FULL PAPER

A Polyrotaxane Series Containing α-Cyclodextrin and Naphthalene-Modified α-Cyclodextrin as a Light-Harvesting Antenna System

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Abstract: Supramolecular light-harvesting antenna systems were constructed by using polyrotaxanes, in which cyclodextrin (CD) rings of α-CD and naphthalene (energy donor)-appended α-CD are threaded by a poly(ethylene glycol) chain with anthracene (energy acceptor) units at both ends (**5 – 8**). The effects of the component ratio of the polyrotaxanes on the efficiencies of energy migration and energy transfer were examined by fluorescence emission and excitation spectra and anisotropy and by fluorescence decay measurements. The observed results were explained by using the Förster mechanism.

Introduction

Photoinduced electron and energy transfer are fundamental processes in nature.[1] There has been widespread interest in mimicking the natural photosynthesis process which involves both energy and electron transfer.[2] In one approach, photon-harvesting polymers have been studied, in which the capture of a photon by one chromophore in the polymer chain is followed by energy transfer among many chromophores to reach an energy acceptor.[3] This process is referred to as the antenna effect by Guillet and Ng.[4] However, conformational flexibility may prevent long-distance energy transfer, because polymer folding permits the formation of energy dissipative excimers or exciplexes.[5] On the other hand, Fox and Watkins reported a vectorial energy migration and electron transfer system in a rigid polymer, where chromophores are attached to polynorbornene backbone.[6] A fundamental question is: Does the antenna effect become remarkable when the number of absorption units increases? Bar-Haim et al. pointed out the importance of the energy gradient theoretically by using dendrimer models.[7] This idea was confirmed by Moore et al. in a dendritic system, where an energy gradient was provided as a function of position from the periphery to the core and the excitation energy efficiently cascaded to the focal point in the system.[8] Recently, Guillet and Gravett and Valeur et al. used the Förster mechanism to both experimentally and theoretically investigate the energy migration between naphthalene units fixed to a cyclodextrin scaffold.[9, 10] From the investigation of the cyclodextrin system, Valeur et al. suggested that a longer distance between chromophores with a more favorable orientation is somewhat equivalent to a shorter distance with a less favorable orientation.[10]

In a natural photosynthesis system, the components of the energy and electron transfer systems are held together by weak noncovalent interactions that result in a spatially well-oriented arrangement. In connection with this, many supramolecular systems, in which donor and acceptor components are linked by noncovalent interactions,[11] such as hydrogen bonding,[12] aromatic π-stacking,[13] and metal–ligand coordination,[14] have been investigated. Here, we report on polyrotaxane-type light-harvesting antenna systems[15] composed of two different CD units: one is native α-CD and the other is naphthalene-modified α-CD (NpCD). In the polyrotaxanes, the rings of α-CD and NpCD are penetrated by polyethylene glycol (PEG) (approximate molecular weight = 2000) bearing an anthracene moiety at both ends. The percentage of NpCD over the total CD units in the polyrotaxanes is varied to produce polyrotaxanes with 0, 20, 60, and 100.0 % NpCD units (see Scheme 1). As there are only through-space interactions between antenna chromophores, it is possible to analyze the energy-transfer efficiency without considering the effect of bond properties.[16, 17] Because all the components of the dendritic light-harvesting system are connected by covalent bonds, a fast intersystem crossing can occur to form dendrimer triplets, which make it difficult to evaluate the relationship

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between energy-transfer efficiency and the number of the antenna units.[8] In our study, this relationship between the energy transfer from the naphthalene chromophore to the anthracene units and the number of naphthalenes was studied by using steady-state emission and excitation spectra and time-resolved fluorescence decay measurements. We attempted to interpret the intramolecular energy transfer within the context of the Förster mechanism.[18, 19] Energy migration between the naphthalene chromophores was also investigated by the anisotropy data of the samples in glassy matrices.

Results and Discussion

Preparation of polypseudorotaxane: The polypseudorotaxanes were prepared by adding α, ω-diamino-polyethylene glycol (diamino-PEG) (MW $= 2000$) into aqueous solutions containing different ratios of naphthalene-modified α-CD (NpCD) and native α-CD (Scheme 1). Here, the NpCD percentages over the total CD units are changed by 0, 20, 60, and 100%. In all cases, white precipitates appeared immedi-
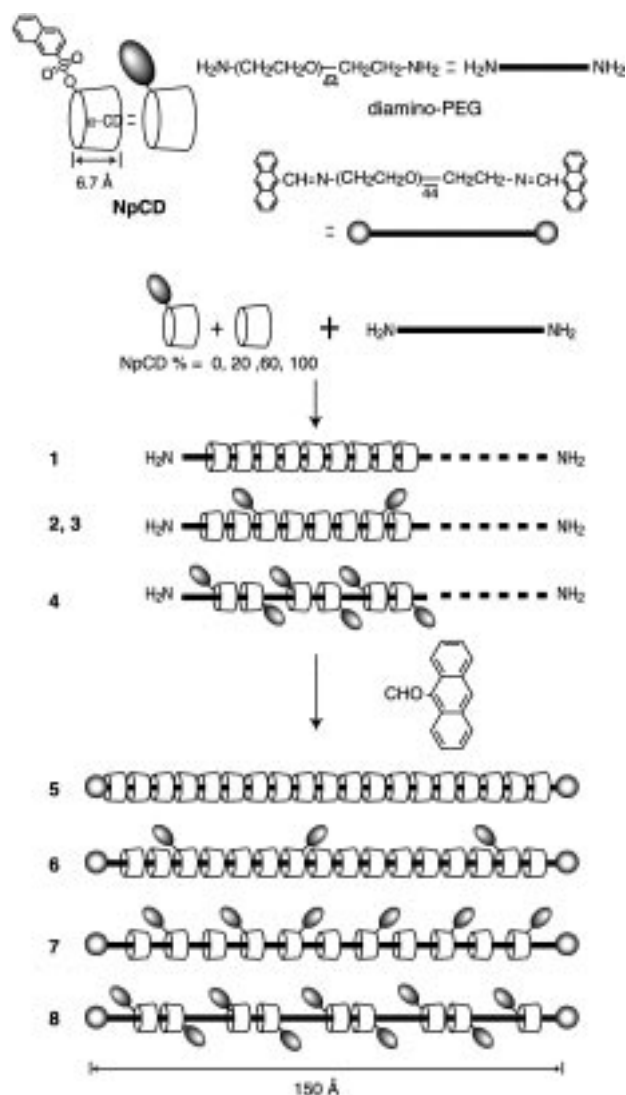
Scheme 1.

