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Effective π-Extension of Carbazole-Based Thiaporphyrins by Peripheral Phenylethynyl Substituents

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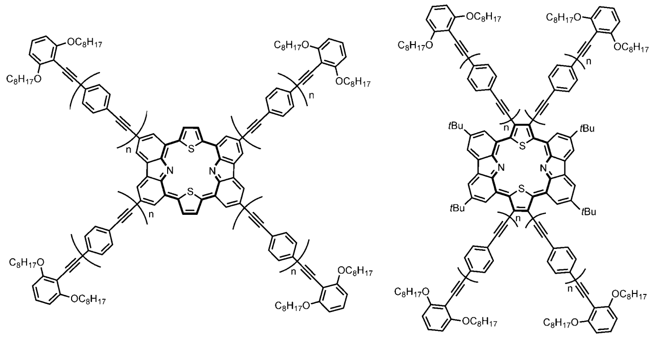
ABSTRACT



Several tetrakis(phenylethynyl)- and (phenylethynylphenylethynyl)-substituted carbazole-based thiaporphyrins were synthesized. These π-extended porphyrins display remarkably intensified and red-shifted absorption bands in the NIR region up to 1126 nm due to perturbation by the phenylethynyl substituents.

Fused porphyrins have received considerable attention due to their unusual optical and electronic properties.[1,2] 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 in photodynamic therapy,[3] nonlinear optical devices,[4] and photovoltaics.[5] These fused porphyrins are typically synthesized via intramolecular oxidative coupling reactions.

Carbazole derivatives have often been studied as novel materials since they are highly emissive, electron conducting, easily modified, and chemically stable.[6] Since carbazole is a benzene-fused pyrrole, its incorporation into fused porphyrins presents interesting possibilities.[7−9] Recently, we reported a multiple annulation strategy which allows the synthesis of novel porphyrinoids from 1,3-butadiyne-bridged cyclic carbazole oligomers.[10] Among these, the

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tetrabenzo-fused core-modified porphyrin **1** exhibits distinct aromaticity and near-infrared (NIR) absorption due to extended π-conjugation over the entire macrocycle. Following this work, we investigated further π-extension of carbazole-based porphyrins. Here we report the synthesis of carbazole-based porphyrins with phenylethynyl or phenylethynylphenylethynyl substituents (Figure 1).[11]

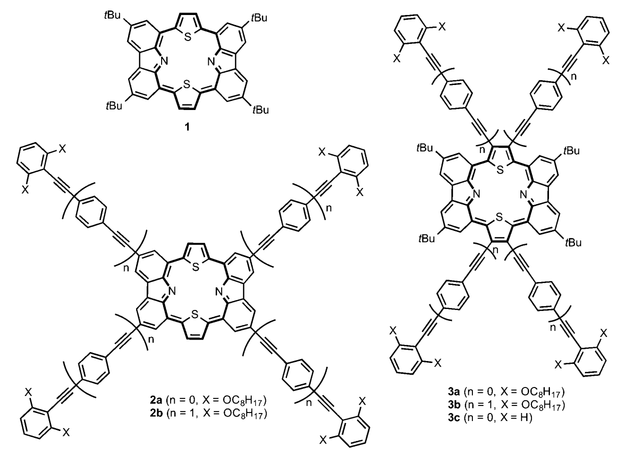

Figure 1. Structures of the carbazole-based porphyrins.

We initially attempted to synthesize **3c** but found it was not possible to isolate the compound, due to its very low solubility. In order to overcome this problem, octyloxy groups were introduced at the terminal phenyl rings as solubilizing groups to prevent aggregation of the products. The phenylethynyltin reagents **7** and **10** were prepared for this purpose, as shown in Scheme S1 in the Supporting Information. Alkylation of 2-iodoresorcinol with 1-bromooctane provided **4**, and the Stille coupling reaction of **4** with tributyl(trimethylsilylethynyl)tin and subsequent silyl deprotection of **5** gave **6**. Lithiation of **6**, followed by reaction with tributyltin chloride, afforded (2,6-dioctyloxyphenylethynyl)tributyltin (**7**), which was then coupled with 1-bromo-4-trimethylsilylethynylbenzene to provide **8**. Trimethylsilyl deprotection of **8**, followed by the stannylation of **9**, generated [4-(2,6-dioctyloxyphenylethynyl)-phenylethynyl]tributyltin (**10**).

