HETEROCYCLES, Vol. 84, No. 2, 2012, pp. 829 - 841. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 29th June, 2011, Accepted, 25th July, 2011, Published online, 2nd August, 2011
DOI: 10.3987/COM-11-S(P)60

# FASILE SYNTHESIS OF 4,9-DIHYDRO-2*H*-BENZ[*f*]- AND 4,11-DIHYDRO-2*H*-NAPHTH[2,3-*f*]-ISOINDOLES AND THEIR UTILITY FOR PORPHYRIN SYNTHESIS

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**Abstract** – Esters of 4,9-dihydro-2*H*-benz[2,3-*f*]isoindole-1-carboxylate and 4,11-dihydro-2*H*-naphth[2,3-*f*]isoindole-1-carboxylate were prepared by the modified Barton-Zard reaction of 2,3-bis(phenylsulfonyl)-1,2,3,4-tetrahydro-naphthalene and anthracene with isocyanoacetate esters, respectively. The bis(phenylsulfonyl) derivatives were, in turn, prepared by the pericyclic reactions of the corresponding sultines with *trans*-1,2-bis(phenylsulfonyl)ethylene. The pyrrole esters were converted to the corresponding *mono*-naphthoporphyrin and *mono*-anthraporphyrin in good overall yields.

*Dedicated to Professor Dr. Albert Padwa on the occasion of his 75th birthday*

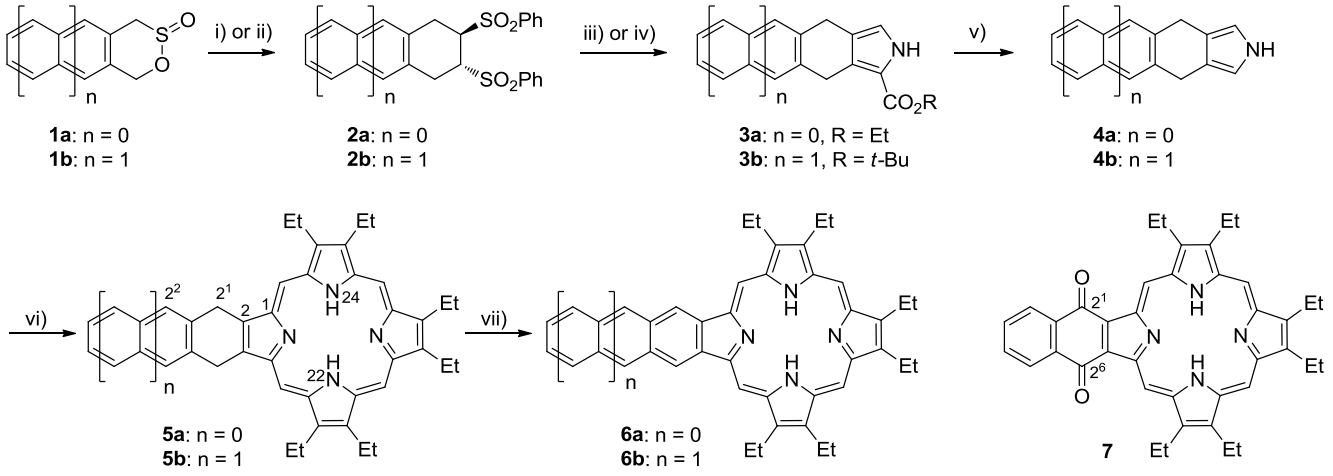
## INTRODUCTION

Inspired by the central role in biological systems, porphyrins have been extensively investigated due to their optical and electronic properties ascribed to their chemical structures. The exploitation of more efficient methodologies for the synthesis of porphyrin derivatives has been stimulated by their ever-expanding applications in biological and opto-electronical fields as photodynamic therapy agents,[1] solar energy conversion materials,[2] materials for nano-molecular devices,[3] and nonlinear optical materials.[4] π-System extension of porphyrins offered possibility of shifting the major UV-vis absorptions to longer wavelengths, a particularly valuable feature that could have wide range of applications. To gain more insights into the effects due to ring fusion on the porphyrin ring, many efforts have been made toward the synthesis of π-extended porphyrins in the last decade.[5] Among the π-extended porphyrinoids, linearly fused aromatic rings exhibited their significant advantages on the

red-shifting effect. However, due to the extreme instabilities of pyrroles bearing linearly-fused acenes such as benzene, naphthalene and anthracene, synthesis of the acene-fused porphyrins still required an expedient tactics. So far, two strategies have been exploited for these porphyrins. One is based on the retro-Diels-Alder extrusion of ethylene from porphyrins fused with a bicyclo[2.2.2]octadiene framework developed by our group.[6] The other is based on the oxidative aromatization of porphyrins fused with non-aromatic saturated hydrocarbon rings. This has been extensively studied by Vinogradov and Cheprakov's groups.[7] With these two strategies, preparations of benzo-, naphtho-, and anthra-porphyrins have made a progress in the past several years. Nevertheless, it still remains a challenge to conveniently enlarge the conjugated system and introduce versatile functional groups on their periphery for their applications in different fields. On the searching of organic compounds with a long and large π-conjugated system for electronic communication between electrodes in nano-scale devices, we focused our attention on the synthetic methodology of linearly π-extended porphyrins, namely oppositely acene-fused porphyrins. We chose [3+1] strategy for such porphyrin synthesis[8] and precursors of acene-fused pyrroles could be used for both preparations of tripyrranes and pyrrole-2,5-dicarbaldehydes. Since *o*-quinodimethane derivatives have been extensively exploited to extend the aromatic systems,[9] we decided to utilize the highly reactive dienes to prepare the precursors. We have already reported the preparation of a bicyclo[2.2.2]octadiene-installed precursor[10] of naphth[*f*]isoindole based on the Diels-Alder reaction of 4,7-dihydro-4,7-ethano-2*H*-isoindole and *α,α'*-dibromo-*o*-xylylene and their application for the synthesis of tetra-anthraporphyrins.[11] Although this method is advantageous for the preparation of these acene-fused porphyrins in a highly pure form, the route is rather tedious and lengthy. Here we present a facile route to the other precursors of acene-fused pyrroles, namely 4,9-dihydro-2*H*-benz[*f*]isoindole (**3a**) and 4,11-dihydro-2*H*-naphth[*f*]isoindole (**3b**), and their utilization for the tripyrrane preparation followed by the [3+1] porphyrin synthesis giving *mono*-naphthoporphyrin and *mono*-anthraporphyrin (Scheme 1).

