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Excitation energy transfer in supramolecular assemblies of aqueous vesicles of 4-(5-dodecyloxynaphthalene-1-oxy) butyl trimethylammonium bromide

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Abstract

A single chain synthetic amphiphile, 4-(5-dodecyloxynaphthalene-1-oxy) butyl trimethylammonium bromide ($C_{12}Naph(1,5)C_4N^+$), can be self-assembled into vesicles in the dilute aqueous solution and subsequently form excimer in the vesicles. The excitation energy transfer has been performed in the $C_{12}Naph(1,5)C_4N^+$ aqueous vesicles. The donor, naphthalene group, was embedded in the interior of the vesicles. The acceptor, titan yellow, with two negatively charged polar groups, was bound electrostatically to the positively charged surface of vesicles. The energy transfer efficiency increased with the increase of the concentration of titan yellow acceptor in the range of $0-1.2 \times 10^{-5}$ mol dm^{-3}. Titan yellow quenched the fluorescence intensity of the naphthalene, which fitted a Stern–Volmer plot, and the Stern–Volmer quenching constant K_{sv} is 1.75×10^4 dm^3 mol^{-1}.

Keywords: Excitation energy transfer; Excimer; Vesicles; Amphiphiles

1. Introduction

Photoexcitation energy transfer has been recognized as the primary step in vivo photosynthesis [1], which is largely dependent on molecular organization and cooperation in membrane protein [2]. For mimicking this process operating in nature, several approaches have been exploited in decades such as Langmuir–Blodgett films, micelles and vesicles [3,4]. Artificial amphiphiles can assembly to vesicles in the dilute aqueous solution and organize functional molecules or ions in their microenvironments [5]. The constrained and organized systems have proved to be useful media for the processes occurring in photosynthesis, such as photoionization [6], electron transfer [7], efficient charge separation [8] and photoexcitation energy transfer [9]. These artificial mimetic media can support a higher local concentration and thus improve energy transfer efficiency [10].

From the viewpoint of molecular architecture, a specific chromophore introduced into the single chain amphiphiles not only increases intermolecular interaction in the aggregates but also provides molecular probe, which can be monitored the changes of molecules or ions in the aggregates and directly obtained information of microenvironment at the molecular levels such phase transition, photoemission and molecular orientation [11]. In general, the single-chain ammonium amphiphile form micelles. However, the introduction of a rigid chromophore, such as azobenzene, benzalaniline, anthryl or biphenyl groups, into the long chain results in

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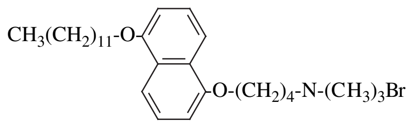
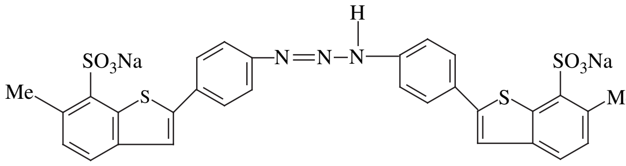
its aggregated structure from micelle to bilayer structure and allows functionalization such as energy transfer and controlled formation of aggregates [12]. We have interested in the photochemical process of synthetic bilayer membranes containing a chromophore and have observed efficient energy transfer in a bilayer membrane with the biphenyl moiety [13]. In the present work, we study further intermolecular energy transfer in the aqueous vesicles of 4-(5-dodecyloxynaphthalene-1-oxy) butyl trimethylammonium bromide (C_{12}Naph(1,5) C_4N^+). The naphthalene group embedded in the vesicles are used as energy donors, the titan yellow (TY) bound to surface of vesicles as acceptor. Meanwhile the naphthalene chromophore introduced can also be as a spectral probe to examine molecular aggregation and to obtain detailed information about the molecular architecture in C_{12}Naph(1,5)C_4N^+ vesicles.

2. Experimental

Synthesis, purification and characterization of C_{12}Naph(1,5)C_4N^+ amphiphile have been described previously [14]. This amphiphile (8×10^{-4} mol dm^{-3}) is given transparent aqueous dispersion by sonication (Branson B-92, ultrasonicator) for ca. 4 h and form stable vesicles. Globular vesicles with diameters ranging from 50 to 200 nm were observed under an electron microscope (JEM-2000 FM). The vesicles were stable in the PH range 4–10 for weeks. The phase transition from crystal to liquid crystal (T_c) determined by differential scanning calorimetry (ca. 1 wt.%, Perkin–Elmer, DSC-2C) is located at 42 °C. The sample of titan yellow (Shanghai General Reagent Works, A.R. grade) was used without further purification. Water was doubly distilled after passing through an ion-exchange resin column. Ethanol (Beijing Chemicals Factory) was redistilled before use. The structure of the C_{12}Naph(1,5)C_4N^+ and titan yellow is shown in Fig. 1.



