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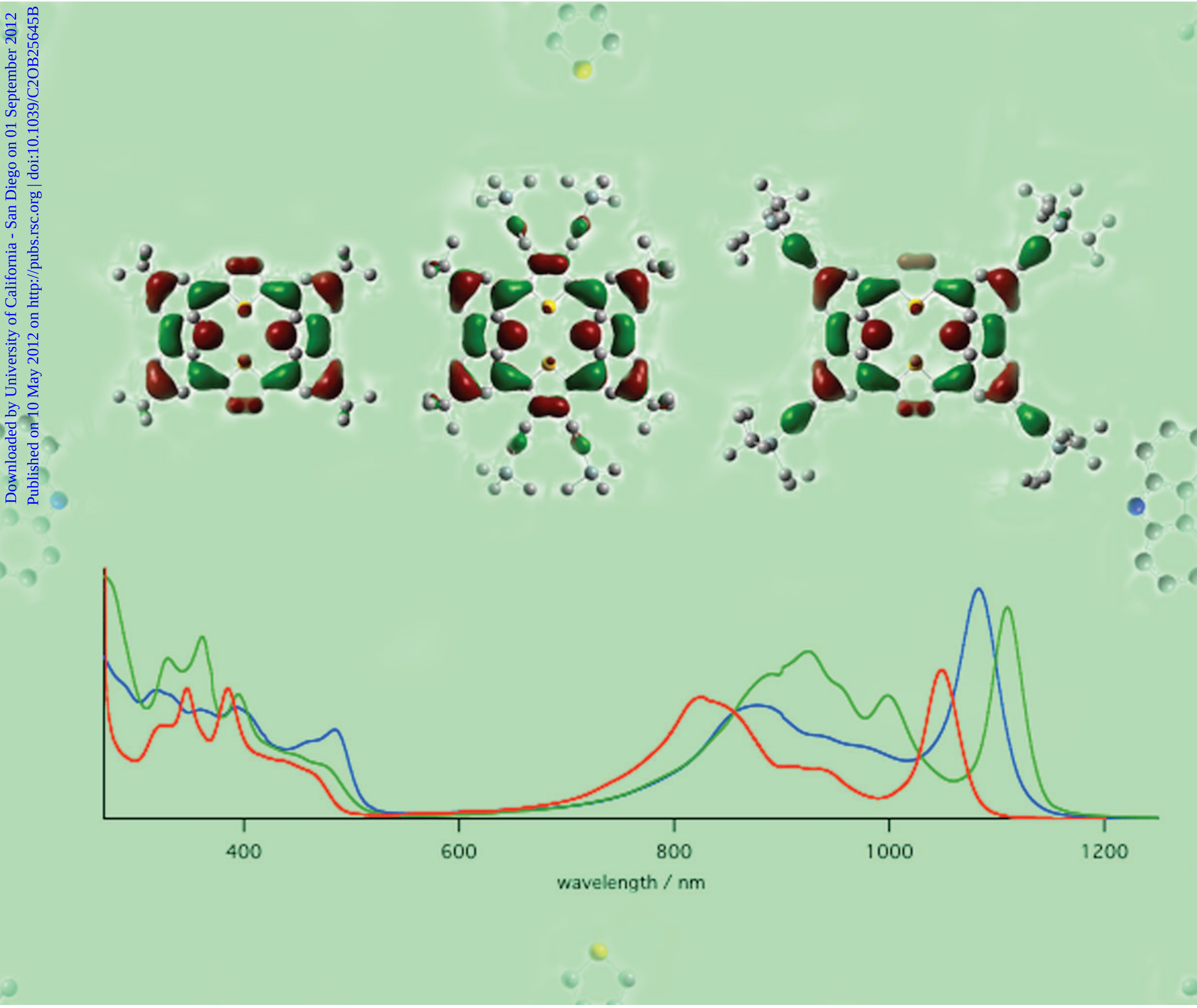

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Peripherally ethynylated carbazole-based core-modified porphyrins†

