Energy Transfer in Compact and Extended Dendrimers

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Introduction

Dendrimers are an exciting class of nanoscale molecules with a wide array of applications. They have a regular and highly branched 3D architecture of which the basic components are: core, branches and end groups.

Dendrimers can be synthesized relatively easily and with few structural defects. Their repetitive nature and uniformity makes it easy to control their size, composition and chemical reactivity very precisely. Because of their versatility they are truly multifunctional nano-devices used in films, membranes, coatings, integrated circuits, sensors, catalysts, drug delivery systems and as light harvesting systems. Dendrimers could be critical to improving the efficiency of current solar technology[1].

In our investigation we mathematically modeled light harvesting reactions and similar diffusion controlled reactions in compact and extended dendrimers. The processes were modeled as a Markovian chains[2-3], where at each step the particle or photon independently jumps to another site on the structure according to some probability distribution until it reaches a reaction center or "trap." The efficiency of energy transfer[4] is analyzed computationally by random walks calculated from each site to the trap and the average random walk on the system.

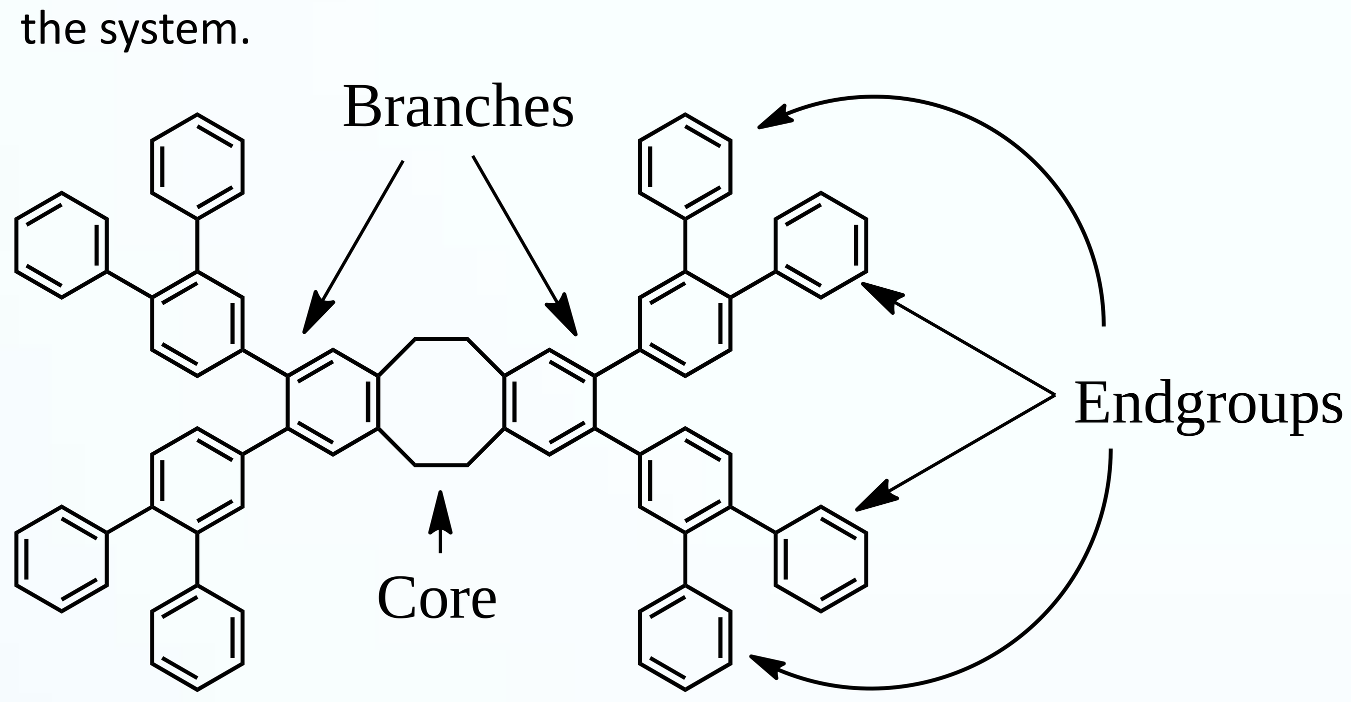


Figure 1. Basic dendrimeric structure. Two branches (b=2), valency of 2 (v=2).

