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Synthesis and properties of BCOD-fused trithiasapphyrin and trithiabenzosapphyrins

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ABSTRACT

Bicyclo[2.2.2]octadiene(BCOD)-fused trithiasapphyrin was prepared by 3+2 condensation of BCOD-fused thiatripyrrane with BCOD-fused bithiophene. The BCOD-fused trithiasapphyrin was successfully converted to pentabenzo[*b*,*g*,*l*,*q*,*v*]sapphyrin by the thermal retro-Diels–Alder reaction. In this case, trithiapentabenzo[*b*,*g*,*l*,*q*,*v*]- and trithiadibenzo[*g*,*q*]sapphyrins were selectively prepared by control of the temperature in the thermal retro-Diels–Alder reaction.

1. Introduction

Recently the interesting aromaticity switching phenomenon between normal Hückel and Möbius[1] was found in a doubly *p*-phenylene-linked dipyrrin by Latos-Grażyński et al.[2] and in octaphyrins and heptaphyrins by Osuka et al.[3] These ring-expanded porphyrins have increasingly attracted much attention due to not only these exotic behavior of their π-systems but also potential applicability toward multi-photon absorbing materials,[4] higher-harmonic generating materials,[5] and light limiters.[6] Generally, these expanded porphyrins had beautiful colors, and this was due to their characteristic electronic spectra showing a strong and sharp Soret-band absorption around 400–500 nm and several weak Q-band absorptions over 500 nm. Hexapyrrolic macrocycles of red-colored rubyrin (hexaphyrin(1.1.0.1.1.0))[7] and amethyrin (hexaphyrin (1.0.0.1.0.0))[8] were named after their ruby-like and amethyst-like colors of precious stones, respectively. Among the expanded porphyrins, sapphyrin (pentaphyrin(1.1.1.1.0)) was the first example, which was serendipitously discovered during the synthesis of vitamin B_{12} by Woodward et al. in 1966.[9] Sapphyrin had a very sharp, strong Soret band and very weak Q bands in the visible region, and the color was quite different from that of porphyrin. Sapphyrin was named after its clear sapphire-like blue color, which was closely related to the characteristics in the electronic absorption spectra. There is no other obvious absorption than the strong Soret band in the visible region. This band was quite sensitive to pH and co-existing anions. Thus, sapphyrin has attracted attention as an anion sensor.[10] During the course of our continuous interest in the preparation of highly expanded π-systems,[11] we have also interested in conjugation-expanded sapphyrins and have reported a preliminary result on the preparation of mono- and di-benzosapphyrins based on the retro-Diels–Alder reaction of the corresponding mono- and di-BCOD-fused sapphyrins.[12] In these sapphyrins, the Soret-band absorptions were still very sharp and red-shifted by 12 nm for benzosapphyrin and 22 nm for dibenzosapphyrin.[12] Moreover, we have recently found the highly site-selective thermolysis of BCOD to benzene in benzoporphyrins and thiabenzoporphyrins.[13] If we prepare a penta-BCOD-fused thiasapphyrin derivative, we may selectively get plural numbers of benzosapphyrins from the same starting material by simply controlling the retro-Diels–Alder reaction temperature. In this paper, we will discuss about the preparation of penta-BCOD-fused trithiasapphyrin and its thermal conversion to the corresponding benzosapphyrins.

2. Results and discussion

2.1. Preparation of BCOD-fused trithiasapphyrin

Since the solubility of benzene-fused porphyrins with no substituent[14] in common solvents was poor, BCOD-fused sapphyrins

