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SYNTHESIS OF MONO-, DI- AND TRIBENZOPORPHYRINS FROM THEIR SOLUBLE PRECURSORS

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Dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday.

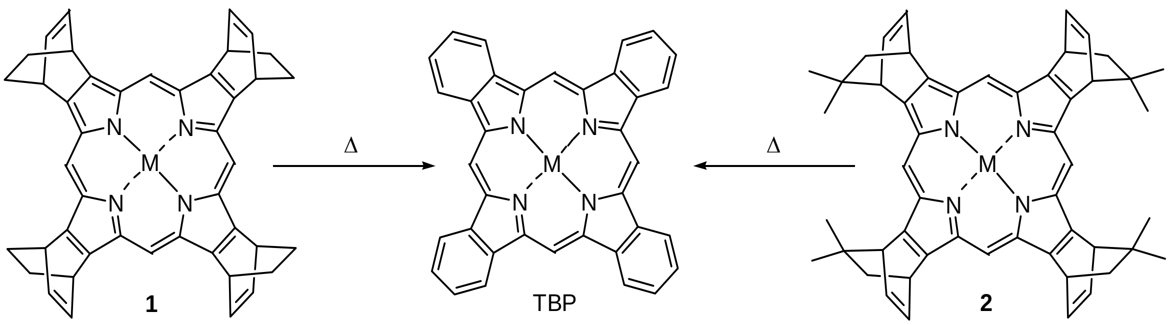
Abstract – Soluble precursors of β-, *meso*-unsubstituted mono-, di- and tribenzoporphyrins were prepared by the reaction of dimethylbicyclo[2.2.2]octadiene-fused pyrrole with appropriate β-free pyrroles. The retro Diels-Alder reaction of these precursors afforded the corresponding benzoporphyrins in quantitative yields.

INTRODUCTION

Recently, much attention has been focused on organic semiconducting π-conjugated molecules due to their potential applications as large-area, low-cost and flexible materials, for example, in light emitting diodes, organic photovoltaics, or organic field-effect transistors (OFETs).[1] Benzoporphyrins and their derivatives have the advantage of easy optimization of molecular structure; low HOMO-LUMO energy gap; and thermal and chemical stability. However, these porphyrins have low solubility and therefore have not been used in solution process suitable for fabricating large-area, low-cost thin-film devices. Improvements in the fabrication of solution-processed thin-film devices are currently driven by two different approaches: introduction of solubilizing groups and of thermally or photochemically removable groups. For example, pentacene is one of the most widely studied organic semiconductors due to its high charge mobility (up to 3 cm^2/Vs).[2] Pentacenes with solubilizing groups have afforded solution-processed OFETs as described by many research groups.[3] Recently, the synthesis of Diels-Alder adducts of pentacene, their thermal conversion to pentacene and application to OFETs were reported by Afzali *et al*.[4]

and Müllen *et al*.[5] We have also reported the preparation of an α-diketone precursor of pentacene and its photochemical conversion.[6,7]

Tetrabenzoporphyrins (TBPs) are also promising semiconductors for practical OFETs. However, only a few examples of soluble precursors of TBPs synthesized utilizing the masked isoindole method have been reported by Cavaleiro and Vinogradov.[8] Recently, we have reported a breakthrough methodology for the preparation of TBPs as shown in Scheme 1, and the fabrication of TBP-based OFETs by a solution process.[7,9–11] Mono-, di- and tribenzoporphyrins are attractive molecules, which are expected to lead to thin-film devices with reduced π-conjugation compared to TBPs and fine tuning of HOMO-LUMO gaps of benzoporphyrins.[9,12,13] Although β-alkyl monobenzoporphyrins[9] and *meso*-aryl dibenzoporphyrins[13] have been prepared starting from pyrroles fused with bicyclo[2.2.2]octadiene (BCOD), the corresponding parent compounds have not been obtained so far.



Scheme 1

In this paper, we report the synthesis of parent mono-, di- and tribenzoporphyrins **3 – 6** from their soluble precursors by the retro Diels-Alder reaction. Since TBP precursors **2** were found to be more soluble than **1**,[10] soluble precursors of β-, *meso*-unsubstituted benzoporphyrins were expected to be derived from pyrroles fused with dimethylBCOD. Therefore we used dimethylBCOD-fused pyrroles as masked isoindoles in the synthesis of the precursors of these porphyrins.

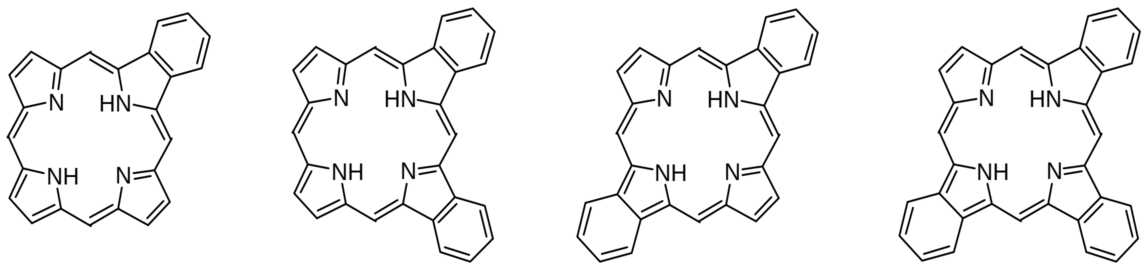
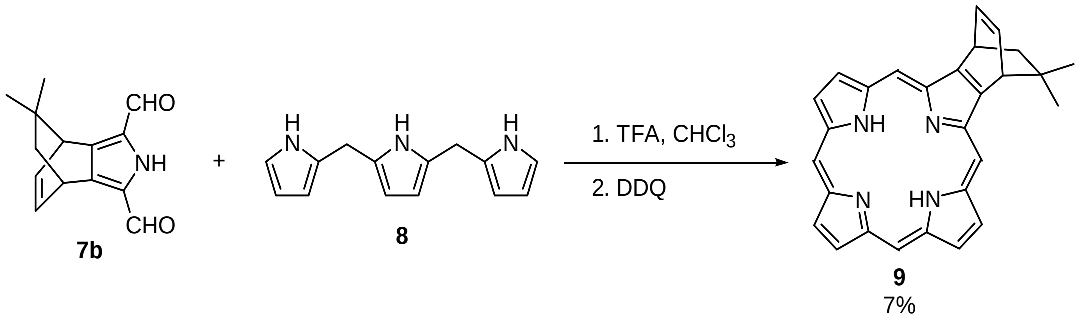


Chart 1

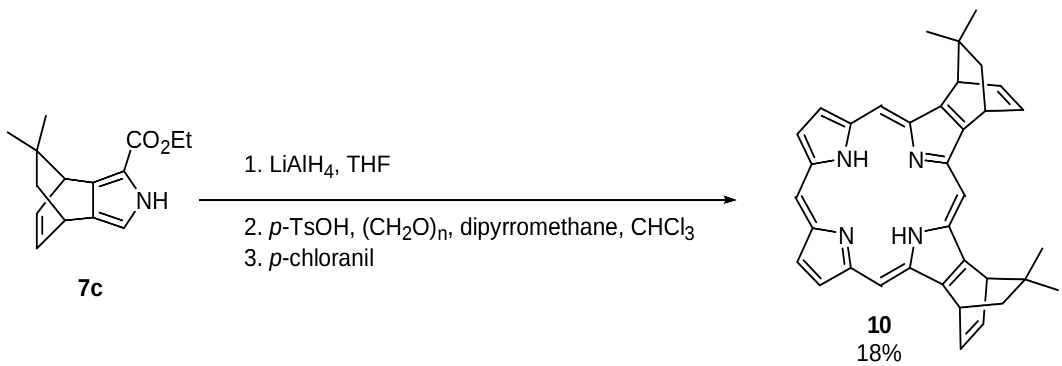
RESULTS AND DISCUSSION

4,7-Dihydro-8,8-dimethyl-4,7-ethano-2*H*-isoindole (**7a**)[10] was treated with methyl orthoformate in TFA to give dialdehyde **7b** in 55% yield. The condensation of tripyrrane **8**[14] with **7b** in $CHCl_3$ in the presence of TFA followed by oxidation with DDQ gave mono(dimethylBCOD)porphyrin **9** in 7% yield (Scheme 2).



