Synthesis and Photophysics of a Water-Soluble, Naphthalene-Containing β-Cyclodextrin

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Abstract: A water-soluble, naphthalene-containing β-cyclodextrin has been synthesized by reaction of 6-hydroxy-2-naphthalene sulfonic acid (disodium salt) with heptakis(6-bromo-6-deoxy)-β-cyclodextrin. Lifetime, fluorescence polarization, and solvent studies show the presence of mainly monomer fluorescence emission with a small amount of excimer. They also show that energy migration occurs. Quenching studies show that singlet energy transfer from the naphthalene substituents to a suitably included acceptor molecule can occur.

Introduction

The synthesis of several "antenna" polymers has been reported.[1-4] These polymers contain various hydrophobic and hydrophilic groups which cause the polymers to adopt a pseudomicellar conformation in dilute aqueous solution. Such conformations result in a preferential solubilization of large hydrophobic molecules which can then act as energy traps. The antenna properties of these polymers result in catalytic effects for the photoreaction[5] and photodecomposition[6] of such solubilized molecules with considerable product selectivity. However, the exact location of these solubilized hydrophobic molecules in the photozymes is still unknown. Thus, if a system which contained well-defined hydrophobic cavities could be synthesized, a better understanding of the catalytic mechanism would be obtained. Furthermore, these systems might show improved selectivity of substrate inclusion. Before this can be achieved, a suitable hydrophobic cavity must be found and tested to see if it has the capability of performing the desired functions of including hydrophobic molecules and allowing energy transfer to occur to an included probe molecule. The present study reports the synthesis of a model compound known to have a hydrophobic cavity and the possibility of exhibiting energy transfer to a suitably included probe molecule.

Cyclodextrins are large molecules consisting of either six, seven, or eight glucose units in a circular arrangement. This results in the formation of a hydrophobic cavity which has a width of 6–10 Å and a depth of 7.8 Å.[7] Cyclodextrins have the well-known ability to act as hosts by including various molecules in this hydrophobic cavity. Thus, a cyclodextrin derivatized with suitable light-absorbing groups would serve as a useful test model. There are many cyclodextrin derivatives,[8] but only a few are photoactive. These include derivatives with benzophenone,[9] rose bengal,[10] porphyrin,[11] and anthraquinone[12] moieties which allow triplet energy transfer, singlet oxygen production, photoreduction, and photooxidation to occur.

Thus, this paper deals with the synthesis and photophysics of a novel water-soluble, naphthalene-containing derivative of β-cyclodextrin.

Experimental Section

β-Cyclodextrin (Aldrich) was recrystallized twice from water and dried under vacuum at 100 °C for 24 h. 2-Naphthol (Aldrich) was recrystallized from methanol and further purified by sublimation. 6-(*p*-Toluidino)-2-naphthalenesulfonic acid (potassium salt) (TNS, Aldrich) was purified by two recrystallizations from water. 2-Aminopyridine (BDH) was recrystallized from Spectro Grade cyclohexane. Anhydrous dimethyl sulfoxide (DMSO, Aldrich), acetone (Caledon, Spectro Grade), methanol (Caledon, Spectro Grade), nitromethane (Fisher, ASC reagent grade), and methyl iodide (Fisher, 99.8%) were used without further purification. Distilled water was passed through a Millipore water purification system prior to use.

^{1}H-NMR and ^{13}C-NMR spectra were obtained by using a Varian Gemini-200 spectrometer. UV/vis spectra were measured by using a Hewlett-Packard 8451A diode-array spectrophotometer. Steady-state fluorescence emission spectra were recorded at room temperature on a SLM 4800S fluorescence spectrophotometer. All fluorescence spectra are uncorrected. For solutions having an absorbance greater than 0.5, front-faced measurements were made. For energy transfer studies, the excitation wavelength was chosen such that most of the incident light was absorbed by the donor species. Quantum yields were determined by integration of the fluorescence peak areas[13] using 2-aminopyridine in 0.1 N H_2SO_4 (ϕ = 0.60, λ_{ex} = 284 nm, 25 °C) as a reference standard.[14] Fluorescence decay curves were measured using a single-photon counting apparatus using monochromators to isolate the excitation and emission wavelengths with the samples being degassed with argon for 20 min prior to measurement.