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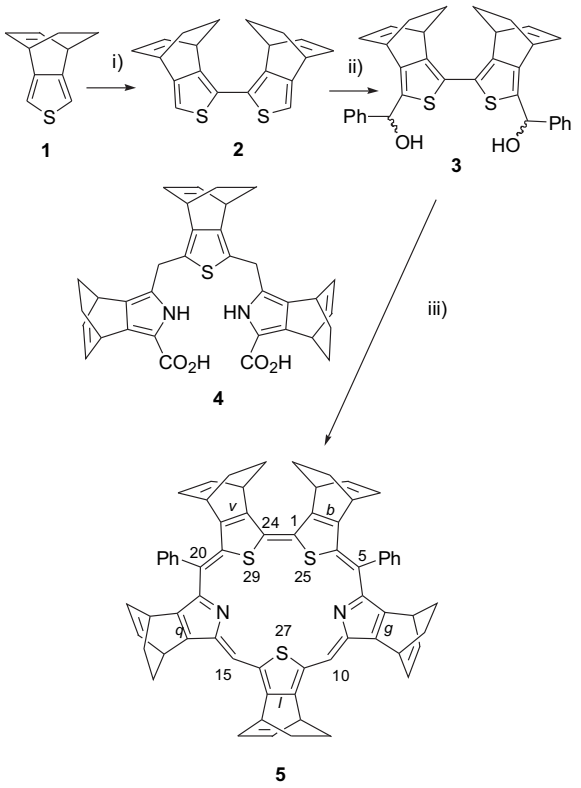
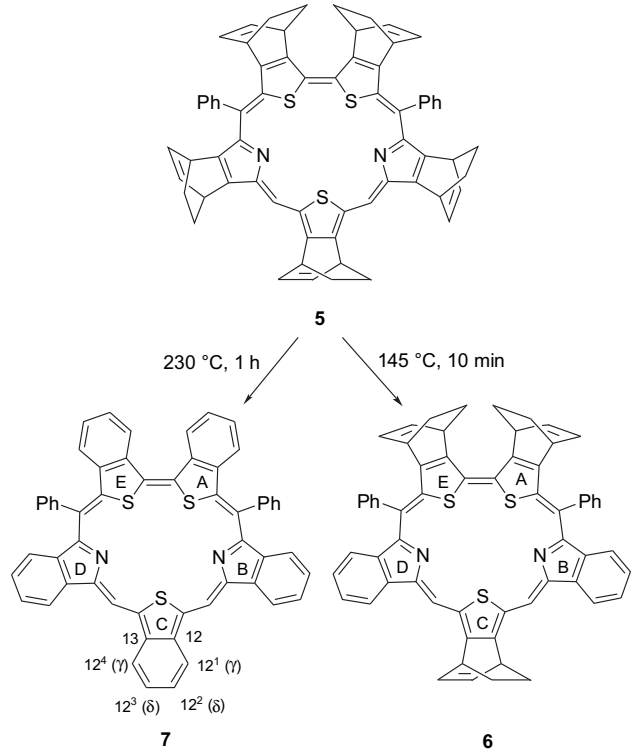
with phenyl substituents were chosen as the first target substances in order to investigate the electronic properties of benzosapphyrins. Our strategy for the preparation of sapphyrins was based on the 3+2 synthesis using BCOD-fused thiatripyrrane **4** (Scheme 1).[13] Sessler et al. reported the scrambling reaction giving a porphyrin derivative as well as the desired sapphyrin in the reaction of tripyrrane with α-(hydroxymethyl)pyrrole under acidic conditions.[15] Combination of tripyrrane and bipyrrole units in addition to acid strength was very important. Preparation of trithiasapphyrin **5** was illustrated in Scheme 1. An α-lithio derivative of BCOD-fused thiophene **1** was oxidatively coupled by $CuCl_2$ to give diastereomeric bithiophene **2**[16] in 62% yield in addition to a small amount of a chlorinated by-product. Dilithiation of bithiophene **2** was accomplished by treatment with *n*-BuLi in the presence of *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA)[16] and then the dilithio derivative was reacted with benzaldehyde to give rather unstable diol **3** in 98% yield. Diol **3** and thiatripyrrane **4**[13] were treated with TFA. After neutralization with Et_3N, the mixture was oxidized with DDQ. Chromatographic purification of the mixture afforded the targeted trithiasapphyrin **5** as a mixture of diastereomers in 13% yield.



Scheme 1. Preparation of BCOD-fused trithiasapphyrin **5**. Reagents, conditions, and yield: (i) *n*-BuLi, THF, −10 °C; CuCl2, −78 °C to rt; 62%; (ii) *n*-BuLi, TMEDA, THF, −70 °C; PhCHO, −50 °C to rt; 98%; (iii) **4**, TFA, rt; **3**, CH2Cl2; Et3N, rt; DDQ, rt; 13%.

2.2. Thermal conversion of the BCOD-fused sapphyrins to benzosapphyrin

The thermal behavior of BCOD-fused trithiasapphyrin **5** was examined by thermogravimetric (TG) analysis. Before the TG experiment, the composition of the sample of **5** was checked by the elemental analysis, because we experienced the BCOD-fused compounds readily co-crystallized with solvent molecules. The elemental analysis revealed the sample of **5** contained one molecule of water. This water molecule would replace co-crystallized solvent molecules during the drying manipulation followed by storage. Since the extrusion of ethylene molecules from the isoindole moieties of BCOD-fused 21,23-dithiaporphyrin[13] occurred during ca. 110–160 °C and that from the isothianaphthene then started at ca. 165 °C, the bulk thermal reactions were performed under the following conditions: 145 °C, 10 min for extrusion of two ethylene molecules from the isoindole moieties and 230 °C, 1 h for extrusion of all ethylene molecules (Scheme 2). In both cases, the targeted dibenzo- and pentabenzo-sapphyrins **6** and **7** were obtained in good yields.



Scheme 2. Thermal conversion of **5**.

