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meso-Porphyrinyl-Substituted Porphyrin and Expanded Porphyrins

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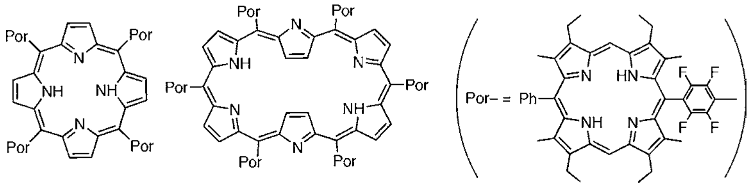
ABSTRACT



A series of *meso*-porphyrinyl-substituted expanded porphyrins were prepared from the 1:1 acid-catalyzed condensation reaction of 4-porphyrinyl-2,3,5,6-tetrafluorobenzaldehyde and pyrrole.

In recent years, expanded porphyrins that bear more than five pyrrolic subunits have been attracting considerable interest in light of their interesting optical, electrochemical, and coordination properties.[1,2] Among these, we reported that a series of *meso*-aryl-substituted expanded porphyrins were prepared in the Rothemund−Lindsey reaction of 2,6-disubstituted aryl aldehyde and pyrrole at a relatively high concentration, ca. 67 mM each.[3] In this paper, we report the extension of this procedure to a formyl-substituted porphyrin substrate that permits the synthesis of *meso*-porphyrinyl-substituted porphyrin and expanded porphyrins. Porphyrin subunits, covalently linked to an expanded porphyrin core, would offer an opportunity of creating interesting electronic interactions between two macrocycles both in the ground and excited states, and such interactions may be tuned by appropriate and selective metalation at porphyrin cores. In addition, covalently linked porphyrin-expanded porphyrin conjugates are expected to undergo distinct multi-redox processes, which may be interesting in view of multibit molecular-based information storage.[4] Despite this rich promise, little attention has been paid to covalently linked porphyrin-expanded porphyrin so far.[5]

In our modified Rothemund−Lindsey protocol for the synthesis of *meso*-aryl substituted expanded porphyrins, aromatic aldehydes are limited to those bearing electron-withdrawing substituents at both *ortho*-positions, and rather high concentrations (ca. of 67 mM) of substrates are necessary for achieving high yields of expanded porphyrins.[3a] Thus, as a precursor of *meso*-porphyrinyl-substituted expanded porphyrins, we designed formyl-substituted porphyrin **3a**, which was prepared in 16% yield by the reaction[6] of 4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,3,5,6-tetrafluorobenzaldehyde (**1**),[7] bis(3-ethyl-4-methyl-2-pyrrolyl)methane (**2**),[8] and

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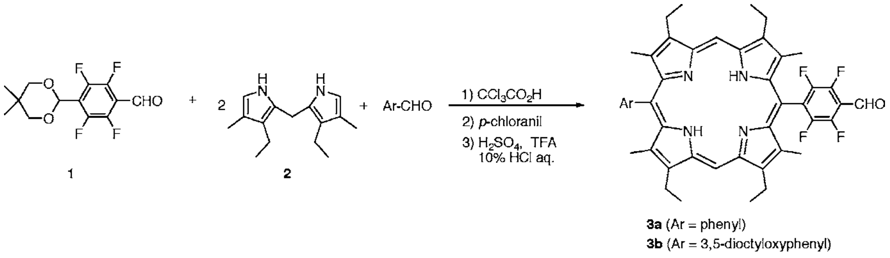
10.1021/ol048953f CCC: $27.50

