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Thermal Behavior of Free-Base and Core-Modified Bicyclo[2.2.2]octadiene-Fused Porphyrins

Hidemitsu Uno,*[a] Yusuke Shimizu,[b] Hiroki Uoyama,[a] Yousuke Tanaka,[a] Tetsuo Okujima,[b] and Noboru Ono[b]

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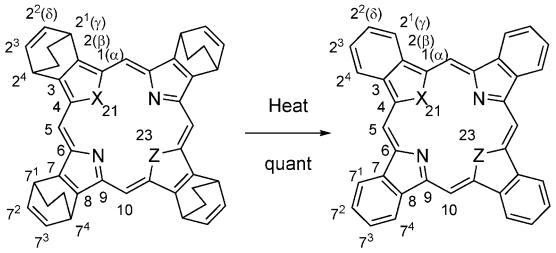
Multistep thermal fragmentation of quadruply bicyclo[2.2.2]-octadiene-fused porphyrins giving tetrabenzoporphyrins was examined in detail. After the first extrusion of an ethylene molecule from the porphyrin derivative, the opposite bicyclo-[2.2.2]octadiene moiety preferentially underwent the second retro-Diels–Alder reaction to give an *opp*-dibenzoporphyrin derivative rather than an *adj*-dibenzoporphyrin derivative. These two benzoporphyrin derivatives then decomposed to give a tribenzoporphyrin derivative in similar rates. The temperature regions of these fragmentations could not be distinguished by thermogravimetric analysis. In contrast, the third and the fourth fragmentations obviously occurred stepwise. There was a temperature region where the tribenzoporphyrin derivative preferentially existed. In the case of the 21,23-dithiaporphyrin derivative, *opp*-21,23-dithiadibenzoporphyrin, possessing benzo moieties fused at the pyrrole parts of the core-modified porphyrin chromophore was predominantly formed during the fragmentation. In the case of the 21-thiaporphyrin derivative, an ethylene molecule was extruded selectively from the bicyclo[2.2.2]octadiene moiety adjacent to the thiophene part to give 21-thiabenzo[*q*]porphyrin and then 21-thiabenzo[*g*,*q*]porphyrin derivatives. In these cases, the last ethylene extrusion also occurred very slowly.

Introduction

Design of molecular electronic structures of porphyrinoids is very important for improving their properties. For example, porphyrinoids utilized for photodynamic therapy (PDT) of tumors[1] are desired to have strong absorption bands in the red region (over 650 nm) for light transparency in living cells, in addition to the ability to generate singlet oxygen by light irradiation,[2] tumor-tissue selectivity,[3] and nontoxic nature in the dark.[4] Requisites of a large absorption cross section for multiphoton absorbing materials[5] and of a large χ^3 coefficient for third-harmonic generation[6] are other examples. Tuning of their molecular electronic structures is mainly achieved by the following methods: introduction of electron-withdrawing and electron-donating groups,[7] deformation of the porphyrin ring by bulky substituents,[8] dissymmetrization of the π-electron system by partial breakage of the extra π bonds,[9] expansion of the porphyrin π system,[10] and substitution of the porphyrin core nitrogen atoms by other atoms involving oxygen, sulfur, carbon, and so on.[11] In order to create a new porphyrin-based π system, we have been developing a new synthesis of highly pure π-expanded porphyrinoids[12] based on the final conversion of the bicyclo[2.2.2]octadinene-fused pyrrole and thiophene moieties into their benzo[*c*] heterocyclic moieties by a thermal retro-Diels–Alder reaction. This method was also successfully applied for the preparation of organic thin-film transistors of tetrabenzoporphyrin derivatives by the spin-coating method.[13] However, little attention has been paid to the thermal fragmentation routes, though the reactions must involve many intermediates. We planned to examine the retro-Diels–Alder reactions of quadruply bicyclo[2.2.2]octadiene-fused porphyrinoids in detail by a combination of thermogravimetric analysis and identification of the intermediates. In this paper, we discuss the



1a: X = Z = NH
1b: X = S; Z = NH
1c: X = Z = S

2a: X = Z = NH
2b: X = S; Z = NH
2c: X = Z = S (1)

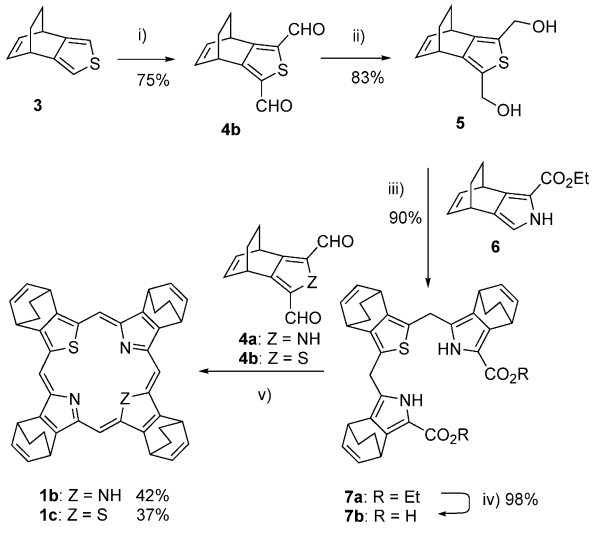
[a] Division of Synthesis and Analysis, Department of Molecular Science, Integrated Center for Sciences (INCS), Ehime University and CREST, Japan Science and Technology Agency (JST), Matsuyama 790-8577, Japan
Fax: +81-89-927-9670
E-mail: uno@dpc.ehime-u.ac.jp
[b] Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan

detailed course of the π-expansion reaction of porphyrin derivatives to give free-base and thiatetrabenzoporphyrins [Equation (1)].

Results and Discussion

Preparation of Quadruply Bicyclo[2.2.2]octadiene-Fused Porphyrins

Bicyclo[2.2.2]octadiene-fused free-base porphyrin **1a** (TBP precursor) was prepared according to the literature procedure[12c] in moderate yields (43–55%). Among the common porphyrin syntheses,[14] we chose the [3+1] approach[15] for thiaporphyrins. The tripyrrane analogues with a central thiophene ring such as **7** were required for the preparation of thiaporphyrins **1b** and **1c**. Acid-catalyzed condensation of thiophene **3** with 3-acetoxymethyl-4,7-dihydro-4,7-ethano-2*H*-isoindole, however, gave none of the targeted compound, and only an intractable mixture was obtained probably due to the labile nature of the starting isoindole under acidic conditions and the rather low reactivity of **3** toward electrophiles. We decided to change the electrophilic species to a thiophene derivative as shown in Scheme 1.



Scheme 1. Preparation of quadruply bicyclo[2.2.2]octadiene-fused thiaporphyrins. Reagents and conditions: i) *n*BuLi, TMEDA, hexane, reflux, 30 min; DMF, THF, –50 °C to r.t.; ii) $NaBH_4$, THF/MeOH, 0 °C; iii) **6**, TFA, $CHCl_3$, 50 °C, 1 h; iv) LiOH, aqueous THF/EtOH, reflux, 16 h; v) **4**, TFA, CH_2Cl_2, r.t., 16 h; Et_3N, DDQ.

According to the literature procedure, ethanoisoindoledicarbaldehyde **4a** was directly prepared in 65% yield by diformylation of 4,7-ethanoisoindole with trimethyl orthoformate in TFA.[16] On the other hand, the reaction of 4,7-ethanoisothianaphthene (**3**) under similar conditions gave a monoformyl derivative. Therefore, lithiation of **3** followed by formylation was examined under several conditions. Treatment of **3** with 2.5 equiv. of LDA or *n*BuLi in THF at –10 °C followed by quenching with DMF, however, also provided only the monoformylated compound. More severe conditions were needed for dilithiation. Thus, thiophene **3** was treated with 2.5 equiv. of *n*BuLi in *n*-hexane in the presence of TMEDA, and then treated with DMF.[17] Diformyl thiophene **4b** was successfully obtained in 75% yield. Reduction of dialdehyde **4b** with $NaBH_4$ in a mixture of THF and methanol gave bis(hydroxymethyl)thiophene **5** in 83% yield. Bis(hydroxymethyl)thiophene **5** was then treated with pyrrolecarboxylate **6** under acidic conditions (TFA, chloroform, 50 °C) to give desired thiatripyrrane **7a** in good yield (90%). Saponification of **7a** with LiOH afforded dicarboxylic acid **7b** in almost quantitative yield (98%). The [3+1] condensation of **7b** with five-membered heterocyclic dicarbaldehydes **4a**,**b** in the presence of TFA followed by neutralization with triethylamine and oxidation with DDQ gave diastereomeric mixtures of targeted thiaporphyrins **1b** and **1c** in respective yields of 42 and 37%.

Retro-Diels–Alder Reaction of Bicyclooctadiene-Fused Porphyrins

The full π-system expansion could be carried out in the solid state under the usual conditions we used (230–250 °C, 30 min, ca. 0.2 Torr). The corresponding tetrabenzo derivatives **2a**–**c** were quantitatively obtained.[12a,12d] There must be a variety of intermediary benzo derivatives during the reactions from precursors **1a**–**c** to final TBP derivatives **2a**–**c**. In order to determine the thermal fragmentation pattern, the recrystallized samples of precursor **1a**–**c** were freed from solvents at 50 °C in vacuo (ca. 2 Torr) overnight and then subjected to thermogravimetric (TG) analysis. In the case of TBP precursor **1a**, one water molecule was involved in the sample, which was proved by combustion analysis. All TG experiments were carried out at a rate of 10 °C min^{-1}, and the TG results are shown in Figure 1.

Close inspection of the TG curve of **1a** revealed that smooth weight loss started after 100 °C and slowed down around 155 °C. Then, there was a turning point around 167 °C (14% weight loss), the curve became rather steep again, and the weight decrease stopped at 200 °C when 20.3% of the initial weight due to one water and four ethylene molecules was lost. The 14% weight decrease before the turning point was thought to be ascribed to three ethylene molecules. The second steep weight decrease after the turning point was due to extrusion of the last ethylene molecule. From Figure 1, precursors **1b**,**c** lost 14.5% (calcd. 17.5%) and 14.0% (calcd. 17.1%) of their weights corresponding to four molecules of ethylene between 100 and 260 °C, respectively. In the TG curves of **1b**,**c**, there were two turning points, both of which were observed around the similar percentage decrease. The decreasing rates became slow after 194 and 207 °C for **1b**,**c**, respectively. At these temperatures, about three quarters of the theoretical amounts had lost. In the TG curve of **1c**, two steep declining curves were clearly observed around 140 and 195 °C. On the other hand, the corresponding turning point was rather ambiguous in the TG curve of **1b**, although the turning point was clearly suggested to exist by the differential TG data.

