Light-harvesting dendrimers

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Natural photosynthetic systems collect sunlight using a vast array of light-harvesting chromophores that channel the absorbed energy to a single reaction center. Recently, it has been realized that dendritic macromolecules can exhibit similar properties, though on a more modest scale. The preparation of dendritic structures and assemblies composed of numerous light-collecting chromophores that transfer their energy to a single energy 'sink' at the core has been achieved in a number of diverse and creative ways. These novel structures are being used as model systems in light-emitting diodes, signal amplifiers, fluorescent sensors, frequency converters, and other photonic devices.

Introduction

It has been estimated that the average yearly incidence of solar radiation at the earth's surface amounts to several orders of magnitude more energy than is consumed by its population.[1] Clearly, harnessing this energy is an important endeavor that will reduce our dependence on fossil fuels. Indeed, our own existence depends on light-harvesting by the plethora of photosynthetic organisms in the biosphere. These organisms have evolved intricate and extremely efficient mechanisms for the transduction of light into chemical energy in the form of ATP.[2] If we are to utilize sunlight in a similar fashion, it is not unreasonable to borrow some design concepts from structures that have evolved over billions of years.

To date, the most studied of all photosynthetic systems is probably that of purple bacteria.[3] The high resolution X-ray crystal structure of the photosynthetic unit (PSU) reveals a central reaction center (RC) that is surrounded by light-harvesting (LH) complexes (Fig. 1).[4] The LH1 complex is composed of a ring-shaped assembly of chlorophyll and
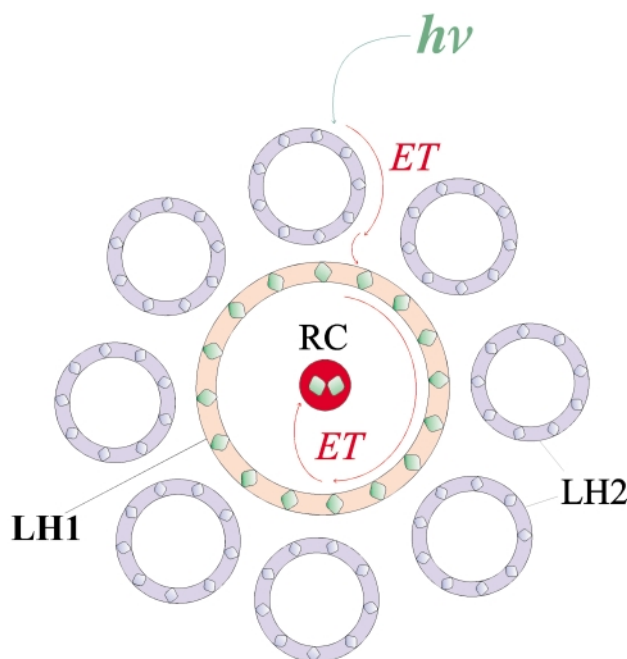

Fig. 1 Schematic representation of bacterial light-harvesting complexes (LH1 and LH2), showing the different protein-embedded light-absorbing porphyrins arranged in circles around the reaction center (RC). The path of energy transfer (ET) is indicated by arrows.

carotenoid moieties embedded in a protein matrix that immediately surrounds the RC. Similar ring-shaped assemblies, somewhat further removed from the RC, make up the LH2 and LH3 complexes.[3] The role of these chlorophyll-containing assemblies is that of an antenna, absorbing photons that strike the relatively large surface area that they cover. Remarkably, the energy of any photon that strikes any of the several hundred chlorophylls within the extensive LH system is transferred to the RC with unit efficiency.[3]

Dendrimers are perfectly branched synthetic macromolecules having numerous chain ends all emanating from a single core.[5–8] Their synthesis, first reported in 1985 by the groups of Tomalia[9] and Newkome,[10] involves a divergent iterative coupling and activation protocol[9–12] that results in the formation of concentric layers of building blocks terminated by a large number of reactive moieties. The convergent synthesis we introduced later[13] provides for growth through a single focal point, an approach that affords even better control over both the dendrimer backbone structure and the placement of functional groups within it. Overall, the accurate positioning of chromophores can be achieved, locating them at the core, focal point, periphery, or even at each branching point of the dendritic structure (Fig. 2). This schematic diagram of a dendrimer is reminiscent of the architecture of natural light-harvesting complexes, where antenna molecules surround the central RC. Although the appropriate placement of chromophores is

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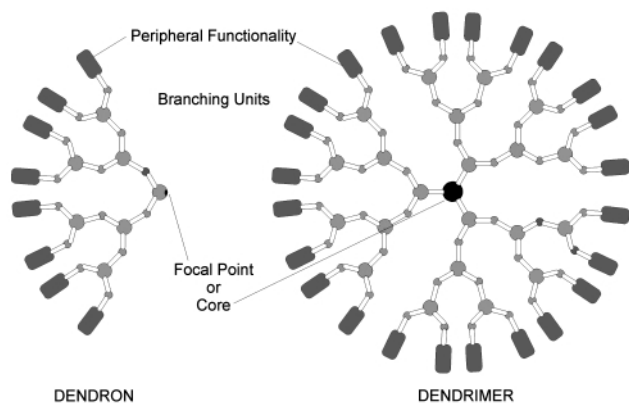
Fig. 2 Schematic diagram of the structure of a dendron and a dendrimer, highlighting the focal point or core (black) surrounded by rings of branching units (gray circles) and end-groups (rectangles).

important, judicious choices must be made both for the selection of the chromophores themselves, and for the design of each successive layer in order to maximize favorable energy transfer interactions.

Over the past several decades, there has been much work done on a number of synthetic light-harvesting complexes in which energy transfer is demonstrated. After a brief introduction to energy transfer, this article will focus on the more recent dendrimer-based light-harvesting structures.

Energy transfer and the choice of chromophores

In a bichromophoric system where one chromophore (the energy donor, D) is in its excited state and the other (the energy acceptor, A) is in its ground state, energy transfer can occur such that the donor returns to its ground state simultaneously with the promotion of the acceptor to its excited state (Fig. 3).[14] This
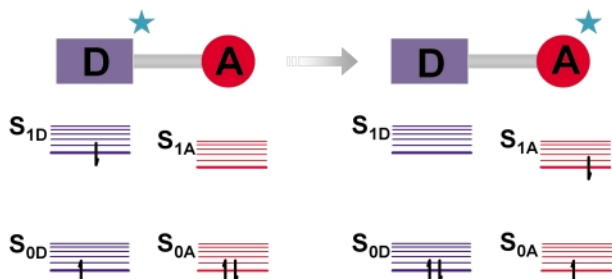

Fig. 3 The process of energy transfer involves the migration of excitation energy from an excited-state donor (D) to a nearby ground-state acceptor (A).

transfer can occur by either a through-bond[15] (Dexter) or through-space[16,17] (Förster) mechanism. In the former, an electron exchange occurs from the S_1 state of the donor to the S_1 state of the acceptor, with a simultaneous exchange of an S_0 electron from acceptor to donor (Fig. 3). This electron exchange requires strong D–A orbital overlap and is therefore a short-range (< 10 Å) interaction that diminishes exponentially with distance.[14] The rate constant for this process is described by eqn. (1):

$$k_{ET} = KJ\exp(-2R_{DA}/L) \tag{1}$$

where K is related to the specific orbital interactions, J is the spectral overlap integral (see below) normalized for the extinction coefficient of the acceptor, and R_{DA} is the donor–acceptor separation relative to their van der Waals radii, L.[14]

