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Enhancement of Energy Utilization in Light-Harvesting Dendrimers by the Pseudorotaxane Formation at Periphery

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Abstract: A series of water-soluble naphthyl terminal-decorated dendrimers G0−3NapH were synthesized. Fluorescence studies reveal that strong interactions among peripheral chromophores occur in these dendrimers according to the intensive excimer emission and the low fluorescence quantum yields (Φ_f = 0.12, 0.097, 0.065, and 0.062 for G0−3NapH). Through assembly of dendrimer with cucurbit[7]uril (CB[7]), the well-defined pseudorotaxane assemblies G*n*NapH·*x*CB[7] (x = 4, 8, 16, 32 for n = 0−3, respectively) form and the energy dissipation is entirely suppressed, resulting in a dramatic increase of the fluorescence quantum yields of dendrimers (Φ_f = 0.18, 0.19, 0.19, and 0.20 for 0−3 generations, respectively). The noncovalent modification is a reversible process, and CB[7] can be unthreaded from the dendrimer periphery by adding 1-amimoadamantane, which can form a more stable complex with CB[7]. Furthermore, 9-anthracenecarboxylic acid (AN), an energy acceptor, was introduced into the dendritic system to investigate the harvested energy utilization. Steady-state fluorescence investigations demonstrate that the energy transfer efficiencies from naphthyl to AN in G3NapH·32CB[7]−AN and G2NapH·16CB[7]−AN are enhanced 100 and 70% compared with those without CB[7] complexation. This study provides a new strategy for developing controllable light-harvesting or -emitting dendritic systems.

Introduction

Since several types of dendrimers were created by pioneer researchers in the past decades,[1] a huge number of dendrimers with a variety of structures and special functions have been synthesized and investigated. Such blossoming development in dendrimer chemistry has extended their applications in many research fields, such as host−guest chemistry, chemosensor, catalysis, drug delivery, and light-harvesting systems.[2] Recently, light-harvesting properties of dendrimers have been widely studied as their regular and hierarchically branched structure, which can be functionalized with plentiful antenna chromophores at the periphery and make dendrimer a mimic of natural photosynthetic systems.[3] However, compared with natural systems, the close-packed periphery and the backbone conformational freedom in artificial light-harvesting dendrimers result in some disadvantageous situations, such as excimer formation and energy annihilation due to the interactions between the antenna chromophores, especially at higher generations.[4] Those drawbacks affect the energy transfer efficiency within dendrimers, but there are a few examples dealing with them. Müllen and co-workers utilized a rigid dendrimer scaffold to overcome those difficulties.[5] Fréchet's group chose proper

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antenna chromophores to avoid self-quenching caused by chromophore aggregation.[6]

The interest in light-harvesting dendrimers[7] urges us to develop an efficient way to avoid the undesired interactions between the peripheral chromophores. The noncovalent modification of the periphery of dendrimers[8] displays advantages such as reversibility, selectivity, and tunability, in comparison with the covalent one. In the present work, we synthesized a new series of water-soluble polyamidoamine (PAMAM) dendrimers with naphthyl chromophores at the periphery as light-harvesting antenna. These dendrimers can form a pseudorotaxane-terminated structure via the supramolecular assembling of peripheral chromophores threaded into cucurbit[7]uril (CB[7])[9] in water; hence, the interactions between peripheral chromophores are restrained, and the undesired excimer formation or energy annihilation is eliminated. Furthermore, we use 9-anthracenecarboxylic acid (AN) as an energy acceptor to investigate the energy transfer process in these light-harvesting systems. The steady-state photophysical studies indicate that the energy utilization is evidently improved by the noncovalent modification.

Experimental Section

Materials. Reagents were purchased from Acros, Alfa Aesar, or Aldrich and used without further purification, unless otherwise noted. Milli-Q water was used in aqueous experiments. Dichloromethane (CH_2Cl_2) was distilled from CaH_2, and methanol was dried with $CaSO_4$ and distilled.

Instrumentation. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained from a Bruker Avance Π-400 spectrometer. IR spectra were recorded on a Varian Excalibur 3100 spectrometer. MALDI-TOF mass spectra were carried out on a Bruker Microflex spectrometer. ESI mass spectra were recorded on a Shimadzu LCMS-2010 apparatus. Absorption and emission spectra were run on a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively.

