

Dendrimers as Controlled Artificial Energy Antennae

Arie Bar-Haim,[†] Joseph Klafter,^{*,‡} and Raoul Kopelman^{*,‡}

School of Chemistry, Tel Aviv University
Tel Aviv 69978, Israel
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109-1055

Received March 27, 1997

The tree-like 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.^{3–5} What makes these supramolecules promising candidates as artificial antennae is the large number of absorbing units that grows exponentially with their generation number² and the relatively short distance of the periphery from the center, where a fluorescent trap, a reaction center, or a chemical sensor can be located. Dendrimers are therefore expected to harvest light and transfer it to a trap at the center with high efficiency. We have recently demonstrated⁵ some characteristic antenna properties in a family of symmetric dendrimers and distinguished between compact and extended structures. The absorption spectra of the latter suggest the existence of an energetic funnel that may channel optical excitations to the center.^{5,6}

Here we present an exact solution for the mean first passage time (MFPT), $\langle \tau \rangle$, *i.e.*, the mean time for an excitation that starts at the periphery to reach the center. The MFPT is a measure of the efficiency of the collection process and can be directly determined from experiments. We discuss the dependence of the MFPT on the size of the dendrimer and on the interplay between geometric and energetic aspects. Figure 1 presents schematically a symmetric dendrimer of four generations ($g = 4$), with a trap at the center and with coordination number $z = 3$, which means that each branch splits into $z - 1 = 2$ new branches. The special case $z = 2$ corresponds to a linear chain. An excitation on the dendrimer migrates to a nearest site of a higher generation with a rate K_1 and to a nearest site of a lower generation with a rate K_2 . Both rates depend on the coordination number and on the local rates k_{up} ($n \rightarrow n + 1$) and k_{down} ($n \rightarrow n - 1$) correspondingly; n is the generation number, $1 \leq n \leq g$.

From simple probabilistic considerations, one concludes that for coordination number z ($z > 2$) the rate “up”, toward the periphery, is

$$K_1 = k_{\text{up}}(z - 1) \quad (1)$$

and the rate “down”, toward the trap, is

$$K_2 = k_{\text{down}} \quad (2)$$

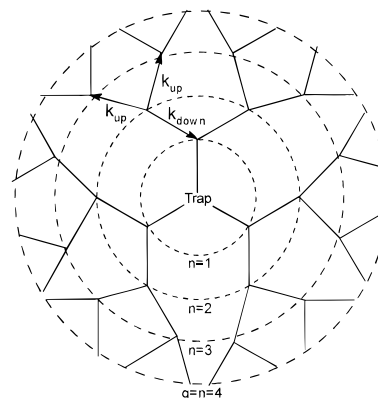


Figure 1. Schematic presentation of a dendrimer of four generations, $g = 4$, and branching $z = 3$.

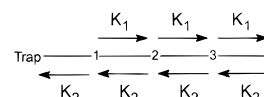


Figure 2. One-dimensional equivalent of Figure 1. The origin corresponds to the trap and sites 1, 2, 3, and 4 to the four generations.

Migration on the dendrimer in Figure 1 can be shown to be equivalent^{7,8} to a random walk on a *one-dimensional chain*, shown in Figure 2, where each site represents the corresponding generation in the dendrimer and with jump rates K_1 and K_2 .

This equivalence between dynamics on a dendrimeric structure and on a chain enables calculation, in a simple way, of some of the quantities related to energy migration in dendrimers. The rates k_{up} and k_{down} are usually distance dependent and may have also an energy difference contribution. If $k_{\text{up}} = k_{\text{down}}$, only the spatial geometry enters, so that $K_1 > K_2$. Namely, symmetric dendrimers are characterized by an *inherent, geometrically induced bias* toward the periphery. To our knowledge, this is a property unique to these supermolecules. One can now superimpose on the geometric bias an energetic funnel, descending from the periphery to the origin, which acts as a counterbias to the geometric one. The competing biases introduce the possibility for a novel control of the energy transfer and trapping efficiency.

