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SYNTHESIS OF DI(3-THIENYL)BENZOPORPHYRIN

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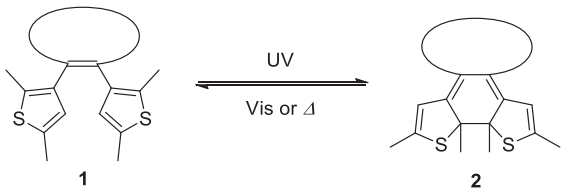
Dedicated to Professor Tohru Fukuyama on the occasion of his 70th birthday

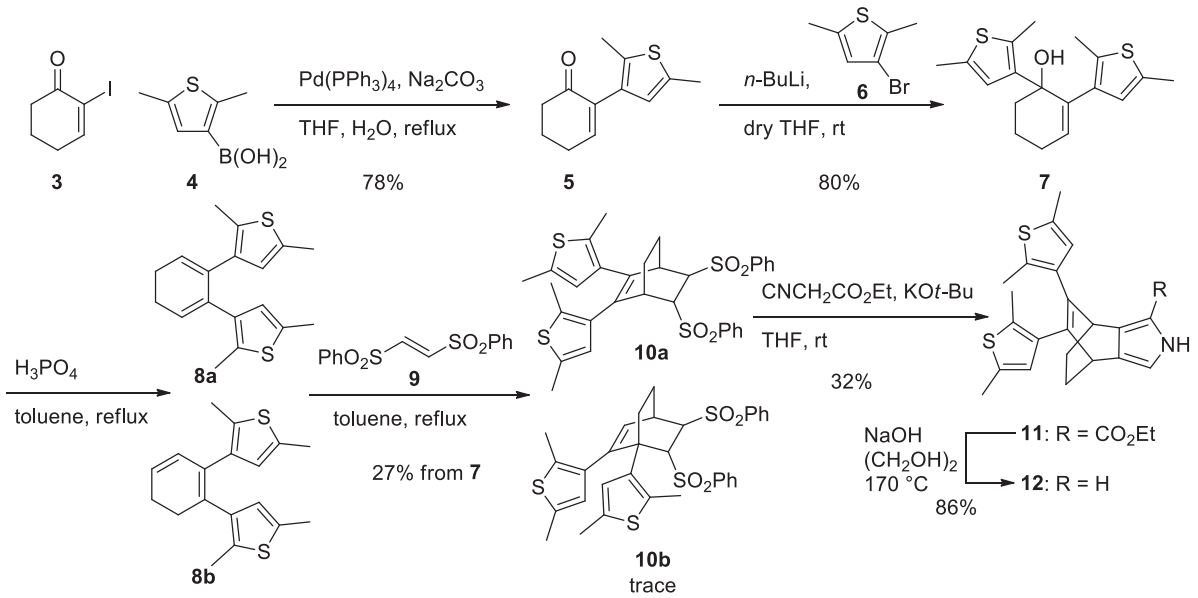
Abstract – We have successfully synthesized 2,3-di(3-thienyl)benzo[*b*]porphyrin based on retro Diels–Alder reaction of bicyclo[2.2.2]octadiene(BCOD)-fused porphyrin and investigated its photoisomerization reaction.

1,2-Diarylethene skeletons are attractive due to the reversible photochemical ring-closure/opening reactions.[1] 1,2-Bis(2,5-dimethyl-3-thienyl)ethene derivatives **1** are well-known as a photochromic compound, which could be isomerized into cyclohexadienes **2** under irradiation by UV light with change of the color (Scheme 1). These photochromic diarylethenes have been investigated as photoswitchable luminescent materials[2] and conductive molecular wire.[3] In 2001, two papers on 1,2-di(3-thienyl)perfluorocyclopentene bearing porphyrin were reported as photoswitchable fluorophore and phosphorophore.[4] These photochromic molecules showed reversible photoisomerization between their closed and open forms by irradiation with UV and visible light. In these molecules, dithienylperfluorocyclopentene moiety undergoes photoisomerization reaction, while porphyrin moiety shows photoluminescent property. In closed form, dihydrobenzodithiophene unit is not conjugated to porphyrin ring directly. Herein we report synthesis of 2,3-di(3-thienyl)benzo[*b*]porphyrin based on retro Diels–Alder reaction of bicyclo[2.2.2]octadiene(BCOD)-fused porphyrin precursor and its photoisomerization reaction.