C_{12}Naph(1,5)C_4N^+



Titan yellow

Fig. 1. Structural formulae of C_{12}Naph(1,5)C_4N^+ amphiphile and titan yellow(TY).

Steady-state fluorescence spectra were recorded on a Spex Fluorolog spectrophotometer, by using front-face angle illumination. Time-resolved fluorescence measurements were carried out with an SP-70 time-domain fluorescence spectrophotometer, operating on the single-photon counting principle, with appropriate deconvolution-fit programs. UV spectra were measured with a Shimadzu UV-3100 spectrophotometer. Since N_2-bubbled and air-saturated solutions gave the same results, the data presented here are all for air-saturated solutions.

3. Results and discussion

3.1. Excimer formation in C_{12}Naph(1,5)C_4N^+ aqueous vesicles

Fig. 2 shows the fluorescence spectra of C_{12}Naph(1,5)C_4N^+ amphiphile in chloroform and aqueous solution at room temperature, respectively. The emission spectra of C_{12}Naph(1,5)C_4N^+ in water and chloroform exhibit a structural band with maxima at 367 nm, 348 nm and 336 nm, which ascribed to monomer emission of naphthalene molecules in the amphiphiles [9]. However, there is not any fluorescence band for the chloroform solution of C_{12}Naph(1,5)C_4N^+ (a), but a weak and broad band appears centred at ca. 430 nm in the spectrum (b) of its aqueous solution in the region of 400–500 nm. The difference in the aqueous solution and chloroform ascribed to excimer formation

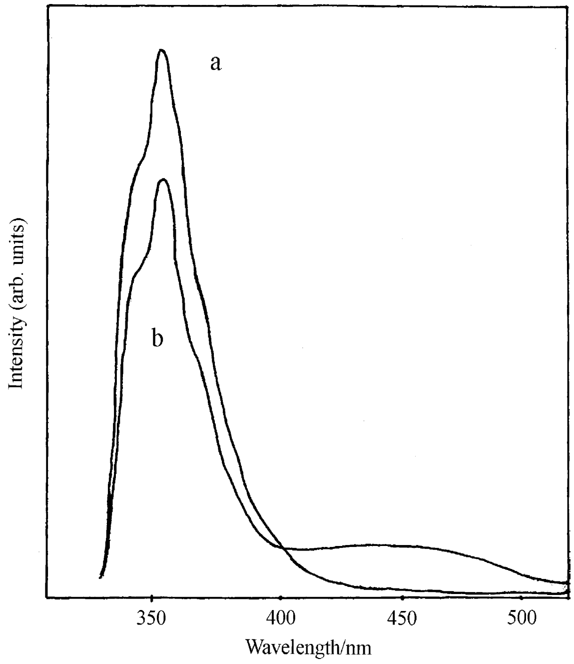


Fig. 2. Emission spectra of C_{12}Naph(1,5)C_4N^+ amphiphile in chloroform (a) and aqueous solution (b).

in the aqueous solution [9], in which the $C_{12}Naph(1,5)C_4N^+$ amphiphilic molecules self assembled into vesicles with closely stacking arrangement of molecules, while the amphiphile takes monodispersion form in chloroform solution. As we known that the excimer is usually considered to be the plane-to-plane sandwich structure constructed by the excited and ground states of the plane molecules. In vesicles, the naphthalene ring might closely arrange into parallel to each other and subsequently formed excimers which yielded a weak and broad fluorescence band near 430 nm [9,15,16]. In monodisperse system of the chloroform solution, the naphthalene molecules were not closely packing, so no corresponding band turns up in spectrum of Fig. 2(a). Several typical packing fashion of naphthalene rings of amphiphilic molecules in vesicles might be inferred to be that illustrated in Fig. 3. It is well known that the excimer formation is related to the distance and overlap extent of naphthalene rings in vesicles. Complete overlap of the naphthalene rings in vesicles (Fig. 3(a)) is suitable for producing excimers, while partial overlap of the naphthalene rings (b) is slightly, although it is impossible to describe precisely the packing geometries of naphthalene units in the vesicles at the present stage [17].

