Synthesis and Characterization of Fully Conjugated Porphyrin Tapes

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Abstract. *meso–meso*, *β–β*, *β–β* Triply-linked zinc(II) porphyrin tapes were synthesized by powerful oxidation of *meso–meso*-linked zinc(II) porphyrin arrays up to tetramers with DDQ-$Sc(OTf)_3$. Coordination of butylamine to zinc(II) ions of porphyrin rings dissociates their aggregation, resulting in clear NMR spectra and sharper red-shifted absorption bands.

INTRODUCTION

Discrete π-conjugated porphyrin arrays with extensive electronic delocalization are of interest as conducting organic materials, near-infrared dyes, nonlinear optical (NLO) materials, molecular devices, and so forth.[1–3] Along this line, a variety of porphyrin arrays that have large inter-porphyrin conjugation have been extensively exploited.[4–11] One of the promising approaches is to make multiple covalent linkages between porphyrins.[7–11] Recently, we reported synthesis of *meso–meso*, *β–β*, *β–β* triply-linked zinc(II) porphyrin tapes from corresponding *meso–meso* singly-linked zinc(II) porphyrin arrays. The porphyrin tapes thus prepared exhibit unprecedented red-shifted absorption bands that reach into the infrared region. However, solubility of these porphyrin tapes is quite low due to their self-assembling nature by π–π stacking, hampering further characterization by means of ^{1}H NMR and UV-vis absorption spectra. Here, we prepared triply-linked porphyrin arrays **2–4** as shown in Scheme 1. Butylamine-induced dissociation of porphyrin aggregate in solution was observed in ^{1}H NMR and absorption spectra, which provided information on the original nature of porphyrin tapes.

RESULTS AND DISCUSSION

Synthesis

The synthetic route of porphyrin monomer is shown in Scheme 2. Alkylation of 4-bromobenzaldehyde was performed by the Grignard reagent to give 1-(4-bromophenyl)-1-hydroxynonane (**5**), which was then iodinated with $(Me)_3SiCl$ and NaI, and reduced with $NaBH_4$ to 1-bromo-4-nonylbenzene (**6**).[12] 4-Nonylbenzaldehyde (**7**) was obtained by formylation of **6** with butyllithium and then DMF. 5,15-Di(4-nonylphenyl)-porphyrin **8** was synthesized from **7** and dipyrromethane in 30% yield. **8** was transformed into zinc complex **1a**. 5,15-Di(4-nonylphenyl)-10-phenyl Zn(II) porphyrin **1b** was prepared from **8** with phenyllithium in 79% yield.[13] All these compounds were characterized by means of ^{1}H NMR, FAB MS, and UV-vis spectra.

Triply-linked porphyrin dimer **2a** was prepared by direct oxidation of 10-capped-5,15-diarylporphyrins **1b**.[14] The oxidation of **1b** with 5 equivs of DDQ and $Sc(OTf)_3$ in refluxing toluene gave *meso–meso*, *β–β*, *β–β* triply-linked diporphyrin **2a** in 76% yield. MALDI-TOF mass spectrum of **2a** showed its parent peak at m/z = 1703 (calcd for $C_{112}H_{114}N_8Zn_2$ = 1703).

The synthesis of higher oligomers was accomplished according to Scheme 3. The key oligomerization reaction utilizes a random oxidative coupling of diaryl- and triaryl-derivatives, which effectively proceeded to form trimer and tetramer. The yield of each product is acceptably high. This approach also has the great advantage of the favorite one-pot availability of homologues.

Ag^I-promoted oxidation of a mixture of **1a** and **1b** (1:7)

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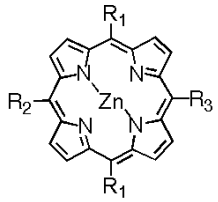
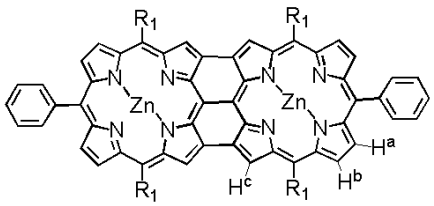


1a R_1 = 4-nonylphenyl, $R_2 = R_3 = H$

1b R_1 = 4-nonylphenyl, R_2 = Ph, R_3 = H

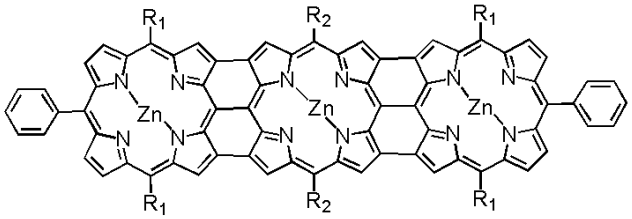
1c R_1 = 3, 5-di-*t*-butylphenyl, $R_2 = R_3 = H$

