HETEROCYCLES, Vol. 86, No. 1, 2012, pp. 515 - 534. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 22nd June, 2012, Accepted, 23rd July, 2012, Published online, 2nd August, 2012
DOI: 10.3987/COM-12-S(N)50

SYNTHESIS OF BIS-NAPHTHOPORPHYRINS

Hiroki Uoyama, Hiroko Yamada, Tetsuo Okujima, and Hidemitsu Uno*

Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan. Fax: (+81)89-927-9670; E-mail: uno@dpc.ehime-u.ac.jp

Abstract – Ethanonaphthoporphyrins with a halogen atom at the ζ position were prepared by the [3+1] porphyrin synthesis of halogen-substituted ethanobenz[*f*]isoindole with a tripyrrane derivative. The halogeno porphyrins were converted to the corresponding ethynyl and pinacolatoboronyl compounds by Sonogashira and borylation reactions, respectively. Suzuki, Sonogashira, and Glaser coupling reactions of these ethanonaphthoporphyrins gave bis-porphyrins connected with no atom, acetylene, and butadiyne, respectively. Retro Diels-Alder reaction of these bis-porphyrins brought about the conversion of bicyclo[2.2.2]octadiene (BCOD) to benzene moieties to give bis-naphthoporphyrins, quantitatively.

Dedicated to Professor Dr. Eiichi Negishi on the occasion of his 77th birthday

INTRODUCTION

Porphyrin dimers, trimers and oligomers[1] have continuously attracted attention as host molecules for carbon materials such as fullerenes and nanotubes,[2] as near infrared dyes,[3] and as artificial models for a light harvesting antenna porphyrin system.[4] For these applications, not only the electronic properties of porphyrins but also the spacer between the porphyrins are important. When the porphyrin rings are directly connected, interaction of the porphyrin π-systems is small because these porphyrin rings tend to orient nearly perpendicularly due to steric repulsion regardless of the connecting positions.[5] Therefore, electronic structures of the oligomers are not greatly different from those expected by summation of the monomeric porphyrins and only small perturbation to electronic states is observed. When spacer groups are employed to connect the porphyrin rings, the spacer properties become important. In the case of aryl spacers, the π-planes of spacers and porphyrin rings tend to be perpendicular and the interaction is small, too.[6] When alkyl chains are used, the length is important for communication of the porphyrin

chromophores.[7] On the other hand, alkyne spacers are quite different and electronic states of the porphyrin rings are well mixed to form large delocalized chromophores.[8] Introduction of the alkyne groups can be achieved by the reliable method, namely Sonogashira reaction.[9] As the alkyne groups are easily converted to other functional groups, many successful examples for the modification of porphyrin chromophores were reported.[10] For Sonogashira reaction, porphyrin halogenated at a desired position is required. Selective halogenation of porphyrin is rather difficult because easily available porphyrins such as tetraphenylporphyrin and octaethylporphyrin have high symmetry of D_{4h}.[11] An alternative method for preparation of halogenated porphryins from pyrroles bearing halogen atoms become important. When a pyrrole derivative bearing iodine atoms at β-positions was employed for the porphyrin synthesis, the aimed diiodoporphyrin was obtained only in a very low yield.[12] During the porphryin synthesis under such acidic conditions, a halogen atom directly substituted on the pyrrole ring is sometimes lost by electrophilic attack of proton on the pyrrole ring.[13] Therefore, the pyrroles with halogen atoms in distal positions were preferably employed for this purpose.[14] The connecting moieties between pyrrole nucleus and halogen atoms are important. During the course of our continuous investigation for the preparation of π-expanded porphyrins, we prepared pyrroles connected with halogenated benzene through bicyclo[2.2.2]octadiene in order to combine the porphyrin chromophores. In this paper, we demonstrate the synthesis of halogenated ethanonaphthoporphyrins **1** and their conversion to naphthoporphyrins **8** and diporphyrins **2**–**7**.

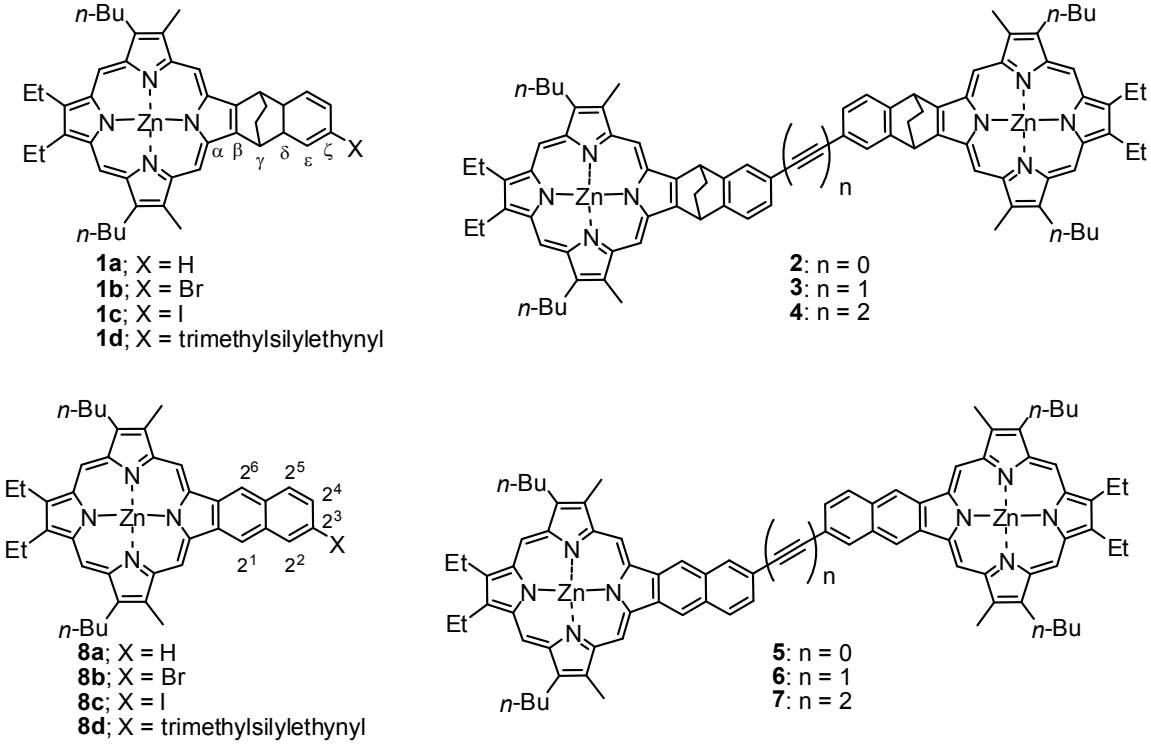
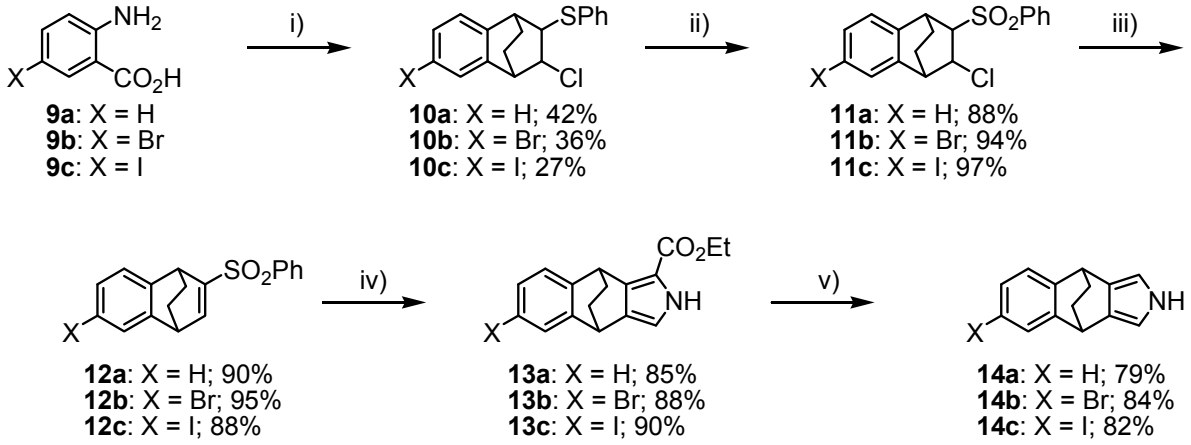


Figure 1. Naphthoporphyrins **8**, bis-naphthoporphyrins **5**-**7**, and their precursors **1**–**4**

RESULTS AND DISCUSSION

Synthesis

The new halogenated pyrroles **14b** and **14c** were prepared according to the modified method reported in the literature (Scheme 1).[15] The Diels-Alder reaction of benzynes generated from anthranilic acids **9** with 1,3-cyclohexadiene gave 1,4-dihydro-1,4-ethanonaphthalene derivatives,[16] which were roughly purified by silica-gel column chromatogaphy and used without further purification. Treatment of the crude products with benzenesulfenyl chloride gave sulfides **10** in moderate yields (two steps). Sulfides **10** were oxidized with mCPBA to give β-chloro sulfones **11** in good yields. Elimination of hydrogen chloride from **11** with DBU afforded α,β-unsaturated sulfones **12** in good yields. Pyrrolecarboxylate esters **13** were obtained in good yields by the modified Barton-Zard pyrrole synthesis using sulfones **12** and ethyl isocyanoacetate with the aid of KO-*t*-Bu. Removal of the ester moiety from pyrrolecarboxylates **13** was achieved by heating **13** with KOH in ethylene glycol at 175 °C for 2 h. α-Free pyrroles **14** were obtained in good yields. The total yields of pyrroles **14a**, **14b**, and **14c** from corresponding anthranilic acids **9** were 22, 24, and 17%, respectively.

