Review

Mechanisms of Light Energy Harvesting in Dendrimers and Hyperbranched Polymers

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Abstract: Since their earliest synthesis, much interest has arisen in the use of dendritic and structurally allied forms of polymer for light energy harvesting, especially as organic adjuncts for solar energy devices. With the facility to accommodate a proliferation of antenna chromophores, such materials can capture and channel light energy with a high degree of efficiency, each polymer unit potentially delivering the energy of one photon—or more, when optical nonlinearity is involved. To ensure the highest efficiency of operation, it is essential to understand the processes responsible for photon capture and channelling of the resulting electronic excitation. Highlighting the latest theoretical advances, this paper reviews the principal mechanisms, which prove to involve a complex interplay of structural, spectroscopic and electrodynamic properties. Designing materials with the capacity to capture and control light energy facilitates applications that now extend from solar energy to medical photonics.

Keywords: light-matter interactions; dendrimers; photons; energy harvesting; nonlinear optics; chromophore arrays; photochemistry; photophysics

1. Introduction

In the photosynthetic realm of the biosphere, highly efficient biomolecular systems daily harness the energy of sunlight, intercepting and trapping radiant energy with complex arrays of light-harvesting

chromophores [1–3]. Research teams across the globe have long sought clues to the structure-property features responsible for the high levels of efficiency in the wide variety of such systems, in the hope of informing the design of artificial energy harvesting materials. A key aim has been, and remains, the accomplishment of similar levels of efficiency in synthetically less demanding materials, achieved by emulating the photobiological principles of photon capture [4–8]. In the whole field of molecular science, multi-chromophore dendrimers represent the single type of material that has most significantly fulfilled this promise [4,5,9–19]. Typically, these materials are built in a quasi-fractal geometry from chemically similar, strongly absorbing chromophores organized around a core that acts as an energy trap [10,18]. Solar energy capture in such materials is not in general aimed at accomplishing biochemical synthesis, but rather as a means of harnessing the energy of light in the cause of effecting molecular-level charge separation. This represents the primary step in a wide range of potential device and materials applications, leading into areas that extend well beyond the scope of this article.

Photobiological and dendrimeric systems deploy similar energy harvesting mechanisms in photon absorption and energy transfer to a central trap [20–22]. The photochemical features which they share include: a multiplicity of peripheral chromophores that can initially absorb light, producing short-lived electronic excited states; a mechanism for rapid transfer of the resulting excitation towards a trapping site (stepwise *resonance energy transfer*, RET); a geometric layout that expedites trap-directed routing, governed by chromophore separation and orientation, and a process for collecting and capturing the energy acquired at the trap. In the construction of light-harvesting dendrimers, each of these photochemical and photophysical principles is put to highly effective use: the repeated branching of the polymer structure, together with the three-dimensional folding that occurs in all but the smallest systems, supports a special proliferation of chromophores on the outermost surface, and the inner, building-block chromophores act with high efficiency as transient hosts for the excitation energy en route to the core. Moreover, the convergence of the dendrimer branches towards the core also assists the pooling of energy, in the event that more than one photon is initially captured upon the outer surface.

As it transpires, it is usually important to fulfil one further, rather less obvious condition in the photophysics: the efficiency of energy harvesting is generally enhanced by ensuring a degree of intramolecular relaxation, so that each stage of excitation transfer within the dendrimer is accompanied by minor energy losses. This feature, in turn, requires that each energy migration route traverses chromophores with progressively red-shifted excited states, a property known as a *spectroscopic gradient*, which can be established through an intramolecular variation of electronic environment for successively encountered chromophores [23–27]. The virtue of this characteristic is that it confers directionality towards the trap, obviating the random-walk behaviour that would otherwise lead to significantly longer trapping times. Alternatively, an entirely different compound can be used for the trap, as is the case in clathrate dendrimers designed to accommodate smaller dye molecules, such as eosin within their internal cavities [28].

Understanding the multi-step flow of excitation energy in these systems is crucial for determining material architectures that can operate as solar (or other light) energy collectors with high efficiency; in the following, we identify the key properties and mechanisms.

2. Constituent Chromophores: The Properties and Layout

For the efficient absorption of radiation, the antenna chromophores of light-harvesting dendrimers, commonly the species from which the polymer is constructed, should display strong absorption in a suitable part of the electromagnetic spectrum—generally the visible range of solar radiation that retains significant intensity after passage through the Earth's atmosphere. Photobiological systems commonly accommodate adjunct chromophores to expand the wavelength range for effective absorption, a device that synthetic materials may also emulate. The most important property to determine absorption strength is the electric dipole transition moment. In the survey of theory presented below, the transition dipole of a chromophore in electronic decay, acting as donor, is denoted μ_D, and the counterpart moment for the electronic excitation of a neighbouring chromophore acting as acceptor is represented μ_A. Both transition dipoles are vector quantities having fixed angular disposition relative to the dendrimer; these orientations can be computed using quantum chemistry software, and the magnitudes either by computation or by calculation from the absorption spectrum. Although the primary absorption of radiation has an efficiency that depends on the orientation of any individual transition dipole with respect to the electric vector of the input light, it is not usually a factor that needs consideration, since each dendrimer carries a multitude of antenna chromophores disposed at a variety of angles, each contributing to the eventual energy trapping. In consequence the response from any single dendrimer effectively corresponds to a spatial averaging of the absorption dipole moments.

The chromophores from which dendrimers are built, often involving benzene rings, are commonly large enough for them to support local vibrational modes, of a sufficient number that the corresponding quantum levels overlap in a broad continuum. In consequence, there is a significant bandwidth to the corresponding absorption profile, and the electronic excitation of each such chromophore is usually also accompanied by significant engagement with the vibrational modes. Ultrafast processes of intramolecular vibrational relaxation (IVR) ensue, before decay of the electronic excited state (usually a singlet state) occurs; the level in the electronic excited state from which decay occurs is then, in general, the lowest in its vibrational continuum. Whereas the chromophore in isolation might decay by fluorescent emission, the key to light-harvesting efficiency in dendrimers is intramolecular RET, so that the energy is not lost to the system but passed on to another chromophore component. Again, the linkages between chromophore units, such as ethynyl or ether groups, are commonly chosen to preclude an alternating bond conjugated structure that would expedite electronic delocalisation (which would result in longer-wavelength absorption). Electron exchange within the dendrimer thus becomes essentially negligible [29,30]. Accordingly the dominant energy transfer mechanism is RET, whose mechanism is traditionally conceived in terms of a coupling between the transition dipoles.

To understand more of the specific properties that will expedite RET, we first need to consider the mechanistic details of pair-wise energy transfer between an excited donor *D** and *A*, an acceptor; *A* becomes excited on acquisition of the energy lost in the decay of *D**:

$$D^* + A \xrightarrow{\text{RET}} D + A^*$$ (1)

(not showing the initial step of single photon absorption at *D*). The excited acceptor, *A**, can then act as donor for the next transfer in the sequence, eventually terminating at the excitation trap; the extent to which such steps can be regarded as separable will be considered in more detail in Section 5.

