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Cascade energy transfer in a conformationally mobile multichromophoric dendrimer

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Received (in Cambridge, UK) 13th August 2002, Accepted 4th October 2002
First published as an Advance Article on the web 25th October 2002

A conformationally flexible, generation-2,3 poly(aryl ether) dendrimer favors quantitative cascade fluorescence resonance energy transfer without the appearance of undesired chromophore self-quenching interactions such as excimer formation.

Natural photosynthetic systems employ several light-harvesting complexes containing many chromophores that efficiently transfer absorbed radiation unidirectionally over nanometer distances.[1–5] In the past, our group has designed and prepared dendritic materials inspired by this energy transfer component of the photosynthetic pathway,[2,3] utilizing fluorescence resonance energy transfer (FRET) to concentrate absorbed energy at a single center.[4,5] Systems capable of directional FRET between several chromophores[6] have been the object of much attention.[7–10] Recently, cascade FRET was reported[11] using a conformationally rigid dendrimer that was thought to curtail energy losses resulting from interactions between chromophores. However, in the absence of a measurement of the energy transfer (ET) efficiency from the initial donor to the final acceptor chromophore it is not possible to ascertain whether ET occurs *via* sequential transfer from one donor to the other donor and then to the acceptor, or includes a component of direct ET from each donor to the acceptor. We now report the design and synthesis of a cascade light-harvesting system based on a flexible dendrimer scaffold. This system demonstrates that, with proper chromophore selection, FRET is favorable in a vectorial cascade process, and that shape-persistence is not needed to avoid self-quenching through chromophore aggregation and excimer formation.

The design of the cascade ET system (**1**, Fig. 1) places coumarin 2 (D1) at the third branch point of a poly(aryl ether) dendrimer and fluorol 7GA (D2) at the second branch point—closer to the core—representing spatially the desired direction of FRET. The final energy acceptor (Ac) consists of a perylenebis(dicarboximide) derivative at the core of the dendrimer. Earlier studies have demonstrated that the dendritic backbone selected does not participate in the ET process[5] and energy is transferred through space, as in natural photosynthetic systems, rather than through the dendritic scaffold. The three laser dyes were chosen for their spectral properties as well as their thermal and chemical stability.[5,12] A requirement for FRET is that there be an overlap of the donor chromophore fluorescence with the absorption of the acceptor chromophore.[13,14] Consistent with this requirement, ET is favored from coumarin 2 to fluorol 7GA, and from fluorol 7GA to the perylene core. In addition, ET is disfavored between coumarin 2 and the perylene core due to a much smaller spectral overlap of coumarin 2 fluorescence with the core absorption, and the increased interchromophoric distance between the two dyes.

Preparation of the target compound starts by coupling fluorol 7GA to the protected AB_2 dendritic monomer[3] **2** followed by removal of the hexadecanesulfonyl protecting group using NaOH in ethanol (Scheme 1). The resulting generation 1 (G-1) dendron **3** was attached to a *tert*-butyldiphenylsilyl (TBDPS) protected AB_2 dendritic monomer[3] (**4**) using a 20 : 1 ratio of **4** : **3** to form the mono-coupled product (**5**). Coupling the coumarin 2 labeled G-2 dendron[3] **6** with **5** under standard Williamson ether conditions, followed by removal of the TBDPS group using CsF in DMF afforded **7**. Finally, the mixed bichromophoric G-2, G-3 dendron **8** was obtained from **7** by reaction with succinic anhydride using a catalytic amount of DMAP in acetone.

The perylenebis(dicarboximide) acceptor core (**11**) was synthesized as illustrated in Scheme 2. Aromatic substitution of Br_2 onto **9**[15] followed by imidation using propylamine[16] afforded **10** in 78% overall yield. This compound was then coupled to 4-(hydroxymethyl)phenylboronic acid under Suzuki conditions and treated with CBr_4 in the presence of triphenylphosphine to afford **11**. Compound **1** (Scheme 3) was then obtained by coupling **8** and **11** using K_2CO_3 in DMF.

In order to establish which of the two possible ET pathways illustrated in Fig. 2 apply to **1**, two key model compounds were required in addition to **7**. Dendrimer **12** (Scheme 3), containing D2 and Ac, was synthesized by coupling **11** with **13** using K_2CO_3 in DMF. Dendrimer **14**, containing D1 and Ac, was synthesized by coupling **11** with **15**.[17] Several preparative TLC purifications were performed on all model compounds to ensure their purity prior to performing absorption and emission measurements.

