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A NEW SYNTHESIS OF MONO- AND DIBENZOSAPPHYRINS

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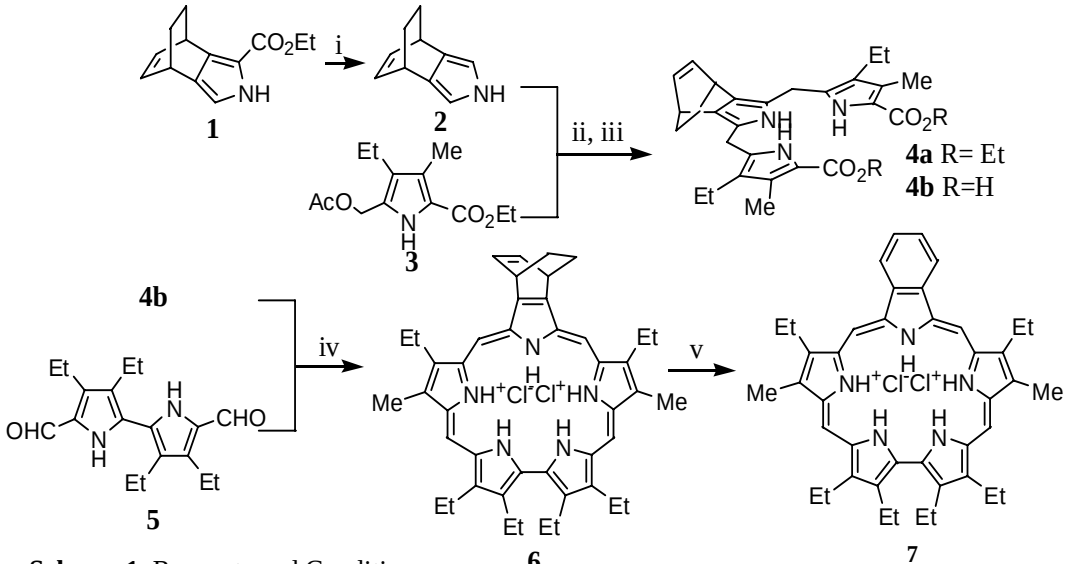
Dedicated to Professor Leo A. Paquette on the occasion of his 70th birthday

Abstract – Sapphyrins fused with mono-bicyclo[2.2.2]octadiene (BCOD) and di-BCOD units are prepared, which are converted into mono- and dibenzosappyrins by heating at 200 ˚C; soret bands are red shifted by 10-20 nm by introduction of fused benzene rings, but Q bands are not much affected in benzosapphyrins.

Sapphyrins (pentapyrrolic expanded porphyrins) are the first expanded porphyrins,[1] and now various expanded porphyrins and related porhyrinoids such as pentaphyrins, hexaphyrins, rubilins or hexadecaphyrins have been prepared.[2, 3] Such expanded porphyrins are important from various reasons, namely, they have larger cavities, altered electronic properties, and enhanced basicity. Thus protonated sapphyrins have been used as receptors for various anions,[4] and also expanded porphyrins are also important for medicinal applications such as phthodynamic therapy (PDT).[5] Among expanded porphyrins, sapphyrins are particularly important for optical materials, for their absorption bands are extremely narrow. For example, chromophores with narrow absorption bands are suitable for non -linear optical applications, because reducing the bandwidth increases the change in absorption or change in refractive index by applying an electric field or forming the excited state, respectively. So it is useful to find ways of tuning the wavelength of the sapphyrin absorption spectrum without increasing the band width. In this paper we present a new method to control the electric properties of sapphyrins by introducing benzo-fused pyrrole ring, namely, isoindole. Benzoporphyrins exhibit the red-shifted absorption and raise the HOMO energy levels (low oxidation potentials). So the similar changes are expected in benzosapphyrin. Although several synthetic methods of benzoporphyrins have been reported,[2]

benzosappyrins have not been prepared so far. This is due to the difficulty of the introduction of isoindole units in sapphyrin cores. Recently we have reported an improved method for the preparation of bezoporphyrins *via* the retro Diels-Alder reaction of porphyrins fused with bicyclo[2.2.2]octadiene (BCOD) units. [6,7] This method has several merits over the old methods. (1) Stable pyrrole fused with BCOD is used in stead of unstable isoindole. (2) Porphyrins with BCOD rings are converted into benzoporphyrins in quantitative yields by heating. (3) Benzoporphyrins are insoluble in organic solvents, but the precursors are soluble in solvents. (4) Spin coating method is used to get thin film of benzoporphyrins. So, it is very useful if this strategy can be extended to the preparation of expanded porphyrins such as sapphyrins.

