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DERIVATIZATION OF TETRAFLUOROBENZO[*c*]THIOPHENE. PREPARATION OF TETRAFLUOROTHIABENZOPORPHYRIN

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Abstract – The Diels-Alder reactions of tetrafluorobenzo[*c*]thiophene with electron-deficient olefins such *p*-benzoquinone and bis(phenylsulfonyl)ethylene gave adducts in moderate yields, while no product was obtained in the reaction with butyl vinyl ether. The Vilsmeier reaction gave tetrafluorobenzo[c]thiophene-1-carbaldehyde in good yield. The aldehyde was converted to tetrafluorothiabenzoporphyrin.

Dedicated to the great contribution to heterocyclic chemistry of Professor Dr. Ivar Ugi

INTRODUCTION

Polythiophenes and their related compounds have been attracting great interest from many scientists as conducting polymers[1] and light-emitting materials.[2] Special attention has been paid for poly(benzo[*c*]thiophene), because it has a very low-band gap (*ca*. 1.0 eV)[3] and its almost-colorless thin film doped with halogen shows high conductivity (*ca*. 50 Scm^{-1}).[4] These properties of polythiophenes were easily modified by introduction of substituents on the thiophene ring such as alkyl, alkoxy, aryl, and halogen groups.[5] On the other hand, in the case of poly(benzo[*c*]thiophene), modification of the properties was difficult due to lack of an efficient derivatization method of rather unstable 1,3-free benzo[*c*]thiophene derivatives,[6] preparation of which requires introduction of the aimed substituent before construction of the heterocyclic ring system. Among the 1,3-free benzo[*c*]thiophene derivatives, 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**1**) was reported to be much stable than parent benzo[*c*]thiophene[7] due to the low HOMO level.[8] Although its polymer[9] and co-polymers[10] with thiophene were

investigated, intrinsic reactivity of 4,5,6,7-tetrafluorobenzo[*c*]thiophene was not reported so far. During our study on preparation of compounds with a novel π-system for organic electronic materials,[11] we planned to utilize 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**1**) as a synthon of tetrafluoro-*o*-quinodimethane. In this paper, we discuss our results of its Diels-Alder and Vilsmeier reactions as well as preparation of tetrafluorothiabenzoporphyrin.

RESULTS AND DISCUSSION

4,5,6,7-Tetrafluorobenzo[*c*]thiophene (**1**) was prepared in 30% overall yield from hexafluorobenzene according to the literature procedure.[7] The sublimed crystalline material of **1** was stable and stored in a refrigerator without decomposition for a long time and, fortunately enough, was suitable for the X-ray analysis.[12,13] As far as we know, this X-ray analysis is the second example of benzo[*c*]thiophene derivative with no substituent on the five-membered ring.[14] The Ortep packing diagram and molecular structure are shown in Figures 1 and 2. The molecules lie in a line along with C2 axes forming molecular tapes (see Figure 1). Close contact [2.49(2) Å] is observed between the H^1(H^3) hydrogen and F^4(F^7) fluorine atoms in the neighboring paralleling tapes forming a two-dimensional sheet. The sheets are stacked in an anti-parallel fashion and the distance of the molecular planes of **1** in the neighboring sheets is 3.337(2) Å. In this crystal, the most reactive carbons at 1- and 3-positions of benzo[*c*]thiophene are nicely protected by fluorine atoms of the stacking molecules. This may be one of the reasons of great stability of 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**1**).

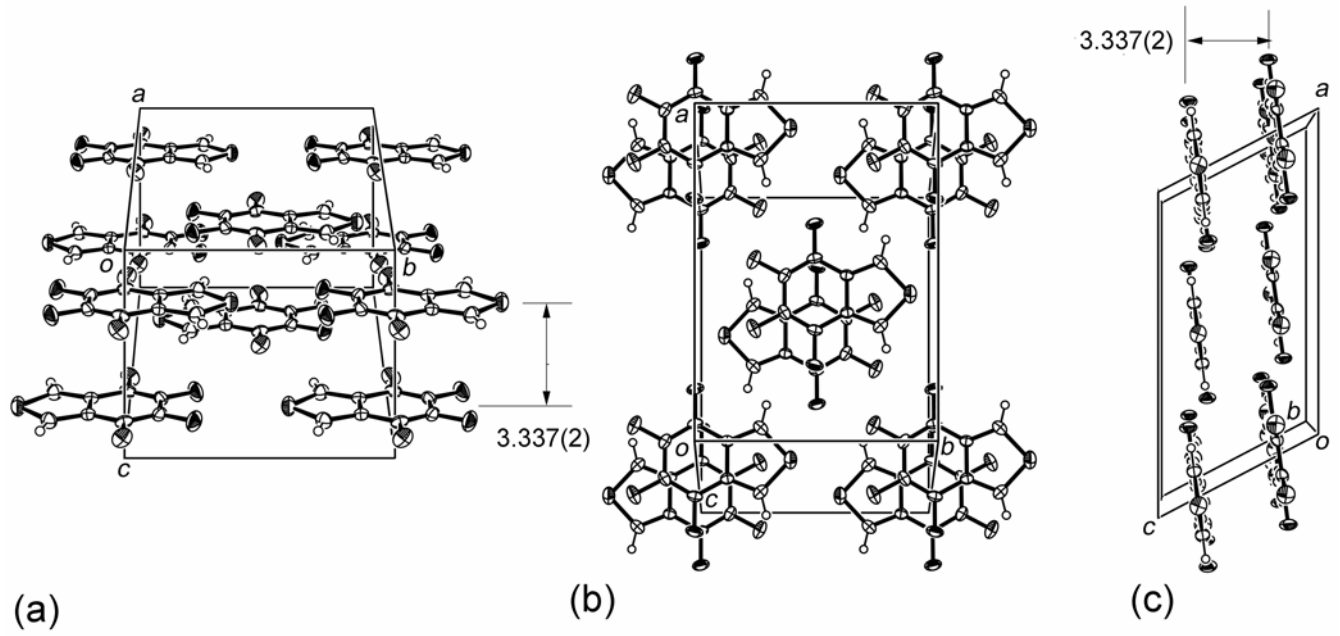


Figure 1. Ortep packing diagram of **1**. (a) View perpendicular to the *bc* plane; (b) View perpendicular to the *ab* plane. (c) View perpendicular to the *ac* plane.

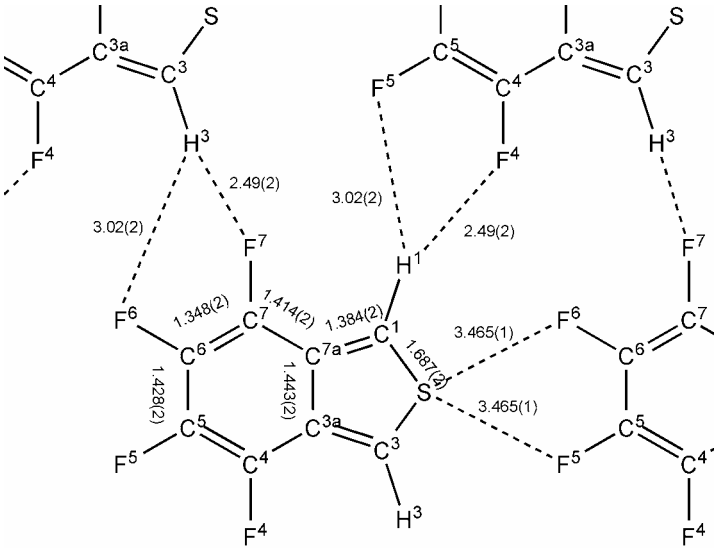
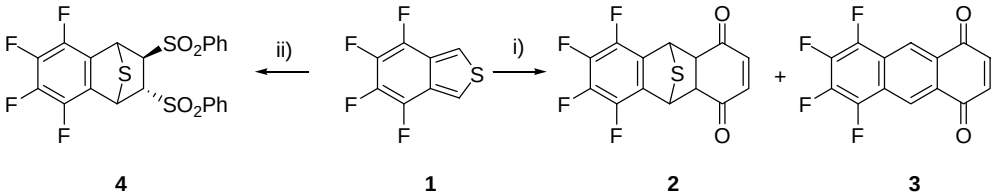


Figure 2. Molecular network of **1**.

