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SYNTHESIS OF TETRABENZOPORPHYRINS FUSED WITH FLUORANTHENES

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Dedicated to Professor Emeritus Akira Suzuki on the occasion of his 80th birthday

Abstract – Tetrabenzoporphyrins fused with fluoranthenes were prepared by the retro Diels-Alder reaction of the precursors composed of a porphyrin and four fluoranthenes connected with bicyclo[2.2.2]octadiene (BCOD). These porphyrins exhibited the Soret (480–494 nm, $\epsilon = 243,000$ – $277,000$) and intense Q bands (739–760 nm, $\epsilon = 375,000$ – $509,000$). Free bases and Zn complexes of them fluoresce at 760 nm and 746 nm with small Stokes shifts and high quantum yields of 30 and 10 %, respectively.

INTRODUCTION

Linearly π -expanded porphyrins have attracted the interest of many research groups for applications such as light emitting displays, thin film transistor, solar cells, photosensitizers for photodynamic therapy (PDT), or other opt-electronic materials.¹ One of the simple strategy for π -expansion of porphyrin is fusion of aromatic rings such as benzene ring at β -positions. Although tetrabenzoporphyrins (TBPs) are most extensively studied porphyrinoid fused with benzene rings, little is known about tetra[2,3]naphtho- and tetra[2,3]anthraporphyrins without *meso*-substituents compared to TBPs.^{2–5} Linearly ring-expansion results in the destabilization against oxidation and reduction as predicted by the molecular orbital calculation by Kobayashi et al.⁶ In spite of the instability, we have succeeded in the synthesis of tetra[2,3]anthraporphyrins by retro Diels-Alder strategy from the BCOD-fused precursors, which showed strong absorptions in the near-IR region.⁷ On the other hand, the porphyrins fused with polycyclic

aromatic rings such as acenaphthylene or phenanthrene show weak Q bands at 600–900 nm.^{8–10} In 2006, we have reported the synthesis of fluoranthobenzoporphyrin **1** by the [3 + 1] porphyrin synthesis and the subsequent retro Diels-Alder reaction.¹¹ The porphyrin **1** showed a strong absorption at 651 nm ($\log \varepsilon 5.45$) for S_0-S_1 transition. Both Soret and Q bands are very strong absorptions with large molar absorption coefficient over $10^5 \text{ M}^{-1}\text{cm}^{-1}$. The fused aromatic ring in **1** consists of naphthalene and acenaphthylene. Thus, this strategy is expected to afford efficiently π -expanded porphyrins with intense absorptions in the near-IR region. We report herein the synthesis of tetra[8,9]fluoranthoTBPs **2** and **3**, which are expected to be more stable linearly π -expanded porphyrins than tetra[2,3]anthraporphyrins, from the BCOD-fused precursors by the retro Diels-Alder reaction.