Scheme 1. Photo-induced ring-closure/opening reaction of 1,2-bis(2,5-dimethyl-3-thienyl)ethene

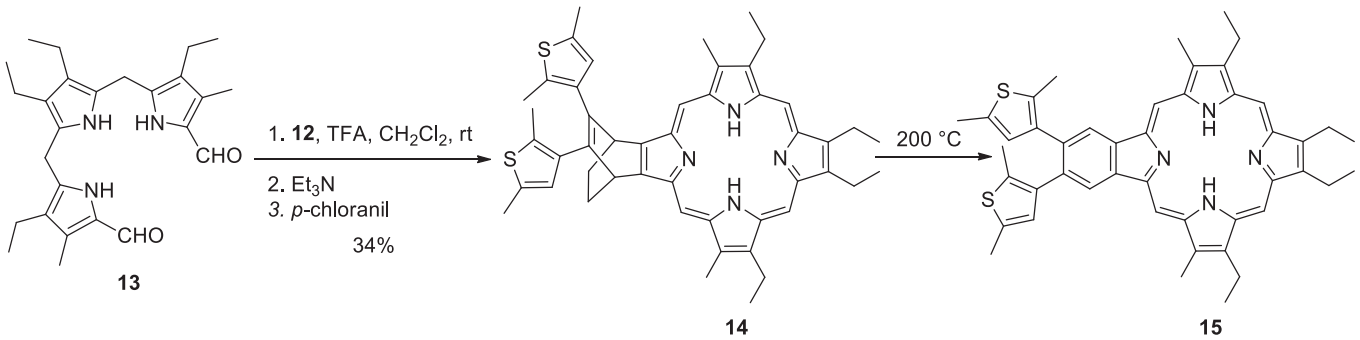
Synthetic methods of peripheral substituted benzoporphyrin were reported by several groups. Vinogradov and co-workers have reported synthesis of tetrabenzoporphyrins (TBP) with alkoxycarbonyl or alkoxy groups at the benzo moieties by oxidative aromatization of porphyrin fused with cyclohexene at β-pyrrolic positions.[5] We have also reported thermally convertible precursors of TBP utilizing retro Diels–Alder strategy, which afforded octamethoxycarbonylTBPs.[6] More recently, Ito and co-workers reported the Suzuki–Miyaura coupling of brominated BCOD-fused pyrrole to give phenyl, 2-naphthyl, and methylBCODpyrroles, which could afford substituted TBPs.[7] We synthesized thiophene-substituted BCODpyrrole **12** as shown in Scheme 2. Suzuki–Miyaura coupling of **3**[8] and **4** afforded **5** in 78% yield. 3-Thienyllithium generated from **6** with *n*-BuLi *in situ* reacted with **5** to give dithienylcyclohexenol **7**, which was dehydrated by treatment with H_3PO_4[9] to give a mixture of **8a** and **8b** with a ratio of 1:1 determined by NMR. The products could not be separated by column chromatography and were treated with **9** in refluxing toluene to give a Diels–Alder adduct **10a** as a major product, recovered unreacted **8b** and a trace amount of **10b**. The structure of **10a** was confirmed by X-ray crystallographic analysis of the single crystals obtained by recrystallization from $CHCl_3$/MeOH as shown in Figure 1a. Barton–Zard pyrrole synthesis from **10a**, followed by removal of ester group by heating **11** with NaOH in ethylene glycol at 170 °C gave pyrrole **12**. Diformyltripyrrane **13**[10] was treated with **12** in the presence of TFA, followed by oxidation with *p*-chloranil to give **14** in 34% yield (Scheme 3).[11]



Scheme 2. Synthesis of dithienylBCODpyrrole **12**

When **14** was heated as solids at 200 °C in a glass tube *in vacuo*, 2,3-di(3-thienyl)benzo[*b*]porphyrin **15** was formed in nearly quantitative yield. Porphyrins **14** and **15** were characterized by physical and spectral methods including X-ray crystallographic analysis in the case of **15**. Single crystals of **15** were obtained

after recrystallization from $CHCl_3$/MeOH. The crystal structure is shown in Figure 1b, and the crystallographic data is summarized in experimental section. Porphyrin **15** crystallized in a triclinic cell, space group $P\bar{1}$ with Z=2. The CNC angles of 107.06° and 104.87° were observed for isoindole and diethylpyrrole moieties, while the CNC angles of 110.53° and 110.54° were observed for ethylmethylpyrrole moieties. These observation supported the position of pyrrolic NHs as shown in Figure 1b. The porphyrin moiety adopted a nearly planar structure. Dihedral angles of 52.85° and 61.70° were observed between benzo moiety and thiophene rings.