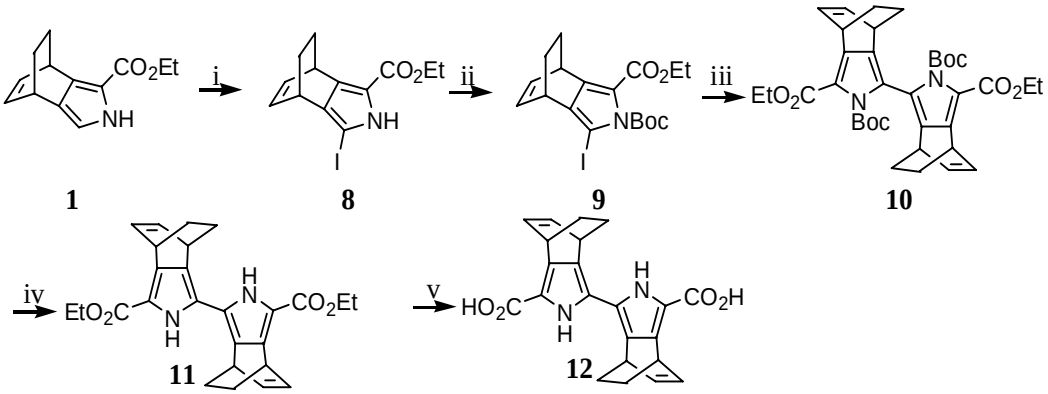
Sapphyrins have been prepared either by "3 + 2" or "4 + 1" approach.[8] The requisite materials for "3 + 2" approach are bipyrroles and tripyrranes. On the other hand,"4 + 1" approach requires tetrapyrranes which are not readily available. As synthesis of bipyrroles and tripyrranes have been well established, we adopt "3 + 2" approach for the synthesis of monobenzosaphyrin **(7)** and dibenzosapphyrin **(17)** (Schemes 1 and 3). As isoindoles are generally unstable, these units are introduced at the final stage *via* the retro Diels-Alder reaction of 4,7-dihydro-4,7-ethano-2*H*-isoindole **(2)** units. The requisite pyrroles **(1)** and **(2)** were prepared by the method previously reported. [7] The reaction of **2** with 2-acetoxypyrrole **(3)** gave tripyrrane **(4a)**, which was converted into **4b** in excellent yields by reported methods.[1, 9] The requisite diformyl bipyrrole **(5)** was prepared in good yield by the Vilsmeier formylaltion of 3,3',4,4'-tetraethylbipyrrole.[1, 10, 12] Acid catalyzed condensation of **4b** with **5** and oxidation by bubbling air gave sapphyrin **(6)** in 43 % yield. For analytical purpose, sapphyrin **(6)** was isolated as HCl-salt. Heating **(6)** at 200 ˚C for 10 min under vacuum (10 mmHg) gave the mono -benzosapphyrin **(7)** in quantitative yield.



