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Synthesis of a Tetrabenzotetraaza[8]circulene by a “Fold-In” Oxidative Fusion Reaction**

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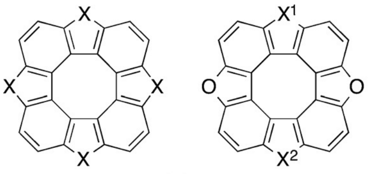
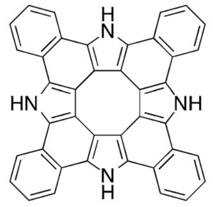
Abstract: *Tetrabenzotetraaza[8]circulene (**1**) has been synthesized in good yield by a “fold-in” oxidative fusion reaction of a 1,2-phenylene-bridged cyclic tetrapyrrole. X-ray diffraction analysis of **1** has revealed a planar square structure with a central cyclooctatetraene (COT) core that shows little alternation of the bond lengths. Despite these structural features, **1** shows aromatic-like character, such as sharp absorption bands, high fluorescence quantum yields (Φ_F = 0.55 in THF), and a single exponential fluorescence decay with τ_F = 3.8 ns. These observations indicate a dominant contribution of an [8]radialene-like π conjugation and hence aromatic character of the local aromatic segments in **1**.*

Hetero[8]circulenes with O, N, S, and Se atoms have been attracting considerable interest in light of their enforced planar structures and presumed 8π antiaromaticity at the cyclooctatetraene (COT) center as well as their potential applications for OLEDs and OFETs.[1–5] We also became interested in tetrabenzotetraaza[8]circulene (**1**) since it corresponds to the central moiety of porphyrin sheet **3**, which displays remarkably strong antiaromatic character owing to its planar COT unit.[6] We envisioned that tetraaza[8]circulene **1** may be a benchmark molecule to assess the roles of the porphyrin segments in the antiaromatic character of **3**. In addition, compound **1** is an interesting molecule on its own, since tetraaza[8]circulene has remained unexplored to date.



Hetero[8]circulenes

X = O, S, Se X^1 = N*n*Pr or NBn, X^2 = O
X^1 = X^2 = N*n*Pr or NBn



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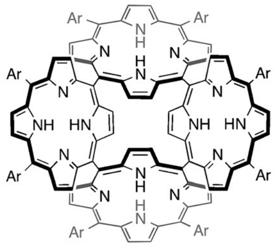

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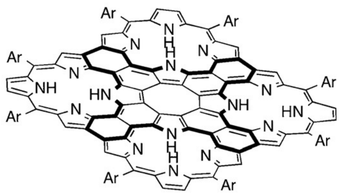

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Porphyrin sheet **3** was synthesized by oxidative fusion of meso-meso-linked 5,10-porphyrin cyclic tetramer **2**. This transformation can be regarded as a “fold-in” oxidative fusion reaction. While “fold-in” approaches have been shown to be effective for the synthesis of bowl-shaped fused aromatic molecules,[7] they have not been employed for the synthesis of heterocirculenes. Since the discovery of tetraoxa[8]circulene in 1968, the synthesis of hetero[8]circulenes has long relied on classical acid-catalyzed condensation reactions of benzoquinones.[2,3] Herein, we report an effective synthesis of **1** by a “fold-in” oxidative fusion reaction of a cyclic tetrapyrrolic precursor **5**.

First, 1,2-di(pyrrol-2-yl)benzene (**4**)[8] was brominated at the 5,5′-positions and the resulting dibromide was directly coupled with 1,2-di(pinacolatoboryl)benzene[9] under palladium-catalyzed conditions. Cyclic tetrapyrrole **5** was obtained in 11 % yield after repetitive purifications by column chromatography on silica gel (Scheme 1). The structure of **5** has been confirmed by X-ray diffraction analysis (Figure 1 a). In the solid state, **5** takes on a twisted figure-eight conformation with an average dihedral angle between the pyrrole rings and 1,2-phenylene bridges of 30.2°. The ^{1}H NMR spectrum of **5** in $CDCl_3$ exhibited a broad singlet corresponding to the pyrrolic NH protons at 8.70 ppm, a singlet corresponding to the pyrrolic β protons at 6.43 ppm, and two signals corresponding to the phenylene protons at 7.41 and 7.20 ppm, thus indicating its high symmetry (D_{4h}). These spectral features remain unchanged even at −80 °C (Figures S3 and S4). From the lower symmetry structure in the solid state, it is concluded that **5** is in dynamic conformational equilibrium in solution.

