



Retaining individualities: the photodynamics of self-ordering porphyrin assemblies†

Wen-Dong Quan,^{ab} Anaïs Pitto-Barry,^a Lewis A. Baker,^{ab} Eugen Stulz,^c
Richard Napier,^d Rachel K. O'Reilly*^a and Vasilios G. Stavros*^a

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The retention of photochemical properties of individual chromophores is a key feature of biological light harvesting complexes. This is achieved despite extensive aggregation of the chromophores, which in synthetic chromophore assemblies often yields a change in spectral characteristics. As an alternative approach towards mimicking biological light harvesting complexes, we report the synthesis of porphyrin assemblies which retained the photochemical properties of the individual chromophore units despite their substantial aggregation. These new materials highlight a new bottom-up approach towards the design and understanding of more complex biomimetic and naturally occurring biological systems.

One of the most important processes for life on earth is photosynthesis, which is performed by plant and photosynthetic micro-organisms such as cyanobacteria. Nature uses light harvesting complexes (LHCs) to efficiently channel photoexcited energy on ultrafast time frames.^{1–5} This extraordinarily efficient process is enabled by the elegant and precise arrangement of chromophores,^{3,6–8} through sophisticated yet naturally-occurring self-assembly processes, and is an exemplar of evolution's phenomenal achievements. Natural LHCs have inspired numerous attempts to create synthetic mimics of such cyclic arrays of chromophores to enhance, for example, the efficiencies of photovoltaic cells.^{9–11} A template-directed synthetic method, elegantly demonstrated by the Anderson group, produced some of the closest mimics.^{12–14} These assembly processes and the requirement for covalent conjugation generally lead to altered spectral characteristics of the individual chromophores. Whilst this does extend the spectral coverage of single chromophoric

systems, this is in contrast to biological LHCs, in which the UV-visible (UV-Vis) spectrum of the assembled system can usually be reconstructed by summing the UV-Vis spectra of the individual chromophores.^{8,15,16} Large aggregated and cross-linked systems are commonly utilised in biology for functions such as mechanical movements (actin filaments), photoprotection (melanin) and structural support (cross-linked cellulose and pectin), whereas the chromophores in LHCs are uniquely arranged through weak intermolecular interactions.^{4,7,8} Thus, the lack of covalent conjugations of these selected chromophores might be key to the functionalities of LHCs. Further, most of these synthetic assemblies require relatively high concentrations of the chromophores, and often challenging and complicated synthetic steps thus limiting their scalability and wider adoption.

In recent years, researchers have produced well-defined polymer-based self-assembled structures with relatively simple synthetic methods that are easily scaled up.^{17–21} In a handful of studies, various functionalised porphyrins, which are close mimics of some biological LHC chromophores, have been incorporated into these polymeric systems. These porphyrin-polymer conjugates were utilised in a range of applications such as photodynamic therapy (PDT),^{22–24} cell-imaging,^{25,26} initiators for complex polymers²⁷ and simple proof-of-concept experiments for potential self-assembly methodologies.^{28,29} However, the only excited state dynamics studies performed involved long time scales (> nanoseconds), as the majority of the systems were oriented towards PDT applications.^{30,31} However, ultrafast dynamics of chromophores is a determinant of light energy harvesting efficiency.^{1–3,32–37} It is therefore crucial to understand the effects of such aggregation processes on the ultrafast photodynamics of individual chromophores to facilitate rational designs of LHC mimics based on non-covalent self-assembling polymers.

