Interlayer Energy Transfer from Naphthalene to Anthracene Chromophores Organized in Langmuir-Blodgett Films

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Abstract: Interlayer energy transfer between 2, 3-naphtho-10-hexadecylaza-15-crown-5 (NC16) and N-[1-(9-methoxyanthryl)]decylaza-15-crown-5 (A10C) within multilayer Langmuir-Blodgett films has been studied by steady-state fluorescence spectra. The donor and acceptor could be separated precisely by inserting stearic acid (SA) spacers. The efficiency of the energy transfer increases with the decrease in the donor-acceptor distance by a quadratic manner, suggesting the donor excitations are delocalized in the layer.

Keywords: Energy transfer, L-B film, naphthalene, anthracene.

In plant photosynthesis the photo energy absorbed by the "antenna" chromophores may migrate on the two dimensional (2D) surface of the biomembranes, and eventually is transferred to the photosynthetic reaction centers. The dynamics and mechanism for such energy transfer and migration are largely controlled by the topological structure of the photosynthesis systems. Elucidation of the relationship between the mechanism of the energy transfer and the topological structure of the systems is essential for understanding photosynthesis, and also for the construction of functional molecular assemblies. To mimic the efficient photon harvesting occurring in plant photosynthesis and to provide the base for designing molecular devices, energy transfer and migration in 2D chromophoric assemblies have been extensively examined[1-4], and Langmuir-Blodgett (L-B) technique is particularly suitable for such studies[5]. In the present work the interlayer excitation energy transfer between a naphthalene derivative, 2,3-naphtho-10-hexadecylaza-15-crown-5 (NC16), and an anthracene derivative, N-[1-(9-methoxy-anthryl)]decylaza-15-crown-5 (A10C, **Scheme 1**) in L-B film has been examined. The distance between the donor NC16 and the acceptor A10C was varied by interposing stearic acid (SA) monolayers. A quadratic dependence of the energy transfer efficiency on the separation distance between the donor and acceptor monolayers was observed, suggesting delocalization of the excitation energy on the donor monolayer.

NC16 and A10C were synthesized and will be published elsewhere. These molecules form stable compressible floating monolayers at the air/water interface on a 0.1 mol/L NaCl aqueous subphase upon mixing with SA in 1:1 molar ratio.

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Figure 1 shows the pressure-area isotherms obtained for mixed monolayers of the chromophores and SA. These monolayers can easily be transferred onto a quartz substrate. AFM measurements show that the film is uniform. The areas per molecular pairs of NC16-SA and A10C-SA at 20 mNm^{-1} surface pressure are *ca.* 0.55 and 0.52 nm^2 respectively, which are consistent with a space-filling molecular model for approximately vertical packing of the hydrocarbon chain and close contact of the crown-ethers with the water surface. From the mean molecular areas, the surface densities of the chromophores naphthalene and anthracene at the deposition pressure were estimated to be *ca.* 1.82 and 1.92 molecules per nm^2 respectively.

Scheme 1 The structure of NC16 and A10C


NC16   A10C
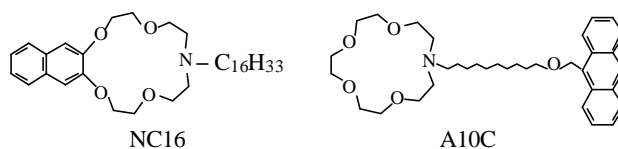
Multilayers deposited on quartz plates were also prepared in the following order: (1) monolayer of NC16-SA, (2) variable layers of SA, and (3) monolayer of A10C-SA. The structures of the L-B film used for energy transfer study are illustrated schematically in **Figure 2**.

Figure 1 The π-A isotherm curves of NC16-SA and A10C-SA on a 0.1 mol/L NaCl aqueous subphase at 20°C
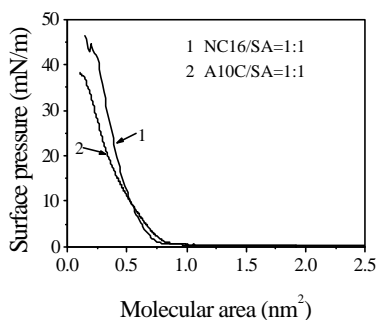
Figure 2 Schematic illustration of the structure of the L-B films used in the present study

1 NC16/SA=1:1
2 A10C/SA=1:1

⇒ SA
⇒ C10An
⇒ NC16
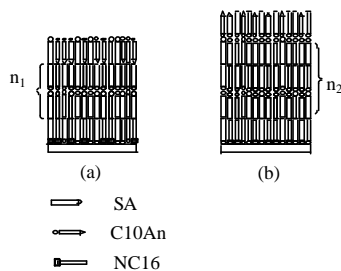
(a) The donor and acceptor monolayers are interspaced by even number of SA monolayers;
(b) The donor and acceptor monolayers are interspaced by odd number of SA monolayers

