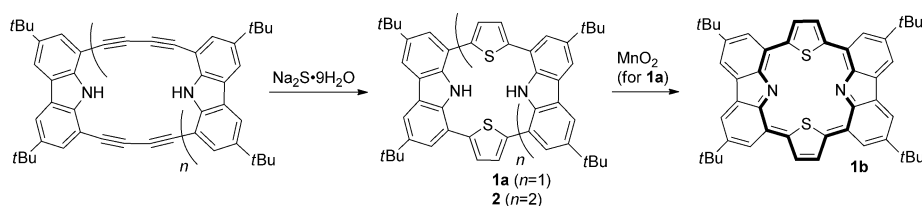


Synthesis and Characterization of Carbazole-Based Expanded Thiaporphyrins

Motoki Masuda and Chihiro Maeda*^[a]

Expanded porphyrins, composed of more than four pyrroles or other equivalent subunits, have received considerable attention as a result of their unique properties.^[1] Of particular interest is the extended π conjugation of these macrocycles, as compared to regular porphyrins, which may lead to the application of such compounds as photosensitizers^[2] and near-infrared (NIR) dyes^[3] as well as in photodynamic therapy^[4] and nonlinear optical devices.^[5] The conjugation system within a porphyrin may be extended by the introduction of ethynyl groups^[6] or by the fusion of aromatic rings to the porphyrin core.^[7] However, such peripheral modifications have rarely been applied to expanded porphyrins.^[8]

Carbazole-based materials have also been extensively studied due to their unique properties. They can be highly emissive and electron conducting and are also both chemically stable and capable of polymerization and metal-catalyzed cross-coupling.^[9] Because a carbazole is simply a benzene-fused pyrrole, the incorporation of carbazole units into fused porphyrins presents interesting possibilities. Despite the potential usefulness of such carbazole-based porphyrinoids, only a few examples have been reported to date.^[10–12] Recently, we reported a multiple annulation strategy, which allows the synthesis of novel porphyrinoids from 1,3-butadiyne-bridged cyclic carbazole oligomers (Scheme 1).^[10a]



Scheme 1. Synthesis of the carbazole-based porphyrins **1a**, **1b**, and **2**.

Among these, the tetrabenzofused core-modified porphyrin **1b** exhibits distinct aromaticity and NIR absorption due to extended π conjugation over the entire macrocycle. Following this work, we investigated the ring expansion of such core-modified porphyrins in order to obtain expanded porphyrins with extended conjugation systems. Herein, we report the synthesis and characterization of oligothiophene-bridged carbazoles as novel carbazole-based expanded thiaporphyrins.

The synthetic procedures used in this work are shown in Scheme 2. A combination of both coupling and annulation reactions played a key role in the synthesis of these oligothiophene-bridged species. Bisthiophene-bridged carbazoles were synthesized through Stille coupling. A solution of 3,6-di-*tert*-butyl-1,8-dibromocarbazole (**9**)^[13] and bis(tributylstannyl)bisthiophene in toluene in the presence of a catalytic amount of [Pd(PPh₃)₄] was heated to reflux for 12 h. After separation by gel permeation chromatography, the bisthiophene-bridged carbazole dimer **3** and the trimer **4** were obtained in 12 and 7.6% yields, respectively. Trithiophene-bridged carbazoles, however, were prepared in a manner similar to the synthesis of compound **1a**. The Glaser coupling reaction of 3,6-di-*tert*-butyl-1,8-bis(5-ethynylthien-2-yl)carbazole (**10**) and a subsequent annulation reaction with

