Notes

Structural Characterization of Meso Aryl Sapphyrins

Alagar Srinivasan, Anand V. G.,
S. Jeyaprakash Narayanan, Simi K. Pushpan,
M. Ravi Kumar, and Tavarekere K. Chandrashekar*

Department of Chemistry, Indian Institute of Technology, Kanpur, U.P. 208 016, India

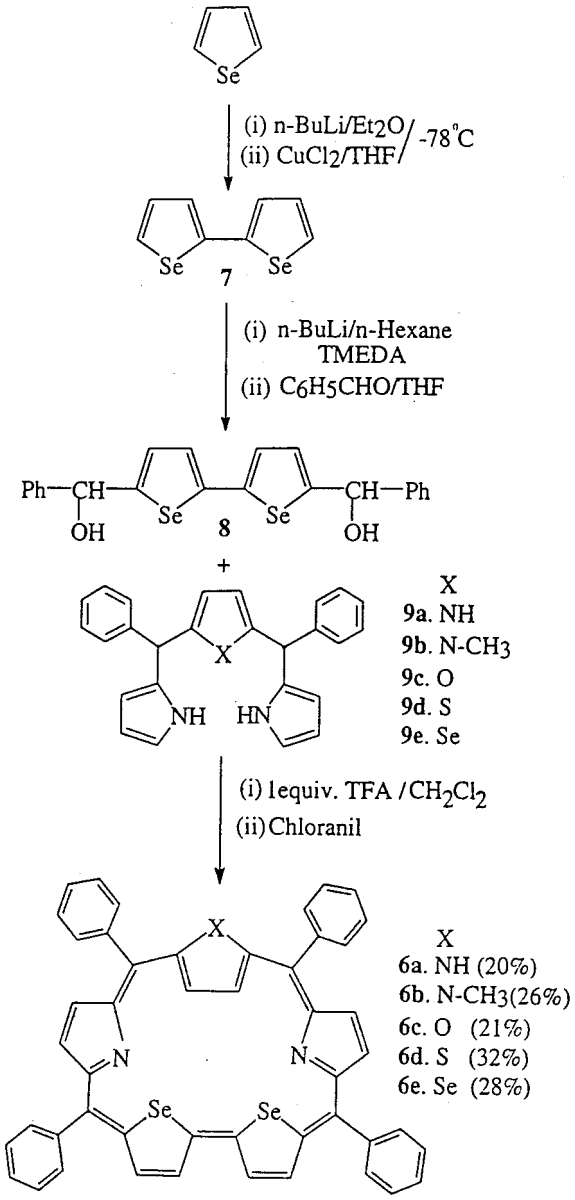
Ken-ichi Sugiura and Yoshiteru Sakata

Institute of Scientific and Industrial Research, Osaka University, Osaka 567, Japan

Received April 30, 1999

Studies on expanded porphyrins are receiving increased attention in view of their diverse applications.[1] Among the expanded porphyrins, the chemistry of β-substituted sapphyrins has been well studied because of the availability of easy and efficient synthetic methods.[2] In contrast, the *meso* aryl sapphyrin **1** was isolated only recently as a byproduct in 1% yield in the Rothemund reaction.[3] Later studies from Dolphin's group,[4] Latos-Grazynski's group,[3,6] and from this laboratory[5] have reported synthesis of a variety of *meso* aryl sapphyrins. Unlike β-substituted sapphyrins, the *meso* aryl sapphyrins show structural diversity.[3] On the basis of spectroscopic studies, Latos-Grazynski[3,6a] and co-workers suggested that **1** has an inverted structure in its free base form in which the pyrrole ring opposite to the bipyrrole unit is inverted and on protonation a 180° ring flipping takes place to get a planar structure. Recent spectroscopic and X-ray structural data from this laboratory[5b] suggested that **3** and **4** has a planar structure where the pyrrole ring opposite to bipyrrole is not inverted and protonation does not lead to any structural change. On the other hand, spectroscopic data[7] reveal that *meso* aryl sapphyrins **5a**−**5e** (Chart 1) exhibit an inverted structure

Scheme 1. Synthesis of Core Modified *Meso* Aryl Sapphyrins



where the heterocyclic ring opposite to bithiophene unit is inverted and protonation does not show any of the ring flipping observed for **1**. To understand the reasons and the circumstances which lead to ring inversion, we have synthesized a new series of sapphyrins **6a**−**6e** and solved first single-crystal X-ray structures of two inverted sapphyrins **5e** and **6b.** In addition, in this paper we report a comparative X-ray structural data as well as spectroscopic data. The data analysis reveal that larger core sizes and the presence of small heteroatoms (N or O) adjacent to the heterocyclic ring lead to inverted structures, while the presence of bigger heteroatoms

* Corresponding author. Telefax: Int. code + (512) 590 007/597 436. e-mail: tkc@iitk.ernet.in.

