Energy Transfer in a Rotaxane with a Naphthalene-modified α-Cyclodextrin Threaded by Dansyl-terminal Poly(ethylene glycol)

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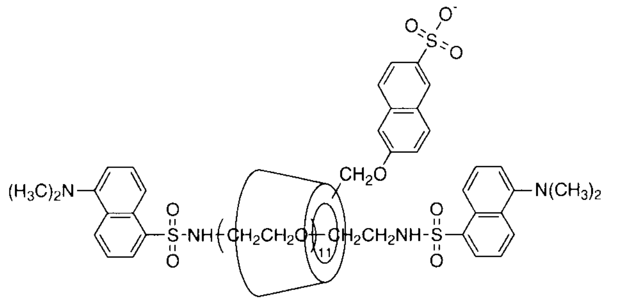
A rotaxane with a naphthalene-modified α-cyclodextrin penetrated by a dansyl-terminal poly(ethylene glycol) was prepared. In the rotaxane, singlet energy transfer occurs from the naphthalene moiety to the terminal dansyl units.

Rotaxanes are compounds with rings threaded by a linear molecular chain that has bulky units at both ends, and are members of supramolecular systems. Recently, a variety of rotaxanes composed of one or plural rings have been prepared.[1-5] However, rotaxanes with ability of particular functions are limited.[4,5] It is therefore important to construct rotaxanes which exhibit unique molecular functions. We have attempted to construct energy transfer systems with rotaxanes, and report here, for the first time, the energy transfer accomplished with a rotaxane (**1**) composed of α-cyclodextrin(α-CD) with a naphthyl moiety and dansyl-terminal poly(ethylene glycol).



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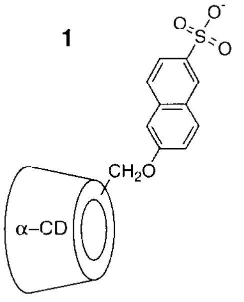

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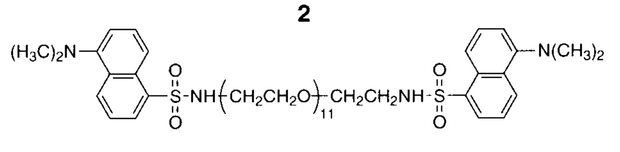

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Synthesis of **2** was performed by a reaction of sodium 6-hydroxy-2-naphthalenesulfonate and 6-O-(2-naphthalenesulfonyl)-α-CD in dimethylsulfoxide with sodium hydride.[6] The mixture of **2** (100 mg, 84.8 μmol) and ω,ω'-diamino-poly(ethylene glycol) (DP=12, 3.84 mg, 7.07 μmol), which had been prepared according to the procedure reported by Harada et al.,[7] was allowed to react with dansyl chloride in aqueous buffer solution at pH 9.5, and formed rotaxane **1** was separated and purified by column chromatography with Sephadex G-15 (yield 6.6%). Dansyl-terminal poly(ethylene glycol) (**3**) was also prepared by a reaction of ω,ω'-diamino-poly(ethylene glycol) and dansyl chloride. The identification of **1** was performed by ^{1}H-NMR (500-MHz).[8]

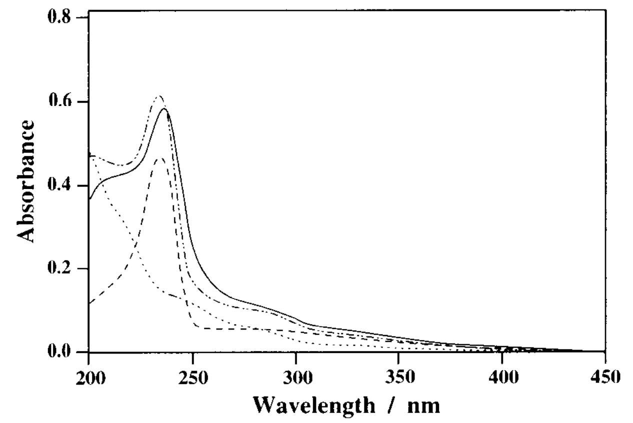


Figure 1. UV-vis absorption spectra of **1** (——), **2** (- - - -), **3** (······), and 1:1 mixture of **2** and **3** (–·–·–) at room temperature in H_2O. Concentrations of **1**, **2**, and **3** are 12 μmol dm^{-3}. The mixture contains 12 μmol dm^{-3} of each component.

