Through-Space and Through-Bond Effects on Exciton Interactions in Rigidly Linked Dinaphthyl Molecules

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Abstract: Electronic absorption spectra of a series of dinaphthyl molecules, in which the naphthyl moieties are separated by a rigid polynorbornyl bridge, together with a corresponding model compound have been measured in *n*-hexane and acetonitrile solvents. Resonance (molecular exciton) splittings of the naphthalene $^1A_g \rightarrow 2^1B_{3u}$ electronic transition are observed and found to be substantially greater than predicted by the usual dipole–dipole model. For the two-bond bridged compound a description of the exciton interaction requires consideration of direct through-space orbital overlap between naphthalenes. Through-space interchromophore orbital overlaps in the four-bond and the six-bond bridged compounds are negligible, and it is concluded that for these systems a significant contribution by a through-bond interaction (involving the σ- and σ^*-orbitals of the bridge) leads to the efficient delocalization of the excitation observed. This is the first evidence that exciton interactions can be enhanced by a through-bond interaction.

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Introduction

The absorption of light and subsequent energy relaxation of a system consisting of two or more proximate, identical chromophores is an important phenomenon relevant to the photochemical properties of crystalline solids,[1,2] polymers,[3,4] solid-state inclusion compounds,[5] organized molecular assemblies,[6] ordered phases,[7] molecular clusters,[8] aggregates,[9] and various dimers[10] and double molecules.[11,12]

In a system of *N noninteracting* chromophores, with one chromophore raised to an excited electronic state, the energy of the system would be unchanged by transferring the excitation to any other chromophore in the system. In a real system, however, the small but finite interchromophore interactions remove this *N*-fold degeneracy since it is impossible to construct a stationary state for the system wherein one select chromophore is excited. The correct zero-order states for the system with one quantum of electronic excitation correspond to a delocalization of the energy over all chromophores.[13,14] Förster refers to this as the "non-additivity of excited state properties".[15] The phenomenon is known as a molecular exciton interaction, and it is the subject of the present contribution.

As proposed by Förster[15,16] and by Simpson and Peterson[17] it is convenient to categorize the interaction into three cases. In case A, the strong coupling regime, the rate of excitation transfer between chromophores is much larger than the frequency of molecular vibrations, which results in a delocalization of the excitation over the entire system. Major differences, such as shifts or splittings, in the absorption spectra of the interacting system relative to an isolated molecule are observed. Case B, the weak coupling case, exhibits less profound spectral perturbations, and the rate of energy transfer is approximately comparable to the frequency of molecular vibrations. In case C, the very weak coupling limit, little or no variation exists between the electronic absorption spectra of the isolated and interacting systems, and to a reasonable approximation the electronic excitation may be regarded as temporarily localized on one chromophore. Observed effects may then be interpreted in terms of excitation transfer.

It is important to note that the Coulombic and the exchange terms which describe the exciton interaction are, in general, additive, although there are two important limits. At very small interchromophore separations, or in the case of triplet–triplet energy transfer, the interaction is governed by exchange effects, which depend on interchromophore orbital overlap (as described by Dexter[18]), while at large separations the Coulombic interaction dominates.[19,20] Intermolecular overlap between adjacent chromophores is most obviously realized in a direct "through-space" fashion. That is, the two chromophores are close enough spatially that there is an overlap of their electron density distributions. These interactions together with the long-range Coulombic (dipole–dipole) interactions are referred to as *through-space interactions* (TS interactions).

It was first demonstrated by Hoffmann,[21] and subsequently by other workers,[22–29] that, in addition to the TS interaction, there

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may be indirect orbital overlap via an intervening σ-framework connecting the chromophores. This is referred to as *through-bond interaction* (TB interaction). This TB interaction is capable of promoting electronic coupling between chromophores over very large spatial separations.

