

Development of the energy flow in light-harvesting dendrimers

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Modeling the multistep flow of energy in light-harvesting dendrimers presents a considerable challenge. Recent studies have introduced an operator approach based on a matrix representation of the connectivity between constituent chromophores. Following a review of the theory, detailed applications are now shown to exhibit the time development of the core excitation following pulsed laser irradiation and the steady-state behavior that can be expected under conditions of constant illumination. It is also shown how energy capture by whole dendrimers can be analytically related to chromophore pair-transfer properties and, in particular, the spectroscopic gradient toward the core. Indicative calculations also illustrate the consequences of tertiary folding. In each respect, the model affords opportunities to derive new, physically meaningful information on the photophysical and structural features of dendrimeric systems. © 2007 American Institute of Physics.

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I. INTRODUCTION

The science of energy harvesting has recently seen dramatic growth in the development of molecular materials specifically designed to emulate some of the key structural and mechanistic principles that operate in biological photosystems. Dendrimers (multibranched polymers with a constant repeat motif) are a prime example of these new materials,¹⁻¹³ in common with photosynthetic complexes, each kind comprises an array of chromophores with broad, intense absorption bands, held together in a molecular superstructure. Following the absorption of light, excitation energy is efficiently conveyed through the system by a series of ultrafast steps.¹⁴ Each such step generally progresses toward a unit that absorbs at a longer wavelength, conferring significant directionality as the energy advances through a series of different chromophores.^{15,16} Eventually, at a trap or reaction center, the energy of captured light serves to trigger a process such as electron transfer. Applications include solar energy conversion,^{10,11} illumination devices,¹¹ luminescence detectors,⁴ analyte-specific sensors,⁸ nonlinear optical materials,⁷ and photodynamic therapy.^{9,11}

In a typical dendrimer, the mechanism for each interchromophore step, in the flow of energy toward the core, is resonance energy transfer.¹⁷ The fundamental electromagnetic nature of each such move is well understood; however, modeling the overall multistep flow presents a considerable challenge.¹⁸ To this end some recent exploratory studies^{19,20} have introduced an operator approach, based on an adjacency matrix representation of the chemical connectivity between chromophores. Preliminary results have already indicated a promising potential for accurately representing the net en-

ergy flow, together with a capacity to interpret kinetic data in terms of new, physically meaningful quantities with a clear molecular interpretation. Other forms of matrix representation, also used to describe the intramolecular energy redistribution,^{1,21} have proved to be amenable for some specific cases. For example, in the work by Blumen *et al.*,²¹ an exact solution is derived for hyperbranched fractal polymers in which all chromophores have the same absorption cross section, and all rates of transfer between nearest neighbors are equal. Other more radical approaches to the problem have also been attempted, such as modeling the diffusion of the excitation under a constant force as a continuum process²² or using the Eyring (membrane permeation) model to treat the energy flux as diffusion in a potential energy landscape with thermal barriers.²³

In this paper, following a brief review of the adjacency matrix model in the specific form we have previously introduced, more detailed applications are developed and shown to exhibit: (i) the time development of the core excitation following pulsed irradiation, (ii) steady-state behavior that can be expected under conditions of constant illumination, (iii) the significance of a spectroscopic gradient in driving excitation toward the core, and (iv) the dynamical effects of solvent-induced tertiary folding. In each respect the new model offers a means of determining valuable new information on the photophysical and structural features of dendrimeric systems.

II. DESCRIPTION OF THE MODEL

By processes to be examined below, the illumination of a light-harvesting dendrimer results in a photoexcitation of the core, which is a function of the intensity of the light, the absorption cross section of the dendrimer and its component chromophores, and the characteristics of energy transfer between those chromophores. As described in our previous work,²⁰ the model for our calculations is cast in the form of

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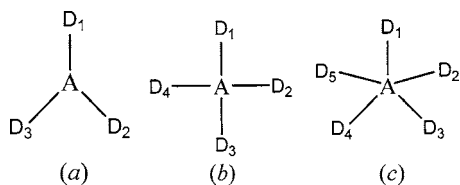


FIG. 1. First-generation dendrimers, $\rho(a)=3$, $\rho(b)=4$, and $\rho(c)=5$.