In contrast, the Förster mechanism does not require electron exchange and is rather a through-space dipole–dipole interaction.[18] In this case, D–A orbital overlap is not necessary, allowing the chromophores to be separated by a relatively large distance (10–100 Å). The Förster energy transfer rate constant is described by eqn. (2):

$$k_{ET} = \frac{9000(\ln 10)\kappa^2\phi_D J}{128\pi^5 n^4 N \tau_D R_{DA}^6} \tag{2}$$

where κ^2 is the orientation factor (related to the relative orientation of the donor and acceptor transition dipole moments), ϕ_D is the donor quantum yield in the absence of the acceptor, J is the overlap integral, n is the index of refraction of the solvent, N is Avogadro's number, τ_D is the donor lifetime in the absence of the acceptor, and R_{DA} is the inter-chromophoric distance in cm. The overlap integral J (cm^6 mol^{-1}) is given by eqn. (3):

$$J = \int f_D(\nu)\varepsilon_A(\nu)\nu^{-4}d\nu \tag{3}$$

where $f_D(\nu)$ is the fluorescence intensity of the donor, $\varepsilon_A(\nu)$ is the molar extinction coefficient of the acceptor, and the integral is calculated over the whole spectrum with respect to the frequency expressed in wavenumbers. This integral represents the overlap between the donor emission spectrum and the acceptor absorption spectrum, and is closely related to the probability of energy transfer from the donor to the acceptor.

Unlike the Dexter interaction, where normalization of J diminishes its significance, Förster energy transfer is greatly influenced by this parameter.[14] In addition, the transition dipole moments of the interacting chromophores play a large role in the energy transfer efficiency of the through-space mechanism.[18] Hence, the bridging moiety plays a crucial role in Dexter energy transfer, where rigidity and conjugation are the key parameters, whereas the properties of the chromophores themselves (transition dipole moments and spectral overlap of donor emission and acceptor absorption) as well as the interchromophoric distance play the more important role in Förster energy transfer.

Within dendritic structures, practically all of the above parameters can be controlled and varied. Chromophore functionalization of the dendrimer can involve only the core and the end-groups, or it can involve the entire dendrimer backbone. The rigidity, conjugation, size, and polarity of the dendritic backbone all depend on the type of branched monomer that is utilized. Hence, the choice of the monomer will affect the overall properties and the energy transfer mechanism of the dendritic system. As the dendrimer generation increases, two competing factors become prevalent (Fig. 4). The number of
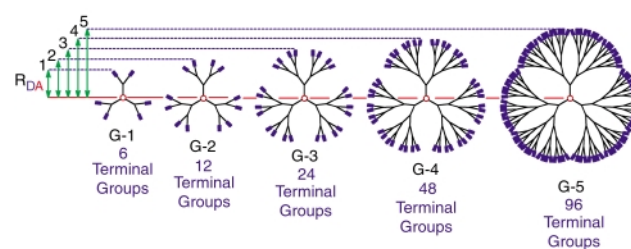

Fig. 4 As dendrimer generation increases, the number of terminal groups doubles, but the distance between the terminal groups (energy donors) and the core (energy acceptor) also increases.

monomer units, closely reflected by the number of end-groups surrounding the core, doubles with each successive generation, and the distance between the core and the end-groups increases. If each branching point or end-group acts as a chromophore, then increasing the generation allows for the harvesting of increasing amounts of light by the molecule. However, at a certain dendrimer generation, or size, it is expected that R_{DA} will become too large to sustain efficient energy transfer. It is thus necessary to reach a balance between the light-harvesting capacity of the dendritic shell, and the energy transfer efficiency to the core.

In the following paragraphs, some key examples of light-harvesting dendrimers will be highlighted.

Chromophoric dendrimer backbones and the role of an energy gradient

The initial reports of multichromophoric dendrimers undergoing intramolecular energy transfer were published by Balzani and coworkers in 1992.[19,20] Their 'complexes as metals/complexes as ligands' strategy provided a means of selectively incorporating different metal and ligand combinations into these low-generation dendrimers. Ru and Os were the metals of choice in this work owing to the ideal luminescence and redox properties of their polypyridine complexes.[20,21] The schematic representation of these molecules (Fig. 5) indicates the presence
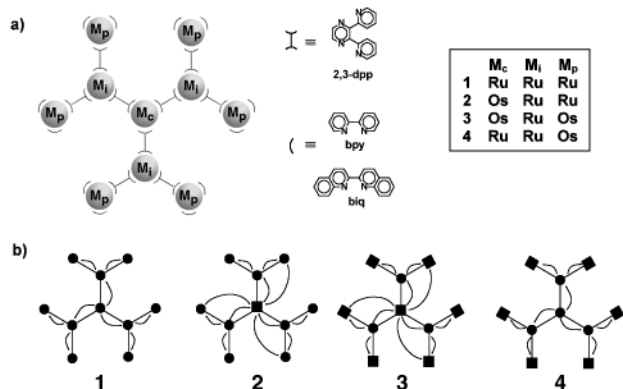

Fig. 5 (a) Schematic representation of metallodendrimers having branching ligands and different combinations and positions of Ru and Os metals. (b) Direction of energy transfer (indicated by arrows) in the different structures depicted in (a). ● = Ru, ■ = Os.

of three distinct metal-binding positions: a single core site; three intermediate sites; and six peripheral sites. In addition, it is well known that the oxidation potential of the metal ion in these polypyridyl complexes can depend on the nature of the coordinated ligands.[21] Hence, bandgap energies of the metal complexes located at the different sites (core, intermediate, and peripheral) within the dendrimer are controlled by both the nature of the metal (Ru complexes have larger bandgap energies than the corresponding Os complexes) and the nature of the surrounding ligands. Balzani and coworkers showed that metal complex bandgap energies depend on the ligands in the order dpp > biq > bpy.[22] Indeed, it was found that energy transfer in the all-Ru compounds (**1**) occurred from the internal higher energy units (dpp ligands) to the external lower energy units having bpy or biq ligands.[20] In the heterometallic complexes, energy migration predominantly occurred from the Ru-containing units to the Os-containing units. Hence, controlled energy migration from the internal units to the external units could be achieved by complexes **1** and **4**. Conversely, energy migration from the dendrimer periphery to the core was more difficult to achieve owing to the lower energy of the outermost complexes *vs.* the intermediate ones [Fig. 5(b)].

In all of these structures, energy transfer is dominated by the Dexter electron exchange mechanism,[20,23] which precludes long-range interactions between the periphery and the core. Indeed, in the third-generation structure having an Os core, it was again shown that energy migrates from the intermediate higher bandgap units to the lower bandgap units at either the periphery or the core.[24,25] Although the concept of intramolecular energy transfer within dendritic structures was clearly illustrated by these initial reports, the structures synthesized did not ideally function as photosynthetic mimics, where numerous peripheral light-harvesting chromophores channel absorbed energy in a unidirectional manner to a single, central, energy acceptor complex.

