A NEW SYNTHESIS OF ACENAPHTHOBENZOPORPHYRIN AND FLUORANTHOBENZOPORPHYRIN

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Dedicated to Professor B. M. Trost on the occasion of his 65th birthday.

Abstract – Benzoporphyrins fused with acenaphthylene or fluoranthene (**3**) and (**4**) were prepared by the condensation of bicyclo[2.2.2]octadiene(BCOD)-fused tripyrrane (**5**) with appropriate pyrrole dialdehydes (**13**) or (**14**) and the subsequent retro Diels-Alder reaction. The absorptions of these new porphyrins were very intense at both Soret and Q bands, which might be useful as organic dyes for solar cells.

INTRODUCTION

Organic conjugated materials are important as active elements in light emitting displays, thin film transistor, solar cells, or other opt-electronic applications.[1] Conjugated cyclic systems like porphyrins and phthalocyanines provide suitable materials for such applications. Their UV-VIS characteristic absorption bands are called Q and B band (or Soret band). The Q band (650-730 nm) of phthalocyanine is intense compared to the B band (320-340 nm). On the other hand, the B band of porphyrins (390-410 nm) is more intense than the Q band (500-600 nm). Extensive reviews of synthesis, spectroscopic properties, and application of porphyrins and phthalocyanines are available.[2] When they are used for organic solar cells, the absorption characteristics of the organic layer should match the solar spectrum as closely as possible.[3] They are also useful for non-linear optical materials such as optical limiting, for they have low ground state absorption over a wide spectral bandwidth and strong excited-state absorption across the same region.[4] As the Q bands are intense in phthalocyanines, phthalocyanines are in principle useful for applications to solar cells. However, synthetic methods of phthalocyanines are limited, and fine tuning of their electronic properties is not easy. On the other hand, recent development of porphyrin synthesis

makes possible the fine tuning of their properties.[2] For example, porphyrin oligomers connected with double or triple bonds,[5] *meso-meso*, β-β, β-β triply linked porphyrin arrays,[6] and expanded porphyrins such as sapphyrins or hexaphyrins[7] extend their conjugation effectively to show remarkable bathochromic shift in near IR regions. In the manipulation of large π-conjugated molecules, one serious problem is poor solubility. In order to resolve such a problem, we employed the retro Diels-Alder strategy. For example, bicyclo[2.2.2]octadiene (BCOD)-fused porphyrin (**1**) is soluble in organic solvents and can be purified by column chromatography. Heating pure **1** affords pure tetrabenzoporphyrin (**2**) in quantitative yield without any purification procedures (Scheme 1).[8] The conversion from **1** to **2** was applied to fabrication of organic thin film transistor. Spin coating of **1** gives amorphous thin film of **1**, which is converted into polycrystalline thin film of **2** by heating at 200 °C. The thin film shows good transistor properties.[9]
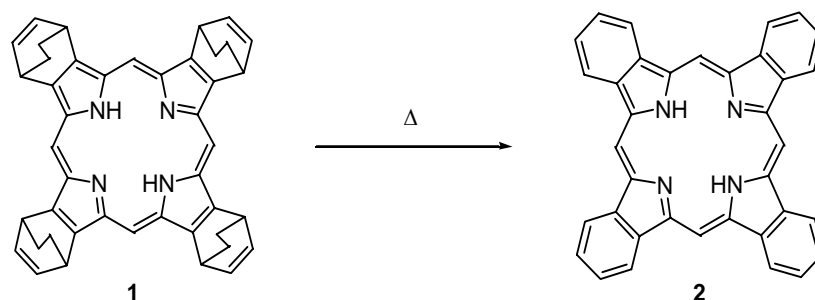
Scheme 1.

In this paper we report a synthesis of acenaphthobenzoporphyrin (**3**) and fluoranthobenzoporphyrin (**4**), which are expected to have intense absorptions near IR region (Chart 1). The longest wave length absorption (S_0-S_1) of **1** or **2** is weak due to symmetrical structure (forbidden). In contrast, S_0-S_1 transition of **3** or **4** is allowed to be intense due to their lower symmetry, which is suitable as dyes for solar cells. Lash and we have prepared a new class of highly conjugated porphyrin chromophores fused with polycyclic aromatic rings.[10,11] Pyrroles fused with polycyclic aromatics such as acenaphthylene or fluoranthene are prepared by the reaction of the corresponding nitro aromatics with ethyl isocyanoacetate.[12] However, available pyrroles are limited in this procedure and we need another strategy for the preparation of **3** and **4**. We have used BCOD-fused tripyrrane (**5**) for the preparation of core-modified tetrabenzoporphyrins.[14] The tripyrrane is now used for the preparation of **3** and **4**.
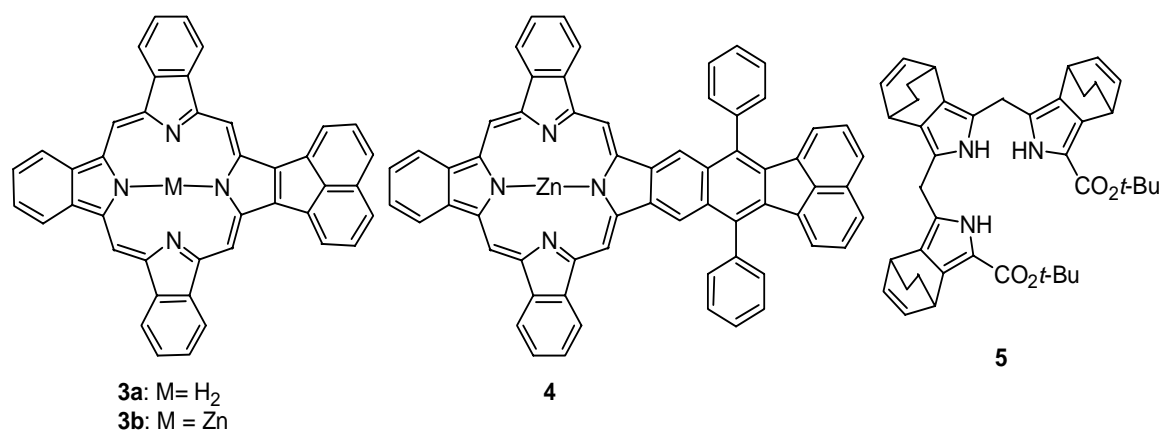
3a: M= H$_2$
3b: M = Zn

