Energy Transfer and Guest Responsive Fluorescence Spectra of Polyrotaxane Consisting of α-Cyclodextrins Bearing Naphthyl Moieties

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We constructed a polyrotaxane (**1**) composed of about 15 α-cyclodextrins, each bearing roughly two naphthalene units and a polyethylene glycol (PEG) as a threading chain with adamantane groups at both ends. The product was characterized by ^{1}H NMR, ^{13}C NMR, and absorption spectroscopies. We observed that photoenergy transfer occurs from the naphthalene units of **1** to 5-dimethylamino-1-naphthalenesulfonyl (dansyl) of dansyl modified β-cyclodextrin (Dnsβ-CD) when Dnsβ-CD forms a complex with each terminal adamantane moiety of the polyrotaxane. This energy transfer was reduced by the addition of adamantanol, which acts as a competitive binder for Dnsβ-CD.

Various energy and electron transfer systems have been reported as models for photosynthesis systems. Since many components are arranged in the membrane of chloroplast in natural systems, artificial membranes like micelles,[1] liposomes,[2—5] and bilayer membrane[6] are expected to be excellent scaffolds, in which the systems of photoenergy-harvesting, charge separation and electron transfer are constructed. Steinberg-Yfrach et al. constructed a proton transfer liposomal system, in which a pH gradient between inside and outside of the liposome is generated, the system then catalytically produces ATP from ADP by photoirradiation.[7,8] On the other hand, some model system, which have rigid and well-defined structures, with donor and acceptor linked by covalent bonds have been investigated.[9—11] Sisido et al. used an α-helical polypeptide as a scaffold of donor and acceptor for energy transfer to clarify the effects of distance and pathway on the phenomena.[12] Recently, the dendrimeric architecture has been used for photoenergy-harvesting systems.[13,14] On the contrary, in the natural system, the components of energy and electron transfer system are held together in a spatially well-oriented arrangement by weak non-covalent interactions. In connection with this, many supramolecular systems, in which donor and acceptor components are linked by non-covalent interactions[15] such as hydrogen bonding,[16,17] aromatic π-stacking,[18] and metal-ligand coordination,[19] have been constructed. Tamiaki et al. reported a supramolecular light-harvesting system, in which efficient energy transfer occurs from about 50—100 self-assembled zinc chlorines to a single metal-free bacteriochlorin.[20] Among the supramolecules, rotaxanes were used as the model systems to study the electron transfer process in relation with the distinction between through-bond and through-space mechanisms.[21,22] Rotaxanes have also been constructed as molecular machines, which change their structures or intramolecular ring motions in response to external stimuli such as light irradiation[24,25] or pH variation.[26] Recently, Harada et al. reported that rotaxane chemistry can be developed to polymer-like chemistry by showing a polyrotaxane, in which many α-cyclodextrin (α-CD) units are threaded by polyethylene glycol and stoppered by terminal bulky units.[27,28] On this basis, we attempted to prepare a rotaxane as an energy transfer system, in which α-CD bearing a naphthyl moiety is threaded by polyethylene glycol and stoppered by terminal dansyl units.[29] Here, we report on a polyrotaxane as a light-harvesting antenna, in which many α-CD units bearing multiple naphthyl units are threaded by a polyethylene glycol chain and stoppered by adamantane units (**1**). The polyrotaxane **1** has about 30 naphthalene units arranged along the polyrotaxane axis. It has a less flexible extended structure, so excimers are difficult to form because of restricted motion, and thus contrasts to the flexible chromophore-appended polymers, in which excimers are easily form.[30—33] To our knowledge this is the first example, in which many chromophores are bound together mechanically. We will discuss the energy transfer system using polyrotaxane **1** as the model system of light-harvesting antenna, in which energy transfer from donors to an acceptor occurs via non-covalent bond (Chart 1). In the system, the dansyl moiety of dansyl-modified β-CD (Dnsβ-CD) is designed to play a role as an acceptor of singlet excitation energy from the naphthalene units of **1** when Dnsβ-CD is bound to the adamantane units of **1** by hydrophobic interaction.

Results and Discussion

Preparation of 1. The synthesis of **1** is shown in Scheme 1. Polypseudorotaxane, in which α-CD units are threaded by poly(oxyethylene)diamine (approximate M.W. = 2000) (Diamino-PEG) (**2**), was obtained by adding Diamino-PEG to a saturated aqueous solution of α-CD at room temperature.[28] According to Harada's research, the

