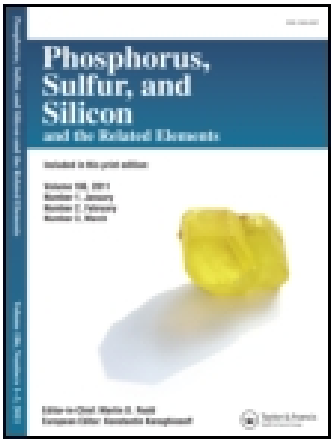


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Synthesis of 2,3-Dihydrobenzo[1,4]dithiin-Fused Porphyrins

Guangnan Jin [a], Tetsuo Okujima [a], Yusuke Hashimoto [a], Hiroko Yamada [a b], Hidemitsu Uno [c] & Noboru Ono [a]

[a] Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama, Japan

[b] PRESTO, Japan Science and Technology Agency, Kawaguchi, Japan

[c] Department of Molecular Science, Integrated Center for Science, Ehime University, Matsuyama, Japan

Published online: 27 May 2010.

To cite this article: Guangnan Jin, Tetsuo Okujima, Yusuke Hashimoto, Hiroko Yamada, Hidemitsu Uno & Noboru Ono (2010) Synthesis of 2,3-Dihydrobenzo[1,4]dithiin-Fused Porphyrins, Phosphorus, Sulfur, and Silicon and the Related Elements, 185:5-6, 1108-1116, DOI: 10.1080/10426501003773449

To link to this article: http://dx.doi.org/10.1080/10426501003773449

Phosphorus, Sulfur, and Silicon, 185:1108–1116, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003773449

SYNTHESIS OF 2,3-DIHYDROBENZO[1,4]DITHIIN-FUSED PORPHYRINS

Guangnan Jin,[1] Tetsuo Okujima,[1] Yusuke Hashimoto,[1] Hiroko Yamada,[1,2] Hidemitsu Uno,[3] and Noboru Ono[1]

[1]*Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama, Japan*
[2]*PRESTO, Japan Science and Technology Agency, Kawaguchi, Japan*
[3]*Department of Molecular Science, Integrated Center for Science, Ehime University, Matsuyama, Japan*

This article describes the preparation of (ethylenedithio)bicyclo[2.2.2]octadiene-fused porphyrins 13 and 14a,b as soluble precursors of 2,3-dihydrobenzo[1,4]dithiin-fused porphyrins and the retro Diels–Alder conversion of the precursors 13 and 14a,b.

Keywords Benzo[1,4]dithiin; benzoporphyrin; retro Diels–Alder reaction; ring expansion reaction of 1,3-dithiolane

INTRODUCTION

The π-conjugated porphyrins with exocyclic rings have been extensively studied because of their special optical and electrical properties.[1] Their chemistry has been investigated for the applications to photoelectronic materials and molecular devices.[2] Alternatively, numerous molecules with the ethylenedithio group have also attracted the interest of the many research groups for the preparation of the organic ferromagnets. For example, benzo[1,4]dithiin system or bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is a well known compound that gives the conducting radical ion salts.[3–7] These dihydro-1,4-dithiin rings are prepared by ring expansion reaction of 1,3-dithiolanes upon treatment with various reagents such as Br_2,[4,8] NBS,[9] NCS,[10] PhSeCl,[11,12] or $TeCl_4$.[13,14] The 1,3-dithiolanes can be obtained by the dithioacetalization of the corresponding carbonyl compounds with 1,2-ethanedithiol. Recently, we have reported the synthesis of 4,7-dihydro-2*H*-isoindoles via Diels–Alder reaction of ethynyl *p*-tolyl sulfine with several 1,3-cyclohexadienes.[15] The Diels–Alder adduct with a trimethylsilyloxy group was converted into pyrrole with fused

Received 10 December 2008; accepted 26 December 2008.

Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

This work was partially supported by the Sasagawa Scientific Research Grant from The Japan Science Society (G.J.). We used ethyl isocyanoacetate from the Nippon Synthetic Chem. Ind. (Osaka Japan).