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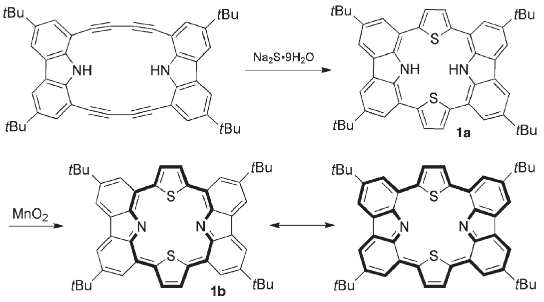
Peripherally ethynylated carbazole-based core-modified porphyrins were synthesized by sequential metal-catalyzed coupling and annulation reactions. Experimental results and DFT calculations both confirm that the π-conjugated networks of the resulting porphyrins effectively delocalize over the entire macrocycle, including the ethynyl substituent groups.

Significant effort has been devoted to the synthesis of porphyrins and porphyrinoids. Both are of exceptional importance in various biological processes, such as photosynthesis, and have numerous applications in catalysis, anion sensing and optical devices.[1] One of the most intriguing aspects of porphyrin chemistry is the potential for expansion of the π-conjugated system within the molecule, since such extended conjugation allows tailoring of the various useful properties of these macrocycles. To date, this expanded conjugation has been achieved by the introduction of acetylene moieties,[2] the fusion of aromatic rings,[3] and ring expansion.[4]

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 catalysed cross coupling.[5] Since a carbazole is simply a benzene-fused pyrrole, the incorporation of carbazole units into fused porphyrins presents interesting possibilities. However, despite the potential usefulness of such carbazole-based porphyrinoids, only a few examples have been reported to date.[6,7] Recently, we reported a multiple annulation strategy which allows the synthesis of novel porphyrinoids from 1,3-butadiyne-bridged cyclic carbazole oligomers (Scheme 1).[8] Among these, the tetrabenzo-fused core-modified porphyrin **1b** exhibits distinct aromaticity as well as near infrared (NIR) absorption up to 1050 nm. It is evident that the π-conjugated circuit of **1b** can be considered as an expanded 34 π electron system, the presence of which is likely responsible for the significant red-shifted absorption of this molecule. The addition of various substituent groups to this macrocycle is seen as a means to further modify its optical and electronic properties. As a result of pursuing this strategy, we report the peripheral ethynylation of the core-modified porphyrin **1b**.



Scheme 1 Synthesis of **1a** and **1b**.

Initial work focused on the peripheral functionalization of **1a**. Reaction of **1a** with Br_2 resulted in a mixture of several brominated products which could not be readily separated from one another. However, treatment of **1a** with 5 equiv. of NBS gave the tetrabrominated compound **2** in 88% yield. The Stille coupling reaction of **2** with tributyl(trimethylsilylethynyl)tin provided the tetrakis(trimethylsilylethynyl)-substituted product **3a**. Slow diffusion of methanol vapor into a dichloromethane solution of **3a** produced crystals with quality suitable for X-ray diffraction analysis. The crystal structure data resulting from this analysis provides unambiguous elucidation of the structure of **3a**, confirming the presence of four trimethylsilylethynyl substituents at the thiophene moieties (Fig. 1).‡ Product **3a** was next oxidized to **3b** using MnO_2. Subsequently, a series of synthetic procedures was performed in order to attach ethynyl groups to the carbazole moieties. The intermediate 3,6-dibromo-1,8-diiodocarbazole (**4**) was first prepared from 3,6-dibromocarbazole by reaction with iodine monochloride. The Sonogashira coupling reaction of **4** with trimethylsilylacetylene provided 3,6-dibromo-1,8-bis(trimethylsilylethynyl)carbazole (**5**). The bromo substituents of **5** were converted into triisopropylsilylethynyl groups through a Stille coupling reaction. The trimethylsilyl protecting groups of **6** were then selectively removed by reaction with 2.5 equiv. of tetrabutylammonium fluoride to give **7**. The Glaser coupling reaction of **7** gave the cyclic carbazole dimer **8** in 27% yield. Finally, the double annulation reaction of **8** with Na_2S afforded **9a**.[9] The high-resolution electrospray-ionization (HR-ESI) mass spectrum of **9a** exhibited the parent ion peak at $m/z = 1214.6260$ (determined from $C_{76}H_{97}N_2S_2Si_4$ $[M–H]^- = 1214.6207$). Similar to **3a**, **9a** was oxidized to **9b** using MnO_2 (Scheme 2) .

