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Porphyrins

Synthesis of Carbazole-Containing Porphyrinoids by a Multiple Annulation Strategy: A Core-Modified and π-Expanded Porphyrin**

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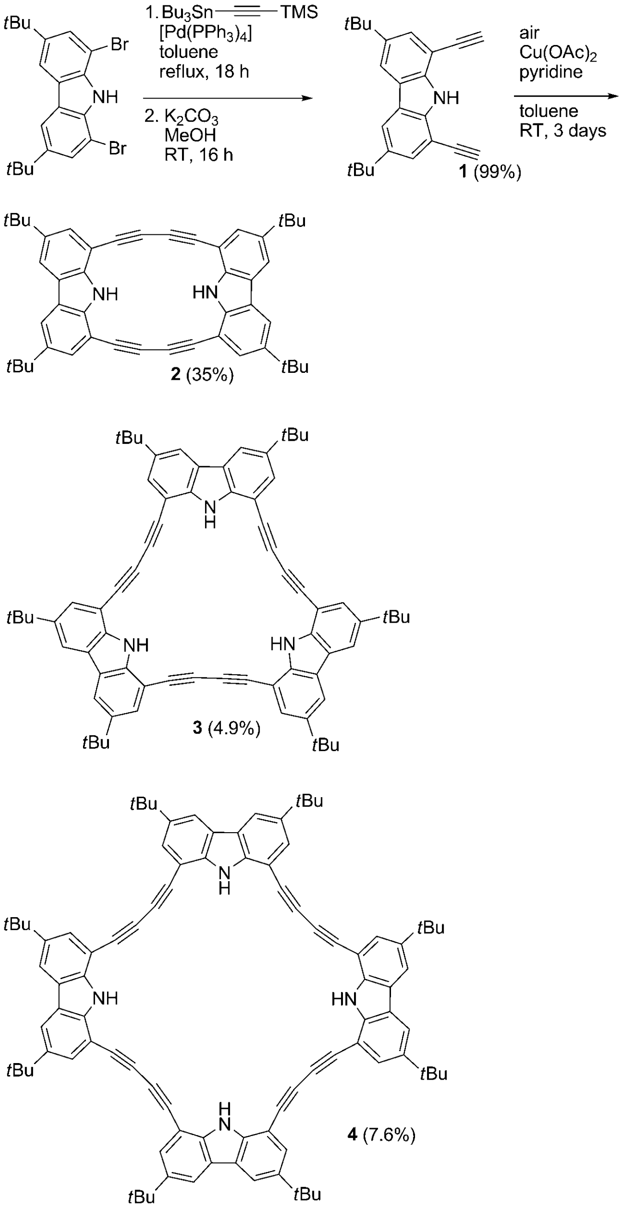
Porphyrins are the most important pyrrolic macrocycles in light of their biological importance and ability to serve as efficient catalysts and functional pigments. Most porphyrins and porphyrinoids have been synthesized by the acid-catalyzed condensation of pyrroles and aldehydes, or their equivalents.[1] The exception are those in which the pyrrole rings are connected either directly or through vinylene linkages, and these have been synthesized by the oxidative coupling of pyrroles[2] and McMurry coupling reactions.[3] New synthetic protocols for porphyrins are desirable, since they may allow the more efficient preparation of porphyrins or the exploration of structurally unique porphyrins that are otherwise very difficult to prepare. Carbazole-based materials have been extensively studied in view of their highly emissive and electron-conducting properties, chemical stabilities, and compatibilities with various transformations such as polymerizations and metal-catalyzed cross-coupling reactions.[4] Despite these developments, porphyrins containing carbazole moieties have rarely been explored.[5–7]

Herein we disclose a multiple annulation strategy that allows the synthesis of novel porphyrinoids from 1,3-butadiyne-bridged cyclic carbazole oligomers. This approach was encouraged by our recent synthesis of diporphyrins linked through their meso pyrrole positions by a copper(I)-mediated annulation reaction of 1,3-butadiyne-brigded diporphyrins with amines;[8] cyclic oligothiophenes were prepared by a similar annulation reaction by Bäuerle and co-workers.[9]

Firstly, 1,8-diethynylcarbazole **1** was prepared through a Stille coupling reaction of 1,8-dibromo-3,6-di-*tert*-butylcarba-



Scheme 1. Synthesis of 1,3-butadiyne-bridged cyclic carbazole dimer **2**, trimer **3**, and tetramer **4**.

