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Journal of Photochemistry and Photobiology A: Chemistry 173 (2005) 271–278
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Efficient inclusion complexation and intra-complex excitation energy transfer between aromatic group-modified β-cyclodextrins and a hemicyanine dye

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Available online 23 May 2005

Abstract

A hemicyanine dye, 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (4-ASP) forms inclusion complexes with β-cyclodextrin (β-CD) and modified β-CDs having a sulfonaphthyl (β-CD-NS) or a pyrenyl group (β-CD-py) at the primary face. The complexation constants in water were determined by fluorescence titration and found to be $4.7 \times 10^4\ M^{-1}$ with β-CD-NS and $3.6 \times 10^4\ M^{-1}$ with β-CD-py, while it is $730\ M^{-1}$ with β-CD. Compared to 4-ASP in water, the emission maximum of 4-ASP of the inclusion complexes is blue-shifted by about 20 nm, and emission intensity is higher by 6.4-fold for β-CD, 14-fold for β-CD-NS and as much as 56 fold for β-CD-py complexes. These are much greater than the 3 nm blue shift and 3.3-fold enhancement of emission intensity when the solvent medium is changed to CH_3OH. Good overlap between the emission bands of β-CD-appended aromatic groups and absorption band of 4-ASP results in the excitation energy transfer from the excited aromatic groups to 4-ASP and the efficiency of the intra-complex transfer is near 100%. ^{1}H NMR spectra and molecular modeling of the 4-ASP complexes with β-CD-NS and β-CD-py indicated that *N*-methyl-pyridinium moiety of 4-ASP is outside the primary face of β-CD cavity. The interaction between the *N*-methyl-pyridinium group and the appended aromatic groups appear to result in the high stability of the complexes. The high fluorescence intensity of 4-ASP in the complexes with β-CD-NS and β-CD-py was explained in terms of hindrance of the formation of the non-fluorescent twisted intramolecular charge transfer (TICT) states by the interaction and confinement in cavity.

Keywords: Hemicyanine dye; Solvatochromism; β-Cyclodextrin; Inclusion complex; Excitation energy transfer

1. Introduction

Excitation energy and photoinduced electron transfer reactions play a central role in photobiological processes and in various light-driven physical and chemical processes, and have drawn much interests in view of designing photomolecular devices [1–9]. A strategy to bring the reacting pairs in close proximity is to synthesize the covalently linked donor/acceptor systems [1–3]. However, this usually requires a great deal of synthetic effort. An alternative approach is to make donor- or acceptor-tethered host molecules and assemble them with complementary acceptor or donor molecules via host–guest interaction [4–14]. Cyclodextrins (CD), a family of torus-shape cyclic oligosaccharides capable of forming inclusion complexes with a variety of hydrophobic species from aqueous solutions, have been widely utilized as the host moiety [15]. Electron acceptors [4] or photoactive groups such as aromatic molecules [5–12] and metal complexes [13,14] were attached to CD and efficient excitation energy or photoinduced electron transfer reactions between the CD-appended groups and/or guest molecules encased in the cavity of CD has been demonstrated.

Naphthalene-modified CDs have been extensively investigated as light harvesting host molecules transferring the excitation energy to other appended chromophores [5] and/or guest acceptors included in the CD cavity [6–8]. The naphthyl group-tethered β-CDs were also used as molecular photoreactors for inducing selective photoreactions via photo-energy transfer within the cavity [9]. Rotaxanes with

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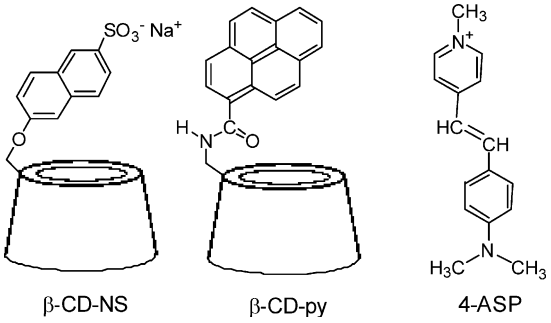
doi:10.1016/j.jphotochem.2005.04.006

naphthalene-modified α-CD threaded by poly(ethyleneglycol) chains with terminal acceptor units were also constructed and excitation transfer from the naphthalene group to the terminal units were demonstrated [10]. Pyrenyl group absorbs light at longer wavelength and has much larger molar absorptivity than the naphthyl group. The pyrene-modified CDs have been used as fluorescent chemosensors for molecular detection utilizing the host–guest interaction [11,12].

