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Effect of Meso Aryl Substituents on the Synthesis of Core-Modified Expanded Porphyrins

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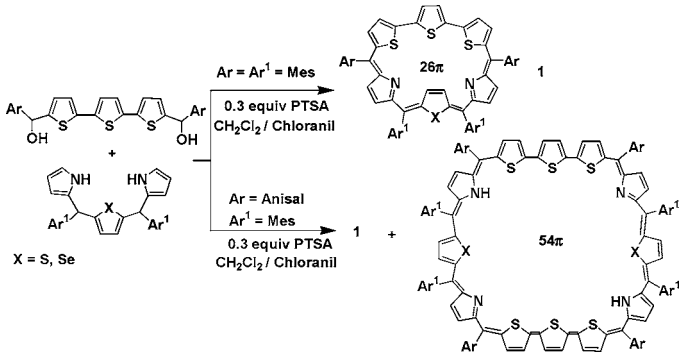
ABSTRACT



Synthesis and characterization of core-modified [26]hexaphyrin (1.1.1.1.0.0). A meso aryl rubyrin isomer and a new 54π-modified dodecaphyrin are reported.

Expanded porphyrins continue to attract the attention of synthetic chemists because of their diverse applications in material science, in molecular recognition, in medicine, and as anion binding agents.[1] Rubyrin **1** is a class of compound in which six pyrrole rings are linked to each other through four meso bridges. Unlike **1**, the meso aryl rubyrins **3**−**6** in which the pyrrole rings are unsubstituted exhibit structural diversity.[2] Depending upon the nature of the link and the heteroatom present in the cavity, two structural congeners, normal as in **5** and inverted as in **3**, **4**, and **6**, are known in the literature[3] (Figure 1). Sessler and co-workers reported the synthesis of **2** by an acid-catalyzed condensation reaction of diphenyltripyrrane with diformylhexamethylterpyrrole by cleverly choosing two precursors: one of them is a β-sub-

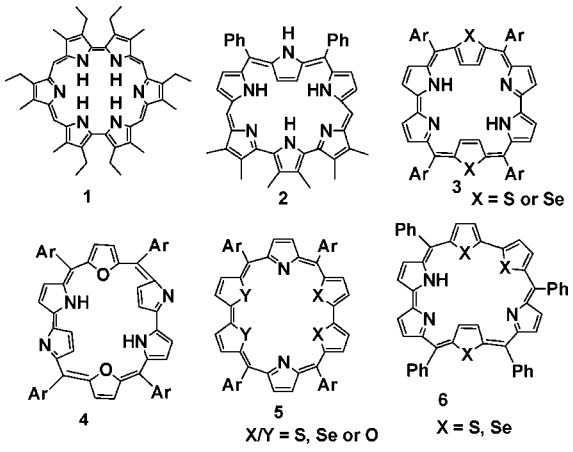


Figure 1. Different rubyrin isomers known in the literature.

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(1) (a) Sessler, J. L.; Weghorn, S. J. Expanded porphyrins. In *The Porphyrin Handbook*; Kadish, K. M, Ed.; Academic Press: San Diego, 2000; Vol. 2 and references cited therein. (b) Chandrashekar, T. K.; Venkatraman, S. *Acc. Chem. Res.* **2003**, *36*, 677. (c) Sessler, J. L.; Gebauer, A.; Weghorn, S. J. In *Expanded Porphyrins*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; San Diego, 2000. (d) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, *97*, 2267.

(2) Narayanan, S. J.; Srinivasan, A.; Sridevi, B.; Chandrashekar, T. K.; Senge, M. O.; Sugiura, K.-I.; Sakata, Y. *Eur. J. Org. Chem.* **2000**, 2357.

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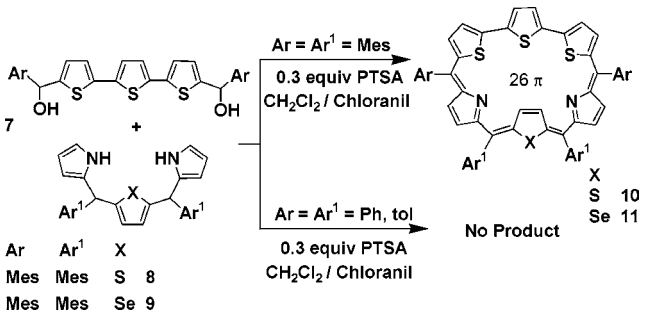
stituted pyrrole derivative, and the other precursor is a meso phenyl substituted derivative.[4] Therefore, in **2**, the pyrrole ring adjacent to meso phenyl substituents is inverted. These studies clearly reveal that the structure of the rubyrins is dependent upon the meso substituents present in the precursors before the condensation or coupling reaction. To understand this aspect further, we have looked into this condensation reaction using different meso substituents on the precursors, the diols, and the tripyrranes.