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. This matrix operates upon a vector representation of the (arbitrary) initial population conditions; iteration of the procedure models the temporal evolution of energy flow. We assume that successive generations of the polymer are built with a repeating structural motif, characterized by a vertex degree ρ , signifying the number of chemical links to each chromophore; it is also assumed that all the chromophores in a given shell are of the same type—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. The core acceptor or trap thus has ρ equivalent chromophores in the first generation shell surrounding it; in each successive generation, the number of chromophores in the shell grows by a factor of $\rho-1$. Figure 1 illustrates various first generation dendrimers with different vertex degrees ρ .

For clarity, we begin by illustrating the adjacency matrix for a first generation symmetric dendrimer with $\rho=3$, corresponding to the architecture of many of the most common (1,3,5) trisubstituted benzene dendrimers,

$$\mathbf{C} = \begin{pmatrix} 1-a-2f & f & f & \varepsilon^{-1}a \\ f & 1-a-2f & f & \varepsilon^{-1}a \\ f & f & 1-a-2f & \varepsilon^{-1}a \\ a & a & a & 1-3\varepsilon^{-1}a-\xi \end{pmatrix}. \quad (1)$$

The first three elements in the diagonal of the matrix are written in a form that reflects energy conservation (i.e., the sum of elements in each column of the matrix is unity): a is the propensity for the energy to be transferred from any chro-

mophore in the shell to the core, and f represents transfer between chromophores in the same shell. In the last column of matrix \mathbf{C} the propensity for back transfer, from the core to any chromophore in the shell, is written as $\varepsilon^{-1}a$ (corresponding to b in Ref. 20), where ε is the ratio of propensities for inward and outward energy transfers. In passing, we note that the latter parameter has been the subject of another recent study,²⁴ where its detailed dependence on spectral overlap has been explored. Finally, the parameter ξ is introduced to signify possible losses associated with emission or irreversible energy utilization at the core. In this simple case, the initial state can be represented by the vector,

$$\mathbf{s} = (1 \ 0 \ 0 \ 0)^T, \quad (2)$$

where the first three elements denote the excited state populations of the donors (only one is assumed to be excited) and the fourth element is the population of the acceptor. Through a progression of n repeated operations of \mathbf{C} upon the column matrix [Eq. (2)], we obtain the full time evolution of the energy flow up to a time $n\Delta t$, where Δt is the increment of time for which the propensities in the matrix (1) have been defined. The extent of core excitation after the n th iteration is, therefore, given by

$$G_n = [C^n \mathbf{s}]_4, \quad (3)$$

where the index on the right designates the fourth (core) element of the resulting column matrix. the result is a polynomial in a , of order n ; explicit expressions for the first few iterations are as follows:

$$G_1 = a, \quad (4a)$$

$$G_2 = (2 - \xi)a - (1 + 3\varepsilon^{-1})a^2, \quad (4b)$$

$$G_3 = (3 - 3\xi + \xi^2)a - (3 - \xi - 6\varepsilon^{-1}\xi + 9\varepsilon^{-1})a^2 + (1 + 6\varepsilon^{-1} + 9\varepsilon^{-2})a^3, \quad (4c)$$

$$G_4 = (4 - 6\xi + 4\xi^2 - \xi^3)a - (6 - 4\xi + \xi^2 - 24\xi\varepsilon^{-1} + 9\xi^2\varepsilon^{-1} + 18\varepsilon^{-1})a^2 + (4 - \xi - 12\xi\varepsilon^{-1} - 27\xi\varepsilon^{-2} + 24\varepsilon^{-1} + 36\varepsilon^{-2})a^3 - (1 + 9\varepsilon^{-1} + 27\varepsilon^{-2} + 27\varepsilon^{-3})a^4, \quad (4d)$$

