A starburst porphyrin polymer: a first generation dendrimer

Tyler Norsten and Neil Branda*†

Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2E1

**Tetra(chlorobenzyl)porphyrin 3b reacts with 4 equiv. hydroxyphenylporphyrin 2 to give the first example of a pentaporphyrin that can be considered to be a first generation dendrimer.**

Porphyrins and metalloporphyrins are fascinating chromophores due predominantly to the fact that their photophysical behaviour is sensitive to the type and position of substitution within or around the ring, as well as the presence of neighbouring porphyrins or other chromophore centres. To better understand the complexity of the electronic or photonic communication between porphyrins,[1] covalently linked conjugated[2] and non-conjugated[3] oligomeric porphyrin assemblies, as well as non-covalently linked supramolecular chromophoric assemblies[4] have been prepared and studied. These short, multiply linked chromophoric polymers are successfully paving the way to a better understanding of the fundamental interactions between neighbouring porphyrin centres.

Dendrimers are a specific class of compounds that comprise one of the fastest growing areas of polymer research.‡[5] These hyperbranched starburst polymers differ from their traditional linear counterparts in that the repeating units cascade outwardly from a central core rather than elongating in a linear fashion. The attraction here is that as successive generations are iterated, dendrimers become increasingly globular and exhibit intriguing structural properties such as internal voids and cavities created by the multiple branches folding back upon themselves. Knowing this, we were surprised when we could not find any examples of a fully porphyrinic dendrimer. There are several examples of the two extreme cases: (1) multiple porphyrins covalently linked onto a non-porphyrin core,[6] and (2) non-porphyrin dendrimer branches fused to a singular porphyrin core.[7] Here we report the first example of a dendrimer where the core and repeating polymeric unit are themselves both porphyrins. It is hoped that this new class of branched chromophores will combine the advantages of the hybrid properties of both porphyrins and dendrimers.

With a divergent§ synthetic approach in mind, the polymeric cycle leading to dendrimer **1** was designed to consist of ester-reduction, activation of the resulting alcohol and coupling to form an ether linkage. The ether linkage was chosen because of its chemical stability towards a wide range of synthetic conditions including those required for future iterations. Another attractive feature of this approach is that both the precursor to the active core **3b** [*meso*-tetrakis(4-methoxy-carbonylphenyl)porphyrin **3a**] and the repeating unit [5,10,15-tris(methoxycarbonylphenyl)-20-(4-hydroxyphenyl)-porphyrin **2**] can be prepared in the same one-pot procedure as previously reported.[8] Porphyrins **2** and **3a** are easily separated and purified by trituration with acetone followed by column chromatography (SiO₂). Porphyrin **3a** was reduced[9] with LiAlH₄ and the resulting tetraalcohol chlorinated[10] to give the core **3b** following known procedures. The first generation dendrimer **1** was prepared from building blocks **2** and **3b** in one step as outlined in Scheme 1, by coupling 4 equiv. **2** to 1 equiv. **3b** in the presence of NaOH in DMF at 80–100 °C for 24 h. Pentaporphyrin **1** was isolated as a purple solid in 48% yield after purification by column chromatography (SiO₂, CHCl₃–2% CH₃CN) and by GPC.

Pentaporphyrin **1** was highly soluble in a wide range of organic solvents such as THF, CHCl₃ and CH₂Cl₂. It is
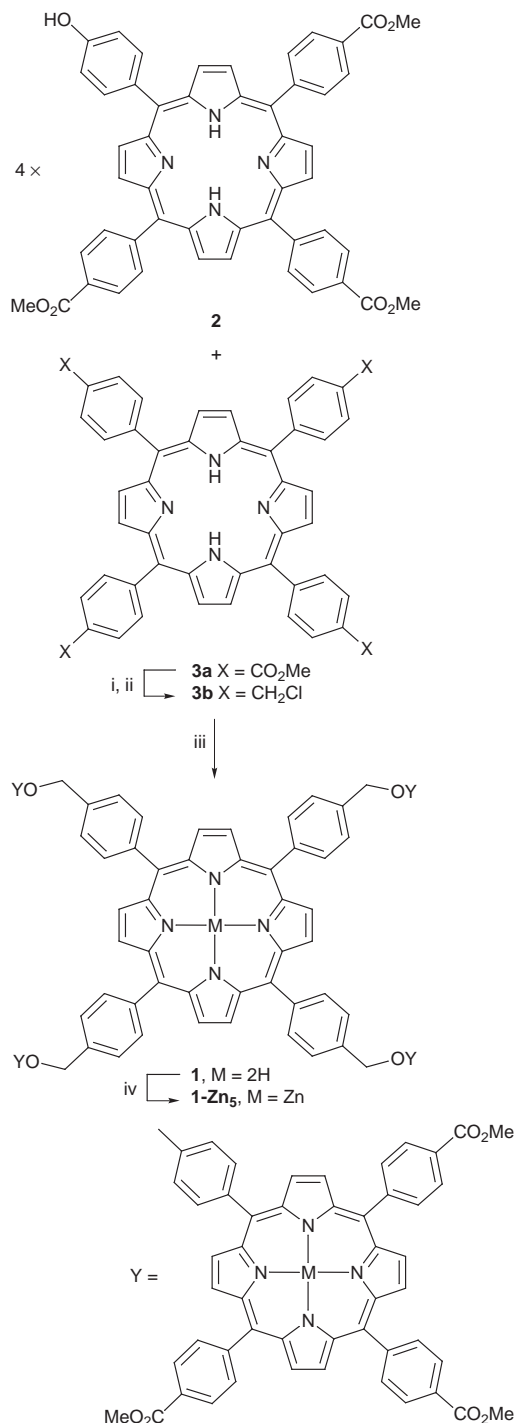
Scheme 1 *Reagents and conditions*: i, LiAlH₄, THF, reflux; ii, SOCl₂; iii, NaOH, DMF, 80–100 °C; iv, Zn(OAc)₂·2H₂O, MeOH, CHCl₃

interesting to note that it is in fact significantly more soluble than either building blocks **2** or **3**. The pentaporphyrin **1** displays 12 divergent ester groups suitable for submission to future dendrimeric cycles.

