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Theory of Directed Electronic Energy Transfer

David L. Andrews · Richard G. Crisp

Abstract The migration of electronic energy between molecules or chromophores in molecular solids is a well-studied phenomenon. The ability to exert control over the directionality of this transfer, by a variety of methods involving applied electrical or optical fields, holds promise for advances in fields including nanoelectronics and energy harvesting materials. In this paper, we review in detail a number of methods for directing energy transfer, also identifying potential applications.

Keywords Dendrimers · Energy transfer · Nanophotonics · Optical switching · Photosynthesis

Introduction

Molecular origins of energy transfer

The primary result of UV–Visible absorption in non-homogeneous molecular materials is the population of short-lived electronic excited states in individual molecules or chromophores. One or more intermolecular transfers of electronic excitation energy may occur between the initial absorption and eventual fluorescence emission events, commonly on an ultrafast timescale and with an associated degree of intramolecular vibrational redistribution. The routing of energy flow is determined by a sequence of transfer steps, which begins and ends at chromophores that differ either chemically or, if the chromophores are chemically equivalent, through local modifications in energy-level struc-

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ture arising from differences in electronic environment. At the molecular scale, each elementary transfer step is a radiationless pairwise interaction, generally occurring between an electronically excited donor and an electronically distinct acceptor initially residing in its ground state. Förster [1] first demonstrated the Coulombic origin of this interaction, now commonly known as resonance energy transfer (RET), also deriving its inverse sixth power dependence on the donor–acceptor separation. It has since been shown [2–7] that the Förster interaction is the short-range limit of a more general result given by a unified transfer theory—A theory that is valid over any distance and which includes additional terms with inverse fourth power and inverse square dependences on the separation. At large donor–acceptor separations, it naturally emerges that energy transfer is a radiative process involving the distinct emission and subsequent absorption of a photon. At shorter separations, the radiationless process is exhibited. In each case, the efficiency of transfer depends on the extent of overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. The transfer efficiency is also strongly influenced by the donor–acceptor geometry.

In an optically dense system containing a large number of chromophores, many pairwise interactions typically occur before the system enters in a stable state, and the energy transfer path accordingly features a series of short hops rather than one long one—largely as a result of the inverse sixth power distance dependence. Such multi-step resonance energy transfer might be expected to have the character of a random walk, as indeed occurs in homogeneous single-component systems. However, with suitable chromophore differentiation, functionally unidirectional transfer is exhibited in multi-chromophore systems, assisted by suitable chromophore disposition, and often the operation of a *spectroscopic gradient*.

Multi-chromophore systems

Directional RET is an extremely significant process in the operation of photosynthetic and biomimetic light-harvesting units. The light-harvesting systems of purple bacteria in particular have been extensively studied and characterized, and the emulation of their high efficiency is a key goal in the development of new energy harvesting materials [8–14]. In order to most effectively utilize the sunlight that falls on them, photosynthetic organisms have a system of antenna complexes surrounding the reaction centers where photosynthesis takes place. The complexes absorb sunlight and the acquired energy migrates towards the reaction center by a series of short-range, radiationless energy transfer steps. In the overall migration of energy from the site of its initial deposition to the site of its chemical action, the spectroscopic gradient is one of the key directional principles obviating random diffusion. Specifically, a small amount of energy is lost after each transfer step, such that the species acting as the next acceptor receives energy associated with a longer optical wavelength than the donor initially acquired. This causes back-transfer to be very inefficient, due to the poorer overlap of the acceptor emission and donor absorption spectra. By such means, energy absorbed by outlying complexes is quickly and efficiently directed towards the reaction center—a process often referred to as *channeling* or *funneling*. Not only does this allow an organism to harvest light incident on a large surface area, but by pooling energy from a large number of antenna chromophores, energy of a higher equivalent frequency can be produced. This is essential, since the majority of the incident light from the sun has too low a frequency for its individual photons to effect photosynthesis.

It is not only spectroscopic properties of the chromophores that determine the direction of energy flow; the chromophore positioning and orientation are also important. Two-dimensional optical spectroscopy can unveil the intricate interplay between spectral and spatial overlap features in light-harvesting complexes, as beautifully exhibited in recent studies on the Fenna-Olsen-Matthews bacteriochlorophyll *a* protein of green sulfur bacteria [15]. Interrogating the system with a sequence of ultrashort laser pulses, the optical response of the sample can be interpreted to reveal linear absorption processes as well as couplings between chromophores, and dynamical aspects of the energy transfer. The results show that excitation relocation does not simply proceed by stepwise transfer from one energy state to another of nearest energy—it depends on strong coupling between chromophores, determined by the extent of their spatial overlap. Thus, excitation relocation may involve fewer intermediary chromophores than might otherwise be expected.