Polarization measurements were made using a SLM 4800S fluorescence spectrophotometer with 10-mm Glan–Thompson calcite prism polarizers. The samples for fluorescence polarization measurements were prepared by introducing microliter quantities of the required stock solutions into 10 mL of propylene glycol. The samples were placed in a quartz cell, and the fluorescence intensity reading was averaged over 30 s. The samples were cooled by suspending them in a dry ice/acetone bath and then dipping them in liquid N_2 prior to measurement. The cell holder was cooled by circulating water at 0 °C.

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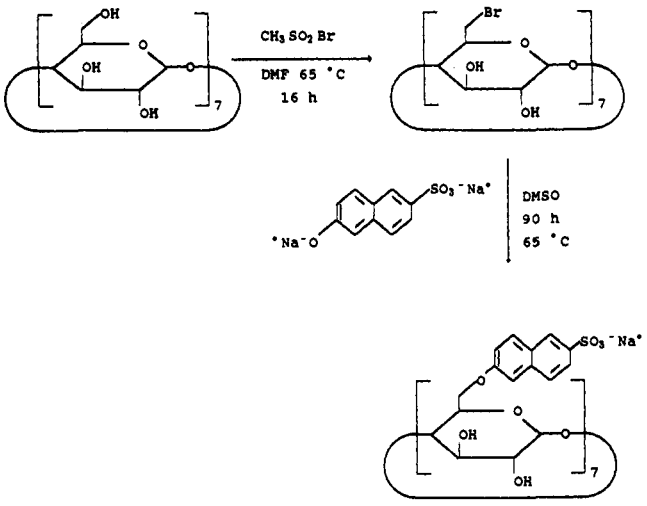
Scheme I



Heptakis-6-*O*-(2-sulfonato-6-naphthyl-β-cyclodextrin, Heptasodium Salt (1). Heptakis(6-bromo-6-deoxy)-β-cyclodextrin[15] (9.25 g, 5.87 mmol) and 6-hydroxy-2-naphthalenesulfonic acid[16] (HNSA, disodium salt, 22.0 g, 82.2 mmol) were dissolved in 60 mL of DMSO. The reaction mixture was kept at 65 °C for 90 h under nitrogen. After being cooled, the resultant reaction mixture was poured into excess acetone with rapid stirring. The light-brown precipitate was filtered and placed under vacuum for 24 h. The precipitate, which had now become a dark-brown viscous syrup, was dissolved in a minimum volume of water. Aliquots of this solution were then chromatographed on a Sephadex G-10 size exclusion column (65 cm × 2.5 cm) using water as an eluent. The desired product was eluted in the first 15–25 fractions (6-mL each). These fractions were combined, concentrated under vacuum, and precipitated out by addition to excess acetone.

The precipitate was filtered and dried under vacuum. The chromatographic process was then repeated. The precipitate was again dissolved in water, precipitated out in acetone, filtered, washed with chloroform, and dried at 60 °C for 24 h to yield the final product (10.25 g, 64%): mp 252–258 °C dec; ^{13}C NMR (D_2O) δ 160.0, 140.8, 137.8, 133.6, 130.4, 130.2, 128.3, 125.9, 121.6, 109.9, 105.1, 84.8, 75.7, 74.7, 73.7, 69.8; ^{1}H NMR (D_2O) δ 8.166–6.34 (m, 6 H), 4.98 (s, 1 H), 4.05–3.98 (m, 3 H), 3.61 (br s, 3 H); UV (H_2O) λ (log ε) 280 (4.53), 314 (3.84), 328 nm (3.77). Anal. Calcd for $C_{112}H_{105}O_{56}Na_7S_7 \cdot 5H_2O$: C, 47.67; H, 4.11; O, 34.58; S, 7.95. Found: C, 47.54; H, 4.50; O, 34.05; S, 7.51.