In recent years there have been a number of studies investigating TB interaction between distant groups connected by saturated hydrocarbon bridges. Much valuable data have been acquired through photoelectron spectroscopy and examination of intramolecular electron transfer.[23,24,29-33] Evidence for electronic coupling through rigid saturated bridges extending up to twelve σ bonds has been presented.[33] Experimental and theoretical studies have demonstrated that the efficiency of hydrocarbon bridges to mediate TB interactions depends strongly on their structure and conformation. Such effects have also been observed in polysilanes in which electronic $\sigma \rightarrow \sigma^*$ excitation occurs into a suitable oriented backbone.[34] A recent study has reported observations of a TB mechanism in triplet and singlet energy transfer in carotene–porphyrin dyads.[35] Given the efficiency of TB interaction through an optimally configured σ-framework it is not unreasonable to anticipate that molecular exciton interactions may also be enhanced considerably in some supramolecular multichromophoric systems.

The purpose of the present work is to explore the role played by TS and TB coupling on exciton interactions by examining electronic absorption spectra of the naphthalene–bridge–naphthalene systems DN-2, DN-4, and DN-6, in which the pair of naphthalene chromophores are held at well-defined distances and orientations by a rigid polynorbornyl-type bridge of variable length (two, four, or six σ bonds, respectively). The exciton resonance may be represented as A*–L–B ↔ A–L–B*, where L is the rigid spacer and the entire molecule has a well-defined geometry.[36] Electronic absorption spectra of the intense naphthalene S_3 ($^1A_g \rightarrow 2^1B_{3u}$) band are reported here, since its high oscillator strength should make it more amenable to analysis by simple exciton theory using the dipole approximation (in the absence of any overlap effects). The effect of solvent dielectric constant is also discussed.

Experimental Section

Synthesis of the compounds examined in this paper has been reported previously.[37] The geometry of each was determined by using MNDO geometry optimization within the C_{2v} symmetry constraint.

The concentration of solutions (*n*-hexane, Ajax Spectrosol; acetonitrile-210, Ajax Unichrom, HPLC grade) used for the electronic absorption experiments was typically 2.0–3.0 × 10^{-5} M. At these concentrations intermolecular interactions can be excluded and maximum absorbances were in the range 0.1 to 0.8. Absorption spectra were recorded at 295 K in 1 mm path length quartz cuvettes on a Cary 5 UV-VIS-NIR spectrophotometer (spectral band width 0.4 nm, data interval 0.1 nm).

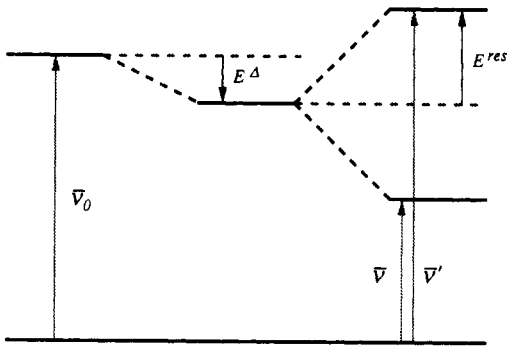

Figure 1. Partitioning of experimentally observed exciton splitting of an electron absorption band into resonance, E^{res}, and electrostatic (plus polarization plus some dispersion), E^{Δ}, contributions. Absorption of an isolated chromophore is indicated by $\bar{\nu}_0$.

Intermolecular Interactions

It has been shown that the term corresponding to the interaction energy between two identical chromophores with one in an excited electronic state may be given the general form

$$E^{int} = E^{\Delta} \pm E^{res} \quad (1)$$

where E^{Δ} contains electrostatic, polarization, and dispersion contributions[38] and E^{res} is the important resonance interaction which effectively splits the excited state surface into two sheets. The effect of these two contributions in producing the new spectral splitting lines $\bar{\nu}$ and $\bar{\nu}'$ from the transition energy $\bar{\nu}_0$, in the isolated chromophore, is illustrated in Figure 1.

In general E^{res} is given (to first order) as a sum of Coulombic and exchange interactions between the transition charge densities which relate the excitation resonance between two identical chromophores, labeled A and B

$$A^*B \leftrightarrow AB^* \quad (2)$$

So, formally, de-excitation of A is accompanied by excitation of B. Thus the Coulombic contribution to E^{res} is related to the relevant transition moment and is large and positive, while the exchange contribution, which can be considered as a simultaneous electron and hole transfer between the chromophores, depends on interchromophore overlap and is in general small and negative. As a first approximation, the exchange contribution to E^{res} is usually ignored.