(1) (a) Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted and Isomeric Porphyrins*; Elsevier: Oxford, 1997. (b) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, *97*, 2267−2340 and references therein.

(2) (a) Sessler, J. L.; Lisowski, K. A.; Boudreaux, K. A.; Lynch, V.; Barry, J.; Kodadek, T. J. *J. Org. Chem.* **1995**, *60*, 5975−5978. (b) Paolesse R.; Licoccia, S.; Spagnoli, M.; Boschi, T.; Khoury, R. G.; Smith, K. M. *J. Org. Chem.* **1997**, *62*, 5133−5137. (c) Lash, T. D.; Richter, D. T. *J. Am. Chem. Soc.* **1998**, *120*, 9965−9966.

(3) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K. *Chem. Eur. J.* **1995**, *1*, 68−73.

(4) Bruckner, C.; Sternberg, E. D.; Boyle, R. W.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1997**, 1689−1690.

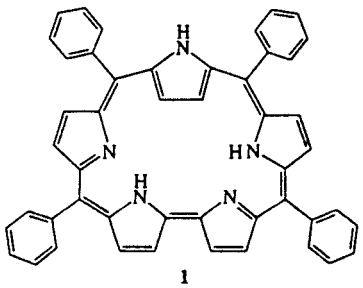
(5) (a) Srinivasan, A.; Mahajan, S.; Pushpan, S. K.; Ravi Kumar, M.; Chandrashekar, T. K. *Tetrahedron Lett.* **1998**, *39*, 1961−1964. (b) Jeyaprakash Narayanan, S.; Sridevi, B.; Chandra shekar, T. K.; Vij, A.; Roy, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 3394−3397. (c) Jeyaprakash Narayanan, S.; Sridevi, B.; Srinivasan, A.; Chandrashekar, T. K.; Roy, R. *Tetrahedron Lett.* **1998**, *39*, 7389−7392. (d) Pushpan, S. K.; Jeyaprakash Narayanan, S.; Srinivasan, A.; Mahajan, S.; Chandrashekar, T. K.; Roy, R. *Tetrahedron Lett.* **1998**, *39*, 9249−9252.

(6) (a) Rachlewicz, K.; Sprutta, N.; Latos-Grazynski, L.; Chmielewski, P. J.; Szterenberg, L. *J. Chem. Soc., Perkin Trans.* 2 **1998**, 959−968. (b) Rachlewicz, K.; Sprutta, N.; Chmielewski, P. J.; Latos-Grazynski, L, *J. Chem. Soc., Perkin Trans.* 2 **1998**, 969−975.

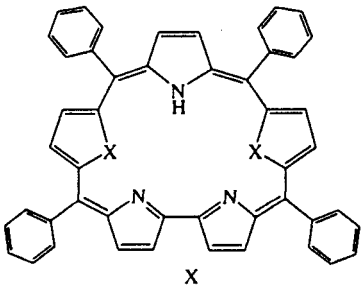
(7) Srinivasan, A.; Pushpan, S. K.; Ravi Kumar, M.; Mahajan, S.; Chandrashekar, T. K.; Roy, R.; Ramamurthy, P. *J. Chem. Soc., Perkin Trans.* 2 **1999**, 961−968.

10.1021/jo990729u CCC: $18.00
Published on Web 10/23/1999

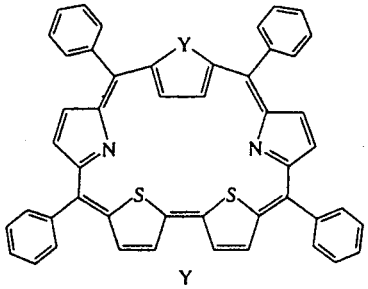
Chart 1



1



X
2. O
3. S
4. Se



Y
5a. NH
5b. N-CH$_3$
5c. O
5d. S
5e. Se

Table 1. ^{1}H NMR Chemical Shifts of β-CH Protons of the Inverted Ring before and after Protonation

compd	inverted ring	free base (ppm)	$\Delta\delta$	dication[b] (ppm)
5a	pyrrole	−0.84	9.70	−1.06
6a		−0.55	9.54	−0.32
1[a]		−1.49	11.60	8.58
5b	*N*-methylpyrrole	−1.15	10.03	−1.09
6b		−0.36	9.34	−0.38
5c	furan	0.61	9.18	0.31
6c		0.31	9.13	−0.31
2[a]		−0.85	10.64	−2.20
5d	thiophene	−0.73	9.40	−1.20
6d		−0.68	9.47	−0.65
5e	selenophene	−0.27	9.10	−1.17
6e		−0.82	9.58	−0.98

[a] Data taken from refs 3 and 6b, respectively. [b] Dications are generated by adding a dilute solution of CF_3COOH in $CDCl_3$.

