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Synthesis of A_2B-type 22-oxacorroles bearing two different five-membered heterocycles at *meso* positions

Umasekhar Booruga and Mangalampalli Ravikanth*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

Dedicated to Professor Atsuhiro Osuka on the occasion of his 65th birthday.

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ABSTRACT: A series of 22-oxacorroles containing mixed substituents such as either two five-membered heterocycles and one six-membered aryl group or three five-membered heterocycles at three *meso* positions were synthesized by 3 + 2 oxidative coupling of appropriate 16-oxatripyrrane and *meso*-substituted dipyrromethane under mild acid catalyzed conditions. The identities of the 22-oxacorroles were confirmed by the respective molecular ion peaks in HR-MS spectra and the structures were deduced by detailed 1D and 2D NMR spectroscopy. NMR studies clearly showed upfield or downfield shifts of core pyrrole and furan protons and inner NH protons depending on the type of substituent present at the *meso* positions. All 22-oxacorroles absorb in the 410–655 nm region, and the position of the absorption bands depends on the type of *meso* substituents. The A_2B oxacorroles showed one broad and weak fluorescence band in the 600–700 nm region with low fluorescence quantum yields in the 0.05–0.12 range. Electrochemical studies revealed that the A_2B-type 22-oxacorroles are easier to oxidize and also easier to reduce than triphenyl 22-oxacorroles. Thus, the electronic properties of 22-oxacorroles were significantly altered when six-membered aryl groups were replaced with five-membered heterocycles as reflected in spectral and electrochemical measurements.

KEYWORDS: corroles, 22-oxacorrole, five-membered heterocycle, electrochemical studies, fluorescence.

INTRODUCTION

Corroles are aromatic tetrapyrrolic macrocycles where four pyrrole rings are connected with three *meso* carbons and possess one direct pyrrole–pyrrole linkage [1, 2]. Thus, corroles have one *meso* carbon fewer than porphyrins but contain three inner pyrrole NH atoms, unlike porphyrins which have two inner NH atoms. Hence, corroles have a greater ability to stabilize metals in higher oxidation states than porphyrins [3–5]. This is indeed shown by several studies demonstrating that corroles have ability to stabilize metals in higher oxidation states than porphyrins. Corroles, like porphyrins, have rich coordination chemistry, and many coordination complexes such as P(V) and Ge(IV) corroles are strongly fluorescent compounds with high fluorescence quantum yields [6]. Corroles can be modified further by replacing one or two pyrrole rings with other heterocycles such as thiophene, furan, selenophene and telluorophene and the resulting core-modified corroles or heterocorroles are expected to possesses different physicochemical properties from regular tetrapyrrolic corroles [7–10]. Interestingly, there are very few reports on heterocorroles because of lack of proper synthetic strategies and also partly due to their 'inherent instability.' In fact, to the best of our knowledge, only oxa- and thiacorroles have been synthesized and characterized so far, but the synthesis of many other heterocorroles are yet to be developed [11–12]. Among oxa- and thiacorroles, the chemistry of oxacorroles is relatively more explored because of their better-developed synthetic strategies and their high stability. *Meso*-tri(*p*-tolyl) 22-oxacorrole **1** was obtained

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*Correspondence to: Mangalampalli Ravikanth, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India, Email: ravikanth@chem.iitb.ac.in.

as a side product along with expanded porphyrin, 25-oxasmaragdyrin by (3 + 2) oxidative coupling of 16-oxatripyrrane and *meso*-tolyl dipyrromethane under mild acid-catalyzed conditions. *Meso*-triaryl 22-oxacorroles such as **1** are strongly fluorescent and show an ability to form coordination complexes [8]. Recently, we reported the synthesis of 22-oxacorroles containing one *meso*-pyrrolyl group such as compound **2** under the same (3 + 2) oxidative coupling conditions [12] and we used these corroles to prepare novel BODIPY-bridged 22-oxacorrole dyads by utilizing the reactivity of the α position of the *meso*-pyrrolyl group of 22-oxacorroles. We further developed a straightforward, simple strategy to prepare ABC-type 22-oxacorroles bearing three different five-membered heterocycles at the *meso* positions [13]. Our studies indicated that the electronic properties of 22-oxacorroles were significantly altered by replacing the six-membered aryl groups with three different five-membered heterocycles such as pyrrole, thiophene and furan [13]. In continuation of our work on 22-oxacorroles, herein we report synthesis and properties of different 22-oxacorroles containing mixed substituents such as a combination of a six-membered aryl group and five-membered heterocycles or a combination of different five-membered heterocycles at the *meso* positions and we compare the properties with appropriate *meso*-substituted 22-oxacorroles. The studies show that the properties of 22-oxacorroles are dependent on the type of substituents present at the *meso* positions.