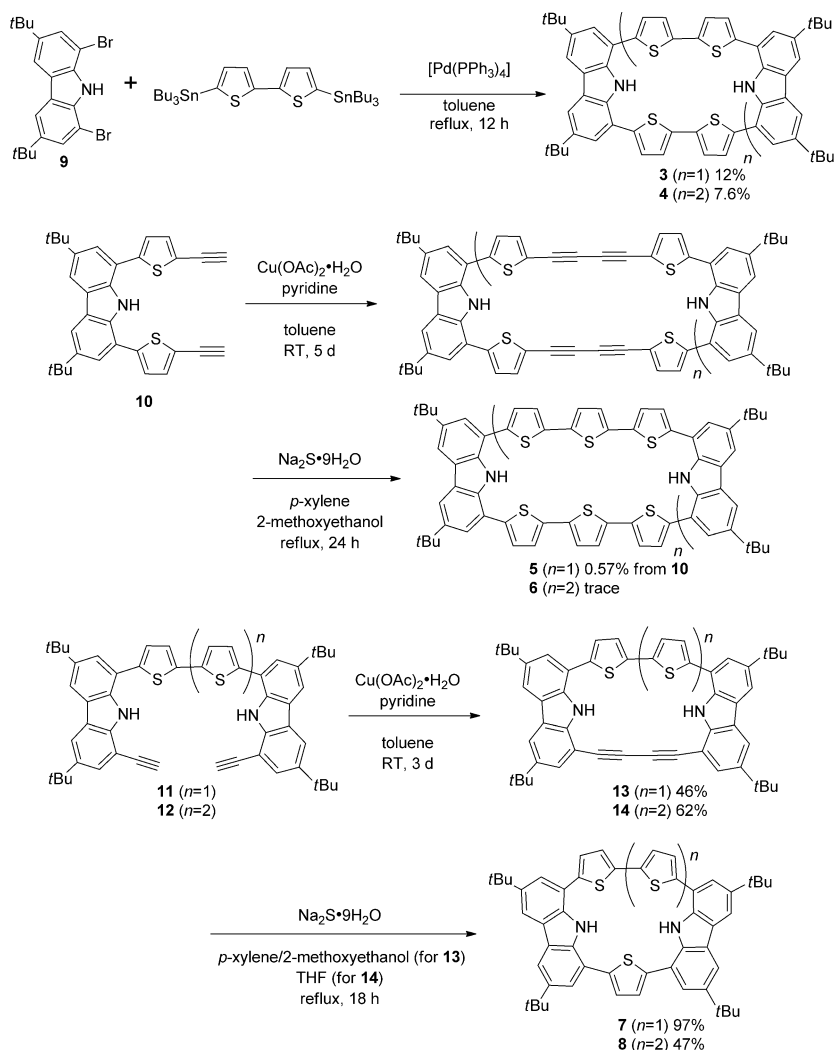
Na₂S^[14] provided the trithiophene-bridged carbazole dimer **5** and the trimer **6**. In addition, the carbazole dimers **7** and **8**, incorporating both thiophene and bisthiophene or trithiophene linkages, were also prepared. The intramolecular cyclization of compounds **11** and **12** were achieved by Glaser coupling under dilute conditions, resulting in either compound **13**

or compound **14**, respectively. Finally, the annulation reactions of **13** and **14** with Na₂S provided compounds **7** and **8**.

The structures of these compounds were characterized by both spectroscopic and X-ray diffraction analyses. The ¹H NMR spectra of these macrocycles were fully consistent with their proposed structures, with the exception of compound **5**. At room temperature, the NMR spectrum of this compound consists of rather broad, unresolved signals, whereas at 140 °C in [D₂]tetrachloroethane, a single set of peaks is evident (see the Supporting Information). These re-

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Scheme 2. Synthesis of compounds **3–8**.

sults suggest restricted rotation of the single bond linkages in **5** at ambient temperature and free rotation at higher temperatures. Slow vapor diffusion of methanol into a solution of **3** in dichloromethane provided crystals qualitatively suitable for analysis. X-ray diffraction analysis provided unambiguous elucidation of the structure of compound **3**, indicating that the four sulfur atoms are oriented towards the interior of the macrocycle (Figure 1a).^[15a] The lattice contains two independent molecules of compound **3**, which are coordinated through CH– π interactions (Figure S29 in the Supporting Information). The dihedral angles between the two carbazole planes are 37.1 and 13.2°, respectively. The structure of the cyclic compound **13** in the solid state was also confirmed by X-ray diffraction analysis (Figure 1b).^[15b] This lattice also contains two independent molecules of compound **13**, although the molecules are stacked through π – π interactions (Figure S30 in the Supporting Information). The dihedral angles between the two carbazole planes in this species are 16.9 and 16.2° and the mean plane deviations are 0.197 and 0.115 Å, indicating a highly planar structure.

