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Journal of Photochemistry and Photobiology A: Chemistry 179 (2006) 13–19
Journal of Photochemistry and Photobiology A:Chemistry
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Spectroscopic study on the interaction of cyclodextrins with naphthyl groups attached to poly(acrylamide) backbone

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Received 24 February 2005; received in revised form 29 March 2005; accepted 17 April 2005
Available online 4 June 2005

Abstract

The interaction of β-cyclodextrin (β-CD) with (1-naphthyl)methyl (1Np) and (2-naphthyl)methyl (2Np) groups attached to the poly(acrylamide) backbone was investigated by several techniques, including steady-state fluorescence and circular dichroism (cd) spectroscopies. When β-CD was added to polymer aqueous solutions, the fluorescence intensity increased remarkably, indicative of the formation of inclusion complexes of β-CD with polymer-carrying Np groups. Comparison of these fluorescence data with those for the guest model compounds, (1-naphthyl)methanol and (2-naphthyl)methanol (2NpMeOH), indicated that, upon complex formation, the polymer main chain effectively protects Np groups of the singlet excited state from the contact of water molecules. Using steady-state fluorescence data at varying concentrations of β-CD, association constants (K) were determined to be $(1.1 \pm 0.3) \times 10^2$ and $(2.0 \pm 0.4) \times 10^2$ M^{-1} for the complex formation of β-CD with polymer-carrying 1Np and 2Np groups, respectively. The structures of inclusion complexes of β-CD with Np groups were investigated by cd spectroscopy for the polymers and the model compounds in the presence of β-CD and by X-ray crystallographic analysis for the inclusion complex of β-CD with 2NpMeOH. These data indicated that β-CD included polymer-carrying 1Np groups shallowly, but it included polymer-carrying 2Np groups deeply to form inclusion complexes, in which the longer axis of the 2Np group is rather parallel to the rotation axis of β-CD. On the basis of these data, plausible structures of the inclusion complex of β-CD with polymer-carrying 2Np groups were proposed.

Keywords: Cyclodextrin; Steady-state fluorescence spectroscopy; Circular dichroisum spectroscopy; Naphthyl group; Poly(acrylamide)

1. Introduction

Macromolecules are identified by other molecules through recognition of their main chains and side chains. In biological systems, recognition of side chains plays an important role in constructing supramolecular structures which express various functions necessary to maintain living activities [1]. For example, anitigens are identified by antibodies through recognition of their side chains [2].

We have been aware of the importance of polymer side chains in the macromolecular recognition in biological systems, and thus studying in detail on the interaction of cyclodextrins (CDs) with several guest moieties attached to water-soluble polymers as model systems for the macromolecular recognition in biological systems [3,4]. In our previous study, we investigated the interaction of CDs with alkyl side chains attached to the poly(acrylamide) backbone by NMR spectroscopy [3]. We have found that CDs interact selectively with alkyl side chains of a size and shape matching their cavities and that the selectivity of CDs is higher for polymer-carrying alkyl groups than for low-molecular-weight model compounds. This may be because

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doi:10.1016/j.jphotochem.2005.04.026

CDs include polymer-carrying alkyl side chains from one direction restricted by the polymer main chain.

As an extension of our research on the recognition of polymer side chains by CDs, we have chosen naphthyl groups as guest moieties. Since naphthyl groups absorb UV light and emit fluorescence, it is possible not only to determine association constants for the formation of inclusion complexes but also to investigate the structure of inclusion complexes by spectroscopic techniques. In this study, we investigate the interaction of CDs with (1-naphthyl)methyl (1Np) and (2-naphthyl)methyl (2Np) groups attached to the poly(acrylamide) backbone by several techniques, including steady-state fluorescence and circular dichroism spectroscopies. Since our preliminary study indicated that either α-CD or γ-CD did not interact considerably with polymer-carrying Np groups, we are focusing on the interaction of β-CD in the present paper.

2. Experimental

2.1. Materials

(1-Naphthyl)methanol (1NpMeOH) and (2-naphthyl) methanol (2NpMeOH) (Nacalai Tesque) were purified by recrystallization in methanol. Acrylamide (AAm) (Wako) was purified by recrystallization from ethyl acetate. *N*,*N*-dimethylformamide (DMF) used as a solvent for polymerization was dried with calcium hydride, and purified by distillation under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) (Wako) was recrystallized from methanol, and β-cyclodextrin (β-CD) was purified by recrystallization from water. Milli-Q water was used for all measurements. Other reagents were used without further purification.

