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Light-Harvesting Dendrimers: Efficient Intra- and Intermolecular Energy-Transfer Processes in a Species Containing 65 Chromophoric Groups of Four Different Types[**]

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Dedicated to J. Fraser Stoddart
on the occasion of his 60th birthday

An antenna for light harvesting is an organized system in which several chromophoric molecular species absorb the incident light and channel the excitation energy to a common acceptor component.[1] Light-harvesting antennas are essential devices for natural photosynthetic processes.[2] In the last decade, dendrimers[3] have been extensively used to construct artificial antenna systems as suitable chromophoric groups may be incorporated into their regular branched structures.[4,5] Another interesting aspect of dendrimer chemistry is the presence of internal cavities where ions or neutral molecules can be hosted.[6,7] Energy-transfer processes between the

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chromophoric units present in the dendrimer branches and hosted species have also been investigated.[7a,e,f]

Continuing our studies in this field,[8] we have designed and synthesized a dendrimer that 1) contains 64 chromophoric units of three different types, and 2) is able to host a dye molecule. We have found that in such a host–guest system the encapsulated dye molecule collects electronic energy from all of the 64 chromophoric units of the dendrimer with high efficiency.

Dendrimer **1** (Scheme 1) consists of a polyamine core surrounded by 8 dansyl-, 24 dimethoxybenzene-, and 32 naphthalene-type units (dansyl is the commonly used name for the 5-dimethylamino-1-naphthalenesulfonyl chromophoric group). It can be viewed as the combination of the poly(propylene amine) (POPAM) dendrimer **2** with eight attached dendrons **3** (Scheme 1).

The absorption and emission spectra of dendrimer **2**, dendron **3**, and eosin **4** are shown in Figure 1. Dendron **3** contains three dimethoxybenzene- and four naphthalene-type chromophoric units, whose absorption and fluorescence bands strongly overlap. The fluorescence band maximum (λ_{max}), quantum yield (Φ), and lifetime (τ) of dendron **3** are 336 nm, 0.019, and 4.6 ns, respectively. Dendrimer **2** exhibits the absorption bands of its dansyl chromophoric units ($\lambda_{max} = 255$ nm, $\varepsilon = 96300\,\text{M}^{-1}\text{cm}^{-1}$; $\lambda_{max} = 340$ nm, $\varepsilon = 29500\,\text{M}^{-1}\text{cm}^{-1}$). The broad fluorescence band shows a maximum at 514 nm with $\Phi = 0.27$ and $\tau = 16$ ns. Since eosin is not soluble in CH_2Cl_2, solubilization was achieved by addition of [18]crown-6.[7f,8c] Under such conditions, a solution of eosin in CH_2Cl_2 shows a strong absorption band in the visible region ($\lambda_{max} = 529$ nm, $\varepsilon = 61000\,\text{M}^{-1}\text{cm}^{-1}$), and a fluorescence band with $\lambda_{max} = 555$ nm, $\Phi = 0.65$, and $\tau = 3.8$ ns. It is noticeable (Figures 1 a and b) that the fluorescence band of dendron **3** strongly overlaps the absorption band of dendrimer **2**, and that the fluorescence band of dendrimer **2** strongly overlaps the absorption band of eosin **4**.