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† Electronic supplementary information (ESI) available: Experimental details and compound data. CCDC 871499. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25645b

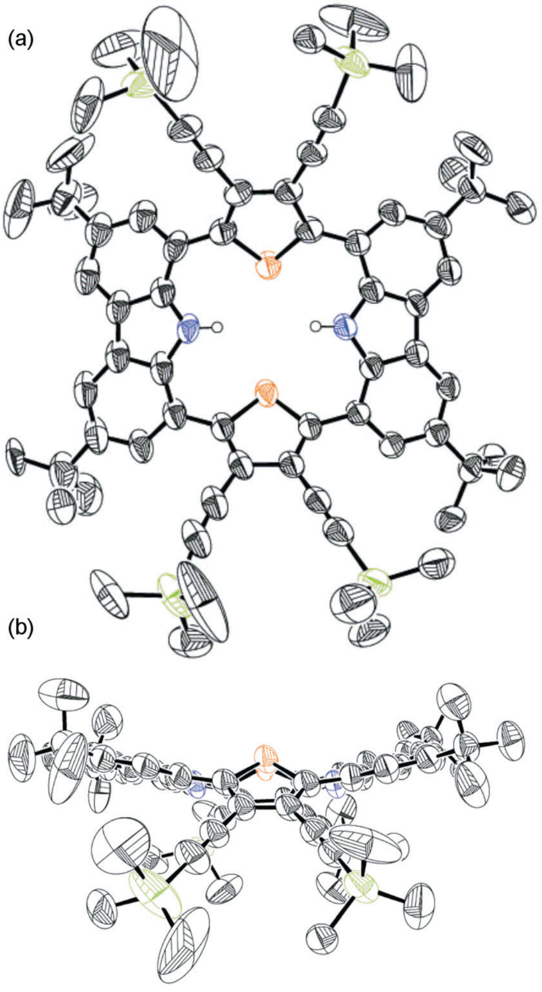
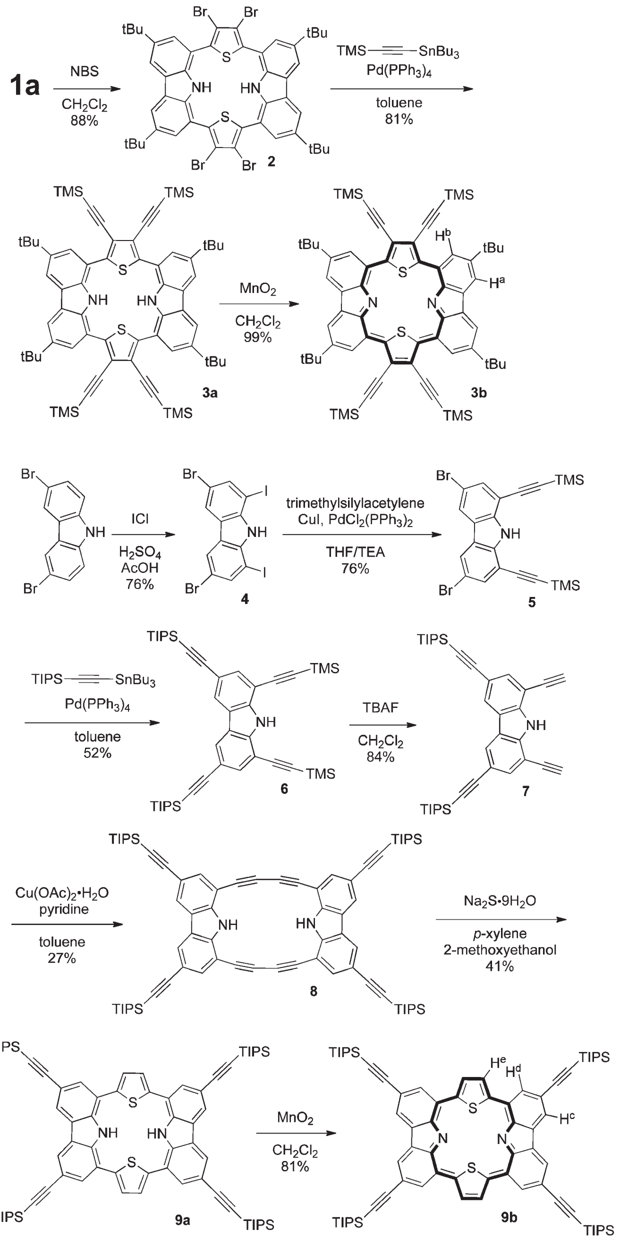


Fig. 1 X-ray crystal structure of **3a**: (a) top view and (b) side view. Hydrogen atoms except for NH protons are omitted for clarity. The thermal ellipsoids were at the 50% probability level.

