Mechanisms of excitation energy transport in macromolecules

Kenneth P. Ghiggino *, Edwin K.L. Yeow, David J. Haines, Gregory D. Scholes,
Trevor A. Smith

Photophysics Laboratory, School of Chemistry, University of Melbourne, Melbourne, 3052 Vic., Australia

Abstract

Recent developments in our understanding of the mechanisms of singlet excitation energy transfer (EET) in multichromophoric assemblies are reviewed. Particular emphasis is placed on the role of superexchange interactions involving the molecular framework linking the chromophores in the mediation of EET processes. Experimental measurements of the rates of EET in rigidly linked model bichromophoric compounds demonstrate that, under certain conditions, a through-bond interaction can dominate the energy transport process. High rates of EET in synthetic macromolecules are also observed, and the possible pathways of energy migration and trapping in these systems are outlined.

Keywords: Energy transfer; Energy trapping; Macromolecules; Superexchange

1. Introduction

Macromolecules, which consist of arrays of chromophores covalently linked via a molecular framework, provide a unique environment for many photochemical processes. The high local concentration of chromophores present in such systems is conducive to excitation energy transfer (EET), which can effectively delocalize the energy away from the initial site of light absorption. In the natural photosynthetic systems of plants and algae, arrays of chlorophyll pigments serve as a very efficient energy gathering "antenna", transporting absorbed light energy to the reaction centre, where it is used to drive the chemical reactions necessary for biological functioning. Energy migration among the chromophores in synthetic aromatic polymers is also recognized to be an important process in polymer photophysics [1–4]. It has been shown that the incorporation of chromophores of lower energy along the polymer backbone can trap the migrating energy and sensitize useful photochemical processes. In these natural and synthetic arrays, the absorption cross-section of the trap chromophore is effectively increased by the EET process. Understanding the mechanisms by which energy migration and trapping occur in macromolecules, and devising means for developing optimized synthetic "light harvesting" systems, are major challenges for photochemists and underlie the development of useful photomolecular devices. In this paper, recent developments in our understanding of energy transfer processes are reviewed, and experi-

mental results of the rates of energy transport in model compounds and macromolecules are presented.

2. Developments in theory

The rate of singlet–singlet EET is often written in the form first derived by Förster [5]

$$k_{EET} \approx \frac{9000(\ln 10)}{128\pi^5 R^6 L} \frac{\kappa^2 J \Phi_D}{\eta^4 \tau_D} \tag{1}$$

where Φ_D and τ_D are the fluorescence quantum yield and lifetime of the donor respectively, κ^2 and J are the orientation factor and spectroscopic overlap integral respectively (as defined elsewhere [5]), η is the refractive index of the solution, L is Avogadro's number and R is the interchromophore separation. This equation may be rearranged [6] to mirror the general quantum mechanical rate expression

$$k_{EET} = \frac{2\pi}{\hbar} |\tilde{T}_{DA}|^2 \delta(E_D - E_A) \tag{2}$$

in which T_{DA} is the electronic transfer matrix element (ETME) connecting donor and acceptor states (denoted D and A) and the tilde indicates that vibrational overlap factors are included. The Dirac delta term ensures energy conservation between the donor and acceptor (cf. the spectral overlap integral J in Eq. (1)).

Recently, a unified theory for the electronic factors responsible for EET has been developed [7,8]. It accounts for the

---

* Corresponding author.

mixing of locally excited (LE) configurations (A*B or AB*) with charge-separated configurations (A$^+$B$^-$ and A$^-$B$^+$) in the donor and acceptor states. The resultant ETME contains contributions from a coulombic interaction for singlet–singlet EET only (u^{Coul}, e.g. dipole–dipole) as well as interchromophore orbital overlap-dependent terms present for both singlet–singlet and triplet–triplet EET. In many cases, the most significant overlap-dependent interactions are mediated via the charge-separated configurations and are termed through-configuration interactions. Thus we have

$$^{1,3}T_{DA}^{(EET)} \approx u^{Coul} + u^{IOO} + {}^{1,3}U^{TC} \qquad (3)$$

where superscript numbers differentiate between singlet EET and triplet EET, u^{Coul} is the coulombic interaction, U^{TC} is the through-configuration interaction and u^{IOO} encompasses the remaining orbital overlap-dependent terms (e.g. penetration terms).