In order to clarify the fragmentation pathway, incomplete fragmentation of **1a** was conducted. Thus, TBP pre-

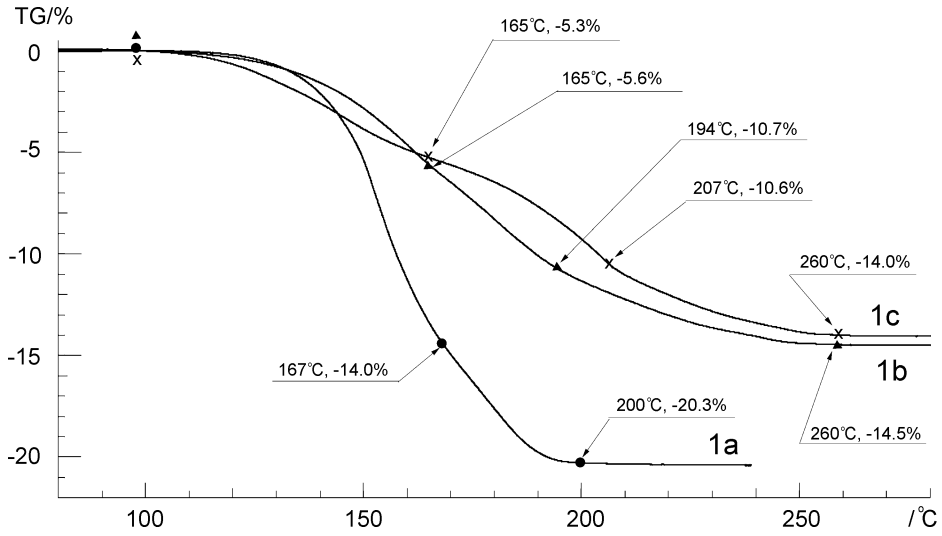


Figure 1. Thermogravimetric analysis of bicyclo[2.2.2]octadiene-fused porphyrins **1a**–**c**.

cursor **1a** was heated at 140 °C for 10 min and 15% of the initial weight was lost. The mixture was subjected to NMR and UV spectroscopic analysis. The ^{1}H NMR spectrum was carefully taken by dissolving 1 mg of the mixture in $CDCl_3$ in order not to affect the mixture composition. The UV spectra were obtained by diluting the NMR sample. From the UV spectra, TBP **2a** certainly existed in the mixture in a fair amount. Therefore, absorptions due to **2a** had to exist in the NMR spectra, although no NMR spectroscopic data of free base **2a** was recorded in $CDCl_3$ without an acid as a result of its poor solubility. In the ^{1}H NMR spectrum shown in Figure 2a, four strong absorptions are observed in the *meso* proton region (10–11 ppm). It was quite difficult to analyze the NMR spectra because starting TBP precursor **1a** was a diastereomeric mixture. Therefore, mono- and dibenzo derivatives would possibly consist of three and four isomers, respectively. We decided to isolate the intermediary benzo derivatives.

The mixture was subjected to GPC separation, and only two fractions were recognized and collected. The combined recovery of two fractions was 61%. From their UV and NMR spectra, the first and second fractions did not contain free base TBP **2a**, and they were determined to consist of dibenzoporphyrins **9a** and tribenzoporphyrin **10a**, respectively. In the ^{1}H NMR spectrum of the first fraction, diastereomers of *opp*-dibenzoporphyrins *opp*-**9a** dominantly existed, and the ratio of *opp*-**9a** and *adj*-**9a** was 3:1 (Figure 2c). This finding is in accord with the fact that the 22π-electron system involving the inner lone pair of electrons depicted as the light grey region in *opp*-**9a** (Scheme 2) plays a more important role than that in *adj*-**9a**.[18] Free-base TBP **2a**, which surely existed in the mixture, was irreversibly adsorbed on a filter membrane and/or GPC polystyrene gel. In the ^{1}H NMR spectrum of tribenzoporphyrin **10a** recorded at ambient temperature, all absorption signals were unambiguously assigned, although the signals were rather broad and the chemical shifts were concentration- and tem-

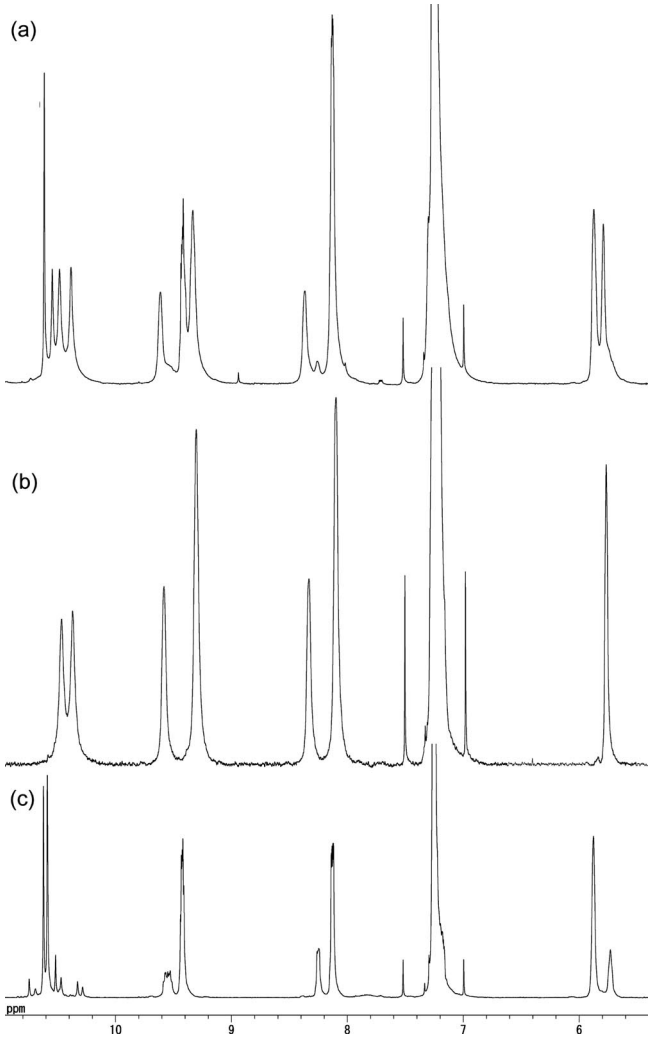
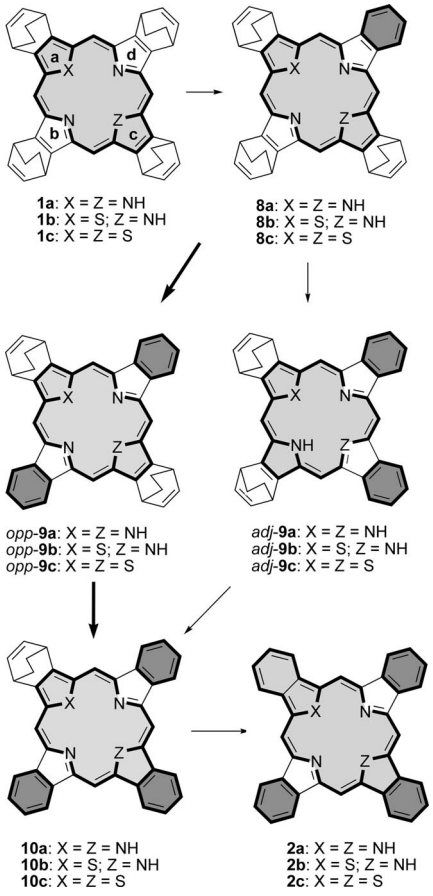


Figure 2. NMR spectra in $CDCl_3$: (a) the mixture obtained in the incomplete fragmentation; (b) tribenzoporphyrin **10a**; (c) dibenzoporphyrin **9a**.

perature-dependent due to stacking. The spectra of isolated dibenzoporphyrins **9a** and tribenzoporphyrin **10a** are compared with the mixture spectrum in Figure 2. From Figure 2, four major *meso* proton signals could be assigned, and the mixture was concluded to consist of *opp*-**9a**, *adj*-**9a**, **10a**, and TBP **2a** in a roughly estimated ratio of 6:2:10:3.



Scheme 2. Reaction pathway to tetrabenzoporphyrins.

Next, the fragmentation of **1a** was carried out at 130 °C for 10 min and 2% of the initial weight was lost. In the ^{1}H NMR and UV spectra of the mixture, only the starting porphyrin and monobenzoporphyrins **8a** as a diastereomeric mixture were found. GPC separation of the mixture afforded diastereomeric monobenzoporphyrins **8a** as well as recovered starting precursor **1a**. The ratio of **8a** and **1a** was ca. 4:5. This fact means that the first and the second fragmentation rates of **1a** were surely different, though no step was observed between them by TG analysis. The importance of the 22π-electron system in *opp*-**9** over *adj*-**9** was clearly exemplified by the incomplete fragmentation of thiaporphyrin **1b** when heated at 130 °C for 10 min. Under these conditions, the bicyclo[2.2.2]octadiene parts of the pyrrole moieties (Scheme 2, rings b and d) adjacent to the thiophene units (Scheme 2, ring a) predominantly (ca. 90%) underwent the retro-Diels–Alder reaction by examination of the ^{1}H NMR spectrum of the mixture: proton signals of the adjacent benzo moieties (Scheme 2, rings b and d) appeared in higher regions (9.29 ppm for the γ protons and 8.06 ppm for the δ protons) than those of the opposite benzo moiety (ring c: 9.75 ppm for the γ protons and 8.36 ppm for the δ protons) due to fixation of the major contributing 22π-electron system by replacement of the core atom with sulfur.[11] Thiabenzo[*q*]porphyrin **8b** and thiadibenzo[*g*,*q*]porphyrin *opp*-**9b** were obtained in yields of 38 and 35%, respectively, by GPC separation.

Because the fragmentation of 4,7-ethanoisoindole occurred at a lower temperature (170 °C) than that of ethanoisothianaphthene **3** (200 °C),[16] the selective extrusion of ethylene molecules to afford the isoindole moieties was expected to occur at the first steep declining curve in the TG experiment of bicyclo[2.2.2]octadiene-fused dithiaporphyrin **1c**. *opp*-Dibenzo derivatives would predominantly exist at the flat region around 165 °C. This assumption was proven to be the case. The thermal fragmentation of **1c** was conducted at 145 °C for 10 min and the partially decomposed mixture was then subjected to NMR spectroscopic analysis. From the ^{1}H NMR spectra, diastereomeric *opp*-dibenzo isomers *opp*-**9c** were preferentially formed in over 80% selectivity in addition to a small amount of tribenzoporphyrin **10c**. Preparative GPC isolation of the mixture afforded pure isomers of *opp*-**9c** in a combined yield of 60%.

As the last ethylene molecule slowly came off after 195 °C in the thermal fragmentation of **1b**,**c** (Figure 1), tribenzoporphyrin derivatives **10b**,**c** could be obtained if the fragmentation conditions were properly controlled. Therefore, **1b** and **1c** were respectively heated at 170 and 180 °C for 10 min, and the mixtures were subject to the GPC separation. Core-modified tribenzoporphyrins **10b**,**c** were obtained in 40 and 67% yields, respectively. In all cases, the fourth extrusion of ethylene unit required a rather high energy. This is rationalized by the local aromatization energy in the benzene ring formation (dark grey parts in Scheme 2) and the porphyrin macrocyclic 22π-electron systems (light grey parts in Scheme 2) in each step. In the last step, only the 10π-electron system of isoindole or isothianaphthene is formed in the important 22π-electron system, whereas the benzene moiety is produced without significant interference to the 22π-electron system in other steps.

