Pergamon

Tetrahedron 55 (1999) 6671–6680

TETRAHEDRON

Novel Heteroatom Containing Rubyrins

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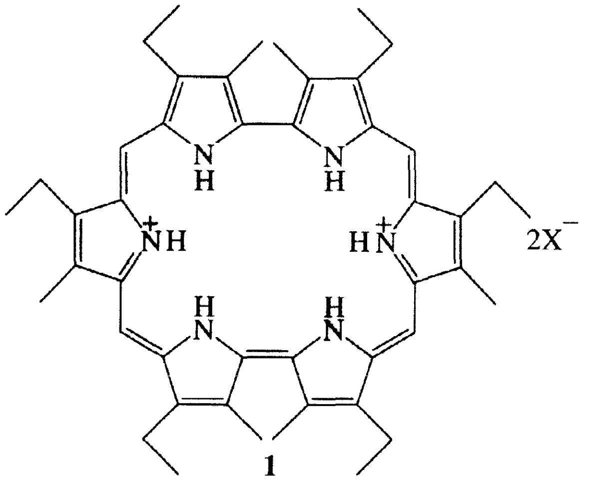
Received 4 January 1999; revised 15 March 1999; accepted 31 March 1999

Abstract: Synthesis of rubyrins containing two or three heteroatoms (O, S, Se) in the core is accomplished using modified diols and tetrapyrromethanes. Substitution of heteroatoms leads to significant reductions in HOMO-LUMO gap and easier oxidations and reductions reflecting the changes in electronic structure of the rubyrin skeleton. © 1999 Elsevier Science Ltd. All rights reserved.

Research on the development of easy and efficient methods for the synthesis of expanded porphyrins is receiving attention in view of their diverse applications in photodynamic therapy (PDT), as contrasting agents for magnetic resonance imaging (MRI) and as anion receptors.[1] The majority of the expanded porphyrins reported to date are confined to β-substituted pyrrole containing macrocycles linked through methine bridges.[1,2] Expansion of the ring increases the number of π-electrons in conjugation. 22π-Electron macrocycles are referred to as sapphyrins while rubyrins contain 26π-electrons. Sessler and coworkers reported the first β-substituted rubyrin **1**, formed by a [4+2] acid catalysed condensation of appropriate precursors.[2] Replacement of one or more pyrrole nitrogens by other heteroatoms such as O, S and Se from the rubyrin skeleton leads to new rubyrins with altered electronic structure and core sizes.[3,4] We have recently reported the synthesis and properties of modified *meso* substituted rubyrins **2** and **3**.[3a] In this paper, we wish to report the synthesis, spectral and electrochemical properties of modified rubyrins containing Se_4N_2, $S_2O_2N_2$, $Se_2O_2N_2$ and $Se_2S_2N_2$ cores.



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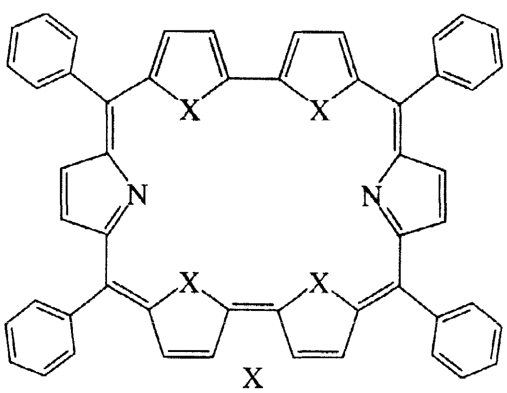


