

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 ¹H 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 ¹H 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

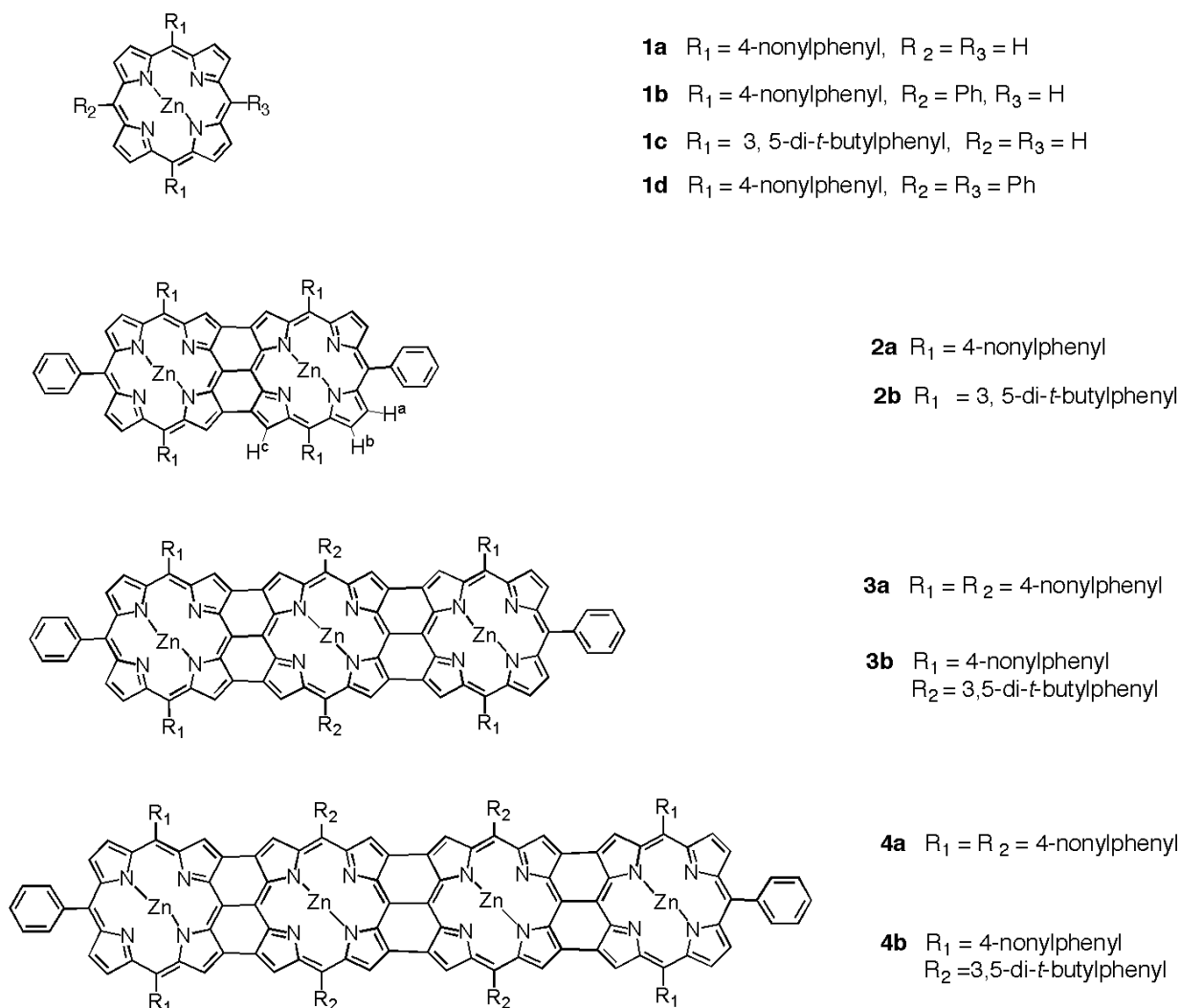
performed by the Grignard reagent to give 1-(4-bromophenyl)-1-hydroxynonane (**5**), which was then iodinated with (Me)₃SiCl and NaI, and reduced with NaBH₄ to 1-bromo-4-nonylbenzene (**6**).¹² 4-Nonylbenzaldehyde (**7**) was obtained by formylation of **6** with butyllithium and then DMF. 5,15-Di(4-nonylphenyl)-porphyrin **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 ¹H 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 C₁₁₂H₁₁₄N₈Zn₂ = 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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Scheme 1. Molecular structures.