The above discussion refers explicitly to a simple donor–acceptor system in which electronic coupling occurs directly between the chromophores of interest; however, such interactions may be promoted over large through-space separations via a connecting molecular framework, intervening chromophores or intermediate states. This relayed interaction or superexchange, as first suggested by McConnell [9], is well known to promote long-range electron transfer [10,11] and can similarly enhance rates of EET [12,13] relative to that due to direct coupling only.

The relayed interactions may be considered to be a multistep mechanism in which each step proceeds by the same mechanism as for direct electronic coupling. In this picture, the complete relayed interaction is described by a sum over all possible pathways leading from the initial to the final state. An important aspect of a relayed mechanism is that energy does not need to be conserved in each step, since states representing localization of excitation on a relay unit are virtual states, and thus the energies of the intermediate states can be entirely different from that of the initial and final states as long as there is an overall conservation of energy between the initial and final states of the transition. Overlap-dependent interactions, for example, can be promoted over large through-space separations essentially by delocalization (or mixing) of the donor and acceptor wavefunctions into the orbitals of a connecting bridge. Donor and acceptor wavefunctions may then effectively overlap appreciably, even at separations far exceeding their van der Waals' radii. Details of this mechanism have been discussed recently [14–18].

A schematic diagram of certain matrix elements which may be important in describing the transport of excitation energy in a vinyl aromatic polymer containing pendant "donor" chromophores (phenyl groups) and a lower energy "trap" chromophore (naphthyl moiety) is shown in Fig. 1(a). These matrix elements can be dissected into contributions by superexchange pathways including those mediated by the linking σ bonds of the polymer backbone (see Fig. 1(b)). The overall effect of these superexchange pathways is to increase substantially the coupling and thus the rate of EET
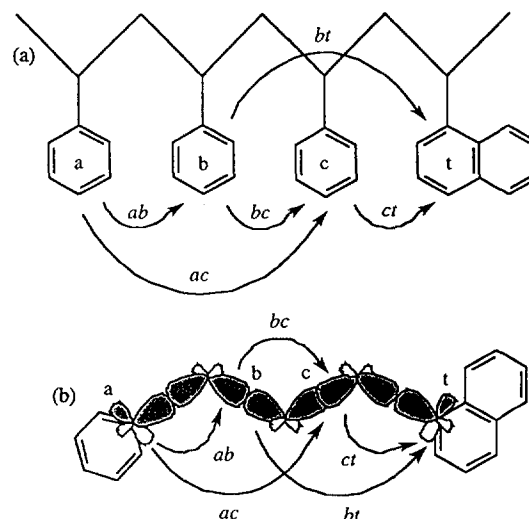

Fig. 1. (a) Schematic diagram of possible matrix elements for energy migration among chromophores a, b and c and for transfer to a trap, t. (b) Resolution of matrix element ct into contributions by superexchange pathways involving the saturated carbon–carbon bonds of the polymer backbone.

between the donor and acceptor above that expected for direct through-space orbital overlap-dependent or coulombic mechanisms.

3. EET in model bichromophoric systems

Recently, EET has been studied in several model bichromophoric systems in which the chromophores are separated by a rigid polynorbornane bridge, allowing separation and orientation of the donor and acceptor to be controlled [19,20]. Examples of the structures studied are given in Fig. 2. For naphthalene and anthracene chromophores rigidly linked by a polynorbornane bridge with six carbon–carbon bond separation (A-6-N; centre-to-centre interchromophore distance, 12.2 Å), the rate of energy transfer was determined from time-resolved fluorescence measurements of the grow-in of anthracene emission following picosecond pulsed laser excitation of the naphthalene chromophore at 292 nm. The
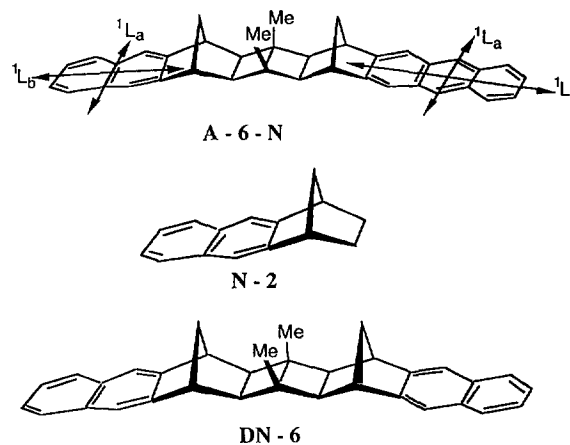