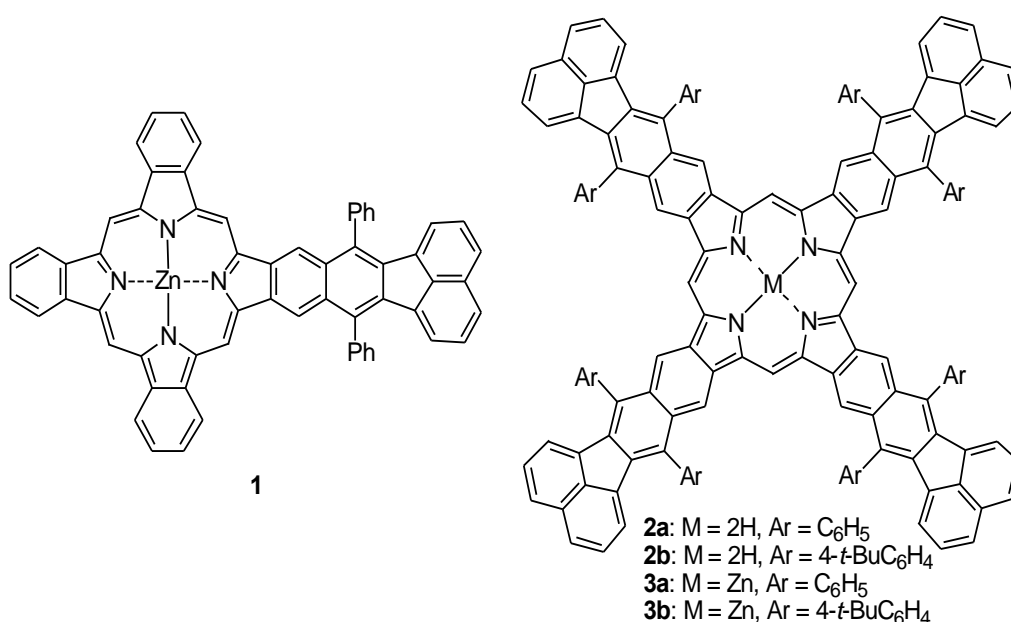


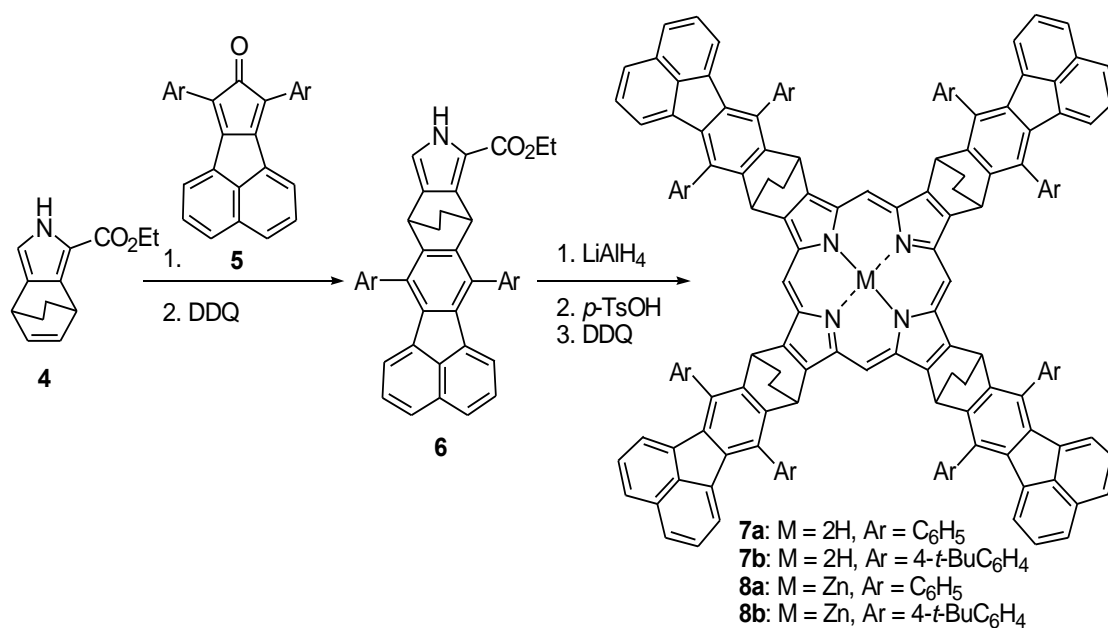
Chart 1

RESULTS AND DISCUSSION

Synthesis of BCOD-fused porphyrins **7** and **8** is summarized in Scheme 1. Diels-Alder reaction of **4**^{11,12} with **5**¹³ followed by oxidation with DDQ afforded fluorantho[8,9-*f*]isoindoles **6** in good yields. Porphyrins **7** were synthesized by reduction of **6** with LiAlH₄ followed by tetramerization and oxidation with DDQ¹⁴ and purified by column chromatography on silica gel with CHCl₃ to give two fractions of R_f 0.9 and 0.4 for **7a** and R_f 0.5 and 0.2 for **7b**, respectively. The relative ratio of R_f 0.9/0.4 (**7a**) is 69/31 and that of R_f 0.5/0.2 (**7b**) is 35/65. Free base porphyrins **7a** and **7b** were treated with Zn(OAc)₂ to give their zinc complexes **8a** and **8b** in 77% and 96% yields, respectively.

¹H NMR spectra of **7a** and **7b** in aromatic region are shown in Figure 1. *Meso*-CH signals of **7a** (R_f 0.4) and **7b** (0.2) were observed as a singlet peak, while those of **7a** (0.9) and **7b** (0.5) were observed as two intense and several small singlet peaks, and a number of singlet peaks, respectively. This indicates that **7a**

(0.4) and **7b** (0.2) consist of a single isomer and have either cone- or 1,3-altenative-typed configuration.