The monomers used in this study, (1-naphtyl)methyl acrylate (1NpA) and (2-naphtyl)methyl acrylate (2NpA), were prepared from acryloyl chloride and the corresponding alcohols, respectively. Both the monomers were fully characterized by ^{1}H NMR spectroscopy and elemental analysis [5].

2.2. Polymerization

Typical procedure for radical polymerization is described below.

AAm (1.1 g, 15.4 mmol), 2NpA (55 mg, 0.26 mmol), and AIBN (13 mg, 0.08 mmol) were dissolved in DMF (30 mL) under an argon atmosphere. The solution was warmed with an oil-bath thermostated at 60 °C. After 24 h, methanol (ca. 300 mL) was poured into the mixture to obtain copolymer of AAm and 2NpA as precipitate. The polymer obtained was purified by reprecipitation from a DMF solution into excess methanol, and was dried in vacuo: yield 0.84 g, 72%. ^{1}H NMR (270 MHz, D_2O): δ 1.3–1.8 (methylene protons in the polymer main chain), 2.0–2.4 (methine protons in the polymer main chain), 5.1–5.4 (methylene protons in the 2NpA unit), 7.3–7.6 (aromatic protons), 7.7–8.0 (aromatic protons).

2.3. Measurements

2.3.1. Gel permeation chromatography (GPC)

GPC measurements were performed at 40 °C with a JASCO GPC-900 system equipped with a Shodex OHpak SB-806M HQ column in combination with JASCO UV-975 and RI-930 detectors. A mixed solvent of water and DMF (7/3, v/v) containing 0.050 M LiBr was used as an eluent with an elution rate of 1.0 mL/min. The molecular weights were calibrated with standard poly(ethylene glycol) and poly(ethylene oxide) samples (Science Polymer Products, Inc.).

2.3.2. Absorption spectroscopy

Absorption spectra were recorded on a Shimadzu UV-2500PC spectrophotometer using a 1.0 cm path length quartz cuvette.

2.3.3. Steady-state fluorescence

Steady-state fluorescence spectra were measured on a Hitachi F-2500 fluorescence spectrophotometer using a 1 cm path length quartz cuvette. Emission spectra were measured with excitation at 281 and 275 nm for (1-naphthyl)methyl (1Np) and (2-naphythyl)methyl (2Np) groups, respectively. The slit widths for both excitation and emission sides were kept at 10 nm during measurement.

2.3.4. Circular dichroism (cd) spectroscopy

Cd spectra were recorded on a Jasco J-820 spectropolarimeter using a 1 mm path length quartz cuvette.

2.3.5. X-ray crystallographic analysis

A saturated aqueous solution of β-CD was prepared at room temperature. 2NpMeOH (100 mg) was dissolved in the saturated aqueous solution of β-CD (ca. 300 mL) at 50 °C. The solution was cooled down slowly and kept at 30 °C. After a few days, colorless crystals of the β-CD–2NpMeOH inclusion complex were obtained.

A crystal of the β-CD–2NpMeOH inclusion complex suitable for X-ray diffraction studies was mounted on a cryoloop. The measurement was carried out on a Rigaku R-AXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$). Relevant crystal and data statistics are summarized in Table 1. Indexing was performed from three oscillations which were exposed for 3.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A symmetry-related absorption correction using the program ABSCOR [6] was applied. Data were corrected for Lorentz and polarization effects. The structure of the inclusion complex was solved by direct methods (SHELXS-97) [7], expanded using Fourier techniques (DIRDIF 94) [8], and refined by full-matrix least

Table 1
Crystal data and collection parameters for the β-CD–2NpMeOH complex

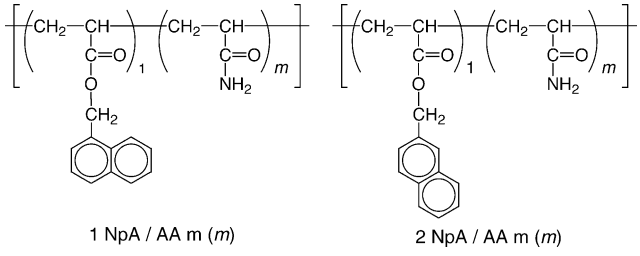
Formula	$C_{106}H_{98}O_{102}$
Formula weight	3003.84
Crystal system	Triclinic
Space group	P1 (#1)
a (Å)	15.444(7)
b (Å)	15.337(6)
c (Å)	17.904(7)
α (°)	98.90(3)
β (°)	113.90(3)
γ (°)	103.90(3)
V (Å^3)	3609(3)
Z	1
D_{calcd} (g/cm^3)	1.382
F(0 0 0)	1550
μ [Mo Kα] (cm^{-1})	0.127
Temperature, K	150(2)
Scan speed (°/min)	3
Scan width (°)	3
$2\theta_{max}$ (°)	55.2
No. of observations	15275
No. of variables	1751
R	0.0985
R_w	0.3051
GOF	1.227