For the particular bichromophoric molecules studied in this work E^{res} can be partitioned into contributions from through-space (TS) and through-bond (TB) interactions:

$$E^{res} = E^{res}(TS) + E^{res}(TB) \quad (3)$$

where $E^{res}(TS)$ is a through-space interaction which, in the absence of direct interchromophore overlap, is given by the usual dipole–dipole approximation (see, e.g., ref 39):

$$E^{res}(TS) \approx (1.070685 \times 10^{10}) f\eta/(\bar{\nu}_0 R^3) \quad (4)$$

the units for E^{res} and $\bar{\nu}_0$, the transition energy in the absence of an interaction, are cm^{-1}, and R, the interchromophore separation, is given in Å. f is the transition oscillator strength, and η describes the relative orientations of the transition dipoles.

$E^{res}(TB)$ can occur because the chromophore π and π^* orbitals overlap with the bridge σ and σ^* orbitals, providing a mechanism by which the exciton interaction may be mediated by the bridge.

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It is likely that interactions depending upon interchromophore orbital overlap, such as the exchange interaction, contribute to E^{res}(TB).

When electronic coupling is mediated by a pathway involving the intervening bonds of the spacer (bridge) McConnell[40] has shown that the energy splitting, S, of π or π^* orbitals of the chromophores due to mixing with the orbitals of the bridge is approximately given by

$$S = -2(T^2/\Delta)(t/\Delta)^{n-1} \quad (5)$$

where n is the number of bonds in the bridge, T is a measure of the coupling of the chromophores to the bridge, t gives the coupling between two adjacent bridge subunits, and Δ is the energy gap separating the chromophore π (π^*) orbitals with the localized bridge σ (σ^*) orbitals. The McConnell model, useful for a qualitative understanding of TB effects, is discussed in detail in two recent reviews.[22,41]

From consideration of this model it is anticipated that the magnitude of the TB coupling matrix element for processes such as electron transfer and energy transfer will decay exponentially with the number of bonds in the spacer,[33,42] as given by eq 6.

$$H = H_0 \exp[-\beta(n-1)/2] \quad (6)$$

Here H_0 is the electronic coupling matrix element for one subunit and β is a constant, scaling the distance dependence, which describes the coupling of the chromophore to the bridge as well as the interaction between bridge subunits. Closs et al.[43,44] considered such an exponential distance dependence in the analysis of through-bond triplet–triplet energy transfer (which is mediated by an electron exchange interaction). Deviations from this behavior are sometimes expected,[41] and recent theoretical studies of polynorbornadienes have suggested significant deviations from exponential behavior for shorter bridges.[45]

Results

The MNDO-optimized structures of the dinaphthopolynorbornyl molecules are shown in Figure 2, where N-2 is the (two-bond) model chromophore and DN-n symbolizes an n-bond dinaphthyl compound. σ bond lengths (r_n) and angles (a_n) in the spacer group are collected in Table I along with three interchromophore separations R_1, R_2, and R_3, representing C1–C1′, C3–C3′, and C5–C5′ through-space distances, respectively. R_2 defines the separation, R, between centers of the electric dipole transition moments. The orientation factor, $\eta = \cos\alpha + 3\cos^2\theta$, relevant to eq 4 along with the angles α and θ defining the orientation of transition dipole moments (cf. Figure 2) for each compound are also listed.

Electronic absorption spectra of each molecule in n-hexane solvent are illustrated in Figure 3, which shows clearly the splitting of the intense naphthalene $^1A_g \rightarrow 2\,^1B_{3u}$, S_3, absorption band as a function of interchromophore separation. Perturbations to the S_2 vibronic band are also evident. The shoulder on the high-energy side of the S_3 band for N-2, which also appears in the DN-n spectra, is absent in the S_3 (condensed phase) absorption band of 2,3-dimethylnaphthalene.[46] A similar shoulder was, however, observed in the gas-phase absorption spectrum of naphthalene,[47] although its assignment was ambiguous. Since this shoulder does not appear to be split independently of the S_3 band in the DN-n spectra, it is more likely to be 0–0 plus a vibrational frequency rather than a higher electronic state. The major observations are collected in Table II, together with the resonance energy calculated from the dipole approximation (eq 4).

