Geometric versus Energetic Competition in Light Harvesting by Dendrimers

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A property, unique to the treelike structure of dendrimers, is predicted. We show that for ideal dendrimers, with a superimposed energy funnel descending from the periphery to the center, one should be able to control the preferred location of the excitation by monitoring the temperature relative to the energy funnel. This opens the possibility for a controlled drive of photochemical processes in these supermolecules.

Introduction

The treelike structure of dendrimers,[1,2] which are made up of repeating units arranged in a hierarchical, self-similar fashion around a core, raises the possibility of their application as artificial antenna systems.[3−7] Two basic properties make these supramolecules promising candidates for light harvesting: (a) the large number of absorbing units that grow exponentially with their generation number[1] and (b) the relatively short distance of the periphery from the center, where a photochemical sensor can be located.[7] We have recently demonstrated some characteristic antenna properties in a family of symmetric dendrimers and distinguished between compact and extended structures.[5] We outlined ways to control the efficiency of light collection by superimposing an energetic funnel on the branched dendrimer structure.[6]

Here we predict the possibility of a controlled drive of photochemical processes in molecules, or molecular groups, located at the core of the dendrimer by tuning the temperature. We show that the unique structure of dendrimers allows one to dictate, by change of temperature, the "preferred location" of the excitation, namely, core or periphery.

Let us consider the temperature dependence of energy transfer from an initially excited state on a dendrimer, with a *linear excitation energy funnel*, to a trap of finite depth located at its center. The energy-transfer process will be dominated by two trends: (a) an entropic one, which stems from the branching at each generation, and (b) an energetic one, which is due to an energy funnel that directs the excitation toward the trap. We calculate the free energy, as a function of the position of the excitation, for different temperatures, and also the mean first passage time (MFPT) in the case of an *irreversible* trap. The MFPT provides a measure of the efficiency of the collection processes and can be obtained from the experimentally measured survival probability.[8] We demonstrate that the effective rate of capture of an excitation by the trap depends on the temperature, the size of the dendrimer, the coordination number, the nature of the funnel, and the initial conditions.

Model and Thermodynamics

Figure 1 presents schematically a symmetric dendrimer of four generations, $g = 4$, with a trap at the center, with

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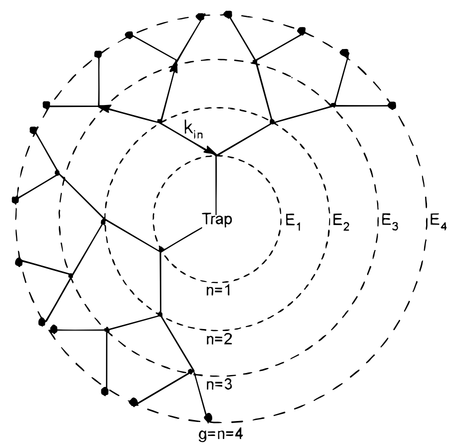

Figure 1. Schematic presentation of a dendrimer of four generations, $g = 4$, coordination number $Z = 3$, and core branching $C = 2$.

coordination number $Z = 3$ and with a core branching $C = 2$. Consider an excitation that migrates, by nearest-neighbor jumps, on a dendrimer that has a reversible trap at the origin and a linear energetic funnel toward it. Namely, the trap captures the energy but releases it with a rate that depends on the trap depth and the temperature. For a dendrimer with excitation energies that descend from the periphery by an amount of U at each generation, the funnel is

$$E_0 = \epsilon \qquad (1)$$

$$E_n = \epsilon + \Delta + (n-1)U \qquad 1 \le n \le g$$

where E_0 is the excitation energy of the trap, Δ is the difference between the excitation energy of the trap and the first generation, and n is the generation number. ϵ, Δ, and U are assumed to be positive. Figure 2 shows the energy funnel as a function of the generation number. The excitation energy is $\epsilon + \Delta + (g - 1)U$ at the periphery and ϵ at the center. The structure of dendrimers, having branching $Z - 1$, $Z > 2$, at each generation and a core branching C, leads to the degeneracy $f_n = C(Z - 1)^{n-1}$, for $n \ge 1$, in the occupancy of the nth generation by the excitation. This entropic contribution makes dendrimers drastically different from one-dimensional structures when considering light harvesting.