Address correspondence to Tetsuo Okujima, Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan. E-mail: tetsuo@chem.sci.ehime-u.ac.jp

bicyclo[2.2.2]octenone by hydrolytic removal of the silyl group, acetalization, and the modified Barton–Zard reaction. Therefore, this pyrrole could be the key compound in the synthesis of peripheral functionalized benzoporphyrins (BPs) by the substitution reaction of the carbonyl moiety and the retro Diels–Alder reaction of the bicyclo[2.2.2]octadiene (BCOD) moiety. We report in this article the synthesis of 4,7-ethano-5,6-ethylenedithio-4,7-dihydro-2*H*-isoindoles **1a**–**c**; the condensation of diformyltripyrrane **12** with **1a** and the tetramerization of **1c** followed by the oxidation to give the corresponding porphyrins **13** and **14a**,**b**; and the retro Diels–Alder conversion of them into mono(4,5-ethylenedithio)benzoporphyrin (MEDT-BP **2**) and tetrakis(4,5-ethylenedithio)tetrabenzoporphyrins (TEDT-TBPs **3a**,**b**) in Chart 1.

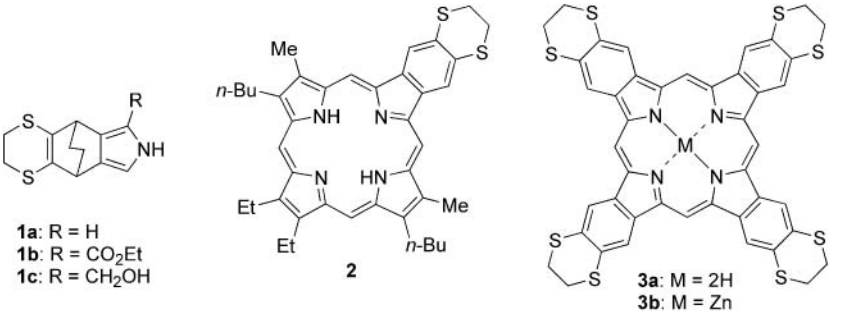
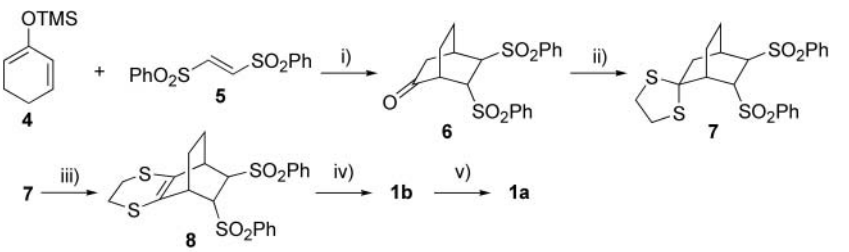


Chart 1

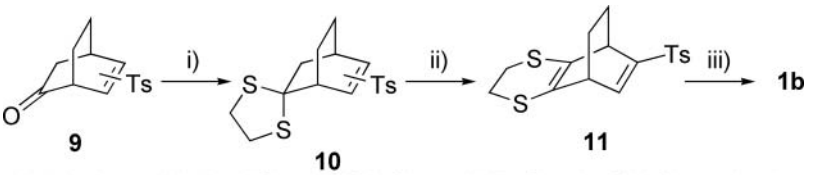
RESULTS AND DISCUSSION

Synthesis of 5,6-ethylenedithioisoindole derivatives **1** is summarized in Scheme 1. Bicyclo[2.2.2]octanone **6** was prepared by the Diels–Alder reaction of 2-trimethylsilyloxy-1,3-cyclohexadiene (**4**) with *trans*-1,2-bis(phenylsulfonyl)ethylene (**5**) and the subsequent desilylation in 76% yield.[16] The thioacetalization of **6**, followed by the ring expansion reaction with $TeCl_4$ as a Lewis acid oxidant gave 2,3-ethylenedithiobicyclo[2.2.2]oct-2-ene **8**, which was converted into the corresponding pyrrole **1b** by the modified Barton–Zard reaction.[17,18] Removal of the ethoxycarbonyl group by heating **1b** with NaOH in ethylene glycol at 170°C gave α-free pyrrole **1a** in 49%. Pyrrole **1b** was also prepared starting from **9** [15] by the similar procedure as shown in Scheme 2.



