Evaluation of energy transfer in perylene-cored anthracene dendrimers†

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Quantitative evaluation of Förster-type fluorescence resonance energy transfer (FRET) was undertaken by statistical investigations on perylene-cored anthracene dendrimers.

A light-harvesting process is a first crucial step among complex reaction cascades evolved in natural photosynthetic organisms on earth.[1] The development of nanostructured materials inspired by biological energy transduction is therefore of great significance in engineering new applications for solar energy conversion.[2,3] However, detailed descriptions quantifying the relative extent of energy transfer in multichromophoric architectures remain a standing concern. In this context, utilization of dendrimer structures for exploratory investigations of energy transfer processes may be advantageous for a deeper understanding of the fundamental aspects of the complex photophysics because the dendrimer systems make it possible to bring a well-defined packing arrangement of chromophores in a nanoscale volume element.[4,5] We report herein a remarkable finding observed for perylene-cored anthracene dendrimers, which exhibit distance independent behavior in all possible energy transfer pathways.

Our general design of the dendrimer systems involves one perylene core surrounded by clustering domains of anthracene groups (Fig. 1). These multichromophoric environments may allow funneling of energy from the peripheral clusters to the core, thus introducing the light-harvesting functionality into the dendrimer systems. With the conceptual basis for creating light-harvesting systems, six different variants of dendrimers **1–6** were prepared by combinatorial covalent attachment of three types of anthracene peripheral units (**A1–A3**) to two types of perylene cores (**P1** and **P2**) as outlined in Scheme 1.[6]

The resulting dendrimer systems allowed simplified spectral characterization in the light absorbing features. Accordingly, the UV-vis spectra of **1–6** exhibited common vibronic structures with three strong peaks due to the π,π* transition of the anthracene groups at 350–410 nm and two clearly structured bands due to the perylene groups at 430–500 nm (Fig. 2A). Remarkably, a linear correlation was seen between extinction coefficients at the three anthracene peaks and the total number of anthracene units present in the dendrimers (inset of Fig. 2A), while the coefficients of the two perylene peaks appeared to be close to unity in all cases. This indicates the individual chromophores behaved substantially as monomeric species with absorption characteristics unaffected by the presence of the other species.[7] The existence of efficient intramolecular energy transfer in the dendrimer systems could be observed in steady-state fluorescence emission measurements. Fig. 2B depicts the fluorescence spectra for **1–6** upon direct excitation of the anthracene groups at 378 nm, which are shown normalized to the emission maxima at 500 nm. At this point, it should be noted that these spectra displayed strong fluorescence

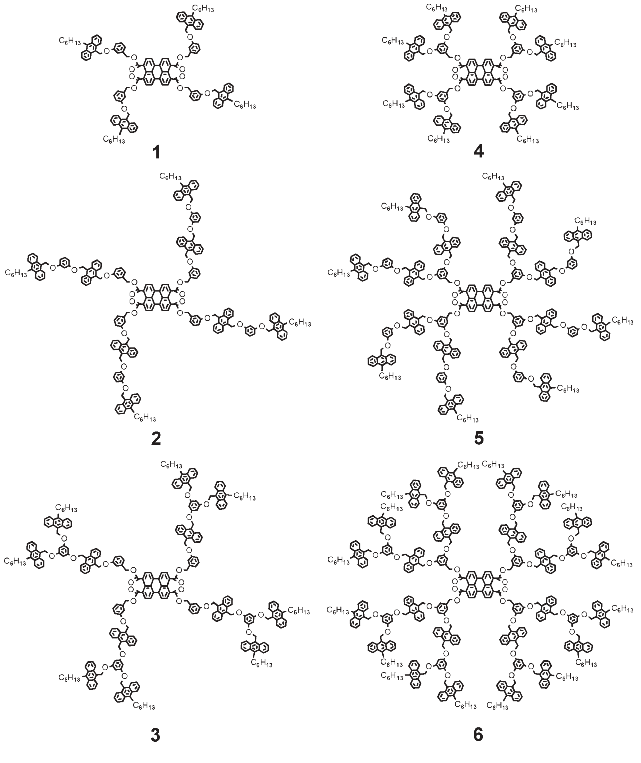
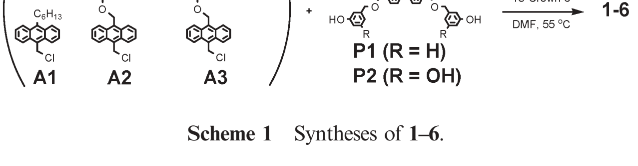


Fig. 1 Structures of perylene-cored anthracene dendrimers.



Scheme 1 Syntheses of **1–6**.

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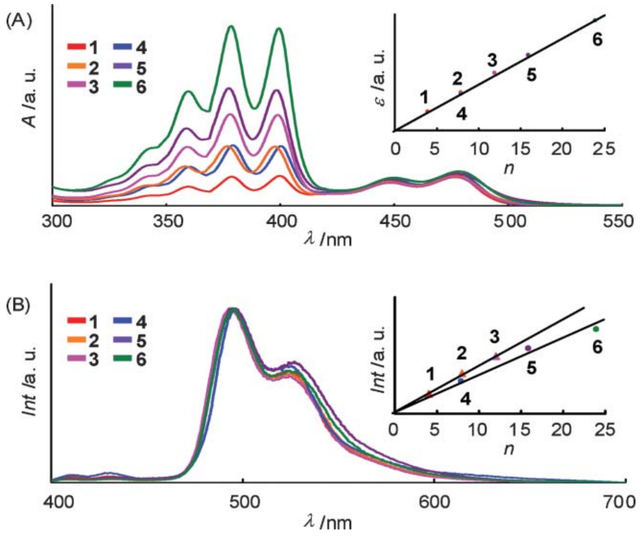

