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Aromaticity

β-Octamethoxy-Substituted 22π and 26π Stretched Porphycenes: Synthesis, Characterization, Photodynamics, and Nonlinear Optical Studies

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Abstract: Three *meso*-expanded tetrapyrrolic aromatic macrocycles, including 22π and 26π acetylene–cumulene bridged stretched octamethoxyporphycenes and octamethoxy[22]porphyrin-(2.2.2.2), are reported, for the first time, by modification of previously reported synthetic methods. This strategy led to an enhancement in the overall yield of their corresponding octaethyl analogues. The methoxy-substituted expanded porphycenes display slightly blueshifted absorption relative to their ethyl analogues, along with very weak fluorescence, probably due to efficient intramolecular charge transfer (ICT). Additionally, the two-photon absorption (TPA) cross sections of these macrocycles were evaluated; these are strongly related to core expansion of the porphyrin aromaticity through increased *meso*-bridging carbon atoms as well as conformational flexibility and substitution effects at the macrocyclic periphery. In particular, the octamethoxy stretched porphycenes display strong TPA compared with the octaethyl analogues due to the dominant ICT character of methoxy groups with a maximum TPA cross section of 830 GM at 1700 nm observed for 26π-octamethoxyacetylene–cumuleneporphycene.

Introduction

Expanded porphyrins endowed with a larger central core have more than 16 atoms.[1] These synthetic analogues can be schematically derived either by increasing the number of *meso*-methine groups or by introducing additional heterocyclic rings into the conjugation pathways. As a result of core expansion, these expanded porphyrins often possess novel spectral and electronic features, unprecedented capability to coordinate both cations and anions, and unique structures with nonplanar figure-of-eight motifs.[1] This success in pioneering a new area of porphyrin chemistry motivated researchers to investigate expanded porphycenes because the structures and photophysical properties of porphycenes are more sensitive than those of porphyrins.[2] In this direction, core expansion of porphycenes by using an even number of bridging *meso*-carbon atoms between the constituent pyrrole units was reported by Vogel et al. in 1990.[3] Owing to the occurrence of pairwise linear $C_{sp^2}C_{sp}C_{sp}C_{sp^2}$ structural units, the resultant macrocycles are called acetylene–cumulene porphyrinoids, whereas the corresponding reduced product [22]porphyrin-(2.2.2.2)[4] is named a stretched porphycene, owing to its closer relationship to porphycene. Although these macrocycles were anticipated to have potential utility as an effective photosensitizer for photodynamic therapy (PDT), previous reports showed limitations in their application because of their low triplet energy gap, and hence, poor singlet oxygen generation ability.[5] Also, porphycenes have recently emerged as promising candidates for third-order nonlinear optical (NLO) materials.[6] However, to the best of our knowledge, there no reports have illustrated NLO studies on their expanded analogues.

In this regard, we have synthesized two new acetylene–cumulene porphyrinoids with 22π and 26π aromatic conjugation pathways and a new [22]porphyrin-(2.2.2.2) derived from 3,4-dimethoxypyrrole by modification of previously reported synthetic methods, by which we could enhance the yields of their ethyl analogues. Additionally, we have investigated their third-order NLO properties along with substituent effects on their structures, photophysical properties, and electrochemical properties.

Results and Discussion

Synthesis of expanded porphycenes

Syntheses of 22π and 26π aromatic acetylene–cumulene porphyrinoids was achieved by McMurry coupling of the corresponding mono- and diacetylenic bipyrroledialdehydes. They were synthesized from mono- and diacetylene-bridged bipyr-

