Porphyrinoids

DOI: 10.1002/ange.200801192

Effective Expansion of the Subporphyrin Chromophore Through Conjugation with *meso*-Oligo(1,4-phenyleneethynylene) Substituents: Octupolar Effect on Two-Photon Absorption**

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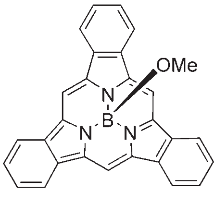
Subporphyrin, a ring-contracted porphyrin with a bowl-shaped structure, has emerged as a promising functional pigment because of its intense absorption and bright green fluorescence which arise from its 14π-conjugated aromatic circuit.[1–3] The chemistry of subporphyrins **1** and **2** has remained in its infancy, compared to the chemistry of subphthalocyanines **3** that has been extensively studied[4] since the first report by Meller and Ossko in 1972.[5] In porphyrin chemistry, the *meso*-aryl substituents in **4** have served as key synthetic handles for the covalent linkage of functional units, the anchoring of chelating units for controlling the reactivity of metalloporphyrins, for providing steric hindrance to the central metal center thus protecting metalloporphyrins from intermolecular interference, and so forth.[6] As such, the roles of *meso*-aryl substituents are in most cases limited to being structural through providing sites for functional fabrications with well-defined geometries with respect to the porphyrin plane. In other words, the electronic impact of *meso*-aryl substituents on the porphyrin π-system is only marginal, this is due mainly to their restricted perpendicular arrangements to the porphyrin plane. This marginal influence is consistent with small ρ values for Hammett plots of the redox potentials of porphyrins ($\rho = 0.073$ and 0.065 V in the plot of $E_{1/2,\mathrm{red}}$ or $E_{1/2,\mathrm{ox}}$ vs. $4\,\sigma$).[7] In contrast, we have recently revealed that the ρ values are large (0.124 and 0.105 V) for subporphyrins,[1b] which indicates a large electronic influence of the *meso*-aryl substituents. This interesting property is aided by the free rotation of the *meso*-aryl substituents and the large orbital coefficients at the *meso*-position in the HOMO and LUMO. Herein, we report the synthesis and nonlinear optical (NLO) properties of 5,10,15-tris-oligo(1,4-phenyleneethynylene) substituted subporphyrins **10**–**13** (see Scheme 1), in which the π-electron system of the subporphyrins is effectively delocalized over the whole molecule including the oligo(1,4-phenyleneethynylene)[8] arms.



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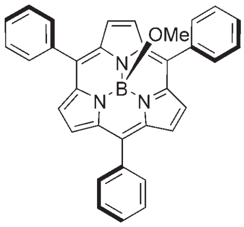

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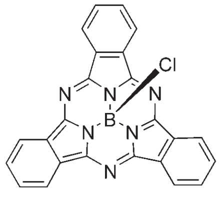

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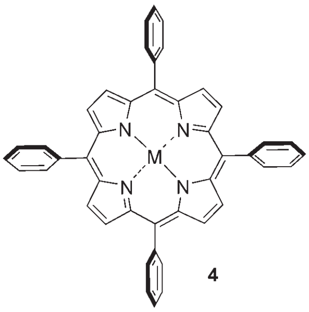

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Scheme 1 outlines the synthetic routes to **10**–**13**. Sonogashira coupling reactions of 4-bromophenyl-substituted subporphyrin **5** with trimethylsilylacetylene (**6**), phenylacetylene (**7**), and 4-(phenylethynyl)phenylacetylene (**8**) proceeded quantitatively to give **10**–**12** in 96, 96, and 95%, yields respectively. It is worth noting that subporphyrins **10**–**12** are readily soluble in CH_2Cl_2, $CHCl_3$, and toluene despite the presence of three oligo(1,4-phenyleneethynylene) units without any bulky substituents. The yield of **13** was only 58%, probably because of the poor solubility of the acetylene precursor **9**. Subporphyrins **10**–**13** exhibit similar ^{1}H NMR spectral patterns, featuring a singlet in the range of $\delta = 8.12$–8.17 ppm for the peripheral β-protons and a single set of signals without discrimination of the two phenylene protons at the 2,6- or 3,5-positions for the 1,4-phenyleneethynylene groups. These ^{1}H NMR data indicate the C_3-symmetry for the subporphyrins **10**–**13** and free rotation of the *meso*-aryl substituents.