Sodium 6-Methoxy-2-naphthalenesulfonate (MNSS). MNSS was synthesized in a manner similar to that used by Kornblum et al.[17] HNSA (disodium salt, 1.0 g, 3.73 mmol) was dissolved in 20 mL of anhydrous DMSO. Methyl iodide (4 mL, 64.3 mmol) was added at a rate slow enough to ensure that the temperature did not rise above 30 °C. The reaction mixture was then stirred for an additional 15 min at room temperature. The reaction mixture was added to 100 mL of acetone to precipitate the desired product. The white precipitate was filtered, washed thoroughly with acetone and then ether, and finally dried under vacuum (0.74 g, 80%): mp >300 °C; ^{1}H NMR (D_2O) δ 8.22 (s, 1 H), 7.79 (m, 3 H), 7.15 (m, 2 H); ^{13}C NMR (D_2O) δ 161.7, 140.7, 138.7, 133.8, 131.1, 130.7, 128.6, 125.7, 122.6, 109.4, 58.4; UV (H_2O) λ (log ε) 278 (3.640), 312 (2.951), 328 nm (2.869).

Results and Discussion

Synthesis. Compound **1** was prepared by nucleophilic substitution of bromide by HNSA (disodium salt) (Scheme I). Since the oxy anion is a stronger nucleophile than the sulfonate group, linkage of sodium 6-hydroxy-2-naphthalenesulfonate (HNSS) to β-cyclodextrin was expected via an ether group and thus the reaction was allowed to proceed for 90 h to ensure that this was the case. Integration of the ^{1}H NMR shows a 7:1 ratio between naphthalenesulfonate and β-cyclodextrin while the ^{13}C-NMR spectrum shows a complete disappearance of the C6–Br peak (34.6 ppm) and the appearance of a peak at 69.8 ppm which is indicative of substitution at C6. The UV spectrum of **1** is virtually identical to that of sodium 6-hydroxy-2-naphthalenesulfonate, indicating that attachment to the cyclodextrin ring has little affect on the naphthalenesulfonate chromophore.[18]

Compound **1** was soluble in H_2O and DMSO while insoluble in solvents such as methanol, DMF, and pyridine.

Photophysics. Sodium 6-methoxy-2-naphthalenesulfonate (MNSS) rather than HNSS was used as a model compound for lifetime measurements since the pK_a of the hydroxy group changes from 9.1 to 1.6[19] upon excitation in aqueous solution. Therefore, the predominant excited species at neutral pH is the ionized form which has an emission maximum at 430 nm.

The decay curve for model compound MNSS was found to be single-exponential with lifetime $\tau = 9.0$ ns. In contrast, solutions of **1** in water or mixtures of water and THF required a sum of three exponential decays to give a satisfactory fit (Table I).

Due to the proximity (~7 Å) of the naphthalenesulfonate moieties on cyclodextrin, some excimer formation is expected, although the emission spectrum of **1** in pure water shows very little difference from that of MNSS. Excimer formation can be identified as having a lifetime longer than that of the individual chromophores[4,20] and red-shifted with respect to normal fluorescence emission.[21]

The steady-state fluorescence spectrum of **1** (Figure 1) shows that there is a small amount of a longer-wavelength component (λ_{max} = 400 nm) in the fluorescence spectrum of **1** compared to that of MNSS, which we attribute to that of the excimer. The low-excimer probability in **1** can be explained by the mutual

Table I. Fluorescence Decay Parameters[a] for **1** (2.3 × 10^{-6} M) and Sodium 6-Methoxy-2-naphthalenesulfonate (3.0 × 10^{-6} M)

1, H_2O		1, 90% THF		MNSS, H_2O	
lifetime (ns)	fraction (%)	lifetime (ns)	fraction (%)	lifetime (ns)	fraction (%)
3.7	12.2	2.0	18.3	9.0	100
9.8	77.6	9.2	54.4		
23.2	9.9	19.0	27.3		
χ^2 = 1.14		χ^2 = 1.08		χ^2 = 1.17	

[a] λ_{ex} = 280 nm; λ_{em} = 355 nm.