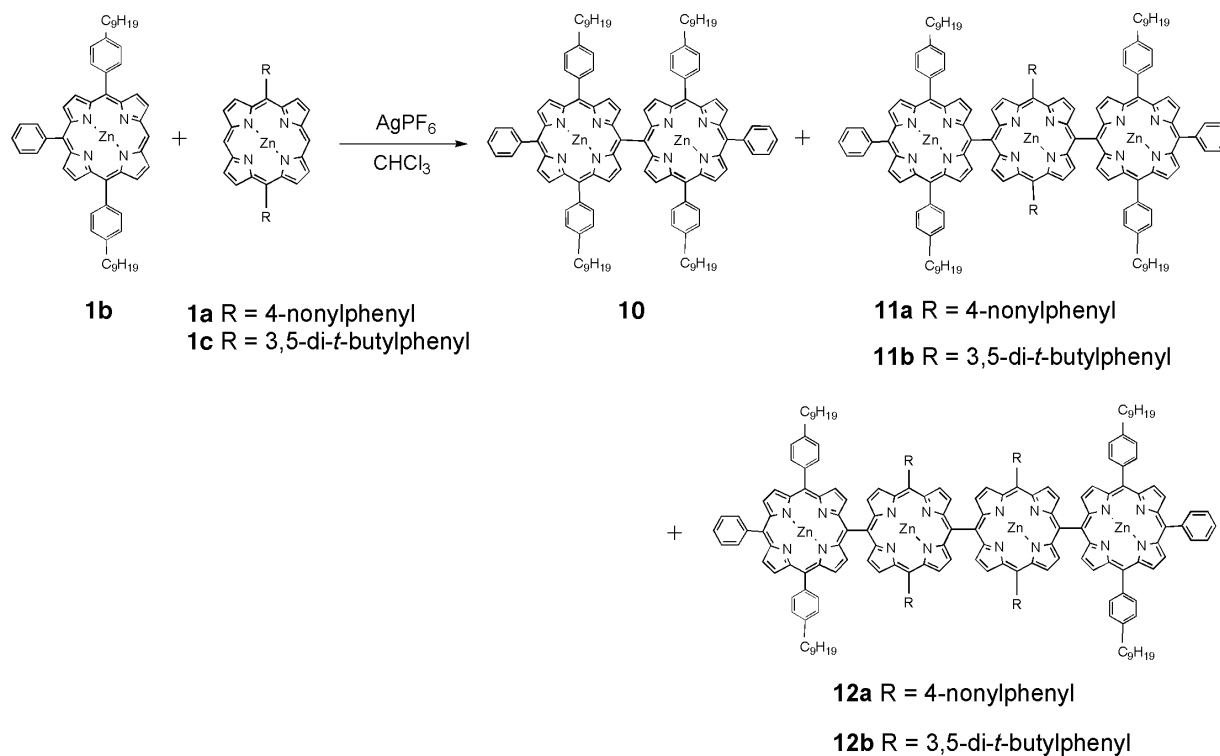
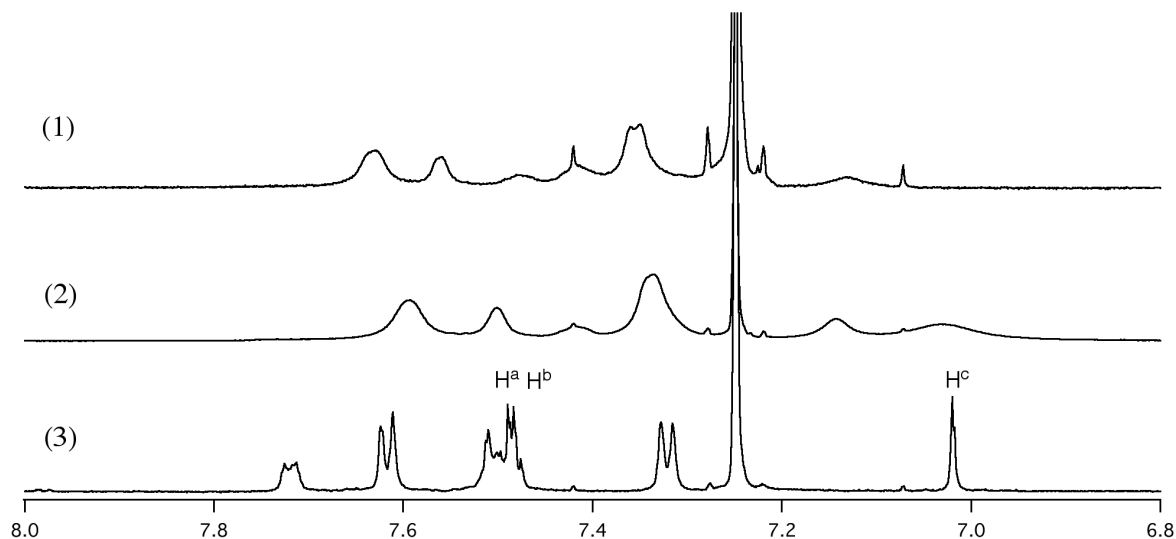
gave *meso-meso*-linked porphyrin dimer (**10**), trimer (**11a**), and tetramer (**12a**) in 63% yield for **11a** and 20% yield for **12a** based on **1a**. The reaction mixture was easily separated by GPC-HPLC. The DDQ-Sc(OTf)₃ oxidation of **11a** was performed in toluene at 100 °C, which gave *meso-meso*, 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 C₁₆₂H₁₆₄N₁₂Zn₃, 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** C₂₁₂H₂₀₈N₁₆Zn₄ = 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 give 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 C₁₆₀H₁₆₀N₁₂Zn₃, 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 C₂₁₂H₂₁₄N₁₆Zn₄, 3191), indicating that aggregation was suppressed by peripheral bulky substituents.