For an ideal host–guest system of efficient excitation energy transfer, large absorptivity and emission intensity of the light harvesting chromophore (energy donor), a good overlap between the emission spectrum of the energy donor and the absorption spectrum of an energy acceptor, and the high binding affinity of the guest molecule to the host are required. For sensitized emission, high emission quantum yield of the acceptor in the assembly is also required. In this paper, we report that the host–guest systems composed of naphthalene- or pyrene-tethered β-CDs (β-CD-NS or β-CD-py) and a hemicyanine dye, 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (4-ASP) meet the requirements. Large complexation constants of 4-ASP with the aromatic group-modified β-CDs, almost 100% efficiency of the intra-complex excitation energy transfer, and the high emission intensity of 4-ASP in the complexes are demonstrated.



2. Experimental

2.1. Materials

Sodium salt of mono-6-*O*-(2-sulfonato-6-naphthyl)-β-CD (β-CD-NS) was prepared by reacting 6-mono-tosylated β-CD and sodium 6-hydroxy-2-naphthalenesulfonate in dry DMF as described elsewhere [16]. The synthesis of mono-6-deoxy-(pyrene-1-carboxamido)-β-CD (β-CD-py) by amide coupling of mono-6-deoxy-6-amino-β-CD with 1-pyrenecarboxylic acid was reported in a previous paper [17]. Iodide salt of 4-[4-(dimethylamino)styryl]-1-methylpyridinium dye (4-ASP) was obtained from Molecular Probes and used without further purification. β-CD (Aldrich) was recrystallized from water and vacuum dried.

2.2. Spectroscopic measurements and molecular modeling

Fluorescence spectra were obtained with a Hitachi F-3010 spectrofluorimeter. UV–vis spectra were recorded with a GBC Cintra 20 spectrophotometer. ^{1}H NMR spectra were taken with a Bruker DPX-250 spectrometer. The chemical shifts (in ppm) were given relative to the external sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d^4 acid. All spectroscopic measurements were done at 25 °C using appropriate temperature controllers. Unless otherwise specified, the ionic strength of the solutions was fixed at 0.1 M with NaCl.

Molecular modeling calculation was performed using CVFF force field in an Insight II/Discover program package [18]. A water sphere of diameter 15 Å provided by Insight II and relative permittivity of 78 were used. The cut-off distances for the van der Waals and electrostatic interactions were set to 100 Å to include all possible interactions.

3. Results and discussion

3.1. Spectral overlaps and the choice of 4-ASP as energy acceptor

Fig. 1 compares the absorption and emission spectra of β-CD-NS and β-CD-py with the absorption spectrum of

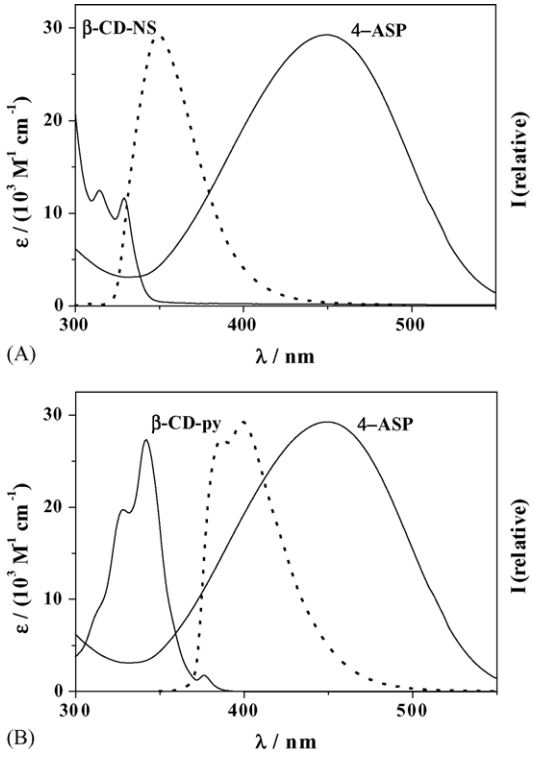


Fig. 1. (A) Absorption and fluorescence spectra of β-CD-NS and absorption spectrum of 4-ASP. (B) Absorption and fluorescence spectra of β-CD-py and absorption spectrum of 4-ASP. Note that the absorption spectrum of β-CD-NS in (A) is expanded by 10 times. Dotted spectra are the fluorescence spectra.

4-ASP. For the long-wavelength absorption band, the absorption band of β-CD-py appears at about 20 nm longer wavelength with about 25 times larger molar absorptivity than β-CD-NS. Good overlaps between the emission bands of aromatic group of the modified β-CDs and absorption band of 4-ASP, enabling one to expect an efficient energy transfer from the excited aromatic groups to 4-ASP, are observed. Besides the spectral overlap for the energy transfer, there are a few other reasons for choosing 4-ASP as energy acceptor in the study: (1) 4-ASP shows moderate binding affinity to β-CD cavity, and the emission intensity of 4-ASP is greatly enhanced upon binding [19] and in less-polar media [20]; (2) the dye has been widely used as a fluorescent probe for biological systems and supramolecular assemblies [21]; (3) 4-ASP molecule is long enough to place the positively charged pyridinium moiety outside the β-CD cavity and the protruded part of the molecule may interact with the appended aromatic groups via electrostatic, cation–π, and/or π–π interaction to result in enhanced binding affinity to the antenna β-CDs; (4) 4-ASP is one of hemicyanine dyes which exhibit various interesting and potentially applicable photoelectric characteristics [22].