(S or Se) leads to planar structures. NMR data indicates that the inverted structures show reduced diatropic ring currents.

Results and Discussion

The synthesis of core-modified *meso* aryl sapphyrins **6a**−**6e** was accomplished by a TFA-catalyzed condensation reaction between biselenophene diol **8** with modified tripyrranes **9a**−**9e**[7] followed by chloranil oxidation (Scheme 1).^{1}H NMR, analytical, mass, and UV−visible spectral data are consistent with the proposed composition.

The first clue that the heterocyclic ring opposite to the bipyrrole, bithiophene, and biselenophene unit is inverted came from chemical shift observed for β-CH protons of the inverted ring (Table 1). It is seen from Table 1 that the β-CH protons of the inverted ring are highly shielded and appear in the range from +0.61 ppm to −1.49 ppm, suggesting that these protons are experiencing the ring current of the macrocycle. Upon protonation, there are only small differences in the chemical shift of these protons, suggesting that the heterocyclic ring remains inverted on protonation. This observation is in total contrast to that observed for **1** where dramatic shielding and deshielding of pyrrole NH and β-CH protons suggested the 180° ring flipping to get back the planar structure.[3,6a] The $\Delta\delta$ values[3] which represent the extent of aromaticity are reduced considerably in the inverted sapphyrins relative to **3** and **4** which show a planar structure ($\Delta\delta$ value for **3** and **4** are 14.87 and 15.32, respectively).[5b,6b]

The ring inversion in the solid state was confirmed by single-crystal X-ray analysis of **5e** and **6b** (Figures 1 and 2). The sapphyrin skeleton show small deviation from planarity; the deviation of meso carbons for **6b**[8] are C(9) −0.035(4), C(14) 0.051(4), C(19) −0.049(4), C(24) 0.031(4) except for the pyrrole ring containing *N*-methyl group. The pyrrole ring is inverted where the *N*-methyl group is pointing away from the macrocyclic ring. The β-CH protons of this ring are near the ring current region consistent with the solution^{1}H NMR chemical shifts. The dihedral angle between the *N*-methyl pyrrole ring and the mean plane of the sapphyrin is 46.48°. For **5e**,[9] the deviations for meso carbons are C(9) 0.094(5), C(14) −0.133(5), C(19) 0.139(5), C(24) −0.091(5) except for the selenophene ring which is inverted, and the selenium atom is pointing away from the ring current of the macrocycle while the β-CH protons are experiencing the ring current of the macrocycle. The dihedral angle between the inverted selenophene ring and the mean plane of the sapphyrin is 20.56°.

Table 2. Selected X-ray Structural Data for Planar and Inverted *Meso* Aryl Sapphyrins

compd	ring	bond lengths (Å) $C_\alpha-X^b$	$C_\alpha-C_\beta$	$C_\beta-C_\beta$
3[a]	pyrrole	1.361(5)	1.451(6)	1.337(6)
4[a]	pyrrole	1.366(6)	1.446(7)	1.328(7)
5e	selenophene	1.907(6)	1.406(7)	1.338(8)
6b	*N*-methylpyrrole	1.383(5)	1.411(6)	1.378(6)

	nonbonded distances (Å)	
3[a]	26S·····28S	4.346
4[a]	26Se·····28Se	3.932
5e	26N·····28N	6.449
6b	26N·····28N	6.403

	torsion angles (deg) 13C−14C−15C−16C	13C−14C−15C−X[b]
3[a]	168.5(4)	−11.1(6)
4[a]	170.0(5)	−9.1(8)
5e	7.6(8)	−165.0(4)
6b	35.3(7)	−149.0(4)

[a] Data taken from ref 5b. [b] X: N1 or Se1 or N2.

(8) Crystal data for **6b**: $C_{50}H_{34}N_3Se_2Cl_3$, crystal from $CHCl_3$:CH_3OH (1:1), crystal dimensions 0.50 × 0.25 × 0.20 mm, M = 941.12, monoclinic, space group $P2_1/n$, a = 17.1534(3), b = 9.8246(3), c = 25.0922(6) Å, β = 106.151(1)°, V = 4061.8(2) Å^3, Z = 4, D_c = 1.539 g/cm^3, $F(000)$ = 1896, T = 199 K, μ(Mo Kα) = 20.59 cm^{-1}, 6826 reflections, [$I > 3.00\sigma$], R = 0.058, R_w = 0.083.