Scheme 3. Synthetic scheme of *meso-meso*-linked porphyrin arrays.Fig. 1. ¹H NMR spectra of **2a** in CDCl₃ 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

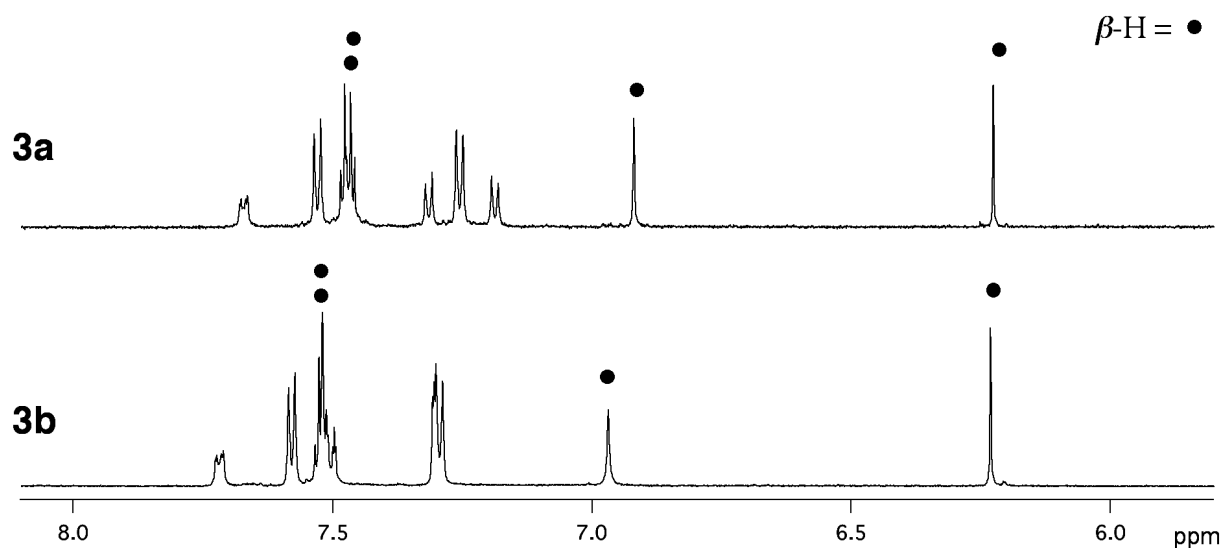


Fig. 2. ^1H NMR spectra of **3a** and **3b** in CD_2Cl_2 at room temperature.