1d R_1 = 4-nonylphenyl, $R_2 = R_3$ = Ph



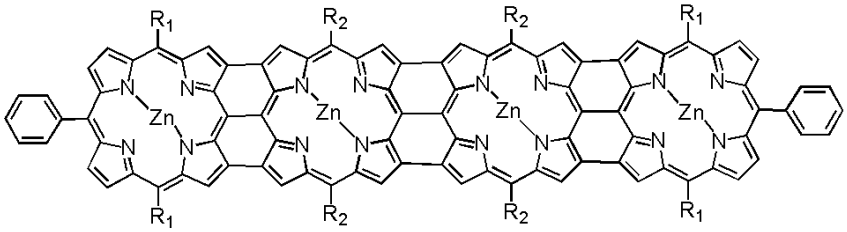
2a R_1 = 4-nonylphenyl

2b R_1 = 3, 5-di-*t*-butylphenyl



3a $R_1 = R_2$ = 4-nonylphenyl

3b R_1 = 4-nonylphenyl
R_2 = 3,5-di-*t*-butylphenyl



4a $R_1 = R_2$ = 4-nonylphenyl

4b R_1 = 4-nonylphenyl
R_2 =3,5-di-*t*-butylphenyl

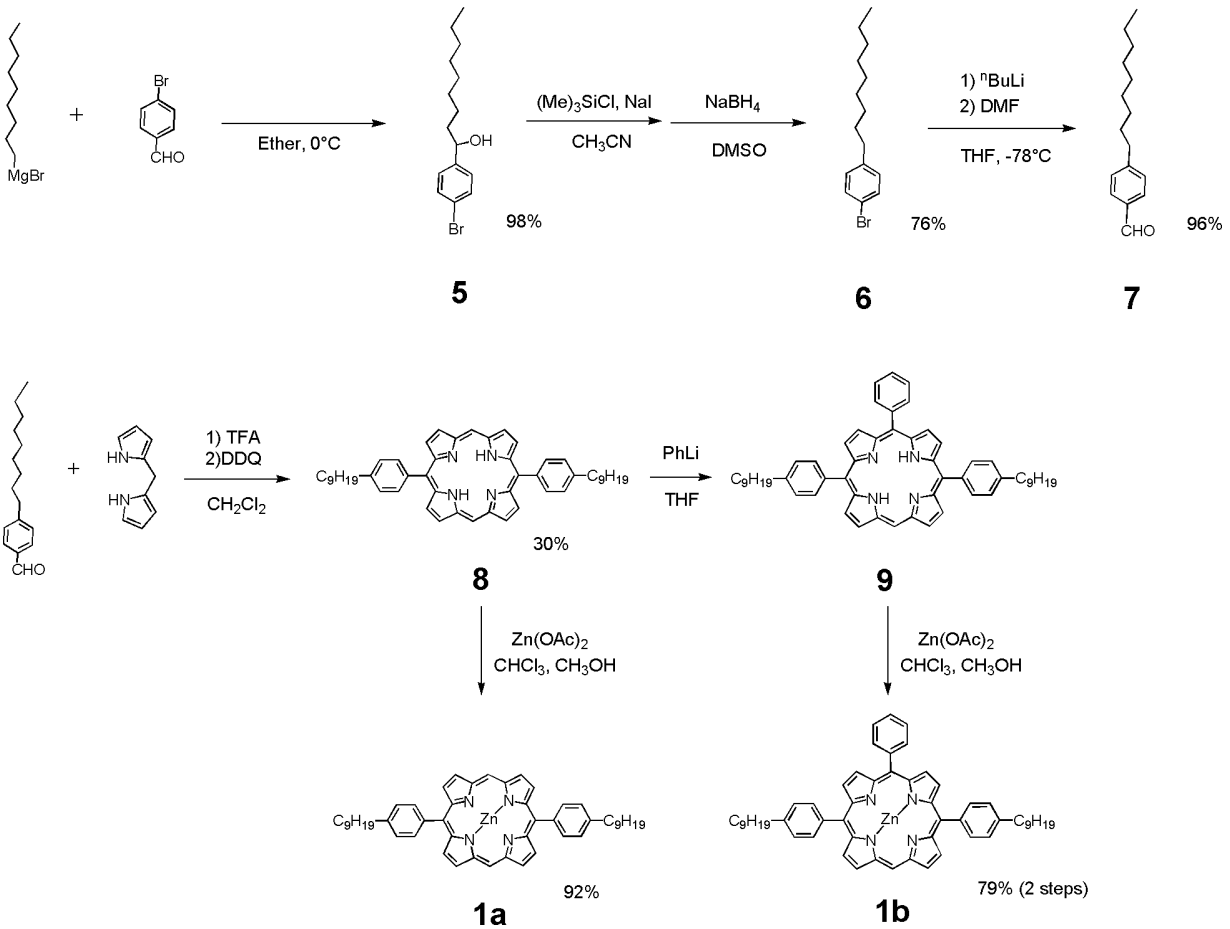
Scheme 1. Molecular structures.

gave *meso–meso*-linked porphyrin dimer (**10**), trimer (**11a**), and tetramer (**12a**) in 63% yield for **11a** and 20% yield for **12a** based on **1a**. The reaction mixture was easily separated by GPC-HPLC. The DDQ-$Sc(OTf)_3$ oxidation of **11a** was performed in toluene at 100 ºC, which gave *meso–meso*, *β–β*, *β–β* triply-linked triporphyrin **3a** in 68% yield. The MALDI-TOF mass spectrum of **3a** appeared at *m*/*z* = 2474 (calcd for $C_{162}H_{164}N_{12}Zn_3$, 2475).

The oxidation of **12a** was attempted with 9 equivs of DDQ and $Sc(OTf)_3$ in refluxing toluene, which gave *meso–meso*, *β–β*, *β–β* triply-linked tetraporphyrin **4a** in 63% yield. MALDI-TOF mass spectrum showed its peaks at *m*/*z* = 6390 and 9599 corresponding to dimeric and trimeric aggregates (calcd for **12a** $C_{212}H_{208}N_{16}Zn_4$ = 3241), indicating that **4a** tends to form quite strong aggregation.

In order to improve the above problem, more bulky substituents were introduced in **1c**. Ag^I-promoted oxidative coupling reaction of **1c** and **1b** (1:7) was performed to form *meso–meso*-linked porphyrin dimer (**10**), trimer (**11b**), and tetramer (**12b**) in 64% yield for **11b** and in 15% yield for **12b** based on **1c**. The further oxidation of **11b** was performed with 7 equivs of DDQ and $Sc(OTf)_3$ in refluxing toluene, to gave triply-linked triporphyrin **3b** in 67% yield. The molecular weight of **3b** has been confirmed by MALDI-TOF mass spectrum (*m*/*z* = 2447, calcd for $C_{160}H_{160}N_{12}Zn_3$, 2446).

The oxidation of **12b** was attempted with 9 equivs of DDQ and $Sc(OTf)_3$ in refluxing toluene, which gave triply-linked tetraporphyrin **4b** in 61% yield. In contrast to **4a**, MALDI-TOF mass spectrum showed its parent peak (*m*/*z* = 3195, calcd for $C_{212}H_{214}N_{16}Zn_4$, 3191), indicating that aggregation was suppressed by peripheral bulky substituents.



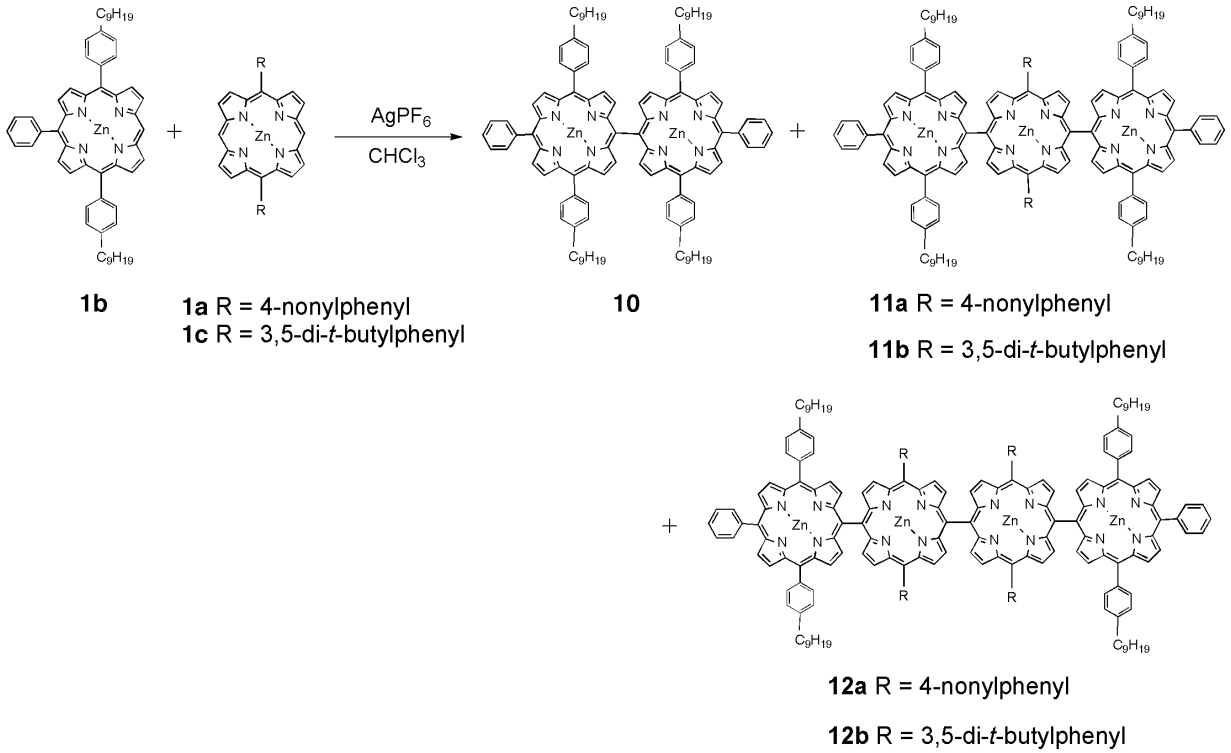
Scheme 2. Synthetic scheme of **1a** and **1b**.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of **2a** in $CDCl_3$ showed quite broad peaks, while **2b** showed sharper peaks, probably due to steric effects of the *meso*-aryl substituents that suppress aggregation. Figure 1 illustrates the concentration dependence of the ^{1}H NMR spectra of **2a** from 0.5 mM to 4.0 mM. The broad spectrum indicated aggregation in chloroform even at 0.5 mM concentration, and the spectrum as a whole was slightly high-field-shifted at 4.0 mM. Upon addition of butylamine, the ^{1}H NMR spectrum of **2a** became sharper, featuring signals of the peripheral β-protons at 7.49, 7.48, and 7.02 ppm as a pair of doublets and a singlet, and the aromatic protons of the *meso*-4-nonylphenyl groups at 7.62 and 7.32 as a pair of doublets, and the aromatic protons of the *meso*-phenyl groups at 7.71, 7.50, and 7.49 ppm. It has been shown that aggregation of **2a** is released in the presence of 5% butylamine in $CDCl_3$, and the spectrum shown in Fig. 1c is rather concentration independent.