Scheme 3. Synthesis of di(3-thienyl)benzoporphyrin **15**

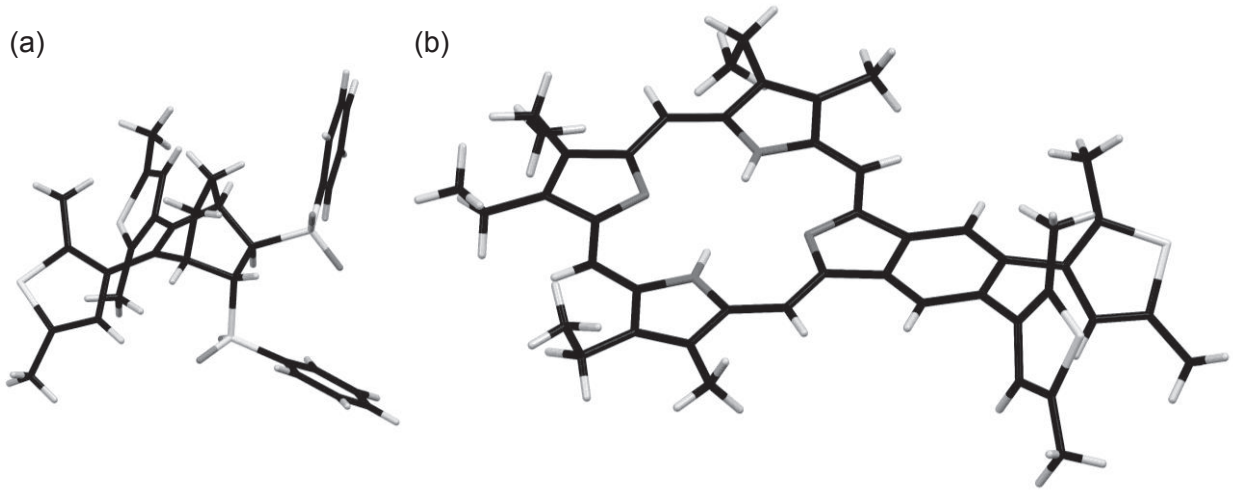


Figure 1. Molecular structures of (a) **10a** and (b) **15**. Disordered (less popular) atoms of thienyl moiety in **15** are omitted for clarity.

While signals for *meso* and thienyl protons of **14** are observed at 10.23 and 10.12 ppm, and 6.77 ppm, those of **15** are also observed at similar region, 10.42 and 10.13 ppm for *meso* protons and 6.77 ppm for thienyl proton as singlet peaks (Figure 2). In **14**, a bridge head signal of BCOD moiety is observed at 5.84 ppm. This signal is not observed and a benzo signal is observed at 9.28 ppm in **15**.