Scheme 1

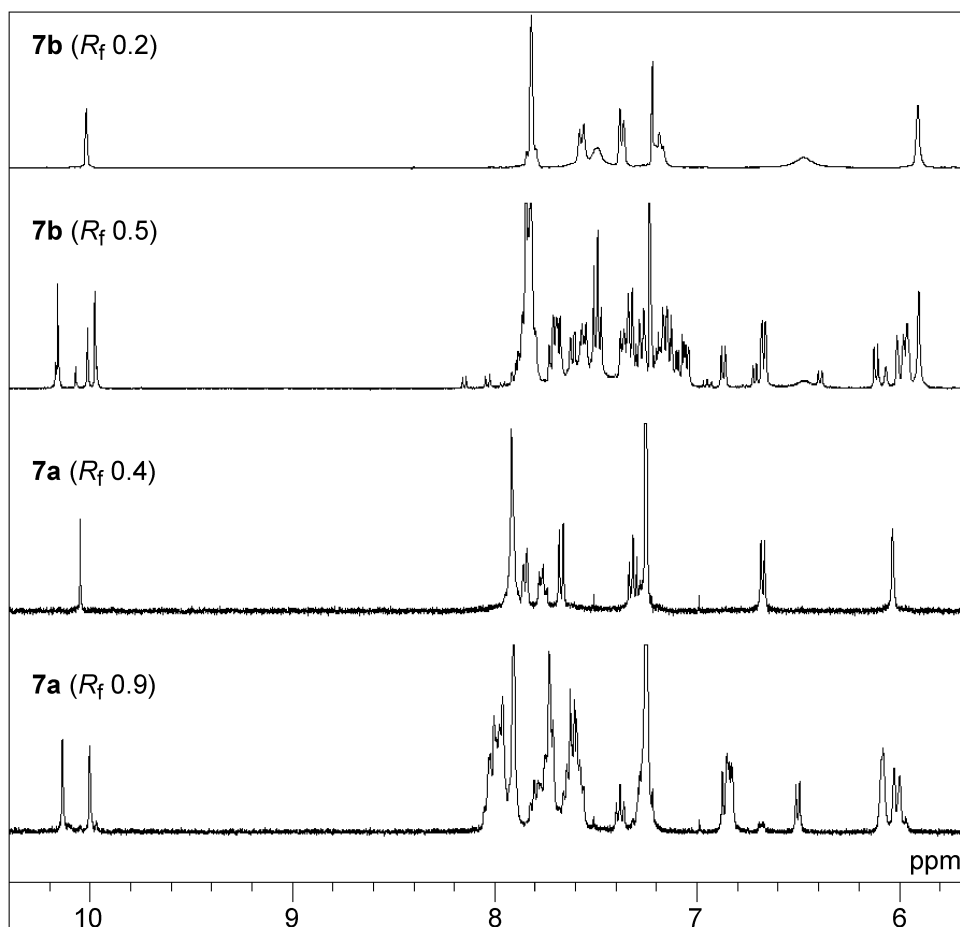


Figure 1. 1H NMR spectra of **7a** and **7b**.

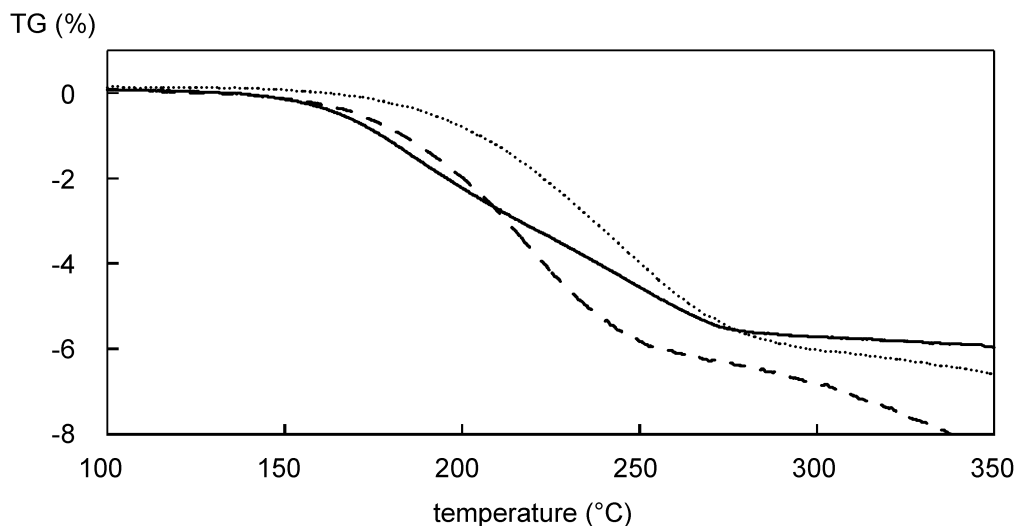


Figure 2. TGA of **7a** (R_f 0.4) (solid line), **7a** (0.9) (dotted line), and **8a** (broken line).

The first fraction of **7a** and **7b** would be a mixture of other isomers. This selectivity would be derived from the bulky *tert*-butyl groups at phenyl groups. However, their configuration is not clear and under investigation.

Thermogravimetric analysis (TGA) curves of **7a** and **8a** are shown in Figure 2. The weight loss of **7a** started at around 180 °C and ceased after 280 °C. The loss of weight was ca. 6%, consistent with the calculated value of 5.81%. Similarly, the retro Diels-Alder reactions of **7b**, **8a**, and **8b** started at 150–200 °C and were completed by 250–300 °C. The loss of weight corresponded to the elimination of four ethylene molecules. The retro Diels-Alder reaction of **7** and **8** was carried out at 330 °C for 1 h *in vacuo* in a glass tube oven to give tetra[8,9]fluoranthoTBPs **2** and **3** in nearly quantitative yields.