3.2. Solvatochromism of 4-ASP

Hemicyanine dyes including 4-ASP are solvatochromic dyes exhibiting a bathochromic shift of the long-wavelength absorption band as the solvent polarity decreases [20]. To correlate the environments of 4-ASP in inclusion complexes with β-CD and the aromatic group-modified β-CDs to that in bulk medium, we obtained absorption spectra of 4-ASP in 1.0×10^{-2} M native β-CD and in 5.0×10^{-4} M aromatic group-modified β-CDs and compared them with the spectra of 4-ASP taken in various compositions of CH_3OH/H_2O mixtures: the fractions of 4-ASP present as complexed forms in above host concentrations are estimated to be ≥0.9 from complexation constants (see Section 3.3). The results are shown in Fig. 2 and the absorption parameters are summarized in Table 1. The order of the extent of bathochromic shifts of 4-ASP, relative to the spectrum in H_2O, is β-CD < β-CD-NS < β-CD-py < CH_3OH.

It was suggested that the 4-ASP has two resonance structures, benzenoid form (as shown in Section 1) and quinoid form in which the positive charge on pyridinium nitrogen atom is transferred to aniline nitrogen atom [23]. It is believed that quinoid structure has more delocalized π-electron and is more favored as solvent polarity decreases. This was used to explain the solvent effect on λ_{max} of absorption spectra [23]. Taking this, the appended 2-sulfonaphthyl and pyrenyl groups in the modified β-CDs can be regarded as hydrophobic caps providing extra less-polar environment to 4-ASP included in the β-CD cavities.

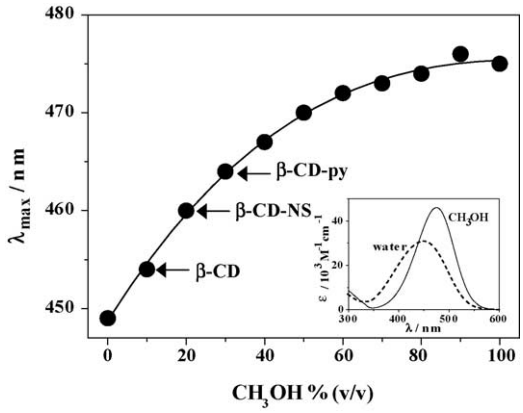


Fig. 2. Variation of absorption maximum of 4-ASP on the methanol content in methanol/water mixtures. The maxima in the presence of 1.0×10^{-2} M β-CD, 5.0×10^{-4} M β-CD-NS, and 5.0×10^{-4} M β-CD-py in aqueous media are marked as arrows. Inset shows the absorption spectra of 4-ASP in water and in methanol. The spectra were taken with 2.0×10^{-5} M 4-ASP solutions.

The emission intensity of 4-ASP is greatly enhanced and the emission maximum shifts to blue side by about 20 nm in the presence of β-CD or the aromatic group-modified β-CDs (Fig. 3 and Table 1). The addition of 1-adamantanemethylammonium chloride, which has high binding affinity to β-CD [24] and thus replaces 4-ASP from β-CD cavity, decreased the emission intensity (see spectrum E in Fig. 3). These facts indicate clearly that the emission spectral changes are due to the transfer of 4-ASP molecule from aqueous medium to β-CD cavities by inclusion complexation.

The blue shift of emission band of 4-ASP and other hemicyanine dyes as solvent polarity decreases was explained in terms of transfer of positive charge on the pyridinium moiety to the aniline moiety on excitation [25,26]. This is similar

Table 1
Absorption and fluorescence characteristics of 4-ASP, and complexation constants (K_h) of 4-ASP with β-CD and aromatic group-modified β-CD at 25 °C

Medium[a]	Absorption	Fluorescence		K_h[c] ($\times 10^4$ M^{-1})
	λ_{max} (nm) (ε (M^{-1} cm^{-1}))	λ_{max} (nm)	I[b] (rel.)	
CH_3OH	475 (44000)	587	3.3	–
Water	450 (29000)	590	1.0	–
10×10^{-3} M β-CD	455 (31000)	569	6.4[c]	0.073 (±0.002)
0.50×10^{-3} M β-CD-NS	460 (31000)	569	14[c]	4.7(±0.3)
0.50×10^{-3} M β-CD-py	466 (33000)	566	56[c]	3.6 (±0.1)

[a] Except CH_3OH, aqueous solutions containing 0.10 M NaCl.
[b] Excited at 447 nm and monitored at 570 nm.
[c] Determined from the fluorescence titrations of 4-ASP with hosts and corresponds to I_c/I_w (see text).