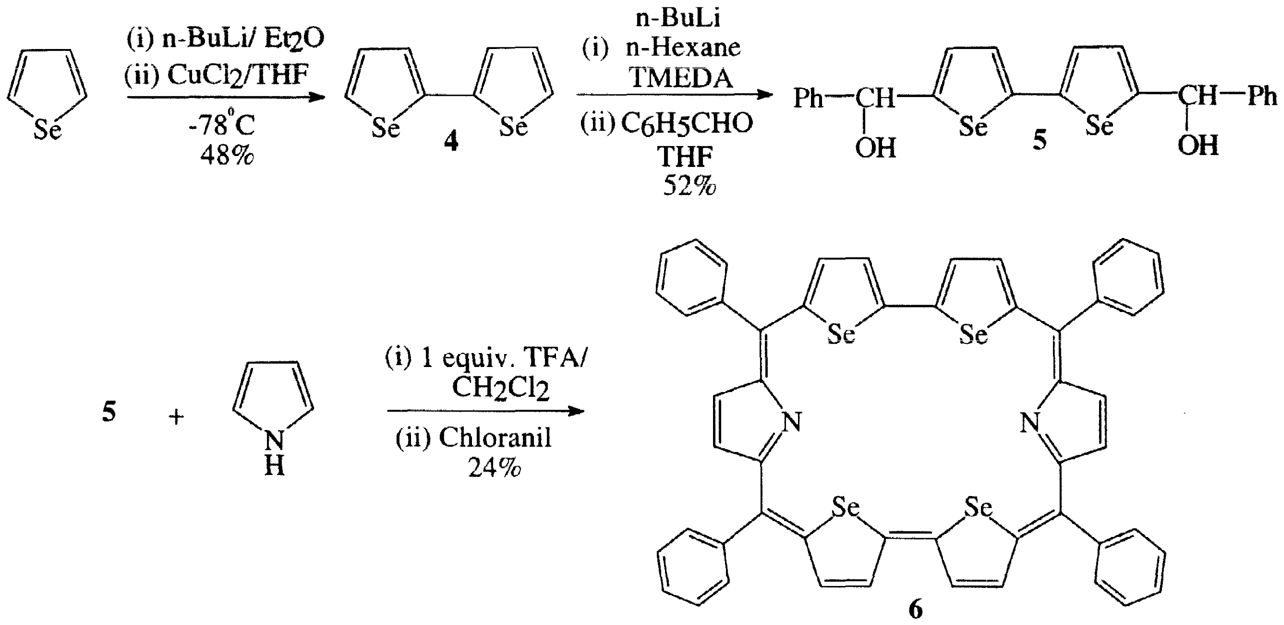
X
2. S
3. O

PII: S0040-4020(99)00313-0

RESULTS AND DISCUSSION:

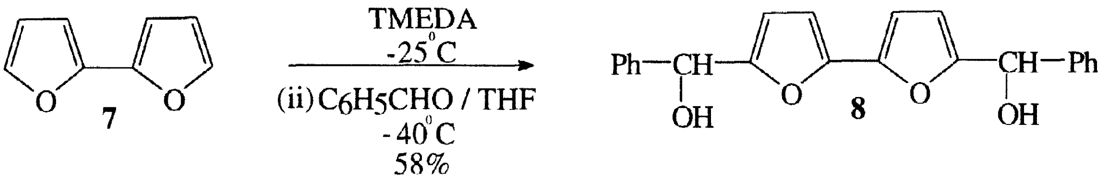
The methodology followed for the synthesis of various rubyrins is similar to one used for the synthesis of **1** or **2**. Thus, the synthesis of **6** (Scheme 1) required hitherto unknown precursors **4** and **5**. Biselenophene **4** was synthesised through the catalytic oxidative coupling reaction between monolithiated selenophene and $CuCl_2$ in THF at -78 °C in 48% yield. Lithiation of **4** followed by reaction with benzaldehyde afforded **5** in 52% yield.[3] **6** was isolated in 24% yield by condensation reaction of **5** with pyrrole in CH_2Cl_2/TFA followed by chloranil oxidation.