The most striking feature is the bond lengths of **1** shown in Figure 2. Distinctive bond alteration is observed even in the benzene ring; C^4-C^5(C^6-C^7) bonds [1.348(2) Å] are shorter than C^5-C^6 [1.428(2) Å] and C^{3a}-C^4 (C^7-C^{7a}) bonds [1.414(2) Å], and the inner bond (C^{3a}-C^{7a}) is extremely elongated to be 1.443(2) Å. This fact means that the 10π-electron system of 2-benzothiophene overwhelms the local 6π benzene aromaticity.[15] The molecular structure was quite similar to that of a benzo[*c*]thiphene-$Cr(CO)_3$ complex.[14]

First, we examined the Diels-Alder reactions of **1**. As the parent benzo[*c*]thiophene and naphtho[2,3-c]thiophene smoothly reacted with electron-deficient dienophiles such as phenyl maleimide[16] and 1,4-benzoquinone,[17] the Diels-Alder reaction of **1** with 1,4-benzoquinone was conducted at room temperature. However, no reaction was observed. Therefore, **1** and 1,4-benzoquinone was heated in neat at 110 °C, and 9,10-epithioanthracenedione **2** and anthracenedione **3** were obtained in respective yields of 24 and 5% (Scheme 1). From the NMR spectra of **2**, this adduct was proved to consist of a *ca*. 1:1 mixture of *endo* and *exo* isomers. Stereochemistry of the *endo* and *exo* isomers could not be determined by difference of the coupling constants between the bridge-head and carbonyl α-methine protons,[18] because exact determination of their coupling constants was difficult: the intrinsic spin system



Scheme 1. *Reagents and conditions:* i) *p*-benzoquinone, 110 °C, 5 h; ii) bis(phenylsulfonyl)ethylene, toluene, 140 °C, 14 h.

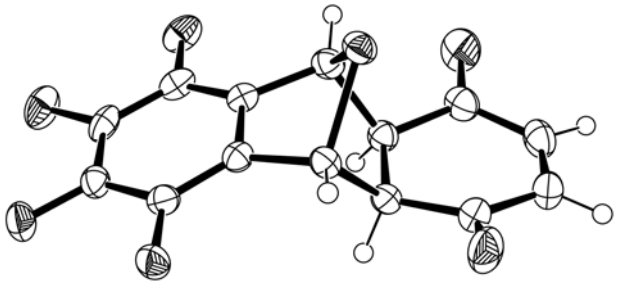
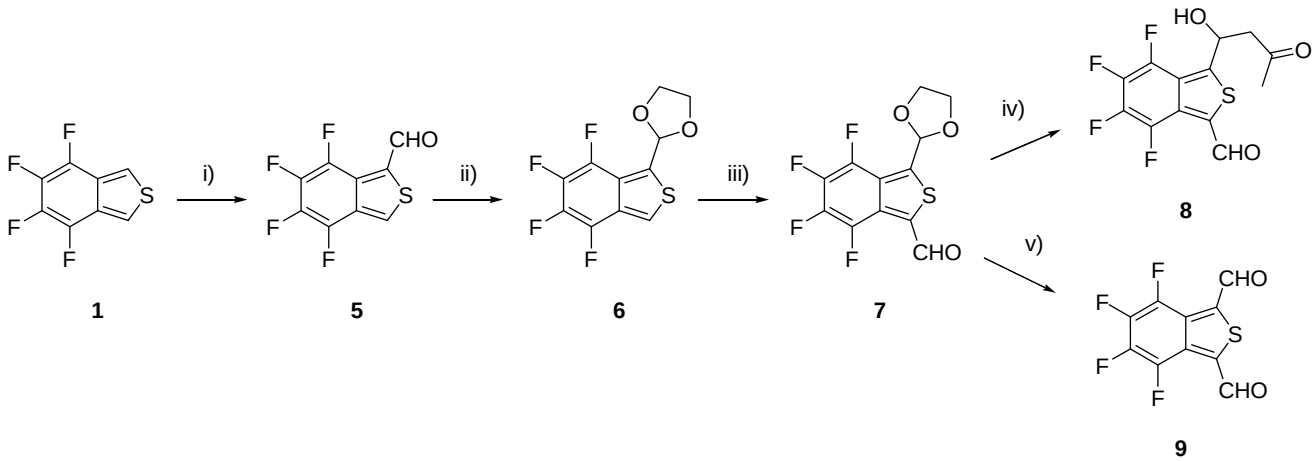


Figure 3. Ortep drawing of *exo*-**2**

of the symmetric bicyclo[2.2.1] skeletal system is AA'XX' or AA'BB'. Moreover, the difference was very small (*ca*. 1 Hz for one isomer and *ca*. 0 Hz for another isomer). On the other hand chemical shifts were very informative for the determination: The olefinic protons of one isomer appeared at a higher field (6.44 ppm) than those of anothor isomer (6.90 ppm) due to the anisotropic effect of the benzene ring. Therefore, the former and the latter isomers were assigned to be *endo* and *exo*, respectively. Finally the stereochemistry was unambiguously determined by the X-ray analysis of exo-2 (Figure 3).[19] The other product **3** was thought to be formed by thermal elimination of hydrogen sulfide from the adduct **2**. The product ratio of **3**/**2** was increased by elongation of the reaction time. When the reaction of **1** with *trans*-bis(phenylsulfonyl)ethylene was conducted in toluene at 140 °C in a sealed tube, adduct **4** was obtained in 36% yield. Contrary to these electron-deficient dienophiles, no reaction of **1** with butyl vinyl ether was observed in spite of all of our efforts.

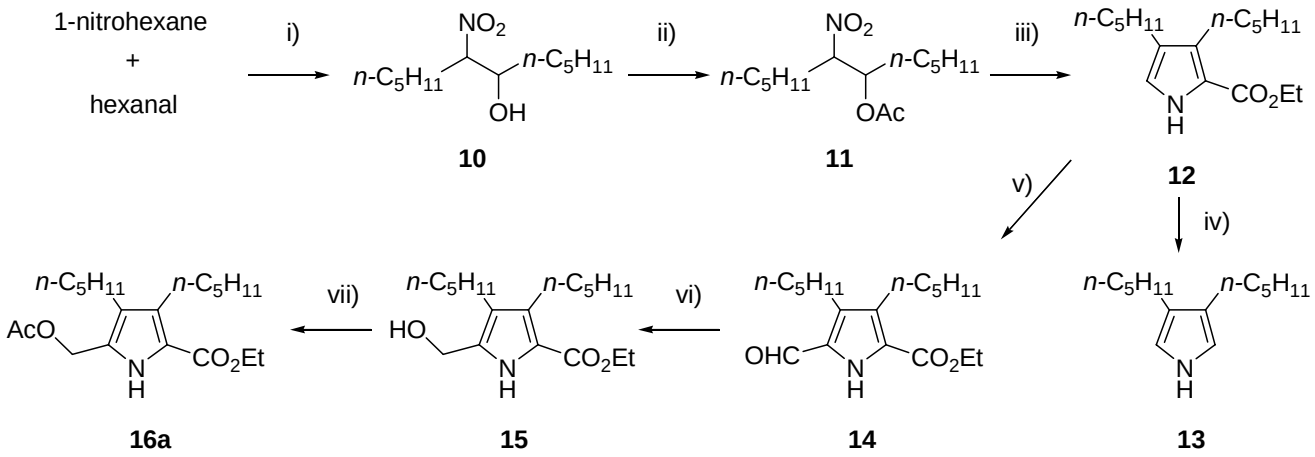
Next, we planned to prepare thiaporphyrin derivatives bearing a tetrafluorobenzo moiety by the [3+1] porphyrin synthesis. As fluorine atoms on the tetrafluorobenzo moiety can be replaced by alkoxide and alkylthiolate anions,[20] tetrafluorothiabenzoporphyrin with long alkyl groups would become a versatile starting compound for preparation of porphyrinoids with a discotic liquid-crystalline property.[21] For this