(9) Crystal data for **5e**: $C_{49}H_{32}N_2S_2SeCl_2$, crystal from CH_2Cl_2:CH_3OH, crystal dimensions 0.53 X 0.18 X 0.03 mm, M = 862.79, monoclinic, space group $P2_1/n$, a = 17.752(2), b = 11.020(1), c = 21.341(2) Å, β = 106.958(3)°, V = 3993.47(7) Å^3, Z = 4, D_c = 1.435 g/cm^3, $F(000)$ = 1760, T = 199 K, μ(Mo Kα) = 12.17 cm^{-1}, 7767 reflections, [$I > 3.00\sigma$], R = 0.070, R_w = 0.083.

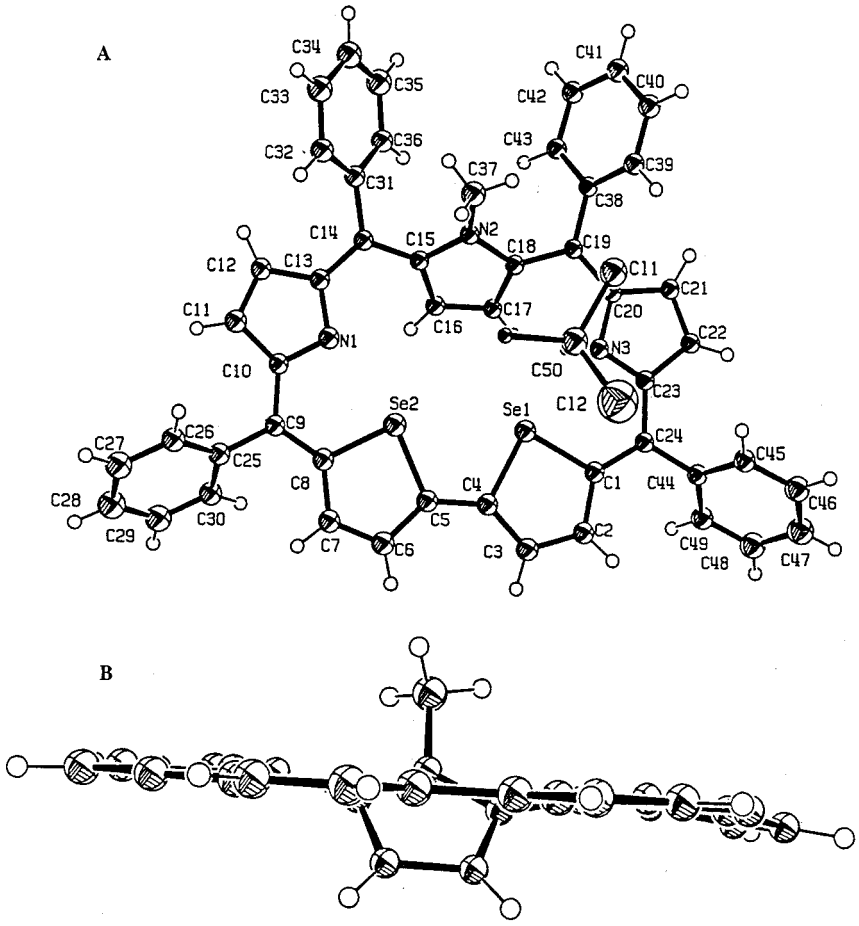


Figure 1. Single-crystal X-ray structure of **6b**: (A) top view, (B) side view showing the atomic labeling scheme. The *meso* aryl rings are deleted for clarity in the side view.

Table 2 lists the relevant bond distances of the inverted ring, the nonbonded distances, and the torsion angles. A comparison of bond lengths of $C_\alpha-X$, $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ observed for the heterocyclic ring opposite to the bipyrrole, bithiophene, and biselenophene unit in **3, 4, 5e** and **6b** with that of the free heterocyclic ring system suggests small decreases in $C_\alpha-X$ and $C_\alpha-C_\beta$ distances and small increases in $C_\beta-C_\beta$ distances due to the modified aromatic delocalization[5b] pathway in sapphyrins relative to free heterocyclic rings. The bonding pattern in the biselenophene moiety for **6b** is reversed if we look at the $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ bond length of biselenophene 1.424 and 1.378 Å, respectively, compared to free selenophene ring ($C_\alpha-C_\beta$ 1.369 and 1.433 Å). However, the $C_\alpha-Se$ (1.899 Å) bond experiences very little change relative to free selenophene ring (1.855 Å).[10] There are no significant differences in these bond lengths for the planar and the inverted sapphyrins. However, there are significant differences in the torsion angles C13−C14−C15−C16 and C13−C14−C15−X. Furthermore, between **5e** and **6b**, the higher torsion angle observed for **6b** clearly suggests significant deviations from the planarity relative to **5e**, and this is clearly seen in the side view of Figures 1 and 2.