2.3. Spectroscopic and X-ray analyses of trithiasapphyrins

Electronic spectra of sapphyrins **5**, **6**, and **7** are shown in Figure 1. The spectrum shape of **5** was quite similar to that reported for *meso*-tetraphenyl-25,27,29-trithiasaphyrin, although all of the absorption peaks of **5** were blue shifted (Soret for 45 nm and Q band for 24–81 nm) probably due to the lack of two phenyl groups at *meso*-positions.[17] There were rather broad and strong Soret-band absorption at 480 nm with a shoulder peak at 455 nm as well as four weak Q-band absorptions at 614 (IV), 654 (III), 705 (II), and 783

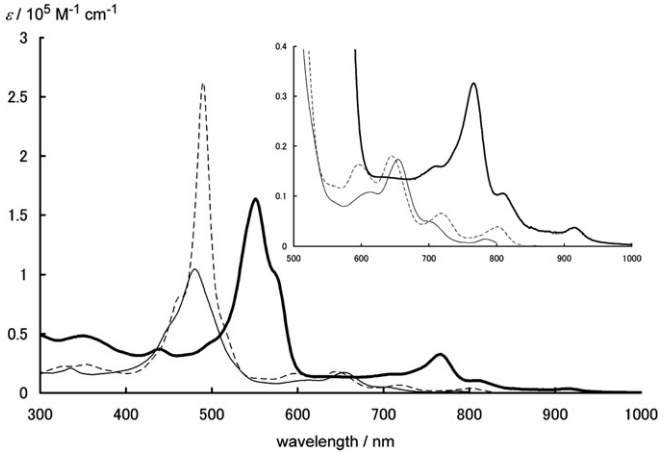


Figure 1. Electronic spectra of sapphyrins **5** (solid line), **6** (broken line), and **7** (bold line).

(I) nm. Among the Q-band absorptions, the peak of III was the highest. Fusion of five benzene rings to the trithiasapphyrin chromophore brought about considerable red-shift and enhancement of the absorptions, although their shapes were quite similar. The Soret- and four Q-band peaks of **7** were 551, 710, 766, 810, and 915 nm, respectively. On the other hand, sharp and strong Soret absorption was observed at 490 nm in the spectrum of **6** as well as four Q bands (596, 645, 718, and 803 nm). Rather small red shifts (10–20 nm) observed in **6** was well rationalized by consideration of the 22π-electron system of the 25,27,29-trithiasaphyrin chromophore (Fig. 2). The benzene rings hardly contributed the expansion of 22π system, but perturbed the π system as phenyl substituents at the α-positions.

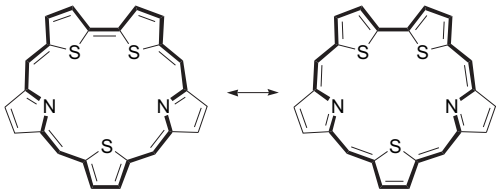


Figure 2. 22π-Electron system of 25,27,29-trithiasapphyrin with major contribution.

Next, we carried out the X-ray analysis of sapphyrins **5**, **6**, and **7**, single crystals of which were successfully obtained by slow diffusion of methanol vapor into the solutions in chloroform. In the cases of sapphyrins **5** and **6** bearing BCOD moieties co-crystallized with solvent molecules to form **5**·3$CHCl_3$ and **6**·2$CHCl_3$·CH_3OH, respectively. On the other hand, no solvent was involved in the crystal of pentabenzosapphyrin **7**. Crystallographic data and Ortep drawings are shown in Table 1 and Figure 3, respectively.

Table 1
Crystallographic data of **5**, **6**, and **7**

Compound	**5**·3$CHCl_3$	**6**·2$CHCl_3$·CH_3OH	**7**
Formula	$C_{69}H_{55}Cl_9N_2S_3$	$C_{65}H_{50}Cl_6N_2OS_3$	$C_{56}H_{32}N_2S_3$
FW	1327.46	1183.98	829.06
Temp/K	150	150	103
Space group	*P*−1	*P*−1	*P*−1
a/Å	11.5991(17)	11.891(4)	11.97520(10)
b/Å	16.975(2)	14.878(5)	12.4358(4)
c/Å	17.200(2)	16.708(5)	15.04840(10)
α	101.919(6)	92.818(4)	82.157(13)
β	98.965(7)	95.521(5)	66.972(10)
γ	107.659(5)	107.731(6)	75.951(11)
V/Å^3	3069.5(7)	2792.8(16)	1998.59(18)
Z	2	2	2
μ/mm^{-1}	0.558	0.467	0.230
Unique refln.	14,025	12,593	8977
No. obs.[a]	11,721	7394	8180
No. var.	753	811	551
Restrained	0	343[b]	0
R_{merge}	0.0269	0.0399	0.0295
R_1	0.0620	0.0753	0.0591
wR_2	0.1759	0.1950	0.1171
GOF	1.112	1.118	1.165

[a] $I>2\sigma(I)$.
[b] Atomic coordinates of disordered solvent molecules are restrained.

In the structure of **5**·3$CHCl_3$, two of three chloroform molecules were found on the pyrrole moieties of **5** and the C–H bonds bounded to the imino nitrogen moieties. Similarly, one of two chloroform and methanol molecules were found on the isoindole moieties of **6** and the chloroform C–H and methanol O–H bounded to the imino nitrogen moieties in **6**·2$CHCl_3$·CH_3OH. In this structure, the non-coordinated chloroform molecule was found to heavily disorder and was treated as three molecules with 0.442, 0.426, and 0.132 occupancies. The coordinated chloroform molecule also disordered and the structure was refined as two molecules with 0.84 and 0.16 occupancies, although both C–H bonds directed toward the imino nitrogen.

