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Synthesis and Characterization of Tetraanthroporphyrins

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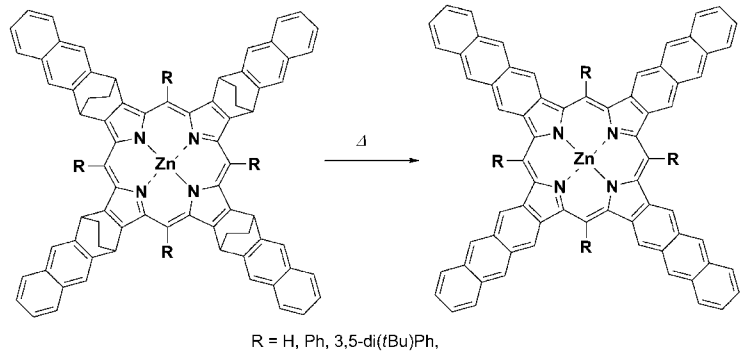
ABSTRACT



Linearly π-expanded novel tetraanthroporphyrins with and without aromatic rings at the *meso*-positions were prepared quantitatively for the first time from the corresponding precursors by a retro-Diels−Alder reaction.

Tetrabenzoporphyrins (TBPs) and linearly π-expanded derivatives, tetranaphthoporphyrins (TNPs) and tetraanthroporphyrins (TAnPs), have attracted great attention for applications such as dye stuffs, optical materials, nonlinear optics, conducting materials, photosensitizers for photodynamic therapy (PDT), and solar systems.[1] Although TBPs, TNPs, and nonlinearly expanded TAnP analogues have been reported to date, linearly expanded TAnPs have been rarely reported to our knowledge.[2] As Kobayashi et al. have theoretically predicted, π-ring expansion results in the destabilization of the third LUMOs and the first HOMOs of the porphyrins, and therefore, they become unstable against oxidation and reduction.[3] The π-expansion also induces strong π−π stacking between molecules, which results in low solubility of the porphyrins and difficulties in purification and derivatization. To overcome these obstacles, a few methods have been reported in the synthesis of TBPs and TNPs,[1,2,4,5] e.g., an introduction of bulky substituents at the meso positions or peripheral aromatic rings, and an annealing of peripheral cyclohexyl structures to the aromatic rings in the presence of oxidants such as DDQ.[6] However, these

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(1) Lash, T. D. *The Porphyrin Handbook*; Academic Press: New York, 2000; Vol. 2.
(2) Lash, T. D. *J. Porphyrins Phthalocyanines* **2001**, *5*, 267.
(3) (a) Kobayashi, N.; Konami, H. *J. Porphyrins Phthalocyanines* **2001**, *5*, 233. (b) Mack, J.; Asano, Y.; Kobayashi, N.; Stillman, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 17697.
(4) Kopranenkov, V. N.; Vorotnikov, A. M.; Dashkevich, S. N.; Luk'yanets, E. A. *Zh. Obsch. Khim. (Russ.)* **1985**, 900.
(5) Rein, M.; Hanack, M. *Chem. Ber.* **1988**, *121*, 1601.
(6) (a) Finikova, O. S.; Cheprakov, A. V.; Carroll, P. J.; Vinogradov, S. A. *J. Org. Chem.* **2003**, *68*, 7517. (b) Rozhkov, V. V.; Khajehpour, M.; Vinogradov, S. A. *Inorg. Chem.* **2003**, *42*, 4253. (c) Finikova, O. S.; Cheprakov, A. V.; Beletskaya, I. P.; Carroll, P. J.; Vinogradov, S. A. *J. Org. Chem.* **2004**, *69*, 522. (d) Finikova, O. S.; Aleshchenkov, S. E.; Briňas, R. P.; Cheprakov, A. V.; Carroll, P. J.; Vinogradov, S. A. *J. Org. Chem.* **2005**, *70*, 4617–4628. (e) Finikova, O. S.; Cheprakov, A. V.; Vinogradov, S. A. *J. Org. Chem.* **2005**, *70*, 9562–9572.