## RESULTS AND DISCUSSION

We chose sultines as precursors for the generation of *o*-quinodimethane derivatives, because they were usually stable at room temperature and reacted thermally under mild conditions. As shown in Scheme 1, the modified Barton-Zard synthesis of pyrroles was employed.[12] Bis-sulfones **2a** and **2b** were prepared by the Diels–Alder cycloaddition of *trans*-1,2-bis(phenylsulfonyl)ethylene and the corresponding *o*-quinodimethanes generated by the retro-Diels-Alder reaction of benzosultine[13] and naphthosultine[14] in refluxing solvents in 89 and 67% yields, respectively. Then, the *α,β*-unsaturated sulfones generated by elimination of a phenylsulfinate anion from the bis-sulfones under the basic conditions of *t*-BuOK were reacted with isocyanoacetate esters to yield pyrrole esters **3a** and **3b** in 76 and 63% yields, respectively.




**Scheme 1**. *Reagents, conditions, and yields*: i) *trans*-1,2-bis(phenylsulfonyl)ethylene, toluene, reflux; 89% for **2a**; ii) *trans*-1,2-bis(phenylsulfonyl)ethylene, *o*-dichlorobenzene, reflux; 67% for **2b**; iii) $CNCH_2CO_2Et$, *t*-BuOK, THF, rt; 76% for **3a**; iv) $CNCH_2CO_2$-*t*-Bu, *t*-BuOK, THF, rt; 63% for **3b**; v) KOH, $(CH_2OH)_2$, 175 °C; 80% for **4a**, 72% for **4b**; vi) *tert*-butyl 5-(acetoxymethyl)-3,4-diethylpyrrole-2-carboxylate, $CH_2Cl_2$, montmorillonite K-10, rt; TFA, rt; 3,4-diethylpyrrole-2,5- dicarbaldehyde, $CH_2Cl_2$, rt; $Et_3N$, DDQ, rt; 25% for **5a**, 13% for **5b**; vii) DDQ, toluene, reflux; 75% for **6a**, 65% for **6b**.

Removal of ester groups from **3** was achieved by heating at 175 °C with KOH in ethylene glycol to give $\alpha$-free pyrroles **4a** and **4b** in 80 and 72% yields, respectively.

With $\alpha$-unsubstituted pyrroles **4a** and **4b** in hand**,** dihydronaphtho- and dihydroanthra-porphyrins **5a** and **5b** were prepared by well-established method *via* a [3+1] approach.[15] Pyrroles **4** and two equivalents of *tert*-butyl 5-(acetoxymethyl)-3,4-diethylpyrrole-1-carboxylate were reacted under the catalysis of montmorillonite K-10 to afford di-*tert*-butyl tripyrrane-1,14-dicarboxylates, which were used without purification. The *tert*-butyl ester group of the tripyrranes was removed by treatment with TFA at room temperature, the $\alpha$-free tripyrranes were reacted with 3,4-diethylpyrrole-2,5-dicarbaldehyde, and then the resulted tetrapyrrolic compounds were oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) at room temperature to give dihydroporphyrins **5a** and **5b** in 25 and 13% yields, respectively. These dihydroporphyrins were rather unstable and were gradually oxidized under air. One of the oxidation products from **5a** was unambiguously assigned as quinone-fused porphyrin **7** by the X-ray and MS analyses. A plausible mechanism giving **7** is as follows. Auto-oxidation of **5a** would afford a hydroperoxylated dihydroporphyrin, which would then give hydroxylated aromatized porphyrin by the fission of the O-O bond. Further oxidation gave quinone **7.** The porphyrins **5** were converted to $\pi$-extended porphyrins **6a** (75%) and **6b** (65%) by oxidation with DDQ in refluxing toluene. The similar results were obtained by the direct oxidation after the [3+1] porphyrin synthesis.

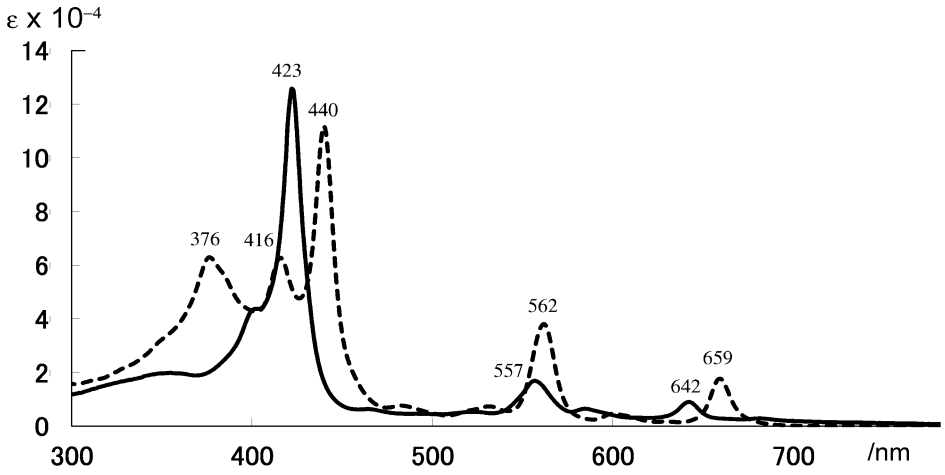



**Figure 1**. UV-vis spectra of naphthoporphyrin **6a** (solid line) and anthraporphyrin **6b** (dotted line) in $CHCl_3$.

