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Investigation on photophysical properties of a substituted 3*H*-indole-modified β-cyclodextrin

II. Efficient photoinduced energy transfer with naphthalene and its derivatives

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Abstract

Photoinduced energy transfer is observed in the supramolecular assemblies of mono-6-deoxy-(2-[(*p*-amino) phenyl]-3,3-dimethyl-5-carboxyl-3*H*-indole)-β-CD (compound A) with naphthalene and its derivatives, which are stabilized via hydrophobic interactions in aqueous solutions. According to Förster theory, the critical transfer radius R_0 was calculated. It was found that the energy transfer efficiency from naphthalene and its derivatives to compound A is very high and is increased with increasing their inclusion percents in the β-CD cavity of compound A. Energy transfer efficiencies for 2-methoxynaphthalene and 2-naphthol are not much different, but larger than that of naphthalene at the same molar ratio of donor to acceptor. But, when the molar ratio reaching 1:10, the difference in the energy transfer efficiency for the three donors is negligible.

Keywords: Supramolecular assemblies; Energy transfer; Time-resolved fluorescence

1. Introduction

As photoinduced energy transfer (PET) plays a key role in photosynthesis [1], it has been frequently applied to probe biology and estimate chromophore separation and structure on the nanometer scale [2]. It provides information about distances on the order of 10–100 Å and is thus suitable for investigating spatial relationships of interest in biochemistry [3]. Large amounts of research on covalently linked chromophore arrays for exploring long-range energy transfer and electron transfer phenomena have been documented [4], and the research concerning non-covalently linked chromophore arrays has also been described [5]. Generally speaking, the energy transfer mechanism in the non-covalent systems is more complicated than that in the covalent systems. Non-covalent interactions including hydrogen bonding, π-stacking, metal-ligand coordination and hydrophobic interactions often help assemble energy transfer donors and acceptors [6–10]. To further understand and mimic the energy transfer mechanism in biological systems where hydrophobic interactions are usually dominant, some research groups designed and synthesized artificial systems of photoinduced electron transfer in which the donor and acceptor were held together via hydrophobic interactions [11,12]. Ueno and co-workers investigated the quenching mechanism of the fluorescence of naphthalene by the combination process of Förster energy transfer and electron transfer to the trinitrophenyl units [13].

Cyclodextrin, containing 6 (α-CD), 7 (β-CD), or 8 (γ-CD) D-glucose units, is one of the most popular host molecules to construct various supramolecular assemblies. A wide variety of cyclodextrin derivatives have been designed and synthesized for their application on enzyme mimics and as supramolecular receptors and chiral selectors in separation science and technology, pharmaceutical chemistry, food technology and analytical chemistry [14]. Very recently, we have synthesized a new compound, mono-6-deoxy-(2-[(*p*-amino)phenyl]-3,3-dimethyl-5-carboxyl -3*H*-indole)-β-CD (compound A) [15,16]. Both experimental and computational analyses show that the substituted 3*H*-indole moiety of compound A adopts rim-covering conformation in

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aqueous solution [16]. It undergoes novel recognition mechanism, in contrast to the conventional CD-based chemosensors that exhibit self-inclusion conformation [16]. The substituted 3*H*-indole moiety of compound A located at the rim of the β-CD cavity is surrounded by water molecules both inside and outside of the cavity. Upon addition of guests, some water molecules inside the cavity are excluded leading to the substituted 3*H*-indole moiety transferring from a hydrophilic microenvironment to a less hydrophilic one and thus an increase in its fluorescence intensity [16]. In this article, we will report that a photoinduced energy transfer phenomenon occurs from naphthalene and its derivatives to compound A, which can afford deeper insight into the mechanism of energy transfer in the non-covalent systems. Naphthalene and its derivatives are included in the β-CD cavity of compound A through hydrophobic interaction. In these supramolecular assemblies, the energy transfer from naphthalene and its derivatives (donors) to the substituted 3*H*-indole moiety of compound A (acceptor) is very efficient.

2. Experimental

2.1. Materials

β-CD (Beijing Shuanghuan, China) was recrystallized three times from tridistilled water. Naphthalene, 2-naphthol and 2-methoxynaphthene were purified by sublimation at reduced pressure. All other chemical reagents were of analytical grade.