$$G_5 = (5 - 10\xi + 10\xi^2 - 5\xi^3 + \xi^4)a - (10 - 10\xi + 5\xi^2 - \xi^3 - 60\varepsilon^{-1}\xi + 45\varepsilon^{-1}\xi^2 - 12\varepsilon^{-1}\xi^3 + 30\varepsilon^{-1})a^2 + (10 - 5\xi + \xi^2 - 60\varepsilon^{-1}\xi - 18\varepsilon^{-1}\xi^2 - 135\varepsilon^{-2}\xi + 54\varepsilon^{-2}\xi^2 + 60\varepsilon^{-1} + 90\varepsilon^{-2})a^3 - (5 - \xi - 18\varepsilon^{-1}\xi - 81\varepsilon^{-2}\xi - 108\varepsilon^{-3}\xi + 45\varepsilon^{-1} + 135\varepsilon^{-2} + 135\varepsilon^{-3})a^4 + (1 + 12\varepsilon^{-1} + 54\varepsilon^{-2} + 108\varepsilon^{-3} + 81\varepsilon^{-4})a^5. \quad (4e)$$

Although the parameter f in Eq. (1) generally enters the calculation of energy transfer between arbitrarily chosen chromophores, it is important to note that the result for the core excitation is independent of f , i.e., it is not in any way influenced by any transfer between chromophores in the same

shell. (This is readily verified not only for this first generation case but also for dendrimers of any higher generation.) Figure 2 illustrates the development of the core population as a function of time (the iteration count representing time in arbitrary units) for various values of the parameters a , ε , and

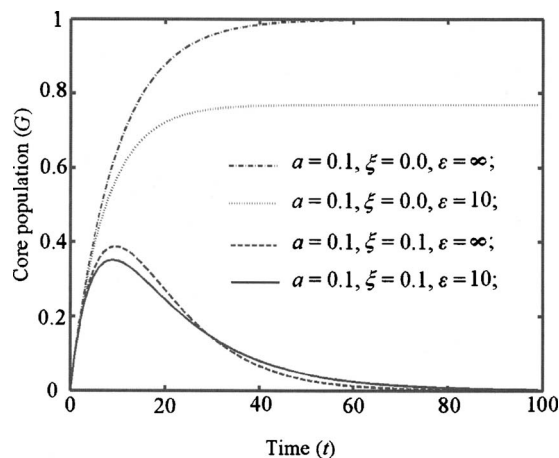


FIG. 2. Extent of core excitation as a function of the iteration count, for different values of propensities a , ξ , and ε in the matrix (1).

ξ in the matrix (1). The uppermost curve, corresponding to the set of values $a=0.1$, $\xi=0$, and $\varepsilon=\infty$, exhibits the simplest case, where there are no losses and no back-transfer processes, and the core works most effectively as an energy trap; in a second case ($a=0.1$, $\xi=0$, and $\varepsilon=10$), also loss less, a steady state is reached where the energy is distributed within the molecule, the exact form of that distribution being determined by the parameters a and b . In all such cases where losses can be neglected, the asymptotic value of the core excited state population is

$$\tilde{\mathbf{C}} = \begin{pmatrix} 1 - a_3 & 2\varepsilon_3^{-1}a_3 & 0 & 0 \\ a_3 & 1 - a_2 - 2\varepsilon_3^{-1}a_3 & 2\varepsilon_2^{-1}a_2 & 0 \\ 0 & a_2 & 1 - a_1 - 2\varepsilon_2^{-1}a_2 & 3\varepsilon_1^{-1}a_1 \\ 0 & 0 & a_1 & 1 - 3\varepsilon_1^{-1}a_1 - \xi \end{pmatrix}, \quad (6)$$

where a_i is the propensity for transfer from a chromophore in the i th shell to another, to which it is chemically bonded, in the $(i-1)$ th shell (or to the core, if $i=1$), ε_i is the ratio of efficiencies for inward and outward energy transfers between the same pair of chromophores, and ξ again signifies possible losses associated with emission or irreversible energy utilization at the core. Here and below, the tilde is employed to denote the reduced, shell-based representation. One ancillary advantage of this representation is that it obviates any need to consider the chromophores of any given shell as equivalent in their individual propensities, i.e., it is no longer necessary to assume a rotational symmetry that chemical connectivity would suggest. This is a facet, that is, of particular relevance when issues of folding are to be entertained.