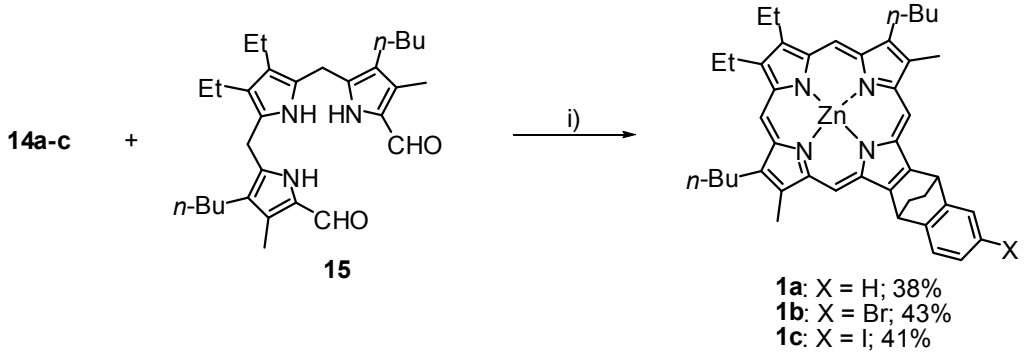


Scheme 1. *Reagents and conditions*: i) isopentyl nitrite, TFA, THF; 1,3-cyclohexadiene, 1,2-dichloroethane; PhSCl, CH_2Cl_2; ii) mCPBA, CH_2Cl_2; iii) DBU, CH_2Cl_2; iv) ethyl isocyanoacetate, KO-*t*-Bu, THF; v) KOH, ethylene glycol, 175 ˚C

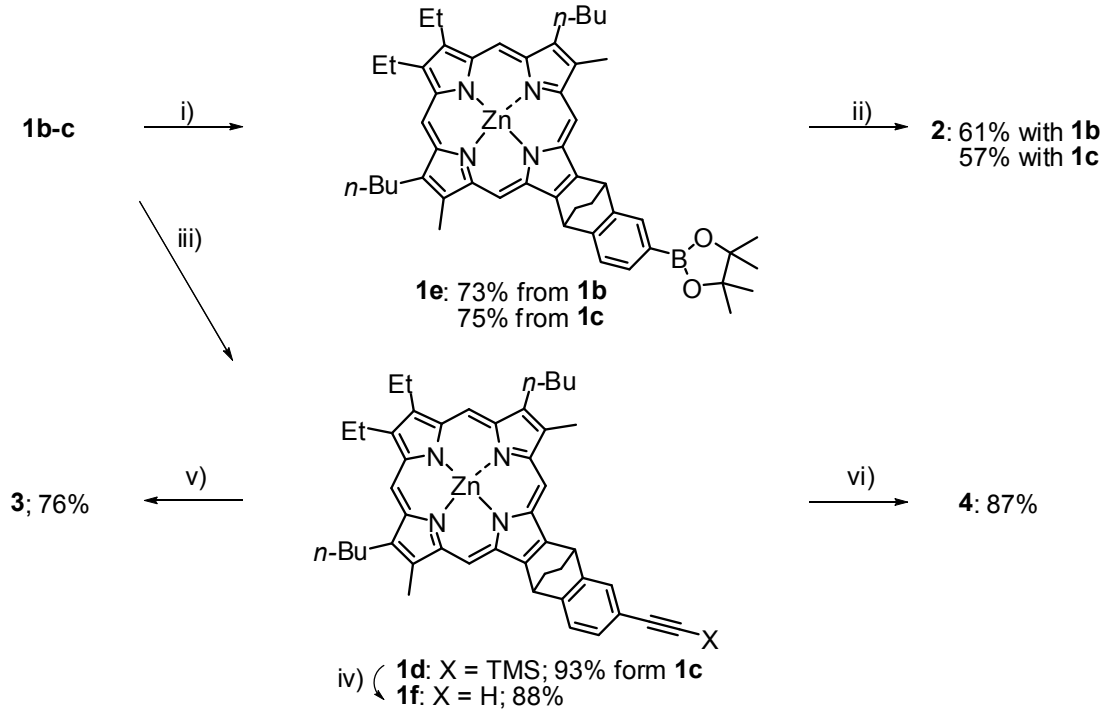
Porphyrins **1a**–**c** were obtained by using the inverse mode[17] of [3+1] method (Scheme 2).[18] Condensation of the pyrrole **14** and tripyrranedicarboaldehyde **15**[19] followed by oxidation with DDQ and treatment with $Zn(OAc)_2 \cdot 2H_2O$ gave porphyrins **1a**, **1b**, and **1c** in respective yields of 38, 43, and 41%.

Preparation of bis-porphyrins **2**–**4** are shown in Scheme 3. Since the preparation of directly linked bis-porphyrin **2** by the Ullmann homo coupling reaction of either **1b** or **1c** with Cu failed, we employed the Suzuki-Miyaura coupling reaction. Pinacolatoboronyl derivative **1e** was obtained by the reaction of porphyrins **1b**–**c** and bis(pinacolato)diboron with $PdCl_2(PPh_3)_2$ in 73 and 75% yields, respectively. The

Suzuki-Miyaura cross coupling reaction between **1b–c** and pinacolatoboronated porphyrin **1e** led to formation of **2** in 61 and 57% yields, respectively. The Sonogashira coupling reaction between iodoporphyrin **1c** and trimethylsilylacetylene gave acetylene-substituted porphyrin **1d** in a 93% yield, while the similar reaction of bromo derivative **1b** was unsuccessful. The trimethylsilyl group of **1d** was removed with tetrabutylammonium fluoride to give **1f** in an 88% yield. Acetylene-linked porphyrin dimer **3** was prepared by the Sonogashira coupling reaction between porphyrins **1c** and **1f** in a 76% yield. On the other hand, butadiyne-linked bis-porphyrin **4** was synthesized by the Eglinton modification of the Glaser coupling reaction of **1f** in an 87% yield.



Scheme 2. *Reagents and conditions*: i) TFA, CH_2Cl_2; DDQ; $Zn(OAc)_2 \cdot 2H_2O$.



Scheme 3. *Reagents and conditions*: i) bis(pinacolato)diboron, $PdCl_2(PPh_3)_2$, KOAc, DMSO, 100 ˚C; ii) **1b–c**, $PdCl_2(PPh_3)_2$, K_2CO_3, DMSO, 100 ˚C; iii) trimethylsilylacetylene, diisopropylamine, $PdCl_2(PPh_3)_2$, PPh_3, CuI, diisopropylamine, THF, reflux; iv) tetrabutylammonium fluoride, THF; v) **1b–c**, diisopropylamine, $PdCl_2(PPh_3)_2$, PPh_3, CuI, THF, reflux; vi) $Cu(OAc)_2$, pyridine

Preparative conversions of the BCOD-fused porphyrins and bisporphyrins **1**–**4** were performed at 290 °C under a reduced pressure (*ca*. 7 Pa) for 10 min according to our previous report,[15] whereby the naphthoporphyrin derivatives **5**–**8** were obtained in quantitative yields. Bis-naphthoporphyrins **5**–**7** were insoluble in common solvents such as chloroform, dichloromethane, and toluene, but slightly soluble in pyridine and THF.

UV-vis Spectra of Properties and DFT calculations

UV-vis spectra of BCOD-fused porphyrins **1a**, **2**, **3**, and **4** in $CHCl_3$ are shown in Figure 2. BCOD-fused porphyrin monomer **1a** showed the Soret band absorption at 402 nm and two Q band absorptions at 531 and 570 nm. In BCOD-fused porphyrin dimers **2**, **3**, and **4**, the Soret and Q bands showed strong absorptions with no bathochromic shift compared to those of monomeric **1a** and **1d** because each porphyrin π-electronic system of **2**, **3**, and **4** was separated by the BCOD moiety.

UV-vis spectra of naphthoporphyrins **5**–**8** in pyridine are shown in Figure 2. Bathochromic shift of Soret- and Q-band absorptions was observed in naphthoporphyrins **5**–**8** compared to those of the corresponding BCOD-fused porphyrins **1**–**4**. UV-vis spectra of bis-naphthoporphyrins **5**–**7** showed only small change compared to those of naphthoporphyrins **8**. Soret band absorptions of bis-naphthoporphyrins **5**–**7** were quite similar and became broad with a slight bathochromic shift, while the Q band absorptions only looked like the sum of the Q band signals of naphthoporphyrin **8a**.

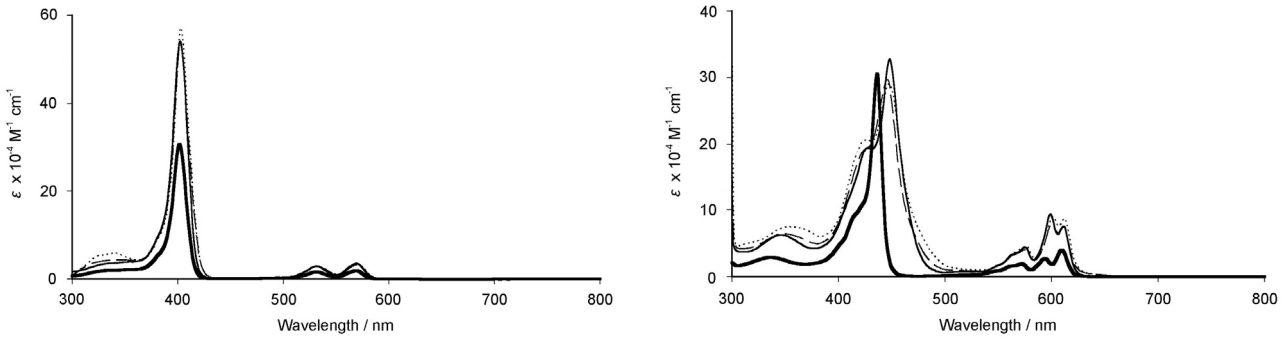


Figure 2. UV-Vis spectra of BCOD porphyrins (left) in $CHCl_3$: **1a** (bold line), **2** (solid line), **3** (broken line), and **4** (dotted line) and naphthoporphyrins (right) in pyridine: **8a** (bold line), **5** (solid line), **6** (broken line), and **7** (dotted line)

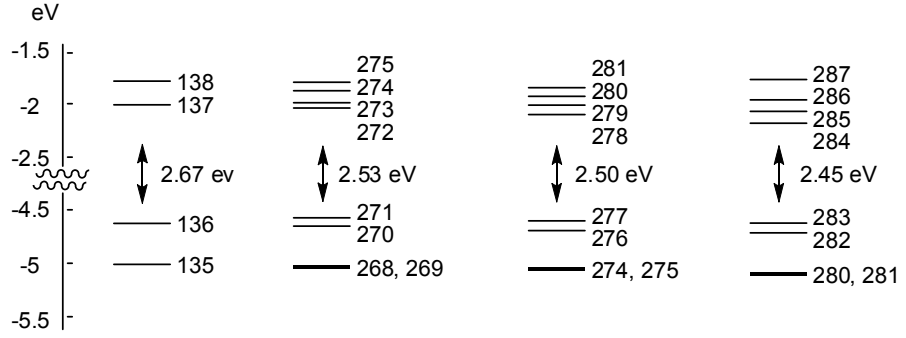


Figure 3. Energy diagrams of **8a** (left), **5** (middle left), **6** (middle right), and **7** (right)

