

## Alternative Resonance Energy Transfer Mechanisms in Polymer Light Harvesting

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### ABSTRACT

Dendrimeric polymers are a subject of considerable interest, particularly for their applications in energy harvesting devices, but also in organic light-emitting diodes, photosensitizers, quantum logic devices and low-threshold lasers. The distinctive light harvesting characteristics of these materials owe their origin to the speed, efficiency and highly directed nature of the multi-step processes that deliver captured light energy to the core.

Recently it has been shown how iterative calculations, based on a matrix representation of the connectivity and propensity for energy transfer between different chromophores, effectively model the time-dependent flux of energy within dendrimer materials. This paper reports the formulation and results of an extended approach, accommodating additional mechanisms by means of which excitations of energy higher than the incoming photons can be generated and propagated towards a trap. It is also shown how the structure of the dendrimer and the operation of a spectroscopic gradient affect this energy flow. These mechanisms explain experimental observations in which energy coupling of four photons or more is observed in large aryl ether azodendrimers, at relatively low levels of irradiance.

### I. INTRODUCTION

In a wide range of materials, resonance energy transfer (RET) is the principal phenomenon responsible for intermolecular and intramolecular electronic energy redistribution following the absorption of ultraviolet/visible radiation [1]. The detailed elucidation of the principles for energy flow in complex systems has led to the devising of new energy-harvesting materials specifically tailored for a host of nanophotonic applications. Chief amongst these new materials are dendrimeric polymers – multiply-branched structures of essentially fractal geometry. Such materials are highly efficient in the capture of optical radiation, as a result of their multiplicity of antenna chromophores and efficient mechanisms for channeling energy to a central core [2]. When ultraviolet or visible radiation of a suitable wavelength impinges on a non-homogeneous dendritic polymer, the absorption of light primarily populates the lowest electronic excited states of the constituent chromophores. A rapid degradation of the acquired energy typically ensues – largely a stochastic process of vibrational dissipation, with the energy losses ultimately to be manifest as heat. Excepting the case of thermal energy harvesting, the operation of an optical energy capture system is generally based on establishing more directional and energy-retaining, less random and dissipative, pathways for the flow of energy between the sites of its initial deposition, to centers where it can be efficiently captured. To optimize harvesting efficiency, it is necessary for such pathways to have a competitive edge over thermal degradation. The primary equation for the rate of RET, beyond regions of wavefunction overlap, is generally derived from the formulation of an electrodynamical coupling between transition dipoles. For many purposes, the original Förster theory of ‘radiationless’ energy transfer is applicable, though from quantum electrodynamic studies it has emerged that both ‘radiative’ and Förster transfer are in fact the long- and short-range limits of a more comprehensive phenomenon [3, 4].

To begin, consider the pairwise transfer of excitation between two chromophores, a donor  $A$  and an acceptor  $B$ . Let it be assumed that prior excitation of the donor generates an

electronically excited species  $A^*$ . Forward progress of the energy is then accompanied by donor decay to the ground electronic state. Acquiring the energy,  $B$  undergoes a transition from its own ground state to an excited level. The explicit result for the rate of this process depends on: the overlap integral,  $S$ , of the fluorescence and absorption spectra,  $F_A$  and  $\sigma_B$ , of the donor  $A$  and acceptor  $B$ , respectively; the distance  $R$  between the two chromophores and their relative orientation factor  $\kappa$ , the refractive index  $n$  of the host material, and the donor lifetime,  $\tau_A$ . In terms of the given parameters the rate of energy transfer from  $A$  to  $B$  is as follows:

$$w_F = \frac{9\kappa^2 c^4}{8\pi\tau_A n^4 R^6} \int F_A(\omega)\sigma_B(\omega)\omega^{-4}d\omega, \quad (1)$$