To continue with the three-generation example, an initial population vector similar to Eq. (2) can also be written in this case, where the elements of the vector $\tilde{\mathbf{s}}$ are now the excited state populations of the entire shells and the core,

$$G_\infty = \frac{1}{1 + 3\varepsilon^{-1}}, \quad (5)$$

as can trivially be shown by imposing the limiting condition that operation of the adjacency matrix \mathbf{C} regenerates the existing energy distribution. Clearly, the state population in this limit depends only on the spectral overlap for forward and backward transfers.²⁴

Returning to Fig. 2, one can observe in the lower two curves the very substantial differences in behavior that occur when losses are present. Both curves—one with back transfer ($a=0.1$, $\xi=0.1$, and $\varepsilon=10$) and the other without ($a=0.1$, $\xi=0.1$, and $\varepsilon=\infty$)—exhibit the patterns of flow in a molecule where energy, once transferred to the core, is irreversibly expended or harvested. A comparison between these latter curves shows that allowing a small degree of back transfer is largely inconsequential. It is apparent from the graphs that the model can properly simulate the flow of energy through dendrimeric systems with a range of photo-physical characteristics. Moreover, application of the results will enable information on the individual propensity parameters to be obtained from experimental measurements of the core excitation.

When higher generation dendrimers are studied it is more convenient to consider each shell as an effective donor or acceptor, significantly reducing the dimensionality of the transfer matrices. For a *three*-generation dendrimer, for example, the corresponding matrix in the shell basis may be written as follows (see the Appendix):

$$\tilde{\mathbf{s}} = (1 \ 0 \ 0 \ 0)^T. \quad (7)$$

This representation of the initial state, in which only the excitation of an outer chromophore is entertained, again reflects the strongest probability for photons to be absorbed in the outermost shell, due to the larger number of chromophores it contains.

III. STEADY-STATE BEHAVIOR

The model as previously described is an approximation in which the excited state populations are not continuous functions of time; energy is transferred between donors and acceptors on every iteration—which can be associated with a finite time interval Δt . The fidelity of this representation is improved if the transfer propensities are decreased in value

(thus requiring a larger number of iterations); in this sense, the above calculations in Sec. II have an improved accuracy over our earlier work.²⁰ Clearly, the best representation is where the energy flow is continuous in time, i.e., when the

propensities are redefined for infinitesimal time intervals, as will be assumed in the following. For example, for a three-generation dendrimer, we can write the adjacency matrix in the form

$$\tilde{\mathbf{C}} = \begin{pmatrix} 1 - w_{a3}dt & 2\varepsilon_3^{-1}w_{a3}dt & 0 & 0 \\ w_{a3}dt & 1 - 2\varepsilon_3^{-1}w_{a3}dt - w_{a2}dt & 2\varepsilon_2^{-1}w_{a2}dt & 0 \\ 0 & w_{a2}dt & 1 - 2\varepsilon_2^{-1}w_{a2}dt - w_{a1}dt & 3\varepsilon_1^{-1}w_{a1}dt \\ 0 & 0 & w_{a1}dt & 1 - 3\varepsilon_1^{-1}w_{a1}dt - \Gamma dt \end{pmatrix}, \quad (8)$$

where w_{ai} is the rate of rotational energy transfer (RET) corresponding to the propensity a_i in Eq. (6) and Γ is the rate of energy utilization by the core.

