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Synthesis of Carbazole-Based Selenaporphyrin *via* Annulation

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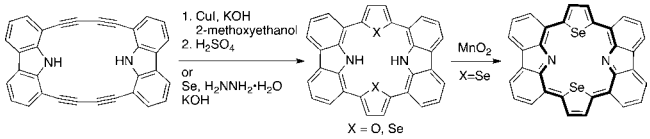
ABSTRACT



Cu(I)-mediated alkoxylation of doubly 1,3-butadiyne-bridged carbazole dimer 1, followed by acid-catalyzed cyclization, provided furan-bridged carbazole dimer 3, while annulation reaction of 1 with selenium in the presence of hydrazine monohydrate provided selenophene-bridged carbazole dimer 5a. Oxidation of isophlorin 5a afforded carbazole-based selenaporphyrin 5b, which possessed distinct aromaticity and produced intensified and red-shifted absorption bands in the near-IR region.

Porphyrins are a class of tetrapyrrolic ligands that are of exceptional importance in biological processes such as photosynthesis, and which also have applications in catalysis, anion sensing, and optical devices.[1] Both peripheral and core modifications of porphyrins are interesting because they can change porphyrin properties dramatically. Peripheral modifications include the introduction of acetylene moieties or the fusion of additional aromatic rings at the porphyrin periphery, which results in expanded π-conjugation and additional absorption within the near-infrared (NIR).[2,3] Core modifications change the electronic and electrochemical properties and coordination abilities of the porphyrin base system.[4]

Carbazole derivatives are compounds of interest because they are highly emissive, electron conducting, easily modified, and chemically stable.[5] Since carbazole is a benzene-fused pyrrole, its incorporation into fused porphyrins presents interesting possibilities.[6,7] Recently, a multiple annulation strategy that allows the synthesis of novel

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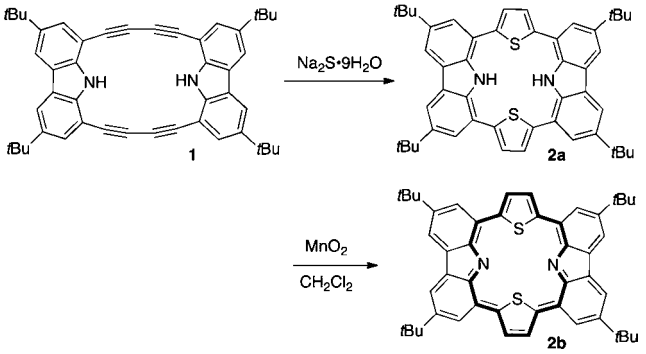
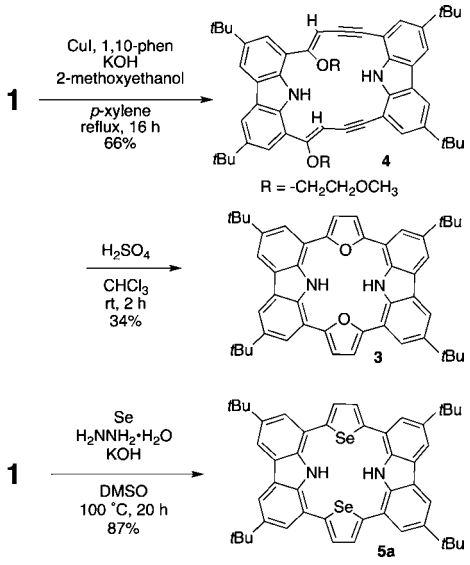
porphyrinoids from 1,3-butadiyne-bridged cyclic carbazole oligomers was reported (Scheme 1).[8,9] Among the porphyrinoids, the tetrabenzo-fused core-modified porphyrin **2b** exhibited distinct aromaticity and NIR absorption due to extended π-conjugation over the entire macrocycle. Following this work, the synthesis of novel carbazole-based core-modified porphyrins was investigated because 1,3-butadiyne moieties of **1** can be converted into five-membered heterocycles. The present report describes the synthesis of the carbazole-based oxaporphyrin and selenaporphyrin, which are 15-group core-modified porphyrins with a thiaporphyrin.