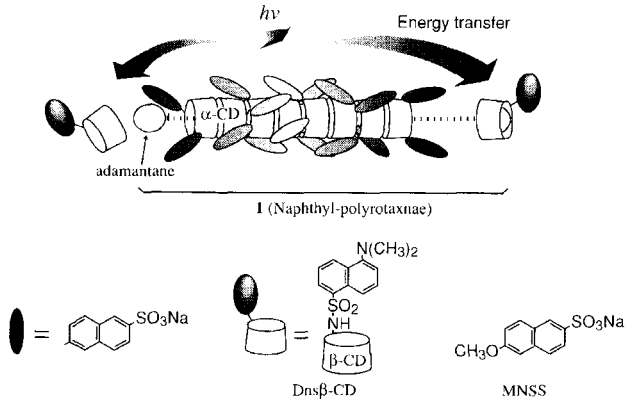
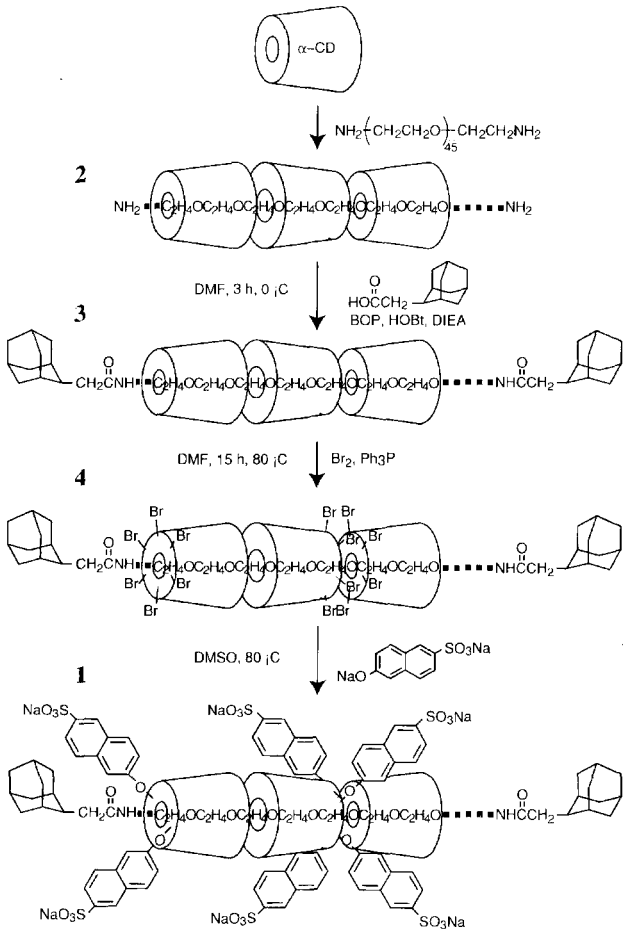


Chart 1.



Scheme 1.

stoichiometries of ethylene glycol unit and α-CD of the polypseudorotaxane were 2 : 1, so α-CD molecules were almost closely packed from end-to-end of the Diamino-PEG chain in this stoichiometry.[34] 1-Adamantaneacetic acid, which was large enough to keep α-CD on Diamino-PEG chain, was attached to both Diamino-PEG ends of polypseudorotaxane to get adamantane terminated polyrotaxane (**3**). As a next step, we added Br_2 to a solution of **3** and triphenylphosphine (Ph_3P) in DMF.[35] This solution was refluxed; after cooling, its pH was adjusted to 9—10. This solution was poured into ice water and the precipitate was collected by filtration. The product was washed by water and MeOH to remove Br_2 and Ph_3P. According to this procedure, only the primary hydroxy group of α-CD in the polyrotaxane was selectively replaced by bromide to yield **4**.[36] Polyrotaxane **1** was prepared by nucleophilic substitution of bromide of **4** by disodium 6-hydroxy-2-naphthalenesulfonate. Since the oxide anion is a stronger nucleophile than the sulfate group, the naphthyl moiety was connected to α-CD via an ether group. The reaction mixture was poured into an excess amount of acetone for precipitation of **1** and other materials. The crude precipitate was dissolved in a small amount of water and purified by Sephadex G-25 column chromatography using water as the eluent to obtain **1**.

Characterization of 3. Polyrotaxane **3** was insoluble in water and in DMF, but was soluble in DMSO. The characterization of **3** was performed by elemental analysis, TLC, and ^{1}H NMR and 2D NOESY NMR spectroscopies. Figure 1a shows the ^{1}H NMR spectrum of **3** in DMSO-d_6. The spectrum shows that the product is composed of CD, PEG, and

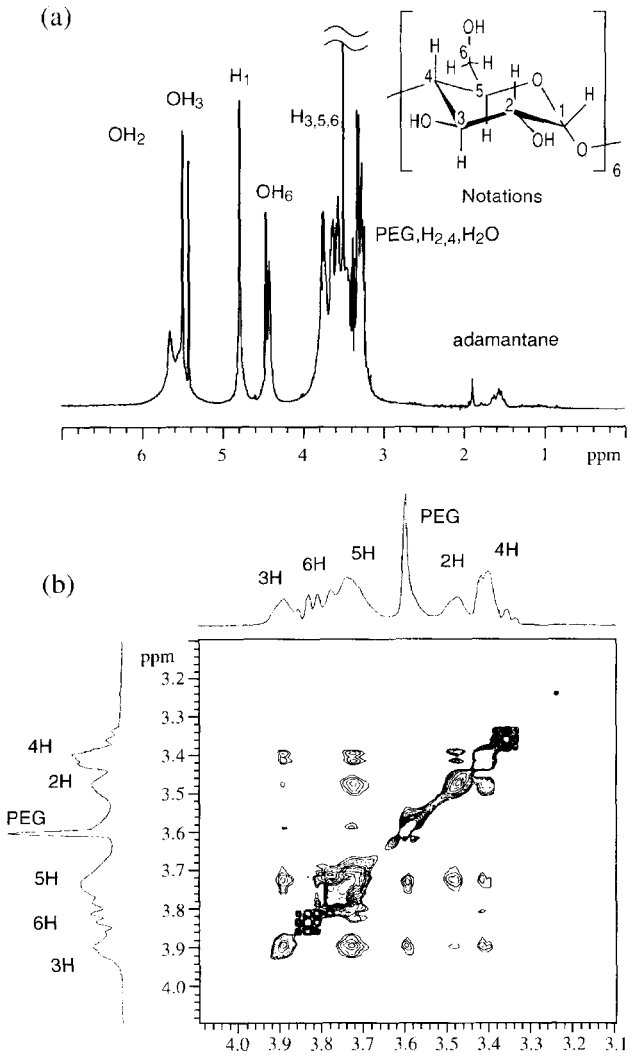


Fig. 1. (a) ^{1}H NMR spectrum of **3** in DMSO-d_6. (b) 2D NOESY NMR spectrum of **3** in 3.5 M NaOD aq.