In considering multi-step processes it is convenient to define a *directional efficiency*,  $\varepsilon$ , for each transfer, expressed as the ratio of the rates or propensities for forward and backward transfer [5]:

$$\varepsilon \equiv \frac{w_F}{w_B} = \frac{\tau_B}{\tau_A} \frac{\int F_A(\omega)\sigma_B(\omega)\omega^{-4}d\omega}{\int F_B(\omega)\sigma_A(\omega)\omega^{-4}d\omega}, \quad (2)$$

where  $\tau_A$  and  $\tau_B$  are the donor and acceptor lifetimes respectively,  $F_B$  is the fluorescence of the acceptor and  $\sigma_A$  is the absorption of the donor. It is important to notice that the lifetime is equal to the normalization factor of the fluorescence for a given chromophore. The parameter  $\varepsilon$  is then a measure of the directionality of the energy migration between two chromophores. Models to describe the energy flow in polymers are discussed in the following sections.

## II. MODEL FOR ENERGY FLOW IN DENDRIMERS

In this section a model is introduced for the description of the multi-step processes that deliver captured light energy to a dendrimeric core. The model for our calculations is cast in the form of an adjacency matrix representation of the *propensities* (probabilities associated with an arbitrary but constant time interval) for energy migration between the individual chromophores comprising the dendrimer [6]. We assume that successive generations of the polymer are built with a repeating structural motif. The core acceptor or trap has  $\rho$  equivalent chromophores in the first generation shell surrounding it – the term ‘shell’ being used to signify the set of monomer units having the same number of branches in its chemical bonding to the core. We begin by illustrating the adjacency matrix for a second generation symmetric dendrimer with  $\rho = 3$ , shown in Fig. 1 (a), corresponding to the architecture of many of the most common (1, 3, 5) tri-substituted benzene dendrimers. For this structure the adjacency matrix is written as;

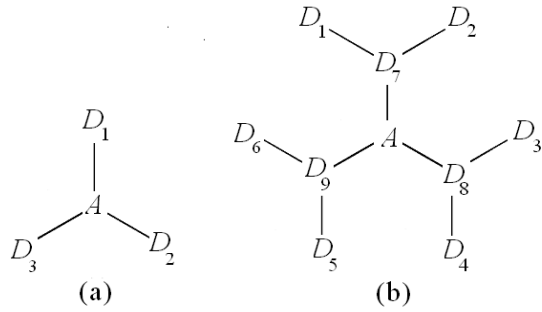
$$C = \begin{pmatrix} 1 - k_{1,2} - k_{1,3} - k_{1,A} & k_{2,1} & k_{1,3} & 0 \\ k_{1,2} & 1 - k_{2,1} - k_{2,3} - k_{2,A} & k_{2,3} & 0 \\ k_{1,3} & k_{2,3} & 1 - k_{1,3} - k_{2,3} - k_{3,A} & 0 \\ k_{1,A} & k_{2,A} & k_{3,A} & 1 \end{pmatrix}. \quad (3)$$

where the scalar  $k_{i,j}$  is the propensity for the energy to be transferred from the chromophore  $D_i$  to the chromophore  $D_j$  or  $A$  ( $j = A$ ). In this simple case the initial state can be represented by the column vector:

$$\mathbf{s} = (s_1, s_2, s_3, s_A)^T, \quad (4)$$

where the first three elements denote the excited state populations of the chromophores  $D_1, D_2$  and  $D_3$ , respectively, and the fourth element,  $s_A$ , is the excitation probability of the core ( $A$ ).

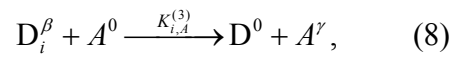
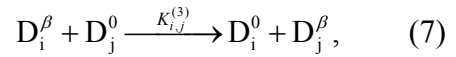
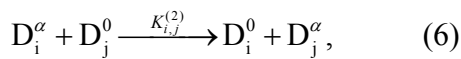
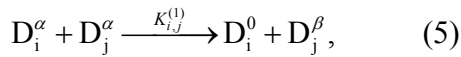
Through a progression of  $n$  repeated operations of  $\mathbf{C}$  upon the column matrix (2), we obtain the time-evolution of the energy flow up to a time  $n\Delta t$ , where  $\Delta t$  is the increment of time for which the propensities in the matrix (1) have been defined. This model is extended to consider energy transport mechanisms that involve pooling of excitations in the following section.