Fig. 2. Structures of rigidly linked bichromophoric systems and model compound.

observed rate of energy transfer for this compound in dilute n-hexane solution at room temperature was 2.9×10^{10} s^{-1}. At the interchromophore separation, there is no direct overlap of the molecular orbitals of the two chromophores, and the rate calculated assuming that a Förster coulombic mechanism alone is operative (1.2×10^9 s^{-1}) is over one order of magnitude lower than that observed experimentally. This remarkable increase in rate was attributed to the presence of the linking bridge, which mediates the orbital overlap-dependent coupling between the two chromophores [19].

In the series of polynorbornane-bridged dinaphthyl compounds DN-n, where n is the number of intervening saturated carbon–carbon bonds, the magnitude of the electronic coupling between the chromophores was determined from the exciton splitting of the S$_3$ absorption band [20]. The centre-to-centre interchromophore separations for DN-2, DN-4 and DN-6 are 6.5 Å, 8.5 Å and 11.3 Å respectively. While some direct through-space orbital overlap of the two chromophores may be expected for the DN-2 compound, such overlap should be negligible for DN-4 and DN-6. However, again, the calculated exciton splittings assuming a coulombic dipole–dipole mechanism were substantially smaller than those observed experimentally, with the largest contribution to the electronic coupling attributed to overlap-dependent interactions relayed by the polynorbornane bridge [20].

We report polarized fluorescence measurements which provide a means of probing directly the rates of energy transfer in the compound DN-6. The fluorescence anisotropy r from a solution of chromophores is defined by

$$r = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp} \qquad (4)$$

where $I_\parallel$ is the fluorescence intensity component parallel to the plane of polarization of the incident radiation and $I_\perp$ is that perpendicular to the plane of polarization of the incident radiation. In a rigid glass, where molecular rotation is absent, the value of r will depend on the relative orientations of the absorption and emission transition moments within the molecule and can take values between 0.4 (absorption and emission transition moments parallel) and -0.2 (absorption and emission transition moments perpendicular) [21]. When excitation is via polarized light pulses and the fluorescence decays are observed through polarizers oriented parallel and perpendicular to the incident polarization, the time-dependent anisotropy $r(t)$ can also be generated using Eq. (4). If energy transfer occurs between chromophores which have their interacting transition moments at different orientations to each other, emission from the accepting chromophore will be depolarized with respect to the fluorescence anisotropy of the donor [21]. The time-dependent decay of the fluorescence anisotropy in such systems has previously been used to characterize rates of energy transfer [22].

If energy transfer occurs between two like chromophores, the observed time-dependent anisotropy will be described by
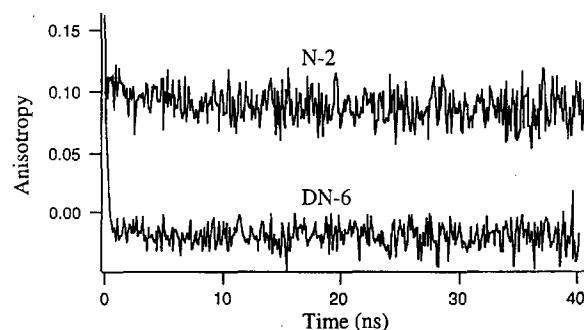

Fig. 3. Time-resolved fluorescence anisotropy for N-2 and DN-6 in MTHF at 77 K. Excitation and emission wavelengths were 296 nm and 318 nm respectively.