The structures of four porphyrins were characterized by $^1$H NMR, MALDI-TOF MS, and UV-vis spectroscopies. In the NMR spectra, the signals arising from methylene protons connecting arene and porphryin rings appeared at 5.50 and 5.67 ppm in **5a** and **5b**, respectively. After oxidative dehydrogenation, the naphthalene and anthracene protons adjacent to the porphyrin ring were found at very lower fields of 9.73 and 9.70 ppm in porphyrins **6a** and **6b**, respectively. In the UV-vis spectra of both dihydroporphyrins **5a** and **5b** in chloroform, slightly broad Soret bands were observed at 399 nm with the molar extinction coefficients (log $\varepsilon$) of 5.09 and 5.14, respectively. These values are smaller than that (log $\varepsilon$ = 5.22) of octaethylporphyrin.[16] This fact supports that the effect of dihydroacene fusion on the porphyrin $\pi$-system is more than that of alkyl substitution, namely the hyperconjugative effect observed in the methylene-connected diporphyrins.[17] The observed red-shifted Q-bands of porphyrins **6a** and **6b** appeared at 642 (log $\varepsilon$ = 3.90) and 659 (log $\varepsilon$ = 4.25) nm, respectively. Additionally, the Soret band of porphyrin **6b** was split into three strong absorptions at 376 (log $\varepsilon$ = 4.80), 416 (log $\varepsilon$ = 4.25), and 440 (log $\varepsilon$ = 5.05) nm**.** These observations exhibited the very close characterization of porphyrins **6** to their respective homologous porphyrins.[18]

Fortunately, single crystals of dihydroacene-fused pyrrole-2-carboxylates **3a** and **3b** and dihydronaphthoporphyrin **5a** were obtained. Ortep drawings of **3a** and **3b** are illustrated in Figure 2. In the structure of **3a**, the molecule is slightly bent at the cyclohexadiene moiety and the torsion angle of the pyrrole and benzene mean planes is 15.6(1)°, while the molecule of **3b** is almost flat and the mean plane angle of pyrrole and naphthalene rings in **3b** is 1.5(1)°. In both structures, the pyrrole ring and the ester moieties are almost coplanar similarly as reported[19] and the torsion angles in **3a** and **3b** are 2.47(8)° and 2.60(9)°, respectively. In these crystal structures, hydrogen bonding motif is quite different. In **3b**, double hydrogen bonding between pyrrole hydrogen and carbonyl oxygen with the neighboring molecule

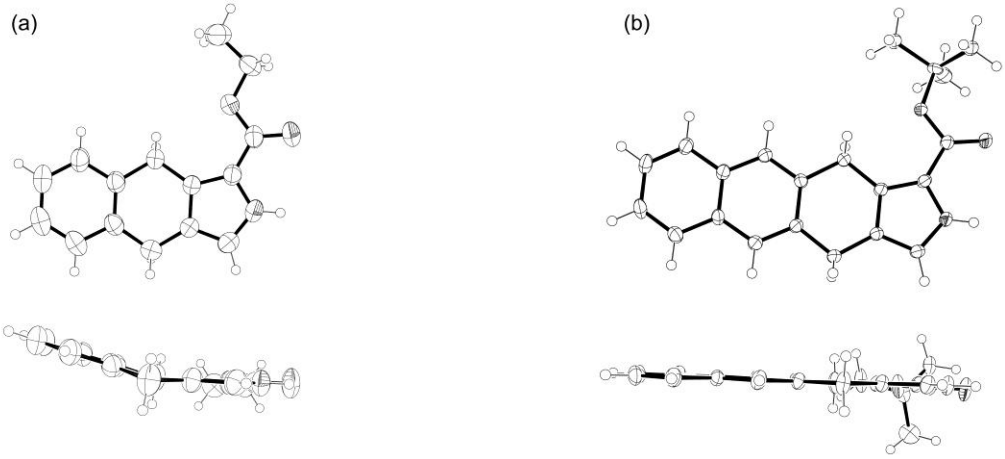



**Figure 2**. Ortep drawings of **3a** and **3b**. (a) upper and lower: top and side views of **3a**; (b) upper and lower: top and side views of **3b**. Less popular atoms in the disordered *t*-butyl group of **3b** are omitted for clarity. Diffraction was measured at room temperature for **3a** and -173 °C for **3b**.