Figure 1 shows absorption spectra of **1**, **2**, **3**, and 1:1 molar mixture of **2** and **3**. Compound **2** shows a peak at 234 nm, where **3** has no particular peak around the wavelength. Rotaxane **1** has a peak at 235 nm and the intensity and absorption pattern are almost the same as the 1:1 mixture of **2** and **3** although its peak position is slightly shifted to the longer wavelength from that of the mixture. The result suggests that in **1** one α-CD ring of **2** is penetrated by poly(ethylene glycol) with one dansyl moiety at each end of the polymer chain, being consistent with the ^{1}H-NMR data of **1**.

Figure 2 shows fluorescence spectra of **1**, **2**, **3**, and the 1:1 mixture of **2** and **3** measured with the excitation wavelength of 234 nm. Compound **2** and the 1:1 mixture of **2** and **3** exhibit almost the same spectra with a peak at 350 nm although the peak intensity is slightly weaker for the mixture than that for **2**. On the other hand, **1** exhibits remarkable decrease in the fluorescence intensity at 350 nm (73% decrease in comparison with the intensity of **2**) with emission in the longer wavelength region of dansyl fluorescence (>450 nm). This observation demonstrates that singlet energy transfer occurs from the naphthyl moiety to the terminal dansyl units in **1**. With regard to the energy transfer phenomenon,

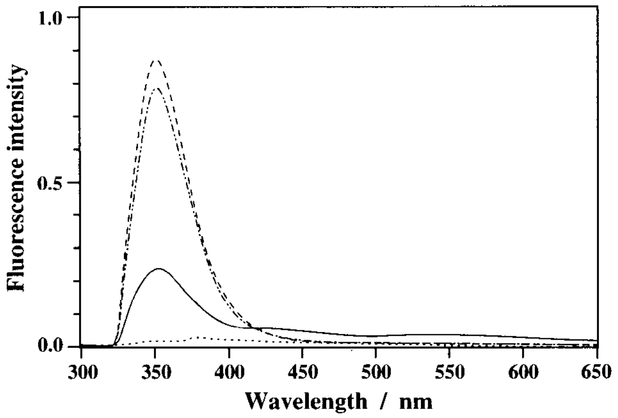
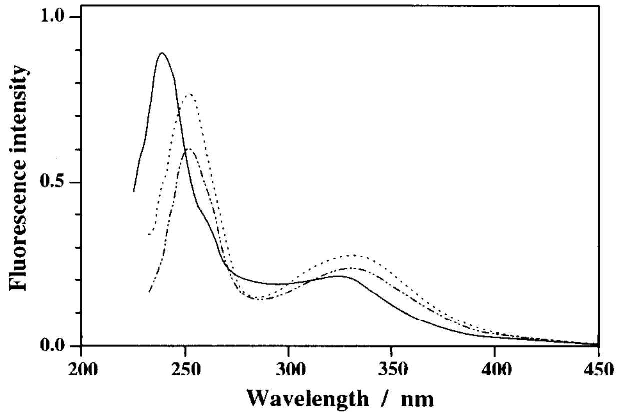


Figure 2. Fluorescence spectra of **1** (———), **2** (- - - - -), **3** (·······), and 1:1 mixture of **2** and **3** (–·–·–) at room temperature in H_2O. Concentrations of **1**, **2**, and **3** are 12 μmol dm^{-3}. The mixture of **2** and **3** contains 12 μmol dm^{-3} of each component. Excitation wavelegth is 234 nm.



