Synthesis and Characterization of Facially Encumbered and Soluble Porphyrin Tapes

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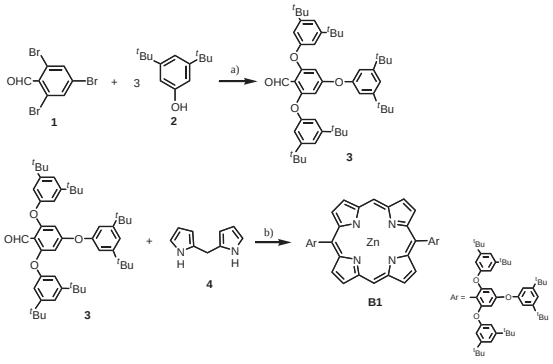
We report the synthesis and characterization of facially encumbered meso–meso-linked and triply fused porphyrin arrays.

Recently, our group has reported singly meso–meso-linked porphyrin arrays[1] and meso–meso, β–β, β–β, triply linked porphyrin arrays (porphyrin tapes),[2] both of which are unprecedented in respects of the molecular length and the extent of π-conjugation. The former arrays have been synthesized up to a discrete 1024-mer, in which the electronic interactions between porphyrin units are small owing to the orthogonal conformations. In contrast, the fully conjugated features of the latter arrays are apparent from the progressive red-shifts of the absorption bands, reaching an exceptionally red-shifted absorption band at 2800 nm for the dodecameric porphyrin tape.[2a] This feature is intriguing, since they do not exhibit effective conjugation length (ECL) behavior[3] up to the dodecamer, hence suggesting ECL of these arrays larger than 12. Despite this promise, the porphyrin tapes have serious problems such as poor solubility and chemical instability, which become more evident with increasing number of porphyrin subunits. Especially, the poor solubility of porphyrin tapes makes it difficult to characterize them by spectroscopic methods. These problems are common for extensively π-conjugated molecules. One of the useful strategies to solve them is to encapsulate the π-conjugated system.[4,5] In this paper, synthesis and properties of a new series of porphyrin arrays that bear bulky aryl groups at 5- and 15-positions are reported. 2,4,6-Tris(3,5-di-*tert*-butylphenoxy)phenyl group was employed for facial encumbrance of porphyrin tapes, which was hoped to suppress aggregation and to improve the chemical stability.

5,15-Bis[2,4,6-tris(3,5-di-*tert*-butylphenoxy)phenyl]porphyrinzinc(II) complex **B1** was synthesized as shown in Scheme 1.



Scheme 1. Synthetic scheme of **B1**. a) Cs_2CO_3, CuCl, AcOEt, toluene, 79%. b) 1) TFA, CH_2Cl_2, 2) DDQ, 3) $Zn(OAc)_2 \cdot 2H_2O$, MeOH, $CHCl_3$, 43%.

Cu(I)-catalyzed coupling reaction of 2,4,6-tribromobenzaldehyde (**1**) and 3,5-di-*tert*-butylphenol (**2**) afforded 2,4,6-tris(3,5-di-*tert*-butylphenoxy)benzaldehyde (**3**) in 79% yield.[6] Acid-catalyzed condensation of **3** and dipyrrylmethane (**4**) followed by oxidation with DDQ provided 5,15-bis[2,4,6-tris(3,5-di-*tert*-butylphenoxy)phenyl]porphyrin in 43% yield, which was converted to Zn(II)–porphyrin **B1** quantitatively by insertion of Zn(II) ion.

Single crystals of **B1** suitable for X-ray analysis were grown by slow diffusion of acetonitrile into a toluene solution (Figure 1).[7] In the molecular structure of **B1**, the ortho-substituted 3,5-di-*tert*-butylphenoxy groups take almost perpendicular conformations with regard to the porphyrin plane, hence providing steric hindrance toward π–π stacking. Actually, there is no sign of π–π stacking in the solid state. In addition, the Zn(II) ion in **B1** is not coordinated with any solvent molecules despite the tendency of Zn(II) porphyrin to bind an axial ligand.