square refinement (SHELXL-97) [7]. In the subsequent refinement, the function $\sum \omega(|F_O| - |F_O|)^2$ was minimized, where $|F_O|$ and $|F_C|$ are the observed and calculated structure factor amplitudes, respectively. The agreement index is defined as $R = \sum ||F_O| - |F_C|| / \sum |F_O|$ and $R_W = \left[\sum \omega(|F_O|^2 - |F_C|^2)^2 / \sum \omega(|F_O|^2)^2\right]^{1/2}$.

3. Results and discussion

3.1. Basic characteristics of the polymers used in this study

In this study, copolymers of AAm with 1NpA or with 2NpA (1NpA/AAm(*m*) and 2NpA/AAm(*m*), respectively, where *m* is the number of AAm units relative to an NpA unit in the copolymers) were used (Scheme 1). Since hydrophobically modified poly(acrylamide)s (HM-pAAm) are a typical example of amphiphilic polymers, it is known that polymer-carrying hydrophobes in HM-pAAm associate with each other at higher hydrophobe contents or at higher



Scheme 1. Chemical structure of the polymers used in this study.

Table 2
Basic characteristics of polymers used in this study

Polymer code	m[a]	M_w ($\times 10^{-3}$)[b]	M_w/M_n[b]
1NpA/AAm(42)	42	8.9	2.5
1NpA/AAm(64)	64	7.5	1.9
2NpA/AAm(52)	52	7.4	2.1
2NpA/AAm(73)	73	5.7	2.0

[a] The number of AAm units relative to an NpA unit in copolymer.
[b] Determined by GPC using a mixed solvent of water and DMF (7/3, v/v) containing 0.050 M LiBr as eluent. Molecular weights were calibrated with standard poly(ethylene glycol) and poly(ethylene oxide) samples.

polymer concentrations [9]. When associations occur between polymer-carrying Np hydrophobes, it becomes complicated to study inclusion complex formation of β-CD with polymer-carrying Np groups. Therefore, we have chosen lower Np contents and lower polymer concentrations, at which no association between Np groups was confirmed in the absence of β-CD by steady-state and time-dependent fluorescence measurements. Since Np contents were considerably low (i.e., *m* values are large) for the polymers used in this study, it is likely that there are no or few blocky sequences of NpA units. As listed in Table 2, M_w and M_w/M_n values for 1NpA/AAm(*m*) and 2NpA/AAm(*m*) were determined to be (5.7–8.9) $\times 10^3$ and 1.9–2.5, respectively, by GPC.

3.2. Steady-state fluorescence study on the interaction of CDs with Np groups

In steady-state fluorescence measurements, it is necessary to use an appropriate excitation wavelength. To determine the excitation wavelength, we measured absorption spectra (data not shown). Absorption spectra for 1NpA/AAm(*m*) and 2NpA/AAm(*m*) in the presence of 8.0 mM β-CD were practically the same as those in its absence, respectively. From the spectra, the excitation wavelength was fixed at 281 and 275 nm in steady-state fluorescence measurements for 1NpA/AAm(*m*) and 2NpA/AAm(*m*), respectively. Fig. 1 shows steady-state fluorescence spectra for 1NpA/AAm(42) and 2NpA/AAm(52) in the presence and absence of 8.0 mM β-CD. In the presence of β-CD, the fluorescence intensities are about 1.4 times and twice as high as those in its absence for 1NpA/AAm(42) and 2NpA/AAm(52), respectively. These data indicate that β-CD interacts with polymer-carrying 1Np and 2Np groups to form inclusion complexes.