The ^{1}H NMR spectra of **3a** and **3b** were broader in the absence of butylamine in either $CDCl_3$ or CD_2Cl_2, reflecting a stronger assembling nature. Similar to the case of **2a**, the ^{1}H NMR spectra of **3a** and **3b** in CD_2Cl_2 become sharper with 5% butylamine, exhibiting the β-pyrrolic protons at 6.29, 6.97, 7.53, and 7.53 ppm, and 6.23, 6.97, 7.52, and 7.53 ppm, respectively (Fig. 2).

The ^{1}H NMR spectra of **1d**, **2a**, **3b**, and **4b** at 25 °C in CD_2Cl_2 with 5% butylamine are shown in Fig. 3. The pyrrolic β-protons of the monomer **1d** appear at 8.84 (4H) and 8.87 (4H) ppm, while those of **2a** appear at high-field position (7.05 (4H) and 7.51 (8H) ppm). In longer conjugated arrays **3b** and **4b**, the pyrrolic β-protons are found at 7.53, 7.52, 6.97, and 6.23 ppm, and 7.45, 7.45, 6.87, 6.29, and 6.23 ppm, respectively, again indicating the high-field shifts compared with the corresponding *meso–meso* singly-linked porphyrin arrays. The reason for these high-field shifts is not clear, but one may suggest the weakened aromatic ring current due to the enhanced electronic communication between neighboring porphyrins through the triple linkage.



Scheme 3. Synthetic scheme of *meso–meso*-linked porphyrin arrays.

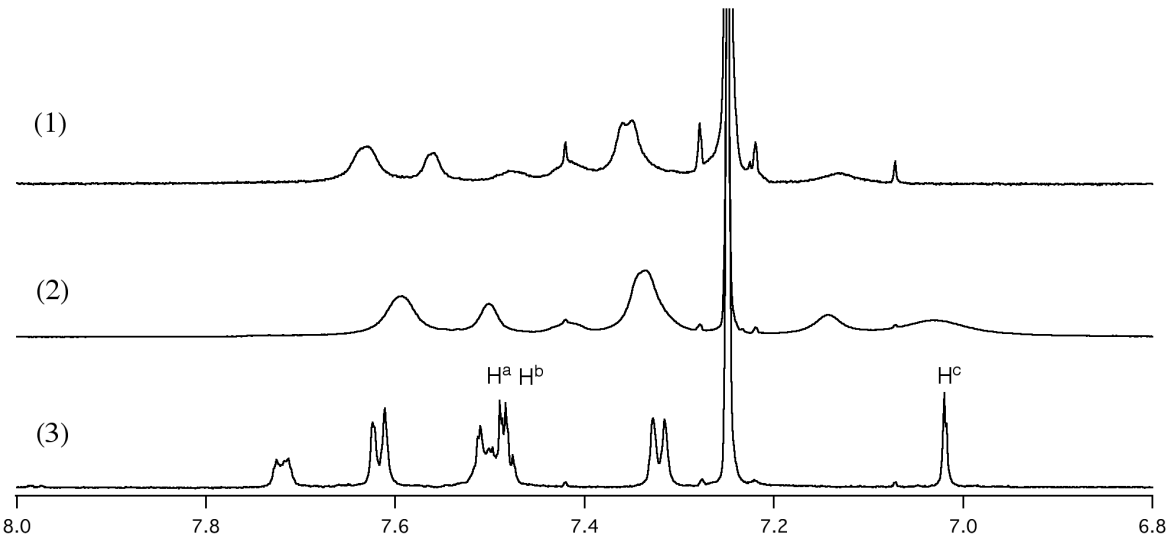


Fig. 1. ^{1}H NMR spectra of **2a** in $CDCl_3$ at room temperature. (1) 0.5 mM, (2) 4.0 mM, (3) 4.0 mM with butylamine.

*X-ray Crystal Structure of **2a** Along With Two Axial Butylamine Molecules*

The molecular structure of **2a** with two butylamine molecules was confirmed by single-crystal X-ray diffraction analysis (Fig. 4). Two butylamine molecules are coordinated with the central zinc(II) ions of **2a** in a trans fashion. The X-ray structure shows the two porphyrin rings are fused to form a coplanar saddle-like conformation with a mean plane deviation of 0.16 Å for the 25 core atoms. The crystal packing of **2a** is like a parallel sheet with an interporphyrin separation of approximately 9.3 Å, featuring no significant aggregation in the solid state. The

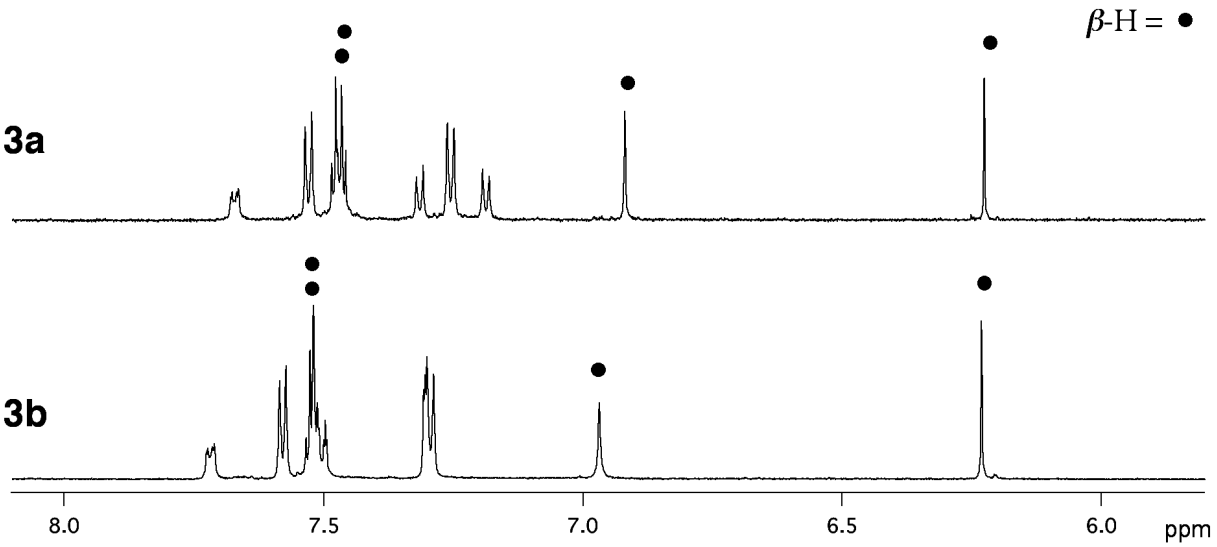


Fig. 2. ^{1}H NMR spectra of **3a** and **3b** in CD_2Cl_2 at room temperature.