The efficiency of photosynthetic units has encouraged the design of a variety of synthetic light-harvesting systems that can mimic their energy funneling properties. The materials that have received most attention are dendrimers—macromolecules consisting of molecular units repeatedly branching out from a central core designed to act as an excitation trap [16, 17]. The branching functionalization of terminal groups leads to successive generations of structures, each with an increased number of peripheral antenna chromophores. In ideal cases the requisite spectroscopic gradient is established through chemically similar chromophores in generationally different locations having different electronic properties, due to subtly differing chemical environments. This arrangement expedites emulation of the energy funneling observed in natural light-harvesting systems, with the peripheral chromophores absorbing incident photons, excitation energy relocating across the structure [18, 19], and ultimately being funneled into the core [20]. Striking examples of this principle can be seen in early work on perylene-functionalized phenylacetylene dendrimers [21, 22]. More recent work on dendrimers has seen a number of variations on the basic dendrimeric structure, mostly with branching motifs of threefold and fourfold local symmetry based on (1,3,5)-substituted benzene and porphyrin rings, respectively [23–26].

Electrical and optical control

Whilst the spectral and geometric principles that govern the directionality of energy flow in multi-chromophore systems are largely understood, recent developments have identified new possibilities for effecting externally determined directional control. In particular it transpires that, by a variety of means, optical and electronic perturbations of light-harvesting systems can exert significant additional directing influences on the energy transit. The delineation and analysis of these novel mechanisms is the main subject of the following sections in this paper. In the section Molecular Quantum Theory, the general theory underlying such mechanisms is reviewed, and in section Energy Transfer Between Dipole Arrays, a model utilizing the principles is explored. In particular, it is shown how RET can be tailored, through the involvement of ancillary chromophores or non-resonant throughput radiation, to more efficiently direct the flow of excitation energy. Future prospects for the utilization of directional control are discussed in the concluding section Future Applications.

Molecular Quantum Theory

In order to understand the multi-step energy transfer that typifies the operation of many complexes, it is appropriate to begin with the theory for the prototypical case of energy transfer between one specific excited chromophore and another in its ground state. This is discussed in the first subsection—The following deal with modifications to the basic process,

Fig. 1 Depictions of:
(a) Resonance energy transfer;
(b) electric field induced energy
transfer; (c) third-body energy
transfer; (d) laser-assisted
resonance energy transfer. In
each case, energy transfers from
the donor on the *left* to the
acceptor on the *right*; in the
latter three cases, an auxiliary
influence affects the rate of
transfer
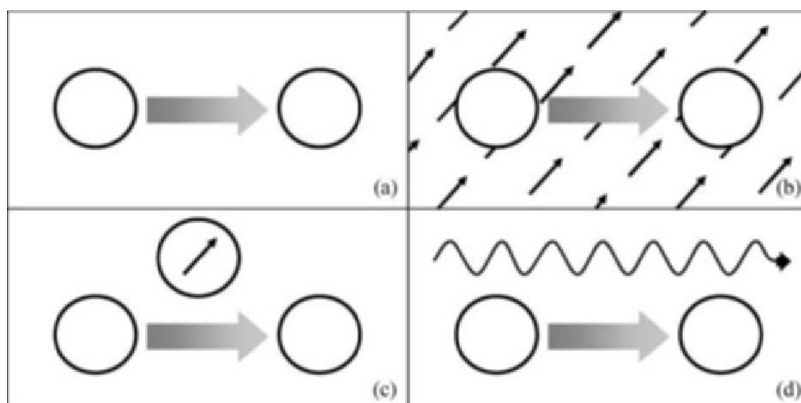
including the influence of a nearby third chromophore and of an applied non-resonant radiation field. A depiction of the four processes to be covered is given in Fig. 1.

Fundamental theory for energy transfer in a donor–acceptor pair

The pairwise transfer of energy between two chromophores D and A can be described by the equation:

$$D^* + A \rightarrow D + A^*, \tag{1}$$

where ξ^* denotes an excited state for chromophore ξ. Chromophore D is designated the *donor* and A the *acceptor*, although it should be emphasized that D and A may each adopt the alternative role in another part of a sequential transfer processes. For the description of this primary event, neither the mechanism for the excitation of D nor the subsequent decay of A comes into play; these are kinetically separable events. Using the Fermi rule, the rate of energy transfer is given by the unified theory [27] as:

$$W_{DA} = \frac{9}{8\pi c^2 \tau_D} \int F_D(\omega)\, \sigma_A(\omega)\, \omega^2 \eta^{DA}(\omega, \boldsymbol{R}_{DA})\, d\omega, \tag{2}$$

where $\sigma_A(\omega)$ is the absorption cross-section of the acceptor, $F_D(\omega)$ the donor emission spectrum (here normalized to unity) and $\hbar\omega$ the energy transferred—the integration is performed over a frequency range that is specifically limited to the salient donor emission and acceptor absorption regions. Also in Eq. (2), τ_D is the donor radiative lifetime (the product of the measured fluorescence lifetime and the fluorescence quantum yield), $\boldsymbol{R}_{DA} = R_D - R_A$ the vector separation of the chromophores, and

$$\eta^{DA}(\omega, \boldsymbol{R}_{DA}) = \frac{c^6}{\omega^6 R_{DA}^6} \left(\kappa_3^{DA}\right)^2 + \frac{c^4}{\omega^4 R_{DA}^4}$$
$$\times \left[\left(\kappa_3^{DA}\right)^2 - 2\kappa_3^{DA}\kappa_1^{DA}\right] + \frac{c^2}{\omega^2 R_{DA}^2} \left(\kappa_1^{DA}\right)^2. \tag{3}$$

