Cruciform porphyrin pentamers

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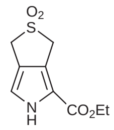
Cruciform porphyrin pentamers 15 and 16 are obtained in good yield by acid-catalyzed tetramerization of Zn^{II}–pyrroloporphyrin 14, followed by oxidation with DDQ; pyrroloporphyrins are in turn obtained from the corresponding pyrrolochlorins by Diels–Alder type reactions of porphyrins involving thermal extrusion of sulfur dioxide from a pyrrole-fused 3-sulfolene.

Syntheses of covalently-linked porphyrin arrays have recently attracted much attention due to their unique photoelectronic properties and potential applications as mimics of light-harvesting in photosynthesis, and as electron/energy transfer moieties in molecular wires.[1–4] A variety of model structures have been reported, mostly containing two or three porphyrin units, either directly coupled,[2] bridged by coplanar aromatic systems,[3] or beta-fused.[4] Coplanar-linked porphyrin arrays are believed to lead to more efficient energy- and electron-transfer superstructures. Recently, a linear beta-fused trimer[4] was prepared from a fused pyrroloporphyrin.[5] Herein we describe the first synthetic route to covalently-linked cruciform pentamer porphyrins, one of which is planar and fully conjugated.

One of our long term objectives is to modify porphyrin macrocycles for use both as dienes and dienophiles. The synthesis and cycloaddition reactions of a pyrrole-fused 3-sulfolene **1** with standard dienophiles were recently reported,[6] and porphyrins have also been shown to react with electron-rich dienes.[7] Thus, when TPP **2** was heated at 240 °C in the presence of an excess of pyrrole **1** and 4 Å molecular sieves, the pyrrolochlorin **3** was produced as a mixture of enantiomers in 20–22% yield. Two minor products are also obtained from this reaction: pyrroloporphyrin **4** (6–10% yield) and isoindoloporphyrin **5** (usually $<1\%$ due to its ready transformation into further products). Trace amounts of bacteriochlorin were also detected by spectrophotometry. Based on recovered starting material **2**, the yield of products **3–5** was quantitative. Products obtained simply from the dimerization and polymerization of the reactive pyrrolodiene, generated *in situ* from **1**, were also identified by ^{1}H NMR and mass spectrometry. Products **4** and **5** were obtained from pyrrolochlorin **3** by oxidation with *p*-chloranil or DDQ. The Ni^{II} and Zn^{II} complexes of TPP reacted under similar conditions to afford the same products in lower yields due to increased susceptibility toward unwanted oxidation reactions. When the same reaction conditions were applied to octaethylporphyrin **6**, the pyrrolochlorin **7** was obtained in low yield (2–5%). Under the same conditions the iron(III) complex **8** afforded pyrrolochlorin **9** in 6% yield (unoptimized). In contrast, the electron-deficient *meso*-tetra(pentafluorophenyl)porphyrin **10** readily reacted to afford only two products, the pyrrolochlorin **11** (32–39% yield) and the bacteriochlorin **12** (5–10%). When the same reaction was applied to a porphyrin or chlorin bearing a β-vinyl substituent the cycloaddition reaction took place predominantly at the vinyl group. Reactions of pyrrole **1** with functionalized chlorins led to mixtures of products which include bacteriochlorins, isoindolochlorins, and products resulting from addition of another pyrrole to the isoindolochlorin.

All new compounds possessed spectroscopic data in accord with the assigned structures. Pyrrolochlorins **3**, **7**, **9** and **11** possess typical chlorin absorption spectra, with a strong band at λ_{max} 652 nm; pyrroloporphyrin **4** shows an electronic absorption spectrum similar to that of TPP **2**, and isoindoloporphyrin **5** shows a type of rhodo-visible spectrum characteristic of monobenzoporphyrins. Compound **12** (λ_{max} 746 nm) displayed an optical spectrum characteristic of a bacteriochlorin.

Insertion of zinc into pyrroloporphyrin **4** yielded complex **13** in 85–90% yield. The ester function of compound **13** was reduced with LiAlH$_4$ to give alcohol **14** which afforded the crude pentamer **15** after treatment (*e.g.* ref. 8) with acid and



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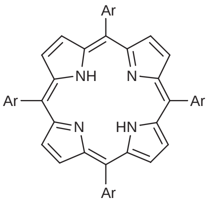
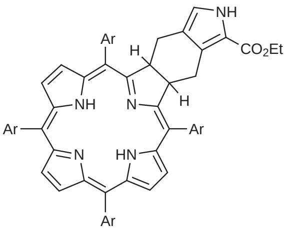
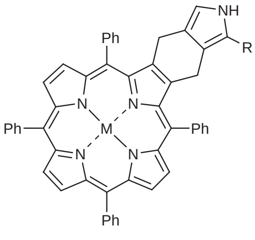