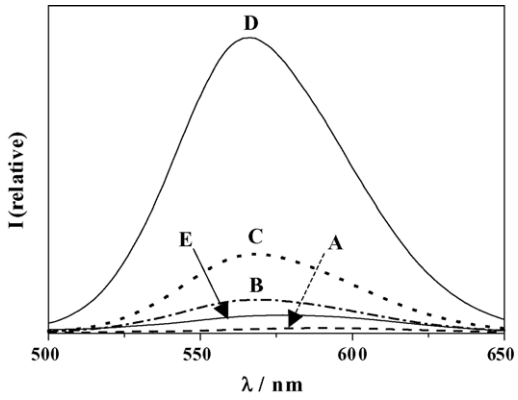


Fig. 3. Fluorescence spectra of 5.0×10^{-6} M 4-ASP in water (A), and in the presence of 1.0×10^{-2} M β-CD (B), 5.0×10^{-4} M β-CD-NS (C), and 5.0×10^{-4} M β-CD-py (D), and 5.0×10^{-4} M β-CD-py + 1.0×10^{-2} M 1-adamantanemethylammonium chloride (E). The excitation wavelength was 447 nm. The spectrum in CH_3OH, which overlaps closely with the spectrum E was omitted for clarity.

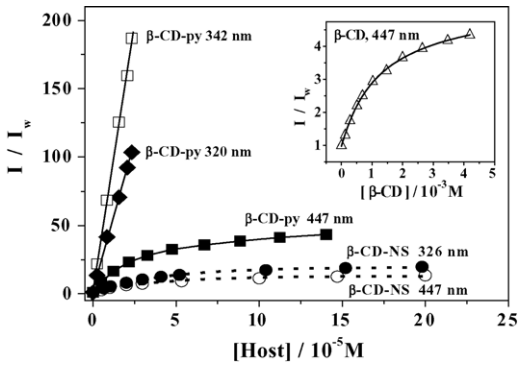


Fig. 4. Dependence of fluorescence intensity of 4-ASP on the concentration of β-CD (△), β-CD-NS (●, ○) and β-CD-py (□, ■, ♦). The additives and excitation wavelengths are shown in the figure. The concentration of 4-ASP was 2.5×10^{-5} M ((□, ♦), 5.0×10^{-6} M (■), or 2.0×10^{-6} M (△, ●, ○). The fluorescence intensities were monitored at 570 nm and normalized to the intensities (I_w) taken with the corresponding 4-ASP solutions in the absence of the additives.

to the explanation of the solvent effect on λ_{max} of absorption spectra [23]. However, as much as 20 nm blue shift of emission of 4-ASP in the complexes is quite unexpected, as the emission shift is usually only a few nm in most of bulk media [20,26,27]. Mishra et al. observed 20–30 nm blue shift of the emission maximum of 4-ASP in $CHCl_3$ and benzene media and attributed the shift to the 'specific' solvent–ASP dye interaction [27]. However, the detailed nature of the interaction between 4-ASP with the solvents as well as in the present systems, and the mechanism of the large blue shit of the emission band are not clear at this point. The emission properties of 4-ASP in the complexes will be discussed in more detail in the following section.

3.3. Inclusion complexation constants and the emission properties of 4-ASP in the complexes

The complexation constants of 4-ASP with β-CD or its derivatives and the emission properties of the complexes were obtained from the fluorescence titration of 4-ASP solutions with the hosts [19]. For this purpose, the solutions were excited at 447 nm, where only 4-ASP absorbs the light. The titration results are included in Fig. 4. In all cases, the large enhancement of emission intensity upon the addition of the hosts and leveling-off of the intensity at high concentration of the hosts are seen.

We have shown in a previous paper that 4-ASP forms 1:1 complex with β-CD [19]. For 1:1 complexation of 4-ASP with a host, Eq. (1), the change of emission intensity (ΔI) caused by the addition of a host is related to the equilibrium concentration of the host by Eq. (2) [19]:

$$\text{4-ASP} + \text{host} \rightleftarrows \text{4-ASP–host};$$

$$K_h = [\text{4-ASP–host}]/\{[\text{4-ASP}][\text{host}]\} \quad (1)$$

$$\Delta I/[\text{host}] = \Delta I_\infty K_h - \Delta I K_h \quad (2)$$

where ΔI_∞ is the maximum change in emission intensity when all of 4-ASP molecules are complexed with the host. The ratio of emission of the complex (I_c) to that of 4-ASP in bulk water (I_w) becomes $I_c/I_w = \Delta I_\infty/I_w + 1$.