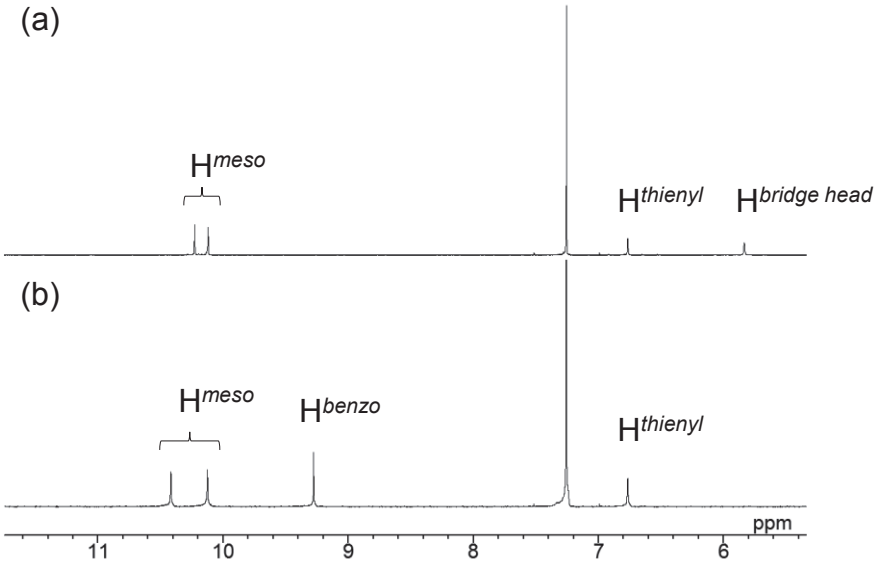


Figure 2. ^{1}H NMR spectra (aromatic region) of (a) **14** and (b) **15** in $CDCl_3$

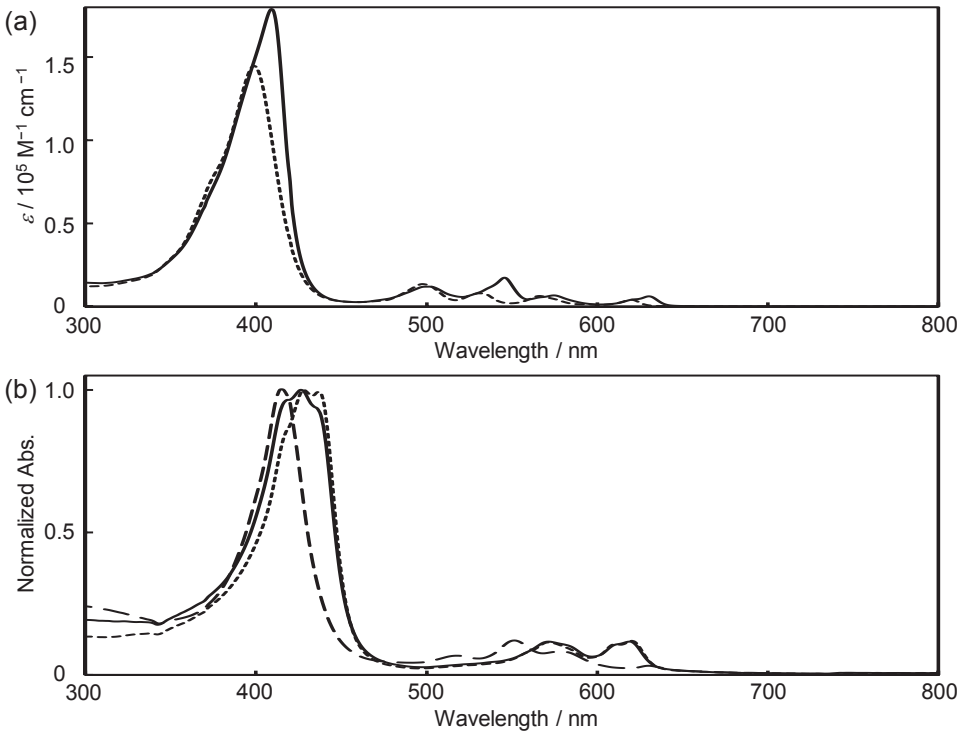
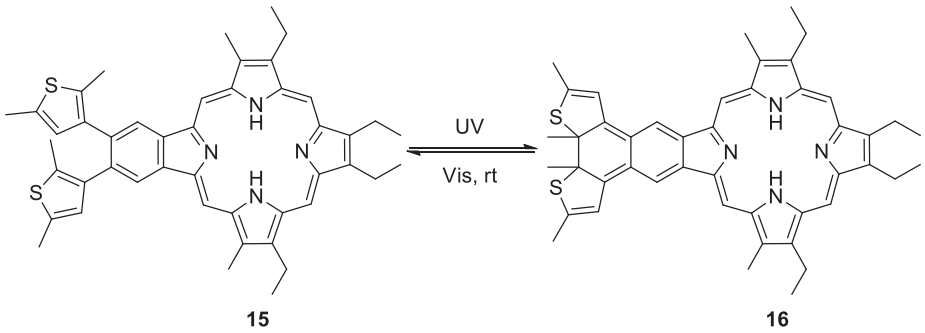


Figure 3. Absorption spectra of (a) **14** (dotted) and **15** (solid), and (b) **15** recorded after irradiation of UV light at 254 nm for 1 min (dotted), 3 min (solid), and after irradiation followed by standing at room temperature under room light (dashed) in $CHCl_3$.