When β-CD was added to aqueous solutions of 1NpA/AAm(42) and 2NpA/AAm(52), the absorbance did not change very much, while the fluorescence intensity increased significantly. These data indicate that the formation of inclusion complexes of β-CD with polymer-carrying 1Np and 2Np groups enhances the fluorescence quantum yields for both the Np groups. On the basis of a recent photophysical study on the inclusion complexes of CDs with naphthalene [10], we can explain these observations as follows: Since, in the inclusion complex, β-CD protects the singlet-excited Np

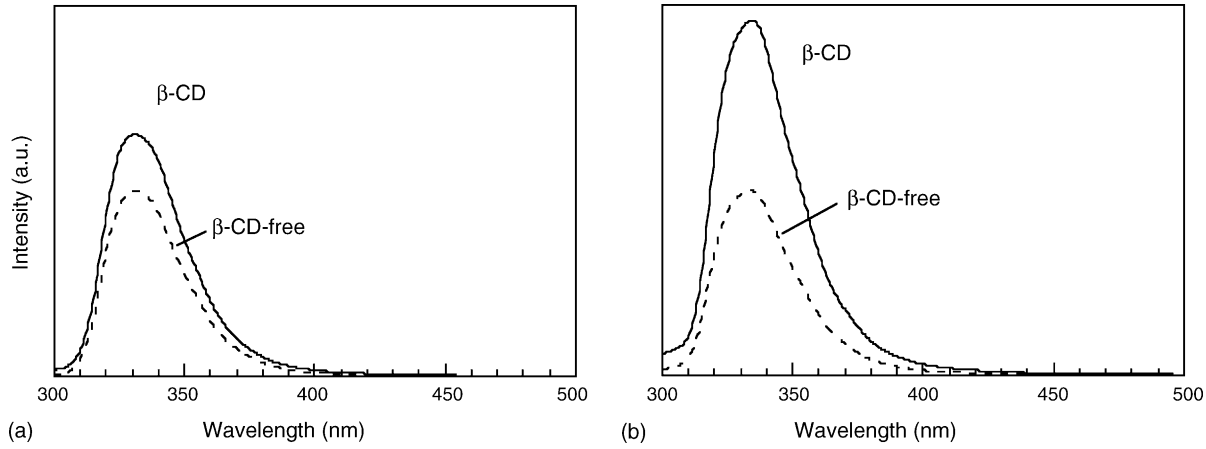


Fig. 1. Steady-state fluorescence spectra for 1NpA/AAm(42) (a) and 2NpA/AAm(52) (b) in the presence and absence of 8.0 mM β-CD.

group from the contact of water molecules, the intersystem crossing of the singlet-excited Np group is markedly retarded, resulting in an increase in the fluorescence quantum yield. Furthermore, since the increase in the fluorescence intensity is larger for 2NpA/AAm(52) than for 1NpA/AAm(42), β-CD protects polymer-carrying 2Np group more efficiently.

To estimate association constants (K) for the β-CD–1NpA/AAm(42) and β-CD–2NpA/AAm(52) systems, steady-state fluorescence spectra were recorded at varying β-CD concentrations ([β-CD]). Using these spectra, the ratios (I/I_0) of the fluorescence intensities in the presence of β-CD and in its absence were calculated, and plotted in Fig. 2 as a function of [β-CD]. For both the polymers, I/I_0 increases with [β-CD] and shows a slight tendency for saturation at higher [β-CD]. For both the cases, Benesi–Hildebrand plots (data not shown) were fitted well with a straight line, indicative of the formation of 1:1 complexes of β-CD with 1Np and 2Np groups. Therefore, K values were determined to be 1.4×10^2 and $2.3 \times 10^2\ M^{-1}$ for the complex formation

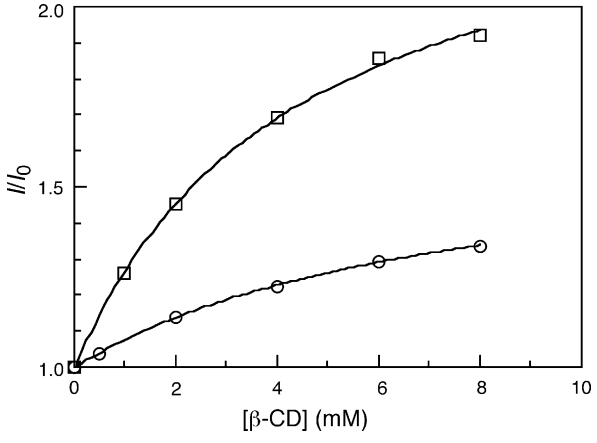


Fig. 2. I/I_0 as a function of [β-CD] for the β-CD–1NpA/AAm(42) (◯) and β-CD–2NpA/AAm(52) (□) systems.

of β-CD–1NpA/AAm(42) and β-CD–2NpA/AAm(52), respectively, by fitting plots in Fig. 2 with the following equation [11]:

$$\frac{I}{I_0} = \frac{1 + aK[\beta - \mathrm{CD}]}{1 + K[\beta - \mathrm{CD}]} \quad (1)$$

where a is a constant.