In case of the titration with β-CD, the total concentration of β-CD, $[\beta\text{-CD}]_0$, is much higher than the total concentration of 4-ASP, $[\text{4-ASP}]_0$. Thus, we can use $[\beta\text{-CD}]_0$ as [host] of Eq. (2). However, in titration with β-CD-NS and β-CD-py, the concentrations of hosts are not large enough to assume that the total concentrations of the hosts, $[\text{host}]_0$, are the same as the concentration of the non-complexed host (C_{nc}). The C_{nc} can be corrected by Eq. (3). Another complication in the analysis of the titration data of β-CD-NS and β-CD-py is dimerizations of the modified β-CDs. We have reported that β-CD-NS [16] and β-CD-py [17] form dimers with the dimerization constants (K_D) of 9700 ± 2500 and $270 \pm 20\ M^{-1}$, respectively. Since β-CD cavities of the dimers are pre-occupied with the pendant groups, the dimers cannot form inclusion complex with 4-ASP. Considering the monomer–dimer equilibrium of the non-complexed host molecules, the concentration of monomeric host in equilibrium with 4-ASP is given as Eq. (4):

$$C_{nc} = [\text{host}]_0 - \Delta I/\Delta I_\infty [\text{4-ASP}]_0 \quad (3)$$

$$[\text{host}] = [\text{host}]_{\text{monomer}} = \{(8K_D C_{nc} + 1)^{1/2} - 1\}/(4K_D C_{nc}) \quad (4)$$

The plot of β-CD titration data to Eq. (2) is straightforward. For β-CD-NS and β-CD-py, we first assumed ΔI value taken at the highest concentration of the host as trial ΔI_∞, and calculated concentrations of non-complexed host for each data point using Eq. (3). Then, the concentrations of monomeric hosts, $[\text{host}]_{\text{monomer}}$, were evaluated from Eq. (4) using the reported K_D values, and then the calculated $\Delta I/[\text{host}]_{\text{monomer}}$ values were plotted against ΔI according to

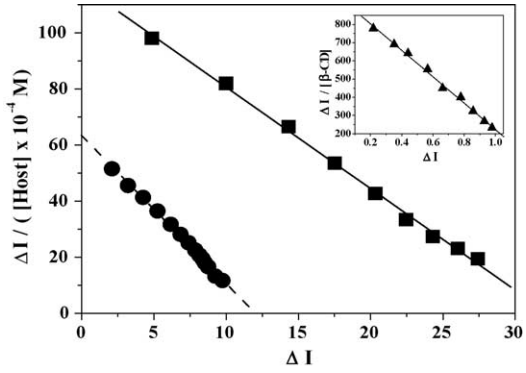


Fig. 5. Benesi-Hildebrand type plots (Eq. (2)) of the fluorescence titration data of 4-ASP with β-CD (▲), β-CD-NS (●), and β-CD-py (■). The excitation and emission wavelengths were 447 and 570 nm, respectively.

Eq. (2). Linear regression of the plot gave the calculated ΔI_∞, which replaces the trial value. This process was repeated until we obtain a satisfactory linear relationship between the calculated $\Delta I/[\text{host}]_{\text{monomer}}$ and ΔI. The plots were shown in Fig. 5. The good linearity of the plots confirms 1:1 stoichiometry of the complexes. The K_h and I_c/I_w values obtained from the plots were included in Table 1.

The complexation constants of 4-ASP with β-CD-NS and β-CD-py are about 50 times greater than that with native β-CD. This is reminiscent of the large binding constant of a merocyanine dye, 4-(dicyanomethylene)-2-methyl-6-[*p*-bis(hydroxyethyl)aminostyryl]-4H-pyran (DCM-OH) with a β-CD derivative (CD-NA) having seven naphthyl groups [6]. The interaction between the appended aromatic groups with the pyridinium moiety of 4-ASP can account for the extra stability of the complexes.

Another interesting feature of the 4-ASP complexes with aromatic group-tethered β-CD is the large emission intensity: the intensity of 4-ASP is about 6 times in β-CD complex, 14 times in β-CD-NS complex, and as much as 56 times greater in β-CD-py than that in water. These enhancements in emission intensity upon inclusion complexation are much larger than the 3.3-fold enhancement when the solvent medium was changed to CH_3OH from water (Table 1). Also, the enhancement of emission intensity of 4-ASP upon inclusion complexation with β-CD-NS and β-CD-py are much larger than the reported 5-fold increase in the emission lifetime of DCM-OH on the binding to CD-NA [6].