Facially encumbered meso–meso-linked porphyrins **B***n* were synthesized by Ag(I)-promoted oxidative coupling.[1] Monomer **B1** was stirred in the presence of 3 equiv. of $AgPF_6$ at 40 °C for 72 h to afford **B2** (21%), **B3** (8%), and **B4** (2%) along with the recovery of **B1** (48%). In contrast to the previously reported cases, the coupling reaction of **B2** was found to be very sluggish even under rather forcing conditions, probably because of the serious buttressing steric hindrance arising from the bulky *meso*-aryl substituents.

In general, the oxidation of meso-free meso–meso-linked porphyrins with DDQ-$Sc(OTf)_3$ tends to give polymeric products as a result of intermolecular coupling. Therefore, the synthesis of the porphyrin tapes required the protection of the free meso-positions before the double ring closure reaction. In con-

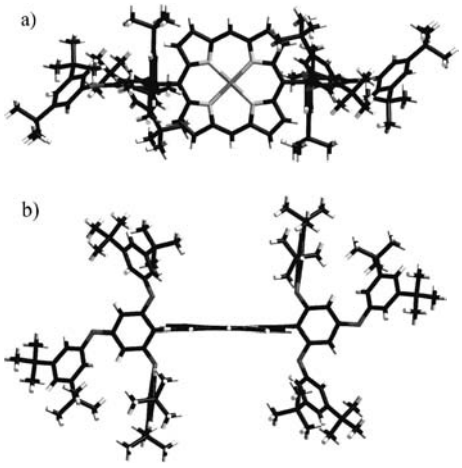


Figure 1. X-ray crystal structure of **B1**. (a) Top view. (b) Side view.

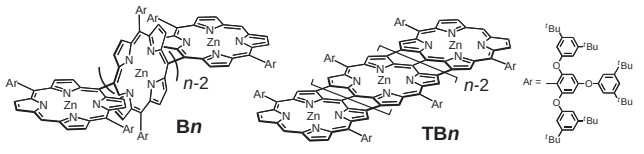


Chart 1.

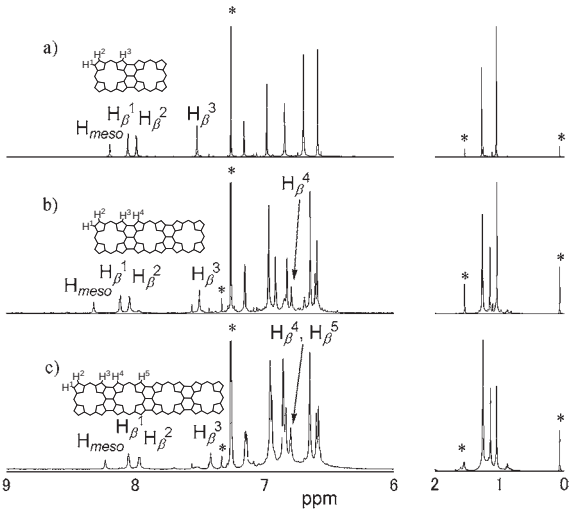


Figure 2. ^{1}H NMR spectra in $CDCl_3$. a) **TB2**, b) **TB3**, and c) **TB4**. *shows solvents and impurities.

trast, the oxidation of **B***n* with DDQ-Sc(OTf)$_3$ in toluene at 80 °C for 2 h provided meso-free porphyrin tapes **TB***n* bearing free meso-postions in moderate yield (23–56%) without any noticeable amount of oligomeic porphyrin products (Chart 1). Porphyrin tapes **TB2**, **TB3**, and **TB4** thus synthesized exhibited parent molecular ion peaks at *m*/*z* 3492.51 (calcd for 3497.49, $C_{232}H_{274}N_8O_{12}Zn_2$), *m*/*z* 5241.40 (calcd for 5243.22, $C_{348}H_{416}N_{12}O_{18}Zn_3$), and *m*/*z* 6986.33 (calcd for 6988.93, $C_{464}H_{542}N_{16}O_{24}Zn_4$), respectively, as revealed by MALDI-TOF mass spectroscopy.