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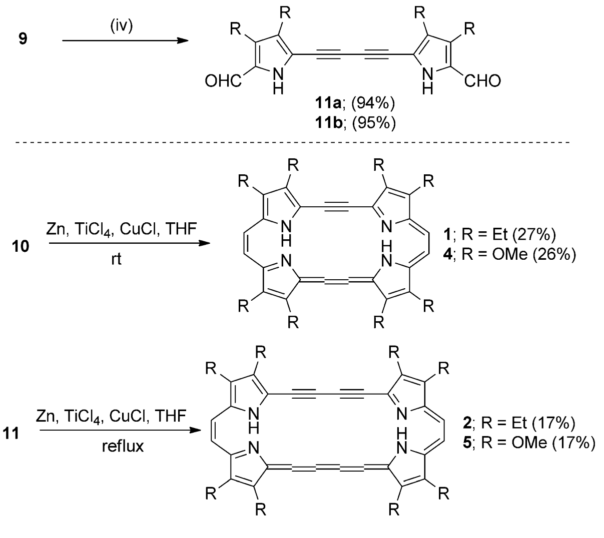
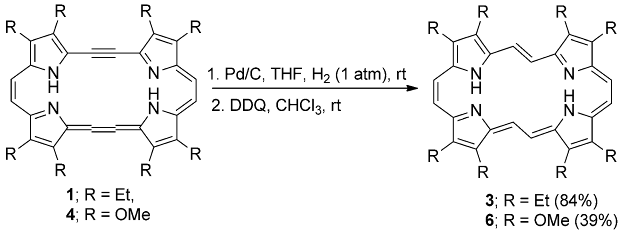
role dialdehyde precursors, which were synthesized by using a modified method reported in the literature, starting from iodopyrrole aldehydes **7a** (see the Supporting Information) and **7b**[7] (Scheme 1). Briefly, Sonogashira coupling of **7a** and **7b** with trimethylsilylacetylene in the presence of [PdCl$_2$(PPh$_3$)$_2$] and CuI led to trimethylsilylacetylinic pyrrole aldehydes **8a** and **8b** in 87 and 88% yield, respectively. Subsequent removal of the trimethylsilyl group with TBAF provided acetylenic pyrrole derivatives **9a** and **9b** in 97 and 99% yield, respectively, at room temperature.[8] Sonogashira coupling of **9a** and **9b** led to the successful synthesis of acetylene-bridged bipyrroledialdehydes **10a** and **10b** in 62 and 89% yield, respectively.[8] To improve the yield of the desired product, we employed a modified Glaser–Hay coupling protocol, in which oxidative coupling of **9a** and **9b** in the presence of a catalytic amount of [PdCl$_2$(PPh$_3$)$_2$] and CuI with a base under an oxygen atmosphere led to the desired diacetylene-bridged bipyrroledialdhydes **11a** and **11b** in 94 and 95% yield at room temperature, respectively. McMurry coupling of **10b** with Zn/TiCl$_4$ in the presence of CuCl under reflux conditions, followed by oxidation in air gave desired β-octamethoxy 22π-acetylene–cumuleneporphycene **4** in very poor yield with reduced 22π β-octamethoxy[22]porphyrin-(2.2.2.2) **6** as the major product.[3] Because the 3,4-dimethoxypyrrole analogue is a highly activated system, we performed the McMurry coupling reaction by slow addition of **10b** at room temperature and this modification led to the formation of the desired product **4** as the major product and reduced products as a minor component. Although it was difficult to purify the mixture of products by column chromatography, we could obtain pure compound **4** in 26% yield (Scheme 1), by simply washing with hexane and chloroform (1:1). Interestingly, the McMurry coupling of **10a** in the same manner resulted in the exclusive formation of the desired 22π-β-octaethylacetylene–cumuleneporphycene **1** without any additional reduced products. The 27% yield in this reaction was much improved compared with that reported by Vogel et al. (18%).[3] Syntheses of 26π-β-octasubstituted acetylene–cumuleneporphycenes (**2** and **5**) were achieved by McMurry coupling of diacetylene-bridged bipyrroledialdhydes **11a** and **11b** under reflux conditions; this led to the formation of compounds **2** and **5** both in 17% yield. Again our method led to the formation of **2** in much higher yield than that reported by Vogel et al. (9%).[5]



Scheme 1. Synthesis of 22π and 26π expanded acetylene–cumuleneporphycenes. Reagents and conditions: i) [PdCl$_2$(PPh$_3$)$_2$] (4 mol%), CuI (8 mol%), THF, 50 °C; ii) tetrabutylammonium fluoride (TBAF), THF, RT; iii) [PdCl$_2$(PPh$_3$)$_2$] (4 mol%), CuI (8 mol%), THF, reflux; iv) [PdCl$_2$(PPh$_3$)$_2$] (5 mol%), CuI (10 mol%), O$_2$, THF, RT.

22π-Acetylene–cumuleneporphycenes (**1** and **4**) were reduced with Pd/C in the presence of 1 atm of H$_2$ gas followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which gave [22]porphyrins-(2.2.2.2) (**3** and **6**) in good yield (Scheme 2). Octamethoxy-substituted acetylene–cumuleneporphycene **4** undergoes a relatively slow reduction (48 h) compared with the octaethyl analogue (20 h). Our method shows an distinct advantage over the method reported by Vogel et al., which used Lindlar catalyst (35% yield),[4] with much improved yield of **3** (84%). A moderate yield for **6** may be attributed to the longer reaction time. Furthermore, the direct reductive McMurry coupling of 3,4-dimethoxypyrrole-2,5-dialdehyde[9] led to **6** in 1.4% yield as the only non-polymer product.[4]



Scheme 2. Synthesis of [22]porphyrins-(2,2,2,2).

^{1}H NMR spectroscopy analysis of expanded porphycenes

The macrocycles revealed aromatic features in the ^{1}H NMR spectra because the outer *meso* protons were shifted downfield and the inner NH protons were shifted upfield. The ^{1}H NMR spectrum of **4** indicates that the *meso* protons are marginally perturbed, whereas the NH protons are significantly shifted upfield ($\delta = 0.86$ ppm), in comparison to the octaethyl analogue **1** ($\delta = 2.19$ ppm). This may be attributed to increased electron density in the aromatic core of **4** due to the increased electron-donating ability of methoxy substituents at its periphery. A similar trend is also observed for **26π-acetylene–cumuleneporphycene analogues, in which the NH protons are shifted upfield by 1.19 ppm for the methoxy analogue ($\delta = 0.77$ ppm for **5** and $\delta = 1.96$ ppm for **2**). Similar to octaethyl analogue **3**, octamethoxy[22]porphyrin-(2.2.2.2) **6** displays outer *meso*-Hs at C-5, 11 and 12 that are shifted downfield, whereas the inner *meso*-H at C-6 is shifted upfield. For example, in the case of **6**, the H-5 protons are shifted downfield by 0.21 ppm ($\delta = 11.98$ ppm for **6** and $\delta = 11.77$ ppm for **3**), the H-6 protons are shifted upfield by 0.5 ppm ($\delta = -7.97$ ppm for **6** and $\delta = -7.47$ ppm for **3**), and the NH protons are shifted upfield by 0.5 ppm ($\delta = 0.83$ ppm for **6** and $\delta = 1.33$ ppm for **3**); these results clearly indicate a stronger substituent effect for this class of macrocycles than those of the acetylene–cumulene types.

