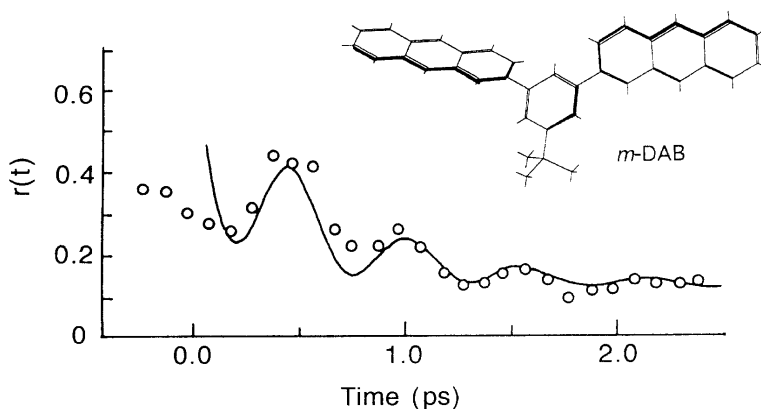


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Observation of Quantum Coherence for Recurrence Motion of Exciton in Anthracene Dimers in Solution

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Most of the previous studies on intermolecular excitation energy transfer have been directed toward the *irreversible* transfer under the very weak interaction limit ($\beta < 1 \text{ cm}^{-1}$) in the Förster's dipole–dipole interaction mechanism.¹ For bichromophoric molecules in which two identical molecules are connected closely, $\beta > 10 \text{ cm}^{-1}$, the quantum mechanical theory predicts that the exciton state expressed as a superposition of two degenerate locally excited states undergoes a recurrence motion of local excitation between the two chromophores.^{2–6} However, such a predicted phenomenon is essentially difficult to observe experimentally, because of very fast phase randomization.^{7,8} Here we report a coherent recurrence motion of exciton, which was observed as damped oscillations on fluorescence anisotropy decays in anthracene dimers in room-temperature solution. The oscillatory curves were fitted reasonably to the theoretical equation.

A schematic diagram of the exciton interaction is shown in Figure 1 for a bimolecular system. When the superposition states of two locally excited states split by an interaction energy 2β are photoexcited coherently, they undergo a time evolution such that the excitation moves back and forth between the coupled chromophores with a time period of $h/2\beta$ due to the interference term.⁹ In conventional experiments, the macroscopic quantum coherence of an ensemble is lost rapidly in solution due to solute–solvent interaction. This is observed if the oscillation period is shorter than the electronic dephasing time. In an experiment based on fluorescence anisotropy decay, an additional condition with regard to dimer structure is that the lab frame orientation of the electronic transition moments of absorption or emission is different between the different halves of bichromophores. Hochstrasser et al.^{7,8} investigated this problem using 2,2'-binaphthyl and 9,9'-bifluorene. Recently, we reported a damped oscillation which appeared on the fluorescence anisotropy decay in an anthracene dimer, dithianthracenophane (DTA, see Figure 2).⁹ Although their oscillatory curves are quite impressive as evidenced by the close agreement with the theoretical prediction, the amplitude of oscillation is rather small for examination along the theory of coherent dynamics.

Two anthracene dimers (Figure 2) were synthesized: 1,2-bis-(anthracen-9-yl)benzene (*o*-DAB) and 3,5-bis-(anthracen-2-yl)-*tert*-butylbenzene (*m*-DAB). The X-ray crystallography for *o*-DAB showed a dihedral angle of 66.2° between the two anthracene rings with the center-to-center distance $r_0 = 5.13 \text{ \AA}$. For *m*-DAB, the dihedral angle in the most stable conformation was estimated to be ca. 60° and $r_0 = 11 \text{ \AA}$ from MO calculation. All the experiments were carried out on toluene and THF solutions with a concentration of ca. 10^{-5} M at room temperature (296 K).

The absorption spectra of *m*-DAB and *o*-DAB are similar to that of the anthracene monomer with well-defined vibronic bands. The

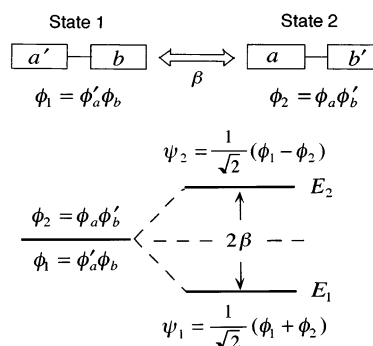


Figure 1. Diagrammatic illustration of the interchromophore interaction (b) in a dimer of a and b, and the creation of the two superposition states ϕ_1 and ϕ_2 split by 2β . In the expression $\phi_a \phi'_b$ or $\phi'_a \phi_b$, the prime stands for the excited singlet state of the chromophore.