ately. It is known that if diamino-PEG is added to a native α-CD aqueous solution, polypseudorotaxane, in which α-CD rings are threaded by a diamino-PEG chain, is formed as a white precipitate.[20] So we regarded the white precipitates formed in our study as polypseudorotaxanes, in which the CD rings of NpCD and α-CD were threaded by a diamino-PEG chain. The precipitates were collected and they were designated as **1**, **2**, **3**, and **4** corresponding to starting mixture solutions of 0, 20, 60, and 100% NpCD, respectively. The ratios of the NpCD in the polypseudorotaxanes were analyzed by comparing ^{1}H NMR peak integrals (Table 1). The ratios of

Table 1. Numbers of α-CD and NpCD and the Percentages of NpCD in the Polypseudorotaxanes.[a]

	1	**2**	**3**	**4**
Initial NpCD [%][b]	0.0	20.0	60.0	100.0
CD$_{number}$[c]	24.9	19.8	17.8	11.2
NpCD$_{number}$[d]	0.0	3.6	10.7	11.2
NpCD [%][e]	0.0	20.0	60.1	100.0

[a] The number of α-CD and NpCD were estimated from the ^{1}H NMR spectra measured at 25 °C in D$_2$O solution, which contains a little amount of [D$_6$]DMSO. [b] Initial NpCD content over total CD content when the polyrotaxanes were synthesized. [c] Number of total CD units in the polypseudorotaxanes. [d] Number of NpCD in the polypseudorotaxanes. [e] NpCD$_{number}$/CD$_{number}$ × 100 (%).

NpCD in polypseudorotaxane are roughly the same as those in the starting mixture solutions. The polypseudorotaxanes were formed through a transition process, in which the two processes of threading or dethreading of the PEG chain into the CD and NpCD cavity are in equilibrium. If there were some selectivity for CD or NpCD, or some bias to concentrate CD or NpCD existed in the threading process, the percentages of NpCD over total CD units in the polyrotaxanes, which are products from the equilibrium state, would not coincide with those in the starting mixture solutions and those in the reaction solvent at the equilibrium. In all cases, (0, 20, 60, and 100%) the percentages of NpCD in the polypseudorotaxane were the same as those of the starting solutions. From these observations, we think that there is no selectivity for CD or NpCD in the threading process and the NpCD dispersions are uniform in the polypseudorotaxanes. However, the total number of CD units decreases with increasing NpCD ratio in the polypseudorotaxanes, showing 24.6 CD units for **1** and 11.2 CD units for **4**. This result suggests that a remarkable steric hindrance exists between the NpCD units in the polypseudorotaxanes.

Preparation of polyrotaxane: The polypseudorotaxanes were converted into polyrotaxanes by the reaction of the amino groups of a diamino-PEG chain with 9-anthraldehyde for 2 h in DMF (Scheme 1). The anthracene moiety is large and consequently acts as a stopper to keep α-CD and NpCD in the polyrotaxanes. The reaction products were washed with acetone to remove unreacted 9-anthraldehyde and then washed with water to remove the components of unreacted

polypseudorotaxane. According to this procedure, polyrotaxanes **5–8** were prepared from **1–4**, respectively. In the polyrotaxanes **6** and **7** the NpCD dispersion may be uniform with a set distance between the units, which are related with the NpCD arrangement in the polypseudorotaxanes. All these polyrotaxanes were soluble in DMSO, DMF, and propylene glycol.

^{1}H NMR study of polyrotaxanes: ^{1}H NMR spectra in [D$_6$]DMSO of **5–8** show peaks corresponding to CD, diamino-PEG, naphthalene units, and anthracene units. For instance, the ^{1}H NMR spectrum of **6** is shown in Figure 1b.
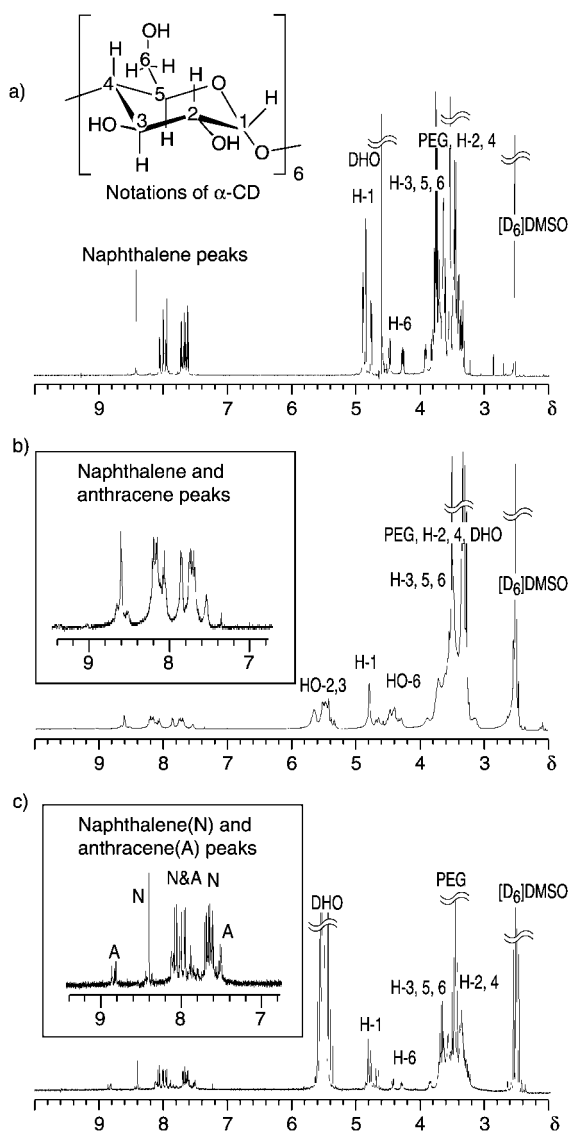

Figure 1. The ^{1}H NMR spectra of **2** (a) and **6** (b) in [D$_6$]DMSO, and **6** (c) in 1.5 N DCl aqueous solution at 25 °C. The ^{1}H NMR spectrum of **6** in a 1.5 N DCl aqueous solution at 25 °C was measured after **6** was dissolved in 1.5 N NaOD aqueous solution and kept at room temperature for 1.5 h.