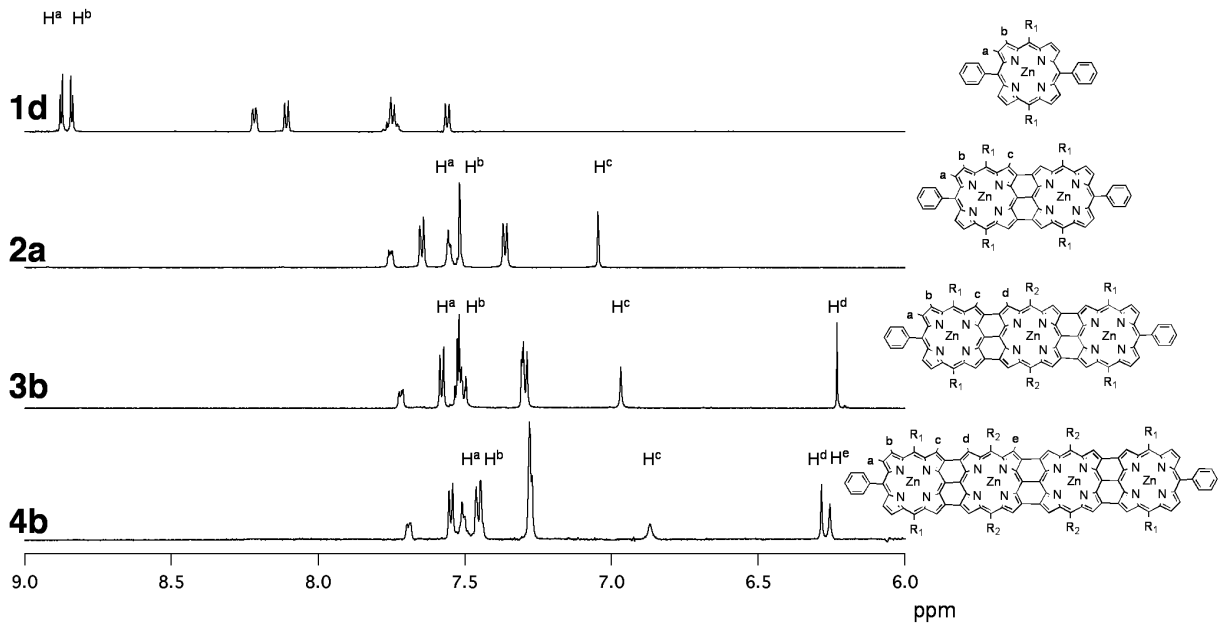


Fig. 3. ^{1}H NMR spectra of **1d**, **2a**, **3b**, and **4b** in CD_2Cl_2 with 5% butylamine at room temperature.

newly formed two C_β–C_β bonds are both 1.44 Å, and the bond length of C_{meso}–C_{meso} is 1.48 Å. X-ray structure of **2b**[10] with ethanol exhibits a flat coplanar conformation with a mean plane deviation (0.23 Å).

UV-vis Absorption Spectra

Although the electronic conjugation is almost disrupted in the *meso–meso* singly-linked porphyrin oligomers due to perpendicular conformation, triply-linked porphyrin arrays are fully conjugated over the whole array, which results in drastically red-shifted absorption spectra that reach to the far-infrared region. The absorption spectra of triply-linked porphyrin arrays exhibit three distinct broad absorption bands in $CHCl_3$ (designated as bands I, II, III in Fig. 5a). Upon addition of 5% butylamine, the absorption bands, especially bands II

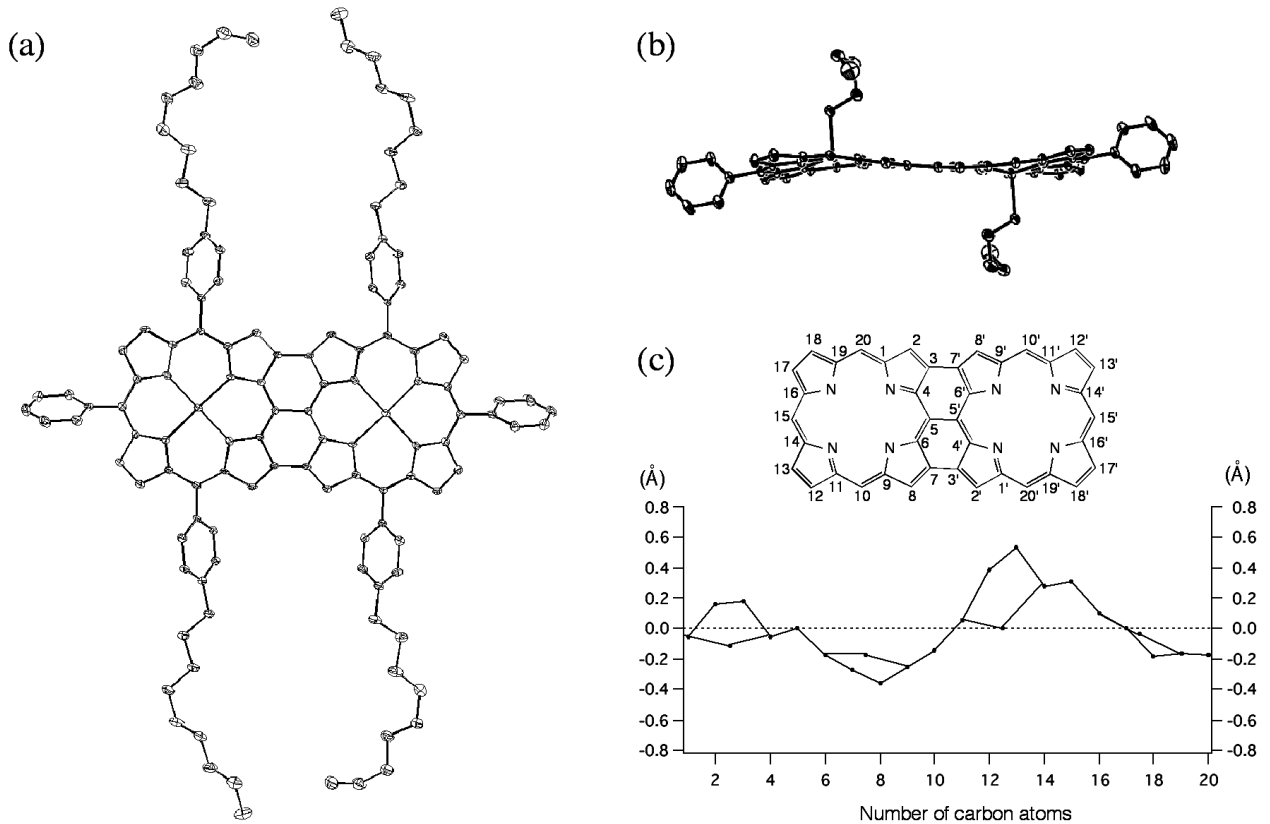


Fig. 4. X-ray structure of **2a** with butylamine, top view (a) and side view (b). Displacements of the peripheral carbon atoms from the mean plane of 24 atoms (c). Hydrogen atoms and butylamines are omittied for clarity in (a), and hydrogen atoms and 4-nonylphenyl substituents are omitted for clarity in (b).

and III, become sharpened as a consequence of coordination-induced dissociation.

In the case of **2a**, two strong absorption bands, I and II, are observed at 420 and 583 nm, respectively, and a broad band, III, at 1061 nm. Upon addition of butylamine, the strong absorption bands remain nearly at the same position, but the Q-band-like absorption is shifted to the low-energy side at 1146 nm, with distinct sharpening and vibrational structures.

Essentially the same tendency was observed for **3b** and **4b**. Two strong Soret-like bands I and II, of **3b** are observed at 416 and 670 nm, respectively, and a broad Q-band-like absorption III at 1290 nm in $CHCl_3$. Upon the addition of butylamine, the high-energy Soret band remains at the same position, but the low-energy Soret band is sharpened and Q-bands are shifted to the low-energy side at 1494 nm. In the case of **4b**, two strong Soret-like bands, I and II, are observed at 405 and 776 nm, respectively, and a broad Q-band is observed at 1652 nm. Upon the addition of butylamine, band I remains, but the low-energy Soret band II is sharpened and Q-band III is shifted to the low-energy side at 1813 nm. These experiments revealed that very broad Q-band-like lowest-energy absorptions of the porphyrin tapes are due to their aggregation, and disaggregation caused by the addition of coordinative butylamine led to the sharpening of these bands with vibrational structures that are quite similar to those of porphyrin monomers. The molecular coefficient of the lowest energy absorption (band III) is steadily increased with the increase in the number of the porphyrins, reaching a value of 340,000 $M^{-1}cm^{-1}$ for **4b**.