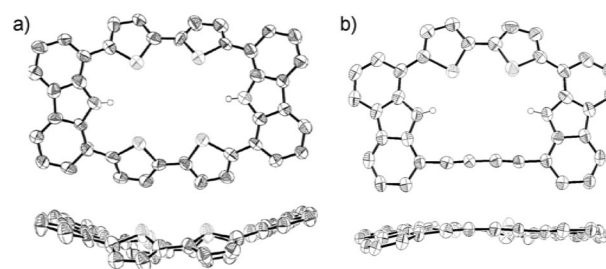


Figure 1. X-ray crystal structures of a) compound **3** and b) compound **13**; top view (top) and side view (bottom). *tert*-Butyl groups and hydrogen atoms (except for NH protons) are omitted for clarity. The thermal ellipsoids are at the 50% probability level.

0.5 V except for compound **8**, which shows a lower potential of 0.26 V. DFT calculations were performed to further clarify the structures and electronic properties of these compounds.^[16] Product **8** possesses the highest HOMO level, consistent with the cyclic voltammetry results. In addition, the LUMO level of **8** is exceptionally stabilized, resulting in

The UV/Vis absorption and fluorescence spectra of compounds **1a**, **3**, and **5** are relatively similar, although the emission maxima of those compounds show a distinct red shift going from **1a** to **3** to **5** as the number of thiophene spacers increases. In the case of the carbazole trimers, both absorption and fluorescence spectra show a red shift going from **2** to **4** to **6**. The spectrum of compound **7** is slightly red shifted and broadened in comparison to that of compound **1a**, whereas that of compound **8** exhibits an additional red-shifted band at $\lambda = 455$ nm. The quantum yields are reduced going from **1a** to **3** to **5**, whereas the other products simply display moderate yields with no distinct pattern.

Cyclic voltammetry of these products was carried out and the resulting oxidation potentials are summarized in Table 2. The cyclic voltammograms exhibited quasi-reversible oxidation potentials at approximately

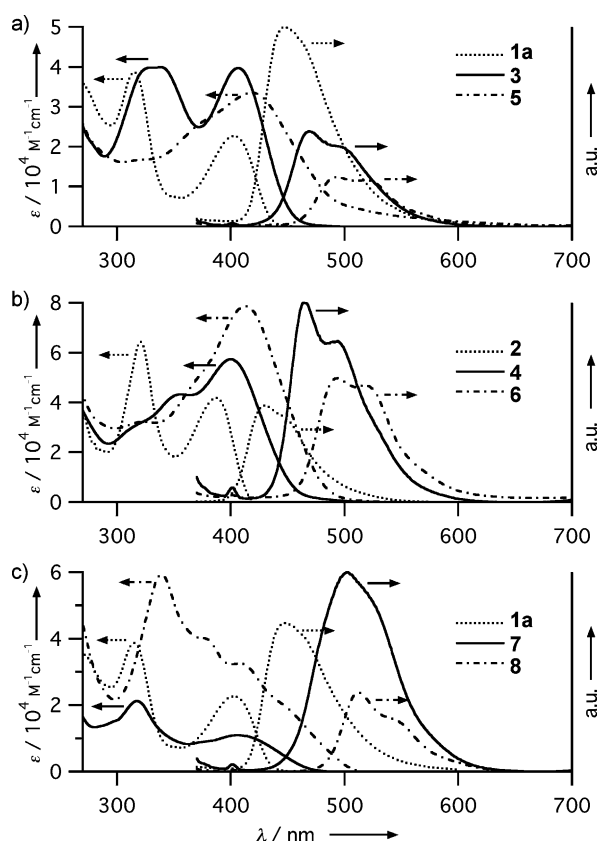


Figure 2. UV/Vis absorption (left axis) and fluorescence (right axis) spectra in CH_2Cl_2 . a) Compounds **1a**, **3**, and **5**. b) Compounds **2**, **4**, and **6**. c) Compounds **1a**, **7**, and **8**.