Absorption spectra of **14** and **15** are shown in Figure 3a. The intense Soret bands are observed at 399 nm (log ε 5.16) for **14** and 409 nm (log ε 5.25) for **15**. Their weak Q bands appear at 460–650 nm. These

bands of **15** are red-shifted by ca. 10 nm compared to those of **14**. The longest wavelength absorption of **15** is observed at 630 nm (log ε 3.79) while that of **14** is observed at 620 nm (log ε 3.62). Photochromic behavior of **15** was investigated such as shown in Scheme 1. When a solution of **15** in $CHCl_3$ (ca. 2.6 × 10^{-3} mM) was irradiated by UV light at 254 nm, a color change was observed from purple to green after 3 min. The red-shifted Soret band was observed at 430 nm and the Q bands at 570 and 620 nm (Figure 3b). The longest wavelength absorption maximum showed slightly blue-shift whereas the absorption edges of **15** and the product were observed at around 650–660 nm. Thus the porphyrin skeleton persists in the product and photoreaction of *o*-dithienylbenzo moiety would undergo by UV irradiation. The solution after irradiation for 3 min was left at room temperature for 1 d to give almost same spectrum shape to **15**. These results suggests the formation of dihydronaphthodithiophene-fused porphyrin **16** *via* photoisomerization from **15** similar to reported 1,2-di(3-thienyl)ethenes as shown in Scheme 1. Therefore, 2,3-di(3-thienyl)benzo[*b*]porphyrin **15** showed a reversible photochromic behavior between purple and green with ring-opening/closure reaction (Scheme 4).



15 **16**

Scheme 4. Plausible photoisomerization of **15**

In summary, we synthesized di(3-thienyl)BCODporphyrin **14** via [3+1] porphyrin synthesis. The retro Diels–Alder reaction of **14** afforded 2,3-di(3-thienyl)benzo[*b*]porphyrin **15** in nearly quantitative yield. The molecular structure was revealed by X-ray crystallographic analysis. The absorption spectra of **15** after irradiation of UV light indicated the formation of ring-closed product **16**. Porphyrin **15** exhibited a reversible photochromic behavior. The synthetic strategy for **15** is expected to prepare peripheral substituted benzoporphyrins and further work on their synthesis is under way.

EXPERIMENTAL

General. Melting points were determined on a BÜCHI melting point apparatus M-565 and are uncorrected. EI and FAB mass spectra were measured on a JEOL JMS-700. MALDI–TOF mass spectra were measured on a JEOL JMS-S3000. UV–vis absorption spectra were measured on a JASCO V-570

spectrophotometer. ^{1}H NMR (^{13}C NMR) spectra were recorded on a JEOL AL-400 at 400 MHz (100 MHz). Elemental analyses were performed at the Advanced Research Support Center, Ehime University.

Crystallographic analysis. The diffraction data were corrected for Lorentz, polarization, and absorption effects. The structures were solved with SIR2004[12] and refined with SHELXL-97.[13] All calculations were performed by using the Crystal Structure crystallographic software package.[14] CCDC-1876271 for **10a** and 1876272 for **15** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data of **10a**: $C_{32}H_{32}O_4S_4$, FW 608.85, monoclinic, $P2_1/n$, Z = 4, a = 9.9993(19) Å, b = 12.446(2) Å, c = 23.923(5) Å, β = 98.661(3)°, V = 2943.3(10) Å^3, μ (Mo$K\alpha$) = 0.360 mm^{-1}, unique 8951, R_{int} 0.0508, obs. 7631, param. 365, R_1 (I > 2σ(I)) 0.0573, $_wR_2$ (all data) 0.1096, GOF 1.104; **15**: $C_{46}H_{48}N_4S_2$, FW 721.03, triclinic, $P\bar{1}$, Z = 2, a = 8.8534(3) Å, b = 12.7796(5) Å, c = 17.2143(6) Å, α = 81.310(3)°, β = 88.711(3)°, γ = 83.129(3)°, V = 1911.47(12) Å^3, μ (Mo$K\alpha$) = 0.178 mm^{-1}, unique 8787, R_{int} 0.06336, obs. 5900, param. 545, R_1 (I > 2σ(I)) 0.1051, $_wR_2$ (all data) 0.1808, GOF 1.039.