The orientation factors κ_3^{DA} and κ_1^{DA} are defined as:

$$\kappa_q^{DA} = \left(\hat{\boldsymbol{\mu}}^D \hat{\boldsymbol{\mu}}^A\right) - q\left(\hat{\boldsymbol{\mu}}^D \hat{\boldsymbol{R}}_{DA}\right)\left(\hat{\boldsymbol{\mu}}^A \hat{\boldsymbol{R}}_{DA}\right), \tag{4}$$

with $\hat{\boldsymbol{\mu}}^D$, $\hat{\boldsymbol{\mu}}^A$, $\hat{\boldsymbol{R}}_{DA}$ being unit vectors in the direction of the dipole transition moments and the donor–acceptor separation vector. The κ factors embody one important facet of the energy transfer, an orientational dependence determined by the chromophore architecture. For certain orientations of the displacement vector and dipole transition moments—for example, if all three are mutually orthogonal—the κ factors vanish, resulting in zero energy transfer. At the other extreme, optimization of the energy transfer rate is achieved by both transition moments being parallel or antiparallel to the separation vector [28]. Analysis of Eq. (2) indicates that the energy transfer rate is also strongly influenced by the separation and spectral features of the two chromophores, in addition to the relative orientation of the transition dipoles.

Equation (2) incorporates both the commonly termed "radiative" and "radiationless" processes through $\eta^{DA}(\omega, \boldsymbol{R}_{DA})$, where ω is a typical frequency within the spectral overlap region. In the far-zone ($R \gg c/\omega$, corresponding to distances well in excess of the wavelength associated with the transfer energy), the third term in Eq. (3) dominates and the radiative rate $W_{DA} \propto \kappa_1^2/R^2$ is observed. Conversely, in the near-zone ($R \ll c/\omega$, as is usual for condensed phase energy transfer) Eq. (2) produces the Förster rate of RET:

$$W_{DA}^{RET} = \frac{9c^4 \kappa_3^2}{8\pi \tau_D R_{DA}^6} \int F_D(\omega)\, \sigma_A(\omega)\, \omega^{-4} d\omega, \tag{5}$$

with a dependence on R^{-6} and κ_3^2. The latter "radiationless" process is by far the most significant for the near-neighbor transfers that occur in light-harvesting materials, though in optically dilute systems with chromophore spacings of about a hundred or a few hundred nanometers, all three terms in Eq. (3) become comparable in magnitude and Eq. (5) no longer applies.

Influence of a static electric field

If a donor–acceptor pair of chromophores is placed in a static electric field, the rate of energy transfer between them will be modified by their interaction with the electric field [29]. In detail, it transpires that the mechanism for delivery of energy to the acceptor then comprises four pathways, to be understood as follows. The quantum amplitude for the overall process is dominated by the usual field-independent term, but also comprises correction terms—the most significant two of which entail linear coupling of the static field with either D or A, and another involves coupling of the static field at both D and A. Moreover, when the static field engages with a transition, it is associated with different selection rules—which can be formally identified with those of a *two-quantum* transition.

From the Fermi rule, the rate of energy transfer is in turn determined from the square of the quantum amplitude. To elicit most clearly the principles that operate, it is expedient to apply a two-level approximation to the chromophores—fully justified if the donor and acceptor excited states are the lowest electronically excited levels of each chromophore, and other energy levels are of significantly higher energy. Provided this is applicable, the rate of energy transfer between the two chromophores in a static electric field is given by:

$$
\begin{aligned}
W^{\mathrm{DA}} = \frac{9}{8\pi c^2 \tau_{\mathrm{D}}} &\times \left[\int F_{\mathrm{D}}(\omega)\sigma_{\mathrm{A}}(\omega)\omega^2 \eta^{\mathrm{DA}}(\omega, \boldsymbol{R})\, \mathrm{d}\omega \right. \\
&+ \frac{E}{\hbar}\{|d^{\mathrm{D}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{D}}) + |d^{\mathrm{A}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{A}})\} \int F_{\mathrm{D}}(\omega)\sigma_{\mathrm{A}}(\omega)\,\omega \\
&\times \eta^{\mathrm{DA}}(\omega, \boldsymbol{R})\, \mathrm{d}\omega + \frac{E^2}{\hbar^2}\{[|d^{\mathrm{D}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{D}}) + |d^{\mathrm{A}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{A}})]^2 \\
&+ 2|d^{\mathrm{D}}\|d^{\mathrm{A}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{D}})(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{A}})\} \int F_{\mathrm{D}}(\omega)\sigma_{\mathrm{A}}(\omega) \\
&\times \eta^{\mathrm{DA}}(\omega, \boldsymbol{R})\mathrm{d}\omega - \frac{E^3}{\hbar^3}\{|d^{\mathrm{D}}\|d^{\mathrm{A}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{D}})(\hat{E}.\hat{\mu}^{\mathrm{A}}) \\
&\times [|d^{\mathrm{D}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{D}}) + |d^{\mathrm{A}}|(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{A}})]\} \int F_{\mathrm{D}}(\omega)\sigma_{\mathrm{A}}(\omega)\omega^{-1} \\
&\times \eta^{\mathrm{DA}}(\omega, \boldsymbol{R})\, \mathrm{d}\omega + \frac{E^4}{\hbar^4}|d^{\mathrm{D}}|^2|d^{\mathrm{A}}|^2(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{D}})^2(\hat{\boldsymbol{E}}\hat{\boldsymbol{\mu}}^{\mathrm{A}})^2 \\
&\left. \times \int F_{\mathrm{D}}(\omega)\sigma_{\mathrm{A}}(\omega)\omega^{-2}\eta^{\mathrm{DA}}(\omega, \boldsymbol{R})\, \mathrm{d}\omega \right]
\end{aligned}
\tag{6}
$$