The absorption and emission data and the absolute quantum yields (Φ) of **2**, **3**, **7**, and **8** are summarized in Table 1, and the typical spectra of **3a** and **8a** are shown in Figure 3. The absorption spectra were dramatically changed by retro Diels-Alder reaction of the BCOD-fused precursors as shown in Figure 3a. The Soret band of **3a** showed a remarkable bathochromic shift from 402 nm for **8a** ($\log \epsilon$ 5.31) to 480 nm (5.42). The Q bands of **3a** were also red shifted by 120–150 nm and very intense compared to that of **8a**. The Soret and Q bands of fluoranthoTBPs **2** and **3** were observed at 480–500 and 670–760 nm with large molar absorption coefficient over $10^5 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The intensity of the Q bands was stronger than that of the Soret bands as shown in Table 1. Thus, **2** and **3** were expected to be suitable dyes for PDT. BCOD-porphyrins **7** and **8** showed the strong Soret band ($\log \epsilon$ ca. 5.3) at 400–420 nm and the weak Q bands at 500–620 nm similar to those of typical porphyrins. The emission spectra with excitation at their Soret bands showed two bands at 620 and 700 nm for **7** and 580 and 630 nm for **8** with Φ values of 2–4%. On the other hand, fluoranthoTBPs **2** and **3** showed a strong emission at 750–770 nm and two weak bands at 790–850 nm. The intensities of them were stronger than those of BCOD-porphyrins **7** and **8**. This

observation was consistent with their absolute quantum yields. FluoranthoTBPs showed relatively high Φ values of ca. 35% for free base porphyrins **2** and 10% for the zinc complexes **3** compared to [2,3]naphthoporphyrins (13% in DMF) and *meso*-fluorene-substituted porphyrins (22% in toluene).^{15,16}

Table 1. Absorbance, Fluorescence, and Absolute Quantum Yields (Φ) of **2**, **3**, **7**, and **8**

compd	$\lambda_{\text{abs}} / \text{nm} (\log \epsilon)$			$\lambda_{\text{em}} / \text{nm}^a$	$\Phi (\%)^a$
2a	494 (5.44)	679 (4.64), 712 (4.60), 751 (5.63)			38
2b	499 (5.39)	687 (4.64), 722 (4.65), 760 (5.57)			33
3a	480 (5.42)	672 (4.59), 703 (4.61), 739 (5.71)			9
3b	484 (5.44)	677 (4.65), 710 (4.66), 747 (5.68)			8
7a (R_f 0.9)	400 (5.31)	499 (4.27), 531 (3.99), 566 (3.89), 619 (3.24)			4
7a (R_f 0.4)	402 (5.31)	502 (4.28), 534 (4.01), 569 (3.90), 621 (3.24)			4
7b (R_f 0.5)	403 (5.31)	501 (4.29), 535 (4.01), 569 (3.93), 622 (3.35)			4
7b (R_f 0.2)	407 (5.25)	506 (4.27), 537 (3.93), 576 (3.89), 623 (3.28)			3
8a	402 (5.31)	534 (4.01), 569 (3.90)			3
8b	417 (5.40)	540 (4.28), 571 (4.18)			2