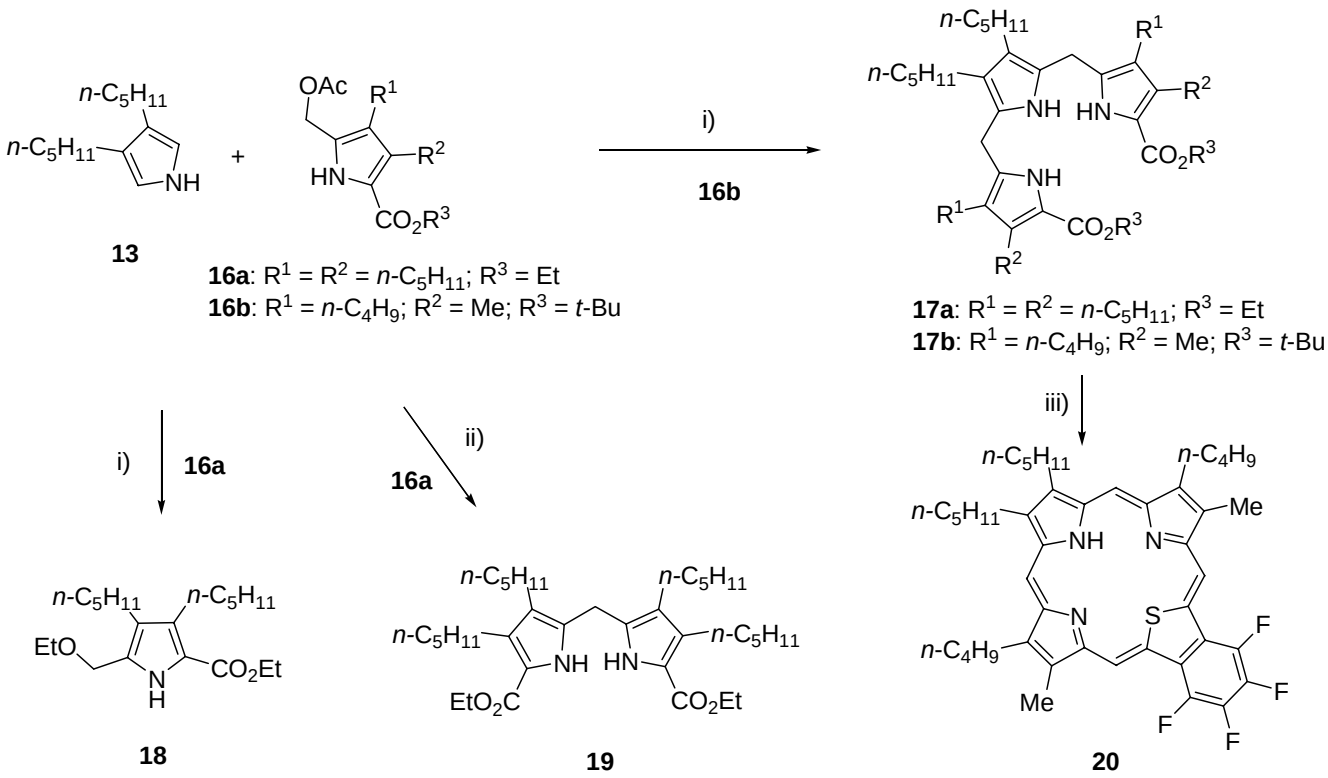
Scheme 2. *Reagents and conditions*: i) *N*-methylformanilide, $POCl_3$, THF, rt. ii) ethylene glycol, *p*-TSA, toluene, reflux. iii) *n*-BuLi, TMEDA; DMF, THF, -50 °C. iv) *p*-TSA, *aq*-acetone, reflux. v) HCl, *aq*-THF, rt.

purpose, we require a diformyl derivative of **1** and tripyrrane with long alkyl chains. Since pyrrole derivatives could be diformylated under proper reaction conditions,[22] we treated 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**1**) with orthoformate derivatives under various reaction conditions. However, no diformyl derivative was formed. We decided to make a detour to the dialdehyde (Scheme 2). The Vilsmeier reaction of **1** using N-methyl formanilide and phosphoryl chloride gave 4,5,6,7-tetrafluorobenzo[*c*]thiophene-1-carbaldehyde (**5**) in good yield (90%). Protection of the formyl group as 1,3-dioxolane with ethylene glycol gave **6** in 95% yield. Lithiation of dioxolanylisothianaphthene **6** with *n*-BuLi and TMEDA followed by treatment with DMF afforded aldehyde **7** in 80% yield. Deprotection of the dioxolanyl group of **7** was first carried out in aqueous acetone in the presence of *p*-toluenesulfonic acid under reflux conditions. The aimed dialdehyde **9** was not obtained at all, and acetone adduct **8**, instead, was obtained in quantitative yield. The deprotection of **7** was successfully done by changing the conditions (HCl in *aq*-THF at room temperature). The aimed aldehyde **9** was obtained in quantitative yield. High susceptibility of the dialdehyde **9** toward the nucleophilic attack even under acidic conditions was well understood by the *o*-quinonoid character of benzo[*c*]thiophene.

Preparation of tripyrrane with long alkyl chains was examined. Due to availability of the starting materials, we chose 3,4-dipentylpyrroles as a component of such a tripyrrane (Scheme 3). The Henry reaction of hexanal and 1-nitrohexane gave a diastereomeric mixture of nitro alcohol **10** in 82% yield. Acetylation of **10** followed by the Barton-Zard reaction[23] with ethyl isocyanoatetate gave ethyl pyrrole-1-carboxylate **12** in 66% yield (2 steps). Removal of the ester group gave 2,3-dipentylpyrrole (**13**) in 74% yield. The Vilsmeier formylation of ethyl pyrrole-1-carboxylate **12** afforded formyl compound **14** in 97% yield. Reduction of aldehyde **14** with $NaBH_4$ in the presence of $CeCl_3$ followed



Scheme 3. *Reagents and conditions:* i) DBU, THF, rt. ii) Ac_2O, H^+, $CHCl_3$, rt. iii) ethyl isocyanoacetate, DBU, THF, rt. iv) KOH, ethylene glycol; 180 °C. v) DMF, $POCl_3$, $C_2H_4Cl_2$, 0 °C. vi) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, THF/EtOH, 0 °C. vii) Ac_2O, pyridine, rt.



Scheme 4. *Reagents and conditions*: i) AcOH/EtOH, reflux. ii) AcOH/CF_3CH_2OH, reflux. iii) **9**, TFA, CH_2Cl_2, rt; Et_3N; DDQ.

by acetylation with acetic anhydride in pyridine provided 5-acetoxymethyl derivative **16a** in 96% yield (2 steps).

We attempted to prepare tripyrrane with six pentyl groups **17a** by the condensation of α-free pyrrole **12** with acetoxymethylpyrrole carboxylate **16a** (Scheme 4). When pyrroles **12** and **16a** in acetic acid and ethanol were refluxed according to the literature procedure,[24] only 5-(ethoxymethyl)pyrrole **18** was isolated instead of the targeted tripyrrane **17a**. By changing the solvent system to a less nucleophilic mixture of acetic acid and trifluoroethanol, dipyrromethane **19** was only obtained. We had already encountered the similar technical difficulty in the preparation of a hexaethyl tripyrrane derivative: diethyl hexamethyltripyrranedicarboxylate was prepared only in 29%, while the corresponding butyl methyl tripyrrane derivative was obtained in 72% yield under the similar conditions.[25] Therefore, we changed the target to tripyrrane **17b**. When pyrrole **13** was reacted with butyl methyl derivative **16b** under the similar conditions, the targeted tripyrrane **17b** was obtained in 77% yield.

The [3+1] porphyrin synthesis of 4,5,6,7-tetrafluorobenzothiphene-1,3-dicarbaldehyde (**9**) with tripyrrane **17b** was conducted under the usual conditions[26] to give tetrafluorothiabenzoporphyrin **20** in 10% yield. The UV-vis spectra of **20** and 12,13-diethyl-7,18-dibutyl-8,17-dimethylbenzo[b]porphyrin (**21**)[27] are shown in Figure 3. Thiabenzoporphyrin **20** showed a rather broad Soret absorption band at 417 nm

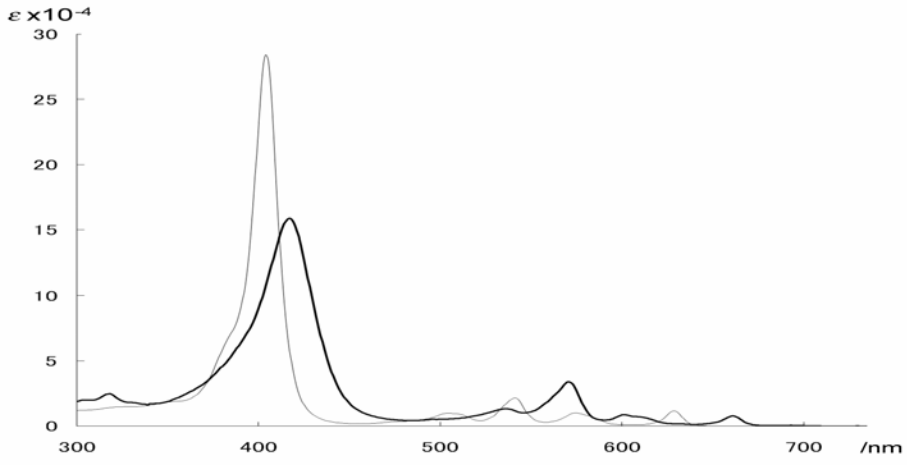


Figure 4. UV-vis spectra of thiabenzoporphyrin **20** (bold line) and benzoporphyrin **21** (solid line)

compared to benzoporphyrin **21** (404 nm). The Q band absorptions were observed at 495 (shoulder), 536, 571, 601, 613 (shoulder), and 661 nm. The lowest energy absorption band of **20** was 32-nm bathochromically shifted from that of **21**. This fact clearly suggests that the porphyrinoid π-system of **20** was expanded more effectively by incorporation of the benzo[*c*]thiophene moiety than by simple fusion of the benzo moiety.