**Figure 1.** (a) First and (b) second generation dendrimers with chromophores  $D$  and core  $A$ . The indices are used to distinguish the chromophores  $D$ , which may be chemically identical.

### III. EXTENDED MODEL: EXCITATION POOLING

When there are large number of chromophores in the dendrimer and/or when the irradiance of the incoming light is relatively high, photophysical processes that involve more than one excited chromophore may occur with higher probability within the dendrimer. The model introduced in the previous section is now extended to accommodate a pooling of the energy of electronic excitations generated by two individual photon absorptions. While the rate of two-photon absorption at individual centers would only be proportional to the number of chromophores in the dendrimer,  $N$ , the net rate of pooling mechanisms as considered here is proportional to  $N(N - 1)$ . Consequently, excitation coupling can be observed even at relatively low levels of irradiance for large dendrimers. We assume the energy flow, in a dendrimer with chromophores  $D$  and core  $A$ , can be described through the following RET processes;



where the rate constants  $K_{i,j}^{(1)}$  etc., designated as shown in the above equations, carry subscripts that denote specific chromophores in the dendrimer – see Fig. 1. The process shown in (5) implies transfer of the energy of the electronic transition  $\alpha \rightarrow 0$  to another chromophore in the electronic state  $\alpha$ , to generate an excitation of higher energy,  $\beta$ , as illustrated in Fig. 2 (a). The latter process is followed by vibrational relaxation, implying that the energy of the electronic state  $\beta$  is lower than twice the energy of the electronic transition  $0 \rightarrow \alpha$ . We assume that there

is no overlap between the absorption spectrum associated with the electronic transition  $0 \rightarrow \alpha$  and the emission spectrum associated with the transition  $\beta \rightarrow \alpha$ , and consequently the process inverse to the latter coupling, i.e. excitation reverting from the acceptor core to the antenna chromophores, does not occur. Energy transferred to the core is immediately used in a chemical process or photon emission. The other processes, eqs. (6), (7), and (8), are responsible for the multi-step RET of the energy associated with the electronic transitions  $0 \rightarrow \alpha$  and  $0 \rightarrow \beta$ . Also the absorption spectrum of  $A$  does not overlap with the  $\alpha \rightarrow 0$  donor emission; hence there is no RET from the  $\alpha$  level to  $A$  – only the energy from the electronic state  $\beta$  is transferred to  $A$ .

To describe the energy flow under these conditions, we first define vector states for the probability of each chromophore to be excited by the two individual photon absorptions  $\alpha$  and  $\alpha'$  and by the excitation resulting from the coupling of these two excitations  $\beta$ :

$$\mathbf{s}(\alpha) = (s_1(\alpha), s_2(\alpha), \dots, 0)^T, \quad (9)$$

$$\mathbf{s}(\alpha') = (s_1(\alpha'), s_2(\alpha'), \dots, 0)^T, \quad (10)$$

$$\mathbf{s}(\beta) = (s_1(\beta), s_2(\beta), \dots, s_A(\beta))^T, \quad (11)$$