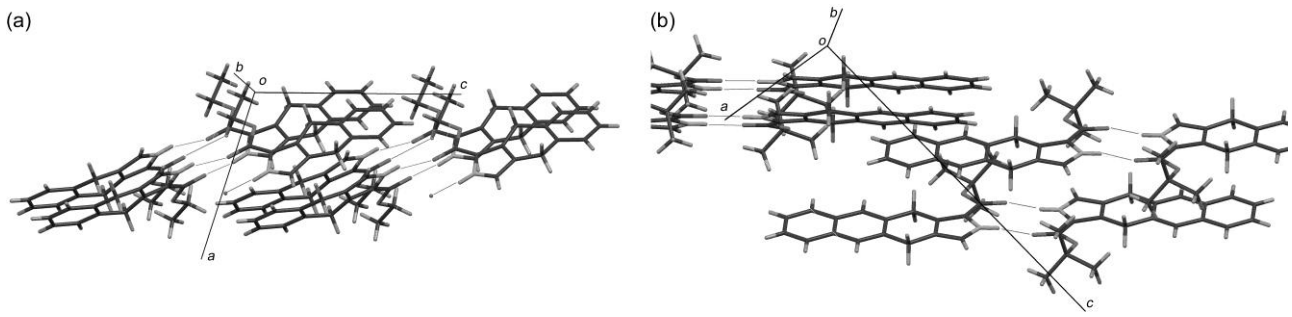



**Figure 3**. Packing diagrams of (a): **3a** and (b): **3b**. Disordered atoms in **3b** are omitted for clarity.

giving a dimer structure is observed and the N-H···O distance is 2.837(4) Å (Figure 3b). As an inversion center exists between pyrrole rings of the dimeric structure, the torsion angle of pyrrole rings is completely parallel. The torsion angle between the mean planes of five pyrrolic atoms and four hydrogen bonding atoms of nitrogen and oxygen is 3.0(1)°. This means that all atoms in the dimer of **3b** are almost in the same plane except for atoms in the *tert*-butyl group. On the other hand, two kinds of the hydrogen bonds are observed in **3a** (Figure 3a). Pyrrolic hydrogen of one molecule bonds to carbonyl oxygen of a neighboring molecule (2.789(4) Å), pyrrolic hydrogen of which bonds to carbonyl oxygen of another molecule (2.876(4) Å). Therefore, the hydrogen bonding shows a zigzag motif. The dihedral angle between the pyrrole rings is 58.9(1)°.

Two kinds of single crystals were obtained by slow diffusion of an *i*-propanol vapor into a chlorobenzene solution of dihydronaphthoporphyrin **5a**. Ortep drawings are illustrated in Figure 4. One crystal **A** is composed of **5a** and $2^1,2^6$-dioxo-$2^1,2^6$-dihydronaphthoporphyrin **7** in a ratio of 7:1. The latter is unambiguously assigned by the X-ray and MS analyses. Another crystal **B** consists of **5a** and solvent

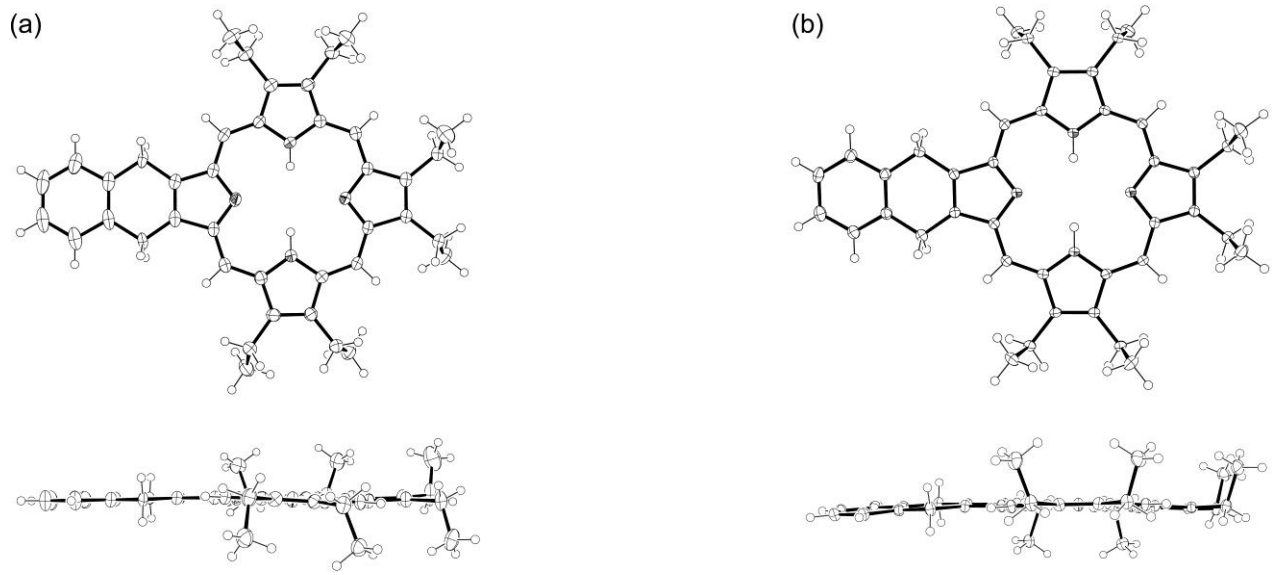



**Figure 4**. Ortep drawings of dihydronaphthoporphyrin **5a**. (a): Top (upper) and side (lower) views of structure **A**. Contaminated molecule **7** is omitted for clarity. (b): Top (upper) and side (lower) views of structure **B**. The solvent chlorobenzene molecule is omitted for clarity.

chlorobenzene. In this crystal **B**, no other porphyrinic compound is found. In both structures of **5a**, porphyrin and benzene rings are almost coplanar, and dihedral angles of these mean planes are 1.49(7)° for **A** and 7.24(5)° for **B**. The very small value of the angle in structure **A** may be due to the contamination of flat **7**. Pyrrolic hydrogen atoms are placed at the electron peaks found in the differential Fourier maps. In the structure **B** of pure **5a**, pyrrolic hydrogen atoms are found at the pyrrole moieties adjacent to the dihydrobenz[*f*]isoindole unit. Although substituent effects on the tautomerism of inner porphyrin protons are rather difficult to discuss,[20] the hyperconjugative effect of the coplanar dihydronaphthalene moiety may control the porphyrinic macrocyclic ring currency similarly as found in the aromatic ring fusion.[21]

In conclusion, we have developed a facile approach for dihydrobenz[*f*]isoindole and dihydronaphth[*f*]isoindole by using *o*-quinodimethane intermediates generated from sultines. These dihydro isoindoles were successfully converted to the $\pi$-extended porphyrins. Due to the ready accessibility of sultines, we believe that the current approach could provide a facile route to naphthoporphyrins and anthraporphyrins with various substitutents, and open new possibilities for the engagement of these molecules into applied researches.

