meso-Aryl sapphyrins with heteroatoms; synthesis, characterization, spectral and electrochemical properties

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The synthesis, characterization and spectral properties of six new *meso*-aryl core modified sapphyrins are described. An efficient approach involving an acid catalyzed condensation of bithiophene diol **1** and modified tripyrranes **2a**–**2e** allows preparation of the desired *meso*-aryl sapphyrins in 16–36% yield. The product distribution and the isolated yield were found to be dependent on the nature of the acid catalyst (Lewis acid or protic acid) and its concentration. Protic acid catalyst exclusively gave the expected sapphyrins while two additional products, an 18π tetraphenylporphyrin and a 26π modified rubyrin, were isolated under Lewis acid catalysis. An analysis of proton NMR and absorption spectral data suggests that in free base sapphyrins, the heterocyclic ring opposite to the bithiophene unit is inverted as in N-5 *meso*-aryl sapphyrin and the degree of inversion is dependent on the nature of the heterocyclic ring. The energy optimized structure calculated from the semi-empirical method substantiates such a conclusion. Protonation of sapphyrins generates respective mono- and dications and the heterocyclic ring retains an inverted structure in contrast to normal N-5 sapphyrins. The triplet excited lifetimes for free base and protonated derivatives are similar both under argon saturated and air equilibrated conditions, indicating that the triplet state quenching by oxygen is minimal. Cyclic voltammetric studies reveal easier reductions and harder oxidations relative to *meso*-aryl porphyrins and the Δ_{redox} observed for **3d** suggests significant reduction of the HOMO–LUMO energy gap consistent with the large red shift observed for the Soret band.

Introduction

Research on expanded porphyrins[1] in general and sapphyrins[2] in particular has received considerable attention in recent years because of their potential biomedical applications as, for example, photosensitizers for PDT, MRI contrasting agents[3] and macrocyclic receptors for transport of neutral[4] and anionic substrates.[4a,b,5] They are also of interest in terms of aromaticity in large conjugated systems[6] and the range of coordination environment available for transition metals.[5d,7] Synthetic methods available in the literature for the synthesis of sapphyrins include: a traditional [3 + 2] acid catalysed MacDonald condensation between the appropriate precursors,[1] reaction of diformylbipyrrole with benzaldehyde and pyrrole,[8] an acid catalysed condensation of biladienes-*ac* with pyrrole-2-carbaldehyde[9a] and of terpyrranedicarboxylic acid with pyrrole-2,5-dicarbaldehyde.[9b] The majority of the sapphyrins reported to date are limited to β-pyrrole substituted macrocycles linked through *meso*-carbon bridges. Only recently, an N-5 *meso*-aryl sapphyrin was isolated as a byproduct from a Rothemund reaction[10a] and from an acid catalysed self coupling reaction of dipyrromethane.[10b]

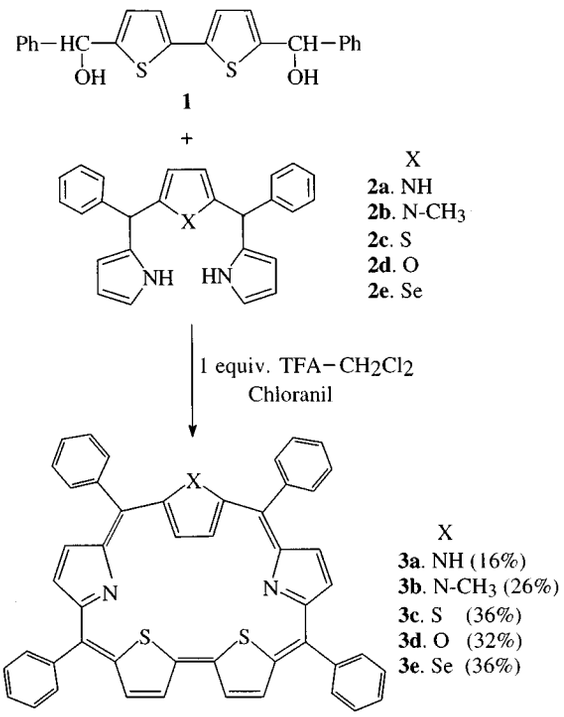
Core modification by replacement of one or more pyrrolic units by other heterocycles such as furan, thiophene and selenophene leads to a new class of sapphyrins. These macrocycles by virtue of their altered electronic structure are expected to have optical, electrochemical and excited state properties different from all their pyrrolic counterparts.[11] A perusal of the literature reveals only limited reports on core modified expanded porphyrins. Sessler and coworkers have reported a series of core modified β-substituted sapphyrins containing furan, thiophene and selenophene rings and core modified β-substituted isosmaragdyrins containing a furan ring.[12] The other reports include ozaphyrins and bronzaphyrins,[13] thiophene and furan containing annulenes,[14] selenium and sulfur containing pentaphyrins[15] and furan containing 26π expanded macrocycles.[16] Recent studies from this laboratory and of others describe the synthesis of *meso*-aryl sapphyrins with heteroatoms.[17,25]

An understanding of the spectral and electrochemical properties of sapphyrins in the ground and excited states is an important first step towards their potential biomedical application. In this direction, only β-substituted sapphyrin dication has been probed for its redox behaviour,[5a] photoexcited singlet[5a] and triplet state properties[18,19] and photodynamic activity.[20] However, to the best of our knowledge there are no systematic studies on the *meso*-aryl sapphyrins in general and core modified sapphyrins in particular. In this paper, we wish to report not only the synthesis of a series of *meso*-aryl sapphyrins bearing heteroatoms, but also their spectral and electrochemical behaviour. A comparison of their properties with those observed for β-substituted sapphyrins reveals some important differences attributable to the effect of *meso*-substitution and the presence of heteroatoms. Unlike β-substituted sapphyrins, the sapphyrins reported here show inversion of the heterocyclic ring opposite to the bithiophene unit in their free base as well as in their protonated forms. However, a complete flip of the inverted heterocycle upon protonation as reported for N-5 *meso*-aryl sapphyrin is not observed in the core modified *meso*-aryl sapphyrins reported here.[10a]

Results and discussion

(a) Synthesis and characterization

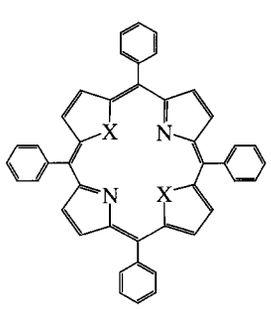
The synthetic method followed here is basically a modified [3 + 2] MacDonald condensation which has been traditionally