The ^{1}H NMR spectra of **TB2**, **TB3**, and **TB4** taken in $CDCl_3$ are shown in Figure 2. In contrast to the previously reported porphyrin tapes,[2b] **TB***n* displayed relatively sharp peaks even without axial ligand such as butylamine, suggesting suppressed aggregation. Compared to **B1** and **B2**, *meso* and β protons of **TB2**, **TB3**, and **TB4** exhibit up-field shifts, which has been interpreted in terms of weakened ring current of porphyrin tapes compared with that of porphyrin or meso–meso-linked porphyrin.[2b,2c] The clear spectra of **TB3** and **TB4** encouraged us to compare the ring current of inner and outer units of porphyrin tapes. Signals due to H_β^1 and H_β^2 of **TB2**, **TB3**, and **TB4** appear at nearly the same region, while signals due to H_β^3 are slightly shifted to up-field upon elongation of the array. Interestingly signals due to H_β^4 and H_β^5 of **TB3** and **TB4** are more upfield shifted at ca. 6.8 ppm, suggesting that the ring current of inner porphyrins is weaker than that of outer porphyrins.

The UV–vis absorption spectra of **TB***n* taken in $CHCl_3$ are shown in Figure 3. The absorption spectra of **TB***n* exhibit split Soret bands and significantly red-shifted Q-bands, which are similar to those of the previously reported porphyrin tapes.[2] However, it is worthy to note that the broadening of absorption bands caused by aggregation was less serious and the vibronic

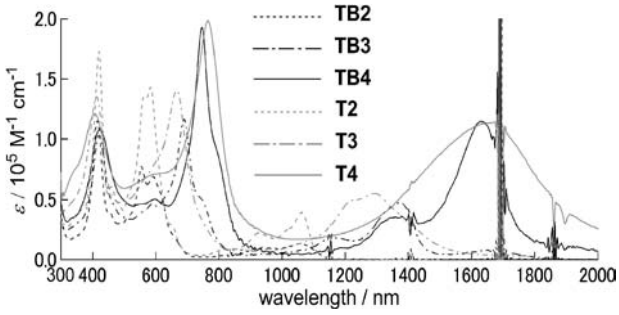


Figure 3. UV–vis absorption spectra of **TB***n* and **T***n* in $CHCl_3$. Structures of **T***n* are shown in Supporting Information.

structures of Q-bands are well preserved up to **TB4** compared to sterically nonencumbered porphyrin tape **T***n*,[2c] probably reflecting facial encumbrance effects of the bulky aryl groups that suppress the aggregation.

In summary, the synthesis and characterization of the facially encumbered porphyrin arrays were reported. The bulky groups are suitable for suppression of aggregation. In addition, such bulky groups allowed for the synthesis of meso-free porphyrin tapes, which may be fabricated towards further elaborated molecules. The ^{1}H NMR spectra of the meso-free porphyrin tapes revealed the attenuated ring current of porphyrins. Detailed examinations of these soluble and chemically stable porphyrin tapes **TB***n* with respect to their promising attributes[8] will be worthy of further investigation.

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7 Crystallographic data for **B1**: $C_{116}H_{140}N_4O_6Zn_1$, M_r 1751.79, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.692(3)$, $b = 12.860(5)$, $c = 20.454(6)$ Å, $\alpha = 102.36(1)$, $\beta = 92.912(9)$, $\gamma = 95.12(1)°$, $V = 2473(1)$ Å^3, $D_{calcd} = 1.176$ g/cm^3, $Z = 1$, $R_1 = 0.0970$ ($I > 2\sigma(I)$), R_w ($I > 2\sigma(I)$) = 0.2500, GOF = 1.036. CCDC 604851.

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