Figure 1. Energetics for pair-wise RET and associated spectral overlaps: (top) transfer from *D* to *A*; (below) potential backward transfer, *A* to *D*: *F*—fluorescence spectrum; σ—absorption spectrum; IVR—intramolecular vibrational relaxation.
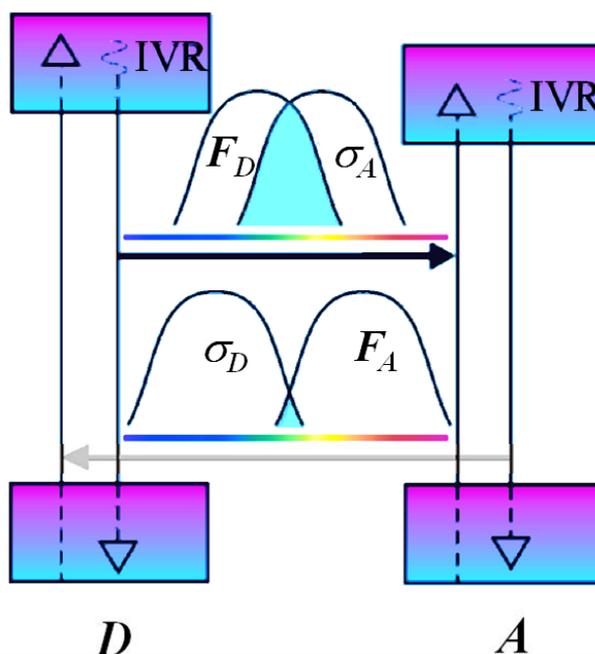
Since the electronic levels of both the donor and acceptor are broadened by their coupling with local vibrations, it follows that energy transfer can occur at any level within the region of overlap between the donor emission and acceptor absorption bands, as illustrated in Figure 1. This process is generally described by Förster theory, from which the following expression arises for the rate of pair-wise transfer, w_F, for any donor-acceptor separation, *R*, substantially smaller than optical wavelengths [31]:

$$w_{\mathrm{F}} \propto \frac{\kappa^2}{\tau_{D*}R^6} \int F_D(\omega)\sigma_A(\omega)\frac{\mathrm{d}\omega}{\omega^4} \tag{2}$$

In Equation (2), ω is an optical frequency and $F_D(\omega)$ represents the normalized line-shape for the fluorescence spectrum of the donor (τ_{D*} being the associated radiative decay lifetime); $\sigma_A(\omega)$ is the corresponding line-shape for the linear absorption cross-section of the acceptor. The inverse proportionality of the rate with the lifetime of the donor signifies the fact that energy transfer is generally expedited by excited states that have the faster decay rates. The integral within which the line-shape product appears, known as the *spectral overlap*, is one of the key determinants of energy transfer efficiency [32]. Another prominent feature in Equation (2) is the κ factor, which depends on the orientations of the donor and acceptor with respect to each other, and also with respect to their mutual displacement vector *R*;

$$\kappa = (\boldsymbol{\mu}_D \cdot \boldsymbol{\mu}_A) - 3(\boldsymbol{R} \cdot \boldsymbol{\mu}_D)(\boldsymbol{R} \cdot \boldsymbol{\mu}_A) \tag{3}$$

where carats denote unit vectors. Whilst the possible values of κ^2 are readily shown to lie in the range (0, 4), the result for a specific pair of chromophore in mutually fixed positions and orientations can be cast as a function of three independent angles, shown and defined in Figure 2:

$$\kappa = \cos\theta_T - 3\cos\theta_D\cos\theta_A \tag{4}$$

Unfavourable orientations can indeed reduce the rate of energy transfer to zero; the relative angular disposition of the chromophores is therefore a very important facet, and it is one reason why one cannot usually expect credible results from calculations unless account is taken of three-dimensional folding in the dendrimer [33–35]. One further complication is that the electronic donor or acceptor transitions in molecules of sufficiently high symmetry may relate to a degenerate excited state—as for example occurs with the square-planar porphyrin derivatives studied by Galli *et al*. [36]. The added complication that each of these effects brings into energy transfer has been extensively researched by van der Meer [37].

Figure 2. Relative orientations and positions of donor and acceptor and their transition moments: angles θ_D and θ_A are subtended by the donor and acceptor dipole transition moments ($\boldsymbol{\mu}_D$ and $\boldsymbol{\mu}_A$, respectively) against the inter-chromophore displacement vector, $\boldsymbol{R}$; θ_T is the angle between the transition moments.
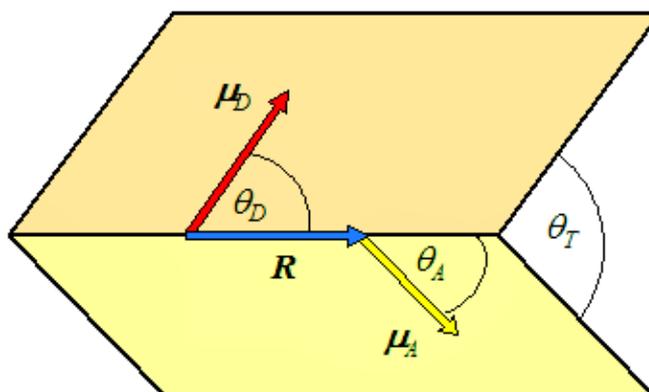
The last and arguably most important feature of the rate Equation (2) is its inverse sixth power dependence on *R*. This signifies that, in any classical trajectory of energy through the dendrimer, the migration from a peripheral antenna chromophore to a central (or other remotely positioned) trap will mostly operate through a sequence of short hops between neighbouring chromophores. In such a multi-step pathway, which is in general greatly more efficient than one long hop, any unit that has acquired electronic energy (by direct photon activation or through playing the role of acceptor) adopts the role of donor in the subsequent step—see Figure 3. Thus, a distinct hopping rate or propensity can be associated with possible transfer between each pair of adjacent sites. However, in a system configured with multiple transfer pathways, where excitation might undergo stepwise propagation between the antenna and trap by two or more routes of broadly similar efficiency, quantum interference might also be manifest. Here, one has to cast theory in terms of the quantum amplitudes for the coupling between neighbouring chromophores (which accordingly have an inverse cubic dependence on *R*), to allow for quantum coupling between different transfer pathways; these possibilities require different methods of dynamical modelling, a subject to which we shall return in detail in Section 5.