CONCLUSION

Triply-linked porphyrin arrays tend to aggregate extensively due to their planar large π-conjugated framework. Upon addition of butylamine, clear ^1H NMR and UV-vis absorption spectra were observed for trimer and tetramer, allowing the investigation on the intact elec-

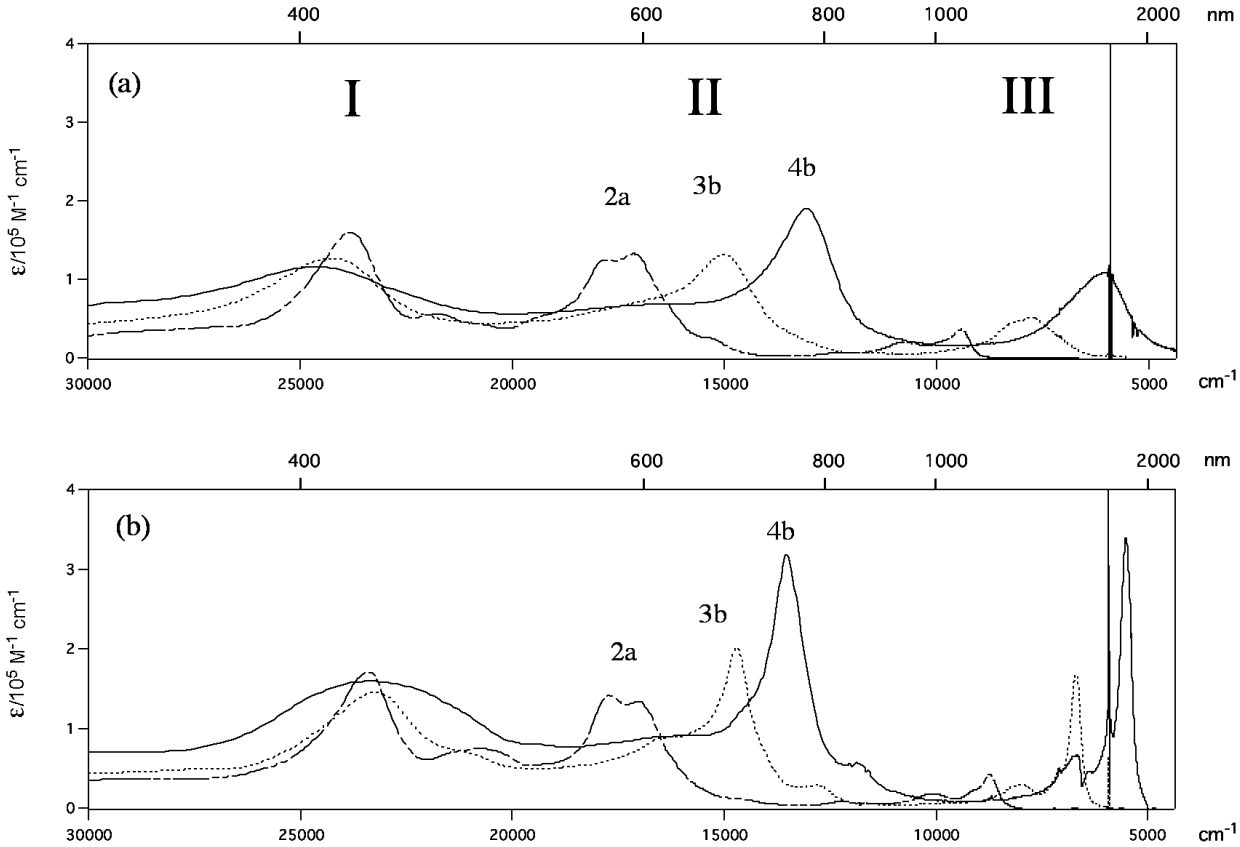


Fig. 5. UV-vis absorption spectra of **2a**, **3b**, and **4b** in $CHCl_3$ at room temperature. (a) Without butylamine. (b) With 5% butylamine. The background absorbance at 6000 cm^{-1} may arise from the overtones of C–H vibration of $CHCl_3$.

tronic structure of porphyrin tapes. Further studies about the photophysics of fully-conjugated porphyrin tapes are currently under way.

EXPERIMENTAL

General Procedure

All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. ^{1}H NMR spectra were recorded on a JEOL delta-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CH_2Cl_2 (δ 5.32 ppm) and $CHCl_3$ (δ 7.26 ppm). Spectroscopic grade CH_2Cl_2 was used as solvent for all spectroscopic studies. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Mass spectra were recorded on a JEOL HX-110 spectrometer using the positive-FAB ionization method with accelerating voltage 10 kV and a 3-nitrobenzylalcohol matrix. MALDI-TOF mass spectra were recorded on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer using a positive-MALDI-TOF method with/without a sinapinic acid matrix. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-300). Recycling preparative GPC-HPLC was performed for separation of the porphyrin oligomers (Japan Analytical Industry Co., LTD LC-908 with JAI-GEL 2.5H and 3H column series with $CHCl_3$ as an eluent.).

Synthesis

*1-(4-Bromophenyl)-1-hydroxynonane (**5**)*

Octylmagnesium bromide was prepared from magnesium (2.44 g, 100 mmol) and 1-octylbromide (21.6 g, 100 mmol) in diethyl ether at room temperature. Then, 1-bromobenzaldehyde (13.5 g, 80 mmol) was added to the mixture in diethyl ether at 0 ºC. The combined organic solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The resulting yellow residue was taken up in hexane and purified by silica gel chromatography with a mixture of hexane: AcOEt, 3:1, as an eluent. The yield of **5** was 98% (29.2 g). ^{1}H NMR($CDCl_3$): δ = 0.87 (3H, t, *J* = 6.9 Hz), 1.24 (7H, m), 1.36 (2H, m), 1.66 (2H, m), 1.73 (2H, m), 1.99 (1H, s), 4.62 (2H, m), 7.21 (2H, d, *J* = 8.0 Hz), and 7.45 (2H, d, *J* = 8.0 Hz); FAB MS: calcd for $C_{15}H_{23}BrO$: 299.2; found: 299.2 [M^+].

*4-Bromophenylnonane (**6**)*

A mixture of **5** (29.95 g, 0.1 mmol), trimethylsilylchloride (55.4 mL, 0.6 mol), and NaI (89.9 g, 0.6 mol) in CH_3CN solution (300 mL) was stirred under N_2 for 12 h at room temperature. Then, the organic residue was washed with $Na_2S_2O_3$ solution, dried over anhydrous Na_2SO_4 and evaporated. The resulting orange residue was stirred with $NaBH_4$ (5.7 g, 0.15 mol) in DMSO (300 mL) under N_2 for 12 h at room temperature. The mixture was extracted with hexane. Combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated. The yellow residue was taken up in hexane and purified by silica gel chromatography with hexane as an eluent. The first band was **6** (21.52 g, 76%). ^{1}H NMR($CDCl_3$): δ = 0.89 (3H, t, *J* = 6.0 Hz), 1.28 (12H, m), 1.59 (2H, m), 2.55 (2H, m), and 7.05 (2H, d, *J* = 8.4 Hz), and 7.39 (2H, d, *J* = 8.4 Hz); FAB MS: calcd for $C_{15}H_{23}Br$: 282.2; found: 282.2 [M^+].