EXPERIMENTAL

All chemicals were used as received unless otherwise noted. All solvents were of at least reagent grade and dried if necessary. The ^{1}H, ^{11}B, ^{19}F and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker 400 or 500 MHz instruments. The frequency of 101 and 126 MHz is used for the ^{13}C nucleus. Tetramethylsilane $[Si(CH_3)_4]$ was used as an internal standard for ^{1}H and ^{13}C NMR. Absorption and steady-state fluorescence spectra were obtained with a Cary series UV-vis/NIR spectrophotometer and a Varian–Cary Eclipse spectrofluorometer, respectively. The fluorescence quantum yields (Φ_f) were estimated from emission and absorption spectra by the comparative method at an excitation wavelength of 440 nm using H_2TTP ($\Phi_f = 0.11$) as the standard. Cyclic voltammetric studies were carried out with a BAS electrochemical system utilizing a three electrode configuration consisting of glassy carbon working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode. The experiments were done in dry CH_2Cl_2 using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Half-wave potentials were measured using DPV (differential pulse voltammetry) and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated *vs.* the saturated calomel electrode by the addition of ferrocene as an internal standard, taking $E_{1/2}$ (Fc/Fc^+) = 0.42 V *vs.* SCE. All the solutions were purged with argon gas prior to electrochemical and spectral measurements. High resolution mass spectra (HRMS) were recorded with a Bruker Maxis Impact and Q-TOF micro mass spectrometer. For UV-vis and fluorescence titrations, the stock solutions of all compounds (1×10^{-3} M) were prepared by using a HPLC grade chloroform solvent.

Synthesis of compounds 3–7

Samples of 16-oxaripyrrane (500 mg, 1.58 mmol) **8**, **12** and **13** and *meso*-heterocyclic-substituted dipyrromethane **9–11** and **14–16** were dissolved in CH_2Cl_2 (150 mL) and stirred under a nitrogen atmosphere for 5 min. A catalytic amount of TFA (12 μL, 0.106 mmol) was added and stirring was continued for a further 1.5 h under an inert atmosphere. DDQ (1.077 g, 4.74 mmol) was added and stirring was continued in open air for an additional 2 h. The solvent was removed under reduced pressure and the crude compound was subjected to silica gel column chromatography purification. The desired 22-oxacorrole was collected using petroleum ether/dichloromethane (3:1) to afford pure 22-oxacorroles **3**–**7** as purple solids in 6–12% yield.

***Compound* 3.** Yield 8%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H in ppm -1.55 (s, 2H, –NH), 2.9 (s, 3H, CH_3), 6.75 (d, 1H, *J* = 4.2 Hz, pyrrole ring), 6.80 (d, 1H, *J* = 3.0 Hz, pyrrole ring), 7.09 (s, 1H, pyrrole ring), 7.19 (s, 1H, pyrrole ring), 7.21 (d, 1H, *J* = 4.2 Hz, pyrrole ring), 7.50 (s, 1H, pyrrole ring), 7.65 (d, 2H, *J* = 6.32 Hz, aryl ring), 8.15 (d, 2H, *J* = 6.32 Hz, aryl ring), 8.49 (d, 1H, *J* = 4.3 Hz, pyrrole core), 8.51 (d, 1H, *J* = 5.04 Hz, pyrrole ring), 8.91–9.00 (m, 3H, pyrrole core, β-furyl), 8.95 (d, 1H, *J* = 4.5 Hz, pyrrole core), 9.15 (m, 2H, β-furyl and β-pyrrole), 9.09 (br.s, 1H, –NH), 9.39 (br.s, 1H, –NH).; ^{13}C NMR (100 MHz, $CDCl_3$; Me_4Si): δ_C in ppm 108.7, 110.0, 111.4, 116.0, 119.6, 119.5, 122.2, 123.5, 125.5, 126.5, 126.8, 130.2, 136.1, 137.7, 139.8, 141.5, 144.5, 151.7, 161.9; HR-MS calcd for $C_{34}H_{26}N_5O$ $(M + H)^+$ *m/z* 520.2132, observed 520.2132.

