

Functionalized porphyrin derivatives for solar energy conversion



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ABSTRACT

In this review, we discuss a collection of three sets of porphyrin-based systems recently synthesized in our group. In the first set we improve the light harvesting ability of porphyrins by preparing arrays in which strongly absorbing boron dipyrin (BDP) chromophores are combined with porphyrins, either by covalent attachment to the periphery of the porphyrin ring or by axial coordination to a tin(IV) porphyrin. We observe that BDP increases significantly the light absorption capability of porphyrins by efficient BDP to porphyrin excitation energy transfer. Further functionalization of the arrays with redox active groups such as phenolate ligands or fullerenes gives rise to interesting electron transfer dynamics in the excited state. In the second set, we use porphyrins as sensitizers in photocatalytic hydrogen production schemes with cobaloxime catalysts either in supramolecular or diffusion controlled systems. Photocatalytic experiments, detailed spectroscopic studies on our systems and recent literature results show that attachment of a photosensitizer to a catalyst is in fact detrimental to H₂ production. Diffusion controlled systems show considerably increased photocatalytic activity mainly because deleterious effects such as back electron transfer are avoided. In the final set, porphyrins are used as light harvesting dyes in dye-sensitized solar cells (DSSCs). Aiming to extend the light absorption range of the sensitizing dyes, to achieve enhanced solar cell performances, appropriately functionalized porphyrins with carboxylic acid anchoring groups are synthesized. These include porphyrins with π -conjugated groups at *meso* positions, “push–pull” porphyrins, porphyrins with bridges between the macrocycle and the anchoring group, and covalently linked arrays of porphyrins and other chromophores. Porphyrins with pyridyl anchoring groups are also utilized, in order to get insight into the effect of the nature and strength of the porphyrin binding on the solar cell efficiency. Devices with photovoltaic efficiencies higher than the average values of solar cells sensitized by simple porphyrin and other hybrid-porphyrin derivatives are obtained, particularly after reduction of dye-aggregation by means of chemical co-adsorbents, and by using co-sensitization, modified photoanodes, molten electrolytes and electrolyte additives.

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1. Introduction

The harvesting and storage of solar energy by means of multi-chromophoric assemblies has been an active field of research over the last few decades [1]. The early stages of photosynthesis, where solar energy is absorbed and channeled to a reaction center through a series of energy and electron transfer steps, have been a major source of inspiration for the construction of artificial mimics [2]. Due to their importance in natural photosynthesis, porphyrins have been widely investigated as key constituents of artificial photosynthesis systems as they exhibit strong absorption in the

visible region and highly redox active excited states. In the present review, we summarize recent results from our group on the use of porphyrins as light harvesting and energy storage agents in three different contexts: (i) synthesis and photophysical study of multi-chromophoric systems involving porphyrins, (ii) the use of porphyrins as sensitizers in photocatalytic hydrogen production schemes and (iii) porphyrin derivatives as light harvesting dyes in dye sensitized solar cells (DSSCs).

2. Electron and energy transfer in porphyrin derivatives

Despite of their favorable properties, one major drawback of porphyrin derivatives as light-harvesters is their relatively poor absorption cross section in the blue-green region of the spectrum (430–550 nm). This issue can be tackled by coupling porphyrins with chromophores, which absorb strongly in the desired spectral

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region and are thus able to sensitize the porphyrin excited state via efficient intramolecular energy transfer. Boron dipyrin (BDP), see [scheme 1](#), dyes are particularly attractive as “antenna” chromophores for porphyrins as they combine the following characteristics: (i) BDPs are well-known for their high extinction coefficients in the 450–550 nm region (ii) high fluorescence quantum yields and long-lived excited states and (iii) excellent photostability, and stability in many solvents [3]. In addition, the absorption and emission properties of BDP dyes can be easily tuned in the 450–680 nm range owing to the ease of synthetic modification of the BDP core. Indeed, a wealth of studies exist in which, BDP chromophores transfer excitation energy to porphyrins thereby mimicking the photosynthetic antenna-reaction center [4]. In our studies, we combined the BDP chromophore with porphyrins in two ways: (i) covalent attachment of BDP to the periphery of the porphyrin ring and (ii) axial attachment of BDP antennas on a porphyrin via coordination bonds.