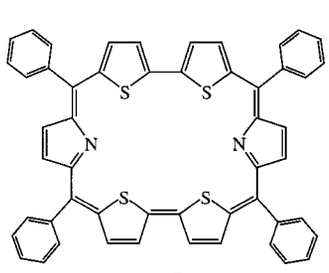
Scheme 1 Synthetic scheme for the preparation of core modified *meso*-aryl sapphyrins.

used for the synthesis of sapphyrins[1] (Scheme 1). Only recently, Smith and coworkers[9] have reported a new method which avoids preparation of the bipyrrole precursor and is different from the MacDonald approach. The present method is based on Ulman's reaction reported for the synthesis of core modified mono- and dithia porphyrins.[21] The key precursors required for the synthesis were modified tripyrranes **2a**–**2f**. The tripyrranes **2a**, **2c**, **2d** and **2f** were already known in the literature[22] and hitherto unknown **2b** and **2e** were synthesised by a similar method by the reaction of 2,5-bis(phenylhydroxymethyl)-*N*-methylpyrrole and 2,5-bis(phenylhydroxymethyl)selenophene with pyrrole in the presence of 0.1 equivalent of TFA as the catalyst in 33 and 72% yield respectively. Thus, the reaction of **2a**–**2e** with bithiophene diol synthesised from an earlier reported method,[23] on condensation in dichloromethane containing one equivalent of TFA gave the desired core modified sapphyrins **3a**–**3e** in moderately good yields. The yields compare well with those reported by Dolphin and coworkers[24] for the synthesis of *meso*-aryl N-5 sapphyrins (up to 39%) and are better than those reported for 5,10-*meso*-diphenylsapphyrin[8] (10%) and tetraphenylsapphyrin (1.1%), (7.5%),[10] and 26,28-dithia, dioxa and diselena substituted sapphyrins (15%).[25]

Change of catalyst from protic acid to Lewis acid changes the product distribution and yield. For example, use of $BF_3{\cdot}OEt_2$ (3.05×10^{-5} M) as the catalyst and **2c** as the substrate under similar conditions gave two additional products **4** and **5** in addition to **3c** in 4, 2 and 30% yield respectively. A higher concentration of $BF_3{\cdot}OEt_2$ (6.05×10^{-5} M) produced more of **4**



4
X_2TPP



5
S_4 Rubyrin

Table 1 The chemical shifts of the protons of the inverted heterocyclic ring opposite to the bithiophene unit before and after protonation

			Chemical shift (ppm)	
Compound	Inverted ring	Proton	Free base ($\Delta\delta$)[b]	Dication[c]
3a	Pyrrole	NH	11.35	13.60
		β-CH	−0.84 (9.70)	−1.06
		NH[a]	—	−4.11
3b	*N*-methyl-pyrrole	*N*-CH_3	2.71	2.71
		β-CH	−1.15 (10.03)	−1.09
		NH[a]	—	−3.67
3c	Thiophene	β-CH	−0.73 (9.40)	−1.20
		NH[a]	—	−3.15
3d	Furan	β-CH	0.61 (9.18)	0.31
		NH[a]	—	−1.25
3e	Selenophene	β-CH	−0.27 (9.10)	−1.17
		NH[a]	—	−2.50

[a] Corresponds to NH protons of pyrrole after protonation. [b] Corresponds to difference in the chemical shift of the ring inverted β-protons and the adjacent pyrrole ring β-protons. [c] Dications were generated by adding trifluoroacetic acid in $CDCl_3$ solution.

(15%) and **5** (5%) at the expense of **3c** (7%). Change of Lewis acid to $SnCl_4$ (4.35×10^{-4} M) also gave **5** (11%), **4** (3%) and **3c** (20%).

The cyclization has to occur through the formation of a carbocation in **1** by the acid catalyst. The sole formation of the expected sapphyrins with one equivalent of TFA indicates that the generation of carbocation occurs through protonation followed by elimination of water from **1**. The formation of additional products **4** and **5** in the presence of $BF_3{\cdot}OEt_2$ catalysts can be explained by acidolysis of tripyrromethanes on the time scale of sapphyrin formation in addition to carbocation generation. It is possible that the metal on the Lewis acid coordinates to the heteroatom on the tripyrrane, triggering its acidolysis. The observed increase in the yields of **4** and **5** at the expense of **3c** on increasing the concentration of Lewis acid supports such a possibility. There is spectroscopic evidence that the tripyrromethanes undergo acidolysis. For example: (a) stirring of **2c**, **2d** or **2e** with benzaldehyde in CH_2Cl_2 under nitrogen atmosphere for 15 min followed by addition of $BF_3{\cdot}OEt_2$ (6.09×10^{-4} M) and subsequent oxidation with chloranil under reflux for an hour resulted in the formation of ~2% *meso*-tetraphenylporphyrin and monothia, monooxa or monoselena porphyrin respectively. (b) The gradual decrease in the absorbance of tripyrrane in CH_2Cl_2 in the UV–Visible spectrum (475 nm) upon addition of $BF_3{\cdot}OEt_2$ with time and subsequent TLC analysis (silica gel, ethyl acetate–petroleum ether (1:9)) of the mixture reveal a decrease in concentration of tripyrrane and a new purple spot (R_f: 0.23) was noticed suggesting the formation of uncyclized conjugated macrocycles. Further support for the acidolysis of precursors dipyrromethane or tripyrrane comes from recent work of Lindsey,[22a] Lash[22c] and coworkers.