$$r(t) = \frac{I_1(t)}{I_1(t) + I_2(t)} r_1 + \frac{I_2(t)}{I_1(t) + I_2(t)} r_2 \qquad (5)$$

where $I_1(t)$ and $I_2(t)$ are the time-dependent excited state populations of molecules 1 (donor) and 2 (acceptor) respectively and r_1 and r_2 are the fluorescence anisotropies. r_1 and r_2 will not be equal if the transition moments of the donor and acceptor are in different directions with respect to each other (such is the case for DN-6). $I_1(t)$ and $I_2(t)$ will be determined by the rate of energy transfer and the rates of radiative and other non-radiative processes depleting the excited state, and can be calculated from survival probabilities of excitation on the chromophores derived from a 2×2 probability transition matrix as a solution of the Pauli master equation [23] for this system. This approach assumes very weak coupling conditions and the excitation transport can be described by an incoherent random walk. For a pair of identical chromophores, as considered here, the analysis may not be so straightforward [24]. A more rigorous approach requires a careful choice of representation of the initial and final states, which will be influenced by the magnitude of the electronic coupling relative to the spectral bandwidth (cf. weak and strong coupling cases [6]). Complications arise in the present case due to broad overlapped absorption and emission spectra and the presence of mixtures of pure electronic transitions and vibronically allowed intensity. Relevant theoretical approaches have been described recently [25–27].

Excitation of the model monomeric naphthalene compound N-2 in a rigid methyltetrahydrofuran (MTHF) glass at 77 K using polarized light pulses at 296 nm leads to fluorescence with an anisotropy value of 0.092 which is invariant with time (see Fig. 3). However, a similar experiment with the bichromophoric compound DN-6 results in a very rapid decay of anisotropy to a final value of -0.017 (Fig. 3). The short-time decay behaviour of the anisotropy for DN-6, together with the theoretically predicted curve (see Eq. (5)) assuming a Förster dipole–dipole mechanism for energy transfer, is shown in Fig. 4. The rate constant for energy transfer in the DN-6 molecule, used in the calculation of the predicted curve, was 0.264 ns^{-1}, determined from Eq. (1) with parameters $\Phi_D = 0.251$, $\tau_D = 72.0$ ns, $\kappa^2 = 2.50$, $J = 2.747 \times 10^{-16}$ cm^3, $\eta(\text{MTHF}) = 1.406$ and $R = 11.6$ Å.
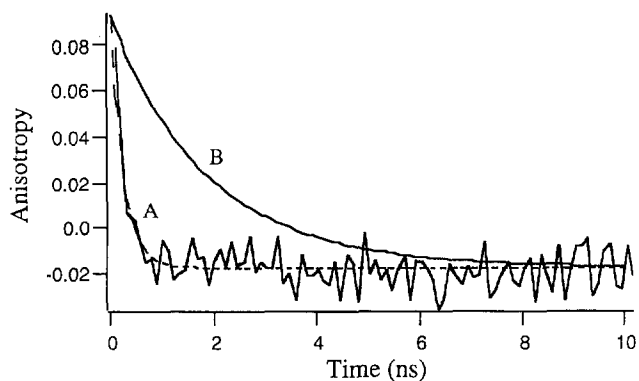
Fig. 4. Experimental (A) and simulated (B) time-resolved fluorescence anisotropy decay profiles for DN-6 in MTHF at 77 K. Simulated curve (B) based on a coulombic transfer mechanism with $k_{EET} = 0.264$ ns^{-1}. Broken line is an empirical fit of the data with $k_{EET} = 2$ ns^{-1}.

It should be noted that, at long times after excitation of DN-6, the observed fluorescence anisotropy becomes invariant with time, since after the initial rapid energy transfer steps the survival probabilities of excitation on the two chromophores become equal (i.e. $I_1(t) = I_2(t)$); thus from Eq. (5), $r(t) = (r_1 + r_2)/2$ where r_1 and r_2 are 0.092 and -0.13 respectively.