Fig. 3 shows the absorption and emission spectra (λ_{ex} = 342, 418 and 555 nm) of **1** in chloroform. While the absorption spectrum is a composite of those of the three chromophores, the emission spectra show a near complete quenching of the D1 and D2 emissions when **1** is excited at 342 nm (λ_{max} of D1). This results in a 6.9-fold increase in Ac emission, relative to the direct excitation of Ac at 555 nm. This very significant 'antenna effect' (calculated using the ratio of integrated emission of Ac

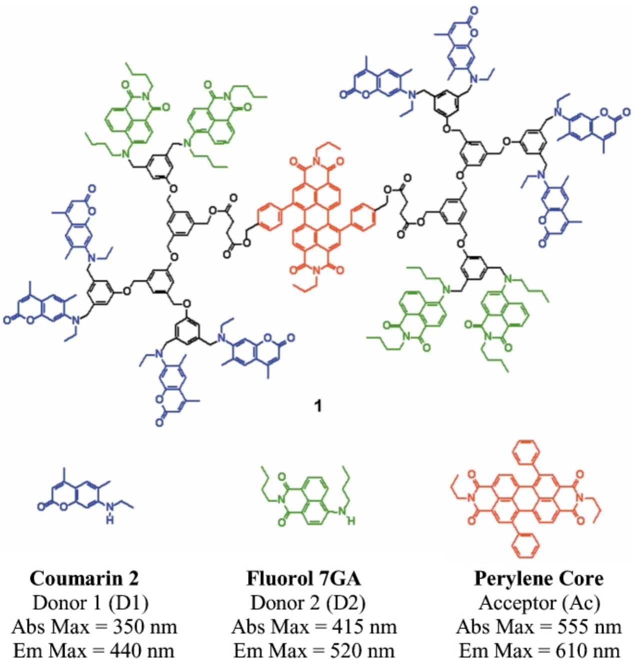
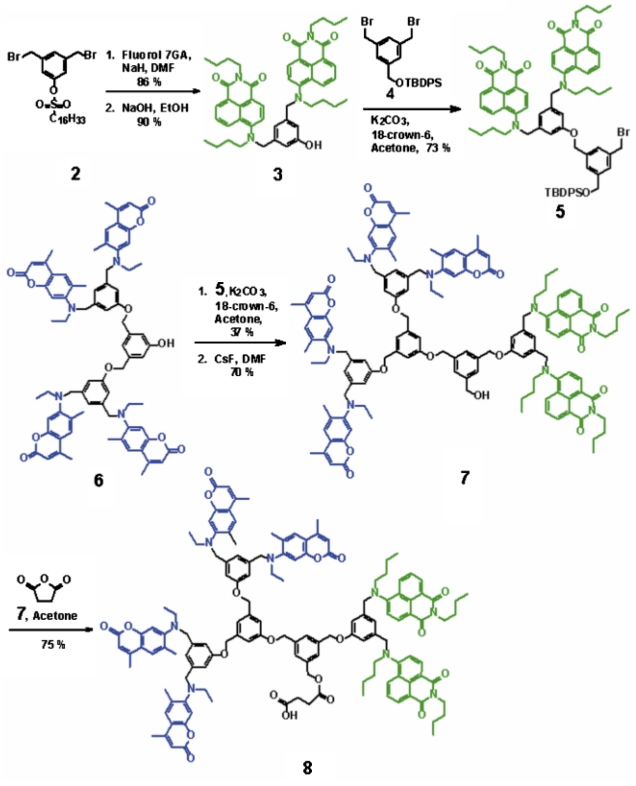


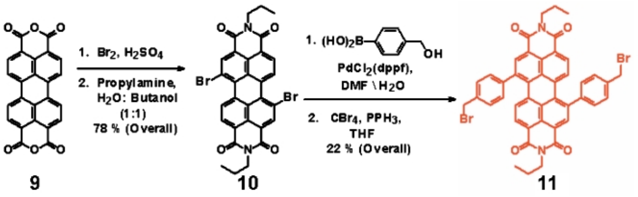
Fig. 1 Structure of the directional cascade ET system (**1**) and the component donor and acceptor chromophores.