2.2. Instrumentations

Absorption spectra were recorded on UV-3010 (Hitachi) spectrophotometer using 1 cm quartz cells. Steady-state fluorescence measurements were performed on F-4500 (Hitachi) spectrofluorimeter. The excitation and emission bandpasses were 10 and 5 nm, respectively. Each solution was excited near its maximum absorption wavelength using 1 cm quartz cells. Fluorescence lifetime measurements were made on a multiplexed time-correlated single-photon counting fluorimeter FLS920 (EDINBURGH). The fluorescence lifetime was determined from data on the fluorescence transient waveform of the material to be tested and the lamp waveform data using the least-squares iterative deconvolution method [17]. Three thousand counts were collected for each sample.

2.3. Methods

Tridistilled water and fresh sample solutions were used throughout the experiments. The pH value of solutions, fixed at 9.5, was adjusted by adding NaOH and no buffers were used [18]. Stock solutions of naphthalene and its derivatives were prepared in methanol. The fluorescence spectra for the mixture of the donor naphthalene with the acceptor compound A and for the acceptor compound A only were recorded under same conditions. The latter has been subtracted from the former to give accurate spectral information and the net change in the fluorescence intensities for both donor and acceptor. The influence of dissolved oxygen on the systems in the present work was investigated and it was found to be typically less than 5%. Thus, all samples for the measurements were not deoxygenated and measured directly in the air.

3. Results and discussion

The interaction between compound A and naphthalene in aqueous solution has been studied with absorption and steady-state fluorescence spectra. As can be seen from Fig. 1, there is much overlap between the emission spectrum of naphthalene and the absorption spectrum of compound A. This indicates that the occurrence of the photoinduced energy transfer from naphthalene (donor) to the substituted 3*H*-indole moiety of compound A (acceptor) is possible [19].

The fluorescence spectra for the mixture of naphthalene at fixed concentration and compound A at various concentrations are shown in Fig. 2. Considering the fact that the fluorescence

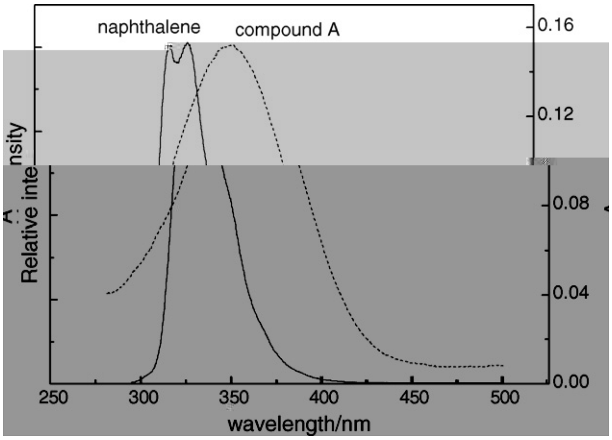

Fig. 1. Fluorescence emission of naphthalene (10 μM) and absorption of compound A (10 μM) in aqueous solution.

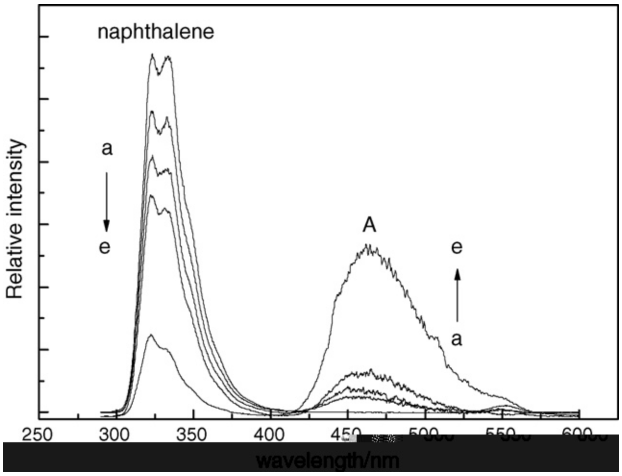

Fig. 2. Fluorescence spectra of naphthalene (10 μM) in the presence of compound A at various concentrations (from (a) to (e): 0, 10, 20, 30 and 100 μM). The excitation wavelength = 275 nm. Note that the spectrum of the compound A only has been subtracted from the fluorescence spectra of the mixture of donor naphthalene and acceptor compound A, which gives net changes of fluorescence intensities for both donor and acceptor.