In conclusion, we utilized 4,5,6,7-tetrafluorobenzo[*c*]thiophene (**1**) as a building block for preparation of tetrafluorobenzo-fused aromatic compounds. The first X-ray analysis of **1** explained the stability in solid. Tetrafluorothiabenzoporphyrin was prepared and the π-system was revealed to be effectively expanded.

EXPERIMENTAL

General

Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were obtained with a JEOL AL-400 or EX-400 spectrometer at the ambient temperature by using $CDCl_3$ as a solvent, tetramethylsilane as an internal standard for ^1H and ^{13}C, $CFCl_3$ as a standard for ^{19}F. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. Mass spectra (EI, 70 eV) were measured with a JEOL JMS-700. Elemental analyses were performed with a Yanaco MT-5 elemental analyzer. X-ray measurements of the single crystals were done with Rigaku AFC8S Mercury CCD (1.5 kW Mo sealed tube). UV-vis spectra were measured in chlorofom with a HITACHI U-2810 spectrophotometer. Dehydrated tetrahydrofuran and dichloromethane were purchased from Kanto Chemical Co. and used without further purification. Toluene and TMEDA were distilled from CaH_2 under a nitrogen atmosphere and stored over molecular sieves 4A. DMF and DBU were distilled under

a reduced pressure and stored over molecular sieves 13X. 1,4-Benzoquinone was sublimed under a reduced pressure prior to use. Triethylamine and ethylene glycol were distilled prior to use. Potassium *tert*-butoxide was sublimed at 200 °C under a reduced pressure (*ca.* 0.1 mmHg) and dissolved in dry THF (1.0 mol L^{-1}). Ethyl isocyanoacetate[28] and *trans*-bis(phenylsulfonyl)ethylene[29] were prepared according to the literature procedures. Other commercially available materials were used without further purification.

Diels-Alder reaction of 1 with *p*-benzoquinone

4,5,6,7-Tetrafluorobenzo[*c*]thiophene (**1**; 128 mg, 0.62 mmol) and *p*-benzoquinone (134 mg, 1.24 mmol) was dissolved in $CHCl_3$ (1 mL) and placed in a tube. After the solvent was mostly removed by evaporation, the tube was sealed and heated at 110 °C for 5 h. After cooling, the mixture was chromatographed on silica gel to give 5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9,10-epithioanthracene-1,4-dione (**2**; 11 mg, 24%) and 5,6,7,8-tetrafluoroanthracene-1,4-dione (**3**; 3 mg, 5%). **2**: yellow crystals, R_f 0.3 (15% EtOAc/hexane); ν_{max} (KBr)/cm^{-1} 1660, 1496, 1122, 1080, and 1033; HRMS (EI) Calcd for $C_{14}H_6F_4O_2S$: 314.0025. Found: 314.0023. *exo*-**2**: mp >137 °C (decomp.); δ_H ($CDCl_3$) 3.30 (2H, s), 5.38 (2H, s), and 6.90 (2H, s); δ_F ($CDCl_3$) -142.6 (2F, m) and -156.1 (2F, m). *endo*-**2**: mp 126-129 °C; δ_H ($CDCl_3$) 3.94 (2H, m), 5.38 (2H, m), and 6.44 (2H, s); δ_F ($CDCl_3$) -142.4 (2F, m) and -154.9 (2F, m). **3**: yellow crystals, mp 117-119 °C, R_f 0.3 (15% EtOAc-hexane); δ_H ($CDCl_3$) 7.15 (2H, m) and 8.88 (2H, m); δ_F ($CDCl_3$) -145.5 (2F, m) and -151.9 (2F, m); ν_{max} (KBr)/cm^{-1} 1660, 1471, 1301, 1122, 1055, and 962; MS (EI) *m/z* (rel. intensity) 280 (M^+, 100), 252 (20), 224 (74), and 198 (70). HRMS (EI) Calcd for $C_{14}H_4F_4O_2$: 280.0147. Found: 280.0148.

***trans*-5,6,7,8-Tetrafluoro-2,3-bis(phenylsulfonyl)-1,2,3,4-tetrahydro-1,4-epithionaphthalene (4)**

A solution of **1** (102 mg, 0.48 mmol) and *trans*-bis(phenylsulfonyl)ethylene[29] (410 mg, 1.33 mmol) in dry toluene (12 mL) was placed in a sealed tube, the tube was flashed with nitrogen, and the tube was heated at 140 °C for 14 h. After cooling, the solvent was removed and the residue was chromatographed on silica gel to afford 59 mg (36%) of the title compound as pale yellow crystals: mp 159-162 °C, R_f 0.3 (30% EtOAc/hexane); δ_H ($CDCl_3$) 4.10 (1H, d, J = 4.6 Hz), 4.90 (1H, m), 5.00 (1H, dd, J = 4.6 and 3.1 Hz), 5.27 (1H, br s), and 7.5-7.95 (10 H, m); δ_F ($CDCl_3$) -139.9 (1F, t, J = 17 Hz), -142.5 (1F, t, J = 17 Hz), -154.9 (1F, t, J = 17 Hz), and -155.2 (1F, t, J = 17 Hz); ν_{max} (KBr)/cm^{-1} 1508, 1485, 1448, 1330, 1151, and 1079; MS (EI) *m/z* (rel. intensity) 514 (M^+, 28), 373 (50), 309 (25), 247 (38), 231 (47), 200 (56), 141 (55), 125 (77), and 77 (100); HRMS (EI) Calcd for $C_{22}H_{14}F_4O_2S_3$: 513.9990. Found: 513.9990.

4,5,6,7-Tetrafluorobenzo[*c*]thiophene-1-carbaldehyde (5)

To a stirred solution of *N*-methylformanilide (0.8 mL) was added $POCl_3$ (1.0 mL) by a syringe at rt, and the mixture was stirred for 30 min. A solution of **1** (300 mg, 1.46 mmol) in dry THF (5 mL) was added

dropwise to the mixture. After being stirred for 6 h at rt, the reaction was quenched with water, and the mixture was extracted with Et_2O. The ethereal extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel to give **5** (285 mg, 90%) as yellow powdery crystals: mp 173-175 °C, R_f 0.7 (30% EtOAc/hexane); δ_H ($CDCl_3$) 8.42 (1H, s) and 10.43 (1H, s); δ_C ($CDCl_3$) 126.0 (dd, J = 17 and 5 Hz), 126.9 (dd, J = 19 and 8 Hz), 127.2 (d, J = 9 Hz), 135.0 (m), 136.7, (dt, J = 255 and 16 Hz), 138.7 (dm, J = 257 Hz), 139.7 (dm, J = 255 Hz), 140.4 (dtd, J = 259, 16, and 2 Hz), and 181.8 (d, J = 10 Hz); δ_F ($CDCl_3$) -143.0 (t, J = 17 Hz), -145.9 (t, J = 17 Hz), -158.3 (t, J = 17 Hz), and -160.7 (t, J = 17 Hz); ν_{max} (KBr)/cm^{-1} 1649, 1576, 1541, 1491, 1363, 1234, 1173, and 1034; MS (EI) *m/z* (rel. intensity) 234 (M^+, 100), 206 (37), and 161 (31). Anal. Calcd for $C_9H_2F_4OS$: C, 46.16; H, 0.86. Found: C, 46.32; H, 1.26%.