4

5

Chart 1.

RESULTS AND DISCUSSION

Synthesis of BCOD-fused pyrroles (**7**) and their conversion into acetoxymethylpyrrole (**10**) or pyrrole dialdehyde (**13**) are summarized in Scheme 2. The Diels-Alder reaction of *trans*-1,2-bis(phenylsulfonyl)ethylene[14] with 1,3-cyclohexadiene, followed by the treatment with ethyl isocyanoacetate or *tert*-butyl isocyanoacetate gave pyrrole (**7a**) (R = CO$_2$Et) or (**7b**) (R = CO$_2$t-Bu), respectively. In previous papers the pyrroles (**7**) were prepared *via* the Diels-Alder reaction of β-phenylsulfonylnitroethylene with 1,3-cyclohexadienes.[8] As *trans*-1,2-bis(phenylsulfonyl)ethylene is more readily prepared than β-sulfonylnitroethylene (it is also commercially available), the present method is more convenient than the original one. Acetoxymethylpyrrole (**10**) was prepared by the formylation of **7b** with POCl$_3$ and DMF, followed by reduction with NaBH$_4$ and acetylation. De-ethoxycarbonylation by heating **7a** with KOH in ethylene glycol at 170 °C gave α-free pyrrole (**7c**). Tripyrranes are generally prepared by the reaction of α-free pyrrole with α-acetoxymethylpyrrole under acidic conditions using *p*-TsOH or AcOH in EtOH, CH$_2$Cl$_2$, or MeCN. However, BCOD-fused tripyrrane (**5**) could not be survived under these conditions. Tripyrrane (**5**) was obtained with mild conditions using Montmorillonite K-10 in dry CH$_2$Cl$_2$ at room temperature. Tripyrrane (**5**) was used without purification for 3 + 1 porphyrin synthesis, as it was decomposed during purification by column chromatography with silica gel. The 3 + 1 porphyrin synthesis was first used in 1994 by Momenteau,[15] then this strategy have been extensively used for the preparation of various kinds of porphyrins and related compounds.[16] Fluoranthoisoindole-1,3-dicarbaldehyde (**13**) and acenaphtho[1,2-*c*]pyrrole-2,9-dicarbaldehyde (**14**) were used as pyrrole dialdehydes. Cyclopenta-fused polycyclic compounds are key compounds in C$_{60}$ structure, and they provide interesting π-conjugation.[17] Therefore, porphyrins (**3**) and (**4**) may be useful as new dyes for opt-electronic materials. Dialdehyde (**13**) was prepared by the Diels-Alder reaction of 7,9-diphenyl-8*H*-cyclopenta[*l*]acenaphthylen-8-one (**12**)[18] with isoindole-1,3-dicalbaldehyde (**11**),[8]