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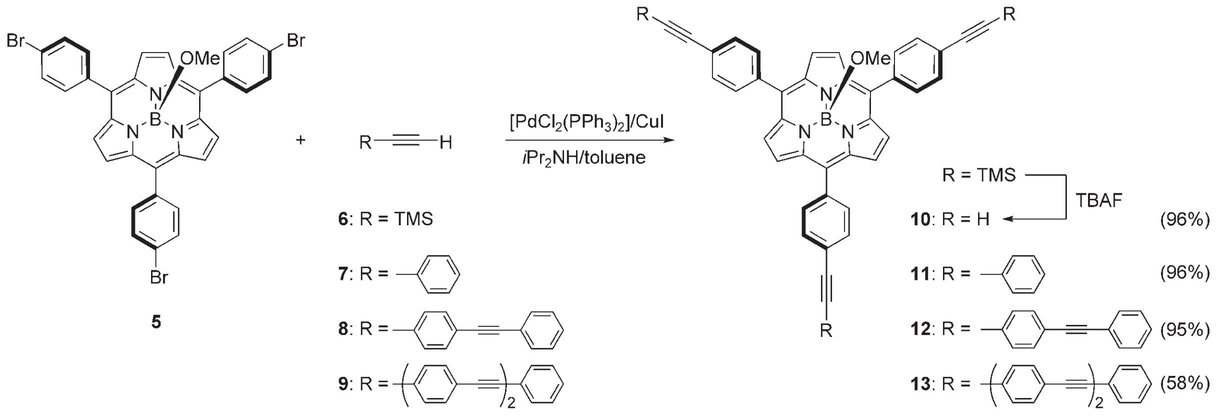
[**] This work was partly supported by a Grants-in-Aid (A) (No. 19205006) for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (Japan). Y.I. thanks the JSPS Research Fellowships for Young Scientists. The work at Yonsei University was supported by the Star Faculty program from the Ministry of Education and Human Resources Development, Korea. S.E., S.Y.J., and K.S.K. acknowledge BK21 fellowship.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthesis of subporphyrins **10–13**; TBAF = tetrabutyl ammonium fluoride.

Single crystals of **10** and **11** suitable for X-ray diffraction analysis were grown in a mixture of CH_2Cl_2/methanol.[9] These two structures show bowl-shaped triangular frameworks, in which the sides are approximately 17 Å for **10** and 24 Å for **11** (Figure 1). The bowl-depth, defined by the distance between center boron atom and the mean plane of peripheral six β-carbon atoms, has been calculated to be 1.33 Å both for **10** and **11**. The dihedral angles of the *meso*-aryl substituents with respect to the mean plane are 50.2, 51.5, and 57.3° for **10**, and 45.8, 48.7, and 52.0° for **11**.

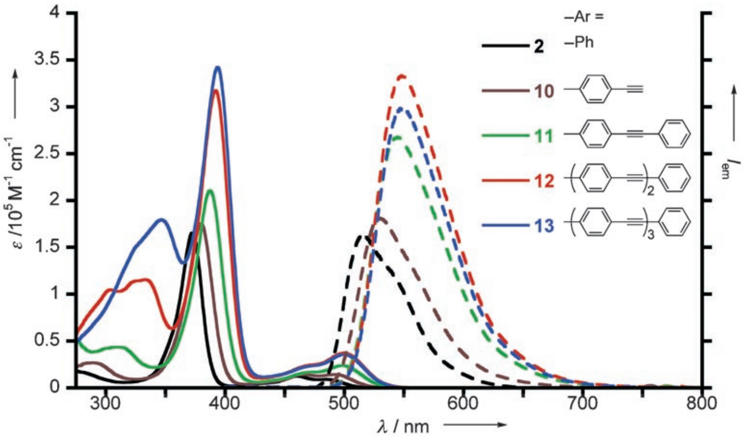


Figure 2. UV/Vis absorption (solid lines) and fluorescence (dashed lines) spectra of subporphyrins **2** and **10–13** in CH_2Cl_2.