Absorption and Emission Measurements. All the absorption and fluorescence examinations were performed in 30 mM $CH_3COONa-CH_3COOH$ buffered water (pH = 4.5) using 1 cm path length cells. UV and fluorescence titrations were performed by adding stock solutions of host compounds into the guest buffer solutions at certain concentration. For the energy transfer experiments, the donor group (naphthyl) concentrations were kept at ca. 5×10^{-5} M and the concentrations of acceptor (9-anthracenecarboxylic acid) were ca. 2.5×10^{-5} M. The excitation wavelength was 276 nm for the fluorescence measurements unless otherwise noted, and the spectra were normalized to a constant absorbance at the excitation wavelength. Fluorescence quantum yields were measured in buffer by using anthracene in deaerated ethanol as a reference ($\Phi_r = 0.27$) and calculated with the equation $\Phi = \Phi_r(I/I_r)(A_r/A)(n^2/n_r^2)$, where the r subscript refers to the reference compound, Φ is the quantum yield, I is the integrated intensity of emission, A is the absorbance at the excitation wavelength, and n is the refractive index of solvent.[17]

General Synthetic Procedure of Naphthyl-Modified Dendrimers (G*n*Nap). One equivalent of G*n* PAMAM dendrimer ($n = 0-3$, the terminal chromophores are 4, 8, 16, 32, respectively) and $1.2x$ equiv of 2-naphthaldehyde (x = the number of terminal amino groups of G*n* PAMAM dendrimer) were dissolved in anhydrous dichloromethane/methanol (1:2, v/v). The mixture was stirred with excess anhydrous Na_2SO_4 under argon atmosphere at 40 °C for 16 h. A 3-fold excess of $NaBH_4$ was added as the mixture was cooled to room temperature, and then the reduction was held overnight. After that, the solvents were evaporated and products were extracted by CH_2Cl_2. The organic layer was thoroughly washed with brine, then concentrated and precipitated in excess Et_2O. Repeated precipitation from CH_2Cl_2 into Et_2O three times and finally dialysis against methanol for 12 h gave the G*n*Nap ($n = 0-3$) products as glassy solid in 45, 52, 54, and 66% yield for G0Nap−G3Nap, respectively. The G*n*Nap dendrimers were dissolved in a small amount of methanol followed by the addition of HCl, and then excess Et_2O was added to the solution to precipitate the protonated dendrimer G*n*NapH ($n = 0-3$, Scheme 1), the target dendritic molecules in the present work.

Results and Discussion

Preparation of Functionalized Dendrimers and Model. The PAMAM dendrimer was chosen as the scaffold of the target system because of its convenient synthesis and water solubility, which makes dendrimer a better mimic of natural systems. The PAMAM dendrimers described here (zeroth- to third-generation, G0−G3 PAMAM, with 4, 8, 16, and 32 terminal chromophores, respectively) possess a diaminododecane core, which provides a hydrophobic region and has potential to host substrate

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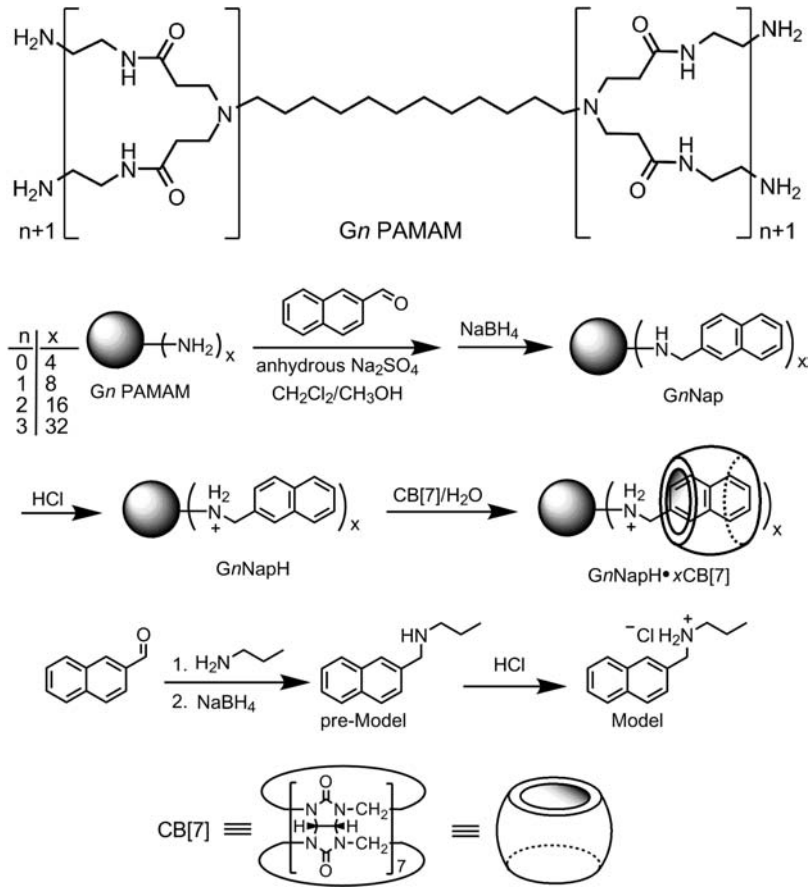
Scheme 1. Synthesis of Dendrimers, Model, and Dendritic Assemblies