Structural analysis of expanded porphycenes

The molecular structures of **4** and **6** were characterized by X-ray crystallography (Figure 1).[10] The crystal structure of expanded porphycene **4** possesses a near-planar macrocyclic core with a mean deviation of 0.05 Å for the nitrogen atoms from the average macrocyclic plane. The structure of the acetylene–cumulene bridge $C_{sp^2}C_{sp}C_{sp}C_{sp^2}$ appears to be equivalent on both sides of **4**, which suggests that **4** exists in the form of a resonance hybrid. The nitrogen atoms of **4** form a rectangular core similar to that in **1**, with N1···N2 and N2···N3 distances of 5.355 and 2.608 Å, respectively. X-ray crystal-structure analysis of **6** confirms the *cis*, *trans*, *cis*, *trans* configuration of the compound; however, the core of this macrocycle is slightly more distorted (0.087 Å) than **3** (0.05 Å) with a mean deviation of the nitrogen atoms from the mean ring plane.[4] The four nitrogen atoms of **6** define a near-parallelogram core geometry (N1-N2-N3 = 77.9°, N1-N4-N3 = 77.8°).

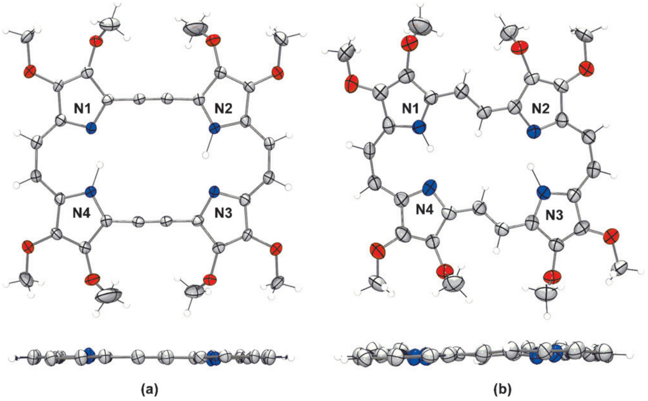


Figure 1. X-ray crystal structures of a) **4** and b) **6** (top: front view, bottom: side view) scaled to the 35 % probability level. In the side views, the methoxy groups are omitted for clarity. Color code: C, gray; N, blue; O, red; H, white.

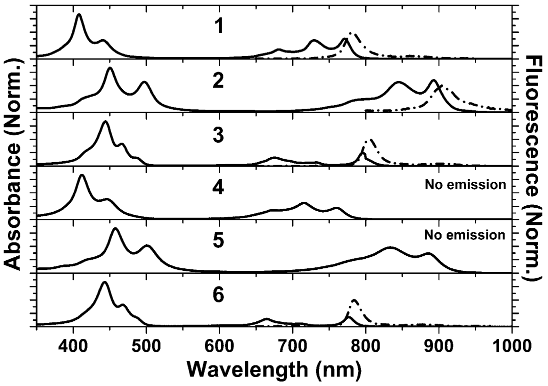


Figure 2. Normalized UV/Vis absorption (——) and fluorescence spectra (–•–•) of compounds **1**–**6** in chloroform.

Absorption and emission properties

The UV/Vis absorption and fluorescence spectra of compounds **1**–**6** were recorded in chloroform at room temperature (Figure 2 and Figures S16 and S17 in the Supporting Information). The introduction of acetylene spacers into the bipyrrolic units of octamethoxyporphycene[7] gives rise to a huge change in the UV/Vis absorption spectra. Both the split Soret and Q bands are bathochromically shifted for **4** and **5** relative to those of octamethoxyporphycene, due to the increased conjugation pathway (22π and 26π vs. the 18π-electron system). The addition of two acetylene spacers to methoxy-substituted bipyrrole resulted in a redshift of the lowest energy band from $\lambda = 636$ to 758 nm, and further redshifted to $\lambda = 884$ nm upon the addition of two more acetylene spacers. The UV/Vis absorption spectra of **4** and **5** show marginal changes in the absorption maxima compared with their ethyl analogues.[3,5] However, there is a discernible difference in the spectral patterns, in particular, in the Q-band region, where the methoxy derivatives display the second band as the most intense one of the three, whereas for the ethyl analogues, the lowest energy band is the most intense one. Again the effect of substituents is more apparent in the case of [22]porphyrin-(2.2.2.2), with the absorption spectrum of **6** showing the lowest energy Q band blueshifted by about 17 nm compared with that of **3**.[4] We could not detect any fluorescence for **4** and **5**. Also, compared with **3**, the stretched porphycene **6** exhibits weaker fluorescence at $\lambda_{max} = 779$ nm ($\varphi_f = 0.0095$). These results support that the methoxy-substituted macrocycles possess an efficient intramolecular charge-transfer (ICT) characteristic. Additionally, we can assume that acetylene–cumulene porphyrinoids have a stronger ICT character than that of β-octamethoxy[22]porphyrin-(2.2.2.2).