Upon elongation of the *meso*-oligo(1,4-phenyleneethynylene) chain lengths, the Soret- and Q-bands are red-shifted and progressively intensify (Figure 2 and Table 1). While the Q(1,0) band is more intense than the Q(0,0) band in the case of **2**, the relative intensity of Q(0,0) band progressively increases with the increasing length of the substituted 1,4-phenyleneethynylene chains. These spectral changes reveal the electronic interactions between subporphyrin core and *meso*-oligo(phenyleneethynylene) chains, however it reaches a saturation point at **12**, beyond that no significant spectral change occurs. Nonetheless the absorption bands characteristic of oligo(1,4-phenyleneethynylene) moieties observed at 309, 333, and, 347 nm for **11**, **12**, and **13**, respectively, are in line with the elongation of π-conjugation length. The steady-state fluorescence spectra are observed at 518, 536, 554, 554, and 555 nm for **2**, **10**, **11**, **12**, and **13**, respectively, and are a mirror image of

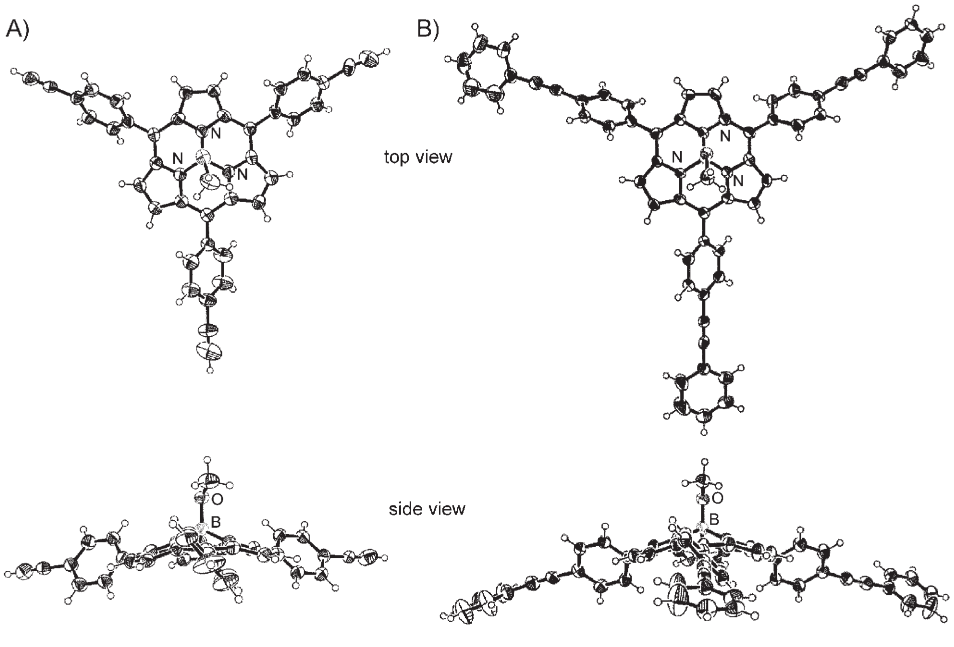


Figure 1. Crystal structures of A) **10** and B) **11**.

Table 1: Summary of optical measurements.