2-(2,5-Dimethyl-3-thienyl)cyclohex-2-enone 5

To a degassed solution of **3** (14.23 g, 64.1 mmol), **4** (14.96 g, 95.9 mmol), Na_2CO_3 (72.29 g, 682.0 mmol) in water (350 mL) and THF (400 mL) was added $Pd(PPh_3)_4$ (3.90 g, 3.4 mmol) under Ar atmosphere. The resulting mixture was refluxed for 16 h. The reaction mixture was concentrated under reduced pressure and extracted with $CHCl_3$. The organic layer was washed successively with aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc/hexane (1/9) to give **5** (10.37 g, 78%).

Dark brown oil; MS (EI) m/z 206 (M^+), HRMS calcd for $C_{12}H_{14}OS$ 206.0765, found 206.0767; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, 1H, J = 4.4 Hz, H-3), 6.47 (s, 1H, H-4'), 2.56 (t, 2H, J = 6.4 Hz, H-6), 2.51 (m, 2H, H-4), 2.39 (s, 3H, Me), 2.25 (s, 3H, Me), 2.10 (tt, 2H, J = 6.4, 6.4 Hz, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.97, 148.80, 135.87, 134.80, 133.55, 132.84, 127.28, 38.79, 26.32, 22.91, 15.01, 13.86.

1,2-Bis(2,5-dimethyl-3-thienyl)cyclohex-2-enol 7

To a stirred solution of **6** (8.59 g, 44.9 mmol) in dry THF (114 mL) was slowly added a solution of *n*-BuLi (2.67 M, 17 mL) in hexane at −78 °C under Ar atmosphere. The resulting mixture was stirred at same temperature for 2 h. After addition of a solution of **5** (9.00 g, 43.6 mmol) in dry THF (35 mL) over 20 min at −78 °C, the mixture was stirred at room temperature for 18 h. The reaction was quenched by

addition of sat. aqueous NH_4Cl (50 mL). The reaction mixture was concentrated under reduced pressure and extracted with EtOAc. The organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc/hexane (1/9) to give **7** (11.05 g, 80%).

Yellow oil; MS (EI) *m*/*z* 318 (M^+); HRMS calcd for $C_{18}H_{22}OS_2$ 318.1112, found 318.1120; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 1H, thienyl), 6.10 (s, 1H, thienyl), 5.76 (t, 1H, *J* = 3.6 Hz, H-3), 2.34–2.18 (m, 2H), 2.16–2.08 (m, 1H), 2.42 (s, 3H, Me), 2.37 (s, 6H, Me), 2.27 (s, 3H, Me), 1.97 (s, 1H, OH), 2.02–1.90 (m, 1H), 1.80–1.70 (m, 1H), 1.69–1.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.76, 137.82, 135.83, 134.83, 134.61, 133.22, 131.60, 129.51, 127.93, 125.74, 74.51, 38.50, 25.58, 19.08, 15.17, 15.10, 14.51, 14.14.

2,3-Bis(2,5-dimethyl-3-thienyl)-5,6-bis(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene 10a

A mixture of **7** (3.11 g, 9.8 mmol) and H_3PO_4 (0.50 mL) in dry toluene (30 mL) was refluxed for 35 min. The reaction mixture was washed with sat. aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane to give a mixture of **8a** and **8b** (2.20 g) with a ratio of 1:1 determined by ^{1}H NMR. A solution of **8a**/**8b** (1.83 g) and **9** (921 mg, 3.0 mmol) in toluene (24 mL) was refluxed for 16 h. After removal of solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ to give **10a** (694 mg, 27%), **10b** (trace) and recovered **8b**.

