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Supramolecular array of imizazolylethynyl-zinc-porphyrin

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Abstract

Novel imidazolylethynyl-zinc-porphyrin **1a** and its *meso*,*meso*-linked bisporphyrin **5M** were synthesized effectively by the reaction of the corresponding bromoporphyrins and 2-imidazolylethyne in the presence of palladium-arsenic catalyst. The complementary coordination of monomer **1a** into dimer **2a** was observed by ^{1}H NMR and UV–Vis spectroscopy. Self-association constant of **1a** to **2a** in $CHCl_3$ (including 0.5% ethanol) was determined as 1.84×10^7 M^{-1} by UV–Vis titration of **2a** with *N*-methylimidazole. UV–Vis absorption and fluorescence spectra of **1a**, **2a**, monomer **5M**, and its polymer **5P** were compared.

Keywords: Supramolecular; Porphyrin

1. Introduction

Supramolecular porphyrin arrays are interesting material for light-harvesting antenna and non-linear optical device [1]. Characteristic organizations, especially, into face-to-face and slipped cofacial arrangements of porphyrins have been achieved by use of several non-covalent interactions, such as coordination bonding [2], hydrogen bonding [3], π–π interaction [4], and electrostatic interaction [5]. We have examined supramolecular organization using imidazolyl-zinc-porphyrin motif, in which a large self-association constant was achieved by complementary coordination [6]. By use of this unique motif, supramolecular light-harvesting antenna [7], special pair complex in photosynthetic reaction center [8] and non-linear optical materials [9] have been constructed.

We will report here a novel complementary coordination dimer **2** of imidazolylethynyl-zinc-porphyrin **1** as another supramolecular motif. Introduction of the ethynyl unit allows effective synthesis of the motif by Sonogashira coupling. The supramolecular structure of complementary dimer **2** is generated by molecular mechanics calculation on Cerius2® and illustrated in Fig. 1 in reference to the previous imidazolyl-zinc-porphyrin dimer **4**. Inter zinc-to-zinc distances are estimated as 8.4 Å for **2** and 6.2 Å for **4**. Formation of dimer **2** from **1** and absorption and fluorescence spectra are examined in view of the effect of insertion of the ethynyl unit. Further, *meso*,*meso*-linked bis(imidazolylethynylporphyrin) **5M** was prepared by the similar coupling reaction and its linear array formation (**5P**) are described. Comparison of UV–Vis spectra between **5** and **6** is also discussed.

2. Results and discussion

Free base imidazolylethynylporphyrin **9** was prepared from porphyrin **7** by monobromination and Sonogashira coupling [10] as shown in Scheme 1. Porphyrin **7** obtained by the reported procedure [11] was brominated with *N*-bromosuccinimide in the presence of pyridine at −40 °C to give monobromoporphyrin **8** (48%) along with *meso*-dibromoporphyrin (35%). Bromide **8** was isolated by chromatography and coupled with 1-methyl-2-imidazolylethyne in the presence of $Pd_2(dba)_3CHCl_3$ and $AsPh_3$ as catalyst to afford **9** in 84% yield. Treatment of $Zn(OAc)_2$ with **9** gave the corresponding zinc porphyrin **1a**, which was organized spontaneously into **2a** in non-coordinating solvents. Free base and zinc porphyrins **9** and **1a** (**2a**) were identified by NMR spectroscopy and mass spectrometry.

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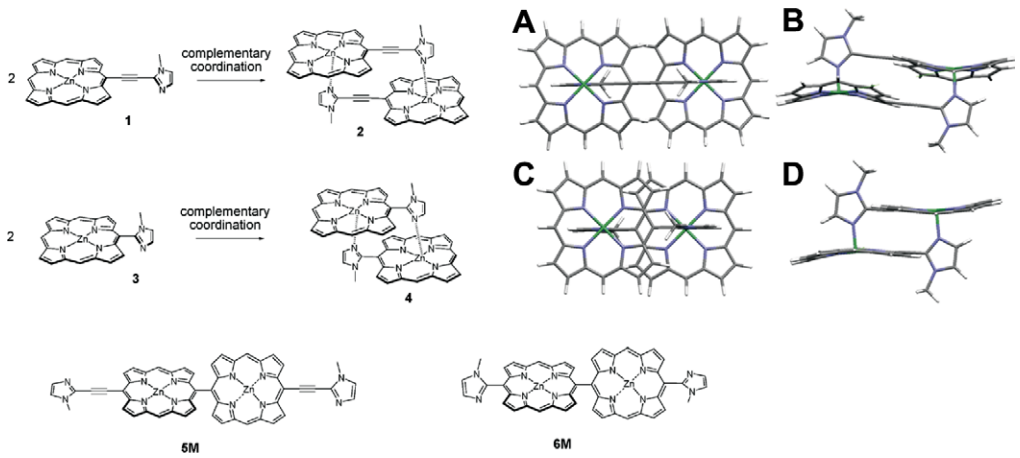
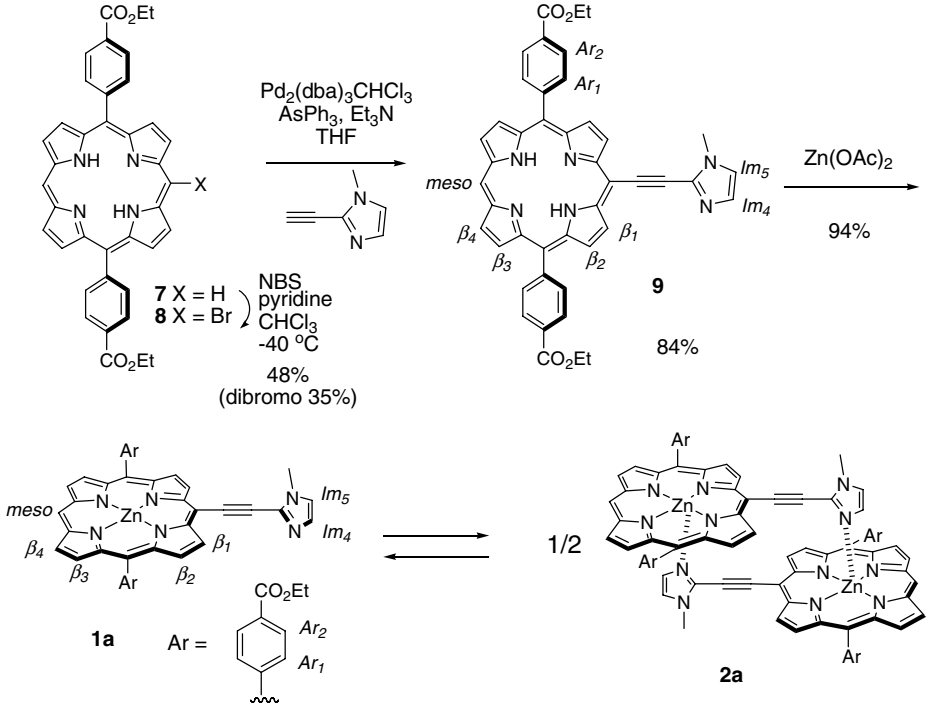


Fig. 1. Upper left: Structures of imidazolylethynyl-zinc-porphyrin **1** and imidazolyl-zinc-porphyrin **3**, and their respective coordination dimers **2** and **4**. Upper right: molecular models constructed by molecular mechanics calculation. (A) Top and (B) side views of **2**. (C) Top and (D) side views of **4**. Lower: Structures of **5M** and **6M**.