Fugure 3. Fluorescence excitation spectra of **1** (———), **3** (·······), and 1:1 mixture of **2** and **3** (–·–·–) at room temperature in H_2O. Concentrations of **1** and **3** are 12 μmol dm^{-3}. The mitxture of **2** and **3** contains 12 μmol dm^{-3} of each component. Emission wavelength is 570 nm.

we also measured excitation spectra of **1**, **3**, and the 1:1 mixture of **2** and **3** with the emission wavelength of 570 nm. Similar excitation spectra were observed for **3** and the 1:1 mixture although the fluorescence intensity of the mixture at 252 nm is 18% smaller than that of **3** due to the fact that the excitation light is partly absorbed by **2**. The remarkable feature of the excitation spectra is that the peak wavelength of **1** is shifted from 252 nm of **3** and the 1:1 mixture of **2** and **3** to 238 nm, which corresponds to the absorption wavelength of the naphthyl moiety of **2**. This observation confirms again that energy transfer occurs from the naphthyl moiety to the dansyl units in **1**.

Table 1 shows the lifetimes of **1**, **2** and **3**. The two lifetimes 5.7 ns and 10.4 ns of **2** suggest that the naphthyl moiety is located in two different environments. In the longer lifetime species, the naphthyl moiety may interact with the mouth of the hydrophobic cavity while in the shorter lifetime species the naphthyl moiety may be located in the bulk water environment apart from the CD unit. It is interesting that **3** has two lifetimes 3.8 ns and 13.0 ns in spite of the fact that the two dansyl moieties are located at both ends of one linear chain. It might reflect that poly(ethylene glycol) takes a folded conformation in which the dansyl is involved in the hydrophobic region of the folded chain or exposed to bulk water outside of the folded structure. On the other hand, rotaxane **1** exhibits four lifetimes 0.9, 3.6, 7.1, and 13.1 ns. Among them, 3.6 ns and 13.1 ns may be attributed to the lifetimes of the dansyl moiety. On this basis, we may attribute other lifetime species to those of the naphthyl unit quenched by energy transfer to the dansyl units. If 0.9 ns and 7.1 ns are lifetimes shortened by the energy transfer from 5.7 ns and 10.4 ns of **2**, respectively, the corresponding energy transfer efficiencies are ca. 80% and ca. 30%. These two cases might be related to the different locations of the CD ring in **1**.

Table 1. Fluorescence decay parameters of **1**, **2** and **3** in H2O at 25 ℃^{a}

1		**2**		**3**	
lifetime (ns)	fraction (%)	lifetime (ns)	fraction (%)	lifetime (ns)	fraction (%)
0.9	48.1	5.7	53.8	3.8	44.4
3.6	21.5	10.4	46.2	13.0	55.6
7.1	20.1				
13.1	10.3				
χ^2=1.04		χ^2=1.09		χ^2=1.10	

^{a}Concentrations of **1**, **2** and **3** are 12 μmol dm^{-3}. λ_{ex}=276 nm; $\lambda_{em} \geqq$320 nm.

The study on the construction of supramolecular systems, in which energy transfer occurs from many antenna chromophores to terminal chromophores, is now under way.

References and Notes

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6 ^{1}H-NMR (500 MHz, D_2O) δ 3.40-4.00 (br), 4.20 (dd, 1H, J=9.8, 4.5 Hz), 4.46 (dd, 1H, J=9.8, 4.5 Hz), 4.80-5.10 (m, 6H), 7.30 (dd, 1H, J=4.5, 1.3 Hz), 7.39 (s, 1H), 7.75 (dd, 1H, J=4.5, 1.3 Hz), 7.88 (d, 1H, J=4.5 Hz), 7.95 (d, 1H, 4.5 Hz), 8.25 (s, 1H). MALDI-TOF-MS m/z 1177 [M + Na]$^+$; TLC Rf=0.41 (BuOH, MeOH, H_2O 5:4:3). A related compound was previously prepared: M. Nowakowska, V. P. Foyle, and J. E. Guillet, *J. Am. Chem. Soc.*, **115**, 5975 (1993).
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8 ^{1}H-NMR (500 MHz, D_2O): δ 2.61 (br, 6Hx2, CH_3 of Dansyl), 3.30-4.50 (m, 36H, C-2 H, C-3 H, C-4 H, C-5 H, C-6 H of α-CD; 4Hx12, CH2 of poly(ethylene glycol)), 4.80-5.10 (m, 6H, C-1 H of α-CD), 7.00-8.50 (m, 6H, Naphthyl; m, 6Hx2, Dansyl).