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Core-Modified Smaragdyrins: First Examples of Stable Meso-Substituted Expanded Corrole

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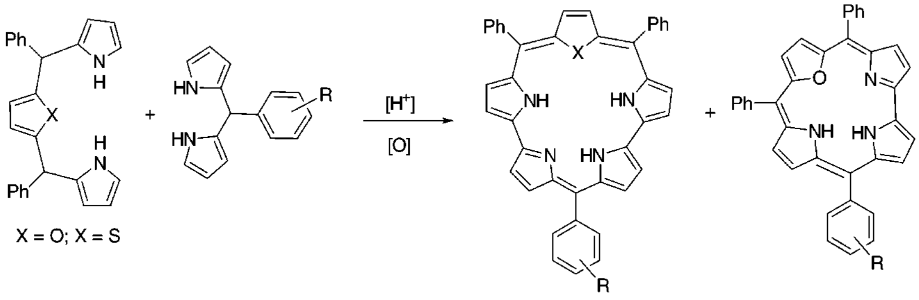
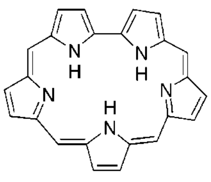
ABSTRACT



X = O, **1**; X = S, **2**

A synthetic access to the first members of expanded corroles 1 and 2 is achieved through formation of two direct pyrrole–pyrrole links by an oxidative coupling reaction. Spectroscopic and structural analysis reveal that 1 and 2 are 22Π aromatic macrocycles despite the nonplanar structure and properties resemble that of isocorroles rather than 22Π sapphyrins.

Sapphyrin **1** is an example of the simplest possible expanded porphyrin with 22Π electrons.[1] The existence of sapphyrins was been reported long ago, but their rich and diverse chemistry has been explored only recently after the development of efficient synthetic methodologies allowing their preparation in gram quantities. Removal of one meso carbon from the sapphyrin skeleton results in a new 22Π electron macrocycle with two direct pyrrole−pyrrole links. This structural principle is referred to as "smaragdyrin" **2** in the literature.[2,3] The structural relationship between **1** and **2** is analogous to that between a porphyrin and a corrole;



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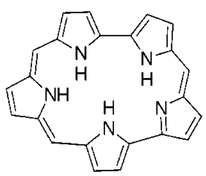

2

therefore, the chemistry of smaragdyrins is expected to resemble that of corroles.[4] Two previous attempts to syn-

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[1] For the recent reviews and papers on the expanded porphyrins, see: (a) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, *97*, 2267−2340. (b) Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted & Isomeric Porphyrins, Tetrahedron Organic Chemistry Series, Vol. 15*; Pergamon: New York, 1997. (c) Sessler, J. L.; Hoehner, M. C.; Gebauer, A.; Andrievsky, A.; Lynch, V. *J. Org. Chem.* **1997**, *62*, 9251−9260. (d) Paolesse, R.; Licoccia, S.; Spagnoli, M.; Boschi, T.; Khoury, R. G.; Smith, K. M. *J. Org. Chem.* **1997**, *62*, 5133−5137. (e) Srinivasan, A.; Reddy, M. V.; Narayanan, S. J.; Sridevi, B.; Pushpan, S. K.; Ravikumar, M.; Chandrashekar, T. K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2598−2601. (f) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Vij, A.; Roy, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3394−3397. (g) Pushpan, S. K.; Narayanan, S. J.; Srinivasan, A.; Mahajan, S.; Chandrashekar, T. K.; Roy, R. *Tetrahedron Lett.* **1998**, *39*, 9249−9252. (h) Rachlewicz, K.; Sprutta, N.; Chmielewski, P. J.; Latos-Grazynski, L. *J. Chem. Soc., Perkin Trans. 2* **1998**, 969−975. (i) Lash, T. D.; Richter, D. T. *J. Am. Chem. Soc.* **1998**, *120*, 9965−9966.