1-(1,3-Dioxolan-2-yl)-4,5,6,7-tetrafluorobenzo[*c*]thiophene (6)

A solution of **5** (800 mg, 3.42 mmol), distilled ethylene glycol (0.40 mL, 7.0 mmol), and *p*-TSA·H_2O (0.6 mg, 0.03 mmol) in dry THF (30 mL) was heated at reflux under N_2 for 1.5 h with azeotropic removal of water by a Dean-Stark apparatus filled with molecular sieves 4A. The mixture was cooled to rt, and an aqueous solution of $NaHCO_3$ was added. The organic layer was separated and aqueous layer was extracted with ether. The combined ethereal extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel to give 904 mg (95%) of **6** as white powder: mp 35-39 °C, R_f 0.3 (40% $CHCl_3$/hexane); δ_H ($CDCl_3$) 4.06-4.24 (4H, m), 6.65 (1H, s), and 7.82 (1H, s); δ_C ($CDCl_3$) 65.6 (s), 98.9 (d, J = 6 Hz), 115.3 (d, J = 9 Hz), 122.4 (dd, J = 17 and 6 Hz), 126.5 (dd, J = 19 and 7 Hz), 133.8 (m), 136.2 (dt, J = 251 and 17 Hz), 137.6 (ddm, J = 248 and 17 Hz), 138.1 (ddm, J = 240 and 17 Hz), 138.8 (dm, J = 257 Hz), and 140.1 (dm, J = 13 Hz); δ_F ($CDCl_3$) -147.9 (t, J = 16 Hz), -148.9 (t, J = 16 Hz), -161.3 (t, J = 16 Hz), and -161.1 (t, J = 16 Hz); ν_{max} (KBr)/cm^{-1} 1684, 1550, 1495, 1375, 1171, 1088, and 985; MS *m/z* (rel. intensity) 278 (M^+, 100), 262 (77), and 183 (66). Anal. Calcd for $C_{11}H_6F_4O_2S$: C, 47.49; H, 2.17. Found: C, 47.51; H, 2.22%.

3-(1,3-Dioxolan-2-yl)-4,5,6,7-tetrafluorobenzo[*c*]thiophene-1-carbaldehyde (7)

To a solution of **6** (780 mg, 2.80 mmol) and TMEDA (0.73 mL, 4.24 mmol) in THF (14 mL) was added dropwise a 1.58-M hexane solution of *n*-BuLi (1.94 mL, 3.07 mmol) at -78 °C under N_2, and the mixture was stirred at -10 °C for 30 min. Dry DMF (0.33 mL, 4.3 mmol) was added at -50 °C and the mixture was slowly warmed up to rt. The reaction mixture was quenched with an aqueous saturated solution of NH_4Cl. The mixture was extracted with Et_2O. The ethereal extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel to give 682 mg (80%) of **7** as yellow powder, mp 106-109 °C, R_f 0.4 (60% $CHCl_3$/hexane); δ_H ($CDCl_3$) 4.13-4.21 (4H, m), 6.68 (1H, s), and 10.42 (1H, s); δ_C ($CDCl_3$) 56.9, 98.6 (d, J = 6 Hz), 123.0 (dd, J = 17 and 8 Hz), 127.0 (dd, J = 17 and 6 Hz), 132.9 (t, J = 9 Hz), 137.4 (dt, J = 254 and 17 Hz), 139.3 (dm, J = 259 Hz),

139.9 (dt, *J* = 259 and 17 Hz), 147 (m), 182.2 (d, *J* = 11 Hz), and one carbon could not be found; δ_F ($CDCl_3$) -142.3 (t, *J* = 17 Hz), -143.8 (t, *J* = 17 Hz), -154.4 (t, *J* = 17 Hz), and -160.0 (t, *J* = 17 Hz); ν_{max} (KBr)/cm^{-1} 1655, 1577, 1533, 1485, 1373, 1230, and 1146; MS (EI) *m/z* (rel. intensity) 306 (M^+, 82), 234 (100), 217 (80), and 161 (36). Anal. Calcd for $C_{12}H_4F_4O_3S$: C, 47.49; H, 2.17. Found: C, 47.51; H, 2.22%.

4,5,6,7-Tetrafluoro-3-(3-oxo-1-hydroxybutyl)benzo[*c*]thiophene-1-carbaldehyde (8)

A solution of **7** (56 mg, 0.183 mmol) and *p*-toluenesulfonic acid (1 mg) in acetone (30 mL) and water (1 mL) was refluxed overnight under an inert atmosphere. After cooling, the mixture was concentrated to a half volume and the residue was extracted with $CHCl_3$. The organic extract was washed successively with an aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel to give 58 mg (99%) of **8** as yellow powder: mp 124-126 °C, δ_H ($CDCl_3$) 2.27 (3H, s), 2.86 (1H, dd, *J* = 18.2 and 9.8 Hz), 3.12 (1H, dt, *J* = 18.2 and 2.0 Hz), 4.24 (1H, d, *J* = 3.2 Hz; OH), 6.00 (1H, ddd, *J* = 9.8, 3.2 and 2.0 Hz), and 10.37 (1H, d, *J* = 1.6 Hz); δ_C ($CDCl_3$) 30.6, 51.5, 66.3 (d, *J* = 5 Hz), 120.3 (dd, *J* = 16 and 8 Hz), 126.7 (dd, *J* = 17 and 6 Hz), 131.8 (m), 137.0 (dt, *J* = 258 and 16 Hz), 139.0 (m), 139.5 (m), 139.6 (m), 153.3 (m), 181.5 (d, *J* = 11 Hz), and 207.5; δ_F ($CDCl_3$) -141.9 (1F, t, *J* = 17 Hz), -145.7 (1F, t, *J* = 17 Hz), -154.7 (1F, t, *J* = 17 Hz), and -161.0 (1F, *J* = 17 Hz); ν_{max} (KBr)/cm^{-1} 3253, 1716, 1627, 1490, 1240, 1147, and 1093; MS (EI) *m/z* (rel. intensity) 320 (M^+, 14), 263 (72), 235 (100), 206 (30), 161 (33), and 157 (31). Anal. Calcd for $C_{12}H_6F_4O_3S$: C, 47.06; H, 1.97. Found: C, 47.22; H, 2.12%.

4,5,6,7-Tetrafluorobenzo[*c*]thiophene-1,3-dicarbaldehyde (9)

To a stirred solution of **7** (670 mg, 2.19 mmol) in THF (24 mL) was added 1.5 M aqueous HCl (20 mL) at rt. After 1 h, the mixture was extracted with $CHCl_3$. The organic extract was washed successively with aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated in vacuo to give 574 mg (100%) of **9** as yellow powder: mp 143-145 °C, R_f 0.4 (60% $CHCl_3$/hexane); δ_H ($CDCl_3$) 10.60 (s); δ_C ($CDCl_3$) 126.3 (t, *J* = 12 Hz), 139.6 (dm, *J* = 264 Hz), 140.0 (dm, *J* = 257 Hz), 141.0 (m), and 182.2 (t, *J* = 6 Hz); δ_F ($CDCl_3$) -140.1 (m) and -153.5 (m); ν_{max} (KBr)/cm^{-1} 1654, 1485, 1230, 1146, and 1066; MS (EI) *m/z* (rel. intensity) 262 (M^+, 100), 233 (36), and 161 (53). Anal. Calcd for $C_{11}H_2F_4O_2S$: C, 45.81; H, 0.77. Found: C, 45.75; H, 1.02%.

7-Nitro-6-dodecanol (10)

To a stirred solution of hexanal (6.98 mL, 50.0 mmol) and 1-nitrohexane (6.15 mL, 50.0 mmol) in THF was added DBU (0.74 mL, 5.0 mmol) by a syringe at rt under nitrogen. After 8 h, a 1.0-M HCl solution was added and then the mixture was extracted with EtOAc. The organic extract was washed successively with water, a saturated aqueous $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The

residual liquid was distilled under a reduced pressure and the distillate at 112-115 °C/0.01 mmHg was collected to give 9.46 g (82 %) of diastereomeric **10** (6:4) as a pale yellow oil: R_f 0.25 (15% EtOAc/hexane); δ_H ($CDCl_3$) 0.90 (6H of both isomers, m), 1.2-1.6 (14H of both isomers, m), 1.65-2.1 (2H of both isomers, m), 2.1-2.6 (1H of both isomers, br m), 3.87 (1H of one isomer, m), 4.00 (1H of another isomer, m), and 4,3-4.5 (1H of both isomers, m); δ_C ($CDCl_3$) 13.8, 13.9, 22.2, 22.4, 24.9, 25.2, 25.3, 25.6, 27.9, 30.6, 31.0, 31.1, 31.4, 31.5, 33.1, 33.5, 72.1, 72.4, 92.4, and 92.9; ν_{max} (KBr)/cm^{-1} 3437, 1550, 1458, 1379, 1126, and 1072; FAB^+ *m/z* 232 ($M+H^+$). Anal. Calcd for $C_{14}H_{25}NO_4$: C, 62.30; H, 10.89; N, 6.05. Found: C, 62.53; H, 10.75; N, 5.78%.