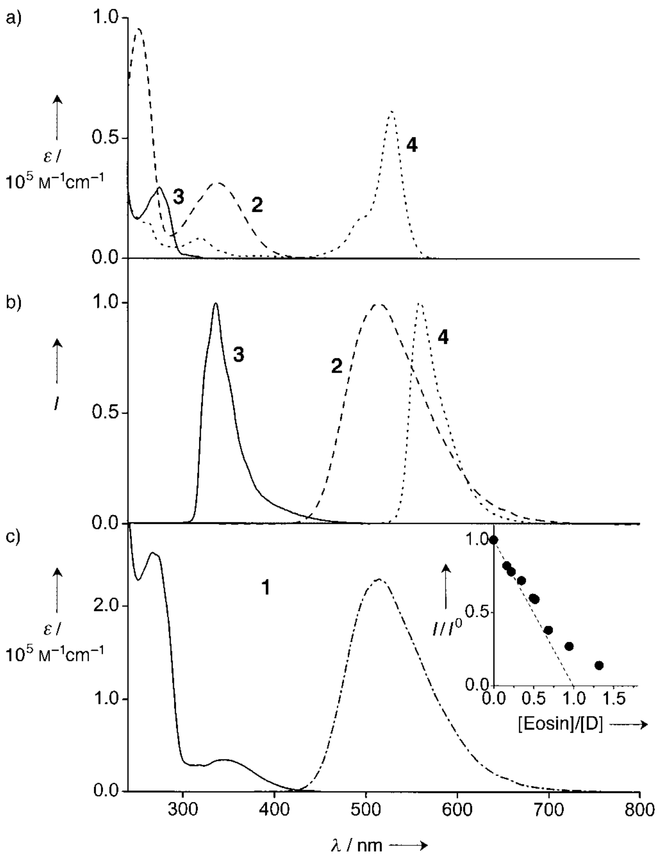
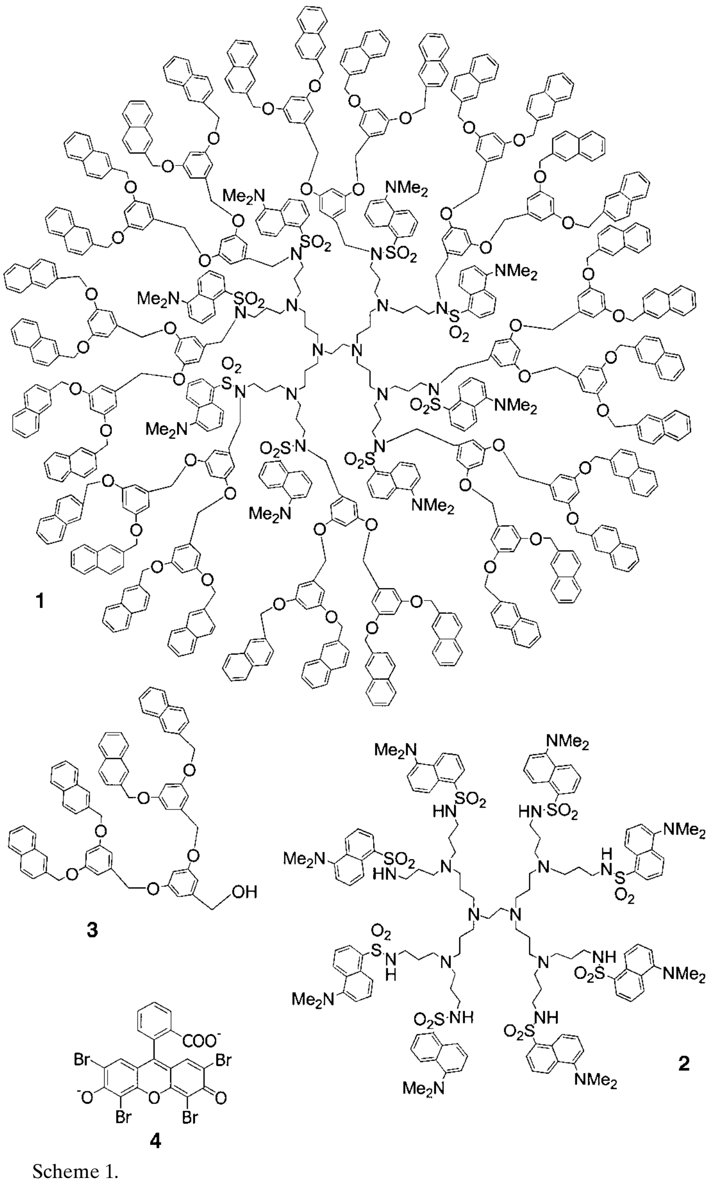