followed by oxidation with DDQ. Dialdehyde (**14**) was prepared from acenaphtho[1,2-*c*]pyrrole according to the literature.[19]
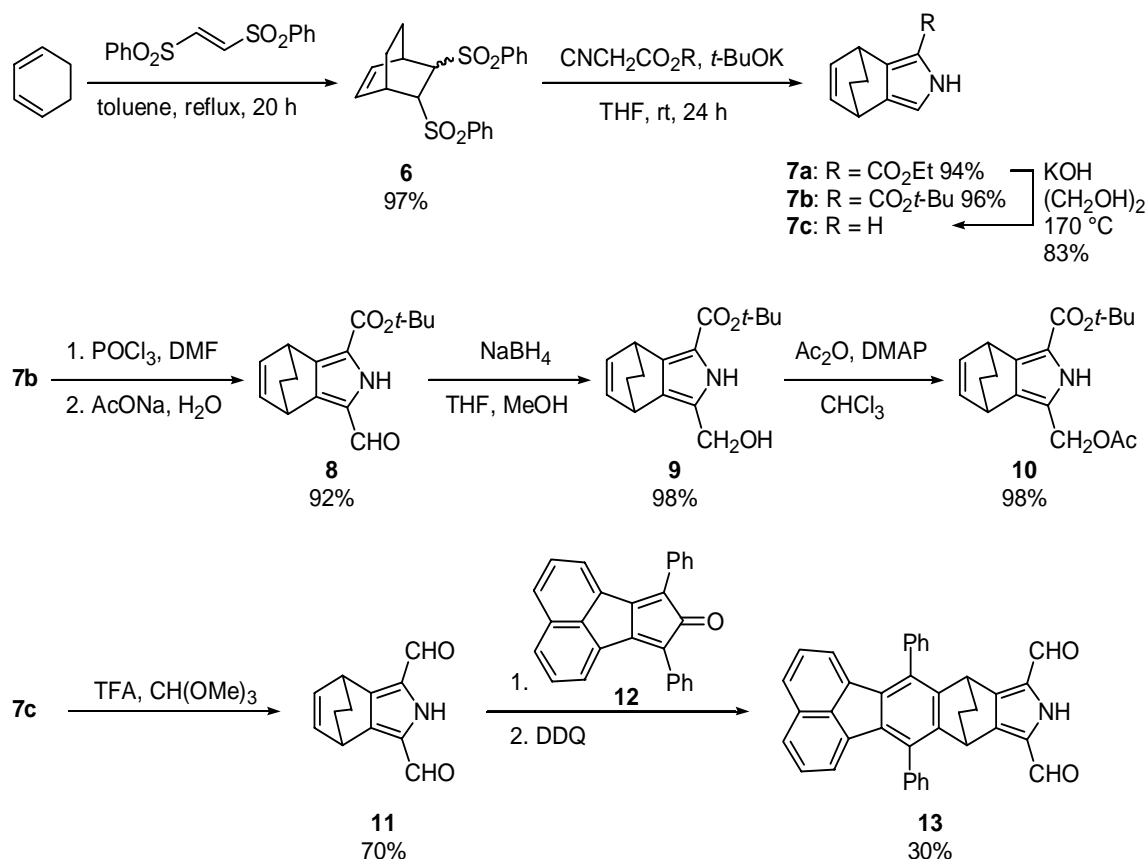
Scheme 2.

The 3 + 1 porphyrin synthesis is shown in Scheme 3. A mixture of crude tripyrrane (**5**) and **14** in CHCl$_3$ containing TFA was stirred at room temperature for 11 h followed by oxidation with DDQ to give porphyrin (**15a**) in 14 % yield. Porphyrin (**15a**) was purified by column chromatography on silica gel and converted into the zinc complex (**15b**) on treatment with Zn(OAc)$_2$. The similar reaction of **5** with **13** yielded the corresponding porphyrin. However, the reaction mixture could not be purified to separate the porphyrin and unreacted **13** and then treated with Zn(OAc)$_2$ to give Zn-porphyrin (**16**) in 24% yield. Heating **15a** at 230 °C for 3 h *in vacuo* resulted in clean retro Diels-Alder reaction to give acenaphthotribenzoporphyrin (**3a**) in quantitative yield. Zinc complex (**15b**) was also converted into **3b**, which proceeded slightly at lower temperature (200 °C) for 3 h. The retro Diels-Alder reaction of **16** proceeded stepwise at 170 and 270 °C by TG analyses. At first, three ethylene units were eliminated from BCOD rings and then another ethylene unit was eliminated by heating. When **16** was heated at 270 °C for 3 h, the color of the crystals was changed from red to deep green to give zinc complex (**4**) in quantitative yield without purification.
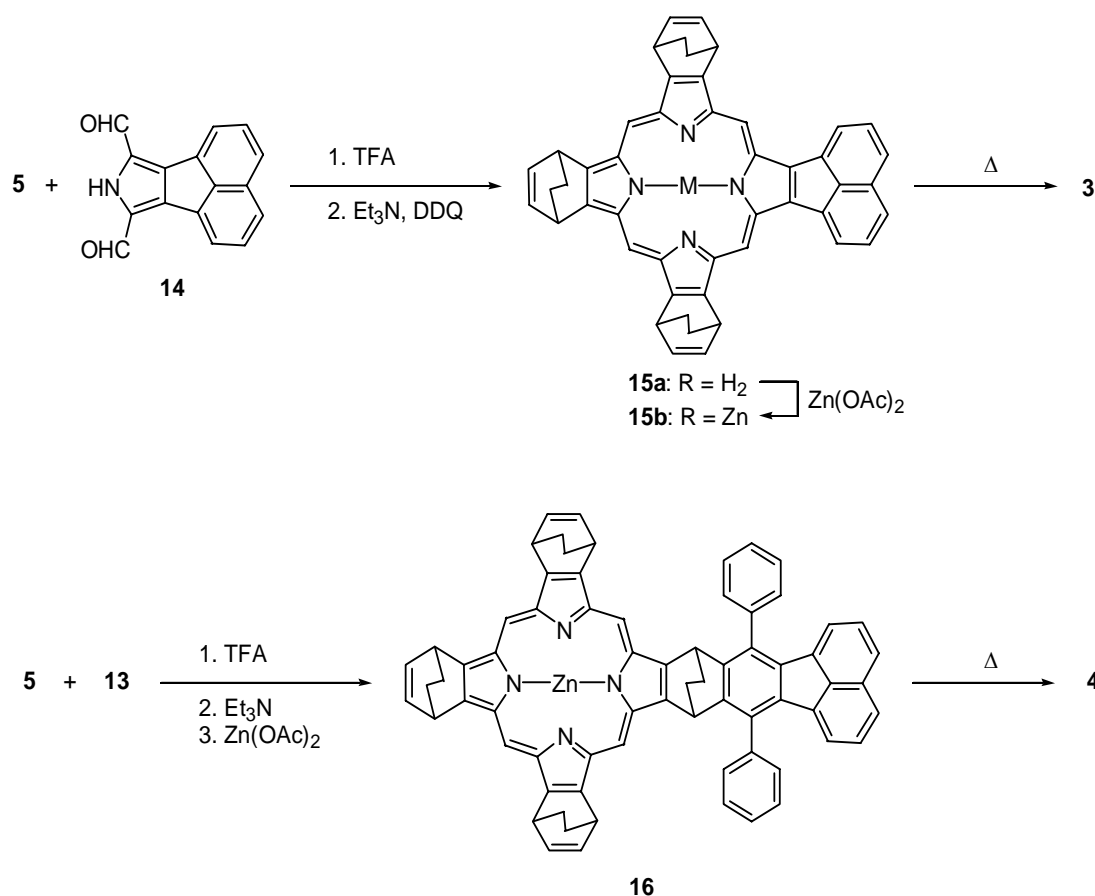
Scheme 3.

