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Excitation Hopping Behavior between Two Naphthyl Moieties Spatially Fixed in Triptycene Structure

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Abstract Spatially fixed bichromophoric systems with nonidentical chromophores have been extensively employed for studies of electron transfer and excitation transfer. Excitation hopping behavior between two naphthyl moieties in 7, 14-dihydro-7, 14-ethanodibenz[a,h]anthracene(DEA) has been explored by the time-resolved fluorescence anisotropy measurements. The experimentally obtained value of the hopping rate in DEA agrees at least qualitatively with that calculated on the basis of the Dexter's theory, but disagrees with that calculated on the basis of the Förster's theory, indicates that for a pair of donor and acceptor with inter-chromophore separation as short as 4.5 Å, excitation transfer via electron exchange is a predominant process.

INTRODUCTION

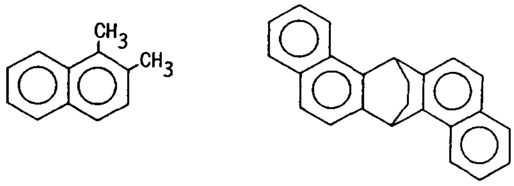
In previous works[1~4], excitation hopping behavior between two identical chromophores attached to both ends of alkanes and polystyrene chains was explored by time-resolved fluorescence anisotropy measurements[1,2]. The observed decays of fluorescence anisotropy, r(t), were analyzed on the basis of the results of the conformational analysis of the bichromophoric molecules. Although the conformational analysis employed in the previous papers[1,2] seems to reflect precisely the interchromophore distance ($\underline{R}$) and angular distribution of the relevant chromophores and hence the experimentally observed decay curves of r(t) were well reproduced by the simulated curves, the most adequate system for the study of the excitation transfer may be bichromophoric systems with spatially fixed chromophores. In these systems, both R and orientation of the two chromophores are unequivocally determined by structural analysis of the compounds such as X-ray analysis.

Such spatially fixed bichromophoric systems with nonidentical chromophores have been extensively employed for studies of electron transfer and excitation transfer[7,8]. In the present work, the author has selected triptycene as a frame structure to spatially fix two naphthyl moieties and synthesized 7, 14-dihydro-7, 14-ethanodibenz[a,h]anthracene (DEA). Excitation hopping behavior between two naphthyl moieties in triptycene has been explored by the time-resolved fluorescence anisotropy measurements.

EXPERIMENTAL

Materials

Structures of the model compound and bichromophoric compound used in this study are shown in Fig. 1. 1,2-Dimethylnaphthalene (DMN) was used as a model compound with a si-



DMN DEA

Fig. 1. Structure of DMN and DEA used in this study

ngle chromophore in a molecule and was purified by distillation under reduced pressure.

Measurements

Absorption and fluorescence spectra were measured as described in previous papers[1,2]. Time-resolved measurements of fluorescence and fluorescence anisotropy were conducted by the time-correlated single-photon counting method described in previous papers[1~4].

In order to exclude the contribution of rotational diffusion of the chromophores to fluorescence depolarization, the fluorescence anisotropy, r(t), was measured in a rigid matrix of 2-methyltetrahydrofuran (MTHF) at 77 K.

RESULTS

Absorption and Fluorescence Spectra, and Fluorescence Lifetimes

Fig. 2 shows absorption spectra of DEA and its model compound, DMN, in MTHF at room temperature. DEA exhibited a similar spectrum to that of DMN, but red-shifted by ~3 nm than that of DMN.

The same tendency was observed in excitation spectra of DEA and DMN as shown in Fig. 3 where excitation spectra of both compounds at room temperature (A) and at 77 K (B) are indicated for comparison. It is clear that at 77 K the peak of ^1L_b band at ~325 nm is enhanced in its intensity both in DEA and DMN in comparison with that at room temperature.