Other polyrotaxanes **5–8** exhibit similar spectral features, showing that all peaks of the ^{1}H NMR spectra are broadened, in contrast to polypseudorotaxanes **1–4**, which exhibit sharp ^{1}H NMR peaks in [D$_6$]DMSO (Figure 1a). This result may

arise from the fact that the movement of each component in the polyrotaxanes is restricted and that NpCD and α-CD are closely packed in the limited space between two stoppers, while the incorporated CD units are not tightly packed in **1–4** because of the absence of any stopper. Such ^{1}H NMR peak broadening is consistent with the previously reported results for the CD-based polyrotaxanes.[20] The ratio of NpCD and α-CD in the polyrotaxanes can be analyzed by comparing the ^{1}H NMR peak area of the naphthalene moiety with the areas of α-CD and diamino-PEG chain. However, each of these peaks is too broad to estimate the molar ratio correctly. Therefore, the large stoppers (anthracene) at the ends of **5–8** were removed by cleaving the bond with acid (1.5 N DCl/[D$_6$]DMSO v:v = 1:1 solution) at room temperature to produce free CD units (Figure 1c). After the cleavage, the NMR peaks became sharp. These results indicate that each component of **5–8** is released from the supramolecular system under the conditions. After the reaction is completed, it is possible to compare the areas of the component ^{1}H NMR peaks. The results are summarized in Table 2. The percentages of NpCD in **5–8** are nearly similar to those of pseudopolyrotaxanes **1–4**, but during the capped reaction, about 25% of the polypseudorotaxane CD units were dethreaded.

Table 2. Numbers of CD and NpCD and the percentages of NpCD in the Polyrotaxanes.[a]

	5	**6**	**7**	**8**
CD$_{number}$[b]	19.1	15.8	10.7	9.3
NpCD$_{number}$[c]	0.0	3.2	6.4	9.3
NpCD [%][d]	0.0	20.0	60.0	100.0
MW[e]	21 000	18 400	14 050	13 200

[a] The number of α-CD and NpCD were estimated from the ^{1}H NMR spectra measured at 25 °C in 1.5 N DCl aq./[D$_6$]DMSO (v:v = 1:1) solution. [b] Number of total CD units in the polyrotaxane. [c] Number of NpCD units in the polyrotaxanes. [d] NpCD$_{Number}$/ CD$_{Number}$ × 100 (%). [e] Molecular weights (MW) of the polyrotaxanes were estimated from CD$_{Number}$ and NpCD$_{Number}$, using the following equation: 972.85 × (CD$_{Number}$ − NpCD$_{Number}$) + 1163.07 × (NpCD$_{Number}$) + 2420.85, where 972.85, 1163.07 and 2420.85 are the molecular weights of native α-CD, NpCD and diamino-PEG, which bear an anthracene unit at both ends, respectively.

UV/Vis absorption spectra: The UV/Vis absorption spectra of the polyrotaxane antenna series in propylene glycol are shown in Figure 2a and summarized in Table 3. There are two distinct absorption bands between 270 and 450 nm, one is at 340–440 nm, and the other is at 270–335 nm. The absorption around 270–335 nm is due to the naphthalene units, having peaks at 277, 312, and 327 nm, while the absorption around 340–440 nm is due to the anthracene units, having peaks at 350, 368, 387 nm. As can be seen in the spectra of **5–8**, the molecular coefficient around 270–335 nm increases linearly with the increasing number of NpCDs, while the molecular extinction coefficient around 340–440 nm remains constant (Figure 2b). In this case, no spectral broadening or spectral shift was observed for the samples with different concentrations of NpCD. These results indicate that there is no strong
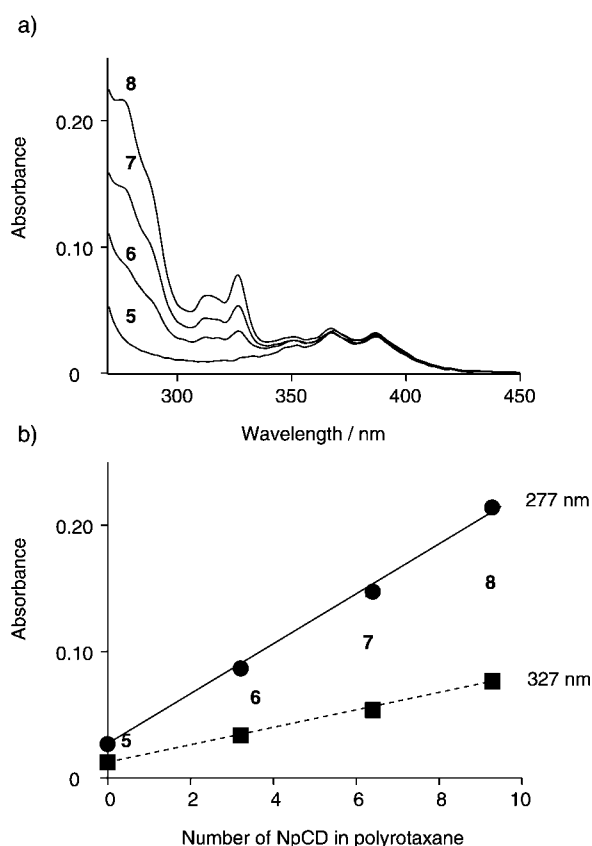
a)

b)

Figure 2. UV/Vis absorption spectra (a) and absorbance (b) of polyrotaxanes **5**, **6**, **7**, and **8** at 25 °C in propylene glycol. Absorption spectra were measured for the polyrotaxanes (1.8 μM) using a 1 cm path length cell. Extinction coefficients of the polyrotaxanes **5**, **6**, **7**, and **8** at 277 nm (—●—) and 327 nm (--■--) in propylene glycol at 25 °C were presented as a function of the NpCD number in the polyrotaxanes.