Scheme - 1



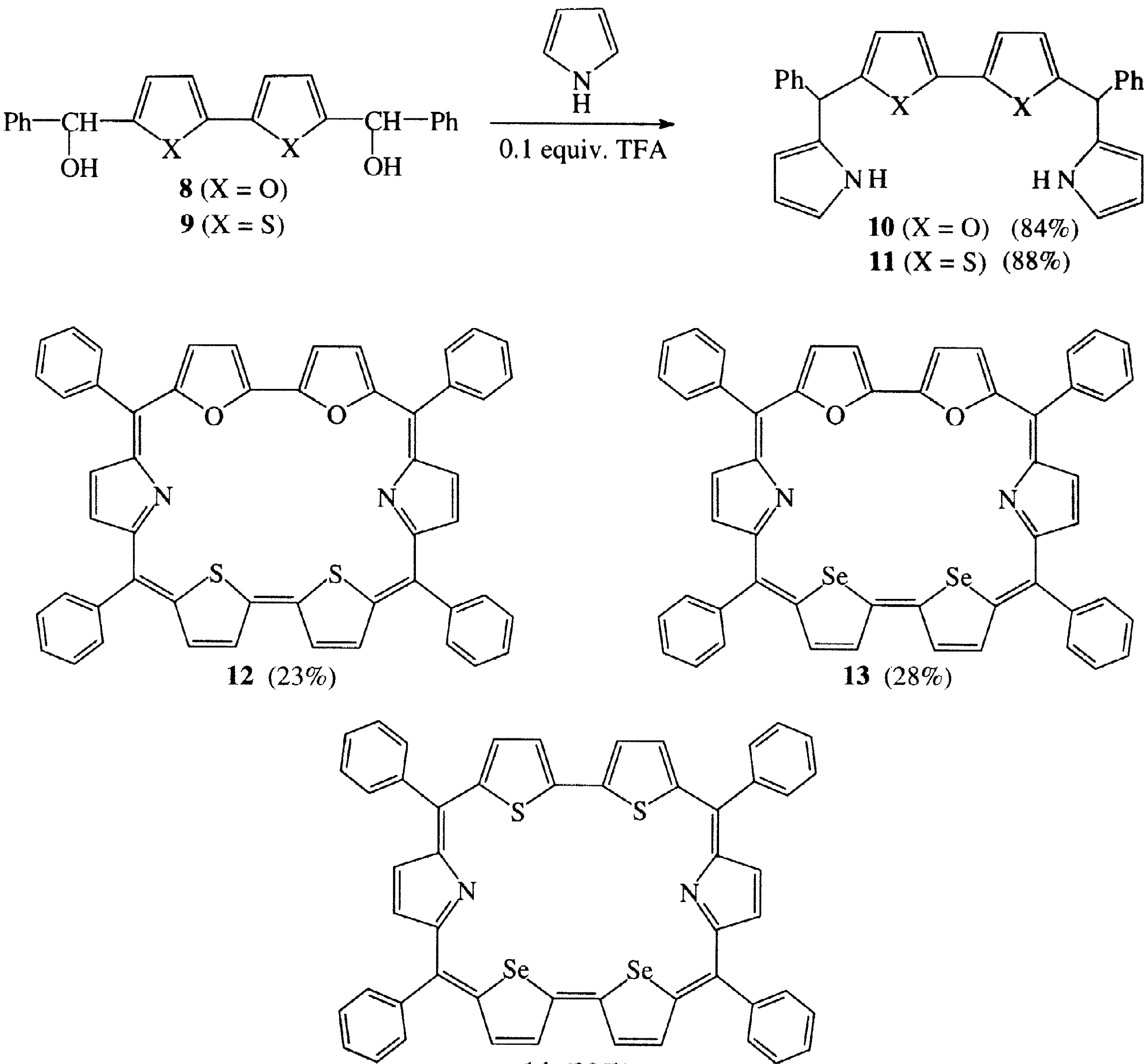
The synthesis of three heteroatom containing rubyrins **12**, **13** and **14** required a [4+2] MacDonald type condensation between the hitherto unknown norbilanes **10** and **11** and the corresponding diols **8** and **9**. Bifuran **8** was synthesised in 58% yield by a different route (Scheme 2) than known in literature[3a] by lithiation of **7**, followed by reaction with benzaldehyde in THF at -40°C. Rubyrin precursors **10** and **11** were prepared by reaction of the appropriate diol with pyrrole (Scheme 3) in the presence of 0.1 equivalent of TFA under a

Scheme - 2



nitrogen atmosphere in 84% and 88% yield respectively. Condensation of **8** and **11** in CH_2Cl_2 containing one equivalent of TFA followed by chloranil oxidation afforded **12** in 23% yield. Similar reaction of **10** with **5** and **11** with **5** afforded **13** and **14** in 28% and 20% yield respectively. The simplicity of the method lies in the fact that in all the condensations, rubyrin was the sole product making the separation much easier and the yields are moderately good.

Scheme - 3



The composition of the rubyrins reported here were confirmed by analytical, Electrospray mass spectrometry and ^{1}H NMR spectral data. Compound **6** was the simplest to analyze which showed two doublets (12.15 and 11.03 ppm) and a singlet (9.31 ppm) assigned to biselenophene and pyrrole protons respectively. The phenyl protons resonate as two multiplets at 8.63 and 8.03 ppm. Compounds **12**, **13** and **14** exhibit six doublets for bithiophene/bifuran/biselenophene and pyrrole from 9.20 to 12.35 ppm and two multiplets for the phenyl protons. The nonplanarity of the macrocyclic ring results in the appearence of two doublets for the pyrrole protons instead of a singlet.

The UV-Visible absorption spectral data of the rubyrins and their respective dications are tabulated in Table 1 and representative spectra of **14** and its dication are shown in the Figure. The absorption data reveals