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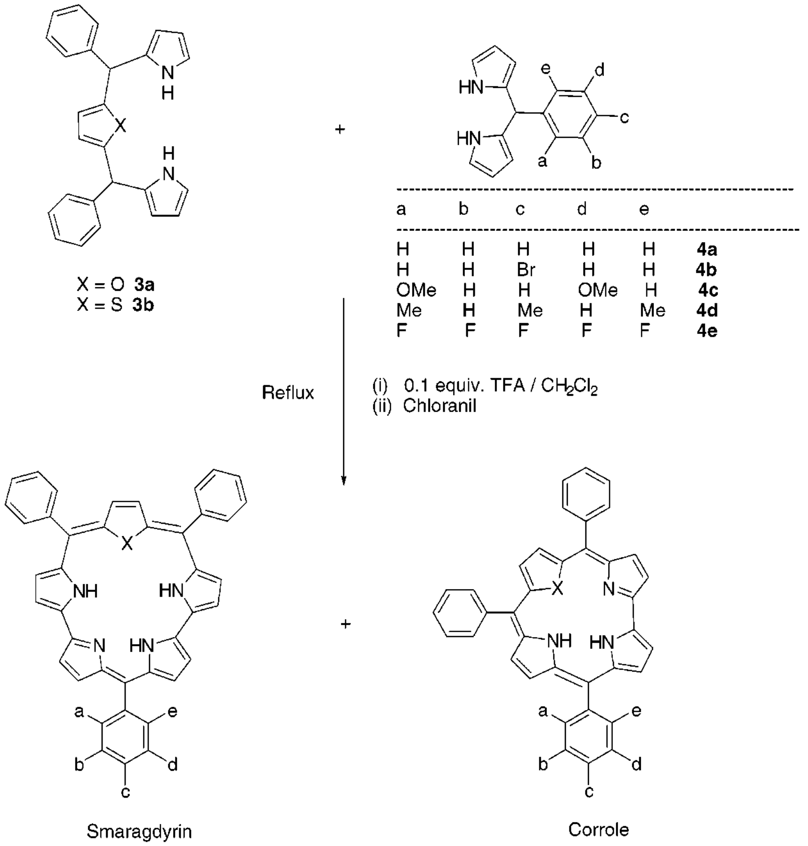
Scheme 1. Synthesis of Smaragdyrins and Corroles



a	b	c	d	e	
H	H	H	H	H	**4a**
H	H	Br	H	H	**4b**
OMe	H	H	OMe	H	**4c**
Me	**H**	Me	H	Me	**4d**
F	F	F	F	F	**4e**

X	a	b	c	d	e	
O	H	H	H	H	H	**5a**
O	H	H	Br	H	H	**5b**
O	OMe	H	H	OMe	**H**	**5c**
O	Me	H	Me	H	Me	**5d**
O	F	**F**	F	**F**	**F**	**5e**
S	H	**H**	H	H	H	**5f**

X	a	b	c	d	e	
O	H	H	H	H	H	**6a**
O	H	H	Br	H	H	**6b**
O	OMe	H	H	OMe	H	**6c**

thesize β-substituted smaragdyrins were only partially successful due to their inherent instability toward light and acid.[2,3] Very recently, Sessler and co-workers have observed that β-substituted smaragdyrins are highly unstable and reported the successful synthesis of an isomer of β-substituted smaragdyrin as a chloride salt.[5] In this Letter, we present the first synthesis of stable meso aryl substituted smaragdyrins by an acid-catalyzed oxidative coupling reaction of modified tripyrranes with meso aryl substituted dipyrromethanes (Scheme 1). It has been demonstrated that unlike sapphyrins the structure, coordination, and spectral behavior of smaragdyrins resemble those of corroles, thus qualifying them to be referred to as expanded corroles.[6]

To the best of our knowledge there are only two reports in the literature on the synthesis of meso aryl substituted corroles:[7] the acid-catalyzed condensation of benzaldehyde with 2 equiv of dipyrromethanedicarboxylic acid and the self-condensation of 3,4-dimethyl-2-(α-hydroxybenzyl)pyrrole-5-carboxylic acid. Both methods are confined to the synthesis of regular corroles and require Co^{3+} ion in the final step of the condensation. The key step in the synthesis of meso substituted aryl smaragdyrins is the introduction of two direct pyrole–pyrrole links. This can be achieved in two ways: (a) by using precursors containing pyrrole–pyrrole links or (b) through the formation of pyrrole–pyrrole link in the final step of condensation. The difficulty of synthesising precursors with direct pyrrole–pyrrole links lies in the inherent instability of the respective material.[2] In the present method, this problem has been solved by introducing the pyrrole–pyrrole link in the final step of condensation between the

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(2) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2111–2116.