Scheme 2

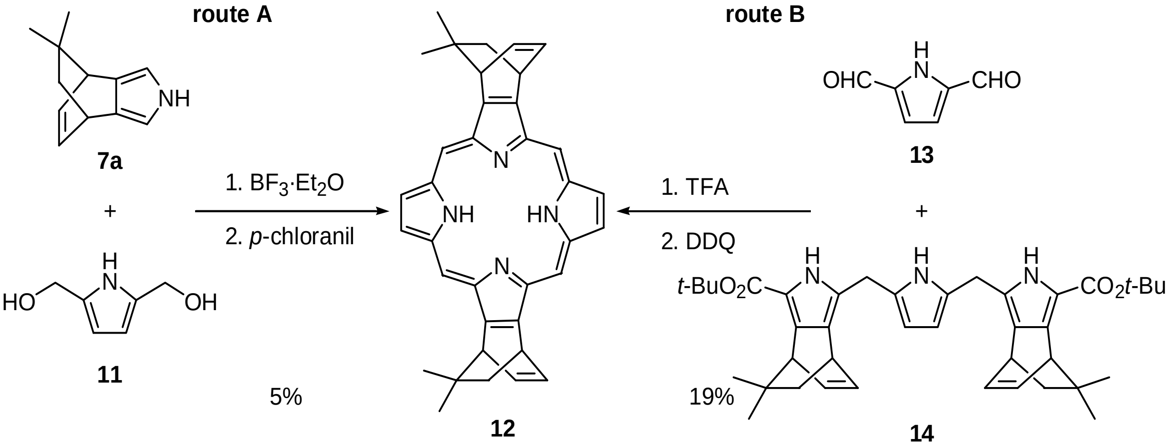
Syntheses of dibenzoporphyrins are shown in Schemes 3 and 4. There are two stereoisomers of dibenzoporphyrin: *adj*-type **4** and *opp*-type **5**. To prepare the *adj*-type precursor, a reaction was carried out using dipyrromethane[15] with two equimolar amounts of (hydroxymethyl)pyrrole fused with dimethylBCOD and an equimolar amount of formaldehyde (Scheme 3). Reduction of dimehylBCOD-fused pyrrole **7c** with $LiAlH_4$ gave the corresponding (hydroxymethyl)pyrrole, which was treated with paraformaldehyde and dipyrromethane in the presence of *p*-TsOH and then oxidized with *p*-chloranil to give *adj*-bis(dimethylBCOD)porphyrin **10** as a mixture of diastereomers in 18% yield. These isomers could not be isolated by column chromatography or recrystallization. Since the yield in the deesterification of α-bis(ethoxycarbonyl)dipyrromethane fused with dimethylBCOD was very low, 2+2 condensation of α-free dimethylBCOD-fused dipyrromethane with α-diformyldipyrromethane was not carried out.



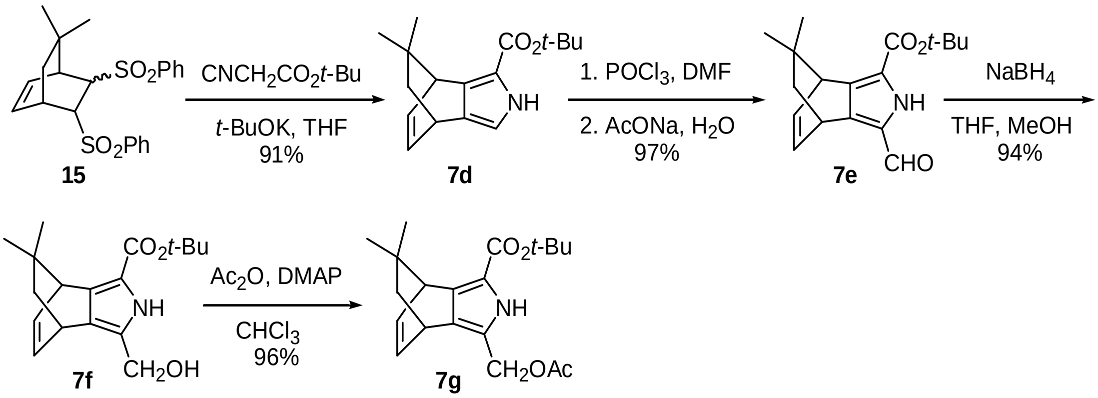
Scheme 3

The synthesis of the precursor of *opp*-dibenzoporphyrin **5** is summarized in Scheme 4. Acid-catalyzed condensation of **7a** with 2,5-bis(hydroxymethyl)pyrrole (**11**) afforded *opp*-bis(dimethylBCOD)porphyrin **12** as a mixture of diastereomers in 5% yield (route A). Porphyrin **12** was also prepared by 3+1 condensation of tripyrrane **14** with **13** (route B). (Acetoxymethyl)pyrrole **7g** was prepared by the

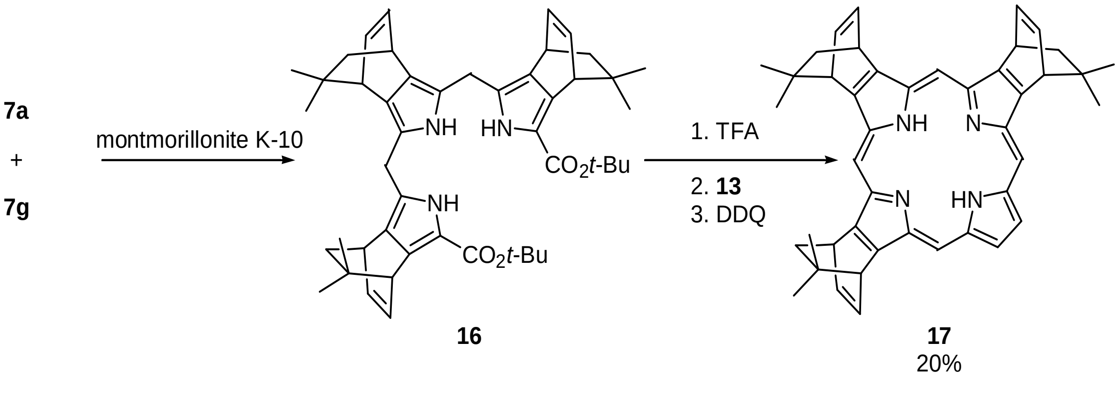
Barton-Zard reaction followed by a Vilsmeier-Haack reaction, reduction and acetylation as shown in Scheme 5.[16] The condensation of the parent pyrrole with **7g** catalyzed by montmorillonite K-10 afforded tripyrrane **14**, which was used in the reaction with **13** without further purification after work-up.[16,17] Tripyrrane **14** was deesterified by TFA. The resulting mixture was diluted with $CHCl_3$ and treated with **13**. After oxidation of the porphyrinogen with DDQ, work-up of the reaction mixture furnished *opp*-bis(dimethylBCOD)porphyrin **12**.