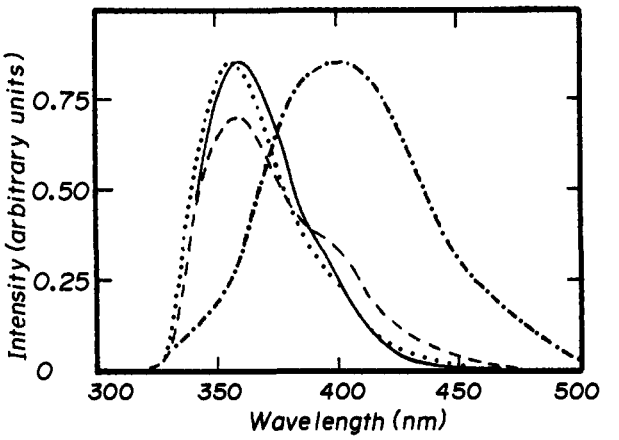


Figure 1. Fluorescence emission spectra: (···) sodium 6-methoxy-2-naphthalenesulfonate, 4.0 × 10^{-5} M (H_2O); (—) **1**, 4.0 × 10^{-6} M (H_2O); (- - -) **1**, 4.0 × 10^{-6} M (90:10 THF/H_2O); and (-·-) partially sulfonated poly(2-vinylnaphthalene).

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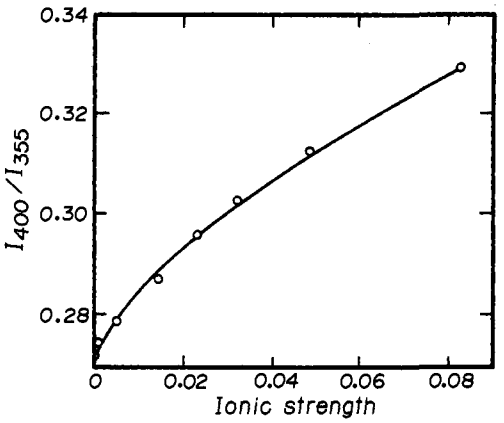

Figure 2. I_{400}/I_{355} ratio of **1** (2.8×10^{-6} M) as a function of the ionic strength of the solution. λ_{ex} = 280 nm.

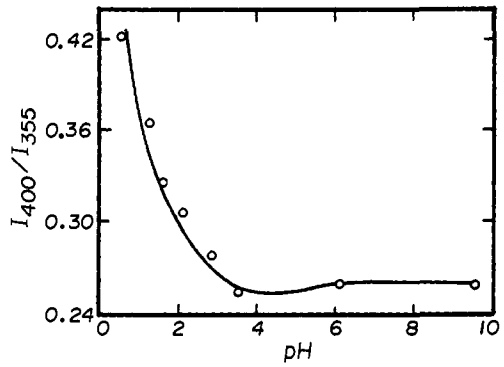

Figure 3. I_{400}/I_{355} ratio of **1** (1×10^{-6} M) as a function of pH. λ_{ex} = 280 nm.

repulsion of the negatively charged sulfonate groups attached to the cyclodextrin ring. By contrast, the emission spectrum of partially sulfonated poly(vinylnaphthalene) shows only excimer emission[22] (Figure 1, curve d). In the latter case, it is the hydrophobic, unsulfonated naphthalene groups which form the excimer traps.

