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Porphyrin arrays as models for light-harvesting systems involved in photosynthesis

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Introduction

Our research has been directed towards developing an artificial mimic of the whole purple bacterial photosynthetic cycle; here we concentrate on the initial light-harvesting process.^{1,2}

The self-assembled wheel-like arrangement of the bacteriochlorophyll chromophores in light-harvesting complexes LH1 and LH2, revealed in the outstanding X-ray crystallographic studies of the photosynthetic bacterium *Rhodospseudomonas acidophila* by the University of Glasgow group,³ is an attractive target for an artificial mimic. In the LH2 system, eighteen bacteriochlorophyll *a* molecules are held together by apoprotein in such a way that they form a continuous overlapping ring (wheel). Another nine bacteriochlorophyll *a* molecules are positioned perpendicular to this ring (Fig. 1).

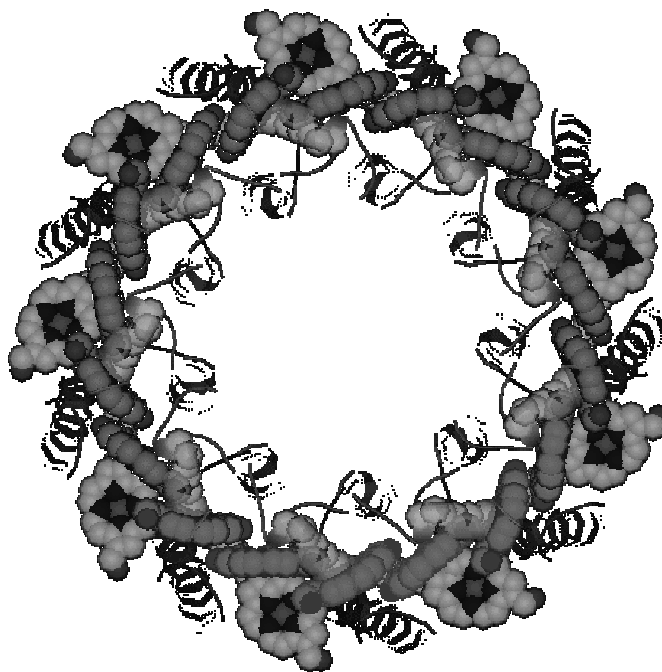


Fig. 1. View of the periplasmic face of the LH2 complex of the photosynthetic bacterium *Rhodospseudomonas acidophila* showing the 27 bacteriochlorophyll molecules as space-filling structures [from the X-ray crystal structure: McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature (London)* **1995**, 374, 517-521].

This system is not only able to capture light very efficiently, but it is also able to store the energy by multi-step energy transfer processes until the LH1 centre is "ready" to accept the energy and convert it into chemical energy. The LH1 system is apparently made of the same sub-units as LH2 but is a larger continuous overlapping ring and contains 32 bacteriochlorophyll *a* molecules and 16 bacteriochlorophyll *a* molecules are positioned perpendicular to this ring.

This paper presents work done toward the design, synthesis and properties of artificial porphyrin arrays used to mimic the energy capture and transfer properties of the natural light-harvesting antennae assemblies. The systems reported herein combine the advantages of a large number of porphyrin chromophores being contained within a discrete rationally designed supramolecular structure. They promote the very rapid energy delocalisation over available chromophores seen as an essential characteristic of natural light harvesting systems. Initial investigations have shown these constructs to be good models for the energy capture and transfer properties of the LH1 and LH2 systems with the largest giving rise to a particularly long-lived excited species.

Results and discussion

Bacteriochlorophyll molecules are relatively labile outside of biological systems. Any attempt to mimic the properties of the light-harvesting arrays is more likely to succeed by making use of synthetic porphyrins in their place. Not only is there a vast number of porphyrins that have been synthesised in the laboratory, it is relatively easy to modulate and control their chromophoric properties. Use of synthetic porphyrins offers the possibility of examining a range of exciting variations of the natural light-harvesting systems by the use of metalloporphyrins with many different metal ions other than magnesium(II), thereby shedding light on the reasons for nature's choice.