The ^{1}H NMR spectra of **3b** and **9b** show considerable downfield shifts for the peripheral protons; for **3b**, H^a and H^b appear at 10.48 and 8.65 ppm, respectively, and for **9b**, H^c, H^d and H^e appear at 9.08 and 8.97 ppm and 8.42 ppm, respectively, indicating strong diatropic ring currents (ESI†). The UV-vis absorption spectra of **3b** and **9b** display intensified and extremely red-shifted Q-like bands at 877, 976, and 1083 nm for **3b**, and 925, 998, and 1110 nm for **9b**.[10] These bands display a greater degree of red-shift as compared to those of the previously synthesized compound **1b** (Fig. 2). The absorption red-shift observed for **9b** suggests that the π-conjugation system of this core-modified porphyrin has expanded considerably, extending up to the benzo moieties. Additionally, the molar absorption coefficient of Soret-like bands for these core-modified porphyrins is significantly lower than that for regular porphyrin.[11]

The oxidation and reduction potentials of **3b** and **9b** were measured by cyclic voltammetry and the resulting voltammograms, along with that of **1b**, are shown in Fig. 3. Product **3b** exhibits oxidation waves at 0.53 and 1.01 V with reduction waves at −0.41 and −0.73 V, while **9b** shows oxidation waves at 0.62, 0.83, and 1.15 V with reduction waves at −0.32, and −0.57 V. Both the first oxidation and reduction potentials



Scheme 2 Synthesis of tetraethynyl-substituted porphyrins **3a**, **3b**, **9a**, and **9b**.

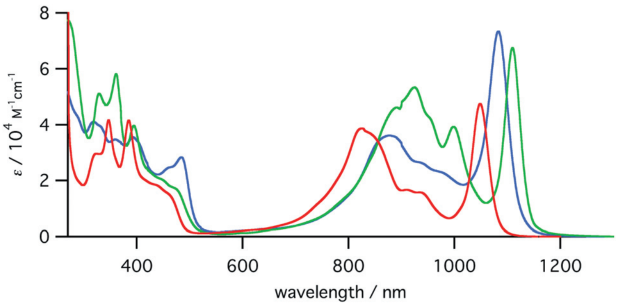


Fig. 2 UV/Vis/NIR absorption spectra of **1b** (red), **3b** (blue), and **9b** (green) in CH_2Cl_2.

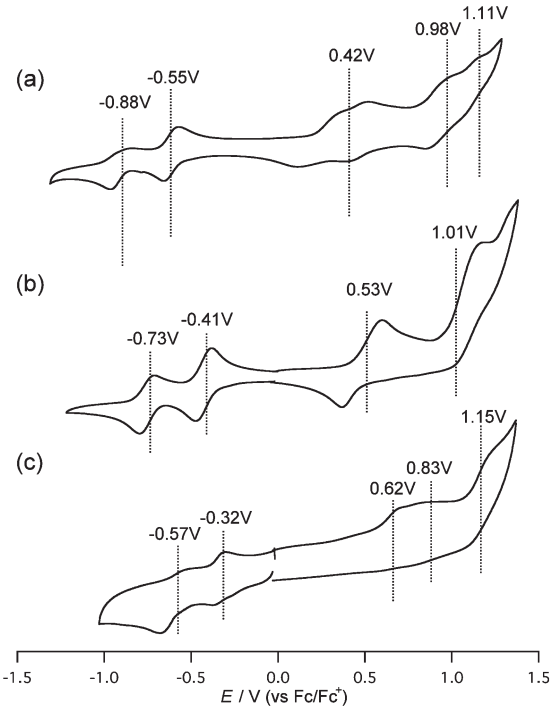


Fig. 3 Cyclic voltammograms of (a) **1b**, (b) **3b**, and (c) **9b** (solvent: CH_2Cl_2, supporting electrolyte: Bu_4NPF_6 (0.10 M), counter electrode: Pt, reference electrode: Ag/Ag$^+$, scan rate: 0.05 V s^{-1}). Accurate potentials were determined by the differential pulse voltammetry method (ESI†).