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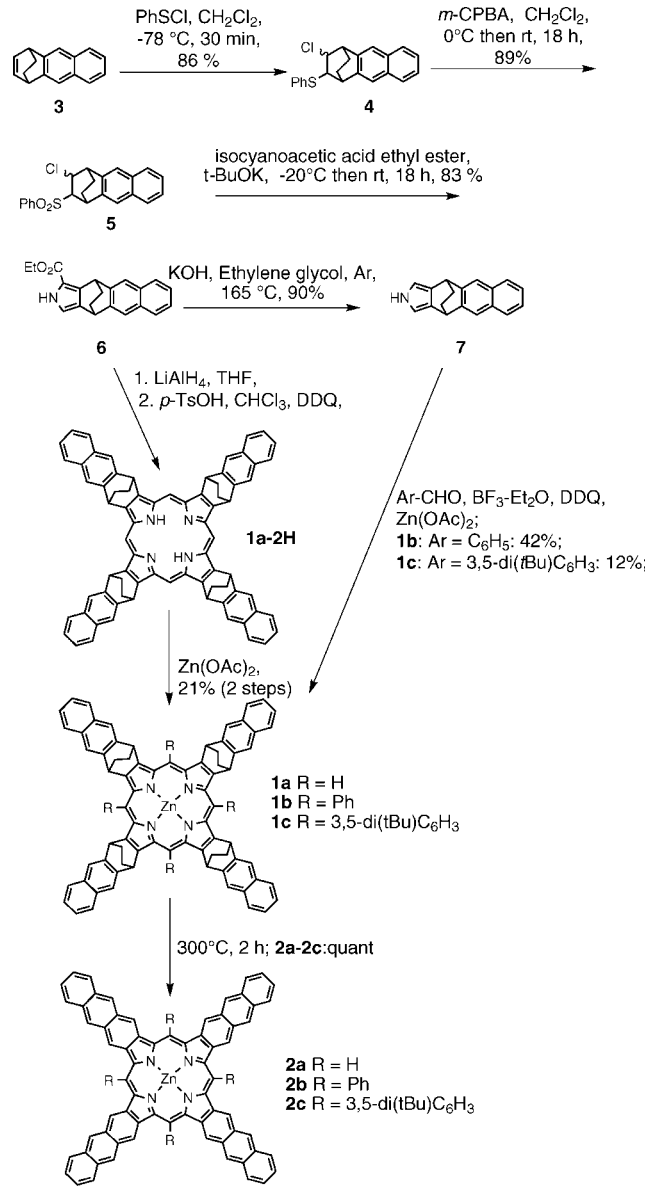
methodologies are not suitable for preparing TAnPs because TAnPs are less stable against oxidants compared to TNPs and TBPs, and only 5,10,15-tribiphenyl-ZnTAnP has been reported so far.[7,8]

Recently, we have developed an efficient synthetic method for various benzoporphyrin-type compounds including TBPs and TNPs using a retro-Diels−Alder reaction.[9,10] With this method, soluble porphyrins fused with bicyclo[2.2.2]octadiene were converted quantitatively into insoluble benzoporphyrins by simply heating at around 200−290 °C; which temperature to use was decided by thermogravimetric analysis (Tg) and differential thermal analysis (DTA) measurements. As the thermal process does not require any reagents, solvents, or purification steps, it is the ideal method for the preparation of low-soluble and highly planar π-conjugated porphyrins. Aramaki et al. and Kanicki et al. have observed comparable performance with pentacene in carrier mobility using TBP films prepared by spin coating of bicyclo[2.2.2]octadiene-fused porphyrins on a silicon substrate followed by heating.[11,12] Yamada et al. have reported the photoenergy conversion system of BPs and PCBM prepared by spin-coating.[13] Using this procedure, we have succeeded in preparing meso-free and meso-substituted TAnPs **2a**−**c** from the corresponding bicyclo[2.2.2]octadiene-fused precursors (**1a**−**c**), as shown in Scheme 1.