Values of K were determined for the complex formation of β-CD with polymers of different m in the same manner, as listed in Table 3. K values are $(1.1 \pm 0.3) \times 10^2$ and $(2.0 \pm 0.4) \times 10^2\ M^{-1}$ for 1NpA/AAm(m) and 2NpA/AAm(m), respectively, indicating that β-CD forms inclusion complexes more strongly with polymer-carrying 2Np groups than with polymer-carrying 1Np groups.

To study the effect of the polymer main chain on the complex formation of β-CD with Np groups, the interaction of β-CD with guest model compounds, 1NpMeOH and 2NpMeOH, was also investigated by steady-state fluorescence. Fig. 3 shows steady-state fluorescence spectra for 1NpMeOH and 2NpMeOH in the presence and absence of 8.0 mM β-CD. For both the cases, when β-CD was added, the fluorescence intensity increased, indicating that β-CD interacts with these model compounds to form inclusion complexes. The noteworthy is that the increase in the fluorescence intensity upon the complex formation is larger for

Table 3
Association constants (K) of the complex formation of β-CD with polymer-carrying Np groups[a] and guest model compounds

Guest	K (M^{-1})
1NpA/AAm(42)	1.4×10^2
1NpA/AAm(64)	7.0×10^1
1NpMeOH	2.4×10^2
2NpA/AAm(52)	2.3×10^2
2NpA/AAm(73)	1.6×10^2
2NpMeOH	7.4×10^2

[a] Based on a side chain repeat unit, provided no interactions between complex sites.

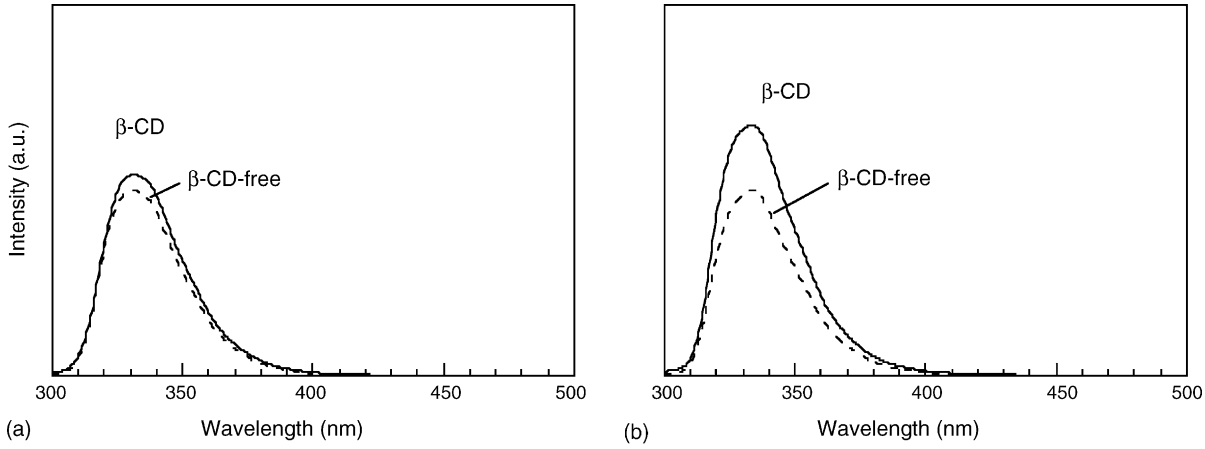


Fig. 3. Steady-state fluorescence spectra for 1NpMeOH (a) and 2NpMeOH (b) in the presence and absence of 8.0 mM β-CD.

polymer-carrying Np groups than for the guest model compounds. These observations indicate that the polymer main chain in the inclusion complex effectively protects a polymer-carrying Np group of the singlet excited state from the contact of water molecules. On the basis of these observations, we will discuss the structure of inclusion complexes of β-CD with polymer-carrying Np group in the later subsection.