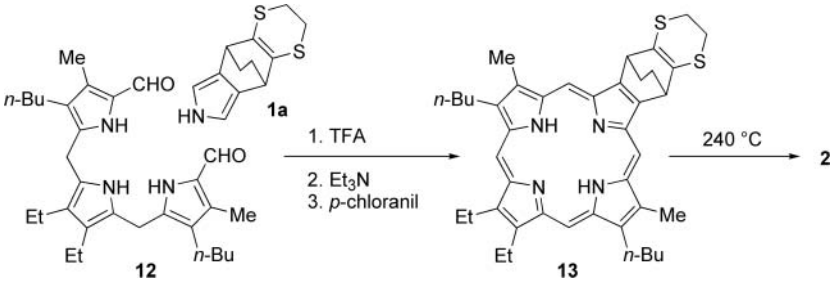
i) 1. toluene, 130 °C, 5 d, autoclave, 2. SiO_2, 76%; ii) 1,2-ethanedithiol, $AlCl_3$, dry CH_2Cl_2, rt, 2 h; iii) $TeCl_4$, dry CH_2Cl_2, rt, 2 h, 74% (2 steps); iv) $CNCH_2CO_2Et$, t-BuOK, THF, rt, 21 h, 91%; v) NaOH, $(CH_2OH)_2$, 170 °C, 1.5 h, 49%.

Scheme 1

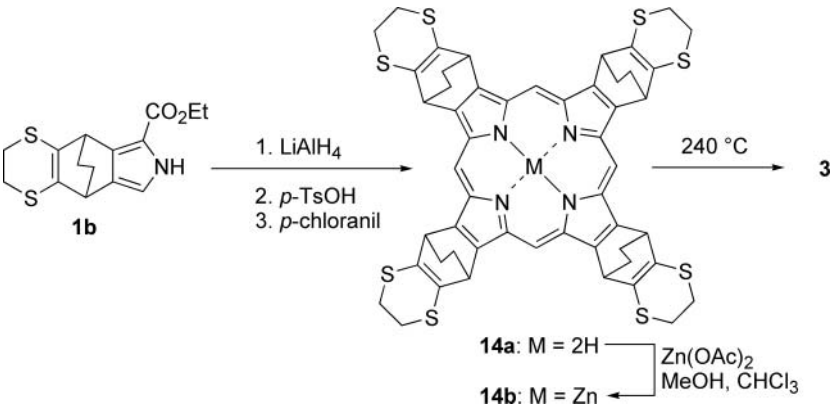


Scheme 2

The condensation of tripyrrane **12** [19] with **1a** in $CHCl_3$ in the presence of TFA followed by oxidation with *p*-chloranil gave **13** in 22% yield as shown in Scheme 3. Tetrakis(ethylenedithioBCOD)porphyrin **14a** was synthesized by reduction of **1b** with $LiAlH_4$ followed by tetramerization and oxidation with *p*-chloranil (Scheme 4).[20] Zinc complex **14b** was prepared on the treatment of **14a** with zinc acetate.



Scheme 3



Scheme 4

The retro Diels–Alder reaction of **13** was carried out at 240°C in vacuo in a glass tube oven. MEDT-BP **2** was quantitatively obtained. Thermogravimetric analysis (TGA) curves of **13** and **14a**,**b** are shown in Figure 1. The weight loss of **13** started at around 200°C and ceased after 230°C. The loss of weight was ca. 5%, consistent with the calculated value

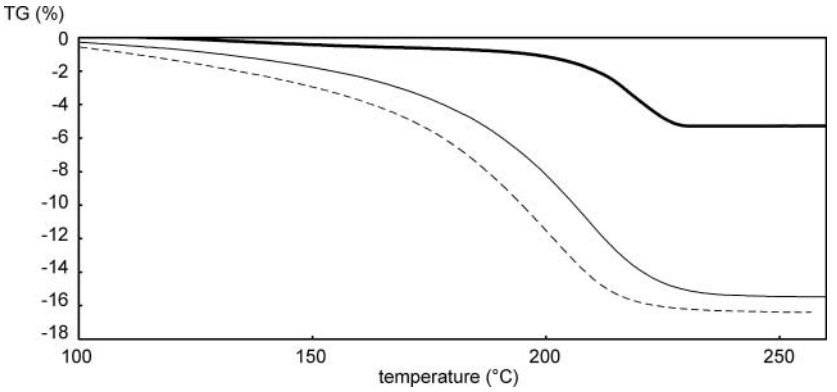


Figure 1 TGA of **13** (bold line), **14a** (solid line), and **14b** (broken line).

of 4.2%. Tetrakis(ethylenedithioBCOD)porphyrins **14a** and **14b** were also converted into TEDT-TBPs **3** by heating at 240°C under same conditions in nearly quantitative yields.