Scheme 1. Reagents and Conditions:

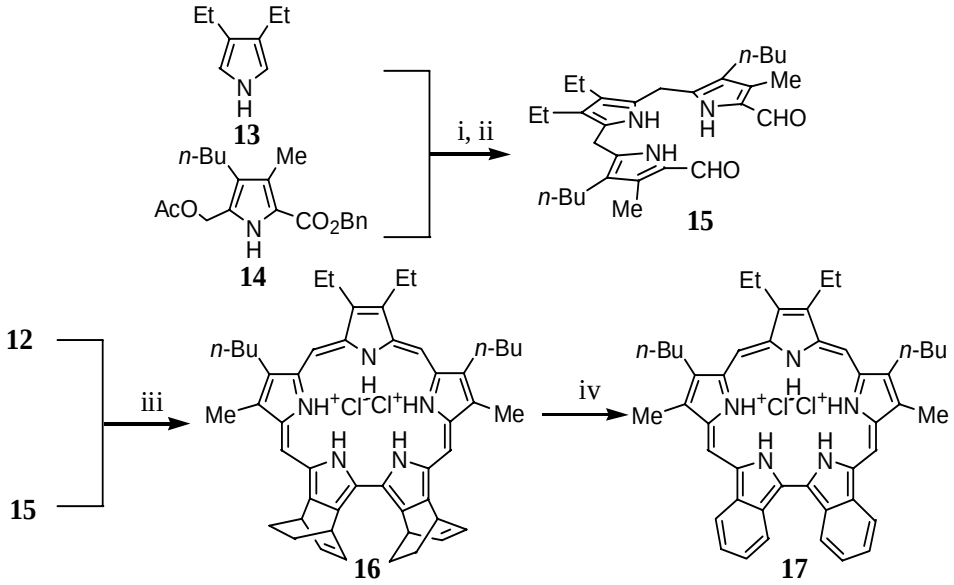
i) KOH, $HOCH_2CH_2OH$, 160 ºC, 2 h; ii) AcOH, 2-Propanol, reflux, 16 h; iii) LiOH, H_2O, reflux, 3 h ; iv) *p*-TsOH, O_2, EtOH, rt, 16 h; 2N-HCl, $CHCl_3$, rt, 5 min, v) 200 ºC, 10 min.

Dibenzosapphyrin **(17)** was prepared as shown in Scheme 3. In order to get **17** bipyrrole **(12)** which is fused with BCOD ring is required. The Ullmann coupling reaction of alkyl substituted α-iodopyrrole gives 2,2'-bipyrroles in about 50 % yield as reported previously. [1, 10, 11] However, the coupling reaction of **8** did not give the desired C-C coupling product **(11)**, but affords N-C coupling product mainly. In order to prevent the N-C coupling, N-Boc pyrrole **(9)** was used.[11] The Cu-catalyzed coupling reaction of **9** gave **10** in 55 % yield. Removal of Boc from **10** followed by hydrolysis of the ester with LiOH gave **12**. Decarboxylation of **12** resulted in polymerization to give black polymer, and **12** was used directly for the next step. Bipyrrole **(12)** must be important for the preparation of various expanded porphyrins containing fused aromatic rings. The reaction of **12** with tripyrrane **(15)** in the presence of acid gave sapphyrin **(16)** in 18% yield. Heating **16** at 200 ˚C gave dibenzosapphyrin **(17)** in quantitative yield.



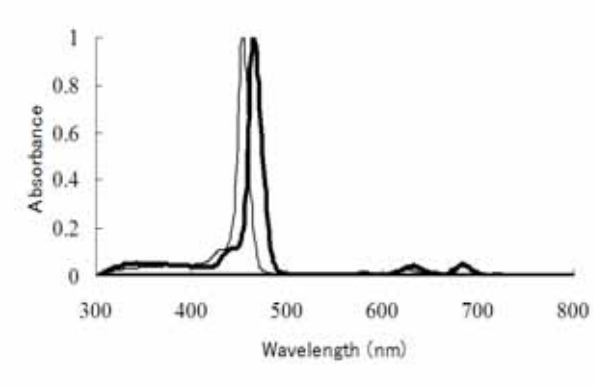
Scheme 2. Reagents and Conditions:

i) $BTMAICl_2$, $CaCO_3$, reflux, 2 h; ii) $(Boc)_2O$, DMAP, Et_3N, reflux, 2 h; iii) Cu, dry-DMF, 110 ºC, 5 h; iv) HCl, EtOAc, rt, 14 h; v) LiOH, THF, EtOH, H_2O, 85 ºC, 3 h.