The preparation of the TAnPs is shown in Scheme 1. The addition of phenylsulfenyl chloride to 1,4-dihydro-1,4-ethanonanthracene **3**[14] at −78 °C gave compound **4** in 86% yield, and the oxidation of **4** with *m*-CPBA gave **5** in 89% yield. When a dry THF solution of **5** was treated with isocyanoacetate ethyl ester in the presence of 2.7 equiv of *t*-BuOK at −20 °C, followed by stirring at room temperature for 18 h, pyrrole **6** was obtained in 89% yield. Treatment of pyrrole **6** with potassium hydroxide gave pyrrole **7**.

Scheme 1. Preparation of TAnPs **2**



Porphyrin **1a-2H** was prepared from pyrrole **6** in two steps: (1) reduction of pyrrole **6** by LAH and (2) acid-catalyzed condensation in $CHCl_3$ in the presence of *p*-toluenesulfonic acid, followed by oxidation with DDQ. Metalation of porphyrin **1a-2H** with $Zn(OAc)_2$ gave porphyrin zinc complex **1a**. Porphyrin **1a** was converted into pure TAnP **2a** quantitatively by heating at around 300 °C under vacuum for 2 h. The temperature of the retro-Diels−Alder reaction was determined by thermogravimetric analyses of porphyrin **1a** as shown in Figure 1. The weight loss seen in the retro-Diels−Alder reaction was 11.1%, which is similar to the calculated value of 10.3%. Porphyrin **1a** was characterized by FAB and MALDI-TOF mass spectrometry, ^{1}H NMR spectroscopy, and elemental analysis. Although it is a mixture of isomers, the NMR spectrum of **1a** was relatively simple as shown in Figure S7 (Supporting Information). Because of its planarity, the solubility of tetraanthroporphyrin **2a** was

(7) (a) Sapunov, V. V.; Solov'ev, K. N.; Kopranekov, V. N.; Vorotnikov, A. M. *Opt. Spectrosc. (USSR)* **1988**, *64*, 464. (b) Vorotnikov, A. M.; Kopranekov, V. N.; Luk'yanets, E. A. *Zh. Obsch. Khim. (Russ.)* **1991**, *61*, 1241.

(8) Kobayashi, N.; Nevin, W. A.; Mizunuma, S.; Awaji, H.; Yamaguchi, M. *Chem. Phys. Lett.* **1993**, *205*, 51.

(9) (a) Ito, S.; Murashima, T.; Ono, N.; Uno, H. *Chem. Commun.* **1998**, 1661. (b) Ito, S.; Murashima, T.; Ono, N.; Uno, H. *Chem. Commun.* **1999**, 2275. (c) Ito, S.; Ochi, N.; Murashima, T.; Ono, N.; Uno, H. *Chem. Commun.* **2000**, 893. (d) Ito, S.; Uno, H.; Murashima, T.; Ono, N. *Tetrahedron Lett.* **2001**, *42*, 45. (e) Okujima, T.; Komobuchi, N.; Shimizu, Y.; Uno, H.; Ono, N. *Tetrahedron Lett.* **2004**, *45*, 5461. (f) Okujima, T.; Jin, G.; Hashimoto, Y.; Yamada, H.; Uno, H.; Ono, N. *Heterocycles* **2006**, *70*, 619. (g) Okujima, T.; Komobuchi, N.; Uno, H.; Ono, N. *Heterocycles* **2006**, *67*, 255. (h) Yamada, H.; Kushibe, K.; Okujima, T.; Uno, H.; Ono, N. *Chem. Commun.* **2006**, 383. (i) Uno, H.; Nakamoto, K.-I.; Kuroki, K.; Fujimoto, A.; Ono, N. *Chem. Eur. J.* **2007**, *13*, 5773.

(10) (a) Giraud-Roux, M.; Proni, G.; Nakanishi, K.; Berova, N. *Heterocycles* **2003**, *61*, 417. (b) Senge, M. O.; Bischoff, I. *Tetrahedron Lett.* **2004**, *45*, 1647.

(11) Aramaki, S.; Sakai, Y.; Ono, N. *Appl. Phys. Lett.* **2004**, *84*, 2085.