The medium dependent fluorescence emissions of conjugated *N*,*N*′-dialkylaniline derivatives having electron acceptor moiety have been explained in terms of the formation of twisted intramolecular charge transfer (TICT) state [28]. However, the emission behaviors of hemicyanine dyes are different from those of most TICT state molecules: hemicyanine dyes do not show dual fluorescence, one from local excited state and the other from TICT state. Cao et al. attributed this to that TICT states of hemicyanine dyes are not fluorescent and showed theoretically that rotations of the pyridyl and aniline rings are the major channels for the formation of TICT states in the excited 4-ASP and the rotations enhance the charge transfer [26]. Confinement of 4-ASP molecule in β-CD cavity and interaction of the pyridinium moiety with the appended aromatic groups of β-CD-NS and β-CD-py (see Section 3.5) would hinder the formation of TICT states. This can explain why 4-ASP in β-CD and the aromatic group-modified β-CDs complexes shows greater enhancement of emission intensity than in CH_3OH, despite it experiences more polar environment in the complexes than in the bulk CH_3OH as judged from the shift in the absorption spectra.

3.4. Intracomplex excitation energy transfer

The excitation energy transfer from the appended aromatic groups of β-CD-NS and β-CD-py to 4-ASP included in their β-CD cavities was studied by two methods. One is the quenching of the emission from the excited aromatic groups by 4-ASP. The other is enhanced emission of 4-ASP upon excitation of the aromatic groups. Fig. 6 shows the change of emission spectra of 2.0×10^{-6} M β-CD-NS solutions by the presence of various concentrations of 4-ASP. As the concentration of 4-ASP increases, the emission from the naphthyl group is strongly quenched and 4-ASP emission is observed. After correcting the inner filter effect, $I = I_{obs} \times \text{antilog}[(A_{ex} + A_{em})/2]$, the corrected emission intensity was plotted against the concentration of free 4-ASP (see inset of Fig. 6): A_{ex} and A_{em} are the absorbances of the solutions at excitation and emission wavelengths, respectively. The concentrations of free 4-ASP were calculated from the initial 4-ASP concentrations and emission intensities of naphthyl group assuming that the 4-ASP/β-CD-NS complex does not show the naphthyl fluorescence. The emission intensity versus $[\text{4-ASP}]_{\text{free}}$ profile fitted well to 1:1 complexation scheme and gave the complexation constant $K_{\beta\text{-CD-NS}}$ as $4.2(\pm 0.5) \times 10^4\ \text{M}^{-1}$. Similarly, the emission

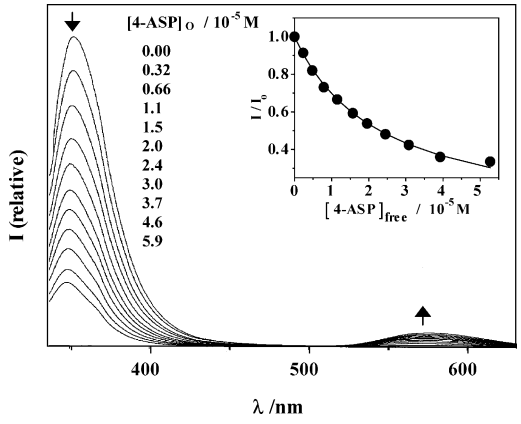


Fig. 6. Quenching of naphthalene fluorescence of 2.0×10^{-6} M β-CD-NS excited at 326 nm by 4-ASP. Inset shows the plots of I/I_0 at 350 nm against the equilibrium concentration of 4-ASP calculated by assuming that the naphthyl group in β-CD-NS/4-ASP complex is not fluorescent. The inner filter effect was corrected for the I/I_o vs. [4-ASP] plot.

from the pyrene moiety of β-CD-py was quenched by 4-ASP and the plot of the corrected pyrene emission intensity against free 4-ASP gave $K_{\beta\text{-CD-py}}$ as $3.5(\pm0.3) \times 10^4\ M^{-1}$. The complexation constants estimated from the quenching are in good agreement with the corresponding values obtained in the previous section. This indicates that the fluorescence of the appended aromatic groups in the 4-ASP complexes is totally quenched, i.e. efficiency of the excitation transfer is close to 100%.