Table 3. Absorption maxima and extinction coefficients of polyrotaxanes **5, 6, 7**, and **8**.[a]

5		6		7		8	
λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
387.0	10 300	387.0	10 300	387.0	10 300	387.0	10 300
369.0	10 700	367.0	11 300	367.2	11 300	367.2	11 700
352.6	7 700	350.0	8 700	351.0	9 000	351.2	9 700
		327.0	11 300	327.0	18 000	327.0	26 000
		313.0	9 700	313.0	14 700	313.0	20 700
		277.0	29 000	277.0	49 000	277.0	72 000

[a] All parameters were recorded in propylene glycol at 25 °C. λ_{max} in nm; ε in $M^{-1}cm^{-1}$.

electronic coupling between the naphthalene units and between the naphthalene and anthracene units in the ground state.[8, 19]

Steady-state fluorescence spectroscopy: Figure 3a shows the steady-state emission spectra ($\lambda_{ex} = 277$ nm) of **6–8** and the mixture solutions of NpCD and **5**. The concentrations of the naphthalene and anthracene units in the mixture solutions were adjusted to become the same as those of the solutions of polyrotaxanes **6–8**. The naphthalene fluorescence intensities of **6–8** are smaller than those of the mixture solutions, while
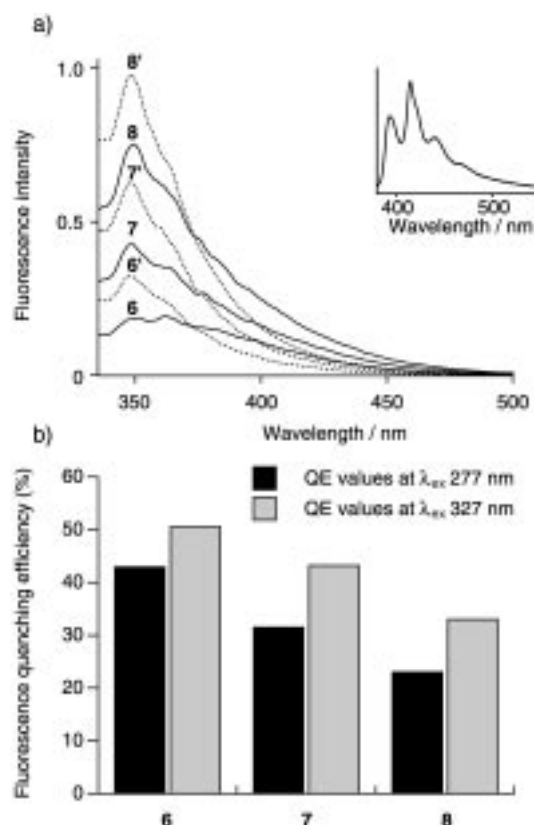
a)

b)

Figure 3. Steady-state corrected fluorescence emission spectra ($\lambda_{ex} = 327$ nm) of polyrotaxanes **6–8** (1.8 μM) and the mixtures of **5** (1.8 μM) and NpCD (**6′**, **7′**, and **8′**) in propylene glycol at 25 °C (a), and fluorescence quenching efficiencies (QE) obtained by excitation at 327 nm and 277 nm as a function of the number of NpCDs in the polyrotaxanes (b). Inset shows the fluorescence spectrum ($\lambda_{ex} = 367$ nm) of **5** (1.8 μM). Each mixture contains the same naphthalene unit as the corresponding polyrotaxane (5.8 μM in **6′**, 11.5 μM in **7′**, and 16.7 μM in **8′**). QE values were calculated by the equation, QE (%) = $(1 - I_{poly}/I_{mix}) \times 100$, where I_{poly} is the fluorescence intensity of polyrotaxane at 347.5 nm ($\lambda_{ex} = 277$ nm and 327 nm) and I_{mix} is that of the corresponding mixed solution of **5** and NpCD.

the anthracene fluorescence intensities of **6–8** in the region of 390–460 nm are enhanced compared with those of the mixture solutions. It is noted that the anthracene fluorescence of **5** ($\lambda_{ex} = 367$ nm) was observed around 380–460 nm (inset) and has three peaks at 393.5, 415, and 438.5 nm. If the naphthalene units formed an excimer, this excimer emission could be observed around 400 nm. However, in the polyrotaxane that has trinitrophenyl moieties as the terminal caps instead of the anthracene moieties, the excimer emission was not observed under the same conditions.[21] On this basis, we think that the longer wavelength fluorescence of **6–8** does not involve excimer emission. The results suggest that excited energy transfer from the naphthalene units to the terminal anthracene moieties in the polyrotaxanes enhanced the anthracene fluorescence, and the energy transfer results in the decrease in the naphthalene fluorescence. There is a large spectral overlap between naphthalene fluorescence and anthracene absorption, so energy transfer may occur from the naphthalene units to the anthracene moieties by a dipole–dipole interaction (Förster-type) mechanism.[18, 19] Compared to the decrease in the naphthalene fluorescence intensity, the increase in the anthracene fluorescence intensity seemed