Scheme 4



Scheme 5



Scheme 6

A similar 3+1 porphyrin synthesis afforded the tribenzoporphyrin precursor. DimethylBCOD-fused tripyrrane **16** was prepared by montmorillonite-catalyzed condensation of **7a** with **7g**, and a subsequent 3+1 reaction of **16** with **13** in the presence of TFA followed by oxidation with DDQ gave tris(dimethylBCOD)porphyrin **17** (Scheme 6). These porphyrins fused with dimethylBCOD **9**, **10**, **12** and **17** were stable and soluble in $CHCl_3$. They were fully characterized by their spectral data as shown in the experimental section.

Thermogravimetric analysis (TGA) curves of dimethylBCOD-fused porphyrins are shown in Figure 1. The weight loss of **9** started at around 150 ºC and ceased after 180 ºC. The loss of weight was ca. 14%, consistent with the calculated value of 13.5%. Similarly, the retro Diels-Alder reactions of **10**, **12** and **17** started at 140 – 150 ºC and were completed by 180 – 190 ºC. The loss of weight was 22% (for **10**), 30% (**12**), and 38% (**17**), corresponding to the elimination of two or three isobutene molecules and any included solvents. The retro Diels-Alder reaction of **9** was carried out at 200 ºC for 10 min *in vacuo* in a glass tube oven to give β-, *meso*-unsubstitued benzoporphyrin (**3**) in nearly quantitative yield.

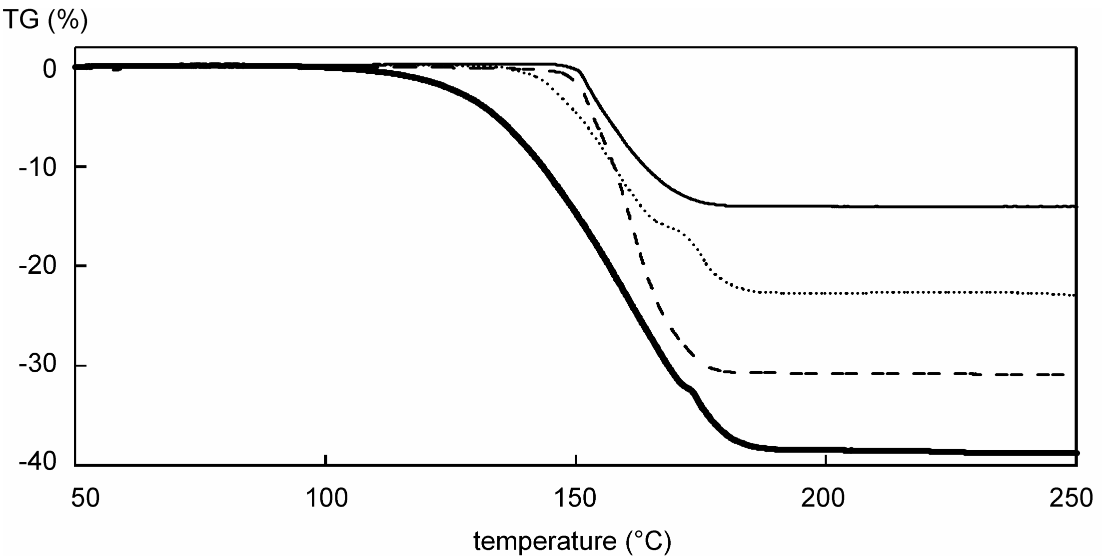


Figure 1. TGA of **9** (solid line), **10** (dotted line), **12** (broken line) and **17** (bold line).

The absorption spectra of **9** and **3** are shown in Figure 2. The Soret band of **3** appeared at 402 nm, while that of **9** appeared at 397 nm. Heating **10**, **12**, and **17** at 200 ºC also resulted in clean formation of **4**, **5**, and **6**, respectively. The Soret bands showed a gradual bathochromic shift as the number of fused benzene rings increased (Figure 3). The absorption and fluorescence data and spectra are contained in Table 1 and Figure 4, respectively. The HOMO-LUMO energy gaps E_g of **3**–**6**, which were estimated from the longest absorption maxima and emission maxima in $CHCl_3$ solution, were 1.98, 1.97, 1.92 and 1.91 eV, respectively. The longest absorption maxima of **4** and **5** were about the same as for **3** and **6**, respectively, though both **4** and **5** were dibenzoporphyrins. On the other hand, in ^{1}H NMR spectroscopy of **3**–**6**, signals of the β-pyrrolic protons in **3** were observed at 9.58 ppm for two *adj*-pyrroles to isoindole and

9.38 ppm for a *opp*-pyrrole. Benzo protons of **3** showed two multiplet signals at 9.36 and 8.13 ppm. These porphyrins **3** – **6** exhibited the ring current effect similar to that reported for benzoporphyrins fused with BCODs.[18]

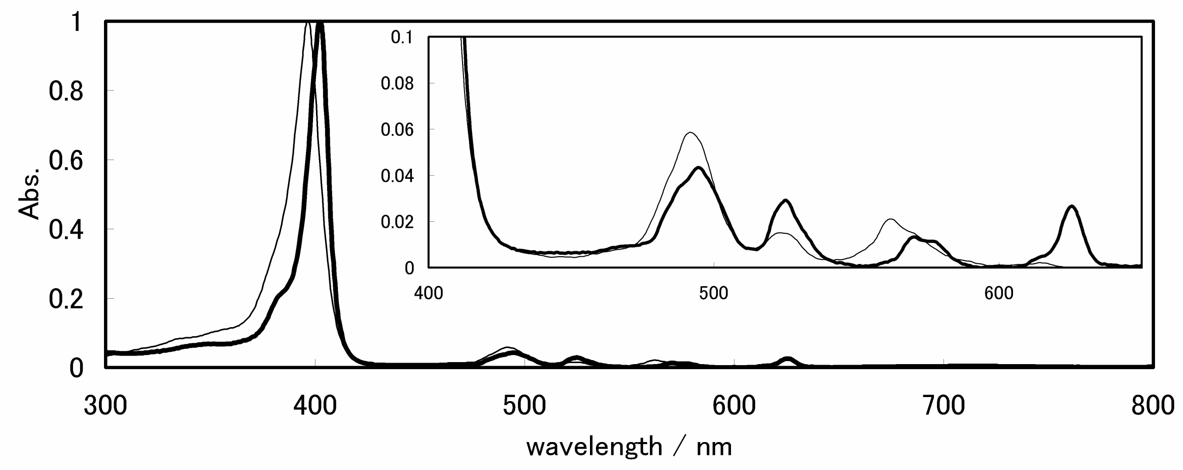


Figure 2. UV-vis spectra of **9** (solid line) and **3** (bold line) in $CHCl_3$.