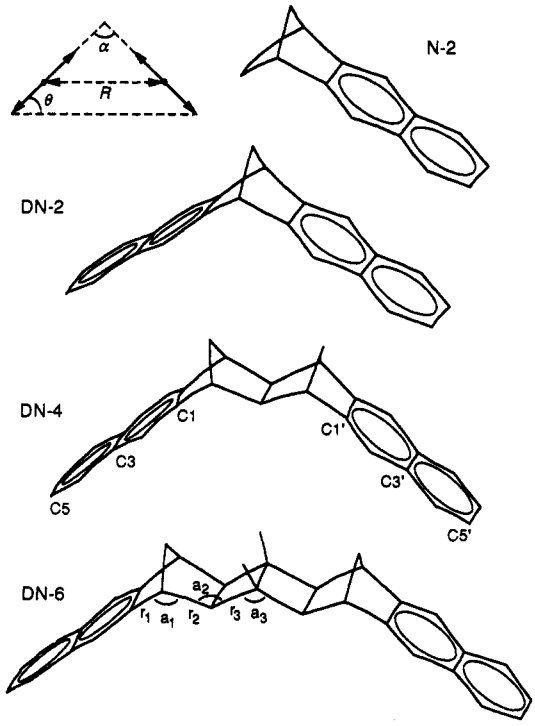

Figure 2. The polynorbornyl-bridged dinaphthyl molecules examined in this study (DN-2, DN-4 and DN-6) together with the model chromophore (N-2). Geometry labels relevant to Table I are indicated, as is an illustration of the orientation of transition dipole moments.

The oscillator strength of the N-2 S_3 transition in n-hexane solvent was calculated by integrating from 42 000 to 50 000 cm^{-1} and was found to be 1.0.

In acetonitrile solvent negligible solvent shift relative to n-hexane was detected for N-2, and resonance energies for the DN-n series were only up to 100 cm^{-1} larger. A comparison between DN-2 spectra in the two solvents is shown in Figure 4.

Discussion

From the data presented in Table II it is evident that the observed resonance splittings, E^{res}, of the naphthalene $S_0 \rightarrow S_3$ transition in all the DN-n molecules are considerably larger than the E^{res}(TS) values calculated by using the dipole–dipole model, eq 4. An ab initio (RHF method, 3-21G and 6-31+G basis sets) study of the π^* splittings in ethene dimers has shown that direct TS orbital overlap is strongly attenuated with distance and is significant to a separation of 5 Å only.[23] An extensive series of similar calculations on polynorbornadienes found that TS interchromophore overlap was important in the two-bond diene but insignificant for longer bridges.[23] Thus, while direct TS overlap might be expected to enhance the resonance splitting in DN-2, it is unlikely that direct TS orbital overlap is affecting the resonance splitting of the S_3 transition in DN-4 and DN-6. For these two molecules any TS interaction will be Coulombic in origin.

It is appropriate to represent the Coulombic interaction by the multipole expansion only when the two charge distributions are non-overlapping.[48] It is thus inappropriate to use eq 4 for DN-2;

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Table I. Optimized Geometry Parameters As Determined by the MNDO Method[a]

compd	r_1, Å	r_2, Å	r_3, Å	a_1, deg	a_2, deg	a_3, deg	R_1, Å	R_2, Å	R_3, Å	α, deg	θ, deg	η
DN-2	1.531			106.0			2.45	6.50	10.59	112.79	33.6	1.695
DN-4	1.534	1.568		105.5	122.3		4.89	8.46	12.07	94.4	42.8	1.538
DN-6	1.531	1.564	1.553	105.9	119.8	117.0	7.56	11.26	15.00	98.9	40.5	1.580

[a] As depicted in Figure 2, r_1, r_2, and r_3 define bridge C–C bond lengths, a_1, a_2, and a_3 define bridge bond angles, R_1, R_2, and R_3 define interchromophore separations. The orientation of the transition dipole moment is given by the angles α and θ, which are used to calculate the orientation factor η.