Mimicry of multi-porphyrin systems presents a challenge of considerable complexity – the need to control interporphyrin distances and relative orientations. In order to avoid creating huge structures in which the porphyrins would assemble into predefined locations, it should be evident that accurate chemical models for these multiporphyrin systems can only be obtained if the porphyrins are linked directly.

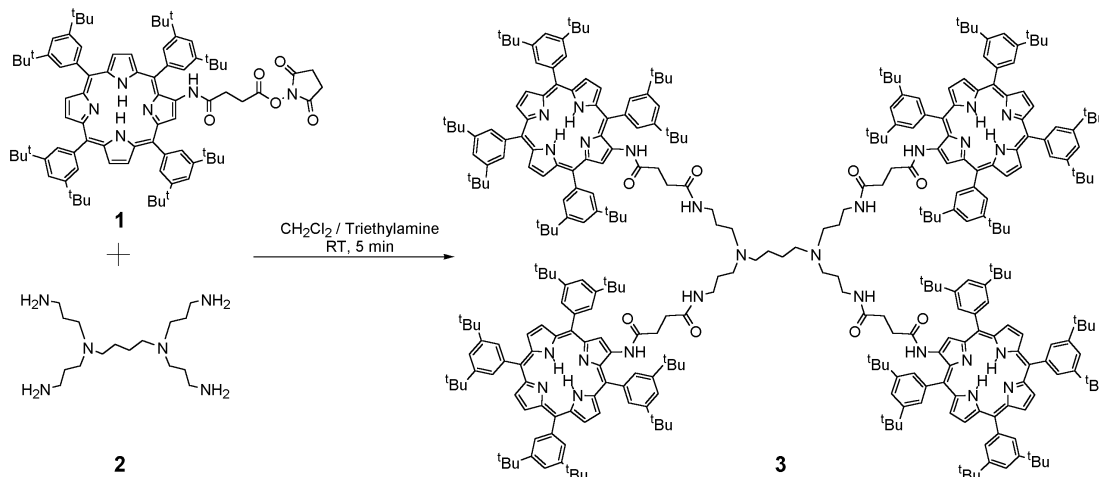
A porphyrin array assembled in a cyclic or spherical structure is of special interest. Dendrimers are well-defined hyperbranched polymers with variable sizes up to the nanometer range,⁴ and therefore these molecules are ideal building blocks to construct functional supramolecular assemblies. The functionalisation of dendrimers with porphyrins on the periphery would lead to spherical arrays, which might mimic the LH1 and LH2 systems. Subsequent modifications might allow the core of the dendrimer to be replaced by a photoactive component or this component might be bound as a guest molecule in the innerspace of the dendrimer.

We have coupled a porphyrin active ester to the amines of polypropylenimine dendrimers. This synthetic route results in fully functionalised dendrimers. 2-Amino-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrin was heated at reflux in toluene with succinic anhydride to give 4-{amino-2-[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinyl]}-4-oxo-butanoic acid in 80% yield. This porphyrin was activated (DCC and *N*-hydroxysuccinimide) giving the active ester **1** in 85% yield and subsequently coupled to the amino groups of the dendrimer DAB-*dendri*-(NH₂)₄, **2**, yielding the corresponding DAB-*dendri*-(NH-CO-CH₂CH₂-CO-NH-porphyrin)₄ **3** (Scheme 1). The reaction was carried out in dichloromethane for 5 minutes and only 4.1 molar equivalents (1.025 stoichiometric equivalents) of the active ester were

required to give near quantitative yield of **3**. According to TLC analysis, IR and ^1H NMR spectroscopy the product was pure.

Scheme 1

The synthesis of related 2-, 8-, 16-, 32-, and 64-porphyrin systems was readily



achieved from peptide coupling reactions of the porphyrin active ester **1** and appropriate dendrimers. The 16-porphyrin compound **4** is shown in Fig. 2 and the 64-porphyrin compound **5** is shown in Fig. 3.