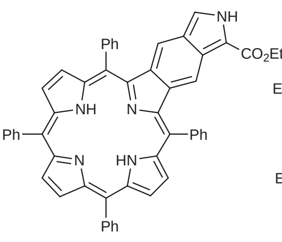
2 Ar = Ph
10 Ar = C$_6$F$_5$



3 Ar = Ph
11 Ar = C$_6$F$_5$



4 M = 2H, R = CO$_2$Et
13 M = Zn^{II}, R = CO$_2$Et
14 M = Zn^{II}, R = CH$_2$OH



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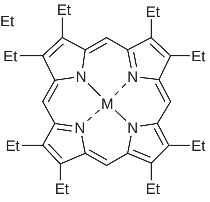
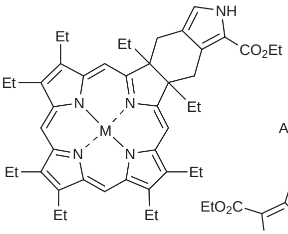
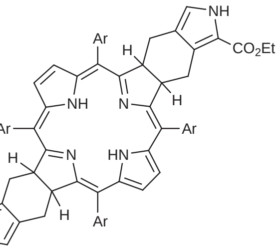


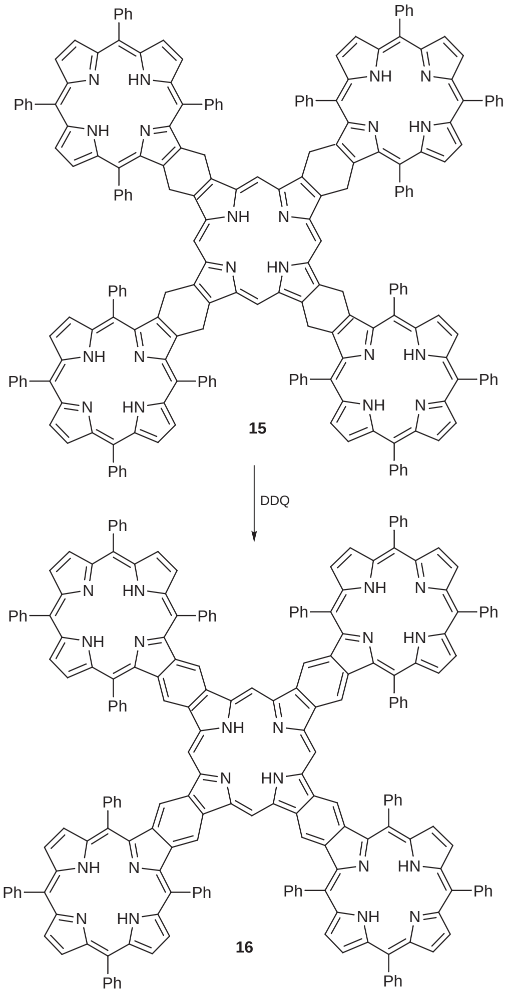
6 M = 2H
8 M = Fe^{III}Cl



7 M = 2H
9 M = Fe^{III}Cl



12 Ar = C$_6$F$_5$
(mixture of isomers)



Scheme 1

oxidation with *p*-chloranil. Filtration through Sephadex G-25 resulted in isolation of **15** in 65–75% yield. Mass spectrometry was performed on **15** using matrix-assisted laser desorption ionization (MALDI) with a Fourier transform mass spectrometry (FTMS) analyzer.† This technique has been shown to be highly effective for high resolution MS determinations of large porphyrin compounds.[9] The ^{1}H NMR spectrum of **15** showed only broad bands, even upon addition of TFA, possibly due to aggregation effects of these high molecular-weight molecules. Treatment of pentamer **15** with an excess of DDQ gave the fully conjugated pentamer **16** in quantitative yield (Scheme 1). Compound **16** was also characterized by MALDI-FTMS;† its absorption spectrum showed a long-wavelength band at λ_{max} 774 nm (838 nm in acid). Pentamers **15** and **16** display good solubilities in most organic solvents. The methodology described above offers the opportunity for synthesis of novel heterobimetallic cruciform porphyrin pentamers, and this work is in progress.

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Notes and references

† *Selected data* for **15**: $C_{204}H_{134}N_{20}$ requires 2863.1099; found: 2862.8791 (M^+). For **16**: $C_{204}H_{126}N_{20}$ requires: 2855.0474; found 2854.9263 (M^+).

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