^aexcited at Soret band

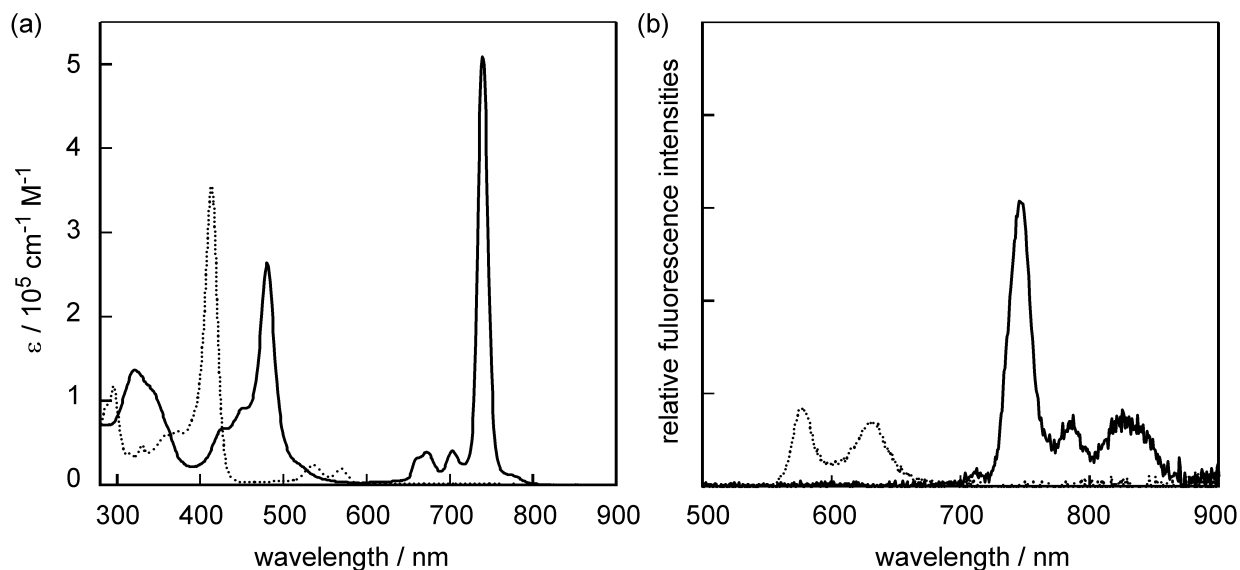


Figure 3. (a) UV-vis absorption and (b) fluorescence emission spectra of **3a** (solid line) and **8a** (dotted line) in CHCl_3 .

In summary, tetra[8,9]fluoranthoTBPs have been synthesized from the BCOD-fused porphyrins by the retro Diels-Alder reaction. FluoranthoTBPs **2** and **3** showed red-shifted Soret band at ca. 500 nm and Q bands in near-IR region. Although porphyrins fused with polycyclic aromatic rings such as acenaphthylene or phenanthrene also show the Q bands in this region, their Q bands are weak similar to those of typical porphyrins.^{8–10} On the other hand, linearly π -expanded porphyrins, tetra[2,3]naphtho- or tetra[2,3]anthraporphyrins, are relatively unstable, while they show strong red-shifted Q bands. Thus,

FluoranthoTBPs **2** and **3** are stable and exhibit strong absorptions over wide range of the visible-near-IR region, which are expected to show potential application for solar cells or other optics.

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. MALDI-TOF mass spectra were measured on an Applied Biosystems Voyager de Pro. TG analysis was 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. The fluorescence emission spectra and the Φ values were measured on a Hamamatsu Photonics K.K. absolute PL quantum yield measurement system C9920-03. ^1H 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 Science, Ehime University.

[8,9]fluoranthoBCODpyrrole **6a**

A solution of **4** (501 mg, 2.31 mmol) and **5a** (714 mg, 2.00 mmol) in xylene (20 mL) was stirred at 135 °C for 3 days. After the solvent was removed under reduced pressure, a mixture of the residue and DDQ (454 mg, 2.00 mmol) in CHCl_3 (70 mL) was stirred at rt for 21 h. The reaction mixture was poured into sat. aqueous NaHCO_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 /hexane to give **6a** (824 mg, 76%)

pale yellow powder; mp > 300 °C; MS (70 eV) m/z (relative intensity) 544 ($\text{M}^+ + 1$, 9%), 515 (100), and 470 (69); IR (KBr disk) ν_{max} 3305, 3053, 2935, 2863, and 1685 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.43 (br, 1H), 7.36–7.46 (m, 12H), 7.23 (m, 2H), 6.62 (d, 2H, $J = 6.6$ Hz), 6.61 (s, 1H), 4.82 (m, 1H), 4.30 (m, 1H), 4.20 (q, 2H, $J = 7.1$ Hz), and 1.16 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 161.69, 142.87, 142.15, 139.23, 139.07, 136.72, 136.67, 135.15, 134.52, 134.48, 132.71, 130.61, 129.82, 129.52, 129.40, 129.34, 128.88, 128.84, 128.68, 128.63, 127.54, 127.49, 127.40, 127.36, 125.92, 125.89, 122.51, 122.44, 114.94, 113.64, 59.89, 34.68, 34.19, 27.63, 27.01, and 14.42. Anal. Calcd for $\text{C}_{39}\text{H}_{29}\text{NO}_2 \cdot 1/2\text{MeOH}$: C, 84.77; H, 5.58; N, 2.50. Found: C, 84.90; H, 5.35; N, 2.66.