Next, we turned our attention to distortion of the sapphyrin rings because out-of-plane and in-plane distortions were well affected by macrocyclic ring currency of core-modified porphyrins.[18] No inversion of the five-membered rings was observed in all trithiasapphyrins due to β-substituents. Out-of-plane deviation from the mean planes of sapphyrins is illustrated in Figure 4 and dihedral angles between the five-membered heterocyclic moieties are listed in Table 2. The ring undulation and tilting angles of five-membered rings became larger as the number of benzene ring increased. As small bond alteration was observed in all benzene moieties of **6** and **7**, the local benzene aromaticity was preserved even in the isothianaphthene moieties of **7** (see Supplementary Table S1). This is quite different from the core-modified benzoporphyrins.[14,18] From Table 2, dihedral angles of the bithiophene moiety increased by fusion of benzene rings: 32.57 (5)° for **5**, 34.44 (7)° for **6**, and 39.84 (5)° for **7**. This is well rationalized by the sterical effects of BCOD and benzo moieties. Only the methine protons of BCOD and the *peri*-protons of benzo moiety were needed to be considered in the in-plane sterical hindrance, because these moieties were rigid. Since the bond angle in sp^3 carbon are narrow compared to that in sp^2 carbon, the benzo fusion more effectively hinders the in-plane adjacent positions than the BCOD fusion. In these sapphyrin structures, most striking feature was the bond lengths of bithiophene moieties. The bonds between the thiophene moieties of **5**, **6**, and **7** were 1.437 (3), 1.440 (5), and 1.404(3) Å, respectively. The bond between the isothianaphthene moieties was obviously shorter than those between the thiophene moieties. The plane dihedral angles between the thiophene and fused benzo moieties (B-5 angles of rings A, C, and E in Table 2) were also worthy to mention. These angles were rather large compared to those of thiabenzoporphyrins.[14,18] These facts suggested that the benzene rings little contributed expansion of the macrocyclic ring current.

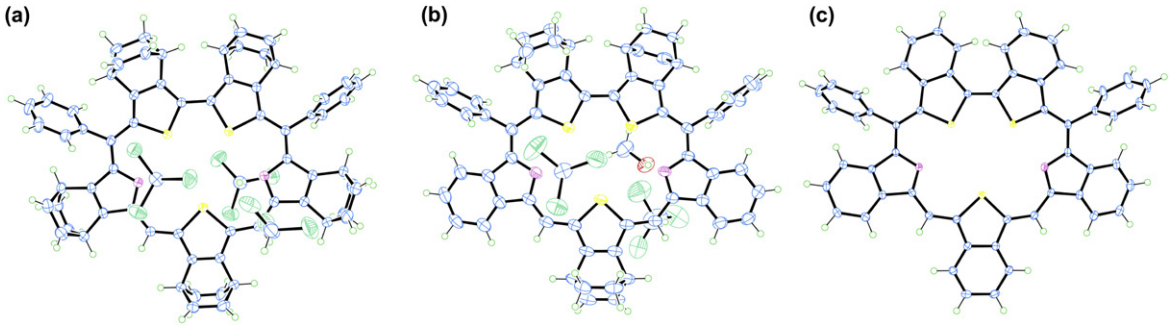


Figure 3. Ortep drawings of (a): **5**·3$CHCl_3$, (b): **6**·2$CHCl_3$·CH3OH, and (c): **7**. Disordered atoms with less occupancy are omitted for clarity.

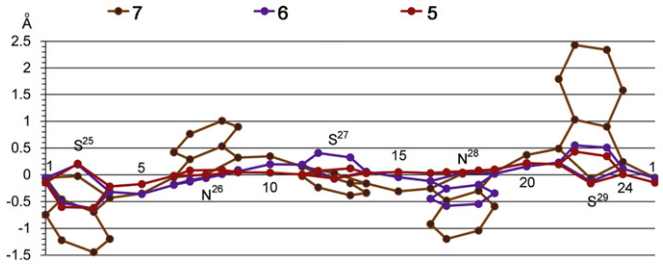


Figure 4. Out-of-plane distortion of sapphyrins **5** (red line), **6** (purple line), and **7** (brown line).

Table 2
Plane angles in sapphyrins **5**, **6**, and **7**

Compound	Ring/degree °					
	Angles	A	B	C	D	E
5	Dihedral[a]	19.22(5)	−2.84(8)	−3.88(5)	−1.80(9)	−13.35(5)
	Tilt[b]	19.2(1)	−2.2(1)	−3.8(1)	−0.6(1)	−12.7(1)
	Undulation[c]	−1.6(1)	1.7(1)	0.6(1)	1.8(1)	−4.2(1)
6	Dihedral[a]	19.07(7)	6.4(1)	−10.38(8)	7.6(1)	−15.37(6)
	Tilt[b]	18.1(1)	−0.2(1)	−10.1(1)	−0.1(1)	−15.3(1)
	Undula tion[c]	−5.9(1)	6.5(1)	−2.9(1)	3.6(1)	−2.6(1)
	B-5[d]	—	1.0(2)	—	1.8(2)	—
7	Dihedral[a]	15.28(5)	−14.53(7)	7.51(6)	13.49(7)	−24.56(4)
	Tilt[b]	12.7(1)	−10.3(1)	2.2(1)	10.7(1)	−24.4(1)
	Undula tion[c]	−8.6(1)	9.6(1)	−7.2(1)	7.9(1)	−5.4(1)
	B-5[d]	6.20(7)	0.62(9)	3.85(7)	6.83(9)	12.68(7)