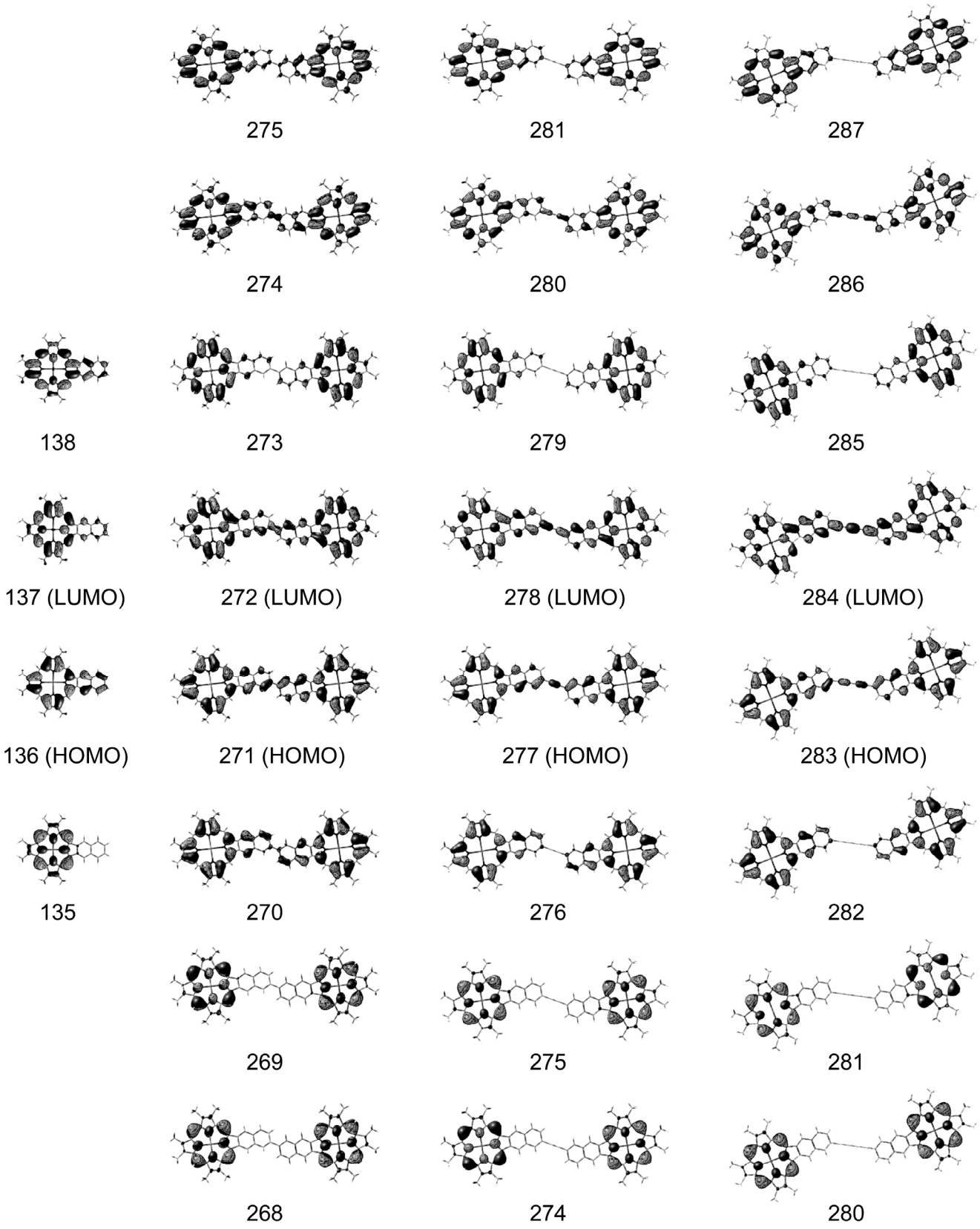


Figure 4. Frontier MO diagrams of naphthoporphyrin **8a** (left) and bis-naphthoporphyrins **5** (middle left), **6** (middle right), and **7** (right)

In order to figure out electronic properties of bis-naphthoporphyrins, we performed DFT calculation (B3LYP/6-31G(d)-LanL2DZ) of **5**, **6**, **7**, and **8a**. Figures 3 and 4 show energy levels and some frontier MO diagrams of naphthoporphyrin **8a** and dimers **5**-**7**. The eight molecular orbitals (HOMO−3 ~ LUMO+3) of dimers **5**–**7** can be approximately described as linear combinations of four molecular orbitals (HOMO−1 ~ LUMO+1) of constituent monomers.[20] The HOMO−1, HOMO, LUMO, and LUMO+1 of monomer constitute the following pairs of dimer orbitals: HOMO−3/HOMO−2, HOMO−1/HOMO, LUMO/LUMO+1, and LUMO+2/LUMO+3. AO coefficients at ζ-positions of naphthoporphyrin are nearly zero in HOMO−1 and small in HOMO, LUMO, and LUMO+1. Therefore, those of HOMO−3 and HOMO−2 of dimers are also nearly zero, because HOMO−3 and HOMO−2 of dimers consist of linear combination of HOMO-1 orbitals of the monomer. Thus, the HOMO−2/HOMO−3 pair shows no energy splitting. On the other hand, as HOMO−1 ~ LUMO+3 of dimers have small AO coefficients on the connecting ζ-positions, the HOMO/HOMO − 1, LUMO/LUMO+1, and LUMO+2/LUMO+3 pairs of dimers exhibit small energy splitting. Consequently, very similar electronic spectra are obtained especially in the Q-band region.

In conclusion, we have achieved the synthesis of ethanonaphthoporphyrins with a bromine or iodine atom at the ζ position and their conversion to the corresponding ethynyl and pinacolatoboronyl compounds by Sonogashira and borylation reactions. These monomeric porphyrin compounds were successfully dimerized by the Suzuki, Sonogashira, and Glaser coupling reactions. Fully conjugated naphthoporphyrin dimers connected directly and with acetylene and butadiyne at ζ-positions were obtained by the retro Diels-Alder reaction. These naphthoporphyrin dimers are revealed to show the similar UV-vis absorptions to the corresponding monomers especially in the Q-band region.

EXPERIMENTAL

General: Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. Otherwise noted, NMR spectra were obtained in $CDCl_3$ with a JEOL AL-400 or EX-400 spectrometer at the ambient temperature by using tetramethylsilane as an internal standard for ^1H and ^{13}C. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. EI and FAB MS were measured with a JEOL JMS-700. MALDI-TOF MS were measured on a Voyager DE Pro instrument (Applied Biosystems). Elemental analyses were performed with a Yanaco MT-5 elemental analyzer. Preparative GPC was carried out on a JAI LC-9801 chromatograph equipped with JAI-1H (*Φ*20 x 600 mm) and JAI-2H (*Φ*20 x 600 mm) columns. UV-vis spectra were measured with a HITACHI U-2810 spectrophotometer. All solvents and chemicals were reagent grade quality, obtained commercially, and

used without further purification except as noted. Dry CH_2Cl_2 and THF were purchased from Kanto Chemical Co. Triethylamine, pyridine, and DBU, were distilled from calcium hydride and then stored on appropriate Molecular Sieves. Solvents for chromatography were purified by distillation. For spectral measurements, spectral grades of pyridine and chloroform were purchased from Nacalai Tesque Co. Thin-layer (TLC) and column chromatography with silica gel was performed on Art. 5554 (Merck KGaA), Silica Gel 60N (Kanto Chemical Co.). Tripyrrane **15** was prepared according to the literature.[19]

General procedure for preparation of sulfide 10: To a solution of anthranilic acid **9** (25.0 mmol) in THF (40 mL) was added CF_3CO_2H (0.04 mL) at 0 °C. The mixture was stirred for 10 min and isopenyl nitrite (5.01 mL, 3.75 mmol) was slowly added at the same temperature. The mixture was warmed to room temperature and stirred for 1.5 h. The mixture was cooled to 0 °C and white solid was formed. The solid was filtered and then washed with cooled $ClCH_2CH_2Cl$. *Caution: The diazonium salt must be wet with the solvent, or it explodes!* The wet solid was suspended in $ClCH_2CH_2Cl$ (10 mL) and added to a refluxed solution of 1,3-cyclohexadiene (4.77 mL, 50.0 mmol) in $ClCH_2CH_2Cl$ (150 mL). After the addition, the mixture was stirred for 2 h under reflux. The mixture was cooled to room temperature and concentrated under a reduced pressure. The black residue was purified by short column chromatography on silica gel ($CHCl_3$, $R_f = 0.9$) to give a colorless crude product. Benzenesulfenyl chloride was added to a stirred solution of the crude product in dry CH_2Cl_2 (100 mL) at -78 °C under N_2 until the orange color of PhSCl no more disappeared. The mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic extract was washed successively with aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was chromatographed on silica gel to give **10**.

2-Chloro-3-phenyltho-1,4-dihydro-1,4-ethanonaphthalene (10a): Yield, 42%; colorless oil, $R_f = 0.45$ (30% EtOAc/hexane); ^{1}H NMR δ 7.43 (2H, m), 7.28 (5H, m), 7.23 (2H, m), 3.83 (1H, m), 3.59 (1H, m), 3.22 (1H, m), 3.10 (1H, m), 2.38 (1H, m), 1.91 (1H, m), 1.54 (1H, m), and 1.34 (1H, m); ^{13}C NMR δ 139.84, 139.19, 135,27, 134.43, 131.98, 129.18, 128.92, 127.19, 127.06, 125.75, 124.38, 124.22, 64.89, 57.23, 42.89, 40.32, 26.15, and 18.49; IR (KBr) ν_{max}/cm^{-1} 1583, 1481, 1439, 1101, 742, and 690; MS (EI) *m/z* (rel. intensity) 300 (M^+, 100), 191 (13), 128 (29), and 77 (9). Anal. Calcd for $C_{18}H_{17}ClS+1/2H_2O$: C, 69.77; H, 5.86. Found: C, 70.14; H, 5.85%.

6-Bromo-2-chloro-3-phenyltho-1,4-dihydro-1,4-ethanonaphthalene and 6-bromo-3-chloro-2-phenyltho-1,4-dihydro-1,4-ethanonaphthalene (10b): Yield, 36%; colorless oil, R_f = 0.45 (30% $CHCl_3$/hexane); ^{1}H NMR (diastereomeric mixture) δ 7.38–7.45 (3H, m), 7.23–7.35 (5H, m), 7.05 (1H, m), 3.78 (1H, m), 3.55 (1H, m), 3.20 (1H, m), 3.06 (1H, m), 2.37 (1H, m), 1.91 (1H, m), 1.52 (1H, m), and 1.33 (1H, m); ^{13}C NMR (typical signals) δ 141.87, 141.31, 138.71, 138.10, 133.90, 132.16, 132.05, 130.00, 129.92, 128.95, 128.93, 128.77, 127.44, 127.39, 127.37, 127.32, 125.93, 120.81, 120.51, 64.12,

64.11, 56.84, 56.81, 42.62, 42.36, 40.23, 39.83, 25.88, 25.81, and 18.22; IR (KBr) ν_{max}/cm^{-1} 1574, 1475, 1439, 1414, 1259, 1238, and 1024; MS (EI) *m/z* (rel. intensity) 380 [M^+(^{79}Br)+1, 100], 271 (49), 235 (31), 208 (62), and 128 (83). Anal. Calcd for $C_{18}H_{16}BrClS$: C, 56.93; H, 4.25. Found: C, 56.94; H, 4.20%.