Table 1. Selected photophysical properties of compounds **1a** and **2–8** in CH_2Cl_2

	λ_A [nm]	λ_F [nm] ^[a]	Φ_F ^[b]
1a	315, 403	448	0.271 ^[c]
2	320, 386	432	0.144 ^[c]
3	329, 338, 407	469, 498	0.144
4	312, 356, 400	464, 494	0.311
5	318, 368, ^[d] 419	503, 532	0.065
6	322, ^[d] 413	494, 518	0.207
7	318, 406	502	0.370
8	339, 380, 408, 455 ^[d]	513, 541 ^[d]	0.139

[a] Excitation wavelengths are $\lambda = 360$ nm. [b] Fluorescence quantum yields were determined with reference to the value of **1a** (0.271) in CH_2Cl_2 . [c] Absolute fluorescence quantum yields with the excitation at $\lambda = 360$ nm. [d] Shoulder.

a narrow calculated HOMO–LUMO gap, which is also consistent with the results of absorption spectroscopy. The HOMO levels of these core-modified porphyrins exhibit electronic coefficients on the whole macrocycles, whereas the LUMO levels exhibit electronic coefficients predominantly on the thiophene moieties, which becomes more clear as the number of thiophene units increases, suggesting that such oligothiophenes will become stronger acceptors as the number of thiophene units increases (Figure S25 in the

Table 2. First oxidation potentials versus ferrocene/ferrocenium (Fc/Fc^+) (E_{ox1}),^[a] calculated HOMO and LUMO levels,^[b] and optical HOMO–LUMO gaps (ΔE_{opt})

	E_{ox1} [V]	HOMO [eV]	LUMO [eV]	$\Delta E_{\text{HOMO–LUMO}}$ [eV]	ΔE_{opt} [eV]
1a	0.47	−4.78	−1.56	3.22	3.08
2	0.56	−5.03	−1.76	3.27	3.21
3	0.49	−4.94	−1.59	3.35	3.05
4	0.51	−4.99	−1.77	3.22	3.10
5	0.49	−4.87	−1.85	3.02	2.96
6	0.35	−4.88	−1.95	2.93	3.00
7	0.64	−4.92	−1.74	3.18	3.05
8	0.26	−4.76	−2.08	2.68	2.76

[a] Determined by cyclic voltammetry; solvent: CH_2Cl_2 , supporting electrolyte: Bu_4NPF_6 (0.10 M), scan rate: 0.05 V s^{-1} . [b] Calculated at the B3LYP 6-31G* levels.

Supporting Information). The electron coefficients for the LUMO levels of compounds **7** and **8** are practically localized at the bithiophene moiety and the trithiophene moiety, respectively. These electrochemical results indicate that the broadened bands in the absorption spectrum of product **7**, as well as the additional band at $\lambda = 455$ nm observed for compound **8**, may be considered as resulting from intramolecular electron transfer.

Finally, the chemical oxidation of the dicarbazoles **3**, **5**, **7**, and **8** was investigated. In contrast to earlier results with **1a**, which was oxidized by MnO_2 to give **1b**, no changes were observed following the attempted oxidation of compounds **3**, **5**, **7**, and **8** with MnO_2 .^[17] Treatment of **1a**, **3**, **5**, **7**, and **8** with excess of NOSbF_6 , however, produced dramatic changes, with the reaction mixtures displaying NIR absorption bands in the region of $\lambda = 1000$ – 2000 nm (Figure 3). In

