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Synthesis of *meso-β* doubly linked porphyrin tapes†

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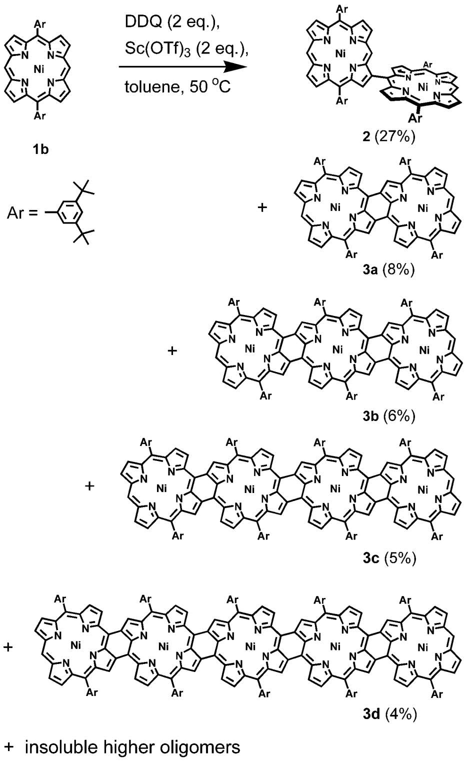
The oxidation of 5,15-bis(3,5-di-*tert*-butylphenyl) Ni(II)-porphyrin 1b with Sc(OTf)$_3$ and DDQ led to production of *meso-β* doubly linked Ni(II)-porphyrin tapes that have large π-electronic communications over the arrays.

Discrete π-conjugated porphyrin arrays with extensive electronic delocalization are of interest as conducting organic materials, near-infrared dyes, nonlinear optical (NLO) materials, molecular wires, molecular devices, and so forth.[1–3] In these studies, one of the central issues is to increase the electronic interaction between the constituent porphyrins and hence decrease the HOMO-LUMO gap. Along this line, a variety of new conjugated porphyrin arrays have been actively exploited.[4–12] A straightforward strategy for maximizing π-overlap may be to hold the π-systems coplanar within a tape-like framework by fusing the units edge-to-edge, hence forcing a flat π-network.[7–12] Another feature desirable for molecular wire may be sufficient molecular length for separating two termini and a synthetic handle for attachment to electrodes or other functional groups.[2]

Recently, we have found that oxidation of metalloporphyrins bearing sterically uncongested *meso*-positions provides effective synthetic routes towards directly linked and fused porphyrin oligomers. Ag(I)-salt promoted coupling reaction of Zn(II)-porphyrins afforded *meso-meso* linked porphyrin arrays,[13] and subsequent oxidation with a combination of Sc(OTf)$_3$ and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) led to the fully conjugated porphyrin tapes.[12] The former arrays adopt a nearly orthogonal conformation that tends to minimize the electronic interaction between the neighboring porphyrins, whereas the latter adopt a tape-shaped coplanar structure that leads to extremely red-shifted absorption bands owing to extensive π-conjugation. On the other hand, *meso-β* doubly-linked diporphyrin was prepared in 53% yield from oxidation of 5,10,15-tris(3,5-di-*tert*-butylphenyl) Ni(II)-porphyrin (**1a**) with (p-BrC$_6$H$_4$)$_3$NSbCl$_6$,[10] but its extension to higher arrays using 5,15-bis(3,5-di-*tert*-butylphenyl) Ni(II)-porphyrin (**1b**) as a starting substrate was difficult due mainly to the extensive peripheral halogenation. Here we report a simple synthesis of oligomeric *meso-β* doubly-linked Ni(II)-porphyrin arrays by the oxidation with DDQ and Sc(OTf)$_3$.