[a] The angle between the five-membered heterocycle and the mean plane of 29 sapphyrin atoms. The sign is arbitrary.
[b] The angle is between the mean plane of 29 sapphyrin atoms and the vector calculated by summation of two C^{β} to hetero-atom vectors. The sign is arbitrary.
[c] The angle is between the mean plane of 29 sapphyrin atoms and the vector of C^{α} to C^{α}. The sign is arbitrary.
[d] The dihedral angle between the five-membered heterocycle and the fused benzene ring.

The results obtained in trithiapentabenzosapphyrin **7** are a little confusing, because both canonical 22π-electron forms **A** and **B** of trithiasapphyrin in Figure 2 did not satisfy the facts we observed. The canonical structure **A** would be supported by the short bond between the isothianaphthene moieties, while their larger dihedral angle would support larger contribution of the canonical structure **B**. Absence of bond alteration in the benzo moieties as well as the large B-5 angles did not support either. Taking these facts into an account, a 22π-electron circuit in the inner 19 atoms involving all heteroatoms shown in Figure 5 would fairly contribute the aromaticity of trithiapentabenzosapphyrin.[19] As the electronic spectrum shapes of **5** and **7** were very similar, the similar circuit would be important even in trithiasapphyrin.

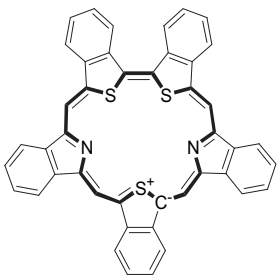


Figure 5. Another proposed 22p-electron circuit of trithiapentabenzosapphyrin.

To estimate the electron distribution of trithiasapphyrins **5**–**7**, sapphyrin, and 5,20-diphenylsapphyrin, we have performed the B3LYP/6-31G(*) density functional theory calculations of HOMO and LUMO orbitals (See the Supplementary data).[20] The electron distribution of **5** was quite similar to that of **6** for the four orbitals, LUMO+1, LUMO, HOMO, and HOMO−1. Their HOMO–LUMO energy gaps were estimated same values of 2.13 eV. This result suggested that two fused-benzene rings of isoindole moieties were localized and not included in sapphyrin macrocycle. On the other hand, the gap of **7** (ΔE=1.86 eV) was narrower than those of **5** and **6**. LUMO+1 and LUMO in **7** showed the same distribution for LUMO and LUMO+1 in **5** and **6**, respectively. The similar results were obtained for HOMO and HOMO−1 as shown in Figures S1–S3. Parent sapphyrin and 5,20-diphenylsapphyrin showed similar electron-distribution of sapphyrin moiety to trithiasapphyrins **5**–**7**.

3. Conclusion

We prepared BCOD-fused trithiasapphyrin **5**, which was selectively converted either to trithiadibenzosapphyrin **6** and trithiapentabenzosapphyrin **7** by controlling the retro-Diels–Alder temperature. The UV and X-ray analyses of the thrithiasapphyrins revealed contribution of the 22π-electron circuit on the 19 inner atoms involving all five heteroatoms.

4. Experimental section

4.1. General

Melting points were measured with a Yanaco M500-D melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 or -EX 400 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Hitachi 270-30 as KBr disks. FAB and DI-EI mass spectra were measured on a JEOL JMS-700 instrument. MALDI-TOF mass spectra were measured on a Voyager DE Pro instrument (Applied Biosystems). Elemental analyses were performed on 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, TMEDA, and chloroform were distilled from calcium hydride and then stored on appropriate Molecular Sieves. Solvents for chromatography were purified by distillation. For spectral measurements, spectral grades of toluene, dichloromethane, 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. 4,7-Dihydro-4,7-ethano-2-benzothiophene (**1**)[16] and $2^{1},2^{4},5,7^{1},7^{4},10,12^{1},12^{4},15$,17-dodecahydro-$2^{1},2^{4};7^{1},7^{4};12^{1},12^{4}$-triethano-16-thiatribenzo[*b*,*g*,*l*]tripyrrin-1,14-dicarboxylic acid (**4**)[14] were prepared according to the literature procedure.

