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Sequential Energy and Electron Transfer in Aggregates of Tetrakis[oligo(*p*-phenylene vinylene)] Porphyrins and C_{60} in Water

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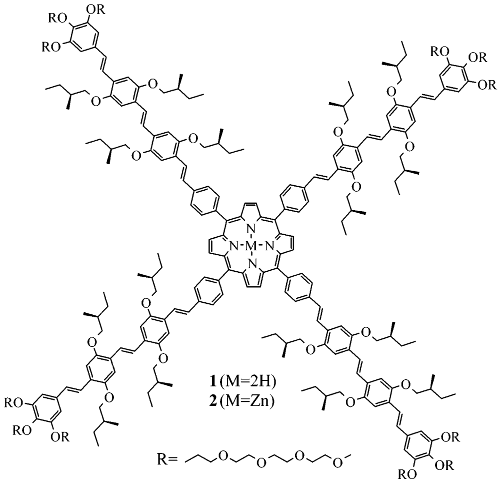
Efficient cascade energy and electron transfer in natural photosynthetic systems depends highly on the molecular structure of chlorophylls and the way in which they are mesoscopically ordered.[1] Since interchromophoric order is crucial for efficient functioning of organic electronic devices, understanding and mimicking photosynthetic processes may eventually lead to improved design principles for such devices based on noncovalent interactions. Energy[2] and electron[3] transfer processes in π-stacked architectures have been reported;[4] however, the use of sequential energy and electron transfer steps has been far more elusive and has, up until now, only been observed in, for example, elegantly designed covalent molecules[5] or supramolecular dimers.[6] To the best of our knowledge, we report here the first approach to cascade energy and electron transfer in mixed π-conjugated assemblies in water, based on our previous experience with water-soluble oligo(*p*-phenylene vinylene)s (OPVs).[7] For this purpose, we constructed mixed assemblies consisting of $(OPV4)_4$ porphyrins **1** and **2**. When these assemblies are formed in water, excitation of OPV4 should result in energy transfer from OPV4 via Zn porphyrin to free-base porphyrin. Moreover, incorporation of C_{60} into aggregated **1** or **2** results in redox-active assemblies yielding an additional electron transfer step to C_{60}. Compounds **1** and **2** have been synthesized and fully characterized.[8] Absorption spectra of **1** and **2** in chloroform clearly show the distinctive Q-bands of the porphyrin,[9] although the Soret band is remarkably shifted and broadened, suggesting a certain degree of ground state interaction of the separate chromophores. Photoluminescence spectra of **1** and **2** in chloroform show that upon predominant excitation of OPV4 ($\lambda_{ex} = 346$ nm) the OPV emission is strongly quenched whereas almost exclusive emission of the porphyrin is observed, indicating efficient intramolecular energy transfer from the OPVs to the porphyrin (see the Supporting Information for a comparison of **1** with reference compounds).

Chart 1. $(OPV4)_4-H_2$ Porphyrin (**1**) and $(OPV4)_4-Zn$ Porphyrin (**2**)



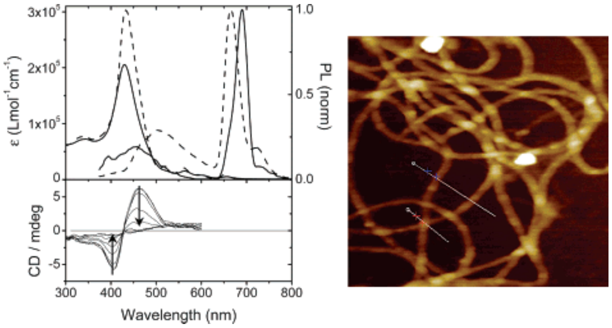


Figure 1. UV/vis and PL of **1** (10^{-5} M, $T = 20$ °C) in water (solid line, $\lambda_{ex} = 344$ nm) and chloroform (dashed line, $\lambda_{ex} = 337$ nm) and temperature-dependent CD spectra of **1** in water (5×10^{-6} M, $T = 10-80$ °C). Tapping mode AFM image showing fibers of **1**, dropcast from water (10^{-5} M) onto a MICA surface (420 nm × 420 nm).