Complementary evidence of the efficient excitation energy transfer was obtained from the larger enhancement of 4-ASP fluorescence in the presence of β-CD-NS or β-CD-py when the excitation wavelength is changed from 447 nm (where only 4-ASP absorbs) to shorter wavelength where both 4-ASP and the β-CD appended aromatic groups absorbs the light (Fig. 4). Fig. 4 shows clearly that the emission intensity versus [β-CD-NS] profiles obtained by exciting 447 and 326 nm exhibit almost the same [β-CD-NS] dependence. However, at a given concentration of β-CD-NS, the enhancement of the emission intensity (I/I_w) taken with $\lambda_{ex} = 326$ nm is 1.3 times greater than that obtained with $\lambda_{ex} = 447$ nm. The 1.3 times difference in the enhancement of emission intensity is close to ratio of the sum of molar absorptivities of 4-ASP and β-CD-NS ($\varepsilon_{4\text{-ASP}} + \varepsilon_{\beta\text{-CD-NS}}$) to the molar absorptivity of 4-ASP ($\varepsilon_{4\text{-ASP}}$) at 326 nm: the ε values of 4-ASP and β-CD-NS are 3000 and 1040 $cm^{-1}\ M^{-1}$, respectively. For β-CD-py, I/I_w ratios were increased to 4.5 and 7.8 times when the exciting wavelengths were changed to 320 and 342 nm, respectively, from 447 nm. Again, the ratios are close to those of the sum of the molar absorptivities 4-ASP and β-CD-py to the molar absorptivity of 4-ASP at the exciting wavelengths: the ε value of 4-ASP is 3250 $cm^{-1}\ M^{-1}$ at both wavelengths, and that of β-CD-py is 12600 $cm^{-1}\ M^{-1}$ at 320 nm and 27300 $cm^{-1}\ M^{-1}$ at 342 nm, giving the $(\varepsilon_{4\text{-ASP}} + \varepsilon_{\beta\text{-CD-py}})/\varepsilon_{4\text{-ASP}}$ ratios as 4.9 at 320 nm and 9.4 at 342 nm. These results indicate clearly that the sensitized fluorescence via the absorption-energy transfer-emission contributes to the fluorescence of 4-ASP when the excitation wavelength is in the aromatic group absorption regions. Though there are slight differences between the I/I_w and $(\varepsilon_{4\text{-ASP}} + \varepsilon_{host})/\varepsilon_{4\text{-ASP}}$ ratios, presumably due to the solvatochromism of 4-ASP as shown in Section 3.2, the closeness of the two ratios supports that the excitation energy transfer in the 4-ASP/host complexes occurs with nearly 100% efficiency.

As far as the sensitized fluorescence emission is concerned, β-CD-py appears to be far more superior sensitizer to β-CD-NS for 4-ASP. Its 4-ASP complex shows similar stability to the β-CD-NS complex, but the emission intensity of 4-ASP is about three times higher in β-CD-py cavity than in β-CD-NS cavity. Moreover, the maximum absorptivity of β-CD-py in near UV region is about 25 times larger that that of β-CD-NS. These give as much as 75 times higher sensitizered fluorescence intensity with β-CD-py than that with β-CD-NS, when the same concentration of the host sensitizers is used.

3.5. Structural features of 4-ASP/host complexes

To obtain the structural features of 4-ASP/host complexes, we obtained ^{1}H NMR spectra of 4-ASP and 1:1 mixtures of 4-ASP and host in D_2O (Fig. 7). The assignments of peaks were made with the aid of 2-D COSY spectra. In the presence of β-CD, resonance signals from protons of ethenyl and phenyl groups appear at slightly upfield than those in the absence of β-CD. This indicates that the groups are inside the β-CD cavity and experience shielding effect from the change of the microenvironment. The presence of β-CD-NS and β-CD-py affects the chemical shifts of 4-ASP drastically and the effect of β-CD-py on the chemical shifts is much greater than that of β-CD-NS. The protons a–d shift upfield much more than the protons e and f. This indicates that the former protons experience more ring current effects from the appended aromatic groups than the latter protons. This suggests that the pyridinium moiety of 4-ASP is outside the primary rim of β-CD, where the aromatic groups are attached, keeping the phenyl ring inside the cavity.

To get the better insight on the structures of the complexes, we performed modeling calculations for the complexes. The energy-minimized structure of β-CD-NS complex is shown in Fig. 8. In the complex, the ethenyl and phenyl groups are appeared to be inside the β-CD cavity. The *N*-methyl pyridinium and dimethyl groups protrude the β-CD cavity from the primary and the secondary side, respectively. This agrees well with the conclusion from NMR spectra. The distance between the nitrogen atom of pyridinium moiety and the nearest oxygen atom of sulfonate group is estimated to be 3.7 Å. The center-to-center distance between pyridinium and naphthalene rings is also 3.7 Å and the rings are in almost