where the shorthand $\boldsymbol{R}$ has been used for $\boldsymbol{R}_{\mathrm{DA}}$. In the above, $\hat{\boldsymbol{E}}$ is the electric displacement unit vector of the static field, whose magnitude is E, and $d^{\xi} = \mu^{ee(\xi)} - \mu^{00(\xi)}$ is the absolute difference between the magnitudes of the excited state (e) and ground state static dipole moments of chromophore ξ—all other terms are as given in the previous section. Here, it is assumed for simplicity that all static and transition dipole moments associated with the same chro-
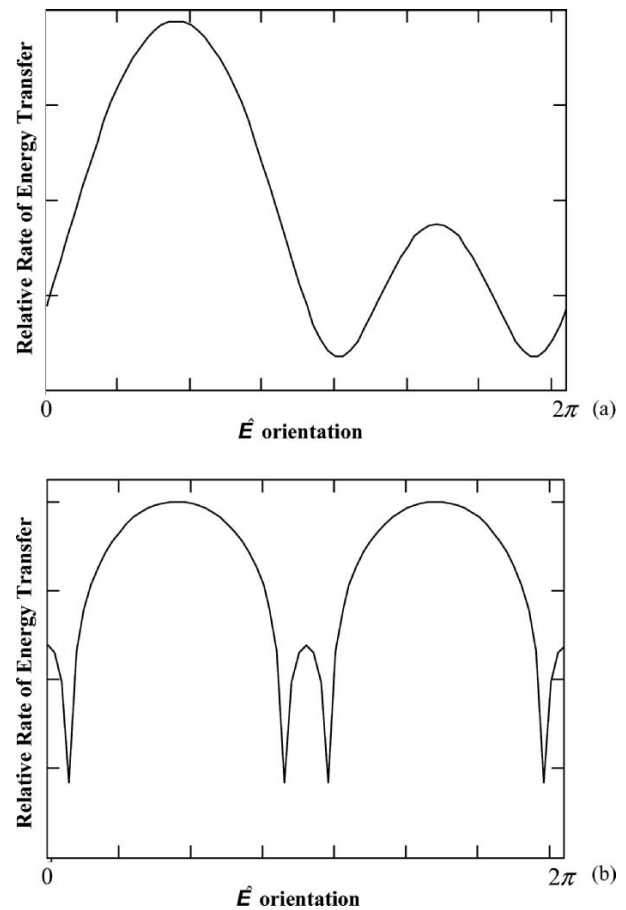

Fig. 2 Influence of a static field on energy transfer as the polarization vector of the static field is rotated relative to the transfer pair. (a) The donor and acceptor transition moments are parallel, and the static-field strength is 10^{10} V m^{-1}. (b) The donor and acceptor transition moments are antiparallel to each other and the static-field strength is 10^{11} V m^{-1}

mophore are parallel, although those associated with D can have arbitrary orientation with respect to those associated with A. Figure 2 exhibits graphs constructed based on typical values for the static-field strength and transition dipole moments.

Equation (6) can be understood as a series expansion in powers of E, with the first term representing the normal rate of energy transfer (i.e., excluding static-field coupling), and the following terms signifying corrections of successively diminishing importance. The term describing energy transfer with one static interaction is in fact the third term, and the last term describes energy transfer involving coupling of both chromophores with the static field. The other terms represent interference between the various pathways, of which the second term in Eq. (6) is linear in E and generally the most significant correction. However, if either the donor or acceptor transition is electric dipole-forbidden, the first and second terms of (6) vanish and the third term provides the leading rate contribution. If both the donor *and* acceptor transitions are electric dipole-forbidden, only the final term

will provide any meaningful contribution to the rate. It is important to note that, with increasing order of E in successive terms of Eq. (6), the powers of ω in the spectral overlap integral decrease. This indicates an increasing weighting towards the long-wavelength end of the spectral overlap between the donor emission and acceptor absorption curves, especially in connection with the nonlinear terms. The amenability of the static field-induced mechanism to directing energy transfer is easily seen in the case of a chromophore with a dipole-forbidden transition—energy may not transfer to or from such a species without the presence of a static field, allowing a switchable electric field to control the delivery of energy to the acceptor.