molecules (Scheme 1).[10] The terminal modification of dendrimers by naphthyl chromophores involves a condensation of the amino group and the aldehyde followed by a reduction of Schiff base (Scheme 1).[11] The average functionalization extents of the periphery amino groups were 95, 89, 82, and 83% for G0Nap−G3Nap, respectively, according to their ^{1}H NMR spectra. The structure of the modified dendrimers G*n*Nap was characterized by means of ^{1}H and ^{13}C NMR spectra, MALDI-TOF mass spectrometry, and IR spectra (Supporting Information). Because of the hydrophobic effect of naphthyl groups, the naphthyl-terminated dendrimers need to be protonated to improve their water solubility. As a reference compound for G*n*NapH, *N*-propyl-2-naphthalenemethanamine hydrochloride (Model) was synthesized by using the same procedure described for G*n*NapH previously (Scheme 1).

Reversible Noncovalent Modification. To obtain an excellent assembly system, CB[7], one member of the cucurbit[*m*]uril family (CB[*m*], $m = 5-10$),[9,12] is chosen as the host molecule. The cucurbit[*m*]uril family, a series of synthetic macrocyclic compounds, has shown specific self-assembly properties such as high affinity, good selectivity, and high chemostability compared with the traditional supramolecular receptors, such as cyclodextrins, crown ethers, calixarenes, and many others, which have been widely studied over past decades. Consequently, CB[*m*] has attracted increasing interest and became a brilliant building block for supramolecular assemblies.[13] As CB[7] has a suitable hydrophobic cavity to bind the naphthalene group, it is expected that CB[7] can encapsulate the terminal naphthyl chromophore within its cavity through ion-dipole and hydrophobic interactions, which will isolate each periphery chromophore and diminish the interactions among them.

To understand the binding affinity of naphthyl toward CB[7], the UV titration experiment of Model with CB[7] was carried out. The binding mode between Model and CB[7] was elucidated by UV spectra shown in Figure 1a. The UV absorption spectra of Model show an evident drop at short wavelength region and a slightly bathochromic shift with the addition of CB[7]. The inset shows a plot of the absorbance at 223 nm vs the concentration of CB[7], and the optimum fit of the data gives a 1:1 binding model with $K_a = (4.8 \pm 0.5) \times 10^6$ M^{-1}.

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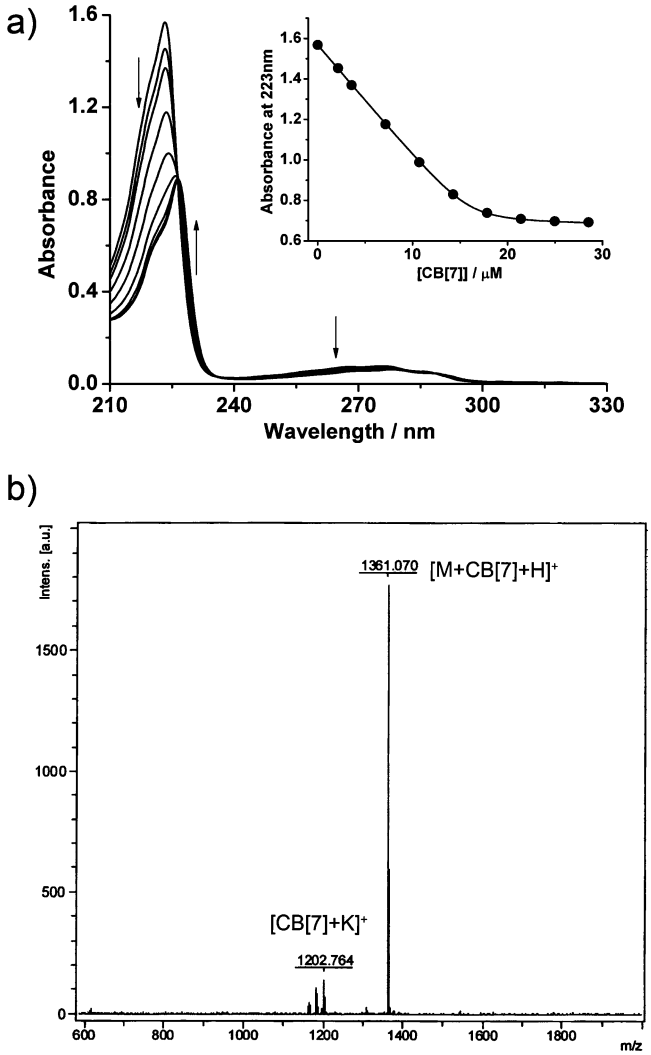
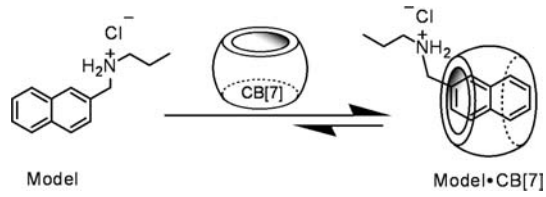