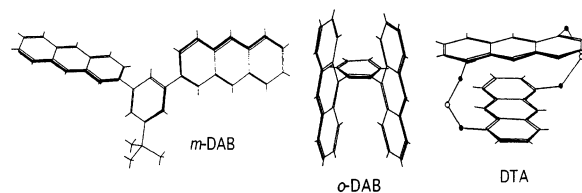


Figure 2. Molecular structures of *m*-DAB and *o*-DAB examined in the present study, and of dithianthracenophane (DTA) studied in ref 9.

bandwidth of the 0-0 band is $300\text{--}400 \text{ cm}^{-1}$, caused by overlap with a fairly strong $\nu_{12} (A_{1g})$ vibrational band of anthracene. The dimers were excited at the 0-0 band of the $S_1 \leftarrow S_0 (L_a)$ absorption with a pulsed laser (pulse width 70 fs, spectral width $\Delta\nu = 211 \text{ cm}^{-1}$). The fluorescence anisotropy decays $r(t)$ were measured with the fluorescence up-conversion method, where $r(t)$ is defined as the difference of the probe signals parallel (I_{\parallel}) and perpendicular (I_{\perp}) to the excitation laser polarization, i.e., $r(t) = \{I_{\parallel}(t) - I_{\perp}(t)\} / \{I_{\parallel}(t) + 2I_{\perp}(t)\}$. The $r(t)$ curves (Figure 3) exhibited distinct oscillation in the 0–2 ps time region, followed by slow decays due to rotational diffusion ($\tau_{\text{rot}} = 50\text{--}90 \text{ ps}$). The time period in *o*-DAB (0.34 ps) is significantly shorter than that in *m*-DAB (0.91 ps) in toluene, and the dephasing time is longer in *o*-DAB (1.0 ps) than in *m*-DAB (0.73 ps). Also, it is seen that the oscillatory behavior depends on solvent as seen in *m*-DAB. On the other hand, the population decay showed only a smooth curve.

The oscillation patterns in anisotropy decays were analyzed with the theoretical equation formulated by Hochstrasser's group.^{2,3} First, the time evolution of density matrix elements ρ_{11} and ρ_{22} for the populations of the states ϕ_1 and ϕ_2 , respectively, is derived from the optical Bloch equation as

$$\Delta n(t) = \frac{\Delta n(0)}{\cos \delta} e^{-(1/T_1 + 1/T_2)t} \cos(\omega_{\text{osc}} t + \delta) \quad (1)$$

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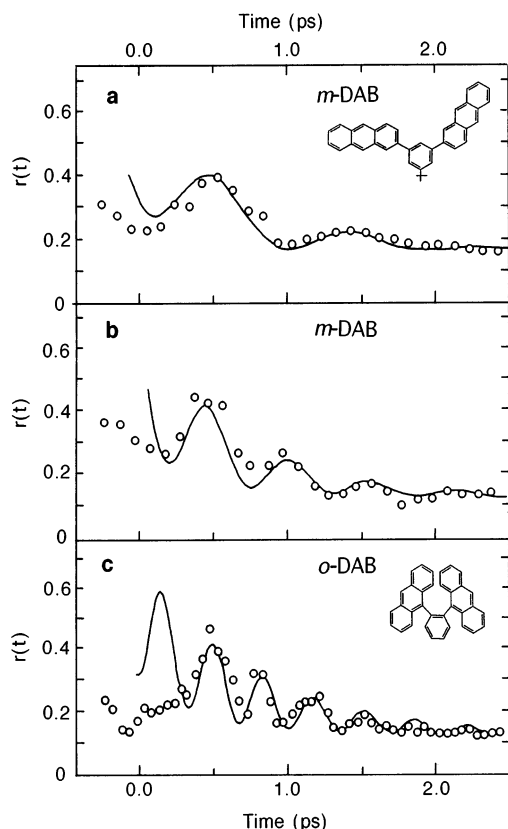