Spectroscopic Analyses of the Porphyrins

The ^{1}H NMR spectra of bicyclo[2.2.2]octadiene-fused porphyrins **1a**–**c** were very complicated due to the diastereomeric nature of the bicyclo[2.2.2]octadiene moieties. The ^{1}H NMR spectra of **1a**–**c** in $CDCl_3$ showed no dependence on temperature or concentration. Absorptions due to the *meso* protons between the thiophene and pyrrole moieties appeared in the lower region at about 10.95–10.94 ppm; the *meso* protons between the pyrrole moieties appeared at 10.40–10.39 ppm. Broad signals due to the inner pyrrolic protons of **1a**,**b** were observed at –4.80 and –4.61 ppm, respectively. In diastereomeric *opp*-dibenzoporphyrins *opp*-**9a**, absorptions due to the *meso* protons appeared at about 10.61 ppm as an overlapped singlet signal or as two singlet

signals depending on the low or high concentration, respectively. Similarly, signals due to the *meso* protons adjacent to the benzo moiety of monobenzoporphyrins **8a** appeared around 10.6 ppm, whereas the *meso* proton signals between the bicyclo[2.2.2]octadiene moieties were observed around 10.3 ppm. The *meso* proton signals of isomeric *adj*-**9a** appeared at 10.74, 10.68 (between benzo moieties), 10.52, 10.47 (between benzo and bicyclooctadiene moieties), 10.33, and 10.29 (between bicyclooctadiene moieties) ppm. In the case of tribenzoporphyrin **10a**, the chemical shifts and widths of the absorption signals were highly dependent on the measuring conditions, such as concentration and temperature. A narrow singlet signal due to the *meso* protons was observed at 10.15 ppm in the case of a saturated solution of **10a** in $CDCl_3$ at ambient temperature. The signal shifted downward with broadening, and finally split into two broad signals at 10.48 and 10.38 ppm, as the concentration was lowered (Figure 2b).

Chemical shifts of the aromatic protons were sensitively affected by the diamagnetic ring current effect of the macrocyclic ring systems. Signals of the benzo moieties in monobenzoporphyrins **8a** and *opp*-dibenzoporphyrins *opp*-**9a** were observed at 9.42 (γ protons: $H2^1$ and $H2^4$ for **8a**; $H2^1$, $H2^4$, $H12^1$ and $H12^4$ for *opp*-**9a**) and 8.12 (δ protons: $H2^2$ and $H12^3$ for **8a**; $H2^2$, $H2^3$, $H12^2$ and $H12^3$ for *opp*-**9a**) ppm, whereas the benzo proton signals of *adj*-**9a** were observed at the lower regions of 9.55 (γ protons) and 8.25 (δ protons) ppm. This is well understood by the major contribution of the 22π-electron system[10,18] involving the lone pair of electrons of two five-membered ring heterocycles (which is depicted as the light grey regions of **8a** and *opp*-**9a** in Scheme 2) to the porphyrin macrocyclic system. Namely, the chromophores of **8a** and *opp*-**9a** are the highly symmetric 22π-electron system (light grey) having coplanar benzene units (dark grey) rather than expanded 26π- and 30π-electron systems. In *adj*-**9a**, the lower-contributing 22π-electron system can only be drawn if two benzene rings are depicted (Scheme 2). Therefore, the diamagnetic macrocyclic ring current affects more on the benzene rings of *adj*-**9a** than on those of **8a** and *opp*-**9a**. This is also supported by the NMR analysis of tribenzoporphyrins **10a**–**c**: The benzo protons on the center benzene rings appeared always lower than those on the edge benzene rings (see Figure 2b and Experimental Section). The X-ray analysis of **10a**–**c** also suggested this effect (vide post).

The UV/Vis spectra[12d] of bicyclooctadiene-fused porphyrins **1a**–**c** closely resembled those reported for the corresponding octaalkyl-substituted porphyrins,[19] and proportional bathochromic shifts were observed in the absorption bands as the number of the sulfur atoms and fused benzene rings increased. Electronic spectra of the free-base porphyrins are shown in Figure 3 for the qualitative discussion of the π-system expansion. As a result of the bulky bicyclo[2.2.2]octadiene moieties, porphyrins **1a**, **8a**, **9a**, and **10a** were quite soluble in common solvents such as chloroform, and no aggregative behavior was observed under UV-measuring conditions. On the other hand, free-base TBP **2a** was poorly soluble in chloroform and molar extinction coefficients could not be calculated. From Figure 3a, the Soret band absorptions were bathochromically shifted from 386 ($\log_{10}\varepsilon$ = 5.13, **1a**) to 401 (5.42, **8a**), 410 (5.78, **9a**), and 415 (5.65, **10a**) nm by benzene-ring expansion of the porphyrin chromophore. The Q–I band absorptions were also redshifted from 614 ($\log_{10}\varepsilon$ = 3.09, **1a**) to 625 (3.98, **8a**), 642 (4.44, **9a**), and 648 (4.49, **10a**) nm. These spectra were quite similar to those reported for mono- and dibenzoporphyrins.[12c,20] In the case of TBP **2a** in chloroform, however, Soret and Q–I bands appeared at 413 and 648 nm, respectively (Figure 3b). Close inspection of the spectra of TBP **2a** in chloroform revealed the presence of shoulders in these peaks at about 427 and 661 nm. The shoulder peaks greatly increased when the solvent was changed to 5% pyridine/THF. TBP **2a** in a 5% pyridine/THF solution had obvious split Soret bands at 412 and 427 nm corresponding to B_y and B_x[21] with similar molar extinction coefficients, and a fused Q–I band at 661 nm as reported by Koehorst et al.[22]

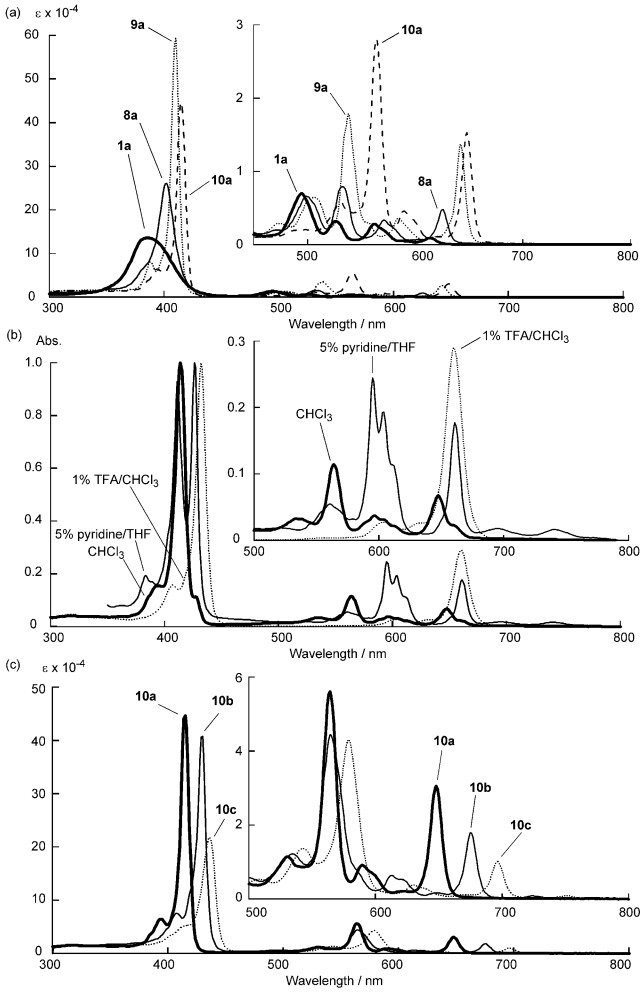


Figure 3. UV/Vis spectra of benzoporphyrins: (a) **1a** (bold line), **8a** (solid line), **9a** (dotted line), and **10a** (broken line) in $CHCl_3$; (b) **2a** in $CHCl_3$ (bold line), 5% pyridine/THF (solid line), and 1%TFA/CH_2Cl_2 (dotted line); (c) **9a** (bold line), **9b** (solid line), and **9c** (dotted line) in $CHCl_3$.

In the UV spectra of tribenzoporphyrins (Figure 3c), proportional bathochromic shifts were observed as the number of sulfur atoms increased. In the spectra of thiatribenzoporphyrins **10b**,**c**, new absorption bands with very long wavelengths were observed at 724 ($\log_{10} \varepsilon = 2.96$) and 750 (2.99) nm, respectively. No corresponding absorption band was found either in the spectra of tribenzoporphyrin **10a** or in those of thiatetrabenzoporphryins **2b**,**c**.

X-ray Structural Analysis

As electronic spectra of porphyrinoids were greatly affected by the structures, we carried out the X-ray analysis of the porphyrins. Porphyrins were dissolved in chloroform, benzene, chlorobenzene, or pyridine, and the solutions were placed in a vapor of methanol or 2-propanol. Good single crystals of **1a**·3PhH, **1a**·2/3PhCl, **8a**·5/2PhCl, *cis*-*opp*-**9c**·2($CHCl_3$), *trans*-*opp*-**9c**·1/2($CHCl_3$), and **10a**–**c** were obtained. In the case of **1a**·2/3PhCl, other solvent molecules surely existed around special positions in a heavily disordered fashion. We failed to model these solvent molecules. Thus, the porphyrin and chlorobenzene molecules were refined without the disordered molecules by the Platon squeeze technique.[23] In the case of **8a**·5/2PhCl, residual values were rather high due to slight disorder of solvent chlorobenzene molecules. The residual values were greatly improved by removal of the solvent molecules with Platon squeeze. Of course, **1a** and **8a** used for the X-ray experiment were diastereomeric mixtures. Therefore, the ethylene and ethynylene bridges of bicyclo[2.2.2]octadiene moieties were treated as disordered structures, and the populations were calculated except for some cases, where the bond characters could be unambiguously assigned by their bond lengths. In the cases of tribenzoporphyrins **10a**–**c**, ethylene and ethynylene bridges could not be distinguished and treated as disordered structures. In the cases of **1a**·2/3PhCl and *trans*-*opp*-**9a**·1/2($CHCl_3$), two crystallographically independent molecules were found in the asymmetric unit cells. In the cases of **1a**·3PhH, **1a**·2/3PhCl (one molecule), and *trans*-*opp*-**9a**·1/2($CHCl_3$) (both molecules), the porphyrin molecules occupied special positions with –1 symmetry. The results are summarized in the Experimental Section and the ORTEP edge views along the facing core heteroatoms (left column: along heteroatoms 21 and 23; right column: along nitrogen atoms 22 and 24) are shown in Figure 4.