*4-Nonylbenzaldehyde (**7**)*

To a solution of 4-bromophenylnonane (8.5 g, 30 mmol) was added a hexane solution of butyllithium (57 mL, 92 mmol) in dry THF (200 mL) at –78 °C. After stirring at –78 ºC for 1 h, DMF (6.1 mL, 92 mmol) was slowly added to the mixture. After the reaction temperature was increased gradually until room temperature, the mixture was poured into iced water and extracted with hexane. The combined organic extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The organic residue was taken up in hexane and purified by silica gel chromatography with a mixture of hexane: AcOEt, 3:1, as an eluent. The yield of 4-nonylbenzaldehyde was 93% (6.45 g). ^{1}H NMR($CDCl_3$): δ = 0.85 (3H, t, *J* = 7.0 Hz), 1.22 (10H, m), 1.28 (2H, m), 1.61 (2H, m), 2.65 (2H, m), 7.29 (2H, d, *J* = 8 Hz), 7.65 (2H, d, *J* = 8.0 Hz), and 9.93 (1H, s); FAB MS: calcd for $C_{15}H_{23}BrO$: 232.3; found: 232.3 [M^+].

*5-15-Di(4-nonylphenyl)porphyrin (**8**)*

A solution of dipyrromethane (458 mg, 3.1 mmol) and **7** (630 mg, 3.1 mmol) in dry CH_2Cl_2 (600 mL) was stirred under N_2 for 15 min. TFA (0.13 mL, 2.0 mmol) was added to the solution via syringe, the flask was shielded from light, and the solution was stirred for 3 h at room temperature. DDQ (1.15g, 5 mmol) was added, and the solution was stirred for an additional 2 h. The mixture was passed directly through an alumina column and evaporated. The yield of **8** was 30% (668 mg). ^{1}H NMR($CDCl_3$): δ = –3.09 (2H, s), 0.94 (6H, t, *J* = 6.6 Hz), 1.36 (16H, m), 1.52 (4H, m), 1.59 (4H, m), 1.94 (4H, m), 2.97 (4H, t, *J* = 7.3 Hz), 7.61 (4H, d, *J* = 7.6 H), 8.17 (4H, d, *J* = 7.6 Hz), 9.11 (4H, d, *J* = 2.3 Hz) 9.38 (4H, d, *J* = 2.3 Hz), and 10.29 (2H, s); FAB MS: calcd for $C_{50}H_{58}N_4$: 715.5; found: 715.5 [M^+]; UV ($CHCl_3$): λ_{max} = 409, 503, 538, 576, and 630 nm.

*Zn (II) 5-15-Di(4-nonylphenyl)porphyrin **1a***

A saturated solution of $Zn(OAc)_2$ in CH_3OH (3 mL) was added to a solution of **8** (200 mg, 0.28 mmol) in $CHCl_3$ (150 mL) and the resulting mixture was stirred for 3 h at 60 ºC. Then, the organic residue was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The solid was taken up in CH_2Cl_2 and purified by silica gel chromatography by CH_2Cl_2. The yield of **1a** was 92% (200 mg). ^{1}H NMR($CDCl_3$): δ = 0.94 (6H, t, *J* = 6.4 Hz), 1.32~1.45 (16H, m), 1.51 (4H, m), 1.59 (4H, m), 1.95 (4H, m), 2.98 (4H, t, *J* = 7.8 Hz), 7.59 (4H, d, *J* = 7.4 Hz), 8.15 (4H, d, *J* = 7.4 Hz), 9.16 (4H, d, *J* = 4.1 Hz), 9.41 (4H, d, *J* = 4.1 Hz), and 10.29 (2H, s); FAB MS: calcd for $C_{50}H_{56}N_4Zn$: 776.4; found: 776.4 [M^+]; UV ($CHCl_3$): λ_{max} = 413 and 540 nm.

*Zn (II) 5-15-Di(4-nonylphenyl)-10-phenylporphyrin **1b** and Zn (II) 5-15-di(4-nonylphenyl)-10,20-diphenylporphyrin **1d***

8 (157 mg, 0.22 mmol) was dissolved in dry THF (50 mL) under N_2 and the solution was cooled at 0 °C, to which PhLi (1.4 mL, 1.5 M solution in ether) was added dropwise, and the reaction flask was removed from the cooling bath and allowed to warm to room temperature and stirred for 30 min. Then, the reaction mixture was treated with 50% aqueous THF (1 mL). DDQ (100 mg, 0.44 mmol as a CH_2Cl_2 solution) was added and stirred for 15 min. The organic residue was washed with water, dried over anhydrous Na_2SO_4, and evaporated. Then, the product separation was performed on a preparative-size exclusion column (recycling preparative GPC-HPLC) for **8**, 5,15-di(4-nonylphenyl)-10-phenylporphyrin **9**, and 5,15-di(4-nonylphenyl)-10,20-diphenylporphyrin. A solution of **9** in $CHCl_3$ was stirred under N_2 for 15 min at room temperature. A saturated $Zn(OAc)_2$ in CH_3OH (3 mL) was added to the solution and it was stirred for 3 h at 60 °C. Then, the organic solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The solid was taken up in CH_2Cl_2 and purified by silica gel chromatography by CH_2Cl_2. The yield of Zn(II) 5,15-di(4-nonylphenyl)-10-phenylporphyrin **1b** was 79% (149 mg). A solution of 5,15-di(4-nonylphenyl)-10,20-diphenylporphyrin in $CHCl_3$ was stirred under N_2 for 15 min at room temperature. A saturated $Zn(OAc)_2$ in CH_3OH (3 mL) was added to the solution and it was stirred for 3 h at 60 ºC. Then, the residue was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The solid was taken up in CH_2Cl_2 and purified by silica gel chromatography by CH_2Cl_2. The yield of Zn(II) 5,15-di(4-nonylphenyl)-10,20-diphenylporphyrin **1d** was 5.4% (11 mg). **1b**: ^{1}H NMR($CDCl_3$): δ = 0.94 (6H, t, *J* = 6.9 Hz), 1.36–1.42 (16H, m), 1.51 (4H, m), 1.59 (4H, m), 1.95 (4H, m), 2.98 (4H, t, *J* = 7.8 Hz), 7.57 (4H, d, *J* = 7.3 Hz), 7.74 (2H, m), 7.77 (1H, m), 8.14 (4H, d, *J* = 7.8 Hz), 8.21 (2H, d, *J* = 6.5 Hz), 8.96 (2H, d, *J* = 4.6 Hz), 9.02 (2H, d, *J* = 4.2 Hz), 9.12 (2H, d, *J* = 4.6 Hz), 9.37 (2H, d, *J* = 4.6 Hz), and 10.22 (1H, s); FAB MS: calcd for $C_{56}H_{60}N_4Zn$: 852.5; found: 852.5 [M^+]; UV ($CHCl_3$): λ_{max} = 417 and 545 nm. **1d**: ^{1}H NMR($CDCl_3$): δ = 0.91 (6H, t, *J* = 6.4Hz), 1.33–1.42 (16H, m), 1.47 (4H, m), 1.56 (4H, m), 1.92 (4H, m), 2.95 (4H, t, *J* = 7.8 Hz), 7.54 (4H, d, *J* = 7.8 H), 7.74 (4H m), 7.75 (2H m), 8.10 (4H, d, *J* = 7.9 Hz), 8.21 (4H, m), 8.92 (4H, d, *J* = 4.6 Hz), 8.96 (4H, d, *J* = 4.6 Hz); FAB MS: calcd for $C_{62}H_{64}N_4Zn$: 928.5; found: 928.5 [M^+]; UV ($CHCl_3$): λ_{max} = 422.5 and 552.5 nm. **1d** with butylamine: ^{1}H NMR($CDCl_3$): δ = 0.94 (6H, t, *J* = 6.9Hz), 1.35–1.45 (16H, m), 1.49 (4H, m), 1.58 (4H, m), 1.93 (4H, m), 2.95 (4H, t, *J* = 7.8 Hz), 7.56 (4H, d, *J* = 7.6 Hz), 7.74 (4H, m), 7.76 (2H, m), 8.14 (4H, d, *J* = 7.8 Hz), 8.22 (2H, d, *J* = 6.5 Hz), 8.84 (4H, d, *J* = 4.6 Hz), and