10a: Colorless powder; mp >194.7 °C (decomp); MS (EI) *m*/*z* 608 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2H, Ph), 7.68 (m, 1H, Ph), 7.59 (m, 3H, Ph), 7.53 (m, 2H, Ph), 7.42 (m, 2H, Ph), 6.48 (s, 1H, thienyl), 6.31 (s, 1H, thienyl), 4.07 (m, 1H, H-5 or H-6), 4.00 (dd, 1H, *J* = 6.0, 2.0 Hz, H-5 or H-6), 3.44 (m, 1H, H-1 or H-4), 3.01 (m, 1H, H-1 or H-4), 2.48 (m, 1H, H-7 or H-8), 2.36 (s, 3H, Me), 2.34 (s, 3H, Me), 1.95–1.70 (m, 1H, H-7 or H-8), 1.84 (s, 3H, Me), 1.75 (s, 3H, Me), 1.64 (m, 1H, H-7 or H-8), 1.33 (m, 1H, H-7 or H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.31, 137.91, 135.87, 135.78, 135.59, 135.38, 135.16, 133.97, 133.67, 132.93, 129.18, 128.96, 128.73, 128.68, 125.85, 125.57, 64.96, 62.51, 38.50, 38.05, 24.63, 20.62, 15.20, 15.12, 14.04, 14.00; Anal. Calcd for $C_{32}H_{32}O_4S_4 \cdot 1/3CHCl_3 \cdot 1/3MeOH$: C, 59.51; H, 5.15. Found: C, 59.37; H, 4.95.

10b: Colorless powder; MS (FAB) *m*/*z* 609 $[M+H]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (m, 2H, Ph), 7.71 (m, 1H, Ph), 7.63 (m, 2H, Ph), 7.47 (m, 3H, Ph), 7.33 (m, 2H, Ph), 6.75 (s, 1H, thienyl), 6.38 (d, 1H, *J* = 6.4 Hz, H-3), 5.47 (s, 1H, thienyl), 4.74 (d, 1H, *J* = 6.0 Hz, H-6), 4.50 (dd, 1H, *J* = 6.0, 2.8 Hz, H-5), 3.44 (m, 1H, H-7 or H-8), 3.30 (m, 1H, H-4), 2.44 (s, 3H, Me), 2.42 (s, 3H, Me), 2.11 (s, 3H, Me),

1.82(m, 1H, H-7 or H-8), 1.64 (m, 2H, H-7 or H-8), 1.18 (s, 3H, Me); Anal. Calcd for $C_{32}H_{32}O_4S_4 \cdot 1/2CHCl_3$: C, 58.39; H, 4.91. Found: C, 58.63; H, 4.89.

Ethyl 4,7-dihydro-5,6-bis(2,5-dimethyl-3-thienyl)-4,7-ethano-2*H*-isoindole-1-carboxylate 11

To a stirred solution of **10a** (935 mg, 1.5 mmol) and ethyl isocyanoacetate (210 μL) in dry THF (5.6 mL) was added dropwise a solution of KO*t*-Bu (585 mg, 5.2 mmol) in dry THF (5.4 mL) at 0 °C under Ar atmosphere. The resulting mixture was stirred at room temperature for 2 d. After addition of 1 M HCl (6 mL), the reaction mixture was concentrated under reduced pressure, and extracted with $CHCl_3$. The organic layer was washed with sat. aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$, followed by recrystallization from $CHCl_3$/MeOH to give **11** (209 mg, 32%).

Colorless crystals; mp 142.4 °C; MS (FAB) *m*/*z* 437 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (bs, 1H, NH), 6.59 (d, 1H, *J* = 2.4 Hz, H-3), 6.41 (s, 1H, thienyl), 6.36 (s, 1H, thienyl), 4.53 (m, 1H, H-7), 4.38 (dq, 1H, *J* = 10.8 and 7.2 Hz, CO_2Et), 4.30 (dq, 1H, *J* = 10.8 and 7.2 Hz, CO_2Et), 4.01 (m, 1H, H-4), 2.36 (s, 3H, Me), 2.33 (s, 3H, Me), 1.96–1.76 (m, 2H, H-8,9), 1.87 (s, 3H, Me), 1.75–1.50 (m, 2H, H-8,9), 1.69 (s, 3H, Me), 1.38 (t, 3H, *J* = 7.2 Hz, CO_2Et); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.80, 139.26, 138.56, 137.04, 136.73, 136.31, 135.21, 134.82, 131.94, 131.61, 131.23, 126.36, 125.51, 114.01, 113.15, 59.85, 40.43, 40.03, 27.57, 26.66, 15.16, 15.12, 14.54, 13.95, 13.80; Anal. Calcd for $C_{25}H_{27}NO_2S_2 \cdot 1/2H_2O$: C, 67.23; H, 6.32; N, 3.14. Found: C, 67.52; H, 6.16; N, 2.97.