adamantane groups. The peaks of α-CD, PEG, and adamantane groups of **3** are broadened. This result indicates that the movements of the molecules are restricted. This is the typical feature of polyrotaxanes.[28] The R_f value of **3** was 0.00, while the R_f value of the polypseudorotaxane **2** was 0.48, which is the same as that of α-CD. Figure 1b shows the 2D NOESY NMR spectrum of **3** in 3.5 M NaOD solution (1 M = 1 mol dm^{-3}). The signals of C3–H and C5–H of α-CD, which are placed inside the cavity of α-CD, show NOEs with the CH_2 of Diamino-PEG. On the contrary, the signals of C1–H, C2–H, and C4–H, which are located outside the cavity, do not indicate the NOEs with PEG. These results confirm that PEG chain actually exists inside α-CD cavities in **3**. In the same concentration of the mixture of α-CD and Diamino-PEG, no NOEs between C3, C5–H of α-CD and CH_2 of PEG were observed. This result confirmed that α-CDs of **3** are mechanically interlocked on the Diamino-PEG chain by the adamantane groups as stoppers.

Characterization of 4. Polyrotaxane **4** is not dissolved in water, but did dissolve in DMSO and DMF, in which **3** can not be dissolved. The characterization of **4** was performed by ^{1}H NMR and ^{13}C NMR spectra. Figure 2a shows the ^{1}H NMR spectrum of **4**. The signal of O6–H of α-CD, which was detected at δ = 4.54 in **3**, was not observed in **4**. Figure 2b shows the ^{13}C NMR spectrum of **4**. The peak of C6 was observed at δ = 34.2, which was shifted to the high magnetic field from δ = 60 where that of native α-CD is observed. This remarkably high magnetic field shift in the ^{13}C NMR spectrum may be explained in terms of the change from a hydroxy group to a heavy atom like bromide on the carbon. These results mean that the O6–H of α-CD is replaced by bromide in **4**.

Characterization of 1. Compound **1** was purified with a Sephadex G-25 size exclusion column (1.7×70 cm) using water as the elution solvent. The compound was detected by UV (280 nm) and TLC (R_f = 0.00), appearing as the first component of the fractions. Figure 3a shows the ^{1}H NMR spectrum of **1** in D_2O. The peaks of adamantane groups were observed from δ = 1.5 to δ = 2.2, and the peaks of α-CD and Diamino-PEG were observed from δ = 3.5 to δ = 5.5. On the other hand, the peaks of the naphthyl group were detected in the region from δ = 7.0 to δ = 8.8. These peaks were remarkably broadened. This broadening confirmed that the product was the polyrotaxane. From the ^{1}H NMR, it is difficult to identify the peaks of **1**. Figure 3b shows that the ^{13}C NMR spectrum of **1** in D_2O, which clearly shows that there are α-CD, Diamino-PEG, adamantane, and naphthyl units. It is noted that all these peaks are also broadened. As described in the next section, about two of the six bromides of **4** were replaced by the naphthalene moieties and the rest of the bromides were hydrolyzed, returning to hydroxy groups.

Numbers of α-CD and Naphthalene in 1. The num-

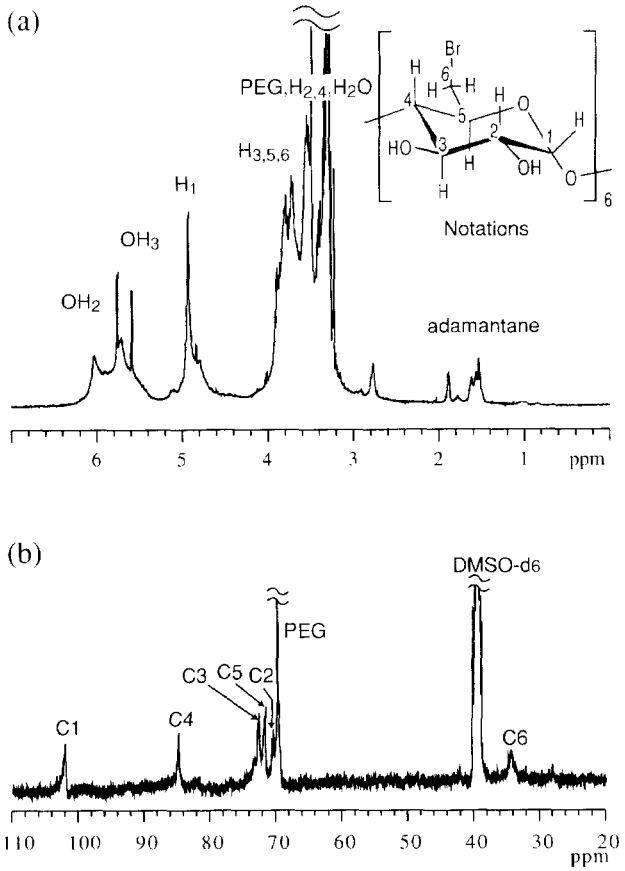


Fig. 2. (a) ^{1}H NMR spectrum of **4** in DMSO-d_6. (b) ^{13}C NMR spectrum of **4** in DMSO-d_6.