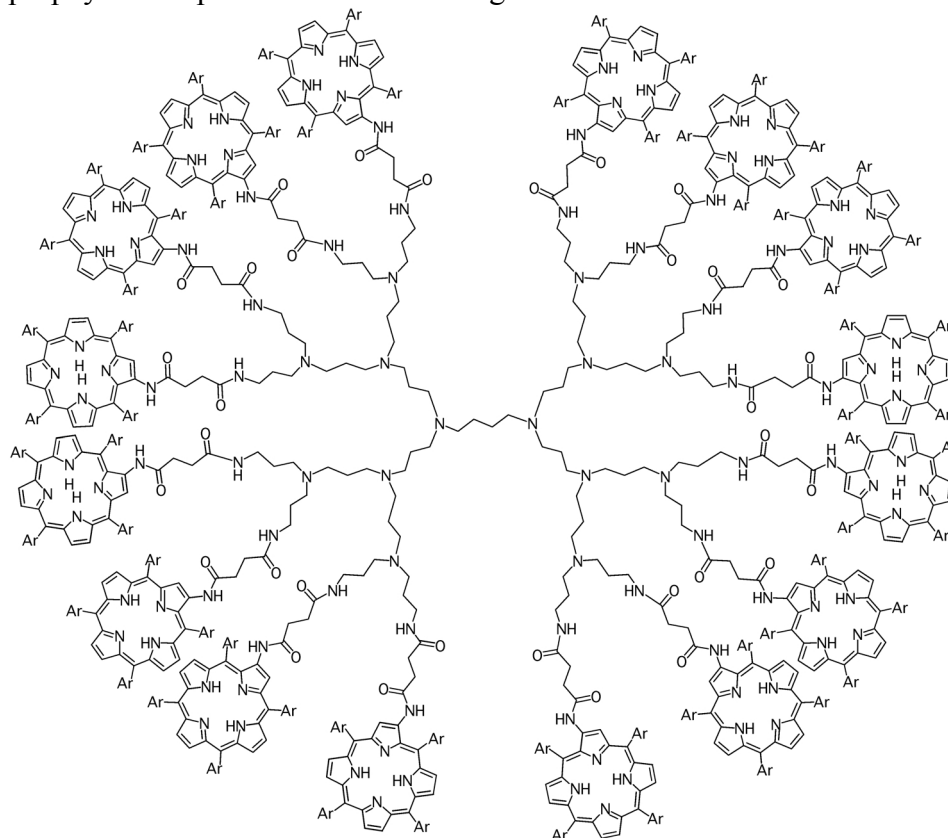


Fig. 2. Third generation porphyrin-appended dendrimer **4**. Ar means 3,5-di-*tert*-butylphenyl.