Scheme 1

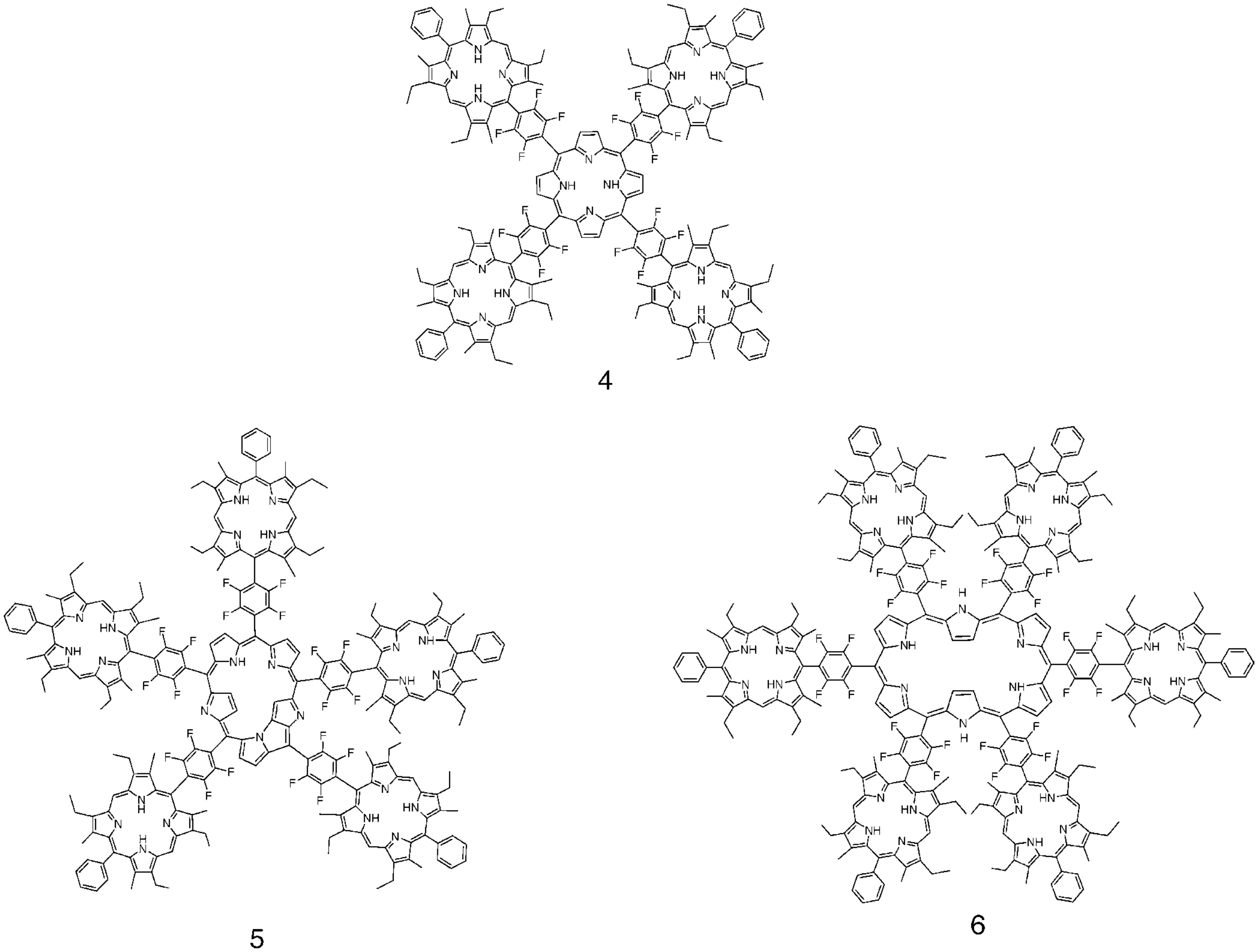


1

2

3a (Ar = phenyl)
3b (Ar = 3,5-dioctyloxyphenyl)

benzaldehyde followed by acidic hydrolysis (Scheme 1). However the poor solubility of **3a** hampered its dissolution at 67 mM in CH_2Cl_2, and thus, a more soluble porphyrin substrate **3b** was prepared from the reaction of **1**, **2**, and 3,5-dioctyolxybenzaldehyde in 29% yield. Initially, the porphyrin **3b** was reacted with an equimolar amount of pyrrole at ca. 67 mM in the presence of $BF_3{\cdot}OEt_2$ (3 equiv) followed by oxidation with DDQ. But this reaction gave only polymeric intractable materials. Meanwhile, it was found that a similar reaction at ca. 100-fold dilute concentration (ca. 0.60 mM) afforded *meso*-porphyrinyl-substituted porphyrin and expanded porphyrins (Figure 1). Because of much simpler ^{1}H NMR spectra of the products, we focused on the reaction of **3a** with pyrrole. A solution of **3a** and pyrrole (0.60 mM each) was treated with $BF_3{\cdot}OEt_2$ for 2 h in the dark and was subsequently oxidized with DDQ for overnight. Separation by silica gel column gave pentakis(porphyrinyl)-N-fused pentaphyrin **5** (8.2%, m/z = 3885; calcd for $C_{245}H_{215}N_{25}F_{20}$ = 3887) and a fraction that contained many expanded porphyrin products. Further separation of this fraction by