The ring inversions in the sapphyrins are found to be dependent on the nature of the heterocyclic ring which is adjacent to the inverted ring. For example, when the adjacent ring contains a small heteroatom like N, the ring is inverted as in **1**, **2**, **5a**−**5e**, and **6a**−**6e**, while in **3** and **4**, which shows a planar structure, the adjacent ring contains bigger S or Se atoms. A comparison of the nonbonding distances shown in Table 2 clearly suggests that this distance depends on the nature of X-atom present at the 26th and 28th positions and significant decreases are observed for X = S or Se. For example, in **4** this distance is 3.932 Å, while for **5e** it is 6.449 Å. This decrease in the distance will not only prevent accommodation of two carbon atoms separated by at least ~1.35 Å (average $C_\beta-C_\beta$ distance) but also hinders any possible free rotation along C14−C15 or C18−C19 required for the inversion of the ring, and consequently the sapphyrin is forced to adopt a planar structure. If this is true, then one would expect that replacement of S or Se atoms at 26 and 28 positions by O atoms (which has similar size as that of N) in **3** and **4** should lead to inversion of the ring. Indeed, very recently independent work from this laboratory[5b] as well as that of Latos-Grazynski[6b] reveals that the analogous 26,28-dioxasapphyrin shows an inverted structure.

An analysis of X-ray structural data of **3, 4, 5e**, and **6b** and the ^{1}H NMR chemical shifts shown in the Table 1 reveal the following: (a) The inverted sapphyrins show significantly smaller $\Delta\delta$ values relative to planar sapphyrins due to the reduced aromaticity caused by nonplanar structures of inverted sapphyrins. (b) The presence of bigger heteroatoms such as S or Se at the 26 and 28 positions leads to planar structures, while the pres-

(10) Latos-Grazynski, L.; Pacholska, E.; Chmielewski, P. J.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1996**, *35*, 566−573.

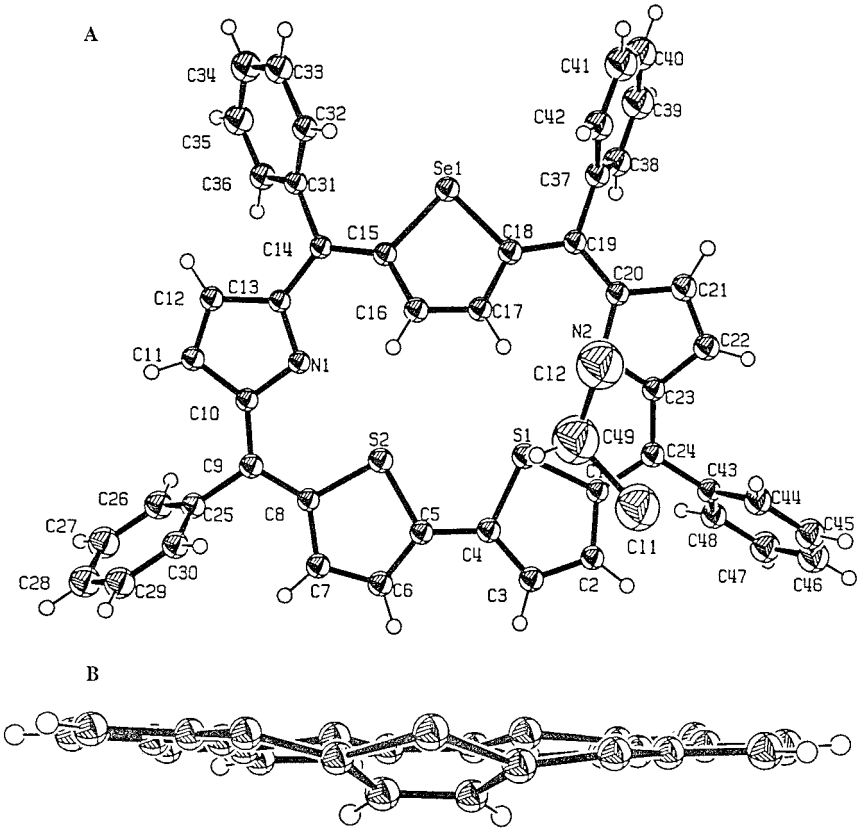


Figure 2. Single-crystal X-ray structure of **5e**: (A) top view, (B) side view showing the atomic labeling scheme. The *meso* aryl rings are deleted for clarity in the side view.

ence of smaller heteroatom like N or O leads to inverted structures. (c) The ring inversion does not depend on the heteroatom present on the bipyrrolic unit. These conclusions are in accordance with the structures of all the *meso* aryl sapphyrins reported to date.