The MFPT, $\langle \tau \rangle$, which measures the trapping efficiency, is obtained by solving the set of differential equations which describes the one-dimensional equivalent system in Figure 2:

$$\dot{p}_1(t) = K_2 p_2(t) - (K_1 + K_2) p_1(t) \quad (3)$$

$$\dot{p}_n(t) = K_2 p_{n+1}(t) + K_1 p_{n-1}(t) - (K_1 + K_2) p_n(t) \quad (1 < n < g)$$

$$\dot{p}_g(t) = K_1 p_{g-1}(t) - K_2 p_g(t) \quad (\text{reflecting boundary condition})$$

where $p_n(t)$ is the probability that there is still an excitation at time t in the n th generation ($1 \leq n \leq g$). The survival probability of an excitation, initially prepared in the periphery, is

$$\Phi(t) = \sum_{n=1}^g p_n(t) \quad (4)$$

The above set of differential equations has a matrix representation:

$$\overrightarrow{\dot{P}}(t) = \mathbf{A} \overrightarrow{P}(t) \quad (5)$$

Diagonalizing the matrix leads to the survival probability⁸

[†] Tel Aviv University.

[‡] University of Michigan.

(1) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, 132, 875.

(2) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 138.

(3) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, 118, 9635.

(4) Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, 118, 4354.

(5) Kopelman, R.; Shortreed, M.; Shi, Z. Y.; Tan, W.; Xu, Z.; Moore, J. S.; Bar-Haim, A.; Klafter, J. *Phys. Rev. Lett.* **1997**, 78, 1239. Shortreed, M.; Shi, Z. Y.; Kopelman, R. *Mol. Cryst. Liq. Cryst.* **1996**, 28, 95.

(6) The funnel in the extended dendrimers⁵ is achieved by phenyl-acetylene chains of varying lengths: shorter at the periphery and longer toward the center.

(7) Hughes, B. D.; Sahimi, M. *J. Stat. Phys.* **1982**, 781. Monthus, C.; Texier, C. *J. Phys. A: Math. Gen.* **1996**, 29, 2399.

(8) Bar-Haim, A.; Rozman, M. G.; Klafter, J. Manuscript in preparation.

$$\Phi(t) = \sum_{i=1}^g c_i e^{-\lambda_i t} \quad (6)$$

where $-\lambda_i$, $1 \leq i \leq g$, are eigenvalues of the matrix **A**. The survival probability is the experimental observable in time evolution experiments of trapping. The MFPT is directly related to the survival $\Phi(t)$ and is given by⁹

$$\langle \tau \rangle = \int_{t=0}^{\infty} \Phi(t) dt \quad (7)$$

We now present the dependence of $\langle \tau \rangle$ on the size (number of generations of the dendrimer) and on the rates toward and from the periphery. A complete calculation, and the analogy of the solution to queueing theory, will be presented elsewhere.⁸

$$\langle \tau \rangle = \frac{K_1((K_1/K_2)^g - 1)}{(K_1 - K_2)^2} - \frac{g}{K_1 - K_2} \quad K_1 \neq K_2 \quad (8)$$

$$\langle \tau \rangle = \frac{g(g+1)}{2K_1} \quad K_1 = K_2$$

For a finite but large dendrimer ($g \gg 1$), the different behaviors can be classified as follows:

$K_1 > K_2$ (bias to the periphery)	$K_1 = K_2$	$K_1 < K_2$ (funnel to the trap)
<i>exponential</i>	<i>square</i>	<i>linear</i>
$\langle \tau \rangle = \frac{K_1}{(K_1 - K_2)^2} e^{g \ln(K_1/K_2)}$	$\langle \tau \rangle = \frac{g^2}{2K_1}$	$\langle \tau \rangle = \frac{g}{K_2 - K_1}$

The competition between K_1 and K_2 opens the possibility for controlling the trapping efficiency, covering a range from *exponential* (less efficient trapping) dependence to *linear* (very efficient trapping) dependence of $\langle \tau \rangle$ on size.