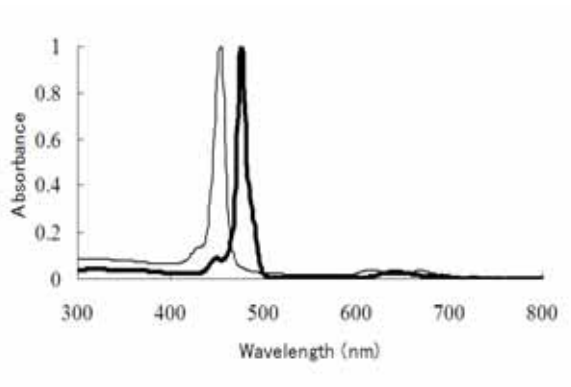
Scheme 3. Reagents and Conditions:

i) AcOH, EtOH, reflux, 18 h; ii) $Pd(OH)_2$, Et_3N. TFA, $CH(OMe)_3$; iii) TFA, 55 ºC, 11 h. O_2, rt, 5 h. 2N-HCl, rt, 5 min, iv) 200 ºC, 30 min.



	Soret	Q band
	λ/ nm (log ε)	λ/ nm (log ε)
6	453 (5.83)	623 (4.22), 679 (4.41)
7	465 (5.65)	632 (4.22), 683 (4.31)

Figure 1. UV-Vis spectra of **6** (—)and **7** (▬) in CH_2Cl_2



	Soret	Q band
	λ/ nm (log ε)	λ/ nm (log ε)
16	454 (5.91)	618 (4.50), 668 (4.51)
17	476 (5.65)	640 (4.36)

Figure 2. UV-Vis spectra of **16** (—)and **17** (▬) in $CHCl_3$

The UV-Vis spectra of sapphyrins **(6)**, **(7), (16)** and **(17)** are shown in Figures 1 and 2. The UV- Vis spectra of **6** and **16** are similar to those of alkyl substituted sapphyrins (λ max = 456, 576, 624, 681 nm). [2,8] The very strong Soret band and weak Q bands are characteristic of sapphyrins. Thus, fused bicyclo rings do not alter electronic properties of sapphyrins. However, absorption of **7** and **17** are red shifted by 12 and 22 nm, respectively. Soret bands of **7** and **17** are intense, but Q bands of **7** and **17** are weak. These results are very interesting, compared to the case of benzoporphyrins.[6,7] The Soret bands of mono- and dibenzoporphyrins are red shifted by about 6 and 10 nm, and those of Q bands are red - shifted by 10 and 21 nm, respectively. Furthermore, Q bands of benzopohyrins become more intense as numbers of benzo-fused rings increase. Thus, fused benzene ring affects Soret bands mainly in sapphyrin cases. On the other hand, Q bands are more affected in benzoporphyrins. These findings are very important to get new dyes, which have intense and narrow absorption at near 500 -700 nm. Tri-, tetra- and pentabenzosapphyrins might be interesting chromophores, which are now targets in our laboratory. Alkyl substituted 2,2'-bipyrroles are critical precursors required for the synthesis of large expanded porphyrins (those containing eight or more pyrrole rings). [3] BCOD fused 2,2'-pyrrole such as **12**, which was prepared for the first time, might be useful for the synthesis of new expanded porphyrins.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a JEOL-JNM-GSX 270 or JNM-EX 400 specrometer using tetramethylsilane as an internal standard. IR and UV-Vis spectra were obtained with a Hitachi 270-30 and a Shimadzu UV-2200 spectrophotometer, respectively. MS spectra were measured with a Hitachi M80B

spectrometer. FAB Ms spectra of porphyrins were measured with a JEOL JMS-DX 300 or JMS-LX 2000 spectrometer; samples were dissolved in *m*-nitrobenzyl alcohol was used as a matrix. Elemental analysis was performed with a Yanako MT-5.