The absorption and fluorescence spectra of **3a**,**b** and **14a**,**b** are shown in Figure 2. The Soret band of **14b** appeared at 404 nm, while that of **3b** appeared at 442 nm. The absorption maxima of **14a**,**b** showed a bathochromic shift as they were converted into TEDT-TBPs **3a**,**b**. The emission spectra of zinc complexes **3b** and **14b** with excitation at their Soret bands showed a single band at 657 nm. The values of their absolute quantum yields (Φ) in $CHCl_3$ solution were in the range of 0.10–0.11. On the other hand, the emissions of free base porphyrins **3a** and **14a** were observed at around 670 nm and 688 nm with Φ values of 0.24 and 0.16, respectively.

In summary, 2,3-dihydro-1,4-dithiin-fused BPs, MEDT-BP **2**, and TEDT-TBPs **3a**,**b** were synthesized from (ethylenedithioBCOD)porphyrins **13** and **14a**,**b** by the retro Diels–Alder reaction in nearly quantitative yield. Both the Soret and Q bands of **2** and **3a**,**b** exhibited a bathochromic shift compared to their precursors **13** and **14a**,**b**. Free base

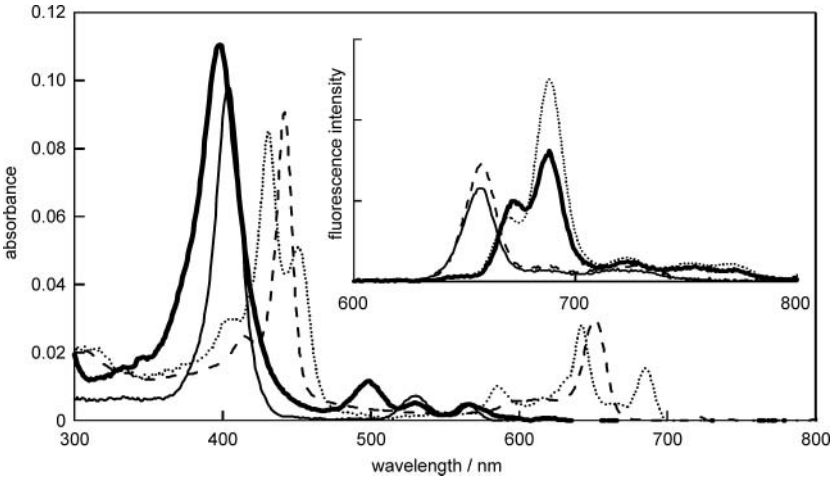


Figure 2 Absorption and fluorescence emission (inset) spectra of **3a** (dotted line), **3b** (broken line), **14a** (bold line), and **14b** (solid line) in $CHCl_3$.

porphyrin **3a** fluoresces with Φ values of up to 0.25. Further works on application of these porphyrins such as solution-processed fabrication for organic field-effect transistors are underway.

EXPERIMENTAL

Melting points were determined on a Yanaco micro melting point apparatus MP500D and are reported here uncorrected. DI-EI and FAB mass spectra were measured on a JEOL JMS-700. TG analyses were performed on an SII Exstar 600 TG/DTA 6200. UV-vis spectra were measured on a JASCO V-570 spectrophotometer. The fluorescence emission spectra and the Φ values were measured on a Hamamatsu Photonics K.K. absolute PL quantum yield measurement system C9920–03. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL AL-400 at 400 MHz (100 MHz). Elemental analyses were performed at the Integrated Center for Sciences, Ehime University.

5,6-Bis(phenylsulfonyl)bicyclo[2.2.2]octan-2-one (6)[16]

A solution of **4** (4.0 mL, 21 mmol) and **5** (3.05 g, 9.89 mmol) in toluene (80 mL) was heated at 130°C in an autoclave for 5 d. After addition of silica gel (ca. 20 g), the resulting mixture was stirred at room temperature overnight. The reaction mixture was filtered with Celite and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$/hexane to give **6** (3.05 g, 76%) as colorless crystals.