2-Chloro-6-iodo-3-phenyltho-1,4-dihydro-1,4-ethanonaphthalene and 3-chloro-6-iodo-2-phenyltho-1,4-dihydro-1,4-ethanonaphthalene (10c): Yield, 27%; colorless oil; R_f = 0.25 (10% $CHCl_3$/hexane); ^{1}H NMR (diastereomeric mixture) δ 7.50–7.67 (2H, m), 7.42 (2H, m), 7.23–7.32 (3H, m), 6.93 (1H, m), 4.68 (one of isomers, 1H, m), 3.92 (one of isomers, 1H, m), 3.78 (one of isomers, 1H, m), 3.53 (one of isomers, 1H, m), 3.33 (one of isomers, 1H, m), 3.10 (1H, m), 3.04 (one of isomers, 1H, m), 2.35 (one of isomers, 1H, m), 2.14 (one of isomers, 1H, m), 1.87 (, 1H, m), 1.49 (, 1H, m), 1.30 (one of isomer, 1H, m), and 1.08 (one of isomers, 1H, m); ^{13}C NMR (typical signals) δ 144.43, 143.22, 142.22, 141.60, 139.43, 138.84, 136.70, 136.05, 134.97, 134.07, 133.99, 133.84, 133.25, 132.16, 132.08, 131.06, 127.73, 127.43, 127.37, 127.12, 126.28, 124.22, 92.59, 91.94, 64.13, 58.62, 56.72, 55.96, 51.13, 42.86, 42.35, 39.85, 29.14, 25.86, 25.73, and, 24.33; IR (KBr) ν_{max}/cm^{-1} 1583, 1473, 1408, 1259, 1173, 955, 820, 742, and 690; MS (EI) *m/z* (rel. intensity) 426 (M^+, 100), 317 (40), 281 (37), 254 (31), and 128 (65). Anal. Calcd for $C_{18}H_{16}ClIS$+1/8H_2O: C, 50.40; H, 3.82. Found: C, 50.20; H, 3.86%.

General procedure for oxidation of sulfide 10 to sulfone 11: To a solution of **10** (7.00 mmol) in dry CH_2Cl_2 (70 mL) was added mCPBA (16.8 mmol) at 0 °C. The mixture was then stirred for 2 h at room temperature. The mixture was quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2. The organic extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was chromatographed on silica gel to give **11**.

2-Chloro-3-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene (11a): Yield, 88%; colorless powder, mp 177–180 °C; R_f = 0.3 (30% EtOAc/hexane); ^{1}H NMR (diastereomer mixture) δ 7.85 (2H, m), 7.67 (1H, m), 7.56 (2H, m), 7.29 (3H, m), 7.21 (1H, m), 4.25 (1H, m), 3.72 (1H, m), 3.56 (1H, m), 3.31 (1H, m), 2.34 (1H, m), 1.97 (1H, m), 1.56 (1H, m), and 1.42 (1H, m); ^{13}C NMR (typical signals) δ 138.56, 138.01, 137.70, 133.77, 129.10, 128.61, 127.54, 127.27, 125.24, 124.16, 72.49, 56.85, 42.80, 34.64, 26.75, and 18.10; IR (KBr) ν_{max}/cm^{-1} 1444, 1302, 1146, 1086, 754, and 723; MS (EI) *m/z* (rel. intensity) 332 (M^+, 20), 191, (100), 162 (8), 129 (93), and 77 (17). Anal. Calcd for $C_{18}H_{17}ClO_2S$+1/2H_2O: C, 63.24; H, 5.31. Found: C, 63.48; H, 5.12%.

6-Bromo-2-chloro-3-phenylfulfonyl-1,4-dihydro-1,4-ethanonaphthalene and 6-bromo-3-chloro-2-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene (11b): Yield, 94 %; colorless powder, mp 56–58 °C, R_f = 0.4 (30% EtOAc/hexane); ^{1}H NMR (diastereomer mixture) δ 7.78–7.82 (2H, m), 7.51–7.67 (3H, m), 7.31–7.45 (2H, m), 7.14 (one isomer, 1H, m), 7.03 (another isomer, 1H, m), 4.18 (1H, m), 3.70 (another isomer, 1H, m), 3.63 (one isomer, 1H, m), 3.50 (1H, m), 3.25 (1H, m), 2.30 (1H m),

1.94 (1H, m), 1.53 (1H, m), 1.35 (1H, m); ^{13}C NMR (typical signals) δ 140.59, 139.73, 137.91, 137.67, 137.50, 134.35, 134.06, 134.00, 130.67, 130.32, 130.16, 129.74, 129.25, 129.19, 128.73, 128.66, 128.45, 128.21, 127.37, 127.28, 127.02, 125.85, 121.30, 120.97, 72.36, 72.19, 56.44, 42.64, 42.38, 34.65, 34.18, 26.64, 26.54, 17.99, and 17.94; IR (KBr) ν_{max}/cm^{-1} 1477, 1444, 1411, 1295 and 1147; MS (EI) *m/z* (rel. intensity) 412 [M^+(^{81}Br), 92], 207, (51), 162 (71), and 128 (53). Anal. Calcd for $C_{18}H_{16}BrClO_2S$+1/4CH_2Cl_2: C, 50.63; H, 3.84. Found: C, 50.35; H, 3.68%.

2-Chloro-6-iodo-3-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene and 3-chloro-6-iodo-2-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene (11c): Yield, 97%; colorless solid, mp 48–56 °C; R_f = 0.45 ($CHCl_3$); ^{1}H NMR (diastereomer mixture) δ 7.91–7.94 (1H, m), 7.76–7.81 (1H, m), 7.49–7.70 4H, m), 6.71 (another isomer, 1H, m), 6.90 (one isomer, 1H, m), 5.17 (another isomer, 1H, m), 4.16 (one isomer, 1H, m), 3.63 (both isomers, 1H, m), 3.48 (both isomers, 1H, m), 3.40 (another isomer, 1H, m), 3.22 (one isomer, 1H, m), 2.64 (another isomer, 1H, m), 2.27 (one isomer, 1H, m), 2.09 (another isomer, 1H, m), 1.92 (one isomer, 1H, m), 1.52 (another isomer, 1H, m), 1.27 (one isomer, 1H, m), 1.07 (another isomer, 1H, m), and 0.91 (one isomer, 1H, m); ^{13}C NMR (typical signals) δ 143.00, 141.52, 140.84, 139.89, 138.15, 137.90, 137.62, 136.61, 136.25, 134.14, 134.06, 133.97, 133.10, 129.55, 129.23, 129.16, 128.72, 128.65, 127.76, 127.22, 126.04, 123.94, 92.76, 92.13, 72.26, 71.23, 56.43, 53.59, 48.63, 42.43, 40.69, 34.37, 29.14, 26.60, 24.10, and 17.94; IR (KBr) ν_{max}/cm^{-1} 1473, 1446, 1317, 1147, 1083, 957, and 723; MS (EI) *m/z* (rel. intensity) 458 (M^+, 100), 422 (3), 394 (12), 333 (6), 317 (76), 281 (30), 254 (19), and 128 (83). Anal. Calcd for $C_{18}H_{16}ClIO_2S$+1/8H_2O: C, 46.90; H, 3.55. Found: C, 46.50; H, 3.55%.

General procedure for α,β-unsaturated sulfone 12: To a stirred solution of **11** (7.00 mmol) in dry CH_2Cl_2 (70 mL) was added DBU (7.7 mmol) at room temperature under N_2. After 1 h, a 1.0-M aqueous HCl solution was added to the reaction mixture. The mixture was extracted with CH_2Cl_2. The organic extract was washed successively with saturated aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was chromatographed on silica gel to give **12**.

2-Phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene (12a): Yield, 90%, colorless oil, R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR δ 7.79 (2H, m), 7.55 (1H, m), 7.46 (3H, m), 7.15 (1H, m), 7.07 (1H, m), 7.03 (1H, m), 6.99 (1H, m), 4.20 (2H, m), and 1.54 (4H, m); ^{13}C NMR δ 146.98, 144.60, 144.48, 141.17, 139.47, 133.08, 128.98, 127.59, 125.80, 125.66, 123.05, 122.64, 41.40, 40.49, 26.16, and 25.54; IR (KBr) ν_{max}/cm^{-1} 1610, 1460, 1311, 1149, 1090, 746, and 690; MS (EI) *m/z* (rel. intensity) 296 (M^+, 5), 268 (100), 127 (21), and 77 (9).

6-Bromo-2-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene and 7-bromo-2-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene (12b): Yield, 95%; colorless powder, mp 191–193 °C, R_f = 0.3 (30% EtOAc/hexane); ^{1}H NMR (diastereomer mixture) δ 7.81 (2H, m), 7.47–7.61(4H, m), 7.10–7.32 (2H, m),

7.04 (one isomer, 1H, m), 6.82 (another isomer, 1H, m), 4.17 (2H, m), and 1.46–1.61 (4H, m); ^{13}C NMR (typical signals) δ 147.06, 144.40, 142.87, 143.82, 143.60, 140.78, 140.43, 139.39, 133.45, 133.36, 129.23, 129.19, 128.88, 128.71, 127.79, 126.44, 125.98, 124.71, 124.23, 119.83, 119.46, 41.14, 40.95, 40.26, 40.07, 25.89, and 25.26; IR (KBr) ν_{max}/cm^{-1} 1606, 1471, 1411, 1300, 1242, 1155, and 1090; MS (EI) *m/z* (rel. intensity) 376 [M^+(^{81}Br), 39], 348 (100), 267 (8), 235 (35), 154 (51), and 126 (97). Anal. Calcd for $C_{18}H_{15}BrO_2S$: C, 57.61; H, 4.03. Found: C, 57.31; H, 3.97%.

6-Iodo-2-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene and 7-iodo-2-phenylsulfonyl-1,4-dihydro-1,4-ethanonaphthalene (12c): Yield, 88%, colorless solid, mp 179–185 °C; R_f = 0.25 ($CHCl_3$); ^{1}H NMR (diastereomer mixture) δ 7.80 (1H, m), 7.60 (1H, m), 7.34–7.53 (4H, m), 7.30 (1H, m), 6.92 (one isomer: 1H, d, J = 7.8 Hz), 6.70 (another isomer: 1H, d, J = 7.8 Hz), 4.15 (2H, m), and 1.44–1.55 (4H, m); ^{13}C NMR (typical signals) δ 147.44, 147.08, 144.40, 144.12, 143.88, 143.86, 141.47, 141.21, 139.42, 134.95, 134.78, 133.47, 133.37, 132.18, 131.73, 129.24, 129.20, 127.82, 127.80, 125.09, 124.61, 91.05, 90.81, 41.03, 40.97, 40.16, 40.09, 25.88, 25.83, 25.29, and 25.21; IR (KBr) ν_{max}/cm^{-1} 3061, 1468, 1444, 1404, 1230, 1228, 1146, and 1088; MS (EI) *m/z* (rel. intensity) 422 (M^+, 46), 394 (100), 281 (22), 153 (21), and 126 (37). Anal. Calcd for $C_{18}H_{15}IO_2S$: C, 51.20; H, 3.58. Found: C, 50.88; H, 3.66%.