DOI: 10.1039/b207905d

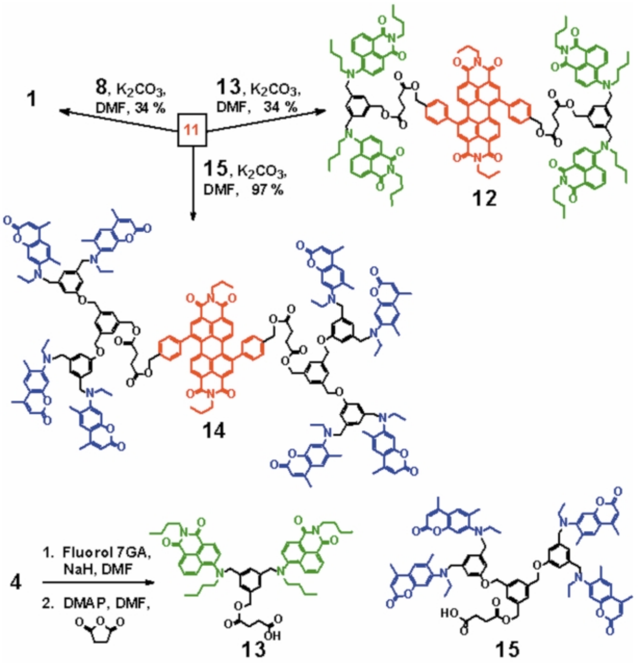
when excited at 342 nm, over the integrated emission when excited at 555 nm) demonstrates how light energy can be concentrated at a single center using a large, multi-chromophoric antenna. A similar effect is seen when **1** is excited at D2 (λ_{ex} = 418).



Scheme 1



Scheme 2



Scheme 3

Steady-state photophysical measurements of **7**, **12** and **14** in chloroform enabled the determination of approximate FRET efficiencies from D1 to D2, D2 to Ac, and D1 to Ac, respectively. The donor to acceptor FRET efficiencies were calculated by comparing the integrated donor emission when in the presence of the acceptor relative to the donor emission in the absence of the acceptor.[5] This is demonstrated using model dendrimer **14**, whose absorption and emission properties, along with those of **6**, are shown in Fig. 4 (**6**: λ_{ex} = 342 nm; **14**: λ_{ex} = 342 and 555 nm). The coumarin 2 absorption is well separated from that of the perylene core. Coumarin 2 emission from **14** is quenched by 79% (FRET efficiency) relative to its emission in **6**. Considering that the average distance from D1 to Ac in **14** is less than in **1**, this value can be taken as the upper limit of FRET efficiency between these chromophores in **1**. In addition, the spectral overlap between D1 to D2 in **1** is larger than the spectral overlap between D1 and Ac, further increasing the Förster rate constant for ET in the desired direction.[14] Similar studies using **3**, **6**, **7** and **12** resulted in calculated FRET efficiencies of 99 % from D1 to D2, and 96 % from D2 to Ac (Fig. 5).

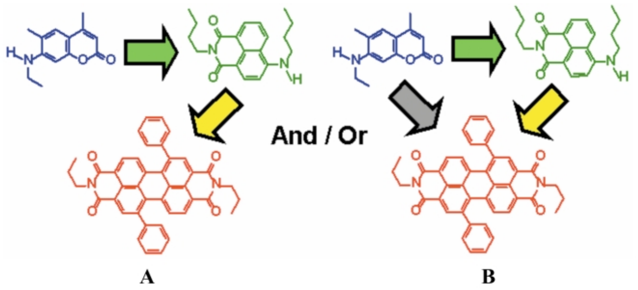


Fig. 2 The two possible pathways of FRET. **A** = Directional cascade FRET. Energy is transferred from D1 to D2 to Ac. **B** = Bi-directional FRET. Energy is transferred from both donor chromophores directly to the acceptor.