The exponential dependence of $\langle \tau \rangle$ on g corresponds to the geometrically dominated regime, while the linear g dependence stems from the energy funnel effect. The crossover case $K_1 = K_2$ has a typical one-dimensional behavior $\langle \tau \rangle \approx g^2$. In Figure 3, we display the MFPT vs the number of generations of a dendrimer for different values of the rates K_1 and K_2 . The problem solved here is closely related to the effect of a bias in a protein folding model discussed by Zwanzig et al.,¹⁰ where calculation of the MFPT to reach the native configuration demonstrates a change from an inefficient random search (exponential in the number of building unit) to an efficient

(9) Van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North-Holland: Amsterdam, 1981. Weiss, G. H. *Adv. Chem. Phys.* **1966**, *13*, 1.

(10) Zwanzig, R.; Szabo, A.; Bagchi, B. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 20.

(11) Balzani, V.; Campagne, S.; Denti, G.; Alberto, J.; Serroni, S.; Venturi, M. *Sol. Energy Mater. Sol. Cells* **1995**, *38*, 159.

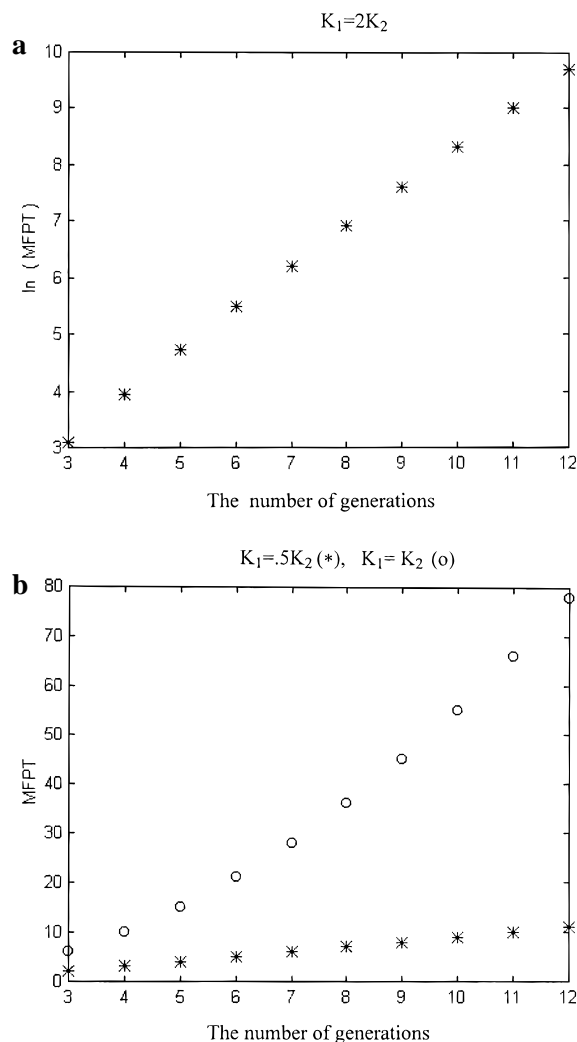


Figure 3. Dependence of the MFPT, $\langle \tau \rangle$, on dendrimer size, g . Plotted are the different cases in the table. Note the large effect of the energetic bias. As an example for $g = 10$, $\langle \tau \rangle$, in $1/K_1$ units, scales as 4072:55:9 for $K_1 = 2K_2$, $K_1 = K_2$, and $K_1 = 0.5K_2$, respectively.

biased search. This again emphasizes the difference between random and funnel-assisted exploration of space to reach a trap. The idea to control the trapping process by using the interplay between geometric bias and energetic funnel in dendrimers should be considered when designing artificial antennae.¹¹ Synthesizing extended vs compact dendrimers is the first step in this direction.⁵

Acknowledgment. We thank Dr. G. M. Rozman for fruitful discussions. J.K. acknowledges the support of the German Israeli Foundation (GIF). R.K. acknowledges NSF Grant DMR-9410709.

JA970972F