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

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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, rational designs of LHC mimics based on non-covalent self-assembly challenges, as well as to obtain further insight into ultrafast photodynamics of 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 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 properties of the individual chromophores, 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...
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 con-
densed phase ultrafast transient electronic absorption spectroscopy
(TEAS). Together with static photochemical studies, we demon-
strate that the photochemical properties of individual chromo-
phores 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 macro-
biological 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 removal\(^{44}\) of the start-
ing 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 conju-
gated product is strongly coloured; dioxane was then removed
effectively by lyophilisation. The resulting Zn-dPP-pDMA was
assembled at 3 mg mL\(^{-1}\) (230 \(\mu\)M) by solvent switch from
dioxane with slow addition of 18.2 \(\text{M} \text{2cm water (see ESI}^{†}\)).
Although we expected the formation of small micelles, cysrogene
transmission electron microscopy (cryo-TEM) revealed surpris-
ingly 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) \(\approx 470 \text{ nm and } R_h\) (hydrodynamic radius) \(\approx 190 \text{ nm} (R_g/R_h = 2.4),\) 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 experi-
ments 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 filtra-
tion (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
(\(\approx 414-420 \text{ nm, } S_2 \leftarrow S_0\) and Q-band (\(\approx 500-625 \text{ nm, } S_1 \leftarrow S_0\))
are red-shifted by \(ca. 5 \text{ 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 Mg · · · Mg
non-bonding distance was determined to be \(ca. 6.5-7.5 \text{ Å.}^{48}\) 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 Kash’s exciton theory,\(^{51}\) leads us
to propose that while the chromophores are held at close

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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) BF\(_3\)Et\(_2\)O, CH\(_2\)Cl\(_2\), N\(_2\), RT, 45 min; (ii) DDQ, toluene, N\(_2\), reflux, 3 h; (iii) Zn(OAc)\(_2\)-2(H\(_2\)O), CH\(_2\)Cl\(_2\), 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) Cu-P(OEt)\(_3\), dimethylformamide, N\(_2\), RT, 48 h. Detailed procedures are provided in the ESI.\(^†\)
proximity to each other, extensive stacking is prevented, resulting in the chromatophores of the aggregates being weakly coupled. This is very likely the result of the repulsive interactions between the polymer chains.\textsuperscript{19,20}

After having established the general chromophore arrangement, we determined the excited state dynamics of the three systems (Zn-dPP, Zn-dPP-pDMA unimers solvated in dioxane; and Zn-dPP-pDMA assembled in 18.2 MΩ cm water), using TEAS following photoexcitation to the S\textsubscript{2} state with 400 nm radiation. We first examined Zn-dPP, in which the transient absorption spectra (TAS) show two dominant features: the large ground state bleach (GSB) in the Soret region (ca. 416 nm) and the excited state absorption shoulders (ESA, ca. 450 nm, Figs. 2a, 2b). Global fitting the TAS\textsuperscript{52–54} reveals two ultrafast processes (Table 1): internal conversion (IC) of S\textsubscript{2} to S\textsubscript{1} (\(\tau\text{IC} \approx 1\) ps) and intramolecular vibrational energy transfer (IET) between the Zn-dPP S\textsubscript{1} excited state and the dioxane solvent bath (\(\tau\text{IET} \approx 21.8\) ps). These time constants and corresponding processes are comparable to the previously studied model Zn-tetraphenyl-porphyrin (Zn-tPP) reported by Zewail and co-workers (see ESI\textsuperscript{†}).\textsuperscript{55} We note that in addition to these two extracted time-constants, there is a time-constant that extends beyond the temporal window of our measurements (2 ns) which, in accord with previous studies,\textsuperscript{55} we attribute to inter-system crossing (ISC) of S\textsubscript{1} \(\rightarrow\) T\textsubscript{0} (\(\tau\text{ISC}\)) (see Table 1, footnote a).

The shapes of the decay associated spectra (DAS, Fig. 2c) are highly informative in guiding the interpretation of the TAS. In particular, any negative components correspond to an exponential rise in that population whilst any positive components correspond to an exponential decay in population. The flow of excited state populations can be visualised in the DAS when a positive and negative features appear concomitantly. This can be interpreted as either a change in electronic state (IC or ISC), or relaxation within a single electronically excited state (IET).\textsuperscript{52,56}

Remarkably, almost identical features are observed in the TAS of the functionalised systems (Zn-dPP-pDMA unimers in dioxane and assembled in water, see ESI\textsuperscript{†}). Furthermore, these are fitted with almost identical time constants (Table 1 and Fig. 2c) revealed no discernible differences in their features. Of these, \(\tau\text{IC}\) showed insignificant variations. The slightly faster \(\tau\text{IET}\) observed in the assembled system (15.2 ps cf. 20.3 ps in dioxane) suggests that the vibrational frequency match between the Franck-Condon active modes of the photo-excited Zn-tPP and the instantaneous normal modes of its surrounding molecules might be different between each system, as inferred in previous studies.\textsuperscript{55,57} However, the differences are within the 95% confidence interval of each other (Table 1 and ESI\textsuperscript{†}), which makes this supposition tentative. The final ISC process demonstrated no discernible difference within the window of our experiments (Table 1 and Fig. 2c).

In conclusion, we have presented a study on a basic system of solvated and aggregated porphyrin molecules assembled via solvophobicity. The photodynamic studies presented demonstrate that the individual Zn-dPP molecules retained their overall photo-chemical properties following the addition of a large polymer (pDMA), even following assemblies into macromolecular vesicles. The fact that the addition of such a large polymer has very little effect on the photochemical properties of the porphyrin adds credence to the ‘bottom-up’ approach towards understanding the photochemistry and photophysics of complex biological systems.\textsuperscript{56–61} Coupled with the relatively high yielding synthetic steps and simple assembly method, these types of polymer-chromophore conjugates could be opportune building blocks for more complex biomimetic systems. We propose that this proof of concept study should facilitate future modular designs of photo-active biomimetic arrays which do not rely on the complex covalent conjugation of multiple chromophores, thereby allowing full exploitation of individual pigment characteristics.

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References