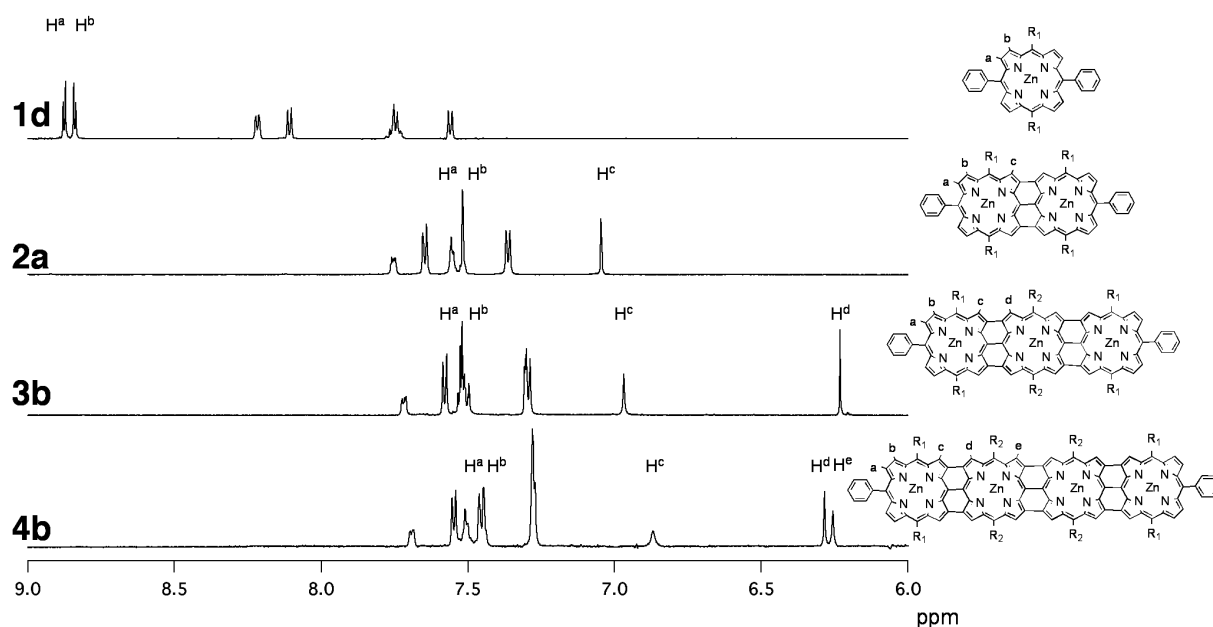


Fig. 3. ^1H NMR spectra of **1d**, **2a**, **3b**, and **4b** in CD_2Cl_2 with 5% butylamine at room temperature.

newly formed two $\text{C}_\beta\text{--C}_\beta$ bonds are both 1.44 Å, and the bond length of $\text{C}_{\text{meso}}\text{--C}_{\text{meso}}$ 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 oligo-

