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# Fluorescence Quenching in a Perylenetetracarboxylic Diimide Trimer

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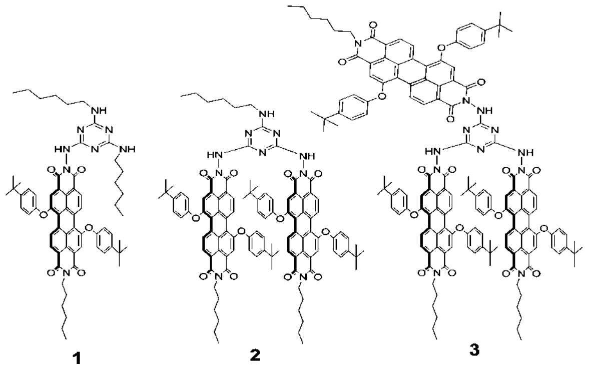
Energy transfer (ET) and migration in natural light harvesting systems (LHs) are highly efficient despite involving complex structures with many different chlorophyll molecules.[1] Great efforts have been devoted to the synthesis and characterization of artificial systems that can elucidate or mimic key mechanisms of ET in natural LHs.[2] Recently the ET in more complicated systems, such as molecular aggregates with precisely controlled structure, has generated a lot of interest because the crystal structure of LHs has revealed the dominating role of aggregated bacterio-chlorophylls (BChl) in the ET process in photosynthesis.[2c,3]

To understand the photophysical properties of molecular aggregates, the study on the photophysical interactions between monomeric and aggregated molecules is necessary because the self-aggregation normally leads to equilibrium between aggregates and monomeric molecules in solution. An energy transfer from a diphenylacetylene monomer to dimer has recently been reported in a DNA triplex templated supramolecular system,[4] but the dynamics and the efficiency of this ET are still unknown. To elucidate the detail of the ET from monomer to dimer, new models with relative simple but well-defined structure are necessary. We designed a trimeric perylenetetracarboxylic diimide (PDI) molecule, with three PDI molecules connected by a melamine, **3** in Figure 1.



**1** **2** **3**

***Figure 1.*** Molecular structures of the compounds.

Because the face-to-face structure formed by the two chromophores linked by melamine has been well documented in literature,[5] we expect a face-to-face dimeric conformation for two of the three PDIs in the molecule; the third one appended acts as a monomer, which partially resembles the structural block in the LH2 complex, that is, B800 BChl monomer and B850 BChl dimer.[1b] Our design is structurally different from the flexible linear PDI trimer[6] as well as the rigid cofacially stacked PDI trimer[7] and should be an ideal model for the study of the photophysical interactions between a covalently linked monomer and dimer.

Compound **3** together with monomer **1** and dimer **2** were prepared by the condensation of 1,7-di(4′-*t*-butyl)phenoxy-perylene-9,10-(*N*-hexyl)-dicarboxyimide-3,4-dicarboxylic anhydride with corresponding melamine derivatives.[8] The synthesis and structure characterization are described in the Supporting Information.

The absorption spectra of compounds **1**−**3** show two intense absorption bands peaked at about 502 and 542 nm, but with varied relative intensity between these two peaks (Figure 2). Apparently the relative peak-intensity of the dimer **2** is reversed from that of the monomer **1**. This intensity reversing can be attributed to the formation of a face-to-face stacked PDI dimer.[6] It is noteworthy that the absorption spectrum of compound **3** presents two peaks with almost equal intensity and is concentration independent in the range of $10^{-4}-10^{-6}$ mol $L^{-1}$, indicating that the peak at 502 nm is not due to the intermolecular aggregation, but a intramolecular aggregation instead. More interestingly, the spectrum of compound **3** is almost identical to the sum of that of **1** and **2**, which suggests that compound **3** is composed of a "dimer" and a "monomer" as expected, and there is no significant interactions between them at ground state. This is also supported by the $^1$H NMR spectra of **1**, **2** and **3** (Figure S2 in Supporting Information).

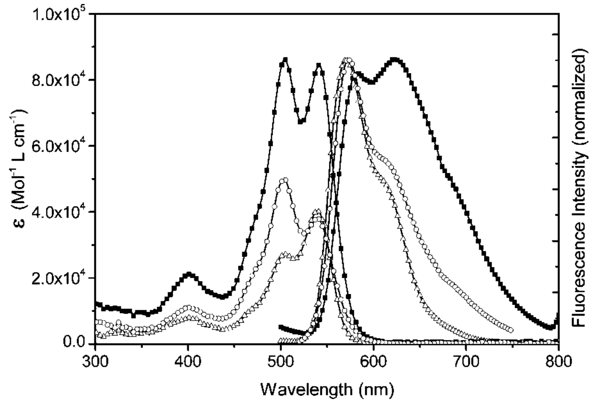


***Figure 2.*** UV−vis absorption and fluorescence spectra of monomer **1** (Δ), dimer **2** (○), and trimer **3** (■) in toluene.