2,3-Ethylenedithio-5,6-bis(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (8)

To a solution of **6** (8.08 g, 20.0 mmol) in dry CH_2Cl_2 (40 mL), 1,2-ethanedithiol (4.0 ml, 48 mmol) and powdered $AlCl_3$ (0.95 g, 7.1 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. The reaction was quenched with sat. aqueous $NaHCO_3$, and the insoluble material was removed by filtration with Celite. The filtrate was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. After addition of ether, the mixture was cooled in a refrigerator overnight. The precipitate was collected by filtration as crude thioacetal **7** (9.22 g).

To a solution of crude **7** (4.81 g) in dry CH_2Cl_2 (40 mL), powdered $TeCl_4$ (1.92 g, 7.13 mmol) was added at 0°C. After stirring at room temperature for 2 h, sat. aqueous $NaHCO_3$ was poured into the reaction mixture. The resulting black precipitate was removed by filtration with Celite. The filtrate was washed with 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 CH_2Cl_2/hexane to give **8** (3.69 g, 74%).

Colorless crystals; mp 198.2–200.1°C; MS (FAB) *m/z* 478 (M^++H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, 2H), 7.84 (m, 2H), 7.68 (m, 1H), 7.65 (m, 1H), 7.59 (m, 2H), 7.54 (m, 2H), 3.90 (dd, 1H, J = 2.2, 5.6 Hz), 3.83 (m, 1H), 3.14–3.26 (m, 4H), 3.04 (dd, 1H, J = 2.7, 5.6 Hz), 2.69 (m, 1H), 2.35 (m, 1H), 1.70 (m, 1H), 1.62 (m, 1H), and 1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.04, 137.64, 133.98, 133.90, 129.10, 129.07, 128.99, 128.66, 123.89, 123.21, 65.74, 62.70, 39.03, 38.87, 28.27, 28.14, 24.96, and 21.67. Anal. Calcd for $C_{22}H_{22}O_4S_4$: C, 55.20; H, 4.63. Found: C, 54.92; H, 4.62.

2,3-Ethylenedithio-5-tosylbicyclo[2.2.2]octa-2,5-diene (11)

To a solution of **9** (0.91 g, 3.3 mmol) in dry CH_2Cl_2 (10 mL), 1,2-ethanedithiol (0.35 ml, 4.2 mmol) and powdered $AlCl_3$ (165 mg, 1.24 mmol) were added. The resulting mixture was stirred at room temperature overnight. The reaction was quenched with sat. aqueous $NaHCO_3$, and the insoluble material was removed by filtration with Celite. The filtrate was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. After addition of ether, the mixture was cooled in a refrigerator overnight. The precipitate was collected by filtration as crude thioacetal **10** (0.84 g).

To a solution of crude **10** (0.36 g) in dry CH_2Cl_2 (10 mL), powdered $TeCl_4$ (259 mg, 0.961 mmol) was added at 0°C. After stirring at room temperature for 0.5 h, sat. aqueous $NaHCO_3$ was poured into the reaction mixture. The resulting black precipitate was removed by filtration with Celite. The filtrate was washed with 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 CH_2Cl_2/hexane to give **11** (0.22 g, 44%).

Colorless crystals; mp 117.2–118.6°C; MS (FAB) *m/z* 350 (M^++H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 2H, $H^{2',6'}$), 7.31 (m, 2H, $H^{3',5'}$), 7.23 (dd, 1H, $J = 2.1$, 6.3 Hz, H^6), 3.60 (dd, 1H, $J = 2.6$, 4.8 Hz, H^4), 3.52 (ddd, 1H, $J = 2.6$, 2.6, 6.3 Hz, H^1), 2.98–3.06 (m, 4H, -SCH_2CH_2S-), 2.42 (s, 3H, CH_3), 1.64 (m, 1H, H^7 or H^8), 1.54 (m, 1H, H^8 or H^7), 1.41 (m, 1H, H^7 or H^8), and 1.27 (m, 1H, H^8 or H^7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.23, 144.04, 142.57, 136.55, 129.67, 127.64, 123.92, 123.55, 44.67, 43.72, 27.79, 27.69, 26.73, 25.94, and 21.63. Anal. Calcd for $C_{17}H_{18}O_2S_3$: C, 58.25; H, 5.18. Found: C, 57.95; H, 5.06.