mers 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

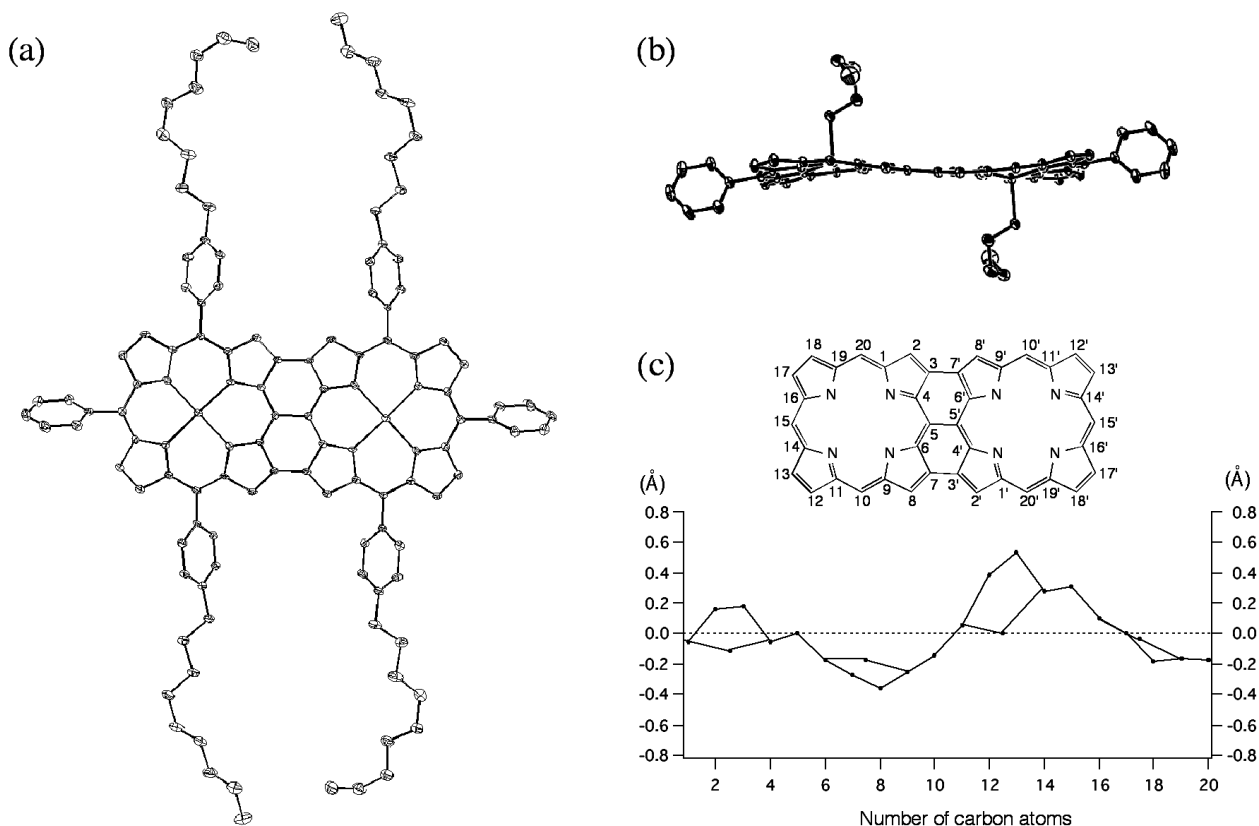


Fig. 4. X-ray structure of **2a** with butylamine, top view (a) and side view (b). Displacements of the peripheral carbon atoms from the mean plane of 24 atoms (c). Hydrogen atoms and butylamines are omitted for clarity in (a), and hydrogen atoms and 4-nonylphenyl substituents are omitted for clarity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

mains, 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 $340,000 \text{ M}^{-1}\text{cm}^{-1}$ 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-