## 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 and tetramethylsilane as an internal standard for $^1H$ and $^{13}C$. IR spectra were measured as a KBr pellet with a Horiba FT-720 infrared spectrophotometer. EI and FAB MS spectra were measured with a JEOL JMS-700 in Integrated Center for Sciences. MALDI TOF MS spectra were measured with a Voyager DE Pro instrument in Venture Business Laboratory. Elemental analysis was performed with a Yanaco MT-5 elemental analyzer in Integrated Center for Sciences. X-Ray diffraction was measured with Rigaku AFC8S Mercury (for **3a**) or Rigaku VariMax Saturn-724 (for **3b** and **5a**). All solvents and chemicals were reagent grade quality, obtained commercially, and used without further purification except for otherwise noted. Dry solvents were purchased from Kanto Chemical Co. Solvents for chromatography were purified by distillation. Thin-layer (TLC) and column chromatography with silica gel were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.

***trans*-2,3-Bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene (2a):** Benzosultine (**1a**, 2.52 g, 15.0 mmol) in 10 mL of toluene was slowly added into the refluxing solution of *trans*-1,2-bis(phenylsulfonyl)ethylene (4.62 g, 15.0 mmol) in 150 mL of toluene. After addition the solution was refluxed for 3 h. After cooling to room temperature and standing for several hours, the precipitation was collected by vacuum filtration to give 6.0 g of the crude product containing a small amount of 1,3-dihydroisothianaphthene *S,S*-dioxide and *trans*-1,2-bis(phenylsulfonyl)ethylene. Recrystallization of the crude product from THF gave 5.5 g (89%) of **1a** as a white solid: mp 187.2 °C; IR /$cm^{-1}$ 1446, 1295, 1145, 1083; $^1H$ NMR $\delta$ 3.15 (m, 4H), 4.16 (m, 2H), 7.05 (m, 2H), 7.14 (m, 2H), 7.57 (m, 4H), 7.69 (m, 2H), 7.81 (m, 4H); $^{13}C$ NMR $\delta$ 27.27, 58.13, 127.08, 127.79, 128.80, 129.27, 132.41, 134.13, 137.15; MS (FAB): *m/z* 413 ($M^+$+1). Anal. Calcd for $C_{22}H_{20}O_4S_2$: C, 64.05; H, 4.89%. Found: C, 63.81; H, 4.86.

***trans*-2,3-Bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene (2b):** Naphthosultine (**1b**, 0.436 g, 2.00 mmol) in 10 mL of *o*-dichlorobenzene was slowly added into the refluxing solution of *trans*-1,2-bis(phenylsulfonyl)ethylene (0.616 g, 2.00 mmol) in 10 mL of *o*-dichlorobenzene. After addition, the solution was refluxed for 3 h. After cooling down to room temperature and standing for several hours, the precipitates were collected by filtration to give a crude product containing 1,3-dihydronaphthothiphene *S,S*-dioxide and *trans*-bis(phenylsulfonyl)ethylene. Recrystallization of the crude product from THF gave 0.62 g (67%) of pure **1b** as a white powder: mp 278 °C; IR (KBr) /$cm^{-1}$ 1450, 1304, 1142, 1080; $^1H$ NMR $\delta$ 3.25 (dd, $J$ = 20.0, 5.5 Hz, 2H), 3.35 (dd, $J$ = 20.0, 5.5 Hz, 2H), 4.23 (t, $J$ = 5.5 Hz, 2H), 7.42 (m, 2H), 7.54 (m, 6H), 7.71 (m, 2H), 7.73 (m, 2H), 7.82 (m, 4H); $^{13}C$ NMR $\delta$ 28.12, 58.47, 125.71, 126.29, 127.30, 128.93, 129.28, 130.81, 132.73, 134.19, 137.06; MS (FAB) *m/z* 463

($M^+$+1). Anal. Calcd for $C_{26}H_{22}O_4S_2$+1/2$H_2O$: C, 66.22; H, 4.92%. Found: C, 66.24; H, 4.88.