Ethyl 4,7-Ethano-5,6-ethylenedithio-4,7-dihydro-2*H*-isoindole-1-carboxylate (1b)

From 8. A solution of potassium *t*-butoxide (1.34 g) in dry THF (15 mL) was added to a stirred solution of **8** (2.44 g, 5.10 mmol) and ethyl isocyanoacetate (1.3 mL) in dry THF (30 ml) at 0°C under an Ar atmosphere. The resulting mixture was stirred at room temperature for 21 h. The reaction mixture was poured into 1 M HCl (10 mL), evaporated and extracted with $CHCl_3$. The organic layer was washed successively with sat. 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 $CHCl_3$ followed by recrystallization from $CHCl_3$/methanol to give **1b** (1.43 g, 91%).

From 11. The above procedure was followed by using **11** (83 mg, 0.24 mmol), ethyl isocyanoacetate (0.1 ml) in dry THF (7 mL), and 1 M potassium *t*-butoxide solution in dry THF (2 mL). Chromatographic purification on silica gel with $CHCl_3$ and recrystallization from $CHCl_3$/hexane gave **1b** (56 mg, 77%)

Colorless crystals; mp 189.5–191.4°C; MS (70 eV) *m/z* (relative intensity) 307 (M^+, 44%), 279 (M^+–C_2H_4, 85), and 233 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (br, 1H, NH), 6.58 (d, 1H, $J = 2.7$ Hz, H^3), 4.31 (q, 2H, $J = 7.1$ Hz, 1-CO_2Et), 4.10 (m, 1H, H^4), 3.60 (m, 1H, H^7), 3.12 (s, 4H, -SCH_2CH_2S-), 1.82 (m, 2H, H^8 and H^9), 1.52 (m, 2H, H^8 and H^9), and 1.36 (t, 3H, $J = 7.1$ Hz, 1-CO_2Et); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.40, 134.58, 129.87, 126.16, 125.32, 114.11, 112.73, 60.00, 40.95, 40.66, 28.49, 28.00, 27.97, 27.87, and 14.59. Anal. Calcd for $C_{15}H_{17}NO_2S_2$: C, 58.60; H, 5.57; N, 4.56. Found: C, 58.34; H, 5.60; N, 4.59.

4,7-Ethano-5,6-ethylenedithio-4,7-dihydro-2*H*-isoindole (1a)

A solution of **1b** (464 mg, 1.51 mmol) and NaOH (375 mg) in ethylene glycol (10 mL) was heated at 170°C for 1.5 h under an Ar atmosphere in a shaded vessel. The reaction mixture was poured into water and extracted with $CHCl_3$. 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 $CHCl_3$ and washed with $CHCl_3$/hexane to give **1a** (173 mg, 49%).

Colorless crystals; mp 180.0–182.0°C; MS (FAB) *m/z* 235 (M^+) and 207 (M^+–C_2H_4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (br, 1H, NH), 6.46 (d, 2H, $J = 2.4$ Hz, $H^{1,3}$), 3.59 (m, 2H, $H^{4,7}$), 3.11 (s, 4H, -SCH_2CH_2S-), 1.82 (m, 2H, H^8 and H^9), and 1.55 (m, 2H, H^8 and H^9); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.88, 126.03, 108.05, 40.73, 29.00, and 27.97. Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95. Found: C, 61.03; H, 5.44; N, 5.86.

Mono(ethylenedithioBCOD)porphyrin 13

To a solution of **12** (233 mg, 0.488 mmol) and **1a** (118 mg, 0.503 mmol) in dry CH_2Cl_2 (30 mL), TFA (1 mL) was added at room temperature under an Ar atmosphere in a shaded vessel. After stirring overnight, the reaction mixture was neutralized with triethylamine, treated with *p*-chloranil (0.12 g, 0.49 mmol) for 4 h with stirring at room temperature, and evaporated. After dilution with $CHCl_3$, the mixture was washed successively with sat. 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 $CHCl_3$ followed by recrystallization from hexane to give **13** (72 mg, 22%).