much smaller. Actually we obtained a very small quantum yield for this anthracene moiety (0.017), in comparison with that of anthracene (0.30). This result may be due to the fact that the anthracene moiety bound to PEG chain exists as a Schiff base. Energy transfer efficiency of the polyrotaxanes was estimated by comparing the naphthalene fluorescence intensity of polyrotaxanes at 347.5 nm ($\lambda_{ex} = 277$ nm and 327 nm) in propylene glycol (I_{poly}) with that of NpCD and **5** mixed solutions (I_{mix}). Here we defined the fluorescence quenching efficiency (QE) as follows: QE (%) = $(1 - I_{poly}/I_{mix}) \times 100$. The QE values of the polyrotaxanes are shown in Figure 3b. The highest quenching efficiency was observed for **6**, the values being 48.2% ($\lambda_{ex} = 277$ nm) and 40.3% ($\lambda_{ex} = 327$ nm), while the lowest quenching efficiency was observed for **8**, the values being 31.7% nm ($\lambda_{ex} = 277$ nm) and 25.4% ($\lambda_{ex} = 327$ nm). Devadoss et al. reported the energy transfer from branched light-absorbing units to an acceptor core in a dendritic system, in which the efficiency of energy transfer decreases with increasing generation of the dendrimer. In this case, Bar-Haim et al. explained this phenomenon by evaluation of the mean time for the excitation energy transfer that starts from the periphery to the center using a one-dimensional energy migration model.[7] The mean time increased linearly to the square of generation because of the increase in the frequency of energy hopping between antenna units. In the case of polyrotaxane antenna series, there may be energy migration (energy hopping) among the naphthalene units, and the fluorescence radiation may occur during this energy migration process. This energy wandering process may result in a less efficient antenna effect.

Figure 4a shows the steady-state fluorescence excitation spectra of **5–8** ($\lambda_{em} = 440$ nm) and the mixture solutions of NpCD and **5**. Here, the concentration of the naphthalene and anthracene units in the mixture solutions is the same as those of the solutions of the polyrotaxanes **6–8**. The shape of the excitation spectrum of polyrotaxane **5** is the same as its absorption spectrum. On the other hand, polyrotaxanes **6–8** not only have peaks of anthracene absorption but also have the band of the naphthalene absorption in the region of 300–330 nm with a peak at 327 nm. Although there is a similar naphthalene absorption band in the mixture solutions, the excitation intensities of polyrotaxanes **6–8** at 327 nm are much larger those of the corresponding mixture solutions. This result demonstrates that the energy transfer occurs from the naphthalene units to the anthracene units in polyrotaxanes **6–8**. The reason why the naphthalene excitation band appears for the mixture solutions is that the tail of naphthalene fluorescence still exists around 440 nm, and the fluorescence quantum yield of anthracene is rather small. The relative efficiency of the antenna effect (Figure 4b) was evaluated as the increase in excitation intensity defined by the equation of $(E_{poly} - E_{mix})/(E_6 - E_{mix6})$. Here, E_{poly} is the excitation intensity of polyrotaxane ($\lambda_{ex} = 327$ nm), E_{mix} is the excitation intensity of the corresponding mixture ($\lambda_{ex} = 327$), and E_6 and E_{mix6} are the excitation intensities ($\lambda_{ex} = 327$) of **6** and the mixture solution for **6**. The highest antenna effect was observed for **8** (1.58), confirming that the antenna effect depends on the number of NpCDs in the polyrotaxanes. The energy transfer quantum yield can be estimated by comparing
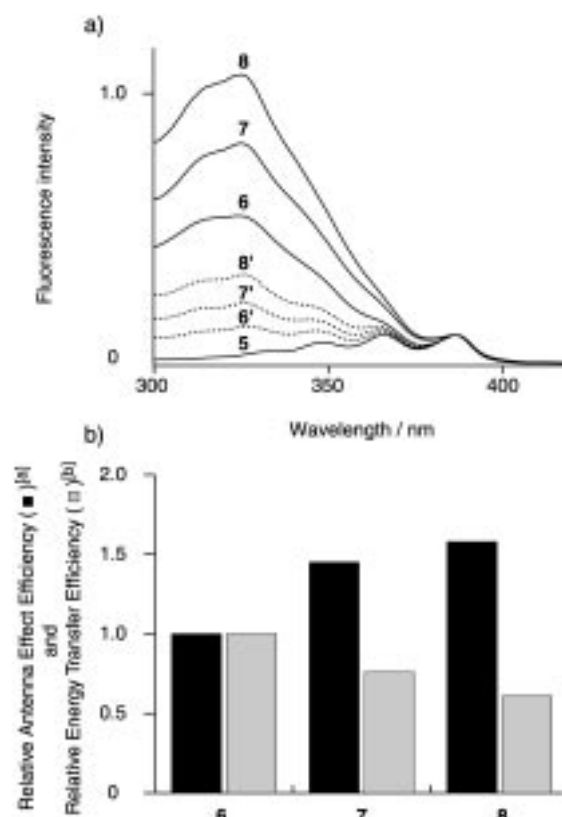

Figure 4. Steady-state corrected fluorescence excitation spectra ($\lambda_{em} = 440$ nm) of polyrotaxanes **5–8** (1.8 μM) and the mixtures of **5** (1.8 μM) and NpCD (a), and the relative antenna and energy transfer efficiencies (b) in propylene glycol at 25 °C. Each of the mixtures contains the same naphthalene unit as the corresponding polyrotaxane (5.8 μM in **6′**, 11.5 μM in **7′**, and 16.7 μM in **8′**). The absorbance of each sample in the recorded wavelength range is smaller than 0.08. Relative antenna effect efficiency was defined as follows: $(X_{poly} - X_{mix})/(X_{poly6} - X_{mix6})$. X_{poly} is the excitation intensity at 327 nm of polyrotaxanes ($\lambda_{em} = 440$ nm) and X_{mix} is the excitation intensity ($\lambda_{em} = 440$ nm) of the corresponding mixture solution. E_{poly6} and E_{mix6} are the excitation intensities of **6** and the corresponding mixture soluion at 327 nm. Relative energy transfer efficiency was defined as follows, $(E_{poly} - E_{mix})/N_{poly}$. E_{poly} is the excitation intensity of polyrotaxanes ($\lambda_{ex} = 327$ nm), E_{mix} is the excitation intensity of the corresponding mixture ($\lambda_{ex} = 327$), and N_{poly} is the number of NpCD units in polyrotaxanes. The values are normalized so that the value for **6** is 1.0.