**Ethyl 4,9-dihydro-2*H*-benz[*f*]isoindole-1-carboxylate (3a):** To a stirred suspension of *trans*-2,3-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene (**2a**, 1.65 g, 4.00 mmol) and ethyl isocyanoacetate (0.48 mL, 4.4 mmol) in 50 mL of dry THF, 20 mL of a 0.5 M *t*-BuOK solution (1.12 g in 20 mL of dry THF) was added slowly at room temperature. After the reaction mixture was stirred overnight, 10 mL of aqueous HCl and 100 mL of $CHCl_3$ were added. The organic phase was separated, washed with water and brine, and dried over $Na_2SO_4$. Purification on the silica-gel column eluting with EtOAc/hexane (1/3) gave 0.73 g (76%) of **3a** as a pale yellow solid: mp 161.2 °C; IR /$cm^{-1}$ 3301, 1668; $^1$H NMR $\delta$ 1.41 (t, $J$ = 7.0 Hz, 3H), 3.89 (s, 2H), 4.17 (s, 2H), 4.35 (q, $J$ = 7.0 Hz, 2H), 6.81 (s, 1H), 7.19-7.31 (m, 4H), 8.96 (br s, 1H); $^{13}$C NMR $\delta$ 14.72, 27.00, 28.32, 60.08, 117.42, 117.83, 120.46, 125.82, 125.96, 126.23, 128.87, 129.17, 134.83, 135.09, 161.35; MS (EI$^+$) *m/z* 241, 212, 194, 167. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81%. Found: C, 74.60; H, 6.28; N, 5.82. Single crystals were obtained by recrystallization from $CHCl_3$/hexane. *Crystallographic data*: $C_{15}H_{15}NO_2$; *FW* = 241.29, pale yellow block, 0.40 x 0.30 x 0.20 mm, *monoclinic*, *P2₁*, $Z$ = 2 in a cell of dimensions $a$ = 9.060(4) Å, $b$ = 6.753(3) Å, $c$ = 10.688(4) Å, $\beta$ = 105.894(8)°, $V$ = 628.9(4) Å$^3$, $D_{calc}$ = 1.274 g·cm$^{-3}$, *Mo Kα*, $F$(000) = 256, $T$ = 298, 2249 unique reflections, 1281 with $F^2 > 2\sigma(F^2)$. Friedel pairs are merged. The final $R_1$ = 0.0451, $wR_2$ *(all)* = 0.1141, goodness-of-fit = 1.084 for 165 parameters with no restrain refined on $F^2$, CCDC No. 830979.

***tert*-Butyl 4,11-dihydro-2*H*-naphth[2,3-*f*]isoindole-1-carboxylate (3b):** To a stirring suspension of 2,3-bis(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene (**2b**, 0.92 g, 2.0 mmol) and *tert*-butyl isocyanoacetate (0.30 g, 2.4 mmol) in 50 mL of dry THF, 5 mL of 1 M *t*-BuOK solution was added slowly at room temperature. After the reaction mixture was stirred overnight, 10 mL of aq. HCl and 100 mL of $CHCl_3$ were poured into. The organic phase was washed with water and brine, and dried over $Na_2SO_4$. Purification on silica gel eluting with EtOAc/hexane (1/3) gave 0.40 g (63%) of **3b** as a white solid: mp 226 °C; IR /$cm^{-1}$ 3309, 3047, 1658 ; $^1$H NMR $\delta$ 1.64 (s, 9H), 4.05 (s, 2H), 4.33 (s, 2H), 6.82 (d, $J$ = 2.9 Hz, 1H), 7.41 (m, 2H), 7.73-7.79 (m, 4H), 8.86 (br s, 1H); $^{13}$C NMR (typical signals) $\delta$ 27.80, 28.64, 28.87, 80.73, 116.97, 118.70, 120.98, 125.15, 126.98, 127.04, 132.11, 132.20, 134.38, 134.51, 160.86; MS (FAB) *m/z* 320 ($M^+$+1). Anal. Calcd for $C_{21}H_{21}NO_2$+1/8$H_2O$: C, 78.42; H, 6.66; N, 4.35%. Found: C, 78.20; H, 6.74; N, 4.35. Single crystals were obtained by recrystallization from chloroform/methanol. *Crystallographic data*: $C_{21}H_{21}NO_2$; *FW* = 319.40, pale yellow needle, 0.40 x 0.10 x 0.03 mm, *monoclinic*, *P2₁/c*, $Z$ = 4 in a cell of dimensions $a$ = 6.238(2) Å, $b$ = 10.247(3) Å, $c$ = 25.951(9) Å, $\beta$ = 97.356(6)°, $V$ = 1645.2(9) Å$^3$, $D_{calc}$ = 1.289 g·cm$^{-3}$, *Mo Kα*, $F$(000) = 680, $T$ = 100, 3653 unique reflections, 2465 with $F^2 > 2\sigma(F^2)$. The final $R_1$ = 0.0700, $wR_2$ *(all)* = 0.1791,

goodness-of-fit = 1.008 for 246 parameters with 126 restrains refined on $F^2$, CCDC No. 830980.

**4,9-Dihydro-2*H*-benz[*f*]isoindole (4a):** A stirring mixture of pyrrole ester **3a** (0.96 g 4.0 mmol) and KOH (1.2 g, 20 mmol) in 25 mL of ethylene glycol was heated at 175 °C under $N_2$ for 2 h. The reaction mixture was poured into ice water, and then extracted with $CHCl_3$ (50 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ solution, water and brine, and dried over $Na_2SO_4$. After removal of the solvent under the vacuum, the residue was purified by flash chromatography eluting with $CHCl_3$ to give 0.54 g (80%) of **4a** as a pale gray powder: mp 97 °C; IR /cm$^{-1}$ 3428, 3378; $^1$H NMR $\delta$ 3.90 (s, 4H), 6.59 (d, $J$ = 2.9 Hz, 2H), 7.15 (m, 2H), 7.24 (m, overlapped with solvent, 2H), 7.91 (br s, 1H); $^{13}$C NMR $\delta$ 27.63, 112.53, 118.47, 125.57, 128.84, 136.45; MS (FAB) *m/z* 170 ($M^+$+1). Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28%. Found: C, 85.08; H, 6.70; N, 8.15.