If a dendrimer is irradiated with constant intensity light, then a steady state is reached when the energy expended in the core equals that captured by the dendrimer during the same time interval. The state populations become independent of time and may be expressed as follows:

$$\tilde{\mathbf{s}} = (G^{(4)}, G^{(3)}, G^{(2)}, G^{(1)}), \quad (9)$$

$$\sum_{i=1}^4 G^{(i)} = 1. \quad (10)$$

This distribution of excitation is subject to the recursive condition,

$$\tilde{\mathbf{s}} = \tilde{\mathbf{p}} + \tilde{\mathbf{C}}\tilde{\mathbf{s}}, \quad (11)$$

in which $\tilde{\mathbf{p}}$ represents the incremental extent of excitation, due to the light, in the interval dt ,

$$\tilde{\mathbf{p}} = G^{(1)}Z\Gamma dt(N_4\sigma^{(4)}, N_3\sigma^{(3)}, N_2\sigma^{(2)}, N_1\sigma^{(1)}). \quad (12)$$

Here the normalizing factor Z is defined by

$$Z^{-1} = \sum_{i=1}^4 N_i\sigma^{(i)}, \quad (13)$$

and $\sigma^{(i)}$ signifies the individual absorption cross-section for each of the N_i chromophores in the $(i-1)$ th shell. Substituting Eqs. (8), (9), and (12) in Eq. (11) and using Eq. (10), the state population in the core of the molecule is expressed as

$$G^{(1)} = \frac{1}{\left(1 + \frac{3}{\varepsilon_1} \left(1 + \frac{2}{\varepsilon_2} \left(1 + \frac{2}{\varepsilon_3}\right)\right)\right) + \Gamma \left(\frac{P_1}{w_{a3}} + \frac{P_2}{w_{a2}} \left(1 + \frac{2}{\varepsilon_3}\right) + \frac{P_3}{w_{a1}} \left(1 + \frac{2}{\varepsilon_2} \left(1 + \frac{2}{\varepsilon_3}\right)\right)\right)}, \quad (14)$$

where

$$\begin{aligned} P_1 &= ZN_4\sigma^{(4)}, \\ P_2 &= Z(N_4\sigma^{(4)} + N_3\sigma^{(3)}), \\ P_3 &= Z(N_4\sigma^{(4)} + N_3\sigma^{(3)} + N_2\sigma^{(2)}). \end{aligned} \quad (15)$$

It is interesting to consider a limiting case where Γ , the rate of energy loss by the core, can be neglected. (In fact, since the practical objective of an energy-harvesting dendrimer is delivery to the core specifically in order for the energy to be expended there, the exclusion of Γ is consistent with a focus on the efficiency of excitation arrival.) Equation (14) reduces still further if it is assumed that all the directional efficien-

cies, ε , between chromophores in adjacent shells, are equal. Then, the core population can be written as

$$G^{(1)} = (1 + 3\varepsilon^{-1} + 6\varepsilon^{-2} + 12\varepsilon^{-3})^{-1}. \quad (16)$$

In order to compare the core populations of *different* dendrimeric systems, under the conditions described for Eq. (16), it is necessary to account for the different net absorption cross sections of these systems—which can be assumed to vary in proportion to the total number of chromophores N which they comprise. Figure 3 shows the suitably scaled extent of core excitation $NG^{(1)}$ as a function of the directional efficiency, for three-, four-, and five-generation dendrimers. The result shows the rapid increase in the extent of total core

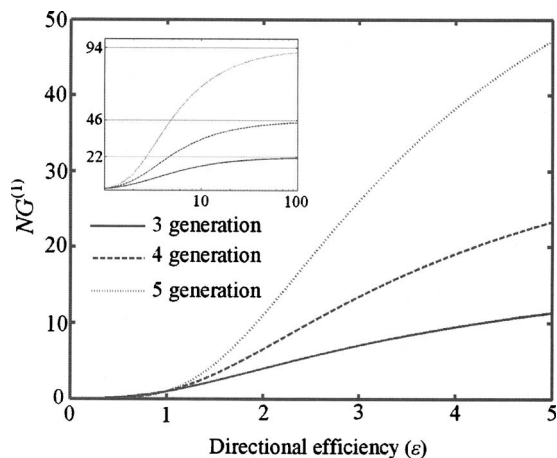


FIG. 3. Core excited state population scaled by the total number of chromophores N in dendrimers of vertex degree $\rho=3$, plotted as a function of the directional efficiency of intershell RET, for three-, four-, and five-generation dendrimers.

excitation with the growth of successive generations; as can be physically expected, the asymptotic behavior for large ε corresponds to the total number of chromophores.