6-Acetoxy-7-nitrododecane (11)

To a stirred solution of **10** (9.25 g, 40.0 mmol) and acetic anhydride (5.67 mL, 60.0 mmol) was added conc. H_2SO_4 (0.02 mL) at 0 °C. After the mixture had been stirred for 4 h at rt, a saturated aqueous $NaHCO_3$ was added and then the mixture was extracted with $CHCl_3$. The organic extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residual liquid was distilled under a reduced pressure and the distillate at 133-135 °C/0.01 mmHg was collected to give 8.96 g (82 %) of **11** (6:4) as a colorless oil: R_f 0.4 (15% EtOAc-hexane); δ_H ($CDCl_3$) 0.89 (6H of both isomers, m), 1.31 (10H of both isomers, m), 1. 5-1.75 (4H of both isomers, m), 2.00 (2H of both isomers, br m), 2.10 (3H of one isomer, s), 2.16 (3H of another isomer, s), 4.60 (1H of both isomers, m), 5.16 (1H of another isomer, m), and 5.29 (1H of one isomer, m); δ_C ($CDCl_3$) 13.77, 13.82, 20.65, 20.73, 22.2, 22.3, 24.2, 24.9, 25.2, 25.5, 28.9, 29.6, 29.7, 30.7, 30.96, 31.01, 31.2, 31.4, 72.7, 72.9, 89.6, 90.1, 169.8, and 170.2; ν_{max} (KBr)/cm^{-1} 2958, 2931, 2862, 1749, 1558, 1478, 1373, 1228, and 1122; FAB^+ *m/z* 274 ($M+H^+$). Anal. Calcd for $C_{14}H_{27}NO_4$: C, 61.51; H, 9.96; N, 5.12. Found: C, 61.32; H, 9.75; N, 5.11%.

Ethyl 3,4-dipentylpyrrole-2-carboxylate (12)

To a stirred solution of **11** (8.20 g, 30.0 mmol) and ethyl isocyanoacetate (3.93 mL, 36.0 mmol) in dry THF (30 mL) was added DBU (10.7 mL) (72.0 mmol) by a syringe at 0 °C under N_2. The mixture was warmed to rt and then stirred for 8 h. The reaction was quenched by adding a 1.0-M aqueous HCl solution. The mixture was extracted three times with $CHCl_3$. The organic extract was washed successively with a saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed through a short silica-gel column with 15% EtOAc/hexane. The eluate was concentrated, the residue was distilled under a reduced pressure, and the distillate at 142-144 °C/0.03 mmHg was collected to give 6.68 g (80%) of **12** as a pale yellow oil: R_f 0.2 (15% EtOAc/hexane); δ_H ($CDCl_3$) 0.90 (6H, m), 1.35 (11H, m), 1.52 (4H, m), 2.39 (2H, t, J = 7.8 Hz), 2.70 (2H, t, J = 7.8 Hz), 4.30 (2H, q, J = 7.2 Hz), 6.66 (1H, s), and 8.86 (1H, s, br); δ_C ($CDCl_3$) 14.0, 14.1, 14.5, 22.5, 22.6, 24.8, 24.9, 30.3, 30.9, 31.7, 32.1, 59.7, 118.2, 119.6, 125.2, 131.3, and 161.6; ν_{max} (KBr)/cm^{-1} 3496, 3321, 1670, 1466, 1414, 1277, 1144, and 1117; MS (EI) *m/z* (rel. intensity) 279 (M^+, 44), 223 (44), 207 (42), 166 (66),

150 (88), 120 (39), and 94 (100). Anal. Calcd for $C_{17}H_{29}N$: C, 73.07; H, 10.46; N, 5.01. Found: C, 73.01; H, 10.56; N, 5.00%.

3, 4-Dipentylpyrrole (13)

To ethyl pyrrolecarboxylate **12** (2.79 g, 10.0 mmol) were added KOH (2.0 g) and ethylene glycol (40 mL). The mixture was heated at 180 °C under nitrogen. After 2 h, the mixture was cooled to rt and extracted with EtOAc. The organic extract was washed successively with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was distilled under a reduced pressure and the distillate at 95-97 °C/0.03 mmHg was collected to give 1.54 g (74 %) of **13** as a colorless oil: R_f 0.45 (15% EtOAc/hexane); δ_H ($CDCl_3$) 0.90 (6H, t, J = 6.6 Hz), 1.35 (8H, m), 1.56 (4H, m), 2.41 (4H, t, J = 7.6 Hz), 6.50 (2H, s), and 7.76 (1H, br s); δ_C ($CDCl_3$) 14.1, 22.6, 25.3, 30.2, 32.0, 114.8, and 123.1; ν_{max} (KBr)/cm^{-1} 3496, 3392, 2956, 2927, 2856, 1460, and 1063; MS (EI) *m/z* (rel. intensity) 207 (M^+, 33), 150 (44), 136 (12), 108 (22), and 94 (100). Anal. Calcd for $C_{14}H_{25}N$: C, 81.09; H, 12.15; N, 6.75. Found: C, 80.81; H, 12.25; N, 6.67%.

Ethyl 5-formyl -3,4-dipentylpyrrole-2-carboxylate (14)

To a solution of *N,N*-dimethylformamide (1.2 mL, 5.0 mmol) was added dropwise $POCl_3$ (8.4 mL, 90 mmol) at 0 °C under a N_2 atmosphere. The mixture was stirred at rt for 15 min and then the mixture was diluted with 1,2-dichloroethane (50 mL). A solution of **12** (1.40 g, 5.00 mmol) in 1,2-dichloroethane (25 mL) was added dropwise to the reaction mixture at 0 °C and the mixture was then stirred at rt for 1.5 h. An aqueous NaOAc was added at 0 °C and then the mixture was refluxed for 15 min. The mixture was exacted with CH_2Cl_2 and the organic extract was washed successively with a saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel with 20% EtOAc/hexane to give **14** (1.49 g, 97%) as colorless crystals: mp 55-57 °C, R_f 0.4 (20% EtOAc/hexane); δ_H 0.90 (6H, m), 1.37 (11H, m), 1.54 (4H, m), 2.71 (4H, m), 4.36 (2H, q, J = 7.2 Hz), 9.54 (1H, brs), and 9.75 (1H, s); δ_C 13.9, 14.0, 14.3, 22.4, 22.5, 23.4, 24.4, 30.9, 31.7, 32.0, 32.4, 60.9, 124.6, 129.9, 131.9, 135.0, 160.7, and 179.2; ν_{max} (KBr)/cm^{-1} 3280, 1689, 1673, 1545, 1483, 1367, and 1257; MS (EI) *m/z* (rel. intensity) 307 (M^+, 100), 278 (31), 251 (44), 234 (44), 194 (74), and 189 (25). Anal. Calcd for $C_{18}H_{29}NO_3$: C, 70.32; H, 9.51; N, 4.56. Found: C, 70.07; H, 9.34; N, 4.40%.

Ethyl 5-hydroxmethyl-3,4-dipentylpyrrole-2-carboxylate (15)

To a solution of **14** (1.23 g, 4.00 mmol) in dry THF (30 mL) was added $CeCl_3 \cdot 7H_2O$ (1.49 g, 4.00 mmol) in EtOH (10 mL) at rt and then $NaBH_4$ (0.15 g, 4.00 mmol) was added at 0 °C. The mixture was warmed to rt and then stirred for 1 h. The reaction was quenched by adding a 1.0-M aqueous HCl solution. The mixture was extracted three times with EtOAc. The organic extract was washed successively with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give **15** (1.21 g,

98%) as colorless powder: mp 98-100 °C, R_f 0.25 (40% EtOAc/hexane); δ_H 0.89 (6H, m), 1.34 (11H, m), 1.43 (2H, m), 1.51 (2H, m), 2.01 (1H, br s), 2.38 (2H, t, J = 7.6 Hz), 2.67 (2H, t, J = 8.1 Hz), 4.30 (2H, q, J = 7.2 Hz), 4.64 (2H, s), and 9.18 (1H, br s); δ_C 14.0, 14.1, 14.7, 22.5, 22.6, 23.8, 25.1, 31.2, 31.7, 31.8, 32.2, 56.5, 59.9, 117.8, 122.2, 131.9, 132.3, and 161.8; ν_{max} (KBr)/cm^{-1} 3439, 3288, 1676, 1288, 1240, and 1045; MS (EI) *m/z* (rel. intensity) 309 (M^+, 100), 252 (70), 218 (68), 196 (97), 180 (66), and 150 (56). Anal. Calcd for $C_{18}H_{31}NO_3$: C, 69.86; H, 10.10; N, 4.53. Found: C, 69.61; H, 10.03; N, 4.52%.