Experimental Section

All the chemicals used for the synthesis were reagent grade unless otherwise specified. Solvents for spectroscopic measurements were purified and dried according to the standard methods. Compounds **9a**−**9e** were synthesized following the literature procedure.[7] The instrumentation used for UV−visible, IR, ^{1}H NMR, ^{13}C NMR, mass, and elemental analysis were the same as described previously.[7] Crystal measurements were made on a Rigaki TAXIS−IV imaging plate area detector with graphite monochromated Mo−Kα radition. Indexing was performed from four oscillations which were exposed for 3.3 min. The crystal-to-detector distance was 86.60 mm with the detector at the zero swing position. Readout was performed in the 0.100 mm pixel mode. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

Syntheses. 2,2′-Biselenophene (7). To a solution of selenophene (1 g, 7.63 mmol) in a 1:1 mixture of dry ether (20 mL) and dry THF (20 mL) was added *n*-butyllithium (5.4 mL, 8.39 mmol) at −70 °C and allowed to stir for 2 h at the same temperature. Then, $CuCl_2$ (1.85 g, 13.7 mmol) was added to the above mixture at −70 °C followed by dry THF (20 mL) and allowed to stir for 2 h. The reaction mixture was quenched with saturated NH_4Cl solution (25 mL) at −30 °C and extracted with ethyl acetate (100 mL). The organic layers were combined and washed with brine (100 mL) and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel 100−200 mesh). A colorless fraction eluted with petroleum ether gave a yellow solid identified as 2,2′-biselenophene. Yield 480 mg, 48%; mp 40−42 °C. Anal. Calcd for $C_8H_6Se_2$: C, 36.95; H, 2.33. Found: C, 37.36; H, 2.12%. IR ν_{max} (Nujol) 2920, 2860, 1460, 1380, 1250, 1040, 825, 760, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87−7.86 (d, J = 4 Hz, 2H), 7.21−7.27 (m, 4H). ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 144.7, 130.2, 129.6, 126.7. EI mass: m/z 260 (100%) [M$^+$].

5,5′-Bis-(phenylhydroxymethyl)-2,2′-biselenophene diol (8). To a solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.8 mL, 11.4 mmol) in dry *n*-hexane (90 mL) was added *n*-butyllithium (7.3 mL, 11.4 mmol) followed by 2,2′-biselenophene (1 g, 3.82 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h and later heated under reflux for 1 h. The reaction mixture was then allowed to attain 25 °C. Benzaldehyde (1 mL, 9.53 mmol) in dry THF (25 mL) was added dropwise to the reaction mixture at 0 °C. After the addition was over, the reaction mixture was allowed to attain 25 °C, saturated ammonium chloride solution (40 mL) was added, and it was then extracted with ether or chloroform (100 mL). The organic layers were combined and washed with brine (100 mL) and dried over anhydrous Na_2SO_4. The crude product obtained on evaporation of the solvent was recrystallized from dry toluene to afford the diol as a pale yellow solid. Yield 940 mg, 52%; mp112 °C. Anal. Calcd for $C_{22}H_{18}O_2Se_2$: C, 55.95; H, 3.84. Found: C, 56.32; H, 4.12%. IR ν_{max}(Nujol) 3500−3100 (br), 2920, 2860, 1450, 1370, 1040 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26−7.47 (m, 10H), 7.00−7.01 (d, J = 3 Hz, 2H), 6.88−6.89 (d, J = 3 Hz, 2H), 5.97 (s, 2H), 2.5 (brs, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 154.6, 145.0, 143.1, 128.6, 128.1, 127.2, 126.2, 125.9, 74.2. EI mass: m/z 472 (100%) [M$^+$].

5,10,15,20-Tetraphenyl-25,29-diselenasapphyrin (6a). 5,5′-Bis(phenylhydroxymethyl)-2,2′-biselenophene (200 mg, 0.424 mmol) and 5,10-diphenyltripyrrane (160 mg, 0.424 mmol) in dry dichloromethane (200 mL) were stirred under nitrogen atmosphere for 15 min at room temperature. TFA (0.033 mL, 0.424 mmol) was added to the above mixture. The solution was stirred for further 1 h under dark conditions. The resulting solution was opened to the air, chloranil (313 mg, 1.272 mmol) was added, and the mixture was heated to reflux in a preheated oil bath at 50 °C for 1 h. After removal of the solvent, the crude product was purified by column chromatography (basic alumina). An