Two-photon absorption studies

Two-photon absorption (TPA) is a third-order NLO phenomenon, the probability of occurrence of which is closely related to π-electron behavior. Recent theoretical and experimental studies have indicated that ICT character could lead to an enhancement of the TPA cross-sectional values.[11] In this context, to investigate different degrees of ICT character between ethyl and methoxy analogues, TPA measurements for **1**–**6** were conducted by the Z-scan technique in toluene at $\lambda = 1300$–1900 nm, at which the contribution from one-photon absorption (OPA) is negligible (Figure 3 and Figure S18 in the Supporting Information). The TPA profiles revealed spectral features that were in a good agreement with those of the lowest

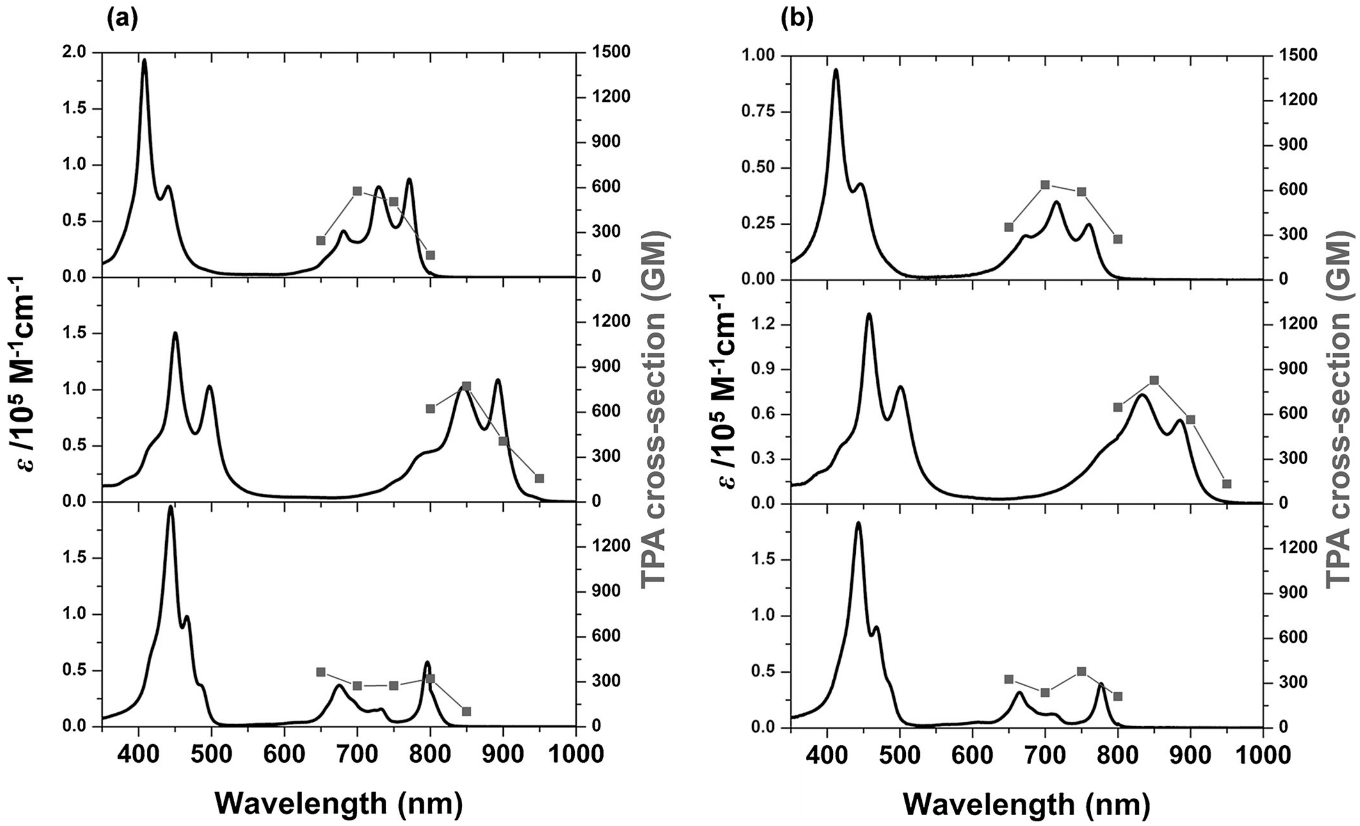


Figure 3. a) OPA (——) and TPA spectra (■) of **1** (top), **2** (middle), and **3** (bottom) in toluene. b) OPA (——) and TPA spectra (■) of **4** (top), **5** (middle), and **6** (bottom) in toluene. The TPA spectra are plotted at $\lambda_{ex}/2$ for comparison with the OPA spectra.

OPA band. The maximum TPA cross sections of **1**, **2**, and **3** were measured to be 580, 770, and 370 GM at $\lambda = 1400$, 1700, and 1300 nm, respectively. Meanwhile, the maximum TPA cross sections of **4**, **5**, and **6** were measured to be 640, 830, and 380 GM at $\lambda = 1400$, 1700, and 1500 nm, respectively. Based on the observed trends, we can conclude that the TPA cross sections of the methoxy analogues are larger than those of the ethyl analogues due to a greater ICT character. Furthermore, we have observed higher TPA cross sections for 26π-acetylene–cumulene porphycenes compared with the corresponding 22π-acetylene–cumulene porphycenes due to the more extended π-conjugated network for the former. Additionally, the TPA cross sections of isoelectronic [22]porphyrins-(2.2.2.2) are smaller than those of 22π-acetylene–cumulene porphyrinoids. Herein, we note that the TPA cross section is closely related to conformational flexibility in the π-conjugated network.[12] We can see that acetylene–cumulene porphyrinoids are much rigid and tend to be more effectively conjugated than [22]porphyrins-(2.2.2.2) with a vinylinic linker, which is known to undergo an isodynamic transformation involving rotation around *trans* −CH=CH− bonds[4] and lead to a relatively low TPA cross section. Interestingly, expansion of the aromaticity could be clearly observed for all expanded porphycenes as evident from their higher TPA cross section values compared with their porphycene analogues.[6e]