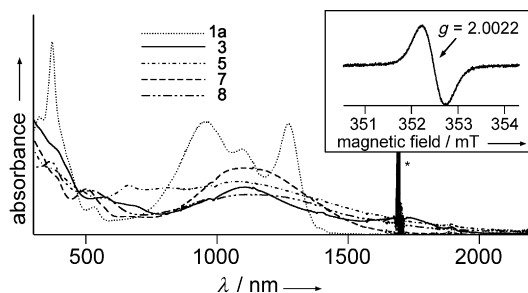


Figure 3. UV/Vis/NIR absorption spectra with NOSbF_6 in CH_2Cl_2 . The inset shows the ESR spectrum of compound **3** with NOSbF_6 in CH_2Cl_2 . The asterisk marks vibrational overtones of the solvent.

this case, the spectrum of **1a** is similar to that obtained previously for **1b**, exhibiting a Q-like band, whereas the spectra of compounds **3**, **5**, **7**, and **8** are instead relatively broad. Importantly, the spectrum resulting from **1a** with NOSbF_6 agrees with that obtained for a combination of **1b** with trifluoroacetic acid (TFA) (Figure S27 in the Supporting Information), indicating that reaction with NOSbF_6 results in the two-electron oxidation of **1a** to afford the protonation state of **1b**.^[18] The observation that the ESR spectrum of the re-

action solution of compound **1a** was silent further suggests that this is the case. Conversely, the ESR spectra of compounds **3**, **5**, **7**, and **8** with NOSbF_6 confirmed the presence of radical species with g values of 2.0022, 2.0020, 2.0024, and 2.0033, respectively (Figure 3 and Figure S28 in the Supporting Information), suggesting radical cations. Although these observations are typical for oligothiophenes,^[19] the absorption seen here is extremely red shifted, indicating that the π -conjugated network of compounds **3**, **5**, **7**, and **8** is effectively delocalize over the entire macrocycles in the oxidized state.

In summary, we have successfully synthesized carbazole-based expanded thiaporphyrins utilizing a coupling and annulation strategy. The structures and electronic properties of these macrocycles have been investigated by both spectroscopic methods and DFT calculations. These compounds were observed to undergo oxidation by NOSbF_6 , following which they exhibited significantly shifted NIR absorption. Further investigations involving novel carbazole-based porphyrinoids and their metal complexes are currently underway in our laboratory.

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Keywords: carbazoles • NIR absorption • π interactions • porphyrinoids • thiophenes

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- [15] a) Crystallographic data for compound **3**: formula: $\text{C}_{56}\text{H}_{54}\text{N}_2\text{S}_4$; $M_w = 883.25$; triclinic; space group: $P\bar{1}$; $a = 13.1318(4)$, $b = 18.7704(7)$, $c = 20.6485(6)$ Å; $\alpha = 97.2537(19)$, $\beta = 95.2711(18)$, $\gamma = 95.3477(19)^\circ$; $V = 4999.2(3)$ Å³; $Z = 4$, $\rho_{\text{calcd}} = 1.174$ g cm⁻³; $T = -180^\circ\text{C}$; 14207 measured reflections; 6329 unique reflections ($R_{\text{int}} = 0.1191$); $R_1 = 0.0994$ ($I > 2\sigma(I)$); $wR_2 = 0.2296$ (all data); GOF = 1.035. The contribution to the scattering arising from the presence of the disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package (see ref. [20]); b) Crystallographic data for compound **13**: formula: $4(\text{C}_{52}\text{H}_{50}\text{N}_2\text{S}_2) \cdot 2.54(\text{CCl}_2) \cdot 2(\text{O}) \cdot 1.06(\text{CO})$; $M_w = 842.77$; triclinic; space group: $P\bar{1}$; $a = 13.6379(3)$, $b = 19.9820(4)$, $c = 20.0082(4)$ Å, $\alpha = 112.6846(8)$, $\beta = 97.8256(8)$, $\gamma = 105.9883(9)^\circ$; $V = 4652.00(17)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.203$ g cm⁻³; $T = -180^\circ\text{C}$; 15722 measured reflections; 8532 unique reflections ($R_{\text{int}} = 0.0964$); $R_1 = 0.0927$ ($I > 2\sigma(I)$); $wR_2 = 0.2428$ (all data); GOF = 1.038. CCDC 884500 (**3**) and 884501 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

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