***Compound* 4.** Yield 12%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H in ppm -1.99 (s, 2H, –NH), 2.50 (s, 3H, $-CH_3$), 6.85 (d, 1H, *J* = 3.0 Hz, pyrrole ring), 6.95 (s, 1H, *J* = 4.6 Hz, pyrrole ring), 7.10 (s, 1H, pyrrole ring), 7.35 (d, 1H, *J* = 3.6 Hz, furyl ring), 7.40 (s, 1H, furyl ring), 7.60 (d, 2H, *J* = 6.32 Hz, aryl ring), 8.19 (d, 2H, *J* = 6.32 Hz, aryl ring), 8.55 (d, *J* = 4.0 Hz, 1H, furyl ring), 8.60 (d, 1H, *J* = 5.04 Hz, pyrrole ring), 8.95–9.00 (m, 3H, pyrrole core, β-furyl), 9.01 (d, 1H, *J* = 4.6 Hz, pyrrole core), 9.15 (m, 2H, β-furyl and β-pyrrole), 9.21 (d, 1H, J = 4.3, pyrrole core), 9.40 (br.s, 1H, –NH).; UV-vis (in CH_2Cl_2, λ_{max}/nm (log ε): 428 (5.7), 522 (4.2), 562 (4.1), 601 (4.5), 659 (4.9); λ_{em} (nm): 665. HR-MS calcd for $C_{34}H_{24}N_4O_2$ $(M + H)^+$ *m/z* 521.1972, observed 521.1970.

***Compound* 5.** Yield 9%. ^{1}H NMR (400 MHz; CDCl$_3$; Me$_4$Si): δ_H in ppm -2.0 (br s, 2H, –NH), 2.90 (s, 3H, –CH$_3$) 6.78 (d, 1H, J = 4.1 Hz, pyrrole ring), 7.00 (d, 1H, J = 3.0 Hz thiophene ring), 7.29 (d, 1H, J = 4.0 Hz, pyrrole ring), 7.50 (d, 1H, J = 4.6 Hz, pyrrole ring), 7.57 (d, 1H, J = 3.2 Hz, thiophene ring), 7.49 (d, 1H, J = 3.8 Hz, thiophene ring), 7.55 (d, 1H, J = 3.9 Hz, pyrrole core), 7.62 (d, 2H, J = 7.2 Hz, aryl ring), 7.99 (m, 1h, pyrrole core), 8.15 (d, 2H, J = 7.6 Hz, aryl), 8.59 (d, 1H, J = 4.2 Hz, core), 9.05–9.10 (multiplet, 4H, core), 9.09 (d, 1H, J = 4.0 Hz β-furyl), 9.11 (d, 1H, J = 4.4 Hz, pyrrole), 9.25 (br s, 1H, NH); UV-vis (in CH$_2$Cl$_2$, λ_{max}/nm (log ε): 423 (5.7), 505 (2.15), 537 (1.50), 593 (1.90), 645 (2.00): HR-MS calcd for C$_{31}$H$_{21}$N$_4$O$_2$S (M + H)$^+$ *m/z* 537.1744, observed 537.1742.

***Compound* 6.** Yield 8%. ^{1}H NMR (400 MHz; CDCl$_3$; Me$_4$Si): δ_H in ppm -2.60 (s, 2H, –NH), 6.79 (m, 1H, pyrrole), 7.10 (s, 2H, pyrrole ring, furyl ring), 7.30 (s, 2H, furyl ring), 7.59 (s, 2H, pyrrole), 7.89 (s, 1H, pyrrole), 7.99 (s, 1H, furyl) 8.19 (d, 2H, β-furyl, pyrrole ring), 8.25 (d, 2H, β-furyl, pyrrole ring), 8.39 (d, 2H, β-furyl, pyrrole ring), 9.10 (d, 2H, β-furyl, pyrrole), 9.19 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl$_3$; Me$_4$Si): δ_C in ppm 108.0, 108.3, 110.6, 115.2, 118.8, 121.1, 122.6, 124.7, 125.7, 126.1, 126.3, 128.0, 129.5, 135.4, 136.9, 139.0, 140.7, 143.7, 151.0, 161.2: UV-vis (in CH$_2$Cl$_2$, λ_{max}/nm (log ε): 425 (5.7), 522 (4.0), 565 (3.9), 601 (3.5), 658 (4.9). LR-MS calcd for C$_{31}$H$_{20}$N$_4$O$_3$ (M + H)$^+$ *m/z*, observed 496.2975.