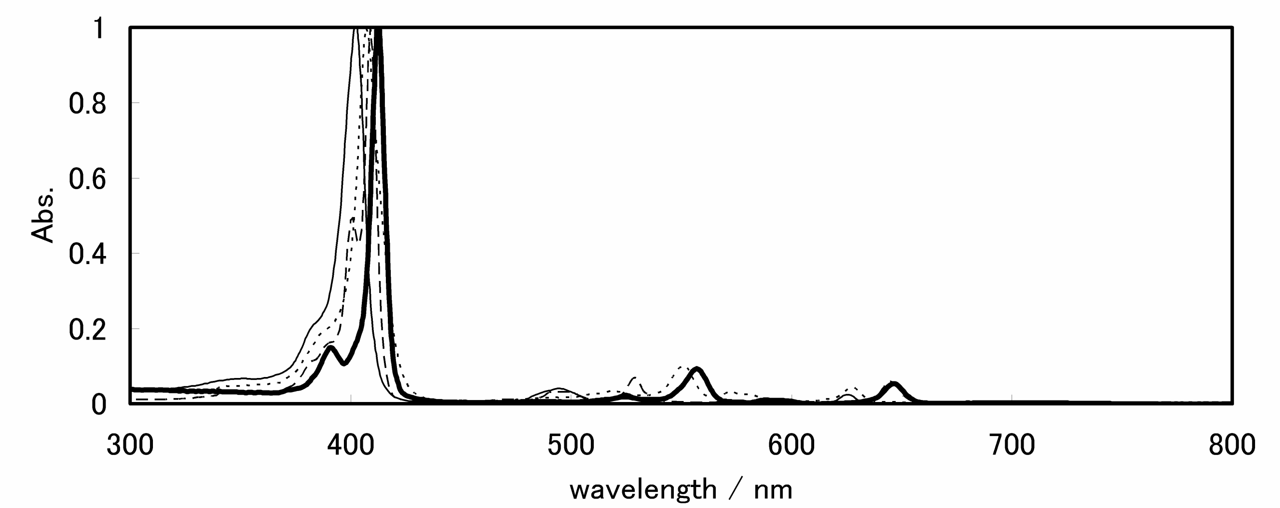


Figure 3. UV-vis spectra of **3** (solid line), **4** (dotted line), **5** (broken line), and **6** (bold line) in $CHCl_3$.

Table 1. Absorption and Fluorescence Data and HOMO-LUMO Energy Gaps of **3**–**6**

	Soret band λ_{ex} / nm	Q bands λ_{abs} / nm				λ_{em} / nm	E_g / eV[a]
3	402	495	525	570	626	628.2	1.98
4	407	520	551	571	627	630.4	1.97
5	409	492	529	593	645	647.5	1.92
6	412	525	557	588	646	649.0	1.91

[a] E_g is the solution optical gap calculated from the longest wavelength absorption and λ_{em}.
$E_g = 2hc / (\lambda_{abs}+\lambda_{em})$; *h*: Planck constant; *c*: light speed

In summary, we have shown that β-, *meso*-unsubstituted mono-, di-, and tribenzoporphyrins were synthesized from their soluble dimethylBCOD-fused precursors by the retro Diels-Alder reaction in nearly quantitative yield. Further work on fabricating OFETs based on these porphyrins by a solution process is under way.

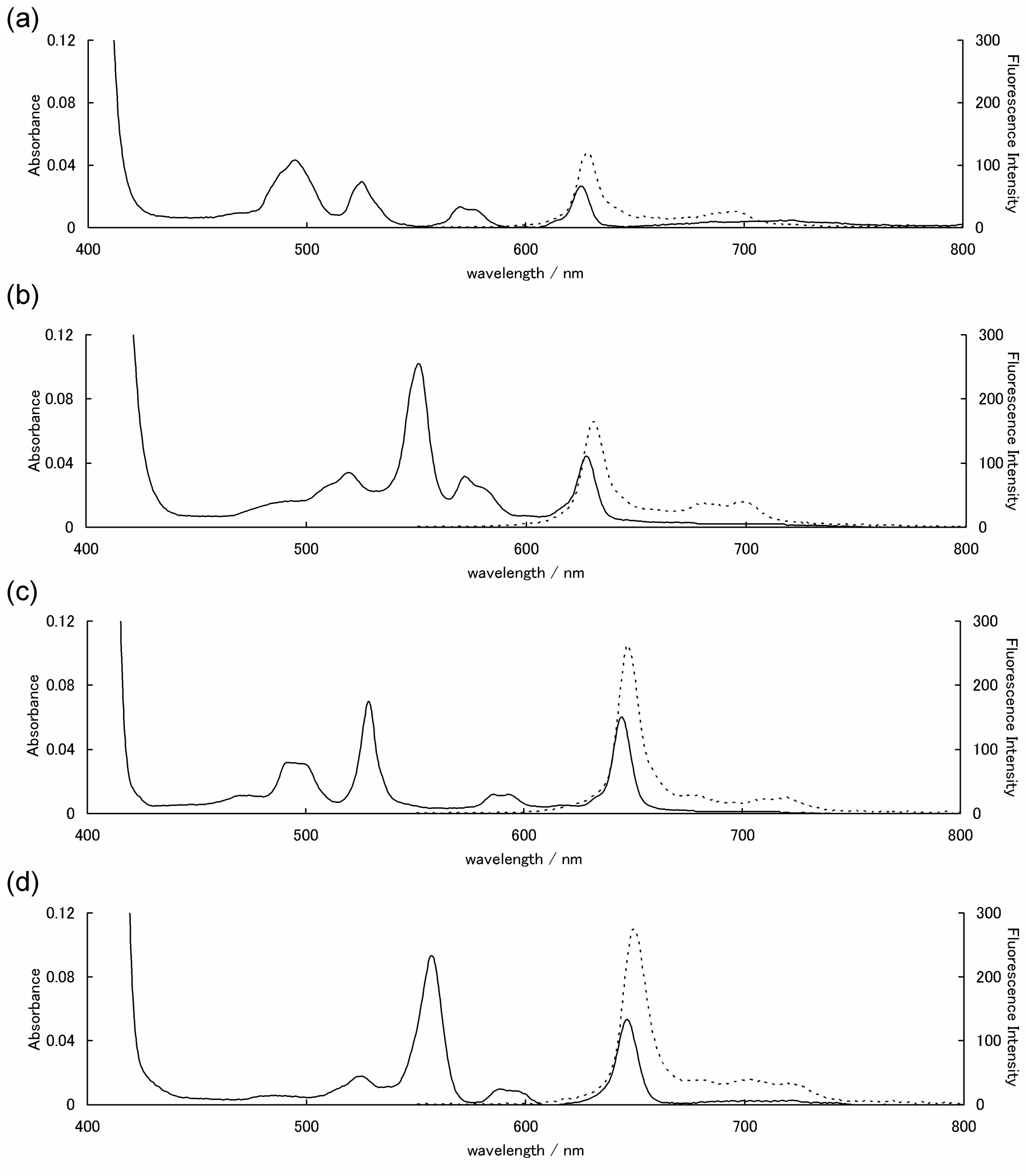


Figure 4. Absorption (solid line) and fluorescence (dotted line) spectra of (a) **3** (λ_{ex} = 402 nm, Soret band), (b) **4** (λ_{ex} = 407 nm), (c) **5** (λ_{ex} = 409 nm), and (c) **6** (λ_{ex} = 412 nm).