the absorption spectrum and excitation spectrum of polyrotaxane ($\lambda_{em} = 440$ nm). However, in our case, when the excitation spectra and absorption spectra were normalized by the anthracene absorption, the excitation intensity in the naphthalene absorption region was larger than the naphthalene absorption intensity. This discrepancy was considered to come from the existence of the fluorescence emission from the naphthalene unit at 440 nm. Thus, it is difficult to estimate the energy transfer efficiency by this method. Therefore, we defined the energy transfer efficiency as follows, $(E_{poly} - E_{mix})/N_{poly}$, where N_{poly} is the number of NpCDs in the polyrotaxanes. After obtaining the values from this equation, the relative energy transfer efficiency of each polyrotaxane was calculated, normalizing the value of **6** as one. These relative energy transfer efficiencies are shown in Figure 4b. The results indicate that the antenna effect increases, but the relative energy transfer efficiency decreases with the increasing content of NpCD in the polyrotaxanes.

Anisotropy measurement: To confirm this energy hopping in the polyrotaxane, we measured the anisotropy in glassy matrices.[9, 10] The relative orientations of the absorption and emission dipoles of a chromosphere are fixed in a rigid medium, and thus the emission will retain the memory of the excitation anisotropy. The degree of anisotropy r is defined as $r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH})$, where I_{VV} and I_{VH} are the fluorescence intensities observed through a polarizer oriented parallel and perpendicular to the plane of polarization of the excitation beam, and G is an instrumental correction factor. If energy migration occurs, however, the chromophore that absorbs light is different from the chromophore that emits light and the retention of anisotropy will be lost, thereby resulting in a value of r closer to zero. The anisotropy measurements were undertaken at 348 nm of naphthalene fluorescence using 277 nm as the excitation wavelength. Under the conditions used (propylene glycol, $-70\,°C$), the fluorophore should remain stationary during the lifetime of the excited state, thereby effectively removing any depolarization effect due to fluorophore motion. One can expect the anisotropy value for the naphthalene of NpCD to be similar to that of the polyrotaxanes if energy migration does not occur between the naphthalene units. However, if energy migration does occur within these polyrotaxanes, the anisotropy value should become smaller. The anisotropy values of **6–8** and NpCD are summarized in Table 4. It is clear that the

Table 4. Anisotropy of polyrotaxanes **6**, **7**, **8**, and NpCD (1.8 μM).

6	7	8	NpCD
0.150	0.094	0.081	0.184

All parameters were recorded in propylene glycol at $-70\,°C$; $\lambda_{ex} = 277$ nm and $\lambda_{em} = 348$ nm.

anisotropy values of the polyrotaxanes are smaller than the value of NpCD and that the anisotropy decreases with increasing content of NpCD in the polyrotaxanes. This observation suggests that energy migration occurs between the naphthalene units in the polyrotaxanes and that the frequency of energy hopping depends on the density of the naphthalene units.

Time-resolved fluorescence spectroscopy: The naphthalene fluorescence lifetimes of **6–8** and the mixture solutions of NpCD and **5** were measured in propylene glycol using a time-correlated single photon-counting instrument ($\lambda_{ex} = 327$ nm). The fluorescence decays were well fitted by a double exponential decay function but cannot be fitted by a single exponential decay function. The values of the fluorescence lifetimes are given in Table 5. The decay curve for NpCD was found to have lifetimes of 5.2 ns (93.1 %) and 15.3 ns (6.9 %). This may suggest that the naphthyl moiety is located in two different environments.[22] In the longer lifetime species, the naphthyl moiety may be included in the hydrophobic CD cavity while in the shorter lifetime species, which is the

Table 5. Fluorescence lifetime parameters.[a]

	$\tau 1$ [ns]	$\tau 2$ [ns]	χ^2	D.W.
NpCD	5.2 (93.1 %)	15.3 (6.9 %)	1.16	1.81
6[b]	1.1 (75.1 %)	5.6 (24.9 %)	1.22	1.81
7[b]	1.2 (69.9 %)	5.7 (30.1 %)	1.21	1.89
8[b]	1.3 (65.8 %)	5.9 (34.2 %)	1.26	1.93
mix for **6**[c]	5.1 (91.9 %)	13.3 (8.1 %)	1.23	1.78
mix for **7**[c]	5.2 (93.4 %)	14.4 (6.6 %)	1.14	1.89
mix for **8**[c]	4.9 (92.2 %)	14.0 (7.8 %)	1.16	2.00

[a] Fluorescence decay parameters were measured in polypropylene glycol at 25 °C. $\lambda_{ex} = 312$ nm; $\lambda_{em} = 350$ nm. [b] The concentration of polyrotaxanes **6–8** is 1.8 μM. [c] The mixture solutions of **5** (1.8 μM) and NpCD, each having the same naphthalene concentration as the corresponding polyrotaxane (5.8 μM in mix for **6**, 11.5 μM in mix for **7**, and 16.7 μM in mix for **8**).