8.87 (2H, d, *J* = 4.6 Hz); UV ($CHCl_3$): λ_{max} = 430, 565, and 606 nm.

meso–meso, β–β, β–β *Triply-linked Zn(II)-diporphyrin **2a***

1b (100 mg, 0.118 mmol) was oxidized with DDQ (133.9 mg, 0.59 mmol) and $Sc(OTf)_3$ (253 mg, 0.59 mmol) in toluene at 60 ºC for 30 min under N_2. After addition of THF to the mixture, the resulting solution was directly passed through an alumina column and then evaporated. The yield of **2a** was 86%. **2a**; MALDI-TOF MS: calcd for $C_{112}H_{116}N_8Zn_2$: 1705; found: 1703; UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 420 (174000), 562 (136000), 583 (144000), and 1061 (39600) nm. **2a** with butylamine; ^{1}H NMR (CD_2Cl_2): δ = 0.92 (12H, t, *J* = 6.7 Hz), 1.20–1.35 (16H, m), 1.44 (8H, m), 1.50 (8H, m), 1.80 (8H, m), 2.81 (8H, t, *J* = 7.6 Hz), 7.05 (4H, s), 7.36 (8H, d, *J* = 7.8 Hz), 7.51 (8H, s), 7.55 (2H, m), 7.55 (4H, m), 7.65 (8H, d, *J* = 7.8 Hz), and 7.75 (8H, m); UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 425 (173000), 563 (143000), and 1146 (44400) nm.

meso–meso *Singly-linked Zn(II) di-, tri-, and tetraporphyrin **10**, **11a**, and **12a***

1a (40 mg, 0.051 mmol) and **1b** (320 mg, 0.374 mmol) were dissolved in $CHCl_3$ (200 mL), and the reaction vessel was covered with foil. A solution of 0.1 M $AgPF_6$ in CH_3CN (0.24 mmol) was added all at once. After stirring for 12 h, the mixture was diluted with water and the porphyrin products were extracted with $CHCl_3$. The combined organic extract was washed with water and dried over anhydrous Na_2SO_4. Then, separation by recycling preparative GPC-HPLC afforded three major fractions that eluted in the following order: **10** (216.3 mg, 0.12 mmol), **11a** (79.4 mg, 0.032 mmol), and **12a** (16.7 mg, 0.005 mmol). **10**: ^{1}H NMR ($CDCl_3$): δ = 0.81 (12H, t, *J* = 6.9 Hz), 1.2–1.3 (32H, m), 1.35 (8H, m), 1.44 (8H, m), 1.79 (8H, m), 2.92 (8H, t, *J* = 7.3 Hz), 7.45 (8H, d, *J* = 7.8 Hz), 7.79 (4H, m), 7.80 (2H, m), 8.07 (4H, d, *J* = 4.5 Hz), 8.08 (8H, d, *J* = 7.8 Hz), 8.29 (4H, m), 8.66 (4H, d, *J* = 4.5 Hz), and 8.98 (8H, s); MALDI-TOF MS: calcd for $C_{112}H_{118}N_8Zn_2$: 1707; found: 1707; UV ($CHCl_3$): λ_{max} = 422, 458, and 563 nm. **11a**: ^{1}H NMR ($CDCl_3$): δ = 0.75 (6H, t, *J* = 6.9 Hz), 0.88 (12H, t, *J* = 6.9 Hz), 1.16–1.39 (60H, m), 1.41 (4H, m), 1.49 (8H, m), 1.72 (4H, m), 1.85 (8H, m), 2.76 (4H, t, *J* = 7.4 Hz), 2.89 (8H, t, *J* = 7.4 Hz), 7.37 (4H, d, *J* = 8.3 Hz), 7.49 (8H, d, *J* = 8.3 Hz), 7.81 (2H, m), 7.82 (4H, m), 8.12 (4H, d, *J* = 8.7 Hz), 8.16 (8H, d, *J* = 7.4 Hz), 8,18 (4H, d, *J* = 4.6 Hz), 8.23 (4H, d, *J* = 4.6 Hz), 8.31 (4H, m), 8.73 (4H, d, *J* = 4.6 Hz), 8.75 (4H, d, *J* = 4.6 Hz), 9.02 (4H, d, *J* = 4.6 Hz), and 9.04 (4H, d, *J* = 4.6 Hz); MALDI-TOF MS: calcd for $C_{162}H_{172}N_{12}Zn_3$: 2483; found: 2480; UV ($CHCl_3$): λ_{max} = 419, 479, and 571 nm. **12a**: ^{1}H NMR ($CDCl_3$): δ = 0.76 (12H, t, *J* = 6.9 Hz), 0.86 (12H, t, *J* = 6.9 Hz), 1.16–1.36 (80H, m), 1.38 (8H, m), 1.49 (8H, m), 1.74 (4H, m), 1.85 (8H, m), 2.77 (4H, t, *J* = 7.3 Hz), 2.88 (8H, t, *J* =7.4 Hz), 7.40 (8H, d, *J* = 7.8 Hz), 7.50 (8H, d, *J* = 8.3 Hz), 7.80 (2H, m), 7.81 (4H, m), 8.14 (8H, d, *J* = 7.4 Hz), 8.17 (8H, d, *J* = 7.4 Hz), 8,18 (4H, d, *J* = 4.6 Hz), 8.23 (4H, d, *J* = 4.6 Hz), 8.28 (4H, d, *J* = 4.6 Hz), 8.31 (4H, m), 8.75 (4H, d, *J* = 4.6Hz), 8.76(4H, d, *J* = 4.6Hz), 8.79 (4H, d, *J* = 4.6Hz), 9.02 (4H, d, *J* = 4.6Hz), and 9.04 (4H, d, *J* = 4.6 Hz); MALDI-TOF MS: calcd for $C_{212}H_{226}N_{16}Zn_4$: 3259; found: 3256; UV ($CHCl_3$): λ_{max} = 418, 489, and 575 nm.