IV. SPECTROSCOPIC GRADIENT

It is interesting to illustrate the transparent linkage afforded by the present model, between the light-harvesting properties of a dendrimer entity, and the detailed optical properties of the constituent chromophores. To this end we focus on the critical role of a *spectroscopic gradient*, the progressive bathochromic shift that enhances efficient funneling of energy from the peripheral chromophores to the core.²⁵ A general relationship between the relative directional efficiency ε and the spectroscopic gradient has recently been established.²⁴ In the simplest case, where the spectral bands of the chromophores are represented by Gaussian functions of similar width and where the absorption and fluorescence maxima are separated by a constant Stokes shift, this relationship is as follows:

$$\varepsilon = 2^{(8\omega_C\omega_S/\Delta\omega_{1/2}^2)} = e^{\tilde{\omega}_G\tilde{\omega}_S}. \quad (17)$$

Here $\Delta\omega_{1/2}$ is the full width at half maximum, ω_G is the absorption frequency shift between successive generation chromophores, and ω_S is the Stokes Shift. The simplified expression on the right-hand side of Eq. (17) is obtained by rewriting in terms of $\tilde{\omega}_S = (2\sqrt{2}\ln(2)/\Delta\omega_{1/2})\omega_S$ and $\tilde{\omega}_G = (2\sqrt{2}\ln(2)/\Delta\omega_{1/2})\omega_G$, dimensionless measures of the Stokes shift and spectroscopic gradient, respectively. To illustrate the effect of the spectroscopic gradient, we plot the core excitation of a three-generation dendrimer as a function of the spectroscopic gradient $\tilde{\omega}_G$, in Fig. 4, based on an excited state population given by Eq. (16). The figure shows the sensitive dependence of the light-harvesting efficiency on the spectroscopic gradient, a feature which also increases in importance with the Stokes shift exhibited by the chromophores.

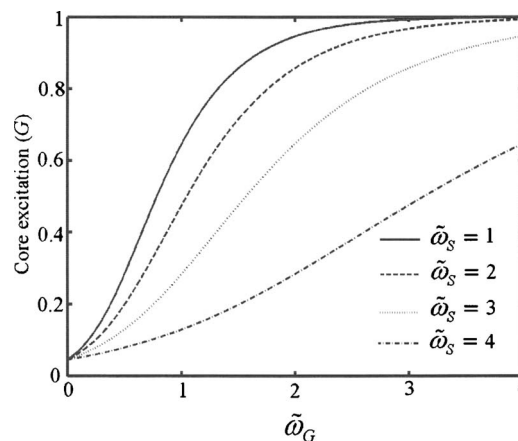


FIG. 4. Core excitation G of a three-generation dendrimer [described by Eqs. (16) and (17)], plotted as a function of $\tilde{\omega}_G$ (measure of the spectroscopic gradient) for different values of $\tilde{\omega}_S$ (the relative Stokes shift).

V. DISCUSSION

In this paper, we have developed a comprehensive framework for the theory of energy flow in dendrimeric polymers. In Sec. II, a more compact form has been secured for the basic adjacency matrix representation of energy flow. The methodology has been shown to offer a robust representation that can accommodate a variety of chemically and photophysically significant parameters—especially the relative propensities for inward and outward energy flows, itself a sensitive function of the spectral overlap for the donor emission and acceptor absorption curves. In Sec. III, it has been shown how to determine the steady-state behavior, representing equilibrium conditions that will arise under conditions of constant illumination, and where the directional efficiency again proves a key determinant of the core excitation. Bridging two levels of theory, Sec. IV has exhibited the connections that can be made, using the matrix theory, between the light-harvesting characteristics of a dendrimer and the detailed spectroscopic properties of the constituent chromophores.