predominant species, the naphthyl moiety may be located in the bulk solution.[22] One can expect that the environment around the naphthalene moiety of the polyrotaxanes is similar to that of the shorter lifetime species of NpCD (5.2 ns), meaning that the naphthalene moiety is located outside the CD cavity and exists in the bulk solution. We actually observed species with similar lifetimes ($\tau = 5.6 - 5.9$ ns); however, we also observed species with very short lifetimes ($\tau = 1.1 - 1.3$ ns), much shorter than 5.2 ns of NpCD. We attribute the shorter lifetime species of **6–8** to the naphthalene units quenched by the energy transfer to the anthracene units. In the mixture solutions, the lifetimes, and the ratio of the shorter and longer lifetime components are almost the same as those of NpCD. Energy transfer efficiency (E_T) by the Förster mechanism can be evaluated by the equation: $E_T = 1 - (\tau'/\tau)$; where τ is the lifetime without an acceptor and τ' is the lifetime quenched by energy transfer to an acceptor. The average energy transfer efficiency for short lifetime species can be estimated by the equation. Based on the fraction of the lifetime, the percentage of naphthalene acting as the energy transfer donor over the whole naphthalene content can be estimated. We use $\tau = 5.2$ ns for NpCD as the lifetime without an acceptor. The evaluated energy transfer efficiencies are 78.8, 76.9, and 75.0 % for the short lifetime species of **6**, **7**, and **8**, respectively. The interesting result from the fluorescence decay measurements is that the ratio of the shorter lifetime species decreases, and the ratio of the longer lifetime species increases with the increasing number of naphthalene units. In **6**, about 75 % of NpCD acts as an energy donor with an energy transfer efficiency of about 79 %, while in **8**, the content of NpCD acting as an energy donor decreases to 66 % with an energy transfer efficiency of 75 %. These results support the idea that increasing the number of the antenna chromophores may not result in higher energy transfer efficiency in the antenna system without any energy gradation to the acceptor. It should be pointed out that the overall mechanism of energy migration and energy transfer will be very complex and consequently it is difficult to obtain the overall rate of energy transfer precisely. What is more, various ranges of distances between moieties are present in the polyrotaxane, and, in addition, which naphthalene is initially excited cannot be ascertained.

Energy transfer mechanism: The mechanism for singlet–singlet energy transfer is interpreted in terms of the Förster mechanism, which involves the long distance dipole–dipole interaction. The Förster radius (R_0), where the energy transfer efficiency is 50% between naphthalene and anthracene, can be obtained from Equation 1 where k^2 is the molecular

$$R_0 = 8.785 \times 10^{-25} k^2 \phi n^{-4} J \tag{1}$$

orientation factor, which is 2/3 in random distribution between the donor and acceptor, ϕ is the fluorescence quantum yield of the donor in the absence of an acceptor (the measured ϕ value of NpCD is 0.158 in polypropylene glycol), n is the refractive index of the solvent (the value for propylene glycol is 1.432), and J is the overlap integral between fluorescence spectrum of donor and the absorption spectrum of acceptor.

The overlap integral J is given by Equation 2 where F_D is the relative fluorescence intensity of the donor normalized on the wavenumber scale (v), and $\varepsilon_A(v)$ is the excitation coefficient of the acceptor at the wavenumber.

$$J = F_D(v)\varepsilon_A(v)v^{-4}dv \tag{2}$$

The R_0 value was calculated to be 23 Å based on the above equations. From the fluorescence decay measurement, about 75% of the singlet excited state energy of the naphthalene units in **6** transfers to the anthracene moiety, where the energy transfer efficiency is about 80%. The rate constant of the energy transfer k_{ET} in the Förster mechanism is given by Equation (3), where N is Avogadro's number, and R is the distance between the centers of the two dipoles for the donor and acceptor molecules.

$$k_{ET} = \frac{9000(\ln 10)k^2 \phi J}{128\pi^5 n^4 N\tau R^6} \tag{3}$$

Based on these equations, the relationship between the energy transfer efficiency (E_T) and distance is defined by Equation (4).

$$\frac{E_T}{1 - E'} = \left(\frac{R_0}{R}\right)^6 \tag{4}$$

Using this equation, the distance between naphthalene and anthracene was calculated to be about 19 Å when the energy transfer efficiency is 80%. To coincide with the data for the fluorescence decay, about 2.4 NpCD units of the 3.2 NpCD units in **6** (75%) should be located 19 Å apart from the two anthracene moieties. Because the length of the PEG chain is about 150 Å in its extended form, **6** may not exist as a straight structure. Using the above equations, the Förster radius between naphthalene units is calculated to be about 14 Å, which is twice the length of the α-CD height (7 Å). Thus, the energy migration between the naphthalene units can occur and facilitate the energy transfer to the anthracene moiety from the distant naphthalene units. There are fewer total CD units in **7** and **8** than in **6**. So the flexibility of **7** and **8** should be greater than that of **6**. Although energy transfer for the polyrotaxane with the higher proportion of NpCD units may be expected to be more easily facilitated, the observed energy transfer efficiency actually decreased with increasing content

of NpCD. The energy loss associated with energy transfer to anthracene may be explained by emission from the naphthalene group during energy migration between the naphthalene units. Actually, anisotropy measurements showed that the energy migration in **7** and **8** was more remarkable than that of **6**.

Conclusion

A polyrotaxane series as a light-harvesting antenna model was constructed, which consists of various ratios of α-CD and NpCD threaded by a polyethylene glycol chain bearing anthracene moieties at each end. In this system, the naphthalene and anthracene moieties act as energy donor and energy acceptor, respectively. The energy transfer from the naphthalene units to the anthracene units was analyzed by steady state fluorescence excitation and emission spectra and by fluorescence decay measurements. Glass-matrix anisotropy measurements also suggested that energy migration between naphthalene units occurred. These results indicate that the antenna effect becomes more marked with increasing number of NpCD units in the polyrotaxanes. However, the energy transfer efficiency from naphthalene to anthracene decreases with increasing number of NpCDs in the polyrotaxanes.

Experimental Section

Materials: α-CD was a kind gift from Nihon Shokuhin Kako Co., Ltd. Poly(oxyethylene)diamine (Approximate MW = 2000). (Diamino-PEG) was purchased from Scientific Polymer Products and was used without further purification.

Measurements: ^{1}H NMR spectra were recorded on a Varian VXR 500 S 500 MHz NMR spectrometer. Chemical shifts were referenced to those of the solvent values ($\delta = 2.62$ for DMSO and 4.7 for HOD). The UV/Vis absorption spectra were recorded on a Shimazu model UV-3100 spectrometer using 1 cm quartz cells. Fluorescence spectra were taken on a Hitachi Fluorescence Photometer F-2500. The fluorescence quantum yields were determined using quinine sulfate solution in 0.1 N H_2SO_4 ($\phi_n = 0.55$) as the standard. Fluorescence and excitation spectra were corrected for the wavelength dependence of detector sensitivity and the excitation light source output. The spectra were recorded using a 1 cm quartz cell. Fluorescence lifetimes were measured on a time-correlated single photon counting fluorometer (Horiba NAES-550). A total of 10000 counts were collected in the maximum channel. The absorbances of the solutions were between 0.1 and 0.3 at the excitation wavelength. The fluorescence decay profile was analyzed by reconvolution of the instrumental response function and monoexponential or multiexponential decay of the emission using an iterative nonlinear least squares method. The goodness-of-fit was assessed using the plots of weighted residuals, reduced χ^2 values, and Durbin–Watson parameters. The Analytical Division of the Research Laboratory of Resources Utilization of Tokyo Institute of Technology performed the elemental analyses.