The absorption data of porphyrins (**3**), (**4**), (**15**), and (**16**) are summarized in Table 1. Some typical spectra are shown in Figure 1. While porphyrins fused with BCOD such as **15a**, **15b** and **16** were soluble in CH_2Cl_2, benzoporphyrins (**3a**), (**3b**), and (**4**) were insoluble in CH_2Cl_2. The absorption spectra of BCOD-fused porphyrins were similar to those of typical β-substituted porphyrins like octaethylporphyrin. Spectra of them were dramatically changed by the retro Diels-Alder reaction as shown in Figure 1. Such dramatic changes are induced just by heating. They may be useful for color sensor of temperature. Porphyrins (**3**) and (**4**) have some important features in absorption spectra. As expected, the Q bands of **3** and **4** were highly red shifted and very intense compared to those of symmetrical benzoporphyrin (*e.g.* Zn-**2**: λ_{max} 425, 622 nm). For example, zinc complexes (**3b**) and (**4**) showed strong absorptions at 669 (log ε 5.04) and 651 (5.45) nm for S_0-S_1 transition, respectively. The Soret bands of them were also very intense with large molar absorptivity over 10^5 $M^{-1}cm^{-1}$. Thus, **3** and **4** have strong absorptions over wide range of visible region, which may be useful as dyes for solar cells or other optics. Such dyes are quite rare. For example, absorptions of porphyrins are strong near 400 (log ε *ca.* 5) nm, weak near 500-600 (*ca.* 3-4) nm. Intensity of absorptions of phthalocyanines is reverse, strong absorption near 700 (log ε *ca.* 5) nm and weak absorption near 350 (*ca.* 3-4) nm. Tetraacenaphthoporphyrins are known to show long wavelength electronic absorption.[10b,11] Absorptions of zinc complex of tetraacenaphthoporphyrin with

four phenyl groups at the *meso*-positions appear at 558 (log ε 5.35) and 672 (4.39) nm.[10b,11b] The red shifted Soret band of this porphyrin is remarkable, but the Q bands are weak and not so red shifted. On the other hand, **3b** showed intense absorptions at 415 (log ε 5.00), 440 (5.05), 461 (5.11), and 669 (5.04) nm. The Q band of **4** (651 nm, log ε 5.45) was strong and sharp. Thus, benzoporphyrins with another fused aromatic ring are expected to afford useful dyes with strong absorption at 650-670 nm.

In conclusion, BCOD-fused acenaphtho- and fluoranthoporphyrins (**15**) and (**16**) were synthesized by 3 + 1 porphyrin synthesis of BCOD-fused tripyrrane (**5**) with dialdehydes. These porphyrins were cleanly converted into unsymmetrical π-expanded porphyrins (**3**) and (**4**) by retro Diels-Alder reaction. Both of Soret and Q bands of them exhibited strong absorptions with a bathochromic shift compared with those of BCOD-fused ones. Application of these dyes for solar cells is under investigation in our group.