Efficient, unidirectional energy transfer from a dendritic framework to a single core chromophore was first reported in elegant work by Xu and Moore.[26] The robust, high-yielding synthesis of their phenylacetylene dendrimers allowed for the preparation of high-generation (G-*n*) molecules, up to G-6.[27,28] These cross-conjugated structures (Fig. 6) exhibit strong UV
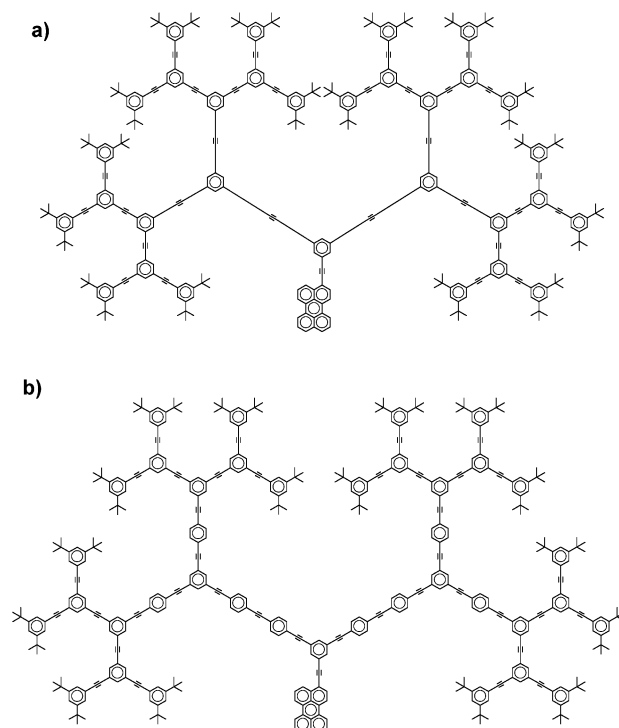

Fig. 6 Chemical structure of perylene-functionalized phenylacetylene dendrimers without (a) and with (b) an energy gradient.

absorption features in the 250–350 nm range that double in magnitude with increasing generation.[29] Additionally, it was found that these dendrimers act as luminescent chromophores that have an emission in the 350–450 nm range. By functionalizing the core of these structures with the lower bandgap perylene chromophore, the authors introduced an energy 'sink' into the system. Hence, the phenylacetylene monomer units act as the peripheral energy donors, and the perylene acts as the central energy acceptor. Excitation of the dendrimer backbone at 312 nm resulted in emission emanating solely from the perylene dye (450–600 nm), with nearly complete quenching of the dendrimer emission.[29]

Further, the versatile synthetic scheme allowed for the synthesis of dendrimers having a directional energy gradient, with the bandgap energy of each branch decreasing owing to increasing conjugation length [Fig. 6(b)].[30,31] Interestingly, it was found that this energy gradient dramatically increases (by two orders of magnitude) the energy transfer rate constant within the dendrimer.[29] Hence, the directional energy transfer from periphery to core must be greatly facilitated by the built-in energy gradient. Indeed, theoretical work by Klafter and coworkers afforded the same conclusion, suggesting that 'random walk' energy transfer from periphery to core, as in the former structures, is much less productive than the directional multi-step process.[32–34] These structures represent the first examples of effective photosynthetic mimics, and the latter molecules remain the *only* example of built-in multi-step energy gradients within dendritic macromolecules. However, the mechanism of energy transfer in these systems was difficult to ascertain. Owing to the cross-conjugated dendrimer backbone, orbital overlap contributions to the energy transfer cannot be ruled out. In addition, spectral overlap between donor emission and acceptor absorption is not very large in this case, and would

preclude the Förster mechanism alone from producing in the high energy transfer efficiencies that were observed.

Poly(benzyl ether) dendrimers and the 'antenna effect'

Several years ago our group studied the encapsulation of lanthanide ions (Ln^{3+}) by dendritic ligands in the context of a possible application for optical signal amplification. The impetus for this project originated from the self-quenching of fluorescence by lanthanide ions, such as erbium, when they are clustered together in the solid state. This self-quenching limits their effectiveness as signal amplifiers for optical fiber communications, since the poor solubility of Ln^{3+} ions in substrates such as silica leads to the formation of ion clusters.[35,36] Encapsulation of individual Er^{3+} and Tb^{3+} ions within a dendritic shell (Fig. 7) was expected to lead to their
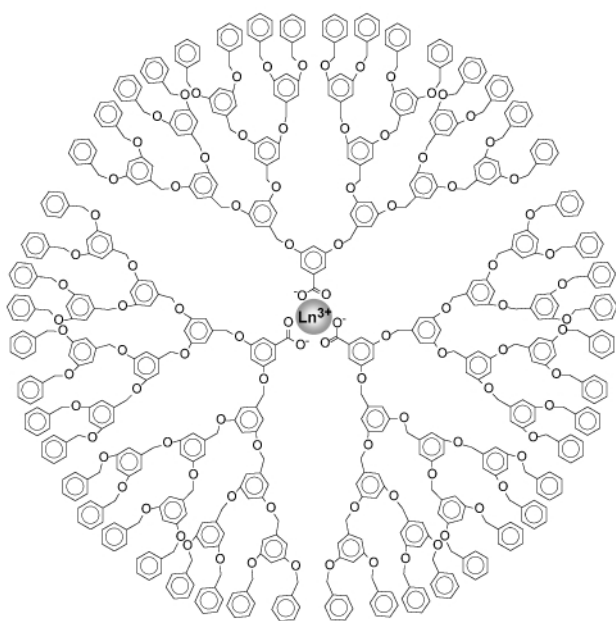

Fig. 7 Structure of a lanthanide-cored poly(benzyl ether) dendrimer.

site-isolation, thereby increasing interchromophoric distance and decreasing the self-quenching effect. Indeed, this site-isolation was realized by self-assembly of suitably function-alized carboxylate-cored dendrons around the lanthanide ion, and the resulting assemblies possessed all the characteristics desired for use in signal amplification. During the course of photophysical studies on these ionically bound supramolecular assemblies, it was found that irradiation at wavelengths where the dendrimer backbone absorbed (280–290 nm) resulted in strong luminescence from the lanthanide core.[37,38] Apparently, energy absorbed by the peripheral dendrimer shell was efficiently transferred to the luminescent Ln^{3+} at the focal point by a mechanism postulated to be of the Förster type. At these wavelengths, energy transfer to Tb^{3+} was found to be more efficient than in the case of Er^{3+}, likely due to the better overlap of dendrimer emission with Tb^{3+} absorption. This channeling of excitation energy from a dendrimer shell to a single core unit was termed the 'antenna effect'. Interestingly, it was also found that this energy transfer phenomenon was critically dependent on the substitution pattern within the dendritic shell. When the isomeric dendrons having 2,5- rather than 3,5-substitution at the focal aromatic ring were utilized, the energy transfer interaction practically disappeared.