Table 1
Förster energy transfer parameters, inclusion association constants of donor–acceptor pair and the inclusion percents of donor in the β-CD cavity of compound A

Donor	R_0 (Å)	K_1 ($\times 10^3$ M^{-1})	Molar ratio (donor:acceptor)	Inclusion percent of donor (%)	E_{ET}	R (Å)
Naphthalene	20.8	7.2 ± 0.9	1:1	6	0.10	30.0
			1:2	11	0.23	25.3
			1:10	40	0.80	16.5
2-Naphthol	26.6	11.1 ± 0.6	1:1	9	0.27	31.0
			1:2	16	0.41	28.4
			1:10	51	0.83	20.4
2-Methoxy naphthalene	33.4	12.4 ± 0.1	1:1	10	0.22	40.9
			1:2	18	0.38	36.3
			1:10	54	0.84	25.3

spectra for both donor and acceptor are net ones, we can see that the PET phenomenon does take place. Since compound A adopts the rim-covering conformation, energy transfer can undergo in two routes, one is the dyra1(Sinc20.5(dyraquench-381.6(dyrabetweeJT*[(undeound)-250(406)-1A0(406)5)-354.406)-1-405.1(6)-

[21], i.e.:

$$k_{\text{diff}} = \frac{8kT}{3\eta} = 6.6 \times 10^{9}\,\text{M}^{-1}\,\text{s}^{-1} \qquad (3)$$

This leads us to conclude that molecular dynamic diffusion is not the unique mechanism for the quenching studied herein. According to the literature, the bimolecular quenching concerning the singlet state of an organic molecule is mostly attributed to the long-range Förster energy transfer [22], or electron transfer [23].

In the time-resolved fluorescence measurements, the lifetime of naphthalene in pure water was estimated to be 35.3 ns. For we measured the sample directly in the air, the possible weak quenching of O_2 [19] made the value slightly lower than 39.0 ns reported in the literature [24]. For the same reason, the lifetime of naphthalene in the aqueous solution of β-CD (10 mM) was estimated to be 56.3 ns, also slightly lower than 60.9 ns reported in the literature [24]. To our knowledge, the 1:1 (guest:host) inclusion complex was formed between naphthalene of low concentration and β-CD in aqueous solution, whereas the 2:2 inclusion complex was formed at high concentration of naphthalene [24,25]. Thus, naphthalene in the hydrophobic cavity of β-CD can be well shielded from water molecules. This can reduce the intersystem crossing rate of naphthalene to some extent and results in a much longer lifetime [24]. To the mixture of naphthalene and compound A at the molar ratio of 1:2 (donor:acceptor) that was excited at 275 nm, the fluorescence decay curves at emission wavelengths of 333, 365, 47kr0.61dm3ofth42d(mea819.9he)pleo.3(w)10ymea819.9(se322.5(lifetime)]TJ1.3143 0 tor, and R_0 is the Förster or critical transfer distance at which the energy transfer rate is equal to the decay rate. R_0 being a function of the spectral properties of a donor–acceptor pair can be represented as [27]:

$$R_0^6 = \frac{(9000 \ln 10)\kappa^2\phi_\mathrm{D}}{128\pi^5 n^4 N} \int_0^\infty F_\mathrm{D}(\lambda)\varepsilon_\mathrm{A}(\lambda)\lambda^4 \, \mathrm{d}(\lambda)$$
$$= 8.79 \times 10^{-5} \, (\kappa^2 n^{-4} \phi_D J(\lambda)) \tag{5}$$

where κ^2 is the orientation factor related to the geometry of the donor–acceptor dipoles and for random orientation as in fluid solution $\kappa^2 = 2/3$, n the refractive index of the medium, ϕ_D the quantum yield of the donor in the absence of acceptor, N the Avogadro number, $F_\mathrm{D}(\lambda)$ the spectral distribution of corrected donor emission, and $\varepsilon_\mathrm{A}(\lambda)$ is the extinction coefficient of the acceptor [28]. For this naphthalene-compound A pair, the spectral overlap integral $J(\lambda)$ was calculated to be $1.514 \times 10^{14}\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}\ (\mathrm{nm})^4$ for the emission spectrum of naphthalene and the absorption spectrum of compound A. Thus, the value of R_0 was estimated to be 20.8 Å, which is in the range of 20–60 Å for a typical donor–acceptor pair [29]. Based on Eq. (4) and Fig. 2, we know that4[e0.8(thatnapr)18(gy0.8(that4he)sfkr0.8(thatn41.6(coef)cD[(y0.8(that)-241.68(thRat178ongly0.8(thatdepe-28)2531(fluid[d)-4519nu

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