Influence of a neighboring dipole

The previous sections describe energy transfer in terms of the usual model of coupling between two electronically isolated chromophores. However, in reality most systems comprise many chromophores, and each transfer event takes place in an electronic environment that may be modified by one or more other chromophores in proximity to the interaction pair. In this connection it is possible for a variety of species to play the role of a "third body" M. For example, in a dendrimeric system the latter might be another chromophore of the same type as either donor or acceptor, in the same general vicinity. In a photosynthetic complex, the third body might be an ancillary pigment, or even one residue of a support protein unit. The possible involvement of such species in exerting an influence on the rate of donor–acceptor transfer has received surprisingly little attention, yet it transpires that surrounding chromophores, especially any that are strongly polar, can substantially affect the rate of energy transfer without themselves changing state. This mechanism can be represented in general terms by:

$$D^* + A + M \rightarrow D + A^* + M. \tag{7}$$
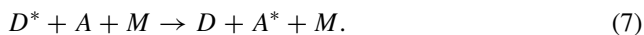
Associated with this mechanism, in addition to the quantum amplitude for direct transfer not involving the chromophore M, as described in the initial section, three further distinct contributions to the amplitude can be identified: A static dipole of M interacts with either D or A, or a dynamic dipole of M acts as an intermediary for the energy transfer. In a sense the static interaction is comparable to that described in the last subsection, except that here the field is produced *in situ* rather than being externally delivered. The total rate of energy transfer between two chromophores in the presence of a third body is [30]:

$$W_{DA} = \frac{9}{8\pi c^2 \tau_D} \int F_D(\omega) \sigma_A(\omega) \omega^2 \eta^{DA}(\omega, \boldsymbol{R}_{DA}) \, d\omega$$

$$+ \frac{9}{128\pi^3 \hbar^2 c^2 \varepsilon_0^2 \tau_D} \left\{ \left[\frac{|d^D|^2 (\kappa_3^{DM})^2}{R_{DM}^6} + \frac{|d^A|^2 (\kappa_3^{AM})^2}{R_{AM}^6} \right. \right.$$

$$+ \frac{|d^D||d^A|\kappa_3^{DM}\kappa_3^{AM}}{R_{DM}^3 R_{AM}^3} \left] |\mu^M|^2 \int F_D(\omega) \sigma_A(\omega) \right.$$

$$\times \eta^{DA}(\omega, \boldsymbol{R}_{DA}) d\omega + \hbar^2 \int F_D(\omega)\sigma_A(\omega)|\alpha^M(\omega)|^2 \omega^2$$

$$\times \eta^{DM}(\omega, \boldsymbol{R}_{DM}) \eta^{AM}(\omega, \boldsymbol{R}_{DA}) d\omega + \left[\frac{|d^D|\kappa_3^{DM}}{R_{DM}^3} \right.$$

$$+ \frac{|d^A|\kappa_3^{AM}}{R_{AM}^3} \left] 4|\mu^M|\hbar \int F_D(\omega) \sigma_A(\omega) \omega \right.$$

$$\times \eta^{DA}(\omega, \boldsymbol{R}_{DA}) d\omega + \left[\frac{|d^D|\kappa_3^{DM}}{R_{DM}^3} + \frac{|d^A|\kappa_3^{AM}}{R_{AM}^3} \right]$$

$$\times \frac{|\mu^M|\hbar c^6}{R_{DA}^3 R_{DM}^3 R_{AM}^3} \int F_D(\omega) \sigma_A(\omega) |\alpha^M(\omega)|\omega^{-5}$$

$$\times \chi(\omega, \boldsymbol{R}_{DA}, \boldsymbol{R}_{DM}, \boldsymbol{R}_{AM}) d\omega + \frac{4\pi\varepsilon_0 \hbar^2 c^6}{R_{DA}^3 R_{DM}^3 R_{AM}^3}$$

$$\times \int F_D(\omega) \sigma_A(\omega) |\alpha^M(\omega)|\omega^{-4}$$

$$\times \chi(\omega, \boldsymbol{R}_{DA}, \boldsymbol{R}_{DM}, \boldsymbol{R}_{AM}) d\omega \right\} \tag{8}$$

where μ^M and α^M are, respectively, the static dipole moment and the dynamic polarizability (at frequency ω) of M and, as defined previously, d^ξ is the difference between the static excited state and ground state dipole moments of chromophore ξ. Additionally, $\chi(\omega, R_{DA}, R_{DM}, R_{AM})$ is given by;

$$\Re e \left\{ \left[\left(1 - \frac{i\omega R_{DA}}{c} \right) \kappa_3^{DA} - \frac{\omega^2 R_{DA}^2}{c^2} \kappa_1^{DA} \right] \right.$$

$$\times \left[\left(1 + \frac{i\omega R_{DM}}{c} \right) \kappa_3^{DM} - \frac{\omega^2 R_{DM}^2}{c^2} \kappa_1^{DM} \right]$$

$$\times \left[\left(1 + \frac{i\omega R_{AM}}{c} \right) \kappa_3^{AM} - \frac{\omega^2 R_{AM}^2}{c^2} \kappa_1^{AM} \right] \right\} \tag{9}$$

