



Gap-filling functionality of energy transmitter on cascade energy transfer in a unimolecular anthracene/perylene/rhodamine system



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ABSTRACT

This work reports an intriguing finding that a newly designed anthracene/perylene/rhodamine system makes it possible to achieve efficient cascade energy transfer. The results of comparative spectroscopic studies on the protonated compounds provided a direct proof that the perylene dye can promote gap-filling functionality as an energy transmitter to enhance overall efficiency for the energy flow.

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Introduction

A cascade energy transfer occurring among the photosynthetic antenna pigments is the crucial event for the solar energy conversion by the natural light-harvesting photosystems, which results in an electronically excited 'special pair' of the reaction center, facilitating efficient charge separation to generate usable chemical energy.¹ This sophisticated strategy for the directional energy transport relies on a synergistic use of multi-component energy gradients, given by regularly arrayed chromophoric units, such as carotene, monomeric chlorophyll, and its dimeric species of the 'special pair', to organize extended Förster resonance energy transfer (FRET) networks via filling spectral gaps that result from unsatisfactory interactions between energy donor and acceptor elements.² In the context of engineering technologies for exploiting this gap-filling functionality,³ potential advantages have been demonstrated in the solar cell applications which dramatically improve the photovoltaic performance with superior light-absorbing characteristics to cover a broad range of the spectrum.⁴ Despite the crucial importance in manufacturing future devices, as exemplified by high performance solar cells and artificial photosynthetic mimics,⁵ a mechanistic understanding of this photofunctionality still remains limited, with the exception of only a very small number of implicit knowledge gained on specific types of molecular

systems.⁶ Thus, addressing the nature of the gap-filling phenomenon underlying the extended FRET networks is one of the most important challenges in modern science and technology.⁷ Here we report an intriguing finding that a well-ordered energy gradient of a newly designed molecular system, which is composed of anthracene, perylene, and rhodamine fluorophores, can promote the effective gap-filling functionality to enhance the cascade energy flow of light captured by the highest energy donors, funneling toward the lowest energy acceptor.

The present study was motivated by a concern about what impact would be seen when spectrally complementary dye component is incorporated into energetically incompatible donor/acceptor FRET systems. To realize this concept, we designed a primitive model of the three-component energy gradient system as represented by structure **1** in Figure 1. The perylene dye in this structure may play a role as the energy transmitter to relay the light energy transferred from the anthracene, the highest energy donor, to the rhodamine, the lowest energy acceptor of the present molecular system. For comparison purposes, we also used an analogous system **2**, where the perylene dye replaces a structurally similar but functionally inert naphthalene moiety. These two compounds could be synthesized by condensation of rhodamine B with the relevant alcohols **3** and **4** that are readily accessible by use of the previously established procedure⁸ or a modified one from a common benzylamine intermediate **5** and the corresponding imide anhydrides **6** and **7** (Scheme 1), and were fully characterized by analytical methods.

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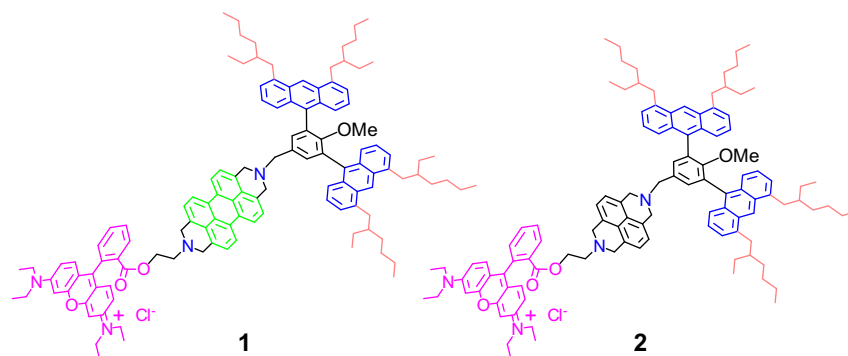
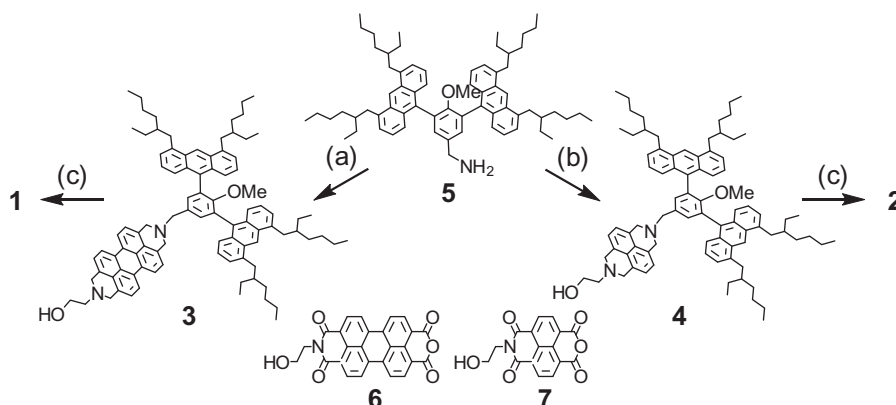


Figure 1. Structures of energy gradient systems.