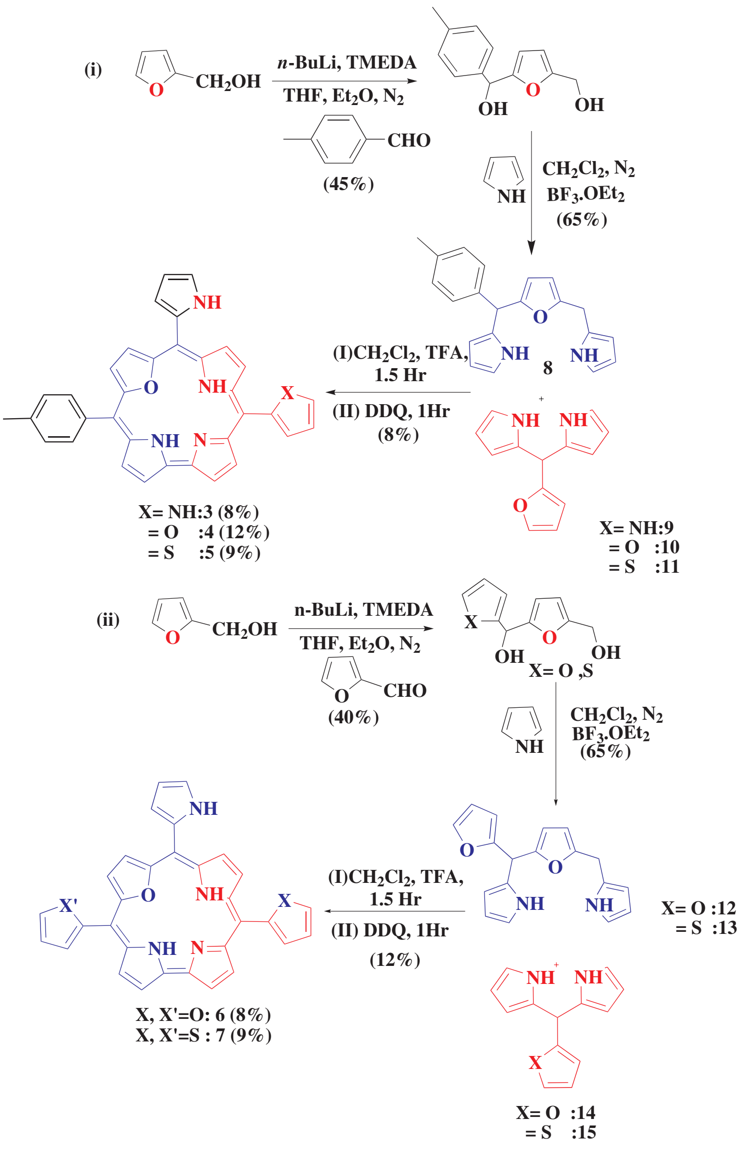
***Compound* 7.** Yield 9%. ^{1}H NMR (400 MHz; CDCl$_3$; Me$_4$Si): δ_H in ppm -2.55 (s, 2H, –NH), 7.15 (m, 4H, pyrrole, thianyl ring), 7.39 (s, 1H, pyrrole), 7.58 (d, 4H, pyrrole, thianyl ring), 8.30 (m, 2H, pyrrole), 8.39 (m, 2H, β-furyl, pyrrole ring), 8.61 (br.s, 4H, β-furyl, pyrrole), 9.05 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl$_3$; Me$_4$Si): δ_C in ppm 109.7, 117.0, 122.8, 123.2, 124.5, 126.5, 127.56, 127.85, 131.2, 131.5, 133.5, 134.8, 137.2, 140.8, 142.5, 152.7; UV-vis (in CH$_2$Cl$_2$, λ_{max}/nm (log ε)): 413 (5.4), 496 (3.1), 528 (3.1), 567 (3.5), 633 (4.2). HR-MS calcd for C$_{31}$H$_{20}$N$_4$OS$_2$ (M + H)$^+$ *m/z* 528.1102, observed 528.1106.

RESULTS AND DISCUSSION

The 22-oxacorroles containing mixed *meso*-substituents **3–7** (Chart 1) were synthesized as presented in Scheme.1. The required precursors, different dipyrromethanes such as 5-(*p*-tolyl)-dipyrromethane [12], 5-pyrrolyldipyrromethane **9** [15], 5-thienyldipyrromethane **10** [13] and 5-furyldipyrromethane **11** [13] and 16-oxatripyrranes such as 5-(*p*-tolyl)-10,15,17-trihydro-16-oxatripyrrane **8** [12], 5-(furyl)-10,15,17-16-oxatripyrrane **12** [13] and 5-(thienyl)-10,15,17-trihydro-16-oxatripyrrane **13** [13] were synthesized by following the literature procedures and the characterization data was matched with the reported data. 22-Oxacorroles containing two five-membered heterocycles and one six-membered aryl group present at the *meso*-positions (**3–5**) were synthesized by condensing one equivalent of 5-(*p*-tolyl)-10,15,17-trihydro-16-oxatripyrrane **8** with one equivalent of appropriate dipyrromethane, 5-pyrrolyl dipyrromethane **9**, 5-furyl dipyrromethane **10** and 5-thienyl dipyrromethane **11**, whereas 22-oxacorroles containing three mixed five-membered heterocycles at the *meso* positions (**6–7**) were synthesized by condensing appropriate 16-oxatripyrrane, 5-(furyl)-10,15,17-trihydro-16-oxatripyrrane **12** or 5-(thienyl))-10,15,17-trihydro-16-oxatripyrrane **13** with 5-furyl dipyrromethane **14** and 5-thienyl dipyrromethane **15** under mild acid-catalyzed inert conditions for 1 h followed by oxidation with DDQ in open air for an additional 1 h. The progress of the reaction was followed by TLC analysis and absorption spectroscopy. The crude compounds were subjected to alumina column chromatographic purification and afforded pure 22-oxacorroles containing mixed five/six-membered heterocycles/aryl groups at *meso* positions **3–7** in 8–9% yields. The identities of 22-oxacorroles **3–7** were confirmed by corresponding molecular ion peaks in HR-MS spectra and characterized in detail by 1D and 2D NMR spectroscopy.