Fluorescence spectra of DMN are shown in Fig. 4 in which a spectrum indicated by solid line corresponds to that of room temperature while one indicated by dotted line was obtained at 77 K. It is recognized that the peak positions are insensitive to temperature while their intensities are affected by temperature, but only to some extent. On the other hand, fluo-

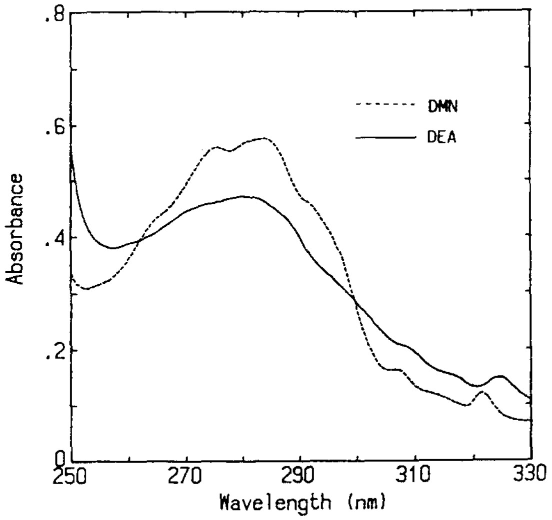


Fig. 2. Absorption spectra of DMN and DEA in MTHF at room temperature.

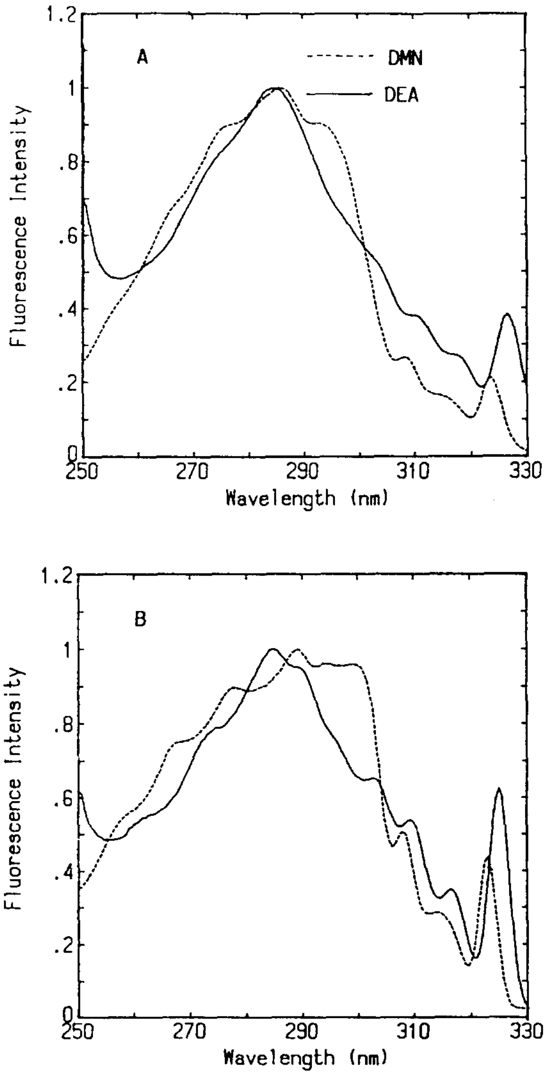


Fig. 3. Excitation spectra of DMN and DEA in MTHF at room temperature (A) and 77 K (B), respectively.

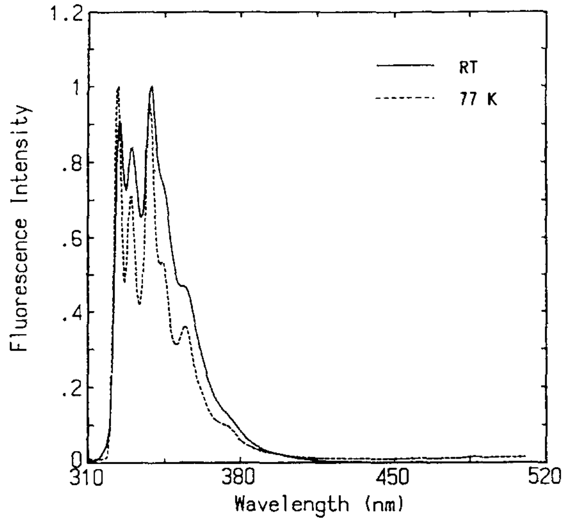


Fig. 4. Fluorescence spectra of DMN in MTHF at room temperature and 77 K.