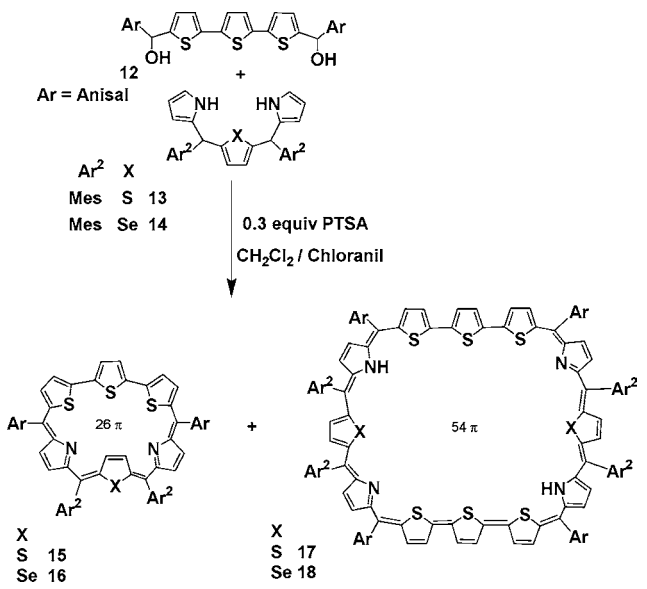
In this letter, we have shown that the nature of the expanded porphyrin and its structure depend on the meso substituents present on the precursors. It has been shown that a new isomer of rubyrin (**10** and **11**) can be obtained when at least one of the meso substituents is mesityl in one of the precursors (Scheme 1), whereas the change of mesityl

Scheme 1



substituents with a *para*-methoxy substituent in the terthiophene diol results in the formation of a [3 + 3 + 3 + 3] condensation product which is 54π octathia dodecaphyrin **17** and hexathiabiselena dodecaphyrin **18** in addition to the expected tetrathia rubyrin **15** and terthiaselena rubyrin **16** (Scheme 2).

Scheme 2



In the present synthesis, an efficient approach involving a [3 + 3] acid-catalyzed condensation[5] of terthiophene diol[6] **7** and tripyrranes[7] **8** and **9** in the presence of 0.3 equiv of *para*-toluenesulfonic acid (PTSA) in dry dichloromethane in the dark at room temperature was applied. After 90 min of stirring under a nitrogen atmosphere followed by chloranil oxidation in air, purification by column (alumina, grade III) chromatography using dichloromethane/hexane (1:4) as eluent gave **10** and **11** in 20−25% yield. The advantage of this methodology is the isolation of a single product leading to easy purification by column chromatography. With 0.3 equiv of acid concentration, we did not observe any partial acidolysis of the precursor, tripyrrane, leading to the formation of other products also during the reaction. A procedure similar to that described above was followed by using terthiophene diol **12** and tripyrranes **13** and **14**, and we got the expected tetrathia rubyrin **15** and terthiaselena rubyrin **16** in 15% yield and octathia dodecaphyrin **17** and hexathiabiselena dodecaphyrin **18** in 6 and 8% yield. It is important to note here that formation of a 12-membered macrocycle, i.e., dodecaphyrin, was achieved only when a meso aryl group in the terthiophene diol was *para*-methoxy. The exact reason for the formation of this compound only with the *para*-methoxy group is not yet established.

The FAB mass spectra and the detailed ^{1}H and 2D NMR spectral analyses of **10** and **11** confirmed the proposed compositions. Hexaphyrin **10** exhibited its parent ion peak at $m/z = 981$ (M^+), and dodecaphyrin **17** exhibited its parent ion peak at $m/z = 2011$ (M^+).