In 90% THF/H_2O, the dielectric constant of the medium is much lower, leading to a reduction in the repulsive charge interactions between naphthalenesulfonate groups, thereby increasing the probability of formation of an excimer site. In keeping with the mechanisms which are generally accepted for polymer photophysics, we attribute the short lifetime species (τ = 2–4 ns) to naphthalene moieties quenched by energy migration to either emitting or nonemitting excimers. The major species in both cases for **1** has a normal fluorescence with $\tau \cong 9$ ns and an emitting excimer at τ = 19–23 ns.

Increasing the ionic strength of an aqueous solution of **1** would be expected to decrease the electrostatic repulsion between the naphthalenesulfonate units due to partial charge neutralization from the counterions. The expected increase in excimer emission is shown in Figure 2 where the ratio of the fluorescence emission at 400 nm (excimer) to that of normal fluorescence at λ_{355} is plotted as a function of ionic strength. Similar results are obtained by reducing the pH.

The naphthalenesulfonic acid group has a pK_a of 0.57,[23] and thus, if the solution pH is decreased, the degree of ionization of the sulfonate groups can be changed, thereby reducing the repulsive interactions between naphthalenesulfonate groups and increasing the probability of forming an excimer site.

Figure 3 shows that the ratio I_{400}/I_{355} is essentially the same for the pH range 9.5–3.5 but on further decreasing of the pH, the I_{400}/I_{355} ratio increases, thereby demonstrating increased excimer formation.

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Table II. Fluorescence Depolarization Measurements[a] for **1** (1×10^{-6} M) and Sodium 6-Methoxy-2-naphthalenesulfonate (2×10^{-6} M) at Two Different Temperatures

sample	T (°C)	P	sample	T (°C)	P
1	32.2	0.029	**1**	−70	0.055
MNSS	32.2	0.014	MNSS	−70	0.281

[a] λ_{ex} = 280 nm; λ_{em} = 340 nm.

Due to the closeness of the naphthalenesulfonate moieties, energy migration can also be expected. Fluorescence depolarization studies in glassy matrices have been shown to be a useful method to confirm energy migration.[24] The relative orientations of the absorption and emission dipoles of a chromophore are fixed in a rigid medium, and thus the emission will retain memory of the excitation polarization. The degree of polarization P is defined as[25]

$$P = (I_{\parallel} - GI_{\perp})/(I_{\parallel} + GI_{\perp}) \quad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ are 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 absorption and emission will not involve the same chromophore and so retention of polarization will be lost, thereby resulting in a value of P closer to zero. Fluorescence depolarization measurements were made to confirm this (Table II). The depolarization measurements were determined at 340 nm to ensure that there was no contamination of the monomer fluorescence by excimer fluorescence which is usually depolarized.

Under the conditions used (propylene glycol, −70 °C), the fluorophores should remain stationary during the lifetime of the excited state,[25] thereby effectively removing any depolarization effects due to fluorophore motion. One would expect the polarization values for MNSS to be similar to that of **1** in the absence of energy migration. However, if energy migration within **1** occurs, then the polarization value would be significantly smaller. From Table II, it can be seen that for MNSS, the degree of polarization increased dramatically on cooling to −70 °C, thereby showing the removal of depolarization effects due to molecular rotation. For **1**, however, cooling to −70 °C results in a slight increase in the degree of depolarization, as would be expected for the removal of fluorophore motion. It is clear that with the fluorophore motion having been eliminated, the degree of depolarization of **1** is significantly smaller than that for MNSS. Since the fluorophores are immobile during the fluorescence lifetime, depolarization as a result of excimer formation and dissociation can be excluded and thus, the depolarization of the fluorescence is attributed to energy migration between the naphthalenesulfonate moieties.