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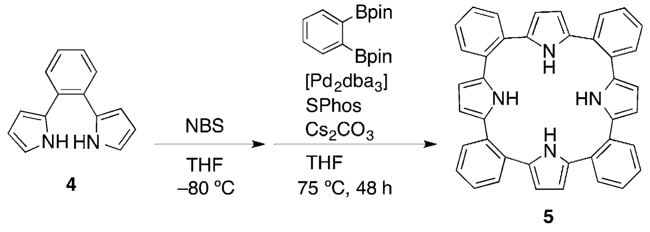


Scheme 1. Synthesis of **5**. Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl, dba = dibenzylideneacetone, NBS = *N*-bromosuccinimide.

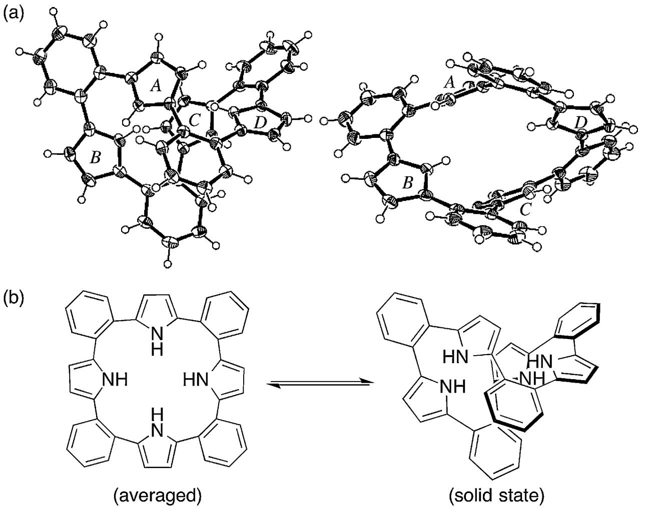
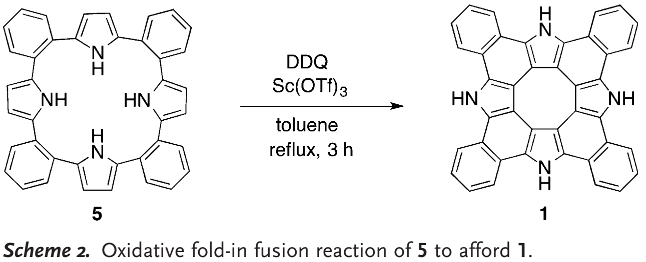


Figure 1. a) X-ray crystal structure of **5**. The thermal ellipsoids were scaled to 50% probability. b) Dynamic equilibrium of **5**.

Despite its formal [24]porphyrin(2.2.2.2) expanded-porphyrin-like structure, **5** is non-aromatic, as judged from its ^{1}H NMR and UV/Vis spectra.[10]

In the next step, the intramolecular oxidative fusion reaction of **5** was examined (Scheme 2). After extensive optimization of the conditions, we were delighted to find that tetrabenzotetraaza[8]circulene (**1**) was cleanly synthesized in a high yield of 96% by oxidation of **5** with DDQ/Sc(OTf)$_3$.[11] Compound **1** is poorly soluble in CHCl$_3$, toluene, and other nonpolar solvents, but soluble in THF and DMSO. The ^{1}H NMR spectrum of **1** in [D$_8$]THF exhibited a signal at 11.77 ppm corresponding to the pyrrolic NH protons and two signals at 8.83 and 7.76 ppm corresponding to the phenylene protons. The ^{13}C NMR spectrum of **1** showed five sharp signals at 130.4, 124.4, 122.6, 121.9, and 114.0 ppm, again highlighting its D_{4h}-symmetric structure.