General procedure for Barton-Zard reaction of 12: To a stirred solution of **12** (5.00 mol) and ethyl isocyanoacetate (0.66 mL, 6.0 mmol) in dry THF (50 mL) was added a 1.0-M solution of potassium *tert*-butoxide in THF (6.0 mmol) at 0 °C under N_2. The mixture was stirred for 8 h at room temperature. The reaction was quenched by adding a 1.0-M aqueous HCl solution. The mixture was extracted with EtOAc. The organic extract was washed successively with aqueous $NaHCO_3$, water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was chromatographed on silica gel to give **13**.

Ethyl 4,9-dihydro-4,9-ethano-2*H*-benzo[*f*]isoindole-1-carboxylate (13a): Yield, 85%; colorless powder, mp 142–144 °C, R_f = 0.3 (30% EtOAc/hexane); ^{1}H NMR δ 8.81 (1H, br s), 7.25 (1H, m), 7.15 (1H, m), 7.03 (2H, m), 6.56 (1H, d, J = 2.4 Hz), 4.77 (1H, m), 4.31 (2H, q, J = 7.1 Hz), 4.22 (1H, m), 1.69 (4H, m), and 1.35 (3H, q, J = 7.1 Hz); ^{13}C NMR δ 161.57, 144.84, 144.08, 135.50, 130.32, 125.27, 125.20, 123.44, 122.86, 114.49, 113.79, 59.86, 37.47, 37.30, 27.87, 27.24, and 14.52; IR (KBr) ν_{max}/cm^{-1} 3327, 1678, 1423, 1317, 1151, 1088, and 1043; MS (EI) *m/z* (rel. intensity) 296 (M^+, 5), 268 (100), 127 (21), and 77 (9). Anal. Calcd for $C_{17}H_{17}NO_2$+1/8H_2O: C, 75.74; H, 6.45; N, 5.20. Found: C, 75.67; H, 6.44; N, 5.14%.

Ethyl 6-bromo-4,9-dihydro-4,9-ethano-2*H*-benzo[*f*]isoindole-1-carboxylate and ethyl 7-bromo-4,9-dihydro-4,9-ethano-2*H*-benzo[*f*]isoindole-1-carboxylate (13b): Yield, 88%, colorless powder, mp 55–60 °C, R_f = 0.45 (30% EtOAc/hexane); ^{1}H NMR (diastereomer mixture) δ 8.49 (1H, br s), 7.71 (1H,

s), 7.21 (1H, m), 7.07 (1H, m), 6.66 (1H, s), 4.74 (1H, s), 4.34 (2H, q, J = 7.1 Hz), 4.26 (1H, s), 1.64–1.72 (4H, m), and 1.40 (3H, t, J = 7.1 Hz); ^{13}C NMR (typical signals) δ 161.25, 147.14, 146.46, 143.96, 143.23, 130.0, 129.64, 128.11, 1,28.05, 126.70, 126.17, 125.12, 124.54, 118.80, 118.72, 114.80, 114.73, 113.92, 113.86, 60.02, 37.28, 37.27, 37.22, 37.21, 27.62, 27.61, 27.01, 27.00, and 14.54; IR (KBr) ν_{max}/cm^{-1} 3313, 1684, 1315, 114.2, and 1041; MS (FAB) *m/z* 348 [M^+(^{81}Br)+1]. Anal. Calcd for $C_{17}H_{16}BrNO_2$+1/4$CHCl_3$: C, 56.38; H, 4.53; N, 3.81. Found: C, 56.58; H, 4.46; N, 3.91%.

Ethyl 6-iodo-4,9-dihydro-4,9-ethano-2*H*-benzo[*f*]isoindole-1-carboxylate and ethyl 7-iodo-4,9-dihydro-4,9-ethano-2*H*-benzo[*f*]isoindole-1-carboxylate (13c): Yield, 90%; colorless oil, R_f = 0.3 ($CHCl_3$); ^{1}H NMR (diastereomer mixture) δ 8.42 (1H, br s), 7.57 (1H, m), 7.32 (1H, m), 6.94–7.01 (1H, m), 6.65 (1H, m), 4.75 (1H, m), 4.33 (1H, m), 4.23 (1H, m), 1.70 (4H, m), and 1.40 (3H, m); ^{13}C NMR (typical signals) δ 161.38, 161.35, 146.52, 144.46, 143.71, 133.97, 133.90, 132.15, 131.66, 129.60, 129.29, 125.32, 124.77, 123.31, 122.75, 114.50, 114.46, 113.96, 90.22, 90.11, 59.91, 59.87, 37.31, 37.23, 36.84, 36.78, 27.45, 26.87, 26.83, and 14.46; IR (KBr) ν_{max}/cm^{-1} 3296, 1684, 1423, 1315, 1142, 1097, 1039; MS (FAB) *m/z* 394 (M^++1).

General procedure for removal of ester moiety: To a solution of **13** (4.00 mmol) in ethylene glycol (40 mL) was added potassium hydroxide (2.0 g) under N_2. After being heated at 175 °C for 2 h, the mixture was cooled to room temperature and water was added. The mixture was extracted with ethyl acetate. The organic extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was chromatographed on silica gel to give **14**.

4,9-Dihydro-4,9-ethano-2*H*-benz[*f*]isoindole (14a): Yield, 79%; colorless powder, mp 182–184 °C, R_f = 0.35 (30% EtOAc/hexane); ^{1}H NMR δ 7.53 (1H, br s), 7.20 (2H, m), 7.05 (2H, m), 6.53 (2H, d, J = 2.0 Hz), 4.26 (2H, s), and 1.73 (4H, m); ^{13}C NMR δ 145.59, 128.53, 125.19, 123.05, 108.73, 37.46, and 28.43; IR (KBr) ν_{max} /cm^{-1} 3369, 1468, 1396, 1282, 1038, and 750; MS (EI) *m/z* (rel. intensity) 295 (M^+, 33) and 167 (100).

6-Bromo-4,9-dihydro-4,9-ethano-2*H*-benz[*f*]isoindole (14b): Yield, 84%; colorless powder, mp 87–89 °C, R_f = 0.5 (30% EtOAc/hexane); ^{1}H NMR δ 7.58 (1H, br s), 7.35 (1H, d, J = 2.0 Hz), 7.18 (1H, dd, J = 7.8 and 2.0 Hz), 7.07 (1H, d, J = 7.8 Hz), 4.24 (1H, s), 4.23 (1H, s), and 1.68–1.76 (4H, m); ^{13}C NMR δ 147.77, 144.56, 127.90, 127.62, 126.29, 124.66, 118.58, 108.99, 108.92, 37.29, 36.96, 28.12, 28.07, and one carbon signal is not found; IR (KBr) ν_{max} /cm^{-1} 3351, 1454, 1408, 1306, 1157, and 1047; MS (FAB) *m/z* 276 [M^+(^{81}Br)+1]. Anal. Calcd for $C_{14}H_{12}BrN$+1/8CH_2Cl_2: C, 59.70; H, 4.28; N, 4.84. Found: C, 59.51; H, 4.43, N, 4.80%.

6-Iodo-4,9-dihydro-4,9-ethano-2*H*-benz[*f*]isoindole (14c): Yield, 82%; colorless powder, R_f = 0.45 (60% $CHCl_3$/hexane); mp 167–170 °C; ^{1}H NMR δ 7.57 (1H, br s), 7.54 (1H, s), 7.38 (1H, dd, J = 7.8 and

1.5 Hz), 6.96 (1H, d, J = 7.8 Hz), 6.52 (2H, d, J = 1.5 Hz), 4.22 (2H, d, J = 5.4 Hz), and 1.68–1.76 (4H, m); ^{13}C NMR δ 148.12, 145.32, 134.07, 132.03, 127.91, 127.64, 125.11, 108.99, 90.12, 37.15, 37.07, 28.09, and two carbon signals are not found; IR (KBr) ν_{max}/cm^{-1} 3353, 1400, 1305, 1170, 1171, and 1047; MS (FAB) *m/z* 322 (M^++1). Anal. Calcd for $C_{14}H_{12}IN$+1/8CH_2Cl_2: C, 51.13; H, 3.72; N, 4.22. Found: C, 51.50; H, 3.69; N, 4.29%.

General procedure for inverse [3+1] porphyrin synthesis: To a solution of pyrrole **14** (1.00 mmol) and tripyrrane **15** (478 mg, 1.00 mmol) in dry CH_2Cl_2 (100 mL) was added TFA (5.0 mL) at room temperature under N_2 in the dark. After being stirred for 20 h at the same temperature, the mixture was neutralized with triethylamine and treated with DDQ (227 mg, 1.00 mmol) for 4 h. To the mixture was added $Zn(OAc)_2 \cdot 2H_2O$ (329 mg, 1.50 mmol) and stirred for 6 h. Water was added to the reaction mixture. The mixture was extract with CH_2Cl_2. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatographed on silica gel and recrystallized from $CHCl_3$/MeOH to give **1**.

8,17-Dibutyl-12,13-diethyl-7,18-dimethyl-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]porphyrinato-zinc (1a): Yield, 38%; red powder, mp 232 °C (decomp), R_f = 0.35 (10% EtOAc/hexane); UV-vis ($CHCl_3$) λ_{max}/nm (log$_{10}$ ε): 402 (5.49), 531 (4.21), 569 (4.28); ^{1}H NMR δ 9.94 (2H, s), 8.48 (2H, s), 7.92 (2H, m), 7.33 (2H, m), 6.15 (2H, s), 3.38 (6H, s), 3.32 (4H, t, J = 7.6 Hz), 2.46 (2H, d, J = 6.8 Hz), 2.29 (2H, d, J = 6.8 Hz), 1.85 (4H, m), 1.47 (4H, m), 1.35 (6H, t, J = 7.6 Hz), 0.96 (6H, t, J = 7.6 Hz); ^{13}C NMR δ 148.02, 147.27, 146.47, 146.40, 145.51, 141.33, 140.65, 140.33, 135.20, 125.44, 123.88, 97.32, 95.57, 40.55, 35.27, 29.37, 25.61, 23.00, 19.15, 18.38, 14.29, 11.72; MS (FAB) *m/z* 697 (M^++1). Anal. Calcd for $C_{44}H_{48}N_4Zn$: C, 75.68; H, 6.93; N, 8.02. Found: C, 75.61; H, 7.19; N, 8.00%.