Scheme 1. Synthesis of **1a**.

Proton NMR spectra of **9** and **2a** (10 mM as a monomer **1a** in $(CDCl_2)_2$) are shown in Fig. 2. Each signal was assigned from HH-COSY and HMQC correlation spectra. One set of proton signals and characteristically shielded imidazolyl peaks indicate the formation of complementary dimer **2a**. Thus, Im_4 (1.67), Im_5 (5.28), and *N*-Me (2.63 ppm) signals are shifted to upper-fields due to the shielding effect of porphyrin coordinated by the imidazole. The relative upper-field shifts are similar to those on the formation of dimeric imidazolyl-zinc-porphyrin **4** [2a]. The upper-field shift of proton β_1 in **2a**, however, is small as ca. 1 ppm, whereas upper-field shift of ca. 4 ppm is observed in **4** [12]. The smaller shift value is consistent with the dimeric structure of **2a** having a larger center-to-center distance (see Fig. 1).

UV–Vis spectra of **2a** (Fig. 3) were concentration dependent. The peak maximum of Soret band at 434 nm (4×10^{-6} M in $CHCl_3$) was gradually sharpened and red-shifted to 436 nm (8×10^{-8} M^{-1}) on dilution, suggesting dissociation of **2a** into **1a** at the lower concentration limit. The shift of the peak maximum to a longer wavelength side on the structural change of dimer to monomer may correspond to the increase of π-conjugation through all planar conformation in **1a**. In the higher concentration range between 1×10^{-6} and 4×10^{-6} M in $CHCl_3$, the spectra have a similar shape and follow the Beer's law (data not

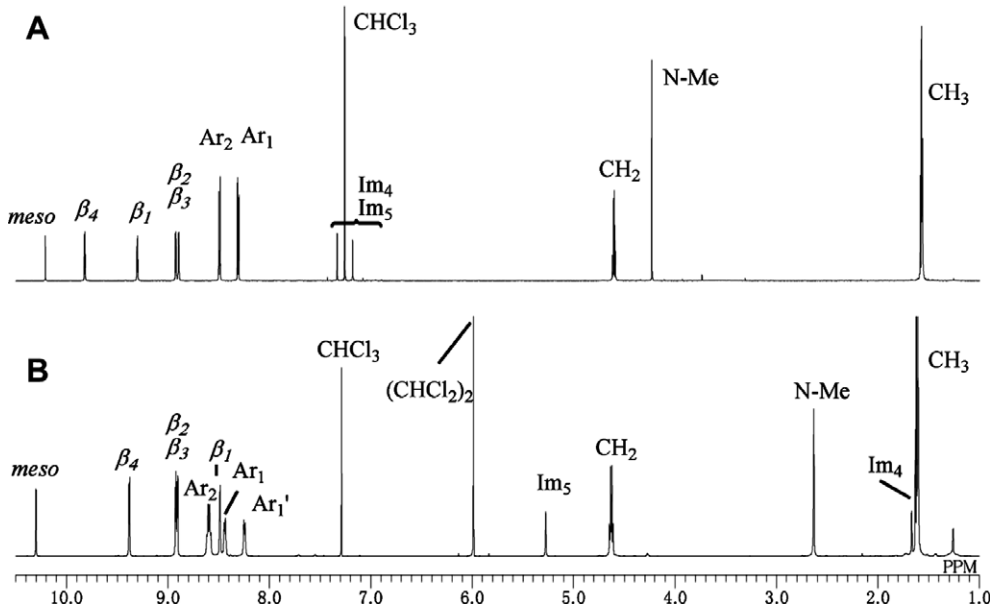


Fig. 2. ^{1}H NMR spectra (600 MHz) of **9** in $CDCl_3$ (**A**) and **2a** in $(CDCl_2)_2$ (**B**).

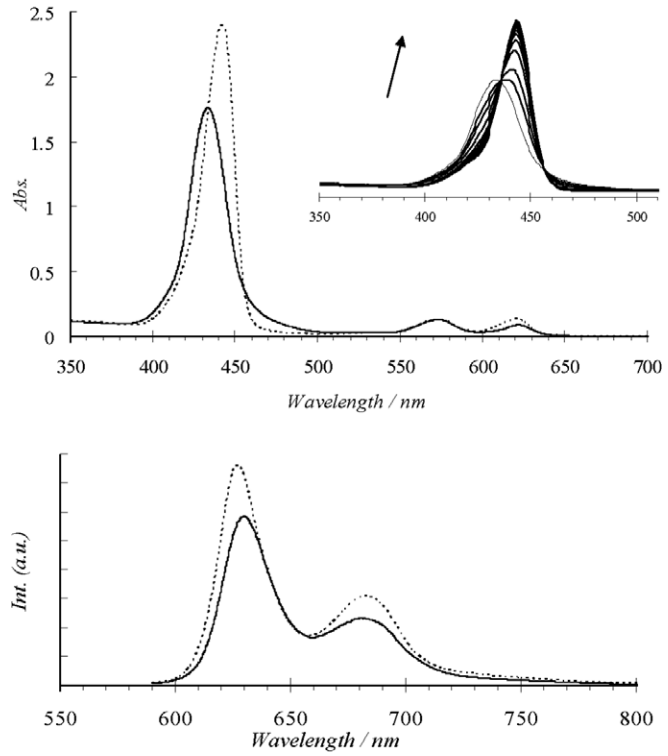


Fig. 3. UV–Vis (upper) and fluorescence (lower) spectra of dimer **2a** (solid line) and monomer **1a** (dotted line) in $CHCl_3$. **2a** (4×10^{-6} M). **1a** was prepared by the addition of pyridine (4×10^{-2} M) to **2a** solution. Fluorescence spectra were measured by excitation at 573 nm (Abs. 0.13 for both **2a** and **1a**). (Upper inset) UV–Vis spectral change of **2a** (2.06×10^{-6} M in $CHCl_3$) to **1a/Im** by the addition of *N*-methylimidazole (0, 80, 160, 320, 480, 640, 800, 960, 1110, 1420, 1570, 3150, 6300, 12600, 25200 eq.) The inset spectra were corrected to eliminate the dilution factor.

