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Synthesis and energy-transfer properties of poly(amidoamine) dendrons modified with naphthyl and dansyl groups

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Abstract

Poly(amidoamine) dendrons of 1–3 generations with naphthyl groups at the periphery and a dansyl group at the focal point were synthesized and carefully characterized. Intramolecular energy-transfer properties of these flexible aliphatic-scaffold light-harvesting dendrons were investigated by UV–vis absorption and fluorescence spectroscopy. Efficient energy transfer from the naphthyl groups to the dansyl group occurred for both the first and the second generation dendrons (the energy-transfer efficiency was 94.3% and 76.9%, respectively), whereas the third generation dendron exhibited a low energy-transfer efficiency of 17.8%. The average donor–acceptor distances between the naphthyl and dansyl groups were calculated for different generation dendrons. Different degrees of the backfolding of dendritic branches were used to interpret the different donor–acceptor distances.

Keywords: Energy transfer; Poly(amidoamine) dendrons; Förster mechanism; Light-harvesting

Light-harvesting systems in natural world have the unique ability to absorb, transfer, and convert the solar energy into the chemical energy.[1] Undoubtedly, designing efficient artificial light-harvesting materials will greatly reduce our dependence on unrenewable energy, such as fossil fuels.[2] Inspired by the nature, artificial light-harvesting systems, which are capable of channeling absorbed energy to a selected site in a unidirectional manner, have recently attracted great attention.[3] Dendrimers and dendrons[4] are recognized as excellent candidates for light-harvesting applications, owing to their well-defined and highly branched structures, possible energy gradient for the energy funneling process and large numbers of peripheral groups that could be used to capture light. In 1994, Xu and Moore reported the first efficient unidirectional energy transfer from a dendritic scaffold to a single-core chromophore.[5] Phenylacetylene dendrimers (up to the sixth generation) with a perylene core were synthesized in their laboratory. When the dendrimer backbone was excited at 312 nm, the fluorescence largely came from the perylene dye with effective quenching of the backbone emission. Following that, various conjugated dendron-based light-harvesting systems were developed.[6] For example, Peng and co-workers explored a novel class of unsymmetrical perylene-core phenylacetylene dendrons, in which the excitation of phenylacetylene backbone resulted in strong emission of the perylene core.[6a,b] De Schryver and co-workers reported an efficient intramolecular energy transfer of poly(phenylene) dendrimers with a perylenediimide core.[6c] Meanwhile, non-conjugated