The different designations of  $\alpha$  and  $\alpha'$ , with their corresponding vector states, are a device used to track the migration of each original excitation through the dendrimer. The energy flow under these conditions can then be modeled using the following recurrence relations:

$$\mathbf{s}^{(n)}(\alpha') = \mathbf{C}^{(2)}\mathbf{C}^{(3)}\mathbf{s}^{(n-1)}(\alpha') - \mathbf{C}'^{(1)}\mathbf{C}'^{(3)}\mathbf{s}^{(n-1)}(\alpha), \quad (12)$$

$$\mathbf{s}^{(n)}(\alpha) = \mathbf{C}'^{(2)}\mathbf{C}'^{(3)}\mathbf{s}^{(n-1)}(\alpha) - \mathbf{C}^{(1)}\mathbf{C}^{(3)}\mathbf{s}^{(n-1)}(\alpha'), \quad (13)$$

$$\mathbf{s}^{(n)}(\beta) = \mathbf{C}^{(4)}\mathbf{s}^{(n-1)}(\beta) + \frac{1}{2}(\mathbf{s}^{(n)}(\alpha) - \mathbf{s}^{(n-1)}(\alpha) + \mathbf{s}^{(n)}(\alpha') - \mathbf{s}^{(n-1)}(\alpha')). \quad (14)$$

These recurrences inter-relate each set of vector states  $\mathbf{s}^{(n)}(\alpha)$ ,  $\mathbf{s}^{(n)}(\alpha')$ ,  $\mathbf{s}^{(n)}(\beta)$ , which give the state of the dendrimer at time  $n\Delta t$ , with the vector states  $\mathbf{s}^{(n-1)}(\alpha)$ ,  $\mathbf{s}^{(n-1)}(\alpha')$ ,  $\mathbf{s}^{(n-1)}(\beta)$  giving the state at time  $(n-1)\Delta t$ . The operators  $\mathbf{C}^{(1)}$ ,  $\mathbf{C}^{(2)}$ ,  $\mathbf{C}^{(3)}$ ,  $\mathbf{C}'^{(1)}$ ,  $\mathbf{C}'^{(2)}$ ,  $\mathbf{C}'^{(3)}$ , and  $\mathbf{C}^{(4)}$  are each  $N \times N$  matrices, where  $N$  is the number of chromophores in the dendrimer, and their matrix elements  $c_{i,j}^{(1)}(\alpha)$ ,  $c_{i,j}^{(2)}(\alpha)$ ,  $c_{i,j}^{(3)}(\alpha)$ ,  $c_{i,j}^{(1)}(\alpha')$ ,  $c_{i,j}^{(2)}(\alpha')$ ,  $c_{i,j}^{(3)}(\alpha')$  and  $c_{i,j}^{(4)}$  are given by;

$$c_{i,N}^{(1)}(x) = c_{i,i}^{(1)}(x) = c_{N,i}^{(1)}(x) = 0 \text{ for } i = 1, 2 \dots N; \quad (15)$$

$$c_{i,i}^{(2)}(x) = 1 - k^{(1)} \sum_{\substack{j \\ j \neq i}} \frac{s_j^{(n-1)}(x)}{r_{ij}^6}, \quad c_{i,N}^{(4)} = c_{i,N}^{(3)}(x) = c_{N,i}^{(3)}(x) = 0, \quad c_{N,i}^{(4)} = \frac{k^{(1)}}{r_{Ni}^6},$$

$$c_{i,i}^{(4)} = 1 - \sum_{\substack{j=0 \dots (N-1) \\ j \neq i}} \left[ \frac{k_{i,j}^{(3)}}{r_{ji}^6} \right] - \frac{k_{i,A}^{(3)}}{r_{Ni}^6}, \quad c_{i,i}^{(3)}(x) = 1 - \left( \sum_{\substack{j \\ j \neq i}} k_{i,j}^{(2)} \left[ \frac{1 - s_j^{(n-1)}(x)}{r_{ij}^6} \right] \right),$$

$$\text{for } i = 1, 2 \dots N-1; \quad (16)$$

$$c_{i,j}^{(1)}(x) = \frac{k_{i,j}^{(1)} s_i^{(n-1)}(x)}{r_{i,j}^6}, c_{i,j}^{(2)}(x) = 0, c_{i,j}^{(3)}(x) = k_{i,j}^{(2)} \left( \frac{1 - s_j^{(n-1)}(x)}{r_{ij}^6} \right), c_{i,j}^{(4)} = \frac{k_{i,j}^{(3)}}{r_{i,j}^6}$$

for  $i = 1, 2 \dots (N-1)$  and  $j = 1, 2 \dots (N-1)$  and  $i \neq j$ ; (17)