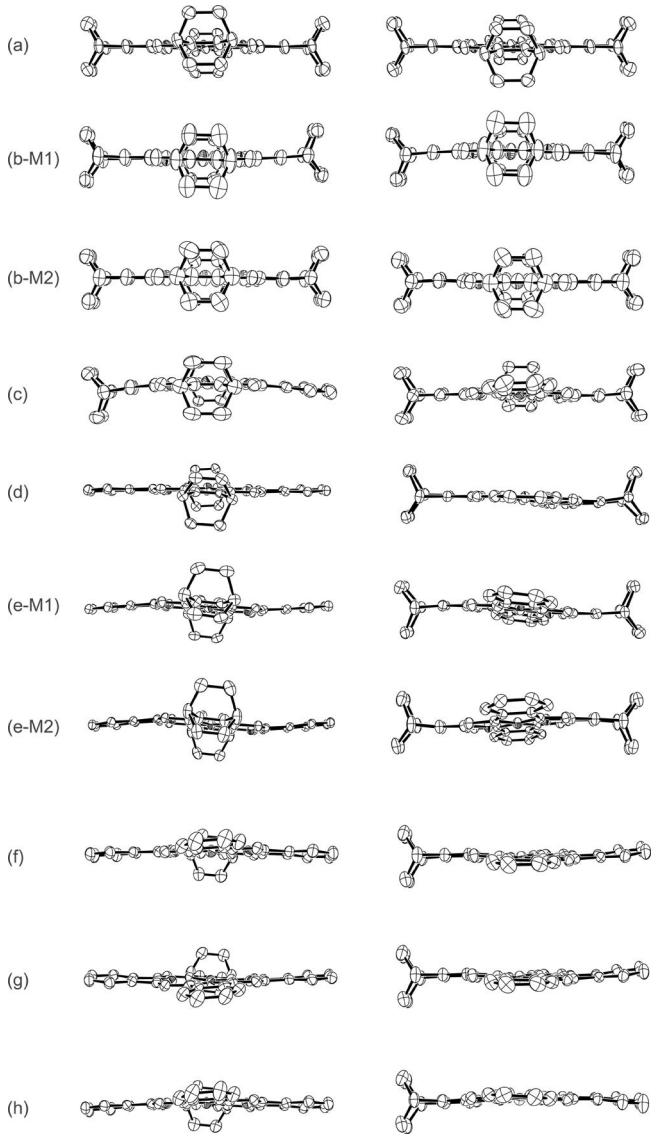


Figure 4. ORTEP edge views of porphyrins (left column: along heteroatoms 21 and 23; right column: along nitrogen atoms 22 and 24). Hydrogen atoms are omitted for clarity. (a) **1a**·3PhH; (b) **1a**·2/3PhCl; (c) **8a**·5/2PhCl; (d) c*is*-*opp*-**9c**·2$CHCl_3$; (e) *trans*-*opp*-**9c**·1/2$CHCl_3$; (f) **10a**; (g) **10b**; (h) **10c**.

We reported that zinc *meso*-tetraphenylporphyrin fused with four bicyclo[2.2.2]octene units at the β,β-positions showed an exceptionally flat structure and adopted very slight wave out-of-plane distortion.[24] In the cases of these bicyclo[2.2.2]octadiene-fused porphyrins, too, no obvious out-of-plane distortion was observed except for *trans*-*opp*-**9c**. Both molecules of *trans*-*opp*-**9c** adopted wave out-of-plane distortion (Figure 4e), whereas the porphyrin plane of *cis*-*opp*-**9c** was almost flat (Figure 4d). The difference between *cis*-*opp*-**9c** and *trans*-*opp*-**9c** is only the bond character of ethylene and ethynylene, and thought to be tiny, because diastereomeric **1a** formed single crystals as a mixture of diastereomers. In these crystals, the molecules of *trans*-*opp*-**9c** and *cis*-*opp*-**9c** occupy special and normal positions, respectively. Therefore, we concluded that the molecules of *meso*-free dibenzoporphyrins were intrinsically flat and the molecules of *trans*-*opp*-**9c** were distorted by the crystal packing.

In the crystal structure of **1a**·3PhH, bicyclo[2.2.2]octadiene moieties and inner pyrrolic protons are completely disordered. The crystal structure of **1a**·3/2PhCl is worthy to mention. In order to understand the relative molecular positions, the crystal packing diagram (ORTEP) is shown in Figure 5. In this crystallizing system, the single crystals grew very slowly and the suitable crystals for the X-ray analysis were obtained after about six months. At –123 °C, two independent molecules M1 and M2 of **1a** were found

at normal and special (–1) positions, respectively. The porphyrin rings of molecules M1 and M2 were in almost the same plane to form a two-dimensional sheet. The dihedral angle between M1 and M2 was 3.46(2)°. In addition to these porphyrin molecules, one chlorobenzene molecule was found at a normal position. Although high electron peaks were found around other special positions, they formed meaningless structures. Even at –180 °C, we failed to model solvent structures from the peaks. In this crystal structure, *ortho* and *meta* protons of the properly modeled chlorobenzene molecule pointed to the core imine nitrogen atoms (22 and 24 positions) of the porphyrin molecule M1 occupying the normal position. The distances of N···H–C were 2.824 (*ortho*) and 2.476 (*meta*) Å, and their angles were 168.9° and 166.5°. The dihedral angle between the porphyrin ring of molecule M1 and chlorobenzene was almost perpendicular [92.26(9)°]. Because of this interaction, the inner pyrrolic hydrogen atoms were nicely fixed at the 21- and 23-positions. Therefore, the C–N–C angles of these pyrrole moieties [110.8(3)° and 111.6(3)°] were wider than those of the imine moieties [105.7(2)° and 105.2(2)°]. One of the bicyclo[2,2,2]octadiene moieties was not disordered and the bond characters were fixed [1.342(3) for the double bond and 1.517(3) Å for the single bond]. Other three bicyclo[2,2,2]octadiene moieties were disordered by diagnosis of the bond lengths, which showed almost an average value of single and double carbon–carbon bonds [1.419(5), 1.479(5), 1.432(4), 1.421(4), 1.442(5), and 1.405(5) Å]. However, one of the bicyclooctadiene moieties neighboring the ordered bicyclo[2.2.2]octadiene was not treated as the disordered structure because the values were rather different [1.419(5) and 1.479(5) Å]. Furthermore, the short intermolecular contact of hydrogen atoms was observed if it was treated as the disordered structure. Another porphyrin molecule occupying a special position was not disordered and the hydrogen atoms on the bridges were correctly found, although they were not refined. The type-IV centrosymmetric one of four possible isomers (*cis–trans–cis–trans* isomer, 25% amount by mathematical calculation) selectively occupied this special position.

In the benzo moieties of **8a** and *opp*-**9c**, their bond lengths were from 1.375(4) to 1.420(4) Å, which were quite typical for benzene. Among them, the bonds at the fused positions (Cβ–Cβ) were rather longer [1.397(3), 1.394(4), 1.420(4), 1.405(4), and 1.407(4) Å] than others. These values were also larger than the Cβ–Cβ bonds fused with bicyclooctadiene [from 1.340(4) to 1.381(4) Å]. This is rationalized by the partial contribution of the π-system expansion from 22π to 26π or 30π. Structures of isoindoles have attracted much attention due to the intrinsic tautomerism between the *2H*- and *1H*-isomers.[25] Large bond alteration of benzene rings in *2H*-isoindole was predicted by calculation[26] and proved by X-ray analysis.[27] Especially, the fused bond between benzene and pyrrole rings was quite elongated: 1.43 Å,[27] and the bond order of the fused bond decreased,[25] because the aromaticity of *2H*-isoindole was mainly ascribed to the peripheral 10π-electron system. On the other hand, the bond alteration in the benzene moiety of *1H*-isoindole was quite smaller and the fused-bond lengths were 1.387–1.415 Å.[27a,28] The benzo structures of **8a** and *opp*-**9c** quite resembled those of *1H*-isoindole. Therefore, the porphyrinic macrocyclic pathway mainly goes through the inner route of these isoindole moieties depicted in Scheme 2.

In tribenzoporphyrins **10a**–**c**, quite interesting bond alteration was observed, and bond lengths of the benzo moieties are listed in Table 1. These crystals had the same space group and the similar cell constants. Their crystal packing diagrams were also similar. From Table 1, the Cβ–Cβ bonds fused with benzene ring had quite similar values [from 1.393(3) for C7–C8 in **10a** to 1.417(5) for C7–C8 in **10c**] to those of **8a**, *opp*-**9c**, and *1H*-isoindoles irrespective of their positions. On the other hand, distinctive bond alteration was only observed in the benzene rings opposite to the bicyclo[2.2.2]octadiene-fused positions, and bond lengths of other benzene rings adjacent to the bicyclo[2.2.2]octadiene-fused positions showed the similar tendency observed in **8a** and *opp*-**9c**. This fact clearly suggests that the major contributing porphyrinic 22π-electron system is effectively expanded by fusion of the center benzene ring and the macro-

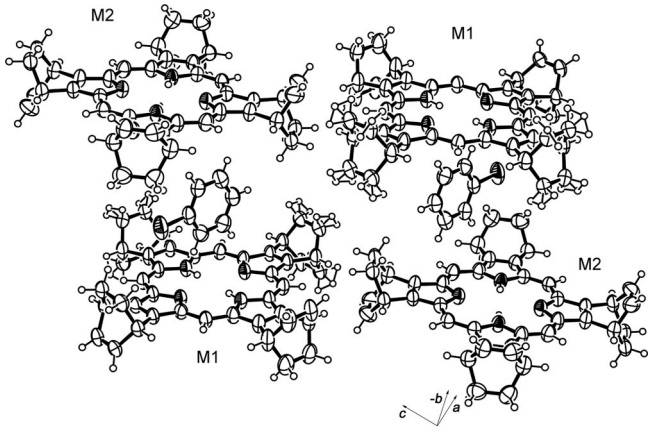


Figure 5. ORTEP packing diagram of **1a**·2/3PhCl.

Table 1. Bond lengths of benzo moieties in tribenzoporphyrins **10a**–**c**.

Compound	Bond lengths of the edge benzene rings /Å				Bond lengths of the center benzene ring /Å			
	Cβ-Cβ	Cβ-Cγ	Cγ-Cδ	Cδ-Cδ	Cβ-Cβ	Cβ-Cγ	Cγ-Cδ	Cδ-Cδ
10a[a]	1.393 1.399	1.390 1.392 1.396 1.398	1.387 1.386 1.385 1.379	1.389 1.391	1.398	1.403 1.403	1.350 1.368	1.404
10b[a]	1.408 1.396	1.383 1.390 1.398 1.395	1.384 1.387 1.383 1.383	1.402 1.396	1.399	1.403 1.402	1.365 1.367	1.402
10c[b]	1.405 1.417	1.384 1.396 1.390 1.389	1.387 1.384 1.389 1.388	1.395 1.390	1.414	1.419 1.403	1.343 1.362	1.410

[a] The s.u. value is 3 or 4. [b] The s.u. value is 5 or 6.

cyclic ring current goes through not the edge but center benzene rings. This is also supported by the chemical shifts of these protons discussed above.