Figure 1. Absorption (a) and emission (b) spectra of dendron **3** (——, $\lambda_{ex} = 287$ nm), dendrimer **2** (- - - -, $\lambda_{ex} = 343$ nm), and eosin **4** (••••, $\lambda_{ex} = 500$ nm). Absorption (——) and emission spectra (–•–, arbitrary unit, $\lambda_{ex} = 370$ nm) of dendrimer **1** (c). Inset: decrease of dansyl fluorescence intensity on increasing [eosin]:[**1**] ratio. Experimental conditions: in dichloromethane at 298 K in all cases.



Scheme 1.

The absorption spectrum of dendrimer **1** (Figure 1 c) is that which may be expected from the sum of the absorption spectra of its components, namely dendrimer **2** and eight dendrons **3**. The emission spectrum of **1** shows a strong dansyl-type fluorescence band, whereas the intensity of the fluorescence band of the units of dendron **3** is almost completely quenched (≧95%). Since the fluorescence lifetime of dendron **3** is 4.6 ns, the rate constant for the quenching process has to be at least $4 \times 10^9\ s^{-1}$. The quenching is accompanied by the sensitization of the dansyl fluorescence, which presumably occurs by singlet–singlet Förster-type energy transfer[9] from the dimethoxybenzene- and naphthalene-type units to the dansyl units. This transfer is favored by 1) the large spectral overlap between donor emission and acceptor absorption, 2) the high molar absorption coefficient of the acceptor, and 3) the high fluorescence quantum yield of the donor.[10] From the experimental viewpoint, however, the energy-transfer efficiency is difficult to measure because of band overlap. The estimated value of 80 ± 25 % does not allow us to rule out the presence of a minor quenching path based on electron transfer.

Previous investigations[7f,8c] have shown that solutions of POPAM dendrimers such as **2** in CH_2Cl_2 are able to extract eosin, presumably in its monoprotonated form, from aqueous solutions. In such host–guest systems, the fluorescence of the dansyl units of the dendritic host was found to be quenched very efficiently by the presence of the guest. Therefore, we thought it was worthwhile investigating whether dendrimer **1**, whose "core" consists of the POPAM dendrimer **2**, was able to host eosin.

When a solution of dendrimer **1** in CH_2Cl_2 (8.2×10^{-6} M) was shaken with aqueous solutions containing eosin, the organic phase became colored, which indicated that eosin had been extracted. We have also confirmed[7f,8c] that, in the absence of dendrimer, extraction of eosin by CH_2Cl_2 was practically negligible. The concentration of eosin extracted by the dendrimer, measured from the increase of the eosin absorption in the CH_2Cl_2 phase, was found to increase with increasing eosin concentration in the aqueous phase. Extraction of eosin is accompanied by the quenching of the dansyl fluorescence, which confirms that eosin interacts with the dendrimer.[11] Eosin is likely to be located in the amine core of the dendrimer since: 1) as we have seen above, eosin is also extracted by dendrimer **2**, which does not contain naphthalene and dimethoxybenzene units, 2) the Fréchet dendron **3** does not extract eosin, thus indicating that the aromatic peripheral groups do not strongly interact with eosin, and 3) one of the major driving forces for the host–guest interaction is an acid (acidic eosin)–base (internal amine units) relationship, as already suggested by Baars and Meijer.[6] for similar xanthene dyes.