increase in the order of **1b** to **3b** to **9b**. The electrochemical HOMO–LUMO gaps of **3b** and **9b** are evidently narrower than that of **1b**, indicating that the introduction of the ethynyl groups reduces the HOMO–LUMO gap.

Finally, DFT calculations at the B3LYP 6-31G* level were performed in order to obtain additional information concerning the electronic properties of these core-modified porphyrins (Fig. 4).[12] Results of these calculations show that both HOMO and LUMO levels are stabilized going from **1b** to **3b** to **9b**, which is consistent with the results of cyclic voltammetry. Importantly, the HOMO levels of both **3b** and **9b** exhibit large electronic coefficients not only on the core macrocycles, but also on the ethynyl moieties, indicating that the electronic π electron networks of **3b** and **9b** extend up to these ethynyl groups. The nucleus-independent chemical shift (NICS) values at the centers of these macrocycles were calculated as −11.09 for **1b**, −10.03 for **3b**, and −10.16 for **9b**. These NICS results, along with the ^{1}H NMR data, indicate that **3b**, **9b**, and **1b** are all strongly aromatic.[13]

Conclusions

In summary, carbazole-based core-modified porphyrins bearing ethynyl substituents on their thiophene or carbazole moieties (**3b** and **9b**) have been synthesized *via* a series of metal-catalyzed coupling and annulation reactions. The effects of adding such ethynyl substituents have been determined based on the results of both experimental work and theoretical calculations. These results demonstrate that the π-conjugated networks of these core-modified porphyrins are extended over the entire macrocycles, including the peripheral ethynyl groups. Further investigations concerning the synthesis and functionalization of novel carbazole-containing porphyrins are currently under way in our laboratory.

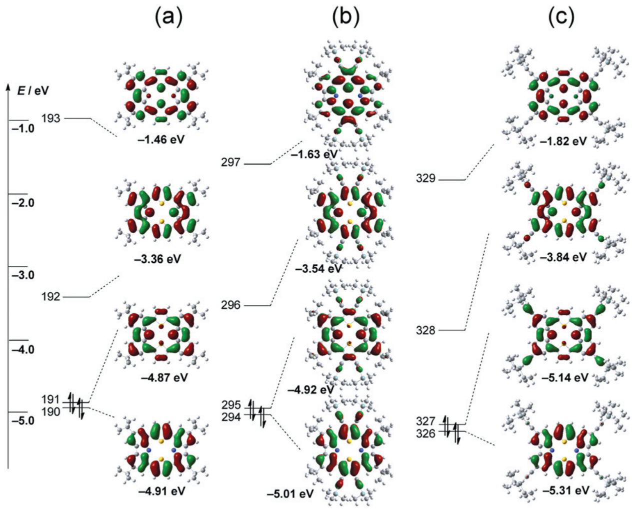


Fig. 4 Molecular orbital diagrams of (a) **1b**, (b) **3b**, and (c) **9b** calculated at the B3LYP 6-31G* levels.

Acknowledgements

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Notes and references

‡ Crystallographic data for **3a**: $C_{68}H_{82}N_2S_2Si_4$, M = 1103.84, monoclinic, space group $P21/n$ (14), a = 19.3107(4), b = 17.0190(4), c = 23.1391(4) Å, β = 93.5198(10)°, V = 7590.3(3) Å^3, Z = 4, ρ_{calcd} = 0.966 g cm^{-3}, T = −180 °C, 10 918 measured reflections, 7314 unique reflections (R_{int} = 0.0798), R_1 = 0.0991 ($I > 2\sigma(I)$), wR_2 = 0.2981 (all data), GOF = 1.150. CCDC 871499 **3a** contains the supplementary crystallographic data for this paper. The contribution to the scattering arising from the presence of disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package.[14]

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