Conclusions

opp-Dibenzoporphyrins were preferentially formed during the thermal fragmentation of quadruply bicyclo[2.2.2]-octadiene-fused porphyrins to tetrabenzoporphyrins. The first and the second fragmentations were not distinguished by the thermogravimetric analysis, although they occurred stepwise. The third extrusion of an ethylene molecule from the 21,23-dithiaporphyrin derivative was very slow and the 21,23-dithiadibenzo[*g*,*q*]porphyrin was obtained with good selectivity. In the case of the 21-thiaporphyrin derivative, an ethylene molecule was extruded selectively from the bicyclo[2.2.2]octadiene moiety adjacent to the thiophene part to give 21-thiabenzo[*q*]porphyrin and then 21-thiadibenzo-[*g*,*q*]porphyrin derivatives. This is rationalized by the fact that the major contributing macrocyclic pathway of the porphyrin chromophore is effectively fixed by replacement of core NH groups by sulfur atoms. In all cases, the last extrusion of ethylene giving tetrabenzoporphyrins required high energy because the energetic merit at this step was a gain of only 10π-electron aromaticity of isoindole or isothianaphthene.

Experimental Section

General: Melting points were measured with a Yanaco M500-D melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-AL 400 or -EX 400 spectrometer by using tetramethylsilane as an internal standard. IR spectra were measured with a Hitachi 270–30 as KBr disks. FAB and DI-EI mass spectra were measured with a JEOL JMS-700 instrument. MALDI-TOF mass spectra were measured with a Voyager DE Pro instrument (Applied Biosystems). Elemental analyses were performed with a Yanaco MT-5 elemental analyzer. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. Dry dichloromethane and THF were purchased from Kanto Chemical Co. Toluene, hexane, triethylamine, pyridine, DBU, and chloroform were distilled from calcium hydride and then stored over appropriate molecular sieves. Solvents for chromatography were purified by distillation. For spectral measurements, spectral grades of toluene and chloroform were purchased from Nacalai Tesque Co. Thin-layer (TLC) and column chromatography was performed on Art 5554 (Merck KGaA) and silica gel 60 N (Kanto Chemical Co.), respectively. Ethyl 4,7-dihydro-4,7-ethano-*2H*-isoindole-1-carboxylate (**6**), 4,7-dihydro-4,7-ethano-*2H*-isoindole-1,3-dicarbaldehyde (**4a**), and TBP precursor **1a** were prepared according to literature procedures.[12]

4,7-Dihydro-4,7-ethano-2-benzothiophene (3): 3-Thiolen-2-one[29] (14.6 g, 146 mmol), 1,3-cyclohexadiene (20.8 mL, 219 mmol), and pyridine (0.05 mL) were placed in a stainless steel cylinder equipped with a magnetic stirring bar. The cylinder was screw-capped and heated at 120 °C for 2 d with stirring. The cylinder was cooled to room temperature, and the cap was carefully unscrewed. The inner mixture was concentrated, and the residue was chromatographed on silica gel (10% EtOAc/hexane) to give 20.2 g (113 mmol; 77%) of *endo*-4-thiatricyclo[5.2.2.0^{2,6}]undec-8-en-3-one[29] as an oil, which solidified in the refrigerator. R_f = 0.35 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.29–6.27 (m, 2 H), 3.47 (dd, J = 11.2, 9.7 Hz, 1 H), 3.04 (m, 1 H), 2.94–2.77 (m, 3 H), 2.72 (m, 1 H), 1.54–1.50 (m, 2 H), 1.31–1.29 (m, 2 H) ppm.

To a stirred solution of *endo*-4-thiatricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (9.01 g, 50.0 mmol) in dry THF (130 mL) was slowly added a solution of LDA (2.0 M in THF, 30.0 mL, 60.0 mmol) at –78 °C under an atmosphere of nitrogen, and the mixture was stirred for 20 min at the same temperature. To this mixture was added a solution of PhSeBr (14.16 g, 60.0 mmol) in dry THF (30 mL) with stirring. After addition, the resulting mixture was warmed up to room temperature and stirred for 1 h. Water was added, roughly a half amount of solvent was removed by evaporation, and the residual mixture was extracted with diethyl ether. The ethereal extract was washed sequentially with water, saturated aqueous $NaHCO_3$, water, and brine and then dried with Na_2SO_4. After removal of the drying agent, the mixture was concentrated and the residual oil was purified by column chromatography on silica gel (10% EtOAc/hexane) to give 15.2 g (45.5 mmol; 91%) of *endo*-2-phenylselenenyl-4-thiatricyclo[5.2.2.0^{2,6}]undec-8-en-3-one as colorless crystals. M.p. 72–73 °C. R_f = 0.35 (10% EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (m, 2 H), 7.42 (m, 1 H), 7.33 (m, 2 H), 6.29–6.20 (m, 2 H), 3.18 (dd, J = 11.4, 10.0 Hz, 1 H), 2.82–2.76 (m, 2 H), 2.64 (m, 1 H), 2.54 (m, 1 H), 2.33 (m, 1 H), 1.69 (m, 1 H), 1.38–1.25 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.3, 137.8, 134.2, 132.5, 129.6, 128.9, 126.7, 66.0, 48.1, 37.6, 36.4, 34.1, 25.8, 20.1 ppm. IR (KBr): $\tilde{\nu}$ = 3046, 2938, 2861, 1670, 1434, 1369, 1299, 1245, 1095 cm^{-1}. MS (EI): *m*/*z* (%) = 336 (71) [M]$^+$, 179 (100), 151 (61). $C_{16}H_{16}OSSe$ (335.32): calcd. C 57.31, H 4.81; found C 57.61, H 5.07.

A solution of *endo*-2-phenylselenenyl-4-thiatricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (15.7 g, 46.8 mmol) in CH_2Cl_2 (300 mL) was cooled to –20 °C and *m*-chloroperbenzoic acid (70% assay; 11.5 g, 46.8 mmol) was added slowly. After the addition, the mixture was warmed to room temperature and stirred for 2 h. Water was added, and the mixture was extracted with CH_2Cl_2. The organic extract was washed sequentially with water, saturated aqueous $NaHCO_3$, water, and brine and then dried with Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (10–20% EtOAc/hexane) to give 6.68 g (37.4 mmol; 80%) of 4-thiatricyclo[5.2.2.0^{2,6}]undeca-2(6),8-dien-3-one as pale yellow crystals. R_f = 0.22 (10% EtOAc/hexane). M.p. 46–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (m, 1 H), 6.37 (m, 1 H), 4.03 (m, 1 H), 3.98 (s, 2 H), 3.83 (m, 1 H), 1.55–1.36 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 173.2, 145.5, 135.4, 132.9, 40.9, 35.3, 34.2, 25.2, 24.8 ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2937, 2868, 1664, 1402, 1367, 1333, 1236, 1200, 1140 cm^{-1}. MS (EI): *m*/*z* (%) = 178 (8) [M]$^+$, 150 (100), 122 (66). $C_{10}H_{10}OS$ (178.25): calcd. C 67.38, H 5.65; found C 67.34, H 5.73.

To a stirred solution of 4-thiatricyclo[5.2.2.0^{2,6}]undeca-2(6),8-dien-3-one (6.23 g, 35.0 mmol) in dry CH_2Cl_2 (80 mL) was slowly added a solution of DIBAL (1.0 M in hexane, 38.5 mL, 38.5 mmol) at –10 °C, and then the mixture was stirred for 30 min at that temperature. An aqueous solution of hydrochloric acid (1.0 M, 100 mL) was added at the temperature, and the mixture was extracted with CH_2Cl_2. The organic extract was washed with water, dried with Na_2SO_4, and concentrated. The oily residue was purified by column chromatography on silica gel (hexane) to give 4.65 g (28.7 mmol, 82%) of **3** as colorless crystals. R_f = 0.43 (hexane). M.p. 57–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.72 (s, 2 H), 6.49 (m, 2 H), 3.87 (m, 2 H), 1.61–1.51 (m, 4 H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 146.5, 135.4, 112.3, 36.5, 26.4 ppm. IR (KBr): $\tilde{\nu}$ = 2950, 2863, 1473, 1392, 1346, 1226 cm^{-1}. MS (EI): *m*/*z* = 162 $[M]^+$, 134. $C_{10}H_{10}S$ (162.25): calcd. C 74.02, H 6.21; found C 73.69, H 6.21.

4,7-Dihydro-4,7-ethano-2-benzothiophene-1,3-dicarbaldehyde (4b): To a stirred solution of **3** (2.43 g, 15.0 mmol) and TMEDA (3.56 mL, 36.0 mmol) in dry hexane (50 mL) was added a solution of *n*BuLi (1.58 M in hexane, 22.7 mL, 36.0 mmol) at room temperature, and the mixture was heated at reflux for 30 min. After being cooled to –50 °C, dry THF (80 mL) and then dry DMF (10 mL) were slowly added with stirring. The mixture was allowed to warm to room temperature and the stirring was continued overnight. The mixture was poured into hydrochloric acid (1.0 M, 50 mL), and the mixture was extracted with $CHCl_3$. The organic extract was washed sequentially with water, saturated aqueous $NaHCO_3$, water, and brine, dried with Na_2SO_4, and concentrated. Column chromatography on silica gel ($CHCl_3$) of the residue gave a crude material, which was further purified by recrystallization from $CHCl_3$/hexane to give 2.47 g (11.3 mmol, 75%) of **4b** as pale yellow crystals. R_f = 0.43 ($CHCl_3$). M.p. 134–135 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.09 (s, 2 H), 6.58 (m, 2 H), 4.55 (m, 2 H), 1.76–1.59 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.2, 155.6, 136.0, 134.7, 34.9, 25.2 ppm. IR (KBr): $\tilde{\nu}$ = 2952, 2830, 1662, 1297, 1226, 1087, 1029 cm^{-1}. MS (FAB): *m*/*z* = 219 $[M + H]^+$. $C_{12}H_{10}O_2S$ (218.27): calcd. C 66.03, H 4.62; found C 65.96, H 4.43.

1,3-Bis(hydroxymethyl)-4,7-dihydro-4,7-ethano-2-benzothiophene (5): To a stirred solution of **4b** (1.30 g, 6.00 mmol) in dry THF (30 mL) and MeOH (5 mL) was added $NaBH_4$ (0.680 g, 18.0 mmol) in a small portion at 0 °C, and the mixture was stirred for 30 min. The mixture was poured into water (50 mL), and the mixture was extracted with diethyl ether. The ethereal extract was washed with water and brine, dried with Na_2SO_4, and concentrated to give a crude material. Recrystallization from $CHCl_3$/hexane gave 1.11 g (5.03 mmol, 83%) of **5** as colorless crystals. M.p. 143–145 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.49 (m, 2 H), 4.75–4.70 (m, 4 H), 3.91 (m, 2 H), 1.62–1.49 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 135.3, 129.4, 57.5, 34.8, 26.0 ppm. IR (KBr): $\tilde{\nu}$ = 3270, 2958, 2865, 1427, 1002 cm^{-1}. MS (EI): *m*/*z* = 222 $[M]^+$, 194, 177, 163, 147, 135, 115. $C_{12}H_{14}O_2S$ (222.30): calcd. C 64.83, H 6.53; found C 64.73, H 6.37.