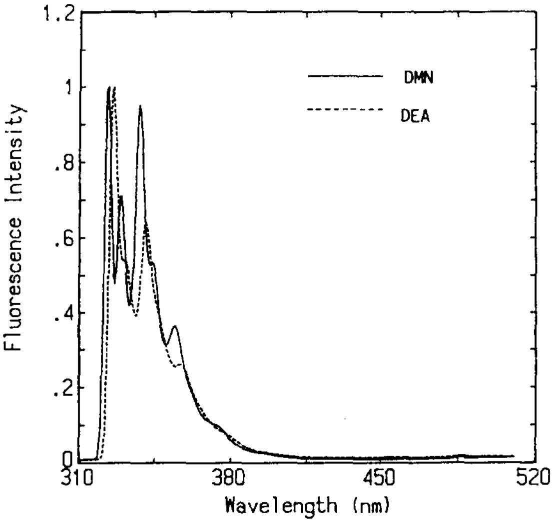


Fig. 6. Fluorescence spectra of DMN and DEA in MTHF at 77 K.

rescence spectra of DEA were significantly affected by the temperature.

As shown in Fig. 5 , the spectrum obtained at room temperature (solid line) was broad and red-shifted remarkably in comparison with that at 77 K (dotted line), demonstrating that some interchromophoric interaction is operative between two naphthyl moieties in triptycene at room temperature. At 77 K, however, both DEA and DMN exhibited similar spectra as shown in Fig. 6, although the spectrum of DEA was red-shifted by ~2.6 nm in comparison with that of DMN. These results indicate that at 77 K the naphthyl moieties in DMN and DEA possess similar properties (e.g. energy level) in the excited state.

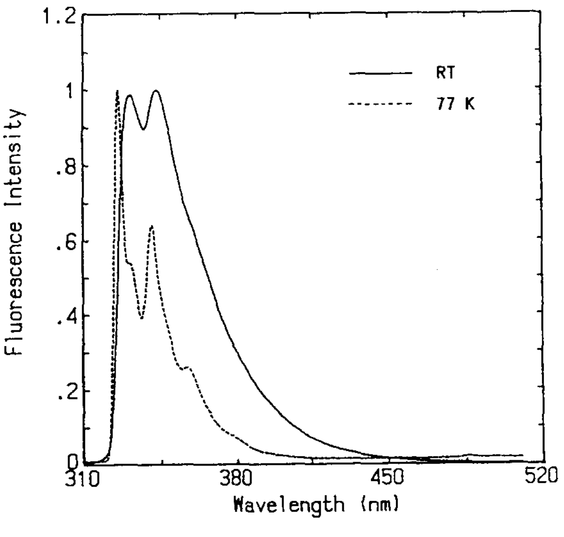


Fig. 5. Fluorescence spectra of DEA in MTHF at room temperature and at 77 K.

Lifetime measurements, however, have revealed quenching of the excited naphthyl moiety in triptycene. The decay profiles of DMN could be analyzed essentially by a single-exponential function at both temperatures : $\tau=56.6$ ns at room temperature ($\chi^2=1.28$, DW$=1.84$) and $\tau=80.7$ ns at 77 K ($\chi^2=1.16$ and DW $=1.72$).

On the other hand, DEA showed much faster decays at room temperature as well as at 77 K, though the decay profiles were similarly analyzed by the single-exponential function. At room temperature, $\tau=25.4$ ns ($\lambda_{ex}=300$ nm, $\lambda_{em}=324$ nm; $\chi^2=1.42$, DW$=1.63$) and at 77 K, $\tau=35.4$ ns ($\lambda_{ex}=300$ nm, $\lambda_{em}=326$ nm; $\chi^2=1.41$, DW$=1.50$). These values of τ are less than half of those of DMN at each temperature.