Compounds **2a** and **2b**, both of which have four phenylethynyl substituents at the carbazole moieties, were subsequently synthesized as follows (Scheme 1). The Stille coupling reaction of 3,6-dibromo-1,8-bis(trimethylsilylethynyl)carbazole (**11**) with **7** provided **12a**. The trimethylsilyl protection was removed by tetrabutylammonium fluoride, and the Glaser coupling reaction of **13a** gave the cyclic carbazole dimer **14a**. The annulation reaction of **14a** with Na_2S provided the isophlorine **15a**.[12] Finally, **15a** was oxidized with MnO_2 to the thiaporphyrin **2a**. The phenylethynyphenylethynyl substituted thiaporphyrin **2b** was prepared from **11** in a similar manner by using **10** instead of **7**. The carbazole-based thiaporphyrins bearing phenylethynyl substituents at the thiophene moieties (**3a** and **3b**) were synthesized as follows. The Stille coupling reaction of the tetrabrominated isophlorine **16** with either **7** or **10** provided **17a** or **17b**, respectively. Although **17a** and **17b** were not oxidized by MnO_2, their reaction with PbO_2 afforded **3a** and **3b**, respectively. The ^1H NMR spectra of the isophlorines **15a**, **15b**, **17a**, and **17b** all exhibit NH peaks at $\delta = 10$ ppm, while the spectra of the oxidized thiaporphyrin products contain no NH signals and exhibit downfield shifts of the peripheral proton signals, indicating a ring current effect.

The UV/vis/NIR absorption spectra of **2a**, **2b**, **3a**, and **3b** all exhibit strong Q-like bands in the NIR region, which are red-shifted in comparison to the same bands of **1** (Figure 2). Interestingly, the central band in the **2a** spectrum (at 1030 nm) is more intense than the equivalent band of **1** (934 nm), while the most pronounced absorption band of **3a** (1111 nm) is more intense than the strongest band of **1** (1049 nm), suggesting that the phenylethynyl substituents result in critical perturbation. Importantly, the spectra of **2a** and **2b** are very similar, as are those of **3a** and **3b**, which indicates that the terminal phenylethynyl groups present in **2b** and **3b** make only minor contributions to the extent of π-conjugation over the macrocycle. In addition, upon excitation at 980 nm, **2a**, **2b**, and **3a** exhibited weak fluorescence with vibration bands at 1140 and 1170 nm (Figure S22 in Supporting Information).[13]

The redox potentials of these compounds were measured by cyclic voltammetry; the resulting electrochemical data are summarized in Table 1. The electrochemical HOMO−LUMO gaps of the substituted porphyrins are all smaller than that of **1**, which is consistent with the optical

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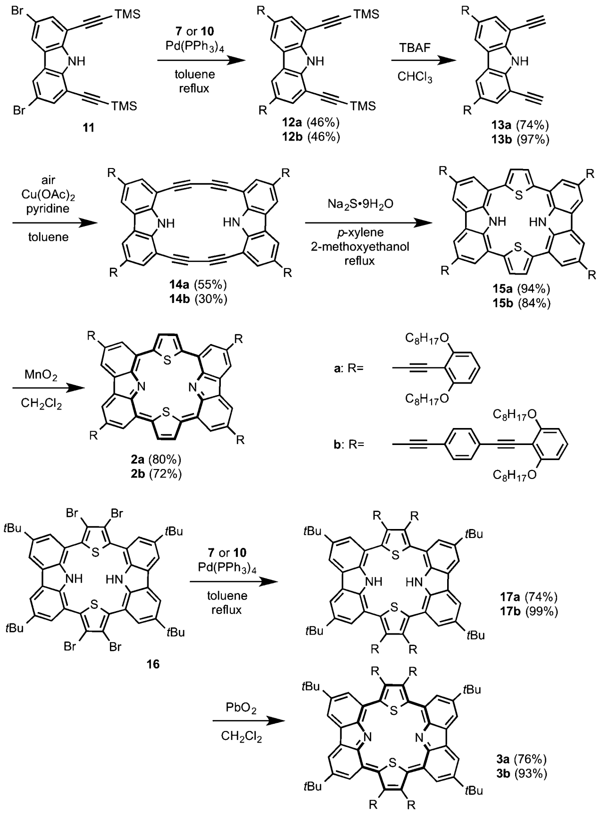
(13) The fluorescence was too weak to detect for **1** and **3b**. The fluorescence was not observed when excited at 400 nm.

Scheme 1. Synthesis of Carbazole-Based Porphyrins **2a**, **2b**, **3a**, and **3b**



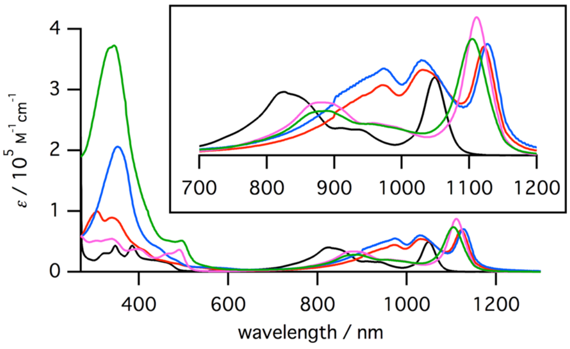


Figure 2. UV/vis/NIR absorption spectra in CH$_2$Cl$_2$ (black line, **1**; red line, **2a**; blue line, **2b**; pink line, **3a**; green line, **3b**). Inset shows the NIR region enlarged. The spectrum of **3b** is normalized.