Figure 3. Two-step energy harvesting illustrated schematically in a second-generation phenylacetylene dendrimer, depicting initial electronic excitation of a peripheral phenyl group, which then acts as a donor for energy transfer to a neighboring first-generation acceptor; this then acts as a donor for energy transfer to the core phenaline core.
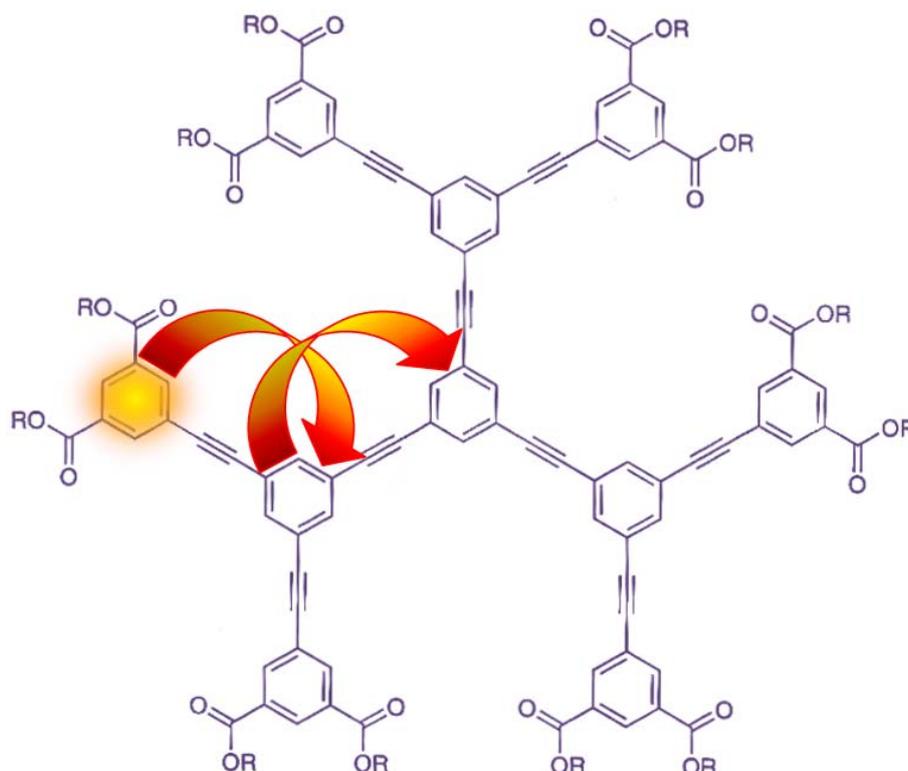

3. Directed Energy Transfer

As mentioned in Section 1, the directionality of energy transfer, within each step of a sequence from a peripheral chromophore to the core via intermediary chromophores, is only ensured through the presence of a spectroscopic gradient—namely, a downward-displacement of energy within the electronic excited state of the acceptor, compared to the donor. This feature, which enables the preferred direction of transfer to be more efficient than the undesirable, reverse direction, can be separately quantified by a directional efficiency, ε, which encapsulates the key spectral information [32]; a detailed discussion on this subject is given in Section 5. As is evident from Figure 1, the central reason that forward transfer can be favoured over backward transfer is a difference between the spectral overlaps for the two processes.

It is also possible to exert control over the directionality of excitation flow by the operation of external influences [38]. Examples of such modifications, produced on application of an electrical or optical stimulus, are illustrated by the simple representations given in Figure 4: (a) depicts the regular form of RET; (b) the application of a static electric field; (c) the incorporation of an ancillary polar species; (d) the throughput of off-resonant electromagnetic radiation. The involvement of static fields in (b) extends in principle to the influence of a host medium, as for example through solvatochromic shifts in the excited-state energy levels of exposed chromophores [39]. Most significantly, based on option (d), an all-optical method has been proven to enable excitation transportation to be completely switched on or off, such that the energy flow from donor to acceptor is subject to a controllable,

photo-activated switch; the detail on all-optical switching of this type is beyond the scope of this review, see [40–43] for greater depth.

Figure 4. Schematic depictions of: (**a**) resonance energy transfer; (**b**) electric-field induced energy transfer; (**c**) third-body (dipole-assisted) energy transfer; (**d**) laser-assisted resonance energy transfer, the throughput beam being off-resonant with respect to the donor and acceptor spectra.
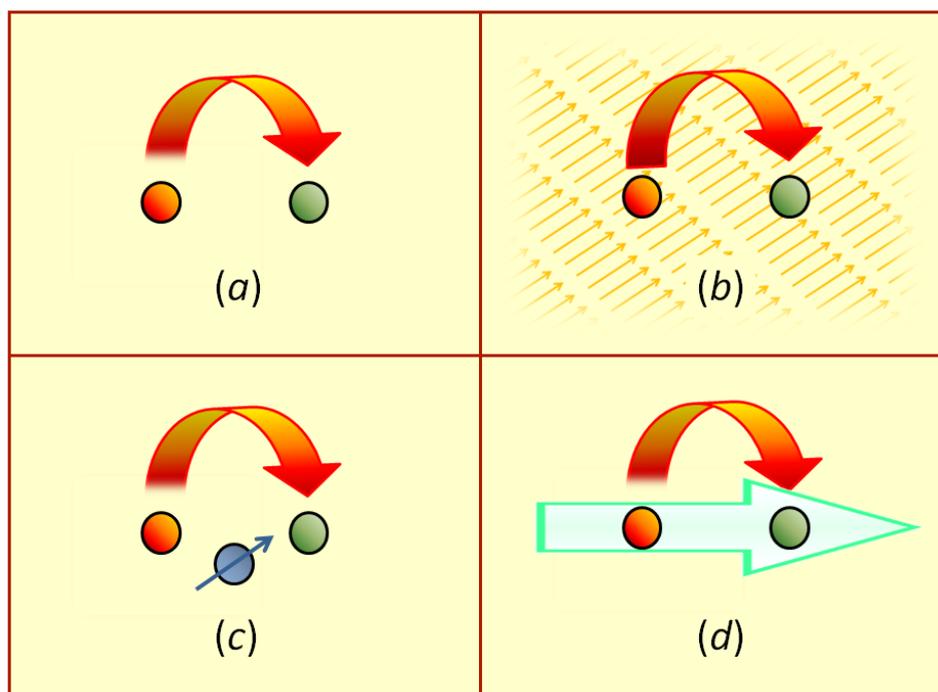
Consider first a donor-acceptor pair positioned in a static electric field, as in Figure 4(b). It has been shown that the rate of transfer between the chromophores will be modified under such conditions, primarily as a result of their state wavefunctions being perturbed by interaction with the field [44]. This is readily understood: for each chromophore, the electron charge distribution of both the ground and excited electronic states will experience a degree of distortion. The graph of Figure 5 exhibits a typical form of variation in the rate of energy transfer, according to the orientation of the static electric field (based on typical values of 1×10^6 V cm^{-1} for the static field strength and ~1.5 D for the transition dipole moments). Moreover, when the static field engages with a transition, it is associated with selection rules that formally identify with those of a *two-photon* transition. Consequently it is possible, in a case where either the donor or acceptor transition is (single-photon) dipole-forbidden, for the application of a static electric field to specifically produce and direct energy transfer, allowing a switchable electric field to control the delivery of energy to the acceptor. In this respect the effect is a static analogue to the all-optical switching mechanism discussed below.