2^3-Bromo-8,17-dibutyl-12,13-diethyl-7,18-dimethyl-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]-porphyrinato zinc (1b): Yield, 43%; red solid, mp 238 °C (decomp), R_f = 0.2 (15% EtOAc/hexane); UV-vis ($CHCl_3$) λ_{max}/nm (log$_{10}$ ε): 402 (5.55), 531 (4.26), and 570 (4.29); ^{1}H NMR δ 10.12 (1H, s), 10.10 (1H, s), 9.40 (2H, s), 8.21 (1H, s), 7.61 (2H, s), 6.08 (1H, s), 6.07 (1H, s), 3.30–3.59 (14H, m), 2.59 (2H, d, J = 8.3 Hz), 2.33 (2H, d, J = 8.3 Hz), 2.02 (2H, m), 1.62 (4H, m), 1.54 (6H, t, J = 7.3 Hz), and 1.05 (6H, t, J = 7.3 Hz); ^{13}C NMR (typical signals) δ 148.75, 147.72, 147.53, 147.51, 147.26, 147.00, 146.10, 145.52, 146.10, 141.11, 140.73, 135.64, 135.59, 128.17, 127.11, 125.37, 118.90, 97.46, 95.96, 40.22, 39.95, 35.20, 28.89, 25.70, 22.91, 19.21, 18.28, 14.15, 11.68, and 11.65; MS (FAB) *m/z* 823 (M^++1).

8,17-Dibutyl-12,13-diethyl-2^3-iodo-7,18-dimethyl-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]-porphyrinato zinc (1c): Yield, 41%; red solid, mp 233 °C (decomp), R_f = 0.2 (15% EtOAc/hexane); UV-vis ($CHCl_3$) λ_{max}/nm (log$_{10}$ ε): 402 (5.55), 531 (4.26), and 570 (4.29); ^{1}H NMR δ 10.12 (1H, s), 10.10 (1H, s), 9.40 (2H, s), 8.21 (1H, s), 7.61 (2H, s), 6.08 (1H, s), 6.07 (1H, s), 3.30–3.59 (14H, m), 2.59 (2H,

d, J = 8.3 Hz), 2.33 (2H, d, J = 8.3 Hz), 2.02 (2H, m), 1.62 (4H, m), 1.54 (6H, t, J = 7.3 Hz), and 1.05 (6H, t, J = 7.3 Hz); ^{13}C NMR (typical signals) δ 149.27, 147.51, 147.20, 147.08, 146.42, 145.47, 140.95, 140.61, 140.37, 135.24, 135.21, 134.36, 132.96, 125.93, 97.24, 95.44, 90.40, 40.13, 40.10, 35.16, 28.96, 28.92, 25.47, 22.91, 19.02, 18.26, 14.21, 11.64, and 11.59. MS (FAB) *m/z* 823 (M^++1). Anal. Calcd for $C_{44}H_{47}IN_4Zn$ C, 64.12; H, 5.75; N, 6.80. Found: C, 64.05; H, 5.80; N, 6.71%.

8,17-Dibutyl-12,13-diethyl-7,18-dimethyl-2^3-trimethylsilylethynyl-2^1,2^6-dihydro-2^1,2^6-ethano-naphtha[2,3-*b*]porphyrinato zinc (1d): Three-times freeze-pump-thaw cycles were performed for a solution of porphyrin **1c** (196 mg, 0.238 mmol), CuI (I) (4.5 mg, 0.024 mmol), triphenylphosphine (6.2 mg, 0.024 mmol), dichlorobis(tripheylphosphine)palladium(II) (16.8 mg, 0.0239 mmol), trimethysilylacetylene (0.34 mL, 2.4 mmol), and diisopropylamine (3.0 mL) in dry THF (30 mL) to remove dissolved O_2 and then the solution was filled by N_2. The mixture was refluxed for 12 h. The mixture was cooled to room temperature and water was added. The mixture was extracted with $CHCl_3$. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel and recrystallized from $CHCl_3$/MeOH to give **1d** (177 mg, 0.223 mmol, 94%) as a red solid, mp 166–172 °C; R_f = 0.3 (30% EtOAc/hexane), UV-vis ($CHCl_3$) λ_{max}/nm ($\log_{10}$ ε) 402 (5.53), 531 (4.21), and 570 (4.23); ^{1}H NMR δ 10.10 (2H, s), 9.39 (1H, s), 9.33 (1H, s), 7.99 (1H, s), 7.78 (1H, d, J = 7.8 Hz), 7.43 (1H, d, J = 7.3 Hz), 6.10 (2H, d, J = 5.9 Hz), 3.65–3.78 (8H, m), 3.57 (3H, s), 3.55 (3H, s), 2.40 (2H, d, J = 8.3 Hz), 2.27 (2H, d, J = 9.3 Hz), 2.09 (4H, m), 1.62–1.69 (14H, m), 1.05 (6H, q, J = 7.3 Hz), and 0.26 (9H, s); ^{13}C NMR (typical signals) δ147.76, 147.73, 147.68, 147.59, 147.39, 147.33, 146.94, 146.56, 146.53, 146.20, 141.54, 141.31, 140.95, 140.90, 135.87, 135.81, 129.27, 127.28, 123.59, 119.91, 105.87, 97.57, 96.36, 96.30, 92.79, 40.19, 40.04, 35.22, 35.19, 28.86, 28.82, 25.85, 25.79, 22.90, 22.86, 19.36, 18.30, 14.10, 14.08, and 11.62; MS (FAB) *m/z* 793 (M^++1). Anal. Calcd for $C_{49}H_{56}N_4SiZn$: C, 74.08; H, 7.10; N, 7.05. Found: C, 73.68; H, 7.15; N, 6.88%.

8,17-Dibutyl-12,13-diethyl-7,18-dimethyl-2^3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]porphyrinato zinc (1e): A solution of halogenated porphyrins **1b** or **1c** (0.200 mmol), KOAc (196 mg, 2.00 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and bis(pinacolato)diboron (254 mg, 1.00 mmol) in DMSO (5.0 mL) was filled with N_2 by freeze-pump-thaw cycles three times. The mixture was heated at 100 °C for 15 h. The mixture was cooled to room temperature and water was added. The mixture was extracted with $CHCl_3$. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel and recrystallized from $CHCl_3$/MeOH to give **1e** (73% and 75% form **1b** and **1c**, respectively) as a red powder, mp >250 °C; R_f = 0.15 (10%

EtOAc/hexane); UV-vis ($CHCl_3$) λ_{max}/nm ($\log_{10}$ ε): 402 (5.52), 531 (4.20), and 559 (4.27); ^{1}H NMR δ 10.01 (1H, s), 9.93 (1H, s), 8.70 (1H, s), 8.48 (1H, s), 8.41 (1H, s), 7.99 (1H, d, J = 7.3 Hz), 7.87 (1H, d, J = 7.3 Hz), 6.17 (2H, m), 3.53 (3H, s), 3.42 (3H, s), 3.17–3.40 (8H, m), 2.45 (2H, m), 2.30 (2H, m), 1.96 (2H, m), 1.86 (2H, m), 1.55 (2H, m), 1.44 (2H, m), 1.37 (6H, s), 1.36 (12H, s), 0.99 (3H, t, J = 7.3 Hz), and 0.93 (3H, t, J = 7.3 Hz); ^{13}C NMR δ 150.04, 148.23, 147.43, 147.36, 147.19, 146.63, 146.38, 145.84, 145.60, 145.49, 141.27, 141.26, 140.69, 140.54, 140.36, 135.38, 135.18, 132.54, 129.87, 123.51, 97.38, 97.28, 95.70, 95.52, 83.71, 40.69, 40.34, 35.32, 35.19, 29.14, 29.13, 25.82, 25.56, 25.04, 24.95, 23.02, 22.91, 19.16, 19.10, 18.34, 18.30, 14.29, 14.23, 11.78, and 11.71; MS (FAB) *m/z* 823 (M^++1). Anal. Calcd for $C_{50}H_{59}BN_4O_2Zn$+CH_2Cl_2: C, 67.37; H, 6.76; N, 6.16. Found: C, 67.60; H, 6.83; N, 6.50%.

8,17-Dibutyl-12,13-diethyl-2^3-ethynyl-7,18-dimethyl-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]-porphyrinato zinc (1f): To a stirred solution of porphyrin **1d** (177 mg, 0.223 mmol) in THF (23 mL) was added 1.0-M tetrabutylammonium fluoride in THF (2.3 mL, 2.3 mmol) at 0 °C. The mixture was stirred at the same temperature for 2 h. Water was added to the reaction. The mixture was extract with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by recrystallization from $CHCl_3$/MeOH to give **1f** (141 mg, 0.195 mmol, 87%) as a red solid, mp 225 °C (decomp.); UV-vis ($CHCl_3$) λ_{max}/nm ($\log_{10}$ ε): 402 (5.51), 531 (4.20), and 570 (4.27); ^{1}H NMR δ 9.91 (1H, s), 9.87 (1H, s), 8.53 (1H, s), 8.49 (1H, s), 7.78 (1H, d, J = 6.4 Hz), 7.87 (1H, m), 7.51 (1H, m), 6.14 (2H, s), 3.41 (3H, s), 3.35 (3H, s), 3.25–3.34 (8H, m), 3.08 (1H, s), 2.48 (2H, m), 2.32 (2H, m), 1.87 (4H, m), 1.50 (4H, m), 1.37 (6H, m), and 0.97 (6H, m); ^{13}C NMR (typical signals) δ 147.55, 147.53, 147.43, 147.30, 147.27, 147.21, 146.63, 146.61, 146.54, 145.74, 141.01, 140.98, 140.84, 140.82, 140.46, 140.39, 135.32, 135.30, 135.28, 129.62, 127.50, 123.82, 119.01, 97.23, 95.59, 84.40, 762.17, 57.51, 57.45, 40.31, 40.16, 35.23, 35.09, 29.96, 25.51, 25.44, 23.10, 22.85, 19.03, 18.17, 14.09, 13.30, 11.54, and 11.45; MS (MALDI-TOF) *m/z* 720.2 (M^+).

Suzuki-Miyaura reaction giving 2: A solution of halogenated porphyrin **1b** or **1c** (0.0400 mmol) pinacolatoboronated porphyrin **1d** (0.0400 mmol), K_2CO_3 (27.6 mg, 0.0800 mmol), and $PdCl_2(PPh_3)_2$ (2.8 mg, 0.0040 mmol) in DMSO (0.5 mL) was degassed by three-times freeze-pump-thaw cycles and then filled with N_2. The mixture was heated at 100 °C for 14 h. The mixture was cooled to room temperature and water was added. The mixture was extracted with $CHCl_3$. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel and recrystallized from $CHCl_3$/MeOH to give bi(21,23-zinco-8,17-dibutyl-12,13-diethyl-7,18-dimethyl-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]-porphyrin-2^3-yl) (**2**; 88% and 83% form **1b** and **1c**, respectively) as a red powder, mp >300 °C; R_f = 0.95 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max}/nm ($\log_{10}$ ε): 402 (5.73), 531 (4.47), and 569 (4.55); ^{1}H NMR (pyridine-d_5) δ 10.95 (2H, s), 10.85 (2H, s), 10.52 (4H, s), 8.12 (2H, m), 7.87 (2H, s), 6.50 (2H, m), 6.41

(2H, s), 4.19 (16H, m), 3.85 (6H, s), 3.78 (6H, s), 2.37 (12H, m), 2.22 (4H, m), 1.96 (6H, m), 1.77 (8H, m), and 1.09 (12H, m); ^{13}C NMR (pyridine-d_5; typical signals) δ 149.25, 149.21, 149.12, 148.46, 147.54, 147. 51, 145.73, 145.68, 143.03, 142.99, 142.97, 142.88, 141.99, 141.96, 139.40, 139.33.137.06, 124.55, 124.48, 124.44, 98.79, 98.74, 97.49, 97.48, 40.96, 40.40, 35.91, 29.75, 29.72, 26.62, 23.30, 20.24, 19.06, 14.45, 12.08, 12.05, and 12.00; MS (MALDI-TOF) *m/z* 1394.8 (M^++H).