Ethyl 5-acetoxymethyl-3,4-dipentylpyrrole-2-carboxylate (16a)

To a solution of **15** (309 mg, 1.00mmol) in dry pyridine (5 mL) was added acetic anhydride (5 mL) by a syringe at rt under nitrogen. After 12 h, the mixture was vacuum distilled to remove the low boiling components (pyridine, acetic anhydride, and acetic acid). The residue was chromatographed on silica gel to give **16a** (344 mg, 98%) as colorless powder: mp 77-79 °C; R_f 0.4 (20% EtOAc/hexane); δ_H 0.90 (6H, m), 1.34 (11H, m), 1.50 (4H, m), 2.06 (3H, s), 2.42 (2H, t, J = 7.8 Hz), 2.67 (2H, t, J = 8.1 Hz), 4.32 (2H, q, J = 7.2 Hz), 5.03 (2H, s), and 9.34 (1H, br s); δ_C 13.9, 14.0, 14.4, 20.8, 22.5, 23.7, 25.1, 31.1, 31.6, 31.7, 32.1, 57.1, 59.9, 118.8, 124.9, 126.9, 131.5, 161.5, and 171.4; ν_{max} (KBr)/cm^{-1} 3301, 1732, 1672, 1469, 1365, 1282, 1242, and 1020; MS (EI) *m/z* (rel intensity) 351 (M^+, 100), 292 (56), 234 (47), 222 (40), 162 (35), and 150 (24). Anal. Calcd for $C_{20}H_{33}NO_3$: C, 68.34; H, 9.46; N, 3.99. Found: C, 68.22; H, 9.34; N, 4.03%.

2,5-Bis(5-*t*-butoxycarbonyl-3-butyl-4-methyl-2-pyrrolylmethyl)-3,4-dipentylpyrrole (17b)

To a solution of 3,4-dipentylpyrrole (**13**) (1.04 g, 5.00 mmol) and **16b**[27] (3.09 g, 10.0 mmol) in EtOH (100 mL) was added AcOH (10 mL) at rt under a N_2 atmosphere. The mixture was refluxed for 12 h. After cooling, the mixture was diluted with EtOH and stirred at -40 °C. White precipitates were formed and collected by filtration to afford **17b** (2.71 g, 77%). This material was pure enough for the next step. **17b**: pale yellow powder, mp 126-128 °C; δ_H ($CDCl_3$) 0.88 (12H, m), 1.31 (16H, m), 1.43 (4H, m), 1.52 (18H, s), 2.23 (6H, s), 3.32 (8H, m), 3.47 (4H, s), 7.09 (1H, br s), and 8.34 (2H, br s); δ_C ($CDCl_3$) 10.6, 13.9, 14.0, 22.5, 22.6, 23.1, 23.7, 24.6, 31.6, 32.1, 33.2, 80.1, 118.6, 120,2, 121.7, 122.2, 126.2, 129.9, and 161.2; ν_{max} (KBr)/cm^{-1} 3448, 3309, 2925, 2856, 1655, 1365, and 1277; HRMS (FAB^+): Calcd for $C_{44}H_{71}N_3O_4+H^+$: 706.5523; found: 706.5528.

Ethyl 5-ethoxymethyl-3,4-dipentylpyrrole-2-carboxylate (18)

To a solution of 3,4-dipentylpyrrole (**13**) (42 mg, 0.20 mmol) and **16a** (141 g, 0.40 mmol) in EtOH (4.0 mL) was added AcOH (0.4 mL) at rt under a N_2 atmosphere. The mixture was refluxed for 12 h. After cooling, the mixture was extracted three times with EtOAc. The organic extract was washed successively with water, saturated aqueous $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel with 20% EtOAc/hexane to give **14** (49 mg, 72%) as colorless

oil, R_f 0.5 (20% EtOAc/hexane); δ_H 0.89 (6H, m), 1.23 (3H, t, J = 7.1 Hz), 2.36 (2H, t, J = 7.8 Hz), 2.67 (2H, t, J = 7.8 Hz), 3.52 (2H, q, J = 7.0 Hz), 4.29 (2H, q, J = 7.2 Hz), 4.43 (2H, s), and 8.67 (1H, br s); δ_C 14.0, 14.1, 14.5, 15.2, 22.5, 22.6, 23.9, 25.1, 31.2, 31.5, 31.8, 32.2, 59.7, 63.8, 66.0, 117.8, 122.7, 129.7, 132.0, and 161.4; ν_{max} (KBr)/cm^{-1} 3313, 1707, 1666, 1458, 1371, 1342, 1247, 1171, and 1097; MS (EI) *m/z* (rel. intensity) 337 (M^+, 100), 292 (42), 281 (32), 236 (41), and 208 (32). HRMS (EI^+): Calcd for $C_{20}H_{35}NO_3$: 337.2617; found: 337.2617.

Bis(5-ethoxycarbonyl-3,4-dipentyl-2-pyrrolyl)methane (19)

To a solution of 3,4-dipentylpyrrole (**13**) (42 mg, 0.20 mmol) and **16a** (141 g, 0.40 mmol) in CF_3CH_2OH (4.0 mL) was added AcOH (0.4 mL) at rt under a N_2 atmosphere. The mixture was refluxed for 12 h. After cooling, the mixture was extracted three times with EtOAc. The organic extract was washed successively with water, saturated aqueous $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated *in vacuo.* The residue was chromatographed on silica gel with 20% EtOAc/hexane to give **14** (86 mg, 76%) as white solid, mp 51-53 °C; R_f 0.4 (20% EtOAc/hexane); δ_H 0.88 (12H, m), 1.28-1.34 (22H, m), 1.50 (4H, m), 1.62 (4H, m), 2.33 (4H, m), 2.65 (4H, m), 3.83 (2H, s), 4.25 (4H, q, J = 7.2 Hz), and 8.67 (2H, brs); δ_C 14.0, 14.1, 14.5, 22.5, 22.6, 23.4, 24.1, 25.3, 31.20, 31.23, 31.9, 32.4, 59.7, 117.5, 122.5, 129.0, 132.6, and 161.5; ν_{max} (KBr)/cm^{-1} 3302, 1651, 1442, 1313, 1250, and 1043; MS (EI) *m/z* (rel. intensity) 570 (M^+, 100), 291 (43), 222 (5), 162 (4), and 134 (4). Anal. Calcd for $C_{35}H_{58}N_2O_4$: C, 73.64; H, 10.24; N, 4.91. Found: C, 73.34; H, 10.22; N, 4.91%.

8,18-Butyl-7,17-dimethyl-12,13-dipentyl-2^1,2^2,2^3,2^4-tetrafluoro-23*H*,21-thiabenzo[*b*]porphyrin (20)

A solution of tripyrrane **17b** (79.2 mg, 0.11 mmol) in trifluoroacetic acid (0.20 mL) was stirred at rt for 15 min under N_2 in the dark. The mixture was diluted with dry CH_2Cl_2 (7.0 mL), and then a solution of diformylbenzo[*c*]thiophene **9** (29 mg, 0.11 mmol) in dry CH_2Cl_2 (3.0 mL) was added. The mixture was stirred at rt for 16 h. The reaction mixture was neutralized with triethylamine and treated with DDQ (27.2 mg, 0.12 mmol) for 2 h. The mixture was washed successively with water and brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was chromatographed on silica gel with EtOAc/hexane and recrystallization of CH_2Cl_2/MeOH gave **20** (8.2 mg, 10%) as purple crystals: mp >250 °C (decomp); δ_H ($CDCl_3$) -3.10 (1H, br s), 1.03 (6H, t, J = 7.3 Hz), 1.15 (6H, t, J = 7.3 Hz), 1.60 (4H, m), 1.80 (8H, m), 2.23 (4H, m), 2,32 (4H, m), 3.25 (6H, s), 3,82 (4H, t, J = 7.6 Hz), 4.07 (4H, t, J = 7.8 Hz), 9.96 (2H, s), and 10.27 (2H, s); δ_C ($CDCl_3$) 11.3, 14.1, 14.2, 22.8, 23.2, 26.2, 26.5, 32.5, 33.6, 35.3, 103.3, 110.9 (m), 121.4 (m), 135.3, 137.2, 137.9 (dm, J = 253 Hz), 138.1, 138.5, 141.9 (dm, J = 266 Hz), 144.7, 151.8, and 157.4; δ_F ($CDCl_3$) -144.2 (2F, m) and -158.1 (2F, m); UV-vis ($CHCl_3$) λ_{max}/nm ($\log_{10}$ ε): 318 (4.40), 417 (5.20), 495 (sh, 3.75), 5.36 (4.13), 571 (4.53), 6.01 (3.94), 6.13 (sh, 3.81), and 661 (3.90). HRMS (FAB^+) Calcd for $C_{44}H_{51}N_3F_4S+H^+$: 730.3818; found: 730.3817. Anal. Calcd for $C_{44}H_{51}F_4N_3S_4+1/8CH_2Cl_2$: C, 71.56; H, 6.98; N, 5.67. Found: C, 71.68; H, 6.80; N, 5.57%.