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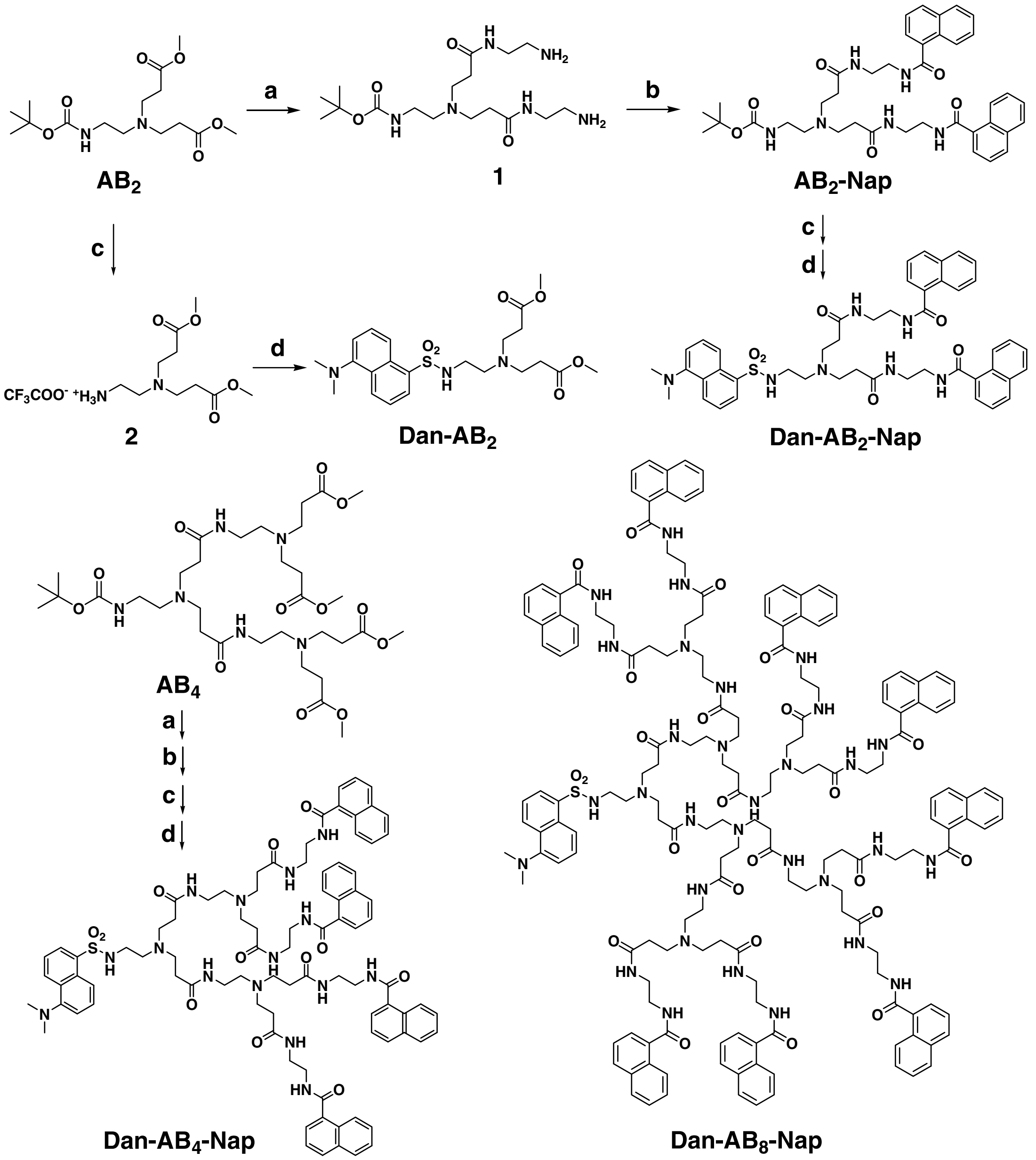
poly(aryl ether) dendron (Fréchet-type dendron) based light-harvesting systems were reported.[7] Particularly, Fréchet and Kawa described the 'antenna effect' in their lanthanide-core poly(benzyl ether) dendrimers.[7a] They also developed a series of light-harvesting poly(benzyl ether) dendrimers containing Coumarin-2 as the energy donor on the periphery and Coumarin-343 as the acceptor at the core.[7b–d] Jiang and Aida reported the energy transfer behavior in porphyrin dendrimers by varying the substituted number of the Fréchet-type dendrons.[7e] Furthermore, they reported blue-luminescent dendronized polymers with poly(phenylene ethynylene) as the backbone and Fréchet-type dendrons as the dendritic shell.[7f]

Non-conjugated poly(benzyl ether) dendron-based light-harvesting systems have been explored intensely; however, up to now, reports about flexible aliphatic-scaffold light-harvesting dendritic systems, such as poly(amidoamine) (PAMAM) dendron-based light-harvesting systems, are still very rare. In fact, high efficiency of energy transfer is possibly allowed because of the relatively short distance from the peripheral donor to the core acceptor due to the backfolding of flexible scaffold.[8] In addition, the flexibility of scaffold would enhance the solubility and processability. Finally, the investigation of intramolecular energy-transfer process in flexible PAMAM dendrons will enrich the large family of light-harvesting dendritic systems including rigid conjugated dendrimers, non-conjugated poly(aryl ether) dendrimers and so on. Therefore, we believe that the study on the energy-transfer properties of flexible aliphatic-scaffold dendritic systems is very important.