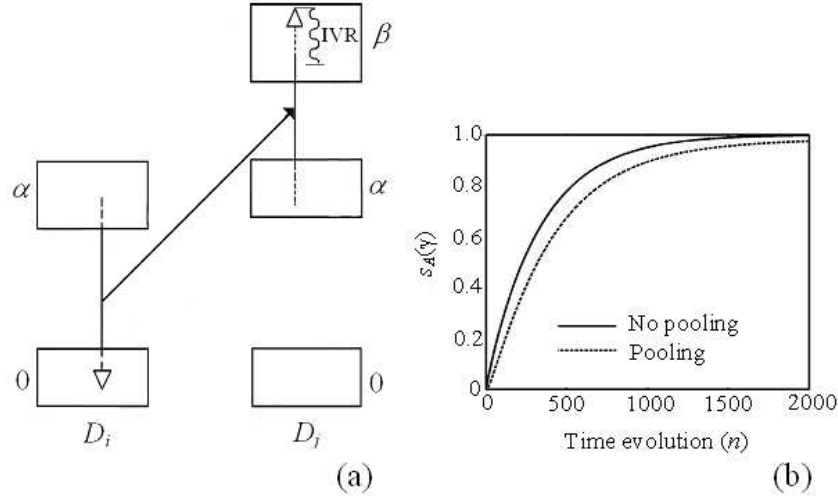
$$c_{N,N}^{(2)}(x) = c_{N,N}^{(3)}(x) = c_{N,N}^{(4)} = 1; \quad (18)$$

where  $x$  is  $\alpha$  or  $\alpha'$ ; the propensities, in a time interval  $\Delta t$ , for the resonance energy transfer processes in (5), (6), (7), and (8) are written with the explicit inter-chromophore separation dependence as follows  $k_{i,j}^{(1)}/r_{i,j}^6$ ,  $k_{i,j}^{(2)}/r_{i,j}^6$ ,  $k_{i,j}^{(3)}/r_{i,j}^6$ , and  $k_{i,A}^{(3)}/r_{i,A}^6$ , respectively. The adjacency matrices  $\mathbf{C}^{(1)}$ ,  $\mathbf{C}'^{(1)}$ ,  $\mathbf{C}^{(2)}$ , and  $\mathbf{C}'^{(2)}$  model the excitation pooling described by eq. (5), while  $\mathbf{C}^{(3)}$ ,  $\mathbf{C}'^{(3)}$ , and  $\mathbf{C}^{(4)}$  model the flow of the excitations  $\alpha$ ,  $\alpha'$ , and  $\beta$  described by eqs. (6), (7), and (8).