Several other research groups have observed similar antenna effects while utilizing different luminescent cores. Jiang and Aida reported that singlet energy transfer could be observed from the same Fréchet-type poly(benzyl ether) dendrons to a core porphyrin ring (Fig. 8).[39] A variety of structures, differing
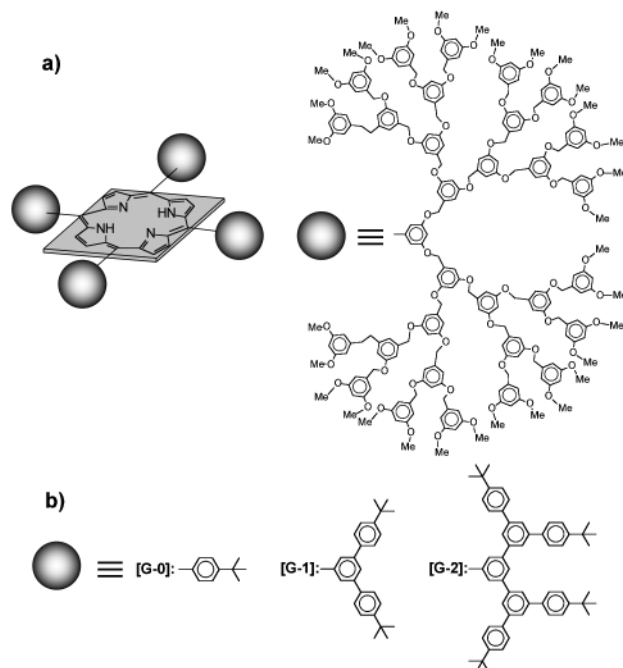

Fig. 8 Schematic representation of porphyrins encapsulated by (a) poly(benzyl ether) dendrimers, and (b) 1,3,5-phenylene-based dendrimers.

in the number of dendrons attached to the central porphyrin, as well as in the generation number of the dendrons, were prepared and studied. A small amount of overlap between the fluor-escence spectrum of the dendrons and the Soret absorption of the porphyrin allows for some degree of energy transfer to occur. Indeed, excitation of the tetra-substituted dendritic porphyrin at 280 nm (dendrimer absorption) resulted in quenching of the dendrimer emission (310 nm), with most of the light being emitted by the porphyrin core (600–750 nm). The energy transfer efficiency in both the G-4 and G-5 analogs was calculated to be approximately 80%. However, if the porphyrin was only partially substituted, with one, two, or three G-5 dendrons instead of four, the energy transfer efficiency dropped dramatically, to 10, 20 and 32%, respectively. Similar phenom-ena were also observed when G-4 dendrons were used. Temperature-dependent effects indicated that increased flex-ibility and conformational freedom were responsible for the decreased energy transfer efficiency. Only the highly crowded molecule having four G-5 dendrons retained a constant level of energy transfer, even at high temperatures. It was also postulated that cooperativity between dendrons is necessary for efficient energy transfer, and this cooperativity appeared to decrease with increasing conformational mobility.

A slight variation of this work was recently published by Kimura *et al.*, who synthesized low-generation (G-1 and G-2) 1,3,5-phenylene-based dendritic porphyrins [Fig. 8(b)].[40] Inter-estingly, the authors found that energy transfer between the dendrimer and the porphyrin was highly efficient at low generations. This seemingly contradictory result may be rationalized by the fact that the energy transfer mechanism may be different in these cross-conjugated molecules than for the dendrimers of Aida and coworkers.[39] Additionally, the authors point out that the spectral overlap between the emission of the dendrons and the absorption of the porphyrin core is larger in this case, which may also have a significant effect on the energy transfer efficiency.

In a more recent publication, Aida and coworkers reported the encapsulation of a poly(phenyleneethynylene) rigid-rod polymer by a poly(benzyl ether) Fréchet-type dendrimer shell.[41] The dendritic shell was again effective as both a steric 'bumper' preventing polymer chains from aggregating, and as a light-harvesting antenna. The authors showed that upon direct

excitation of the polymer backbone, the fluorescence quantum yield remained constant over a wide concentration range only if a large enough dendrimer envelope, composed of G-4 dendrons or higher, was utilized. Additionally, excitation of the dendritic shell at 278 nm resulted in complete quenching of dendrimer emission, and a high fluorescence intensity emanating from the conjugated polymer. It was found that this sensitized polymer fluorescence was greatly enhanced over the emission resulting from direct excitation of the polymer at 425 nm, again illustrating the dendrimer 'antenna effect'. Owing to the importance of such conjugated polymers in organic light-emitting diode (OLED) technology, these findings could have a significant impact on the future of LED devices.

In a separate report, Jiang and Aida have demonstrated an unusual acceleration of the *cis–trans* isomerization within an azobenzene moiety at the core of G-4 and G-5 poly(benzyl ether) dendrimers.[42] This acceleration was observed under low-flux IR irradiation of a stretching vibrational band of the aromatic rings at 1597 cm^{-1}. Interestingly, irradiation at different IR frequencies, such as 2500 or 1155 cm^{-1} resulted in no apparent acceleration above the thermal rate. Additionally, when low-generation dendrimers were utilized, the acceleration was not apparent. Any change in substitution, such as in the mono-dendritic analog (Fig. 9), also eliminated the acceleration.

Fig. 10 Illustration of the electron transfer process occurring through the dendrimer backbone as a result of photoexcitation of the peripheral acceptor chromophores.
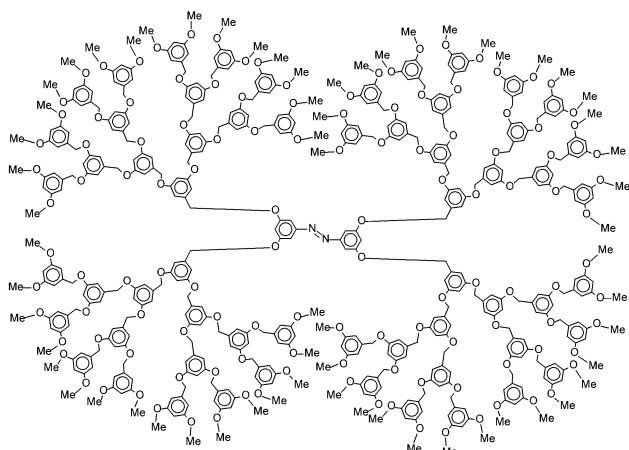

Fig. 9 Structure of a G-5 azobenzene-cored dendrimer.

This latter point is not surprising in light of our own work on encapsulated lanthanide ions (*vide supra*) in which the critical dependence of energy transfer on the substitution pattern of the focal aromatic ring was demonstrated. However, UV irradiation of the dendrons at 280 nm did result in a similar acceleration. In order to rationalize these observations, the authors proposed that the dendritic shell not only insulates the azobenzene core from collisional energy dissipation, but also acts as a photon-harvesting antenna. By comparison with thermally induced accelerations at 60 °C and by determining the dependence of the isomerization rate constant on the applied photon flux, it was found that the energy required for the observed rate acceleration required the simultaneous delivery of the energy of 4.9 IR photons to the azobenzene core. This calculation is consistent with the observed requirement of high-generation dendrons, since the simultaneous absorption of multiple photons from such weak photon sources could only be plausible in extremely large molecules.

Using a different approach, Stewart and Fox[43] utilized the known photoinduced electron transfer interaction between aryl chromophores (naphthyl or pyrenyl) and tertiary amines.[44] Since it is well known that excited states of aryl chromophores are quenched by electron donating amines, it was postulated that excitation of the periphery of dendrimers having naphthyl or pyrenyl groups at their chain ends and an amine at the core, would lead to intramolecular electron transfer through the dendrimer backbone (Fig. 10). Indeed, fluorescence quenching
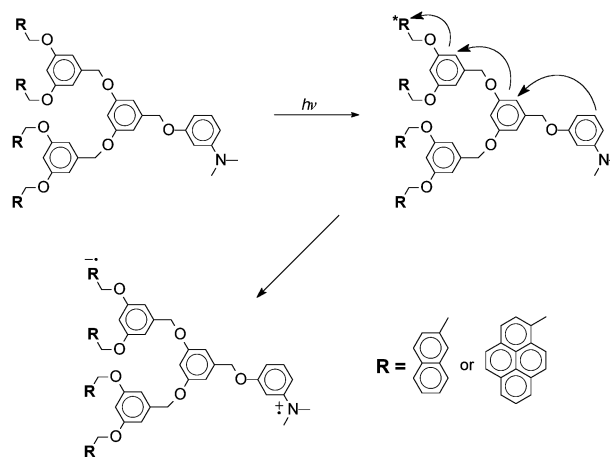
of the peripheral chromophores by the amine core was observed, but only in small dendrons (G-1 and G-2). At higher generations, the quenching efficiency decreased dramatically, probably as a result of the increased distance between periphery and core.