Furthermore, at 77 K, the decay profile of DEA was insensitive to the monitoring wavelength (λ_{em}), while at room temperature the

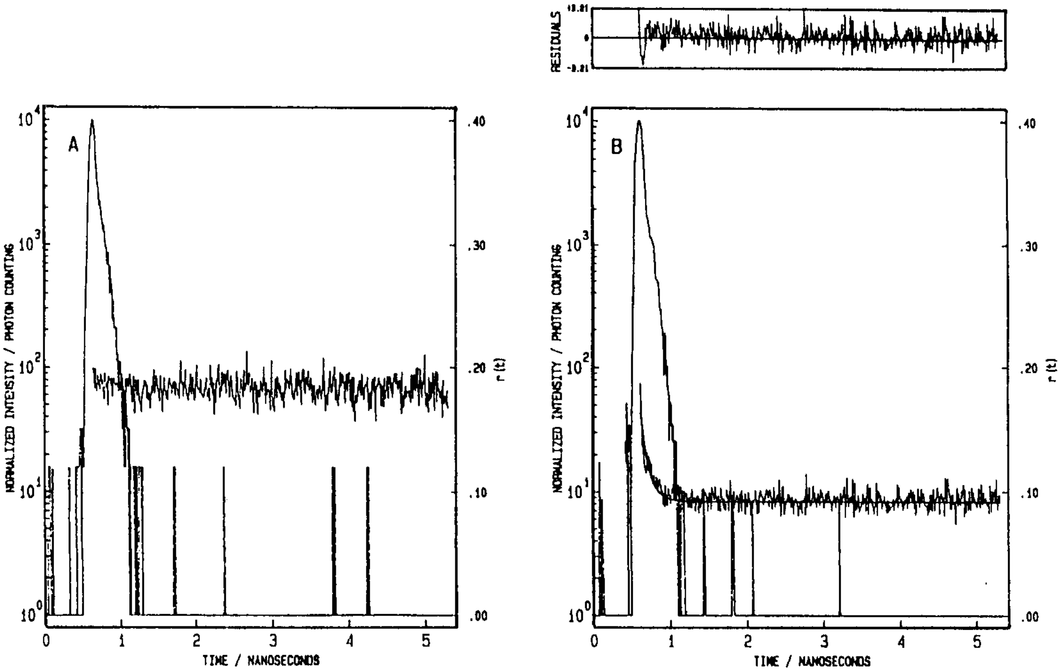


Fig. 7. Fluorescence anisotropy decays of DMN (A) and DEA (B), respectively: The best fit curve based on r(t) = Aexp(-2ωt) + B. Measured in MTHF at 77 K : λ_{ex}=300 nm λ_{em}=326 nm; time division 10.17 ps/channel.

decay behaviors were much different, depending on λ_{em} and they could no longer be analyzed by the single-exponential function.

Fluorescence Anisotropy Decays

Fluorescence anisotropy decay behaviors of DMN and DEA are shown in Fig. 7. The decays of r(t) were measured at 77 K with λ_{ex}= 300 nm and λ_{em}=326 nm for both compounds. The values of r(t) for DMN does not change with time, which indicates that the excited state remained at the originally excited site. On the contrary, r(t) of DEA decayed, which demonstrates clearly that excitation hopping takes place between two naphthyl moieties in triptycene.

DISCUSSION

The present study has clearly shown that excitation hopping takes place between two naphthyl moieties in triptycene. Unlike α, ω,-bis(2-naphthyl)alkanes (Nn) described in previous work[1], DEA possesses spatially fixed naphthyl moieties in a single molecule and hence distribution need not be taken into account on interchromophore distance (R) and orientation of the naphthalene rings. For such a spatially fixed pair of identical chromophores, eq 1 may be strictly applied:

$$r(t)=1/2(r_0-r_1)\exp(-2\omega t)+1/2(r_0-r_1) \qquad (1)$$

where r_0 is the limiting value of r and can be estimated from a case where no fluorescence depolarization occurs as in the case of r for DMN (r_0=0.185). r_1 is the anisotropy of fluorescence emitted entirely by the chromophore which is not originally excited. In Fig. 7B is also included the best-fit curve for the observed decay of r(t) on the basis of eq 2 :

$$r(t)=A\exp(-2\omega t)+B \qquad (2)$$

where A, B and ω are fitting parameters. The values of A, B and ω obtained by the iterative least-squares method are 0.164, 0.092 and 4.7 $\times 10^9$ s^{-1} with χ^2=1.00 and DW = 1.82. This value of hopping rate (ω) is larger by a factor of 26 than that observed for N3 (1,3-bis(2-naphthyl)propane) in previous paper[1], demonstrating that excitation hopping occurs in triptycene quite effectively.