Figure 5. Influence on the rate of energy transfer (arbitrary scale) of a static field, as the polarisation vector of the static field is varied relative to the transfer pair. Here, the donor and acceptor transition moments are assumed to be equal in magnitude (10^{-29} C m) and to have a parallel disposition; the static field strength is 10^{10} V m^{-1}.
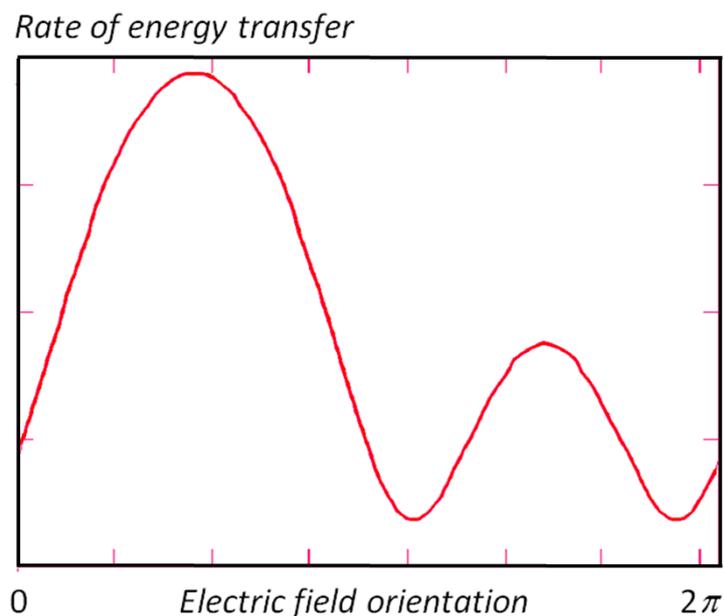
In the conventional cast of theory, RET is described in terms of a coupling between electronically isolated chromophores. In dendrimeric systems, however, each transfer of energy takes place in an electronic environment that may be significantly modified by other chromophores in close proximity to the interacting pair—even if those neighbouring groups, denoted in the following by *M*, do not explicitly participate in excitation routing from *D* to *A*. This can be represented in general terms by:

$$D^* + A + M \xrightarrow{\text{RET}} D + A^* + M \tag{5}$$

If such nearby chromophores are strongly polar, one possible mechanism is immediately evident from the discussion above: it can be expected that the electrostatic fields produced by *M* will influence nearby energy transfer processes, as illustrated in Figure 4(c). With some important exceptions—see for example Bentz and Kozak [45]—such influences on donor-acceptor transfer have received little attention. Nonetheless, it has been shown by quantum electrodynamical methods [46] that adjacent chromophores can produce a very significant effect on the rate of energy transfer. Moreover, it proves strictly unnecessary for *M* to be polar; a *dynamic* dipole (readily produced in polarisable groups such as phenyl derivatives) can also act as an intermediary for the energy transfer. When the neighbour group is positioned within about 1–2 nm from the donor or acceptor, the influence will typically range between a 50% enhancement and a 40% reduction of the transfer rate, the sign of the change being determined by the configuration of the chromophores involved. Generally, the influence of *M* is greatest when located just beyond the region of possible orbital overlap with *D* or *A*, as illustrated in Figure 6. A possible experimental observation of the effect is discussed in [47].

Figure 6. Influence of neighbouring dipole position on the rate of energy transfer between two chromophores. Here, the chromophore transition moments are aligned parallel to the *y*-axis, the ancillary dipole at an angle of $\pi/4$ to the *y*-axis. The influence on the RET rate is diminished in the blue regions, increased in the red regions—up to a 200% increase of rate over the lightest blue areas.
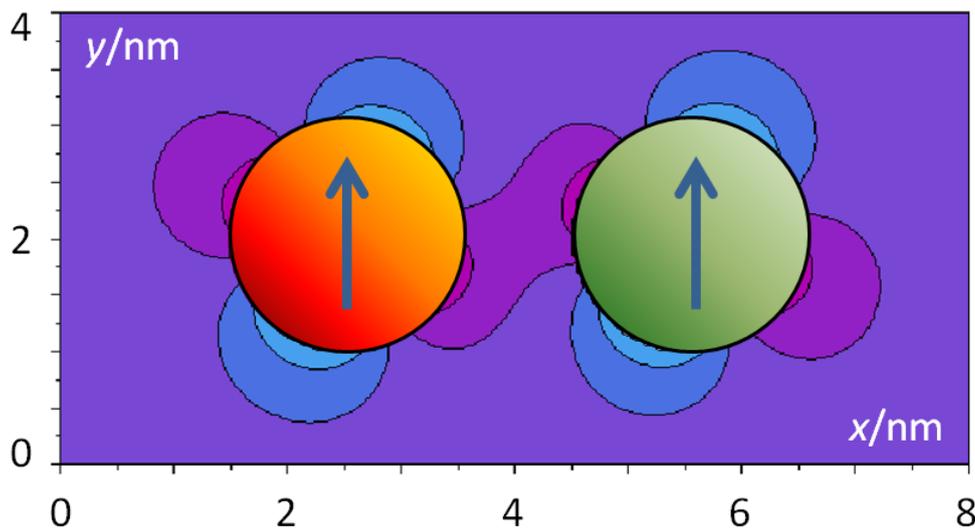
As depicted in Figure 4(d), off-resonant laser light may also modify the rate of pair-wise energy transfer. Here, the mechanism involves cooperative forward Rayleigh scattering by the donor-acceptor pair—a process that leaves the throughput beam unchanged, but which can again either enhance or diminish the efficiency of energy transfer. The more interesting, enhancement case is known as *laser-assisted resonance energy transfer* [48]; it is this phenomenon which has been proposed as the basis for achieving, under certain configurations (Figure 7), the all-optical switching outlined earlier. Perhaps surprisingly, static dipoles of the donor and acceptor do still play a role, despite the oscillatory character of the electromagnetic field—but the dipole moments that enter into the rate expression here relate to electronically excited states. The detailed electrodynamic analysis has shown that, with pulsed laser delivering intensities of around 10^{12} W cm^{-2}, a 10% or more enhancement of the energy transfer rate can be expected for non-polar systems. For systems comprising chromophores that are both polar and chiral, it transpires that additional rate contributions may lead to rate enhancements of 30% or more. The fundamental similarity with the enhancement mechanisms discussed above lies in the fact that this process once again operates by producing shifts in the donor and acceptor charge distributions and, in particular, those involved in the decay and excitation transitions. The use of off-resonant laser light to augment energy transfer shows considerable promise for a variety of applications, since it is a method with the virtues of being easily controlled, rapid in response, and non-contact in operation.

Figure 7. In optimum configurations, off-resonant laser light can enhance or trigger RET. An initially excited chromophore (red dot) transfers energy to its acceptor neighbour beneath only when an off-resonant beam (right) passes through the system.
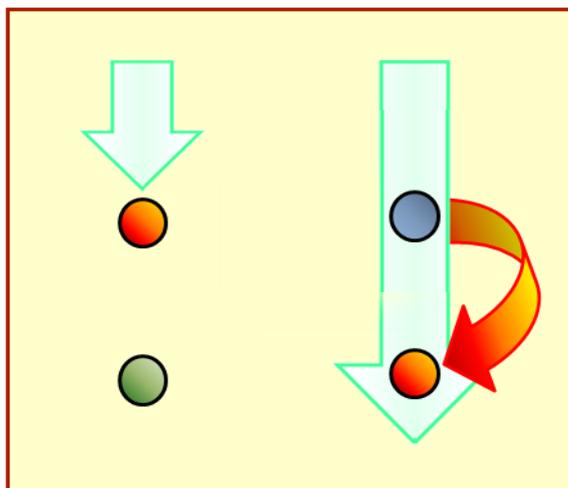
4. Multiphoton Processes

Studies on some dendrimers have produced evidence that their light-harvesting action may, under suitable conditions, entail the collective action of two or more excitations [4,11,49]. Indeed, these compounds often display unusually prominent nonlinear optical properties—including, and extending beyond, a propensity to exhibit multiphoton absorption. In this connection it is worth recalling that, in photosynthetic systems, the ultimately sought charge separation is achieved through the absorption of light quanta that are individually of insufficient energy [50], necessitating the engagement of less familiar photophysical processes—such as excitation pooling—to deliver the necessary energy. In dendrimers, such features are facilitated by fractal structures that offer concurrent channels of energy transfer directed towards the same trapping site.