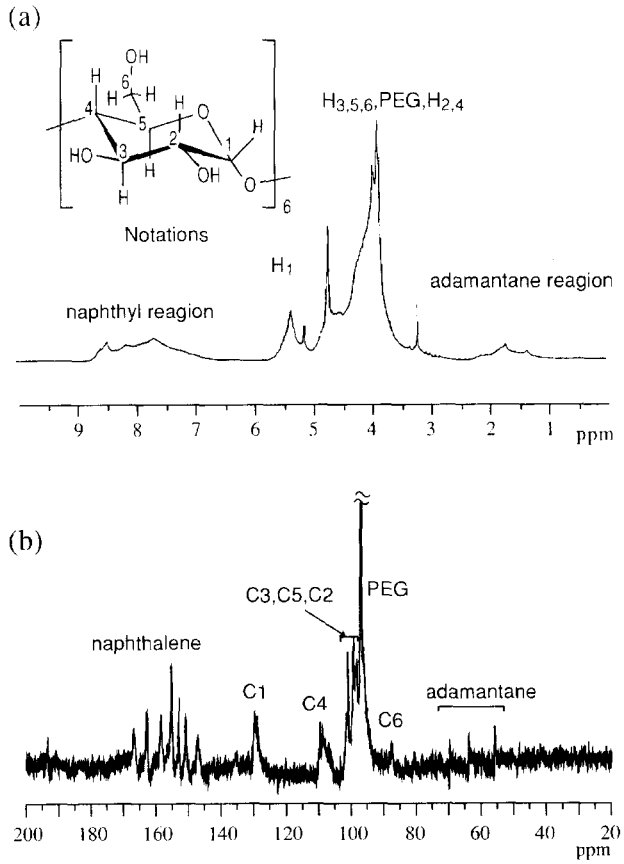


Fig. 3. (a) ^{1}H NMR spectra of **1** in D_2O. (b) ^{13}C NMR spectrum of **1** in D_2O.

bers of α-CD and naphthalene in **1** can be estimated by the comparison of the integration of ^{1}H NMR of α-CD, naphthalene, and adamantane units. However, each of these peaks is too broad to calculate the molar ratio correctly. Therefore, the large stoppers (adamantane unit) at the ends of **1** were removed by cleaving the amide bond with a strong base (3 M NaOD solution) at room temperature to produce free α-CD derivatives. The peaks, which were broadened at first, became sharp after 15 d. These results indicated that each component of **1** was released from the complex in this condition. After the reaction was completed, it was possible to compare the integration of each peak. The comparison of the peak areas of C1–H of α-CD, adamantane, and naphthalene peaks indicate that one polyrotaxane involves approximately 15 α-CDs and each α-CD bears about 2 naphthalene units. It is possible to estimate these values by using the UV-vis absorption spectrum. The number of α-CD (x) and the number of naphthalene units attached to one α-CD (y) can be obtained by equation 1. MW is the molecular weight of **1**.

$$\mathrm{MW} = \frac{x \times y \times c \times \varepsilon \times L}{A} \quad (1)$$

Here c (g dm^{-3}) is the concentration of **1** and ε is the molar extinction coefficient of naphthalene estimated by using the data of sodium 6-methoxy-2-naphthalenesulfonate (MNSS). A is the absorbance and L is the cell length (1 cm). One **1** has xy naphthalene units. The molecular weight was calculated by Eq. 2.

$$\mathrm{MW} = 194 \times 2 + 2000 + x(973 + 228y) \quad (2)$$

The molecular weights corresponding to adamantaneacetyl unit and PEG are 194 and 2000, respectively. When a naphthyl moiety is attached to α-CD unit, molecular weight is increased by 228 from 973, which is the molecular weight of α-CD. From these equations, values of x and y are estimated to be 15 and 1.6, respectively.

Energy Transfer. Polyrotaxane **1** was designed as an effective energy transfer system, in which the photoenergy absorbed by naphthyl chromophores is transferred to the dansyl moiety of Dnsβ-CD, which forms inclusion complexes with the adamantane units at the ends of **1**.[37] It is well known that β-CD binds adamantane derivatives strongly. Hamasaki et al. reported that Dnsβ-CD (Chart 1) binds 1-adamantanol with a binding constant of 11800 M^{-1}.[37] Therefore, Dnsβ-CD is expected to bind strongly the adamantane units at the ends of **1**.

Figures 4a and 4b show absorption spectra and fluorescence spectra of **1** and MNSS in aqueous solution.[35] The absorption spectra of **1** and MNSS are similar and fluorescence spectra of **1** and MNSS are also similar, exhibiting a predominant normal fluorescence peak around 370 nm. However, detailed examination of the fluorescence spectra indicates that **1** shows slightly stronger fluorescence intensity at longer wavelength (>400 nm) than MNSS does. This result suggests that the fluorescence of **1** involves a small amount of excimer emission in the longer wavelength region. This small excimer may be formed between two naphthalene units within the same α-CD unit or between two naphthalene units each attached to different α-CD units in **1**. The reason why excimer probability was low in **1** was explained as follows: (1) **1** has a rod like structure and the flexibility of the naphthalene units is limited; (2) There is ionic repulsion between negatively charged sulfonate groups attached to the naphthalene units.[35] Dnsβ-CD and dansylglycine (DnsGly) have an absorption band with a peak at 340 and 330 nm, respectively. These spectral features confirm that energy transfer may occur from the naphthyl unit of **1** or from MNSS to the dansyl unit of Dnsβ-CD and DnsGly since there exists an overlapping between the fluorescence band of the naphthyl unit and absorption band of the dansyl moiety. Actually, in another rotaxane system, the energy transfer from the naphthyl moiety to the dansyl one was observed.[29]

