Building large porphyrin arrays: pentamers and nonamers

David L. Officer,* Anthony K. Burrell* and David C. W. Reid

Department of Chemistry, Massey University, Private Bag 11222, Palmerston North, New Zealand

A building block approach towards porphyrin arrays is used to construct pentameric and nonameric porphyrin arrays in one step.

The design and construction of a photovoltaic cell based upon the processes used by photosynthetic organisms is a tantalising goal. In photosynthesis, plant cells utilise arrays of up to three hundred porphyrin molecules (chlorophyll) for light capture.[1] A photovoltaic cell could be envisioned as operating in an analogous fashion, effecting the capture of light using large arrays of synthetic porphyrins. However, the exploration of such a possibility has been limited by a lack of appropriate synthetic methodology for the production of large porphyrin arrays. Conventional synthetic strategies to porphyrin arrays have proved quite limiting. They frequently involve large numbers of sequential steps, separation of statistical mixtures and extensive chromatographic purification, always resulting in low product yields. Consequently, we[2,3] and others[4–8] have been developing building block strategies for array formation. We have shown that this approach is versatile, efficient and flexible for the preparation of a variety of free-base and metallated porphyrin monomers, dimers and trimers.[2,3,9] We now demonstrate the inherent flexibility of our building block methodology with the one-step construction of two geometrically different porphyrin pentamers and a nonamer, to our knowledge the largest, non-polymeric, synthetic porphyrin array yet made.[8,10,11,12]

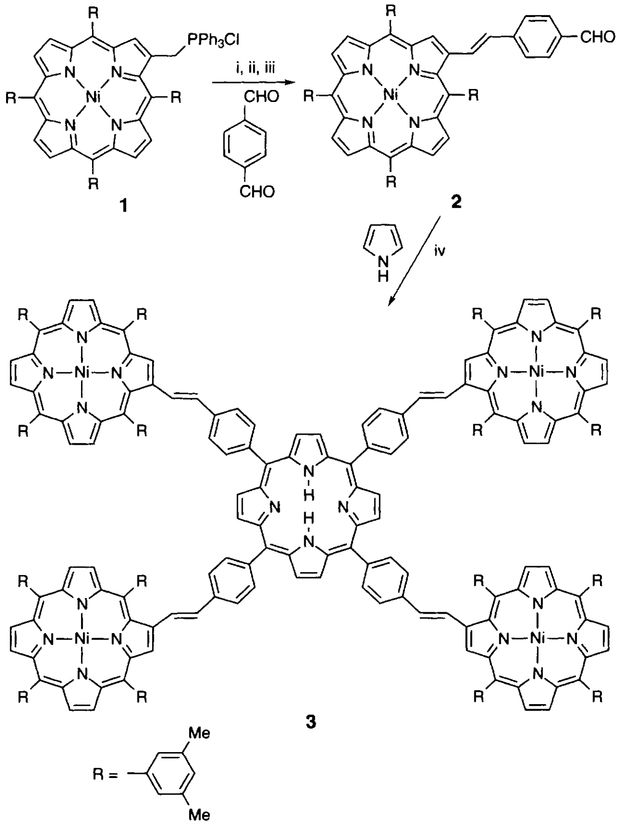
The key to the synthesis of these arrays is the ready availability of appropriately-functionalised porphyrin phosphonium salts. Thus, in 1993 we prepared the tetraphenylporphyrin methyl phosphonium salt (see **1**, R = Ph) and used it to prepare a variety of free-base and metallated porphyrin monomers and dimers.[2] During the development of the building block methodology from this phosphonium salt however, we encountered problems with solubility.[3] Consequently, we have prepared the tetra-*m*-xylyl† derivative **1** which leads to porphyrin arrays that are readily soluble.

Thus, preparation of the nickel tetra-*m*-xylyl building block **2** from **1** was readily achieved in an analogous fashion to that previously described.[3] Condensation of the aldehyde **2** with pyrrole using Lindsey conditions[13] afforded the 'star pentamer' **3** in 39% yield (Scheme 1).‡ Wennerström *et al.* obtained 1% of a phenyl-substituted star pentamer using similar condensation conditions.[14] Pentamer **3** behaves differently from **2** having a higher R_f (R_f: silica, CH_2Cl_2–hexane, 1 : 1, **2** = 0.39, **3** = 0.74). Pentamer **3** is spectroscopically similar in many respects to the starting aldehyde **2**, although the ^1H NMR spectrum revealed the telltale NH resonances at δ −2.5 and the FAB mass spectrum confirmed pentamer formation with ions at 3844 ($[M - H]^+$) and 1922 ($[M - H]^{2+}$).