In water, the absorption spectra of **1** and **2** display a red shoulder at $\lambda = 475$ nm, a decrease in extinction coefficient, and a hypsochromic shift (4 nm) of the Soret band. Moreover, a clear bathochromic shift in their emission maxima (25 nm) and a bisignate Cotton effect in circular dichroism suggest chiral, face-to-face aggregation of pure **1** and **2** in water (Figure 1).[10]

Temperature-dependent UV/vis and CD spectra of **1** and **2** in water show a loss of optical activity at elevated temperatures (Figure 1), while the UV/vis spectra remain unchanged, indicating a transition from chiral to achiral aggregation.[8] AFM measurements of **1** on mica show extended fibers of 3.5 nm in height that coagulate into larger assemblies.[8] If we assume an extended conjugated system, this height corresponds to an angle of 64° between cofacially stacked molecules and the MICA surface if two OPV arms of each molecule interact with the surface.

Mixed assemblies of **1** and **2** were studied in water, based on ubiquitous reports using Zn and free-base porphyrin as energy donor and acceptor, respectively.[11] Aggregates made by premixing **1** and **2** in THF before injection into water[8] showed a clear decrease in the emission of **2** ($\lambda_{max} = 623$ nm, 5×10^{-7} M) and an increase in the fluorescence of **1** ($\lambda_{max} = 666$ nm), indicating cascade energy transfer from OPV4 via zinc porphyrin to free-base porphyrin (Figure 2A). A control experiment performed by the addition of aggregated **1** in water to aggregated **2** in water did not show any significant change in emission of **2** (Figure 2B), indicating absence of energy transfer between separate stacks of **1** and **2**.

To incorporate redox activity, use was made of the specific, attractive interactions of fullerenes with porphyrins.[3b,12] UV/vis spectra of mixed aggregates of C_{60} with either **1** or **2** in water (5×10^{-7} M)[8] exhibited a 5 nm bathochromic shift of λ_{max} and a charge

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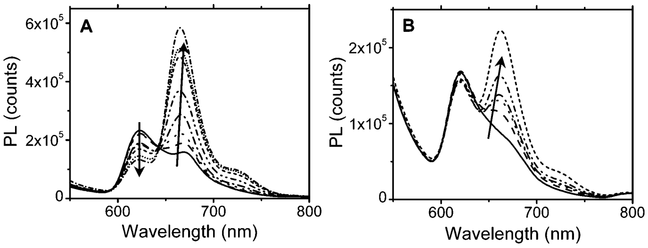

Figure 2. PL spectra for the addition of (A) 0−36 mol % of **1** to **2** in water, (B) 0−30 mol % of **1** in water to **2** in water (in both cases $\lambda_{ex} = 346$ nm, [**2**] $= 5 \times 10^{-7}$ M, $T = 20$ °C).

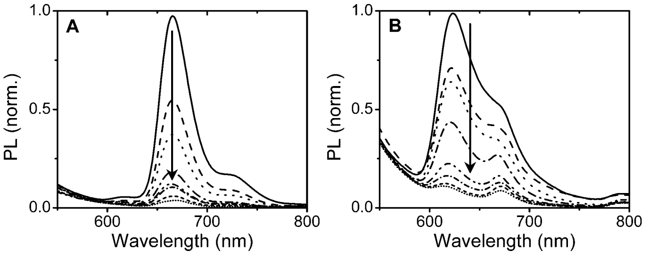

Figure 3. Normalized PL spectra for mixtures containing 0−75 mol % of C_{60} in (A) **1** and (B) **2** in water ($\lambda_{ex} = 346$ nm, 5×10^{-7} M, $T = 20$ °C).