Both the free base and protonated forms of hexaphyrin exhibit well-resolved peaks in ^{1}H NMR at room temperature, and all the peaks were assigned. Specifically, the ^{1}H NMR spectrum of **10** taken in $CDCl_3$ revealed four sets of doublets between 7.61 and 9.61 ppm, integrating to two protons each, which are assigned to the four magnetically distinct β-CH protons. This was further confirmed by 2D NMR. A singlet at 9.75 ppm is ascribed to the β-CH protons of the central thiophene ring of the terthiophene unit, and a singlet at 7.26 ppm is ascribed to the phenyl CH protons of the mesityl ring. As anticipated, the heterocyclic ring opposite to the

(3) (a) Srinivasan, A.; Reddy, V. M.; Narayanan, S. J.; Sridevi, B.; Pushpan, S. K.; Kumar, M. R.; Chandrashekar, T. K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2598. (b) Srinivasan, A.; Pushpan, S. K.; Kumar, M. R.; Chandrashekar, T. K.; Roy, R. *Tetrahedron* **1999**, 6671. (c) Simi, K. P.; Venkataramana, G. A.; Sundararaman, V.; Alagar, S.; Akhilesh, K. G.; Chandrashekar, T. K. *Tetrahedron Lett.* **2001**, *42*, 3391.

(4) Sessler, J. L.; Seidel, D.; Bucher, C.; Lynch, V. *Chem. Commun.* **2000**, 1473.

(5) A typical procedure for the condensation involves stirring of the mesityl-terthiophene diol (0.30g, 0.55 mmol) and 16 tripyrrane (0.27g, 0.55 mmol) in dry dichloromethane (200 mL) under a nitrogen atmosphere for 5 min at room temperature. Then, *para*-toluenesulphonic acid (0.03g, 0.165 mmol) was added to the above mixture. The solution was stirred for an additional 90 minutes. Chloranil (0.410 g, 1.65 mmol) was added, and the reaction mixture was exposed to air and refluxed for a further 90 min. The solvent was evaporated in a vacuum. The residue was purified by chromatography on a basic alumina column. The first red band which eluted with dichloromethane/petroleum ether (1:4) gave **10** in 22.2% yield (0.110 g).

(6) Anand, V. G.; Pushpan, S. K.; Srinivasan, A.; Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Roy, R.; Joshi, B. S. *Org. Lett.* **2000**, *2*, 3829.

(7) Lash, T. D. *Chem.−Eur. J.* **1996**, *2*, 1197.

terthiophene unit is inverted in free base as well as in protonated forms.

In the free base, the inner CH protons of the inverted thiophene ring were not seen even at − 70 °C suggesting a rapid rotation of the ring; however, after protonation with TFA, the inner CH protons resonate as a sharp singlet at −3.64 ppm and the inner NH protons resonate as a broad singlet at −3.21 ppm. These data indicate a diatropic ring current for **10**. The ^{1}H NMR spectra of **17** and **18** were not well-resolved at room temperature; however, fairly well-resolved spectra were obtained in CD_2Cl_2 upon lowering the temperature to 213 K for **17** and **18** in strong support of the well-known fact that larger macrocycles exhibit conformational flexibility; hence, at room temperature, well-resolved peaks could not be obtained (see the Supporting Information). Specifically, the ^{1}H NMR spectrum of **18** in CD_2Cl_2 at 213 K was well-resolved. The peaks in the region 6.0−8.2 ppm have been assigned to the phenyl and β-CH protons of the heterocyclic units. The peak at 3.9 ppm was assigned for methoxy protons, whereas the peaks in the region 1.2−2.4 ppm have been assigned to the methyl protons of the meso mesityl substituents.

Additional evidence for the aromatic nature comes from UV−visible spectral data. The absorption spectrum of free base hexaphyrin **10** exhibited a sharp Soret-like band at 527 nm ($\epsilon = 1.97 \times 10^5$ M^{-1} cm^{-1}) and multiple Q-bands in the region 600−730 nm, and dodecaphyrin **18** exhibited a Soret-like band at 604 nm ($\epsilon = 1.16 \times 10^5$ M^{-1} cm^{-1}). One Q-band at 744 nm confirmed the porphyrinoid nature of macrocycles. The 77 nm shift of the Soret band from **10** to **18** is in line with the extension of π-conjugation from 26π to 54π (Figure 2).

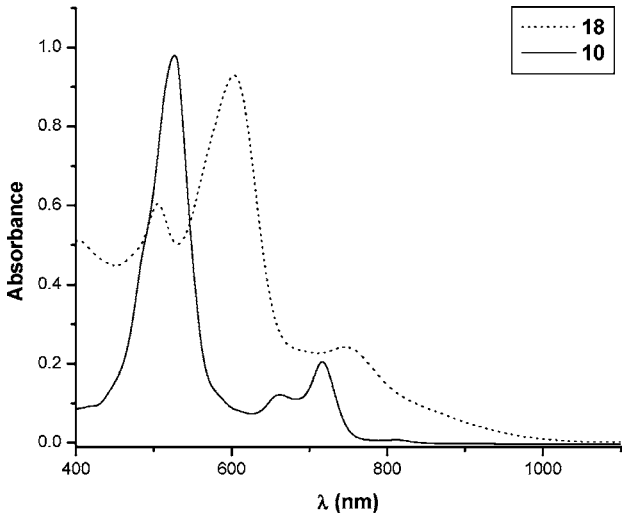


Figure 2. UV−vis spectra of the free base of hexaphyrin **10** and dodecaphyrin **18** in CH_2Cl_2.