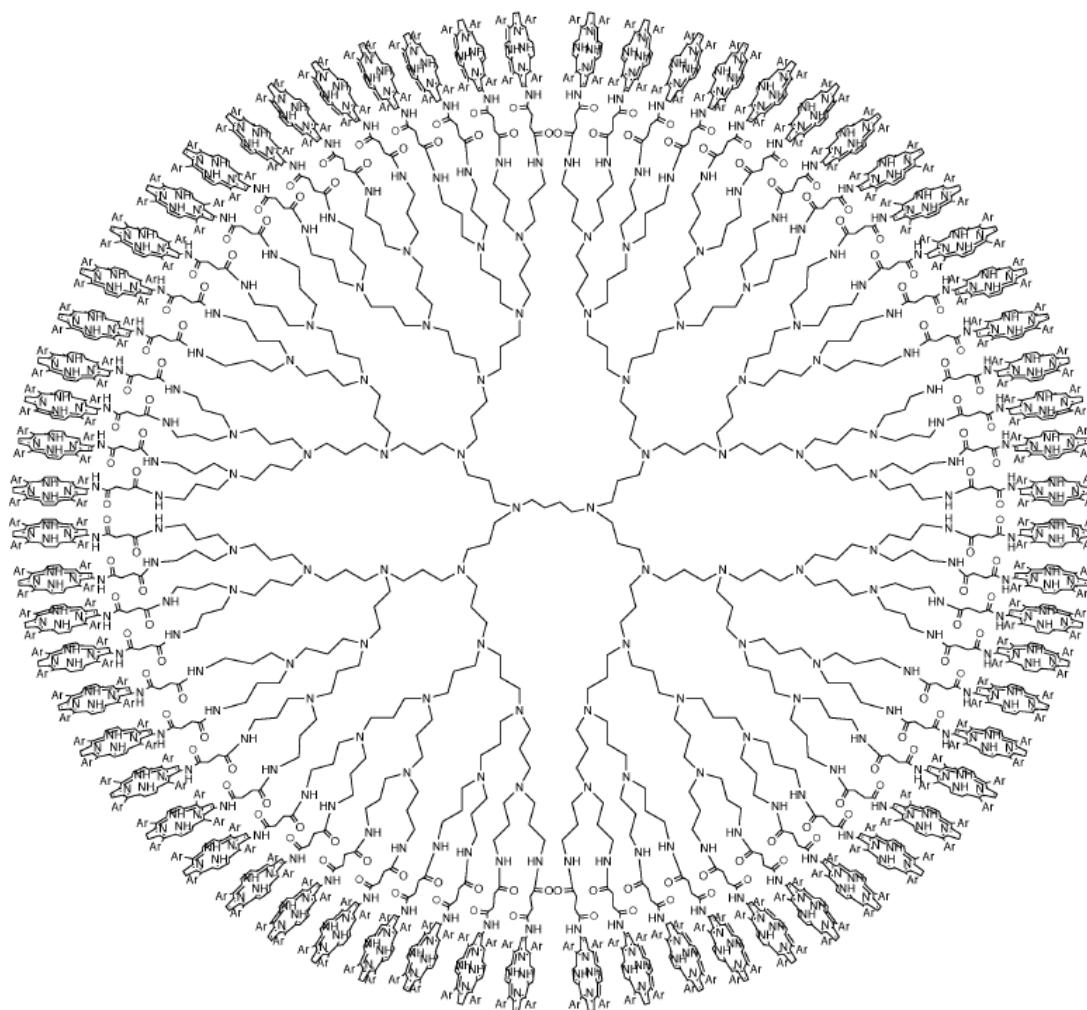


Fig. 3. Fifth generation porphyrin-appended dendrimer **5**: $C_{5496}H_{7088}N_{446}O_{128}$. A novel multi-chromophore “wheel” designed to mimic the energy capture of the bacterial light-harvesting antenna.

Interporphyrin distances in the 32-porphyrin system approximate well those found in bacterial LH2 systems. ^{13}C nmr spectroscopy was used to provide a clear indication as to the full extent of the involved coupling process. ^{13}C nmr spectra showed strong signals arising from the *N*-methylene carbons alpha to the newly formed amide functionality and an absence of any signal associated with *N*-methylene carbons alpha to the amine functionality originally present in the dendrimer starting material. The effectiveness of this approach was reinforced by the results of MALDI-TOF mass spectroscopy for the first three generation compounds, which showed the required parent ion peaks and distinctive fragmentation patterns predicted for each of these compounds.

Subsequent chelation of the free-base porphyrins within the functionalised dendrimers with metal ions such as magnesium(II) demonstrates one possible means for the modulation of the light absorbing characteristics of the chromophore. In this way the 16-porphyrin compound **5** was treated with magnesium iodide and readily converted into the Mg(II) analogue **6** in high yield (Fig. 4).

Investigations into the properties of the porphyrin arrays include efforts to study both the physical and photophysical nature of these macromolecules. Photophysical experiments carried out include fluorescence anisotropy and steady state fluorescence.