In an effort to address the aforementioned synthesis and assembly challenges, as well as to obtain further insight into their ultrafast excited state dynamics, we designed a simple proof-of-concept porphyrin-polymer conjugate (**Zn-dPP-pDMA**, Fig. 1a) to exploit the natural solvophobicity-driven self-assembly

^a Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, UK.
E-mail: v.stavros@warwick.ac.uk, rachel.oreilly@warwick.ac.uk

^b Molecular Organisation and Assembly of Cells Doctoral Training Center (MOAC DTC), University of Warwick, Gibbet Hill Road, Coventry, UK

^c School of Chemistry & Institute for Life Sciences, University of Southampton, Highfield, Southampton, UK

^d School of Life Science, University of Warwick, Gibbet Hill Road, Coventry, UK

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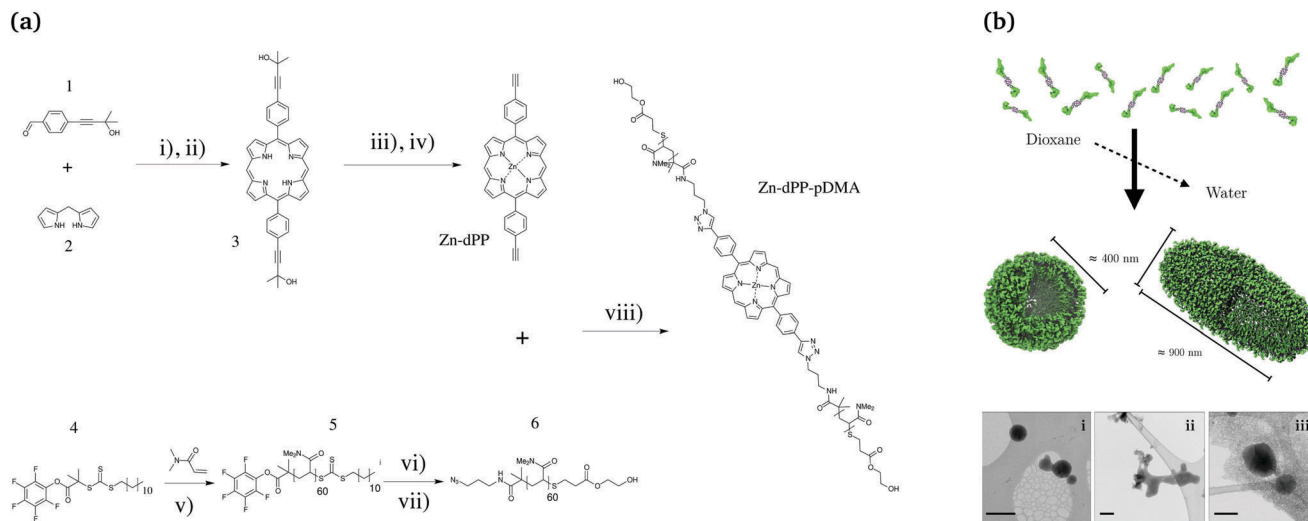


Fig. 1 (a) Scheme for the synthesis of poly(dimethylacrylamide) functionalised Zn-porphyrin (**Zn-dPP-pDMA**). (b) Cartoon representation of the assembly, and their visualisation under cryo-TEM (bottom, i–iii, scale bars = 500 nm). Conditions in (a): (i) $\text{BF}_3 \cdot \text{Et}_2\text{O}$, CH_2Cl_2 , N_2 , RT, 45 min; (ii) DDQ, toluene, N_2 , reflux, 3 h; (iii) $\text{Zn}(\text{OAc})_2 \cdot (\text{H}_2\text{O})_2$, $\text{CH}_2\text{Cl}_2 : \text{MeOH}$ (8 : 1), N_2 , 35 °C, 20 min; (iv) NaOMe , toluene, N_2 , reflux, 18 h; (v) AIBN, 1,4-dioxane, 65 °C, 40 min (80% conversion); (vi) 3-azidopropan-amine, tetrahydrofuran (THF), N_2 , RT, 18 h; (vii) HEA, PBU_3 , N_2 , THF, RT, 24 h; (viii) $\text{Cu} \cdot \text{P}(\text{OEt})_3$, dimethylformamide, N_2 , RT, 48 h. Detailed procedures are provided in the ESI†