3.2. Excitation energy transfer from naphthalene to the membrane-bound TY anions in the vesicles

Fig. 4 shows the excitation and emission spectra of aqueous $C_{12}Naph(1,5)C_4N^+$ bilayer vesicles (a, a′: 8×10^{-4} mol dm^{-3}) and aqueous TY solution (b, b′: 1.6×10^{-4} mol dm^{-3}), respectively. The weak and broad bands at ca. 430 nm of a′ curve indicated the formation of excimers in the vesicles. The spectra of naphthalene centered at 348 nm are similar to those in ethanol solution except for the slight red shift of the corresponding bands [18]. Complete overlap of emission band at 348 nm of naphthalene (a′) with the excitation band at 348 nm of TY (b) suggests possible Förster-type intermolecular energy transfer from the naphthalene rings to the membrane-bound TY anions in the vesicles. Such energy transfer was virtually observed in the presence of $C_{12}Naph(1,5)C_4N^+$ vesicles and TY, as illustrated in Fig. 5. In fact, the excitation of the mixture of $C_{12}Naph(1,5)C_4N^+$ and TY in aqueous solution (Fig. 5, curve 5) at 295 nm, where the direct photon energy absorption of TY is very weak (Fig. 4 curve b′), resulted in an increase of the emission intensity of TY centered at ca. 430 nm and a concomitant decrease of the emission intensity of naphthalene in the vesicles centered at 348 nm. In ethanol solution, however, no energy transfer was observed under the same condition [18]. These results imply that the TY anions were first organized on surface of membrane by electrostatic interaction in aqueous solution and then closed to the distance for energy transfer between naphthalene and titan yellow chromophores. The organization of the $C_{12}Naph(1,5)C_4N^+$ amphiphilic molecules in aqueous solution plays a decisive role in the energy transfer from the naphthalene to TY.

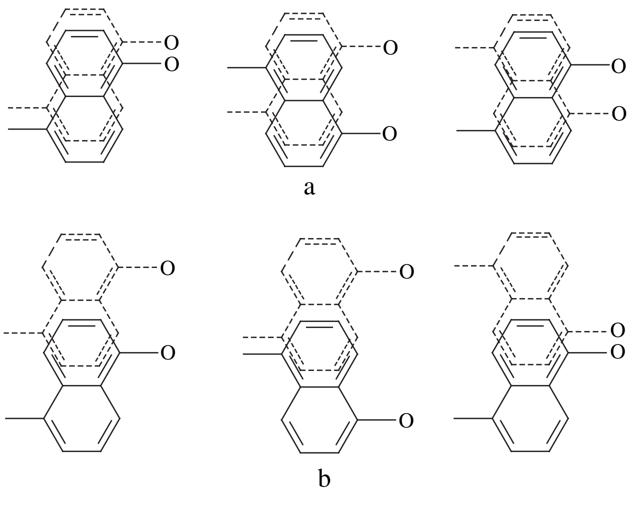


Fig. 3. Possible arrangements for naphthalene rings of $C_{12}Naph(1,5)C_4N^+$ molecules in vesicles. O: Hydrophilic group: $-N^+(CH_3)_3$.

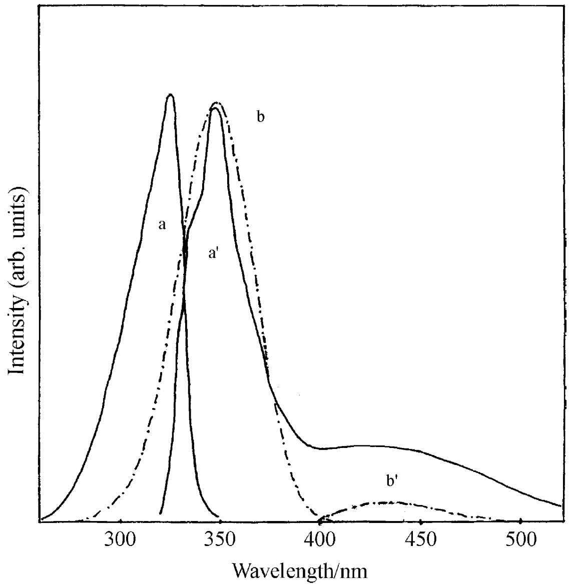


Fig. 4. Excitation and emission spectra of $C_{12}Naph(1,5)C_4N^+$aqueous vesicles (8.0×10^{-4} mol dm^{-3}, curves a and a′); titan yellow (1.6×10^{-5} mol dm^{-3}, curves b and b′). Curves a, b are excitation spectra monitored at 375 nm for a and 437 nm for b, respectively. Curves a′, b′ are emission spectra excited at 295 nm.