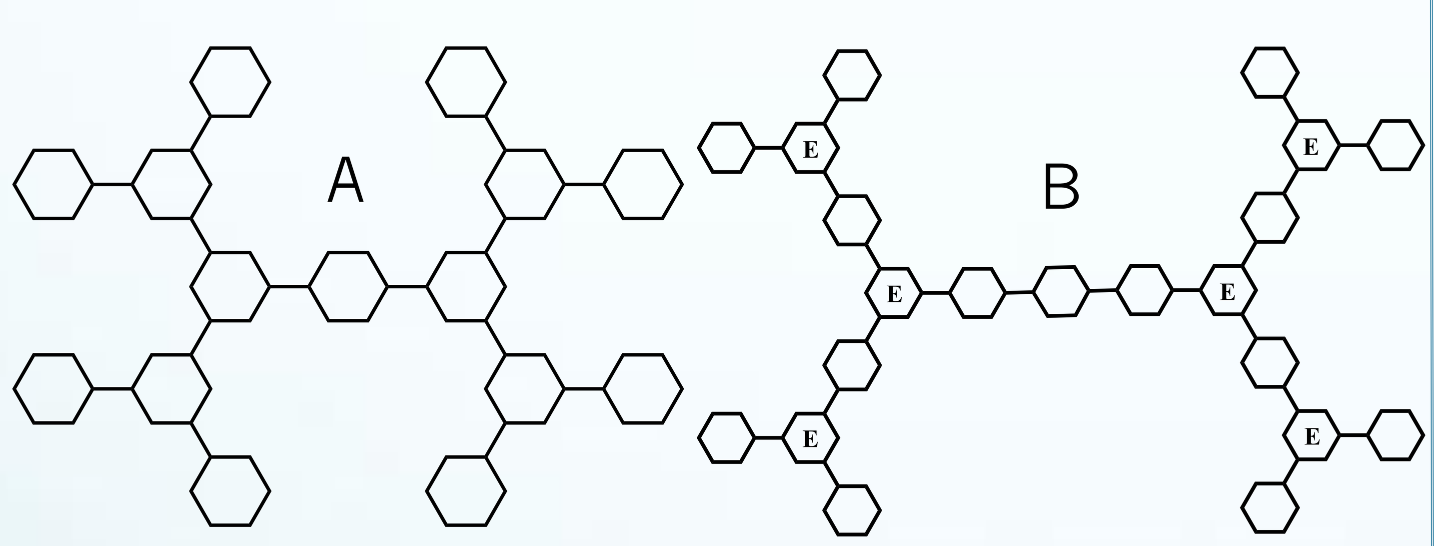


Figure 2. Compact and extended dendrimers. Structure A on the left is a compact dendrimer of the second generation (n=2). Structure B is an extended dendrimer of the same generation with extensions labeled with an E, it has more sites than structure A.