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REFERENCES AND NOTES

1. For reviews, see: A. G. MacDiarmid, *Angew. Chem Int. Ed.*, 2001, **40**, 2581; A. J. Heeger, *Angew. Chem Int. Ed.*, 2001, **40**, 2591.
2. I. F. Perepichka, D. F. Perepichka, H. Meng, and F. Wudl, *Adv. Mater.*, 2005, **17**, 2281.
3. F. Wudl, M. Kobayashi, and A. J. Heeger, *J. Org. Chem*., 1984, **49**, 3382.
4. M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl, and A. Heeger, *J. Chem. Phys*., 1985, **82**, 5717.
5. G. Barbarella, M. Melucci, and G. Sotgiu, *Adv. Mater.*, 2005, **17**, 1581; J. Roncali, P. Blanchard, and P. Frère, *J. Mater. Chem.*, 2005, **15**, 1589.
6. T. L. Gilchrist and S. J. Higgins, "*Benzo[c]thiophenes,*" in "*Hetarenes and Related Ring Systems, Fused Five-Membered Hetarenes with One Heteroatom,*" E. J. Thomas, ed in a series of "*Science of Synthesis*," George Thieme Verlag, Stuttgart, 2000, **10.5**, 185.
7. G. M. Brooke and S. D. Mawson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1919; G. M. Brooke and J. A. K. J. Ferguson, *J. Fluorine Chem.*, 1988, **41**, 263.
8. F. Babudri, G. M. Farinola, F. Naso, and R. Ragni, *Chem. Commun.*, 2007, 1003.
9. G. M. Brooke, C. J. Drury, D. Bloor, and M. J. Swann, *J. Mater. Chem.*, 1995, **5**, 1317; R. Kiebooms, P. Adriaensens, D. Vanderzande, J. Gelan, M. J. Swann, D. Bloor, C. J. Drury, and G. M. Brooke, *Macromolecules*, 1996, **29**, 5981.
10. R. H. L. Kiebooms, P. J. A. Adriaensens, D. J. M. Vanderzande, and J. M. J. V. Gelan, *J. Org. Chem.*, 1997, **62**, 1473.
11. For a recent example, see: H. Uno, K. Nakamoto, K. Kuroki, A. Fujimoto, and N. Ono, *Chem. Eur. J.*, **2007**, *13*, 5773.
12. *Crystallographical data for* **1**: $C_8H_3F_4S$; FW = 206.16, colorless blocks, 0.30 x 0.30 x 0.20 mm, *monoclinic*, *C2/c* (#15), $Z = 4$ in a cell of dimensions $a = 12.771(4)$ Å, $b = 9.219(2)$ Å, $c = 7.086(6)$ Å, $\beta = 117.604(1)^\circ$, $V = 739.3(7)$ Å^3, $D_{calc} = 1.852$ g·cm^{-3}, *Mo Kα*, $F(000) = 408$, $T = 150$, 830 unique reflections, 691 with $F^2 > 2\sigma(F^2)$. The final $R_1 = 0.040$, wR_2 *(all)* = 0.103, goodness-of-fit = 1.01 for 65 parameters refined on F^2, CCDC No. 650401.
13. X-Ray data were processed by CrystalStructure Ver. 3.8.1. Structures were solved by SIR-97 and then refined by SHELXL-97. CrystalStructure Ver. 3.8.1, Crystal Structure Analysis Package, Rigaku (3-9-12 Akishima, Tokyo, Japan) and Rigaku/MSC (9009 New Trails Dr., The Woodlands, TX 77381 USA), (2006). SIR-97: A package for crystal structure solution and refinement, Istituto di

Gristallografia, Italy; A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Cryst.,* 1999, **32,** 115. SHELXL-97: Program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany; G. Sheldrick and T. Schneider, *Methods Enzymol.*, 1997, **277,** 319.

14. J. P. Selegue and K. A. Swarat, *J. Am. Chem. Soc.*, 1993, **115**, 6448.
15. M. Szajda and J. N. Lam,*"Comprehensive Heterocyclic Chemistry* II" A. R. Katritzky, C. W. Rees, and E. F. V. Scriven, eds, Pergamon, Oxford, 1996, Vol 2. 2.09.
16. D. W. H. MacDowell, A. T. Jeffries, and M. B. Meyers, *J. Org. Chem.*, 1971, **36**, 1416.
17. H. F. G. Linde and N. H. Kämer, *Archiv Pharm.*, 1990, **323**, 295.
18. A. P. Marchand, "*Stereochemical Application of NMR Studies in Rigid Bicyclic Systems,*" in "*Methods in Stereochemical Analysis,*" A. P. Marchand ed, Verlag Chemie Int. Inc., Deerfield Beach, 1982, Vol. 1.
19. *Crystallographical data for exo*-**2**: $C_{14}H_6F_4O_2S$; FW = 314.25, colorless platelets, 0.22 x 0.12x 0.03 mm, *monoclinic*, *P2₁/c* (#14), $Z = 4$ in a cell of dimensions $a = 13.352(2)$ Å, $b = 6.3727(9)$ Å, $c = 13.878(2)$ Å, $\beta = 94.196(3)^\circ$, $V = 1177.7(3)$ Å^3, $D_{calc} = 1.772$ g·cm^{-3}, *Mo Kα*, $F(000) = 632$, $T = 150$, 2683 unique reflections, 2126 with $F^2 > 2\sigma(F^2)$. The final $R_1 = 0.058$, wR_2 *(all)* = 0.169, goodness-of-fit = 1.09 for 191 parameters refined on F^2, CCDC No. 656409.
20. M. Matsui, S. Taniguchi, M. Suzuki, M. Wang, K. Funabiki, and H. Shiozaki, *Dyes and Pigments*, 2005, **65**, 211; L. M. Gornostaev, T. I. Lavrikova, and E. V. Arnold, *Zh. Org. Khim.*, 1992, **28**, 2291.
21. T. Murashima, N. Wakamori, Y. Uchihara, T. Ogawa, H. Uno, and N. Ono, *Mol. Cryst. Liq. Cryst.*, 1996, **278**, 165.
22. Y. Shimizu, Z. Shen, S. Ito, H. Uno, J. Daub, and N. Ono, *Tetrahedron Lett*., 2002, **43**, 8485.
23. D. H. R. Barton and S. Z. Zard, *J. Chem. Soc., Chem. Commun*., 1985, 1098.
24. T. D. Lash, P. Chandrasekar, A. T. Osuma, S. T. Chaney, and J. D. Spence, *J. Org. Chem.*, 1998, **63**, 8455.
25. H. Uno, K. Nakamoto, K. Kuroki, A. Fujimoto, and N. Ono, *Chem. Eur. J.*, 2007, **13**, 5773.
26. A. Boudif and M. Momentou, *J. Chem. Soc., Chem. Commun.*, 1994, 2069; J. L. Sessler, J. W. Genge, A. Urbach, and P. Sanson, *Synlett*, 1996, 187.
27. S. Ito, N. Ochi, T. Murashima, H. Uno, and N. Ono, *Heterocycles*, 2000, **52**, 399; T. Itoh, T. Murashima, H. Uno, and N. Ono, *J. Chem. Soc., Chem. Commun.*, 1998, 1661.
28. G. D. Hatman and L. M. Weinstock, *Org. Synth*., *Coll. Vol.,* 1988, **6**, 620.
29. O. De Lucchi, V. Lucchini, L. Pasquato, and G. Modena, *J. Org. Chem.*, 1984, **49**, 596.