The electronic absorption bands of the star pentamer **3** were almost identical to those of its precursor, with the additional absorption band at 654 nm reflecting the formation of the central free-base ring. It is interesting to note that no Soret band splitting is observed as was reported by Wennerström[14] for the analogous pentamer. This suggests a lack of porphyrin–porphyrin interaction which could be due to the increased separation (~15 *vs* ~12.5 Å) of the central and peripheral rings.

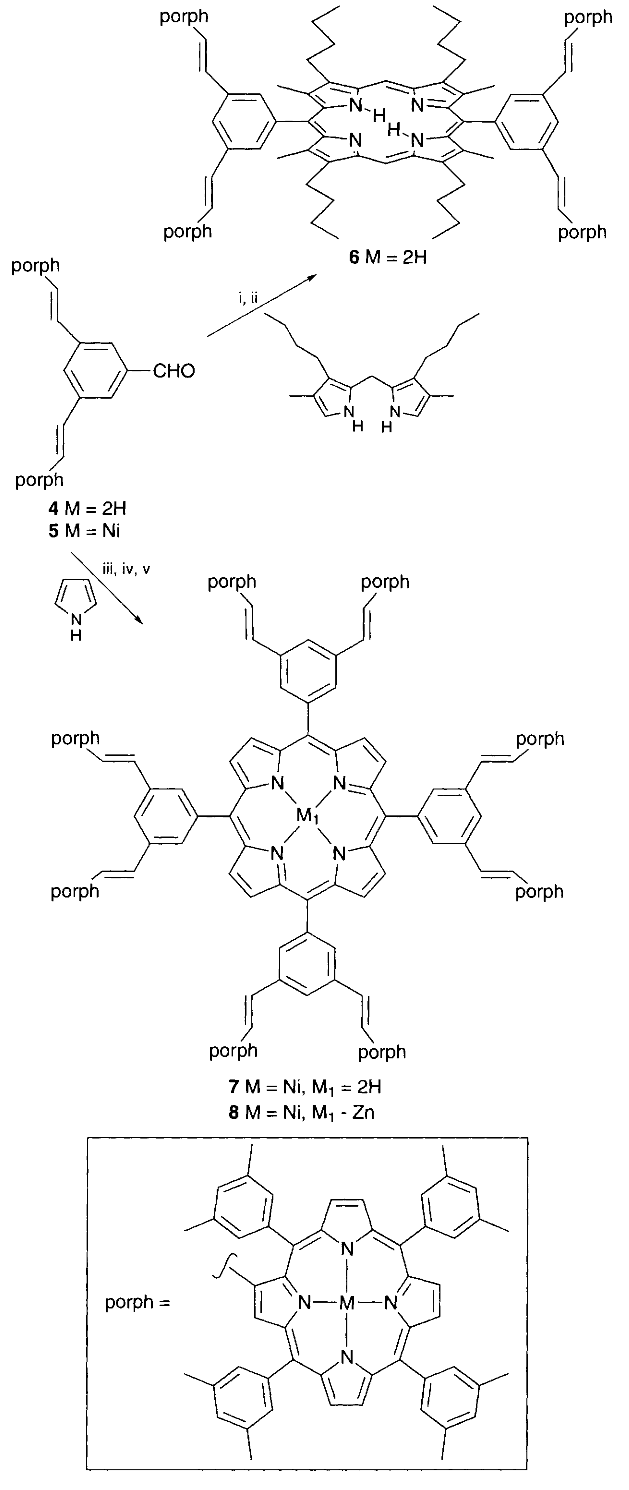
The real strength of this methodology is demonstrated by the facile preparation of a more highly substituted building block resulting in the doubling of array size. Thus, the second generation building block, the porphyrin dimer aldehyde **4**, was synthesised as easily as the monomer building block, in a single step Wittig reaction of **1** with benzene-1,3,5-trialdehyde. A novel 'H-pentamer' **6** was then readily prepared by condensation of the dimer aldehyde **4** with dipyrrylmethane (Scheme 2) (R_f: silica, CH_2Cl_2–hexane, 1 : 1, **4** = 0.46, **6** = 0.63). Given the unique nature of the central porphyrin ring, **6** was easily characterised by spectroscopy. The ^1H NMR spectrum showed a broad singlet at δ −2.51 due to the NH resonances and the typical deshielded central-ring *meso*-proton signal at δ 10.58, along with the characteristic signal pattern for the methyl and butyl substituents. The FAB mass spectrum afforded the anticipated MH^+ ion at 3748. As before, no Soret band splitting or band shifts are observed in the electronic absorption spectrum, the spectrum being almost identical to the starting material but with increased molar absorption coefficients, again reflecting the lack of porphyrin–porphyrin interaction.