Previously, we reported the fluorescence and aggregation behavior of different generation PAMAM dendrimers peripherally modified with aromatic chromophores.[9] Herein, we report the synthesis and energy-transfer properties of a novel series of flexible aliphatic-backbone PAMAM dendrons (from the first to the third generation) that are modified with peripheral naphthyl and focal dansyl chromophore. Energy transfer occurred effectively in these light-harvesting dendrons by the Förster (through-space) mechanism. The effects of the structure and generation of the dendrons on the energy-transfer efficiency are also discussed.

It is known that naphthyl and dansyl chromophores are a pair of energy donor and acceptor, respectively, between which the energy transfer can take place. As shown in Scheme 1, the first to the third generation (G1–G3) light-harvesting dendrons Dansyl-AB$_n$-Naphthyl (**Dan-AB$_n$-Nap**: *n* denotes the number of dendron branches, equal to the number of naphthyl groups) were synthesized by the modification of PAMAM dendrons with naphthyl groups at the periphery to absorb the light and dansyl group at the focal point as the energy acceptor. G1, G2, and G3 light-harvesting dendrons are named as **Dan-AB$_2$-Nap**, **Dan-AB$_4$-Nap**, and **Dan-AB$_8$-Nap** for short, respectively (Scheme 1). To better understand the energy-transfer process, three generations of model compounds having only naphthyl groups (i.e. the donor model compounds **AB$_2$-Nap**, **AB$_4$-Nap**, and **AB$_8$-Nap**) or dansyl group (i.e. the acceptor model compounds **Dan-AB$_2$**, **Dan-AB$_4$**, and **Dan-AB$_8$**) were also synthesized. As an example, the synthetic routes of G1 model compounds (**AB$_2$-Nap** and **Dan-AB$_2$**) and light-harvesting dendron (**Dan-AB$_2$-Nap**) are shown in Scheme 1. The starting material PAMAM dendron **AB$_2$** was prepared according to the method that we reported in the previous paper.[10] The donor model compound **AB$_2$-Nap** was obtained by the standard dicyclohexylcarbodiimide (DCC) coupling of 1-naphthoic acid with the intermediate **1**, which was obtained from by the reaction of **AB$_2$** with excess ethylene diamine. To convert all the terminal amine groups into amide, excess amount of 1-naphthoic acid was used in the reaction. The acceptor model compound **Dan-AB$_2$** was obtained from the reaction of dansyl chloride with another intermediate **2**, which was derived from **AB$_2$** by the removal of the *tert*-butoxycarbonyl (Boc) group with trifluoroacetic acid (TFA). Accordingly, **Dan-AB$_2$-Nap** was prepared by the modification of the focal point of **AB$_2$-Nap** with dansyl group. All the other light-harvesting dendrons and model compounds were prepared in a way similar to the procedures as mentioned above, except that PAMAM dendron **AB$_2$** was replaced with **AB$_4$** and **AB$_8$** for G2, and G3 dendrons, respectively (see Supplementary data). ^{1}H NMR, ^{13}C NMR, EI-MS, and MALDI-TOF MS were used to verify the structures of all the products (see Supplementary data). The results agree with the proposed structures almost without any defect.

As shown in Figure 1a, the absorption spectrum of **Dan-AB$_2$-Nap** matches the sum of the absorption spectra of donor model compound **AB$_2$-Nap** and acceptor model compound **Dan-AB$_2$**, indicating that there is no electronic communication between donor and acceptor chromophores through PAMAM dendritic backbone.[7d] Figure 1b shows that the absorption spectrum of **Dan-AB$_2$** overlaps well with the emission spectrum of **AB$_2$-Nap** (Fig. 1b), fulfilling the requirement for Förster energy transfer. As expected, energy transfer from peripheral naphthyl groups to focal dansyl group occurred efficiently in both G1 and G2 light-harvesting dendrons. Excitation of the naphthyl groups on the periphery at 282 nm resulted in emission emanating mainly from the dansyl group (450–650 nm), with strong quenching of the naphthyl emission (300–450 nm) (Fig. 2). After the energy-transfer process, the focal dansyl group's emission was enhanced when it was compared to the emission that resulted from the direct excitation of the dansyl group at either 282 nm ($\lambda_{\max}$ of naphthyl group, Fig. 2a) or 340 nm ($\lambda_{\max}$ of dansyl group, Fig. 2b), which confirmed the light-harvesting properties of these PAMAM dendrons simultaneously modified with naphthyl and dansyl groups (i.e., **Dan-AB$_2$-Nap** and **Dan-AB$_4$-Nap**). The intramolecular (rather than intermolecular) energy transfer nature of these light-harvesting dendrons was confirmed by the emission spectra of **AB$_2$-Nap**, **Dan-AB$_2$**, and **Dan-AB$_2$-Nap** at lower concentrations (see S-Fig. 1 in Supplementary data). When the concentration