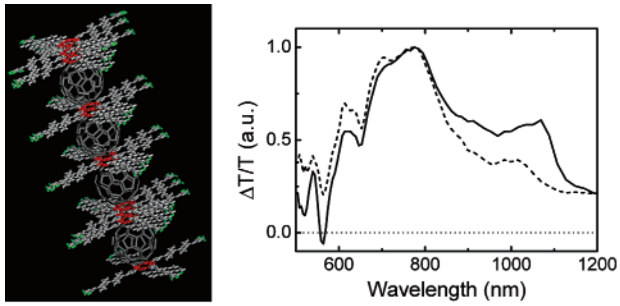

Figure 4. Proposed molecular picture of a co-aggregate of **1** and C_{60}. Photoinduced absorption of **1** (dashed) and of a 1:1 ratio of **1** with C_{60} (solid) ($\lambda_{ex} = 361$ nm, 10^{-4} M, $T = 20$ °C).

transfer band (**1**: $\lambda = 672$ nm, **2**: $\lambda = 625$ nm), both of which are known to be induced by porphyrin−fullerene interactions.[13] Since scattering effects were observed when the C_{60} incorporation exceeded 50 mol %, these collective observations indicate formation of a 1:1 co-aggregate of **1** or **2** with C_{60} in water. These complexes yielded clear solutions that were stable in time. Furthermore, photoluminescence spectra of mixtures ($\lambda_{ex} = 346$ nm, Figure 3) show a dramatic quenching of porphyrin emission upon addition of C_{60} to either **1** or **2**, suggesting electron transfer to incorporated C_{60}. Near quantitative quenching of **1** and **2** luminescence is reached at ∼20 mol % C_{60} incorporation.[8]

To directly prove intermolecular electron transfer to C_{60}, photoinduced absorption (PIA) was performed on a 1:1 mixed assembly of **1** and C_{60} (Figure 4). The PIA spectrum shows a band at $\lambda = 1070$ nm that is characteristic for the C_{60} radical anion.[14] A bleaching band at $\lambda = 550$ nm indicates that less porphyrins occupy their ground state, suggesting that the porphyrin radical cation is responsible for the observed absorption band at $\lambda = 750$ nm. However, on the basis of the Weller equation[15] for these systems, the difference in driving force for charge separation into either OPV4 or porphyrin radical cation and C_{60} radical anion is negligible at room temperature.[8] Therefore, assignment of the band observed at $\lambda = 750$ nm is difficult. A 1:1 mixed assembly of **2** and C_{60} did not show the $\lambda = 1070$ nm band, which will be further investigated on shorter time scales.[8]

Since C_{60} has a higher affinity for free-base porphyrin than for Zn porphyrin,[12a] we aimed at the formation of a mixed aggregate consisting of **2** and 15 mol % of a 1:1 ratio of **1** and C_{60}.[8] Preliminary fluorescence data indicate cascade energy transfer from OPV4 via zinc porphyrin to free-base porphyrin followed by electron transfer from **1** to C_{60}.[8]

In conclusion, we have shown the first examples of energy and electron transfer in multichromophoric, π-conjugated assemblies in water by construction of mixed stacks consisting of $(OPV4)_4$−Zn porphyrin, $(OPV4)_4$−H_2 porphyrin, and C_{60}. Currently, we are determining speeds for the different energy and electron transfer steps.

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Supporting Information Available: Synthetic route to **1** and **2** and their full characterization. Optical comparison of **1** with reference compounds (Figure S1). Solvent and temperature-dependent UV/vis for **1** (Figure S2) and for **2** (Figure S3). AFM and height profile for **1** (Figure S4). UV/vis and quenching data for addition of C_{60} to, respectively, **1** and **2** (Figures S5−S7). PIA spectra (Figure S8) and energetic diagrams for **1** and **2** (Figure S9), including data for the Weller equation (Table S1). PL data for a mixture of **1**, **2**, and C_{60} (Figure S10). This material is available free of charge via the Internet at http://pubs.acs.org.

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