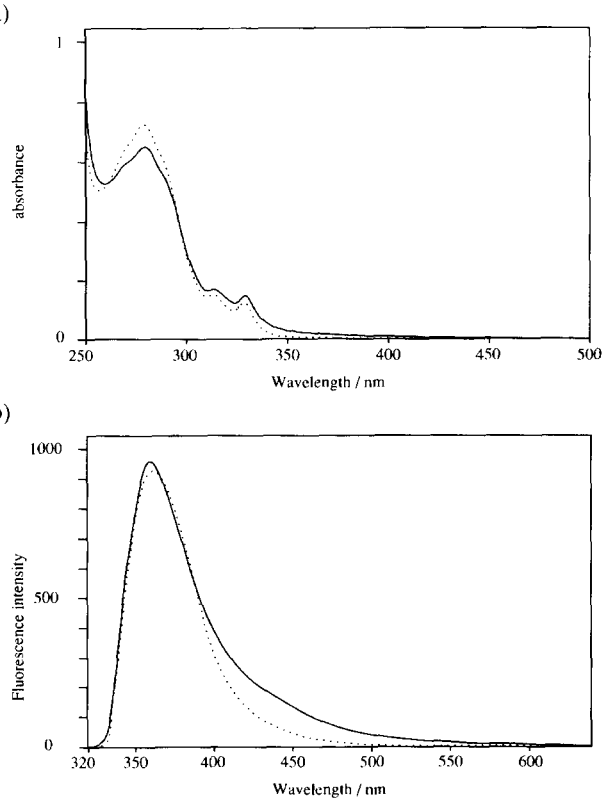


Fig. 4. (a) UV absorption spectra of **1** (—) and MNSS (····) at 25 °C using 1 cm path-length cell. Naphthalene concentration of each sample is 1.20×10^{-4} M. (b) Fluorescence spectra of **1** (—) and MNSS (····) at 25 °C. Excitaion wavelength = 296 nm. Naphthalene concentration of each sample is 1.77×10^{-4} M.

Figure 5 shows fluorescence spectra of **1** in the presence of different concentrations of DnsGly. The fluorescence intensity of the peak around 370 nm remarkably decreases with increasing concentration of DnsGly, while the intensity of the dansyl fluorescence around 580 nm slightly increases. Similar effects of DnsGly were observed for the fluorescence of MNSS (Fig. 6). These data confirm that energy transfer occurs from the naphthyl unit to the dansyl unit in both systems.

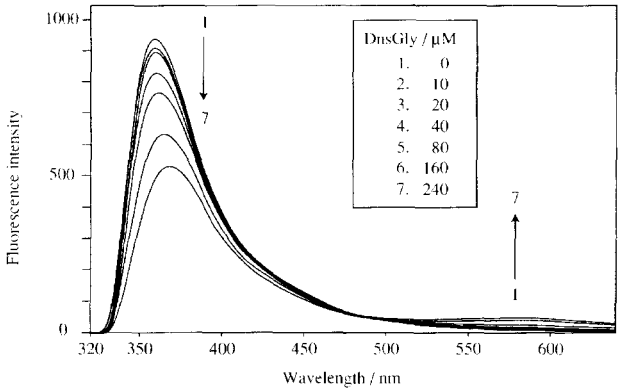


Fig. 5. Fluorescence spectra of **1** (naphthalene concn is 1.77 mM) alone and in the presence of DnsGly at 25 °C. Excitaion wavelength is 296 nm.

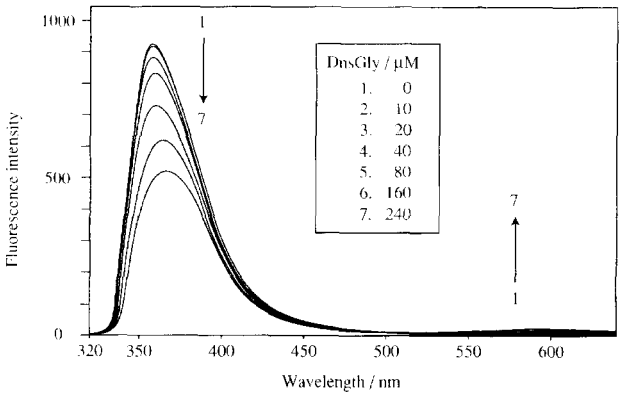


Fig. 6. Fluorescence spectra of MNSS (naphthalene concn is 1.77 mM) alone and in the presence of DnsGly at 25 °C. Excitaion wavelength is 296 nm.