Scheme 1. Structures and synthesis of model compounds and light-harvesting dendrons. Reagents and conditions: (a) ethylene diamine, rt; (b) 1-naphthoic acid, DCC, −10 °C and rt; (c) TFA, rt; (d) dansyl chloride, triethylamine, K_2CO_3, rt. rt = room temperature, DCC = dicyclohexylcarbodiimide, TFA = trifluoroacetic acid.

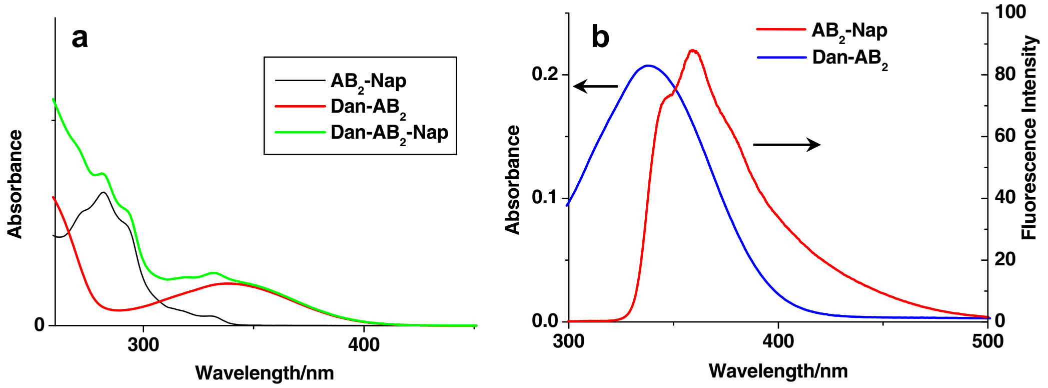


Fig. 1. (a) UV–vis spectra of **AB$_2$-Nap**, **Dan-AB$_2$**, and **Dan-AB$_2$-Nap** at the same concentration; (b) UV–vis spectrum of **Dan-AB$_2$** and fluorescence spectrum of **AB$_2$-Nap** at the same concentration. Concentration: 5.0×10^{-5} mol/L; solvent: $CH_3OH/CHCl_3 = 1/1$ (v/v).