Table 1. Electrochemical Results[a]

	E_{red1} (V)	E_{ox1} (V)	HOMO–LUMO $_{gap}$ ΔE_{CV} (eV)	HOMO–LUMO $_{gap}$ ΔE_{opt} (eV)
1	−0.552	0.424	0.976	1.18
2a	−0.418	0.356	0.774	1.10
2b	−0.361	0.376	0.737	1.10
3a	−0.584	0.364	0.948	1.11
3b	−0.388	0.417	0.805	1.12

[a] Solvent: CH$_2$Cl$_2$. Supporting electrolyte: Bu$_4$NPF$_6$ (0.10 M). Counter electrode: Pt. Reference electrode: Ag/Ag$^+$. Scan rate: 0.05 V/s. Accurate potentials were determined by the differential pulse voltammetry method (Supporting Information).

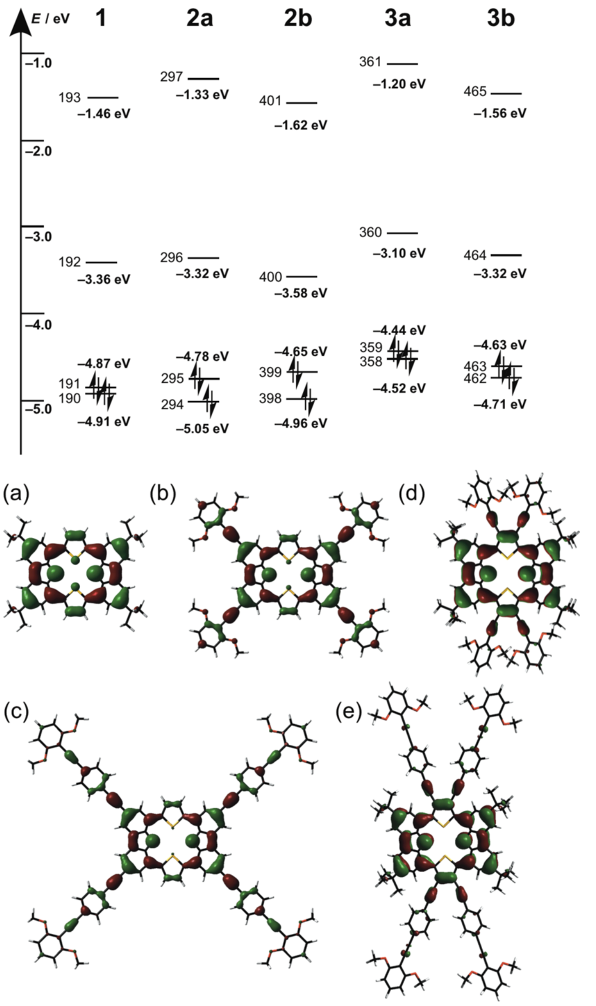


Figure 3. MO diagram and HOMOs of (a) **1**, (b) **2a**, (c) **2b**, (d) **3a**, and (e) **3b** calculated at the B3LYP/6-31G* level.

spectroscopy results.[14] DFT calculations were performed in order to further elucidate the structures and electronic properties of these compounds. In these studies, the octyloxy groups were replaced with methoxy groups in order to reduce the required calculations (Figure 3).[15] The calculated HOMO–LUMO gaps of the ethynylated porphyrins

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[14] There are differences between **3a** and **3b** in the ΔE_{CV} and between **2a** and **3a** in the reduction potentials although they show similar optical properties. This is probably because some favorable conformations exist in the oxidation state or in the reduction state and such species affect the electrochemical behaviors while the absorption spectra reflect the properties of the average structure.

are also smaller than that of **1**. As previously reported, the HOMO of **1** exhibits large electronic coefficients both at the 3,6-positions of the carbazoles and at the thiophene moieties, suggesting that efficient substituent effects occur at these positions. The HOMOs of **2a** and **3a** exhibit electronic coefficients not only at their macrocycles but also at the phenylethynyl moieties, demonstrating effective electronic delocalization. Conversely, the electronic coefficients associated with the terminal phenyl rings of **2b** and **3b** are negligible. From these results, and considering the UV/vis/NIR absorption spectra, we may conclude that directly substituted phenylethynyl groups perturb the macrocycles, whereas the contributions of the terminal phenylethynyl groups of **2b** and **3b** to the macrocyclic π-conjugation are minimal.

In summary, we have synthesized several phenylethynyl and phenylethynylphenylethynyl substituted carbazole-based thiaporphyrins. The photophysical and electrochemical analysis of these products, along with DFT calculations, confirmed effective π-extension resulting from the addition of the phenylethynyl substituents. Further exploration of novel porphyrinoids and their metal complexes is currently underway in our laboratory.

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Supporting Information Available. Experimental procedures and compound data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.