EXPERIMENTAL

General. 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. IR spectra were measured on a Horiba FT-720 infrared spectrophotometer, and UV-vis spectra on a JASCO V-570 spectrophotometer. ^{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.

4,7-Dihydro-8,8-dimethyl-4,7-ethano-2*H*-isoindole-1,3-dicarbaldehyde (7b)

TFA (10 mL) was added slowly to **7a** (879 mg, 5.08 mmol) at 0 ºC under an Ar atmosphere and the mixture was stirred for 5 min. After slow addition of methyl orthoformate (12 mL), stirring was coninued at 0 ºC for 2 h. After neutralization with 20% aqueous NaOH, the mixture was 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 $CHCl_3$/EtOAc to give **7b** (644 mg, 55%).

colorless oil; MS (70 eV) *m*/*z* (relative intensity) 230 (M^++1, 45%) and 174 (100); IR (neat) ν_{max} 3260, 1684, 1647 and 1573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H, 1- or 3-CHO), 9.80 (s, 1H, 1- or 3-CHO), 9.14 (br, 1H, NH), 6.60 (ddd, 1H, *J* = 6.3, 6.0, 1.0 Hz, H_6), 6.54 (ddd, 1H, *J* = 6.3, 6.0, 1.0 Hz, H_5), 4.20 (m, 1H, H_4), 3.73 (dd, 1H, *J* = 6.0, 1.0 Hz, H_7), 1.55 (dd, 1H, *J* = 12.0, 2.7 Hz, H_9), 1.34 (dd, 1H, *J* = 12.0, 2.7 Hz, H_9), 1.13 (s, 3H, 8-Me), and 0.76 (s, 3H, 8-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.38 (1- or 3-CHO), 179.30 (1- or 3-CHO), 140.50 (C_{7a}), 139.13 (C_{3a}), 135.73 (C_6), 134.02 (C_5), 128.67 (C_1 or C_3), 126.54 (C_1 or C_3), 45.32 (C_7), 42.78 (C_9), 37.86 (C_8), 33.81 (C_4), 30.56 (8-Me), and 30.53 (8-Me). Anal. Calcd for $C_{14}H_{15}NO_2$·1/4$CHCl_3$: C, 66.05; H, 5.93; N, 5.41. Found: C, 65.98; H, 5.98; N, 5.42.

***t*-Butyl 4,7-dihydro-8,8-dimethyl-4,7-ethano-2*H*-isoindole-1-carboxylate (7d)**

A solution of potassium *t*-butoxide (8.52 g) in dry THF (75 mL) was added dropwise to a stirred solution of **15** (10.44 g, 25.07 mmol) and *t*-butyl isocyanoacetate (5.3 mL) in dry THF (300 mL) at below 0 °C under an Ar atmosphere. The resulting mixture was stirred at rt for 1 d. The reaction mixture was poured into 1 M HCl, evaporated 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 $CHCl_3$ followed by recrystallization with $CHCl_3$/hexane to give **7d** (6.27 g, 91%).

white powder; mp 180.1–181.9 °C; MS (70 eV) *m*/*z* (relative intensity) 274 (M^++1, 2%), 217 (22), and 161 (100); IR (KBr disk) ν_{max} 3321 and 1682 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (br, 1H, NH), 6.53 (ddd, 1H, *J* = 6.5, 6.1, 1.4 Hz, H_6), 6.51 (d, 1H, *J* = 2.7 Hz, H_3), 6.48 (ddd, 1H, *J* = 6.5, 6.1, 1.4 Hz, H_5), 3.77 (d, 1H, *J* = 6.1 Hz, H_7), 3.72 (m, 1H, H_4), 1.57 (s, 9H, 1-CO_2*t*-Bu), 1.39 (dd, 1H, *J* = 11.7, 2.7 Hz, H_9), 1.21 (dd, 1H, *J* = 11.7, 2.7 Hz, H_9), 1.06 (s, 3H, 8-Me), and 0.71 (s, 3H, 8-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.21 (1-CO_2*t*-Bu), 136.05 (C_6), 135.67 (C_{7a}), 135.19 (C_5), 129.80 (C_{3a}), 117.49 (C_1), 112.07 (C_3), 80.12 (1-CO_2*t*-Bu), 46.46 (C_7), 43.86 (C_9), 37.77 (C_8), 34.63 (C_4), 30.90 (8-Me), 30.28 (8-Me), and 28.60 (1-CO_2*t*-Bu). Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.69;

H, 8.38; N, 5.07.

***t*-Butyl 4,7-dihydro-8,8-dimethyl-4,7-ethano-3-formyl-2*H*-isoindole-1-carboxylate (7e)**

A mixture of DMF (1.5 mL) and phosphoryl chloride (1.3 mL) was stirred at 0 ºC for 30 min under an Ar atmosphere. A solution of **7d** (2.73 g, 10.0 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise to this mixture over 30 min at 0 °C. The mixture was stirred at rt for 3 h. After addition of aqueous NaOAc (2.00 g/20 mL) to the reaction mixture, it was stirred at rt for 30 min. The organic layer was washed succesively with water, sat. aqueous $NaHCO_3$, and brine; dried with Na_2SO_4; and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization with $CHCl_3$/hexane to give **7e** (2.92 g, 97%).

white powder; mp 130.5 – 132.0 °C; MS (70 eV) *m*/*z* (relative intensity) 302 (M^++1, 100) and 245 (64); IR (KBr disk) ν_{max} 3301, 1684 and 1666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H, 3-CHO), 9.00 (br, 1H, NH), 6.59 (ddd, 1H, *J* = 6.5, 6.1, 1.0 Hz, H_6), 6.48 (ddd, 1H, *J* = 6.5, 6.1, 1.0 Hz, H_5), 4.14 (m, 1H, H_4), 3.83 (dd, 1H, *J* = 6.1, 1.0 Hz, H_7), 1.59 (s, 9H, 1-CO_2*t*-Bu), 1.50 (dd, 1H, *J* = 11.7, 2.9 Hz, H_9), 1.28 (dd, 1H, *J* = 11.7, 2.9 Hz, H_9), 1.09 (s, 3H, 8-Me), and 0.73 (s, 3H, 8-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.13 (3-CHO), 160.09 (1-CO_2*t*-Bu), 139.89 (C_{3a}), 136.63 (C_6), 136.22 (C_{7a}), 133.52 (C_5), 124.57 (C_3), 122.54 (C_1), 81.97 (1-CO_2*t*-Bu), 46.11 (C_7), 43.03 (C_9), 37.94 (C_8), 33.93 (C_4), 30.65 (8-Me), 30.18 (8-Me), and 28.41 (1-CO_2*t*-Bu). Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.43; H, 7.72; N, 4.57.