Scheme 1. Synthesis of Carbazole-Based Porphyrinoids **2a** and **2b**



First, the furan-bridged carbazole **3** was synthesized. Recently, Jiang et al. reported the synthesis of furans in high yield *via* Cu(I)-catalyzed annulation of 1,3-butadiynes.[10] This reaction was applied to the preparation of **3**. However, reaction of **1** to **3** did not proceed in DMSO, 1,4-dioxane, or DMF. In contrast, the use of *p*-xylene/2-methoxyethanol as a mixed solvent system provided compound **4**, the bismethoxyethoxy adduct to **1**, in 66% yield (Scheme 2). High-resolution matrix-assisted-laser-desorption-ionization time-of-flight (HR-MALDI-TOF) mass spectral data showed the parent ion peak of **4** at an m/z value of 802.4733 (calcd for $C_{54}H_{62}N_2O_4$ $[M]^+$ = 802.4705). The ^{1}H NMR spectrum of **4** contained two NH peaks at δ = 10.13 and 9.18 ppm. Slow diffusion of methanol vapor into a toluene solution of **4** resulted in the formation of well-defined crystals. X-ray diffraction analysis unambiguously provided the structure of **4**, shown in Figure 1.[11a] The two methoxyethoxy groups are attached at one carbazole side through antiaddition and are oriented in the same direction. Benzofurans are readily synthesized from cyclization of *o*-alkynylphenol ether; therefore **4** should be transformed into the furan-bridged carbazole **3** in a similar manner.[12] Here, the cyclization reaction of **4** to **3** was achieved using sulfuric acid. HR-MALDI-TOF mass spectral data showed the parent ion peak of **3** at an m/z value of 686.3881 (calcd for $C_{48}H_{50}N_2O_2$ $[M]^+$ = 686.3867). The ^{1}H NMR spectrum of **3** contained a furan peak at δ = 7.01 ppm.

Scheme 2. Synthesis of Carbazole-Based Porphyrinoids **3** and **5a**



Additionally, the reaction of **1** with selenium in the presence of hydrazine monohydrate afforded the selenophene-bridged carbazole **5a** in 87% yield.[13] The HR-MALDI-TOF mass spectrum of **5a** showed the parent ion peak at an m/z value of 814.2321 (calcd for $C_{48}H_{50}N_2Se_2$ $[M]^-$ = 814.2309). Slow diffusion of methanol vapor into a CH_2Cl_2 solution of **5a** resulted in the formation of well-defined crystals. X-ray diffraction analysis unambiguously determined the structure of isophlorin **5a**, as shown in Figure 1.[11b] The angle between the two carbazole planes was 8.66°, indicating that **5a** was a relatively flat molecule.

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(11) (a) Crystallographic data for **4**: formula: $C_{54}H_{62}N_2O_4$, M_w = 803.06, triclinic, space group $P\bar{1}$, a = 10.8252(2) Å, b = 14.0413(3) Å, c = 16.0269(3) Å, α = 80.5192(13), β = 80.3028(12)°, γ = 76.9564(13)°, V = 2318.87(8) Å^3, Z = 2, ρ_{calcd} = 1.150 g cm^{-3}, T = −180 °C, 8265 measured reflections, 25 548 unique reflections (R_{int} = 0.0486), R_1 = 0.0938 ($I > 2\sigma(I)$), wR_2 = 0.2320 (all data), GOF = 1.362. (b) Crystallographic data for **5a**: formula: $C_{50}H_{50}N_2Se_2$, M_w = 836.84, triclinic, space group $P\bar{1}$, a = 10.1478(8) Å, b = 12.6951(12) Å, c = 16.6983(12) Å, α = 90.204(4)°, β = 104.566(3)°, γ = 111.507(2)°, V = 1926.1(3) Å^3, Z = 2, ρ_{calcd} = 1.443 g cm^{-3}, T = −183 °C, 6463 measured reflections, 15 836 unique reflections (R_{int} = 0.0469), R_1 = 0.0709 ($I > 2\sigma(I)$), wR_2 = 0.2163 (all data), GOF = 1.253.