shown), indicating that dimer structure looks maintained at concentrations higher than 1×10^{-6} M in $CHCl_3$. It is noted that the chloroform used here contains a stabilizer of 0.5% ethanol which competes the imidazolyl/zinc coordination bond in **2**. The coordinated structure is maintained under more diluted conditions in other solvents free from coordinating stabilizer, such as CH_2Cl_2. The self-association constant of **1a** into **2a** in $CHCl_3$ was determined by UV–Vis titration of **2a** and phenylethynylporphyrin **11** with use of *N*-methylimidazole. (Fig. 3, inset). Absorption spectrum of dimer **2a** (4×10^{-6} M in $CHCl_3$) shows broad Soret band at 434 nm due to weak excitonic coupling between two porphyrins. The Soret band was red-shifted and sharpened by the addition of *N*-methylimidazole. From curve fitting analysis, the equilibrium constant for ligand substitution of **2a** with *N*-methylimidazole was obtained as $K_1 = 21.7\ M^{-1}$. As the reference, the association constant of **11** with *N*-methylimidazole was determined as $K_2' = 2.0 \times 10^4\ M^{-1}$ in $CHCl_3$. Therefore, the self-association constant of **1a** to **2a** was obtained as $K_3 = 1.84 \times 10^7\ M^{-1}$ according to Eq. (4) (Fig. 4). This value is four orders of magnitudes smaller than the self-association constant of imidazolyl-zinc-porphyrin **4**. At the same time, the value is three orders of magnitudes larger than the stability constant of *N*-methylimidazole coordination to zinc porphyrins [13]. It is strong enough to keep the dimer structure almost completely above tens micromolar concentration. Following considerations may be important for understanding the molecular behavior. Before coordination, imidazolyl π-orbitals are conjugated with those of the porphyrin. All planar conformation is energetically favorable, but molecular rotation around the ethynyl bond is allowed. Imidazolyl coordination induces the orientation perpendicular to porphyrin and disrupts the π-conjugation and further loses its rotational freedom. The free energy loss from these contributions may lower the self-association constant. Another factor may arise from the small overlap of porphyrin π-planes due to the presence of acetylenyl linker. Despite these unfavorable

factors, complementarity is effective to increase dramatically the association constant of imidazolyl coordination.

$$K_1 = \frac{[\mathbf{1a}/\mathbf{Im}]^2}{[\mathbf{2a}][\mathbf{Im}]^2}, \quad (1)$$

$$K_2 = \frac{[\mathbf{1a}/\mathbf{Im}]}{[\mathbf{1a}][\mathbf{Im}]}, \quad (2)$$

$$K_2' = \frac{[\mathbf{11}/\mathbf{Im}]}{[\mathbf{11}][\mathbf{Im}]}, \quad (3)$$

$$K_3 = \frac{[\mathbf{2a}]}{[\mathbf{1a}]^2} = \frac{K_2^2}{K_1} \simeq \frac{K_2'^2}{K_1}. \quad (4)$$

Fluorescence spectra of dimer **2a** and monomer **1a** (as a pyridine adduct) are shown in Fig. 3b. Fluorescence quantum yields of **1a** ($\Phi_F = 0.053$) and **2a** ($\Phi_F = 0.043$) were obtained from the fluorescence spectra as a reference with that of ZnTPP ($\Phi_F = 0.033$ in benzene) [14]. It has been established that the fluorescence is not quenched by complementary coordination [7a,7b,7d]. For the decrease of the fluorescence quantum yield by 19% from monomer **1a** to dimer **2a**, the loss of conjugation on coordination with the imidazolyl group may be taken into account. The fluorescence decrease is not fatal and **2a** is more fluorescent than ZnTPP by a factor of 130%. The imidazolylethynyl-zinc-porphyrin motif can be used as a light-harvesting antenna unit even better than imidazolyl-zinc-porphyrin.

The imidazolylethynyl-zinc-porphyrin motif was applied to a bidirectional system to produce linear polymer. *meso*,*meso*-Linked bis(imidazolylethynylporphyrin) **16** was synthesized from **12** according to the route shown in Scheme 2. *meso*,*meso*-Linked porphyrin **13** was prepared by oxidative coupling of **12** [15]. Bromination of **13** followed by demetalation and palladium-catalyzed coupling with imidazolylethyne gave **16** in 47% yield (3 steps). Zinc ion was then introduced into **16** to afford **5P**. Proton NMR spectra of **16** and **5P** (2.5 mM as a monomer) are shown in Fig. 5. Well-resolved sharp signals were observed in **16**, whereas all of the signals except residual $CHCl_3$ appeared broad in **5P**. This peak broadening indicates the formation of polymeric structure of **5M**. Imidazolyl protons Im_5 and *N*-methyl were upper-field shifted characteristically to appear at 5.78 and 3.01 ppm, respectively, with disappearance of non-coordinating imidazolyl protons around at 7.3 ppm. These chemical shifts are close to 5.28 and 2.63 ppm, respectively, observed for dimer **2a**. Considering the fact that these protons are deshielded by another porphyrin plane attached to the coordinating one, most of the imidazolyl parts are participating to the coordination to zinc porphyrin. In other words, the linear array should have a large mean molecular weight. If we assume that the self-association constant of the imidazolylethynyl-zinc-porphyrin part in **5M** is the same as that of **1a** ($1.8 \times 10^7\ M^{-1}$), the mean number of porphyrins in the