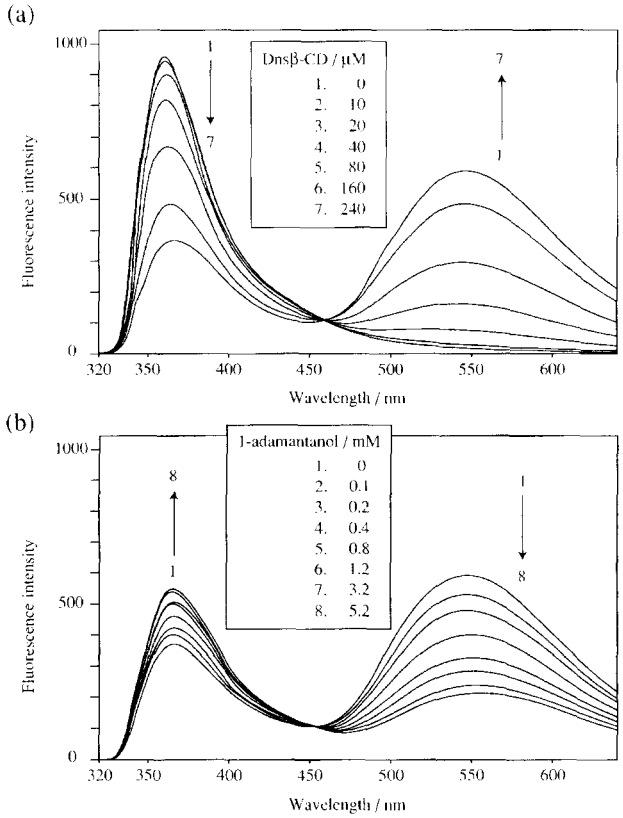


Fig. 7. (a) Fluorescence spectra of **1** (naphthalene concn is 1.77 mM) alone and in the presence of Dnsβ-CD at 25 °C. Excitaion wavelength is 296 nm. (b) Fluorescence spectra of **1** (naphthalene concn is 1.77 mM) with Dnsβ-CD (240 μM), and in the presence of various concentrations of 1-adamantanol at 25 °C. Excitaion wavelength is 296 nm.

Figure 7a shows fluorescence spectra of **1** in the presence of different concentrations of Dnsβ-CD. With increasing concentration of Dnsβ-CD, the intensity of fluorescence around 370 nm decreases but the intensity of the dansyl fluorescence increases with an isoemissive point at 460 nm. This result demonstrates that Dnsβ-CD binds the adamantane moiety located at both ends of **1** and energy transfer effectively occurs in the complex.[38] The importance of the complex formation was confirmed by the observation that the enhancement of the dansyl fluorescence and the depressed naphthyl fluorescence tend to be cancelled upon addition of 1-adamantanol (Fig. 7b). It is obvious that 1-adamantanol added competes with the adamantane ends of **1** in the complex formation with Dnsβ-CD. The recovery of the intensity of the naphthyl fluorescence is ca. 30% and the decrease of the dansyl fluorescence is ca. 65% when 1-adamantanol concentration is changed from 0 to 5.2 mM. It is noted that there exists an unbalance between the ratio of increase in the naphthyl fluorescence intensity and the ratio of the decrease of the dansyl fluorescence. This means that the 30% recovery of the naphthyl fluorescence corresponds to the 65% change of the dansyl fluorescence. Here, the binding constant K_b between Dnsβ-CD and adamantane units of **1** was evaluated as 9800 M^{-1} by using the competitive binding mode with adamantanol, in which recovery of naphthyl fluorescence intensity upon addition of adamantanol was fitted to the theoretical curve. From this K_b value, it was estimated that ca. 65% adamantane units of **1** complexes with Dnsβ-CD before addition of adamantanol in the system. When Dnsβ-CD is replaced by DnsGly, the fluorescence intensity of the naphthyl unit is effectively quenched by DnsGly, as shown in Fig. 5, without any remarkable increase in the dansyl fluorescence. This result indicates that the fluorescence of the naphthyl units can be remarkably quenched by collision without forming any complex with the polyrotaxane. Consequently, there must be two types of energy transfer mechanisms, one resulting in the moderate quenching of the naphthyl fluorescence associated with very slight enhancement of the dansyl fluorescence and the other resulting in the effective quenching of the naphthyl fluorescence associated with marked enhancement of the dansyl fluorescence. One possible explanation for this phenomenon is that there are two naphthyl units in **1**, one being located near the ends (end region) and another being mainly located in the center region of **1**. If **1** contains 15 α-CD units and each CD has two naphthalene units, there are 30 naphthyl units in **1**. In this case, at least 4 units are connected to the end CD units. If

the naphthyl units of another α-CD unit second from the end participate in the energy transfer to the dansyl unit of Dnsβ-CD, the photoenergy from totally 8 naphthyl units around the ends may be transferred to the dansyl units. However, there remains a problem of how much energy migration occurs along the naphthyl units.[39] Table 1 shows fluorescence lifetimes of **1** and MNSS, and rate constant of energy transfer from **1** and MNSS to DnsGly (k_q). The k_q values were estimated by fitting the Sterm–Volmer plots ($I^\circ/I = 1+k_q\tau[Q]$) where [Q] is the concentration of DnsGly. Although MNSS gives 9.4 ns as a fluorescence lifetime, we found two lifetimes for **1** with larger content (85.6%) for shorter lifetime (7.8 ns) and smaller content (14.4%) of longer one (18.1 ns). The two lifetimes of **1** suggest that there are two naphthyl moieties located in different environments. Here, we adopt the shorter lifetime of larger content for rough estimation of the k_q. The obtained k_q values are similar for **1** and MNSS. However, the energy transfer rate from **1** may be considered to be double when the diffusion of **1** is negligible because of its polymeric dimension. This consideration leads us to conclude that some extent of energy migration occurs in **1** and that photoenergy is effectively transferred to Dnsβ-CD. Therefore, the observed effective decrease in the naphthyl fluorescence intensity and marked increase in the dansyl fluorescence as shown in Fig. 7a may be the result of a combination of direct and indirect energy transfer. Since the depth of α-CD is ca. 7 Å and the orientation such as head–head and head–tail arrangement of the α-CD units is not clear, it is not easy to know that energy migration occurs not only between the naphthyl units separated by 7 Å but also between those separated by 14 Å.[38] The flexibility of the naphthyl moieties is another factor to determine the efficiency of the migration.