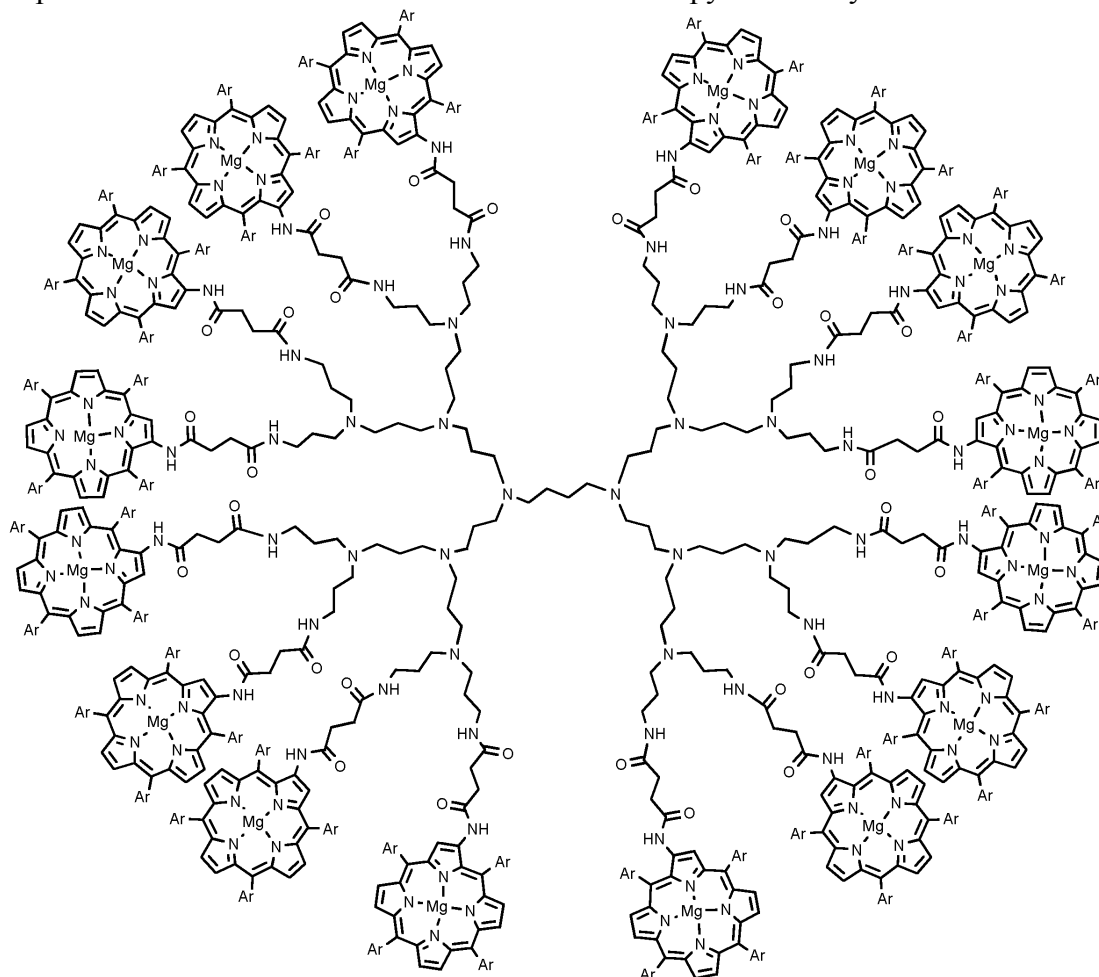


Fig.4. Example of a third generation metalloporphyrin dendrimer **6**. Magnesium (II) chelation with the free-base porphyrin chromophores enables a modification of the absorption spectrum.