Preparation of pyrroles **(1)** and **(2)** was carried out according to the literaure.[7] Bipyrrole **(5)** was prepared by the Ullmann coupling of α-iodopyrrole followed by the Vilsmeyer-Heck reaction according to procedures reported by Guilard *et al*. [12] Tripyrrane **(15)** was prepared by the method of Sessler. [11]

Preparation of mono-bicyclosapphyrin (6)

A solution of 4,7-dihydro-4, 7-ethano-2*H*-isoindole **(2)** (0.73 g, 0.5 mmol) and ethyl 5-acethoxymethyl-4-ethyl-3-methylpyrrole-2-calboxylate **(3)** (0.25 g, 1.0 mmol) in isopropyl alcohol (13 mL) and acetic acid (13 mL) was refluxed under nitrogen for 16 h, then the mixture was poured into water, and saturated aqueous $NaHCO_3$ was added to the solution until the pH was neutral. The solution was extracted with $CHCl_3$, and the extract was washed with water, brine, dried with anhydrous Na_2SO_4 and evaporation. To the residue KOH (0.5 g, 9.0 mmol) and $(CH_2OH)_2$ (15 mL) was added and heated at 160 ˚C under argon for 3 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with water, brine, dried over anhydrous Na_2SO_4 and concentrated to give the crude **4b**. A solution of **4b**, **5** (150 mg, 0.5 mmol) and *p*-toluenesulfonic acid dihydrate (0.59 g, 3.2 mmol) in ethanol was stirred for 16 h while oxygen was bubbled. Then ethanol was removed at reduced pressure, and the residue was dissolved in chloroform and subjected to chromatography over neutral alumina with $CHCl_3$. The green fraction was collected and evaporated to dryness. The residue was dissolved in $CHCl_3$ again, and washed 2 N-HCl (100 mL x 3). Recrystallization from $CHCl_3$-hexane gave **6** (151 mg, 43 %). ^{1}H NMR ($CDCl_3$): δ 11.80 (s, 2 H), 11.72 (s, 2 H), 7.42 (br s, 2 H), 6.34 (br s, 2 H), 4.78 (q, 4 H, *J* = 6.84), 4.62 (q, 8 H, *J* = 6.84), 4.26 (s, 6 H), 2.56-2.09 (m, 4 H), 2.29 (t, 12 H, *J* = 6.84), 2.17 (t, 6 H, *J* =6.84), 2.17 (t, 6H, *J* =6.84), -4.50 (br s, 2H), -4.98 (br s, 1H), -5.19 (br s, 2H); MS (FAB): 686(-1HCl, M +1, 33%), 650 (-2HCl, M+1, 100 %); UV-Vis (CH_2Cl_2) λmax (log ε): 453 (5.83), 577 (3.57), 623 (4.22), 679 (4.41).

Preparation of mono -benzosapphyrin (7)

Sapphyrin **(6)** (14 mg, 0.02 mmol) was heated under vacuum (10 mmHg) at 200 ˚C for 10 min to give **7** (14 mg, 100 %). ^{1}H NMR ($CDCl_3$): δ 11.73 (s, 2 H), 11.52 (s, 2 H), 10.11 (m, 2 H), 8.64 (m, 2 H), 4.67 (q, 4 H, *J* = 7.81), 4.48 (q, 8 H, *J* = 7.32), 4.13 (s, 6 H), 2.22 (t, 12 H, *J* = 7.32), 2.05 (t, 6 H, *J* = 7.81), -2.89 (br s, 1 H), -3.26 (br s, 2 H), -3.66 (br s, 2 H); ^{13}C NMR ($CDCl_3$): δ 114.61, 140.17, 137.25, 136.82, 133.73, 131.94, 131.70, 129.42, 129.30, 122.37, 100.47, 88.68, 29.67, 21.68, 20.87, 20.73, 18.72, 17.69, 17.18, 12.55; MS (FAB): 622 (-2HCl, M+1); UV-Vis (CH_2Cl_2) λmax (log ε): 464 (5.65), 577 (3.31), 632

(4.22), 683 (4.31); Anal. Calcd for $C_{42}H_{49}N_5Cl_2$; C, 72.61; H, 7.11; N, 10.08. Found: C, 72.46; H, 7.20; N, 9.89

Preparation of Ethyl 4, 7-dihydro-4, 7-ethano-9-iodo-4, 7-(*2H*-isoindole)-1-carboxylate (8)