Scheme 1. Reagents and conditions: (a) see Ref. 8; (b) (i) **7**, NMP, 100 °C, 5 h; (ii) AlH_3 , THF, 0 °C to rt, 14 h; 47% (two steps); (c) rhodamine B, DIPC, DCM, rt, 42 h; 28% for **1**, 49% for **2**.

A comparison of absorption profiles obtained with CHCl_3 solutions of the both compounds is given in **Figure 2** to illustrate the spectral contribution of each chromophore unit. Obviously, the anthracene, perylene, and rhodamine dyes incorporated in these molecules behave independently to exhibit their individual characteristic absorption bands, whose maxima are in distinct spectral regions centered around 380, 440, and 560 nm, respectively. This also proved that the spectrum of the perylene-free derivative **2** has a broad valley between the two absorption bands of the constituent dye units, ranging from 410 to 500 nm. The wide separation existing between these bands was thought to cause poor spectral overlap between fluorescence spectrum of the anthracene donor and absorption spectrum of the rhodamine acceptor. We note that the anthracene dye indeed produces fluorescence emission in the wavelength range of 400–480 nm, significantly shorter than the rhodamine absorption region, with its emission tail extending beyond 500 nm.⁸ It is apparent that efficient FRET is unlikely to occur in this donor/acceptor system, in view of very small spectral overlap, representing a poor cooperative situation

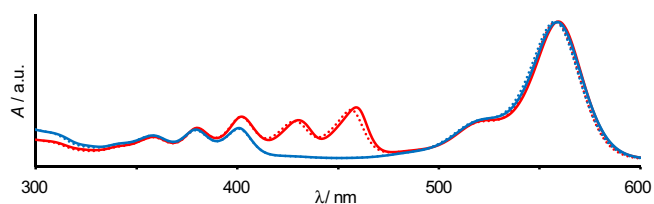


Figure 2. Normalized absorption spectra of **1** (red lines) and **2** (blue lines) in CHCl_3 (solid lines) and $\text{CHCl}_3/\text{AcOH}$ (1.0 M) mixtures (dotted lines).

called the spectral gap state. In this regard, simulations for the spectral overlap integrals (J_{DA}), which are based on normalized emission/absorption spectra of CHCl_3 solutions using dipole orientation factor (κ^2) of 0.476 (represented as randomized static transition dipoles), suggested that the J_{DA} value for the spectral overlap between anthracene emission and rhodamine absorption is 1.21×10^{14} , much smaller than for the one between anthracene emission and perylene absorption (4.53×10^{14}).

With these points in mind, we then investigated the fluorescence behavior of these two molecular systems in CHCl_3 solutions. Upon selective excitation of the anthracene dyes with 370 nm light, distinct emission peaks characteristic of the rhodamine fluorescence were detected at 580 and 570 nm in the cases of **1** and **2**, respectively, (**Fig. 3**). These observations can be understood on the basis of mechanisms that are dominated by the intramolecular FRET interactions,^{9,10} though much greater complexity must exist in the three-component system rather than the other. Furthermore, it should be noted that these fluorescence spectra also show significant amounts of residual emissions from the anthracene and

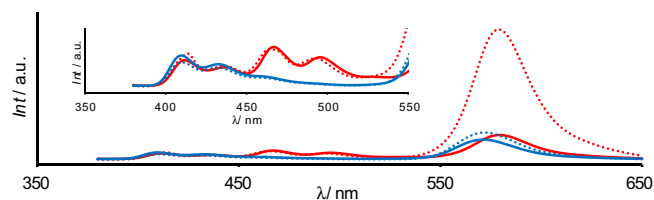


Figure 3. Fluorescence emission spectra (c 1.0×10^{-5} M, λ_{ex} 370 nm) of **1** (red lines) and **2** (blue lines) in CHCl_3 (solid lines) and $\text{CHCl}_3/\text{AcOH}$ (1.0 M) mixtures (dotted lines). (Inset) Expansion of the 350–550 nm region showing ~ 8.5 -fold increase in the emissions from the anthracene and perylene dyes.

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