1,3-Bis(3-ethoxycarbonyl-4,7-dihydro-4,7-ethano-2*H*-isoindolylmethyl)-4,7-dihydro-4,7-ethano-2-benzothiophene (7a): To a stirred solution of bis(hydroxymethyl)thiophene **5** (0.333 g, 1.50 mmol) and pyrrole **6** (0.652 g, 3.00 mmol) in $CHCl_3$ was slowly added TFA (1.0 mL) at 0 °C under an atmosphere of argon. The mixture was stirred at 0 °C for 1 h and then at 50 °C for an additional 1 h. Water was added to quench the reaction at room temperature. The mixture was extracted with $CHCl_3$. The organic extract was washed successively with water, saturated aqueous $NaHCO_3$, water, and brine, dried with Na_2SO_4, and concentrated. Recrystallization of the residue from EtOAc/hexane gave 838 mg (1.35 mmol; 90%) of diastereomeric mixture of **7a** as pale brown powder. R_f = 0.26 ($CHCl_3$). M.p. 199–205 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (br. s, 2 H), 6.52–6.39 (m, 6 H), 4.34–4.28 (m, 2 H), 4.27 (q, *J* = 7.1 Hz, 4 H), 4.02–3.91 (m, 4 H), 3.77–3.60 (m, 4 H), 1.60–1.25 (m, 12 H), 1.34 (t, *J* = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ = 161.6, 143.3 (3 C), 137.3, 136.0, 135.4 (2 C), 135.2, 128.2, 125.2, 125.0 (2 C), 112.5, 59.7, 34.8, 34.7, 33.8, 32.4 (2 C), 31.6, 26.8, 26.3 (2 C), 25.8 (2 C), 24.3 (2 C), 22.6, 14.6, 14.1 ppm. IR (KBr): $\tilde{\nu}$ = 3274, 3043, 2950, 2865, 1666, 1511, 1446, 1307, 1141, 1087 cm^{-1}. MS (EI): *m*/*z* (%) = 620 (24) $[M]^+$, 592 (100), 564 (48), 546 (7), 518 (19). $C_{38}H_{40}N_2O_4S$ (620.80): calcd. C 73.52, H 6.49, N 4.51; found C 73.18, H 6.57, N 4.37.

1,3-Bis(3-carboxy-4,7-dihydro-4,7-ethano-2*H*-isoindolylmethyl)-4,7-dihydro-4,7-ethano-2-benzothiophene (7b): Diester **7a** (0.620 g, 1.00 mmol) was dissolved in THF (10 mL) and a solution of LiOH (0.849 g, 20.0 mmol) in water (12 mL) and EtOH (8 mL) was added. The mixture was heated at reflux under an atmosphere of argon overnight and then an aqueous solution of HCl (1.0 M) was added to acidify (pH = ca. 1) at room temperature. The mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried with Na_2SO_4, and concentrated. The residual solid was dissolved in EtOAc and then hexane was added. The precipitates were collected to give 555 mg (0.983 mmol, 98%) of crude diastereomeric dicarboxylic acid **7b** as pale brown powder. This material was used without further purification. M.p. 117–149 °C. ^1H NMR (400 MHz, [D_6]acetone): δ = 9.68 (br. s, 2 H), 6.51–6.28 (m, 6 H), 4.35–4.22 (m, 2 H), 4.12–3.93 (m, 4 H), 3.90–3.74 (m, 2 H), 3.74–3.59 (m, 2 H), 1.57–1.31 (m, 12 H) ppm.

General Procedure for the [3+1] Condensation of Thiatripyrranedicarboxylic Acid 7b and Dicarbaldehyde: Thiatripyrranedicarboxylic acid **7b** (0.565 g, 1.00 mmol) and a magnetic stirring bar were placed in a 500-mL round-bottomed flask, which was thoroughly wrapped with aluminum foil and then flashed with nitrogen. To this vessel was added TFA (2.5 mL, 34 mmol), and the mixture was stirred for 5 min under an atmosphere of nitrogen. The resulting mixture was diluted with dry CH_2Cl_2 (200 mL) and then a dicarbaldehyde (1.00 mmol) was added. After the mixture was stirred at room temperature overnight, triethylamine (4.8 mL, 34 mmol) was slowly added to neutralize. DDQ (0.272 g, 1.20 mmol) was added, and the mixture was stirred for 2 h at room temperature. The mixture was washed successively with water, saturated aqueous $NaHCO_3$, water, and brine, dried with Na_2SO_4, and concentrated. The residue was chromatographed on basic alumina (an appropriate solvent system). Recrystallization gave pure core-modified porphyrin as a mixture of diastereomers.

$2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4$-Octahydro-$2^1,2^4;7^1,7^4;12^1,12^4;17^1,17^4$-tetraethano-23*H*,21-thiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (1b):[12d] The reaction with pyrroledicarbaldehyde **4a** was performed according to the general procedure. Chromatography (90% CH_2Cl_2/hexane) and recrystallization (CH_2Cl_2/MeOH) gave the title porphyrin in 42% yield as purple crystals: $C_{44}H_{37}N_3S$ (639.85): m.p. >130 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.90 (m, 2H, H_{meso}), 10.39 (m, 2H, H_{meso}), 7.25–7.21 (m, 4 H), 7.06 (m, 4 H), 6.04 (m, 2 H), 5.87 (m, 2 H), 5.57 (m, 4 H), 2.28 (m, 4 H), 2.13 (m, 4 H), 2.01–1.82 (m, 8 H), –4.61 (s, 1 H) ppm. MS (FAB): *m*/*z* (%) = 640 (44) $[M + H]^+$, 612 (10), 584 (9), 556 (32), 528 (100). UV/Vis (CH_2Cl_2): λ ($\log_{10}$ ε) = 394 (5.14), 497 (4.32), 528 (4.08), 590 (3.67), 663 (3.31) nm. $C_{44}H_{37}N_3S \cdot 1/4CH_2Cl_2$ (661.08): calcd. C 80.39, H 5.72, N 6.36; found C 80.30, H 6.00, N 6.17.

$2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4$-Octahydro-$2^1,2^4;7^1,7^4;12^1,12^4;17^1,17^4$-tetraethano-21,23-dithiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (1c):[12d] The reaction with thiophenedicarbaldehyde **4b** was carried out according to the general procedure. Chromatography (CH_2Cl_2) and recrystallization (CH_2Cl_2/MeOH) gave the title porphyrin in 37% yield as purple crystals: $C_{44}H_{36}N_2S_2$ (656.90): m.p. >130 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.94 (m, 4H, H_{meso}), 7.26 (m, 4 H), 7.06–7.03 (m, 4 H), 6.04 (m, 4 H), 5.55 (m, 4 H), 2.29 (m, 4 H), 2.13 (m, 4 H), 2.02–1.83 (m, 8 H) ppm. MS (FAB): *m*/*z* (%) = 657 (35) $[M + H]^+$, 629 (11), 601 (9), 573 (29), 545 (100). UV/Vis (CH_2Cl_2): λ ($\log_{10}$ ε) = 402 (5.12), 502 (4.36), 531 (4.06), 611 (3.47), 680 (3.04) nm. $C_{44}H_{36}N_2S_2 \cdot 1/4(CH_2Cl_2 + H_2O)$ (682.63): calcd. C 77.90, H 5.51, N 4.08; found C 77.64, H 5.80, N 4.01.

General Procedure for Preparative Retro-Diels–Alder Reaction: The precursor bicyclooctadiene-fused porphyrin in a sample tube (ca.

10 mg) was placed in a 25-mL round-bottomed flask. The flask was evacuated by a rotary vacuum pump and then heated at the indicated temperature for the indicated time in a glass tube oven. In the cases of incomplete fragmentation, the mixture was dissolved in chloroform and then filtered (0.45 μm). The filtered sample was subjected to the GPC separation (JAI gel 1H and 2 H). In the cases of complete fragmentation, the reaction mixture was directly subject to all analyses.

Thermal Fragmentation of 1a at 130 °C for 10 min: TBP precursor **1a** (10.5 mg) was heated at 130 °C for 10 min and the weight decreased to 10.3 mg. The mixture was separated by preparative GPC to give **1a** (5.2 mg, 50%) and **8a** (3.9 mg, 39%).

Thermal Fragmentation of 1a at 140 °C for 10 min: TBP precursor **1a** (10.6 mg) was heated at 140 °C for 10 min and the weight decreased to 9.0 mg. The mixture was separated by preparative GPC to give **9a** (2.5 mg, 26%) and **10a** (3.2 mg, 35%).

$2^1,2^4,7^1,7^4,12^1,12^4$-Hexahydro-$2^1,2^4;7^1,7^4;12^1,12^4$-triethano-21*H*,23*H*-tetrabenzo[*b*,*g*,*l*,*q*]porphyrin (8a): $C_{42}H_{34}N_4$ (594.75): red crystals, m.p. >130 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ = 10.63 (s, 2 H, H15, H20), 10.37 (s, 2 H, H5, H10), 9.42 (m, 2 H, $H17^1$, $H17^4$), 8.13 (m, 2 H, $H17^2$, $H17^2$), 7.3–7.1 (m, 6 H), 5.9–5.65 (m, 6 H), 2.3–2.15 (m, 6 H), 1.94 (m, 6 H), –4.34 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ = 152.2, 149.7, 145.8, 144.7, 142.0, 136.9, 136.7, 130.9, 130.0, 127.1, 120.8, 98.0, 94.6, 36.8, 36.6, 36.0, 35.9, 27.9 ppm. UV/Vis ($CHCl_3$): λ ($\log_{10}$ ε) = 401 (5.42), 499 (4.12), 532 (4.20), 570 (3.82), 625 (3.98) nm. HRMS (FAB+): calcd. for $C_{42}H_{35}N_4$ [M + H]$^+$ 595.2862; found 595.2863.