[8,9]fluoranthoBCODpyrrole **6b**

A solution of **4** (236 mg, 1.09 mmol) and **5b** (473 mg, 1.01 mmol) in xylene (10 mL) was stirred at 135 °C for 3 days. After the solvent was removed under reduced pressure, a mixture of the residue and

DDQ (269 mg, 1.18 mmol) in CHCl_3 (70 mL) was stirred at rt for 1 h. The reaction mixture was poured into sat. aqueous NaHCO_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 /hexane to give **6b** (410 mg, 62%)

pale yellow powder; mp 290 °C (decomp); MS (70 eV) m/z (relative intensity) 656 ($\text{M}^+ + 1$, 7%), 627 (12), and 154 (100); IR (KBr disk) ν_{max} 3316, 3064, 2949, 2900, 2864, and 1674 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.49 (br, 1H), 7.56–7.63 (m, 6H), 7.34–7.49 (m, 4H), 7.22 (t, 2H, $J = 7.8$ Hz), 6.63 (d, 2H, $J = 2.7$ Hz), 6.58 (dd, 2H, $J = 5.4$ and 6.9 Hz), 4.84 (m, 1H), 4.35 (m, 1H), 4.19 (m, 1H), 1.58–1.83 (m, 4H), 1.49 (s, 18H), and 1.15 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 161.83, 150.37, 150.16, 143.02, 142.20, 136.92, 136.87, 136.07, 135.24, 134.75, 134.66, 133.23, 132.74, 132.72, 130.75, 129.35, 129.30, 129.07, 128.99, 128.91, 127.37, 127.34, 125.77, 125.74, 125.70, 125.61, 125.52, 125.47, 122.45, 122.41, 114.92, 113.75, 34.84, 34.80, 34.75, 34.18, 31.64, 27.68, and 27.14. Anal. Calcd for $\text{C}_{47}\text{H}_{45}\text{NO}_2$: C, 86.07; H, 6.92; N, 2.14. Found: C, 86.13; H, 6.97; N, 2.11.

Porphyrim 7a

To a solution of **6a** (326 mg, 0.600 mmol) in dry THF (20 mL) was added slowly LiAlH_4 (113 mg, 2.98 mmol) at 0 °C under an Ar atmosphere in a shaded vessel. The resulting mixture was stirred below 0 °C for 4 h. After slow addition of water, the mixture was diluted with CHCl_3 and filtrated with Celite. The organic layer was separated, washed successively with water and brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was diluted with degassed CHCl_3 (150 mL) and $p\text{-TsOH} \cdot \text{H}_2\text{O}$ (11 mg) was added in a shaded vessel. After stirring at rt for 16 h, DDQ (90 mg, 0.40 mmol) was added. The resulting mixture was stirred at rt for 40 min. 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 alumina with CHCl_3 , column chromatography on silica gel with CHCl_3 , and recrystallization from CHCl_3 /MeOH to give **7a** (R_f 0.9) (125 mg, 43%) and **7a** (R_f 0.4) (54 mg, 19%).

7a (R_f 0.9): brown powder; mp 220 °C (decomp); MS (FAB) m/z 1929 ($\text{M}^+ + 2$) and 1816; UV-vis (CHCl_3) λ_{max} , nm (log ϵ) 315 (4.49), 330 (4.60), 400 (5.31), 499 (4.27), 531 (3.99), 566 (3.89), and 619 (3.24); ^1H NMR (400 MHz, CDCl_3) δ 9.95–10.17 (m, 4H), 7.20–8.07 (m, 56H), 6.47–7.00 (m, 8H), 5.94–6.12 (m, 8H), 2.04–2.63 (m, 16H), and -4.61–4.44 (br, 2H). Anal. Calcd for $\text{C}_{148}\text{H}_{94}\text{N}_4 \cdot \text{H}_2\text{O}$: C, 91.33; H, 4.97; N, 2.88. Found: C, 91.36; H, 4.85; N, 2.87.

7a (R_f 0.4): brown powder; mp 220 °C (decomp); MS (FAB) m/z 1929 ($\text{M}^+ + 2$) and 1816; UV-vis (CHCl_3)

λ_{\max} , nm (log ϵ) 315 (4.53), 330 (4.64), 402 (5.31), 502 (4.28), 534 (4.01), 569 (3.90), and 621 (3.24); ^1H NMR (400 MHz, CDCl_3) δ 10.04 (s, 4H), 7.91 (m, 24H), 7.84 (d, 8H, $J = 7.6$ Hz), 7.75 (m, 8H), 7.66 (d, 8H, $J = 8.2$ Hz), 7.31 (dd, 8H, $J = 7.1$ and 8.2 Hz), 6.66 (d, 8H, $J = 7.1$ Hz), 6.02 (m, 8H), 2.20 (m, 8H), 1.69 (m, 8H), and -4.27 (br, 2H). Anal. Calcd for $\text{C}_{148}\text{H}_{94}\text{N}_4 \cdot \text{H}_2\text{O}$: C, 91.33; H, 4.97; N, 2.88. Found: C, 91.09; H, 4.96; N, 2.82.