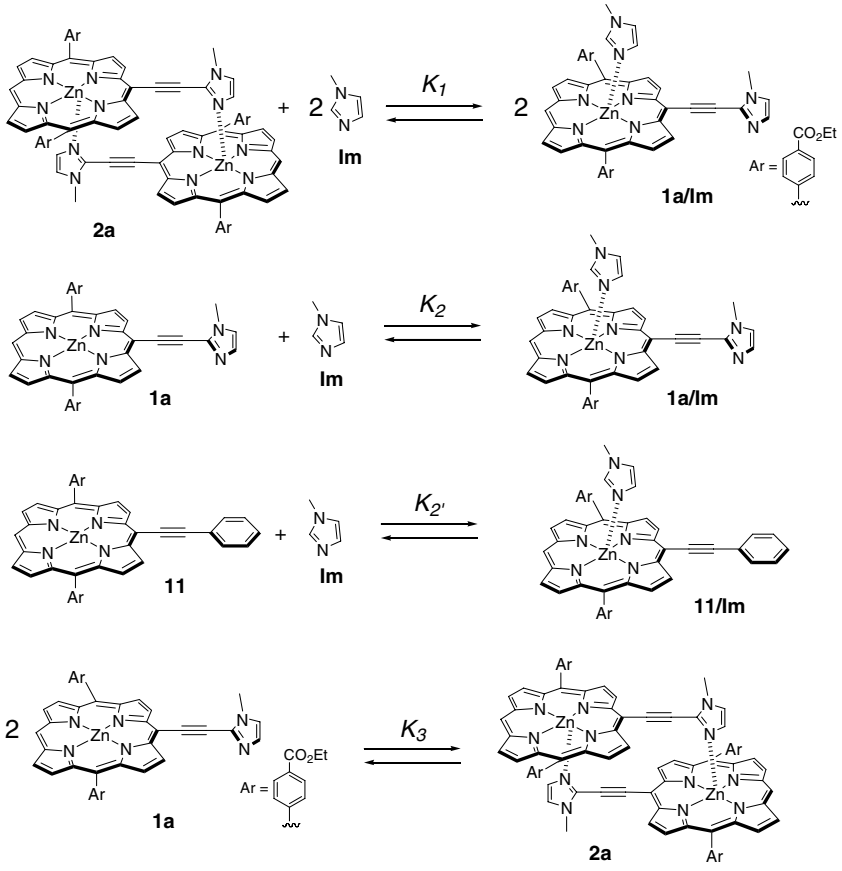
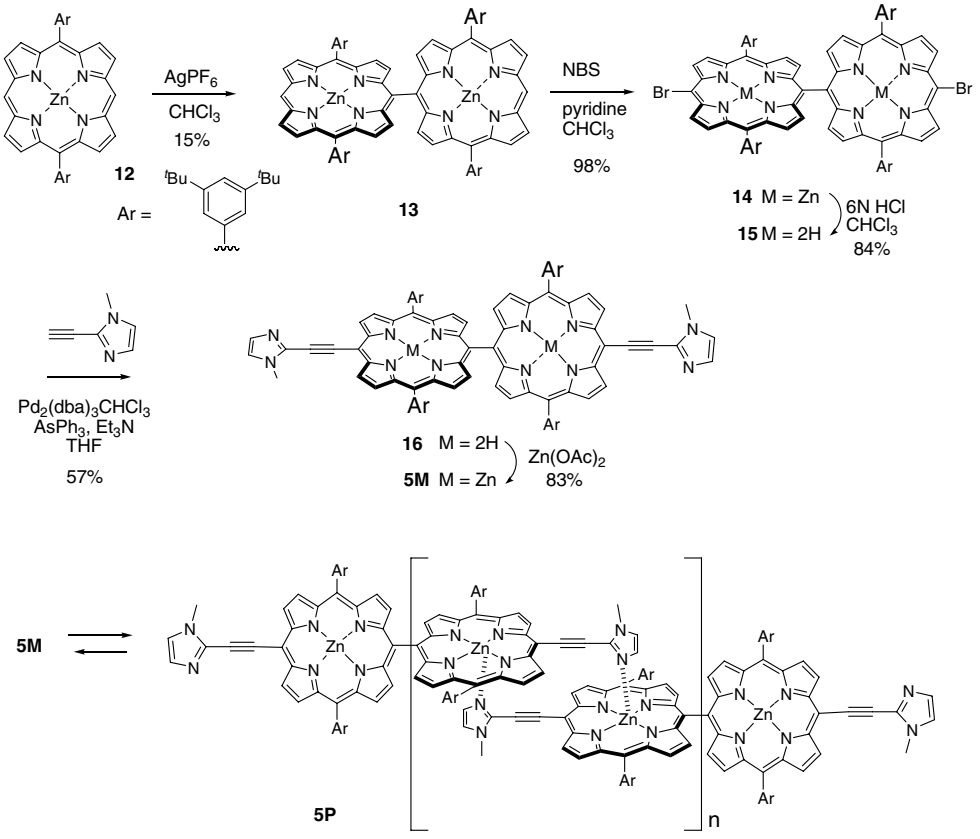


Fig. 4. Coordination equilibria of **1a**, **2a**, and **11** with *N*-methylimidazole (**Im**).



Scheme 2. Synthesis of **5**.

array is estimated as ca. 400 mer at 2.5 mM, indicating that only 0.5% of non-coordinating imidazole exists.

UV–Vis spectra of polymeric form of **5** (hereafter **5P**) (5.8×10^{-5} M in $CHCl_3$, 1 mm cell) [16] and monomeric form of **5** (**5M**) (5.3×10^{-7} M in $CHCl_3$/MeOH, 95/5, v/v) [17], normalized at the lower energy Soret band, are shown in Fig. 6A. In order to examine the effect of ethynyl moiety, UV–Vis spectra of polymeric and monomeric forms of **6** (*meso*,*meso*)-linked bis(imidazoly-zinc-porphyrin) reported previously [7a] are shown in Fig. 6B. The split Soret bands in the both monomeric states (dotted lines) are explained by the simple exciton coupling theory [18].

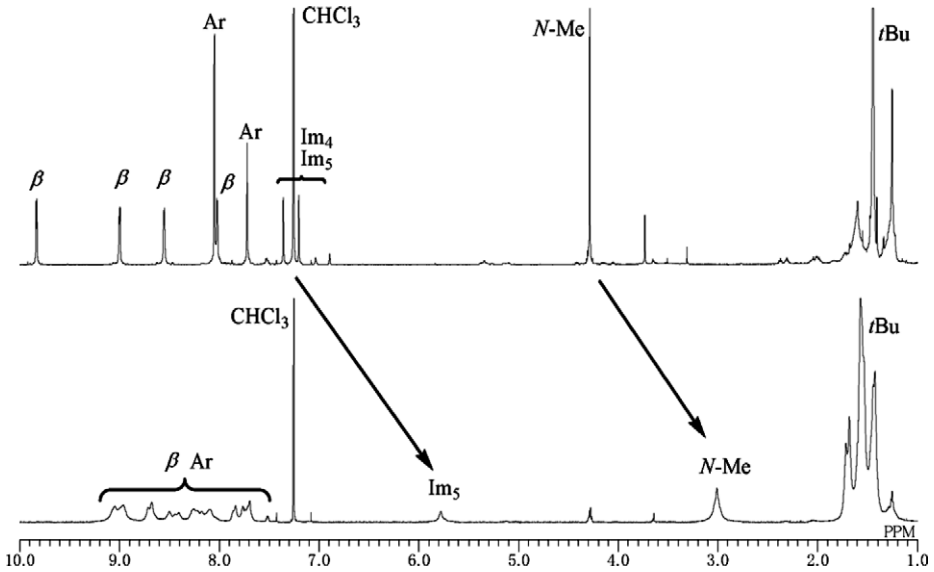


Fig. 5. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of **16** (upper) and **5P** (lower).