Figure 1. (a) Changes in the absorption spectra of Model (20 μM) upon titration with CB[7] (0−29 μM) in buffer. Inset shows the data of absorbance at 223 nm vs CB[7] concentration, and the solid line represents the best fit of the data to a 1:1 binding mode. (b) MALDI-TOF spectra of the Model·CB[7] complex. M represents the unprotonated Model.

Scheme 2. Complex Formation Between Model and CB[7]



Obviously, CB[7] and Model can form quite a stable 1:1 inclusion complex (Scheme 2), which is also confirmed by MALDI-TOF (Figure 1b) and ^{1}H NMR spectra (Supporting Information).

The details of the complexation between the G*n*NapH dendrimers and CB[7] were investigated by the UV and fluorescence titrations and ^{1}H NMR spectra. A 30 mM $CH_3COONa-CH_3COOH$ buffer (pH = 4.5) was used in these measurements. Such buffer is a suitable condition for CB[7] complexation,[13a] which provides an acidic environment to make dendrimers retain a stretched conformation by keeping most of the amino groups within dendrimers protonated. The UV spectra of G*n*NapH show similar changes as Model does

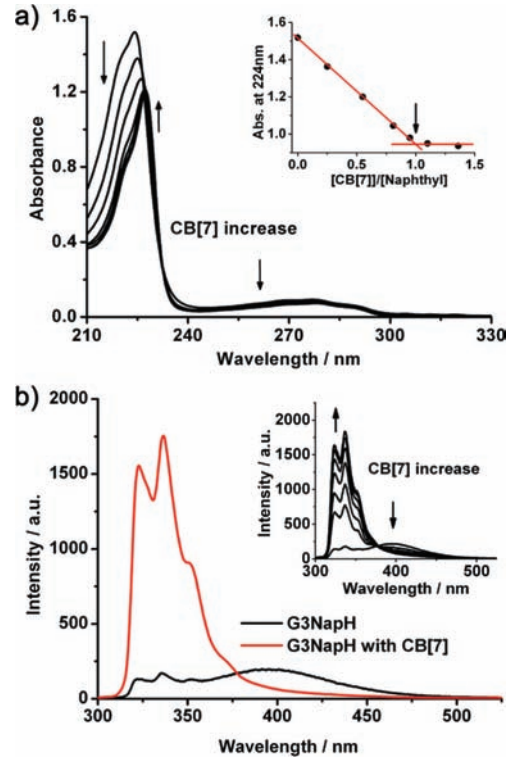


Figure 2. (a) Absorption spectra of G3NapH ([Naphthyl] = 2.3×10^{-5} M) in buffer during addition of CB[7] (0−32 μM). Inset: Plot of absorbance (224 nm) as a function of CB[7] concentration; the arrow indicates the titration end point (the extrapolated intersection of the two linear regions of the plot before and after mole ratio [CB[7]]/[Naphthyl] = 1) where added amount of CB[7] is equal to the naphthyl group in solution. (b) Emission spectra of the buffer solution of G3NapH in the absence (black line) and presence (1 equiv based on the naphthyl group, red line) of CB[7]. Inset shows the G3NapH fluorescence enhancement with the titration of CB[7] (0−32 μM) in buffer ([Naphthyl] = 2.3×10^{-5} M, λ_{ex} = 276 nm).