We now briefly provide a thermodynamic description of our model dendrimer. The partition function, from which other

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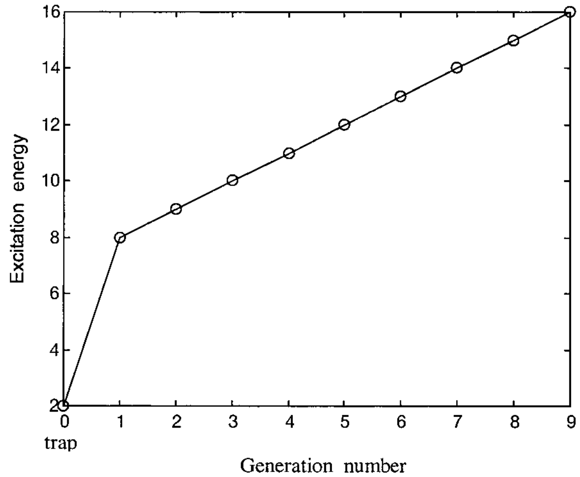

Figure 2. Energy funnel as a function of the generation number. Here $\epsilon = 2$, $\Delta = 6$, and $U = 1$ in a dendrimer of nine generations, $g = 9$. Note that $n = 0$ is the trap.

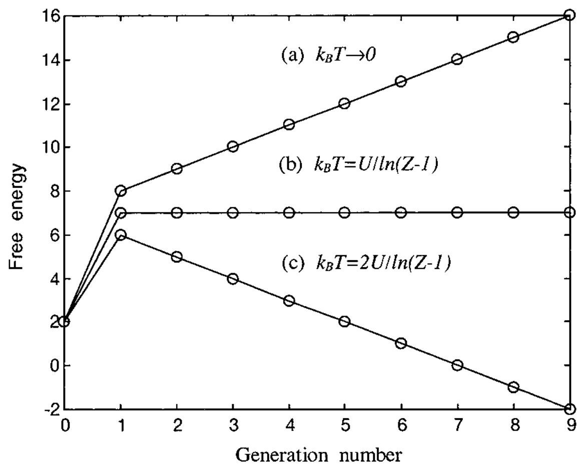

Figure 3. Free energy as a function of the excitation position for three different temperatures for a dendrimer with nine generations, $g = 9$, coordination number $Z = 3$, and core branching $C = 2$.

quantities can be derived, is

$$Q = \sum_{n=0}^{g} f_n\, e^{-E_n/(k_B T)} =$$

$$e^{-\epsilon/(k_B T)} + C\, e^{(-\epsilon-\Delta)/(k_B T)} \sum_{n=1}^{g} [(Z-1)\, e^{-U/(k_B T)}]^{n-1} \quad (2)$$

where k_B is the Boltzman factor. The equilibrium occupation probabilities of the various generations are then

$$P_0 = \frac{1}{Q}\, e^{(-\epsilon/k_B T)} \quad (3)$$

$$P_n = P_0 C\, e^{-\Delta/(k_B T)}[(Z-1)\, e^{-U/(k_B T)}]^{n-1} \qquad 1 \le n \le g$$

From eqs 2 and 3 one obtains the free energy as a function of the generation at which the excitation is located:

$$F_n = -k_B T \ln(P_n Q) = E_n - k_B T \ln f_n \quad (4)$$

In Figure 3 we plot the free energy for three different temperatures: (a) describes the free energy for $T \to 0$, which is similar to the energy funnel in Figure 2; (b) is the free energy for $k_B T = U/\ln(Z-1)$, which corresponds to the case where there is no preference of the system to be in any specific generation for $n \ge 1$; (c) $k_B T > U/\ln(Z-1)$ introduces a second minimum in the free energy, which corresponds to the last generation, $n = g$. Namely, at high temperatures the energetic funnel become less efficient relative to the geometric one, and therefore the excitation prefers to be mainly at the periphery. Figure 4 describes the occupation probability of the excitation as a function of the generation number for high temperatures, $k_B T > U/\ln(Z-1)$, case c in Figure 3. For low temperature, $k_B T < U/\ln(Z-1)$, the excitation would prefer the vicinity of the trap. When compared to a polymer, which has the same energetic funnel toward the trap, we find that the polymer is characterized only by regimes a and b of Figure 3 but does not have the high-temperature behavior, case c. The latter stems from the degeneracy that is special for the dendrimer.

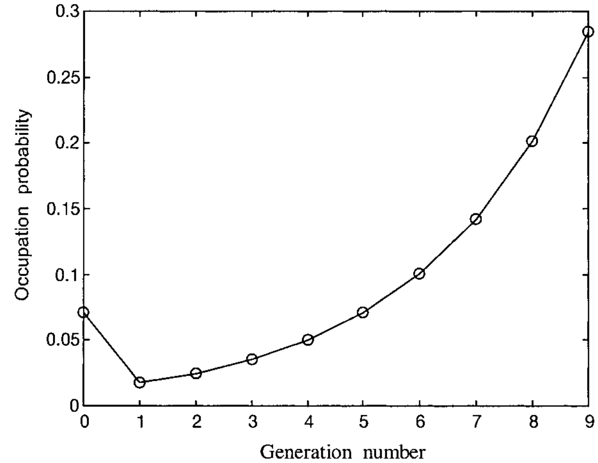

Figure 4. Occupation probability as a function of the generation number for high temperatures, corresponding to graph c in Figure 3.