Grazynski and coworkers[10a] have recently reported that the pyrrole ring opposite to the bipyrrolic unit in *meso*-aryl sapphyrin is inverted in its free base form on the basis of ^1H NMR chemical shifts observed for the NH proton and the β-pyrrole protons of the inverted ring. The chemical shifts observed were 11.76 ppm for the NH proton and −1.28 ppm for the inner β-CH protons. In the *meso*-aryl sapphyrins reported here such a ring inversion is indeed observed and Table 1 lists the chemical shifts of the relevant protons of the inverted heterocyclic ring opposite to the bithiophene unit. Thus, in **3a** the NH proton resonates at 11.35 ppm while β-CH protons resonate at −0.84 ppm. A comparison of $\Delta\delta$ values (calculated from the difference between the chemical shift of the ring inverted β-protons and the adjacent pyrrole ring β-protons) reveals that those in **3a**–**3e** (10.03–9.10 ppm) are slightly smaller as compared to N-5 *meso*-aryl sapphyrin (10.25 ppm),[10a] sug-

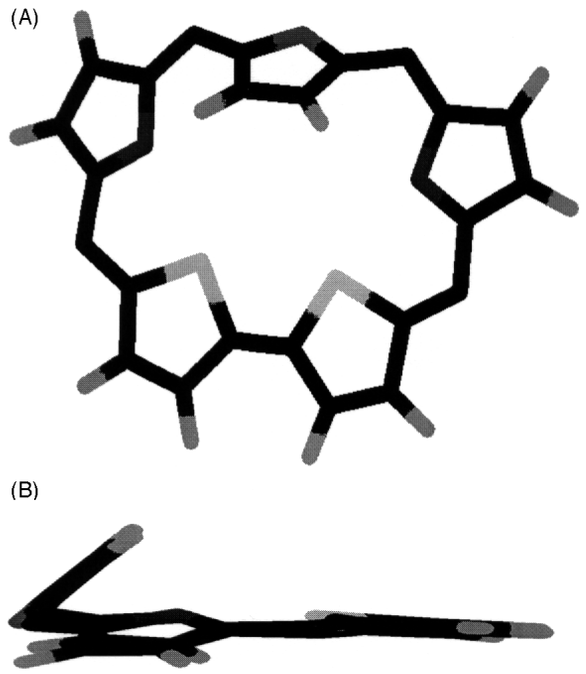


Fig. 1 Geometry optimized structure of **3d**. (A) Top view, (B) side view showing the ring inversion. The *meso*-aryl rings are deleted for clarity.

gesting a small decrease in the ring current. The non-planarity of the sapphyrin on heteroatom substitution accounts for this difference. The geometry optimized structure for **3d** shown in Fig. 1 reveals the ring inversion.

On protonation, N-5 *meso*-aryl sapphyrin undergoes a dramatic 180° flip of the inverted pyrrole ring as evidenced by a large upfield–downfield shift of the NH protons (11.75 to −2.74 ppm) and β-pyrrole protons (−1.21 to 8.87 ppm). Both monocationic and dicationic species have been identified and it has been shown that the ring flipping occurs during formation of dicationic species.[25c,26] The NMR titration studies on **3d** also reveal formation of both mono- and dicationic species (Fig. 2). It has been observed that the bithiophene, pyrrole and *meso*-phenyl protons undergo gradual deshielding (0.28, 0.71 and 0.33 ppm) consistent with the observation of Grazynski.[26] In contrast, the inverted furan ring protons experience shielding (0.31 ppm) suggesting that the dramatic ring flipping observed for N-5 *meso*-aryl sapphyrin does not occur in the modified sapphyrins reported here. This is also consistent with the observation of Grazynski on 26,28-dioxa- and 26,28-dithia-sapphyrins.[25c] It has been shown by detailed NMR studies that in 26,28-dioxasapphyrin, the pyrrole ring opposite to the bi-pyrrole is inverted while 26,28-dithiasapphyrin shows a planar structure.[25c] It is also observed that on protonation no ring flipping takes place in the dioxa case. It is pertinent to point out here that the NH signals were not observed at room temperature because of the possible rapid tautomerism. Formation of mono- and dicationic species is shown in Scheme 2.