Figure 8a shows fluorescence spectra of MNSS in the absence and presence of Dnsβ-CD. The fluorescence intensity of MNSS decreases remarkably and the fluorescence of the dansyl unit increases slightly with increasing concentration of Dnsβ-CD. The spectral behavior is markedly different from that of **1** under the same conditions, since the intensity of the dansyl fluorescence of **1** markedly increases. The quenching shown in Fig. 8a may arise from the complex of Dnsβ-CD and MNSS, so we added 1-adamantanol to the system. If the quenching occurs via complex formation between MNSS and Dnsβ-CD, the strong binding ability of 1-adamantanol to Dnsβ-CD would cancel the quenching phenomenon due to the competition for the cavity of Dnsβ-CD. However, we found a slight increase in the naphthalene fluorescence and negligible depression in the dansyl fluorescence (Fig. 8b). This result suggests that the fluorescence quenching mainly occurs by collision between two species. This also suggests that Dnsβ-CD does not bind naphthalene moieties of **1** directly.

Table 1. Fluorescence Lifetimes of **1** and MNSS and k_q Values of **1** and MNSS for DnsGly

Compound	Lifetime[a]/ns	k_q[d]/s^{-1}M^{-1}
1	7.8 (85.5 %)[b]	4.16×10^{11}
	18.1 (14.4 %)	
MNSS	9.4 (100.0 %)[c]	3.38×10^{11}

a) Fluorescence decay was mesured at room temperature in H_2O. Naphthalene concentrations of each solution are 1.18 mM. Excitation wavelength is 300 nm and the decay of the fluorescence intensity over 320 nm was recorded. b) Dacay profile was satisfactorily fitted to a doublel exponential function (χ^2 = 1.19). c) Dacay profile was satisfactorily fitted to a single exponential function (χ^2 = 1.11).

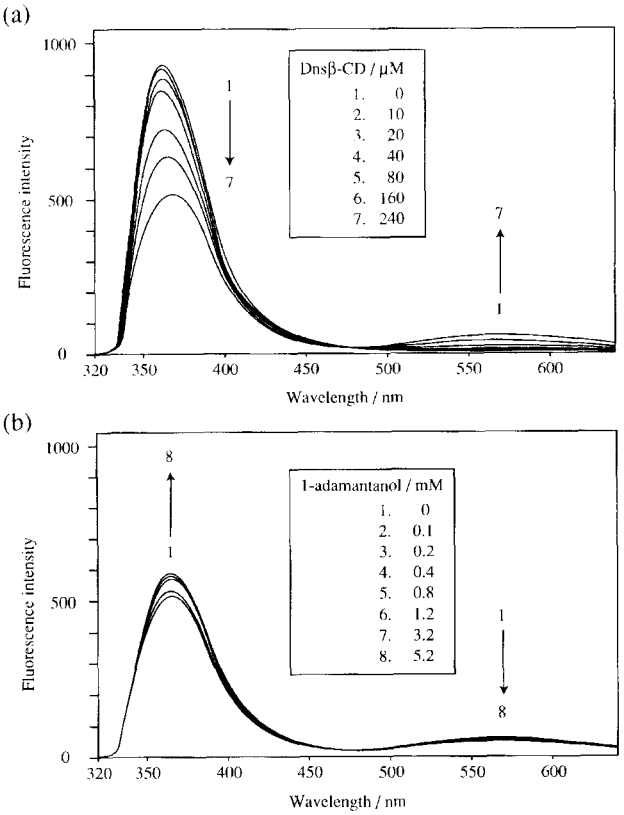


Fig. 8. (a) Fluorescence spectra of MNSS (naphthalene concn is 1.77 mM) alone and in the presence of Dnsβ-CD at 25 °C. Excitaion wavelength is 296 nm. (b) Fluorescence spectra of MNSS (naphthalene concn is 1.77 mM) with Dnsβ-CD (240 μM), and in the presence of various concentrations of 1-adamantanol at 25 °C. Excitaion wavelength is 296 nm.

Dansyl-modified CD was reported to decrease the fluorescence intensity in forming complexes with a variety of guests.[37] This decrease in the fluorescence intensity was explained by the guest-induced location change of dansyl moiety from the hydrophobic cavity to outside water environment. So, it is curious that the complex formation between the adamantane unit of **1** and Dnsβ-CD results in remarkably enhanced dansyl fluorescence despite the exclusion of the dansyl chromophore from hydrophobic cavity of Dnsβ-CD to outside water environment. There might be hydrophobic interaction between the excluded dansyl moiety and the naphthyl unit of **1** so as to decrease the effect of bulk water.

Conclusion. Polyrotaxane **1** has about 15 α-CDs, each bearing ca. two naphthyl units. We concluded that **1** has a

stable rod-like structure, which is the structure suited for energy transfer. The adamantane units located at both ends of **1** form complexes with Dnsβ-CD and energy transfer occurs from several naphthyl chromophores of **1** to the dansyl unit of Dnsβ-CD, resulting in enhanced dansyl fluorescence. This energy transfer was depressed upon addition of 1-adamantanol, due to the competition of adamantane ends of **1** and 1-adamantanol for the cavity of Dnsβ-CD. So, this energy transfer is switched off by adding 1-adamantanol. We are now constructing a variety of supramolecular systems in which energy transfer is controlled by chemical species.