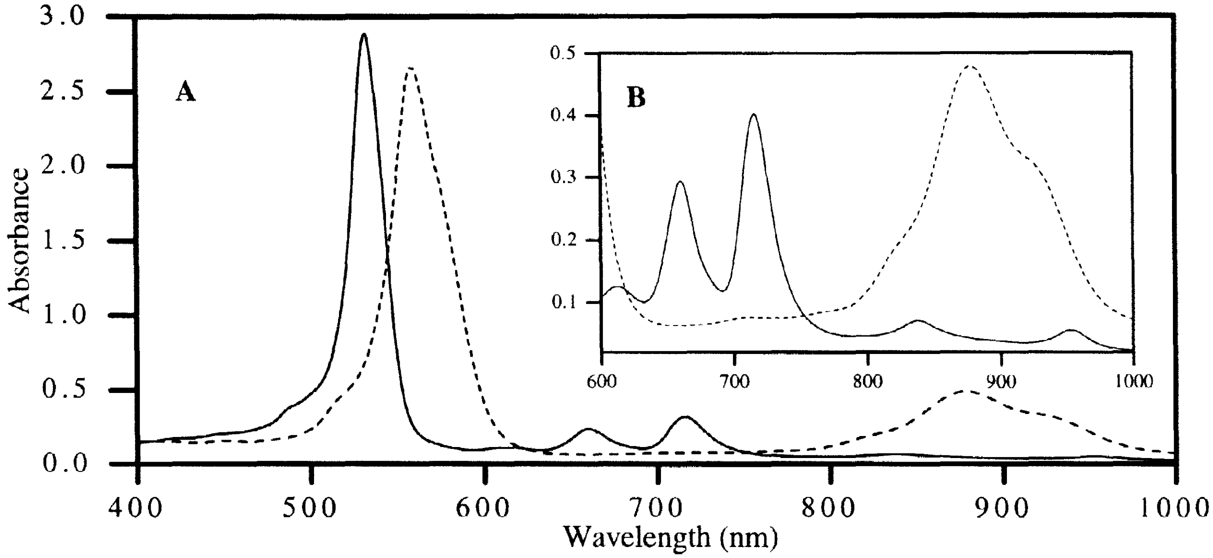


Figure: Absorption spectrum of; (A) **14** and **14**.2H$^+$ (6.40x10^{-5}M) in CH$_2$Cl$_2$. (B) Expansion in the Q-band region.

Table 1

Compound	Soret, λ_{max} (ϵx10^{-5} [mol^{-1}l^{-1}])	Q-band, λ_{max} (ϵx10^{-4}[mol^{-1}l^{-1}])				
		V	IV	III	II	I
6	541 (4.68)	616 (0.82)	667 (3.79)	721 (2.18)	847 (0.37)	964 (0.35)
6.2H$^+$	572 (2.51)	--	--	768 (0.99)	841 (2.96)	937 (1.01)
12	529 (1.70) 552 (1.07)	639sh(0.66)	712 (1.16)	764 (4.89)	866 (0.32)	994 (0.56)
12.2H$^+$	543 (2.44)	--	--	736sh(0.39)	814sh(1.25)	881 (6.14)
13.	539 (0.79) 563 (0.56)	653 (0.51)	706 (1.00)	766 (2.79)	843sh(0.35)	984 (0.24)
13.2H$^+$	568 (0.65) 614 (0.47)	--	--	828sh(0.94)	896 (4.04)	930sh(4.04)
14.	532 (1.59)	613 (0.54)	660 (1.39)	716 (1.94)	838 (0.31)	954 (0.29)
14.2H$^+$	558 (1.21)	--	--	712 (0.25)	878 (3.11)	925 (2.02)

that these are 26π aromatic systems with a porphyrin like behaviour in terms of a strong Soret like band in the region from 500-575 nm and Q-type bands in the region from 600-1100 nm thus making them more suitable for PDT application.[5] Specifically: (a) all the absorption bands are red shifted relative to corresponding 22π sapphyrins suggesting the extension of the conjugation in rubyrins;[4] (b) the ϵ-values vary significantly among the different rubyrins and the extent of variation depends on the number and nature of heteroatoms present in the core. For example; the ϵ-value for **6** in the Soret region is six times higher than that of **13** while the ϵ-value for **12** and **14** are comparable reflecting the electronic effect of the heteroatom present in the core. Addition of a dilute solution of TFA in CH_2Cl_2 leads to protonation of the pyrrole nitrogens forming the dication. Protonation leads to a red shift of the Soret band and a decrease in the number of Q-bands which is typical of *meso* aryl porphyrins. The red shift is attributed to the structural change occurring on protonation promoting resonance interaction between the β-pyrrolic hydrogens and the *meso* aryl substituent.[6]

The redox behaviour of heteroatom rubyrins was followed by cyclic voltammetric studies. These volt ammograms were recorded in CH_2Cl_2 containing 0.1M $TBAPF_6$ as the supporting electrolyte and the potential was scanned from -1.5V to +1.5V vs SCE. The electrochemical data are tabulated in Table 2. In general, rubyrins **6**, **12**, **13** and **14** exhibit two quasi reversible reductions (ΔE_P: 80-160mV) and one irreversible oxidation.