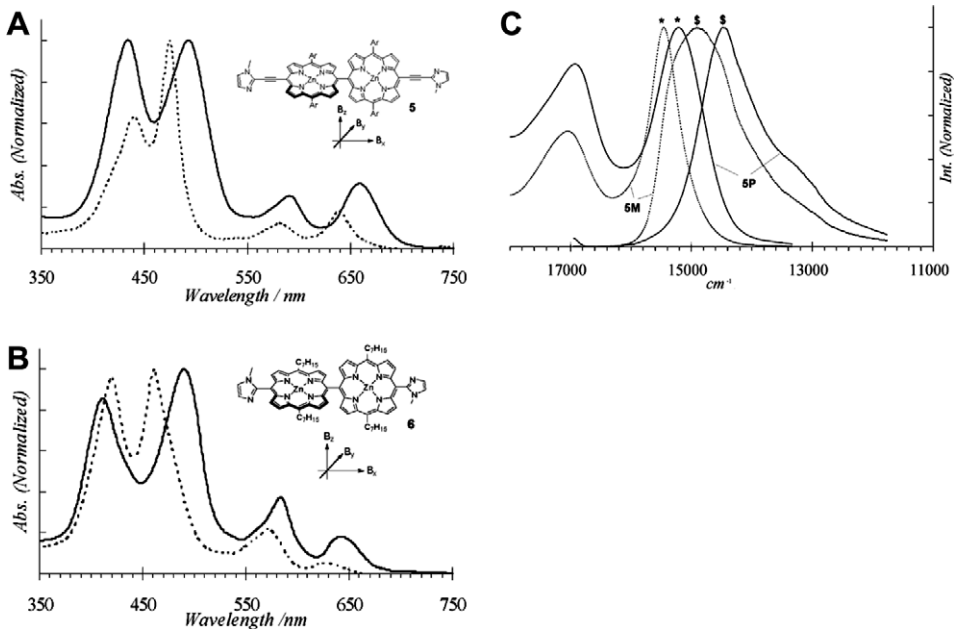


Fig. 6. UV–Vis spectra in $CHCl_3$ of **5** (upper, plain: polymer **5P** 6×10^{-6} M, dotted: monomer **5M** 6×10^{-7} M + MeOH) (A) and **6** (plain: **6P** 10^{-6} M, dotted: **6M** 10^{-6} M + MeOH) (B). Absorption (*) and Fluorescence ($) spectra of **5** (Ex. 479 nm for **5M** (dotted), Ex. 590 nm for **5P** (plain)) (C).

Thus, the transition dipoles of two porphyrins along the *meso*,*meso*-linkage bond (B_x) interact each other in a head-to-tail manner to give the lower energy Soret band. The other Soret band originates in the other transition dipoles (B_y and B_z). If two porphyrins connected at the *meso* position are of an orthogonal conformation, the higher energy Soret band should appear as a sum of two unperturbed degenerated transitions B_y and B_z. When two porphyrin planes rotate to allow the exciton interaction, the higher energy Soret band should contain a blue-shifted band due to the parallel interaction of two transition dipoles at each rotational angle. The resulting effect on the shape of the spectrum may broaden the higher-energy Soret band. This was eventually observed in the spectrum **5M**, in which the absorbance at 444 nm is decreased by broadening with appearance of a shoulder peak at the higher-energy (424 nm). A similar UV–Vis spectral pattern was observed by Osuka et al. in *meso*,*meso*-linked phenylethynyl-zinc-porphyrin [19]. The spectral difference between **5M** and **6M** indicates that the orthogonal conformation is predominant in **6M**, whereas rotational freedom is allowed to some extent in **5M**. When polymeric structures are formed by complementary coordination, similar spectral changes are observed in both **5P** and **6P**. (Fig. 6A and B, plain lines) Thus, the higher-energy Soret band is blue-shifted, whereas the lower energy Soret band and Q-bands are red-shifted. These spectral changes are explained on the basis of the Kasha's theory as reported in our previous paper [7a]. It is noted that the higher-energy Soret band of **5P** shows an absorbance similar to the lower-energy Soret band. Therefore, two spectral patterns of **5P** and **6P** become similar. The result indicates that the orthogonal conformation is predominant in the polymeric state of **5P**. It means that the relatively flexible structure of monomeric form of **5M** was converted to a rigid one by the complementary coordination.

The increase in molecular rigidity on coordination polymer formation is observed in the excited state, too. Absorption and fluorescence spectra of monomeric and polymeric forms of **5** are illustrated by normalized intensity as a function of wavenumber (cm^{-1}) for the qualitative comparison. The fluorescence spectrum of **5M** is very broad. The (0.1) fluorescence band is not a mirror image to the (0.1) absorption band. The broader fluorescence spectrum indicates that more conformational isomers exist in the excited state. On the other hand, (0.1) bands of absorption and fluorescence spectra are more symmetric for **5P**, indicating that the structure becomes rigid by the formation of coordination polymer. The increasing rigidity is probably coming from increased moment of inertia of the rotamer by formation of polymer. Rate of rotation of *meso–meso* bond of **5P** may decrease in the excited state.

3. Conclusion

Novel imidazolylethynyl-zinc-porphyrin **1a** and its *meso*,*meso*-linked bisporphyrin **5** were synthesized by facial coupling reactions of bromoporphyrins with ethynylimidazole. The complementary coordination of **1a** was observed by ^{1}H NMR and UV–Vis spectroscopy. Self-association constant of **1a** to **2a** was determined as 1.84×10^7 M^{-1}, which is larger enough to maintain the complementary coordination structure. A linear polymeric array of porphyrins is obtainable by successive complementary coordination of **5a**. Excitonic coupling between the porphyrins in

2a is very small, whereas that in polymeric species from its *meso*,*meso*-linked dimer **5** is much larger due to the large transition dipole along the linking bond. UV–Vis and fluorescence spectra of **5** indicated that rigid structure of orthogonal orientation formed in the polymeric state.

4. Experimental

4.1. General procedures

^{1}H NMR spectra were recorded on JEOL EX-270 (270 MHz) or ECP-600 (600 MHz) spectrometer using TMS (0 ppm) or the residual proton resonance ($(CHCl_2)_2$ 5.95 ppm) of the solvent as the internal standard. MALDI-TOF mass spectra were obtained with Perseptive Biosystems Voyager DE-STR with dithranol (Aldrich) as a matrix. UV–Vis spectra were obtained with a Shimadzu UV-3100PC spectrometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrometer. Column chromatography was performed with silica gel (63–210 μm, KANTO chemical Co., Inc.). THF was distilled over sodium-benzophenone ketyl radical. Triethylamine was distilled over calcium hydride. All other chemicals obtained from commercial sources were used without further purification, unless otherwise mentioned. 2-Ethynyl-1-methylimidazole [20] was synthesized according to the literature [21].