Purple crystals; mp > 200°C (decomp); MS (FAB) *m/z* 675 (M^++H); UV-vis ($CHCl_3$) λ_{max} (nm) 398, 498, 535, 567, and 621; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 2H), 10.10 (s, 2H), 5.41 (s, 2H), 4.04–4.14 (m,8H), 3.64 (s, 6H), 3.19–3.35 (m, 4H), 2.45 (m, 2H), 2.27 (tt, 4H, $J = 7.3$, 7.6 Hz), 1.97 (m, 2H), 1.93 (t, 6H, $J = 7.6$ Hz), 1.74 (tq, 4H, $J =$ 7.3, 7.3 Hz), 1.11 (t, 6H, $J = 7.3$ Hz), and -3.95 (br, 2H). HRMS calcd for $C_{42}H_{51}N_4S_2$ 675.3555, found 675.3558.

Tetrakis(ethylenedithioBCOD)porphyrin 14a

$LiAlH_4$ (78 mg, 2.1mmol) was added slowly to a solution of **1b** (0.16 g, 0.52 mmol) in dry THF (15 ml) at 0°C under an Ar atmosphere in a shaded vessel, and the resulting mixture was stirred for 2 h. After slow addition of water, the precipitate was removed by filtration with Celite. The filtrate was extracted with ethyl acetate. The organic layer was washed successively with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was diluted with $CHCl_3$ (150 mL). After addition of *p*-TsOH·H_2O (10 mg), the mixture was stirred at room temperature for 12 h, after which *p*-chloranil (0.16 g, 0.65 mmol) was added. After stirring for 1 day, the reaction mixture was washed successively with 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 $CHCl_3$/methanol to give **14a** (65 mg, 51%).

Purple crystals; mp > 200°C (decomp); MS (FAB) *m/z* 984 (M^++H); UV-vis ($CHCl_3$) λ_{max} (nm) (log ε) 398 (5.28), 498 (4.28), 530 (3.89), 566 (3.86), and 618 (3.11); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 4H), 5.47 (br, 8H), 3.27–3.34 (m, 8H), 3.15–3.26 (m, 8H), 2.45–2.51 (m, 8H), 1.93–2.09 (m, 8H), and −4.61 (br, 2H). HRMS calcd for $C_{52}H_{47}N_4S_8$

983.1566, found 983.1568. Anal. Calcd for $C_{52}H_{46}N_4S_8$: C, 63.51; H, 4.71; N, 5.70. Found: C, 63.65; H, 4.74; N, 5.41.

[Tetrakis(ethylenedithioBCOD)porphyrinato]zinc 14b

A saturated solution of $Zn(OAc)_2 \cdot 2H_2O$ in methanol (20 mL) was added to a solution of **14a** (64 mg, 0.065 mmol) in $CHCl_3$ (20 mL) at room temperature under an Ar atmosphere in a shaded vessel. The resulting mixture was stirred at same temperature for 16 h. The reaction mixture was poured into water. 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 $CHCl_3$ followed by recrystallization from $CHCl_3$/methanol to give **14b** (26 mg, 39%).

Purple crystals; mp > 200°C (decomp); MS (FAB) *m/z* 1046 (M^+); UV-vis ($CHCl_3$) λ_{max} (nm) 404, 530, and 563; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 4H), 5.51 (br, 8H), 3.29–3.36 (m, 8H), 3.16–3.23 (m, 8H), 2.50–2.54 (m, 8H), and 2.02–2.12 (m, 8H). HRMS calcd for $C_{52}H_{45}N_4S_8{}^{66}Zn$ 1047.0670, found 1047.0668.

General Procedure for the Retro Diels–Alder Reaction

(EthylenedithioBCOD)porphyrins **13** and **14a**,**b** (ca. 10 mg) were heated at 240°C under reduced pressure in a glass tube to give MEDT-BP **2** and TEDT-TBPs **3a**,**b**, respectively.