(3) Bauer, V. J.; Clive, D. L. J.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429–6436.

(4) (a) Licoccia, S.; Paolesse, R. *Struct. Bonding (Berlin)* **1995**, *84*, 71–133. (b) Neya, S.; Ohyama, K.; Funasaki, N. *Tetrahedron Lett.* **1997**, *38*, 4113–4116. (c) Licoccia, S.; Divona, M. L.; Paolesse, R. *J. Org. Chem.* **1998**, *63*, 3190–3195.

(5) Sessler, J. L.; Davis, J. M.; Lynch, V. *J. Org. Chem.* **1998**, *63*, 7062–7065.

(6) Turcasarin also has been referred to as a possible expanded corrole. For details, see: Sessler, J. L.; Weghorn, S. J.; Lynch, V.; Johnson, M. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1509–1512.

(7) Paolesse, R.; Licoccia, S.; Bandoli, G.; Dolmella, A.; Boschi, T. *Inorg. Chem.* **1994**, *33*, 1171–1176.

easily available precursors. Accordingly, the TFA-catalyzed oxidative coupling between tripyrranes **3a** or **3b**[8a] with dipyrromethanes **4a**−**4e**[8b] gave smaragdyrin as the major product. The minor product is the corresponding corrole. The yields of smaragdyrin and corrole were dependent on the nature of the heteroatom in **3** and the meso-phenyl substituents in **4a**−**4e**. For example, **5a** and **6a** were isolated in 51% and 3% while **5c** and **6c** were isolated in 13% and 6%, respectively.

The analytical and mass spectral data and crystallographic analysis confirm the proposed composition of the new macrocycles. The electronic spectrum exhibit typical Soret type and Q-type absorption bands in the visible region. The red shift (32−64 nm) of all absorption bands in **5a** relative to **6a** confirms extended conjugation.[8c] The emission spectra show strong fluorescence, and **6a** exhibits a unusually high quantum yield ($\phi_f = 0.88$ relative to H_2TPP). ^1H NMR studies reveal a considerable aromatic character for smaragdyrins and corroles. The NH tautomerism in **5a** is rapid from room temperature up to −50 °C, and the three NH protons are exchanging sites between four bipyrrole nitrogen centers, indicating that the molecule adopts an symmetric conformation in solution with respect to the mirror plane passing through the methine bridge and the furan oxygen atom.[9] In contrast, **6a** exhibits asymmetric tautomerism where the NH proton adjacent to the furan ring is localized, and only the NH proton on the bipyrrolic ring is changing sites between the two nitogen atoms of the bipyrrole ring. This observation was confirmed by a 2D TCOSY spectrum.

The single-crystal X-ray analysis of **5a**[10] (Figure 1) reveals the nonplanarity of the smaragdyrin framework, which is mainly due to the strain imposed on the whole molecule by the introduction of an additional pyrrole ring, direct pyrrole−pyrrole interactions, and the steric repulsion between imino hydrogen atoms. Specifically, N2 and N3 are deviated below the mean plane (−0.0171 and −0.0041 Å) while N1 and N4 are located above the plane (0.0145 and 0.0120 Å, respectively). There are two crystallographically independent molecules in the unit cell with three molecules of solvent methanol trapped between the ring with weak interactions. The interplanar distance between the two rings is 6.92 Å. Furthermore, there are strong hydrogen bonding interactions between the protons on the nitrogens and the heteroatom (O1···H1(N1) 2.55 Å, O1···H4(N4) 2.61 Å, N3···H2(N2) 1.81 Å). Interestingly, the imino hydrogen atoms are localized on N1, N2, and N4 in solid state as in octaethylisocorrole.[9] The crystal structure of **6a**[11] is the first reported for free base meso phenyl corrole. **6a** exhibits a nonplanar structure with small deviations of heteroatoms from the mean plane (N1 0.0155, N2−0.0039, N3−0.0046, O1−0.0051 Å). The molecules arrange themselves into a spectacular columnar structure because of the $\Pi-\Pi$ interactions between the macrocycles with average plane to plane separations of 3.613 Å (Figure 2). Both in **5a** and **6a** the C_α- -C_β distances of heterocyclic rings are greater than C_β- -C_β distances, suggesting the aromatic nature of the macrocycles. A similar trend was observed in the structures of corrole[12] and isocorrole.[9]