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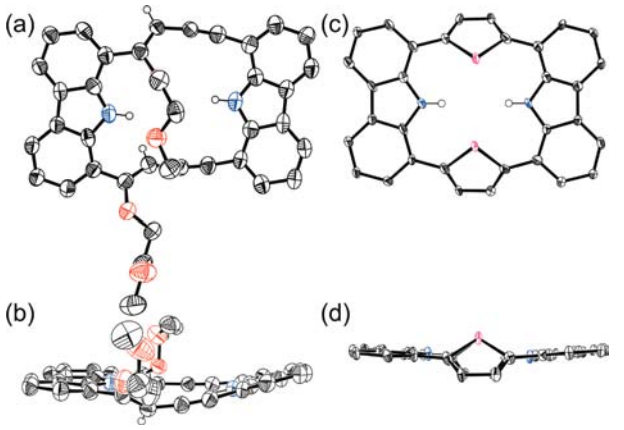


Figure 1. X-ray crystal structures; (a) top view of **4**, (b) side view of **4**, (c) top view of **5a**, and (d) side view of **5a**. *tert*-Butyl groups and hydrogen atoms, except for the NH and vinyl protons, are omitted for clarity. The thermal ellipsoids were at a 50% probability level.

The UV/vis absorption and fluorescence spectra of **2a**, **3**, and **5a** are shown in Figure 2. All of the isophlorins exhibited two similar absorption bands at 310 and 400 nm, which reflect nonaromatic characteristics. Compounds **2a** and **3** exhibited fluorescence with quantum yields of 0.271 and 0.196, respectively, while that of **5a** was less than 0.01, due to the heavy atom effect of selenium moieties.

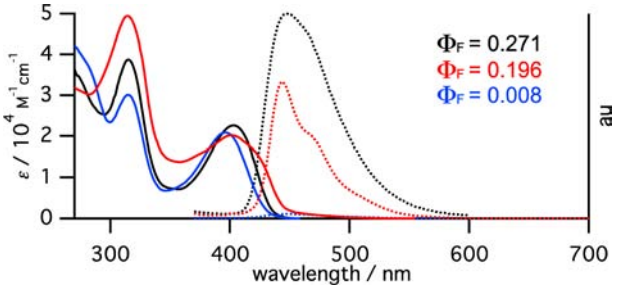


Figure 2. UV/vis absorption (solid) and fluorescence (dotted) spectra in CH_2Cl_2 (black: **2a**, red: **3**, blue: **5a**). The quantum yields of **3** and **5a** were determined by the reference value of **2a** (0.271) in CH_2Cl_2.

Next, the oxidation of **3** and **5a** was examined. Similar to **2a**, the oxidation of **5a** to the selenaporphyrin **5b** was accomplished by MnO_2 in 51% yield with a vivid color change from yellow to green (Scheme 3).[14] In contrast, the

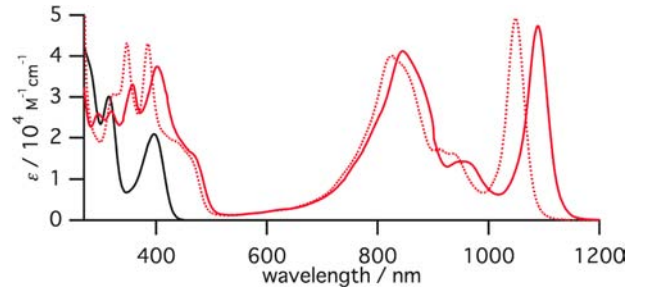
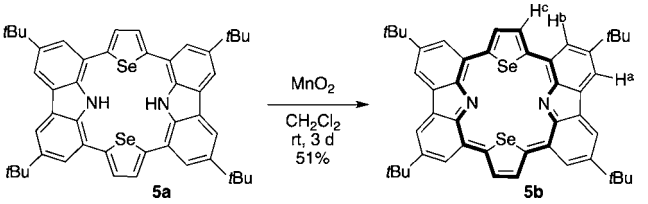


Figure 3. UV/vis/NIR absorption spectra in CH_2Cl_2 (black line: **5a**, red line: **5b**, red dotted line: **2b**).