The observation of increased depolarization of emission from the bichromophore compared with the monomeric model compound N-2 is indicative of energy transfer, but the observed rate of depolarization is much faster than predicted assuming that the coupling arises from a Förster dipole–dipole mechanism alone and that the transfer can be described as an incoherent hopping process. It has been found empirically that the anisotropy data are best fitted when $k_{EET} = 2$ ns^{-1}, a factor of 7.6 faster than the dipole–dipole rate. This increase in rate is of the same order as that observed by time-resolved fluorescence methods for energy transfer in the naphthalene–polynorbornane–anthracene system [19], which has a similar interchromophore spacing, and consistent with ab initio and semi-empirical theoretical calculations [28] on the increase expected at this separation if superexchange interactions involving the linking bridge are operative.

The results presented here on bichromophoric molecules provide evidence that electronic coupling between chromophores can be enhanced over direct through-space coulombic and orbital overlap-dependent interactions by superexchange involving the bonds of the linking molecular framework, at least for the polynorbornane bridges and intermediate chromophore separations investigated, leading to substantial increases in the rate of energy transfer.

4. Energy migration and transfer in vinyl aromatic polymers

Calculation of the time-dependent survival probabilities of excitation via solution of the Pauli master equation [23] can also be used to obtain the fluorescence and fluorescence ani-

sotropy decay kinetics in larger multichromophoric assemblies, such as vinyl aromatic polymer systems. Again, such an approach assumes that the energy transport can be considered as a purely markovian diffusive, or hopping, process. The structure of poly(acenaphthylene) end-tagged with 9-methyl-anthracene (PACE-9MA) as an energy trap, together with a schematic diagram of the one-dimensional model used to simulate energy migration and trapping in this system, is shown in Fig. 5. The master equations needed to solve the probabilities of excitation on chromophore i ($p_i(t)$) and on all traps present ($p_{trap}(t)$) at time t for a polymer of N chromophores are

$$\frac{dp_i(t)}{dt} = \frac{-p_i(t)}{\tau_{fl}} + \sum_{j=1}^{N} k_{ij}[p_j(t) - p_i(t)] - u_i p_i(t) \tag{6}$$

$$\frac{dp_{trap}(t)}{dt} = \frac{-p_{trap}(t)}{\tau_{trap}} + \sum_{i=1}^{N} u_i p_i(t) \tag{7}$$

where k_{ij} is the excitation energy transfer rate between chromophores i and j, u_i is the transfer rate from chromophore i to the traps and τ_{fl} and τ_{trap} are the fluorescence lifetimes of the monomer chromophores and trap respectively. For PACE-9MA, the rate constant for dipole–dipole energy transfer between acenaphthyl chromophores, determined from spectroscopic and photophysical parameters, energy minimized interchromophore spacing and orientation and Eq. (1), is $k_{EET} = 8.41$ ns^{-1}, while the transfer rate from the final acenaphthyl chromophore to the terminal 9MA trap is $u = 223$ ns^{-1}. In order to solve the master equations an $(N+1) \times (N+1)$ probability transition matrix was established and a numerical method algorithm applied to provide the probabilities of energy remaining on any of the chromophores (or trap) after specified time units (time units of 0.1 ps were chosen). The generated theoretical fluorescence anisotropy decay function for the polymer (where $N = 29$) is given in Fig. 6, and the theoretical grow-in and decay of the
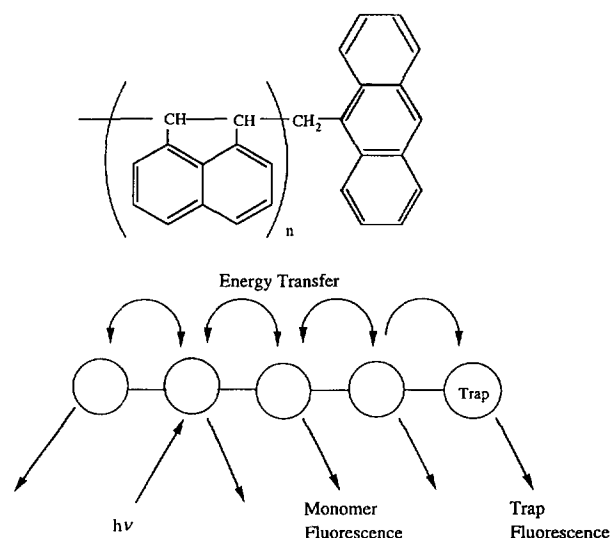