The slope of the fluorescence quenching plot (Figure 1c, inset) at low eosin concentration ([eosin]:[**1**] less than 0.3) is approximately −1, which indicates complete quenching of the fluorescence of any dansyl units of the dendritic host, even when each host can only encapsulate one eosin molecule.[12] Assuming that the intensity of the unquenched fluorescence of a dansyl unit of a dendrimer hosting an eosin molecule is no greater than 5 % of the original intensity (in an "empty" dendrimer), and considering that the intrinsic lifetime of the dansyl fluorescence is 16 ns, the rate constant for the quenching process must be higher than $1.2 \times 10^9\ s^{-1}$. A high quenching constant is indeed expected in view of the strong overlap between the emission spectrum of the dansyl units and the absorption spectrum of the eosin molecules (Figure 1a, b). A value of about $1 \times 10^{11}\ s^{-1}$ can be estimated from the equation of the dipole–dipole (Förster) mechanism taken at an average r value of 1 nm. Comparison between fluorescence intensities obtained upon excitation at 370 nm (dansyl absorption) and 520 nm (eosin absorption) showed that the quenching of the dansyl fluorescence by eosin does occur with high efficiency (at least 0.8). In summary, the excitation spectrum of the host–guest system closely matches the absorption spectrum, which demonstrates that eosin is able to collect light energy from the three different chromophoric groups of the host dendrimer **1**.

Examination of the fluorescence properties of the eosin molecules encapsulated into the dendrimers has revealed other interesting features of this fluorescent-host–fluorescent-guest system. When eosin is hosted in a solution of the dendrimer in dichloromethane, the fluorescence quantum yield is 0.29 and two exponential decays are observed, even at very low eosin concentration where there is a maximum of one eosin molecule per dendrimer. This observation suggests that eosin molecules can occupy two distinct sites (or two families of substantially different sites) in the interior of the dendrimer, a phenomenon that has been previously observed for poly(propylene amine) dendrimers.[7f,8c] At least two different sites for the inclusion of a spin probe within an alternatively functionalized POPAM dendrimer have previously been noted by Jansen and Meijer.[13]

In conclusion, we have shown that an eosin molecule encapsulated into dendrimer **1** (Figure 2) collects electronic energy from all 64 chromophoric units of the dendrimer, which consist of three different chromophoric types. Both intramolecular (that is, within the dendrimer) and intermolecular (dendrimer-host→eosin-guest) energy-transfer processes occur very efficiently by a Förster-type mechanism, because of the strong overlap between the emission and absorption spectra of the relevant donor/acceptor units.

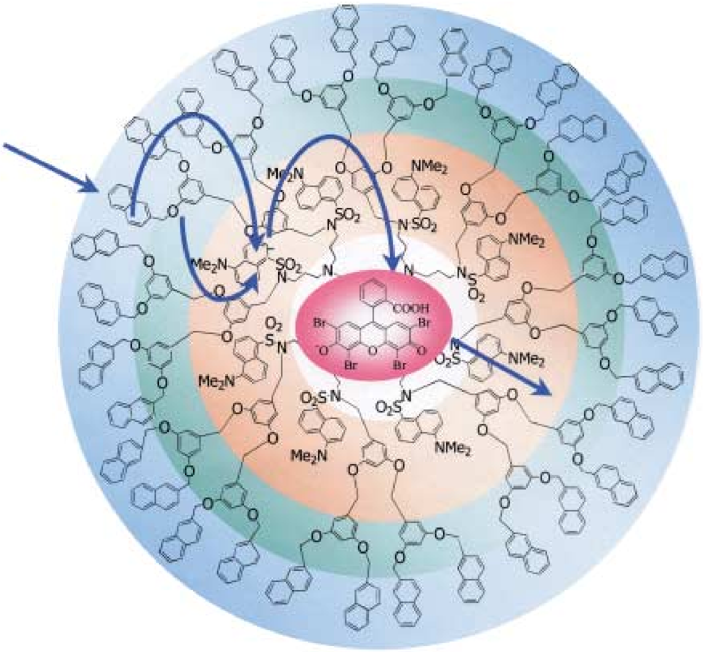


Figure 2. Schematic representation of the intramolecular (that is, within the dendrimer) and intermolecular (dendrimer-host→eosin-guest) energy-transfer processes. The exact eosin location is unknown.