Other studies have included molecular modelling, spin echo n.m.r. experiments and electron microscopy as a means to provide an insight into the three dimensional structure of the compounds both in and out of solution. Preliminary investigations into the electrochemistry of these compounds have also been conducted

In collaboration with Professor Ken Ghiggino and Edwin Yeow, photophysical studies have shown our porphyrin-appended dendrimers to be very good models for the light-harvesting systems involved in photosynthesis.¹ The 16-porphyrin compound **4** has a UV-vis spectra which is virtually the same as that of **1**, indicating that the ground state interaction between the porphyrins is small. This is due to the bulky *tert*-butyl groups of the *meso*-phenyls on the porphyrin rings which prevents a close contact between the porphyrin rings. Fluorescence anisotropy experiments show that these arrays, that have been prepared with 4-, 8-, 16-, and 64-appended porphyrins, provide good models of the energy capture and energy transfer properties of LH1 and LH2 systems. The 16-porphyrin compound **4** has a photosystem that is localised within each 4-porphyrin dendron while the 64-appended porphyrins compound **5** is a completely delocalised photosystem that has a particularly long-lived

excited species with energy transfer between porphyrin units of in the sub-picosecond domain (Fig. 5). These findings are very exciting as they mean that these compounds are the closest chemical model yet reported of the purple bacterial photosynthetic unit.

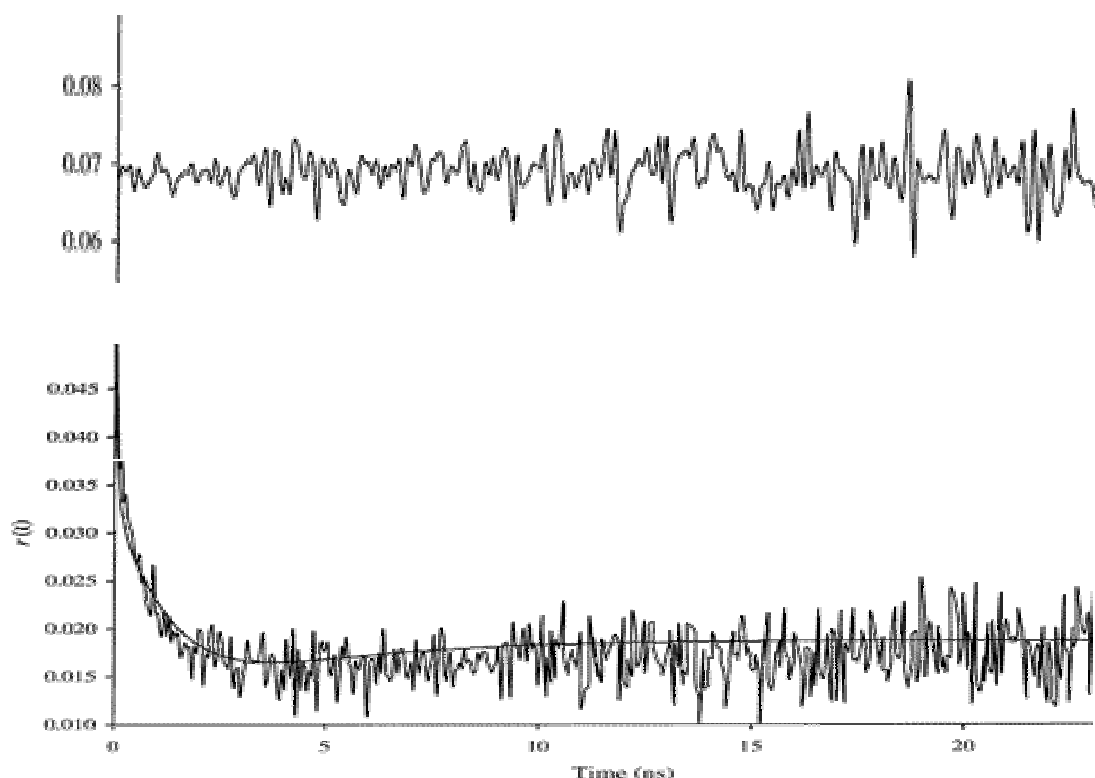


Fig. 5. Initial fluorescence anisotropy measurements on the **5** (bottom) showing rapid and extensive energy delocalisation compared with a single isolated chromophore (top).

Acknowledgements

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