Fig. 5. Structure of PACE-9MA and schematic diagram of the one-dimensional model used to simulate incoherent energy migration and trapping in this polymer.
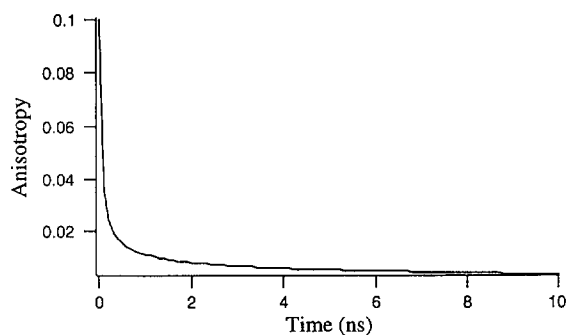
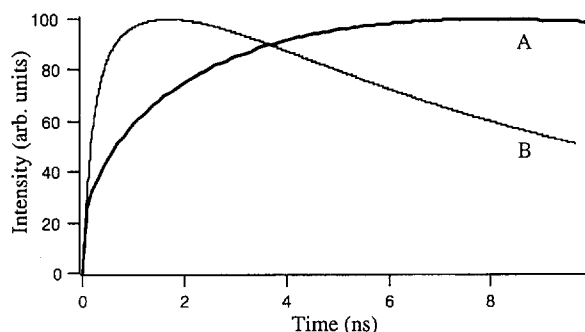Fig. 6. Simulated anisotropy decay profile for PACE-9MA.

Fig. 7. Simulated (A) and experimental (B) fluorescence decay profiles of the anthryl end-trap for PACE-9MA in MTHF glass at 77 K.

9MA end-trap following excitation of the acenaphthyl chromophores are presented in Fig. 7.

The experimental fluorescence decay of 9MA emission, following excitation of the polymer chromophores at 295 nm, for PACE–9MA in an MTHF glass at 77 K is also given with the theoretical data in Fig. 7, and shows a much more rapid population of the trap site than calculated theoretically. For a rigid solution of the polymer model chromophore, acenaphthene, under the same conditions, the fluorescence anisotropy monitored at an emission wavelength of 330 nm was invariant with time with a value of 0.09. This value is somewhat higher than that reported previously [29], although it is known that the fluorescence anisotropy of acenaphthene is strongly dependent on the excitation and emission wavelengths [29,30]. However, the fluorescence anisotropy from the polymer decayed to zero within the time resolution of the time-correlated photon counting detection technique used in this work (less than 80 ps). Thus the rates of energy migration and trapping in the polymer system appear to be much greater than predicted assuming a dipole–dipole mechanism for energy transfer and the rather simple one-dimensional energy hopping model.

As pointed out by Kenkre and Knox [31], the Pauli master equation approach used to describe the energy transport dynamics above disregards the possibility of coherent transport mechanisms and assumes complete vibrational relaxation after each step (i.e. very weak coupling conditions). Kenkre and Knox [31] have developed a generalized master equation, with no thermalization assumption, and in which the transport dynamics can be described by a non-markovian quasi-incoherent model. In the light of this work and other

recent theoretical studies [13,32] of energy transport processes which can operate in multichromophoric assemblies, the following mechanisms can be proposed by which a remote (trap) moiety may be sensitized following excitation of the polymer chromophores.

1. Direct donor-to-trap excitation transfer can occur by a coulombic mechanism at large separations or by a combination of orbital overlap-dependent and coulombic mechanisms if the interchromophore separation is small (less than 5 Å). In the latter case, it has been shown previously [33] that the inclusion of cross terms in the expansion of the golden rule rate expression (Eq. (2)) results in a substantially increased rate of energy transfer above that expected if either mechanism is considered alone. Calculations of direct energy transfer rates to a trap within a polymer coil, assuming a coulombic mechanism, for PACE-9MA [4] and poly(t-butyl-styrene) with an acenaphthyl trap [34] considerably underestimate the experimentally observed rates.