The ^{1}H NMR and ^{1}H–^{1}H COSY NMR spectra of *meso*-bis-pyrrole-substituted 21-oxacorrole **3** are presented in Fig. 1. Compound **3** showed four sets of resonances in the region of 8.50–9.15 ppm corresponding to six *β*-pyrrole protons and two *β*-furan protons. The resonance at 9.15 ppm was identified as a *type-e* proton and showed cross-peak connectivity with a *type-d* proton of *β*-pyrrole appearing at 9.13 ppm. The resonance at 9.00 ppm, due to a *type-j* proton showed cross-peak connectivity with a *type-k* proton of the *β*-furyl ring. The resonance at 8.50 ppm, identified as *type-f* protons, showed cross-peak relation with a *type-g* proton. Furthermore, we also identified and assigned all the *meso*-pyrrolic protons which appeared in the region of 6.60–7.50 ppm by using 1D and 2D NMR spectroscopy. The inner NH resonance appeared as broad resonance at -1.70 ppm whereas the *meso*-pyrrolic NH protons appeared as two broad resonances at 9.09 and 9.39 ppm (Fig. 1a). Compounds **4–7** also exhibited similar NMR features and all resonances were identified and assigned using 1D and 2D NMR spectroscopy. Thus, 1D and 2D NMR techniques were very useful in deducing the molecular structures of 22-oxacorroles **3–7**.

Furthermore, it is noted that the electronic properties of 22-oxacorroles varied depending on the kind of substituents present at the *meso* positions, reflected in the upfield or downfield shifts in the proton resonances of certain core protons of macrocycles **3–7**. The comparison of ^{1}H NMR spectra of 22-oxacorroles **3–5** is shown in Fig. 1a and the relevant NMR data for macrocycles **3–7** is presented in Table 1. As noted from Fig. 2 and the data in Table 1, the protons experienced slight upfield or downfield shifts depending on the type of five-membered