Let's calculate the hopping rate theoretically. The interchromophore distance($\underline{R}$) between two centers of the naphthyl moieties in triptycene was estimated as 4.5 Å for CPK model of this molecule. Furthermore, the angle between the vectors along the long axis of the naphthalene ring was estimated to be 66° by the CPK model. As in previous paper[1], if we assume the ^1L_b band is responsible for the emission, its transition moment lies along the long axis of the naphthalene ring. Thus, the angle between the two transition moment vectors of the donor and the acceptor (θ_{DA}) in DEA is reasonably assumed as $\theta_{DA} = 66°$. Moreover, the angle between two transition moments and $\underline{R}$ (θ_D and θ_A) was calculated as $\theta_D = 45°$ and $\theta_A = 60°$. From these values, the orientation factor was obtained by eq 3 as $\kappa^2 = 0.428$.

$$\kappa = \cos\theta_{DA} - 3\cos\theta_D \cos\theta_A \qquad (3)$$

For calculation of ω on the basis of Förster's theory[5], fluorescence quantum yield of donor (Φ_D), fluorescence lifetime in the absence of acceptor (τ_D) and overlap integral, $J(\upsilon)$, are required in addition to κ as described in previous paper[2]. These values were obtained from Φ_D, and the fluorescence and absorption spectra of DMN at 77 K : $\Phi_D = 0.31$, $\tau = 80.7$ ns, $J(\upsilon) = 1.3 \times 10^{-15}$ cm^6/mol. Using these values ω for DEA was calculated as 1.87×10^{11} s^{-1}.

Owing to proximity of two relevant naphthyl chromophores in triptycene, the Dexter's mechanism[6] may be operative. Next, let's calculate the hopping rate constant on the basis of the Dexter's equation (eq 4); where H is the coupling matrix element, which is assumed to show a single-exponential distance dependence with a preexponential factor H_0 and a fall-off defined by the so-called Bohr radius L, and $f_D(\upsilon)$ and $A(\upsilon)$ are the fluorescence of the donor and the molar extinction coefficient of the acceptor, respectively, as in the case of eq 1. This equation is usually written simply in the form of eq 5.

$$k_D = \frac{4\pi H^2}{h} \frac{\int f_D(\upsilon)\varepsilon_A(\upsilon)d\upsilon}{\int f_D(\upsilon)d\upsilon \int \varepsilon_A(\upsilon)d\upsilon}$$

$$= \frac{4\pi^2 (H_0)^2 e^{-2R/L}}{h} \frac{\int f_D(\upsilon)\varepsilon_A(\upsilon)d\upsilon}{\int f_D(\upsilon)d\upsilon \int \varepsilon_A(\upsilon)d\upsilon} \qquad (4)$$

$$k_D = k_0 \exp(-2R/L) \qquad (5)$$

Very little results have been reported sofar on the absolute value of H_0, however, the value of k_0 has been reported as 6×10^{12} s^{-1} and 1.64×10^{13} s[9,10]. Furthermore, the effective Bohr radius L is twice of the Bohr radius and hence L = 1.07 Å . On the basis of these values and the interchromophore distance estimated for DEA, the hopping rate constant, k_D, was calculated as 1.3×10^9 s^{-1} and 3.6×10^9 s^{-1}, which are in fairly good agreement with the experimentally obtained value of 4.7×10^9 s^{-1}.

The fact that the experimentally obtained value of the hopping rate in DEA agrees at least qualitatively with that calculated on the basis of the Dexter's theory, but disagrees with that calculated on the basis of the Förster's theory, indicates that for a pair of donor and acceptor with interchromophore separation as short as 4.5 Å, excitation transfer via electron exchange is a predominant process.

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