orange band eluted with CCl_4:CH_2Cl_2 (40:60) and gave a green lustrous solid identified as 5,10,15,20-tetraphenyl-25,29-diselenasapphyrin. Yield 70 mg, 20%; mp decomposes above 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.99 (br s, 1H), 10.57 (d, J = 6 Hz, 2H), 10.30 (d, J = 6 Hz, 2H), 8.99 (d, J = 4 Hz, 2H), 8.88 (d, J = 4 Hz, 2H), 8.41−8.45 (m, 4H), 7.91−7.77 (m, 16H), −0.55 (s, 2H). MS (electro spray): m/z 810 (100%) [(M + 2)$^+$]. Anal. Calcd for $C_{48}H_{31}N_3Se_2$: C, 71.38; H, 3.87; N, 5.20. Found: C, 71.42; H, 3.64; N, 5.39%. UV−vis (CH_2Cl_2) λ_{max} [nm] (ϵ): 530 (48000), 659 (5100), 714 (8900), 787 (2600), 889 (3200); UV−vis (CH_2Cl_2/1 equiv of TFA) λ_{max}[nm] (ϵ): 538 (33000), 755 (6400), 800 (9000), 840 (8000). UV−vis (CH_2Cl_2/2.5 equiv of TFA) λ_{max}-[nm] (ϵ): 545 (48000), 815 (15800).

5,10,15,20-Tetraphenyl-27-*N*-methyl-25,29-diselenasapphyrin (6b). 5,5′-Bis(phenylhydroxymethyl)-2,2′-biselenophene-(200 mg, 0.424 mmol), 5,10-diphenyl-16-*N*-methyltripyrrane (166 mg, 0.424 mmol), TFA (0.033 mL, 0.424 mmol), and chloranil (313 mg, 1.272 mmol) under similar reaction conditions as mentioned above gave a green lustrous solid identified as 5,10,15,20-tetraphenyl-27-*N*-methyl-25,29-diselenasapphyrin. Yield 90 mg, 26%; mp decomposes above 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.48 (d, J = 4 Hz, 2H), 10.22 (d, J = 6 Hz, 2H), 8.98 (d, J = 4 Hz, 2H), 8.83 (d, J = 4 Hz, 2H), 8.37−8.40 (m, 4H), 7.94−7.84 (m, 16H), 2.36 (s, 3H), −0.36 (s, 2H). MS (electro spray): m/z 824 (30%) [(M + 2)$^+$]. Anal. Calcd for $C_{49}H_{33}N_3Se_2$: C, 71.62; H, 4.05; N, 5.11. Found: C, 71.89; H, 4.42; N, 5.32%. UV−vis (CH_2Cl_2) λ_{max}[nm] (ϵ): 531 (19600), 662 (1600), 715 (3300), 784 (1100), 883 (1100); UV−vis (CH_2Cl_2/1 equiv of TFA) λ_{max}[nm] (ϵ): 538 (13500), 807 (3300), 847 (3200). UV−vis (CH_2Cl_2/2.5 equiv of TFA) λ_{max}[nm] (ϵ): 548 (15800), 757 (sh, 1700), 822 (4600).

5,10,15,20-Tetraphenyl-27-oxa-25,29-diselenasapphyrin (6c). 5,5′-Bis(phenylhydroxymethyl)-2,2′-biselenophene (200 mg, 0.424 mmol), 5,10-diphenyl-16-oxatripyrrane (160 mg, 0.424 mmol), TFA (0.033 mL, 0.424 mmol), and chloranil (313 mg, 1.272 mmol) under similar reaction conditions as mentioned above gave a green lustrous solid identified as 5,10,15,20-tetraphenyl-27-oxa-25,29-diselenasapphyrin. Yield 72 mg, 21%; mp decomposes above 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.19 (d, J = 3 Hz, 2H), 10.01 (d, J = 6 Hz, 2H), 8.82 (d, J = 6 Hz, 2H), 8.70 (d, J = 3 Hz, 2H), 8.35−8.28 (m, 8H), 7.91−7.73 (m, 12H), 0.31 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$/TFA): δ 10.18 (d, J = 4 Hz, 2H), 10.00 (d, J = 4 Hz, 2H), 8.80 (d, J = 4 Hz, 2H), 8.70 (d, J = 4 Hz, 2H), 8.36−8.26 (m, 8H), 7.88−7.71 (m, 12H), −0.31 (s, 2H). MS (electro spray): m/z 811 (55%) [(M + 2)$^+$]. Anal. Calcd for $C_{48}H_{30}N_2OSe_2$: C, 71.29; H, 3.74; N, 3.46. Found: C, 71.42; H, 3.96; N, 3.27%. UV−vis (CH_2Cl_2) λ_{max}[nm] (ϵ): 532 (96000), 652 (9800), 709 (14300), 818 (1100), 928 (4200); UV−vis (CH_2Cl_2/1 equiv of TFA) λ_{max}[nm] (ϵ): 541 (71200), 662 (3700), 714 (5600), 796 (11300), 862 (11200). UV−Vis (CH_2Cl_2/2.5 equiv of TFA) λ_{max}[nm] (ϵ): 550 (91400), 785 (15700), 856 (13000).