Porphyrin 7b

To a solution of **6b** (262 mg, 0.400 mmol) in dry THF (15 mL) was added slowly LiAlH_4 (75 mg, 1.98 mmol) at 0 °C under an Ar atmosphere in a shaded vessel. The resulting mixture was stirred below 0 °C for 4.5 h. After slow addition of water, the mixture was diluted with CHCl_3 and filtrated with Celite. The organic layer was separated, washed successively with water and brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was diluted with degassed CHCl_3 (150 mL) and *p*-TsOH $\cdot\text{H}_2\text{O}$ (10 mg) was added in a shaded vessel. After stirring at rt for 16 h, DDQ (64 mg, 0.28 mmol) was added. The resulting mixture was stirred at rt for 30 min. 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 alumina with CHCl_3 , column chromatography on silica gel with CHCl_3 , and recrystallization from $\text{CHCl}_3/\text{MeOH}$ to give **7b** (R_f 0.5) (54 mg, 23%) and **7b** (R_f 0.2) (97 mg, 41%).

7b (R_f 0.5): brown powder; mp 220 °C (decomp); MS (MALDI-TOF) m/z 2376 ($\text{M}^+ + 1$), 2349, and 2323; UV-vis (CHCl_3) λ_{\max} , nm (log ϵ) 296 (5.07), 315 (4.54), 330 (4.66), 403 (5.31), 501 (4.29), 535 (4.01), 569 (3.93), and 622 (3.35); ^1H NMR (400 MHz, CDCl_3) δ 9.92–10.21 (m, 4H), 6.97–7.97 (m, 48H), 6.08–6.96 (m, 8H), 5.83–6.08 (m, 8H), 1.73–2.79 (m, 16H), 1.33–1.69 (m, 72H), and -4.61–4.02 (m, 2H). Anal. Calcd for $\text{C}_{180}\text{H}_{158}\text{N}_4 \cdot \text{H}_2\text{O}$: C, 90.26; H, 6.73; N, 2.34. Found: C, 90.40; H, 6.69; N, 2.29.

7b (R_f 0.2): brown powder; mp 210 °C (decomp); MS (FAB) m/z 2376 ($\text{M}^+ + 2$), 2349, and 2321; UV-vis (CHCl_3) λ_{\max} , nm (log ϵ) 296 (5.04), 315 (4.52), 330 (4.64), 407 (5.25), 506 (4.27), 537 (3.93), 576 (3.89), and 623 (3.28); ^1H NMR (400 MHz, CDCl_3) δ 10.01 (s, 4H), 7.82 (m, 24H), 7.57 (d, 8H, $J = 8.1$ Hz), 7.49 (m, 8H), 7.37 (d, 8H, $J = 7.1$ Hz), 7.18 (t, 8H, $J = 7.3$ Hz), 6.47 (m, 8H), 5.91 (s, 8H), 2.27 (m, 8H), 1.95 (m, 8H), 1.49 (s, 72H), and -4.07 (br, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.60, 143.47, 136.73, 136.63, 135.04, 133.40, 132.78, 129.54, 129.38, 129.24, 127.27, 126.68, 126.21, 125.84, 122.68, 96.25, 37.37, 35.02, 31.78, and 27.97. Anal. Calcd for $\text{C}_{180}\text{H}_{158}\text{N}_4$: C, 90.94; H, 6.70; N, 2.36. Found: C, 90.71; H, 6.79; N, 2.31.

(Porphyrinato)zinc(II) 8a

A saturated solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in MeOH (2 mL) was added to a solution of **7a** (R_f 0.4) (11 mg, 0.0065 mmol) in CHCl_3 (50 mL) at rt. The resulting mixture was stirred at same temperature for 1 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 $\text{CHCl}_3/\text{MeOH}$ to give **8a** (9 mg, 77%).

reddish purple powder; mp 210 °C (decomp); MS (FAB) m/z 1991 ($\text{M}^+ + 2$); UV-vis (CHCl_3) λ_{max} , nm (log ϵ) 315 (4.53), 330 (4.64), 402 (5.31), 534 (4.01), and 569 (3.90); ^1H NMR (400 MHz, CDCl_3) δ 10.15 (s, 4H), 7.85–8.02 (m, 32H), 7.76 (m, 8H), 7.67 (d, 8H, $J = 8.0$ Hz), 7.32 (dd, 8H, $J = 7.1$ and 8.0 Hz), 6.66 (d, 8H, $J = 7.1$ Hz), 6.11 (s, 8H), 2.24 (m, 8H), and 1.75 (m, 8H). Anal. Calcd for $\text{C}_{148}\text{H}_{92}\text{N}_4\text{Zn} \cdot 2\text{MeOH}$: C, 87.63; H, 4.90; N, 2.73. Found: C, 87.93; H, 5.19; N, 2.98.