Table 2

Compound	$E_{1/2}^{ox_1}$ (V)	$E_{1/2}^{red_1}$ (V)	$E_{1/2}^{red_2}$ (V)	Δ_{redox} [a] (V)
2	--	-0.86	-1.05	--
3	0.86	-0.78	-1.41	1.64
6	--	-0.89	-1.06	--
12	0.53	-0.76	-0.92	1.29
13	0.55	-0.82	-0.92	1.37
14	--	-0.90	-1.10	--
$TPPH_2$	1.03	-1.23	-1.55	2.26

[a] calculated from difference in $E_{1/2}^{ox_1}$ and $E_{1/2}^{red_1}$

A comparision of the redox data with that of tetraphenylporphyrins reveal several interesting observations:[7] (a) easier oxidation and reduction, (b) stabilization of both HOMOs and LUMOs, (c) significant reduction in the HOMO-LUMO gap which accounts for the large red shift of the absorption bands of rubyrins relative to H_2TPP, (d) the difference in Δ_{redox} of 350mV between **3** and **12** suggests a substituent effect of different heteroatoms. Taken together, the electrochemical data suggest that the presence of different heteroatoms in the core significantly reduces the cavity size especially in the presence of larger S and Se atoms promoting weak interactions between the heteroatoms as observed for dithia and diselena porphyrins[8] thereby altering the electronic structure of the ring.

In conclusion, we have described the synthesis of four novel rubyrins containing different heteroatoms in the core. It has been shown that the substitution of heteroatoms alters the cavity size and electronic structure of the ring which is manifested in the optical and electrochemical properties. Preliminary studies on the protonated derivatives reveal that the rubyrins form stable complexes with anions[9] such as F^-, N_3^- and PO_4^{3-} and the details of these will be reported elsewhere.

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. The instrumentation used for UV-Visible, IR, ^{1}H NMR, ^{13}C NMR, Mass and elemental analysis were same as described previously.[10] Cyclic voltammetric and differential pulse voltammetric studies were performed on a PAR model 273A polarographic analyzer utilizing the three-electrode configuration of a Pt (Beckman) working electrode, a Pt mesh counter electrode and a commercially available saturated calomel electrode as the reference electrode interfaced with the computer. Half wave potentials were measured as the average of the cathodic and the anodic peak potentials.

2,2'-Biselenophene:(4)

To a solution of selenophene (1g, 7.63mmol) in 1:1 mixture of dry ether (20ml) and dry THF (20ml), n-butyllithium (5.4ml, 8.39mmol) was added at -70°C and allowed to stir for 2h at the same temperature. Then, $CuCl_2$ (1.85g, 13.7mmol) was added to the above mixture at -70°C followed by dry THF (20ml) and allowed to stir for 2h. The reaction mixture was quenched with saturated NH_4Cl solution at -30°C and extracted with ethyl acetate (100ml). The organic layers were combined and washed with brine (100ml) 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 (0.480g, 48% yield) identified as 2,2'-biselenophene. Anal.calcd. for $C_8H_6Se_2$: C, 36.95; H, 2.33, found C, 37.36; H, 2.12%. EI mass: m/z: 260 (100%)[M^+].

5,5'-Bis-(phenylhydroxymethyl)-2,2'-biselenophene diol:(5)

To a solution of N,N,N',N'- tetramethylethylenediamine (1.8ml, 11.4mmol) in dry n-hexane (90ml), n-butyllithium (7.3ml, 11.4mmol) was added followed by 2,2'-biselenophene (1g, 3.82mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for1h and later heated under reflux for 1h. The reaction mixture was then allowed to attain 25°C. Benzaldehyde (1ml, 9.53mmol) in dry tetrahydrofuran (25ml) was added dropwise to the reaction mixture at 0°C. After addition was over the reaction mixture was allowed to attain 25°C and saturated ammonium chloride solution was added and it was then extracted with ether or chloroform (100ml). The organic layers were combined and washed with brine (100ml) 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 0.940g, 52%; m.p.112°C. Anal.calcd. for $C_{22}H_{18}O_2Se_2$: C, 55.95; H, 3.84, found C, 56.32; H, 4.12%. ν_{max}(Nujol) 3500-3100(br), 2920, 2860, 1450, 1370, 1040 cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): δ:7.26-7.47 (m, 10H), 7.00-7.01 (d, J=3Hz, 2H), 6.88-6.89 (d, J=3Hz, 2H), 5.97 (s, 2H), 2.5 (brs, 2H). ^{13}C NMR (75.5MHz, $CDCl_3$): 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^+].