Initially, the oxidation of **1b** was attempted with 5 equiv amounts of DDQ and Sc(OTf)$_3$ in refluxing toluene, which gave complicated polymeric products with poor solubility. We thus examined the reaction conditions by changing the amounts of the oxidants and the temperature, and found that the oxidation of **1b** with 2 equiv of DDQ and Sc(OTf)$_3$ in toluene at 50 °C for 12 h gave short and discrete oligomers. The reaction mixture was passed through a short alumina column eluting with THF, and the products were separated by size exclusion chromatography (SEC) and further by silica gel column chromatography, giving *meso-β* singly-linked diporphyrin **2**[14] in 27% yield and *meso-β* doubly-linked oligoporphyrins (2 ~ 5-mer) in the following yields: **3a** (2-mer, 8%), **3b** (3-mer, 6%), **3c** (4-mer, 5%), and **3d** (5-mer, 4%) (Scheme 1). Molecular weights of these arrays were determined by MALDI-TOF mass spectroscopy; **3b** (*m*/*z* = 2216, Calcd for C$_{144}$H$_{148}$N$_{12}$Ni$_3$ 2219), **3c** (*m*/*z* = 2952, Calcd for C$_{192}$H$_{196}$N$_{16}$Ni$_4$ 2957), and **3d** (*m*/*z* = 3694, Calcd for C$_{240}$H$_{244}$N$_{20}$Ni$_5$ 3695). The structures of **3a–d** have been characterized by their ^{1}H-NMR spectra. Typically, the ^{1}H-NMR spectrum of the trimer **3b** shows mutually coupled doublets for eight *β*-protons (δ = 8.44, 8.49, 8.52, 8.71, 8.73, 8.74, 9.08, and 9.38 ppm), singlets for two *β*-protons (8.63 and 8.98 ppm) and *meso*-proton (9.24 ppm), and characteristic three sets of signals for *tert*-butyl, and *para*- and *ortho*-phenyl protons at the peripheral 3,5-di-*tert*-butylphenyl groups (1.52, 1.53, and 1.56 ppm for *tert*-butyl, 7.74, 7.76, and 7.76 ppm for *para*-phenyl, and 7.82, 7.92, and 7.92 ppm for *ortho*-phenyl) (Supporting Information 1†). This spectrum indicating the presence of three identical 3,5-di-*tert*-butylphenyl groups in **3b** is only consistent with anti-arrangement, because the corresponding syn-isomer should exhibit four sets of signals for the 3,5-di-*tert*-butylphenyl groups in a ratio of 2:2:1:1. Similarly, the anti-arrangements have been assigned for the tetramer **3c** and pentamer **3d** on the basis of fully assignable peaks for the protons of the fused porphyrin moieties and the presence of four and five identical 3,5-di-*tert*-butylphenyl groups, respectively.

The absorption spectra of the porphyrin arrays **3a–d** taken in CHCl$_3$ are shown in Fig. 1. The spectra of **3a–d** exhibit roughly distinct three regions as such in the *meso-meso* linked porphyrin arrays[13] and porphyrin tapes[12] (bands I, II, and III as designated



Scheme 1

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra. See http://www.rsc.org/suppdata/cc/b3/b302032k/

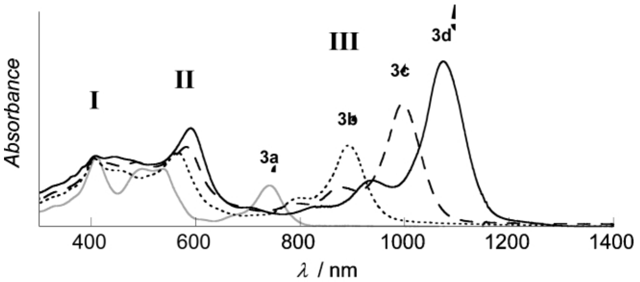

Fig. 1 UV-Vis-NIR absorption spectra of *meso*-β doubly-linked porphyrin arrays **3a–d** taken in $CHCl_3$ at room temperature. The absorption spectra were normalized at 408 nm. λ_{max} (ε) of **3a**: 411 (57900), 498 (33900), 531 (35400), and 741 (22800) nm. λ_{max} (ε) of **3b** : 408 (67000), 567 (64600), 803 (24900), and 892 (60200) nm. λ_{max} (ε) of **3c** : 408 (75000), 583 (92600), 879 (42300), and 996 (143000) nm. λ_{max} of **3d** : 408, 590, 939, and 1075 nm.