To determine K values for the complex formation of β-CD with the guest model compounds, steady-state fluorescence spectra were measured at varying [β-CD]. Using these fluorescence data, I/I_0 values were calculated, and plotted in Fig. 4 as a function of [β-CD]. Since Benesi–Hildebrand plots (data not shown) also exhibited a good linear relationship in the both cases, K values were determined to be 2.4×10^2 and $7.4 \times 10^2\ M^{-1}$ for the complex formation of β-CD–1NpMeOH and β-CD–2NpMeOH, respectively, by fitting plots in Fig. 4 with Eq. (1). As listed in Table 3, K values for polymer-carrying Np groups are smaller than those for the guest model compounds, respectively, indicating that the polymer main chain disturbs the interaction of β-CD with Np groups presumably because of the steric hindrance of the polymer main chain.

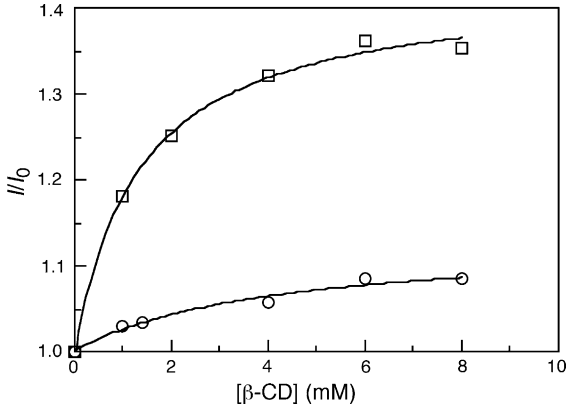


Fig. 4. I/I_0 as a function of [β-CD] the β-CD–1NpMeOH (◯) and β-CD–2NpMeOH (□) systems.

3.3. Structural study of inclusion complexes of β-CD with Np groups

The structures of inclusion complexes were investigated by cd spectroscopy. Fig. 5a shows cd spectra for 1NpA/AAm(42) and 2NpA/AAm(52) in the presence of 8.0 mM β-CD. In the spectrum for the β-CD–1NpA/AAm(42) system, there are no significant cd signals. This spectrum indicates that the substituent at the

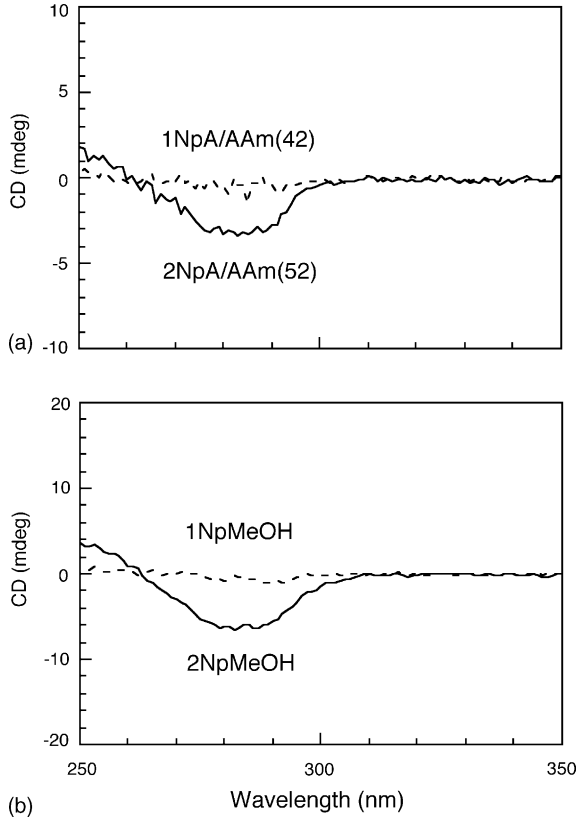


Fig. 5. Cd spectra for the β-CD–1NpA/AAm(42) and β-CD–2NpA/AAm(52) systems (a) and the β-CD–1NpMeOH and β-CD–2NpMeOH systems (b).

1-position of Np group causes a shallow inclusion of β-CD because of the steric hindrance, resulting in undefined structures of the inclusion complex. On the other hand, in the spectrum for the β-CD–2NpA/AAm(52) system, there is a negative induced cd signal ascribable to the ^{1}La transition of the 2Np group in the region of 260–300 nm [12]. This spectrum indicates that the polymer-carrying 2Np group is included deeply in the β-CD cavity to form inclusion complexes, in which the longer axis of the Np group is rather parallel to the rotation axis of β-CD [13]. For comparison, cd spectra for the model compounds were measured in the presence of 8.0 mM β-CD (Fig. 5b). The spectra for the guest model compounds are practically the same as those for the β-CD–polymer systems, respectively, suggesting that the structures of inclusion complexes of β-CD with polymer-carrying Np groups are similar to those of inclusion complexes of β-CD with the model compounds, respectively.