4

5

6

Figure 1. *meso*-Porphyrinyl-substituted porphyrin **4**, N-fused pentaphyrin **5**, and hexaphyrin **6**.

recycling GPC−HPLC chromatography gave tetrakis(porphyrinyl)porphyrin **4** (1.8%, m/z = 3111; calcd for $C_{196}H_{174}N_{20}F_{16}$ = 3111), hexakis(porphyrinyl)hexaphyrin **6** (11.4%, m/z = 4667; calcd for $C_{294}H_{262}N_{30}F_{24}$ = 4668), and higher homologues of *meso*-porphyrinyl-substituted expanded porphyrins.[9] These products elute as a discrete band on GPC−HPLC in the order of decreasing molecular size (Supporting Information).

The absorption spectra of **4**−**6** are shown in Figure 2. These spectra indicate predominant contribution of porphyrin chromophores both in the Soret band (350−450 nm) and Q-band (500−700 nm) regions but reveal distinct differences in the latter region, particularly in the case of **6**. While the Soret band of **4** is split at 411 and 423 nm owing to the exciton coupling between porphyrins bridged by a tetrafluorophenylene spacer,[10] those of **5** and **6** are observed at 408 nm, being nearly at the same position as that (408 nm) of reference porphyrin **3c**.

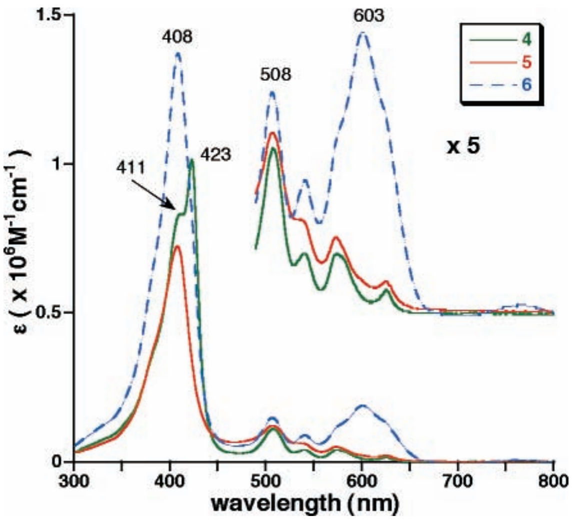
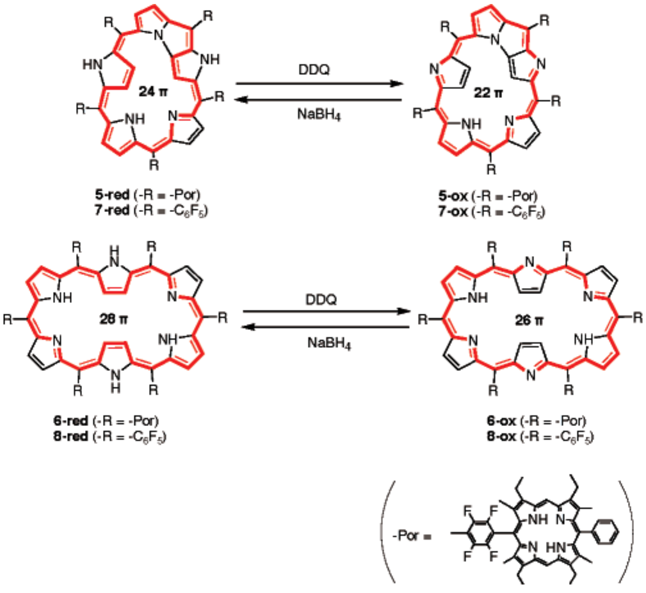


Figure 2. UV−vis absorption spectra of **4**−**6** in CH_2Cl_2.