in Fig. 1). The bands I are observed at 407–410 nm, being nearly the same positions as that of the monomer **1b**, while the bands II are split into two bands and the low-energy bands are modestly red-shifted upon the increase of the number of the porphyrins. More remarkably, the lowest energy bands III are progressively red-shifted and enhanced upon an increase of the number of the porphyrins; 741 nm for **3a**, 892 nm for **3b**, 996 nm for **3c**, and 1075 nm for **3d**, thus realizing far-infrared strong electronic absorption. A plot of absorption maxima (A_{max}) *versus* the reciprocal number of the porphyrins in the array ($1/N$) is a straight line, hence indicating the ECL (effective conjugation length) effect (Fig. 2a), in contrast to the behavior of the *meso-meso*, *β-β*, *β-β* triply linked porphyrin tapes.[12,15] Its intercept is around 1480 nm (6770 cm^{-1}) that may correspond to a limiting value for this array. The enhancement of the bands III can be understood in terms of increasing symmetry lowering upon the increase in the number of the porphyrins on the basis of Gouterman four-orbital theoretical model.[16]

The one-electron oxidation potential of the *meso*-β doubly-linked diporphyrin **3a** was determined to be 0.56 V *versus* $AgClO_4/Ag$ in $CHCl_3$ solution, which is considerably lower than the values for the parent porphyrin monomer **1b** (0.74 V) and *meso*-β linked diporphyrin **2** (0.76 V) but higher than that for completely fused diporphyrin **4** (0.46 V).[10c] Therefore, it may be concluded that the energy level of HOMO orbital is lifted upon expansion of π-system of the porphyrin. This trend is increasingly enhanced upon an increase in the number of the porphyrins (0.44 V for **3b**, 0.38 V for **3c**, and 0.35 V for **3d**) as shown in Fig. 2b, where a plot of the one-electron oxidation potentials *versus* $1/N$ constitutes a nice straight line. The intercept (0.21 V) of the plot may be assigned for the one-electron oxidation potential of the "infinite" *meso*-β doubly-linked porphyrin array.

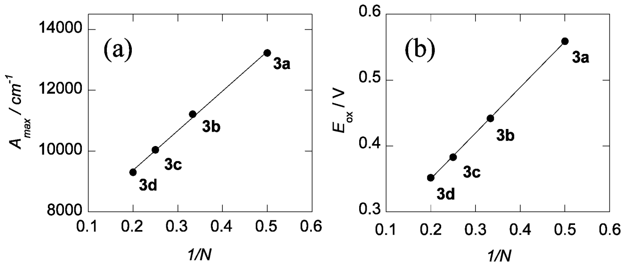

Fig. 2 (a) Plot of absorption maxima (A_{max}) of bands III *versus* the reciprocal numbers of porphyrins ($1/N$) in the *meso*-β fused arrays. (b) Plot of the first oxidation potentials (E_{ox} [V] *versus* $AgClO_4/Ag$ taken in $CHCl_3$) *versus* $1/N$. The first oxidation potentials (E_{ox}) were obtained from cyclic voltammetry. The indicated lines represent by equations: $A_{max} = 13009/N + 6771$ (cm^{-1}) with correlation coefficient, $r^2 = 0.998$, and $E_{ox} = 0.691/N + 0.21$ (V) with correlation coefficient, $r^2 = 0.999$.

In summary, the oxidation of 5,15-bis(3,5-di-*tert*-butylphenyl) Ni(II)-porphyrin **1b** with a combination of DDQ and $Sc(OTf)_3$ provided a series of *meso*-β doubly-linked porphyrin arrays in a one-pot reaction. The porphyrin arrays exhibit remarkably red-shifted and enhanced Q-band-like absorption bands as well as lowered one-electron oxidation potentials upon the increase in the number of the porphyrin, indicating increasing electronic delocalization in the arrays. The longest pentamer **3d** has a molecular length of *ca*. 4.3 nm. In addition, these arrays have free *meso*-positions at both ends, which can be fabricated responding to specific purposes including molecular wires, molecular-scale electronic devices, near-IR sensors and dyes, and materials for nonlinear optics. Further fabrications of these arrays are currently being investigated in our laboratory.

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