Table 1. Absorption Maxima of Porphyrins (**3**), (**4**), (**15**), and (**16**)

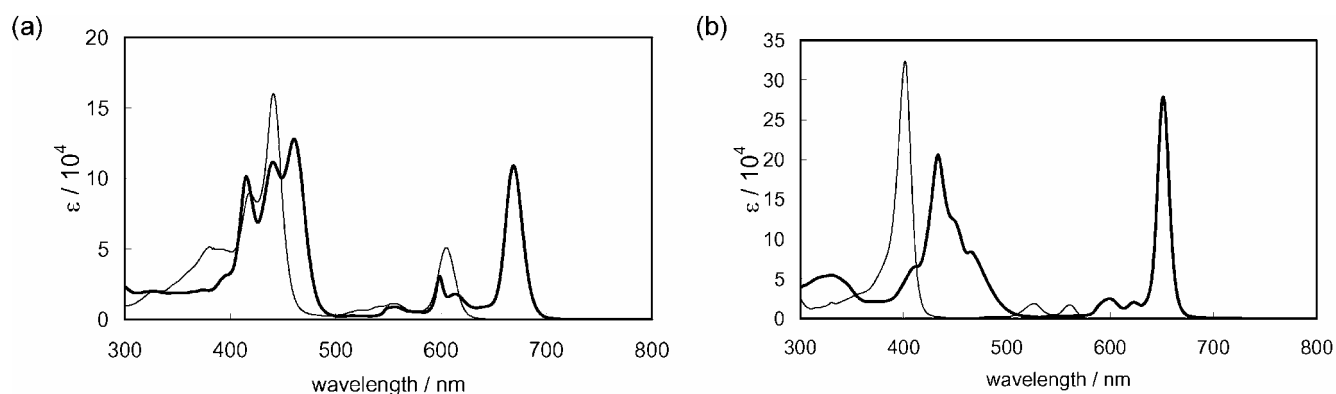| sample	solvent	λ_{max}, nm (log ε)	
15a	CH_2Cl_2	385 (4.83), 430 (5.07)	523 (4.07), 564 (4.45), 584 (4.17), 650 (3.93)
15b	CH_2Cl_2	419 (4.95), 441 (5.20)	555 (4.06), 605 (4.71)
16	CH_2Cl_2	401 (5.51)	526 (4.28), 561 (4.23)
3a	DMF	421 (4.69), 438 (4.85), 461 (4.74)	540 (4.00), 572 (4.33), 633 (3.62), 691(4.58)
3b	DMF	415 (5.00), 440 (5.05), 461 (5.11)	556 (3.96), 599 (4.48), 613 (4.26), 669 (5.04)
4	DMF	433 (5.31), 465 (4.93)	599 (4.40), 623 (4.31), 651 (5.45)

Figure 1. UV-VIS spectra of (a) **15b** (solid line) in CH_2Cl_2, **3b** (bold line) in DMF, (b) **16** (solid line) in CH_2Cl_2, and **4** (bold line) in DMF.

EXPERIMENTAL

General. Melting points were determined on a Yanaco micro melting point apparatus MP500D and are uncorrected. DI-EI and FAB mass spectra were measured on a JEOL JMS-700. MALDI-TOF mass spectra were measured on Voyager DE Pro (Applied Biosystems). IR spectra were taken on a Horiba

FT-720 Infrared Spectrophotometer. UV-VIS spectra were measured on a JASCO V-570 spectrophotometer and a Hitachi U-2810 spectrophotometer. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL AL-400 at 400 MHz (100 MHz). Gel permeation chromatography (GPC) was performed on a JAIGEL 2.5-H. Elemental analyses were performed at Integrated Center for Sciences, Ehime University.

Pyrroles (**7a**) and (**7b**) were prepared by the modified procedure of the original method,[8] and 4,7-dihydro-4,7-ethano-2*H*-isoindole (**7c**) and 4,7-dihydro-4,7-ethano-2*H*-isoindole-1,3-dicarbaldehyde (**11**) were prepared according to the reported procedures.[8]

2,3-Bis(phenylsulfonyl)bicyclo[2.2.2]oct-5-ene (6)[20]

A solution of *trans*-1,2-bis(phenylsulfonyl)ethylene (37.1 g, 120 mmol) and 1,3-cyclohexadiene (18 mL, 180 mmol) in toluene (150 mL) was refluxed for 20 h. The solvent was removed under reduced pressure, and the product was washed with ether to give **6** (45.2 g, 97%) as white powder.

Ethyl 4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (**7a**)

To a stirred solution of **6** (15.5 g, 40.0 mmol) and ethyl isocyanoacetate (5.6 mL, 52.0 mmol) in THF (170 mL) was added a 1 M solution of potassium *tert*-butoxide in THF (120 mL) at 0 °C under an Ar atmosphere. The resulting mixture was stirred at rt for 15 h. The reaction mixture was poured into 1 M HCl and extracted with CHCl$_3$. The organic layer was washed with sat. aqueous NaHCO$_3$, water, brine, and dried with Na$_2$SO$_4$. After removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with CHCl$_3$, followed by recrystallization from CHCl$_3$/hexane to give **7a** (8.16 g, 94%) as white crystals (mp 129-130 °C).

tert-Butyl 4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (**7b**)

To a stirred solution of **6** (9.70 g, 25.0 mmol) and *tert*-butyl isocyanoacetate (5.5 mL, 37.5 mmol) in THF (350 mL) was added a 1 M solution of potassium *tert*-butoxide in THF (75 mL) at 0 °C under an Ar atmosphere. The resulting mixture was stirred at rt for 15 h. The reaction mixture was poured into 1 M HCl and extracted with CHCl$_3$. The organic layer was washed with sat. aqueous NaHCO$_3$, water, brine, and dried with Na$_2$SO$_4$. After removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with CHCl$_3$, followed by recrystallization from CHCl$_3$/hexane to give **7b** (5.86 g, 96%) as white crystals (mp 181.5-183.1 °C).