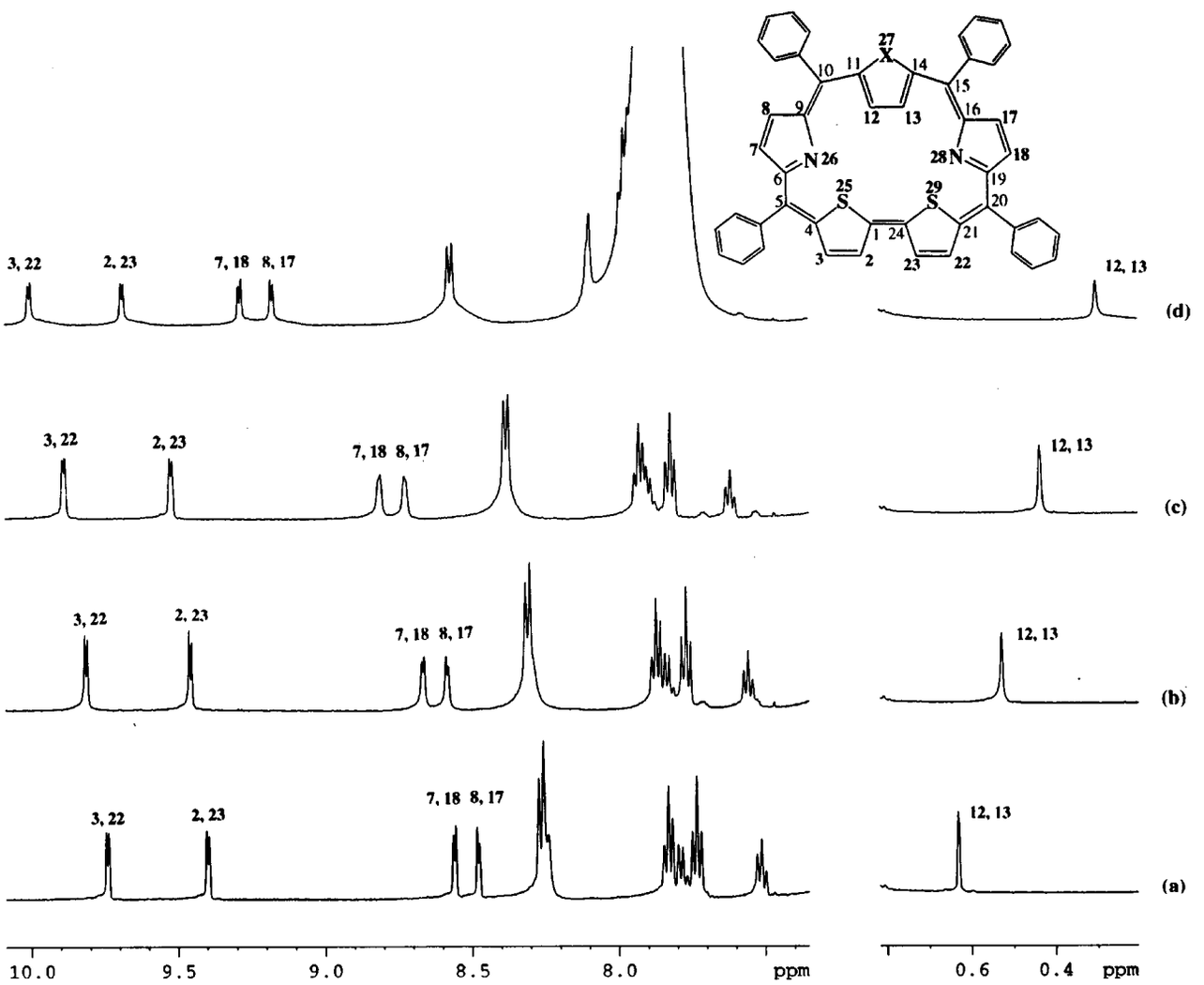
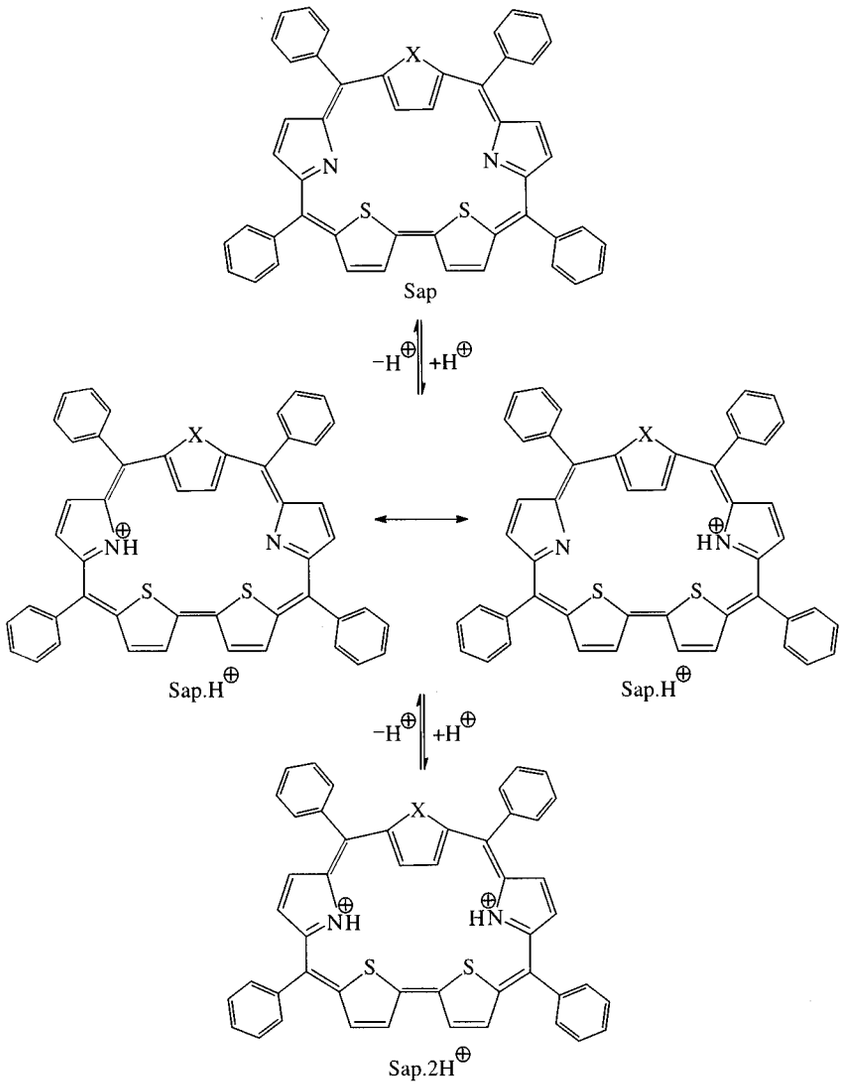


Fig. 2 ^{1}H NMR spectrum of (a) **3d** (1×10^{-4} M) in $CDCl_3$, (b) **3d** (1×10^{-4} M) containing 0.02 equiv. of TFA, (c) **3d** (1×10^{-4} M) containing 0.12 equiv. of TFA, (d) **3d** (1×10^{-4} M) containing 2 equiv. of TFA.



Scheme 2 Protonation scheme for core modified *meso*-aryl sapphyrins.

Table 2 UV–Vis spectral data of *meso*-aryl core modified sapphyrins and their mono- and diprotonated derivatives in CH_2Cl_2

Compound	Soret, λ_{max}/nm ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1})	Q-band, λ_{max}/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1})			
		IV	III	II	I
3a	510 (4.7)	638 (7.0)	698 (10.0)	764 sh (3.7)	864 (4.2)
3a·H$^+$	515 (3.9)		702 (7.1)	768 (7.75)	824 (5.0)
3a·2H$^+$	519 (4.84)				793 (16.75)
3b	510 (6.29)	650 (5.10)	705 (13.33)	770 (2.93)	863 (3.74)
3b·H$^+$	515 (4.51)		709 (4.73)	772 (8.87)	822 (6.0)
3b·2H$^+$	520 (6.67)			658 (3.9)	801 (20.40)
3c	507 (14.27)	622 (9.73)	678 (20.13)	777 (1.87)	875 (4.5)
3c·H$^+$	512 (10.13)	626 (5.2)	677 (10.13)	778 (12.8)	838 (9.7)
3c·2H$^+$	520 (11.05)			778 (20.53)	838 (15.2)
3d	511 (26.93)	624 (23.25)	680 (37.25)	780 (7.75)	883 (10.25)
3d·H$^+$	520 (22.95)		681 (21.5)	773 (32.5)	843 (28.25)
3d·2H$^+$	525 (30)			766 (49)	832 (33.75)
3e	507 (10.25)	598 (9.7)	670 (8.90)	769 (1.5)	871 (2.3)
3e·H$^+$	517 (6.94)	634 (5.1)	670 (5.90)	771 (8.3)	846 (7.5)
3e·2H$^+$	526 (11.20)			778 (16)	842 (13.4)

