ORGANIC
LETTERS

2011
Vol. 13, No. 9
2498–2501

meso-Aryl Triphyrin(2.1.1)

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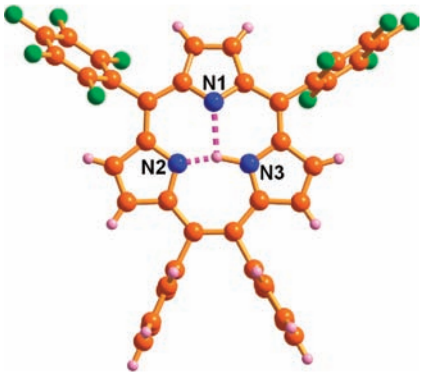
Received March 21, 2011

ABSTRACT



Synthesis, spectral, and single-crystal X-ray structural analysis of *meso*-aryl triphyrin(2.1.1) featuring three pyrrole rings and four *meso*-aryl rings are described. The title compound represents the first example of a ring-*contracted meso*-aryl β-unsubstituted free-base triphyrin containing only pyrrole rings reported to date and generates 2-D supramolecular assembly in the solid state.

Porphyrins, the most widely explored macrocyclic systems, reveal their structural versatility by forming large families of *expanded*, *contracted*, and *isomeric* analogues. Among *contracted* porphyrinoids, subporphyrins are the real ring-*contracted* congener and are relatively new entries. The first subporphyrin, tribenzosubporphine (**3**) with similar electronic structure to subphthalocyanines (**1**),[1] was prepared by the group of Osuka in 2006 as B(III) complex under harsh reaction conditions.[2] Shortly thereafter, the groups of Kobayashi[3a,c] and Osuka[3b] independently reported more facile methods for the syntheses of *meso*-aryl subporphyrins (**4**) (Figure 1). Since then, a variety of substituents have been introduced in the *meso*,[4] β,[5] and axial positions.[2,6] Subporphyrins feature an intense

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10.1021/ol200668a

Soret-like band and rather weak Q-bands, which are blue-shifted compared to porphyrins, due to the *contracted* 14π-electron conjugation pathway, and display a bowl-shaped structure, typical of the other boron contracted subphthalocyanines (**1**) and subporphyrazine (**2**).[1,7] The boron atom is coordinated to the macrocycles (**1**−**4**) in a tetrahedral fashion by three nitrogen atoms of pyrrole rings and one axial ligand such as a halogen atom, hydroxy group, or carboxy group and is an attractive component for supramolecular assembly.

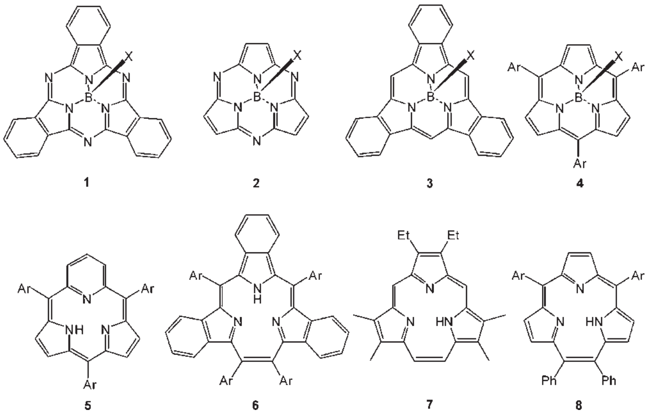
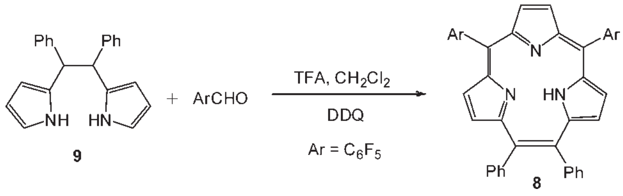


Figure 1

All the above-mentioned reports require B(III) salts as an effective templating agent for subporphyrin synthesis. Among those reported, the only boron free 14π subporphyrins are subpyriporphyrin (**5**)[8] and [14]benzotriphyrin(2.1.1) (**6**)[9] where the replacement of pyrrole by pyridine in the former and insertion of an additional sp^2-hybridized *meso*-carbon atom in the latter stabilizes the free base form by minimizing the steric repulsion. Very recently, a near-planar β-substituted, *meso*-free [14]triphyrin(2.1.1) (**7**) was reported by Yamada and co-workers (Figure 1).[10] However, there is still a great challenge to synthesize *meso*-aryl and β-unsubstituted novel *contracted* 14π porphyrinoids. Herein, we describe the synthesis, spectral, and structural characterization of a novel 14π *meso*-tetraaryl free-base triphyrin(2.1.1) (**8**) featuring three pyrrole rings and four *meso*-aryl rings. To the best of our knowledge, this is the first report on the ring-*contracted* *meso*-aryl free-base triphyrin reported to date.