In conclusion, it is interesting to outline how the overall dendrimer efficiency may depend on tertiary folding. As has been established, the radial flow of energy in dendrimers is extremely sensitive to the separation between successive shells, due to the inverse sixth-power distance dependence of the resonance energy transfer propensities. It is therefore important to register the fact that most dendrimer compounds have a degree of intrinsic flexibility, a feature that grows in significance as the number of generations increases and tertiary folding occurs. This is a facet of the three-dimensional structure that is at present only amenable to empirical modeling. A physical manifestation of the effect is the observation that dendrimer radii prove to be sensitively dependent on both chemical structure and solvent, and a variety of functional forms for the dependence of radius on generation has been found to operate under different conditions.^{25–28} In many cases, the dependence is close to linearity for low generation polymers, suggesting that the separation between successive shells is approximately constant.

It is instructive to visualize the possible effect of this

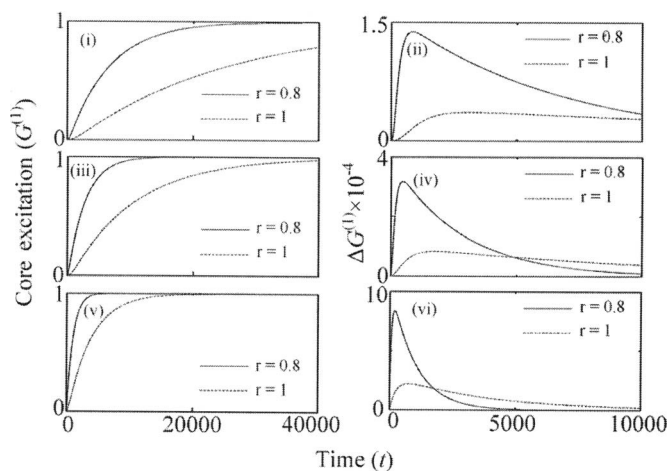


FIG. 5. Time evolution of the excited core population, for $r=1.0$ and 0.8 , for (i) two-generation, (iii) three-generation, and (v) four-generation dendrimers, and their respective increases in core excitation per unit time (ii), (iv), and (vi). The parameter values are $\varepsilon_1=\infty$, $\varepsilon_i=1$ for $i>1$, $\xi=0$, and $a_i'=1 \times 10^{-3}$.

flexibility on the energy flow. To this end, we can recast the propensities in Eq. (6) in a form that expresses their dependence on the distance between shells as $a_i=a_i'/r_i^6$, where r_i is a dimensionless metric of the distance from the i th to the $(i-1)$ th shell (or the core if $i=1$), and a_i' is a corresponding, effective spectroscopic factor. Taking this approach essentially reflects the fact that the energy flow is dominated by transfers between near-neighbor chromophores in adjacent shells. For indicative purposes, let us assume that solvent coordination reduces the distance between successive shells of the dendrimer (and between the first shell and the core) by a constant proportion, i.e., in a geometric progression. Figure 5 shows the effects on the time evolution of the core excited state population for two-, three-, and four-generation dendrimers and the corresponding increases per iteration count. The initial population is as given by Eq. (7) and its counterparts, always featuring one initial excitation in the outermost shell. For comparison, results are shown for the cases where the distance between shells is $r_i=1.0$, and also where the effect of a solvent or other folding process reduces the distance to $r_i=0.8$; we assume that the core is an energy trap imposing the conditions $\varepsilon_1=\infty$ and $\xi=0$, and that the directional efficiency between chromophores in different shells and the core is unity; $\varepsilon_i=1$ and $a_i'=1 \times 10^{-3} \text{ s}^{-1}$ for all the inward transfer.