***t*-Butyl 4,7-dihydro-8,8-dimethyl-4,7-ethano-3-hydroxymethyl-2*H*-isoindole-1-carboxylate (7f)**

Sodium borohydride (802 mg) was added slowly to a solution of **7e** (2.11 g, 7.00 mmol) in THF (35 mL) and MeOH (15 mL) at 0 °C. The resulting mixture was stirred at the same temperature for 2 h. After addition of water, the mixture was extracted with $CHCl_3$. The organic layer was washed succesively with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. A mixture of the residue with hexane was cooled in a refrigerator, and the resulting precipitate was collected by filtration and washed with cold hexane to give **7f** (1.99 g, 94%).

white powder; mp 140.7 –141.5 °C; MS (70 eV) *m*/*z* (relative intensity) 304 (M^++1, 6%), 247 (76), and 191 (100); IR (KBr disk) ν_{max} 3508, 3406, 2970, 2941, 2862 and 1664 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (br, 1H, NH), 6.52 (ddd, 1H, *J* = 6.6, 6.1, 1.2 Hz, H_6), 6.46 (ddd, 1H, *J* = 6.6, 6.1, 1.2 Hz, H_5), 4.61 (d, 2H, *J* = 5.9 Hz, 3-CH_2OH), 3.74 (dd, 1H, *J* = 6.1, 1.2 Hz, H_7), 3.72 (m, 1H, H_4), 2.11 (br, 1H, 3-CH_2OH), 1.56 (s, 9H, 1-CO_2*t*-Bu), 1.39 (dd, 1H, *J* = 11.7, 2.7 Hz, H_9), 1.19 (dd, 1H, *J* = 11.7, 2.7 Hz, H_9), 1.05 (s, 3H, 8-Me), and 0.71 (s, 3H, 8-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.32 (1-CO_2*t*-Bu), 136.13 (C_6), 136.10 (C_{7a}), 134.92 (C_5), 127.37 (C_{3a}), 125.06 (C_3), 116.94 (C_1), 80.33 (1-CO_2*t*-Bu), 56.43 (3-CH_2OH), 46.55 (C_7), 43.74 (C_9), 37.74 (C_8), 33.72 (C_4), 30.86 (8-Me), 30.28 (8-Me), and 28.61

(1-CO_2*t*-Bu). Anal. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62. Found: C, 71.03; H, 8.32; N, 4.60.

_t_-Butyl 3-acetoxymethyl-4,7-dihydro-8,8-dimethyl-4,7-ethano-2*H*-isoindole-1-carboxylate (7g)

To a solution of **7f** (1.73 g, 5.71 mmol) in $CHCl_3$ (25 mL) were added acetic anhydride (0.9 mL) and 4-(dimethylamino)pyridine (21 mg) at rt. After stirring at rt for 2 h, the reaction mixture was poured into sat. aqueous $NaHCO_3$. The organic layer was washed succesively with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was washed with $CHCl_3$/hexane to give **7g** (1.89 g, 96%).

white powder; mp 102.5 – 103.8 °C; MS (70 eV) *m/z* (relative intensity) 346 (M^++1, 3%), 289 (57), and 233 (100); IR (KBr disk) ν_{max} 3303, 1745 1670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (br, 1H, NH), 6.53 (dd, 1H, *J* = 6.9, 6.2 Hz, H_6), 6.47 (dd, 1H, *J* = 6.9, 6.2 Hz, H_5), 5.03 (d, 1H, *J* = 12.9 Hz, 3-CH_2OAc), 4.96 (d, 1H, *J* = 12.9 Hz, 3-CH_2OAc), 3.77 (m, 1H, H_4), 3.75 (d, 1H, *J* = 6.2 Hz, H_7), 2.06 (s, 3H, 3-CH_2OAc), 1.56 (s, 9H, 1-CO_2*t*-Bu), 1.40 (dd, 1H, *J* = 11.6, 2.7 Hz, H_9), 1.19 (dd, 1H, *J* = 11.6, 2.7 Hz, H_9), 1.06 (s, 3H, 8-Me), and 0.71 (s, 3H, 8-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.32 (3-CH_2OAc), 160.89 (1-CO_2*t*-Bu), 136.17 (C_6), 135.36 (C_{7a}), 134.80 (C_5), 129.79 (C_{3a}), 120.19 (C_3), 117.69 (C_1), 80.38 (1-CO_2*t*-Bu), 57.09 (3-CH_2OAc), 46.47 (C_7), 43.60 (C_9), 37.73 (C_8), 33.76 (C_4), 3.82 (8-Me), 30.27 (8-Me), 28.55 (1-CO_2*t*-Bu), and 21.03 (3-CH_2OAc). Anal. Calcd for $C_{20}H_{27}NO_4$: C, 69.54; H, 7.88; N, 4.05. Found: C, 69.31; H, 7.79; N, 4.03.

Mono(dimethylBCOD)porphyrin 9

A solution of **7b** (238 mg, 1.04 mmol) and **8** (234 mg, 1.04 mmol) in $CHCl_3$ (25 mL) was added dropwise over 30 min to a solution of TFA (8.0 mL) in $CHCl_3$ (100 mL) at rt under an Ar atmosphere in a shaded vessel, and the resulting mixture was stirred for 10 min. The reaction mixture was treated with DDQ (68 mg, 0.30 mmol) for 10 min with stirring at rt, and subsequently neutralized with triethylamine. The resulting black precipitate was removed by filtration with Celite. The filtrate was washed succesively 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 with $CHCl_3$/MeOH to give **9** (32 mg, 7%).

red-violet crystals; MS (FAB) *m/z* 417 (M^++1) and 360; UV-vis ($CHCl_3$) λ_{max}, nm 397, 492, 523, and 562; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H, *meso*-H), 10.34 (s, 1H, *meso*-H), 10.33 (s, 2H, *meso*-H), 9.56 (s, 2H, β-H), 9.45 (m, 4H, β-H), 7.23 (dd, 1H, *J* = 6.6, 5.9 Hz, olefin), 7.17 (dd, 1H, *J* = 6.6, 5.9 Hz, olefin), 5.65 (m, 1H, bridge head), 5.18 (d, 1H, *J* = 5.9 Hz, bridge head), 2.10 (dd, 1H, *J* = 11.7, 2.7 Hz, bridge CH_2), 1.75 (dd, 1H, *J* = 11.7, 2.7 Hz, bridge CH_2), 1.55 (s, 3H, Me), 0.64 (s, 3H, Me), and -4.22 (br, 2H, NH). Anal. Calcd for $C_{28}H_{24}N_4\cdot 1/4H_2O$: C, 79.88; H, 5.86; N, 13.31. Found: C, 80.16; H, 5.94; N, 13.27.