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

To a solution of N,N-dimethylformamide (1.1 mL, 14 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise a solution of $POCl_3$ (1.3 mL, 14 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C under an Ar atmosphere. The resulting mixture was stirred at rt for 30 min. A solution of **7b** (2.45 g, 10.0 mmol) in dry CH_2Cl_2 (70 mL) was added dropwise at 0 °C to the reaction mixture and stirred at rt for 1.5 h. After an addition of aqueous sodium acetate to the reaction mixture at 0 °C, the mixture was stirred at rt for 30 min. The organic layer was washed with sat. aqueous $NaHCO_3$, water, brine, and dried with Na_2SO_4. After removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ to give **8** (2.50 g, 92%).

8; colorless plates; mp 100.5–102.0 °C (hexane); MS (70 eV) m/z (rel intensity) 273 (M$^+$, 25%); IR (KBr disk) ν_{max} 3317, 2974, 1697, 1670, 1454, 1369, 1269, 1138, and 687cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.72 (s, 1H), 9.03 (br s, 1H), 6.48–6.57 (m, 2H), 4.39 (d, 1H, J = 4.9 Hz), 4.27 (d, 1H, J = 4.9 Hz), 1.63 (m, 2H), 1.59 (s, 9H), and 1.49 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 178.14, 160.01, 141.04, 136.14, 135.93, 134.39, 124.53, 120.61, 82.08, 33.31, 32.59, 28.39, 26.51, and 26.09; Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.36; H, 7.08; N, 5.12.

***tert*-Butyl 4,7-dihydro-4,7-ethano-3-hydroxymethyl-2*H*-isoindole-1-carboxylate (9)**

To a solution of **8** (2.50 g, 9.15 mmol) in THF/methanol (40 mL/20 mL) was added sodium borohydride (1.04 g, 27.5 mmol) at 0 °C. The resulting mixture was stirred at same temperature for 1 h. After an addition of water, the mixture was extracted with ethyl acetate. The organic layer was washed with water, brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by recrystallization from hexane to give **9** (2.47 g, 98%).

9; white crystals; mp 144.0–146.6 °C (hexane); MS (70 eV) m/z (rel intensity) 275 (M$^+$, 12%); IR (KBr disk) ν_{max} 3425, 3267, 1670, 1647, 1369, 1269, 1142, and 1092 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.61 (br s, 1H), 6.48 (m, 2H), 4.63 (m, 2H), 4.31 (m, 1H), 3.86 (m, 1H), 1.97 (m, 1H), 1.57 (s, 9H), 1.48 (m, 2H), and 1.41 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.05, 136.12, 135.77, 135.50, 128.69, 124.93, 114.82, 80.44, 56.38, 33.71, 32.39, 28.58, 27.09, and 26.35; Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.73; H, 7.69; 5.06.

***tert*-Butyl 3-acetoxymethyl-4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (10)**

To a solution of **9** (2.47 g, 8.97 mmol) in $CHCl_3$ (40 mL) were added acetic anhydride (1.1 mL, 11 mmol) and catalytic amounts of 4-dimethylaminopyridine at rt. After the resulting mixture was stirred at same temperature for 2 h, the reaction mixture was poured into sat. aqueous $NaHCO_3$. The organic layer was washed with water, brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was washed with ether and hexane to give **10** (2.78 g, 98%).

10; white needles; mp 160.4–161.4 °C; MS (70 eV) m/z (rel intensity) 317 (M$^+$, 9%); IR (KBr disk) ν_{max} 3325, 2981, 1739, 1678, 1362, 1338, 1288, 1230, 1165, 1142, 1088, 1022 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.55 (br s, 1H), 6.49 (m, 2H), 5.01 (m, 2H), 4.31 (m, 1H), 3.91 (m, 1H), 2.06 (s, 3H), 1.57 (s, 9H), 1.48 (m, 2H), and 1.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.33, 160.71, 135.65, 135.54, 135.42, 131.12, 120.17, 115.57, 80.51, 57.01, 33.66, 32.44, 28.53, 26.98, 26.32, and 21.01; Anal. Calcd for C$_{18}$H$_{23}$NO$_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 67.83; H, 7.33; N, 4.45.

4,13-Dihydro-5,12-diphenyl-4,13-ethano-2*H*-fluorantho[8,9-*f*]isoindole-1,3-dicarbaldehyde (13)

A solution of **11** (523 mg, 2.60 mmol) and **12** (713 mg, 2.00 mmol) in xylene (20 mL) was stirred at 130 °C for 3 days. After an addition of hexane (100 mL), the mixture was cooled in refrigerator overnight. The precipitate was collected by filtration and the recrystallization from CHCl$_3$/hexane for filtrate gave crystals.