Femtosecond transient absorption studies

To examine the excited-state dynamics of **1**–**6**, we measured femtosecond transient absorption (TA) spectra of these compounds (Figure 4). The TA spectra exhibited ground-state bleaching signals, the spectral features of which corresponded to their ground-state absorption bands. The fitted time components of the ethyl analogues are 630, 36, and 2000 ps for **1**, **2**, and **3**, respectively (Figure S19 in the Supporting Information). These results are in good agreement with those reported previously.[5] Also, the decay times of the methoxy analogues are 11, 7.3, and 370 ps for **4**, **5**, and **6**, respectively (Figure S19 in the Supporting Information). Compared with the ethyl analogues, the methoxy analogues exhibit significantly shorter excited-state lifetimes. This feature could be attributed to the ICT character from the methoxy substituent to the porphyrinoid core. Because the time resolution of our TA setup is about 150 fs, we can assume that the timescale of the ICT process lies within a few hundred femtoseconds, which hinders the direct observation of the ICT process in the TA spectra.

Electrochemical studies

The redox potentials of all expanded porphycenes were analyzed by cyclic voltammetry and differential pulse voltammetry (DPV) in dichloromethane (Figure 5). Similar to β-octamethoxyporphycene,[7] all expanded porphycenes show two reversible

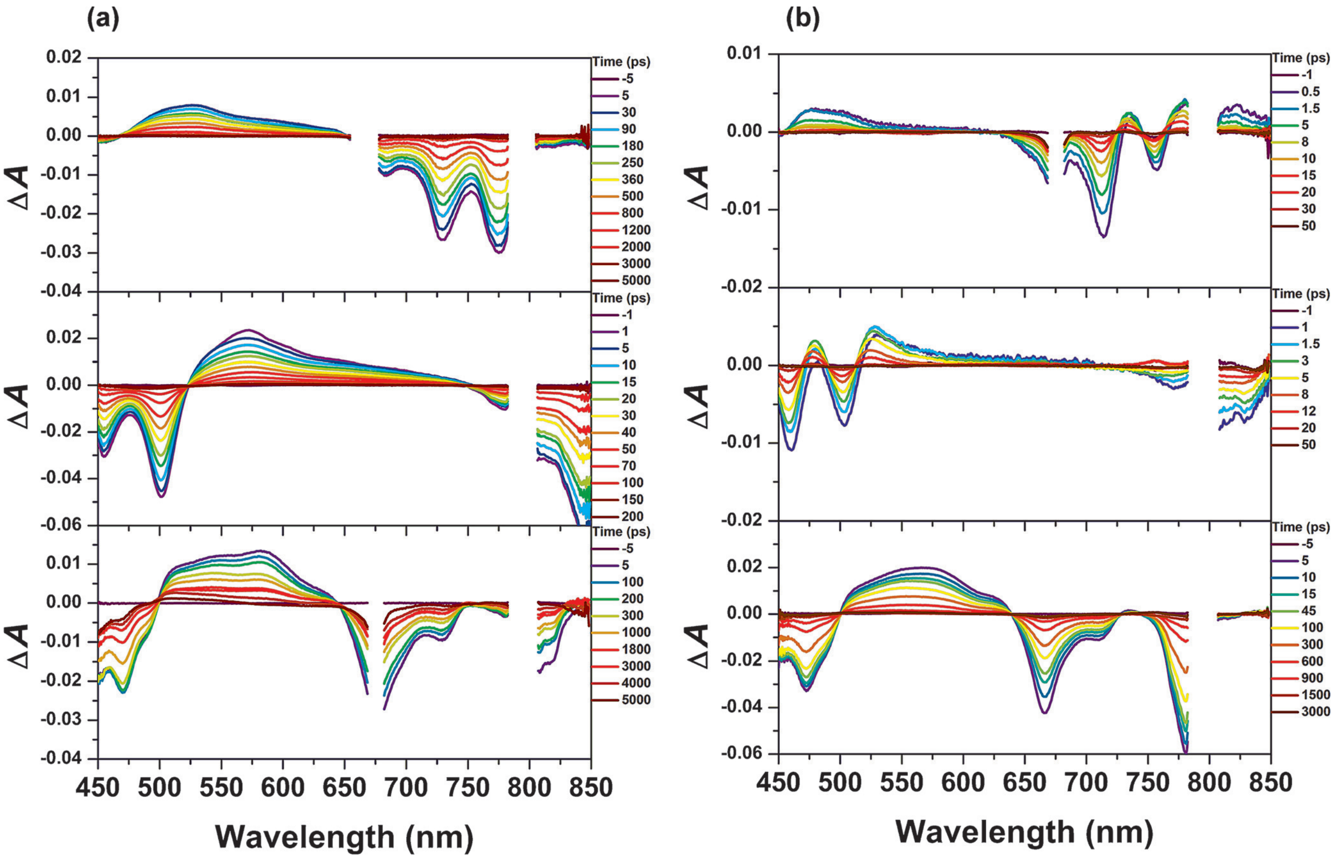


Figure 4. a) TA spectra of **1** (top), **2** (middle), and **3** (bottom) in toluene obtained with photoexcitation at $\lambda = 670$ (top), 830 (middle), and 670 nm (bottom), respectively. b) TA spectra of **4** (top), **5** (middle), and **6** (bottom) in toluene obtained with photoexcitation at $\lambda = 670$ (top), 830 (middle), and 670 nm (bottom), respectively.