**4,11-Dihydro-2*H*-naphth[2,3-*f*]isoindole (4b):** A stirred mixture of pyrrole *tert*-butyl ester **3b** (0.32 g 1.0 mmol) and KOH (0.6 g, 10 mmol) in 10 mL of ethylene glycol was heated at 175 °C under $N_2$ for 1 h. After cooling down to room temperature, the reaction mixture was poured into ice water, and then extracted with $CHCl_3$. The organic phase was washed with saturated $NaHCO_3$ solution, water and brine, and then dried over $Na_2SO_4$. After concentration under vacuum, the residue was purified by flash chromatography on silica gel to give 0.16 g (72%) of **4b** as a beige powder: mp 156 °C; IR /cm$^{-1}$ 3478, 3047; $^1$H NMR $\delta$ 4.06 (s, 4H), 6.68 (d, $J$ = 2.9 Hz, 2H), 7.38 (m, 2H), 7.73-7.77 (m, 4H), 7.96 (br. s, 1H); $^{13}$C NMR $\delta$ 28.39, 112.58, 119.32, 125.04, 126.47, 127.07, 132.19, 136.05; MS (FAB) *m/z* 220 ($M^+$+1). Anal. Calcd for $C_{16}H_{13}N$+1/8$H_2O$: C, 86.75; H, 6.32; N, 6.03%. Found: C, 86.85; H, 6.07; N, 6.36.

**7,8,12,13,17,18-Hexaethyl-2$^1$,2$^6$-dihydro-22*H*,24*H*-naphtho[2,3-*b*]porphyrin (5a)**: A mixture of pyrrole **4a** (84 mg, 0.50 mmol), with *tert*-butyl 5-(acetoxymethyl)-3,4-diethylpyrrole-2-carboxylate (295 mg, 1.00 mmol), and 0.5 g of montmorillonite K-10 clay in 30 mL of $CH_2Cl_2$ was stirred under an atmosphere of nitrogen and protection from light for 3 h. After the clay was filtered off, the solution was shaken in the presence of aqueous $NaHCO_3$ and then washed with water and brine, and dried over $Na_2SO_4$. Removal of the solvent under vacuum gave tripyrrane di-*tert*-butyl ester as a crude product. Without further purification, the foregoing tripyrrane ester was dissolved in 3 mL of trifluoroacetic acid under $N_2$ and protection from light. The mixture was stirred at room temperature for 10 min. The solution was diluted with 100 mL of dry $CH_2Cl_2$, followed immediately by the addition of 3,4-diethylpyrrole-2,5-dicarbaldehyde (89.6 mg, 0.500 mmol), and the resulting solution was stirred at room temperature for 8 h. The mixture was neutralized by the slowly addition of triethylamine (5 mL) and then DDQ (112 mg 0.500 mmol) was added. The mixture was allowed to stir for an additional 2 h. The mixture was washed with aqueous $NaHCO_3$, water, and brine, and dried over $Na_2SO_4$. The solvent was removed under a reduce pressure to give a dark red residue. The residue was purified by flash

chromatography on silica gel eluting with $CHCl_3$ to give a dark red powder (73 mg, 25%). $^1$H NMR $\delta$ -3.73 (br. s, 2H), 1.94 (m, 18H), 4.13 (m, 12H), 5.50 (s, 4H), 7.48 (m, 2H), 7.81 (m, 2H), 10.06 (s, 2H), 10.12 (s, 2H); MALDI-TOF MS *m/z* 580.95 ($M^+$); UV-vis ($CHCl_3$) $\lambda_{max}$/nm (log $\varepsilon$) 644 (3.90), 620 (3.72), 565 (3.80), 550 (4.07), 535 (3.91), 498 (4.04), 468 (3.88), 399 (5.09). HRMS (FAB), calcd for $C_{40}H_{44}N_4$+$H^+$: 581.3644. Found: 581.3655. Three morphologically different crystals were obtained by slow diffusion of an *i*-propanol vapor into a solution of **5a** in chlorobenzene: needles, rhombic platelets, and rectangular rods. The former two crystals are proved to be the same structure of **A** and the last crystals are the structure **B**. *Crystallographic data of structure **A***: $0.88(C_{40}H_{44}N_4)+0.12(C_{40}H_{40}N_4O_2)$; *FW* = 584.18, red needle, 0.40 x 0.10 x 0.06 mm, *triclinic*, *P-1*, *Z* = 2 in a cell of dimensions *a* = 9.013(4) Å, *b* = 11.974(4) Å, *c* = 15.361(7) Å, $\alpha$ = 75.524(15)°, $\beta$ = 84.475(15)°, $\gamma$ = 81.002(15)°, *V* = 1582.5(11) Å$^3$, $D_{calc}$ = 1.226 g·cm$^{-3}$, *Mo K*$\alpha$, *F*(000) = 626.88, *T* = 100, 7199 unique reflections, 4729 with $F^2 > 2\sigma(F^2)$. The final $R_1$ = 0.0722, $wR_2$ *(all)* = 0.1965, goodness-of-fit = 1.090 for 440 parameters with 129 restrains refined on $F^2$, CCDC No. 831582. Similar composition (**5a**:**7** = 7:1) and structures are obtained by the analysis of rhombic platelet crystals (crystal of 0.20 x 0.15 x 0.05 mm: $R_1$ = 0.0677, $wR_2$ *(all)* = 0.1852, goodness-of-fit = 1.075, and crystal of 0.15 x 0.10 x 0.01 mm: $R_1$ = 0.0672, $wR_2$ *(all)* = 0.1938, goodness-of-fit = 1.069). These analysis data as cif files are also deposited (CCDC No. 831583 and 831584, respectively). In order to confirm the contamination of 7,8,12,13,17,18-hexaethyl-2$^1$,2$^6$-dioxo-2$^1$,2$^6$-dihydro-22*H*,24*H*-naphtho[2,3-*b*]porphyrin (**7**), the crystals were subject to MS analysis. In addition to a large peak of *m/z* = 581 due to **5a**+$H^+$, a peak of *m/z* = 609 due to **7**+$H^+$ was observed in the FAB-MS spectrum. The HRMS measurement proved that the composition of *m/z* = 609 was $C_{40}H_{40}N_4O_2$+$H^+$ (Calcd: 609.3230. Found: 609.3225). *Crystallographic data of structure **B***: $C_{40}H_{44}N_4$+$C_6H_5Cl$; *FW* = 693.34, red block, 0.20 x 0.10 x 0.10 mm, *triclinic*, *P-1*, *Z* = 2 in a cell of dimensions *a* = 10.092(3) Å, *b* = 12.233(4) Å, *c* = 16.792(5) Å, $\alpha$ = 91.446(3)°, $\beta$ = 102.979(4)°, $\gamma$ = 114.055(3)°, *V* = 1828.7(10) Å$^3$, $D_{calc}$ = 1.259 g·cm$^{-3}$, *Mo K*$\alpha$, *F*(000) = 740, *T* = 100, 8314 unique reflections, 6575 with $F^2 > 2\sigma(F^2)$. The final $R_1$ = 0.0507, $wR_2$ *(all)* = 0.1501, goodness-of-fit = 1.074 for 466 parameters with no restrain refined on $F^2$, CCDC No. 831585.