Scheme 2. Oxidative fold-in fusion reaction of **5** to afford **1**. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, Tf = trifluoromethanesulfonyl.

Single crystals of **1** were obtained by slow diffusion of hexane into a solution of **1** in a mixture of acetone and THF. X-ray diffraction analysis showed the structure to be a perfectly planar square with a small mean-plane deviation value of 0.025 Å (Figure 2a). All the pyrrole rings point outward, and undergo hydrogen-bonding interactions with the carbonyl oxygen atoms of acetone molecules. The eight C–C bond lengths constructing the central COT are similar, in the range 1.428–1.438 Å, thus indicating no significant alternation of the bond length. Importantly, these bond lengths are longer than those of the optimized D_{8h} COT (ca. 1.40 Å). On the other hand, the C$_\alpha$–C$_\beta$ bond lengths in the pyrrole moieties are distinctly shorter (1.393–1.400 Å). These structural features underline the importance of the contribution of [8]radialene-like conjugation. Single crystals of **1** were also obtained by diffusion of hexane into a solution of **1** in THF, 1,4-dioxane, or DMSO. Although the crystal-packing structures are different, the structures of the molecular frameworks and the hydrogen-bonding interactions of the four pyrrole rings with solvent molecules are nearly the same (see the Supporting Information).

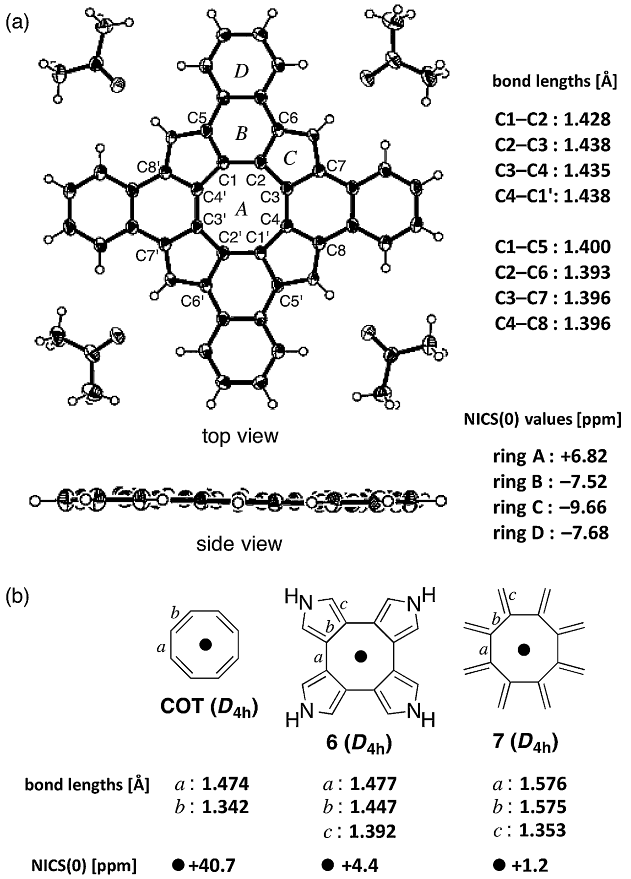


Figure 2. a) X-ray crystal structure of **1**. The thermal ellipsoids were scaled to 50% probability. Acetone molecules coordinating to NH groups by hydrogen bonding are shown. b) Bond lengths and NICS(0) values of reference molecules calculated at the B3LYP/6-311+G(d,p) level.