Fig. 5 shows the changes of the fluorescence spectra of $C_{12}Naph(1,5)C_4N^+$ aqueous vesicles with increasing of the concentration of titan yellow at room temperature, which is below the phase-transition temperature of the vesicles. The fluorescence intensity of the

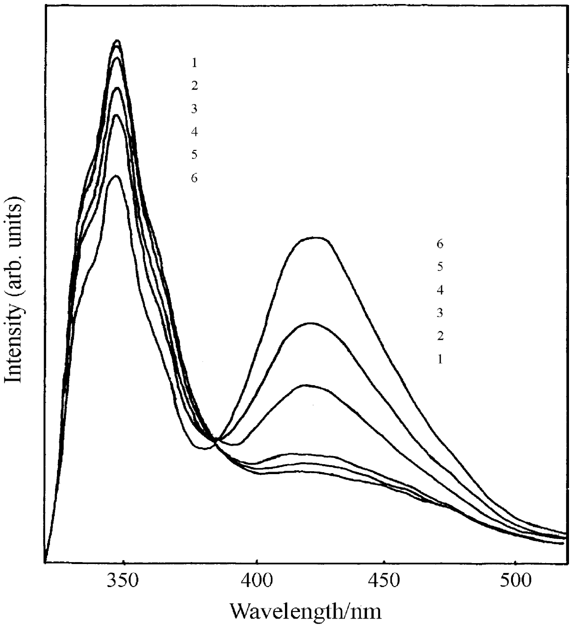


Fig. 5. Energy transfer from a naphthalene chromophore in $C_{12}Naph(1,5)C_4N^+$ vesicle to a membrane-bound titan yellow acceptor at different concentrations of titan yellow. Concentration of $C_{12}Naph(1,5)C_4N^+$ vesicles: 8.0×10^{-4} mol dm^{-3}, excitation at 295 nm. Titan yellow concentration: (1) 0, (2) 8×10^{-7}, (3) 1.6×10^{-6}, (4) 8×10^{-6}, (5) 1.6×10^{-5}, (6) 4×10^{-5} mol dm^{-3}, respectively.

naphthalene emission of $C_{12}Naph(1,5)C_4N^+$ vesicles, which gives a peak centered at 348 nm, gradually decreases with increasing of the concentration of titan yellow in aqueous vesicles. The fluorescence intensity of the emission peak of the titan yellow centred at ca. 430 nm increases with concentration up to a stoichiometric TY concentration of 2×10^{-5} mol dm^{-3}. Beyond this concentration, the fluorescence intensity started to decrease, which is probably due to inner filtering.

It is clear that the titan yellow molecules quench the fluorescence of the naphthalene chromophore in the $C_{12}Naph(1,5)C_4N^+$ vesicles. The concentration quench obeyed the Stern–Volmer relationship, Eq. (1), over the concentration range studied ($0–2 \times 10^{-5}$ mol dm^{-3}), as shown in Fig. 6.

$$I_0/I - 1 = K_{sv}[\text{titan yellow}] \qquad (1)$$

where I_0 and I are the emission intensities of $C_{12}Naph(1,5)C_4N^+$ vesicle in absence and presence of titan yellow, respectively, and K_{sv} is the Stern–Volmer quenching-constant. Quenching data are plotted according to Eq. (1) in Fig. 6. The slope of the Stern–Volmer plot gives $K_{sv} = 1.75 \times 10^4$ mol^{-1} dm^{-3}.

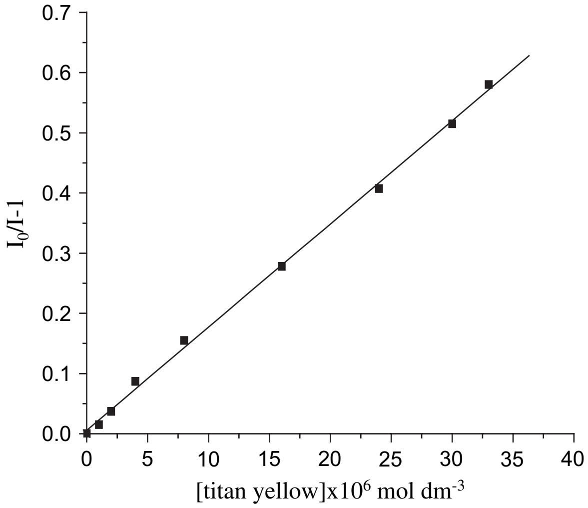


Fig. 6. Stern–Volmer plot of $C_{12}Naph(1,5)C_4N^+$ vesicles.

4. Conclusions

Completely synthetic single chain amphiphile, $C_{12}Naph(1,5)C_4N^+$, can form excimers due to closely ordered arrangement of naphthalene rings in the vesicles. The efficient transfer of excitation energy was performed through the naphthalene chromophore introduced in the amphiphilic molecules of the vesicles to membrane-bound titan yellow molecules. The synthetic bilayer membrane exhibited functions similar to the complex liposomes, but is readily manipulated and functionalized. Thus, specific chromophore-containing vesicles will have many applications in these fields, although the functionalization of aqueous vesicles for practical use is still an exploring subject.

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