A solution of **(1)** (4.36 g, 20 mmol), benzyltrimethylammoniun iodine dichloride ($BTMAICl_2$) (6.96 g, 20 mmol) and $CaCO_3$ (4.32 g, 42.7 mmol) in CH_2Cl_2 (200 mL) and MeOH (80 mL) was refluxed at 50 ˚C for 2 h. Then the reaction mixture was cooled at rt. Organic layer was washed with aqueous $NaHSO_3$ (50 mL x 2), 1 N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL x 2), H_2O (50 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. After evaporation of solvent, crude **8** was purified by column chromatography (silica gel, $CHCl_3$) to give pure **8** as a white powder (6.86 g, 100 %). mp 167-169 ˚C; ^{1}HNMR ($CDCl_3$) δ 8.86 (br s, 1H), 6.42-6.51 (m, 2 H), 4.36 (m, 1 H), 4.33 (q, 2 H, *J* = 7.08), 3.66 (m, 1 H), 1.42-1.59 (m, 4 H), 1.37 (t, 3 H, *J* = 7.08); ^{13}C NMR ($CDCl_3$) δ 160.63, 137.44, 137.24, 135.72, 135.04, 118.80, 61.99, 60.23, 34.14, 33.88, 26.60, 26.14, 14.58; IR (KBr)/cm^{-1} 3275, 3043, 1670, 1052, 845, 694, 597; m/z (FAB) 344 (M+1); Anal. Calcd for $C_{13}H_{14}NO_2I$: C, 45.50; H, 4.11; N, 4 .08. Found: C, 45.50; H, 4.05; N, 4.05.

Preparation of N-Boc-ethyl 4, 7-dihydro-4, 7-ethano-9-iodo-4, 7-(*2H*-isoindole)-1-carboxylate (9)

A solution of **(8)** (6.88g, 20 mmol), dimethylaminopyridine (DMAP, 120 mg), $(Boc)_2O$ (5 mL) and Et_3N (3 mL) in dry-THF (21 mL) was refluxed under Ar at 80 ˚C for 2 h. Then the reaction mixture was cooled at rt. The solvent was removed at reduced pressure, and the residue was dissolved in $CHCl_3$ and organic layer was washed with 1N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), H_2O (50 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude **9** was purified by column chromatography (silica gel, $CHCl_3$) to give pure **9** as a white powder (8.26 g, 93 %). ^{1}H NMR ($CDCl_3$) δ 6.40-6.49 (m, 2 H), 4.30 (q, 3 H, *J* = 7.08), 4.23 (m, 1 H), 3.67 (m, 1 H), 1.60 (s, 9 H), 1.41-1.66 (m, 4 H), 1.36 (t, 3 H, *J* = 7.08); ^{13}C NMR ($CDCl_3$) δ 159.82, 149.16, 140.42, 138.99, 135.28, 134.59, 120.46, 85.14, 77.21, 65.53, 60.49, 34.19, 34.04, 27.69, 26.13, 25.77, 14.50.

Preparation of Bis-(N-Boc-ethyl 4, 7-dihydro-4, 7-ethano-4, 7-(*2H*-isoindole)-1-carboxylate) (10)

A solution of **(9)** (8.26 g, 18.6 mmol) and Cu (7.3 g) in dry-DMF (93 mL) was heated 110 ˚C under Ar for 5 h. Then the reaction mixture was cooled at rt. The solvent was removed at reduced pressure. The residue was dissolved in $CHCl_3$ and organic layer was washed with 1N HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), H_2O (50 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude **10** was purified by column chromatography (silica gel, CH_2Cl_2/ EtOAc) to give pure **10** as a white powder (3.22 g, 55%). mp 223 -224˚C; ^{1}H NMR ($CDCl_3$) δ 6.42 (m, 4 H), 4.34 (m, 4

H), 4.20 (m, 2 H), 3.48 (m, 2 H), 1.35-1.67 (m, 8 H), 1.33 (s, 18 H), 1.22 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 161.09, 148.75, 139.75, 139.75, 139.52, 139.29, 135.27, 135.15, 134.81, 134.48, 133.29, 132.81, 118.69, 118.44, 117.68, 117.59, 83.65, 83.49, 83.41, 83.27, 60.55, 33.28, 33.18, 32.23, 32.19, 32.02, 27.38, 26.63, 26.22, 25.98, 25.84; IR (KBr)/cm^{-1} 3051, 1743, 1709, 1057, 840, 702, 598; Anal. Calcd for $C_{36}H_{44}N_2O_9$: C, 68.34; H, 7.01; N, 4.43. Found: C, 68.10; H, 6.93; N, 4.44.