Nuclear independent chemical shift (NICS) values[12] at the center of each of the ring segments A, B, C, and D were calculated with the GIAO method at the B3LYP/6-311+G(d,p) level to be +6.82, −7.52, −9.66, and −7.68 ppm, respectively (Figure 2a). The calculated positive NICS(0) value in ring A may be regarded as an indication of its antiaromaticity being derived from COT, as discussed for other heterocirculenes.[2–4] However, the observed antiaromaticity in **1** is not as strong as the large positive NICS(0) value (+35.71 ppm) at the center of porphyrin sheet **3**.[6a] Examination of various substructures of **1** such as D_{4h}-symmetric COT, tetrapyrrole **6**, and [8]radialene **7** has revealed that the positive NICS(0) value decreases with elongation of the C−C bond lengths around the COT structure.[13] Therefore, the moderate positive NICS(0) value and weakened antiaromaticity at ring A of **1** may be ascribed to its "stretched" COT segment.[14]

Figure 3a shows the UV/Vis absorption and emission spectra of **1** and **5**. Cyclic tetrapyrrole **5** exhibits a broad absorption band at 326 nm and a broad fluorescence in the range 400–650 nm ($\Phi_F = 0.27$) in THF. Interestingly, solid **5** emits fluorescence in the range 450–700 nm with $\Phi_F = 0.15$ (Figure S6-2). Compound **1** exhibits vibronic-structured absorption bands at 390 and 413 nm and their mirror-image sharp emission bands at 416 and 441 nm with a high quantum yield ($\Phi_F = 0.55$) in THF. Importantly, weak absorption tails in the lower-energy region that are characteristic of antiaromatic porphyrinoids are not detected for **1**.[15] The Stokes shift is only 175 cm^{-1}, thus indicating a rigid structure in the excited state. In line with these absorption and emission features, TD-DFT calculations have indicated intense degenerate bands with $f = 0.22$ at 399 nm to be ascribed to HOMO–LUMO and HOMO-1–LUMO transitions. To gain further insight into the frontier orbital diagrams, the magnetic circular dichroism (MCD) spectrum of **1** was measured in THF. The spectrum exhibits a positive-to-negative sign sequence (negative Faraday A term) corresponding to the main absorption at 416 nm, which indicates that the absorption bands consist of transitions from degenerate orbitals (HOMO and HOMO-1) to a nondegenerate orbital (LUMO; Figure 3b). Overall, these characteristics of **1** suggest an aromatic-like character despite the presence of the central planar COT. On the basis of frontier MO profiles it is considered that the electronic properties of **1** stem from peripheral aromatic segments (Figure S7-6).

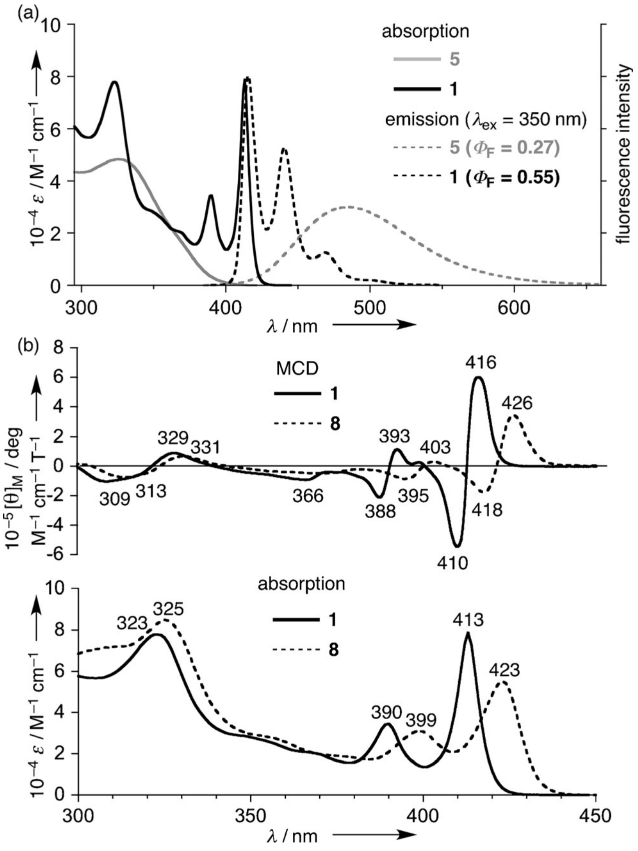
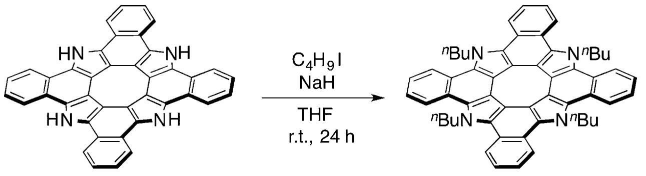


Figure 3. a) UV/Vis absorption (solid) and fluorescence (dashed) spectra of **5** (gray) and **1** (black) in THF. b) MCD (top) and UV/Vis (bottom) spectra of **1** and **8** in THF.