In relatively small dendrimers, it is statistically unlikely for two or more excitations to co-exist, at any one time, within the overall structure. Generally, the timescale for energy delivery from the antenna to the core is shorter than the interval between successive photon capture events—the latter being a time given by $\hbar\omega/I\sigma$, where I is the irradiance, ω is a typical absorption frequency and σ the net absorption cross-section of the entire dendrimer. However in larger systems, where trapping also involves a greater number of energy transfer steps, this is no longer necessarily the case. Indeed, if the intensity of ambient sunlight (typical irradiance at the Earth's surface ~1 kW m^{-2}) is amplified by focussing down to the diffraction limit, the simultaneous presence of two photon energies can then become significant on the picosecond timescale associated with ultrafast trapping. A good example of supporting experimental evidence is the *cis*-to-*trans* isomerisation observed on infrared absorption in large arylether azodendrimers, for which the energetic considerations demand that two (or more) infrared photon energies have to be involved. Notably, isomerisation is not observed in smaller, related families [51].

First, we consider processes that may occur within a dendrimeric superstructure when two or more excitations are present. One obvious possibility is for two components of the migrating energy to

undergo chance convergence at a single site, producing singlet-singlet annihilation. This results in a new, single excitation of greater energy, *i.e.*,

$$D + D + 2\hbar\omega \xrightarrow{\text{absorption}} D^* + D^* \xrightarrow{\text{migration}} D + D^{**} \tag{6}$$
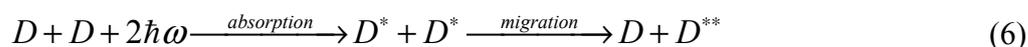
where the double asterisk denotes a doubly excited state. The second stage of Euqation (6), in which energy migrates from one donor to another resulting in excitation merging, clearly depends on a suitably positioned, higher electronic state; the process is simply illustrated in Figure 8. Under such conditions a degree of IVR ensues, significantly reducing the light-harvesting efficiency [52]. However, when another chromophore is located in the vicinity of such a conjunction, it is possible for the merged energy to propagate onwards before there is significant thermalisation. Nonetheless, the small amount of vibrational dissipation that does occur means that the doubly excited level generally possesses a little less than twice the energy of either initial excitation.

Figure 8. A mechanism for delivering the energy of two photons to a single site (specific dendrimer components shown only for illustration); (**a**) two peripheral antenna chromophores are excited; (**b**) the energy acquired by one of the chromophores is transferred to the other, which becomes doubly excited.

(**a**)   (**b**)
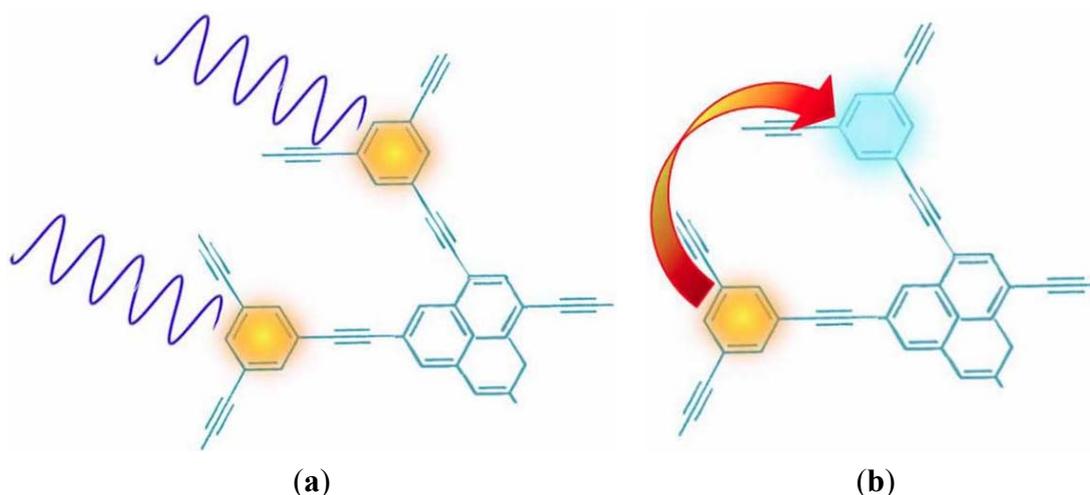
Another stepwise mechanism may also produce higher-level excitation, but without the presence of a second donor:

$$D + 2\hbar\omega \xrightarrow{\text{absorption}} D^* + \hbar\omega \xrightarrow{\text{absorption}} D^{**} \tag{7}$$
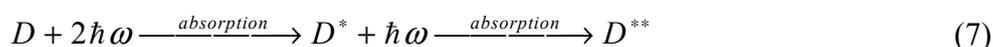
Here, the initial absorption of one photon again results in the population of a physically identifiable electronic level, from which some vibrational relaxation may occur before the arrival of the second photon. Despite having initial and final states that are directly identifiable with those of mechanism (6), the two processes are by no means equally probable. For a dendrimer comprising N chromophores, the excitation merging rate of Equation (6) is proportional to $N(N-1)$, whereas the twin-absorption rate of Equation (7) has a linear dependence on N. As a consequence, mechanism (6) may operate effectively at lower light intensities. Significantly, Monguzzi *et al.* have reported energy up-conversion in a multi-component organic polymer at irradiances as low as 10 W m^{-2}, a level at which the low energy tail of the solar emission spectrum could be captured even without focusing

optics [53]. Earlier reports of exceptionally high two-photon absorption cross-sections and enhanced third-order optical nonlinearity [54–56] have inspired many other suggestions for exploiting dendrimers in a range of applications extending well-beyond energy harvesting [57–65].

Other optical nonlinearities may arise on passage of the excitation to an acceptor, following energy acquisition via two-photon absorption. Again there are two distinct mechanisms, as illustrated by Figure 9, each one subject to minor dissipative losses following the initial absorption. In both of these cases, in contrast to mechanisms (6) and (7), no intermediary energy level is required. The simpler mechanism of two-photon resonance energy transfer (TPRET) [66,67] is initiated by two-photon absorption at a donor, followed by RET directly to the acceptor:

$$D + A + 2\hbar\omega \xrightarrow{\text{absorption}} D^{**} + A \xrightarrow{\text{TPRET}} D + A^* \tag{8}$$

The second mechanism is a *twin-donor* pooling process [68] which, following initial one-photon excitations of two electronically distinct donors, results in the collective migration of donor energies at the acceptor chromophore:

$$D + D + A + 2\hbar\omega \xrightarrow{\text{absorption}} D^* + D^* + A \xrightarrow{\text{pooling}} D + D + A^* \tag{9}$$
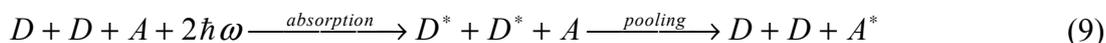
In contrast to TPRET, twin-donor pooling comprises two sub-mechanisms [69]: *cooperative* and *accretive*. In the former, initial one-photon excitations are followed by RET from both donors directly to the acceptor, whereas in the latter, the initial excitation of one donor is passed to its partner and the sum of the two excitations transfers to the acceptor. The balance of factors and constraints that determines the favoured mechanism include: the excitation statistics, the positioning (and symmetry properties) of the energy levels, laser coherence factors, chromophore selection rules and architecture, possibilities for the formation of delocalised excitons, spectral overlap, and the overall distribution of the donors and acceptors [70].