Preparation of Bis-(ethyl 4, 7-dihydro-4, 7-ethano-4, 7-(*2H*-isoindole)-1-carboxylate) (11)

A solution of **(10)** (3.22 g, 5.09mmol) in EtOAc (100 mL), 12 N HCl (33 mL) was stirred at rt for 14 h. Then the mixture was poured into water, and extracted with EtOAc (50 mL x 3). Organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL x 2), H_2O (50 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude **11** was purified by column chromatography (silica gel, $CHCl_3$) to give pure **11** as a white powder (1.78 g, 81 %). ^{1}H NMR ($CDCl_3$) δ 8.81 (br s, 2 H), 6.54 (m, 4 H), 4.40 (m, 2 H), 4.30 (q, 4 H, *J* = 7.08), 3.99 (m, 2 H), 1.48-1.62 (m, 8 H), 1.36 (t, 6 H, *J* = 7.08); ^{13}C NMR ($CDCl_3$) δ 161.71, 137.69, 135.68, 135.57, 135.41, 135.34, 129.13, 129.10, 119.01, 118.99, 60.17, 33.90, 33.87, 33.52, 33.48, 27.03, 26.94, 26.34, 26.27, 14.58; IR (KBr)/cm^{-1} 3325, 3275, 3051, 1685, 1655, 1053, 844, 687, 579; m/z (TOF) 432.6; Anal. Calcd for $C_{26}H_{29}N_2O_4$: C, 72.20; H, 6.53; N, 6.48. Found: C, 71.99; H, 6.53; N, 6.41.

Preparation of Bis-(4, 7-dihydro-4, 7-ethano-4, 7-(*2H*-isoindole)-1-carboxylic acid) (12)

A solution of **11** (0.22g, 0.5 mmol) and LiOH (0.65 g, 15.5 mmol) in H_2O (25 mL), THF (20 mL) and EtOH (14 mL) was refluxed at 85 ˚C for 3 h. Then the reaction mixture was cooled at rt and insoluble materials was removed by filtration, and 1N HCl was added to the solution until the pH was acidic. The solution was extracted with EtOAc (50 mLx3), and the extract was washed with H_2O (50 mL) and brine (50 mLx1), and dried over anhydrous Na_2SO_4, and evaporated to give the crude **12**. This material was used for the preparation of sapphyrin without additional purification.

Preparation of 2, 5-Bis (3-n-butyl-5-formyl-4-methyl-2-pyrrolylmethyl)-3, 4-diethyl-1*H*-pyrrole (15)

This compound was prepared by the similar procedure of reference 13. Analytical data of **15**; ^{1}H NMR($CDCl_3$) δ 0.84 (t, 6 H, *J* = 6.84), 1.15 (t, 6 H, *J* = 7.32), 1.27-1.30 (m, 8 H), 2.23 (s, 6 H), 2.28 (m, 4 H), 2.48 (q, 4 H, *J* = 7.32), 3.51 (s, 4 H), 4.34 (s, 4 H), 6.97 (m, 4 H), 7.20-7.23 (m, 6 H), 8.77 (br s, 1 H), 11.22 (br s, 2 H); ^{13}C NMR($CDCl_3$) δ 11.1, 13.9, 16.9, 17.8, 22.1, 22.8, 23.9, 33.5, 65.2, 117.1, 118.6, 121.6, 122.4, 126.5, 126.6, 127.1, 128.0, 133.4, 137.1, 162.7; IR(KBr) / cm^{-1} 1272, 1454, 1658 (C=O), 2857, 2927, 2958, 3297(NH), 3424(NH); MS (FAB) m/z 689 (M+1); Anal. Calcd for $C_{44}H_{55}N_3O_4$; C, 76.60; H, 8.04; N, 6.09. Found: C, 76.36; H, 8.10; N, 5.86.