reductions and two reversible or quasi-reversible oxidations. Oxidation and reduction potentials referenced versus Ag/AgCl for all expanded porphycenes are summarized in Table 1. The first oxidation potentials for octamethoxy-substituted expanded porphycenes appeared at +0.74, +0.68, and +0.62 V for **4**, **5**, and **6**, respectively, and the first reduction potentials for **4**, **5**, and **6** were observed at −0.58, −0.33, and −0.89 V, respectively. Due to the presence of electron-rich methoxy groups at their periphery, the first oxidation and first reduction potentials are less positive and more negative, respectively, for these expanded porphycenes, which indicate the more electron-rich nature of these macrocycles compared with ethyl-substituted analogues. Interestingly, changes in the oxidation and reduction potentials are marginal, as observed in the corresponding porphycenes (β-ethyl and β-methoxy analogues),[7,14] probably owing to the absence of distortion between adjacent pyrrolic moieties of bipyrrole units (arising from van der Waals repulsion between their inner β substituents), by inserting acetylinic

Table 1. Comparative oxidation and reduction potentials (in V vs. Ag/AgCl) for expanded porphycenes.

	Reduction	Oxidation	HOMO/LUMO [V]
1[a]	−0.88, −0.57	+0.80, +1.09	1.37
2[a]	−0.49, −0.30	+0.72, +0.98	1.02
3[a]	−1.02, −0.87	+0.67, –	1.54
4	−0.76, −0.58	+0.74[b], +1.10[b]	1.32
5	−0.46[b], −0.33[b]	+0.68[b], +0.92[b]	1.01
6	−1.05, −0.89	+0.62, +1.02	1.51

[a] Taken from Ref. [13]. [b] Measured by DPV.

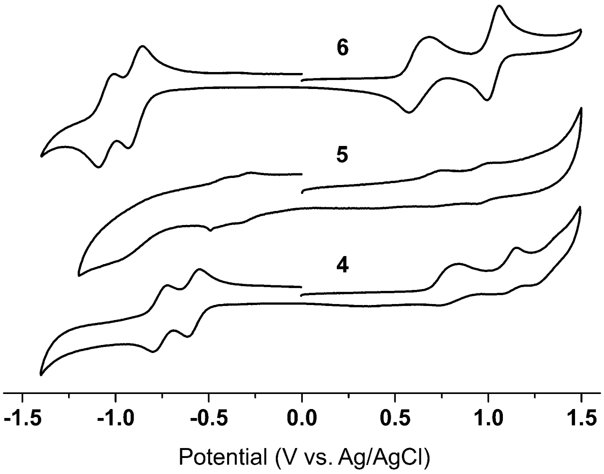


Figure 5. Cyclic voltammograms of **4**, **5**, and **6** in dichloromethane at 25 °C (scan rate: 50 mV s^{-1}).

and vinylinic spacers. Upon extension of the conjugation pathway from 22π to 26π, the changes in the first oxidation potentials were less clear than those of the first reduction potential; this may be attributed to minimal perturbation in the energy levels of the HOMO rather than the LUMO, for these molecules, which indicates that the extension of conjugation leads to greater stabilization of the LUMO.[13] The HOMO–LUMO energy gaps of all methoxy-substituted expanded porphycenes ($\Delta E = E_{\mathrm{ox1}} - E_{\mathrm{red1}}$) were similar to those of ethyl analogues, which was further supported by minimal changes observed in the lowest-energy Q bands in the absorption spectra.

Conclusion

We synthesized β-octamethoxy acetylene–cumulene porphycenes and [22]porphyrin-(2.2.2.2) along with their octaethyl congeners by employing a modified synthetic protocol that gave higher yields. The substituent effect was more severe in the case of [22]porphyrin-(2.2.2.2) than acetylene–cumulene-bridged porphycenes, as observed from their absorption spectra. The dominant ICT character of methoxy groups could be observed through enhanced TPA cross sections for the methoxy-substituted macrocycles compared with their ethyl analogues. From this study, we can conclude that expansion of the π-conjugation network by the introduction of *meso*-methine groups or pyrrole moieties results in a similar NLO response. The NLO properties of the expanded porphycenes studied herein were dominated by the π-conjugated network, but conformation flexibility also played an important role. The ICT property of the methoxy groups led to much shorter excited-state lifetimes for methoxy analogues. Electrochemical studies revealed that the first oxidation and reduction potentials became less positive and more negative, respectively; this complied with the electron-rich character of these octamethoxy-expanded porphycenes.