Figure 9. Alternative mechanisms for delivering the energy of two photons, captured by one or more higher-generation or peripheral antenna chromophores, to a lower generation neighbour (specific dendrimer components shown only for illustration): (**a**) direct transfer of the energy acquired by two-photon absorption in a single outer chromophore (**b**) the pooling of energy from two outer chromophores, each individually excited by single-photon absorption.

(**a**) (**b**)
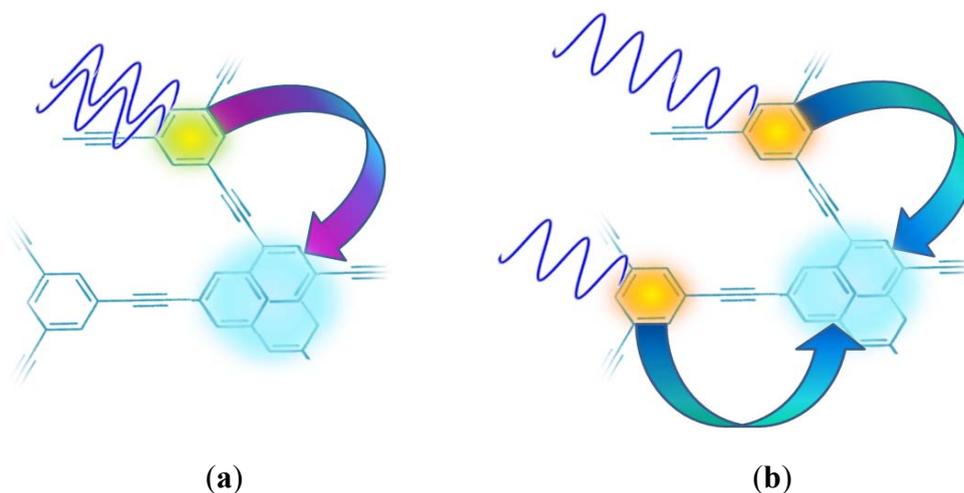
It is instructive to review the interplay of these factors. As regards the electronic properties of the constituent chromophores, it emerges from the detailed theory that optically nonlinear behaviour in dendrimers based on small, essentially non-polarisable chromophores with tightly bound electrons are generally dominated by TPRET, while energy pooling is favoured by systems with tightly packed donors and acceptors. Moreover, systems with a more polarisable acceptor are primarily governed by cooperative pooling, while accretive transfer dominates if it is the donors that are more polarisable. Exciton issues represent another important aspect in the comparison of the two mechanisms. Since TPRET involves only one excited donor, the initially acquired energy is localized to that chromophore; excitons are therefore not relevant for TPRET. However, if two or more chemically identical and proximal donors are electronically coupled to any significant extent, the uncertainty in the location of the excitation may be reflected by formation of an exciton. Generally, exciton formation may occur whenever the number of excitations within an array of chromophores is less than the number of donors [71], provided the electronic environments of those donors render equivalent local geometry and energetics. Twin-donor pooling, which requires two excited donors, may thus engage with three or more equivalent donors to produce an exciton state. An example is afforded by a dendrimer with the common threefold branching motif, organised such that there are chemically identical donors D, D' and D'' at the corners of an equilateral triangle, with an acceptor, A, at the centre. A donor exciton may then form, prior to energy pooling:

$$D + D' + D'' + A + 2\hbar\omega \xrightarrow{\textit{Exciton formation}} \left(D{+}D'{+}D''\right)^{**} + A \xrightarrow{RET} D + D' + D'' + A^* \qquad (10)$$
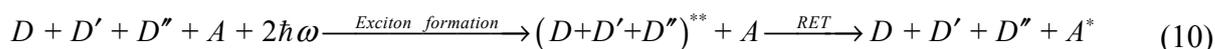
It is worth noting that two further nonlinear mechanisms are, in principle, possible if a significant level of optical radiation is present within the system, during energy transference [72]. One is the process of effective two-photon absorption by an acceptor through the acquisition of one quantum of energy from a singly excited donor, and another quantum from the throughput radiation:

$$D + A + 2\hbar\omega \xrightarrow{\textit{absorption}} D^* + A + \hbar\omega \xrightarrow{\textit{absorption and migration}} D + A^{**} \qquad (11)$$
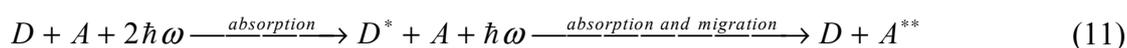
The other possibility is a similar mechanism whereby a singly excited donor is hyper-excited by further photon absorption from the pump radiation field, while energy is simultaneously transferred to the acceptor; this requires levels of intensity usually associated with pulsed radiation but, in contrast to mechanism (11), it need not be a step-wise process. A summary of all the key energetics detailed above is included in Table 1.

To complete the story on nonlinear processes within dendrimers it is important to bear in mind, as mentioned in Section 2, that multiple transfer pathways or mechanisms connecting the same initial and final states should not necessarily be regarded as operating in isolation—it is necessary to ascertain whether or not quantum interference plays a part. Quantum interference should always be considered when designing light-harvesting dendrimers and related polymers, since branched structures especially lend themselves to such effects. For example, the processes of TPRET and twin-donor pooling lead from the same initial state to a final state in which the acceptor is electronically excited. However, the dissipation of energy through IVR in the donor ensemble is different in the two cases so that, whereas these mechanisms may compete (if both are allowed by the selection rules), they cannot display quantum interference. This is not the case, however, when we consider twin-donor pooling operating with concurrent cooperative and accretive sub-mechanisms, because these are *concerted,* not step-wise

processes. Quantum calculations, on twin-donor pooling with both sub-mechanisms present, engender cross-terms that have clear physical significance, directly identifiable with quantum interference. While coherent excitation transfer requires a different, specialized treatment of theory—exemplified by the density matrix approach detailed recently by Huo and Coker [73]—the most significant departures from stepwise Förster transfer are processes in which a bridge chromophore mediates excitation transfer—not by their intermediate excitation but, as described by May [74,75], through their electronic influence on the coupling between a given chromophore pair. In fact, when the usual dipole-dipole coupling entirely fails, energy can still transfer through the operation of higher order interactions [76].

Table 1. Summary of key energetics: second and third columns represent the local energy landscape before and after each form of energy reconfiguration; $\hbar\omega$ denotes a resonant photon, $\hbar\omega'$ one that is specifically non-resonant.