Sonogashira reaction giving 3: Three-times freeze-pump-thaw cycles were applied for a solution of **1f** (78.1 mg, 0.108 mmol), **1c** (89.0 mg, 0.108 mmol), CuI (I) (2.1 mg, 0.011 mmol), triphenylphosphine (2.9 mg, 0.011 mmol), dichlorobis(tripheylphosphino)palladium(II) (7.0 mg, 0.010 mmol), and diisopropylamine (0.5 mL) in dry THF (5.0 mL) to remove dissolved O_2 and then the mixture was filled with N_2. The mixture was refluxed for 14 h. After the mixture was cooled to room temperature and water was added. The mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel and recrystallized from $CHCl_3$/MeOH to give 1,2-di(21,23-zinco-8,17-dibutyl-12,13-diethyl-7,18-dimethyl-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]porphyrin-2^3-yl)ethyne **(3**; 67.4 mg, 0,0424 mmol, 88%) as a red powder, mp >300 °C; R_f = 0.95 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max}/nm ($\log_{10}\varepsilon$): 403 (5.73), 532 (4.47), and 570 (4.53); ^{1}H NMR (THF-d_8) δ 10.29 (2H, s), 10.27 (2H, s), 10.08 (4H, s), 7.88 (2H, s), 7.68 (2H, d, J = 7.6 Hz), 7.32 (2H, d, J = 7.6 Hz), 6.12 (4H, s), 4.09 (16H, m), 3.67 (6H, s), 3.66 (6H, s), 2.41 (4H, m), 2.29 (8H, m), 2.13 (4H, m), 1.88 (6H, t, J = 7.6 Hz), 1.72 (8H, m), and 1.06 (12H, t, J = 7.3 Hz); ^{13}C NMR (THF-d_8) δ 150.81, 150.77, 150.75, 150.72, 150.70, 150.32, 150.10, 149.42, 144.46, 144.34, 144.33, 143.41, 138.53, 138.47, 132.34, 129.84, 126.23, 121.05, 118.51, 100.06, 100.00, 98.92, 84.14, 75.37, 42.83, 42.59, 38.14, 31.38, 28.59, 25.43, 25.42, 25.41, 22.12, 22.10, 20.78, 20.76, 16.21, 13.49, and 13.48; MS (MALDI-TOF) *m/z* 1419.8 (M^+).

Eglinton modification of the Glaser coupling reaction giving 4: Porphyrin **1f** (66.1 mg, 0.0915 mmol) and $Cu(OAc)_2$ (33 mg, 177 mmol) were dissolved in 5 mL of pyridine and the mixture was stirred at room temperature for 12 h. Water was added and the resulting mixture was extract with THF. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by recrystallization from $CHCl_3$/MeOH to give 1,4-di(21,23-zinco-8,17-dibutyl-12,13-diethyl-7,18-dimethyl-2^1,2^6-dihydro-2^1,2^6-ethanonaphtho[2,3-*b*]porphyrin-2^3-yl)-1,3-butadiyne **(4**; 61.6 mg, 0.0427 mmol, 93%) as a red powder, mp >300 °C; R_f = 0.95 ($CHCl_3$); UV-vis ($CHCl_3$) λ_{max}/nm ($\log_{10}\varepsilon$) 403 (5.83), 532 (4.52), and 570 (4.59); ^{1}H NMR (THF-d_8) δ 10.28 (2H, s), 10.27 (2H, s), 10.08 (4H, s), 7.88 (2H, s), 7.70 (2H, d, J = 7.8 Hz), 7.35 (2H, d, J = 7.8 Hz), 6.13 (4H, s), 4.10 (16H, m), 3.66 (12H, s), 2.40 (4H, m), 2.27 (8H, m), 2.11 (4H, m), 1.89 (6H, m), 1.70 (12H, t, J = 7.6 Hz), and 1.06 (12H, t, J = 7.4 Hz); ^{13}C NMR (THF-d_8) δ 147.85, 147.81, 147.73, 147.70, 147.56, 147.46, 147.08, 146.29, 146.28, 146.18, 141.48, 141.46, 141.45, 141.43, 140.44, 140.41, 135.52, 135.48,

128.07, 126.18, 123.02, 120.04, 97.05, 97.03, 95.95, 95.93, 88.39, 39.80, 39.78, 39.73, 35.17, 28.56, 28.54, 28.52, 25.63, 22.47, 22.45, 19.16, 17.81, 13.24, 10.53, and 10.52; MS (MALDI-TOF) *m/z* 1442.7 (M^++H).

General procedure for the preparative retro-Diels-Alder reaction: A sample tube containing appropriate bicyclo[2.2.2]octadiene-fused porphyrin (*ca*. 10 mg) was placed in a glass flask. The flask was evacuated by means of a rotary vacuum pump and then placed in a preheated tube oven at 290 °C. After 1 h, the flask was taken out and then flushed with N_2. The obtained sample was subject to all analysis. The conversion was quantitative.

8,17-Dibutyl-12,13-diethyl-7,18-dimethylnaphtho[2,3-*b*]porphyrinato zinc (8a): Green powder, mp >300 °C; UV-vis (pyridine) λ_{max}/nm ($\log_{10}$ ε): 337 (4.30), 437 (5.48), 572 (4.30), 593 (4.44), and 610 (4.60). ^{1}H NMR (pyridine-d_5; typical signals) δ 10.90 (2H, s), 10.45 (2H, s), 7.85 (2H, m), 4.16 (8H, m), 3.73 (6H, s), 2.36 (4H, s), 1.95 (6H, m), 1.76 (4H, m), and 1.09 (6H, t, J = 8.6 Hz); ^{13}C NMR (pyridine-d_5; typical signals) δ 147.49, 146.98, 146.78, 142.51, 142.01, 133.50, 129.77, 126.27, 120.16, 99.43, 94.34, 35.92, 26.60, 23.34, 20.18, 19.13, 14.47, and 11.96; MS (FAB) *m/z* 669 (M^++1). Anal. Calcd for $C_{42}H_{44}N_4Zn$: C, 75.27; H, 6.62; N, 8.36. Found: C, 75.47; H, 6.91; N, 8.32%.

2^3-Bromo-8,17-dibutyl-12,13-diethyl-7,18-dimethylnaphtho[2,3-*b*]porphyrinato zinc (8b): Brown solid, mp 228-232 °C; UV-vis (pyridine) λ_{max}/nm ($\log_{10}$ ε) 341 (4.53), 439 (5.45), 572 (4.31), 595 (4.48), and 609 (4.60); ^{1}H NMR (pyridine-d_5) δ 10.82 (2H, s), 10.42 (2H, s), 10.21 (1H, s), 10.17 (1H, s), 8.86 (1H, s), 7.76 (1H, d, J = 8.8 Hz), 7.89 (1H, d, J = 8.8 Hz), 4.13 (8H, m), 3.69 (3H, s), 3.68 (3H, s), 2.33 (4H, m), 1.91 (6H, t, J = 7.3 Hz), 1.74 (4H, m), and 1.07 (6H, t, J = 7.3 Hz); ^{13}C NMR (pridine-d_5; typical signals) δ 150.43, 150.38, 147.68, 147.66, 147.18, 147.16, 146.24, 146.09, 142.57, 142.16, 139.67, 139.24, 134.22, 131.53, 131.50, 129.22, 123.99, 120.29, 119.91, 119.20, 99.50, 99.45, 94.53, 94.49, 35.91, 26.60, 23.35, 20.17, 19.11, 14.47, 11.95, and 11.92; MS (FAB) *m/z* 749 [M^+(^{81}Br)+1]. Anal. Calcd for $C_{42}H_{43}BrN_4Zn$: C, 67.43; H, 5.79; N, 7.48. Found: C, 67.29; H, 5.82; N, 7.48%.

8,17-Dibutyl-12,13-diethyl-2^3-iodo-7,18-dimethylnaphtho[2,3-*b*]porphyrinato zinc (8c): Mp >250 °C; UV-vis (pyridine) λ_{max}/nm ($\log_{10}$ ε) 341 (4.59), 416 (5.05), 439 (5.47), 572 (4.35), 594 (4.53), and 610 (4.60); ^{1}H NMR (pyridine-d_5) δ 10.86 (2H, s), 10.46 (2H, s), 10.23 (1H, s), 10.15 (1H, s), 9.14 (1H, s), 8.40 (1H, d, J = 8.8 Hz), 8.11 (1H, d, J = 8.8 Hz), 4.14–4.19 (8H, m), 3.73 (6H, s), 2.39 (4H, m), 1.96 (6H, m), 1.76 (4H, t, J = 7.6 Hz), and 1.11 (6H, t, J = 7.3 Hz); ^{13}C NMR (pyridine-d_5) δ 147.67, 147.16, 146.56, 146.19, 142.56, 142.15, 139.39, 139.24, 138.36, 134.78, 134.37, 131.72, 131.26, 120.26, 119.02, 99.46, 94.50, 92.27, 35.91, 26.60, 23.34, 20.17, 19.11, 14.47, 12.95, and 11.92; MS (FAB) *m/z* 795 (M^++1). Anal. Calcd for $C_{42}H_{43}IN_4Zn$: C, 63.36; H, 5.44; N, 7.07. Found: C, 63.59; H, 5.44; N, 7.01%.

8,17-Dibutyl-12,13-diethyl-2^3-trimethylsilylethynyl-7,18-dimethylnaphtho[2,3-*b*]porphyrinato zinc (8d): Dark blue solid; mp >250 °C; UV-vis (pyridine) λ_{max}/nm ($\log_{10}$ ε): 347 (4.59), 442 (5.42), 574

(4.35), 597 (4.58), and 611 (4.64); ^{1}H NMR δ 9.27 (2H, s), 8.41 (4H, m), 8.41 (1H, m), 8.05 (1H, d, J = 8.8 H), 7.75 (1H, d, J = 8.8 Hz), 3.86 (4H, t, J = 7.6 Hz), 3.57 (4H, m), 2.86 (3H, s), 2.84 (3H, s), 2.05 (4H, m), 1.86 (6H, m), 1.67, (4H, m), 1.10 (6H, t, J = 7.3 Hz), and 0.53 (9H, s); ^{13}C NMR δ 14.73, 147.70, 145.45, 145.44, 143.52, 143.48, 140.95, 140.91, 140.73, 136.57, 136.34, 133.62, 133.58, 133.31, 131.13, 128.73, 127.70, 119.58, 117.62, 117.52, 106.49, 98.24, 94.86, 91.98, 91.81, 35.27, 25.74, 25.71, 23.09, 19.62, 18.66, 14.22, 10.81, 10.75, and 0.34; MS (FAB) *m/z* 765 (M^++1). Anal. Calcd for $C_{49}H_{56}N_4SiZn$: C, 73.65; H, 6.84; N, 7.31. Found: C, 73.98; H, 6.89; N, 7.27%.