2.1. Peripherally substituted porphyrin arrays

2.1.1. Porphyrin arrays linked via a cyanuric chloride bridge

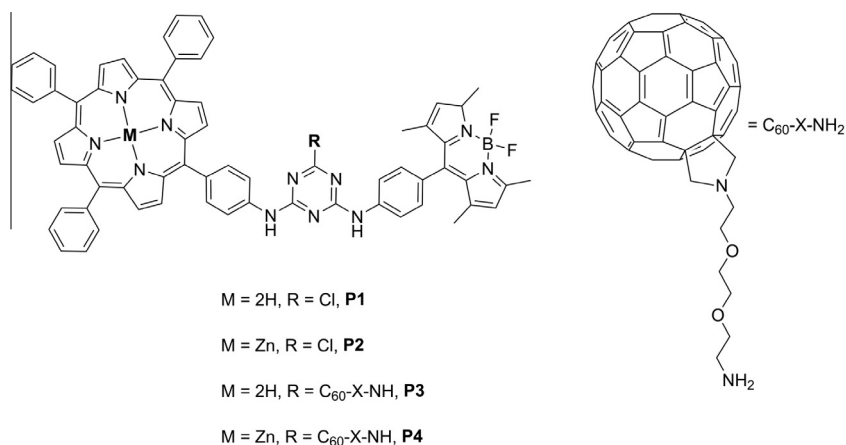
In this first example we exploited the favorable properties of cyanuric chloride, which allows the introduction of up to three different nucleophiles on an s-triazine unit through temperature-dependent sequential substitution of its three chlorine atoms. We thus prepared assemblies **P1** and **P2** in which a BDP chromophore is linked by a flexible cyanuric chloride bridge to either a free-base porphyrin (H_2P) or a Zinc porphyrin (ZnP) [5]. In later work, **P1** and **P2** were further functionalized with an electron accepting fulleropyrrolidine unit [4a,6] through an amino substituted aliphatic chain to give electron donor/acceptor conjugates **P3** and **P4** ([Scheme 1](#)) [7]. Triads **P3** and **P4** show a triangular arrangement of three different photo- and redox- active groups around the central s-triazine linker thereby permitting direct interaction of each chromophore with the other two.

In **P1** and **P2**, steady-state and time-resolved fluorescence studies clearly show that initial excitation of the BDP unit at 490 nm is followed by rapid BDP to porphyrin energy transfer as shown by the greatly reduced BDP fluorescence lifetimes and quantum yields of **P1** and **P2** ($\phi \approx 0.01$, $\tau \approx 0.1$ ns) with respect to the corresponding values of a free BDP control ($\Phi = 0.58$, $\tau = 3.58$ ns). Furthermore, ultrafast transient absorption studies showed that excitation of **P1** and **P2** into their BDP-based singlet $\pi-\pi^*$ excited states is followed by energy transfer to the lowest-lying porphyrin based singlet excited states with rate constants of $k_{P1} = 2.9 \times 10^{10}$ and $k_{P2} = 2.2 \times 10^{10} s^{-1}$. Analysis of the experimental results with

the assistance of DFT calculations on **P1** and **P2** suggested a Förster-type dipole–dipole interaction [8] as the most likely mechanism of BDP to porphyrin energy transfer. Turning to the transient absorption studies of triads **P3** and **P4**, selective BDP excitation at 490 nm results in the immediate formation of the BDP singlet excited state which decays by energy transfer to the porphyrin singlet excited state with time constants of 32 and 26 ps respectively. In contrast to **P1** and **P2** where the porphyrin singlet excited state decays to the ground state by fluorescence and intersystem crossing to the triplet, in **P3** and **P4** it is followed by rapid intramolecular charge separation to yield the metastable radical ion pair states H_2P^+/C_{60}^- (**P3**) and ZnP^+/C_{60}^- (**P4**), which decay back to the singlet ground state with lifetimes of 3000 and 900 ps respectively. It is worth noting, that no evidence of direct electron transfer from BDP to C_{60} was seen in the transient spectra of **P3** and **P4**, following excitation at 490 nm, even though charge separation with a lifetime of 80 ps to afford BDP^+ and C_{60}^- is confirmed as the dominant decay pathway of an analogous BDP- C_{60} dyad which was studied as a control. The absence of a BDP to C_{60} electron transfer pathway in **P3** and **P4** can be attributed to kinetic factors since BDP to H_2P/ZnP (ca. 30–32 ps) energy transfer is faster than that of BDP to C_{60} electron transfer (80 ps).

2.1.2. Porphyrin arrays linked by an amino group

In a next set of compounds ([Scheme 2](#)), we used a palladium-catalyzed coupling reaction to prepare triads **P5** and **P6** where two H_2P or BDP units were linked to the meso positions of a central ZnP via amino groups [9]. In the UV–Vis absorption spectra of **P5** and **P6** we observe features from all their constituent chromophores indicating weak interchromophoric interactions in the ground state (see [Fig. 1](#)). Most notable in the UV–Vis spectra of **P5** and **P6** is their wide range absorption over most of the visible region. When **P5** is excited at either 517 nm (mostly peripheral H_2P chromophores) or 467 nm (mostly central ZnP chromophore) an emission spectrum resembling that of a free base porphyrin is obtained with maxima at 661 and 719 nm, while the excitation spectrum of **P5** shows absorption features from both the central and peripheral porphyrins when monitored at 661 nm. Time resolved emission studies with pulsed excitation of mostly the peripheral porphyrins at 400 nm clearly shows emission from both the constituent chromophores of **P5** as indicated by the dual exponential decay with lifetimes of 2.9 (ZnP) and 9.8 (H_2P) ns. Combination of the steady-state and time-resolved emission results shows **P5** emits from both chromophores regardless of excitation wavelength as excitation of one chromophore results in partial energy transfer to the other. This is expected because the H_2P and ZnP first singlet



Scheme 1. Peripherally substituted porphyrin arrays linked through a cyanuric chloride bridge.

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