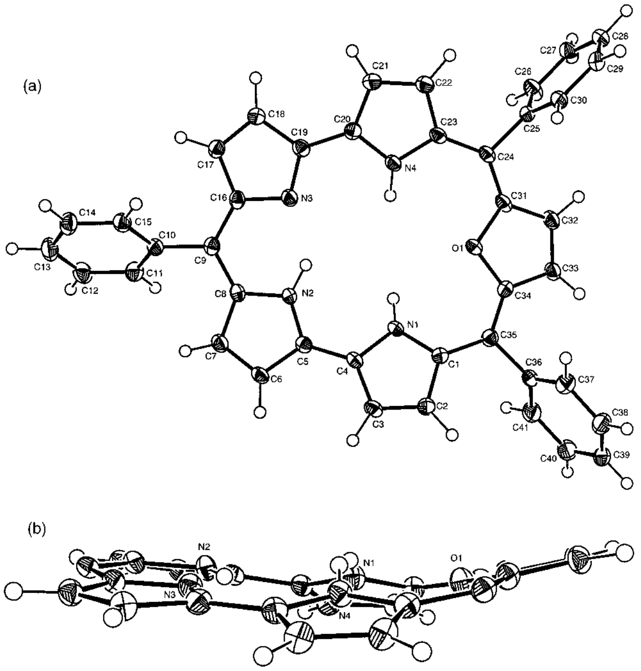

Figure 1. Crystal structure of **5a** (top, plane view; bottom, side view;meso phenyl rings are omitted for clarity). Selected distances [Å]: C1−N1 1.378(3), C1−C2 1.411 (3), C2−C3 1.384(3), C4−C5 1.421(3), C19−N3 1.346(3), C31−C32 1.413(3), C32−C33 1.354(3), N1···N2 2.877, N2···N3 2.636, N3···N4 2.961, N4···O1 3.010, O1···N1 3.078.

Studies on the metalation reactions of **5a** with transition metals, which are currently in progress, reveal formation of stable metal complexes, and the spectral properties resemble that of metallo corroles.[13] Specifically, in the Rh(I) carbonyl

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[8] (a) Sridevi, B.; Narayanan, S. J.; Srinivasan, A.; Reddy, M. V.; Chandrashekar, T. K. *J. Porphyrins Phthalocyanines* **1998**, *2*, 69−78. (b) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440. (c) Narayanan, S. J.; Sridevi, B.; Srinivasan, A.; Chandrashekar, T. K.; Roy, R. *Tetrahedron Lett.* **1998**, *39*, 7389−7392.

[9] Isocorrole also exhibit a similar type of tautomerism. For details, see: (a) Will, S.; Rahbar, A.; Schmickler, H.; Lex, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1390−1393. (b) Vogel, E.; Binsack, B.; Hellwig, Y.; Erben, C.; Heger, A.; Lex, J.; Wu, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2612−2615.

[10] Crystal data for **5a**: $C_{85}H_{68}N_8O_5$, $M_r = 1281.47$ g mol^{-1}; crystals from CH_2Cl_2/CH_3OH (1/1); deep purple blocks of dimensions 0.40 × 0.20 × 0.20 mm^3; triclinic, space group P-1, $a = 11.7055(2)$, $b = 14.8302(1)$, c = 19.6421(4) Å, $\alpha = 80.137$ (1), $\beta = 79.278(1)$, $\gamma = 80.576(1)°$, $V = 3269.95(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.302$ g cm^{-3}; $T(K) = 98$; $F(000) = 1348$; $\mu_{Mo} = 0.082$ mm^{-1}; 14489 independent reflections ($3.6 < 2\theta < 56.6°$); R1 = 0.0541 for 8571 data $I > 2\sigma(I)$, $wR_2 = 0.1232$ for all data. The data were collected utilising a Siemens SMART system, complete with three cycle goniometer and CCD detector as described earlier.