during the titration and reach a planar stage when the addition amount of CB[7] is up to 1 equiv based on the terminal naphthyl (G3NapH as an example shown in Figure 2a). Fluorescence spectra were performed to investigate the protection effect on naphthyl groups from interactions by complexation with CB[7]. The emission spectra of G3NapH are given in Figure 2b as a representative example. The fluorescence characteristic of naphthyl (λ_{max} = 322, 336, and 352 nm) and its excimer[14] (a broad structureless band around 400 nm) was detected for G3NapH in the absence of CB[7]. The excimer emission is remarkable and even more intense than the monomer emission. This phenomenon can be rationalized to the severe interactions between the periphery naphthyl groups in aqueous medium due to the hydrophobic effect and steric repulsion of outer functional groups of dendrimer. Addition of CB[7] to the G3NapH solution results in an increase of the monomer emission and a decrease of the excimer emission. As the amount of added CB[7] is up to 1 equiv based on the naphthyl group the excimer emission disappears, and the intensity of monomer emission reaches a plateau with more than 10-fold increase in intensity compared with the case without CB[7]. G0−2NapH show

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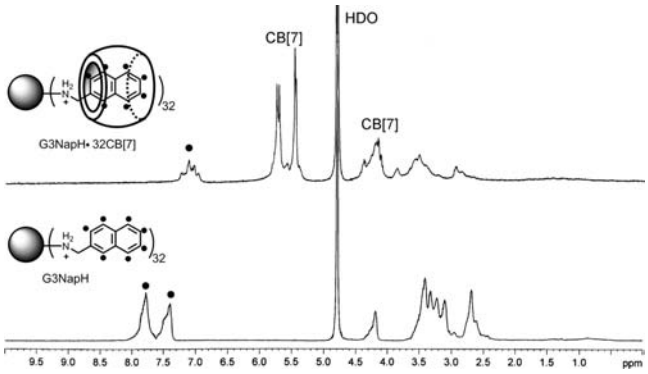


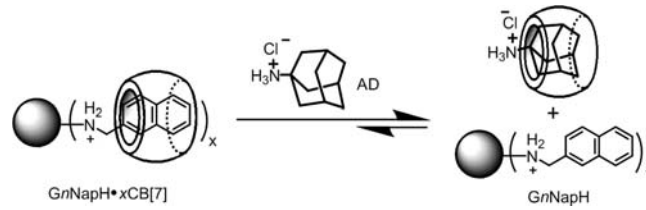
Figure 3. ^{1}H NMR spectra (400 MHz, D_2O) recorded for G3NapH (bottom) and G3NapH in the presence of 1 equiv of CB[7] based on the naphthyl groups (top).

similar phenomena, and their emission spectra are given in Supporting Information. The stoichiometries of the inclusion complexes between G*n*NapH and CB[7] are obtained by the absorption and fluorescence titrations, which are G0NapH•4CB[7], G1NapH•8CB[7], G2NapH•16CB[7], and G3NapH•32CB[7], respectively.

The formation of pseudorotaxane at the dendrimer periphery is further strengthened by the ^{1}H NMR spectra, and an example of the ^{1}H NMR spectra for G3NapH is presented in Figure 3. The signals at 7.3−8.1 ppm assignable to the naphthyl protons of G3NapH shift to the upfield (6.9−7.3 ppm), an ^{1}H NMR shielding region, after the addition of CB[7] (1 equiv based on the naphthyl groups), indicative of the formation of an inclusion complex between the naphthyl and CB[7] and the naphthyl shielded by CB[7]. Additionally, the broadened signals of G3NapH protons also give evidence of the assembling occurrence at the periphery of dendrimer. The attachment of plentiful CB[7] to the periphery diminishes molecular motion of the dendritic shell[8g,k] and makes dendrimer exterior behave similarly to the solid phase consequently broadening the ^{1}H NMR signal. This result is consistent with the absorption and the fluorescence investigations, and the complete encapsulation of periphery groups by CB[7] for all dendrimers is achieved in our experiment conditions according to the upfield shift of all the naphthyl protons. All other generation dendrimer assemblies behave in a similar way as G3NapH does in its ^{1}H NMR investigations. However, we failed to find the molecular ion peak of assemblies in the mass spectra except G0NapH•4CB[7] because of the high molecular weight and charge of dendritic assemblies[8k] (Supporting Information).

The reversibility of the noncovalent modification was also examined. As expected, the noncovalent modification is a reversible process. 1-Amimoadamantane (AD) can form an extremely stable complex with CB[7] ($K_a = (4.23 \pm 1.0) \times 10^{12}$ M^{-1}),[13a] and we chose it as a competition reagent to replace the naphthyl from the inclusion complex G*n*NapH•*x*CB[7] (Scheme 3). The absorption and the fluorescence titration experiments of G*n*NapH•*x*CB[7] with AD were carried out, and an example of the original titration data for G3NapH•32CB[7] is shown in Figure 4. The absorption titration spectra show an opposite trend versus the formation of G*n*NapH•*x*CB[7], an evident increase at short wavelength region and a slightly hypsochromic shift with the addition of AD. It can be understood that the naphthyl of dendrimer is released from the CB[7] cavity because of the competitive complexation of CB[7] with AD. The unthreading process of the inclusion complex G*n*NapH•