$2^1,2^4,12^1,12^4$-Tetrahydro-$2^1,2^4;12^1,12^4$-diethano-21*H*,23*H*-tetrabenzo[*b*,*g*,*l*,*q*]porphyrin (*opp*-9a) and $2^1,2^4,7^1,7^4$-Tetrahydro-$2^1,2^4;7^1,7^4$-diethano-21*H*,23*H*-tetrabenzo[*b*,*g*,*l*,*q*]porphyrin (*adj*-9a): 3:1 mixture: $C_{40}H_{30}N_4$ (566.69): red crystals, m.p. >140 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) *opp*-**9a** (1:1 mixture): δ = 10.63 (s, 4 H of one isomer, H_{meso}), 10.59 (s, 4 H of another isomer, H_{meso}), 9.42 (m, 4 H of both isomers, $H7^1$, $H7^4$, $H17^1$, $H17^4$), 8.12 (m, 4 H of both isomers, $H7^2$, $H7^3$, $H17^2$, $H17^3$), 7.26 (m, 4 H of both isomers), 5.88 (m, 4 H of both isomers), 2.31 (m, 4 H of both isomers), 1.98 (m, 4 H of both isomers), –4.01 (br. s, 1 H of one isomer), –4.09 (br. s, 1 H of another isomer) ppm. ^{1}H NMR (400 MHz, $CDCl_3$) *adj*-**9a** (1:1 mixture, typical signals): δ = 10.75 (s, 1 H of one isomer, H15), 10.67 (s, 1 H of another isomer, H15), 10.51 (s, 2 H of one isomer, H10, H20), 10.46 (s, 2 H of another isomer, H10, H20), 10.32 (s, 1 H of one isomer, H5), 10.28 (s, 1 H of another isomer, H5), 9.53 (m, 4 H of both isomers, $H12^1$, $H12^4$, $H17^1$, $H17^4$), 8.23 (m, 4 H of both isomers, $H12^2$, $H12^3$, $H17^2$, $H17^3$), 7.20 (m, 4 H of both isomers, $H2^2$, $H2^3$, $H7^2$, $H7^3$), 5.72 (4 H of both isomers: $H2^1$, $H2^1$, $H7^1$, $H7^1$) ppm. UV/Vis ($CHCl_3$): λ ($\log_{10}$ ε) = 388 (4.91), 410 (5.78), 474 (3.76), 506 (4.11), 538 (4.55), 557 (3.78), 584 (3.86), 642 (4.44) nm. HRMS (FAB+): calcd. for $C_{40}H_{31}N_4$ [M + H]$^+$ 567.2549; found 567.2549.

$2^1,2^4$-Dihydro-$2^1,2^4$-ethano-21*H*,23*H*-tetrabenzo[*b*,*g*,*l*,*q*]porphyrin (10a): $C_{38}H_{26}N_4$ (538.64): red crystals, m.p. >150 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.48 (s, 2 H, H10, H15), 10.38 (s, 2 H, H5, H20), 9.61 (m, 2 H, $H12^1$, $H12^4$), 9.33 (m, 4 H, $H7^1$, $H7^4$, $H17^1$, $H17^4$), 8.37 (m, 2 H, $H12^2$, $H12^3$), 8.13 (m, 4 H, $H7^2$, $H7^3$, $H17^2$, $H17^3$), 5.79 (m, 2 H, $H2^1$, $H2^4$), 2.30 (m, 2 H), 1.97 (m, 2 H), –3.25 (br. s, 1 H) ppm. UV/Vis ($CHCl_3$): λ ($\log_{10}$ ε) = 394 (4.81), 415 (5.65), 499 (3.61), 530 (4.06), 564 (4.75), 590 (3.96), 648 (4.49) nm. HRMS (FAB+): calcd. for $C_{38}H_{27}N_4$ [M + H]$^+$ 539.2236; found 539.2237.

Thermal Fragmentation of 1b at 180 °C for 10 min: ThiaTBP precursor **1b** (10.2 mg) was heated at 180 °C for 10 min and the weight decreased to 8.6 mg. The mixture consisted of **10b** and **2b**, and was separated by preparative GPC to give **10b** (3.2 mg, 37%).

Thermal Fragmentation of 1b at 170 °C for 10 min: ThiaTBP precursor **1b** (9.6 mg) was heated at 170 °C for 10 min and the weight decreased to 8.5 mg. The mixture consisted of **9b** and **10b**, and was separated by preparative GPC to give **9b** (2.3 mg, 26%) and **10b** (3.3 mg, 40%).

Thermal Fragmentation of 1b at 130 °C for 10 min: ThiaTBP precursor **1b** (10.1 mg) was heated at 130 °C for 10 min and the weight decreased to 8.5 mg. The mixture was separated by preparative GPC to give **8b** (3.7 mg, 38%) and *opp*-**9b** (3.2 mg, 35%).

$2^1,2^4,7^1,7^4,12^1,12^4$-Hexahydro-$2^1,2^4;7^1,7^4;12^1,12^4$-triethano-23*H*,21-thiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (8b): $C_{42}H_{33}N_3S$ (611.80): diastereomeric mixture (the ratio was unknown), red crystals, m.p. >140 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$, asterisks denote changeable assignment): δ = 11.10 (br. s, 1 H, H20), 10.87 (br. s, 1 H, H5), 10.59 (m, 1 H, H15), 10.34 (m, 1 H, H10), 9.33 (m, 1 H, $H17^1$),* 9.29 (m, 1 H, $H17^4$),* 8.07 (m, 2 H, $H17^2$, $H17^3$), 7.25 and 7.08 (m, 6 H, $H2^2$, $H2^3$, $H7^2$, $H7^3$, $H12^2$, $H12^3$), 6.05, 5.88 and 5.57 (m, 6 H, $H2^1$, $H2^4$, $H7^1$, $H7^4$, $H12^1$, $H12^4$), 3.30, 2.14, 1.94 (m, 6 H), –4.29 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ = 153.2, 152.3, 151.8, 150.9, 19.4, 149.0, 146.8, 146.7, 145.7, 142.9, 141.6, 139.1, 137.1, 136.9, 136.7, 136.6, 131.7, 130.86, 127.4, 127.2, 121.1, 120.9, 109.8, 106.5, 100.4, 97.1, 37.9, 37.8, 36.8, 36.1, 36.0, 28.0, 27.7, 27.6 ppm. UV/Vis ($CHCl_3$): λ ($\log_{10}$ ε) = 412 (5.18), 502 (4.19), 534 (4.27), 597 (3.62), 657 (3.51), 690 (3.51). HRMS (FAB+): calcd. for $C_{42}H_{34}N_3S$ [M + H]$^+$ 612.2473; found 612.2476.

$2^1,2^4,12^1,12^4$-Tetrahydro-$2^1,2^4;12^1,12^4$-diethano-23*H*,21-thiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (9b): $C_{40}H_{39}N_3S$ (593.82): 1:1 diastereomeric mixture, ^{1}H NMR (400 MHz, $CDCl_3$, asterisks denote changeable assignment): δ = 11.11 (s, 2 H of one isomer, H5 , H20), 11.06 (br. s, 2 H of another isomer, H5, H20), 10.58 (s, 2 H of one isomer, H10, H15), 10.52 (s, 2 H of another isomer, H10, H15), 9.29 (m, 4 H of both isomers, $H7^1$, $H7^4$, $H17^1$, $H17^4$), 8.07 (m, 4 H of both isomers, $H7^2$, $H7^3$, $H17^2$, $H17^3$), 7.30 (m, 4 H of both isomers, $H2^1$, $H2^4$, $H12^1$, $H12^4$), 6.07 and 5.89 (m, 4 H of both isomers, $H2^1$, $H2^4$, $H12^1$, $H12^4$), 2.32 (m, 4 H of both isomers), 1.98 (m, 4 H of both isomers), –3.85 (br. s, 1 H of one isomer), –4.00 (very br. s, 1 H of another isomer) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, typical signals): δ = 151.1, 146.0, 142.5, 141.4, 137.4, 136.9, 136.7, 131.4, 127.3, 127.0, 121.0, 120.8, 107.4, 97.7, 37.9, 36.1, 28.0, 27.7 ppm. UV/Vis ($CHCl_3$): λ ($\log_{10}$ ε) = 401 (sh, 4.89), 421 (5.48), 477 (3.86), 510 (4.15), 540 (4.57), 607 (3.66), 670 (4.07). HRMS (FAB+): calcd. for $C_{40}H_{40}N_3S$ [M + H]$^+$ 584.2160; found 584.2162.

$2^1,2^4$-Dihydro-$2^1,2^4$-ethano-23*H*,21-thiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (10b): $C_{38}H_{25}N_3S$ (555.69): purple crystals, m.p. >180 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$, asterisks denote changeable assignment): δ = 10.76 (s, 2 H, H5, H20), 10.35 (s, 2 H, H15, H20), 9.56 (m, 2 H, $H12^1$, $H12^4$), 9.21 (m, 2 H, $H7^1$, $H17^1$),* 9.17 (m, 2 H, $H7^4$, $H17^4$),* 8.36 (m, 2 H, $H12^2$, $H12^3$), 8.07 (m, 4 H, $H7^2$, $H7^3$, $H17^2$, $H17^3$), 7.36 (m, 2 H, $H2^2$, $H2^3$), 5.95 (m, 2 H, $H2^1$, $H2^4$) 2.32 (m, 2 H), 1.69 (m, 4 H), –2.89 (br. s, 1 H) ppm. UV/Vis ($CHCl_3$): λ ($\log_{10}$ ε) = 406 (4.88), 429 (5.61), 494 (3.78), 534 (4.09), 564 (4.65), 611 (3.81), 674 (4.25), 724 (2.96) nm. HRMS (FAB+): calcd. for $C_{38}H_{24}N_3S$ [M + H]$^+$ 556.1847; found 556.1849.

23*H*,21-Thiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (2b):[12d] Dark green solid, m.p. >300 °C. UV/Vis (DMF): λ ($\log_{10}$ ε) = 394 (4.41), 423 (4.89), 442 (5.01), 584 (3.94), 620 (4.51), 629 (4.44), 639 (4.29), 692 (4.21) nm. $C_{36}H_{21}N_3S$ (527.64): calcd. C 81.95, H 4.01, N 7.96; found C 81.87, H 4.01, N 7.81.

Thermal Fragmentation of 1c at 145 °C for 10 min: DithiaTBP precursor **1c** (10.2 mg) was heated at 145 °C for 10 min and the weight decreased to 9.0 mg. The mixture was separated by preparative GPC to give *opp*-**9c** (6.0 mg, 67%).

Thermal Fragmentation of 1c at 180 °C for 10 min: DithiaTBP precursor **1c** (2.2 mg) was heated at 180 °C for 10 min and the weight decreased to 2.0 mg. The mixture was separated by preparative GPC to give *opp*-**9c** (0.7 mg, 35%) and **10c** (1.2 mg, 63%).

$2^1,2^4,12^1,12^4$-Tetrahydro-$2^1,2^4;12^1,12^4$-diethano-21,23-dithiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (*opp*-9c): $C_{40}H_{28}N_2S_2$ (600.79): red crystals, m.p. >150 °C (decomp.). MS (MALDI-TOF): *m*/*z* = 600 $[M]^+$, 572 $[M - C_2H_4]^+$, 544 $[M - 2C_2H_4]^+$. UV/Vis (CH_2Cl_2): λ ($\log_{10}\varepsilon$) = 409 (4.89), 429 (5.57), 479 (4.21), 505 (4.25), 514 (4.33), 542 (4.75), 628 (3.65), 694 (4.11) nm. HRMS (FAB): calcd. for $C_{40}H_{29}N_2S_2$ $[M + H]^+$ 601.1772; found 601.1770. The diastereomers were separated by the preparative GPC. Stereochemistry of the less movable isomer was determined to be *cis* by the X-ray analysis. *trans* Isomer *trans-opp*-**9c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.14 (s, 4 H, H_{meso}), 9.26 (m, 4 H, $H7^1$, $H7^4$, $H17^1$, $H17^4$), 8.05 (m, 4 H, $H7^2$, $H7^3$, $H17^2$, $H17^3$), 7.27 (m, 4 H, $H2^2$, $H2^3$, $H12^2$, $H12^3$), 6.06 (m, 4 H, $H2^1$, $H2^4$, $H12^1$, $H12^4$), 2.33 (m, 4 H), 1.97 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 151.2, 142.3, 138.3, 136.9, 127.4, 121.1, 109.2, 37.9, 27.5 ppm. *cis* Isomer *cis-opp*-**9c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.12 (s, 4 H), 9.26 (m, 4 H, $H7^1$, $H7^4$, $H17^1$, $H17^4$), 8.05 (m, 4 H, $H7^2$, $H7^3$, $H17^2$, $H17^3$), 7.29 (m, 4 H, $H2^2$, $H2^3$, $H12^2$, $H12^3$), 6.05 (m, 4 H, $H2^1$, $H2^4$, $H12^1$, $H12^4$), 2.33 (m, 4 H), 1.97 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 151.2, 142.3, 138.2, 137.0, 127.4, 121.1, 109.2, 37.9, 27.5 ppm.