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zole[10] with tributyl(trimethylsilylethynyl)tin and subsequent deprotection with K_2CO_3. A subsequent Glaser coupling reaction of **1** followed by gel-permeation chromatographic separation provided dimer **2** (35 %), trimer **3** (4.9 %), and tetramer **4** (7.6 %; Scheme 1). The ^1H NMR spectra and high-resolution electrospray-ionization (HR-ESI) mass spectra of **2**–**4** are fully consistent with their symmetric structures (see the Supporting Information). Single-crystal X-ray diffraction analysis showed **2** and **3** to be almost planar, with mean deviations from the plane of 0.065 and 0.210 Å, respectively (Figure 1).[11] Interestingly, the 1,3-butadiyne bridges are bent outward in **2** and inward in **3**. Compared to the parent carbazole, 1,8-diethynylcarbazole **1** shows red-shifted absorption bands, while those of the cyclic oligomers **2**–**4** are even more red-shifted (Table 1). The fluorescence quantum yield of **2** is high and comparable to that of **1**, while those of **3** and **4** decrease as the molecular size increases.

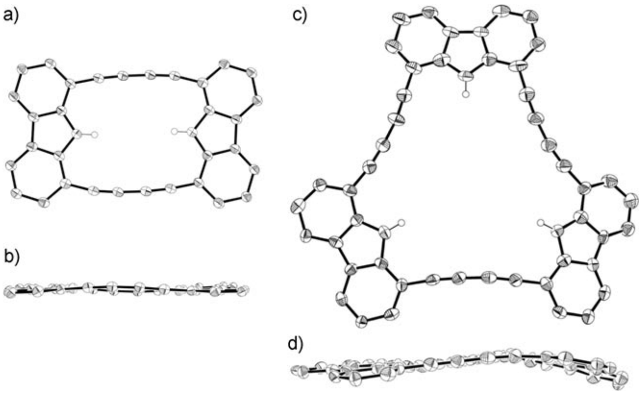


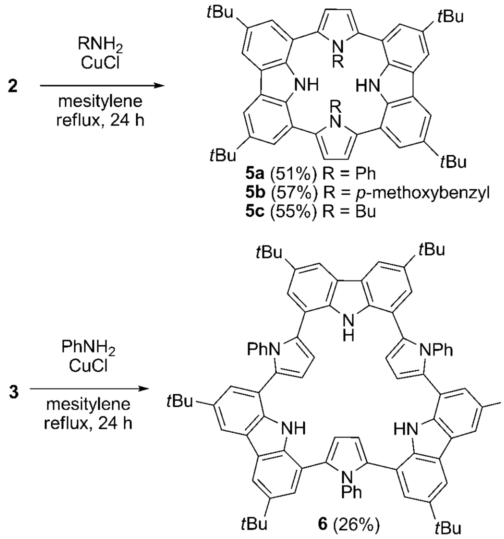
Figure 1. X-ray crystal structures: a) Top view of **2**, b) side view of **2**, c) top view of **3**, and d) side view of **3**. *tert*-Butyl groups, hydrogen atoms except for NH protons, and solvent molecules are omitted for clarity. The thermal ellipsoids are at the 50 % probability level.

Heating a solution of **2** in mesitylene, aniline (25 equiv), and CuCl (2 equiv) at reflux for 24 h afforded *N*-phenyl-pyrrolylene-bridged carbazole dimer **5a** in 51 % after chromatographic separation (Scheme 2). The HR-ESI mass spectrum showed the parent ion signal of **5a** at $m/z = 835.4732$ (calcd for $C_{60}H_{59}N_4$, $[M-H]^- = 835.4745$). Similar annulation reactions with *p*-methoxybenzylamine and butylamine provided the corresponding 2,5-pyrrolylene-bridged carbazole dimers **5b** and **5c**, respectively, in moderate yields. The structure of **5c** was showned by X-ray diffraction analysis to possess a tetrapyrrolic porphyrin-like framework, with a dihedral angle between the pyrrole and carbazole planes of about 52° and with the two butyl groups oriented in the same direction (Figure 2).[11] These 2,5-pyrrolylene-bridged cyclic carbazole dimers **5a**–**c** can be regarded as [20]porphyrins (isophlorins) and are expected to become aromatic after deprotection of the pyrrolic nitrogen atoms and subsequent oxidation. However, deprotection of the pyrrolic nitrogen atoms was unsuccessful, despite extensive attempts using various acids and oxidants.

Table 1: Selected photophysical properties in CH_2Cl_2.

Compound	λ_A [nm]	λ_F [nm][a]	Φ_F[b]
1	310, 364	372, 388[c]	0.408[d]
2	323, 419	431	0.426
3	330, 404	413	0.142
4	325, 387	423,[c] 466	0.061
5a	300, 350	424	0.775
5b	298, 368	417	0.573
5c	297, 368	414	0.704
6	304, 363	401	0.610
carbazole[e]	292, 334	338, 354	0.367

[a] The excitation wavelength is 300 nm. [b] The absolute fluorescence quantum yield with excitation at 360 nm. [c] Shoulder. [d] The fluorescence quantum yield of **1** was determined with reference to that of **2** (0.426) in CH_2Cl_2. [e] The photophysical properties of carbazole was reported by Bonesi and Erra-Balsells.[12]



Scheme 2. Synthesis of pyrrole-bridged carbazole dimers **5a**–**c** and trimer **6**.