Experimental Section

Synthesis of 2,3,8,9,14,15,20,21-octamethoxy-5,6,17,18-tetradehydro[22]porphyrin-(2.2.2.2) (4)

A slurry of activated zinc (1.57 g) and copper(I)chloride (237 mg, 2.4 mmol) were taken in THF (100 mL) under nitrogen and $TiCl_4$ (1.32 mL, 12 mmol) was added slowly. The reaction mixture was then heated at reflux for 3 h with vigorous stirring and the slurry was allowed to come to room temperature. Aldehyde **10b** (200 mg, 0.60 mmol) in THF (100 mL) was added slowly over 5 h at room temperature with vigorous stirring. The reaction mixture was stirred at room temperature for an additional 2 h and then hydrolyzed by slow addition of a 10% aqueous solution of sodium carbonate (ca. 100 mL) to the ice-cooled reaction mixture. Subsequently, chloroform (ca. 100 mL) was added to the reaction mixture and allowed to stir at room temperature in air for an additional 2 h. The reaction mixture was filtered through Celite, the organic layer was separated, and then the Celite portion was taken in a beaker and extracted with chloroform repeatedly until the solution became colorless. The combined organic layer was passed through anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude reaction mixture was purified by column chromatography with methanol/chloroform (1:99) to provide a mixture of **4** with acetylenic dihydro and tetrahydro **6** reduced products. The mixture of products was washed with chloroform/hexane (1:1), filtered and washed with the same solution until the filtrate became colorless, to give **4** as a blue crystalline solid (47 mg, 26%). The filtrate was evaporated to dryness under reduced pressure, which could be reduced to tetrahydro product **6** in good yield by using 20 mol% Pd/C at 1 atm H_2 pressure. M.p. $>300\,^{\circ}$C; IR (KBr): $\tilde{\nu} = 2066\ \mathrm{cm}^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 10.05$ (s, 4H), 5.34 (s, 12H), 4.92 (s, 12H), 0.86 ppm (s, 2H); UV/Vis ($CHCl_3$): $\lambda_{\max}$ ($\log\varepsilon$) = 411 (4.97), 445 (4.65), 672 (4.29), 714 (4.54), 758 nm (4.41); HRMS (ESI+): *m/z* calcd for $C_{32}H_{31}N_4O_8$ [$M+H^+$]: 599.2136; found: 599.2142.

Synthesis of 2,3,8,9,14,15,20,21-octaethyl-5,6,17,18-tetradehydro[22]porphyrin-(2.2.2.2) (1)

The same procedure as that described for **4**, but with aldehyde **10a** (200 mg, 0.62 mmol), was used. The crude reaction mixture was purified by column chromatography on silica gel with chloroform/hexane (1:1) as the eluent to give **1** as a blue crystalline solid (48 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.00$ (s, 4H), 4.46 (q, 8H, $J = 7.6$ Hz), 4.12 (q, 8H, $J = 7.6$ Hz), 2.25 (t, 12H, $J = 7.6$ Hz), 2.19 (s, 2H), 1.94 ppm (t, 12H, $J = 7.6$ Hz); UV/Vis ($CHCl_3$): $\lambda_{\max}$ ($\log\varepsilon$) = 407 (5.29), 440 (4.90), 679 (4.60), 726 (4.88), 768 nm (4.91).

Synthesis of 2,3,10,11,16,17,24,25-octamethoxy-5,6,7,8,19,20,21,22-tetradehydro[26]porphyrin-(2.4.2.4) (5)

A slurry of activated zinc (1.46 g) and copper(I)chloride (221 mg, 2.24 mmol) was taken in THF (100 mL) under nitrogen and $TiCl_4$ (1.23 mL, 11.2 mmol) was added slowly. The reaction mixture was then heated at reflux for 3 h with vigorous stirring. Aldehyde **11b** (200 mg, 0.56 mmol) in THF (100 mL) was added slowly over 2 h with vigorous stirring. The reaction mixture was heated under reflux for an additional 2 h and then hydrolyzed by slow addition of a 10% aqueous solution of sodium carbonate (ca. 100 mL) to the ice-cooled reaction mixture. Subsequently, chloroform (ca. 100 mL) was added to the reaction mixture and allowed to stir at room temperature in air for an additional 2 h. The reaction mixture was filtered through Celite, the organic layer was separated, and then the Celite portion was taken in a beaker and extracted with chloroform repeatedly until the solution became colorless. The combined organic layer was passed through anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude reaction mixture was purified by column chromatography on silica gel by using methanol/chloroform (1:99) as the eluent to provide a mixture of **5** with some impurities. The mixture of product was washed with chloroform/hexane (1:1), filtered, and washed with the same solution until the filtrate became colorless, to give **5** (30 mg, 17%) as a shiny green crystalline solid. M.p. $>300\,^{\circ}$C; IR (KBr): $\tilde{\nu} = 2016\ \mathrm{cm}^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 10.15$ (s, 4H), 5.42 (s, 12H), 4.96 (s, 12H), 0.77 ppm (s, 2H); UV/Vis ($CHCl_3$): $\lambda_{\max}$ ($\log\varepsilon$): 456 (5.10), 500 (4.87), 832 (4.86), 884 nm (4.76); HRMS (ESI+): *m/z* calcd for $C_{36}H_{31}N_4O_8$ [$M+H^+$]: 647.2136; found: 647.2145.