Scheme 1. Synthesis of oxacorroles **3–7**

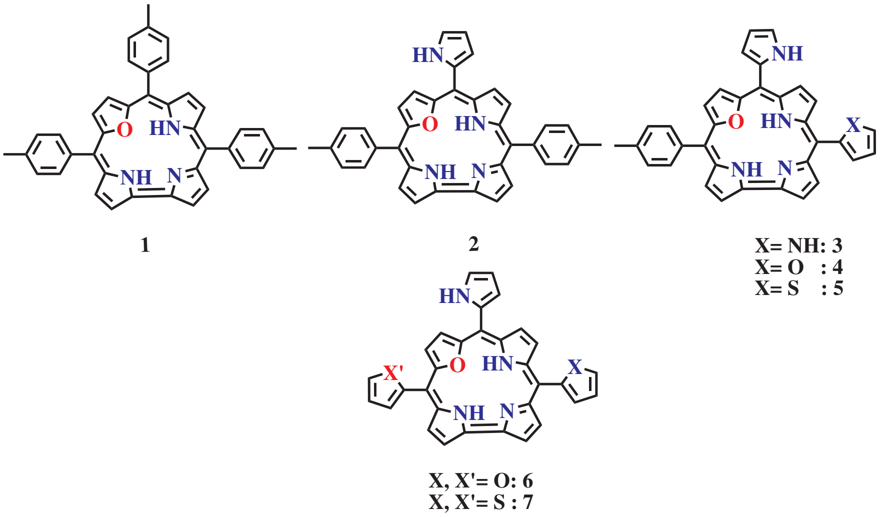


Chart 1. Structures of 22-oxacorroles

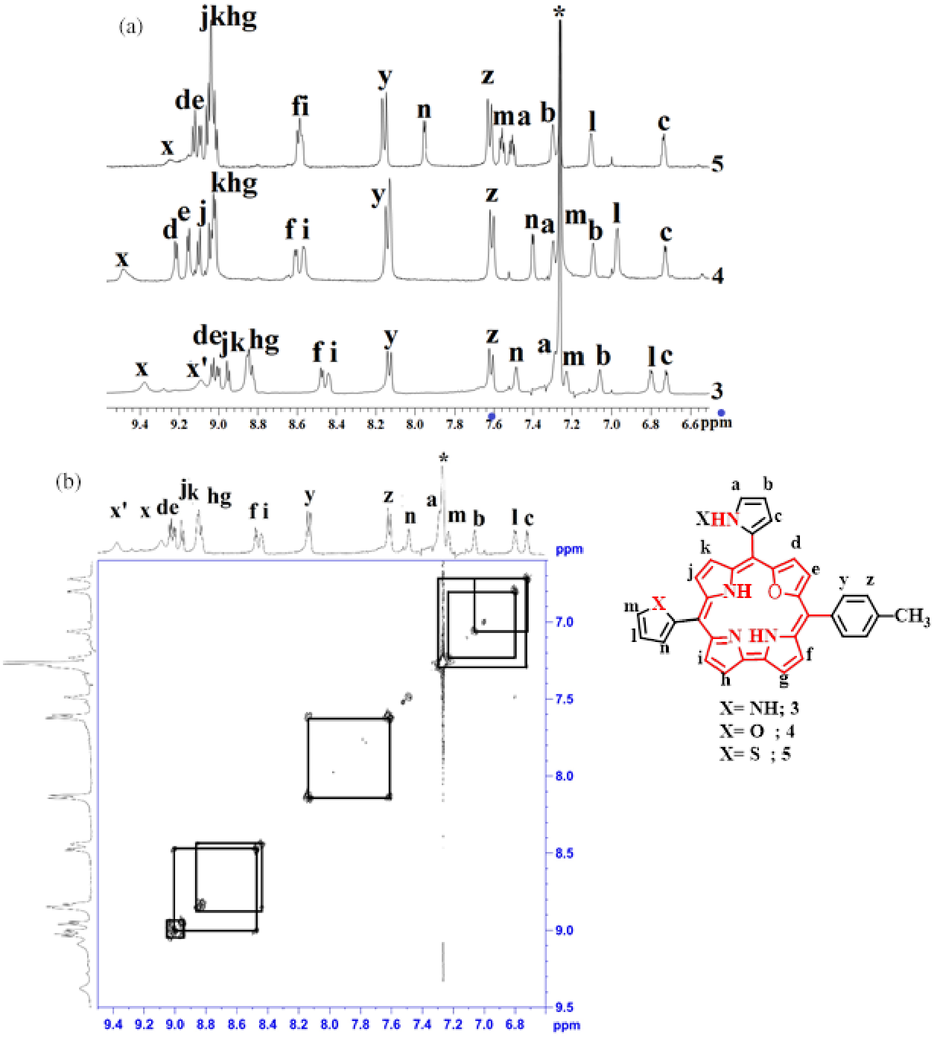


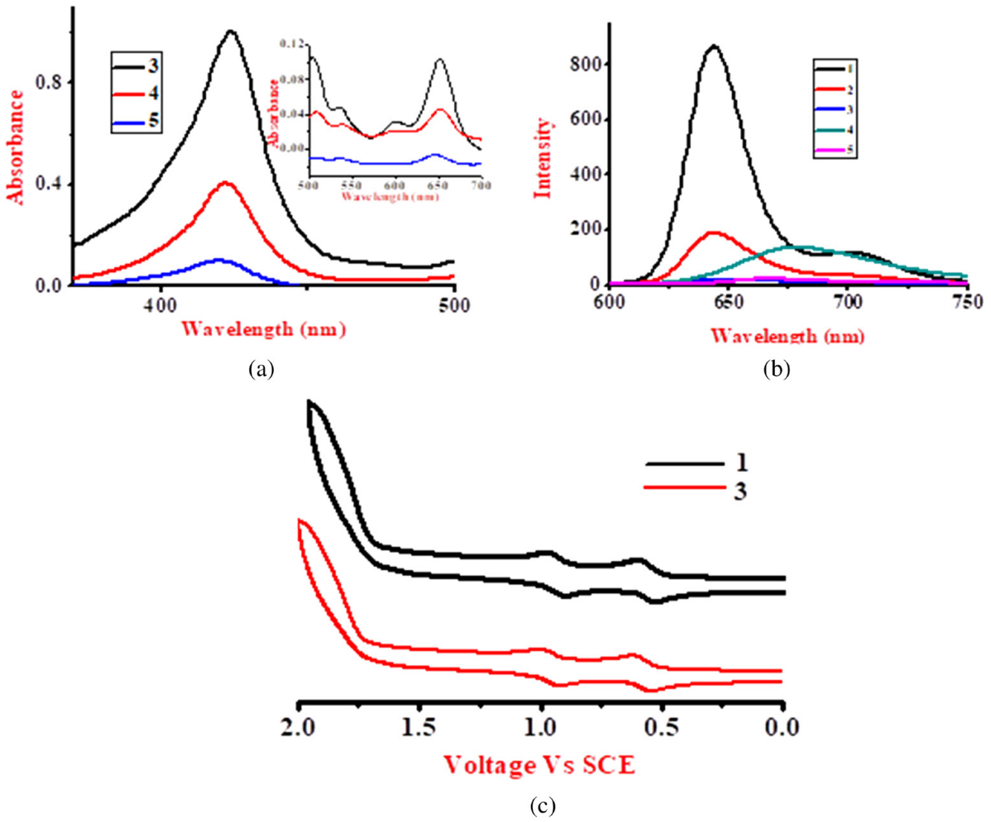
Fig. 1. Comparison of (a) ^{1}H NMR spectra of compound **3–5** in the selected region; (b) ^{1}H–^{1}H COSY spectrum of compound **3** recorded in CDCl$_3$ at room temperature