meso–meso *Singly-linked Zn(II) tri- and tetraporphyrin **11b** and **12b***

1c (30 mg, 0.039 mmol) and **1b** (240 mg, 0.281 mmol) were dissolved in $CHCl_3$ (200 mL), and the reaction vessel was covered with foil. A solution of 0.1 M $AgPF_6$ in CH_3CN (0.24 mmol) was added all at once. After stirring for 12 h, the mixture was diluted with water and the porphyrin products were extracted with $CHCl_3$. The combined organic extract was washed with water and dried over anhydrous Na_2SO_4. Then, recycling preparative GPC-HPLC afforded three major fractions that eluted in the following order: **10** (171 mg, 0.100 mmol), **11b** (61.2 mg, 0.025 mmol), and **12b** (9.6 mg, 0.003 mmol). **11b**: ^{1}H NMR($CDCl_3$): δ 0.85 (12H, t, *J* = 6.9 Hz), 1.20–1.35 (32H, m), 1.41 (8H, m), 1.49 (8H, m), 1.53 (36H, s), 1.83 (8H, m), 2.87 (8H, t, *J* = 7.8 Hz), 7.48 (8H, d, *J* = 8.3 Hz), 7.58 (2H, t, *J* = 1.8 Hz), 7.81 (4H, m), 7.82 (4H, m), 8.07 (4H, d, *J* = 1.8 Hz), 8.14 (8H, d, *J* = 8.3 Hz), 8.16 (4H, d, *J* = 4.6 Hz), 8.24 (4H, d, *J* = 4.6 Hz), 8.31 (4H, d, *J* = 7.7 Hz), 8.72 (4H, d, *J* = 4.5 Hz), 8.75 (4H, d, *J* = 4.5 Hz), 9.01 (4H, d, *J* = 4.6 Hz), and 9.03 (4H, d, *J* = 4.6 Hz). MADLI-TOF MS: calcd for $C_{160}H_{168}N_{12}Zn_3$: 2455; found: 2453; UV ($CHCl_3$): λ_{max} = 418, 477, and 567 nm. **12b**: ^{1}H NMR($CDCl_3$): δ 0.85 (12H, t, *J* = 7.3 Hz), 1.2–1.35 (32H, m), 1.38 (72H, s), 1.39 (8H, m), 1.49 (8H, m), 1.84 (8H, m), 2.88 (8H, t, *J* = 7.8 Hz), 7.50 (8H, d, *J* = 8.3 Hz), 7.62 (4H, t, *J* = 1.9 Hz), 7.81(4H, m), 7.82 (4H, m), 8.11 (8H, d, *J* = 1.9 Hz), 8.16 (8H, d, *J* = 8.3 Hz), 8.19 (4H, d, *J* = 4.6 Hz), 8.27 (4H, d, *J* = 4.6 Hz), 8.32 (4H, d, *J* = 4.6 Hz), 8.33 (4H, m), 8.74 (4H, d, *J* = 4.6 Hz), 8.77 (4H, d, *J* = 4.6 Hz), 8.80 (4H, d, *J* = 4.6 Hz), 9.03 (4H, d, *J* = 4.6 Hz), and 9.50 (4H, d, *J* = 4.6 Hz). MALDI-TOF MS: calcd for $C_{208}H_{218}N_{16}Zn_4$: 3204; found: 3196; UV ($CHCl_3$): λ_{max} = 418, 487, and 574 nm.

meso–meso, β–β, β–β *Triply-linked Zn(II)-triporphyrin **3a***

11a (19.6 mg, 0.008 mmol) was oxidized with DDQ (12.7 mg, 0.056 mmol) and $Sc(OTf)_3$ (24.0 mg, 0.056 mmol) in toluene at 110 ºC for 20 min under N_2. The mixture was directly passed through an alumina column and evaporated. The yield of **3a** was 68% (13.6 mg). **3a**: MALDI-TOF MS: calcd for $C_{162}H_{164}N_{12}Zn_3$: 2475; found: 2474; UV (CH_2Cl_2): λ_{max} = 417, 667, and 1304 nm. **3a** with butylamine: ^{1}H NMR(CD_2Cl_2): δ = 0.84 (6H, t, *J* = 6.9 Hz), 0.91 (12H, t, *J* = 6.9 Hz), 1.16–1.39 (60H, mp), 1.40 (4H, m), 1.48 (8H, m), 1.75 (4H, m), 1.77 (8H, m), 2.72 (4H, t, *J* = 7.8 Hz), 2.77 (8H, t, *J* = 7.8Hz), 6.29 (4H, s), 6.97 (4H, s), 7.24 (4H, d, *J* = 7.8 Hz), 7.31 (8H, d, *J* = 7.8 Hz), 7.37 (4H, d, *J* = 7.8 Hz), 7.53 (4H, *m*-Ph, m), 7.53 (2H, *p*-Ph, m), 7.53 (4H, s), 7,53 (4H, s), 7.58 (8H, d, *J* = 7.8 Hz), and 7.72 (4H, *o*-Ph, m); UV ($CHCl_3$): λ_{max} = 427, 680, and 1491 nm.

meso–meso, β–β, β–β *Triply-linked Zn(II)-triporphyrin **3b***

11b (20.0 mg, 0.008 mmol) was oxidized with DDQ (12.7 mg, 0.056 mmol) and $Sc(OTf)_3$ (24.0 mg, 0.056 mmol) in toluene at 110 ºC for 30 min under N_2. The mixture was directly passed through an alumina column and evaporated. The yield of *meso–meso β–β*, *β–β* triply-linked Zn(II)-diporphyrin was 67% (13.3 mg). MALDI-TOF MS: calcd for $C_{160}H_{160}N_{12}Zn_3$: 2447; found: 2446; UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 416 (128000), 670 (133000), and 1290 (54000) nm. **3b** with butylamine: ^{1}H NMR (CD_2Cl_2): δ = 0.89 (12H, t, *J* = 6.9 Hz), 1.15–

1.25 (32H, m), 1.30 (36H, s), 1.38 (8H, m), 1.44 (8H, m), 1.73 (8H, m), 2.74 (8H, t, J = 7.8 Hz), 6.23 (4H, s), 6.97 (4H, s), 7.23 (8H, d, J = 7.8 Hz), 7.31 (4H, d, J = 1.8 Hz), 7.49 (2H, t, J = 1.8 Hz), 7.51 (4H, m), 7.52 (2H, m), 7.52 (4H, s), 7.53 (4H, s), 7.58 (8H, d, J = 7.8 Hz), and 7.71 (4H, m); UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 431 (146000), 680 (202000), 1249 (32000), and 1494 (170000) nm.

meso–meso, β–β, β–β *Triply-linked Zn(II) tetraporphyrin* ***4a***

12a (15 mg, 0.0046 mmol) was oxidized with DDQ (9.4 mg, 0.041 mmol) and $Sc(OTf)_3$ (17.8 mg, 0.041 mmol) in toluene at 110 ºC for 20 min under N_2. The mixture was passed directly through an alumina column and evaporated. The yield of *meso–meso*, *β–β*, *β–β* triply-linked Zn(II)-diporphyrin was 63% (9.5 mg). UV ($CHCl_3$): λ_{max} = 403, 777, and 1632 nm. **4a** with butylamine: UV (CH_2Cl_2): λ_{max} = 427, 738, and 1808 nm.

meso–meso, β–β, β–β *Triply-linked Zn(II) tetraporphyrin* ***4b***

12b (12 mg, 0.0046 mmol) was oxidized with DDQ (9.4 mg, 0.041 mmol) and $Sc(OTf)_3$ (17.8 mg, 0.041 mmol) in toluene at 110 ºC for 20 min under N_2. The mixture was passed directly through an alumina column and evaporated. The yield of *meso–meso*, *β–β*, *β–β* triply-linked Zn(II)-diporphyrin was 61% (8.5 mg). MALDI-TOF MS: calcd for $C_{212}H_{214}N_{16}Zn_4$: 3191; found: 3195; UV ($CHCl_3$): λ_{max} = 405 (117000), 776 (190000), and 1652 (111000) nm. **4b** with butylamine: ^{1}H NMR (CD_2Cl_2): δ = 0.89–1.40 (124H), 1.44 (8H, m), 1.72 (8H, m), 2.74 (8H, t, J = 7.5Hz), 6.23 (4H, s), 6.29 (4H, s), 6.87 (4H, s), 7.28 (8H, d, J = 7.3 Hz), 7.28 (8H, d, J = 1.4 Hz), 7.45 (4H, s), 7.45 (4H, s), 7.46 (4H, t, J = 1.8 Hz), 7.51 (4H, m), 7.52 (2H, m), 7.55 (8H, d, J = 7.3 Hz), and 7.69 (4H, m); UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 429 (160000), 734 (317000), and 1813 (340000) nm.

Crystallographic data: $C_{120}H_{132}N_{10}Zn_2$, M_W = 1845.10, triclinic, space group P-1 (no. 2), a = 11.9423(14), b = 13.6104(16), c = 16.6785(19) Å, α = 103.596(2) β = 93.325(2), γ = 111.574(2)º, V = 2418.9(5) Å^3, Z = 1, ρ_{calcd} = 1.267 g/cm^3, T = –150 ºC, 14257 measured reflections, 10218 unique reflections (R_{int} = 0.057). R = 0.0587, R_w = 0.1608 (all data), GOF = 0.979. CCDC-261532 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposite@ccdc.cam.ac.uk).

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