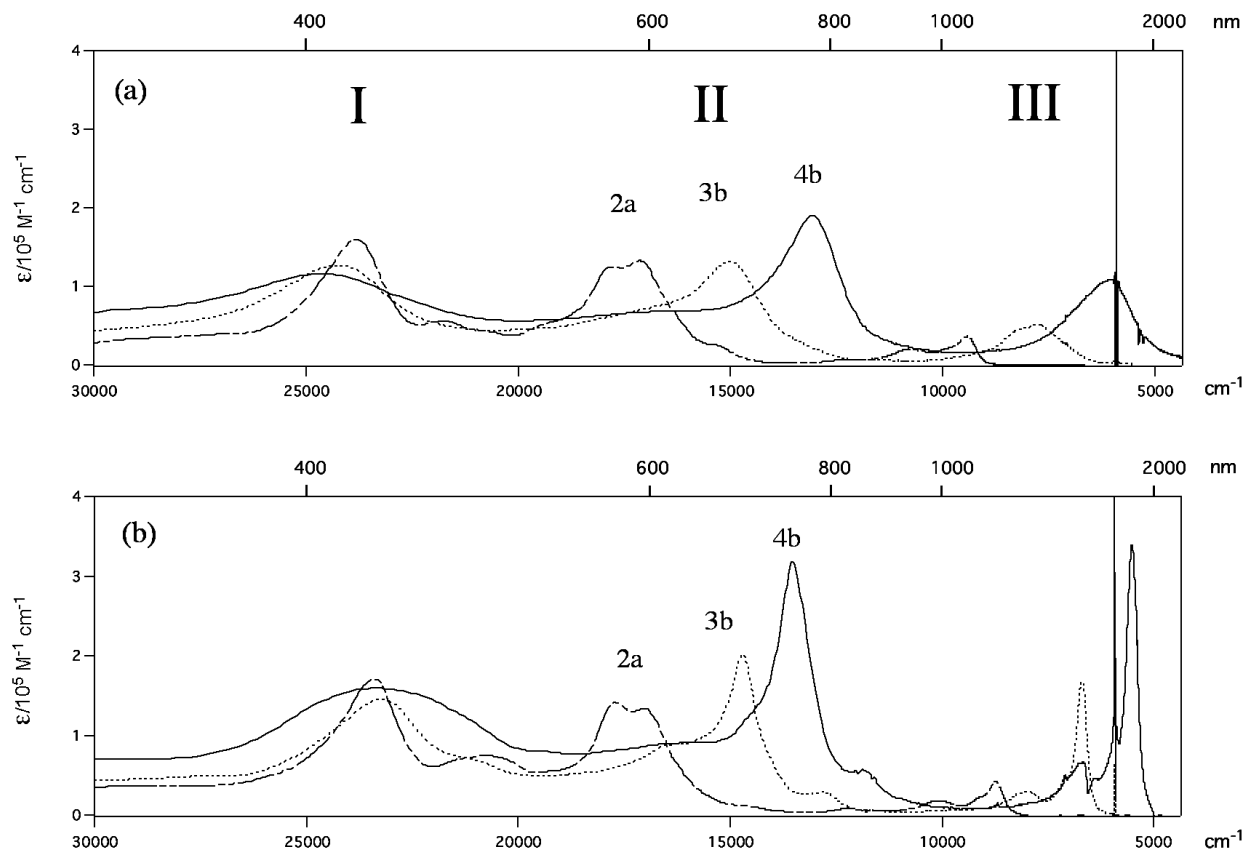


Fig. 5. UV-vis absorption spectra of **2a**, **3b**, and **4b** in CHCl_3 at room temperature. (a) Without butylamine. (b) With 5% butylamine. The background absorbance at 6000 cm^{-1} may arise from the overtones of C–H vibration of CHCl_3 .

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. ^1H 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°C . 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). ^1H 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 $\text{C}_{15}\text{H}_{23}\text{BrO}$: 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 CH₃CN solution (300 mL) was stirred under N₂ for 12 h at room temperature. Then, the organic residue was washed with Na₂S₂O₃ solution, dried over anhydrous Na₂SO₄ and evaporated. The resulting orange residue was stirred with NaBH₄ (5.7 g, 0.15 mol) in DMSO (300 mL) under N₂ for 12 h at room temperature. The mixture was extracted with hexane. Combined organic extracts were dried over anhydrous Na₂SO₄ 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%). ¹H NMR(CDCl₃): 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 C₁₅H₂₃Br: 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 °C 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 Na₂SO₄, 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). ¹H NMR(CDCl₃): 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 C₁₅H₂₃BrO: 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 CH₂Cl₂ (600 mL) was stirred under N₂ 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 (1.15 g, 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). ¹H NMR(CDCl₃): 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 Hz), 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 C₅₀H₅₈N₄: 715.5; found: 715.5 [M⁺]; UV (CHCl₃): 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 CH₃OH (3 mL) was added to a solution of **8** (200 mg, 0.28 mmol) in CHCl₃ (150 mL) and the resulting mixture was stirred for 3 h at 60 °C. Then, the organic residue was washed with water, dried over anhydrous Na₂SO₄, and evaporated. The solid was taken up in CH₂Cl₂ and purified by silica gel chromatography by CH₂Cl₂.