The UV–Visible absorption spectral data of the sapphyrins are tabulated in Table 2. A comparison of this data with those of β-substituted core modified sapphyrins[7c,d,12] reveals interesting substituent effects: (a) In general, the visible spectra of the β-substituted core modified sapphyrins are not too much different from those of the parent N-5 sapphyrins and only small absorption band shifts are observed upon heteroatom substitution. For example, the oxasapphyrins[12] exhibit a small blue shift of the Soret band (1–2 nm) and a red shift of the Q-bands (10–35 nm) with only marginal changes in the ε-values. On the other hand, the *meso*-aryl sapphyrins show a red shift of both Soret and Q-bands upon heteroatom substitution and the magnitude of the red shifts depends on the number and nature of the heteroatoms with significant changes in ε-values. For example, **3d** shows an 18 nm red shift of the Soret band and an 88 nm shift for the Q-I band relative to parent N-5 *meso*-aryl

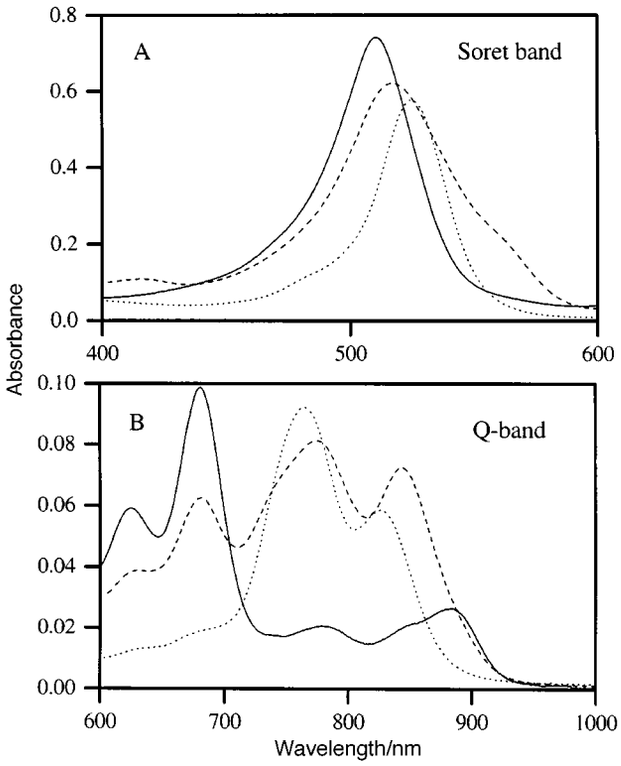


Fig. 3 Absorption spectrum of **3d** in CH_2Cl_2 and its mono- and diprotonated derivative in (A) Soret and (B) Q-band region. (——) Free base (1×10^{-4} M), (----) monocation (1×10^{-4} M containing 0.12 equiv. of TFA) and (....) dication (1×10^{-4} M containing 2 equiv. of TFA).

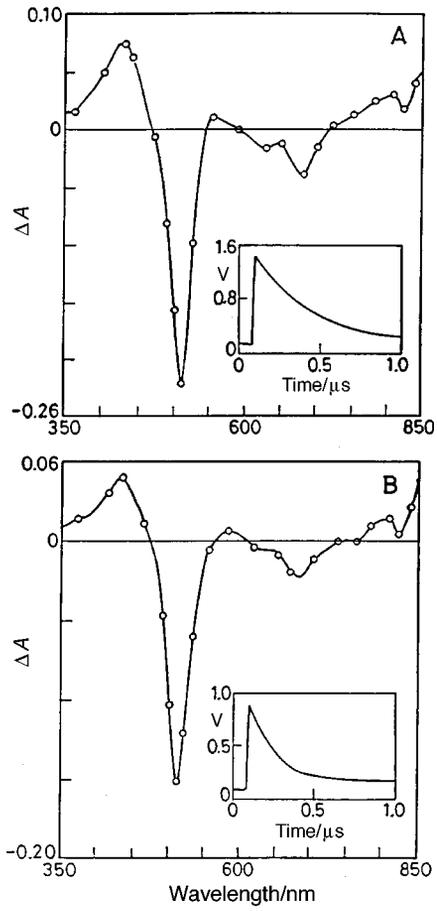


Fig. 4 T–T transient absorption spectrum of (A) **3d** (3.5×10^{-5} M in $CHCl_3$) and (B) its protonated derivative (3.5×10^{-5} M containing ~10^{-3} M of TFA in $CHCl_3$). The inset shows the triplet excited state decay.

sapphyrin[10a] and the ε-value for the Soret band is almost doubled, suggesting that the electronic effect of the heteroatom substitution is significant in *meso*-aryl sapphyrins.[11] (b) Since all the sapphyrins contain two pyridine type nitrogens, they can be either monoprotonated or diprotonated like N-5 *meso*-aryl sapphyrin. The monocations and dications of **3a**–**3e** are identified through UV spectral titrations. A representative spectrum of **3d** is shown in Fig. 3. It is evident that the Soret and Q-I bands of the monocation lie in between those of the free base and the dication, while the other Q-bands almost remain at the same position but with decreased intensity compared to the free base. On further increasing the acid concentration, the Soret band is shifted further towards the red and the number of Q-bands decreases to two from four. Change of solvent from dichloromethane to methanol did not result in any appreciable change, further confirming that the ring flipping is not taking place upon protonation.[26] It is well known that the *meso*-aryl porphyrins[27] undergo a structural change upon protonation by releasing the repulsive interaction between the *ortho*-hydrogens of the *meso*-phenyl rings and the adjacent pyrrole protons. This results in phenyl rings becoming more coplanar with the porphyrin plane, facilitating the delocalization of π-electrons into the phenyl rings by resonance interaction and this is spectroscopically manifested as a red shift of the absorption bands. Such an interaction is not possible in the β-substituted derivatives due to the lack of a *meso*-phenyl substituent. However, it is pertinent to point out here that the N-5 *meso*-aryl sapphyrin shows a blue shift of the Soret band (9 nm) upon protonation[10a] in contrast to the red shift observed for the *meso*-aryl modified sapphyrins. Thus, the *meso*-aryl core modified sapphyrins behave like *meso*-aryl porphyrins while β-substituted sapphyrins resemble octaethyl porphyrins in their spectral behaviour.[27]

(b) Triplet excited state properties

The triplet–triplet transient spectra of **3d** and its protonated derivative, shown in Fig. 4, show bleaching in the Soret and Q-bands of the ground state and a positive absorbance change in the region 380–600 nm. The triplet lifetimes calculated from the decay profiles (Fig. 4 inset) are tabulated in Table 3. Comparison of triplet lifetimes of *meso*-aryl sapphyrins with those of texaphyrins[19] reveals that the lifetimes observed here are about two orders of magnitude lower. The β-substituted sapphyrin dication[18] has a triplet lifetime of 60 ± 5 μs which is again much higher than those of *meso*-aryl sapphyrins. The short lived triplet suggests that the rate of internal conversion from the singlet excited state is much more efficient for *meso*-aryl sapphyrins relative to texaphyrins and sapphyrin dication. Another reason for the short lifetime could be because of the interaction with the solvent $CHCl_3$. It is known that the halogen atoms can affect the non-radiative deactivation process through a spin-orbit coupling effect.[28] Thus, the triplet lifetime data suggest that the β-substituted sapphyrin dication[5a,20] and texaphyrins[19] are better suited for the PDT application in view of their longer triplet lifetimes and better quantum efficiency of singlet oxygen generation[19] than the *meso*-aryl core modified sapphyrins. No attempts were made to measure the quantum yield of singlet oxygen generation.