Experimental Section

All syntheses were routinely carried out under an argon atmosphere. Starting materials (POPAM dendrimer G2, 3,5-dihydroxybenzyl alcohol, 2-bromomethylnaphthalene, dansyl chloride) were purchased from Aldrich. 3,5-Bis(3′,5′-bis(2″-oxymethylnaphthyl)benzyloxy)benzyl bromide (obtained from precursor **3**) and **2** were synthesized according to literature procedures.[14,15]

1:Cesium carbonate (200 mg) was added to a solution of **2** (50.0 mg, 0.019 mmol) in DMF (10 mL) under argon. 3,5-bis(3′,5′-bis(2″-oxymethylnaphthyl)benzyloxy)benzyl bromide (193.0 mg, 0.19 mmol) in DMF (10 mL) was added to this solution, and the mixture was stirred for seven days, then filtered and the solvent evaporated. The residue was dissolved in CH_2Cl_2, washed with water, saturated $NaHCO_3$ solution, and again with water, then dried over Na_2SO_4 and evaporated. Purification by column chromatography on SiO_2 (63–100 μm) with chloroform/methanol (20:1) as eluent yielded a light-yellow solid in 48% yield, m.p. 103–108 °C, $R_f = 0.08$ (chloroform/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.59$ (br s, 24 H, CH_2), 2.13 (br s, 32 H, NCH_2), 2.47 (br s, 52 H, $N(CH_3)_2$ and $N(CH_2)_2N$), 3.35 (s, 16 H, SO_2NCH_2), 4.30 (s, 16 H, SO_2NCH_2Ar), 4.44 (s, 32 H, $ArOCH_2Ar$), 4.97 (s, 64 H, $ArOCH_2Naph$), 6.23 (m, 16 H, CH_{Ar}), 6.35 (m, 8 H, CH_{Ar}), 6.54–6.74 (br m, 56 H, 48 CH_{Ar} and 8 CH_{Dans}), 7.22–7.51 (br m, 104 H, 96 CH_{Naph} and 8 CH_{Dans}), 7.59–7.87 (bm, 136 H, 128 CH_{Naph} and 8 CH_{Dans}), 8.14 (m, 8 H, CH_{Dans}), 8.29 ppm (m, 16 H, CH_{Dans}); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 25.1$, 44.9, 45.1, 50.1, 50.5, 51.2, 101.6 (2 C), 106.6 (2 C), 114.9, 119.3, 123.1, 125.3, 125.9, 126.1, 126.2, 127.6, 127.9, 128.2, 129.3, 129.6, 129.9, 130.1, 130.2, 132.9, 133.1, 134.2, 135.0, 138.6, 139.1, 151.6, 159.8, 159.9 ppm; $C_{654}H_{580}N_{22}O_{64}S_8$; $M_w = 10028.24$.

In all experiments, the aqueous phase was buffered at pH 7.0 using a phosphate buffer. Spectroscopic equipment and techniques have been described elsewhere.[8b] The experiments were carried out in air-equilibrated solutions. Fluorescence quantum yields were standardized[16] using naphthalene ($\Phi = 0.23$ in deaerated cyclohexane)[17a] for dendron **3**, quinine sulfate ($\Phi = 0.55$ in 1 N $H_2SO_{4(aq)}$ solution)[17b] for dendrimers **1** and **2**, and fluorescein ($\Phi = 0.90$ in NaOH; 0.01 M)[17c] for eosin **4**.

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[11] Dynamic quenching can be ruled out because of the short lifetime of dansyl fluorescence and the very low concentration (less than 10^{-5} M) of extracted eosin.

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Synthesis of Amphiphilic Conjugated Diblock Oligomers as Molecular Diodes[**]

Man-Kit Ng and Luping Yu[*]

Nearly three decades ago Aviram and Ratner proposed that individual molecules of the type donor–spacer–acceptor (D-s-A) placed between two electrodes would act as molecular rectifiers under a suitable bias voltage.[1] Previous attempts to provide experimental proof of molecular rectifiers were complicated by difficulty in establishing reproducible electrical contacts between the metal and single molecules, the junction rectifying effect at the metal–molecule interface due

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