To examine the interlayer energy transfer, fluorescence spectra of the L-B films were measured with an excitation wavelength of 290 nm, and are shown in **Figure 3**. At this excitation wavelength, photoenergy is mostly absorbed by the naphthyl chromophore. The monolayer of NC16 exhibits the structured fluorescence character of naphthyl monomer with maxima at 333, 347 and 362 nm and excimer emission with maximum at 425 nm. The bilayer composed of one NC16 layer and one A10C layer shows strong anthryl fluorescence with maxima at 394, 418 and 438 nm and weak fluorescence from the naphthyl group. Using 290 nm as the excitation wavelength, the

fluorescence of A10C monolayer (in the absence of NC16) is very weak. The above observation suggests that efficient interlayer energy transfer occurs from the naphthyl to the anthryl chromophore. It has been established that the naphthyl excimer does not play an important role in the energy transfer to the anthryl, although this energy transfer process is allowed according to the spectral overlap of the naphthyl excimer fluorescence with the anthryl absorption[6-8]. Consequently, the energy transfer is from the naphthyl monomer. Due to the competition between the energy transfer process and the naphthyl excimer formation, efficient energy transfer results in no excimer emission in the above bilayer system. As the distance between the NC16 and A10C momolayers is increased by inserting SA monolayer spacers, the efficiency of the energy transfer is decreased (**Figure 3**). However, even the naphthyl and anthryl monolayers are separated by 5 layers of SA, efficient energy transfer still can occur.

Figure 3 The fluorescence spectra of NC16-SA and A10C-SA organized in the L-B film, λ_{ex} = 290 nm
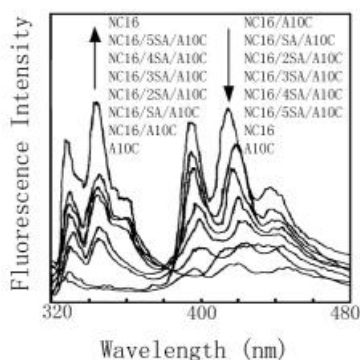
Figure 4 Plot of ($\log(I_0/I-1)$) as a function of the distance between chromophores naphthalene and anthracene
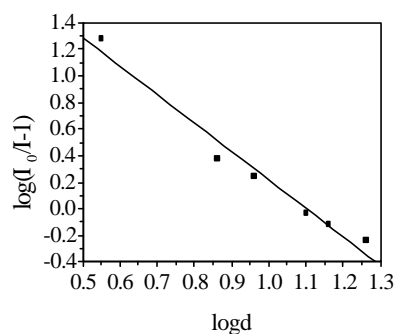
The system studied in the present work involves a donor and an acceptor monolayer separated by a number of SA spacer layers. Each layer of SA represents a distance of *ca.* 2.5 nm[9], and the thickness of each layer of NC16-SA is also 2.5 nm, assuming vertical packing of the hydrocarbon chain and close contact of the crown-ethers with the substrate. In the calculation of the donor-acceptor distance, we assume that the separation between the anthracene chromophore and the crown ether in A10C is *ca.* 1.7 nm. The energy transfer follows Förster theory of dipole-dipole interaction. If the donor excitation is localized on the 2D monolayer, the following equation for the efficiency dependence on distance is applicable[10-13].

$$I/I_0 = 1/[1+(d_0/d)^4] \tag{1}$$

where I and I_0 are the donor fluorescence intensities in the presence and absence of acceptor respectively; *d* is the separation distance between the donor and acceptor layers, and d_0 is the critical energy transfer distance at which the rate of energy transfer equal to the rate of donor de-excitation by all other processes. On the other hand, if the

excitation in the donor layer is delocalized over distance larger compared with the interlayer spacing, the fall-off of energy transfer efficiency with distance is predicted to be quadratic[11-13].

$$I/I_0 = 1/[1+(d_0/d)^2] \qquad\qquad (2)$$

Equations 1 and 2 can be rearranged as

$$(I_0/I-1) = (d_0/d)^k \qquad (3) \qquad\qquad \log(I_0/I-1) = k\log d_0 - k\log d \qquad (4)$$

We measured the naphthyl fluorescence intensities I_0 and I, at 347 nm in the absence and presence of the A10C monolayer from **Figure 3**. The plot of $\log(I_0/I - 1)$ *vis.* $\log d$ is shown in **Figure 4**. The slope of the plot is calculated to be *ca.* 2.1. The critical transfer distance d_0 is found to be *ca.* 12.6 nm, which is consistent with the literature value 13.0 nm[9]. Thus, the energy transfer is expressed by quadratic behavior. This suggests that the donor excitation is delocalized on the NC16 monolayer. This is not surprising by consideration of the high density of the naphthyl chromophore on the donor 2D monolayer.

Acknowledgments

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