The monomer's emission is observed at 570 nm with a lifetime of 4.5 ns while the dimer **2** shows monomer's emission at 570 nm with a broad tail extending to 750 nm (Figure 2). The tail with a lifetime of 20 ns can be assigned to the excimer's emission from the face-to-face stacked PDI dimer.[8] The overall fluorescence quantum yield for dimer **2** (8%) is much smaller than that of the monomer.[2a] On the basis of the results of absorption and fluorescence spectra of compound **3**, one would expect a very strong monomer's emission from compound **3**. However, compound **3** gives a broad emission band in the range of 550−750 nm with a fluorescence lifetime of 22 ns, typical of the excimer's emission rather than that of monomer.[9] This indicates that the fluorescence

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of monomer has been quenched. The excitation spectra of compound **3** (Figure S3), showed clearly the contributions of the monomer's absorption at 542 nm to the emission of dimer at 650 nm, suggesting the presence of ET from monomer to dimer in **3**. It is worth noting that the similar strong excimer-like emission has also been found for a rigid cofacially stacked PDI trimer with strong ground-state interactions among the three PDI units.[7] The emission properties of **3** suggest that the excimer-like emission of PDI trimer can also be achieved by a photoinduced energy transfer between noninteracted monomer and dimer.

To gain an insight into the ET from monomer to dimer in compound **3**, time-resolved transient absorption spectra were recorded[10] (Figure S4). Samples were excited at 400 nm (150 fs in pulse width). In compound **3**, both the monomeric and dimeric subunits would be excited simultaneously, and we employed the method of singular value decomposition (SVD) combined with global fitting procedure to resolve the absorption spectra of the related species and the corresponding kinetics based on a proposed monomeric/dimeric coexcitation model[10a] (Figure 3A). This model involves a single photon excitation of both the monomeric and dimeric subunits with different probability, followed by different energy relaxation paths as shown in Figure 3A. In this model the fast energy relaxing from $M_2$ to $M_1$ and the fluorescence from $M_1$ to $M_0$ of low quantum efficiency are ignored. The excitation probability ratio for these two branches is obtained as a fitting parameter in the model.

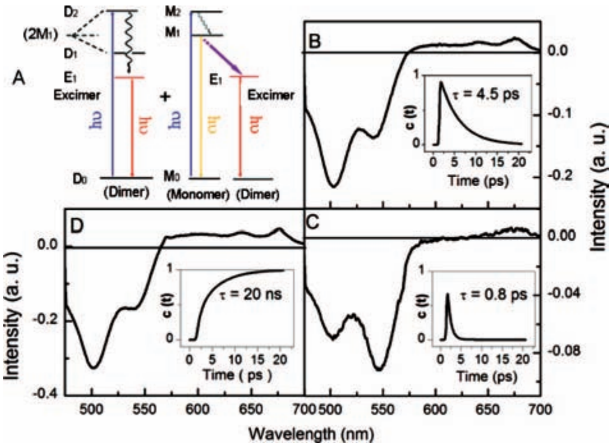

***Figure 3.*** (A) Model for energy relaxation and transfer in the trimer where the monomeric and dimeric subunits are coexcited: (left) dimeric excitation path; (right) monomeric excitation path. $D_n$ ($n = 0-2$) = energy levels of the dimer, where $D_1$ and $D_2$ arise from the energy splitting of the monomeric level because of the formation of H aggregates; $M_n$ ($n = 0-2$) = energy levels of monomer; $E_1$ = the lowest excited energy level of the excimer. Panels B, C, and D show the species associated spectra (SAS) obtained by singular value decomposition (SVD) together with global fitting with the coexcitation model (B, dimer; C, monomer; D, excimer). Graphic inset: the associated population evolution curve of the three components.

We obtained three major components corresponding to monomeric, dimeric, and excimeric subunits in the resolved transient absorption spectra in terms of the coexcitation model. The resolved species associated spectra (SAS) and the associated temporal profile ($C(t)$)[10a] are shown in Figure 3. The inverted bleaching spectra of monomeric and dimeric units are comparable to the absorption spectra of the corresponding monomer and dimer. The lifetime for energy relaxation from the dimer to the excimer is 4.5 ps, while the ET from the monomer to the excimer is 0.8 ps, which is similar to that of B800 to B850 (0.8−0.9 ps).[10b] The obtained excitation probability ratio for the dimeric and monomeric unit is 1.5, which is same as the ratio of the extinction coefficiencies of monomer **1** and dimer **2** at the excitation wavelength.

In conclusion, we have demonstrated for the first time that the fluorescence of a monomeric PDI can be quenched by a covalently linked PDI dimer. Both the excitation and transient absorption spectra support that the efficient and ultrafast ET from PDI monomer to dimer is responsible for this fluorescence quenching. Our finding suggests that the ET can happen efficiently and quickly between a pair of noninteracted PDI monomer and dimer. We believe that this observation is meaningful for the design and construction of novel artificial LH systems.

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**Supporting Information Available:** Details of the synthesis, the $^1$H NMR spectra, results of elemental analysis, the absorption spectra of **3** in dichloromethane with different concentrations, the excitation spectra of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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