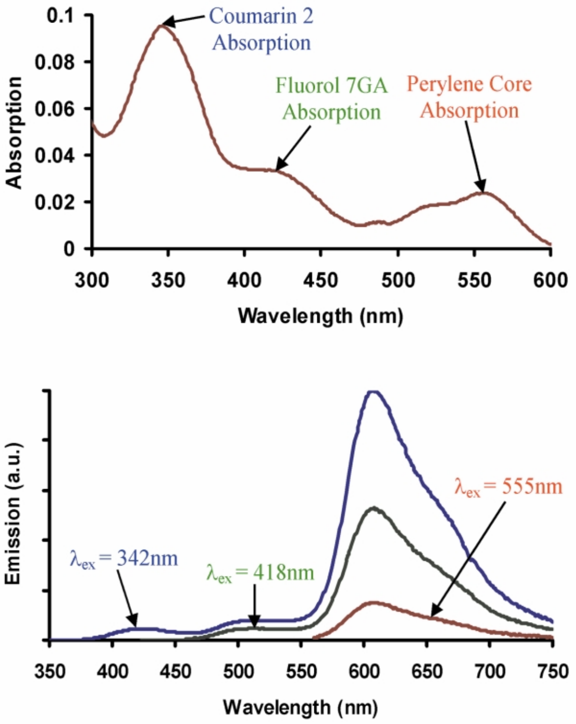


Fig. 3 Absorption spectrum (top) and emission spectra (bottom, λ_{ex} = 342, 418 and 555 nm) of **1** in $CHCl_3$ at rt. Calculated FRET efficiencies and corresponding core emission increases were 98% and 6.9-fold for λ_{ex} = 342 nm, and 97% and 3.6-fold for λ_{ex} = 418 nm, respectively.

Excitation of **1** at 342 nm results in an overall calculated FRET efficiency of more than 95%. More specifically, 98% of the energy D1 absorbs is transferred to D2, and 97% of this energy is transferred to Ac, resulting in a near 7-fold increase in core emission (*vide supra*). The large increase in Ac emission when excited at either donor indicates that there are no major pathways competing with the Ac emission. That is, such an increase in core emission would not be expected if donor chromophore aggregation and self-quenching were competing with ET. This has been demonstrated in similar systems,[5,11] and will be further explored using time-resolved studies. Evidence of core excimer formation was not found in any of the experiments conducted.

Dendrimer **1** represents a novel approach to examine cascade unidirectional FRET in a flexible system. It was shown that ET within this system favors a cascade route, moving from an initial chromophore through an intermediate chromophore and onto a final acceptor chromophore. This is evidenced in the steady-state photophysical analysis of model dendrimer **14**, which places 79% as an upper limit to the amount of FRET that may occur in the undesired direction, *i.e.* directly from D1 to Ac. Time-resolved experiments currently underway should provide a more detailed view of the dynamics occurring within this system.

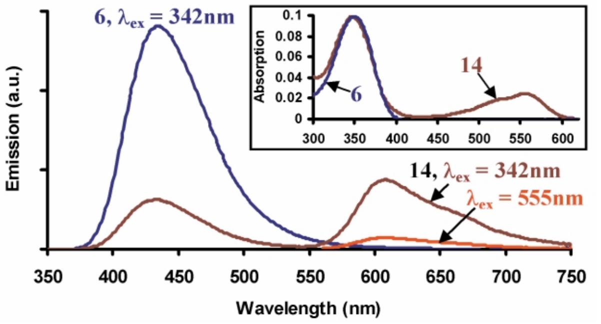


Fig. 4 Emission spectra of **6** (λ_{ex} = 342 nm) and **14** (λ_{ex} = 342 and 555 nm) in $CHCl_3$ at rt. Inset: Absorption spectra of **6** and **14** in $CHCl_3$ at rt.

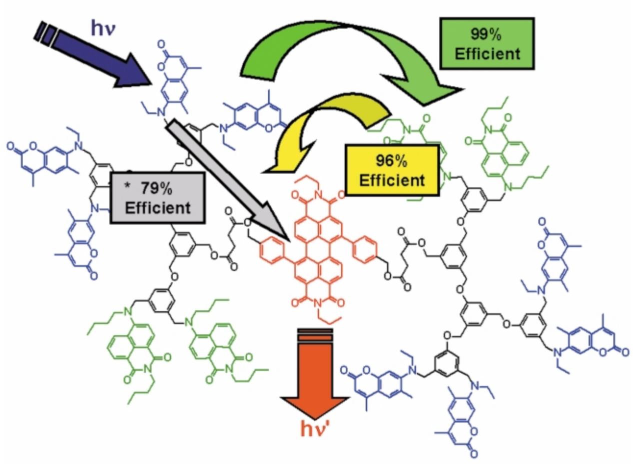


Fig. 5 Diagram illustrating the FRET efficiencies between chromophores in **1**. These calculations were made using model dendrimers **7**, **12** and **14**, and the acceptor-lacking counterparts **3** and **6**. *The 79% FRET from D1 to Ac is an upper limit.

Professor Alex Adronov (McMaster University) is gratefully acknowledged for the synthesis of several starting materials. Financial support of this research comes from the AFOSR (No. FDF-49620-01-1-0167). D. W. B. acknowledges NSERC (Canada) for a post-doctoral fellowship.

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