A mixture of the combined crystals and DDQ (0.45 g) in CHCl$_3$ (100 mL) was stirred at rt for 12 h. The reaction mixture was poured into water. The organic layer was washed with water, brine, and dried with Na$_2$SO$_4$. After removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with CHCl$_3$, GPC with CHCl$_3$, and recrystallization from CHCl$_3$/hexane to give **13** (314 mg, 30%)

13; pale yellow powder; mp 200 °C (decomp); MS (FAB) m/z 528 (M$^+$+1); IR (KBr) ν_{max} 3289, 1678, 1651, 1215, and 775 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.69 (s, 2H), 9.21 (br s, 1H), 7.65 (m, 10H), 7.40 (m, 2H), 7.27 (m, 2H), 6.67 (d, 2H, J = 7.1 Hz), 4.71 (s, 2H), 1.90 (m, 2H), and 1.74 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 179.06, 140.68, 140.10, 138.49, 136.13, 134.93, 133.21, 132.62, 129.25, 129.15, 129.10, 128.94, 128.01, 127.54, 127.26, 126.37, 122.86, 33.39, and 26.72; Anal. Calcd for C$_{38}$H$_{25}$NO$_2$·1/2H$_2$O·1/2CHCl$_3$: C, 77.55; H, 4.48; N, 2.35. Found: C, 77.77; H, 4.55; N, 2.66.

BCOD-fused acenaphthoporphyrin (15a)

Montmorillonite K-10 clay (1.0 g) was added to a degassed solution of **7c** (145 mg, 1.00 mmol) and **10** (635 mg, 2.00 mmol) in dry CH$_2$Cl$_2$ (30 mL) in a shaded vessel. The resulting mixture was stirred at 30 °C for 6 h under an Ar atmosphere. After the insoluble material was removed by filtration, the filtrate was poured into sat. aqueous NaHCO$_3$. The organic layer was washed with water, dried with Na$_2$SO$_4$, and concentrated under reduced pressure.

A solution of the crude **5** in trifluoroacetic acid (2 mL) was stirred at rt for 10 min under an Ar atmosphere in a shaded vessel. The mixture was diluted with CHCl$_3$ (100 mL), followed by an addition of **14** (247 mg, 1.00 mmol) and stirred at same temperature for 11 h. The reaction mixture was neutralized with triethylamine and treated with DDQ (227 mg, 1.00 mmol) for 4.5 h with stirring at rt. The mixture

was washed with water, brine, and dried with Na_2SO_4. After removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ and recrystallization from $CHCl_3$/methanol to give **15a** (95 mg, 14%).

15a; red purple crystals; mp 200 °C (decomp); MS (FAB) *m/z* 669 (M$^+$+1); UV-VIS (CH_2Cl_2) λ_{max} nm (log ε) 385 (4.83), 430 (5.07), 523 (4.07), 564 (4.45), 584 (4.17), and 650 (3.93); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 2H), 10.29 (s, 2H), 8.97 (d, 2H, *J* = 6.3 Hz), 8.00 (d, 2H, *J* = 7.8 Hz), 7.92 (t, 2H, *J* = 7.3 Hz), 7.16 (m, 6H), 5.78 (m, 6H), 1.93-2.27 (m, 12H), and -4.09 (br s, 2H); Anal. Calcd for $C_{48}H_{36}N_4 \cdot 1/2H_2O$: C, 85.05; H, 5.50; N, 8.27. Found: C, 84.97; H, 5.39; N, 8.14.

BCOD-fused [acenaphthoporphyrinato]zinc(II) (15b)

A mixture of **15a** (25 mg, 0.037 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (68 mg, 0.37 mmol) in methanol/$CHCl_3$ (5 mL/20 mL) was stirred at rt for 18 h. After filtration, the filtrate was washed with water, brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was recrystalized from $CHCl_3$/methanol to give **15b** (26 mg, 95%).

15b; black crystals; mp 200 °C (decomp); MS (FAB) *m/z* 730 (M$^+$); UV-VIS (CH_2Cl_2) λ_{max} nm (log ε) 380 (4.71), 419 (4.95), 441 (5.20), 555 (4.06), and 605 (4.71); ^{1}H NMR (400 MHz, pyridine-d_5/$CDCl_3$) δ 10.58 (s, 2H) 10.18 (s, 2H), 8.99 (d, 2H, *J* = 6.6 Hz), 7.99 (d, 2H, *J* = 8.1 Hz), 7.93 (t, 2H, *J* = 7.4 Hz), 7.16 (m, 6H), 5.75 (m, 6H), and 1.83-2.19 (m, 12H); ^{13}C NMR (100 MHz, pyridine-d_5/$CDCl_3$) δ 150.06, 149.93, 149.56, 146.25, 143.71, 143.69, 143.57, 142.66, 140.88, 136.90, 136.83, 135.22, 130.59, 128.16, 126.72, 123.63, 122.59, 100.09, 97.42, 97.34, 36.70, 36.68, 36.63, 36.55, 28.13, 28.05, and 28.01; Anal. Calcd for $C_{48}H_{34}N_4Zn \cdot 2H_2O$: C, 75.04; H, 4.99; N, 7.29. Found: C, 75.30; H, 5.01; N, 7.10.