Experimental

Materials. α-CD was a kind gift from Nihon Shokuhin Kako Co., Ltd. Poly(oxyethylene)diamine (approximate M.W. = 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 VXR500S 500 MHz NMR spectrometer. Chemical shifts were referenced to those of the solvents values (δ = 2.62 for DMSO and 4.7 for HOD). ^{13}C NMR spectra were recorded at 100 MHz on a Unity Plus 400. Fluorescence spectra were taken on a Hitachi Fluorescence photometer 850. Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Gel chromatography (GPC) was carried out with a Sephadex G-25 column (1.7×70 cm) using water as the solvent. Elemental analyses were performed by The Analytical Division of the Research Laboratory of Resources Utilization of Tokyo Institute of Technology. TLC was run with precoated silica gel plates (Merck, 60F 254). The solvent of TLC development was concd NH_3aq–AcOEt–2-propanol–H_2O (1 : 3 : 5 : 4 v/v/v/v).

Preparation of 3. Diamino-PEG 2.29 g (ca. 1.11×10^{-3} mol) was dissolved in a saturated aqueous solution of α-CD 40.0 g (4.11×10^{-2} mol). The mixture was irradiated with ultrasonic waves for 20 min and then allowed to stand overnight at room temperature. The solution was centrifuged and then precipitates were collected and then dried in vacuo to give the polypseudorotaxane **2** (30.0 g). A solution of 1-adamantaneacetic acid 0.32 g (8.29×10^{-4} mol), benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP) 0.73 g (8.29×10^{-4} mol), 1-hydroxybenzotriazole (HOBt) 0.25 g (8.29×10^{-4} mol), and *N*, *N*-diisopropylethylamine (DIEA) 0.29 ml (8.29×10^{-4} mol) in DMF (1 ml) was introduced into a solution of **2** (4.0 g) in DMF (5 ml). The mixture was stirred at room temperature for 3 h. The reaction mixture was then precipitated by addition of acetone (100 ml) to the reaction mixture to remove BOP, HOBt, DIEA, and Diamino-PEG. The precipitate was collected by centrifuging and washed twice with acetone and an aqueous solution, which contains a small amount of ether to break the polypseudorotaxane complex, in order to remove α-CD (2 times). The product was dried under in vacuo to give the **3** (0.92 g). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 1.56—2.06 (br, Adamantane region), 3.18—4.12 (br, C-2 H, C-3 H, C-4 H, C-5 H, C-6 H of α-CD, CH_2 of PEG), 4.54 (br, O-6 H of α-CD), 4.88 (br, C-1 H of α-CD), 5.54—5.93 (br, O-2 H, O-3 H of α-CD). Found: C, 44.81; H, 6.73; N, 0.17%. Calcd for $C_{654}H_{1116}N_2O_{497}(H_2O)_{30}$: C, 44.75; H, 6.78; N, 0.16%.

Preparation of 4. One ml (1.91×10^{-2} mol) of Br_2 was added dropwise to a stirred solution of **3** (1.0 g dried in vacuo at 80 °C over P_2O_5) and Ph_3P (5 g 1.91×10^{-2} mol, dried in vacuo). The mixture was stirred at 80 °C for 15 h, and its pH was adjusted to 9—10 by the addition of 3 M NaOMe in MeOH with external cooling. The solution was stirred for 30 min at room temperature, and then it was poured into ice water (500 ml). The precipitate was collected by filtration, washed by water and redissolved in DMF (50 ml) again. The product was precipitated by addition of MeOH to this solution, washed with MeOH and dried in vacuo to give **4** (0.48 g). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 1.56—1.83 (br, Adamantane region), 3.18—4.12 (br, C-2 H, C-3 H, C-4 H, C-5 H, C-6 H of α-CD, CH_2 of PEG), 5.01 (br, C-1 H of α-CD), 5.66—6.27 (br, O-2 H, O-3 H of α-CD). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 34.24 (br, C-6 of α-CD), 69.77 (br, PEG), 70.39 (br, C-2 of α-CD), 71.63 (br, C-5 of α-CD), 72.66 (C-3 of α-CD), 84.71 (C-4 of α-CD), 101.94 (C-1 of α-CD).

Preparation of 1. Sodium (30 mg, 1.30×10^{-3} mol) was dissolved in EtOH. This solution was added to a stirred solution of sodium 6-hydroxy-2-naphthalenesulfonate (350 mg 1.42×10^{-3} mol) in DMSO (100 ml). EtOH of this solution was removed by using rotary evaporator. And then a solution of **4** (100 mg) in a mixed solution of DMSO (50 ml) and hexamethylphosophoric triamide (HMPA) (3 ml) was added to this solution. The reaction mixture was refluxed at 80 °C for 2 h under Ar atmosphere with stirring. After being cooled, the resultant reaction mixture was poured into an excess amount of acetone with rapid stirring. The precipitate was filtered and placed in vacuo for 24 h. The precipitate was dissolved in a minimum volume of water and then chromatographed on a Sephadex G-25 size exclusion column (1.7×70 cm) using water as eluent. The desired product was eluted in the first 20—35 fractions (3 ml each). These fractions were combined, concentrated in vacuo and lyophilized to give the brown powder of **1** (73.2 mg). ^{1}H NMR (500 MHz, D_2O, 65 °C) δ = 1.40—2.20 (br, Adamantane region), 3.60—4.60 (br, C-2 H, C-3 H, C-4 H, C-5 H, C-6 H of α-CD, CH_2 of PEG), 3.38 (br, C-1 H of α-CD), 7.20—8.80 (br, naphthyl). ^{13}C NMR (100 MHz, D_2O, 20 °C) δ = 56.0—70.0 (adamantane region), 87.42 (br, C-6 of α-CD), 97.16 (br, PEG), 98.78 (br, C-2 of α-CD), 101.12 (br, C-5 of α-CD), 109.61 (C-3 of α-CD), 128.98 (C-4 of α-CD), 135.09 (C-1 of α-CD), 137—167 (br, naphthyl).

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