Scheme 3. Schematic Representation of Unthreading Process of Dendrimers G*n*NapH•*x*CB[7] by Using Competing Agent AD



*x*CB[7] can also be observed in the fluorescence titration experiments. The G*n*NapH•*x*CB[7] solutions show typical naphthyl monomer emission without AD addition. As AD is added into the solution, the monomer emission decreases dramatically and the excimer emission band (at ca. 400 nm) grows simultaneously, and finally the emission reverts to the similar shape as G3NapH does in the absence of CB[7], indicating that CB[7] is gradually removed from the dendrimer periphery and the severe interaction among outer chromophores recurs. In addition, the change of absorption and fluorescence spectra is in proportion to the added amount of AD and reaches a plateau when 1.0 equiv of AD based on CB[7] is added, which means that the removal of CB[7] from the dendrimer periphery is quantitative in our experiment conditions. These titration results reveal that the modification of dendrimer with CB[7] is reversible, and the peripheral threading extent of dendrimer can be tuned by addition of AD.

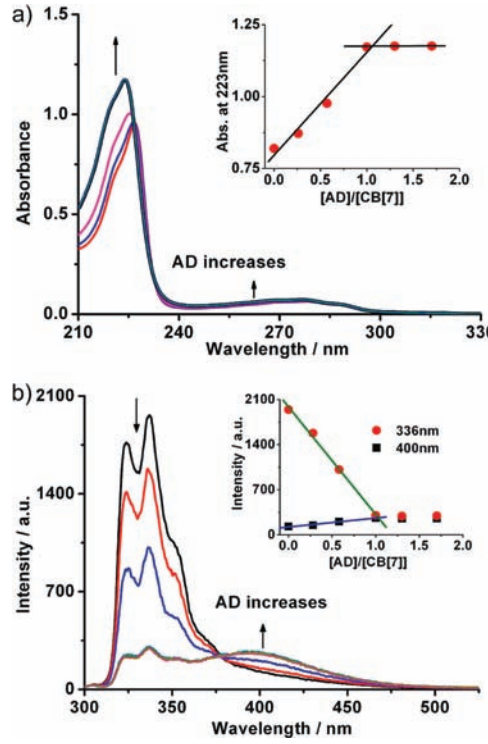


Figure 4. (a) UV spectroscopic titration of G3NapH•32CB[7] ([Naphthyl] = [CB[7]] = 18 μM) with AD (0−31 μM) in buffer. Inset shows the dependence of absorbance (223 nm) on the mole ratio of [AD] to [CB[7]] in the solution, and the solid lines are linear fitting results for [AD]/[CB[7]] < 1 and > 1, respectively. (b) Effect of AD addition (0−31 μM) on the emission spectra of G3NapH•32CB[7] in buffer ([Naphthyl] = [CB[7]] = 18 μM, λ_{ex} = 276 nm). Inset: Fluorescence intensity at 336 nm (red) and 400 nm (black) against the mole ratio [AD]/[CB[7]] with the linear fit in the region of [AD]/[CB[7]] < 1.

Table 1. Emission Data of G*n*NapH and G*n*NapH·*x*CB[7] in Buffer Solution (λ_{ex} = 276 nm)

compounds	emission λ_{max} (nm)	quantum yield (Φ_f)
G0NapH	336, 394	0.12
G1NapH	336, 395	0.097
G2NapH	336, 395	0.065
G3NapH	336, 395	0.062
G0NapH·4CB[7]	336	0.18
G1NapH·8CB[7]	336	0.19
G2NapH·16CB[7]	336	0.19
G3NapH·32CB[7]	336	0.20

Enhancement of Energy Utilization in Light-harvesting Dendrimers by the Pseudorotaxane Formation at Periphery. The parameters of emission spectra for G*n*NapH and G*n*NapH·*x*CB[7] (x = 4, 8, 16, 32 for n = 0−3, respectively) are summarized in Table 1. The original fluorescence spectra of G*n*NapH (n = 0−3) are dominated by the excimer emission band at the longer wavelength. As the generation increases, the fluorescence quantum yield of G*n*NapH (Φ_f) decreases from 0.12 (G0NapH) to 0.062 (G3NapH), which indicates that the periphery of dendrimer molecule becomes more crowded at higher generation, and the interaction between naphthyl groups leads to more energy dissipation.[4] After the complexation of G*n*NapH with CB[7], only the monomer emission of naphthyl can be detected, and the fluorescence quantum yield increases considerably in comparison with that of the corresponding uncomplexed G*n*NapH reaching similar magnitude (0.18−0.20). This remarkable change can be attributed to every naphthyl being embedded into the hydrophobic cavity of CB[7], which protects naphthyl groups from annihilation and quenching by solvent molecules.