4.2. Synthesis

*4.2.1. 4,4′,7,7′-Tetrahydro-4,7;4′,7′-diethano-1,1′-bi(2-benzothiophene) (**2**).* 4,7-Dihydro-4,7-ethano-2-benzothiophene[16] (**1**; 4.86 g, 30.0 mmol) and a magnetic stirring bar were placed in a 200-mL three-necked flask equipped with a rubber septum, a solid dropping funnel containing anhydrous $CuCl_2$ (8.06 g, 60.0 mmol), and a three-way cock connected to a nitrogen inlet and a vacuum pump. The vessel was flashed with nitrogen and dry THF (100 mL) was added by a syringe. The vessel was cooled to −78 °C and then a solution of *n*-BuLi (1.58 M, 20.2 mL, 32 mmol) in hexane was slowly added. The resulting solution was warmed to −10 °C and stirred for additional 30 min. The vessel was again cooled to −70 °C and $CuCl_2$ was slowly added with stirring. After the addition, the mixture was stirred at the same temperature for 2 h and then at

room temperature overnight. The reaction mixture was poured into a 1-M HCl solution and the mixture was extracted with $CHCl_3$. The organic extract was washed sequentially with water, a satd $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (10–20% $CHCl_3$/hexane) to give a small amount of 1-chloro-4,7-dihydro-4,7-ethano-2-benzothiophene and the title compound, latter of which was recrystallized from $CHCl_3$/hexane to give 3.02 g (62%) of the pure dimer as a 1:1 diastereomeric mixture: colorless crystals, mp 197–199 °C; R_f=0.26 (10% $CHCl_3$/hexane); ^{1}H NMR ($CDCl_3$) δ 1.64–1.57 (m, 8H), 3.86 (m, 2H), 4.08 (m, 2H), 6.56–6.48 (m, 4H), and 6.71 (s, 2H); ^{13}C NMR (typical signals, $CDCl_3$) δ 26.0, 26.1, 26.2, 35.5, 35.6, 36.9, 112.0, 123.0, 123.1, 135.3, 135.4, 135.5, 135.6, 143.3, 143.4, and 147.4; MS (EI, relative intensity) m/z 322 (M^+, 29), 294 (23), 266 (100), and 133 (18); IR (KBr) ν/cm^{-1} 3046, 2954, 2861, 1602, 1354, 1378, 1340, and 1135. Anal. Calcd for $C_{20}H_{18}S_2$: C, 74.49; H, 5.63%. Found: C, 74.19; H, 5.78%.

*4.2.2. 3,3′-Bis(1-hydroxybenzyl)-4,4′,7,7′-tetrahydro-4,7;4′,7′-diethano-1,1′-bi(2-benzothiophene) (**3**).* Diastereomeric bi(2-benzothiophene) **2**[16] (806 mg, 2.5 mmol) and TMEDA (1.0 mL, 10 mmol) were dissolved in dry THF (50 mL) under a nitrogen atmosphere and a 1.56-M solution of *n*-BuLi (6.4 mL, 10 mmol) in hexane was added at −78 °C. The mixture was then stirred at room temperature for 30 min. The mixture became turbid. The mixture was cooled to −50 °C and benzaldehyde (1.0 mL, 10 mmol) was added. The mixture was then warmed to room temperature and stirred for 3 h. The mixture became orange and clear. The reaction was quenched with a satd NH_4Cl solution. The reaction mixture was extracted with ether. The ethereal phase was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was triturated with hexane to give 1.32 g (98%) of the title compound as a brown foam, which was used without further purification. ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 2H), 1.2–1.7 (m, 6H), 2.30 (m, 2H), 3.83 (m, 2H), 4.02 (m, 2H), 6.08 (m, 2H), 6.46 (m, 4H), and 7.2–7.5 (m, 10H).

*4.2.3. 5,20-Diphenyl-2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4,22^1,22^4-decahydro-2^1,2^4;7^1,7^4;12^1,12^4; 17^1,17^4;22^1,22^4-pentaethano-25,27,29-trithiapentabenzo[b,g,l,q,v]-sapphyrin (**5**).* To 2^1,2^4,5,7^1,7^4,10,12^1,12^4,15,17-dodecahydro-2^1,2^4;7^1,7^4;12^1,12^4-triethano-16-thiatribenzo[*b,g,l*]tripyrrin-1,14-dicarboxylic acid[14] (**4**, 423 mg, 0.75 mmol) was added TFA (2.0 mL) at room temperature in the dark. The mixture was stirred for 5 min. The mixture was diluted with dry CH_2Cl_2 (200 mL) and bis(1-hydroxybenzyl)bi(2-benzothiophene) **3** (401 mg, 0.75 mmol) was added. The mixture was stirred at room temperature overnight and was neutralized by Et_3N. DDQ (181 mg, 0.80 mmol) was added and the mixture was stirred at room temperature for 2 h. The mixture was washed with a satd $NaHCO_3$ solution and water, dried over Na_2SO_4, and concentrated. The residue was chromatographed on alumina (5% EtOAc/CH_2Cl_2) to give the crude title compound, which was purified by recrystallization from $CHCl_3$/MeOH. The crystals were dried under vacuum (ca. 0.1 Pa) overnight to give 93 mg (13%) of **5** as dark green crystals: ^{1}H NMR ($CDCl_3$) δ 2.8–1.3 (m, 20H), 3.57 (m, 2H), 3.87 (m, 2H), 5.38 (m, 2H), 5.65 (m, 2H), 5.97 (m, 2H), 7.3–6.5 (m, 10H),7.90 (m, 6H), 8.26 (m, 4H), and 10.53 (m, 2H); UV ($CHCl_3$) λ_{max} (log ε) 455 sh (4.79), 480 (5.02), 614 (4.03), 654 (4.24), 705 (3.67), and 783 (3.18); MS (FAB$^+$) m/z 969 (M^++1), 941 (M^++1−C_2H_4), 913 (M^++1−2C_2H_4), 885 (M^++1−3C_2H_4), 857 (M^++1−4C_2H_4), and 829 (M^++1−5C_2H_4). HRMS calcd for $C_{66}H_{53}N_2S_3$: 969.3371. Found: 969.3409. Anal. Calcd for $C_{66}H_{52}N_2S_3\cdot H_2O$: C, 80.29; H, 5.51; N, 2.84%. Found: C, 80.20; H, 5.36; N, 2.67%.