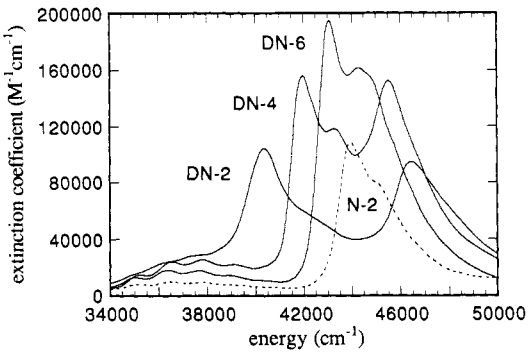

Figure 3. UV absorption spectra of the compounds in *n*-hexane solvent (298 K) in the region of the dipole-allowed naphthalene S_2 and S_3 electronic transitions.

however, it may be applicable to the DN-4 and DN-6 systems. It has been suggested previously that rapid convergence of the multipole expansion to the electric dipole–dipole term may not occur when the molecular size is large compared to the intermolecular separation.[48,49] Due to the high oscillator strength of the naphthalene $S_0 \rightarrow S_3$ transition, the interaction between the chromophores should be well-described as an interaction of two real (transition) dipoles. The ratio of interchromophore separation to transition dipole length (taken to be about 5 Å) in DN-4 and DN-6 is approximately 1.7 and 2.3, respectively. Hence for the orientation of dipoles in these molecules it is expected that terms in the multipole expansion higher than the leading (ie, dipole–dipole) term would act to increase the resonance energy above that calculated with eq 4 by only between 5% and 20%.[48] Hence, if TB interactions were negligible, the resonance energies calculated by eq 4 for DN-4 and DN-6 should be close to those measured experimentally. The much larger spectral splittings measured than predicted in eq 4 for DN-4 and DN-6 must therefore arise from the additional TB mechanism.

In the presence of a TB interaction we may envisage that the "donor" and "acceptor" wavefunctions in the A–L–B systems be written as

$$\Psi_A = N_A(\phi_A + \alpha_A\phi_L) \quad (7a)$$

$$\Psi_B = N_B(\phi_B + \alpha_B\phi_L) \quad (7b)$$

which represents the mixing of the naphthalene chromophore wavefunction with the σ orbitals of the bridge. N_A and N_B are the appropriate normalizing constants, and the mixing coefficients α_A and α_B are determined variationally.[50] The degree to which the excitation is delocalized from one chromophore to another, via the bridge orbitals, is therefore dependent on how effectively the π (π^*) system of each chromophore couples to the bridge σ (σ^*) as well as the degree of coupling between each bridge unit. This dependence is encompassed by the McConnell model, eq 5.

In the following discussion only the results for DN-4 and DN-6 will be considered since direct interchromophore orbital overlap effects are negligible (as discussed above). E^{res}(TB) can be calculated by subtracting E^{res}(TS) from the observed E^{res}, as can be seen from eq 3. To gauge the distance dependence of the TB component to the resonance interaction (in DN-4 and DN-6) the effective exponent for attenuation of the interaction, β in eq 6, can be determined. It is found that $\beta = 0.78$ per bond for the TB component of E^{res}.

The results indicate that there is a substantial contribution to the exciton interaction by a TB mechanism. It should be emphasized that this may not necessarily be the case for lower energy transitions or for less favorable bridge conformations. The question then remains, why is the E^{res}(TB) interaction so strong? This observation is consistent with the classification of the interaction into the Simpson and Peterson strong coupling regime,[17] which is highlighted by the very large transfer frequencies for excitation resonance, ω^{res}, collected in Table II. These were estimated by using the Förster[15] expression for the strong coupling case,

$$\omega^{res}(A^*B \rightarrow AB^*) = 4|M|/h \quad (8)$$

where $|M|$ is the magnitude of the matrix element for the resonance interaction, taken to be E^{res}.

It is likely that one of the most important factors acting to increase the chromophore-bridge electronic coupling is the high energy of the electronic transition being studied, which decreases the π^*–σ^* energy gap. This can be understood within the context of the simple McConnell model (eq 5), from which it can be seen that the effectiveness of a bridge in propagating interactions depends both on the intrabridge coupling matrix elements, t, and on the energy gap, Δ, separating the chromophore π (π^*) orbitals with the localized bridge σ (σ^*) orbitals. As the π^*–σ^* energy gap, Δ, diminishes, the distance dependence gets weaker.