(c) Electrochemical studies

The cyclic voltammograms for **3c** and **3e** in CH_2Cl_2 at 0.1 M in TBAP recorded in the potential region 1.5 to −1.5 V *vs.* SCE are shown in Fig. 5. All the sapphyrins exhibit two quasi reversible reductions (ΔE_p = 90–150 mV) and two irreversible oxidations.[29] However, for **3a** and **3b**, scanning the voltage in the positive potential also showed two irreversible oxidations but on repetitive scans, the peak potentials kept on shifting indicating some decomposition. The $E_{1/2}$ values listed in Table 4 refer to the average of the two peak potentials at slow scan

Table 3 The triplet excited state parameters of core modified *meso*-aryl sapphyrins and their protonated derivatives in $CHCl_3$

			Triplet lifetime/μs			
	Excited T–T absorption/nm		Argon saturated		Air equilibrated	
Compound	Free base	Dication	Free base	Dication	Free base	Dication
3c	435, 570	430, 595	0.88	0.81	0.75	0.70
3d	430, 565	430, 585	1.26	1.44	1.85	1.90
3e	445, 540	440, 570	0.03	0.05	—	—

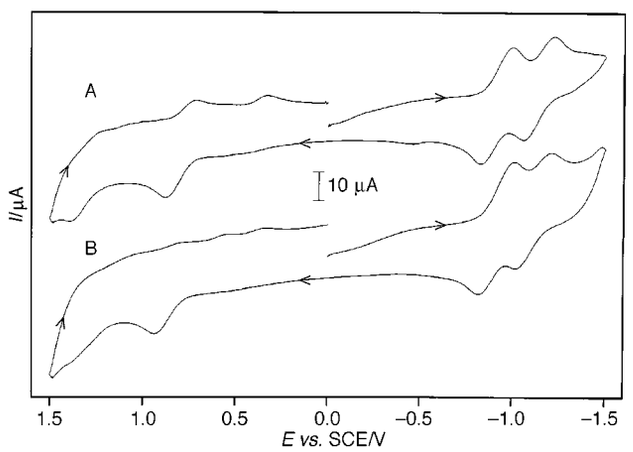


Fig. 5 The cyclic voltammogram of (A) **3c** and (B) **3e** in CH_2Cl_2 containing TBAP (0.01 M) recorded at 50 mV s^{-1} *vs.* SCE. The concentrations of sapphyrins were ~10^{-3} M.

rates (50 mv s^{-1}). In general, there are only minor changes in the reduction potentials among the *meso*-aryl sapphyrins. Comparison of these with the protonated derivatives of β-substituted sapphyrins[5a] (containing Br^- and Cl^- counter anions)[30] suggests easier reductions for the *meso*-aryl core modified sapphyrins by about 120–200 mV. This is not surprising since the substitution of a heteroatom into the porphyrin core leads to easier reductions and harder oxidations relative to the normal porphyrins suggesting changes in the energies of the HOMO and LUMO. Indeed, Ulman and coworkers[31] have shown that in heteroatom substituted porphyrins, both the HOMO and LUMO are stabilized by different mechanisms. In the present study, the Δ_{redox} calculated from the difference of first oxidation potential and first reduction potential indicates significant decreases in the Δ_{redox} values relative to *meso*-aryl porphyrins (2.26 V for H_2TPP).[27b,31] This suggests a decrease in the HOMO–LUMO gap in *meso*-aryl sapphyrins relative to porphyrins. Thus, the observed red shifts of the Soret and Q-bands in the UV–Visible spectra are consistent with this. Among the *meso*-aryl sapphyrins reported here, **3d** has the least Δ_{redox} value and indeed the Soret band of **3d** shows the maximum red shift relative to the others. The redox processes of the *meso*-aryl sapphyrins are summarized in Scheme 3.

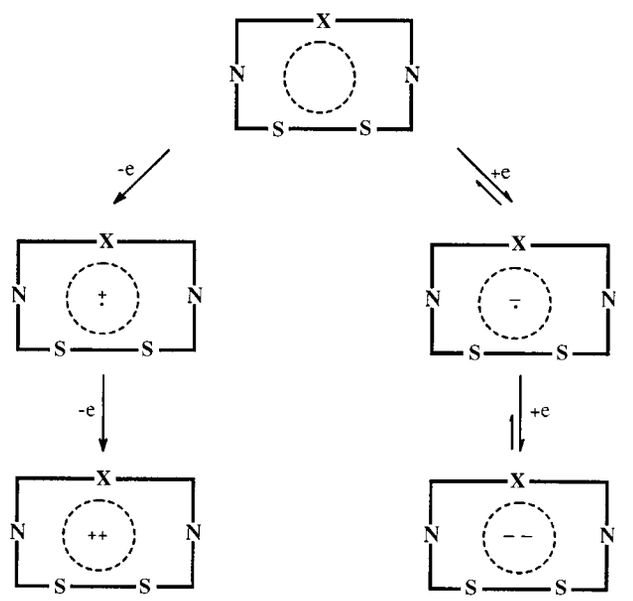
Conclusion

In this paper, we have described the synthesis of five *meso*-aryl sapphyrins bearing heteroatoms. The spectral, electrochemical and excited state studies reveal many interesting differences and similarities relative to β-substituted core modified sapphyrins. It has been shown that the *meso*-aryl hetero sapphyrins behave more like tetraphenyl porphyrins in their spectral and electrochemical behaviour. The hetero sapphyrins have a very short lived triplet excited state relative to β-substituted sapphyrin dication. Preliminary studies on the protonated derivatives of *meso*-aryl hetero sapphyrins suggest binding of the anions similar to that observed for the dicationic β-substituted sapphyrins.[5] Finally, with the availability of good synthetic methodology for the synthesis of core modified expanded porphyrins, we hope to explore their rich and fascinating chemistry in the coming years.