Note again the variable frequency-weighting of the various spectral overlap terms. Previous research into the influence on energy transfer [30] has shown that the third-body chromophore has a significant effect on the rate of energy transfer only when that chromophore is very close to either one of the donor–acceptor pair, typically at distances less then 1.5 nm. In this region, the third-body influence typically ranges from a 50% enhancement of the rate to a 40% reduction, dependent on the arrangement of the chromophores involved. Although the exact rate distribution with respect to position depends on the relative dipole moment orientation of the three chromophores, in general the influence of M is greatest when the dipole is positioned just out-
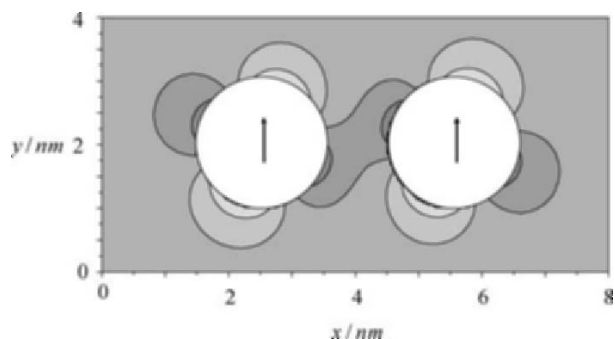
Fig. 3 Influence of a neighboring dipole on the rate of energy transfer between two chromophores, here located at coordinates (25,20) and (55,20). Both chromophore transition moments are aligned parallel to the *y*-axis, the ancillary dipole is oriented at an angle of $\pi/4$ to the *y*-axis. The influence increases as the shade of gray darkens, with the darkest sections displaying a 200% increase of the rate over the lightest area. *White* denotes positions of significant wavefunction overlap, where a different (exchange) mechanism would come into play

side wavefunction overlap of *D* or *A*. An example of this is given in Fig. 3. It is imperative to take this mechanism into account when analyzing systems comprising a large number of closely spaced chromophores, such as most light-harvesting materials.

Influence of throughput radiation

As seen above, ancillary chromophores can exert a significant influence on the inter-chromophore transfer of energy. The rate of pairwise transfer can also be modified by intense, pulsed throughput laser radiation [31]. The radiation is forward Rayleigh scattered cooperatively by the donor–acceptor pair—effectively leaving the radiation unchanged, but either enhancing or diminishing the efficiency of energy transfer between the two chromophores. In the former, more interesting case the process is known as laser-assisted resonance energy transfer (LARET).

For simplicity, we restrict the following consideration to a system of non-polar (or only weakly polar) chromophores, again applying a two-level approximation. In broad terms, the laser-modified mechanism for energy transfer bears some similarity to the static field-induced case described in the section Influence of a Static Electric Field, except that here a dynamic optical field is applied. Surprisingly, static dipoles of the donor and acceptor still play a role, despite the oscillatory character of the field—but those that enter the rate expression now relate to electronically excited states. In other words, this mechanism operates through shifts in the electron distributions, associated with the donor decay and the acceptor excitation transitions. The total rate of energy transfer, in the presence of off-resonant laser light with a frequency ω', is expressible as [31]:

$$W_{DA} = \frac{9}{8\pi c^2 \tau_D} \int F_D(\omega)\sigma_A(\omega)\omega^2 \eta^{DA}(\omega, \boldsymbol{R})\, d\omega$$

$$+ \frac{9|\mu^{ee(D)}||\mu^{ee(A)}|I(\omega')}{32\pi\hbar^2 c^3 \varepsilon_0 \omega'^2 \tau_D} \left\{ \frac{|\mu^{ee(D)}||\mu^{ee(A)}|I(\omega')}{\hbar^2 c\omega'^2 \varepsilon_0} \right.$$

$$\times [(\boldsymbol{e}\cdot\hat{\boldsymbol{\mu}}^D)^2(\bar{\boldsymbol{e}}\cdot\hat{\boldsymbol{\mu}}^A)^2 \int F_D(\omega)\sigma_A(\omega)\eta^{DA}(\omega_+, \boldsymbol{R})\omega_+^2 d\omega$$

$$+ (\bar{\boldsymbol{e}}\cdot\hat{\boldsymbol{\mu}}^D)^2(\boldsymbol{e}\cdot\hat{\boldsymbol{\mu}}^A)^2 \int F_D(\omega)\sigma_A(\omega)\eta^{DA}(\omega_-, \boldsymbol{R})\omega_-^2 d\omega$$

$$+ 2\left[e^{\frac{2i\omega'\boldsymbol{R}}{c}} + e^{-\frac{2i\omega'\boldsymbol{R}}{c}}\right](\boldsymbol{e}\cdot\hat{\boldsymbol{\mu}}^D)^2(\bar{\boldsymbol{e}}\cdot\hat{\boldsymbol{\mu}}^A)^2$$

$$\times \int F_D(\omega)\sigma_A(\omega)\eta^{DA}(\omega_+, \omega_-, \boldsymbol{R})(\omega^2 - \omega'^2)\, d\omega]$$

$$- 4[(\boldsymbol{e}\cdot\hat{\boldsymbol{\mu}}^D)(\bar{\boldsymbol{e}}\cdot\hat{\boldsymbol{\mu}}^A) + (\bar{\boldsymbol{e}}\cdot\hat{\boldsymbol{\mu}}^D)(\boldsymbol{e}\cdot\hat{\boldsymbol{\mu}}^A)]\left[e^{\frac{-i\omega'\boldsymbol{R}}{c}}\right.$$

$$\times \int F_D(\omega)\sigma_A(\omega)\eta^{DA}(\omega, \omega_+, \boldsymbol{R})\omega\omega_+ d\omega + e^{\frac{i\omega'\boldsymbol{R}}{c}}$$

$$\left. \left. \times \int F_D(\omega)\sigma_A(\omega)\eta^{DA}(\omega, \omega_-, \boldsymbol{R})\omega\omega_- d\omega\right]\right\} \qquad (10)$$