To investigate the excited-state properties of **1** and **5**, we measured the dynamics of the S_1 state by using the TCSPC (time-correlated single photon counting) technique (Figures S8-1 to S8-9). In the case of **5**, we could observe biexponential decay profiles and two time constants were estimated to be around 1 and 5 ns. Moreover, the ratio between the two components is slightly different depending on the probe wavelength used. The fast decay component corresponding to 1 ns is too slow to be assigned as structural relaxation dynamics. As mentioned above, however, the various conformers of **5** that exist at both room temperature and even −80 °C probably give rise to the probe wavelength dependent biexponential decay. To gain further insight into this feature, we measured the fluorescence decay of **5** at 77 K to reduce structural heterogeneity. As a result, we found that the biexponential decay of **5** becomes a single exponential decay with a lifetime of around 5.1 ns, regardless of the probe wavelength.

In the case of **1**, the excited-state lifetime was estimated to be 3.8 ns, with a single exponential decay. The measured excited-state lifetime of **1** is much longer than that of the Zn^{II} porphyrin sheet (1.1 ps) measured by the transient absorption technique.[6a] Considering that the Zn^{II} porphyrin sheet shows antiaromaticity above the COT core and nonfluorescent behavior, the well-resolved absorption/fluorescence spectra, high fluorescence quantum yield, and long excited-state lifetime of **1** strongly support its overall aromatic feature being induced by the weakened antiaromatic character of the central COT.

Finally, the fabrication of **1** was examined. Changes in the absorption spectrum of **1** were observed upon addition of tetrabutylammonium fluoride (TBAF), presumably because of deprotonation of the NH protons (Figure S6-4). On the basis of this observation, **1** was treated with an excess of iodobutane in the presence of sodium hydride for 24 h at room temperature to afford tetra-*N*-butylated tetraaza[8]circulene **8** in 77% yield (Scheme 3). This product shows improved solubility in common solvents, such as dichloromethane, chloroform, acetone, and benzene, which would promise its further application as discotic liquid-crystalline mesogens, for example.[2c] The structure of **8** has been



1 **8**

Scheme 3. N-substitution reaction of **1**.

unambiguously determined by X-ray diffraction analysis (Figure S5-6). The core plane was slightly distorted, with an average mean-plane deviation of 0.155 Å. On the other hand, the central COT remained almost unchanged by N substitution. The UV/Vis spectrum of **8** exhibits red-shifted absorption bands at 325, 399, and 423 nm and emissions at 430 and 454 nm, with $\Phi_F = 0.35$. The cyclic voltammetry showed reversible oxidation waves at 0.22 and 0.51 V, while **1** showed a pseudo-reversible peak at −0.01 V versus the ferrocene/ferrocenium ion (Fc/Fc$^+$) couple (Figure S9-1). These results demonstrate the possibility of electronic tuning by an N-substitution reaction.

In summary, tetrabenzotetraaza[8]circulene (**1**) has been synthesized from known compounds in two steps, with a "fold-in" intramolecular oxidative fusion reaction as the key step. Compound **1** is a planar, square molecule that exhibits a sharp absorption spectrum, sharp fluorescence with a high quantum yield, and a long fluorescence lifetime. These features, which are in sharp contrast to porphyrin sheet **3**—which exhibits a strong paratropic ring current—may come from the local aromatic segments fused to the central COT. Antiaromaticity in the central planar COT is considerably weakened, probably because of the elongated C–C bonds around the COT. Further modifications of **1** as well as exploration of all-aza [*n*]circulenes are underway in our laboratory.

Keywords: aromaticity · circulenes · cyclooctatetraene · fused-ring systems · pyrroles

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