The yield of **1a** was 92% (200 mg). ¹H NMR(CDCl₃): 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 C₅₀H₅₆N₄Zn: 776.4; found: 776.4 [M⁺]; UV (CHCl₃): 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 N₂ 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 CH₂Cl₂ solution) was added and stirred for 15 min. The organic residue was washed with water, dried over anhydrous Na₂SO₄, 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 CHCl₃ was stirred under N₂ for 15 min at room temperature. A saturated Zn(OAc)₂ in CH₃OH (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 Na₂SO₄, and evaporated. The solid was taken up in CH₂Cl₂ and purified by silica gel chromatography by CH₂Cl₂. 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 CHCl₃ was stirred under N₂ for 15 min at room temperature. A saturated Zn(OAc)₂ in CH₃OH (3 mL) was added to the solution and it was stirred for 3 h at 60 °C. Then, the residue was washed with water, dried over anhydrous Na₂SO₄, and evaporated. The solid was taken up in CH₂Cl₂ and purified by silica gel chromatography by CH₂Cl₂. The yield of Zn(II) 5,15-di(4-nonylphenyl)-10,20-diphenylporphyrin **1d** was 5.4% (11 mg). **1b**: ¹H NMR(CDCl₃): 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 C₅₆H₆₀N₄Zn: 852.5; found: 852.5 [M⁺]; UV (CHCl₃): λ_{max} = 417 and 545 nm. **1d**: ¹H NMR(CDCl₃): δ = 0.91 (6H, t, *J* = 6.4 Hz), 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 Hz), 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 C₆₂H₆₄N₄Zn: 928.5; found: 928.5 [M⁺]; UV (CHCl₃): λ_{max} = 422.5 and 552.5 nm. **1d** with butylamine: ¹H NMR(CDCl₃): δ = 0.94 (6H, t, *J* = 6.9 Hz), 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 (CHCl₃): $\lambda_{\text{max}} = 430, 565$, 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 °C for 30 min under N₂. 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 C₁₁₂H₁₁₆N₈Zn₂: 1705; found: 1703; UV (CHCl₃): $\lambda_{\text{max}}(\epsilon) = 420$ (174000), 562 (136000), 583 (144000), and 1061 (39600) nm. **2a** with butylamine: ¹H NMR (CD₂Cl₂): $\delta = 0.92$ (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 (CHCl₃): $\lambda_{\text{max}}(\epsilon) = 425$ (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 CHCl₃ (200 mL), and the reaction vessel was covered with foil. A solution of 0.1 M AgPF₆ in CH₃CN (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 CHCl₃. The combined organic extract was washed with water and dried over anhydrous Na₂SO₄. 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**: ¹H NMR (CDCl₃): $\delta = 0.81$ (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 C₁₁₂H₁₁₈N₈Zn₂: 1707; found: 1707; UV (CHCl₃): $\lambda_{\text{max}} = 422, 458$, and 563 nm. **11a**: ¹H NMR (CDCl₃): $\delta = 0.75$ (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 C₁₆₂H₁₇₂N₁₂Zn₃: 2483; found: 2480; UV (CHCl₃): $\lambda_{\text{max}} = 419, 479$, and 571 nm. **12a**: ¹H NMR (CDCl₃): $\delta = 0.76$ (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, $J = 4.6$ Hz), 8.76 (4H, d, $J = 4.6$ Hz), 8.79 (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 C₂₁₂H₂₂₆N₁₆Zn₄: 3259; found: 3256; UV (CHCl₃): $\lambda_{\text{max}} = 418, 489$, 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 CHCl₃ (200 mL), and the reaction vessel was covered with foil. A solution of 0.1 M AgPF₆ in CH₃CN (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 CHCl₃. The combined organic extract was washed with water and dried over anhydrous Na₂SO₄. 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**: ¹H NMR (CDCl₃): $\delta = 0.85$ (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). MALDI-TOF MS: calcd for C₁₆₈H₁₆₈N₁₂Zn₃: 2455; found: 2453; UV (CHCl₃): $\lambda_{\text{max}} = 418, 477$, and 567 nm. **12b**: ¹H NMR (CDCl₃): $\delta = 0.85$ (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 C₂₀₈H₂₁₈N₁₆Zn₄: 3204; found: 3196; UV (CHCl₃): $\lambda_{\text{max}} = 418, 487$, 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 °C for 20 min under N₂. 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 C₁₆₂H₁₆₄N₁₂Zn₃: 2475; found: 2474; UV (CH₂Cl₂): $\lambda_{\text{max}} = 417, 667$, and 1304 nm. **3a** with butylamine: ¹H NMR (CD₂Cl₂): $\delta = 0.84$ (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, $J = 7.8$ Hz), 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 (CHCl₃): $\lambda_{\text{max}} = 427, 680$, 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 °C for 30 min under N₂. 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 C₁₆₀H₁₆₀N₁₂Zn₃: 2447; found: 2446; UV (CHCl₃): $\lambda_{\text{max}}(\epsilon) = 416$ (128000), 670 (133000), and 1290 (54000) nm. **3b** with butylamine: ¹H NMR (CD₂Cl₂): $\delta = 0.89$ (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 (CHCl₃): λ_{max} (ϵ) = 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 °C for 20 min under N₂. 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 (CHCl₃): λ_{max} = 403, 777, and 1632 nm. **4a** with butylamine: UV (CH₂Cl₂): 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 °C for 20 min under N₂. 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 C₂₁₂H₂₁₄N₁₆Zn₄: 3191; found: 3195; UV (CHCl₃): λ_{max} = 405 (117000), 776 (190000), and 1652 (111000) nm. **4b** with butylamine: ¹H NMR (CD₂Cl₂): δ = 0.89–1.40 (124H), 1.44 (8H, m), 1.72 (8H, m), 2.74 (8H, t, $J = 7.5$ Hz), 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 (CHCl₃): λ_{max} (ϵ) = 429 (160000), 734 (317000), and 1813 (340000) nm.