Fig. 2 (A) Absorption and (B) normalized fluorescence spectra (λ_{ex} = 378 nm) of **1–6** in chloroform solutions (c_{abs} 10^{-6}–10^{-5} M, c_{fl} 10^{-8}–10^{-7} M). Insets: plots of (A) extinction coefficients and (B) excitation intensities at 359 nm *vs.* total number of anthracene units (n) in the dendrimer systems. Errors in fitting the experimental data: extinction coefficients of **1–6**, ±4%; excitation intensities of **1–3**, ±4%; excitation intensities of **4–6**, ±7%.

signals assigned to originate from the perylene core with complete disappearance of the anthracene group emission in the shorter-wavelength region (400–460 nm). These observations are consistent with efficient intramolecular energy transfer which may arise from through-space interactions between the excited anthracene units and the perylene core.[8] Moreover, the excitation spectra of **1–6** at λ_{em} of the core at 500 nm matched well the corresponding absorption spectra, exhibiting three distinct maxima attributed to the anthracene groups. In the inset of Fig. 2B, the relative intensities of these peaks, estimated by measuring the height in the spectra normalized with respect to the perylene core excitation at 450 nm, were plotted as a function of the total number of anthracene groups. In contrast to the linear dependence of the absorption feature as mentioned above, the distribution of these data can be well fitted with two comparable linear relationships in accordance with two geometrical types of dendritic architectures ([**1**, **2**, **3**] and [**4**, **5**, **6**]), which are divided according to the number of anthracene chromophores at the closest sites of the dendritic shells (n_1 in Table 1).

By comparing the absorption and excitation spectra normalized at the acceptor peaks, the energy transfer efficiency (Φ_{ET}) was determined for any given dendrimer.[9] As can been seen from Table 1, the energy transfer efficiencies clearly show a bimodal distribution between the two geometrical types of dendritic systems mentioned above. This significant difference in Φ_{ET} can be explained on the basis of intramolecular energy migration in the clustering domains of anthracene groups. Indeed, dense packing of anthracene groups in dendrimer systems has been demonstrated to reduce fluorescence emission efficiency due to energy migration processes as observed with benzene-cored anthracene dendrimers.[6] Such an interpretation can also be applied to account for the slightly decreased Φ_{ET} values for **3** and **6** in comparison to those of the other members that share the common n_1 numbers.

Table 1 Number of anthracenes and energy transfer efficiencies

	1	**2**	**3**	**4**	**5**	**6**
$n_1{}^a$	4	4	4	8	8	8
$n_2{}^b$	0	4	8	0	8	16
n^c	4	8	12	8	16	24
$\Phi_{ET}{}^d$	0.69	0.69	0.65	0.54	0.54	0.48

[a] Number of anthracenes located at close sites of the dendritic shells. [b] Number of anthracenes located at remote sites of the dendritic shells. [c] Total number of anthracene units. [d] Energy transfer efficiencies determined by spectroscopic measurements in chloroform.

On the other hand, it is well accepted that quantum efficiency of fluorescence resonant energy transfer (FRET) depends strongly on the separation distances between the donor–acceptor pairs. In fact, molecular modeling studies of fully extended structures of the dendrimers indicate that averaged center-to-center distances from the perylene core to the anthracene groups located at close and remote sites of the dendritic shells are estimated to be approximately 1.4 and 2.3 nm, respectively.[10] From the viewpoint of possibilities of long-range processes as suggested by these values, Coulombic dipole–dipole interactions (Förster mechanism) would provide a plausible rationale for the observed results.[8] To consider the mechanistic model, one must recall that this type of FRET shows an inverse sixth power dependence of probability on the donor–acceptor separations.[9] However, the similarity in the net Φ_{ET} values given for the related dendrimer series leads to an apparently contradictory result because fractional contributions for all possible FRET pathways in each single molecule are suggested to be closely equivalent regardless of the number of anthracene groups present at the most remote sites (n_2 in Table 1). In other words, an obvious conclusion that can be drawn from these data is that every component of the energy transfer exhibits distance independent behaviour in the dendrimer systems. This remarkable phenomenon can be rationalized in terms of the Förster critical radius (R_0), which is a determinant of the extent of dipole–dipole interaction effects during the FRET processes. From the theoretical treatments, the FRET efficiency should be near unity when the donor–acceptor distance is shorter than $R_0/2$.[9] In comparing the R_0 value of 3.6 nm reported for an analogous anthracene–perylene pair,[11] it is evident that plausible distances between the donor–acceptor pairs are much less than R_0 and even closer to $R_0/2$. These geometrical parameters meet the desired criteria for achieving quantitative processes which provide an effective solution to the observed lack of distance dependence in the FRET efficiencies, although there exist significant differences in the contacts of the core with the two discrete anthracene sites.

In conclusion, we have demonstrated that perylene-cored anthracene dendrimers represent an excellent light-harvesting antenna model. The quantitative analysis of the FRET efficiencies led to a remarkable conclusion that confinement of antenna elements within the nanoscopic dimensions of dendritic architectures, especially inside the reach of the critical radii, would satisfy a primary requirement for creating effective light-harvesting functionalities *via* the Förster mechanism.[12] Extensive research ascertaining whether multistep energy hopping[13–15] is feasible in the dendrimer systems will be addressed elsewhere.[16]

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10. In order to obtain critical distance criteria for the energy transfer processes, we employed the fully extended molecular models, wherein all equivalent dendrimer units should be arranged at the same distances from the perylene core in identical orientation.
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