(12) (a) Shea, P. B.; Kanicki, J.; Cao, Y.; Ono, N. *Appl. Phys. Lett.* **2005**, *87*, 173506. (b) Shea, P. B.; Johnson, A. R.; Ono, N.; Kanicki, J. *IEEE* **2005**, *52*, 1497. (c) Shea, P. B.; Kanicki, J.; Ono, N. *J. Appl. Phys.* **2005**, *98*, 014503. (d) Shea, P. B.; Kanicki, J.; Pattison, L. R.; Petroff, P.; Kawano, M.; Yamada, H.; Ono, N. *J. Appl. Phys.* **2006**, *100*, 034502. (e) Shea, P. B.; Pattison, L. R.; Kawano, M.; Chen, C.; Chen, J.; Petroff, P.; Martin, D. C.; Yamada, H.; Ono, N.; Kanicki, J. *Synth. Met.* **2007**, *157*, 190. (f) Shea, P. B.; Chen, C.; Kanicki, J.; Pattison, L. R.; Petroff, P.; Yamada, H.; Ono, N. *Appl. Phys. Lett.* **2007**, *90*, 233107.

(13) Yamada, H.; Kamio, N.; Ohishi, A.; Mawano, M.; Okujima, T.; Ono, N. *J. Porphyrins Phthalocyanines* **2007**, *11*, 383.

(14) Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1975**, *58*, 380.

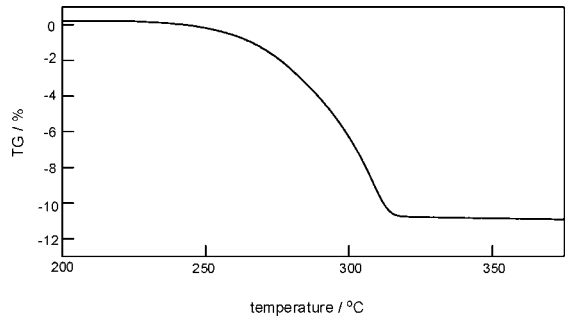


Figure 1. Thermogravimetric analysis of porphyrin **1a**, heating at 10 °C/min.

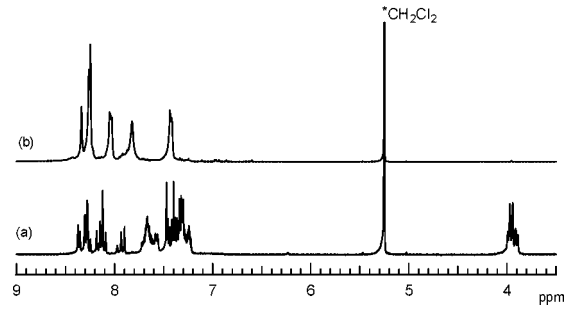


Figure 3. ^{1}H NMR spectra of porphyrins (a) **1c** and (b) **2c** in CD_2Cl_2.

quite poor. Therefore, the characterization of porphyrin **2a** was confirmed only by mass spectroscopy and UV−vis absorption spectroscopy. The absorption and emission spectra of **2a** were measured in the dark because it was unstable in solution under air in the light. The normalized UV−vis and fluorescence spectra of **1a** in $CHCl_3$ and **2a** in pyridine are shown in Figure 2. Compared to the absorption spectrum of **1a**, that of anthroporphyrin **2a** is broad and the Q-band of **2a** was shifted to 800 nm. The relative intensity of the Q-band to the Soret band is high. These changes are due to the effect of the linear expansion of π-conjugation as theoretically predicted.[3] The luminescence of **2a** was shown to occur at around 900 nm, which is in the near-IR region.