Dendrimer-independent energy transfer

In order to create a more versatile system in which the energy transfer between peripheral chromophores and core was not affected by the dendrimer backbone itself, we have designed dendrimers with photochemically silent building blocks. Since the energy transfer process with such structures requires a highly efficient through-space interaction between chromophores located at their focal point and periphery, chromophore selection must meet certain requirements.[45] Specifically, the chromophores should be suitable for Förster energy transfer, with a large spectral overlap between donor emission and acceptor absorption, high transition dipole moments, high extinction coefficients, and high quantum yields of fluorescence.[14] In addition to these photophysical requirements, the chosen chromophores should (i) be soluble in organic solvents—this is particularly important for the peripheral donor chromophores, since the solubility properties of dendrimers are known to be highly sensitive to the nature of the surface groups—and (ii) contain a functional 'handle' through which attachment to the dendritic structure could be achieved.

Amino-functionalized Coumarin-2 and acid-functionalized Coumarin-343 were selected as the donor and the acceptor, respectively (Fig. 11). The solubility of these chromophores was adequate for the preparation of dendrimers up to generation four using an AB$_2$ building block with orthogonal functionalities (Fig. 11).[46] The photophysical properties of these molecules were studied by steady-state and time-resolved absorption and emission spectroscopy.[47] Initially, steady-state data was collected for model compounds containing either the donor chromophores or the acceptor, but not both. These models showed that the large spectral overlap between donor emission and acceptor absorption is preserved after coupling of the chromophores to the dendritic architecture (Fig. 12). Additionally, exclusive excitation of either the donor or the acceptor was found to be possible, simplifying the analysis of fluorescence data for energy transfer calculations.

The steady-state absorption characteristics of the fully-labeled dendrimers showed the expected doubling of donor absorption as a function of dendrimer generation, indicating that no deleterious ground-state aggregation phenomena were occurring in this system [Fig. 13(a)]. The acceptor absorption was shown to remain relatively constant at each generation, with only slight solvatochromic shifts being evident due to the
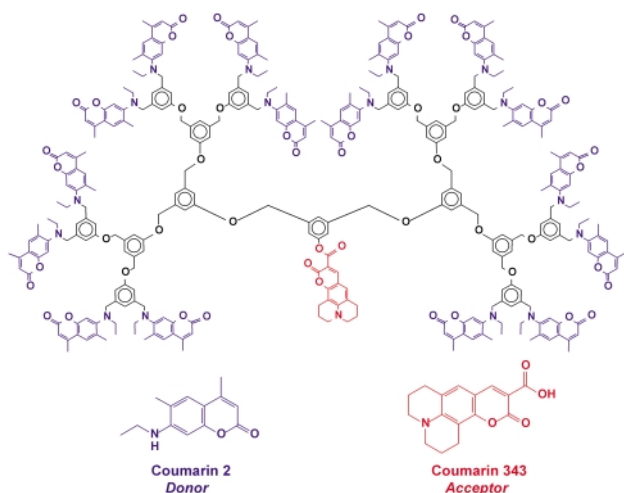
Fig. 11 Chemical structure of the Coumarin-2 donor, Coumarin-343 acceptor, and the fully chromophore-functionalized G-4 dendrimer.
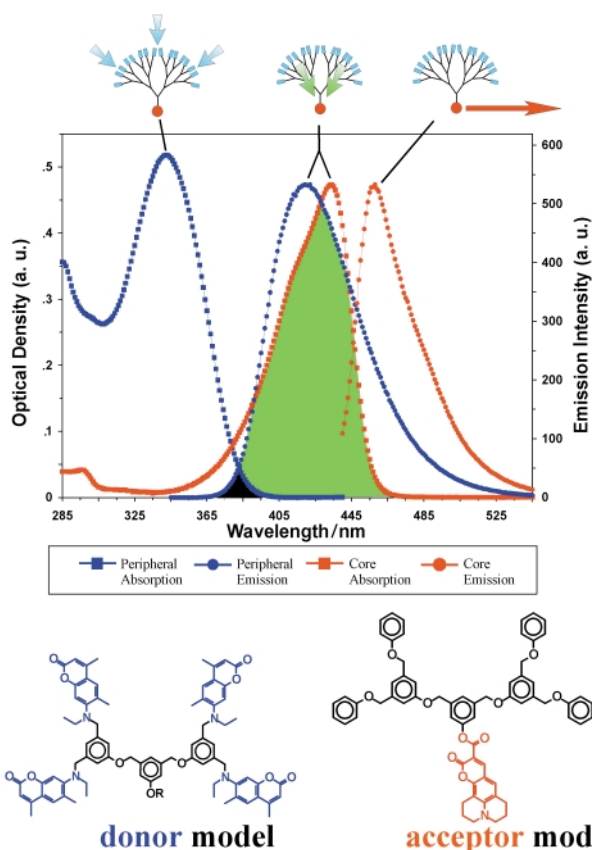

Fig. 12 Structures and spectral properties of donor and acceptor model compounds, indicating the strong overlap between donor emission and acceptor absorption.

Fig. 13 UV–VIS absorption (top) and fluorescence emission (bottom) properties of the Coumarin-functionalized G-1 to G-4 series of dendrimers.