Table 4 Redox potentials of core modified *meso*-aryl sapphyrins

Compound	$E^{ox_1}_{1/2}$/V	$E^{ox_2}_{1/2}$/V	$E^{red_1}_{1/2}$/V	$E^{red_2}_{1/2}$/V	Δ_{redox} [a]/V
3a	—	—	−0.93	−1.39	—
3b	—	—	−1.09	−1.30	—
3c	0.80	1.19	−0.91	−1.12	1.71
3d	0.76	1.14	−0.94	−1.15	1.70
3e	0.82	1.16	−0.92	−1.12	1.74

[a] Calculated from difference in $E^{ox_1}_{1/2}$ and $E^{red_1}_{1/2}$.



Scheme 3 The redox process of core modified *meso*-aryl sapphyrins.

Experimental

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. The instrumentation used for UV–Visible, ^1H NMR, FAB mass and elemental analysis was the same as that described previously.[32] Chemical shifts are given in ppm and *J* values in Hz. For the triplet excited state studies, a Quantel 481 Nd:Yag laser operated in the Q-switched mode was used as excitation source. All the samples were excited at 520 nm. A high intensity Xe-arc lamp was used as monitoring beam. The absorbance changes were detected with a red sensitive photomultiplier tube digitized with a Biomation 8100 recorder before being analysed with a PDP/1170 computer. ILOAR argon degassed 10^{-5} M solutions of sapphyrins were used for all the measurements.

Acid titration

For UV–Visible titration, a constant volume of a dry dichloro-

methane solution of sapphyrin (1×10^{-4} M) was transferred to 10 ml standard volumetric flasks. Then, different equivalents (0.02–1.5) of 1.0×10^{-6} M TFA solution in CH_2Cl_2 were added and the volume was made up to the mark with dry dichloromethane and the absorption spectra in the desired region were recorded in overlay mode. In the case of NMR titration, standard solutions were prepared by using $CDCl_3$.

Molecular mechanics calculations

The geometry-optimized structure was calculated on an HCL-HP Pentium 120 MHz desktop computer using Hyperchem version 5.0. The semiempirical AM1 method and the Polak–Ribiere algorithm with the gradient set at 0.1 were used for the calculation.

5,10-Diphenyl-16-*N*-methyltripyrrane (2b)

A mixture of 2,5-bis(phenylhydroxymethyl)-*N*-methylpyrrole (500 mg, 1.7×10^{-3} mol)[21] and pyrrole (4.73 ml, 6.8×10^{-2} mol) was degassed by bubbling with argon for 10 min. Trifluoroacetic acid (0.01 ml, 1.7×10^{-4} mol) was added and the mixture was stirred for 30 min at room temperature. It was diluted with CH_2Cl_2 (100 ml), then washed with 0.1 M NaOH, followed by water washing. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the unreacted pyrrole was removed by vacuum distillation at room temperature. The resulting viscous dark yellow liquid was purified by column chromatography (silica gel 100–200 mesh, ethyl acetate–petroleum ether (10:90)). After the initial tailing material, a pale orange band eluted which gave orange oil identified as **2b** in 33% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9 (br, s, 2H), 7.12–7.34 (m, 10H), 6.685 (m, 2H), 6.14 (m, 2H), 5.83 (m, 2H), 5.58 (m, 2H), 5.38 (m, 2H), 3.10 (s, 3H). EI mass: *m*/*z* calcd. for $C_{27}H_{25}N_3$ 392, found 389 (37%) [$(M - 3)^+$].

5,10-Diphenyl-16-selenatripyrrane (2e)

2,5-Bis(phenylhydroxymethyl)selenophene (500 mg, 1.46×10^{-3} mol), pyrrole (4 ml, 5.83×10^{-2} mol) and trifluoroacetic acid (0.01 ml, 1.46×10^{-4} mol) under similar reaction conditions as mentioned above gave pale green oil identified as **2e** in 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (br, s, 2H), 7.35–7.24 (m, 10H), 6.80 (s, 2H), 6.68 (m, 2H), 6.16–6.13 (m, 2H), 5.97 (s, 2H), 5.59 (s, 2H). EI mass: *m*/*z* calcd. for $C_{26}H_{22}N_2Se$ 441, found 443 (25%) [$(M + 2)^+$].

5,10,15,20-Tetraphenyl-25,29-dithiasapphyrin (3a)

5,5′-Bis(phenylhydroxymethyl)-2,2′-bithiophene (200 mg, 5.29×10^{-4} mol) and 5,10-diphenyltripyrrane (200 mg, 5.29×10^{-4} mol) in dry dichloromethane (200 ml) were stirred under nitrogen atmosphere for 15 min at room temperature. Trifluoroacetic acid (0.04 ml, 5.29×10^{-4} mol) was added to the above mixture. The solution was stirred for a further 1 h under dark conditions. The resulting solution was opened to air and chloranil (390 mg, 1.58×10^{-3} mol) 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 CH_2Cl_2–ethyl acetate (95:5) gave green lustrous solid identified as **3a** in 16% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.35 (br, s, 1H), 10.31–10.29 (d, 2H, *J* 6), 9.89–9.87 (d, 2H, *J* 6), 8.86–8.85 (d, 2H, *J* 3), 8.78–8.80 (d, 2H, *J* 6), 8.37 (m, 4H), 7.80–8.05 (m, 10H), 7.61–7.67 (m, 6H), −0.84 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$–TFA): δ 13.60 (br, s, 1H), 10.61–10.59 (d, *J* 6, 2H), 10.20–10.18 (d, *J* 6, 2H), 9.65–9.63 (d, *J* 6, 2H), 9.55–9.53 (d, *J* 6, 2H), 8.65 (m, 4H), 8.13–8.07 (m, 10H), 7.99–7.93 (m, 6H), −1.06 (s, 2H), −4.11 (br, s, 2H). MS (electrospray): *m*/*z* calcd. for $C_{48}H_{31}N_3S_2$ 714, found 714 (100%) [M^+]. Anal. calcd. for $C_{48}H_{31}N_3S_2$: C, 80.75; H, 4.38; N, 5.89. Found: C, 80.92; H, 4.15; N, 6.02%.