The first generation dendrimer **1** was characterized by MALDI-TOF mass spectrometry and ^{1}H NMR and UV–VIS absorption spectroscopies. The ^{1}H NMR and COSY spectra of **1** in CDCl$_3$ are consistent with the assigned structure. A significant difference is observed for the resonances of the two core porphyrin N–H hydrogens (−2.61 ppm) and the eight porphyrin N–H hydrogens located within the peripheral porphyrins (−2.75 ppm) of the starburst. Molecular modeling suggests that the radial porphyrin arms are capable of folding back towards the core of the starburst molecule; however, ROSEY NMR studies show no long-range communication. Minimum energy calculations predict that the four radially linked porphyrins ideally exist in a propeller type arrangement around the core with an edge-to-edge distance of 61 Å. The dendrimer exists in the nanoscale range after only one generation!

The MALDI-TOF mass spectrum of **1** shows a peak at 3883.7 mass units (mu) corresponding to the parent ion [M + H], this is in accordance with the calculated value of 3883.3 mu for C$_{248}$H$_{174}$N$_{20}$O$_{28}$. Also evident are fragmentation peaks separated by 804 mu at 3079, 2275 and 1471 mu corresponding to the consecutive loss of a peripheral porphyrin from the central core (Fig. 1).

The UV–VIS spectrum of the porphyrin dendrimer in CHCl$_3$ shows absorption maxima at 424 (2 140 000),[¶] 517 (74 200), 552 (38 200), 591 (23 700) and 647 (17 400) nm. The absorption spectrum of **1** appears to resemble the sum of appropriate model compounds.[‖] Studies to quantify any subtle shifts in absorption and changes in molar extinction coefficients are currently under way.

The pentametallo zinc derivative **1–Zn$_5$** was cleanly prepared by treating a CHCl$_3$ solution of the free base dendrimer with an excess of a saturated MeOH solution of Zn(OAc)$_2$·2H$_2$O. The MALDI-TOF mass spectrum of **1–Zn$_5$** is consistent with the replacement of the 10 porphyrin hydrogen atoms by five zinc

atoms, as is the ^{1}H NMR spectrum with the disappearance of the eight peripheral porphyrin hydrogens at −2.75 ppm and the two core hydrogens at −2.61 ppm. As expected, the addition of five metals to the dendrimer greatly decreased its solubility in chlorinated solvents (CH$_2$Cl$_2$ and CH$_3$Cl), however **1–Zn$_5$** remained highly soluble in THF.

The starbursts **1** and **1–Zn$_5$** represent the birth of a new type of dendrimeric framework. It will be interesting to see what electronic or photonic applications the future holds for the next generation.

Notes and References

† E-mail: neil.branda@ualberta.ca

‡ http://dendrimers.cas.usf.edu/links.html. This web site lists academic and commercial laboratories working on dendrimer research as well as an up to date list of publications on dendrimers.

§ In a divergent approach, dendrimers are constructed from a central core out to the periphery in an iterative fashion of repeating generations. In contrast, a convergent approach builds the dendrimer from the periphery towards the core.

¶ Molar extinction coefficient (ε/M^{-1} cm^{-1}).

‖ Benzyl and phenyl ethers of porphyrins **2** and **3b** respectively were prepared as model compounds for comparative photophysical studies by reacting the hydroxyphenylporphyrin **2** with benzylbromide and by reacting tetrachloroporphyrin **3b** with phenol.

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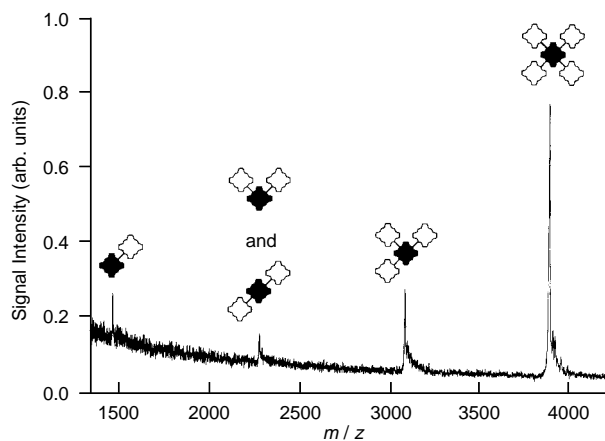11 D. C. Schriemer and L. Liang, *Anal. Chem.*, 1996, **68**, 2721.

Fig. 1 MALDI-TOF mass spectrum of first generation porphyrin dendrimer **1** showing the parent mass peak [M + H] as well as peaks corresponding to the sequential loss of one peripheral porphyrin (unshaded polygons) from the central core porphyrin (shaded polygon). All-*trans*-retinoic acid was used as the matrix without added cation.[11] Synthetic peptides bracketing the mass of interest (4000 mu) were used as external standards for calibration.