It is known that N-fused pentaphyrin **7** can take two stable oxidation states, **7-ox** (22π-electron, aromatic) and **7-red** (24π-electron, nonaromatic),[11] and similarly hexaphyrin **8** can also take two stable oxidation states, **8-ox** (26π-electron, aromatic) and **8-red** (28π-electron, nonaromatic) (Scheme 2).[12] In both cases, these two stable oxidation states are quantitatively interconvertible upon oxidation with DDQ and reduction with $NaBH_4$. These transformations can be monitored by UV−vis spectroscopy as shown in Figure 3.

To determine the oxidation states of expanded porphyrin cores in **5** and **6**, the absorption spectra were corrected by subtracting the absorbance of the porphyrin chromophores from the spectra of **5** and **6** (Figure 4). It is evident that the corrected absorption spectrum of **5** (λ_{max} = 562 nm) is similar to that of oxidized form of N-fused [22]pentaphyrin **7-ox** (λ_{max} = 551 nm).[11] Treatment of **5** with $NaBH_4$ caused a distinct color change from dark red to light orange (λ_{max} = 514 nm), which has been assigned to the formation of a reduced form of *meso*-pentakis(porphyrinyl)-substituted N-fused [24]pentaphyrin, **5-red**, on the basis of the similarity of its corrected absorption spectrum to that of **7-red**. Upon treatment with DDQ, **5-red** was quantitatively oxidized to **5**, as judged from a color change from light orange to dark red (λ_{max} = 562 nm) (Scheme 2). Therefore, the product **5**

Scheme 2



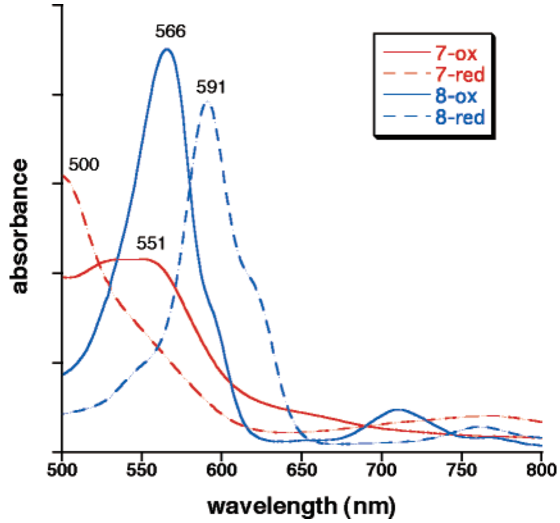


Figure 3. Absorption spectra of *meso*-pentafluorophenyl expanded porphyrins **7-ox**, **7-red**, **8-ox**, and **8-red** in CH_2Cl_2.

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(9) *meso*-Heptakis(porphyrinyl)heptaphyrin (3.1%, m/z = 5442; calcd for $C_{343}H_{305}N_{35}F_{28}$ = 5445) and *meso*-octakis(porphyrinyl)octaphyrin (1.6%, m/z = 6222; calcd for $C_{392}H_{348}N_{40}F_{32}$ = 6223) were isolated but their full characterizations have not been completed.

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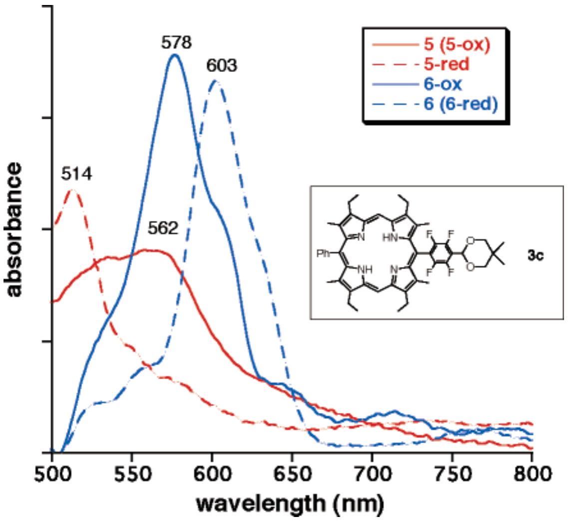

Figure 4. Corrected absorption spectra of **5** (**5-ox**), **5-red**, **6-ox**, and **6** (**6-red**) taken by subtracting the absorbance of the reference porphyrin **3c** from their absorption spectra.