$2^1,2^4$-Dihydro-$2^1,2^4$-ethano-21,23-dithiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (10c): $C_{38}H_{24}N_2S_2$ (572.74): purple crystals, m.p. >150 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.87 (s, 2 H, H10, H15), 10.66 (s, 2 H, H5, H20), 9.66 (m, 2 H, $H12^1$, $H12^4$), 9.09 (m, 4 H, $H7^1$, $H7^4$, $H17^1$, $H17^4$), 8.33 (m, 2 H, $H12^2$, $H12^3$), 8.03 (m, 4 H, $H7^2$, $H7^3$, $H17^2$, $H17^3$), 7.28 (m, 2 H, $H2^2$, $H2^3$), 5.85 (m, 2 H, $H2^1$, $H2^4$), 2.27 (m, 2 H), 1.93 (m, 2 H) ppm. UV/Vis ($CHCl_3$): λ ($\log_{10}\varepsilon$) = 417 (sh, 4.72), 436 (5.34), 509 (3.73), 543 (4.14), 579 (4.63), 630 (3.59), 696 (4.01), 750 (2.99) nm.

21,23-Dithiatetrabenzo[*b*,*g*,*l*,*q*]porphyrin (2c):[12b] Dark green solid, m.p. >300 °C. UV/Vis (DMF): λ ($\log_{10}\varepsilon$) = 399 (4.59), 429 (4.99), 449 (5.11), 593 (4.15), 639 (4.77), 718 (4.30) nm. $C_{36}H_{20}N_2S_2$ (544.69): calcd. C 79.38, H 3.70, N 5.14; found C 79.68, H 3.73, N 5.00.

X-ray Crystal Structure Analysis: Single crystals were prepared by diffusion of methanol into a solution of the compound in $CHCl_3$, benzene, or chlorobenzene. The crystals were taken in Lindeman capillary tubes with a very small amount of the mother liquor, and then the capillary tubes were sealed by candle flame. Determination of cell parameters and collection of reflection intensities were performed with a Rigaku Mercury-8 (3-kW sealed tube) instrument equipped with graphite monochromated Mo-K_α radiation or a Rigaku R-AXIS RAPID (5.4 kW rotating anode). The data were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods (SIR-97[31] or SHELXS-97[32]) and expanded by using the Fourier technique.[33] Hydrogen atoms were placed in calculated positions and refined by using riding models. All calculations were performed by using the CrystalStructure crystallographic software package[34] or WinGX.[35] SHELXL-97[36] was used for structure refinement. In the case of **1a**·2/3PhCl, the reflection intensities were modified by the PLATON squeeze program[23] in order to remove the effect of poorly modeled solvent molecules.

1a·3PhH: Crystal formula: $C_{44}H_{38}N_4 \cdot 3(C_6H_6)$, 0.5 × 0.2 × 0.1 mm, triclinic, space group $P\bar{1}$, a = 9.727(5) Å, b = 11.457(6) Å, c = 11.962(5) Å, α = 115.878(15)°, β = 102.22(3)°, γ = 92.72(3)°, V = 1157.4(10) Å^3, Mo-K_α, T = 150 K, Z = 1, $\rho_{calcd.}$ = 1.230 g cm^{-3}, μ = 0.071 mm^{-1}, F(000) = 456. 8737 measured, 4966 unique, 2142 observed [$I > 2\sigma(I)$]; R_1 = 0.0801 [$I > 2\sigma(I)$], wR_2 = 0.2017 (all); GOF = 1.033. CCDC-648521.

1a·2/3PhCl: The structure was refined without disordered solvent molecules by SHELXL-97 and Platon Squeeze. Refined formula: $3C_{44}H_{38}N_4 \cdot 2(C_6H_5Cl)$, 0.35 × 0.35 × 0.10 mm, monoclinic, space group $P\bar{1}$, a = 11.6067(2) Å, b = 14.3605(3) Å, c = 19.2237(4) Å, α = 107.320(1)°, β = 97.444(1)°, γ = 105.015(1)°, V = 2879.27(10) Å^3, Cu-K_α, T = 93 K, Z = 1, $\rho_{calcd.}$ = 1.207 g cm^{-3}, μ = 0.958 mm^{-1}, F(000) = 1106, 33307 measured, 10311 unique, 5333 observed [$I > 2\sigma(I)$]; R_1 = 0.0789 [$I > 2\sigma(I)$], wR_2 = 0.2222 (all); GOF = 1.026. CCDC-648522. This crystal was also measured at –123.1 °C. Monoclinic, space group $P\bar{1}$, a = 11.632(2) Å, b = 14.429(3) Å, c = 19.287(4) Å, α = 107.413(4)°, β = 97.443(3)°, γ = 104.972(2)°, V = 2907.8(10) Å^3, Mo-K_α, T = 150 K, Z = 1, $\rho_{calcd.}$ = 1.196 g cm^{-3}, μ = 0.114 mm^{-1}, F(000) = 1106, 53952 measured, 13196 unique, 7526 observed [$I > 2\sigma(I)$]; R_1 = 0.0820 [$I > 2\sigma(I)$], wR_2 = 0.2373 (all); GOF = 1.095. CCDC-648523.

8a: This crystal was contaminated with 4% of the corresponding zinc complex. Crystal formula: $0.96(C_{42}H_{34}N_4)0.04(C_{42}H_{32}N_4Zn) \cdot 5/2(PhCl)$, 0.36 × 0.25 × 0.15 mm, triclinic, space group $P\bar{1}$, a = 9.911(6) Å, b = 12.382(7) Å, c = 19.440(10) Å, α = 95.721(7)°, β = 101.142(6)°, γ = 105.624(9)°, V = 2225(2) Å^3, Mo-K_α, T = 150 K, Z = 2, $\rho_{calcd.}$ = 1.307 g cm^{-3}, μ = 0.242 mm^{-1}, F(000) = 917, 20085 measured, 10001 unique, 5406 observed [$I > 2\sigma(I)$]; R_1 = 0.1040 [$I > 2\sigma(I)$], wR_2 = 0.3286 (all); GOF = 1.046. The structure was also refined without solvent molecules by SHELXL-97 and Platon Squeeze and the results are as follows: 4051 observed [$I > 2\sigma(I)$]; R_1 = 0.0687 [$I > 2\sigma(I)$], wR_2 = 0.1521 (all); GOF = 1.017. CCDC-648519 and -648520.

***cis-opp*-9c:** Crystal formula: $C_{40}H_{28}N_2S_2 \cdot 2(CHCl_3)$, 0.35 × 0.25 × 0.10 mm, monoclinic, space group $P2_1/c$, a = 12.814(6), b = 17.536(7), c = 16.535(7) Å, β = 97.651(6)°, V = 3682(3) Å^3, Mo-K_α, T = 150 K, Z = 4, $\rho_{calcd.}$ = 1.514 g cm^{-3}, μ = 0.616 mm^{-1}, F(000) = 1720, 27915 measured, 8426 unique, 6257 observed [$I > 2\sigma(I)$]; R_1 = 0.0696 [$I > 2\sigma(I)$], wR_2 = 0.1847 (all); GOF = 1.120. CCDC No. 637704.

***trans-opp*-9c:** Crystal formula: $C_{40}H_{28}N_2S_2 \cdot 1/2(CHCl_3)$, 0.30 × 0.15 × 0.15 mm, monoclinic, space group $P2_1/a$, a = 11.533(3), b = 19.995(5), c = 13.604(3) Å, β = 97.271(3)°, V = 3111.7(14) Å^3, Mo-K_α, T = 150 K, Z = 4, $\rho_{calcd.}$ = 1.410 g cm^{-3}, μ = 0.335 mm^{-1}, F(000) = 1772.2, 23759 measured, 7114 unique, 5390 observed [$I > 2\sigma(I)$]; R_1 = 0.0661 [$I > 2\sigma(I)$], wR_2 = 0.1638 (all); GOF = 1.122. CCDC No. 637705.

10a: Crystal formula: $C_{38}H_{26}N_4$, 0.37 × 0.13 × 0.08 mm, monoclinic, space group $P2_1/n$, a = 12.0626(16) Å, b = 15.517(2) Å, c = 14.555(2) Å, β = 101.727(3)°, V = 2667.4(6) Å^3, Mo-K_α, T = 150 K, Z = 4, $\rho_{calcd.}$ = 1.341 g cm^{-3}, μ = 0.080 mm^{-1}, F(000) = 1128, 27626 measured, 6090 unique, 4274 observed [$I > 2\sigma(I)$]; R_1 = 0.0815 [$I > 2\sigma(I)$], wR_2 = 0.1989 (all); GOF = 1.140. CCDC-648526.

10b: Crystal formula: $C_{38}H_{25}N_3S$, 0.25 × 0.17 × 0.15 mm, monoclinic, space group $P2_1/n$, a = 12.1857(14) Å, b = 15.0410(16) Å, c = 15.0096(18) Å, β = 103.565(3)°, V = 2674.3(5) Å^3, Mo-K_α, T = 150 K, Z = 4, $\rho_{calcd.}$ = 1.380 g cm^{-3}, μ = 0.156 mm^{-1}, F(000) = 1160, 27696 measured, 6053 unique, 4701 observed [$I > 2\sigma(I)$]; R_1 = 0.0683 [$I > 2\sigma(I)$], wR_2 = 0.1842 (all); GOF = 1.094. CCDC-648525.

10c: Crystal formula: $C_{38}H_{24}N_2S_2$, $0.15 \times 0.10 \times 0.06$ mm, monoclinic, space group $P2_1/n$, a = 12.215(5) Å, b = 14.807(5) Å, c = 15.271(6) Å, β = 102.908(5)°, V = 2692.4(17) Å^3, Mo-K_α, T = 150 K, Z = 4, $\rho_{calcd.}$ = 1.413 g cm^{-3}, μ = 0.231 mm^{-1}, $F(000)$ = 1192, 20489 measured, 6058 unique, 4006 observed [$I > 2\sigma(I)$]; R_1 = 0.0848 [$I > 2\sigma(I)$], wR_2 = 0.2166 (all); GOF = 1.113. CCDC-648518.

CCDC-648518 to -648523, -648525, -648526, -637704, and -637705 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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