Protonation results in further red shifts of the Soret band and the Q-bands. For example, protonation of **10** upon addition of an excess amount of TFA in CH_2Cl_2 led to a red shift, splitting and intensifying the Soret-like band to 558 nm ($\epsilon = 2.62 \times 10^5$ M^{-1} cm^{-1}) and 607 nm ($\epsilon = 1.61 \times 10^5$ M^{-1} cm^{-1}). Protonation of **18** led to a red shift in the Soret-like band to 710 nm ($\epsilon = 1.23 \times 10^5$ M^{-1} cm^{-1}). Similar red shifts are observed in Q-band region (Figure 3).

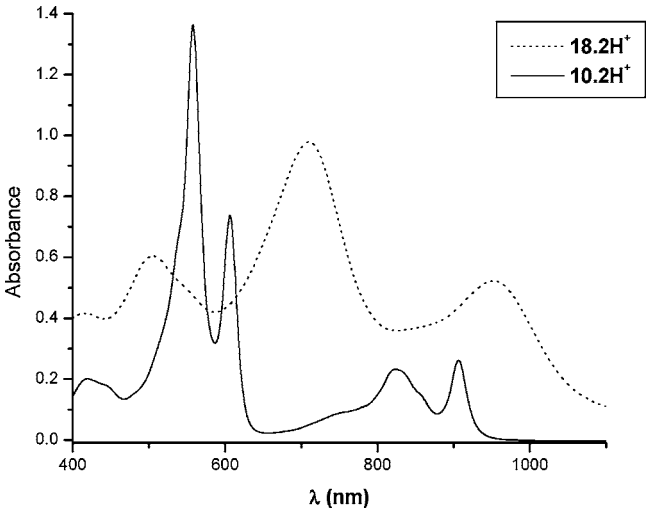


Figure 3. UV−vis spectra of protonated hexaphyrin **10** and protonated dodecaphyrin **18** in CH_2Cl_2.

These absorption bands of hexaphyrin are found to be approximately 25−50 nm red shifted relative to the all-aza analogues, due to the substitution of heteroatoms in the macrocycle core.

Further confirmation of the molecular structure of synthesized hexaphyrin came from single-crystal X-ray analysis[8] of the protonated form of **10** (CCDC-612135). The structure depicted in Figure 4 shows that the thiophene ring opposite

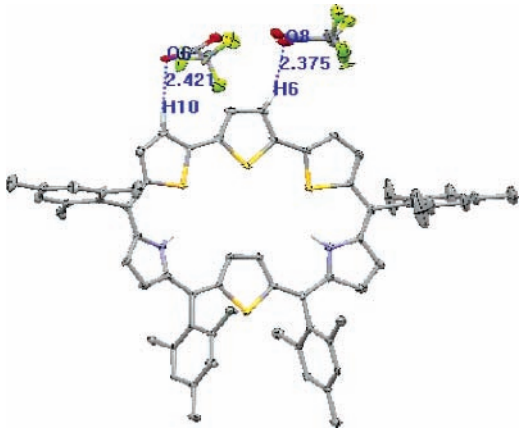


Figure 4. Ortep diagram of TFA-bound hexaphyrin **10**.

to the terthiophene unit is inverted. There are two molecules in an asymmetric unit. There are two C−H−O interactions

[C6−H6−O8, 2.37 Å, 152°; C10−H10−O6, 2.42 Å, 169°]. There is one more C−H−O interaction [C70−H70−O1, 2.49 Å, 163°] with other molecules present in the asymmetric unit (see Supporting Information).

In summary, we have described the syntheses of two new heteroatom substituted aromatic core-modified hexaphyrins and a new 54π dodecaphyrin. The meso aryl group plays an important role, and changing of the meso mesityl group with the meso *para*-methoxy group in diol results in the formation of a 12-membered ring apart from the expected six-membered ring. Further studies to apply this strategy in the synthesis of other new expanded porphyrins and studies on their anion and cation binding to exploit their application as receptors and nonlinear optical properties are underway.

(8) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.

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Supporting Information Available: Experimental procedures and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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