meso substituents present. For example, the inner NH proton in **3** was observed at -1.60 ppm which experienced upfield shift in **4** and **5** and appeared at ~ -2.00 ppm. Similarly, the β-furan protons in **3** appeared as two doublets at 9.13 and 9.15 ppm experienced downfield shifts in compounds **4** and **5**, appearing at ~9.20 and ~9.25 ppm respectively. Thus, the five-membered heterocycles at the *meso* positions alter the electronic properties of 22-oxacorroles.

Photophysical and electrochemical properties

The absorption, fluorescence and electrochemical properties of *meso*-substituted 22-oxacorroles **3–7** were studied along with 22-oxacorroles **1** and **2**. The comparison of absorption spectra of compounds **3–5** is presented in Fig. 2a and the data of all 22-oxacorroles **3–7** along with reference 22-oxacorroles **1** and **2** are presented in Table 2. In general, *meso*-substituted 22-oxacorroles showed one strong Soret band in the region of 410–425 nm and four weak Q bands in the region of 480–680 nm. It is clear from the data presented in Table 2 that compounds **1** and **2** exhibited one Soret band at 412 nm and four well-defined Q bands at 496, 529, 582 and 634 nm. This indicates that the presence of one pyrrole group in place of the aryl group at the *meso* position doesn't alter the electronic properties. However, upon the introduction of two or three five-membered heterocycles such as pyrrole/thiophene/furan in place of the six-membered aryl groups at the *meso* positions, bathochromic shifts were shown in both Soret and Q-band absorption maxima, indicating the alteration of the electronic properties of the 22-oxacorrole macrocycles.

The steady state fluorescence spectra of 22-oxacorroles **1–7** were recorded in CHCl$_3$ and the data are included in Table 2. A comparison of 22-oxacorroles **1–5** is presented



(a) (b)

(c)

Fig. 2. (a) Comparison of absorption spectra of **3**, **4** and **5** recorded in $CHCl_3$. The concentrations used were 1×10^{-5} M; (b) comparison of fluorescence spectra of **1–5** recorded in $CHCl_3$. The concentrations used were 1×10^{-5} M; (c) electrochemical redox data (V) of compounds **1** and **3** recorded in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte using a scan rate of 50 mV/s. $E_{1/2}$ values reported are relative to SCE

Table 1. Comparison of ^{1}H NMR chemical shift values (in ppm) of compound **1–7** recorded in $CDCl_3$ at room temperature

Com	β-furyl		β-pyrrole						Inner –NH
	H_d	H_e	H_{f7}	H_{g6}	H_{h5}	H_{i8}	H_{j3}	H_{k4}	
1	9.03 (d)	8.82 (d)	9.05 (d)	8.57 (d)	8.80 (d)	8.82 (d)	9.09 (d)	8.78 (d)	-1.91 (bs)
2	9.02 (d)	9.10 (d)	8.52 (d)	8.79 (m)	8.91 (d)	8.79 (d)	8.20 (d)	8.19 (m)	-1.85 (bs)
3	9.15 (s)	8.95 (d)	8.50 (d)	8.61 (d)	8.85 (d)	8.43 (d)	8.90 (d)	8.89 (d)	-1.70 (bs)
4	9.20 (d)	9.18 (d)	8.91 (d)	8.99 (m)	8.99 (m)	8.59 (d)	9.05 (d)	8.99 (m)	-1.99 (bs)
5	9.11 (m)	9.09 (d)	8.55 (d)	9.02 (m)	9.01 (d)	8.56 (m)	9.02 (m)	9.02 (m)	-1.92 (bs)
6	9.10 (d)	8.39 (d)	9.10 (d)	8.25 (m)	8.39 (d)	8.40 (d)	8.25 (d)	8.19 (d)	-2.00 (bs)
7	8.61 (s)	8.39 (d)	8.61 (s)	8.61 (s)	8.39 (d)	8.29 (d)	8.29 (d)	8.61 (s)	-1.90 (bs)