In order to improve the solubility, the *meso*-positions of **1a** were substituted with aromatic rings, such as phenyl and 3,5-di(*tert*-butyl)phenyl groups. Porphyrins **1b** and **1c** were prepared by the acid condensation of pyrrole **7** with the corresponding aldehydes in the presence of BF_3·Et_2O followed by oxidation with DDQ and metalation. The porphyrins **1b** and **1c** were converted to TAnPs **2b** and **2c** quantitatively by heating at around 300 °C under vacuum for 2 h. TG analyses of porphyrins **1b** and **1c** are shown in Figure S1 (Supporting Information). The retro-Diels−Alder reaction was performed at 300 °C, and the weight losses were

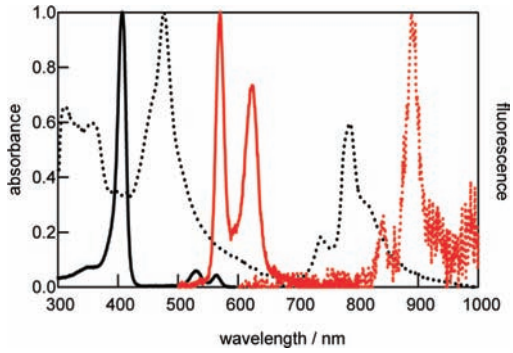


Figure 2. Normalized UV−vis spectra (black lines) and fluorescence spectra (red lines) of porphyrin **1a** in $CHCl_3$ (solid line) and **2a** in pyridine (dotted line). Absorbance and fluorescence are normalized to 1.

11.0 and 5.8%, respectively, which showed good accordance with the calculated values of 8.1 and 6.1%, respectively. The solubility of the TAnPs was improved, and the measurement of ^{1}H NMR spectra of porphyrins **2b** and **2c** was possible in THF-d_8 and CD_2Cl_2, respectively. Porphyrins **2b** and **2c** were not stable in the solution in the light; NMR spectra as well as absorption and emission spectra were measured in the dark. Portions of the NMR spectra of porphyrins **1c** and **2c** are shown in Figure 3 (see also Figures S9 and S12 in the Supporting Information). The aromatic region of **1c** is very complicated because of the existence of isomers of the bicyclo[2.2.2]octadiene moieties. After the retro-Diels−Alder reaction, the NMR spectrum became simple and proton peaks at the bridgehead (3.8−4.0 ppm) disappeared.

The absorption spectra of TAnPs **2b** and **2c** and their precursor porphyrins **1b** and **1c** in $CHCl_3$ are shown in Figure 4, and the data are summarized in Table 1. The Soret peaks of **1b** and **1c** are shown at 430 and 426 nm, respectively, and their Q bands are at 553 and 547 nm, respectively. Soret peaks of **1b** and **1c** are 24 and 20 nm red-shifted, respectively, compared to meso-free porphyrin **1a**, probably because of the distortion from planarity. The Soret band of **1b** with a meso-phenyl group is broadened and 4 nm red-shifted compared to **1c** with its bulky 3,5-di(*tert*-butyl)phenyl substituents at the meso position. The absorption spectra of TAnPs **2b** and **2c** show Soret bands at 498 and 493 nm, respectively, with strong Q bands at 802 and 799 nm, respectively. Because of their low solubility, absorption coefficients could not be determined for **2b** and **2c**. Since π-conjugation was linearly enlarged, broadening and 60 nm red shifts of the Soret and Q bands were observed for **2b** and **2c** compared to precursors **1b** and **1c**. The relative intensities of Q bands to Soret bands of **2b** and **2c** are quite large: 0.98 and 0.94, respectively. The trend of the change and the shift of the absorption spectra are consistent with the results of MO calculations.[3] When the TAnPs were stored in pyridine (**2a**) or $CHCl_3$ (**2b** and **2c**) in UV cells under air under room light, the shape of the absorption spectra changed over several hours. Mass spectroscopy of TAnPs showed an $M^+ + 32$ peak, indicating that a reaction with oxygen had occurred (Figures S11−S13 in the Supporting Information).