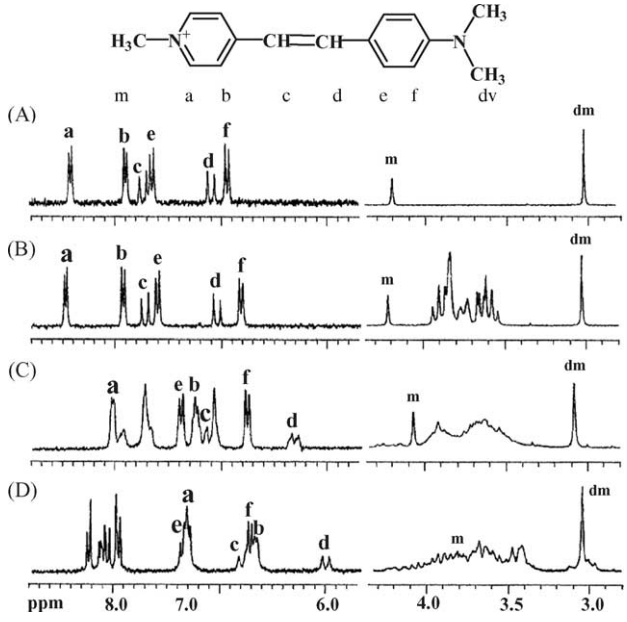


Fig. 7. Partial ^{1}H NMR spectra of 4-ASP (A) and equimolar mixtures of 4-ASP and β-CD (B), β-CD-NS (C) and β-CD-py (D) in D_2O. [4-ASP] = [host] = 2.0×10^{-3} M. The assignments of 4-ASP protons are given.

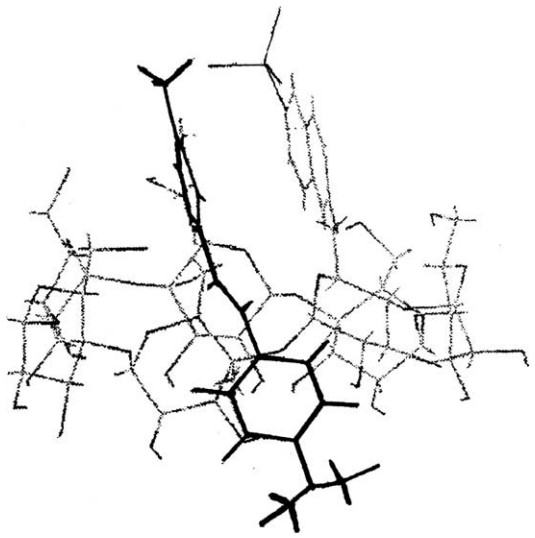


Fig. 8. Energy-minimized structure of 4-ASP/β-CD-NS complex. Note that 4-ASP molecule depicted as darker lines transverses the β-CD cavity. The water molecules were omitted for the sake of clarity.

parallel arrangement. Such arrangement may have advantage for effective π–π and cation–π interactions. The energy-minimized structure also indicates that the 4-ASP skeleton has oblique orientation to the CD axis. Modeling calculation for 4-ASP/β-CD-py complex showed essentially the same structure. We believe that such structures could give extra stability of the complexes through the interactions between pyridinium and the β-CD appended aromatic groups, and hinder the rotation of the pyridinium and aniline groups to produce the non-fluorescent TICT states. The latter can explain the high fluorescence intensity of the complexes.

4. Conclusions

β-CD-NS and β-CD-py form 1:1 inclusion complexes with a hemicyanine dye, 4-ASP, and the stability of the complexes is about 50 times higher than that of β-CD/4-ASP complex. The emission wavelength of 4-ASP in the inclusion complexes is about 20 nm blue-shifted than that in water and in CH_3OH, and the emission intensity is higher by 6.4 times in β-CD, 14 times in β-CD-NS, and 56 times in β-CD-py complexes than that in water. The high stability of the 4-ASP complexes with the aromatic group-modified β-CDs and the high emission intensity of the complexes are due to interactions between the appended aromatic group and *N*-methylpyridinium moiety of 4-ASP and tight binding of 4-ASP in β-CD cavities, which hinder the rotations of pyridinium and aniline groups to produce the non-fluorescent TICT states. ^{1}H NMR spectra and molecular modeling provide evidences of the interactions and tight binding. The excitation energy transfer from the aromatic groups of the modified β-CD to 4-ASP included in the β-CD cavities takes place with nearly 100% efficiency.

The pyrene-modified β-CD, β-CD-py, can be considered as a better light harvesting host for supramolecular photochemical devices than the much studied naphthalene-modified β-CDs, because the molar absorptivity of pyrenyl group is much greater than the naphthyl group, and it shows weaker tendency of dimerization than β-CD-NS. Studies are in progress on using β-CD-py as a photochemical microreactor utilizing the excitation energy transfer or photo-induced electron transfer from the excited pyrenyl group to reactants included in the β-CD cavity.

Acknowledgements

This work was supported by CRM/KOSEF of Korea University. Authors thank Hyun Jung Song for art-works of figures.

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