	Before	After	Equation	Figure
Single site mechanisms				
Single photon absorption	$D, \hbar\omega$	D^*	-	-
Stepwise photon absorption	$D^*, \hbar\omega$	D^{**}	(7)	-
Two-site mechanisms				
Resonance energy transfer	D^*, A	D, A^*	(1)	1
Singlet-singlet annihilation	D^*, D^*	D, D^{**}	(6)	8(b)
Anti-Stokes electronic Raman-induced transfer	$D^*, A, \hbar\omega$	D, A^{**}	(11)	-
Laser-assisted resonance energy transfer	$D^*, A, \hbar\omega'$	D, A^*	-	7
Two-photon resonance energy transfer	D^{**}, A	D, A^*	(8)	9(a)
Three-site mechanism				
Twin-donor pooling	D^*, D^*, A	D, D, A^*	(9)	9(b)

5. Theoretical Methods for Dynamical Analysis

As will be evident from the foregoing survey, the formulation of theory to analyse the dynamics of dendrimeric energy harvesting—crucial for identifying any means of optimising efficiency—represents a considerable challenge. In general, it calls for a framework of theory that can accommodate principles from photophysics, implemented with structural information and data on energy level and transition dipoles from computational quantum mechanics, along with statistical modelling. With a wide variety of different approaches having been attempted, major advances are now being achieved despite the daunting complexity.

Using essentially classical methods of representing energy flow as a series of stepwise processes, Knoester *et al.* [77,78] and also Andrews *et al.* [79–81] have explored the relationships between trapping times and the connectivity of dendrimers. Nonetheless, the formulation of each such step requires quantum methods. Moreover, the transfer of energy from a peripheral chromophore to the core of a dendrimer—especially a folded system—generally affords multiple transfer pathways. As pointed out earlier [82], whenever excitation can propagate from one site to another by more than one route, exciton localization can be compromised by quantum interference [83]. In some beautiful recent work, Cao and Silbey [84] have used chromophore connectivity as the basis for a fully quantum mechanical treatment, securing analytical solutions for simple multi-level systems and interpreting them in terms

of physically intuitive kinetic networks. Their constructs are especially useful for visualizing the connectivity of different energy transfer pathways, and the graphs of average trapping times as a function of phase exhibit the consequences of quantum interference. These results show that, in real, two- or three-dimensional systems, quantum effects due to such pathway interference can produce a significant phase modulation of the energy harvesting kinetics.

To model the detailed dynamics of RET in real dendrimers, numerical computations generally need to be employed. Here, the interplay with advances in characterising the dynamics of photosynthetic systems is evident; notable examples include work by Scholes *et al.* who deploy a generalized Förster approach for Monte-Carlo simulations [85,86]. A semi-empirical quantum chemical approach has been used by Wong *et al.* [87], master equations are employed by several groups [88–91], and an extended Redfield approach, by Ishizaki and Fleming [92,93]. For the modelling of RET dynamics, specifically in dendrimers, significant methods include use of a Pauli master equation by Yeow *et al.* [94], a mixed quantum/classical methodology by May *et al.* [95,96], and non-adiabatic trajectories by Fernandez-Alberti *et al.* [97]. A recent survey of the various methods available for quantum mechanical analysis of RET concluded that: reasonable estimates can be obtained without demanding levels of computer time; moderate basis sets and relatively inexpensive methods are sufficient, especially when deployed with realistic solvation models; the choice of the quantum mechanical level of theory affects the chromophore couplings, and hence the resultant dynamics, much less than the excitation energies [98].

It is well-known that even small departures from planarity, associated with three-dimensional folding of the dendrimer structure, can displace peripheral chromophores sufficiently to produce significant modifications in the dynamics of energy transfer [79]. One of the upshots is that multi-step transfer may not necessarily proceed by the most direct route; folding can facilitate transfers of energy, between chromophores in close proximity, that do not expedite an overall progress of energy towards the core. Moreover, the efficiency of each routing is determined by the architecture of the dendrimer and the photophysical properties of the component chromophores. Attempting to capture such features in recent work, Andrews and Jones have exhibited preliminary results from calculations using an electron dynamics model [99,100]. In these studies, density functional theory (DFT) calculations, employing the B3LYP hybrid density functional in conjunction with the 6-31G(d) basis set, are first used to optimize the molecular geometries of the chromophores, and the phenalene core, of a third-generation phenylacetylene dendrimer. Time-dependent DFT calculations are then employed to calculate the site energies and transition dipole moments for the optimized chromophores and the core molecular structure. On completion of these *ab initio* calculations, optimization of the torsion angles on a three-dimensional graph allows the construction of a physically realistic 3D representation, with the transition dipole moments superimposed on the optimized template. Finally, with a numerical quantum propagator [101] providing for the non-stationary wavefunction to be followed in time, the exciton can be monitored as it moves through the generations of the dendrimer, towards the accepting core. A typical time evolution of the net excitation density for the different dendrimer generations is exhibited in Figure 10 [99]. The results show excitation cascading towards the core through successive spectroscopic gradients; the propensity for each forward (core-directed) transfer is significantly greater than for backward transfer.

Figure 10. Exciton population density in a third-generation dendrimer plotted against time, following initial photon absorption. Populations are calculated from the density matrix, the energy densities of individual sites then being summed to give the total exciton density per generation (with the core and first generation counted together). One branch of the dendrimer with representative chromophores of different generations is shown on the right.
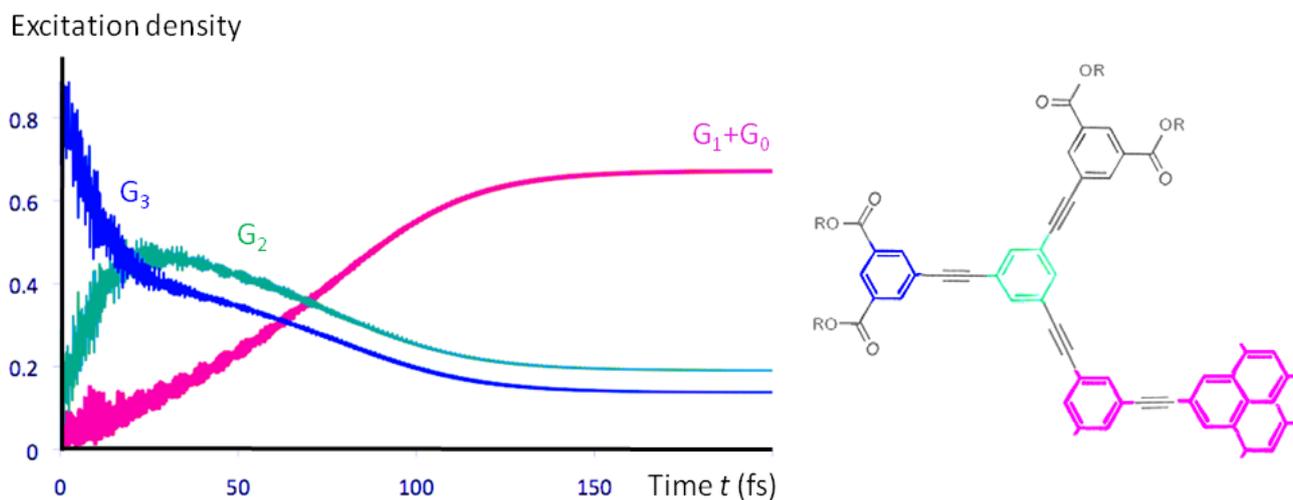
While trapping signifies a vectorial, forward-directed character to the exciton motion, there is a clear similarity between the pair-wise rates for forward and backward transfer, as exemplified by Equation (2): the transfer distances and orientation factors are identical for either direction. Nonetheless an intrinsic directedness arises, for two reasons: fluorescence spectra are generally displaced to longer wavelengths (Stokes-shifted) with respect to the absorption spectra, and IVR usually follows each discrete transfer of energy. In consequence, there may be a sizeable difference in the spectral overlaps for forward and backward transfer; Figure 1 illustrates why forward transfer is generally favoured. To quantify directionality, it is expedient to introduce a parameter directly amenable to spectroscopic determination—the directional efficiency, ε, earlier introduced in Section 3. Encapsulating the key spectral information, the value of this parameter determines the extent to which forward transfer *with* the spectroscopic gradient, $D \rightarrow A$, is favoured over backward transfer *against* it, $A \rightarrow D$ [32]:

$$\varepsilon = \frac{\tau_A \int F_D(\omega)\sigma_A(\omega)\omega^{-4}d\omega}{\tau_D \int F_A(\omega)\sigma_D(\omega)\omega^{-4}d\omega} \tag{12}$$