increasing influence of the polar dendrimer shell around the focal chromophore. Upon irradiation of the donor absorption band, strong fluorescence was observed exclusively from the acceptor chromophore. The complete quenching of the donor chromophores attests to the highly efficient energy transfer occurring in these molecules. Additionally, a comparison of the emission intensity from sensitized acceptor excitation ($\lambda_{ex} = 343$ nm) to that from direct acceptor excitation ($\lambda_{ex} = 440$ nm) could be made [Fig. 13(b)]. It was found that in dendrimer generations beyond G-2, the emission intensity from sensitized excitation was greatly enhanced [Fig. 13(b), dotted curve], confirming that energy transfer efficiency is extremely high in these molecules. Time-resolved experiments indicated that energy migration from the periphery to the core occurred on extremely fast, sub-picosecond timescales. Using single-photon
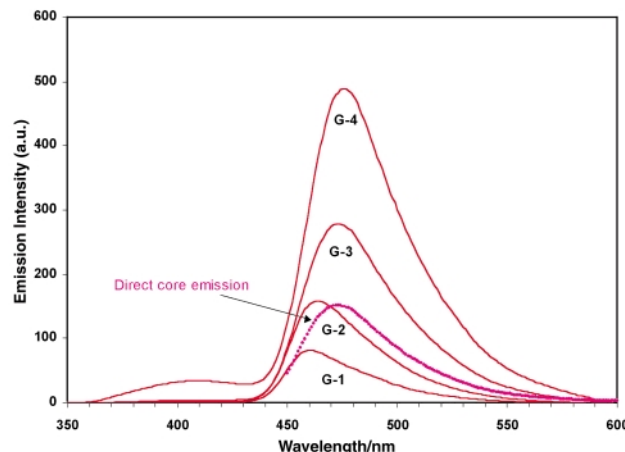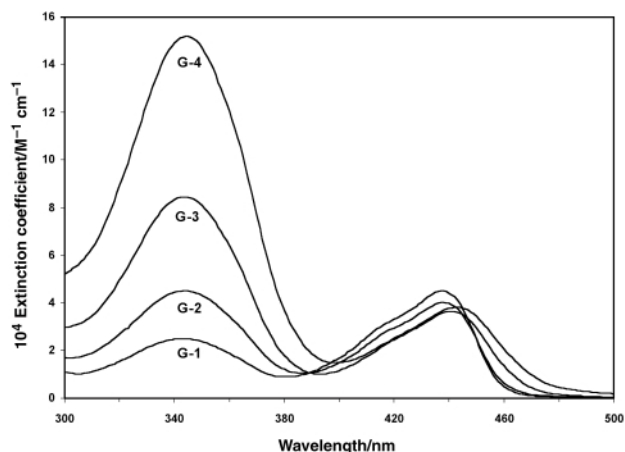
counting, it was not possible to resolve the rise-time of the core excitation upon irradiation of the periphery. Although these preliminary studies indicate that the Förster mechanism is the dominant energy transfer pathway, exact values for energy transfer rate constants must be ascertained before this claim can be fully substantiated. Further spectroscopic experiments with much faster time resolution will enable accurate measurements of the energy transfer rate constants and their quantitative comparison with theoretical calculations from Förster theory and molecular modeling.

Interesting insight into the relative rates of energy transfer *vs.* nonradiative relaxation of Coumarin-2 was provided by a study of the energy transfer dependence on solvent composition. When G-1 and G-2 donor model dendrons were dissolved in methanol (higher generation dendrimers were not soluble), it was found that the Coumarin-2 emission was completely quenched (Fig. 14). This was likely due to hydrogen bonding of the solvent with the tertiary amine lone pair, precluding optimal alignment of this lone pair orbital with the aromatic system of the chromophore. However, upon coupling of the acceptor chromophore to the focal point of these dendrons, excitation of the donors resulted in strong emission from the core. This indicates that, although fast nonradiative decay processes can compete with the nanosecond-scale donor fluorescence, the energy transfer process is much faster and still results in energy localization on the acceptor dye. The acceptor fluorescence is not quenched by the hydrogen bonding solvent presumably because the amine lone pair orbital is kept in conjugation by the two cyclohexyl rings (Fig. 11).

More recent work has shown that replacement of the Coumarin-343 acceptor by other chromophores can result in efficient energy transfer, as long as the absorption spectrum retains good overlap with the donor emission.[48] Oligothiophene
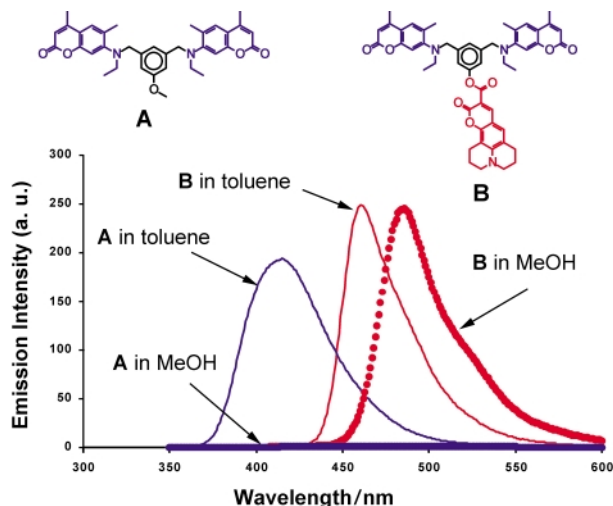
Fig. 14 Emission spectra of G-1 dendrons without (A) and with (B) the core acceptor chromophore in toluene (solid line) and methanol (dotted line).

chromophores proved ideal for this purpose, since it is possible to tune their absorption and emission properties by changing the degree of oligomerization. Two different oligothiophenes—a pentamer linked through its terminal ring, and a heptamer linked through its central ring—were chosen owing to their favorable absorption properties. Dendrimers up to the third generation were prepared, and it was shown that energy transfer was quantitative in all cases. Again, the emission intensity of the oligothiophenes, which have relatively low quantum yields of fluorescence ($\Phi_f = 0.15$), was greatly enhanced by sensitized excitation upon irradiation of the peripheral light-harvesting antenna. This phenomenon may prove useful in the emission enhancement of photonic devices in which it is necessary to utilize components that have low fluorescence quantum yields. Interestingly, the oligothiophenes in this study had emission spectra that were strongly red-shifted from the emission of Coumarin-343. Hence, by simply changing the core function-ality of the dendrimer, it is possible to tune the emission wavelengths across almost the entire visible spectrum, while irradiating at a single wavelength [Fig. 15(b)]. Molecules with this feature serve as ideal probes for experiments requiring simultaneous excitation and detection of several different targets, such as in the area of fluorescent conjugates for biological molecules.

Dendrimer-based light-emitting diodes

The findings made with the dendrimer antennas can be extended to the design of single-layer multichromophoric light-emitting diodes. The dendritic framework provides for both the energy transfer interaction and the site-isolation of different chromo-phores, enabling them to fluoresce simultaneously.[49–51] Sepa-rate emission from each dye is difficult to achieve in classical solid-state devices owing to intermolecular energy transfer to the chromophore with the smallest bandgap. By isolating the different chromophores within a dendritic shell, it should be possible to diminish or even eliminate this energy transfer in their mixture, and enable emission from each individual dye. Dendrimers peripherally-functionalized with hole-transporting triarylamines and core-functionalized with two different fluo-rescent chromophores were synthesized separately, and incor-porated as a mixture into a single-layer light-emitting device (Fig. 16). These structures allowed the excitation energy to be changed from applied light to an applied voltage across two electrodes. Based on the solution work outlined above, the chosen fluorescent chromophores were Coumarin-343 and a pentathiophene, since their absorption bands overlap well with the emission band of the peripheral triarylamine. Our prelimi-nary studies[49–51] indicate that it is possible to observe
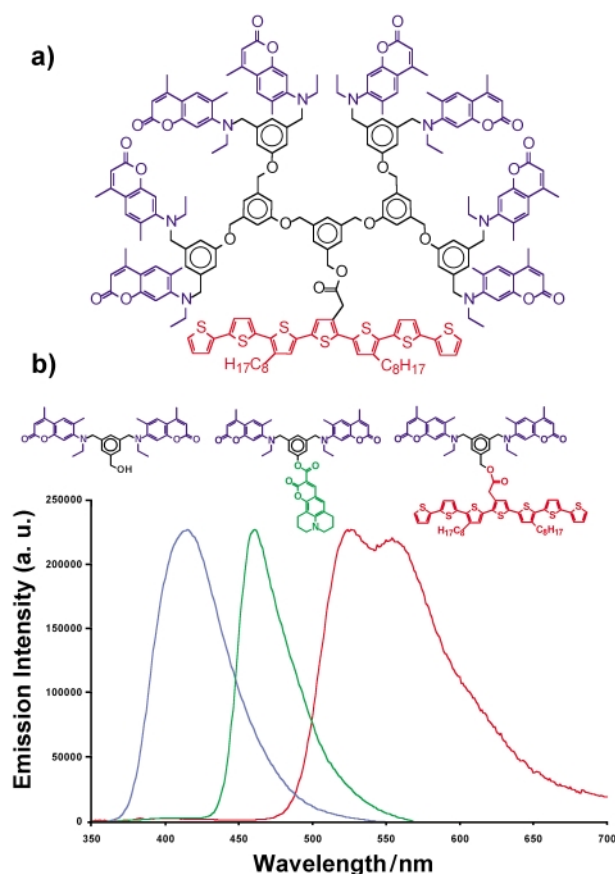