Metallation of building block **4** and reaction of the resulting derivative **5** with pyrrole under Lindsey conditions[13] highlights the value of this approach for porphyrin array synthesis. During



Scheme 1 *Reagents and conditions*: i, DBU, CH_2Cl_2, room temp., 1 min; ii, I_2, CH_2Cl_2, room temp., 16 h; iii, $NiBr_2$, DMF, reflux, 5 min; iv, TFA, CH_2Cl_2, room temp., 3 d; *o*-chloranil, CH_2Cl_2, reflux, 1 h

the course of this reaction, the formation of a new porphyrin-containing material was apparent, somewhat less polar (R_f: silica, CH_2Cl_2–hexane, 1 : 1, **5** = 0.58, **7** = 0.88) than the dimeric nickel aldehyde starting material **5**. The FAB mass spectrum of the resulting deep purple product (29%) gave a peak at 7076 consistent with the M^+ for the expected nonamer **7**. A second ion at 3537 ($[M - 2H]^{2+}$) supports this assignment. While the ^1H NMR spectrum confirms the presence of the central free-base porphyrin ring with two NH singlets (δ −1.73, −1.86), it provides little other evidence for the nonamer structure as the only new signals expected in the ^1H NMR are the β-pyrrolic protons of the central porphyrin. While all of the ^1H resonances are sharp the spectrum is very complex making conclusive assignments impossible. As observed for the H-pentamer **6** no electronic absorption band shifts (relative to **5**) were apparent although there was a large increase in the molar absorption coefficients, indicative of little porphyrin-porphyrin ring interaction. The Soret band molar absorption coefficient is 1.5×10^6 dm^3 mol^{-1} cm^{-1}, one of the largest ever reported for porphyrins. The expected Q-band absorption of the central free-base porphyrin ring was observed at 649 nm, its molar absorption coefficient an order of magnitude smaller than the two other Q-bands.



Scheme 2 *Reagents and conditions*: i, TFA, CH_2Cl_2, room temp., 22 h; ii, *o*-chloranil, CH_2Cl_2, reflux, 4 h; iii, TFA, CH_2Cl_2, room temp., 36 h; iv, *o*-chloranil, CH_2Cl_2, reflux, 3 h; v, $Zn(OAc)_2$, MeOH, CH_2Cl_2, room temp., 10 min

Confirmation of the presence of a free-base porphyrin ring in the nonamer was achieved by the near quantitative preparation of the zinc derivative **8** using standard procedures.[15] The FAB mass spectrum confirmed the insertion of zinc into the nonamer with peaks at 7139 (M^+) and 3569 (M^{2+}). The loss of the NH resonances in the ^1H NMR spectrum and the lowest energy electronic absorption Q-band supported this.

We have demonstrated that large porphyrin arrays can be quickly and easily prepared in reasonable yields in only two or three steps from a phosphonium salt. At no stage in the synthesis of the phosphonium salt, the building blocks or in the array forming reactions are mixtures of porphyrins obtained or extensive purification procedures required. Thus, this building block approach to the construction of porphyrin arrays has significant advantages over other methods. We are currently investigating the physical and electronic properties of these arrays and extending this methodology to the synthesis of arrays of thirteen or more porphyrins.

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Footnotes

† We have chosen to use the older term 'tetra-*m*-xylyl' rather than 'tetrakis-3,5-dimethylphenyl'.

‡ All new compounds were fully characterised by mass, UV–VIS and ^1H NMR spectroscopy.

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