***adj*-Bis(dimethylBCOD)porphyrin 10**

To a solution of **7c** (490 mg, 2.00 mmol) in dry THF was added slowly $LiAlH_4$ (349 mg) at 0 ºC under an Ar atmosphere in a shaded vessel. The resulting mixture was stirred at the same temperature for 3 h. The reaction mixture was poured into water, filtered with Celite, 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 diluted with $CHCl_3$ (300 mL), and dipyrromethane (110 mg, 0.755 mmol) was added at rt under an Ar atmosphere in a shaded vessel. After addition of a solution of *p*-TsOH·H_2O (24 mg) and paraformaldehyde (45 mg) in $CHCl_3$ (100 mL), the mixture was stirred for 25 h, after which *p*-chloranil (214 mg, 0.872 mmol) was added. After stirring at rt for 1 h, the reaction mixture was poured into water. 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 $CHCl_3$ to give **10** (69 mg, 18%).

maroon powder; MS (FAB) *m*/*z* 523 (M^++1), 466, and 410; UV-vis ($CHCl_3$) λ_{max}, nm 394, 493, 523, 563, and 615; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 – 10.34 (m, 4H, *meso*-H), 9.45 – 9.49 (m, 4H, β-H), 7.10 – 7.20 (m, 4H, olefin), 5.55 – 5.61 (m, 2H, bridge head), 5.08 – 5.16 (m, 2H, bridge head), 2.04 – 2.08 (m, 2H, bridge CH_2), 1.73 – 1.78 (m, 2H, bridge CH_2), 1.52 – 1.53 (m, 6H, Me), 0.64 – 0.74 (m, 6H, Me), and -4.26 (br, 2H, NH). Anal. Calcd for $C_{36}H_{34}N_4$·1/2H_2O: C, 81.32; H, 6.64; N, 10.54. Found: C, 81.12; H, 6.60; N, 10.44.

***opp*-Bis(dimethylBCOD)porphyrin 12**

Route A: After bubbling Ar through a solution of **7a** (222 mg, 1.28 mmol) and **11** (163 mg, 1.28 mmol) in $CHCl_3$/MeOH (200 mL/40 mL) in a shaded vessel, BF_3·Et_2O (20 μL) was added at rt under an Ar atmosphere. After the resulting mixture was stirred at the same temperature for 22.5 h, *p*-chloranil (235 mg, 0.956 mmol) was added, and the reaction mixture was poured into water after stirring for 1 h. 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 alumina with $CHCl_3$ and then on silica gel with $CHCl_3$, followed by recrystallization $CHCl_3$/MeOH, to give **12** (16 mg, 5%).

Route B: Tripyrrane **14** was prepared by the reaction of **7g** (345 mg, 1.00 mmol) with pyrrole (35 μL) in the presence of montmorillonite K-10 clay (0.5 g) which was dried by heating at 100 ºC for 30 min *in vacuo*, according to a literature procedure.[16,17] A solution of **14** in TFA (3 mL) was stirred at rt for 10 min under an Ar atmosphere in a shaded vessel. After dilution with $CHCl_3$ (200 mL), **13** (62 mg, 0.50 mmol) was added to the mixture, which was stirred at the same temperature for 22 h. The reaction mixture was neutralized with triethylamine and treated with DDQ (68 mg, 0.30 mmol) for 1 h with stirring at rt. The mixture 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 $CHCl_3$ to give **12** (49 mg, 19%).

red-violet powder; MS (FAB) *m/z* 523 (M^++1), 465, and 410; UV-vis ($CHCl_3$) λ_{max}, nm 398, 496, 529, and 562; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 2H, *meso*-H), 10.35 (s, 2H, *meso*-H), 9.46 (s, 2H, β-H), 9.45 (s, 2H, β-H), 7.25 (ddd, 2H, *J* = 6.3, 5.9, 1.2 Hz, olefin), 7.19 (ddd, 2H, *J* = 6.3, 5.9, 1.2 Hz, olefin), 5.68 (m, 2H, bridge head), 5.20 (dd, 2H, *J* = 5.9, 1.2 Hz, bridge head), 2.12 (dd, 2H, *J* = 11.7, 2.7 Hz, bridge CH_2), 1.76 (dd, 2H, *J* = 11.7, 2.7 Hz, bridge CH_2), 1.56 (s, 6H, Me), 0.63 (s, 6H, Me), and -4.51 (br, 2H, NH). Anal. Calcd for $C_{36}H_{34}N_4\cdot CHCl_3$: C, 69.21; H, 5.49; N, 8.73. Found: C, 68.98; H, 5.56; N, 8.73.

Tris(dimethylBCOD)porphyrin 17

Tripyrrane **16** was prepared by the reaction of **7g** (345 mg, 1.00 mmol) with **7a** (87 mg, 0.50 mmol) in the presence of montmorillonite K-10 clay (0.5 g) which was dried by heating at 100 ºC for 30 min *in vacuo*, as before.[16,17] A solution of **16** in TFA (3 mL) was stirred at rt for 10 min under an Ar atmosphere in a shaded vessel. After dilution with $CHCl_3$ (200 mL), **13** (62 mg, 0.50 mmol) was added to the mixture, which was stirred at the same temperature for 4 h. The reaction mixture was neutralized with triethylamine and treated with DDQ (68 mg, 0.30 mmol) for 30 min with stirring at rt, after which it was poured into aqueous $NaHCO_3$. 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 $CHCl_3$ followed by recrystallization with $CHCl_3$/MeOH to give **17** (66 mg, 20%).

dark violet powder; MS (FAB) *m/z* 629 (M^++1), 572, 515, and 460; UV-vis ($CHCl_3$) λ_{max}, nm 397, 496, 528, 563, and 614; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 – 10.35 (m, 4H, *meso*-H), 9.45 – 9.46 (m, 2H, β-H), 7.08 – 7.26 (m, 6H, olefin), 5.67 – 5.73 (m, 2H, bridge head), 5.53 – 5.58 (m, 1H, bridge head), 5.16 – 5.20 (m, 2H, bridge head), 5.05 – 5.08 (m, 1H, bridge head), 2.05 – 2.14 (m, 3H, bridge CH_2), 1.72 – 1.88 (m, 3H, bridge CH_2), 1.54 – 1.57 (m, 9H, Me), 0.57 – 0.81 (m, 9H, Me), and -4.54 (br, 2H, NH). Anal. Calcd for $C_{44}H_{44}N_4\cdot H_2O$: C, 81.70; H, 7.17; N, 8.66. Found: C, 81.55; H, 6.90; N, 8.38.

Retro Diels-Alder reaction

(DimethylBCOD)porphyrins **9**, **10**, **12**, and **17** (ca. 10 mg each) were heated at 200 ºC under reduced pressure for 10 min in a glass tube to give benzoporphyrins **3 – 6** in quantitative yields.

3: red-violet powder; MS (FAB) *m/z* 360 (M^+); UV-vis ($CHCl_3$) λ_{max}, nm 402, 495, 525, 570, and 626. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 2H, *meso*-H), 10.30 (s, 2H, *meso*-H), 9.56 – 9.60 (m, 4H, pyrrole-β), 9.38 (s, 2H, pyrrole-β), 9.36 (m, 2H, benzo), 8.13 (m, 2H, benzo), and -3.57 (br, 2H, NH); Anal. Calcd for $C_{24}H_{16}N_4$: C, 79.98; H, 4.47; N, 15.55. Found: C, 79.77; H, 4.69; N, 15.32.

4: purple powder; MS (FAB) *m*/*z* 410 (M^+); UV-vis ($CHCl_3$) λ_{max}, nm 407, 520, 551, 572, and 627. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H, *meso*-H), 10.39 (s, 2H, *meso*-H), 10.19 (s, 1H, *meso*-H), 9.52 (m, 2H, benzo), 9.44 (m, 2H, benzo), 9.38 (d, 2H, *J* = 4.2 Hz, pyrrole-β), 9.32 (d, 2H, *J* = 4.2 Hz, pyrrole-β), 8.24 (m, 4H, benzo), and -2.52 (br, 2H, NH); Anal. Calcd for $C_{28}H_{18}N_4$: C, 81.93; H, 4.42; N, 13.65. Found: C, 82.20; H, 4.72; N, 13.36.