4.2. 2-Ethynyl-1-methylimidazole

To a solution of 1-methylimidazole (3.0 g, 36.5 mmol) in THF (100 mL), *n*-BuLi (1.58 M in hexane, 30 mL, 47.5 mmol) was added dropwise slowly during 1 h at −80 °C. The mixture was stirred for 2 h, and the temperature was raised to −60 °C. Iodine (11.12 g, 43.8 mmol) in dry THF (40 mL) was added dropwise. The temperature was raised at RT and the mixture was stirred for 16 h. The mixture was washed with a sodium thiosulfate solution. Organic layer was extracted with $CHCl_3$, washed with brine, dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by SiO_2 column chromatography ($CHCl_3$/MeOH = 10/1) to give **2-iodo-1-methylimidazole** (6.0 g, 79%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.07 (s, 1H, Im), 7.03 (s, 1H, Im), 3.62 (s, 3H, *N*-Me). In a Schlenk tube, $Pd(PPh_3)_2Cl_2$ (14 mg, 19 μmol), CuI (0.9 mg, 4.8 μmol), and **2-iodo-1-methylimidazole** (100 mg, 0.48 mmol) were dissolved in triethylamine (20 mL). Trimethylsilyl acetylene was added to the mixture, and the mixture was stirred at 70 °C for 1.5 h. Solvent was removed under reduced pressure. Water was added to the mixture, and organic layer was extracted with $CHCl_3$. The organic layer was washed with a saturated NH_4Cl solution, brine, and water. After drying over anhydrous Na_2SO_4 and concentration under reduced pressure, the residue was purified by SiO_2 column chromatography (hexane/EtOAc = 4/1 to 1/1) to give **1-methyl-2-trimethylsilylethynylimidazole** (70 mg, 82%) as a yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.81 (d, 1H, $J < 1$ Hz, Im), 6.68 (d, 1H, $J = <1$ Hz, Im), 3.52 (s, 3H, *N*-Me), 0.07 (s, 9H, TMS). To a solution of **2-trimethylsilylethynylimidazole** (70 mg, 0.393 μmol) in $CHCl_3$ (10 mL), *n*-Bu_4NF (1 M in THF, 1.18 mL, 1.18 μmol) was added at RT for 40 min. Water was added to the mixture, and the organic layer was extracted with $CHCl_3$ and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by SiO_2 column chromatography (hexane/EtOAc = 2/1 to 1/1) to give **1-methyl-2-ethynylimidazole** (24 mg, 60%). (This material gradually decomposes even in freezer, so that it should be used for the next coupling reaction as soon as possible.) ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.04 (d, 1H, $J < 1$ Hz, Im), 6.90 (d, 1H, $J < 1$ Hz, Im), 3.74 (s, 3H, N–Me), 3.31 (s, 1H, acetylene).

4.3. 5,15-Bis(ethoxycarbonylphenyl)porphyrin (7)

Dipyrromethane (146 mg, 1 mmol) and 4-ethoxycarbonylbenzaldehyde (178 mg, 1 mmol) were dissolved in $CHCl_3$ (200 mL). Nitrogen gas was passed through the mixture for 10 min to remove dissolved oxygen. Trifluoroacetic acid (TFA, 77 μL, 1 mmol) was added dropwise. The mixture was stirred for 20 h in the dark. Triethylamine (139 mL, 3.1 mmol) and *p*-chloranil (738 mg, 3 mmol) were added to the mixture, and refluxed for 1.5 h. The crude mixture was directly mounted onto SiO_2 column chromatography and eluted with $CHCl_3$ to give **7** (107 mg, 35%) as a purple solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.34 (s, 2H, *meso*), 9.41 (d, 4H, $J = 4.6$ Hz, β), 9.04 (d, 4H, $J = 4.6$ Hz, β), 8.51 (d, 4H, $J = 8.1$ Hz), 8.36 (d, 4H, $J = 8.1$ Hz), 4.61 (q, 4H, $J = 7.3$ Hz, CH_2CH_3), 1.56 (t, 6H, $J = 7.3$ Hz, CH_2CH_3), −3.1 (br, NH). MALDI TOF-Mass (Dithranol) m/z = 607.2 $[M+H]^+$; Calc. for $C_{38}H_{30}N_4O_4 = 606.2$.

4.4. 5,15-Bis(ethoxycarbonylphenyl)-10-bromoporphyrin (8)

To a mixture of **7** (126 mg, 0.208 mmol) and pyridine (170 μL, 2 mmol) in $CHCl_3$ (20 mL), *N*-bromosuccinimide (NBS, 37 mg, 0.208 mmol) in $CHCl_3$ (4 mL) was added at −40 °C. The reaction progress was monitored by TLC (eluent: $CHCl_3$/hexane = 1/4), and three spots corresponding to dibrominated compound, **8**, and **7** were observed. Additional NBS (7 mg, 0.04 mmol) was added to the mixture until monobrominated compounds became a major component. Acetone was added to quench the reaction, and the temperature was raised to RT. Water was added to the mixture, and the organic layer was extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by SiO_2 column chromatography. Monobrominated compound **8** (68 mg, 48%) was eluted after elution of dibromoporphyrin (55 mg, 35%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.17 (s, 1H, *meso*), 9.74 (d, 2H, $J = 4.8$ Hz, β), 9.28 (d, 2H, $J = 4.8$ Hz, β), 8.89 (d, 2H, $J = 4.8$ Hz, β), 8.88 (d, 2H, $J = 4.8$ Hz, β), 8.47 (d, 4H,

$J = 8.1$ Hz), 8.28 (d, 4H, $J = 8.1$ Hz), 4.60 (q, 4H, $J = 7.3$ Hz, CH_2CH_3), 1.56 (t, 6H, $J = 7.3$ Hz, CH_2CH_3), −3.0 (br, 2H, NH). MALDI TOF-Mass (Dithranol) $m/z = 685.1$ $[M+H]^+$; Calc. for $C_{38}H_{29}BrN_4O_4 = 684.1$.

4.5. 5,15-Bis(ethoxycarbonylphenyl)-10-(1′-methyl-2′-imidazolyl)(ethynyl)porphyrin (**9**)

To a solution of bromoporphyrin **8** (62 mg, 90.4 μmol) in dry THF (15 mL), a mixture of THF:Et_3N (5:1, 3 mL), $Pd_2(dba)_3CHCl_3$ (15 mg, 14.5 μmol) and $AsPh_3$ (33 mg, 109 μmol) was added. 2-Ethynyl-1-methylimidazole (29 mg, 270 μmol) in THF (3 mL) was added to the mixture, and the mixture was stirred at 45 °C under Ar. Disappearance of **8** was monitored by TLC after 20 min. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography ($CHCl_3$) and reprecipitation from $CHCl_3$/hexane to give **9** (54 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.21 (s, 1H, *meso*), 9.82 (d, 2H, $J = 4.7$ Hz, β), 9.30 (d, 2H, $J = 4.7$ Hz, β), 8.93 (d, 2H, $J = 4.7$ Hz, β), 8.91 (d, 2H, $J = 4.7$ Hz, β), 8.49 (d, 4H, $J = 8.0$ Hz), 8.31 (d, 4H, $J = 8.0$ Hz), 7.33 (d, 1H, $J = 1.0$ Hz, Im), 7.18 (d, 1H, $J = 1.0$ Hz, Im), 4.61 (q, 4H, $J = 7.2$ Hz, CH_2CH_3), 4,23 (s, 3H, *N*–Me), 1.57 (t, 6H, $J = 7.2$ Hz, CH_2CH_3), −2.61 (s, 2H, NH). MALDI TOF-Mass (Dithranol) $m/z = 710.3$ $[M]^+$; Calc. for $C_{44}H_{34}N_6O_4 = 710.3$.