On inspection of Fig. 5, it is apparent that the time taken for an excitation initially on the outermost shell to reach the core grows with the number of generations, quantifying a trend that can be qualitatively anticipated. In a future work, an extension of the method to dendrimers of a higher generation should enable the detailed form of this dependence to be elicited, accommodating a more general form for the variation of shell radius with generation. The present results, designed to illustrate the principles, show how dramatically the nature of the energy flow changes when the distance between successive shells is reduced, even by as little as 20%, suggesting a considerable solvent-induced enhancement of the energy flow process. Clearly, for each dendrimer

in its folded conformation, compared to its unfolded form, the time taken for excitation to reach the core is very markedly reduced. It is striking that this effect is entirely geometric in its origin. Lastly, the fold-dependent changes in shape in the curves (ii), (iv), and (vi) suggest a basis for interpreting experimentally determined kinetics, based on pulsed laser excitation, in terms of solvent-induced conformational change. These generic results inspire confidence that applications of the theory to specific dendrimer systems will offer considerable interpretive power.

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APPENDIX: ADJACENCY MATRIX DEPENDENCE ON DENDRIMER BRANCHING

In the model previously developed, we showed that the dimensionality of the adjacency matrix can be reduced by considering the shells as effective, composite donors and acceptors.²⁰ In the following, we show the relationship between the propensities in both the original and reduced basis matrices. It is simplest to introduce the relationship by reference to a simple first-generation dendrimer with connectivity $\rho=3$. The matrix representation of the energy flow in the molecule is given by Eq. (1), and in general the initial excited state population can be represented as a four-element population vector \mathbf{s} , whose elements are the degrees of excitation in each chromophore. When the donor shell is considered as a single effective donor or acceptor, we can write a transfer propensity matrix in the form;

$$\tilde{\mathbf{C}} = \begin{pmatrix} 1 - a' & \varepsilon'^{-1}a' \\ a' & 1 - \varepsilon'^{-1}a' - \xi' \end{pmatrix}, \quad (\text{A1})$$

a' being the propensity for transfer from the shell to the core and ε' the ratio of propensities for inward and outward transfers between these two effective chromophores. For the matrix (A1) we can define a reduced population vector as follows;

$$\tilde{\mathbf{s}} = (G^{(2)} + G^{(3)} + G^{(4)}, G^{(1)})^T, \quad (\text{A2})$$

where $G^{(4)}$, $G^{(3)}$, $G^{(2)}$, and $G^{(1)}$ are, respectively, the first, second, third, and fourth elements of \mathbf{s} , whereas the first and second elements of $\tilde{\mathbf{s}}$ are the net excited state populations of the shell and core, respectively. For consistency, the core populations predicted by both models must be equivalent. After one iteration of the usual procedure, by equating the extents of core population delivered by each representation, we have

$$(1 - 3\varepsilon^{-1}a - \xi)G^{(1)} + a(G^{(2)} + G^{(3)} + G^{(4)}) \\ = (1 - \varepsilon'^{-1}a' - \xi)G^{(1)} + a'(G^{(2)} + G^{(3)} + G^{(4)}), \quad (\text{A3})$$

illustrating that the directional efficiency in the matrix (A1) is three times smaller than in the matrix (1), $\varepsilon'=\varepsilon/3$. Consistently with previous works,²⁹ for a G -generation den-

dimer, we find that the nonzero elements of the adjacency matrix in the shell basis are as follows:

$$\begin{aligned}
 C_{1,1} &= 1 - a_G, \\
 C_{i,i} &= 1 - a_i - \beta \varepsilon_{i+1}^{-1} a_{i+1}, \quad 2 \leq i \leq G, \\
 C_{G,G} &= 1 - \rho \varepsilon_1^{-1} a_1 - \xi, \\
 C_{i-1,i} &= \beta \varepsilon_{i+1}^{-1} a_{i+1}, \quad 2 \leq i \leq G+1, \\
 C_{i+1,i} &= a_i, \quad 1 \leq i \leq G,
 \end{aligned}
 \tag{A4}$$

where ρ is the number of chromophores bonded to the core and β is the branch multiplicity from the first shell to the periphery. If the central chromophore is identical to the chromophores in each shell, it follows that $\beta = \rho - 1$.

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