Scheme 1 outlines the synthesis of the macrocycle. The triphyrin (**8**) was synthesized by the reaction of 5,6-diphenyldipyrroethane (**9**)[11] with pentafluorobenzaldehyde in CH_2Cl_2 at room temperature in the presence of trifluoroacetic acid as an acid catalyst followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). The solvent was removed and the residue purified by column chromatography on silica gel, affording **8** as a red solid in 5% yield.[12] The macrocycle is highly soluble in most organic solvents, is air-stable, and affords red diamond-shaped crystals from $CHCl_3$/*n*-hexane.

Scheme 1. Synthesis of **8**



The exact composition of the macrocycle was established by FAB mass spectra which showed a molecular ion signal at *m*/*z* 729.80. The electronic absorption, as well as the emission spectrum, of **8** in $CHCl_3$ is depicted in Figure 2. The absorption spectrum showed a Soret-like band at 373 nm ($6.12 \times 10^4\ M^{-1}\ cm^{-1}$) and Q-bands at 473 ($7.64 \times 10^3$), 519 ($7.78 \times 10^3$), and 564 nm ($1.09 \times 10^4\ M^{-1}\ cm^{-1}$). The emission spectrum showed a band at 586 nm with a quantum yield of 0.008. The Soret-like band is red-shifted by 37 nm as compared to *meso*-free [14]triphyrin (**7**),[10] clearly showing the influence of *meso*-aryl substituents on the electronic properties of triphyrin. On the other hand, the Soret and Q-bands lie at considerably shorter wavelengths than *meso*-tetraaryl porphyrins, reflecting the reduced π-conjugation pathway. Upon protonation with an excess of trifluoroacetic acid, the Soret-like band appeared at 397 nm with a red shift of 24 nm and 2-fold enhancement in the emission intensity as compared to **8**.[13]

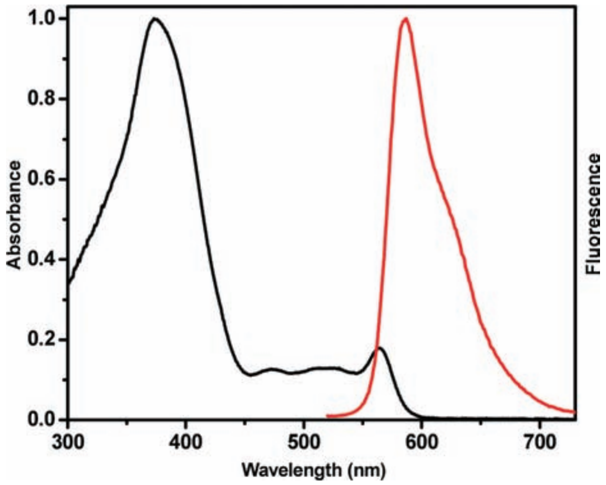


Figure 2. Electronic absorption and emission (red) spectrum of **8** in $CHCl_3$. Emission intensity is normalized to the absorption spectrum.

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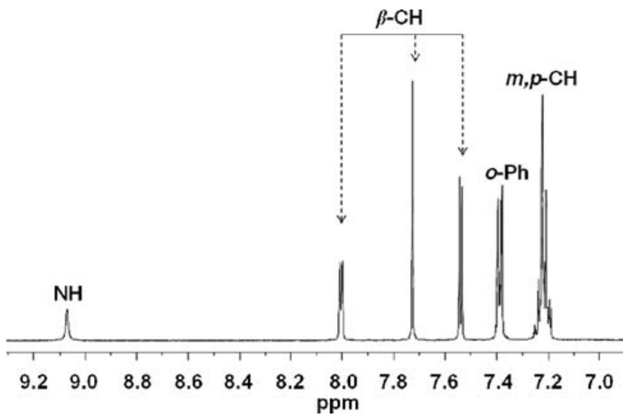

Figure 3. ^1H spectrum of **8** in CD_2Cl_2.