To examine energy utilization in light-harvesting dendrimers, AN, an energy acceptor, was introduced into G*n*NapH. With addition of G*n*NapH, the UV/vis spectra of AN show a gradual decrease and a slightly bathochromic shift, which indicate that AN was encapsulated into a less polar microenvironment inside dendrimers driven by the hydrophobic effect and the electrostatic interaction between the carboxyl group of AN (pK_a = 2.4) and the amine of the dendritic backbone.[14b,15] In addition, AN does not interact with CB[7] in our experiment conditions according to the identical absorption and emission spectra in the absence and presence of CB[7], which may be explained by the hindrance of steric bulk and the negative charge of carboxylic group.[16] The complexation of G*n*NapH with CB[7] has no substantial effect on the encapsulation of AN into G*n*NapH, which makes G*n*NapH·*x*CB[7] show similar encapsulation behavior as G*n*NapH. The UV titration experiments show that AN and G*n*NapH (n = 2, 3) form 1:1 complexes (G2NapH−AN and G3NapH−AN) with binding constants of (2.6 ± 0.5) × 10^5 and (5.6 ± 1.7) × 10^5 M^{-1}, respectively (Supporting Information). The binding affinity of AN toward dendrimer increases with increasing generation, and the lower generation dendrimers, G*n*NapH (n = 0, 1), show weak binding behavior and are not discussed further.

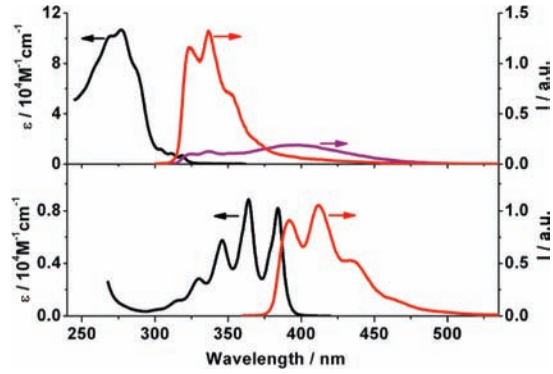


Figure 5. Top: Absorption spectrum of G3NapH and emission spectra (λ_{ex} = 276 nm) of G3NapH (purple) and G3NapH·32CB[7] (red) in buffer. Emission spectra were normalized to the same absorbance at the excitation wavelength. Bottom: Absorption and emission spectra of AN in buffer (λ_{ex} = 346 nm).

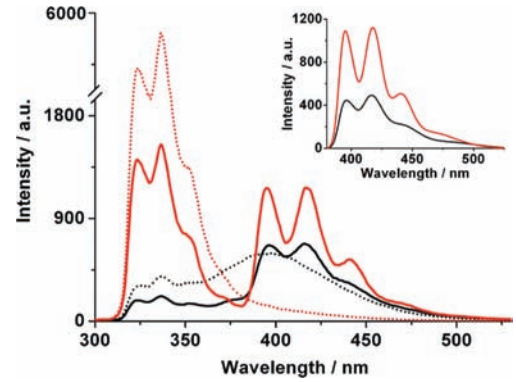


Figure 6. Emission spectra of G3NapH (black dot), G3NapH−AN (black solid), G3NapH·32CB[7] (red dot), and G3NapH·32CB[7]−AN (red solid) in buffer. λ_{ex} = 276 nm and the spectra were normalized to a constant absorbance at the excitation wavelength. Inset shows the corrected emission spectra of AN in G3NapH·32CB[7] (red) and G3NapH (black).

The host−guest systems of G3NapH−AN and G3NapH·32CB[7]−AN are discussed as representative examples, and their absorption and emission spectra in buffer at ambient conditions are presented in Figure 5. Naphthyl and anthryl are a typical energy donor−acceptor pair with proper energy levels and spectral overlap, and the selective excitation of the naphthyl of dendrimer can be achieved by using 276 nm light. With selective excitation of the peripheral naphthyl groups of G3NapH−AN and G3NapH·32CB[7]−AN, the fluorescence efficiency of dendritic hosts is quenched and accompanied by an AN emission indicative of the occurrence of energy transfer from the naphthyl groups to the encapsulated AN. The emission spectra normalized to the absorbance at the excitation wavelength are presented in Figure 6. Since there is a band overlap between the donor and the acceptor emissions, an analysis of emission spectra was done by using the PeakFit program (Systat Software, Inc.). The integrated fluorescence intensities of AN were calculated to give a more direct observation for the utilization of energy in the G*n*NapH−AN and G*n*NapH·*x*CB[7]−AN (n = 2, 3) systems. The corrected fluorescence emissions of AN resulted from the energy transfer process for generation 3 are presented in the inset of Figure 6. Apparently, an increased emission of AN can be observed in the G*n*NapH·*x*CB[7]−AN (n = 2, 3) systems, and the AN emission