4.6. 5,15-Bis(ethoxycarbonylphenyl)-10-(1′-methyl-2′-imidazolyl)(ethynyl)porphyrinatozinc (**1a**, **2a**)

To a solution of free base **9** (25 mg, 35.2 μmol) in $CHCl_3$ (30 mL), zinc acetate dihydrate (232 mg, 1.06 mmol) in MeOH (3 mL) was added at RT, and the mixture was stirred for 2 h. A saturated $NaHCO_3$ solution (10 mL) was added. Organic layer was extracted with $CHCl_3$, dried over anhydrous Na_2SO_4, and evaporated to give **1a** (25.6 mg, 94%). **1a** forms dimer **2a** spontaneously in non-coordinating solvents such as $CHCl_3$ and tetrachroloethane. ^{1}H NMR (600 MHz, $(CDCl_2)_2$) of **2a** δ 10.30 (s, 1H, *meso*), 9.38 (d, 2H, $J = 4.2$ Hz, β), 8.92 (d, 2H, $J = 4.2$ Hz, β), 8.91 (d, 2H, $J = 4.1$ Hz, β), 8.60 (d, 4H, $J = 7.2$ Hz), 8.58 (d, 4H, $J = 7.2$ Hz), 8.49 (d, 2H, $J = 4.2$ Hz, β), 8.44 (d, 4H, $J = 7.2$ Hz), 8.25 (d, 4H, $J = 7.2$ Hz), 5.28 (s, 1H, Im), 4.63 (q, 4H, $J = 7.2$ Hz, CH_2CH_3), 2.63 (s, 3H, *N*–Me), 1.67 (s, 1H, Im), 1.62 (t, 6H, $J = 7.2$ Hz, CH_2CH_3). MALDI TOF-Mass (Dithranol) $m/z = 772.0$ $[M]^+$; Calc. for $C_{44}H_{32}N_6O_4Zn = 772.2$.

4.7. 5,15-Bis(ethoxycarbonylphenyl)-10-bromoporphyrinatozinc (**10**)

To a solution of free base **8** (40 mg, 58.3 μmol) in $CHCl_3$ (20 mL), zinc acetate dihydrate (384 mg, 1.75 mmol) in MeOH (5 mL) was added at RT, and the mixture was stirred for 30 min. A saturated $NaHCO_3$ solution (10 mL) was added. Organic layer was extracted with $CHCl_3$, dried over anhydrous Na_2SO_4, and purified by SiO_2 column chromatography (eluent: $CHCl_3$) to give **10** (40 mg, 92%). ^{1}H NMR (600 MHz, $(CDCl_2)_2$) δ 8.81 (s, 1H, *meso*), 8.43 (d, 2H, β, $J = 4.8$ Hz), 7.98 (d, 2H, β, $J = 4.8$ Hz), 7.61 (d, 2H, β, $J = 4.8$ Hz), 7.59 (d, 2H, β, $J = 4.8$ Hz), 7.04 (d, 4H, Ar, $J = 7,2$ Hz), 6.92 (d, 4H, Ar, $J = 7,2$ Hz), 3.14 (q, 4H, $J = 7.2$ Hz, CH_2CH_3), 0.19 (t, 4H, $J = 7.2$ Hz, CH_2CH_3). MALDI TOF-Mass (Dithranol) $m/z = 747.1$ $[M+H]^+$; Calc. for $C_{38}H_{27}BrN_4O_4Zn = 746.1$.

4.8. 5,15-Bis(ethoxycarbonylphenyl)-10-phenylethynylporphyrinatozinc (**11**)

To a solution of bromoporphyrin **10** (25 mg, 33.4 μmol) in dry THF (7 mL), a mixture of THF:Et_3N (5:1, 1.4 mL), $Pd_2(dba)_3CHCl_3$ (5.5 mg, 5.34 μmol) and $AsPh_3$ (12 mg, 40 μmol) was added. Phenylacetylene (10 mg, 100 μmol) in THF (1 mL) was added to the mixture, and the mixture was stirred at 50 °C under Ar. After 30 min, solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography ($CHCl_3$) twice to give **11** (16.5 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.19 (s, 1H, *meso*), 9.88 (d, 2H, $J = 4.2$ Hz, β), 9.34 (d, 2H, $J = 4.2$ Hz, β), 8.99 (d, 2H, $J = 4.2$ Hz, β), 8.98 (d, 2H, $J = 4.2$ Hz, β), 8.47 (d, 4H, $J = 8.1$ Hz), 8.31 (d, 4H, $J = 8.1$ Hz), 8.04 (d, 2H, $J = 7.8$ Hz, Ph), 7.58 (t, 2H, , $J = 7.8$ Hz, Ph), 7.50 (tt, 2H, , $J = 1.8$, 7.8 Hz, Ph), 4.58 (q, 4H, $J = 7.2$ Hz, CH_2CH_3), 4,23 (s, 3H, *N*–Me), 1.53 (t, 6H, $J = 7.2$ Hz, CH_2CH_3). MALDI TOF-Mass (Dithranol) $m/z = 768.2$ $[M]^+$; Calc. for $C_{46}H_{32}N_6O_4Zn = 768.2$.

4.9. meso,meso-Linked diporphyrinatozinc (**13**) [15]

According to the reported procedure, **13** (15 mg, 15%) was prepared from porphyrin **12** (100 mg, 134 μmol) by oxidative coupling and GPC separation. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.39 (s, 1H, *meso*), 9.49 (d, 2H, $J = 10.2$ Hz, β), 9.19 (d, 2H, $J = 10.2$ Hz, β), 8.75 (d, 2H, $J = 10.2$ Hz, β), 8.13 (d, 2H, $J = 10.2$ Hz, β), 8.114 (s, 4H, Ph), 8.107 (s, 4H, Ph), 7.71 (t, 2H, $J = 3.6$ Hz, Ph), 1.45 (s, 72H, *t*Bu). MALDI TOF-Mass (Dithranol) $m/z = 1496.3$ $[M+H]^+$; Calc. for $C_{96}H_{102}N_8Zn_2 = 1494.7$.