Synthesis of polypseudorotaxanes 1, 2, 3, and 4: The diamino-PEG (0.037 g, 1.83×10^{-5} mol) was added into aqueous solutions (2 ml) of A (α-CD; 0.450 g, 4.63×10^{-4} mol), B (α-CD; 0.360 g, 3.70×10^{-4} mol, NpCD; 0.107 g, 9.20×10^{-5} mol), C (α-CD; 0.180 g, 1.85×10^{-4} mol, NpCD; 0.322 g, 2.77×10^{-4} mol), and D (NpCD; 0.450 g, 3.87×10^{-4} mol). White precipitates were formed in each solution after the addition of diamino-PEG. The precipitates were centrifuged, collected and then dried in vacuo, giving **1** (0.40 g, 1.53×10^{-5} mol, 83.1%), **2** (0.36 g, 1.66×10^{-5} mol, 90.4%), **3** (0.375 g, 1.76×10^{-5} mol, 95.7%), and **4** (0.25 g, 1.69×10^{-5} mol, 92.0%) from solutions A, B, C, and D, respectively. ^{1}H NMR (D_2O): $\delta = 3.40 – 3.60$

(12 H; H-2 and H-4 of α-CD of **1**, **2**, **3**, and **4**), 3.65 (s, 7.3 H, 9.2 H, 10.2 H, and 16.3 H; CH$_2$ of Diamino-PEG of **1**, **2**, **3**, and **4**, respectively), 3.70–4.00 (18 H; H-3, H-5, and H-6 of α-CD of **1**, **2**, **3**, and **4**), 4.85–5.05 (6 H; H-1 α-CD of **1**, **2**, **3**, and **4**), 7.70–8.20 (naphthyl peaks of **2**, **3**, and **4**), 8.54 (s, 0.15 H, 0.60 H, and 1.00 H; H-1 of naphthalene of **2**, **3**, and **4**, respectively).

Synthesis of polyrotaxane 5, 6, 7 and 8: 9-Anthraldehyde (15.0 mg, 7.27 $\times$ 10^{-5} mol) was merged in DMF (30 μM) and then each polypseudorotaxane **1** (0.10 g, 5.33 $\times$ 10^{-6} mol), **2** (0.10 g, 5.86 $\times$ 10^{-6} mol), **3** (0.10 g, 6.62 $\times$ 10^{-6} mol), and **4** (0.10 g, 6.96 $\times$ 10^{-6} mol) was added into this DMF solution individually and kneaded for a few minutes. After standing for 15 h at room temperature, acetone was poured into each cuvette. The precipitates were centrifuged, and the supernatant fluids were then removed. This process was repeated by using acetone (4 $\times$ 45 mL) and then water (2 $\times$ 45 mL) for each reactant. The products were then washed with acetone again and dried in vacuo to obtain yellow powders (**5**, **6**, **7**, and **8** from **1**, **2**, **3**, and **4**, respectively). Yield: **5** (40.0 mg, 1.90 $\times$ 10^{-6} mol, 49.8 %), **6** (23.2 mg, 1.26 $\times$ 10^{-6} mol, 27.5 %), **7** (6.5 mg, 4.63 $\times$ 10^{-7} mol, 9.9 %), **8** (4.2 mg, 3.18 $\times$ 10^{-7} mol, 4.8 %). ^{1}H NMR ([D$_6$]DMSO): δ = 3.00–4.00 (br; H-2, H-3, H-4, H-5, and H-6 of α-CD of **5**, **6**, **7**, and **8**), δ = 3.48–3.52 (br; CH$_2$ of diamino-PEG of **5**, **6**, **7**, and **8**), 4.25–4.58 (br; HO-6 of α-CD of **5**, **6**, **7**, and **8**), 4.60–4.82 (br; H-1 of α-CD of **5**, **6**, **7**, and **8**), 5.24–5.66 (br; HO-2, 3 of α-CD of of **5**, **6**, **7**, and **8**), 7.57–7.59 (br; anthracene peaks of **5**, **6**, **7**, and **8**), 7.68–7.92 (br; naphthalene peaks of **6**, **7**, and **8**), 8.04–8.26 (br; naphthalene and anthracene peaks of **5**, **6**, **7**, and **8**), 8.56 (br; anthracene peaks of **5**, **6**, **7**, and **8**), 8.60 (s, br; naphthalene peak of **6**, **7**, and **8**), 8.68 (br; anthracene peaks of **5**, **6**, **7**, and **8**); elemental analyses calcd (%) for **5** (C$_{805}$H$_{1342}$O$_{616}$N$_2$): C 46.25, H 4.47, N 0.13; found: C 46.14, H 6.74, N 0.26; calcd (%) for **6** (C$_{721.8}$H$_{1169.2}$O$_{526.4}$N$_2$S$_{3.2}$): C 47.11, H 6.41, N 0.15, S 0.56; found: C 46.87, H 6.70, N 0.24, S 0.53; calcd (%) for **7** (C$_{570.2}$H$_{882.4}$O$_{379.8}$N$_2$S$_{6.4}$ $\cdot$ 6 H$_2$O): C 48.38, H 6.39, N 0.20, S 1.45; found: C 48.66, H 6.72, N 0.30, S 1.77; calcd (%) for **8** (C$_{548.8}$H$_{815.8}$O$_{343.6}$N$_2$S$_{9.3}$ $\cdot$ 5 H$_2$O): C 49.46, H 6.25, N 0.21, S 0.24; found: C 49.71, H 6.55, N 0.27, S 1.74.

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