5: red-violet powder; MS (FAB) *m*/*z* 410 (M^+); UV-vis ($CHCl_3$) λ_{max}, nm 401, 409, 492, 529, 586, 593, and 645. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 4H, *meso*-H), 9.60 (s, 4H, pyrrole-β), 9.36 (m, 4H, benzo), and 8.12 (m, 4H, benzo); Anal. Calcd for $C_{28}H_{18}N_4$: C, 81.93; H, 4.42; N, 13.65. Found: C, 81.76; H, 4.58; N, 13.50.

6: dark violet powder; MS (FAB) *m*/*z* 460 (M^+); UV-vis ($CHCl_3$) λ_{max}, nm 391, 412, 525, 557, 588, and 646. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 2H, *meso*-H), 10.38 (s, 2H, *meso*-H), 9.62 (m, 2H, benzo), 9.35 (s, 2H, pyrrole-β), 9.33 (m, 2H, benzo), 9.27 (m, 2H, benzo), 8.36 (m, 2H, benzo), 8.10 (m, 4H, benzo), and -2.35 (br, 2H, NH); Anal. Calcd for $C_{32}H_{20}N_4$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.54; H, 4.50; N, 11.95.

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REFERENCES (AND NOTES)

1. S. R. Forrest, *Nature*, 2004, **428**, 911; A. R. Murphy and J. M. J. Fréchet, *Chem. Rev.*, 2007, **107**, 1066; C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, **14**, 99; Y. -L. Loo, *AIChE Journal*, 2007, **53**, 1066; K. Takimiya, Y. Kunugi, and T. Otsubo, *Chem. Lett.*, 2007, **36**, 578.
2. H. Klauk, M. Halik, U. Zschieschang, G. Schmid, and W. Radlik, *J. Appl. Phys.*, 2002, **92**, 5259; T. W. Kelley, L. D. Boardman, T. D. Dunbar, D. V. Muyres, M. J. Pellerite, and T. P. Smith, *J. Phys. Chem. B*, 2003, **107**, 5877.
3. C. D. Sheraw, T. N. Jackson, D. L. Eaton, and J. E. Anthony, *Adv. Mater.*, 2003, **15**, 2009; F. Würthner and R. Schmidt, *ChemPhysChem*, 2006, **7**, 793;M. M. Payne, S. R. Parkin, J. E. Anthony, C. -C. Kuo, and T. N. Jackson, *J. Am. Chem. Soc.*, 2005, **127**, 4986; Y. Li, Y. Wu, P. Liu, Z.

Prostran, S. Gardner, and B. S. Ong, *Chem. Mater.*, 2007, **19**, 418.

4. A. Afzali, C. D. Dimitrakopoulos, and T. L. Breen, *J. Am. Chem. Soc.*, 2002, **124**, 8812; K. P. Weidkamp, A. Afzali, R. M. Tromp, and R. J. Hamers, *J. Am. Chem. Soc.*, 2004, **126**, 12740; C. R. Kagan, A. Afzali, and T. O. Graham, *Appl. Phys. Lett.*, 2005, **86**, 193505; G. S. Tulevski, Q. Miao, A. Afzali, T. O. Graham, C. R. Kagan, and C. Nuckolls, *J. Am. Chem. Soc.*, 2006, **128**, 1788.
5. A. R. Brown, A. Pomp, D. M. de Leeuw, D. B. M. Klaassen, P. Herwig, and K. Müllen, *J. Appl. Phys.*, 1996, **79**, 2136; P. T. Herwig, and K. Müllen, *Adv. Mater.*, 1999, **11**, 480.
6. H. Uno, Y. Yamashita, M. Kikuchi, H. Watanabe, H. Yamada, T. Okujima, T. Ogawa, and N. Ono, *Tetrahedron Lett.*, 2005, **46**, 1981; H. Yamada, Y. Yamashita, M. Kikuchi, H. Watanabe, T. Okujima, H. Uno, T. Ogawa, K. Ohara, and N. Ono, *Chem. Eur. J.*, 2005, **11**, 6212.
7. H. Yamada, T. Okujima, and N. Ono, *Chem. Commun.*, 2008, 2957.
8. M. G. V. Vicente, A. C. Tomé, A. Walter, and J. A. S. Cavaleiro, *Tetrahedron Lett.*, 1997, **38**, 3639; O. S. Finikova, A. V. Cheprakov, I. P. Beletskaya, P. J. Carroll, and S. A. Vinogradov, *J. Org. Chem.*, 2004, **69**, 522.
9. S. Ito, T. Murashima, H. Uno, and N. Ono, *Chem. Commun.*, 1998, 1661; S. Ito, N. Ochi, T. Murashima, H. Uno, and N. Ono, *Heterocycles*, 2000, **52**, 399.
10. T. Okujima, Y. Hashimoto, G. Jin, H. Yamada, H. Uno, and N. Ono, *Tetrahedron*, 2008, **64**, 2405.
11. S. Aramaki, Y. Sakai, and N. Ono, *Appl. Phys. Lett.*, 2004, **84**, 2085; P. B. Shea, J. Kanicki, and N. Ono, *J. Appl. Phys.*, 2005, **98**, 014503; P. B. Shea, J. Kanicki, L. R. Pattison, P. Petroff, M. Kawano, H. Yamada, and N. Ono, *J. Appl. Phys.*, 2006, **100**, 034502; A. S. Dhoot, S. Aramaki, D. Moses, and A. J. Heeger, *Adv. Mater.*, 2007, **19**, 2914.
12. S. H. Lee and K. M. Smith, *Tetrahedron Lett.*, 2005, **46**, 2009.
13. Y. Inokuma, N. Ono, H. Uno, D. Y. Kim, S. B. Noh, D. Kim, and A. Osuka, *Chem. Commun.*, 2005, 3782.
14. S. Taniguchi, H. Hasegawa, M. Nishimura, and M. Takahashi, *Synlett*, 1999, 73; S. Taniguchi, H. Hasegawa, S. Yanagiwa, Y. Tabeta, Y. Nakano, and M. Takahashi, *Tetrahedron*, 2001, **57**, 2103.
15. R. Chong, P. S. Clezy, A. J. Liepa, and A. W. Nichol, *Aust. J. Chem.*, 1969, **22**, 229; P. S. Clezy and G. A. Smythe, *Aust. J. Chem.*, 1969, **22**, 239; Q. W. Wang and D. W. Bruce, *Synlett*, 1995, 1267.
16. T. Okujima, N. Komobuchi, Y. Shimizu, H. Uno, and N. Ono, *Tetrahedron Lett.*, 2004, **45**, 5461; T. Okujima, N. Komobuchi, H. Uno, and N. Ono, *Heterocycles*, 2006, **67**, 255.
17. A. Boudif and M. Momenteau, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1235.
18. H. Uno, Y. Shimizu, H. Uoyama, Y. Tanaka, T. Okujima, and N. Ono, *Eur. J. Org. Chem.*, 2008, 87; J. Mack, M. Bunya, Y. Shimizu, H. Uoyama, N. Komobuchi, T. Okujima, H. Uno, S. Ito, M. J. Stillman, N. Ono, N. Kobayashi, *Chem. Eur. J.*, 2008, **14**, 5001.