°$, $V = 2768.8(4)$ Å^3, $Z = 1$, $T = 93$ K, $D_{calcd} = 1.426$ g cm^{-3}, $R_1 = 0.0975$ ($I > 2\sigma(I)$), $R_w = 0.2171$ (all data), GOF = 1.080. CCDC 899973 (**7b**) and 899975 (**8c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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