A similar annulation reaction of **3** with aniline gave cyclic carbazole trimer **6** in 26 % yield. The X-ray crystal structure of **6** showed it to have a zigzag triangular shape, in which the pyrrole spacers are inclined by 50–80° toward the neighboring

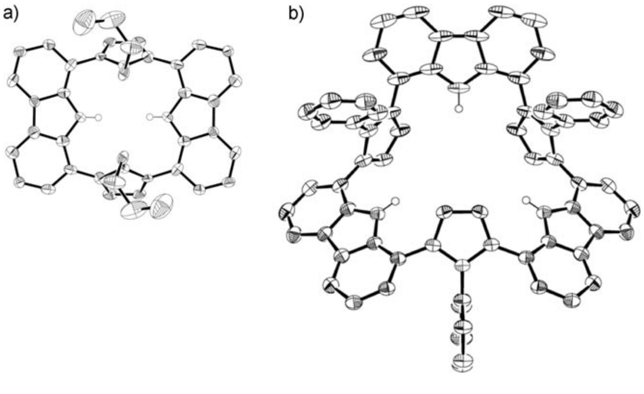


Figure 2. X-ray crystal structures of a) **5c**, and b) **6**. *tert*-Butyl groups, hydrogen atoms except for NH protons, and solvent molecules are omitted for clarity. The thermal ellipsoids are at the 50 % probability level.

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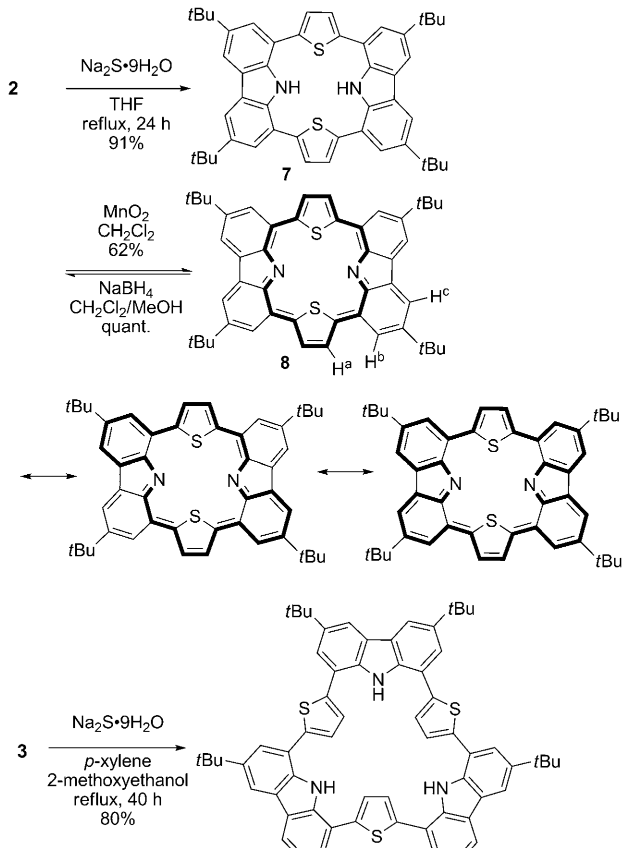
carbazole planes (Figure 2),[11] hence prohibiting conjugation of the overall macrocyclic. The ^{1}H NMR spectrum of **6** is rather broad at room temperature, but the signals become sharper at 50 °C, with signals corresponding to the pyrrole protons observed at $\delta = 6.93$ ppm and phenyl protons at $\delta = 7.30$, 7.08, and 7.03 ppm. This finding suggests there is restricted rotation of the pyrrole bridges at room temperature. The absorption spectra of **5a–c** and **6** are similar, and reflect the nonconjugated characters. Interestingly, the fluorescence quantum yields of **5a–c** and **6** are high (Table 1), which may be ascribed to their conformational rigidities.

Thiophene-containing porphyrinoid **7** was then prepared in 91 % yield by heating **2** at reflux in the presence of $Na_2S{\cdot}9H_2O$ in THF (Scheme 3).[13] The isophlorin structure of **7** was confirmed by X-ray structural analysis to be relatively flat with a mean deviation from the plane of 0.217 Å (Figure 3). The absorption spectrum of **7** is similar to those of **5a–5c**, thus indicating its nonconjugated character. Gratifyingly, the oxidation of **7** with MnO_2 resulted in a vivid color change from yellow to green and formation of core-modified porphyrin **8** in 62 % yield. Porphyrin **8** was reduced quantitatively to **7** with $NaBH_4$. Thiophene-bridged carbazole trimer **9** was obtained in 80 % yield by a similar annulation reaction of **3**, but a subsequent oxidation to an aromatic porphyrinoid has so far been unsuccessful.[14]



Scheme 3. Synthesis of thiophene-bridged carbazole dimers **7**, **8**, and trimer **9**.