Crystallographic data: C₁₂₀H₁₃₂N₁₀Zn₂, 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)°, V = 2418.9(5) Å³, Z = 1, ρ_{calcd} = 1.267 g/cm³, T = -150 °C, 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 deposit@ccdc.cam.ac.uk).

REFERENCES AND NOTES

- (1) (a) Schwab, P.F.H.; Levin, M.D.; Michl, J. *Chem. Rev.* **1999**, 99, 1863. (b) Martin, R.E.; Diederich, F. *Angew. Chem. Int. Ed.* **1999**, 38, 1351.
- (2) (a) Chen, J.; Reed, M.A.; Rawlett, A.M.; Tour, J.M. *Science* **1999**, 286, 1550. (b) Joachim, C.; Gimzewski, J.K.; Aviram, A. *Nature* **2000**, 408, 541.
- (3) Stegmen, G.; Likamwa, P. In *Nonlinear Optical Materials and Devices for Applications in Information Technology*; Miller, A.; Welford, K.R.; Diano, B., Eds.; Kluwer Academic Publishers: Dordrecht, 1995; Vol. 289, pp 285–320.
- (4) (a) Arnold, D.P.; Johnson, A.W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366. (b) Arnold, D.P.; Heath, G.A.; James, D.A. *J. Porphyrins Phthalocyanines* **1999**, 3, 5.
- (5) (a) Lin, V.S.-Y.; DiMaggio, S.G.; Therien, M.J. *Science* **1994**, 264, 1105. (b) Lin, V.S.-Y.; Therien, M.J. *Chem. Eur. J.* **1995**, 1, 645.
- (6) (a) Anderson, H.L. *Inorg. Chem.* **1994**, 33, 972. (b) Taylor, P.N.; Huuskonen, J.; Rumbles, G.; Aplin, R.T.; Williams, E.; Anderson, H.L. *Chem. Commun.* **1998**, 909.
- (7) (a) Crossley, M.J.; Burm, P.L.; Langford, S.J.; Prachar, K.J. *J. Chem. Soc., Chem. Commun.* **1995**, 1921. (b) Reimers, J.R.; Lu, T.X.; Crossley, M.J.; Hush, N.S. *Chem. Phys. Lett.* **1996**, 256, 353.
- (8) (a) Kobayashi, N.; Numao, M.; Kondo, R.; Nakajima, S.; Osa, T. *Inorg. Chem.* **1991**, 30, 2241.
- (9) (a) Vicente, M.G.H.; Jaquinod, L.; Smith, K.M. *Chem. Commun.* **1997**, 177. (b) Jaquinod, L.; Siei, O.; Khoury, R.G.; Smith, K.M. *Chem. Commun.* **1998**, 1261. (c) Vicente, M.G.H.; Cancilla, M.T.; Lebrilla, C.B.; Smith, K.M. *Chem. Commun.* **1998**, 2355. (d) Paoloesse, R.; Jaquinod, L.; Sala, F.D.; Nurco, D.J.; Prodi, L.; Natale, C.D.; D'Amico, A.; Carlo, A.D.; Lugli, P.; Smith, K.M. *J. Am. Chem. Soc.* **2000**, 122, 11295. (e) Aihara, H.; Jaquinod, L.; Nurco, D.J.; Smith, K.M. *Angew. Chem. Int. Ed.* **2001**, 40, 3439.
- (10) (a) Tsuda, A.; Nakano, A.; Furuta, H.; Yamochi, H.; Osuka, A. *Angew. Chem. Int. Ed.* **2001**, 40, 3439. (b) Tsuda, A.; Furuta, H.; Osuka, A. *Angew. Chem. Int. Ed.* **2000**, 39, 2549. (c) Tsuda, A.; Furuta, H.; Osuka, A. *J. Am. Chem. Soc.* **2001**, 123, 10304.
- (11) (a) Tsuda, A.; Osuka, A. *Science* **2001**, 293, 79. (b) Tsuda, A.; Osuka, A. *Adv. Mater.* **2002**, 14, 75.
- (12) Franks, S.; Hartley, F.R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2233.
- (13) Senge, M.O.; Feng, X. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1030.
- (14) Kamo, M.; Tsuda, A.; Nakamura, Y.; Aratani, N.; Furukawa, K.; Kato, T.; Osuka, A. *Org. Lett.* **2003**, 5, 2079.