The ^1H NMR spectrum of **8** in CD_2Cl_2 at room temperature substantiated the expected structure (Figure 3). The NH proton resonated as a singlet at 9.07 ppm and was clearly confirmed by D_2O exchange experiment. The unusual downfield shift of the NH proton suggested a strong intramolecular hydrogen-bonding interaction with the imine nitrogens. The doublets at 8.00 and 7.54 ppm correspond to the four β-CH protons of two pyrrole rings connected through the *meso*-phenyl-substituted vinylene and/or ethylene bridge and is confirmed from $^1H-^1H$ COSY spectral analysis.[13] The remaining two β-CH protons of the third pyrrole ring appeared as a singlet at 7.73 ppm. Furthermore, as compared to 5,6-diphenyldipyrroethane **9**, the pyrrolic β-CH protons in **8** are downfield shifted with a shift difference of 2.01 to 1.82 ppm and the absence of two α-CH protons in the pyrrolic rings which are observed in **9** at 6.47 ppm clearly suggesting the formation of the macrocycle. The *o*-phenyl proton is resonated as a multiplet at 7.39 ppm and the *m*- and *p*-phenyl protons are observed at 7.22 ppm as multiplets.

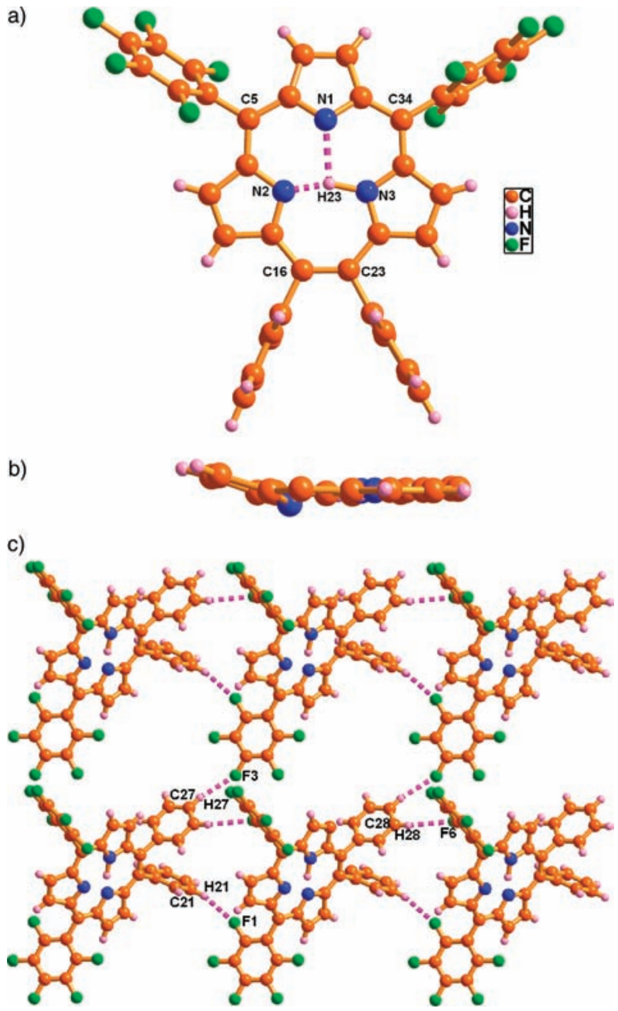

Figure 4. Single-crystal X-ray structure of **8**: (a) top view with intramolecular hydrogen bonding interaction, (b) side view, and (c) 2D-supramolecular assembly. The *meso*-aryl groups are omitted for clarity in the side view.

The structure of the new [14]triphyrin (**8**) was unambiguously determined through single-crystal X-ray diffraction analysis (Figure 4).[14] The compound crystallizes in the monoclinic crystal system with four molecules in a unit cell. Out of the three pyrrole units, one is amino and two are imino in nature, where the amino pyrrole unit is attached directly to the vinylene unit (Figure 4a). The 13-membered ring macrocycle is almost planar with one of the pyrrole rings (N1) slightly tilted up by 20.34° from the mean plane defined by the *meso* carbons C5, C16, C23, and C34 as seen in the side view (Figure 4b), in order to reduce the steric repulsion inside the macrocyclic core. The dihedral angles of the pyrrole rings with N2 and N3 are 1.32° and 1.09°, showing that they hardly deviate from the mean plane. It is pertinent to point out here that there is a strong intramolecular hydrogen bonding interaction with distances and angles of $N3-H23\cdots N2$ and $N3-H23\cdots N1$ 1.40 Å, 1.94 Å and 157.62°, 104.92°. The $N3\cdots N2$ (2.521 Å) and $N3\cdots N1$ (2.515 Å) and $N1\cdots N2$ (2.518 Å) distances are also found to be in the strong hydrogen bonding range,[8,9,11,15] which suggested the formation of a three-centered hydrogen bond. The deviations of the aryl substituents at the *meso* positions with respect to the mean

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(12) In addition to **8**, we also observed a trace amount of [2 + 2] acid-catalyzed condensation product such as porphyrin(2.1.2.1) and the mass spectrum is presented in ref 13.

(13) See the Supporting Information.