Quenching Studies. Quenching studies using nitromethane were performed to see if we could determine whether any of the naphthalenesulfonate moieties were included in the cyclodextrin cavity. Nitromethane quenches excited states by an electron-transfer process which requires the close approach of both species involved.[26] Inclusion of a probe molecule by β-cyclodextrin can result in protection of the probe molecule from the quencher and thus bring about a significant decrease in the bimolecular quenching rate constant, as was shown by Hashimoto and Thomas.[26] In general, a linear Stern–Volmer plot is indicative of a single class of fluorophores, all of which are equally accessible to the quencher. If two classes of fluorophores are present, one

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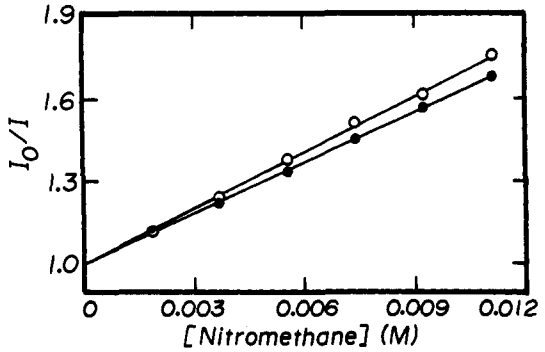

Figure 4. Stern–Volmer plot for quenching of (○) MNSS and (●) **1** by nitromethane. λ_{ex} = 300 nm; λ_{em} = 355 nm.

of which is not equally accessible to the quencher, then the Stern–Volmer plot is expected to deviate from linearity.[25] Thus, if any of the naphthalenesulfonate moieties were included in the cyclodextrin cavity, a decrease in the bimolecular quenching rate constant would be expected, as well as a deviation from linearity of the Stern–Volmer plot.

Fluorescence quenching of **1** by nitromethane was analyzed using the Stern–Volmer equation[20]

$$I_0/I = 1 + K_q\tau[Q] \qquad (2)$$

where I_0 is the fluorescence intensity in the absence of quencher, I is the fluorescence intensity in the presence of quencher, K_q is the bimolecular quenching constant, τ is the lifetime of the fluorophore monomer in the absence of quencher, and [Q] is the quencher concentration used.

Figure 4 shows that Stern–Volmer plots for **1** and MNSS are both straight lines (correlation coefficient = 0.9995 and 0.9997, respectively) showing that there is only one class of fluorophores in each case.

Bimolecular quenching rate constants of 6.2×10^9 and 7.4×10^9 M^{-1} s^{-1} were obtained for **1** and MNSS, respectively. The slightly lower value of the quenching constant obtained for **1** is not totally unexpected since (a) the approach of the nitromethane and naphthalenesulfonate moieties in **1** is hindered by the presence of the β-cyclodextrin ring whereas there is no hindrance in approach for MNSS and nitromethane molecules, and (b) the larger size of **1** compared to that of MNSS results in a smaller diffusion coefficient and thus a slower rate of diffusion.[21] Thus, it can be concluded that all the naphthalenesulfonate groups are exterior to the cavity.

In order to determine whether energy transfer to an included molecule is possible, we performed fluorescence studies using 6-(*p*-toluidino)-2-naphthalenesulfonic acid (TNS) as a probe molecule. TNS has minimal fluorescence emission in water, but in less polar solvents or environments, its fluorescence emission is greatly enhanced.[27]

TNS is known to be included into the β-cyclodextrin cavity with great enhancement of its fluorescence emission.[13,28] Comparison of the TNS absorption spectrum and fluorescence spectrum of **1** (Figure 5) showed that there is significant spectral overlap and thus the possibility of long-range energy transfer by the Förster mechanism is expected.

The radius of interaction R_0 between naphthalenesulfonate moieties and TNS can be obtained by the Förster equation[21,29]

$$R_0^6 = \frac{(8.8 \times 10^{-25})\kappa^2\phi_D}{n^4}\int_0^\infty F_D(\bar{\nu})\,\epsilon_A(\bar{\nu})\,(d\bar{\nu}/\bar{\nu}^4) \qquad (3)$$

where ϵ_A is the extinction coefficient of the acceptor, F_D is the relative fluorescence intensity of the donor at $\bar{\nu}$ satisfying