We successfully obtained crystals of the inclusion complex of β-CD with 2NpMeOH suitable for X-ray crystallographic analysis. Table 1 lists crystallographic data and Fig. 6 shows the crystal structure. As shown in Fig. 6, β-CD and 2NpMeOH form 2:2 inclusion complexes. Two β-CD molecules form a dimer in which the secondary hydroxy group sides face each other. The dimers form layers almost parallel to the *ab* plane with their axis forming an angle of ca. 20° with crystallographic *c* axis. The relative average shifting of two dimers in consecutive layers is ca 6.5 Å. Two 2NpMeOH molecules are accommodated in the β-CD dimer with the hydroxymethyl groups being at the primary edges. These 2NpMeOH molecules form three types of dimers; in two of these three, two Np rings are nearly parallel (Figs. 6b and c), and in one of these three, two Np rings form an angle of ca. 35° (Fig. 6d). Fractions of these dimers are ca. 0.50 (Fig. 6b), ca. 0.25 (Fig. 6c), and ca. 0.25 (Fig. 6d), respectively. These data indicate that 2Np group is included deeply in the β-CD cavity to form an inclusion complex in which the longer axis of the Np group is rather parallel to the rotating axis of β-CD, consistent with the cd spectrum in Fig. 5b. It should be noted here that the crystallographic structure is the structure in the solid state. In aqueous solutions, since fluorescence due to excimer of 2NpMeOH was not observed, it is likely that β-CD and 2NpMeOH form a 1:1 inclusion complex, in which the hydroxyl group in 2NpMeOH is located at the primary hydroxy group side. This proposition was supported by ROESY data for a mixture of β-CD and 2NpMeOH, which showed a significant correlation peak between absorption bands due to C5 protons in β-CD and due to methylene protons in 2NpMeOH (data not shown). This structure may allow water molecules to contact the 2Np group, to some extent, from its secondary hydroxy group side, consistent with the smaller increase in fluorescence quantum yield upon complexation.