Fig. 15 (a) Structure of the G-3 heptathiophene (T-7) core-functionalized dendrimer. (b) Normalized emission spectra of G-1 dendrons having different moieties at the core: (i) no core chromophore; (ii) Coumarin-343; (iii) heptathiophene.

simultaneous emission from both chromophores when they are encapsulated in a dendrimer. In contrast, the light produced by mixtures of the free dyes originates solely from the lower bandgap oligothiophene.[49–51]

Dendrimer-based organic LEDs have also been reported by Moore and coworkers.[52] In this example, phenylacetylene dendrimers were prepared with peripheral triphenylamine groups for hole transport, and a core 9,10-bis(phenylethynyl)-anthracene as the light emitter. Unfortunately, thin films of these molecules exhibited only modest electroluminescence (EL) intensities. Solid-state aggregation of the rigid dendrimers and self-quenching by the low Stokes shift anthracene chromo-phores were the likely causes of diminished EL.

Light-harvesting in self-assembled monolayers

To further simplify the antenna concept without recourse to the tedious preparation of multichromophoric dendrimers, we studied the self-assembly of harvesting antennas and emitting components on silicon surfaces. Small Coumarin-2 function-alized donor dendrons and the Coumarin-343 acceptor chromo-phore (Fig. 17) were therefore functionalized with triethoxy-silane moieties, which could then be adsorbed onto a silicon wafer to form self-assembled monolayers (SAMs).[53] The self-assembly process enables the use of a variety of donor–acceptor ratios by adjusting the adsorbate ratios in solution prior to SAM assembly. The photophysical properties of the monolayers were determined using front-face fluorescence techniques. As ex-pected, variations in the donor–acceptor ratio on the surface had a large effect on the efficiency of energy transfer. Fig. 18(a) illustrates the normalized emission spectra from mixed mono-layers of **6** and **8** having a 2:1 and a 3:1 ratio.[53] The larger average donor–acceptor distance obtained with a 3:1 ratio leads to a broader emission spectrum with contributions from both
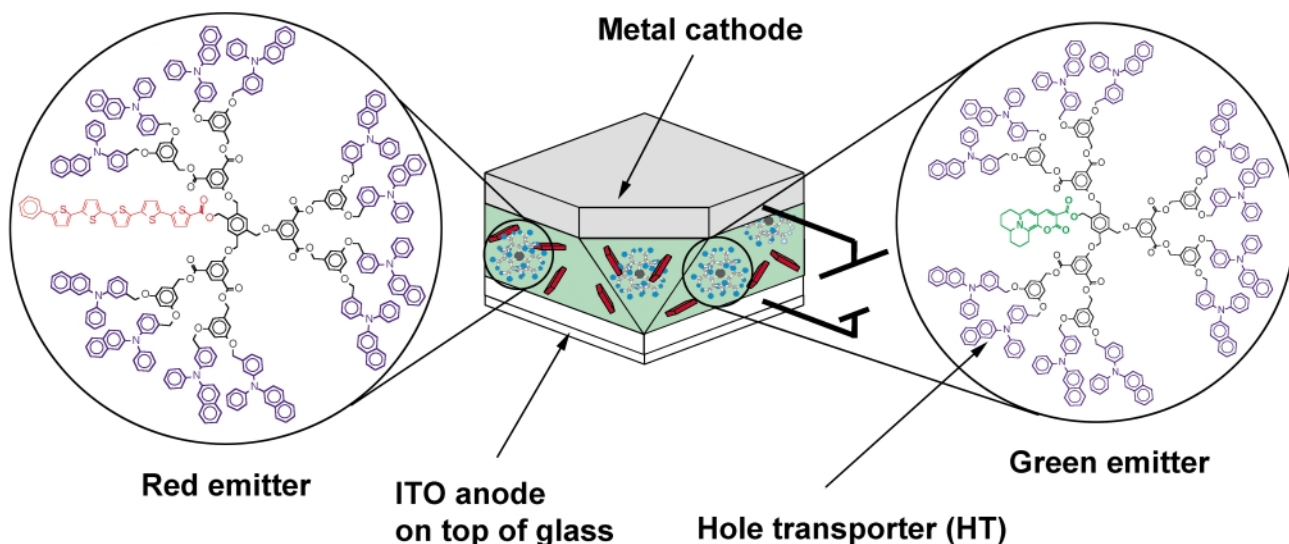
Fig. 16 Schematic diagram of an LED device incorporating hole-transporting dendrimers with pentathiophene (red emitter) and Coumarin-343 (green emitter) cores.
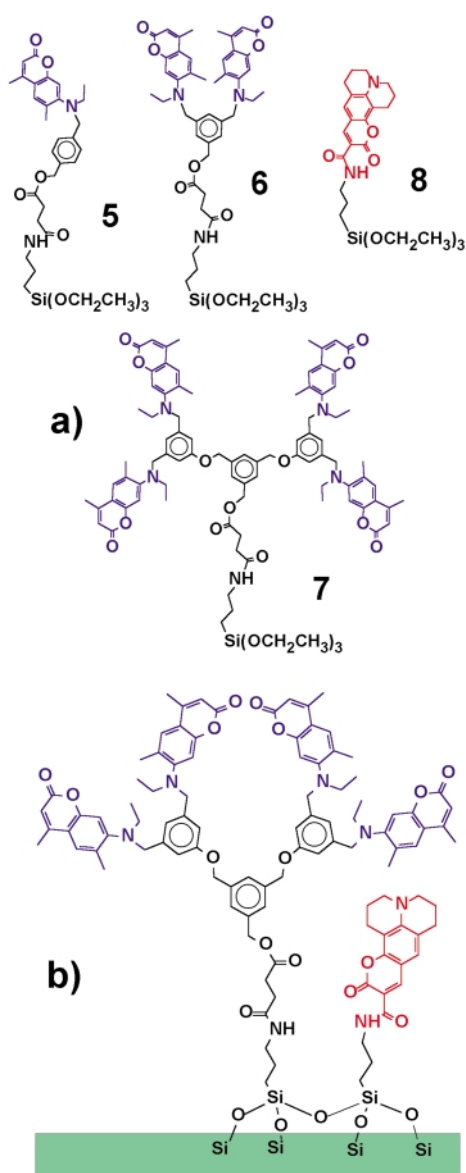