It has been shown that, as for the $^1E_{1u}$ electronic state of benzene,[51,52] π–σ dynamic correlation effects make an important contribution to the 2^1B_{3u} state of naphthalene as a result of its substantial ionic character.[53] This, in turn, may relax the tight-binding approximation for this naphthalene electronic state, which is assumed in the derivation of the McConnell superexchange model. This should significantly increase the electronic coupling of the naphthalene moiety to the bridge.

Changing the dielectric constant of the solvent may affect the resonance interaction in two ways. Firstly, the oscillator strength of the transition may be altered, which would scale eq 4. Secondly, it has been suggested that the solvent dielectric constant may be introduced into expressions such as eq 4 by using the solvent optical dielectric constant,[54] n^2. However, no dramatic solvent effects were detected in this work, presumably since the system is in the strong coupling limit and because the primary mechanism mediating the excitation delocalization is proposed to be a through-bond interaction.

Conclusions

Substantially larger resonance (molecular exciton) splittings are observed for the naphthalene $^1A_g \rightarrow 2^1B_{3u}$ electronic transition in the series of rigidly-linked dinaphthyl molecules, DN-2, DN-4, and DN-6, than are predicted by the usual electric dipole–dipole interaction model.

Two contrasting cases are encountered. For DN-2 direct through-space orbital overlap is considered to dominate the

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Table II. S_3 Absorption Band Maxima ($\bar{\nu}$ and $\bar{\nu}'$) and Extinction Coefficients (ϵ) in *n*-Hexane Solvent, with Experimentally Measured Components of E^{int}, E^{res}, and E^{Δ} (see Figure 1)[a]

						experiment				
compd	$\bar{\nu}$, cm^{-1}	ϵ, M^{-1} cm^{-1}	$\bar{\nu}'$, cm^{-1}	ϵ, M^{-1} cm^{-1}	c, 10^{-5} M	E^{res}, cm^{-1}	E^{Δ}, cm^{-1}	E^{res}(TS), cm^{-1}	E^{res}(TB), cm^{-1}	ω^{res}, 10^{14} s^{-1}
N-2	43 960	108 000			3.0					
DN-2	40 360	104 000	46 470	95 000	2.5	3060	540			3.67
DN-4	41 980	156 000	45 540	152 000	3.8	1780	200	620	1160	2.13
DN-6	43 070	195 000	44 670	162 000	2.3	800	90	270	530	0.96

[a] Resonance energies calculated from eq 4, E^{res}(TS), together with E^{res}(TB) (estimated as the difference between E^{res} and E^{res}(TS)), are included for comparison. Transfer frequencies for excitation resonance (ω^{res}, eq 9) are also included.

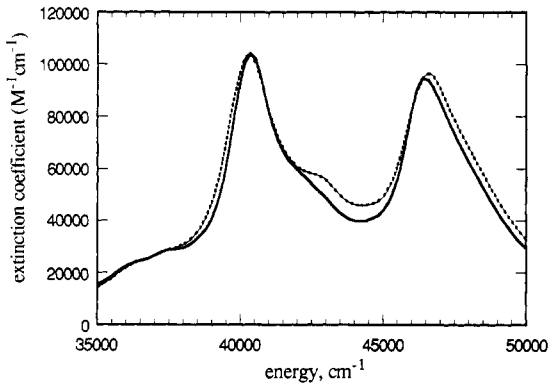

Figure 4. Comparison of DN-2 S_3 absorption bands in *n*-hexane (solid line) and acetonitrile (dashed line).

spectroscopy, although a minor contribution from a through-bond interaction may also be present. A strong spectral splitting is observed and application of the usual multipole expansion is inappropriate.

For DN-4 and DN-6, however, direct through-space interchromophore overlap is very small. It is concluded that the delocalization of electronic excitation through both chromophores is dominated by a through-bond coupling mechanism involving the intervening σ and σ^* orbitals of the bridge, while the through-space dipole–dipole mechanism plays a more minor role.

The results of this study emphasize the importance of through-bond interactions in enhancing energy delocalization in these linked bichromophoric systems, and for the first time the efficiency of a through-bond interaction in mediating a strongly allowed molecular exciton interaction is demonstrated. It is likely that such a mechanism may contribute to the interchromophore energy transfer process in other bichromophoric and polymeric systems.

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