Figure 3. Fluorescence anisotropy decay curves of *m*-DAB in toluene (a) and in THF (b) and *o*-DAB in toluene (c), measured with the fluorescence up-conversion apparatus.

where Δn is the population difference $\Delta n = \rho_{11} - \rho_{22}$, T_1 is the population decay constant, and T_2' is the pure dephasing time. ω_{osc} is the angular frequency $(\omega_{\text{osc}})^2 = 4\beta^2 - (1/T_2')^2$, and δ is the phase shift. Equation 1 means that the excitation population in either half of the bichromophore undergoes an oscillation with an angular frequency ω_{osc} , but it is damped exponentially with a time constant determined by the phase relaxation time, $1/T_1 + 1/T_2' \approx 1/T_2'$ ($T_1 = 3\text{--}7$ ns in the anthracene dimers studied). By further theoretical treatment, the time-dependent anisotropy in a dimer is expressed as:³

$$r(t) = \frac{0.1}{1 + e^{-\gamma t} \cos^2 \theta} [(1 + 3\cos^2 \theta) + 3f(t)(1 - \cos^2 \theta) + (3 + \cos^2 \theta)e^{-\gamma t}] \quad (2)$$

where, $f(t) = \exp(-1/T_2')\cos(\omega_{\text{osc}}t + \delta)$, $\gamma = 2/T_2'$, and θ is the angle between the transition dipole moments of the two chromophores. The second term of eq 2 generates the oscillation with its amplitude depending on θ ; when $\theta = \pi/2$ the amplitude is largest, but when $\theta = 0$ the oscillation is not observed. From the observed $r(t)$ curve, the values for ω_{osc} , T_2' , and θ were derived. Using these values, the theoretical curve of eq 2 was fitted to the experimental curve by varying the δ value until the best fit curve was obtained. It is seen in Figure 3 that the respective experimental curves are fitted reasonably with the theoretical curves (solid lines). The parameter values thus obtained are summarized in Table 1.

Table 1. Characteristics of Coherent Energy Transfer Dynamics of Bichromophores in Solution at 296 K

molecules	solvents	T_{osc} (ps)	T_2' (ps)	β (cm^{-1})	θ (degree)
<i>m</i> -DAB ^a	toluene	0.91	0.73	29.2	57
	THF	0.55	0.78	37.1	72
<i>o</i> -DAB ^a	toluene	0.34	1.02	51.1	65
DTA ^b	THF	1.0	1.2	14.3	88.5
binaphthyl ^c	CCl ₄	1.2	0.18	21	18

^a Present work. ^b From ref 9. ^c From ref 8. All values are with an accuracy of about $\pm 10\%$.

The striking feature of the results is that the interaction energy is two times larger in *o*-DAB (51.1 cm^{-1}) than in *m*-DAB (29.2 cm^{-1}). This is consistent with the difference in r_0 . The interaction energies based on the dipole–dipole interaction were calculated using the known parameter values of r_0 and θ to give $\beta = 30 \text{ cm}^{-1}$ for *o*-DAB and 10 cm^{-1} for *m*-DAB. These values are one-third or half of the experimental values. This difference may be regarded as due to inadequacy of the point dipole approximation and/or an additional contribution from the electron exchange interaction.

Also noteworthy is that the dephasing times T_2' in *o*-DAB are longer than those in *m*-DAB. In *o*-DAB the librational motion of anthracene rings is suppressed by steric hindrance, whereas in *m*-DAB the partial moiety can rotate around a single bond. Note that T_2' is much longer in DTA where the dimer structure is fixed.⁹ It follows that there exists a correlation between the librational motion and the phase relaxation. In fact, the rapid librational motion of naphthalene rings in binaphthyl may cause a faster electronic dephasing.⁸ The observed $r(t)$ curves are not fitted with the theoretical ones at early time < 0.3 ps, particularly in *o*-DAB. This discrepancy might be attributed to a fast depolarizing process like internal vibrational redistribution being involved instead of the dominant coherent process.

The results of our study establish that the coherent cyclic motion of exciton between coupled chromophores survive or outlast the dephasing process even in a room-temperature solution if one uses specially designed molecular systems of rigid dimeric conformation.

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Supporting Information Available: Preparation of compounds and derivation of eq 1 and remarks on the phase δ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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