isolated in the reaction of **3a** and pyrrole has been assigned to **5-ox**. As is the same for **7-ox**, the product **5** displays characteristic low-field shifted six doublet signals due to the outer peripheral β-protons ($\delta = 9.68$, 9.56, 9.14, 9.11, 9.04, and 8.99 ppm) and high-field shifted two doublets ($\delta = 2.88$ and 2.36 ppm) and a singlet ($\delta = -0.48$), indicating the presence of the aromatic ring current in the N-fused pentaphyrin macrocycle. On the other hand, the **5-red** displays no such shifts and displays signals due to the outer peripheral β-protons in 7.2−5.6 ppm.

The corrected absorption spectrum of **6** ($\lambda_{\max} = 603$ nm) is similar to that of **8-red** ($\lambda_{\max} = 591$ nm), and the treatment of **6** with DDQ induced an immediate color change from vivid green to dark purple ($\lambda_{\max} = 578$ nm), indicating the formation of an oxidized form, **6-ox**, which was in turn reduced with $NaBH_4$ to recover **6**. Thus, the product **6** isolated by recycling GPC−HPLC separation has been assigned to be a reduced form, **6-red**. As judged from the color and eluting behavior, the hexaphyrin product isolated from silica gel column is considered to be **6-ox**, which seems to be reduced during the separation by recycling GPC−HPLC with $CHCl_3$ containing a small amount of ethanol. Similar facile reduction of [26]hexaphyrin to [28]hexaphyrin has been often observed in solution containing aliphatic alcohol.

The corrected spectral shapes of **5-ox**, **5-red**, **6-ox**, and **6-red** are, respectively, similar to those of **7-ox**, **7-red**, **8-ox**, and **8-red**, but the peak positions of **5** and **6** are ca. 10-nm red-shifted compared with those of **7** and **8**, respectively. This may be ascribed to the substitution effects of *meso*-attached tetrafluorophenylenylporphyrins. These results indicate that the oxidation and reduction reactions of the expanded porphyrin cores are possible in **5** and **6** with clear color changes without any chemical changes in the peripheral porphyrins.

The electrochemical properties of **3c**, **5**, **6**, **7**, and **8** were comparatively studied by cyclic voltammetry in CH_2Cl_2 versus ferrocene/ferrocenium ion using tetrabutylammonium hexafluorophosphate as an eletrolyte. Porphyrin **3c** undergoes one-electron reduction and oxidation at −1.78 and 0.48 V. Besides these responses, there are additional electrochemical waves associated with the interconversions of the expanded porphyrin cores, −0.58 V for reduction of **5-ox** to **5-red** and −0.13 V for oxidation of **5-red** to **5-ox**, and −0.67 V for reduction of **6-ox** to **6-red** and 0.24 V for oxidation of **6-red** to **6-ox**. These results are similar to the respective potentials of the reference exapanded porphyrins: −0.70 V for reduction of **7-ox** to **7-red**, 0.08 V for oxidation of **7-red** to **7-ox**, −0.67 V for reduction of **8-ox** to **8-red**, and 0.24 V for oxidation of **8-red** to **8-ox**, respectively. These results are in line with the above chemical transformations and indicate that the expanded porphyrin cores in **5** and **6** retain their own electrochemical properties.

Last, the fluorescence from the porphyrin parts is significantly quenched in **4**, **5-ox**, and **6-red** and their quantum yields are quite small, 1.6×10^{-4}, 3.9×10^{-5}, and 1.0×10^{-4}, respectively, in comparison to that of **3c** (0.028).[13] Although the mechanism of this strong fluorescence quenching is not clear at the present stage, intramolecular excitation energy transfer from the porphyrin units to the expanded porphyrin cores or electron transfer involving easily accessible oxidized or reduced state of expanded porphyrin cores can be conceivable, thus suggesting strong electronic interactions in the excited state.

In summary, simple one-pot acid-catalyzed condensation reaction of **3a** with pyrrole provided a series of *meso*-porphyrinyl substituted porphyrin **4** and expanded porphyrins **5** and **6**. Further studies on the property and chemical reactivity of these molecules, particularly on the dynamic interactions between porphyrin and expanded porphyrin are currently under investigation and will be reported in due course.

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

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