Compd	Absorption			Fluorescence				TPA
	λ_{max} [nm] (ε [10^5 M^{-1}cm^{-1}][a])			λ_{max} [nm][b]	Φ_F[c]	τ_f [ns][d]	k_r [s^{-1}][e]	$\sigma^{(2)}$ [GM][f]
2	373 (1.66)	461 (0.13)	484 (0.09)	518	0.13	2.37	5.5×10^7	88
10	380 (1.75)	465 (0.15)	493 (0.15)	536	0.15	2.01	7.5×10^7	270
11	388 (2.11)	466 (0.14)	499 (0.24)	554	0.29	1.93	1.5×10^8	660
12	392 (3.17)	470 (0.24)	500 (0.38)	554	0.34	1.77	1.9×10^8	960
13	394 (3.42)	470 (0.23)	500 (0.36)	555	0.35	1.62	2.2×10^8	1340

[a] Absorption coefficient. [b] Excited at each absorption maximum (373–394 nm). [c] Absolute fluorescence quantum yield. [d] Fluorescence life time. [e] Natural radiative rate constant. [f] TPA cross-section values obtained by excitation at 800 nm (1 GM = 10^{-50} cm^4 s photon^{-1})

the Q-band spectral changes. Thus, these spectral features indicate that the effective conjugative interactions with the subporphyrin moiety are limited up to the 1,4-bis(phenylethynyl)benzene group, that is, **12**. Since the natural radiative lifetime (τ_0) is expected to have a correlation with the actual radiative size of the chromophore and fluorescence lifetime, the natural radiative rate constants calculated from the fluorescence quantum yield and fluorescence lifetime according to the relationship of ($k_r = 1/\tau_0$, $\tau_0 = \tau_f/\Phi_f$) are 5.5×10^7 s^{-1}, 7.5×10^7 s^{-1}, 1.5×10^8 s^{-1}, 1.9×10^8 s^{-1}, and 2.2×10^8 s^{-1} for **2**, **10**, **11**, **12**, and **13**, respectively, in agreement with the increasing size of the effective radiative chromophore with the elongation of *meso*-oligo(1,4-phenyleneethynylene) substituents.[10]

Further information on the electronic conjugative effect of *meso*-oligo(1,4-phenyleneethynylene) substituents on the subporphyrin ring is gleaned from two-photon absorption (TPA) cross-section ($\sigma^{(2)}$) values, which are largely proportional to the electron delocalization strength of the molecule.[11] The TPA cross-section values were measured by the open aperture z-scan method by exciting the molecule at 800 nm using femtosecond Ti:sapphire regenerative amplifier system with 130 fs pulse width.[11] The TPA cross-section values of subporphyrins increase gradually from 88 to 1340 GM as the length of the substituent group increases (Table 1). The TPA cross-section value of **10** is approximately triple that of **2** which can not be solely explained by the elongation of the π-conjugation length by an additional acetylene group. Thus, the observed behavior is attributed to the octupolar structure of these cone shaped subporphyrins because these molecules exhibit larger first-order hyperpolarizabilities (β) than dipolar molecules.[12] The hyperpolarizability (β) and TPA cross-section ($\sigma^{(2)}$) values exhibit a qualitatively linear relationship and these values increase with the increasing π-conjugation length.[13]

It is noteworthy that unlike one-photon absorption, the TPA cross-section values do not show any saturation behavior with respect to *meso*-substituent chain length, hence the enhancement in TPA properties in *meso* substituted subporphyrins would be determined by the octupolar effect rather than the conjugation effect, which shows a saturation behavior as inferred from their one-photon absorption spectra.

Calculations were performed at the B3LYP/6-31G* level with Gaussian03 package.[14] The subporphyrin **2** has degenerate HOMOs and LUMOs. Its HOMO, LUMO and LUMO + 1 have large coefficients at the *meso*-positions, whereas the HOMO−1 has nodal points at *meso*-positions. These orbital characteristics of *meso*-aryl substituted subporphyrins allow large orbital interactions with the *meso*-aryl ring to be predicted. This feature has been confirmed by the calculated molecular orbitals of **10**–**13**. Pairs of strongly degenerated LUMOs are stabilized through the increasing conjugative interactions with the *meso*-1,4-phenyleneethynylene groups progressively from **10** to **13**, although this trend becomes almost saturated at **13**. In contrast, the energy levels of the HOMO orbitals are accidentally rather constant for **2**, **10**, **11**, **12**, and **13**, hence giving rise to a continuous decrease in the HOMO–LUMO gap. To check the validity of these molecular orbitals, the electrochemical properties of the subporphyrins have been examined by cyclic voltammetry (CV) in CH_2Cl_2 containing 0.10 M Bu_4NPF_6 as a supporting electrolyte. The first one-electron oxidation potentials were observed at 0.76, 0.72, and 0.71 V for **11**, **12**, and **13**, respectively, versus the ferrocene/ferrocenium ion couple, while the first one-electron reduction potentials of **10**–**13** were observed at −1.83 to −1.81 V, which are distinctly less negative than that of **2** (−1.97 V). Experimentally determined electrochemical HOMO–LUMO gaps are roughly consistent with the molecular orbital calculation and optical HOMO–LUMO gaps (Table 2 and SI).