The combination of intrinsic Stokes shifts and spectroscopic gradient means that values of $\varepsilon > 1$ are readily attainable, provided there are sufficiently extensive differences in the local electronic environment of chemically similar chromophores. Although dendrimers are usually, by their nature, largely composed of identical units, generation-dependent values of $\varepsilon > 1$ can assist the directed channelling of energy towards the core; a convincing proof of the principle was established in early work by Shortreed *et al.* [23].

Numerical simulations represent the best means of securing detailed dynamical data on specific molecules and, especially, for making quantitative comparisons between the action of dendrimers with different generations or group functionalisation. However, they offer less general information on the fundamental physical parameters responsible for producing the observed patterns of behaviour. For the

latter purpose, a propensity model has proven to offer more fundamental insights; its essence is as follows. An obvious starting point for exploring the dynamics of energy transport, within a dendrimer of generic form, is a model based on bond connectivity between the constituent chromophores; this is readily cast in the form of a graph theoretical adjacency matrix [79–81]. The efficiency of transfer between directly bonded chromophores can then be introduced to give a *propensity matrix* **C**, of the same structure, whose elements C_{rc} denote the relative efficiency of electronic excitation passing to a chromophore r from chromophore c. If interest primarily concerns the efficiency of excitation being trapped at the core, a reduced size matrix based on summed generation populations can again be deployed, as with the quantum model described above. It quickly emerges that the value of ε is itself a simple and powerful indicator of the improvement in efficiency afforded by introducing a spectroscopic gradient.

Despite its simplicity, the propensity model affords considerable scope to explore the effects of varying the inter-chromophore coupling parameters, to gauge their significance in designing for high light-harvesting efficiency. The principles are best illustrated by example: consider a second-generation dendrimer, with the threefold branching motif that is a common feature of phenylacetylene and phenylether dendrimers. This dendrimer comprises ten chromophores: one at the core, three in the first generation surrounding the core, and six at the periphery. Clearly, if there were no spectroscopic gradient, an equal sharing of the excitation would generate a core fractional population of 0.100, neglecting losses. But with a directional efficiency, ε, for coupling between the chromophores in adjacent generations, it is has been shown that the asymptotic population of the core is $(1 + 9\varepsilon^{-1})^{-1}$; a value of $\varepsilon = 1.25$ (25% favour of forward over backward transfer) gives a core population increased by 27%, for example. A closer examination reveals that, if any energy that reaches the trap is irreversibly captured—as is usually the case, then any small degree of back transfer en route is largely inconsequential. In larger dendrimer systems, the onset of significant 3D folding means that energy transfer can no longer be limited to directly bonded chromophore pairs. Moreover, such folding typically introduces geometrical distortions that undermine the symmetry of the propensity matrix, since the latter is generally based on a planar geometry. Indeed, this feature might in principle be utilized to assess the extent of folding, by observing experimental departures from predictions based on a planar model. Nonetheless, the propensity matrix approach is best regarded as a generic tool, a means of securing fundamental design principles. To address any specific dendrimer compound, it makes sense to perform calculations based on the true molecular conformation, derived with the use of quantum chemistry software.

6. Experimental Methods

Although the emphasis in this account has been on theory and mechanism, it is appropriate to briefly point to the kinds of experiment that can provide the supporting data. Such measurements are crucial for eliciting the various intramolecular energy transfer mechanisms that can take place in dendrimeric systems, and for verifying the timescales on which they occur. To monitor the course of the ultrafast processes immediately following the absorption of light calls for time-resolved measurements based on pulsed laser instrumentation—current methods now usually deploying a femtosecond source [102,103]. Typically, such investigations focus on the temporal development of fluorescence

anisotropy. In any molecule lacking energy transfer channels, fluorescence resulting from the decay of an initially excited electronic state would exhibit a well-characterised and significant polarisation anisotropy, consistent with the polarisation of the excitation light. Any subsequent loss of this anisotropy might then be attributed to rotational diffusion—a process that, for dendrimer molecules in solution, has a relatively long timescale. However, when intramolecular energy transfer of any form does occur, between chromophores of different orientation, each step produces a change in the polarisation character of any ensuing fluorescence [94]. Exploiting a pulsed laser configuration, the necessary measurements are commonly made by up-converting the molecular emission through sum-frequency generation in a nonlinear optical crystal, using an optical pump in the form of pulses with a variable delay. With such instrumental methods, the analysis of fluorescence depolarisation features in similarly structured dendrimers of different generations enables the successive stages of energy transfer to be determined—see for example the important work from the Ghiggino and Goodson groups [94,102,103].

7. Summary and Conclusions

In this paper we have seen how the singular photophysical properties of dendritic polymers are engineered and deployed, commonly in the cause of light harvesting. Although much of the context for this analysis has concerned dendrimeric systems acting as solar energy harvesters, there are several other important and emerging areas of application deserving mention, including molecular sensing [104–106], catalysis [104,107], medical photonics [104,108] and light-emitting diodes [109–111]. Most uses exploit the following generic properties: the possession of a multiplicity of chromophores that are responsible for initial photon absorption, and which can also act as relays; these groups display broad and intense absorption bands, and correspondingly strong emission bands; RET mechanisms are in place for the efficient transmission of electronic excitation by a sequence of transfers, providing a means for the direct routing of each excitation from peripheral to core chromophores; irreversibility of energy capture is achieved through intramolecular relaxation (energy losses) at each intervening site.

This review has focused on the mechanisms by means of which the energy of absorbed radiation migrates through energy harvesting dendrimers, from the point of initial excitation to the site at which that energy is ultimately captured. Highlighting the significance of a spectroscopic gradient, it has been shown how multi-step RET processes expedite the flow of acquired energy in these systems. We have seen that excitation flow may be manipulated by the operation of external influences, such as the presence of neighbouring chromophores, the application of a static electric field, or off-resonant electromagnetic radiation. Moreover, a detailed analysis on nonlinear optical mechanisms has been given for cases entailing the collective action of two or more excitations. We have also established the reasons why quantum effects can be anticipated to play a role in the dynamics of internal energy flow. Finally, the paper has illustrated some recent developments in the rich tapestry of theory within this area, drawing upon fundamental principles of electrodynamics, quantum chemistry and computational modelling. With the continued progress in theory taking place alongside advances in synthetic methodology and material characterisation, it can be confidently anticipated that dendrimers will continue to occupy an important position in the future developments of energy materials.

Acknowledgments

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