*4.2.4. 5,20-Diphenyl-2^1,2^4,12^1,12^4,22^1,22^4-hexahydro-2^1,2^4;12^1,12^4;22^1,22^4-triethano-25,27,29-trithiapentabenzo[b,g,l,q,v] sapphyrin (**6**).* BCOD-fused sapphyrin **5** (10 mg, 0.010 mmol) in a small sample tube was placed in a test tube. The test tube was evacuated and heated at 145 °C for 10 min. After the test tube was cooled, the solid material (9.3 mg) was recrystallized from $CHCl_3$/MeOH to give 5.6 mg (60%) of the title compound as a mixture of three possible diastereomers (2:1:1 ratio): green crystals: ^{1}H NMR ($CDCl_3$) δ 1.1–2.0 (m, 10H), 2.25 (m, 2H), 3.69 (m, 2H), 5.48 (m, 2H), 5.88 (m, 2H), 7.05–6.50 (m, 6H), 7.48 (m, 2H), 7.70–7.95 (m, 10H), 8.10–8.30 (m, 4H), 9.00 (m, 2H), 10.56 (s, 2H of another minor isomer), 10.56 (s, 2H of a minor isomer), and 10.57 (br-s, 2H of major isomer); MS (FAB$^+$) m/z 913 (M^++1); UV ($CHCl_3$) λ_{max} (log ε) 463 (4.91), 490 (5.42), 596 (4.21), 645 (4.26), 718 (3.82), and 802 (3.59). HRMS calcd for $C_{62}H_{45}N_2S_3$: 913.2745. Found: 913.2752.

*4.2.5. 5,20-Diphenyl-25,27,29-trithiapentabenzo[b,g,l,q,v] sapphyrin (**7**).* BCOD-fused sapphyrin **5** (16 mg, 0.016 mmol) in a small sample tube was placed in a test tube. The test tube was evacuated and heated at 230 °C for 1 h. After the test tube was cooled, the title compound was obtained in a quantitative yield (13 mg) as dark reddish purple crystals: ^{1}H NMR ($CDCl_3$) δ 7.62 (t, J=7.5 Hz, 2H), 7.72 (t, J=7.5 Hz, 2H), 7.95 (t, J=7.5 Hz, 2H), 8.08 (m, 8H), 8.13 (t, J=7.5 Hz, 2H), 8.41 (m, 4H), 8.55 (m, 2H), 9.39 (d, J=7.3 Hz, 2H), 10.23 (m, 2H), 10.39 (d, J=7.3 Hz, 2H), and 12.11 (s, 2H); UV ($CHCl_3$) λ_{max} (log ε) 439 (4.57), 499 (4.63), 551 (5.21), 574 sh (5.00), 710 (4.20), 766 (4.51), 810 (4.02), and 915 (3.57); MS (FAB$^+$) m/z 829 (M^++1). Anal. Calcd for $C_{56}H_{32}N_2S_3\cdot H_2O$: C, 81.13; H, 3.89; N, 3.38%. Found: C, 80.95; H, 4.17; N, 3.09%.