2: Purple crystals; mp > 250°C; MS (FAB) *m/z* 647 (M^++H); UV-vis ($CHCl_3$) λ_{max} (nm) 413, 509, 548, 577, and 632; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 2H), 10.06 (s, 2H), 9.16 (s, 2H), 4.13 (t, 4H, J = 7.6 Hz), 4.01 (q, 4H, J = 7.6 Hz), 3.68 (s, 6H), 3.58 (s, 4H), 2.28 (tt, 4H, J = 7.3, 7.6 Hz), 1.89 (t, 6H, J = 7.6 Hz), 1.74 (tq, 4H, J = 7.3, 7.3 Hz), 1.12 (t, 6H, J = 7.3 Hz), and -3.67 (br, 2H). HRMS calcd for $C_{40}H_{47}N_4S_2$ 647.3242, found 647.3245.

3a: Purple crystals; mp > 250°C; MS (FAB) *m/z* 871 (M^++H); UV-vis ($CHCl_3$) λ_{max} (nm) 431, 451, 585, 642, and 684. HRMS calcd for $C_{44}H_{31}N_4S_8$ 871.0314, found 871.0310. Anal. Calcd for $C_{44}H_{30}N_4S_8$: C, 60.66; H, 3.47; N, 6.43. Found: C, 60.52; H, 3.58; N, 6.43.

3b: Purple crystals; mp > 250°C; MS (FAB) *m/z* 934 (M^+); UV-vis ($CHCl_3$) λ_{max} (nm) 415, 442, and 651. HRMS calcd for $C_{44}H_{29}N_4S_8{}^{66}Zn$ 934.9418, found 934.9422. Anal. Calcd for $C_{44}H_{28}N_4S_8Zn$: C, 56.54; H, 3.02; N, 5.99. Found: C, 56.25; H, 3.22; N, 5.97.

REFERENCES

1. T. D. Lash, In *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith, and R. Guilard, Eds. (Academic Press, San Diego, 2000), vol. 2, Chap. 10, pp. 125–199.
2. J.-H. Chou, M. E. Kosal, H. S. Nalwa, N. A. Rakow, and K. S. Suslick, In *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith, and R. Guilard, Eds. (Academic Press, San Diego, 2000), vol. 6, Chap. 41, pp. 43–131.
3. S. Murru, V. Kavala, C. B. Singh, and B. K. Patel, *Tetrahedron Lett.*, **48,** 1007 (2007).
4. R. Caputo, C. Ferreri, G. Palumbo, and F. Russo, *Tetrahedron*, **47,** 4187 (1991).
5. R. Lapouyade and J.-P. Morand, *J. Chem. Soc., Chem. Commun.*, 223 (1987).
6. P. Day, *C. R. Chimie*, **6,** 301 (2003).
7. H. Kobayashi, *Curr. Opin. Solid State Mater. Sci.*, **2,** 440 (1997).

8. R. Capuro, C. Ferreri, and G. Palumbo, *Synthesis*, 223 (1991).
9. R. Capuro, G. Palumbo, and S. Pedatella, *Tetrahedron*, **50,** 7265 (1994).
10. K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto, and J. Tanaka, *J. Am. Chem. Soc.*, **109,** 6970 (1987).
11. C. G. Francisco, R. Freire, R. Hernández, J. A. Salazar, and E. Suárez, *Tetrahedron Lett.*, **25,** 1621 (1984).
12. J. R. Williams and P. B. Tran, *Synthesis*, 705 (1988).
13. H. Tani, T. Inamasu, R. Tamura, and H. Suzuki, *Chem. Lett.*, **19,** 1323 (1990).
14. H. Tani, *Bull. Chem. Soc. Jpn.*, **68,** 661 (1995).
15. T. Okujima, G. Jin, Y. Hashimoto, H. Yamada, H. Uno, and N. Ono, *Heterocycles*, **70,** 619 (2006).
16. O. De Lucchi, V. Lucchini, M. Zamai, G. Modena, and G. Valle, *Can. J. Chem.*, **62,** 2487 (1984).
17. D. H. R. Barton, J. Kevagoret, and S. Z. Zard, *Tetrahedron*, **46,** 7587 (1990).
18. Review: N. Ono, *Heterocycles*, **75,** 243 (2008).
19. S. Ito, K.-i. Nakamoto, H. Uno, T. Murashima, and N. Ono, *Chem. Commun.*, 2696 (2001).
20. N. Ono and K. Maruyama, *Chem. Lett.*, **17,** 1511 (1988).