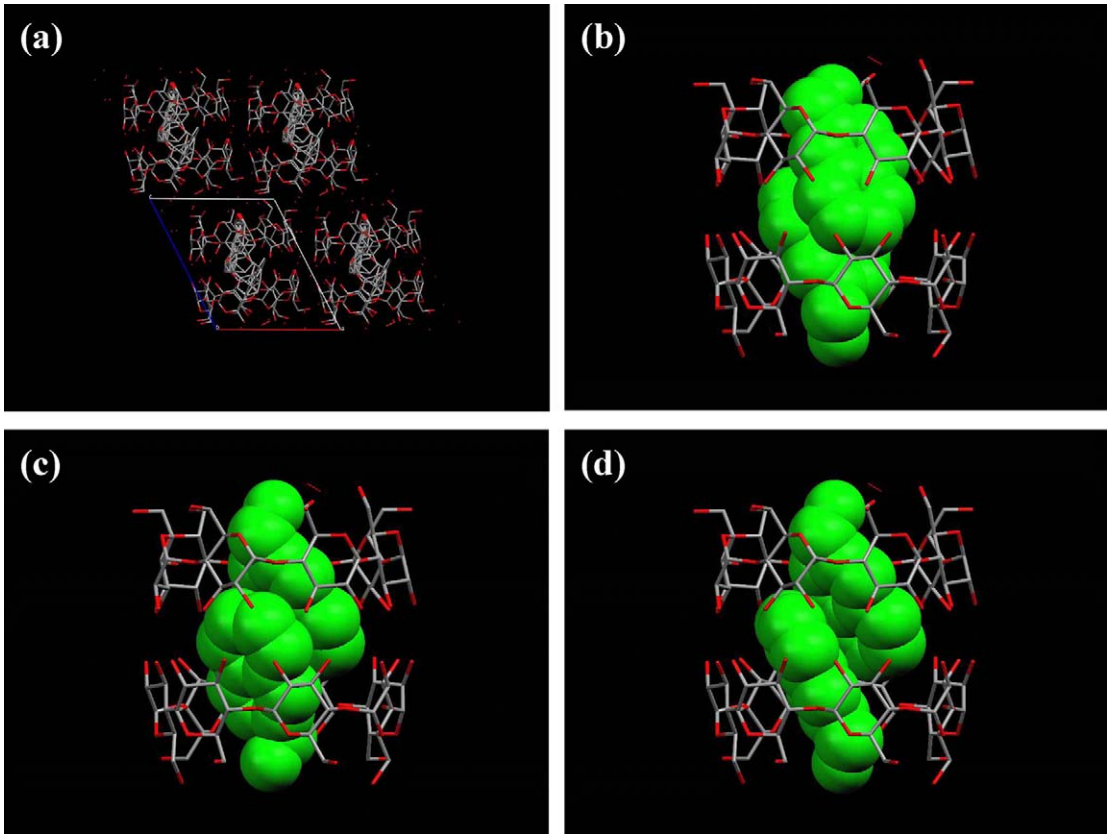


Fig. 6. Crystal packing of the inclusion complex of β-CD with 2NpMeOH (a) and crystal structures of three types of 2:2 complexes of β-CD with 2NpMeOH (b, c, and d), in which carbon and oxygen atoms in β-CD are shown in gray and red, respectively, and 2NpMeOH molecules are shown in green.

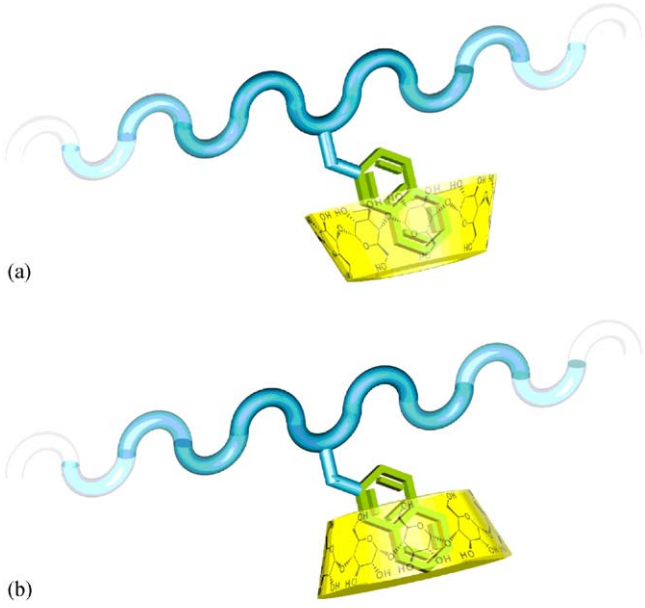


Fig. 7. Plausible structures of the inclusion complex of β-CD with 2NpA/AAm(*m*), in which β-CD includes the polymer-carrying 2Np group from its secondary hydroxy group side (a) and from its primary hydroxyl group side (b).

On the basis of the data described above, we propose here plausible structures of the inclusion complex of β-CD with 2NpA/AAm(*m*) as shown in Fig. 7. Since the inner diameter of the β-CD cavity at the primary edge is smaller than that of the β-CD cavity at the secondary edge, β-CD may include the polymer-carrying 2Np group from its secondary hydroxy group side favorably (Fig. 7a). This proposition is consistent with the remarkable increase in the fluorescence quantum yield, because the polymer main chain and β-CD may efficiently protect the 2Np group from contact of water molecules. When β-CD includes the polymer-carrying 2Np group from its primary hydroxy group side, β-CD may protect the 2Np group from the contact of water molecules less effectively, similar to the β-CD–2NpMeOH system.

4. Conclusion

The interaction of β-CD with 1NpA/AAm(*m*) and with 2NpA/AAm(*m*) was investigated by several techniques, including steady-state fluorescence and cd spectroscopies. When β-CD was added to polymer aqueous solutions, the fluorescence intensity increased remarkably, indicating that β-CD interacts with polymer-carrying 1Np and 2Np groups to form inclusion complexes. Using fluorescence data at varying [β-CD], K values were determined to be $(1.1 \pm 0.3) \times 10^2$ and $(2.0 \pm 0.4) \times 10^2\ M^{-1}$ for the β-CD–1NpA/AAm(*m*) and β-CD–2NpA/AAm(*m*) systems, respectively. Comparison of these K values with those for the guest model compounds, 1NpMeOH (2.4×10^2) and 2NpMeOH (7.4×10^2), indicated that the polymer main chain destabilizes inclusion complexes of β-CD with Np groups. Cd spectra and X-ray crystallographic data indicated that the polymer-carrying 2Np group is included deeply in the β-CD cavity to form an inclusion complex, in which the longer axis of the Np group is rather parallel to the rotation axis of β-CD.

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