Synthesis of 2,3,10,11,16,17,24,25-octaethyl-5,6,7,8,19,20,21,22-tetradehydro[26]porphyrin-(2.4.2.4) (2)

The same procedure as that described for **5**, but with aldehyde **11a** (200 mg, 0.57 mmol), was used. The crude reaction mixture was purified by column chromatography on silica gel with chloroform/hexane (1:1) as the eluent to give **2** as a blue crystalline solid

(30 mg, 17 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.09$ (s, 4 H), 4.57 (q, 8 H, $J = 7.6$ Hz), 4.15 (q, 8 H, $J = 7.6$ Hz), 2.30 (t, 12 H, $J = 7.6$ Hz), 1.98 (t, 12 H, $J = 7.6$ Hz), 1.96 ppm (s, 2 H); UV/Vis ($CHCl_3$): λ_{max} ($\log \varepsilon$): 449 (5.18), 496 (5.01), 841 (5.00), 889 nm (5.03).

Synthesis of 2,3,8,9,14,15,20,21-octamethoxy[22]porphyrin-(2.2.2.2) (6)

Compound **4** (10 mg, 0.017 mmol) and 5 % Pd/C (7 mg) were taken in THF (30 mL) under H_2 (1 atm, balloon). Progress of the reaction was monitored with UV/Vis spectroscopy by taking a small aliquot from the reaction mixture. The reaction mixture was quenched with chloroform and removed from the hydrogen atmosphere after 48 h. Subsequently, DDQ (12 mg, 0.051 mmol) was added and the solution was stirred for another 30 min. The reaction mixture was passed through Celite and washed with chloroform. The combined organic layer was evaporated to dryness under reduced pressure and purified by column chromatography on silica gel by using chloroform as the eluent to afford desired product **6** as a blue crystalline solid (4 mg, 39 %). M.p. 260.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.98$ (d, 2 H, $J = 14.8$ Hz), 9.90 (d, 2 H, $J = 11.2$ Hz), 9.84 (d, 2 H, $J = 11.2$ Hz), 5.05 (s, 6 H), 4.93 (s, 6 H), 4.87 (s, 6 H), 4.82 (s, 6 H), 0.83 (s, 2 H), -7.97 ppm (d, 2 H, $J = 14.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.9$, 145.0, 143.1, 142.9, 139.4, 138.8, 132.0, 131.7, 114.5, 112.8, 109.3, 106.6, 63.61, 63.55, 63.5, 62.1 ppm; UV/Vis ($CHCl_3$): λ_{max} ($\log \varepsilon$): 442 (5.26), 467 (4.96), 665 (4.50), 708 (4.10), 774 nm (4.57); fluorescence ($CHCl_3$): 779 nm ($\lambda_{exe} = 442$ nm); fluorescence quantum yield ($CHCl_3$): 0.0095; HRMS (ESI+): m/z calcd for $C_{32}H_{35}N_4O_8$ $[M+H^+]$: 603.2449; found: 603.2454.

Synthesis of 2,3,8,9,14,15,20,21-octaethyl[22]porphyrin-(2.2.2.2) (3)

Compound **1** (20 mg, 0.034 mmol) and 5 % Pd/C (16 mg) were taken in THF (30 mL) under H_2 (1 atm). The reaction was run for 20 h. The crude product was purified by column chromatography on silica gel by using chloroform/hexane (1:1) as the eluent to afford desired product **3** as a blue crystalline solid (17 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.77$ (d, 2 H, $J = 15.2$ Hz), 9.93 (d, 2 H, $J = 11.2$ Hz), 9.88 (d, 2 H, $J = 11.2$ Hz), 4.68 (q, 4 H, $J = 7.6$ Hz), 4.24 (q, 4 H, $J = 7.6$ Hz), 4.14 (q, 4 H, $J = 7.6$ Hz), 4.09 (q, 4 H, $J = 7.6$ Hz), 2.27 (t, 6 H, $J = 7.6$ Hz), 2.06 (t, 6 H, $J = 7.6$ Hz), 1.93 (t, 6 H, $J = 7.6$ Hz), 1.91 (t, 6 H, $J = 7.6$ Hz), 1.33 (s, 2 H), -7.47 ppm (d, 2 H, $J = 15.2$ Hz); UV/Vis ($CHCl_3$): λ_{max} ($\log \varepsilon$): 442 (5.29), 466 (4.98), 674 (4.56), 728 (4.23), 791 nm (4.71).

Synthesis of 6 by McMurry coupling of 3,4-dimethoxypyrrole-2,5-dialdhyde

A slurry of activated zinc (3.59 g) and copper(I)chloride (544 mg, 5.5 mmol) was taken in THF (100 mL) under nitrogen and $TiCl_4$ (1.23 mL, 11.2 mmol) was added slowly. The reaction mixture was then heated at reflux for 3 h with vigorous stirring. 3,4-Dimethoxypyrrole-2,5-dialdhyde (200 mg, 1.09 mmol) in THF (50 mL) was added slowly over 2 h with vigorous stirring under reflux conditions. The reaction mixture was heated under reflux for an additional 1 h and then hydrolyzed by slow addition of a 10 % aqueous solution of sodium carbonate (ca. 100 mL) to the ice-cooled reaction mixture. The reaction mixture was allowed to stir at room temperature in air for an additional 2 h. The reaction mixture was filtered through Celite and washed with chloroform. The organic layer was separated and the aqueous layer was extracted twice with chloroform. The combined organic layer was passed through anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude reaction mixture was purified by column chromatography on silica gel by using chloroform as the eluent to provide a mixture of **6** as a blue crystalline solid (2.4 mg, 1.4 %).

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