Bi(8,17-dibutyl-12,13-diethyl-7,18-dimethyl-21,23-zinconaphtho[2,3-*b*]porphyrin-2^3-yl) (5): Green powder, mp >300 °C; UV-vis (pyridne) λ_{max}/nm ($\log_{10}$ ε): 355 (4.80), 427 (5.29), 448 (5.52), 558 (4.41), 575 (4.65), 599 (4.97), and 611 (4.88); ^{1}H NMR (pyridine-d_5; typical signals) δ 10.95 (2H, s), 10.91 (2H, s), 10.91 (2H, s), 10.48 (2H, s), 10.45 (4H, s), 10.38 (2H, s), 9.41 (2H, s); 8.90 (2H, d, J = 8.6 Hz), 3.86 (6H, s), 3.83 (6H, s), 2.47 (8H, m), 2.03 (12H, t, J = 7.6 Hz), 1.88 (8H, m), and 1.20 (12H, t, J = 7.3 Hz); MS (MALDI-TOF) *m/z* 1336.7 (M^+).

Di(8,17-dibutyl-12,13-diethyl-7,18-dimethyl-21,23-zinconaphtho[2,3-*b*]porphyrin-2^3-yl)ethyne (6): Green powder, mp >300 °C; UV-vis (pyridne) λ_{max}/nm ($\log_{10}$ ε) 356 (4.80), 426 (sh, 5.29), 446 (5.47), 559 (4.43), 575 (4.61), 600 (4.89), and 611 (4.88); ^{1}H NMR (pyridine-d_5) δ 10.87 (2H, s), 10.85 (2H, s), 10.43 (4H, s), 10.32 (2H, s), 10.26 (2H, s), 9.19 (2H, s), 8.77 (2H, d, J = 8.4 Hz), 8.24 (2H, d, J = 8.4 Hz), 4.23 (16H, m), 3.82 (6H, s), 3.77 (6H, s), 2.48 (8H, m), 2.04 (12H, t, J = 7.6 Hz), 1.88 (8H, m), and 1.21 (12H, t, J = 7.3 Hz); MS (MALDI-TOF) *m/z* 1359.8 (M^++1).

Di(8,17-dibutyl-12,13-diethyl-7,18-dimethyl-21,23-zinconaphtho[2,3-*b*]porphyrin-2^3-yl)-1,3-butadiyne (7): Green powder, mp >300 °C; UV-vis (pyridne) λ_{max}/nm ($\log_{10}$ ε) 356 (4.88), 425 (5.32), 547 (4.19), 560 (4.48), 575 (4.67), 601 (4.96), and 612 (4.94); ^{1}H NMR (pyridine-d_5; typical signals) δ 10.85 (2H, s), 10.84 (2H, s), 10.44 (4H, s), 10.27 (2H, s), 10.23 (2H, s), 9.11 (2H, s), 8.06 (2H, d, J = 8.8 Hz), 4.22 (16H, m), 3.81 (12H, s), 2.48 (8H, m), 2.04 (12H, t, J = 7.8 Hz), 1.89 (8H, m), and 1.21 (12H, t, J = 7.3 Hz); MS (MALDI-TOF) *m/z* 1383.6 (M^++1).

ACKNOWLEDGEMENTS

This work is partially supported by Grant-in-Aids for the Scientific Research (23350020, 23655044, and 23108714 (π-space)) from the Japanese Ministry of Education, Culture, Sports, Science and Technology. Some calculations are done at IMS under the cooperative research program.

REFERENCES

1. D. Kim, ed. "*Multiporphyrin Arrays, Fundamentals and Applications*" Pan Stanford Publishing Pte. Ltd. 2012.

2. K. Tashiro and T. Aida, *Chem. Soc. Rev.,* 2007, **36**, 189; N. Komatsu and F. Wang, *Materials*, 2010, **3**, 3818; T. Yamaguchi, N. Ishii, K. Tashiro, and T. Aida, *J. Am. Chem. Soc.*, 2003, **125**, 13934; S. Campidelli, C. Sooambar, E. Lozano Diz, C. Ehli, D. M. Guldi, and M. Prato, *J. Am. Chem. Soc.*, 2006, **128**, 12544; F. Cheng, S. Zhang, A. Adronov, L. Echegoyen, and F. Diederich, *Chem. Eur. J.*, 2006, **12**, 6062; H. Nobukuni, Y. Shimazaki, F. Tani, and Y. Naruta, *Angew. Chem. Int. Ed.*, 2007, **119**, 9133; X. Peng, N. Komatsu, S. Bhattacharya, T. Shimawaki, S. Aonuma, T. Kimura, and A. Osuka, *Nature Nanotech.,* 2007*,* **2**, 361; H. Uno, M. Furukawa, A. Fujimoto, H. Uoyama, H. Watanabe, T. Okujima, H. Yamada, S. Mori, M. Kuramoto, T. Iwamura, N. Hatae, F. Tani, and N. Komatsu, *J. Porphyrins Phthalocyanines*, 2011, **15**, 951.
3. M.-C. Yoon, Z. S. Yoon, S. Cho, D. Kim, A. Takagi, T. Matsumoto, T. Kawai, T. Hori, X. Peng, N. Aratani, and A. Osuka, *J. Phys. Chem. A,* 2007, **111***,* 9233; K. J. McEwan, P. A. Fleitz, J. E. Rogers, J. E. Slagle, D. G. McLean, H. Akdas, M. Katterle, I. M. Blake, and H. L. Anderson, *Adv. Mater.*, 2004, **16**, 1933; M. Balaz, H. A. Collins, E. Dahlstedt, and H. L. Anderson, *Org. Biomol. Chem.*, 2009, **7**, 874.
4. H. Uoyama, K. S. Kim, K. Kuroki, J.-Y. Shin, T. Nagata, T. Okujima, H. Yamada, N. Ono, D. Kim, and H. Uno, *Chem. Eur. J.,* 2010, **16**, 4063; J. A. A. W. Elemans, R. van Hameren, R. J. M. Nolte, and A. E. Rowan, *Adv. Mater.*, 2006, **18**, 1251; T. Hori, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, M.-C. Yoon, Z. S. Yoon, S. Cho, D. Kim, and A. Osuka, *Chem. Eur. J.,* 2006, **12**, 1319; V. S. Lin, S. G. DiMagno, and M. J. Therien, *Science*, 1994, **264**, 1105.
5. H. Hata, H. Shinokubo, and A. Osuka, *J. Am. Chem. Soc.*, 2005, **127**, 8264; K. Funatsu, A. Kimura, T. Imamura, A. Ichimura, and Y. Sasaki, *Inorg. Chem.*, 1997, **36**, 1625; H. Uno, Y. Kitawaki, and N. Ono, *Chem. Commun*., 2002, 116.
6. D. Holten, D. F. Bocian, and J. S. Lindsey, *Acc. Chem. Res.*, 2002, **35**, 57.
7. R. Selensky, D. Holten, M. W. Windsor, J. B. Paine III, D. Dolphin, M. Gouterman, and J. C. Thomas, *Chem. Phys.*, 1981, **60**, 33.
8. T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwick, and H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 2002, 320; M. K. Kuimova, M. Balaz, H. L. Anderson, and P. R. Ogilby, *J. Am. Chem. Soc.*, 2009, **131** , 7948.
9. (a) Y. Nakamura, N. Aratani, and A. Osuka, *Chem. Soc. Rev.*, 2007, **36**, 831; (b) C.-W. Lee, H.-P. Lu, C.-M. Lan, Y.-L. Huang, Y.-R. Liang, W.-N. Yen, Y.-C. Liu, Y.-S. Lin, E. W.-G. Diau, and C.-Y. Yeh, *Chem. Eur. J.,* 2009, **15**, 1403.
10. L. J. K. Boerner, M. Nath, M. Pink, and J. M. Zaleski, *Chem. Eur. J.*, 2011, **17**, 9311; C. Maeda, T. Yoneda, N. Aratani, M.-C. Yoon, J. M. Lim, D. Kim, N. Yoshioka, and A. Osuka, *Angew. Chem. Int. Ed.*, 2011, **50**, 5691.

11. S. Ito, L. T. Phong, T. Komatsu, N. Igarashi, S. Otsubo, Y. Sakai, A. Ohno, S. Aramaki, Y. Tanaka, H. Uno, T. Oba, and K. Hiratani, *Eur. J. Org. Chem.*, 2009, 5373.
12. P. K. Panda, S. Padhy, K.-S. Ha, and C.-H. Lee, *Bull. Korean Chem. Soc*., 2004, **25**, 1421.
13. D. Kuzuhara, H. Yamada, T. Okujima, and H. Uno, unpublished result.
14. X.-Z. Jiang, C. Cai, J.-T. Liu, and H. Uno, *Org. Biomol. Chem.*, 2012, **10**, 3110; C. Cai, H. Uoyama, M. Nakamura, and H. Uno, *Heterocycles*, 2012, **84**, 829.
15. S. Ito, N. Ochi, H. Uno, T. Murashima, and N. Ono, *Chem. Commun*., 2000, 893.
16. H. E. Simmons, *J. Am. Chem. Soc*., 1963, **85**, 1657; A. M. Braun, *J. Org. Chem*., 1970, **35**, 1208.
17. H. Uno, K. Nakamoto, K. Kuroki, A. Fujimoto, and N. Ono, *Chem. Eur. J.*, 2007, **13**, 5773; S. Ito, K. Nakamoto, H. Uno, T. Murashima, and N. Ono, *Chem. Commun*., 2001, 2696.
18. A. Boudif and M. Momenteau, *J. Chem. Soc. Chem. Commun.*, 1994, 2069; A. Boudif and M. Momenteau, *J. Chem. Soc. Perkin Trans. 1*, 1996, 1235; J. L. Sessler, J. W. Genge, A. Urbach, and P. Sanson, *Synlett*, 1996, 187; T. D. Lash, P. Chandrasekar, A. T. Osuma, S. T. Chaney, and J. D. Spence, *J. Org. Chem*., 1998, **63**, 8455.
19. J. L. Sessler, M. R. Johnson, and V. Lynch, *J. Org. Chem.*, 1987, **52**, 4394; S. V. Shevchuk, J. M. Davis, and J. L. Sessler*, Tetrahedron Lett*., 2001, **42**, 2447.
20. M. Gouterman, *J. Mol. Spectroscopy*, 1961, **6**, 138.