In the above, $\omega_\pm$ represents $\omega \pm \omega'$; $I(\omega')$ is the irradiance of the laser radiation and $\boldsymbol{e}$ is the corresponding polarization vector ($\bar{\boldsymbol{e}}$ being its complex conjugate). The first three η factors are as described previously, with $\omega \pm \omega'$ substituted for ω where appropriate. The other η factors, which arise from interference terms, have a slightly more complicated form and are given by:

$$\eta^{DA}(\omega_1, \omega_2, \boldsymbol{R}) = \frac{c^6}{\omega_1^3 \omega_2^3 R^6}\kappa_3^2 + \frac{c^4}{\omega_1^2 \omega_2^2 R^4}\kappa_3^2 - \left[\frac{c^4}{\omega_1^3 \omega_2 R^4}\right.$$

$$\left. + \frac{c^4}{\omega_1 \omega_2^3 R^4}\right]\kappa_3\kappa_1 + \frac{c^2}{\omega_1 \omega_2 R^2}\kappa_1^2 \qquad (11)$$

where ω_1 and ω_2 stand for ω, ω_+, or ω_- as required by (10).

Detailed analysis of LARET has shown that the standard RET pathway is dominant at incident intensities below about 10^{13} W m^{-2}. At intensities of around 10^{16} W m^{-2} (relatively high, but still easily produced using pulsed lasers) an enhancement to the rate of 10% or more can be observed, for non-polar systems as represented above. However, for chromophores which are both polar and chiral, additional terms arise [31], and these can lead to rate enhancements as high as 30% or more. Due to the linear and quadratic dependencies on irradiance for the LARET rate contributions, any increase in the intensity of the throughput laser light can effect a disproportionately greater enhancement to the rate, although the availability of higher intensities (and the possibility of introducing competing processes such as multiphoton dissociation) must then be taken into account. Using off-resonant laser light to augment energy transfer should find many applications in artificial systems, since it provides an easily

controlled, switchable process that nonetheless has a passive role with regards to the system. We explore this in the following section.

Energy transfer between dipole arrays

In the previous section, a variety of novel means for effecting directed energy transfer have been discussed and key results from the quantum theory have been presented. Each mechanism offers distinct opportunities for future applications, which are being brought closer to fruition as new photonic technology is developed. One of the operational principles under consideration for new devices is to configure a resonant coupling of the energy of throughput optical radiation in matter with a suitable absorption profile, enabling excitation to propagate between nearby particles having a suitably matching frequency response. Many proposed systems thus involve internal transfers of optical excitation energy, the RET activated by an applied electric [32–34] or optical field [35–39], for example. Such devices hold significant promise for the furtherance of ultrafast communication and signal processing systems. Within this context, and as one example of directed energy transfer, we now explore a nanoscale optical switching concept based on LARET. Specifically, this is a scheme using pulsed laser light to selectively channel energy between corresponding pixels in two parallel arrays. Although electrical field influences are also capable of activating forbidden energy transfer, and thus forming the basis for such an application, LARET proves to be the most amenable to controlled nanoscale implementation, as in the system described below.

Suitably configuring an arrangement of transition dipoles, it is possible to design parallel planar arrays of optical donor and acceptor chromophores such that the transfer of energy from any single donor, to its counterpart in the opposing plane, can be switched by throughput laser radiation of an appropriate intensity, frequency and polarization. For simplicity, a pair of two-dimensional arrays can be envisaged, each consisting of equally spaced, identical chromophores arranged on a square lattice. The dipole transition moments of any given chromophore embedded in either structure is parallel to all other transition moments within the same plane; the arrays are arranged such that each particle in one has a counterpart in the other with an orthogonal transition moment. With a single excited donor in the upper array, energy transfer to its counterpart is forbidden, since the κ factor for that transfer is equal to zero. However, the application of laser radiation to the system allows energy to transfer between the two chromophores, via a LARET pathway as described previously. By engineering the separation of the chromophores, this mechanism can be used to direct energy
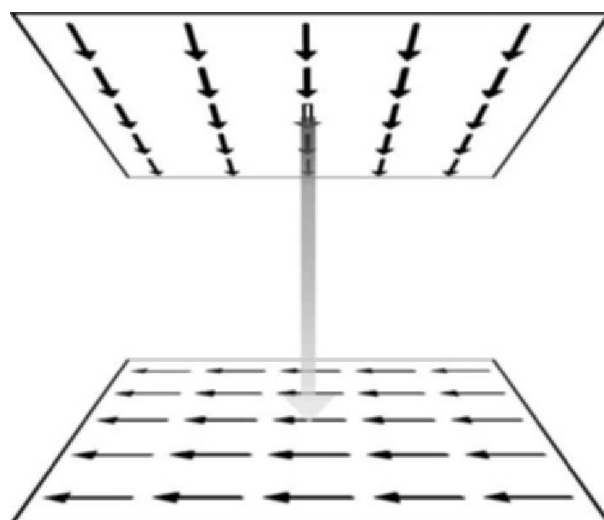