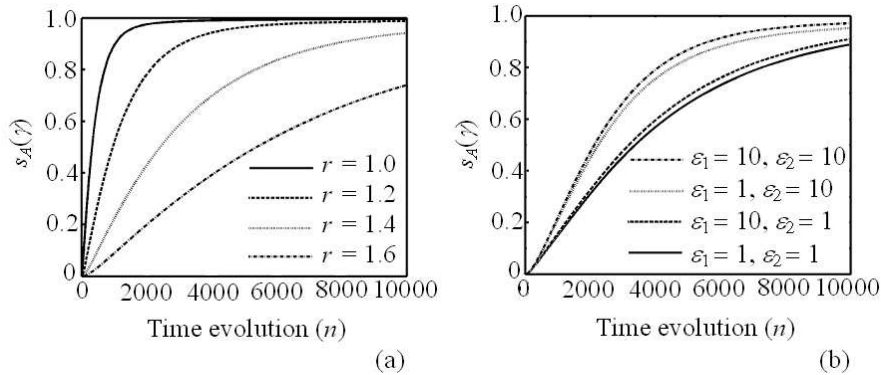
Numerical calculations for the time evolution of the excitation probability at the core of a two-generation dendrimer, such as the one illustrated in Fig. 1 (b), are exhibited in Fig. 2 (b), 3 (a), and 3 (b). It is assumed for simplicity that the dendrimer is planar, and that the lengths of the bonds connecting the chromophores are all given by  $r$ . To count over all possible initial excited states of the dendrimer, the excitation probabilities of all the chromophores  $D$  are made equal in the initial state of the system. There is a directional efficiency for propagation of the excitation  $\alpha$  from the chromophore in the outer shell to the chromophores in the first shell, given by  $\varepsilon_1$ , and another such parameter,  $\varepsilon_2$ , for the propagation of the excitation  $\beta$ . Fig. 2 (b) shows the time evolution of the core population of this dendrimer when any one chromophore is initially excited to the state  $\beta$ , and no pooling of excitations occurs (solid line). The behavior can be compared with the case where two chromophores are excited to the state  $\alpha$  and pooling does subsequently occur (dashed line). This figure shows only a small difference in the time evolution of the energy flows for the two mechanisms, given the assumption of an equal propensity for all processes, indicating that the efficiency of pooling is relatively high. Fig. 3 (a) shows the dependence of the time evolution of the core excitation probability on  $\varepsilon_1$  and  $\varepsilon_2$ , revealing that the energy flow is significantly more sensitive to a change in  $\varepsilon_2$ , the directional efficiency for the excitation  $\beta$ , than to a change of the directional efficiency  $\varepsilon_1$  for  $\alpha$ . Fig. 3 (b) illustrates the time evolution of the same parameter for different values of the separation between bonded chromophores, revealing a significant deceleration in the core excitation as the length of the chemical linkage between chromophores in this planar polymer is increased.

#### IV. CONCLUSION

Mechanisms that imply a pooling of four or more excitations have already been observed experimentally in large aryl ether azodendrimers [7]. These mechanisms are of special interest in the coupling of photons at relatively low levels of irradiance in large dendrimers, where multi-photon absorption may be less probable. The extension of this operator approach for application to mechanisms that imply the pooling of a higher number of excitations, as well as an analysis of the pooling mechanisms in terms of a competition between accretive and cooperative mechanisms, known to be strongly dependent on the dendrimer structure [8], are the subject of ongoing research.



**Figure 2.** (a) Photophysical pooling of excitations. (b) Time evolution of the core excitation probability when any one chromophore is initially in the state  $\beta$  (solid line), and when two chromophores in the dendrimer are initially in state  $\alpha$  and pooling of excitations is present (dashed line).  $k_{i,j}^{(1)} = k_{i,j}^{(2)} = k_{i,j}^{(3)} = k_{i,A}^{(3)} = 0.001$ , for  $i = 1, 2 \dots 9$ ;  $j = 1, 2 \dots 9$ ;  $i \neq j$  and  $r = 1$ .



**Figure 3.** Time evolution of the excitation probability in the core.  $k_{1,7}^{(2)} = k_{2,7}^{(2)} = k_{6,9}^{(2)} = k_{4,8}^{(2)} = k_{3,8}^{(2)} = 0.001$ ,  $k_{1,7}^{(3)} = k_{2,7}^{(3)} = k_{6,9}^{(3)} = k_{5,9}^{(3)} = k_{4,8}^{(3)} = k_{3,8}^{(3)} = 0.001$ ,  $k_{7,A}^{(3)} = k_{8,A}^{(3)} = k_{9,A}^{(3)} = 0.001$ . In (a)  $\varepsilon_1 = 1$ ,  $\varepsilon_2 = 1$ ; in (b)  $r = 1$ :  $\varepsilon_2$ , and  $\varepsilon_1$  are directional efficiencies (see text).

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