of amphiphilic systems. This was based on well-optimised *meso*-functionalised porphyrin synthesis methodologies^{38–42} and reported polymerisation methods.⁴³ The careful selection of synthetic techniques produced **Zn-dPP-pDMA** in gram scale quantities. The relatively large scale synthesis, together with a lowered concentration for solvophobicity-induced assembly, produced polymer assemblies in quantities sufficient for condensed phase ultrafast transient electronic absorption spectroscopy (TEAS). Together with static photochemical studies, we demonstrate that the photochemical properties of individual chromophores are retained in these extensively aggregated systems. These experiments fill a gap in our knowledge, serving as an intermediate case study system that bridges the gap between the photochemical studies of simple small bio-molecules and complex macrobiological and biomimetic systems.

The synthetic scheme for the preparation of **Zn-dPP-pDMA** is shown in Fig. 1a. All the synthetic techniques employed were based on readily optimised procedures,^{38,39,41,43} and resulted in respectable to quantitative yields (see ESI† for further details). The azide-functionalisation and Z-group removal⁴⁴ of the starting **pDMA** (**5**) was performed with an improved one-pot two-step aminolysis method.⁴⁵ The conjugation of **6** and Zn-5,15-bis-(4-ethynylphenyl)-porphyrin (**Zn-dPP**) *via* copper-catalysed azide alkyne cycloaddition was completed at room temperature within 48 h. The excess **pDMA** was easily removed by preparative size-exclusion chromatography (prep-SEC) in dioxane as the conjugated product is strongly coloured; dioxane was then removed effectively by lyophilisation. The resulting **Zn-dPP-pDMA** was assembled at 3 mg mL⁻¹ (230 μM) by solvent switch from dioxane with slow addition of 18.2 MΩ cm water (see ESI†). Although we expected the formation of small micelles, cryogenic transmission electron microscopy (cryo-TEM) revealed surprisingly large vesicular polymersomes with spherical (Fig. 1b, i) and

ellipsoid morphologies (Fig. 1b, iii). The irregular structures observed (Fig. 1b, i and ii) suggested that the assemblies were dynamic and undergoing both fusion and fission processes, similar to other reported polymer-based vesicles.⁴⁶ Static/dynamic light scattering (SLS/DLS) characterisations at room temperature (RT, 20 °C) identified aggregates with R_g (radius of gyration) \approx 470 nm and R_h (hydrodynamic radius) \approx 190 nm ($R_g/R_h = 2.4$), indicating that the majority of assemblies are ellipsoidal or undergoing the fusion/fission processes at RT.⁴⁷ To verify that the large assemblies were indeed formed by the **Zn-dPP-pDMA**, we performed a series of characterisation experiments on samples filtered through membranes of different pore sizes. These studies showed that not only were large amounts of material remaining in the filter, the assemblies also underwent reorganisation, leading to significant change in size upon filtration (see ESI†). Thus, all photochemical experiments of these assemblies were performed with fresh, unfiltered samples, as shown in Fig. 1b.

Despite their extensive aggregation, the spectral features evidenced in the UV-Vis spectrum of **Zn-dPP** are largely retained in the assembled system (Fig. 2a). However, differences are apparent, which warrant discussion. Firstly, the Soret-band (\approx 414–420 nm, $S_2 \leftarrow S_0$) and Q-band (\approx 500–625 nm, $S_1 \leftarrow S_0$) are red-shifted by *ca.* 5 nm. Secondly, a broadening of the Soret band is evident. Lastly, there is an increase in Q-band relative to Soret-band intensities. These changes closely resemble that of a recently reported Mg(II)bisporphyrin system, in which the $\text{Mg} \cdots \text{Mg}$ non-bonding distance was determined to be *ca.* 6.5–7.5 Å.⁴⁸ These observations, taken together with the near identical fluorescence spectra of all the present systems (see ESI†) and the absence of excitonic features, as seen in reported dimers and ordered aggregates,^{49,50} described by Kasha's exciton theory,⁵¹ leads us to propose that while the chromophores are held at close