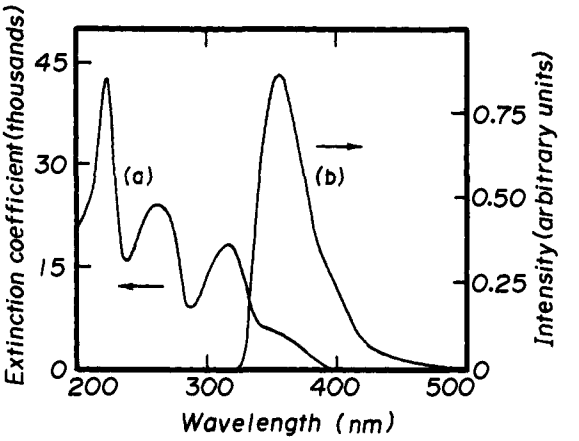

Figure 5. Comparison of the UV absorption spectrum of TNS and the fluorescence emission of **1**.

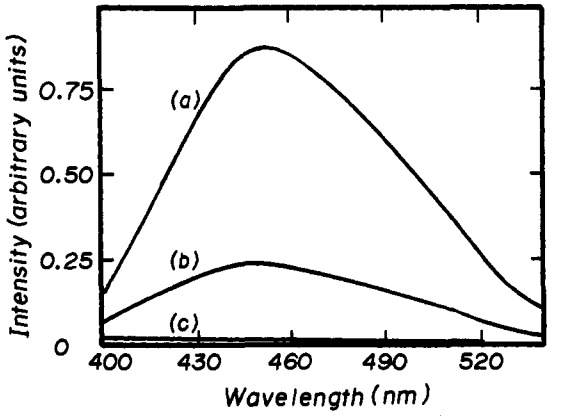

Figure 6. Fluorescence emission spectra: (a) TNS (6×10^{-5} M) and **1** (7.9×10^{-4} M); (b) TNS (1×10^{-5} M) and **1** (7.9×10^{-4} M); and (c) TNS (6×10^{-5} M). λ_{ex} = 366 nm.

$\int_0^\infty F_D(\bar{\nu})\,d\bar{\nu} = 1$, $\int_0^\infty F_D(\bar{\nu})\,\epsilon_A(\bar{\nu})\,d\bar{\nu}$ is the overlap integral between the emission profile of the donor and the absorption spectrum of the acceptor, ϕ_D is the fluorescence quantum yield of the donor in the absence of the acceptor, n is the refractive index of the solvent, and κ^2 is the molecular orientation factor. If the molecular transition dipole moments are averaged over a random distribution of orientations, κ^2 takes a value of two-thirds. A value of 1.33 was used for the refractive index. Since the fluorescence spectrum of **1** is always contaminated with excimer emission, the fluorescence quantum yield of MNSS was measured and used for ϕ_D. The measured fluorescence quantum yield of MNSS was 0.20 ± 0.01. Using the information above, we obtained a critical radius of 25.0 Å for the interaction of naphthalenesulfonate moieties and TNS. This shows that energy transfer by the Förster mechanism from the naphthalenesulfonate moieties to an included TNS molecule is possible.

The fluorescence emission from TNS in water is minimal while the presence of **1** results in a dramatic enhancement of the TNS fluorescence emission (Figure 6), thereby indicating that TNS was included into the hydrophobic cavity. Thus, if energy transfer occurs from the naphthalenesulfonate moieties to TNS not included in the cavity, the fluorescence emission from TNS will be minimal whereas energy transfer to an included TNS molecule will result in significant fluorescence emission from the included TNS.