(Porphyrinato)zinc(II) **8b**

A saturated solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in MeOH (1 mL) was added to a solution of **7b** (R_f 0.2) (30 mg, 0.013 mmol) in CHCl_3 (30 mL) at rt. The resulting mixture was stirred at same temperature for 1 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 $\text{CHCl}_3/\text{MeOH}$ to give **8b** (30 mg, 96%).

red powder; mp 220 °C (decomp); MS (MALDI-TOF) m/z 2439 ($\text{M}^+ + 2$), 2412, 2385, 2358 and 2329; UV-vis (CHCl_3) λ_{max} , nm (log ϵ) 296 (5.06), 315 (4.55), 330 (4.65), 373 (4.80), 417 (5.40), 540 (4.28), and 571 (4.18); ^1H NMR (400 MHz, CDCl_3) δ 10.17 (s, 4H), 7.86 (s, 16H), 7.59 (d, 8H, $J = 8.1$ Hz), 7.54 (d, 8H, $J = 7.6$ Hz), 7.34 (d, 8H, $J = 7.9$ Hz), 7.21 (m, 8H), 6.53 (m, 8H), 5.99 (s, 8H), 2.36 (m, 8H), 2.06 (m, 8H), and 1.49 (s, 72H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.49, 149.76, 143.85, 142.43, 136.72, 136.69, 134.85, 133.31, 132.73, 129.49, 129.34, 129.16, 127.21, 126.65, 126.17, 125.71, 122.64, 97.28, 37.58, 34.92, 31.71, and 28.13. Anal. Calcd for $\text{C}_{180}\text{H}_{56}\text{N}_4\text{Zn} \cdot 1/2\text{CHCl}_3$: C, 86.71; H, 6.31; N, 2.24. Found: C, 86.53; H, 6.46; N, 2.47.

Retro Diels-Alder reaction

Porphyrins **7**, and **8** (ca. 10 mg each) were heated at 330 °C under reduced pressure for 1 h in a glass tube to give fluoranthoTBPs **2** and **3** in nearly quantitative yields.

2a: brown powder; mp > 300 °C; MS (FAB) m/z 1816 ($\text{M}^+ + 1$); UV-vis (CHCl_3) λ_{max} , nm (log ϵ) 314 (5.11), 348 (5.01), 397 (4.71), 494 (5.44), 679 (4.64), 712 (4.60), and 751 (5.63); Anal. Calcd for

C₁₄₀H₇₈N₄: C, 92.59; H, 4.33; N, 3.08. Found: C, 92.42; H, 4.63; N, 3.09.

2b: brown powder; mp > 300 °C; MS (MALDI-TOF) *m/z* 2264 (M⁺+1); UV-vis (CHCl₃) λ_{max}, nm (log ε) 315 (5.14), 348 (5.03), 398 (4.72), 499 (5.39), 687 (4.64), 722 (4.65), and 760 (5.57); ¹H NMR (400 MHz, CDCl₃) δ 10.20 (s, 4H), 9.54 (s, 8H), 9.72 (d, 16H, *J* = 8.1 Hz), 7.71–7.79 (m, 24H), 7.39 (dd, 8H, *J* = 7.1 and 8.1 Hz), 6.52 (d, 8H, *J* = 7.1 Hz), 1.76 (s, 72H), and -0.88 (br, 2H). Anal. Calcd for C₁₇₂H₁₄₂N₄·H₂O: C, 90.49; H, 6.36; N, 2.45. Found: C, 90.46; H, 6.41; N, 2.43.

3a: dark brown powder; mp > 300 °C; MS (FAB) *m/z* 1879 (M⁺+2); UV-vis (CHCl₃) λ_{max}, nm (log ε) 322 (5.14), 480 (5.42), 672 (4.59), 703 (4.61), and 739 (5.71). Anal. Calcd for C₁₄₀H₇₆N₄Zn·H₂O: C, 88.61; H, 4.14; N, 2.95. Found: C, 88.88; H, 4.45; N, 2.99.

3b: dark brown powder; mp > 300 °C; MS (MALDI-TOF) *m/z* 2327 (M⁺+2); UV-vis (CHCl₃) λ_{max}, nm (log ε) 323 (5.24), 484 (5.44), 677 (4.65), 710 (4.66), and 747 (5.68); ¹H NMR (400 MHz, CDCl₃) δ 10.20 (s, 4H), 9.54 (s, 8H), 9.72 (d, 16H, *J* = 8.1 Hz), 7.79–7.71 (m, 24H), 7.39 (dd, 8H, *J* = 7.1 and 8.1 Hz), 6.52 (d, 8H, *J* = 7.1 Hz), 1.76 (s, 72H) and -0.88 (brs, 2H). Anal. Calcd for C₁₇₂H₁₄₀N₄Zn·H₂O: C, 88.04; H, 6.10; N, 2.39. Found: C, 87.83; H, 6.07; N, 2.39.

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