The fluorescence spectra of **1b** and **1c** are shown in Figure 4a, and the data are summarized in Table 1 with absolute

Table 1. Absorbance, Fluorescence, and Absolute Fluorescence Quantum Yields (Φ) of Porphyrins **1a-2H**, **1a**, **1b**, **1c**, **2b**, and **2c** in $CHCl_3$

porphyrins	λ_{max}/nm (log ϵ)	fluorescence/nm	Φ/% (λ_{EX}/nm)
1a-2H	396 (5.22), 496 (4.28), 529 (3.90),564 (3.90), 615 (3.41)	620,685	4.5 (396)
1a	406 (5.42), 530 (4.20), 563 (4.08)	570,623	3.7 (406)
1b	430 (5.56), 553 (4.34)	652	0.7 (430)
1c	426 (5.75), 509 (4.05) 547 (4.46)	645	1.7 (426)
2b	327, 365, 498, 728, 756, 802	819	3.7 (498)
2c	364, 403, 493, 726, 747, 799	811	4.3 (493)

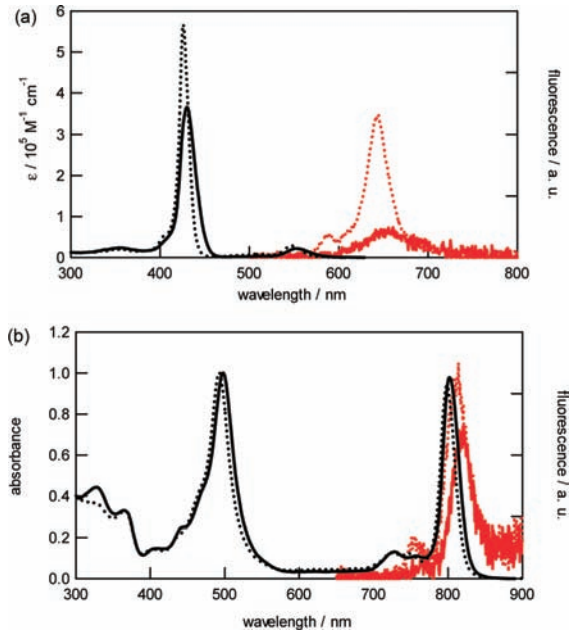


Figure 4. UV−vis absorption and fluorescence spectra of (a) precursors **1b** and **1c** and (b) TAnPs **2b** and **2c** in $CHCl_3$. Solid lines: **1b** and **2b**; broken lines: **1c** and **2c**; black lines: absorption spectra; red lines: fluorescence spectra. (a) Fluorescence spectra were measured at 2.8×10^{-7} M. (b) Absorption spectra were normalized at Soret peaks for TAnPs **2b** and **2c**.

fluorescence quantum yields (Φ). Interestingly, the Stokes shifts for **1b** and **1c** (around 100 nm) are larger than that of **1a** (7 nm). The fluorescence intensity of **1b** is smaller than that of **1c**. These results are consistent with their absolute fluorescence quantum yields (**1b**: 0.7%, **1c**: 1.7%). The reason for the difference in fluorescence intensity is not clear, but it might be because the porphyrin rings are distorted into a saddle shape by the aromatic rings at the *meso*-position. Fluorescence spectra of **2b** and **2c** are shown in Figure 4b. The emission peaks are at 819 and 811 nm, respectively, and are about 160 nm red-shifted compared to the precursors (**1b** and **1c**). Stokes shifts of **2b** and **2c** are only 17 and 12 nm, respectively. Vinogradov has reported that *meso*-arylnaphthoporphyrins show larger Stokes shifts than meso-free tetranaphthoporphyrins.[6e] In that study, the naphthoporphyrins had peripheral 1,4-substituents and might have shown large distortions due to steric hindrance between the *meso*-aryl rings and the substituents on the naphthalene rings. In our case, the anthracene moiety does not have substituents, so the distortion might be smaller. For the precursors **1b** and **1c**, steric hindrance is larger because of the bridgehead protons, and therefore, the Stokes shift might be larger.

We have succeeded in preparing tetraanthroporphyrins for the first time via the retro-Diels−Alder reaction of bicyclo-[2.2.2]octadiene-fused precursors. The compounds have strong absorption in the near-IR region and may have interesting conducting properties.

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Supporting Information Available: Experimental details and thermogravimetric analysis of **1b** and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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