4.3. X-ray crystallography

Single crystals were prepared by slow diffusion of methanol vapor into a solution of compounds **5**, **6**, and **7** in $CHCl_3$. The crystals of **5** and **6** 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. The crystal of **7** was mounted on a glass capillary. Determination of cell parameters and collection of reflection intensities were performed on a Rigaku Mercury-8 (3-kW sealed tube) instrument (Mo Kα) equipped with graphite monochromated Mo Ka radiation. The data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods (Sir-97[21] or Shelxs-97[22]) and expanded using the Fourier technique.[23] Hydrogen atoms were placed in calculated positions and refined by using riding models. Calculations were performed by using the CrystalStructure crystallographic software package.[24] Shelxl-97[22] was used for the structure refinement. The final refined results were validated by Platon CifCheck[25] (see: Supplementary data) and depositted at CCDC. The CCDC numbers of **5**·3$CHCl_3$, **6**·2$CHCl_3\cdot CH_3OH$, and **7** are 772305, 772304, and 772306, respectively.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.06.086. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. Herges, H. *Nature* **2007**, *450*, 36–37.
2. Stępień, M.; Latos-Grażyński, L.; Sprutta, N.; Chwalisz, P.; Szterenberg, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7869–7873.
3. Tanaka, Y.; Saito, S.; Mori, S.; Aratani, N.; Shinokubo, H.; Shibata, N.; Higuchi, Y.; Yoon, Z. S.; Kim, K. S.; Noh, S. B.; Park, J. K.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 681–684.
4. (a) Kim, K. S.; Lim, J. M.; Osuka, A.; Kim, D. *J. Photochem. Photobiol. C.* **2008**, *9*, 13–28; (b) Kim, K. S.; Noh, S. B.; Katsuda, T.; Ito, S.; Osuka, A.; Kim, D. *Chem. Commun.* **2007**, 2479–2481; (c) Mongin, O.; Porrès, L.; Charlot, M.; Katan, C.; Blanchard-Desce, M. *Chem.—Eur. J.* **2007**, *13*, 1481–1498; (d) Drobizhev, M.; Stepanenko, Y.; Rebane, A.; Wilson, C. J.; Screen, T. E. O.; Anderson, H. L. *J. Am. Chem. Soc.* **2006**, *128*, 12432–12433.
5. Rath, H.; Sankar, J.; PrabhuRaja, V.; Chandrashekar, T. K.; Nag, A.; Goswami, D. *J. Am. Chem. Soc.* **2005**, *127*, 11608–11609.
6. McKerns, M. M.; Sun, W.; Lawson, C. M.; Gray, G. M. *J. Opt. Soc. Am. B* **2005**, *22*, 852–861.
7. (a) Sessler, J. L.; Morishima, T.; Lynch, V. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 977–980; (b) Shimizu, S.; Taniguchi; Osuka, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2225–2229.
8. (a) Hannah, S.; Seidel, D.; Sessler, J. L.; Lynch, V. *Inorg. Chim. Acta* **2001**, *317*, 211–217; (b) Sessler, J. L.; Weghorn, S. J.; Hisaeda, Y.; Lynch, V. *Chem.—Eur. J.* **1995**, *1*, 56–57.
9. Bauer, V. J.; Clive, D. L. J.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429–6436.
10. (a) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989–997; (b) Sessler, J. L.; Davis, J. M.; Král, V.; Kimbrough, T.; Lynch, V. *Org. Biomol. Chem.* **2003**, *1*, 4113–4123.
11. A recent example, see: Uoyama, H.; Kim, K. S.; Kuroki, K.; Shin, J.-Y.; Nagata, T.; Okujima, T.; Yamada, H.; Ono, N.; Kim, D.; Uno, H. *Chem.—Eur. J.* **2010**, *16*, 4063–4074.
12. Ono, N.; Kuroki, K.; Watanabe, E.; Ochi, N.; Uno, H. *Heterocycles* **2004**, *62*, 365–373.
13. (a) Shimizu, Y.; Shen, Z.; Okujima, T.; Uno, H.; Ono, N. *Chem. Commun.* **2004**, 374–375; (b) Uno, H.; Shimizu, Y.; Uoyama, H.; Tanaka, Y.; Okujima, T.; Ono, N. *Eur. J. Org. Chem.* **2008**, 87–98.
14. Uoyama, H.; Takiue, T.; Tominaga, K.; Ono, N.; Uno, H. *J. Porphyrins Phthalocyanines* **2009**, *13*, 122–135.
15. Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394–4397.
16. Shimizu, Y.; Shen, Z.; Ito, S.; Uno, H.; Daub, J.; Ono, N. *Tetrahedron Lett.* **2002**, *43*, 8485–8488.
17. Srinivasan, A.; Pushpan, S. K.; Kumar, M. R.; Mahajan, S.; Chandrashekar, T. K.; Roy, R.; Ramamurthy, P. *J. Chem. Soc., Perkin Trans. 2* **1999**, 961–968.
18. Mack, J.; Bunya, M.; Shimizu, Y.; Uoyama, H.; Komobuchi, N.; Okujima, T.; Uno, H.; Ito, S.; Stillman, M. J.; Ono, N.; Kobayashi, N. *Chem.—Eur. J.* **2008**, *14*, 5001–5020.
19. Aihara, J.; Makino, M. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 675–682.
20. The B3LYP/6-31G(*) density functional theory calculations were performed by Gaussian R 03W.
21. SIR-97: A Package for Crystal Structure Solution and Refinement, Istituto di Gristallografia: Italy Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
22. SHELXS-97 and SHELXL-97: Program for Solution and Refinement of Crystal Structures from Diffraction Data; University of Göttingen: Göttingen, Germany; 'A Short History of SHELX' Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.
23. Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M. *DIRDIF2008 program system*; Crystallography Laboratory, University of Nijmegen: The Netherlands, 2008.
24. CrystalClear SM 1.3.6, and CrystalStructure Ver. 3.7.2, Crystal structure analysis packages from X-ray diffraction, Rigaku (3-9-12 Akishima, Tokyo, Japan) and Rigaku/MSC (9009 New Trails Dr., The Woodlands, TX 77381 USA), (2000–2004).
25. PLATON: A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherland Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.