5,10,15,20-Tetraphenyl-27-thia-25,29-diselenasapphyrin (6d). 5,5′-Bis(phenylhydroxymethyl)-2,2′-biselenophene (200 mg, 0.424 mmol), 5,10-diphenyl-16-thiatripyrrane (167 mg, 0.424 mmol), TFA (0.033 mL, 0.424 mmol), and chloranil (313 mg, 1.272 mmol) under similar reaction conditions as mentioned above gave a purple solid identified as 5,10,15,20-tetraphenyl-27-thia-25,29-diselenasapphyrin. Yield 112 mg, 32%; mp decomposes above 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.57 (d, J = 6 Hz, 2H), 10.27 (d, J = 6 Hz, 2H), 8.79 (d, J = 3 Hz, 2H), 8.75 (d, J = 3 Hz, 2H), 8.40−8.37 (m, 4H), 7.94−7.72 (m, 16H), −0.68 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$/TFA): δ 10.16 (d, J = 4 Hz, 2H), 10.01 (d, J = 4 Hz, 2H), 9.26 (d, J = 4 Hz, 2H), 9.16 (d, J = 4 Hz, 2H), 8.63 (m, 8H), 7.84−8.09 (m, 12H), −0.65 (s, 2H). MS (electro spray): m/z 827 (50%) [(M+2)$^+$]. Anal. Calcd for $C_{48}H_{30}N_2SSe_2$: C, 69.90; H, 3.67; N, 3.40. Found: C, 69.63; H, 3.82; N, 3.33%. UV−vis (CH_2Cl_2) λ_{max}[nm] (ϵ): 523 (84200), 644 (12400), 695 (17400), 795 (4000), 903 (4300); UV−vis (CH_2Cl_2/1 equiv of TFA) λ_{max}[nm] (ϵ): 535 (62000), 699 (9700), 767 (14000), 856 (11100). UV−vis (CH_2Cl_2/2.5 equiv of TFA) λ_{max}-[nm] (ϵ): 546 (103000), 731 (17000), 805 (34300), 856 (26600).

5,10,15,20-Tetraphenyl-25,27,29-triselenasapphyrin (6e). 5,5′-Bis(phenylhydroxymethyl)-2,2′-biselenophene (200 mg, 0.424 mmol), 5,10-diphenyl-16-selenatripyrrane (188 mg, 0.424 mmol), TFA (0.033 mL, 0.424 mmol), and chloranil (313 mg, 1.272 mmol) under similar reaction conditions as mentioned above gave a purple solid identified as 5,10,15,20-tetraphenyl-25,27,29-triselenasapphyrin. Yield 105 mg, 28%; mp decomposes above 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.54 (d, J = 6 Hz, 2H), 10.24 (d, J = 3 Hz, 2H), 8.76 (d, J = 3 Hz, 2H), 8.61 (d, J = 3 Hz, 2H), 8.39−8.36 (m, 6H), 7.93−7.69 (m, 14H), −0.82 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$/TFA): δ 10.36 (d, J = 4 Hz, 2H), 10.14 (d, J = 6 Hz, 2H), 8.99 (d, J = 6 Hz, 2H), 8.89 (d, J = 4 Hz, 2H), 8.45−8.38 (m, 8H), 8.00−7.75 (m, 12H), −0.98 (s, 2H). MS (electro spray): m/z 873 (50%) [(M + 1)$^+$]. Anal. Calcd for $C_{48}H_{30}N_2Se_3$: C, 66.14; H, 3.47; N, 3.21. Found: C, 66.32; H, 3.21; N, 3.42%. UV−Vis (CH_2Cl_2) λ_{max}[nm] (ϵ): 527 (88000), 643 (18900), 690 (18300), 803 (sh, 8100), 899 (7500); UV−Vis (CH_2Cl_2/1 equiv of TFA) λ_{max}[nm] (ϵ): 536 (63300), 646 (13500), 698 (15600), 756 (19500), 862 (13300). UV−vis (CH_2Cl_2/2.5 equiv of TFA) λ_{max}-[nm] (ϵ): 543 (65000), 686 (15000), 759 (21300), 862 (16000).

Acknowledgment. This work was supported by a grant from the Department of Science and Technology and Council of Scientific and Industrial Research, New Delhi, India, to T.K.C.

Supporting Information Available: X-ray structural data for **5e** and **6b**, including X-ray experimental, summaries of crystallographic parameters, atomic coordinates, anisotropic displacement parameters, bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990729U