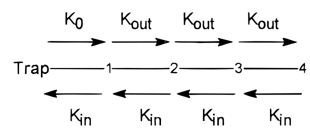

Figure 5. One-dimensional equivalent of Figure 1. Site 0 corresponds to a reversible trap, and sites 1, 2, 3, and 4 correspond to the four generations.

Mean First Passage Time

From the equilibrium condition one obtains

$$P_n K_{n\to n+1} = P_{n+1} K_{n+1\to n} \qquad 0 \le n \le g-1 \quad (5)$$

where $K_{n\to n+1}$ is the rate of energy transfer from the nth generation to the $(n+1)$th generation. Denoting (see Figure 1)

$$K_{n+1\to n} \equiv K_{in} \qquad 0 \le n \le g-1 \quad (6)$$

then by substituting eq 3 and eq 6 into eq 5 we find

$$K_{n\to n+1} = K_{in}(Z-1)\, e^{-U/(k_B T)} \equiv K_{out} \; 1 \le n \le g-1 \quad (7)$$

$$K_{0\to 1} = K_{in} C\, e^{-\Delta/(k_B T)} = K_0 \qquad n = 0$$

Therefore, migration on a dendrimer of size g with a linear excitation energy funnel, as in Figure 2, is equivalent in general to an asymmetric random walk on a one-dimensional chain,[9] as shown in Figure 5. Note that the random walk rate outward, K_{out}, has two competing contributions: a geometric one due to the branching and an energetic one. K_{in} can, of course, be temperature-dependent. To calculate the mean first passage time (MFPT) to the trap at the center of the dendrimer, we now consider the trap as irreversible; namely, $\Delta/k_BT \rightarrow \infty$, so there is no release from the trap, $K_0 = 0$. The exact solution for the MFPT for an excitation that starts at the nth generation to reach the trap according to the simple model shown in Figure 5 with $K_0 = 0$ is given by[6,10,11]

$$\langle\tau(n)\rangle = \frac{n}{K_{in} - K_{out}} - \frac{K_{out}}{(K_{in} - K_{out})^2}\left[\left(\frac{K_{out}}{K_{in}}\right)^{g-n} - \left(\frac{K_{out}}{K_{in}}\right)^{g}\right] \qquad K_{out} \neq K_{in} \quad (8)$$

$$\langle\tau(n)\rangle = \frac{n(2g + 1 - n)}{2K_{in}} \qquad K_{out} = K_{in}$$

Substituting eqs 6 and 7 into eq 8, we get the dependence of the MFPT on the dendrimer size and on temperature, for large dendrimers with a linear excitation energy funnel. The behavior of the MFPT for a finite but large dendrimer, when the excitation starts either at the first generation, $n = 1$, or at the last generation, $n = g$, can be summarized as follows:

	$k_BT > U/\ln(Z - 1)$ bias to the periphery	$k_BT = U/\ln(Z - 1)$ no bias	$k_BT < U/\ln(Z - 1)$ bias to the trap
start at $n = 1$	$<\tau> = \frac{1}{K_{in}}\frac{1}{(K-1)}e^{g \ln K}$	$<\tau> = \frac{1}{K_{in}}g$	$<\tau> = \frac{1}{K_{in}(1-K)}$
start at $n = g$	$<\tau> = \frac{1}{K_{in}}\frac{K}{(K-1)^2}e^{g \ln K}$	$<\tau> = \frac{1}{2K_{in}}g^2$	$<\tau> = \frac{1}{K_{in}(1-K)}g$

where $$K = \frac{K_{out}}{K_{in}} = (Z - 1)\, e^{-U/(k_BT)}$$

Tuning the temperature corresponds to tuning the ratio of the outward to inward biases, as shown in the table. For example, the MFPT for an excitation that starts at the last generation grows as an *exponential* in the generation number, g, at high temperature, $k_BT > U/\ln(Z - 1)$, and is only *linear* in the generation number for lower temperature, $k_BT < U/\ln(Z - 1)$, where the funnel dominates.

Conclusion

The problem solved here is closely related to the effect of a bias in the protein-folding model discussed by Zwanzig et al.,[12,13] where the calculation of the MFPT to reach the native configuration demonstrates a change from an inefficient random search to an efficient biased search as a function of temperature.

The branched structure of dendrimers and the addition of an energetic funnel enable one, by changing the temperature, to determine the "preferred location" of the excitation along the dendrimer structure (if the decay of the excitation is slow compared to the rate of energy migration). Relatively rigid dendrimers can therefore act as sensors for environmental temperature changes or can be used to drive, by temperature changes, photochemical reactions of molecules at the core.

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