(14) Crystal data for **8** (from $CHCl_3$/hexane): $C_{40}H_{17}F_{10}N_3$, M_w = 729.57, monoclinic, a = 13.6059 (4) Å, b = 12.3268(3) Å, c = 20.1794(6) Å, $\alpha = 90°$, $\beta = 105.299(2)°$, $\gamma = 90°$, V = 3264.50(16) $Å^3$, T = 293(2) K, space group $P21/n$, $Z = 4$, D_c = 1.484 mg/m^3, μ(Mo Kα) = 0.128 mm^{-1}, 33928 reflections collected, 6666 unique (R_{int} = 0.0359), R_1 = 0.0533, wR_2 = 0.1546, GOF = 1.019 $\{I > 2\sigma(I)\}$. CCDC-815938 contains the supplementary crystallographic data for **8**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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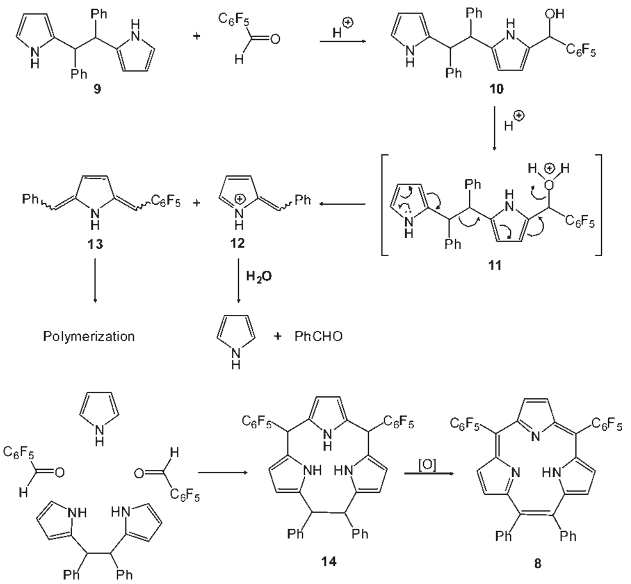
plane are 64.29°, 89.06°, 85.44°, and 83.41°, indicating the near-perpendicular nature as observed in the case of *meso*-tetraaryl porphyrins.

Further crystal analysis of **8** shows three strong intermolecular hydrogen bonding interactions through C−H···F bonds with the distances and angles as 2.58 Å, 165° (C27−H27···F3); 2.78 Å, 158° (C28−H28···F6); and 2.57 Å, 164° (C21−H21···F1), leading to the formation of three one-dimensional arrays. Combining these arrays,[13] the molecule generates two-dimensional supramolecular assembly in the solid state, which is shown in Figure 4c.

Scheme 2. Mechanistic Rationale for the Formation of **8**



Although the mechanism for the reaction is not clear at this moment, a possible mechanism is presented in Scheme 2 to rationalize the formation of triphyrin **8**. The first step involves the TFA-promoted electrophilic substitution reaction of **9** with pentafluorobenzaldehyde to afford compound **10**. In the presence of acidic medium, **10** is further protonated to form **11**, which undergoes the lone pair assisted cleavage at the C5−C5′ position to obtain a highly reactive species **12** and linear intermediate **13**. The intermediate **12** further undergoes hydrolysis to form free pyrrole, while the conjugated triene **13** readily polymerizes yielding the uncharacterizable materials.[16] However, the observed 14π triphyrin **8** formed via the 3-component condensation reaction of free pyrrole, pentafluorobenzaldehyde, and the second unit of **9** leads to the formation of porphyrinogen **14**, which is then finally oxidized by DDQ.

In summary, we have demonstrated the synthesis, spectral, and structural characterization of *meso*-aryl[14]triphyrin(2.1.1). The reported triphyrin is the smallest congener of *meso*-aryl and β-unsubstituted porphyrin containing only pyrrole rings in its free-base form. Furthermore, the single-crystal X-ray analysis reveals the presence of both inter- and intramolecular hydrogen bonding interactions and generates two-dimensional supramolecular assembly. The triphyrin reported here finds potential applications in the near future as the *meso*-aryl groups can be further functionalized. We are currently investigating the coordination properties of this macrocycle in our laboratory.

Acknowledgment. A.S. thanks DST, New Delhi and the Directors, NIIST-CSIR and NISER, for the financial support. A.K.S thanks CSIR for a fellowship. We thank Dr. Babu Varghese SAIF, IIT-Chennai for solving the crystal structure of **8**. We greatly acknowledge Dr. G. Vijay nair, NIIST, CSIR and Dr. S. Peruncheralathan, NISER for valuable discussion. We also acknowledge Mrs. Viji and Mr. Adarsh, NIIST, CSIR, for recording FAB and NMR spectra.

Supporting Information Available. Synthetic procedure and spectral data for **8** and crystal data for **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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