***Tetraselenarubyrin:*(6)**

5,5'-bis(phenylhydroxymethyl)-2,2'-biselenophene (1g, 2.12mmol) and pyrrole (0.15ml, 2.12mmol) in dry dichloromethane (800ml) was stirred under a nitrogen atmosphere for 15 min at room temperature. Tri fluoroacetic acid (0.16ml, 2.12mmol) was added to the above mixture. The solution was stirred for a further 1h under dark conditions. The resulting solution was opened to air and chloranil (0.781g, 3.18mmol) was added and the mixture was heated to reflux in a preheated oil bath at 50°C for 1h. After removal of the solvent, the crude product was purified by column chromatography (basic alumina). A violet band eluted with CH_2Cl_2 : EtOAc (95:5) gave a green lustrous solid identified as Tetraselenarubyrin.Yield 0.250g, 24%; m.p. decomposes above 350°C. Anal.calcd. for $C_{52}H_{32}N_2Se_4$: C, 62.41; H, 3.22; N, 2.80, found C, 62.18; H, 3.44; N, 2.96%. ^1H NMR (300MHz, $CDCl_3$):δ:12.15 (d, J=6Hz, 4H), 11.03 (d, J=6Hz, 4H), 9.31 (s, 4H), 8.61 (m, 8H), 8.02 (m, 12H). ^1H NMR (300MHz, $CDCl_3$/TFA):δ:12.15 (s, 4H), 11.15 (s, 4H), 9.33 (s, 4H), 8.78-8.76 (m, 8H), 8.23-8.14 (m, 8H). MS (Electro spray): m/z: 1003 (70%) [$(M+2)^+$].

***5,5'-Bis-(phenylhydroxymethyl)-2,2'-bifuran diol:*(8)**

To a solution of N,N,N',N'- tetramethylethylenediamine (2.02ml, 13.4mmol) in dry n-hexane (40ml), n-butyllithium (12.9ml, 20.1mmol) was added followed by 2,2'-bifuran (0.900g, 6.7mmol) under an argon atmosphere. The reaction mixture was stirred at -25°C for 2h. Benzaldehyde (1.52ml, 15mmol) in dry tetrahydrofuran (25ml) was added dropwise to the -40°C reaction mixture. After addition was over the reaction mixture was allowed to attain 25°C and saturated ammonium chloride solution was added and it was then extracted with ether or chloroform (100ml). The organic layers were combined and washed with brine (100ml) and dried over anhydrous Na_2SO_4. The crude product obtained on evaporation of the solvent was purified by column chromatography (Silica gel 100-200 mesh). A pale yellow fraction eluted with petroleum ether : EtOAc (75:25) gave a pale yellow solid identified as **8**. Yield 1.35g, 58%; m.p. 102°C. Anal.calcd. for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24; found C, 76.03; H, 5.39%. ν_{max}(Nujol) 3500-3100(br), 2920, 2860, 1450, 1370, 1180, 1015 cm^{-1}. ^1H NMR (60MHz, $CDCl_3$):δ:7.25-7.6 (m, 10H), 6.50-6.60 (d, J=6Hz, 2H), 6.25-6.35 (d, J=6Hz, 2H), 5.9 (s, 2H), 2.3-2.55 (brs, 2H).^{13}C NMR (75.5MHz, $CDCl_3$): δ:155.5, 146.2, 140.5, 128.4, 128.1, 126.6, 109.4, 106, 70. EI mass: m/z: 346 (45%)[M^+].

***5,5'-Bis-(phenylhydroxymethyl)-2,2'-bithiophene diol:*(9)**

To a solution of N,N,N',N'- tetramethylethylenediamine (2.71ml, 18mmol) in dry n-hexane (90ml), n-butyllithium (11.53ml, 18mmol) was added followed by 2,2'-bithiophene (1g, 6.01mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 1h and later heated under reflux for 1h. The reaction mixture was then allowed to attain 25°C. Benzaldehyde (1.52ml, 15mmol) in dry tetrahydrofuran (25ml) was added dropwise to the reaction mixture at 0°C. After addition was over the reaction mixture was allowed to attain 25°C and saturated ammonium chloride solution was added and it was then extracted with ether or chloroform (100ml). The organic layers were combined and washed with brine (100ml) and dried over anhydrous Na_2SO_4. The crude product obtained on evaporation of the solvent was recrystallized from dry toluene afforded the diol as a pale yellow solid. Yield 1.39g, 61%; m.p.126°C. Anal.calcd. for $C_{22}H_{18}O_2S_2$: C, 69.81; H, 4.79; found C, 70.32; H, 5.39%. ν_{max}(Nujol) 3600-3100(br), 2925, 2860, 1450, 1370, 1130, 1020 cm^{-1}. ^{1}H NMR (60MHz, $CDCl_3$):δ:7.2-7.68 (m, 10H), 6.80-6.90 (d, J=6Hz, 2H), 6.60-6.70 (d, J=6Hz, 2H), 5.9 (s, 2H), 2.2-2.45 (brs, 2H). ^{13}C NMR (75.5MHz, $CDCl_3$): δ: 147, 142.7, 137.4, 128.6, 128.1, 126.2, 125.5, 123.1, 72.4. EI mass: m/z: 378 (45%)[M$^+$].