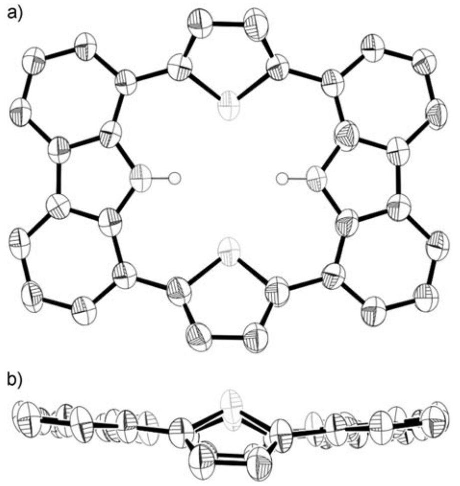


Figure 3. X-ray crystal structure of **7**: a) top view and b) side view. *tert*-Butyl groups and hydrogen atoms except for NH protons are omitted for clarity. The thermal ellipsoids are at the 50 % probability level.

As shown in Scheme 3, the macrocyclic conjugation of the core-modified porphyrin **8** can be drawn as a 18π, 26π, or 34π system, all of which should be aromatic. In line with this, porphyrin **8** exhibits drastically different properties from those of **7**. The ^{1}H NMR spectrum shows considerable downfield shifts of the signals corresponding to the peripheral protons—H^a at $\delta = 9.90$ ppm, H^b and H^c at $\delta = 9.44$ and 8.87 ppm—which indicate a strong diatropic ring current. The absorption spectrum of **8** displays intensified and extremely red-shifted Q-like bands at 845, 934, and 1049 nm (Figure 4).

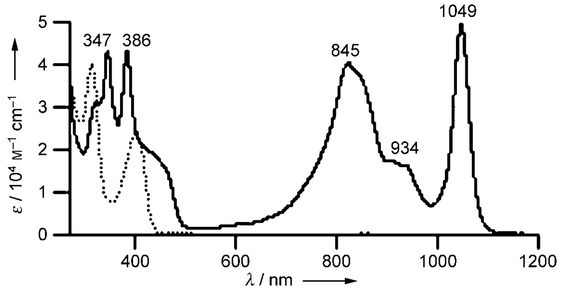


Figure 4. UV/Vis/NIR absorption spectra of **7** (dotted line) and **8** (solid line) in CH_2Cl_2.

Cyclic voltammetry on **8** revealed reduction waves at −0.55, −0.88, and −1.41 V, and oxidation waves at 0.42, 0.98, and 1.11 V. A small electrochemical HOMO–LUMO gap (0.97 eV) is consistent with its optical HOMO–LUMO gap (1.18 eV). Although **7** fluoresces at 448 nm with a quantum yield of 0.27 and a single exponential lifetime of 0.98 ns, porphyrin **8** is nonfluorescent and the lifetime of its S_1 state is very short (6.3 ps), as determined by femtosecond transient absorption spectroscopy, probably because of the acceleration of nonradiaditive relaxation resulting from the smaller HOMO–LUMO gap. Nuclear independent chemical shift (NICS) values at the center of the molecule were calculated to be +1.28 and −11.09 ppm for **7** and **8**, respectively. Collectively, these data indicate the distinct aromaticity of **8**.

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In summary, a copper(I)-promoted annulation reaction of 1,3-butadiyne-bridged cyclic carbazole dimer **2** and trimer **3** with amines provided the porphyrinoids **5** and **6**, respectively, containing carbazole units. A similar annulation reaction of **2** with sodium sulfide produced isophlorin **7** with thiophene-carbazole moieties. Oxidization of **7** with MnO_2 furnished the corresponding porphyrin **8**, which displays a remarkably intensified and red-shifted absorption spectrum that reaches the near infrared region as a result of its distinct aromaticity and expanded π network. This multiple annulation protocol is efficient and useful, and complementary to the conventional acid-catalyzed condensation-based synthesis of porphyrins. Further studies on finding suitable protecting groups for pyrrole rings for the synthesis of aromatic porphyrinoids containing carbazole units are in progress.

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[14] The reason for the unsuccessful oxidation of **9** to the corresponding aromatic macrocycle is currently unclear, but might be ascribed to insufficient steric protection, since carbazole-thiophene hybrid macrocyles bearing peripheral substituents smaller than *tert*-butyl groups were not oxidized to the corresponding aromatic congeners.

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