Preparation of di-bicyclosapphyrin (16)

A solution of **12**, tripyrrane **(15)** (343 mg, 0.7 mmol) and TFA (2.9 mL) in dry CH_2Cl_2 (55 mL) was heated at 55 ˚C for 11 h. Then triethylamine (6 mL) was added to the reaction mixture, then air was bubbled and stirred for 5 h. Reaction mixture was washed with 1N HCl (50 mLx1), saturated aqueous $NaHCO_3$ (50 mLx1), H_2O (50 mLx1), and brine (50 mLx1). The organic layer was dried with Na_2SO_4. Solvent was removed at reduced pressure, and the residue was dissolved in $CHCl_3$ and subjected to chromatography over silica gel with $CHCl_3$ containing 1-2.5% triethylamine The green fraction was collected and evaporated to dryness. The residue was dissolved in $CHCl_3$ again, and washed 2 N-HCl (100 mL x 3) and solvent was removed at reduced pressure. Recrystallization from $CHCl_3$-hexane gave **16** (91 mg, 18 %). ^{1}H NMR ($CDCl_3$) δ 11.86 (s, 2 H), 11.84 (s, 2 H), 7.42 (br s, 2 H), 7.34-7.44 (m, 4 H), 6.58 (br s, 2 H), 6.35 (br s, 2 H), 4.76 (t, 4 H, *J* = 7.33), 4.75 (q, 4 H, *J* = 7.79), 4.31 (s, 6 H), 2.67-2.75 (q, 4 H, *J* = 7.33), 2.20-2.65 (m, 8 H), 2.34 (t, 6 H, *J* = 7.79), 2.10 (m, 4 H), 1.34 (t, 6 H, *J* = 7.79), -5.04 (br s, 3 H), -5.49 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 114.61, 140.17, 137.25, 136.82, 133.73, 131.94, 131.70, 129.42, 129.30, 122.37, 100.47, 88.68, 29.67, 21.68, 20.87, 20.73, 18.72, 17.69, 17.18, 12.55; MS (TOF): 686 (-1HCl, M+1, 33%), 650 (-2HCl, M+1, 100%); UV-Vis (CH_2Cl_2) λmax (log ε): 453 (5.83), 577 (3.57), 623 (4.22), 679 (4.41).

Preparation of di- benzosapphyrin (17)

Sapphyrin **(16)** (10 mg, 0.02 mmol) was heated under vacuum (10 mmHg) at 200 ˚C for 30 min to give **17** (10 mg, 100 %). ^{1}H NMR ($CDCl_3$) δ 12.04 (s, 2 H), 11.93 (s, 2 H), 10.75 (d, 2 H, *J* = 7.33), 10.18 (d, 2 H, *J* = 7.33), 8.59 (m, 4 H), 4.77 (t, 4 H, *J* = 7.33), 4.76 (q, 4 H, *J* = 7.33), 4.22 (s, 6 H), 2.71 (q, 4 H, *J* = 7.33), 2.34 (t, 6 H, *J* = 7.33), 2.14 (m, 4 H), 1.35 (t, 6 H, *J* = 7.33), –4.02 (s, 2 H), -5.02 (s, 1 H), -5.32 (s, 2 H); ^{13}C NMR ($CDCl_3$,) δ 114.61, 140.17, 137.25, 136.82, 133.73, 131.94, 131.70, 129.42, 129.30, 122.37, 100.47, 88.68, 29.67, 21.68, 20.87, 20.73, 18.72, 17.69, 17.18, 12.55; MS (TOF): 622 (-2HCl, M+1); UV-Vis (CH_2Cl_2) λmax (log ε): 464 (5.65), 577 (3.31), 632 (4.22), 683 (4.31); HRMS; calcd 671.3988 for $C_{46}H_{49}N_5$, measured 671.3952

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