***5, 15-Diphenyl-20, 21-dioxo-1-norbilane:*(10)**

A mixture of 5,5'-bis(phenylhydroxymethyl)2,2'-bifuran (0.600g, 1.73mmol) and pyrrole (4.8ml, 69.4 mmol) was degassed by bubbling with argon for 10 min then trifluoroacetic acid (0.01ml, 0.173mmol) was added. This mixture was stirred for 30 min at room temperature. It was diluted with CH_2Cl_2 (100ml), then washed with 0.1N 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, EtOAc:petroleum ether [12:88]). After the initial tailing material, a pale orange band eluted and gave a grey solid identified as **10**. Yield 0.645g, 84%; m.p. 150°C. Anal.calcd. for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30; found C, 81.32; H, 5.39; N, 6.12%. ν_{max}(Nujol) 3400, 2920, 2860, 1450, 1370, 1020cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ:8.02 (brs 2H), 7.21-7.35 (m, 10H), 6.81 (m, 2H), 6.40-6.41 (d, J=2Hz, 2H), 6.14-6.16 (d, J=4Hz, 2H), 6.05-6.07 (d, J=4Hz, 2H), 5.95 (s, 2H), 5.47 (s, 2H). ^{13}C NMR (75.5MHz, $CDCl_3$): δ: 155, 145.9, 140.5, 130.9, 128.6, 128.4, 127.1, 117.4, 109.4, 108.3, 107.4, 105.6, 44.4. EI mass: m/z: 444 (100%) [(M-1)$^+$].

***5,15-Diphenyl-20, 21-dithio-1-norbilane:*(11)**

A mixture of 5,5'-bis(phenylhydroxymethyl)2,2'-bithiophene (0.500g, 1.32mmol) and pyrrole (3.67ml, 52.9mmol) was degassed by bubbling with argon for 10 min then trifluoroacetic acid (0.01ml, 0.132mmol) was added. This mixture was stirred for 30 min at room temperature. It was diluted with CH_2Cl_2 (100ml), then washed with 0.1N 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, EtOAc:petroleum ether [12:88]). After the initial tailing material, a pale orange band eluted and gave a greenish yellow solid identified as **11**. Yield 0.555g, 88%; m.p. 142°C. Anal.calcd. for $C_{30}H_{24}N_2S_2$: C, 75.59; H, 5.08; N, 5.88; found C, 76.02; H, 5.39; N, 6.12%. ν_{max}(Nujol) 3400, 2920, 2860, 1450, 1370, 1020cm^{-1}. ^{1}H

NMR (200MHz, $CDCl_3$): δ:7.91 (brs 2H), 7.25-7.36 (m, 10H), 6.89-6.91(d, J=4Hz, 2H), 6.71 (s, 2H), 6.65-6.67 (d, J=4Hz, 2H), 6.15-6.16 (d, J=4Hz, 2H), 5.95 (s, 2H), 5.60 (s, 2H). ^{13}C NMR (75.5MHz, $CDCl_3$): δ: 145.9, 142.4, 136.7, 132.7, 128.6, 128.3, 127.2, 126.5, 122.8, 117.4, 108.4, 107.7, 45.9. EI mass: m/z: 476 (100%) [$(M-1)^+$].

***Dithiadioxarubyrin:*(12)**

5,5'-bis(phenylhydroxymethyl)-2,2'-bithiophene (0.200g, 0.529mmol) and 20,21-dioxatetrapyrro methane (0.235g, 0.529mmol) in dry dichloromethane (200ml) was stirred under nitrogen atmosphere for 15 min at room temperature. Trifluoroacetic acid (0.04ml, 0.529mmol) was added to the above mixture. The solution was stirred for a further 1h under dark conditions. The resulting solution was opened to air and chloranil (0.195g, 0.794mmol) was added and the mixture was heated to reflux in a preheated oil bath at 50°C for 1h. After removal of the solvent, the crude product was purified by column chromatography (basic alumina). A violet band eluted with CH_2Cl_2 : EtOAc (95:5) gave a green lustrous solid identified as dithiadioxarubyrin.Yield 0.095g, 23%; m.p. decomposes above 350°C. Anal.calcd. for $C_{52}H_{32}N_2O_2S_2$: C, 79.97; H, 4.13; N, 3.59, found C, 80.12; H, 4.42; N, 3.97. ^{1}H NMR (200MHz, $CDCl_3$):δ: 10.57 (brs, 2H), 9.90 (brs, 2H), 8.74 (brs, 2H), 8.54 (m, 6H), 8.27 (m, 4H), 7.82-7.89 (m, 12H), 7.44 (m, 4H). ^{1}H NMR (200MHz, $CDCl_3$/TFA):δ:10.63 (brs, 2H), 9.75 (brs, 2H), 8.82 (brs, 2H), 8.57 (m, 6H), 8.28 (m, 4H), 7.87 (m, 12H), 7.44 (m, 4H). MS (Electrospray) : m/z: 781 (100%) [M^+].