in Fig. 2b. Compound **1** is decently fluorescent and exhibits one band at 643 nm with a fluorescence quantum yield of 0.34. Upon introduction of one pyrrole in place of the aryl group at the *meso* position of 22-oxacorrole, the fluorescence maxima remained unaltered but the fluorescence quantum yield was reduced by ~50%. Compounds **3–5** are weakly fluorescent. The fluorescence maxima were bathochromically shifted by 10–35 nm compared to **1** and **2** and the fluorescence quantum yields were significantly reduced. The 22-oxacorroles **6** and **7** were non-fluorescent. Thus, the presence of five-membered heterocycles in place of six-membered aryl groups at the *meso* positions decreases the fluorescence properties of 22-oxacorroles.

The electrochemical properties of 22-oxacorroles **1–7** were investigated by cyclic voltammetry (CV) in dichloromethane using tetrabutylammonium perchlorate as supporting electrolyte. A comparison of cyclic voltammograms of oxacorrole **3** and oxacorrole **1** is shown in Fig. 2d and the data for compounds **1–5** is

Table 2. Photo physical data of Compounds **3–7** along with **1** and **2**

Compound	Soret band (nm)	Q band (nm) λ_{abs}/nm (log ε/$M^{-1}\cdot cm^{-1}$)	λ_{em}	Φ
1	412 (5.18)	496 (4.03), 529 (3.94), 582 (3.62), 634 (4.01)	643	0.34
2	412 (5.10)	456 (4.01), 497 (4.00), 533 (6.50), 634 (3.58)	643	0.15
3	423 (5.00)	504 (4.00), 537 (2.99), 599 (3.01), 653 (4.01)	643	0.12
4	422 (3.25)	508 (3.56), 538 (2.01), 600 (2.86), 654 (3.21)	677	0.14
5	423 (2.05)	505 (2.15), 537 (1.50), 593 (1.90), 645 (2.00)	655	0.07
6	423 (3.05)	507 (3.55), 534 (3.62), 589 (3.60), 640 (4.02)	—	—
7	423 (3.29)	506 (3.21), 533 (2.51), 584 (3.61), 639 (4.00)	—	—

Table 3. Electrochemical redox data (V) of Compounds **1–7** recorded in dichloromethane containing 0.1 M TBAP as supporting electrolyte using scan rate of 50 mV/s. $E_{1/2}$ values reported are relative to SCE

Compound	I	II&III	I	II
	E_{ox} (V)	E_{ox} (V)	E_{red} (V)	E_{red} (V)
1	0.90	1.10, 1.47	-1.70	-1.93
2	0.77	1.04, 1.24	-1.33	—
3	0.55	0.96	-1.16	-1.44
4	0.53	0.96	-1.14	-1.10
5	0.60	0.97	-1.17	-1.10
6	—	—	—	—
7	—	—	—	—

presented in Table 3. Unlike compound **1**, compound **3** showed four redox processes: two reversible oxidations and two reversible or quasi-reversible reductions. The comparison of redox potentials of compound **3** with those of compound **1** indicated that compound **3** is easier to oxidize and also easier to reduce than compound **1**. Furthermore, compounds **6** and **7** are not stable under the redox conditions.

CONCLUCIONS

We reported the first examples of mixed 22-oxacorroles containing a minimum of two five-membered heterocycles at the *meso* positions. The acid-catalyzed [3 + 2] condensation of appropriate tripyrrane and dipyrromethane yields A_2B and mixed-type 22-oxacorroles containing two or three five-membered heterocycles such as pyrrole, thiophene, furan and aryl groups at *meso* positions in 8–12% yields. All the compounds were characterized by HR-MS, 1D and 2D NMR spectroscopy, absorption, fluorescence and electrochemical measurement techniques. The absorption maxima and fluorescence quantum yields of the oxacorroles altered upon changing the heterocycles at the *meso* positions. The absorption bands appeared in the region of 410–650 with low fluorescence quantum yields (0.05–0.12). The absorption maxima were found to be dependent on the *meso*-heteroaryl substituents and the electrochemical studies reveal that the redox properties of 22-oxacorroles were significantly altered by replacing six-membered *meso*-aryl groups with different heterocycles. The oxacorroles are easier to oxidize and also easier to reduce than triphenyl 22-oxacorroles.

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