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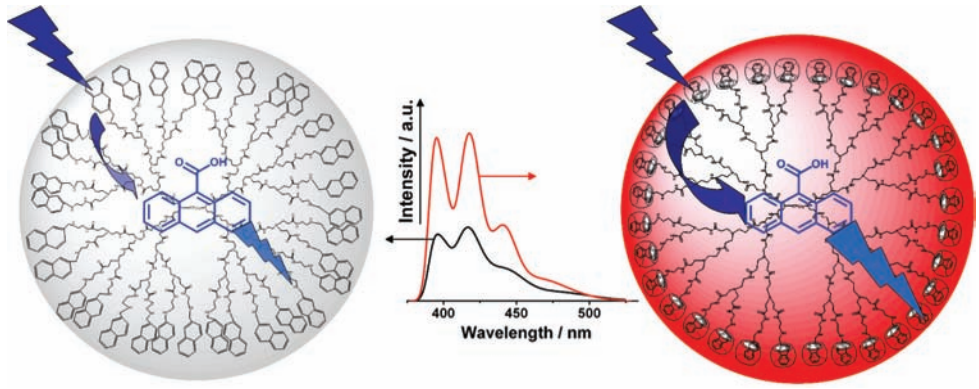

Figure 7. Visual expression of the energy transfer process in different dendritic systems.

efficiencies of G*n*NapH•*x*CB[7]−AN for generations 2 and 3 are 0.7 and 1.0 times higher than those of the corresponding G*n*NapH−AN, respectively. Such an increase of energy transfer efficiency in the G*n*NapH•*x*CB[7] ($n = 2, 3$) systems can be attributed to the suppression of harvested energy dissipation caused by the peripheral chromophore interactions, a competitive way to the energy transfer pass. Since the severe interactions between the peripheral naphthyl groups exist in the G*n*NapH ($n = 2, 3$) systems, the harvested energy by G*n*NapH−AN ($n = 2, 3$) is mostly bypassed. After complexes G*n*NapH•*x*CB[7] ($n = 2, 3$) are formed by the CB[7] decoration, the interactions between the peripheral naphthyl groups are exclusively avoided and the energy harvested by the naphthyl groups of G*n*NapH•*x*CB[7]−AN ($n = 2, 3$) transfers primarily to the acceptor AN. The smaller enhancement effect in the G2NapH/G2NapH•16CB[7]−AN systems can be mainly explained by the lower binding affinity of AN toward G2NapH/G2NapH•16CB[7] and more "empty" dendrimer in our experiment conditions. The peripheral pseudorotaxane formation in our light-harvesting dendrimers evidently improves the energy utilization of the harvested energy, and a visual expression is shown in Figure 7.

Conclusions

In summary, the periphery naphthyl groups of light-harvesting PAMAM dendrimers G0−3NapH show severe interactions in buffer solutions, resulting in excimer formation and self-quenching. Consequently, the efficiency of energy transfer from dendrimers to the encapsulated AN and the intensity of AN emission are low. Through noncovalent interactions, the outer fluorophores of dendrimers can be encapsulated into CB[7] and the well-defined pseudorotaxane assemblies G*n*NapH•*x*CB[7] form. The interactions among the periphery chromophores and the quenching by solvent molecules are avoided because of the protection effect of CB[7], and much higher fluorescence quantum yields are obtained. As a result, higher energy transfer efficiencies from dendritic assemblies to AN are observed and the AN fluorescence emission is remarkably enhanced. Such a noncovalent approach provides a promising way to improve the artificial light-harvesting systems in utilization of harvested photons by decreasing the undesired chromophore interactions and the energy dissipation. Furthermore, the reversibility of noncovalent modification makes the emission property and the peripheral conformation of dendrimers tunable by using a proper competing guest (AD) toward the CB[7] host. The present study provides a new strategy for developing controllable light-harvesting or -emitting dendritic systems.

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Supporting Information Available: Characterization data of the synthetic compounds, ^{1}H NMR spectra, UV titration experiments, and fluorescence spectra of dendritic assemblies with CB[7], UV titration of AN with dendrimers, and emission spectra of energy transfer experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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