Fig. 4 Arrays of donors (*upper array*) and acceptors (*lower array*) aligned with orthogonal dipole transition moments. Throughput laser radiation enables energy transfer from the excited donor (shown in *white*) to its counterpart acceptor. The separation between the arrays is exaggerated for clarity

transfer towards a specific acceptor. A diagram of this system is given in Fig. 4.

To produce a meaningful system, energy transfer from a given donor to its counterpart acceptor must be greatly favorable compared to any involving another acceptor or even another donor—in other words, cross-talk has to be minimized. A detailed analysis of the geometric and orientational features of the system and associated constraints is given elsewhere [40]. The analysis reveals that the probability of transfer to the intended acceptor strongly depends on the aspect ratio—the relative magnitude of the lattice spacing and the spatial separation of the arrays—as well as the intensity of the applied laser radiation. Figure 5 shows
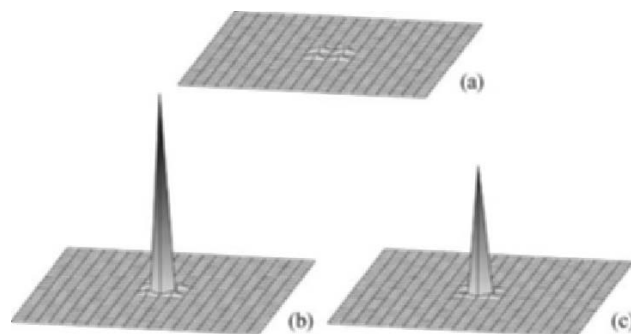

Fig. 5 Energy transfer from a single excited donor to an array of acceptors in (a) the absence and (b, c) presence of throughput laser radiation. In (b), the donor and acceptor array separation is one-tenth that of the lattice spacing of each array, and an irradiance of 10^{14} W m^{-2} is sufficient to direct energy transfer. In (c), the array separation is only half the lattice spacing, requiring an irradiance of 10^{16} W m^{-2} to direct energy transfer. In all cases, the height of the graph represents efficiency of energy transfer to the chromophore at that position in the array

how the variation of these factors affects the efficiency of directing energy transfer. To illustrate with a particularly suitable relative positioning—where the spatial separation is one-tenth that of the lattice spacing—energy can be directed to the intended acceptor on application of laser light with an irradiance in the region of 10^{14} W m^{-2}, for example. The favorability of this configuration is illustrated by the fact that a larger aspect ratio of 1:2 would result in a hundredfold increase in the irradiance required to achieve efficient directed energy transfer. The appraisal of other methods for directing energy transfer in this and related systems, and potential device applications, are the subjects of ongoing research in the quantum electrodynamics group at UEA.

Future applications

The processes presented in this paper represent prospects for a number of different ways in which a vectorial character can be produced or enhanced in resonance energy transfer. Each mechanism is particularly amenable to nanophotonic device implementation, since the propagation of electronic energy by RET is specifically directed over a sub-wavelength scale. Although the mechanisms for controlling energy flow are only just beginning to receive attention, it is already clear that their detailed methods of implementation will differ, according to the mechanism to be deployed.

Exercising electric field control over RET appears to have potential for applications in the optimization of light-harvesting materials. To operate effectively, the mechanism requires levels of field that would be most easily sustained within microscopic or sub-microscopic domains (obviating the extremely high voltages otherwise required), and these may be best achieved through surface field effects. The capacity to switch a directing field on and off offers intriguing possibilities, though one that would necessarily be limited by the speed of the associated electronics. To effect such control more directly at the molecular level, utilizing local fields generated by neighboring dipoles, allows the necessary fields to be produced more readily—but such a system is less amenable to real-time experimental control. Here one might envisage composite materials, whose molecular architecture is designed to deliver optically acquired energy from antenna chromophores to suitable traps, expedited by the incorporation of strongly polar groups.

It appears to be in the last of the mechanisms discussed above, the case of optically induced RET switching, that the most promising opportunities for device implementation will arise. It is highly significant that the laser systems capable of delivering the necessary levels of irradiance are precisely those that also offer directly controllable, ultrafast speeds of switching. The parallel processing possibilities that arise with array implementation suggest a variety of op-

tical interconnect applications, including flat panel displays and optical communications routing technology. The realization of such applications should be viewed in the context of ongoing advances in nanolithographic fabrication, which are driving optical technology to ever greater levels of speed and miniaturization. It will be fascinating to observe how materials science will rise to the challenge of exploiting these possibilities in the years that lie ahead.

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