Fig. 17 (a) Structures of the triethoxysilane-functionalized donor and acceptor adsorbates. (b) Schematic representation of a mixed SAM of separate G-2 donor dendron and the Coumarin-343 acceptor on a silicon surface.
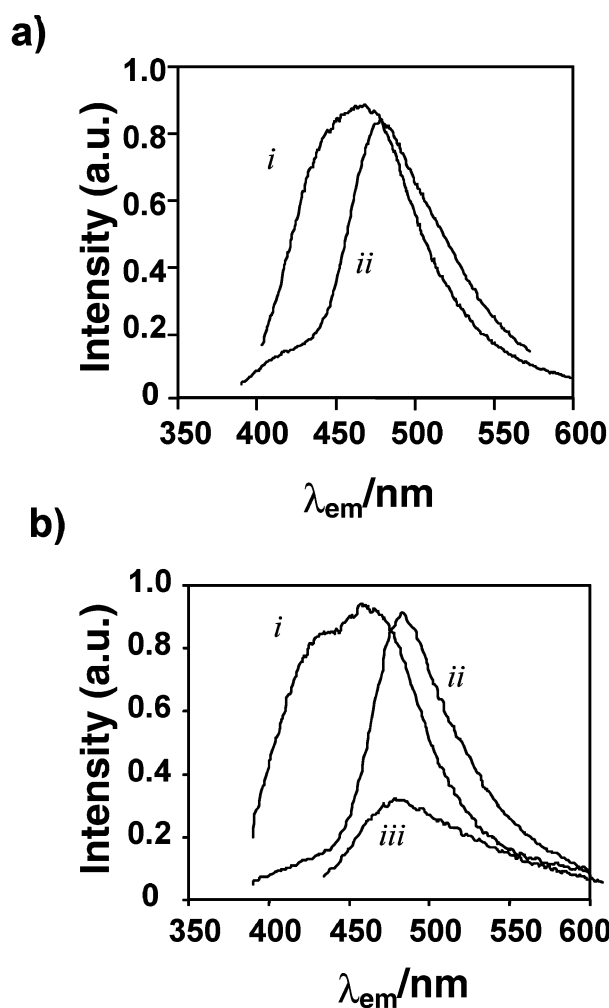

Fig. 18 (a) Normalized emission spectra from mixed monolayers of **6** and **8** having a 3:1 (i) and a 2:1 (ii) ratio. (b) Normalized emission spectra from mixed monolayers of a 4:1 ratio of adsorbates **5** and **8** (i), and a 1:1 ratio of adsorbates **7** and **8** (ii). Emission due to direct excitation of the acceptor at 420 nm is also illustrated (iii).

donor and acceptor as a result of inefficient energy transfer. In contrast, the emission spectrum of a SAM prepared with a 2:1 ratio of **6** to **8** is narrow, resulting purely from Coumarin-343 emission as energy transfer is highly efficient.

The importance of the dendritic character of donor chromophore **7** was confirmed in experiments involving adsorbate **5**

with its single Coumarin-2. The use of a 4:1 ratio of **5** to **8**, equivalent to the 1:1 ratio of **7** to **8**, led to incomplete energy transfer [Fig. 18(b)]. This illustrates the importance of the average inter-adsorbate distance in the energy transfer process as the dendritic nature of **7** facilitates the productive assembly of chromophores in the monolayer. Amplification of acceptor emission by sensitized excitation was clearly illustrated as the light output from the acceptor chromophore is significantly higher when it results from donor excitation at 350 nm than from its direct excitation at 420 nm.

Energy transfer in self-assembled dendritic structures of a different sort have recently been reported by Meijer and coworkers.[54] Poly(propylene imine) dendrimers were surface-modified with oligo(*p*-phenylene vinylene) (OPV) units affording amphiphilic structures that function as hosts capable of extracting water-soluble guests into the organic phase. Since the OPV-surface units are fluorescent, with an emission maximum at 492 nm when excited at 420 nm, it was speculated that energy transfer to a suitable chromophoric guest could occur. Using Sulforhodamine B as the energy-accepting guest (Fig. 19),
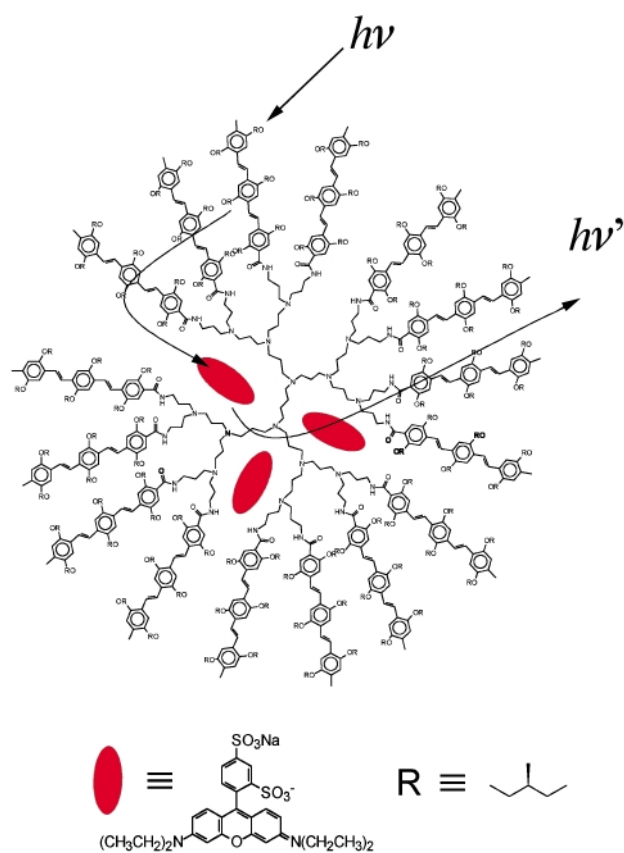

Fig. 19 Schematic representation of energy transfer from the peripheral OPV units to the encapsulated Sulforhodamine B guest within poly-(propylene imine) dendrimers.

energy transfer was indeed observed with an efficiency of roughly 40% at maximal loading. This efficiency is significantly lower than achieved with dendrimers in which donor and acceptor are covalently linked, but this may be due, at least in part, to the poor overlap between donor emission and acceptor absorption.

Conclusions and outlook

In analogy to the natural photosynthetic systems, dendrimers, with their numerous branching units and chain ends uniformly surrounding a single core unit, seem ideally suited to function as light-harvesting structures. The examples illustrated in this article give testimony to our ability, through chemical manipulation, to create effective—if still very simple—mimics of natural photosystems. It is possible to vary the structural units in order to affect the physical properties of these molecules, while still maintaining a well defined, monodisperse macromolecule. Although it is unlikely that the current generation of light-harvesting dendrimers will be utilized in any but the most specialized applications owing to the somewhat tedious and expensive nature of their synthesis, they will prove to be effective model systems that will impact sensor technology, light-emitting diodes, fluorescent labeling of biological molecules, as well as a variety of photonic devices. It should be noted however that new routes to dendrimers[55] and less precise but nevertheless useful hyperbranched polymers[56] and dendritic hybrids are being developed, and some of these have already been applied to easily accessed multichromophoric systems.[57,58] In addition, it is envisioned that future work in this field will advance toward more complex mimics of natural photosynthetic systems, in which the energy absorbed at the dendrimer periphery will be employed to catalyze a chemical reaction. Nature utilizes the sun's energy to enable an electron transfer within the reaction complex, which eventually leads to the production of biologically important molecules such as ATP. Clearly, synthetic antennas have a long way to go as they aim to reach similar goals. The stakes of this research are high, as the development of novel synthetic photocatalysts and more efficient photovoltaic cells, such as the Grätzel cells,[59,60] would expand our ability to better utilize the sun's energy and decrease our dependency on fossil fuels.

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