Fluorescence emission for a **1**/TNS system with the naphthalenesulfonate moieties being excited directly (less than 9% of the incident light is absorbed by included TNS) is shown in Figure 7. There is a decrease in the fluorescence emission of **1** in the presence of TNS while there is an increase in the fluorescence emission in the 440–470-nm region. Subtraction of the normalized

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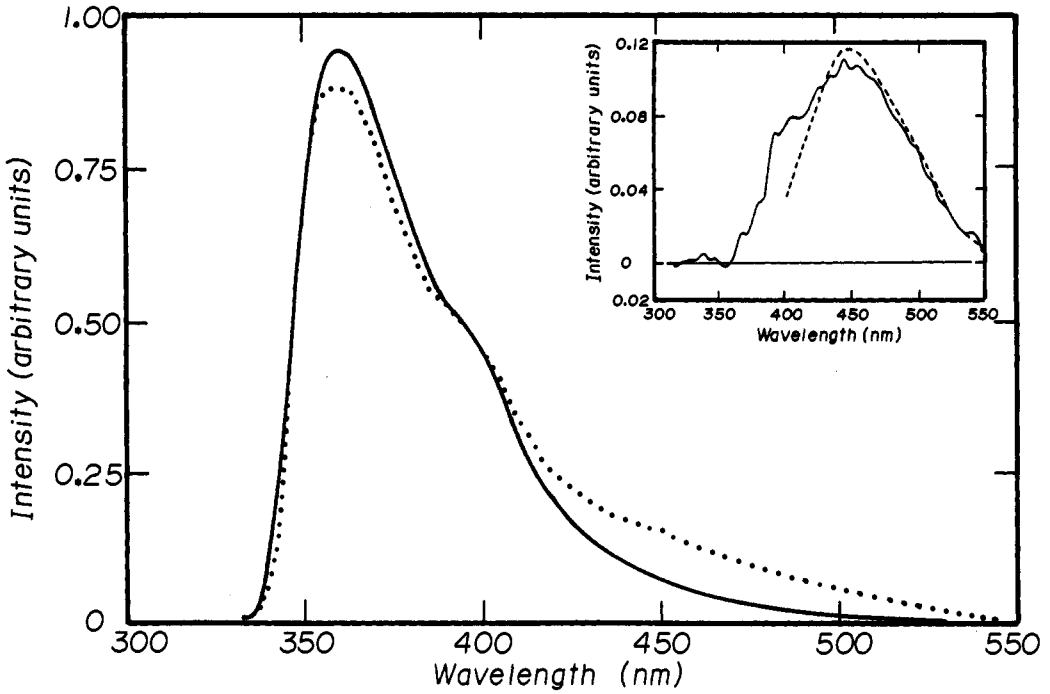

Figure 7. Fluorescence emission spectra: (—) **1** (7.9×10^{-4} M) and (···) **1** (7.9×10^{-4} M) and TNS (1×10^{-5} M). $\lambda_{ex} = 288$ nm. Inset: (—) fluorescence emission obtained from the difference of the normalized spectra of **1** in the presence and absence of TNS and (- - -) typical fluorescence emission spectrum of TNS.

fluorescence spectra of **1** in the presence and absence of TNS (inset) shows that the increased fluorescence in the 440–470-nm region is the same as that for TNS. Thus, this shows that energy transfer from the naphthalenesulfonate moieties to the included probe molecule is occurring.

Conclusion

A water-soluble, naphthalene-containing β-cyclodextrin derivative has been successfully synthesized. Incorporation of the anionic sulfonate groups results in the mutual repulsion of the naphthalene moieties, and thus, this derivative mainly exhibits monomer emission with little energy loss due to excimer emission. Fluorescence depolarization measurements demonstrated that energy migration occurs among the naphthalenesulfonate groups.

Quenching studies showed that the naphthalenesulfonate groups are not included in the cavity, and thus, the inclusion of a guest molecule will not be hindered by any already occupied cavity. Studies using TNS as a probe molecule showed that **1** has the capability of complexing a probe molecule in its cavity and that energy transfer from its naphthalenesulfonate groups to the included molecule is possible. Thus, this derivative has the requirements for use as a hydrophobic cavity component for a photozyme. Methods for incorporation of such cavities into polymeric systems are currently under development. The cyclodextrin derivative by itself may have potential use as a photocatalyst for certain photochemical reactions.

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