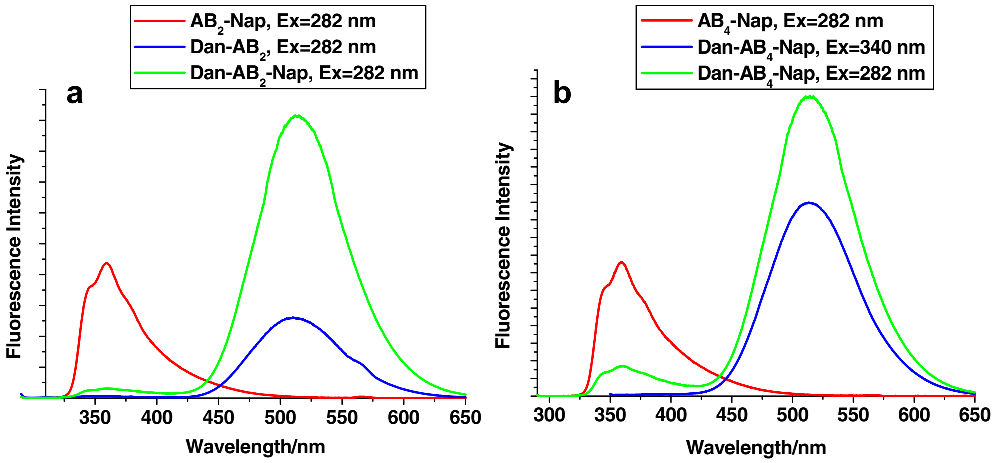


Fig. 2. (a) Emission spectra of **Dan-AB$_2$**, **AB$_2$-Nap**, and **Dan-AB$_2$-Nap** at the same concentration; (b) emission spectra of **AB$_4$-Nap** and **Dan-AB$_4$-Nap** at the same concentration. Concentration: 5.0×10^{-5} mol/L; solvent: $CH_3OH/CHCl_3 = 1/1$ (v/v).

was reduced to 1×10^{-6} mol/L (intermolecular energy transfer hardly occurs in such a dilute solution[11]), energy transfer still occurred with high efficiency (93.9%), indicating that the energy transferred within a dendritic molecule rather than between the molecules.

$$E = 1 - F_{\mathrm{AD}}/F_{\mathrm{D}} \tag{1}$$

$$\begin{aligned} R_0^6 &= [9000(\ln 10)\kappa^2 Q_{\mathrm{D}}]/(128\pi^5 N n^4) \\ &\quad \times \left[\int_0^\infty F_{\mathrm{D}}(\lambda)\varepsilon_A(\lambda)\lambda^4 \mathrm{d}\lambda\right] \Big/ \left[\int_0^\infty F_{\mathrm{D}}(\lambda)\mathrm{d}\lambda\right] \\ &= 0.211^6[\kappa^2 n^{-4} Q_{\mathrm{D}} J(\lambda)] \end{aligned} \tag{2}$$

$$E = R_0^6/(R_0^6 + r^6) \tag{3}$$

The energy-transfer efficiency (E) was calculated to be 94.3%, 76.9%, and 17.8% for **Dan-AB$_2$-Nap**, **Dan-AB$_4$-Nap**, and **Dan-AB$_8$-Nap**, respectively, by using Eqs. 1,[12] where F_{D} is the normalized fluorescence intensity of donor model compounds and F_{AD} is the normalized fluorescence intensity of donor chromophore in **Dan-AB$_n$-Nap.** Förster distance (R_0) and the average distance (r) between donor and acceptor were also calculated by using Eqs. 2 and 3,[12] where κ^2 is the orientation factor (a value of 2/3 was used in our calculations),[7d] Q_{D} is the fluorescence quantum yield of the donor model compounds, N is Avogadro's number, n is the refractive index of solvent, $J(\lambda)$ is the spectral overlap integral, ε_{A} is the molar extinction coefficient of acceptor model compounds, and $F_{\mathrm{D}}(\lambda)$ is the fluorescence intensity of donor model compounds in the wavelength range from λ to $\lambda + \Delta\lambda$. As shown in Table 1, the energy-transfer efficiency decreases in the order of G1 > G2 ≫ G3. Interestingly, it is found that the average distances (r) between the peripheral naphthyl groups and the focal dansyl chromophore for **Dan-AB$_2$-Nap** (10.5 Å) and **Dan-AB$_4$-Nap** (10.3 Å) are very close to each other, although **Dan-AB$_4$-Nap** is one generation higher than **Dan-AB$_2$-Nap**. However, the G3 dendron **Dan-AB$_8$-Nap** was found to show a much larger r value of 15 Å than **Dan-AB$_2$-Nap** and **Dan-AB$_4$-Nap**. These results could be rationalized by the backfolding of flexible dendritic branches and the steric hindrance of naphthyl chromophores.