***Diselenadioxarubyrin*:(13)**

5,5'-bis(phenylhydroxymethyl)-2,2'-biselenophene (0.200g, 0.424mmol) and 20,21-dioxatetrapyrro methane (0.189g, 0.424mmol) in dry dichloromethane (200ml) was stirred under nitrogen atmosphere for 15 min at room temperature. Trifluoroacetic acid (0.03ml, 0.424mmol) was added to the above mixture. The solution was stirred for a further 1h under dark conditions. The resulting solution was opened to air and chloranil (0.156g, 0.636mmol) was added and the mixture was heated to reflux in a preheated oil bath at 50°C for 1h. After removal of the solvent, the crude product was purified by column chromatography(basic alumina). A violet band eluted with CCl_4 : CH_2Cl_2 (50:50) gave a purple solid identified as diselenadioxarubyrin. Yield 0.104g, 28%; m.p. decomposes above 350°C. Anal. calcd. for $C_{52}H_{32}N_2O_2Se_2$: C, 71.40; H, 3.69; N, 3.20, found C, 71.12; H, 3.86; N, 3.42. ^{1}H NMR (200MHz, $CDCl_3$):δ:10.05 (d, J=6Hz, 2H), 9.26 (d, J=4Hz, 2H), 8.42 (d, J=4Hz, 2H), 8.30 (d, J=6Hz, 4H), 8.11 (d, J=4Hz, 2H), 7.78 (m,14H), 7.36(m, 6H). ^{1}H NMR (200MHz, $CDCl_3$/TFA): δ:10.45 (brs, 2H), 9.65 (brs, 2H), 8.67 (m, 2H), 8.40 (m, 4H), 8.21 (m, 2H), 7.82-7.89 (m, 14H), 7.35 (m, 6H). MS (Electrospray): m/z: 877 (45%) [$(M+2)^+$].

***Dithiadiselenarubyrin:*(14)**

5,5'-bis(phenylhydroxymethyl)-2,2'-biselenophene (0.198g, 0.420mmol) and 20,21-dithiatetrapyrro methane (0.200g, 0.420mmol) in dry dichloromethane (200ml) was stirred under nitrogen atmosphere for 15 min at room temperature. Trifluoroacetic acid (0.03ml, 0.420mmol) was added to the above mixture. The solution was stirred for a further 1h under dark conditions. The resulting solution was opened to air and chloranil (0.155g, 0.630mmol) was added and the mixture was heated to reflux in a preheated oil bath at 50°C for 1h. After removal of the solvent, the crude product was purified by column chromatography (basic alumina). A violet band eluted with CH_2Cl_2 : EtOAc (95:5) gave green lustrous solid identified as dithiadiselenarubyrin. Yield 0.075g, 20%; m.p. decomposes above 350°C. Anal. calcd. for $C_{52}H_{32}N_2S_2Se_2$: C, 68.87; H, 3.56; N, 3.09. Found C, 69.02; H, 3.79; N, 3.24. ^{1}H NMR (300MHz, $CDCl_3$):δ:11.80 (d, J=6Hz, 2H), 11.55 (d, J=3Hz, 2H), 10.69 (d, J=6Hz, 2H), 10.40 (d, J=3Hz, 2H), 9.06 (d, J=6Hz, 2H), 9.00 (d, J=6Hz, 2H), 8.52 (m, 8H), 7.98 (m, 12H). ^{1}H NMR (300MHz, $CDCl_3$/TFA):δ:11.91 (d, J=4Hz, 2H), 11.82 (d, J=4Hz, 2H), 11.04 (d, J=4Hz, 2H), 10.73 (d, J=4Hz, 2H), 9.26(d, J=4Hz, 2H), 9.21 (d, J=4Hz, 2H), 8.67 (m, 8H), 8.19 (m, 12H). MS (Electrospray): m/z: 909 (20%) $[(M+2)^+]$.

Acknowledgement:

This work was supported by a grant from the Department of Science and Technology (DST), Government of India, New Delhi, to TKC.

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