Scheme 3. Synthesis of **5b**



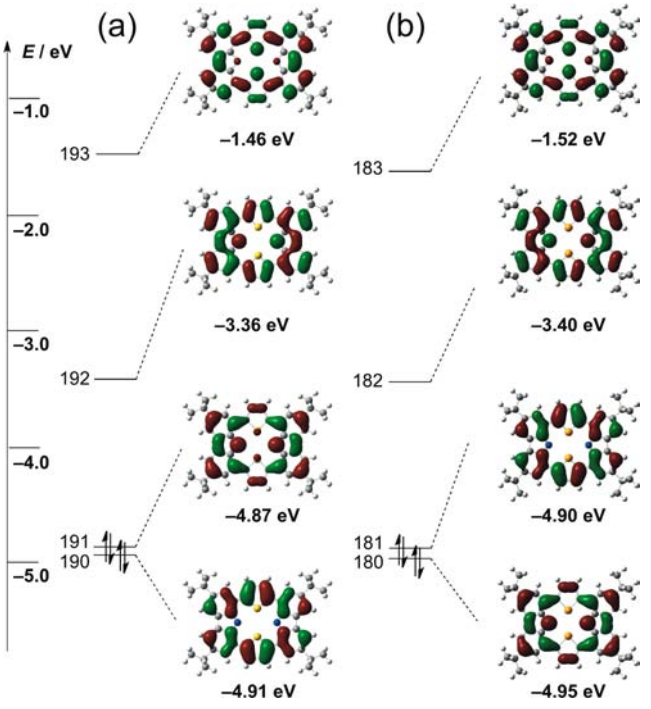


Figure 4. Molecular orbitals of (a) **2b** calculated at the B3LYP/6-31G(d) level and (b) **5b** calculated at the B3LYP/6-31G(d)/LANL2DZ level.

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oxidation of **3** to the corresponding oxaporphyrin did not occur.[15] In line with the dramatic transformation of its electronic state, the ^{1}H NMR spectrum of **5b** contained peripheral protons at 8.93 and 9.49 ppm for H^a and H^b and 10.07 ppm for H^c, indicating a diatropic ring current in **5b**. The UV/vis/NIR absorption spectrum of **5b** exhibited Q-like bands at 845, 952, and 1089 nm, which were more red-shifted in comparison to those of **2b** (Figure 3).[16] The oxidation and reduction potentials of **5b** then were investigated by cyclic voltammetry. The voltammogram of **5b** revealed reduction waves at −0.563 and −0.879 V and oxidation waves at 0.353, 0.505, and 0.973 V (Figure S5 in Supporting Information). A small electrochemical HOMO−LUMO gap (0.916 eV) was consistent with its optical HOMO−LUMO gap (1.14 eV).

DFT calculations were performed to help elucidate the electronic properties of **5b** (Figure 4).[17] Both **2b** and **5b** showed four orbitals characteristic of typical porphyrins, and the electronic coefficients were delocalized over the entire macrocycle. The orbital energies of **2b** and **5b** were similar, while the configurations of HOMO and HOMO−1 were conversed relative to each other. The LUMOs were stabilized, which made such red-shifted NIR absorption possible. Nuclear independent chemical shift (NICS) values at the center of the molecule were calculated to be +0.32 and −14.08 ppm for **5a** and **5b**, respectively. Collectively, these data indicate the distinct aromaticity of **5b**.

In summary, novel benzo-fused porphyrinoids **3** and **5a**, containing both carbazole and furan or selenophene moieties, were synthesized through a cyclization reaction. The MnO_2 oxidation of **5a** afforded **5b** which exhibited distinct aromaticity and NIR absorption. Further exploration of novel porphyrinoids and their metal complexes are currently underway.

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Supporting Information Available. Experimental procedures, compound data, and crystallographic data for **4** and **5a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

(15) We observed the decomposition of **3**.

(16) The fluorescence of **5b** was not observed upon excitation at 400 or 800 nm.

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