Table 1
Light-harvesting properties of naphthyl and dansyl modified PAMAM dendrons

Dendron	R_0[a] (Å)	r[b] (Å)	E[c] (%)
Dan-AB$_2$-Nap (G1)	16.6	10.5	94.3
Dan-AB$_4$-Nap (G2)	12.6	10.3	76.9
Dan-AB$_8$-Nap (G3)	11.7	15.0	17.8

[a] Förster distance in resonance energy transfer.
[b] Average distance between naphthyl and dansyl groups.
[c] Energy-transfer efficiency.

The backfolding of flexible backbone dendrons has been reported by several groups.[13] For example, Li and Yang et al. reported the backfolding of flexible benzyl ether backbone dendrons, in which the intramolecular triplet energy transfer was proposed to proceed between the closest donor and acceptor groups via the backfolded conformation.[13a] Bardeen, Thayumanavan and co-workers also described the dependence of the energy and electron-transfer processes on the generation of dendrimers with regard to the backfolding of non-conjugated flexible dendrons.[13b] In our case, the naphthyl groups on the periphery may approach the focal dansyl group via the backfolding of dendritic branches due to the flexible nature of PAMAM dendron, especially for G1 and G2 dendrons that possess loose and open structures with less periphery groups and steric hindrance. Facile backfolding leads to the comparability of r for **Dan-AB$_2$-Nap** and **Dan-AB$_4$-Nap**. However, as the number of naphthyl groups increased from 4 (**Dan-AB$_4$-Nap**) to 8 (**Dan-AB$_8$-Nap**), the steric hindrance of peripheral naphthyl groups of **Dan-AB$_8$-Nap** may reduce the backfolding to a certain extent. In addition, r for G3 dendron is an average distance between eight naphthyl groups and one dansyl group. Thus, r value of G3 dendron would be larger than that of G1 and G2 dendrons even if one or two branches could backfold to the proximity of the focal dansyl group. To clarify the so-called backfolded conformation, models of the extended and backfolded **Dan-AB$_4$-Nap** dendrons are given in the S-Figure 2 of Supplementary data.

The presence of backfolding in the light-harvesting dendrons is confirmed by the comparison of r values of backfolded dendrons with that of extended dendrons, which are obtained using Hyperchem 7.0 modeling software combined with the sizes of spherical PAMAM dendrimers reported by Tomalia and co-workers.[14] The calculated r values for G1, G2, and G3 extended dendrons are 13.9 Å, 16.4 Å, and 19.9 Å, respectively (see Supplementary data). These values are larger than the experimentally obtained r values shown in Table 1, indicating the backfolded conformation of these light-harvesting dendrons. As shown in Table 1, both the energy-transfer efficiency E and Förster distance R_0 decrease with the generation increasing. The reason for the decrease of R_0 is that more tertiary amine groups in the scaffold would quench the naphthyl fluorescence as the generation increases, since it is known that the excited states of naphthyl groups are quenched by electron donating amines.[2] Thus, although **Dan-AB$_2$-Nap** and **Dan-AB$_4$-Nap** have very similar r values, the latter exhibited a lower energy-transfer efficiency due to the lower R_0 value. While in the case of **Dan-AB$_8$-Nap**, both a larger r value and a smaller R_0 value contribute to the lowest energy-transfer efficiency.

In conclusion, a series of flexible aliphatic-scaffold PAMAM dendrons (from G1 to G3) modified with peripheral naphthyl and focal dansyl chromophores were synthesized and their light-harvesting properties were investigated. Energy transfer from the naphthyl groups to dansyl group occurred efficiently in G1 and G2 light-harvesting dendrons by the Förster mechanism. The average distances between donor and acceptor are comparable for G1 and G2 dendrons because of the backfolding of the flexible PAMAM backbone. The energy-transfer efficiency of G3 dendron was found to be the lowest due to its larger donor–acceptor distance and shorter Förster distance. These flexible-scaffold light-harvesting PAMAM dendrons will further enrich the research field of light-harvesting dendrimers due to their backfolding conformation.

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Supplementary data

Synthetic details and characterization for all the new dendritic compounds, emission spectra of G1 dendrons and simple models of **Dan-AB$_4$-Nap**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.01.083.

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