5,10,15,20-Tetraphenyl-27-*N*-methyl-25,29-dithiasapphyrin (3b)

5,5′-Bis(phenylhydroxymethyl)-2,2′-bithiophene (200 mg, 5.29×10^{-4} mol), 5,10-diphenyl-16-*N*-methyltripyrrane (210 mg, 5.37×10^{-4} mol), trifluoroacetic acid (0.04 ml, 5.29×10^{-4} mol) and chloranil (390 mg, 1.58×10^{-3} mol) under similar reaction conditions as mentioned above gave a green lustrous solid identified as **3b** in 26% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.38–10.36 (d, 2H, *J* 6), 9.94–9.93 (d, 2H, *J* 3), 8.89–8.87 (d, 2H, *J* 3), 8.81–8.80 (d, 2H, *J* 3), 8.40 (m, 4H), 7.92–7.80 (m, 10H), 7.72–7.53 (m, 6H), 2.71 (s, 3H), −1.15 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$–TFA): δ 10.60–10.58 (d, *J* 6, 2H), 10.30–10.28 (d, *J* 6, 2H), 9.53–9.51 (d, *J* 6, 2H), 9.47–9.45 (d, *J* 6, 2H), 8.72–8.60 (m, 4H), 8.20–8.13 (m, 10H), 8.10–8.02 (m, 6H), 2.71 (s, 3H), −1.09 (s, 2H), −3.67 (br, s, 2H). Anal. calcd. for $C_{49}H_{33}N_3S_2$: C, 80.85; H, 4.57; N, 5.77. Found: C, 80.92; H, 4.73; N, 5.62%.

5,10,15,20-Tetraphenyl-25,27,29-trithiasapphyrin (3c)

5,5′-Bis(phenylhydroxymethyl)-2,2′-bithiophene (150 mg, 3.97×10^{-4} mol), 5,10-diphenyl-16-thiatripyrrane (156 mg, 3.97×10^{-4} mol), trifluoroacetic acid (0.03 ml, 3.97×10^{-4} mol) and chloranil (293 mg, 1.191×10^{-3} mol) under similar reaction conditions as mentioned above gave a green lustrous solid identified as **3c** in 36% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.27–10.26 (d, 2H, *J* 3), 9.82–9.80 (d, 2H, *J* 6), 8.67–8.66 (d, 2H, *J* 3), 8.57–8.56 (d, 2H, *J* 3), 8.39–8.32 (m, 8H), 7.91–7.65 (m, 12H), −0.73 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$–TFA): δ 10.61–10.59 (d, *J* 6, 2H), 10.20–10.18 (d, *J* 6, 2H), 9.39–9.38 (d, *J* 3, 2H), 9.33–9.31 (d, *J* 6, 2H), 8.77–8.67 (m, 8H), 8.16–7.95 (m, 12H), −1.24 (s, 2H), −3.10 (br, s, 2H). FAB MS: *m*/*z* calcd. for $C_{48}H_{30}N_2S_3$ 731, found 732 (100%) [$(M + 1)^+$]. Anal. calcd. for $C_{48}H_{30}N_2S_3$: C, 78.87; H, 4.14; N, 3.83. Found: C, 78.52; H, 4.36; N, 3.91%.

5,10,15,20-Tetraphenyl-27-oxa-25,29-dithiasapphyrin (3d)

5,5′-Bis(phenylhydroxymethyl)-2,2′-bithiophene (150 mg, 3.97×10^{-4} mol), 5,10-diphenyl-16-oxatripyrrane (150 mg, 3.97×10^{-4} mol), trifluoroacetic acid (0.03 ml, 3.97×10^{-4} mol) and chloranil (293 mg, 1.191×10^{-3} mol) under similar reaction conditions as mentioned above gave a green lustrous solid identified as **3d** in 36% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75–9.74 (d, 2H, *J* 3), 9.41–9.40 (d, 2H, *J* 3), 8.57–8.56 (d, 2H, *J* 3), 8.49–8.48 (d, 2H, *J* 3), 8.28–8.23 (m, 8H), 7.86–7.49 (m, 12H), 0.61 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$–TFA): δ 10.06–10.05 (d, *J* 3, 2H), 9.63–9.61 (d, *J* 6, 2H), 9.33–9.31 (d, *J* 6, 2H), 9.23–9.21 (d, *J* 6, 2H), 8.60–8.57 (m, 8H), 8.04–7.74 (m, 12H), 0.51 (s, 2H), −1.30 (br, s, 2H). FAB MS: *m*/*z* calcd. for $C_{48}H_{30}N_2S_2O$ 715, found 715 (25%) [M^+]. Anal. calcd. for $C_{48}H_{30}N_2S_2O$: C, 80.64; H, 4.23; N, 3.92. Found: C, 80.87; H, 4.10; N, 3.69%.

5,10,15,20-Tetraphenyl-27-selena-25,29-dithiasapphyrin (3e)

5,5′-Bis(phenylhydroxymethyl)-2,2′-bithiophene (150 mg, 3.97×10^{-4} mol), 5,10-diphenyl-16-selenatripyrrane (176 mg, 3.97×10^{-4} mol), trifluoroacetic acid (0.03 ml, 3.97×10^{-4} mol) and chloranil (293 mg, 1.191×10^{-3} mol) under similar reaction conditions as mentioned above gave a green lustrous solid identified as **3e** in 36% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.65–10.63 (d, 2H, *J* 6), 10.12–10.10 (d, 2H, *J* 6), 8.84–8.82 (d, 2H, *J* 6), 8.55–8.53 (d, 2H, *J* 6), 8.41–8.29 (m, 8H), 7.91–7.63 (m, 12H), −0.27 (s, 2H). ^{1}H NMR (300 MHz, $CDCl_3$–TFA): δ 10.53–10.52 (d, *J* 3, 2H), 10.14–10.13 (d, *J* 3, 2H), 9.29–9.28 (d, *J* 3, 2H), 9.13–9.11 (d, *J* 6, 2H), 8.72–8.65 (m, 8H), 8.15–7.92 (m, 12H), −1.17 (s, 2H), −2.50 (br, s, 2H). FAB MS calcd. for $C_{48}H_{30}N_2S_2Se$ 778, found 778 (50%) [M^+]. Anal. calcd. for $C_{48}H_{30}N_2S_2Se$: C, 74.12; H, 3.89; N, 3.60. Found: C, 74.31; H, 3.56; N, 3.92%.

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