4.10. meso,meso′-Dibrominated meso,meso-linked diporphyrinatozinc (**14**) [19]

According to the reported procedure, **14** (15 mg, 98%) was prepared from porphyrin **13** (14 mg, 9.34 μmol) by bromination with NBS. ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.86 (d, 4H, $J = 4.8$ Hz, β), 9.08 (d, 4H, $J = 4.8$ Hz, β), 8.65 (d, 4H, $J = 4.8$ Hz, β), 8.07 (d, 4H, $J = 4.8$ Hz, β), 8.05 (d, 8H, $J = 1.6$ Hz, Ar), 7.71 (t, 4H, $J = 1.6$ Hz, Ar), 1.44 (s, 72H, *t*Bu). MALDI TOF-Mass (Dithranol) $m/z = 1530.2$ $[M+H]^+$; Calc. for $C_{96}H_{104}Br_2N_8 = 1529.7$.

4.11. meso,meso′-Dibrominated meso,meso-linked diporphyrin (15)

A solution of zinc porphyrin **14** (9 mg, 5.43 μmol) in $CHCl_3$ (10 mL) was added to a 6M HCl aqueous solution. The mixture was stirred under N_2 for 1 h at RT. The mixture was adjusted to pH 8 with a saturated $NaHCO_3$ solution. The organic layer was extracted with $CHCl_3$, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by SiO_2 column chromatography (eluent: $CHCl_3$) to give **15** (7 mg, 84%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.76 (d, 4H, $J = 4.8$ Hz, β), 8.97 (br. d, 4H, $J = 4.8$ Hz, β), 8.65 (d, 4H, $J = 4.8$ Hz, β), 8.07 (d, 4H, $J = 4.8$ Hz, β), 8.05 (d, 8H, $J = 1.6$ Hz, Ar), 7.71 (t, 4H, $J = 1.6$ Hz, Ar), 1.44 (s, 72H, *t*-Bu), −2.15 (br. s, NH). MALDI TOF-Mass (Dithranol) $m/z = 1530.2$ $[M+H]^+$; Calc. for $C_{96}H_{104}Br_2N_8 = 1529.7$.

4.12. meso,meso′-Bis(1′-methyl-2′-imidazolyl)(ethynyl)-substituted meso,meso-linked diporphyrin (16)

To a solution of bromoporphyrin **15** (2.5 mg, 23.5 μmol) in dry THF (5 mL), a mixture of THF:Et_3N (5:1, 1 mL), $Pd_2(dba)_3CHCl_3$ (1.3 mg, 1.25 μmol) and $AsPh_3$ (2.9 mg, 9.4 μmol) was added. 2-Ethynyl-1-methylimidazole (2.5 mg, 23.5 μmol) in THF (1 mL) was added to the mixture, and the mixture was stirred at 45 °C under Ar. Disappearance of **15** was monitored by TLC after 40 min. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography ($CHCl_3$) to give **16** (3.5 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.83 (d, 4H, $J = 4.8$ Hz, β), 9.00 (br. d, 4H, $J = 4.8$ Hz, β), 8.55 (d, 4H, $J = 4.8$ Hz, β), 8.05 (d, 8H, $J = 1.6$ Hz, Ar), 8.02 (d, 4H, $J = 4.8$ Hz, β), 7.72 (br. s, 4H, Ar), 7.36 (s, 2H, Im), 7.20 (s, 2H, Im), 4.29 (s, 6H, *N*-Me), 1.44 (s, 72H, *t*Bu), −1.77 (br. S, NH). MALDI TOF-Mass (Dithranol) $m/z = 1581.5$ $[M+H]^+$; Calc. for $C_{108}H_{114}N_{12} = 1579.9$.

4.13. meso,meso′-Bis(1′-methyl-2′-imidazolyl)(ethynyl)-substituted meso,meso-linked diporphyrinatozinc 5

To a solution of free base **16** (1 mg, 0.633 μmol) in $CHCl_3$ (5 mL), zinc acetate dihydrate (4 mg, 19 μmol) in MeOH (0.5 mL) was added at RT, and the mixture was stirred for 1 h. A saturated $NaHCO_3$ solution (10 mL) was added. The organic layer was extracted with $CHCl_3$, dried over anhydrous Na_2SO_4, and evaporated to give **5** (0.9 mg, 83%). MALDI TOF-Mass (Dithranol) $m/z = 1704.9$ $[M+H]^+$; Calc. for $C_{108}H_{110}N_{12}Zn_2 = 1703.8$. ^{1}H NMR (600 MHz, $(CDCl_2)_2$) of **5P** are shown in Fig. 5.

5. UV–Vis titration

UV–Vis titration shown in Fig. 3 inset was carried out in a Pyrex® glass cuvette (band path 1 cm) filled with a sample solution (4×10^{-6} M, 3 mL) in chloroform. *N*-Methyl imidazole was added as a chloroform solution initially, and then, directly to avoid the volume increase. The mixture was stirred for 2 min at rt and UV–Vis spectra of the solution was measured. The change of absorbance at 443.5 nm was plotted as a function of added *N*-methylimidazole. The curve fitting analysis was carried out by referring to the literature [22].

6. Molecular modeling

Molecular mechanics calculation was performed on Cerius2® (Accelrys Software Inc.) using Universal force field.

7. Estimation of molecular length of 5P

Aggregation numbers of **5P** are estimated from Eqs. (5) and (6) on the basis that the association constant of the zinc porphyrin unit (imidazolylethynyl-zinc-porphyrin moiety) in **5P** is same as that in **2** ($K = 1.8 \times 10^7$ M^{-1}).

$$Z_t = 2[Z_D] + [Z_M], \tag{5}$$

$$\boldsymbol{K} = \frac{[Z_D]}{[Z_M]^2}. \tag{6}$$

Here $[Z_t]$, $[Z_D]$, and $[Z_M]$ are concentrations of total, dimeric, and monomeric zinc porphyrin units, respectively. A mean aggregation number is calculated when an appropriate $[Z_t]$ is defined as the initial concentration of the zinc porphyrin.

8. Deconvolution of Soret bands in 5M

Peak analysis of Soret band of **5M** was performed by using ORIGIN® Pro ver.7 program (Origin Lab Co.). The original spectrum was translated into wavenumber and divided into three components predicted by head-to-tail interaction along B_x–B_x transition, unperturbed B_y and B_z transitions, and parallel interaction of the transition dipoles due to rotation along the *meso–meso* bond. The deconvoluted peak maxima (half band widths) are 21 045 cm^{-1} (475 nm, 971 cm^{-1}), 22 533 cm^{-1} (444 nm, 1562 cm^{-1}), and 23 575 cm^{-1} (424 nm, 2575 cm^{-1}). In the case of **6M**, Soret band can be deconvoluted by two components, 21 536 cm^{-1} (464 nm, 1559 cm^{-1}) and 23 960 cm^{-1} (417 nm, 2109 cm^{-1}).

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