Acenaphtho[*q*]tribenzo[*b,g,l*]porphyrin (3a)

Porphyrin (**15a**) (10 mg) was heated at 230 °C under reduced pressure in grass tube for 30 min to give **3a**.

3a; black crystals; mp >250 °C; MS (MALDI-TOF) *m/z* 584 (M$^+$); UV-VIS (DMF) λ_{max} nm (log ε) 421 (4.69), 438 (4.85), 461 (4.74), 540 (4.00), 572 (4.33), 633 (3.65), and 691 (4.58); (1% TFA/CH_2Cl_2) λ_{max}, nm (log ε) 449 (5.32), 590 (4.04), 637 (4.40), 682 (4.49), and 699 (4.89); Anal. Calcd for $C_{42}H_{24}N_4$: C, 86.28; H, 4.14; N, 9.58. Found: C, 86.09; H, 4.24; N, 9.39.

[Acenaphtho[*q*]tribenzo[*b,g,l*]porphyrinato]zinc(II) (3b)

Porphyrin **15b** (10 mg) was heated at 200 °C under reduced pressure in grass tube for 3 h to give **3b**.

3b; dark green crystals; mp >250 °C; MS (FAB) *m/z* 646 (M$^+$); UV-VIS (DMF) λ_{max} nm (log ε) 415 (5.00), 440 (5.05), 461 (5.11), 556 (3.96), 599 (4.48), 613 (4.26), and 669 (5.04); ^{1}H NMR (400 MHz, pyridine-d_5/$CDCl_3$) δ 9.80 (s, 4H), 9.16 (m, 6H), 8.53 (d, 2H, *J* = 5.9 Hz), 8.15 (m, 6H), 7.95 (d, 2H, *J* =

7.5 Hz), and 7.87 (t, 2H, J = 7.2 Hz); Anal. Calcd for $C_{42}H_{22}N_4Zn \cdot H_2O$: C, 75.74; H, 3.63; N, 8.41. Found: C, 75.35; H, 3.96; N, 8.08.

BCOD-fused fluoranthoporphyrin (16)

Tripyrrane (**5**) was prepared by the reaction of **7c** (73 mg, 0.50 mmol) with **10** (318 mg, 1.00 mmol) in the presence of Montmorillonite K-10 clay (0.5 g). A solution of the crude **5** in trifluoroacetic acid (2 mL) was stirred at rt for 10 min under an Ar atmosphere in a shaded vessel. The mixture was diluted with $CHCl_3$ (100 mL), followed by an addition of **13** (264 mg, 0.500 mmol) and stirred at same temperature for 12 h. The reaction mixture was neutralized with triethylamine, washed with water, brine, and dried with Na_2SO_4. After an addition of methanol (20 mL) and $Zn(OAc)_2 \cdot 2H_2O$ (276 mg, 1.5 mmol), the mixture was stirred at rt for 18 h. The reaction mixture was washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and recrystallization from $CHCl_3$/methanol to give **16** (119 mg, 24%).

16; red crystals; mp 170 °C (decomp); MS (FAB) m/z 1012 (M$^+$+2); UV-VIS (CH_2Cl_2) λ_{max} nm (log ε) 401 (5.51), 526 (4.28), and 561 (4.23); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.40(s, 2H), 10.26 (s, 2H), 7.89 (m, 8H), 7.52-7.68 (m, 4H), 7.16 (m, 8H), 6.74 (m, 2H), 6.08 (m, 2H), 5.70 (m, 6H), and 1.89-2.42 (m, 16H); Anal. Calcd for $C_{70}H_{50}N_4Zn$ 1/2H_2O 3/4$CHCl_3$: C, 76.48; H, 4.69; N, 5.04. Found: C, 76.28; H, 4.74; N, 5.24.

[Fluoranthobenzoporphyrinato]zinc(II) (4)

Porphyrin (**16**) (34 mg) was heated at 270 °C under reduced pressure in grass tube for 3 h to give **4**.

4; dark green crystals; mp >250°C; MS (FAB) m/z 898 (M$^+$); UV-VIS (DMF) λ_{max} nm (log ε) 330 (4.74), 433 (5.31), 465 (4.93), 599 (4.40), 623 (4.31), and 651 (5.45); ^{1}H NMR (400 MHz, pyridine-d_5/CDCl$_3$) δ 9.72 (s, 2H), 9.67 (s, 2H), 9.58 (s, 2H), 9.14 (m, 4H), 8.99 (m, 2H), 8.17 (m, 6H), 8.08 (m, 10H), 7.79 (d, 2H, J = 7.8 Hz), 7.46 (t, 2H, J = 7.4 Hz), and 6.81 (d, 2H, J = 6.9 Hz); ^{13}C NMR (100 MHz, pyridine-d_5/CDCl$_3$) δ 139.72, 136.97, 136.26, 136.06, 134.59, 131.88, 130.58, 130.23, 129.68, 128.30, 127.91, 125.75, 125.63, 121.98, 120.87, 120.65, and 120.57; Anal. Calcd for $C_{62}H_{34}N_4Zn$: C, 82.71; H, 3.81; N, 6.22. Found: C, 82.56; H, 3.98; N, 6.13.

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