[11] Crystal data for **6a**: $C_{37}H_{25}N_3O$, $M_r = 527.60$ g mol^{-1}; crystals from toluene/CH_3OH (1/1); deep purple rods of dimensions 0.70 × 0.15 × 0.10 mm^3; orthorhombic, space group $P2_12_12_1$, $a = 6.4881(10)$, $b = 18.0075(2)$, $c = 22.7207(3)$ Å, $V = 2654.56(6)$ Å^3; $Z = 4$, $\rho_{calcd} = 1.320$ g cm^{-3}; $T(K) = 98$; $F(000) = 1104$; $\mu_{Mo} = 0.080$ mm^{-1}; 4659 independent reflections ($2.9 < 2\theta < 50.00°$); R1 = 0.0762 for 3247 data $I > 2\sigma(I)$, $wR_2 = 0.1870$ for all data. For details, see the Supporting Information.

[12] Harrison, H. R.; Hodder, O. J. R.; Hodgkin, D. C. *J. Chem. Soc. B* **1971**, 640−645.

[13] Will, S.; Lex, J.; Vogel, E.; Schmickler, H.; Gisselbrecht, J. P.; Haubtmann, C.; Bernard, M.; Gross, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 357−361.

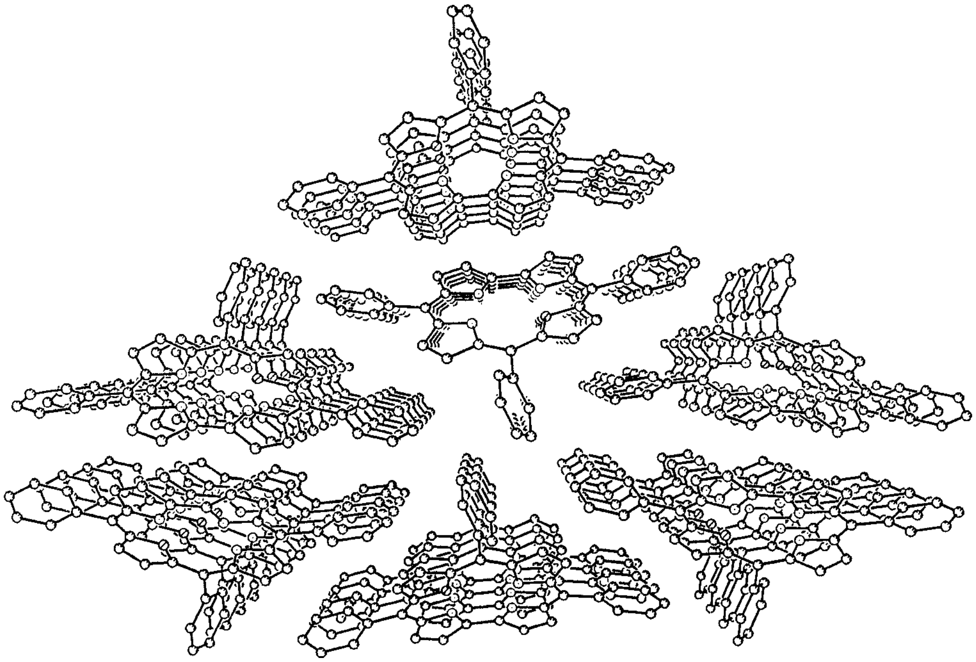

Figure 2. The molecular packing diagram of **6a** showing the columnar arrangement due to the Π−Π interactions. The interplanar distance between the two oxacorrole molecules is 3.613 Å.

complex, only one amino and one imino nitrogen of **5a** are coordinated. The details of their electronic structure and coordination behavior will be reported soon. In conclusion, it is anticipated that this research effort in the field of expanded corroles, which has long stood in the shadow of expanded porphyrins, will now receive renewed impetus as a result of easy synthesis of stable meso-aryl expanded corroles.

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Supporting Information Available: Characterization data, general method of synthesis, and table of yield data of compounds **5a**−**5f** and **6a**−**6c** along with tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic themal parameters for compounds **5a** and **6a** and ORTEP plots for the top view and side view of **6a** and the Rh(I) carbonyl complex of **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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