**7,8,12,13,17,18-Hexaethyl-2$^1$,2$^8$-dihydro-22*H*,24*H*-anthra[2,3-*b*]porphyrin (5b):** The reaction was conducted in the similar manner as described above. Flash chromatography on silica gel eluting with $CHCl_3$ gave 85 mg (13%) of **5b** as a dark purple powder. $^1$H NMR $\delta$ -3.71 (s, 2H), 1.92 (m, 18H), 4.09 (m, 12H), 5.67 (s, 4H), 7.56 (m, 2H), 8.00 (m, 2H), 8.31 (s, 2H), 10.11 (s, 2H), 10.14 (s, 2H); MS (FAB) *m/z* 631 ($M^+$+1); UV-vis ($CHCl_3$) $\lambda_{max}$/nm (log $\varepsilon$) 620 (3.71), 600 (3.20), 566 (3.87), 535 (4.01), 498 (4.08), 399 (5.14). HRMS (FAB), calcd for $C_{44}H_{46}N_4$+$H^+$: 631.3801. Found: 631.3797.

**7,8,12,13,17,18-Hexaethyl-22*H*,24*H*-naphtho[2,3-*b*]porphyrin (6a):** Dihydronaphtho[2,3-*b*] porphyrin **5a** (11.6 mg, 0.020 mmol) was dissolved in 10 mL of toluene. To this solution DDQ (0.020 mmol) was added, and the solution was heated at reflux for 5 min. After cooling, the solvent was evaporated under vacuum, and the residue was washed with copious methanol to give 9 mg (75%) of the title porphyrin as a purple solid. $^1$H NMR $\delta$ -3.29 (s, 2H), 1.89 (t, $J$ = 7.0 Hz, 6H), 1.95 (t, $J$ = 7.0 Hz, 6H), 2.01 (t, $J$ = 7.0 Hz, 6H), 4.01 (q, $J$ = 7.0 Hz, 4H), 4.19 (q, $J$ = 7.0 Hz, 4H), 4.23 (q, $J$ = 7.0 Hz, 4H), 7.81 (m, 2H), 8.55 (m, 2H), 9.73 (s, 2H), 10.06 (s, 2H), 10.42 (s, 2H); $^{13}$C NMR $\delta$ 18.36, 18.41, 18.66, 19.63, 19.68, 19.87, 92.90, 97.56, 118.92, 125.80, 129.17, 132.87, 134.30, 135.89, 137.47, 139.13, 139.83, 143.78, 150.27 and one sp$^2$ carbon is not seen; MALDI-TOF MS *m/z* 578.90; UV-vis ($CHCl_3$) $\lambda_{max}$/nm (log $\varepsilon$) 642 (3.90), 557 (4.22), 518 (3.62), 423 (5.11), 354 (4.25). HRMS (FAB), calcd for $C_{40}H_{42}N_4$+H$^+$: 579.3488. Found: 579.3486.

**7,8,12,13,17,18-Hexaethyl-22*H*,24*H*-anthra[2,3-*b*]porphyrin (6b)**: The reaction was conducted in the similar manner as described above to give 12 mg (65%) of the title porphyrin as a dark red powder. $^1$H NMR $\delta$ 1.90 (m, 18H), 3.97 (m, 4H), 4.14 (m, 8H), 7.61 (m, 2H), 8.21 (m, 2H), 9.04 (s, 2H), 9.70 (s, 2H), 9.97 (s, 2H), 10.21 (s, 2H); MALDI-TOF MS *m/z* 628.79; UV-vis ($CHCl_3$) $\lambda_{max}$/nm (log $\varepsilon$) 659 (4.25), 601 (3.66), 562 (4.58), 529 (3.85), 440 (5.05), 416 (4.80), 376 (4.80). HRMS (FAB), calcd for $C_{44}H_{44}N_4$+H$^+$: 629.3644. Found: 629.3646.

## ACKNOWLEDGEMENTS

This work was partially supported by Grant-in-Aid for Scientific Research B (23350020) from Ministry of Education, Culture, Sports, Science and Technology of Japan.

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