2. Where the molecular framework intermediate between donor and acceptor contains moieties which have quite different excitation energies to that of the donor, excitation transfer may be promoted by a superexchange mechanism involving, for instance, a carbon–carbon bond backbone as illustrated in Fig. 1(b) [19,20]. This indirect coupling is facilitated by a series of virtual excitation transfer steps involving the relay moieties, and thus the energy only needs to be conserved between the initial and final states.

3. When the excitation energies of the intermediate (relay) chromophores are close to those of the donor, an energy migration process may mediate the EET between donor and acceptor. This is illustrated in Fig. 1(a), where the relayed excitation transfer can involve an electronic tunnelling pathway in addition to a random walk "hopping" mechanism. The intermediate chromophores may act as virtual relay states to assist EET via a superexchange-like mechanism. Thus the incoherent and coherent pathways can operate simultaneously.

4. A superexchange mechanism involving higher electronic excited states of intermediate chromophores may assist the energy migration process. This case has been considered recently [32] and will provide significant long-range coherent coupling between chromophores, provided that the energy gap between the states is small and the transition moment of the higher excited state is large.

5. Dispersive excitation transport may provide a further mode of EET [35]. In such an experiment, where the red edge of an inhomogeneously broadened absorption line is excited, energy transport may occur by a coherent (superexchange) mechanism involving chromophores which, due to their local environment, are too high in energy to participate in an incoherent hopping energy migration process.

6. Specific macromolecular systems can be designed in which the mechanism discussed by Kasha et al. [36] may

operate. These systems use antenna-type excitonic arrays and trap molecules, and allow the coupling of long-range Davydov coherent molecular excitonic transfer and Förster transfer processes to a trap. The possibility of realizing such a configuration has been reported recently by Kasha et al. [36], who investigated an "antenna molecule–fluorescence probe pair" as a means of enhancing the efficiency of probe sensitization.

A feature of the discussion above is that other mechanisms, apart from an incoherent hopping process, can contribute to energy transfer in macromolecular systems. In particular, where there are multiple chromophores intermediate between the initially excited donor and acceptor, the intermediate moieties can act as virtual relay states to assist EET via a super-exchange process. This coherent mechanism can occur simultaneously with the incoherent process, such as that used in the modelling of PACE-9MA EET above, and can result in substantial increases in donor–acceptor coupling and hence the rate. As discussed recently, coherence effects [32] can be destroyed if nuclear relaxation occurs within the residence time of excitation on the intermediate chromophores and, as a result, enhanced transport efficiencies may be expected in low temperature glasses and in rigid systems where such relaxation processes are reduced.

5. Conclusions

Mechanisms of energy transfer which may operate in multichromophoric arrays have been outlined in this work. For the case of rigidly linked bichromophores, it is demonstrated that a through-bond interaction can substantially increase the rates of energy transfer above those expected from direct through-space coulombic and orbital overlap-dependent electronic coupling mechanisms. For macromolecular systems consisting of arrays of like chromophores and energy traps, simulations involving a Pauli master equation-type approach, where only nearest-neighbour incoherent transfer steps are considered, can severely underestimate the rates of trap sensitization. Energy migration occurring via "quasi-coherent" pathways has been emphasized, particularly transfer involving intermediate moieties acting as virtual states. Through molecular design, the opportunity exists for the rates and efficiency of energy transfer and trapping in macromolecular arrays to be optimized.