In summary, *meso*-oligo(1,4-phenyleneethynylene)-substituted subporphyrins **10**–**13** were synthesized by Sonogashira-coupling of *meso*-(4-bromophenyl)subporphyrin **5** with ethynes **6**–**9**. The electronic π-networks of subporphyrins are effectively expanded through the conjugation of *meso*-oligo(1,4-phenyleneethynylene) substituents, as has been clearly indicated by the optical and electrochemical properties. These results illustrate the highly tunable electronic properties of subporphyrins by *meso*-aryl substituents, properties which are impossible for porphyrins, hence underscoring versatile and promising potentials of subporphyrinic

Table 2: Electrochemical, optical, and theoretical HOMO–LUMO gaps.

Compd	Redox potential [V][a]		HOMO–LUMO gap [eV]		
	$E_{ox,1}$	$E_{red,1}$	CV	UV/Vis[b]	Calculation[c]
2	0.71	−1.97	2.68	2.56	3.18
10	0.86	−1.81	2.67	2.51	3.05
11	0.76	−1.83	2.59	2.48	2.91
12	0.72	−1.82	2.54	2.48	2.83
13	0.71	−1.81	2.52	2.48	2.80

[a] vs. Ferrocene/ferrocenium ion pair. [b] Calculated from Q(0,0) bands. [c] Performed at the B3LYP/6-31G* level.

chromophores. Furthermore, we have demonstrated that subporphyrins show higher two-photon absorption efficiency by virtue of an octupolar effect, which can be favorably tuned by increasing the arm length. Along this line, our current efforts are directed to explore new properties of subporphyrins by designed introduction of conjugative *meso*-aryl substituents.

Received: March 12, 2008

Keywords: conjugation · fluorescence · porphyrinoids · subporphyrins · two-photon absorption

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[9] Crystallographic data for **10**: $C_{40}H_{24}B_1N_3O_1\cdot CH_3OH$, $M_r = 605.47$, monoclinic, $a = 11.032(6)$, $b = 19.682(8)$, $c = 15.304(9)$ Å, $\beta = 96.020(18)°$, $V = 3305(3)$ Å^3, $T = 123(2)$ K, space group $P2_1/a$, $Z = 4$, $\rho = 1.217$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 0.075$ mm^{-1}, 24698 reflections measured, 5778 unique ($R_{\mathrm{int}} = 0.1496$) which were used in all calculations, $R(F^2) = 0.1679$ (all data), $R_1 = 0.0979$ ($I > 2\sigma(I)$), GOF = 1.039. Crystallographic data for **11**: $C_{58}H_{36}BN_3O$, $M_r = 801.71$, orthorhombic, $a = 24.337(4)$, $b = 17.749(3)$, $c = 22.934(3)$ Å, $V = 9906(2)$ Å^3, $T = 123(2)$ K, space group *Pbcn* (no. 60), $Z = 8$, $\rho = 1.075$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 0.064$ mm^{-1}, 73730 reflections measured, 8703 unique ($R_{\mathrm{int}} = 0.1495$) which were used in all calculations, $R(F^2) = 0.1545$ (all data), $R_1 = 0.0974$ ($I > 2\sigma(I)$), GOF = 1.073. CCDC-680553 (**10**) and CCDC-680554 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The SQUEEZE program in PLATON was used for analysis to remove the solvent densities: a) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194; b) A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, c34.

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[14] Gaussian 03 (Revision B.05): M. J. Frisch et al., see Supporting Information.