4,7-Dihydro-5,6-bis(2,5-dimethyl-3-thienyl)-4,7-ethano-2*H*-isoindole 12

A solution of **11** (207 mg, 0.47 mmol) and NaOH (0.13 g) in ethylene glycol (4 mL) in a shaded vessel was stirred at 170 °C for 2.5 h under N_2 atmosphere. After cooling to room temperature, water (20 mL) was poured into the solution. The mixture was extracted with EtOAc. The organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give **12** (148 mg, 86%).

Colorless powder; mp 142.9 °C; MS (EI) *m*/*z* 365 (M^+), 337 ($M^+-C_2H_4$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (bs, 1H, NH), 6.48 (d, 2H, *J* = 1.6 Hz, H-1,3), 6.38 (s, 2H, thienyl), 3.99 (s, 2H, H-4,7), 2.34 (s, 6H, Me), 1.84 (m, 2H, H-8,9), 1.80 (s, 6H, Me), 1.64 (m, 2H, H-8,9); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.40, 137.37, 134.90, 131.49, 129.14, 126.00, 107.94, 39.98, 27.98, 15.19, 13.95; Anal. Calcd for $C_{22}H_{23}NS_2 \cdot 1/4MeOH$: C, 71.54; H, 6.48; N, 3.75. Found: C, 71.75; H, 6.20; N, 3.50.

Di(3-thienyl)BCODporphyrin 14

To a solution of **12** (164 mg, 0.45 mmol) and **13** (185 mg, 0.44 mmol) in dry CH_2Cl_2 (66 mL) was added TFA (1.4 mL). The resulting mixture was stirred at room temperature for 19 h under Ar atmosphere in the dark. The reaction mixture was neutralized with Et_3N (3 mL) and treated with *p*-chloranil (166 mg) with stirring for 21 h. The mixture was washed with water and brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by column chromatography on alumina with $CHCl_3$, followed by recrystallization from $CHCl_3$/MeOH to give **14** (112 mg, 34%).

Purple crystals; mp >110.9 °C (decomp); MS (FAB) *m*/*z* 749 $[M+H]^+$, 721 $[M+H-C_2H_4]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 2H, *meso*), 10.12 (s, 2H, *meso*), 6.77 (s, 2H, thienyl), 5.84 (s, 2H, bridge head), 4.36–4.02 (m, 8H, Et), 3.64 (s, 6H, Me), 2.52 (m, 2H, bridge), 2.49 (s, 6H, Me), 2.12 (m, 2H, bridge), 1.94 (t, 6H, J = 7.6 Hz, Et), 1.89 (s, 6H, Me), 1.87 (t, 6H, J = 7.6 Hz, Et), −3.95 (bs, 2H, NH); UV–vis ($CHCl_3$) λ_{max}, nm (log ε) 399 (5.16), 498 (4.13), 531 (3.91), 566 (3.81), 620 (3.62); Anal. Calcd for $C_{48}H_{52}N_4S_2$: C, 76.96; H, 7.00; N, 7.48. Found: C, 76.56; H, 6.71; N, 7.31.

Di(3-thienyl)benzoporphyrin 15

Porphyrin **14** (7.5 mg) was heated at 200 °C under reduced pressure for 1 h in a glass tube to give **15** in quantitative yield.

Purple powder; MS (MALDI–TOF) *m*/*z* 721 $[M+H]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 2H, *meso*), 10.13 (s, 2H, *meso*), 9.28 (s, 2H, benzo), 6.77 (s, 2H, thienyl), 4.20 (q, 4H, J = 7.6 Hz, Et), 4.04 (q, 4H, J = 7.6 Hz, Et), 3.74 (s, 6H, Me), 2.53 (s, 6H, Me), 2.37 (s, 6H, Me), 1.91 (t, 6H, J = 7.6 Hz, Et), 1.90 (t, 6H, J = 7.6 Hz, Et), −3.53 (bs, 2H, NH); UV–vis ($CHCl_3$) λ_{max}, nm (log ε) 409 (5.25), 502 (4.08), 546 (4.24), 575 (3.83), 630 (3.79); Anal. Calcd for $C_{46}H_{48}N_4S_2$: C, 76.63; H, 6.71; N, 7.77. Found: C, 76.74; H, 6.57; N, 7.53.

ACKNOWLEDGEMENTS

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