Acknowledgements

References

[1] J.E. Guillet, *Polymer Photophysics and Photochemistry*, Cambridge University Press, Cambridge, 1985.
[2] S.E. Webber, *Chem. Rev., 90* (1990) 1469.
[3] J.E. Guillet and W.A. Rendall, *Macromolecules, 19* (1985) 224.
[4] K.P. Ghiggino and T.A. Smith, *Prog. React. Kinet., 18* (1993) 375.
[5] T. Förster, *Ann. Phys., 2* (1948) 55. T. Förster, in O. Sinanoglu (ed.), *Modern Quantum Chemistry*, Vol. III, Academic Press, New York, 1965.
[6] G.D. Scholes and K.P. Ghiggino, *J. Chem. Phys., 101* (1994) 1251.
[7] R.D. Harcourt, G.D. Scholes and K.P. Ghiggino, *J. Chem. Phys., 101* (1994) 10 521.
[8] G.D. Scholes, R.D. Harcourt and K.P. Ghiggino, *J. Chem. Phys., 102* (1995) 9574.
[9] H.M. McConnell, *J. Chem. Phys., 35* (1961) 508.
[10] G.L. Closs and J.R. Miller, *Science, 240* (1988) 440.
[11] G.L. Closs, M.D. Johnson, J.R. Miller and P. Piotrowiak, *J. Am. Chem. Soc., 110* (1988) 2652.
[12] J. Kroon, A.M. Oliver and M.N. Paddon-Row, *J. Phys. Chem., 97* (1993) 11 871.
[13] G.D. Scholes and K.P. Ghiggino, *J. Photochem. Photobiol. A: Chem., 80* (1994) 355.
[14] A. Kuki, *Structure Bonding, 75* (1991) 49.
[15] K.D. Jordan and M.N. Paddon-Row, *Chem. Rev., 92* (1992) 395.
[16] M.D. Newton, *Chem. Rev., 91* (1991) 767.
[17] J.W. Evans and M. Karplus, *J. Chem. Phys., 96* (1992) 5272.
[18] G.D. Scholes and K.P. Ghiggino, in S.H. Lin, A.A. Villaeys and Y. Fujimura (eds.), *Advances in Multiphoton Processes and Spectroscopy*, World Scientific, Singapore, Vol. 10, 1996.
[19] G.D. Scholes, K.P. Ghiggino, A.M. Oliver and M.N. Paddon-Row, *J. Phys. Chem., 97* (1993) 11 871.
[20] G.D. Scholes, K.P. Ghiggino, A.M. Oliver and M.N. Paddon-Row, *J. Am. Chem. Soc., 15* (1993) 4345.
[21] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum, New York, 1983.
[22] K.A. Peterson, M.B. Zammit, S. Linse, R.P. Dominique and M.D. Fayer, *Macromolecules, 20* (1987) 168.
[23] C.R. Gochanour, H.C. Andersen and M.D. Fayer, *J. Chem. Phys., 70* (1979) 4254.
[24] F. Zhu, C. Galli and R.M. Hochstrasser, *J. Chem. Phys., 98* (1993) 1042.
[25] R.S. Knox and D. Gulen, *Photochem. Photobiol., 57* (1993) 40. T.S. Rhaman and R.S. Knox, *Chem. Phys., 44* (1979) 197.
[26] A.A. Demidov and D.L. Andrews, *Chem. Phys. Lett., 235* (1995) 327. D.L. Andrews and P. Allcock, *Chem. Phys., 198* (1995) 35.
[27] K. Wynne and R.M. Hochstrasser, *Chem. Phys., 171* (1993) 179.
[28] A.H.A. Clayton, G.D. Scholes, K.P. Ghiggino and M.N. Paddon-Row, *J. Phys. Chem., 100* (1996) 10 912.
[29] G. Galli, R. Solaro, E. Chiellini, A. Fernyhough and A. Ledwith, *Macromolecules, 16* (1983) 502.
[30] C. David, D. Baeyens-Volant and M. Piens, *Eur. Polym. J., 16* (1980) 413.
[31] V.M. Kenkre and R.S. Knox, *Phys. Rev. B, 9* (1974) 5279.
[32] G.D. Scholes and K.P. Ghiggino, *J. Chem. Phys., 103* (1995) 8873.
[33] G.D. Scholes, A.H.A. Clayton and K.P. Ghiggino, *J. Chem. Phys., 97* (1992) 7405.
[34] K.P. Ghiggino, D.J. Haines, T.A. Smith and G.J. Wilson, *Can. J. Chem., 73* (1995) 2015.
[35] A.D. Stein, K.A. Peterson and M.D. Fayer, *J. Chem. Phys., 92* (1990) 5622.
[36] M. Kasha, A. Sytnik, J.C. Baum and R.L. Christensen, *Abstracts XVI International Conference on Photochemistry*, Vancouver, Canada, 1993, p. 57.