Objective

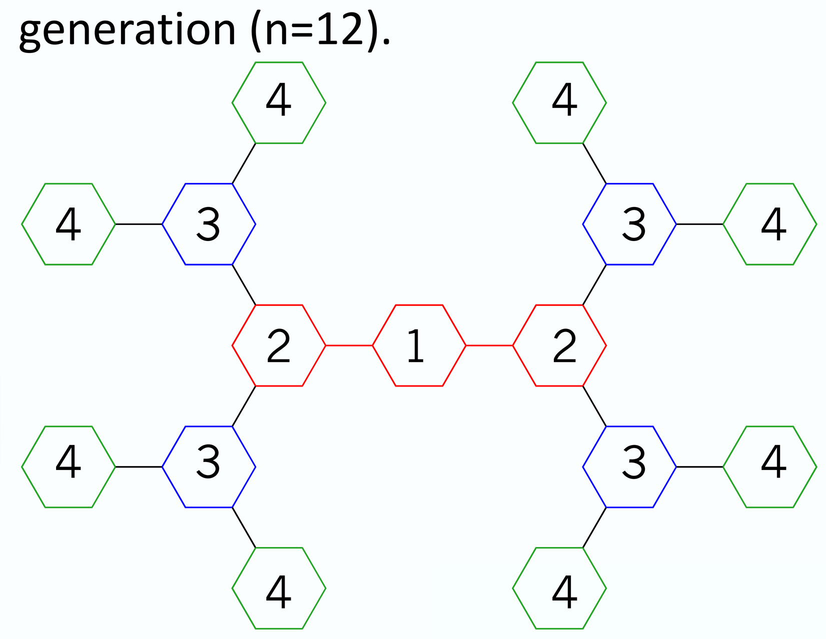
To understand the influence of growth and expansion of a system on the walklengths and by extension the efficiency of the dendrimeric systems. And to understand how energy attracting or particle absorbing endpoint functional groups can influence the efficiency of the systems.

Acknowledgements

I would like to thank Dr. Roberto Garza-López, Chair of the Chemistry Department at Pomona College for his guidance and the Howard Hughes Medical Institute for its support.

Methods

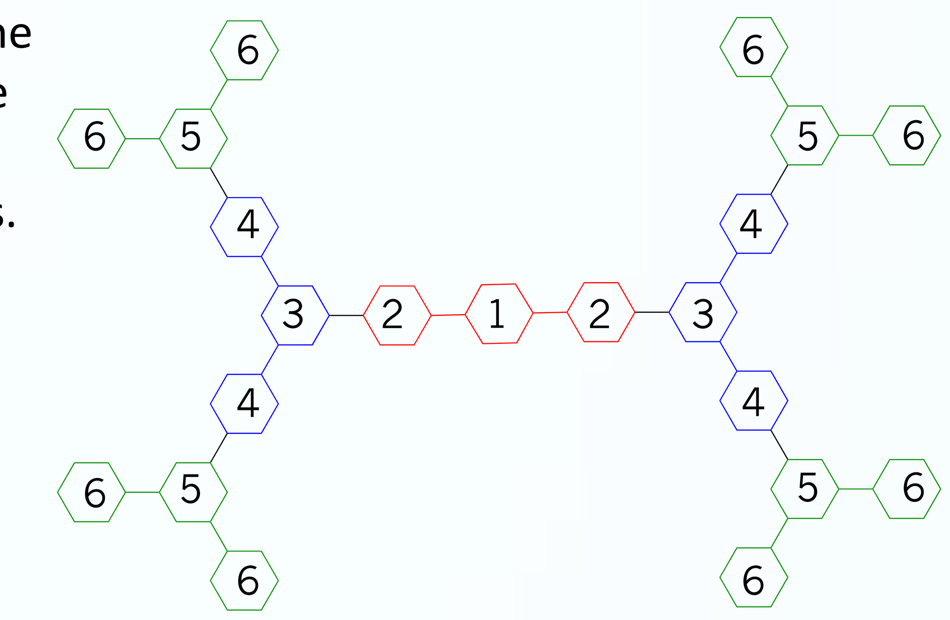
Visual representations of two families of dendrimers with 3 and 4 branched growths (b=3 and b=4) were constructed. Using a systematic numbering/labeling system, based on the symmetry of the fractal-like structures, we labeled all corresponding active sites in each dendrimer for growths up to the 12th generation (n=12).



Using Microsoft Excel® equations are constructed representing walklengths from each site in terms of the probability of a sample particle, jumping to its neighboring sites. Next, the equations are stored as systems of equations on Maple® a computational engine. Using the software we solve the systems for the particular walklengths of each active site on the structure and for the average walklength of all active sites.

Figure 3 & 4. 3rd Growth (b=3) compact and extended dendrimers with symmetrically numbered active sites. Each growth denoted by a different color.

After initial calculations we decided to vary the absorbency of the endpoints on each structure as this would relate better to energy transfer in dendrimeric systems. Walklength for members of each dendrimer family with endpoint transmittance at 0% and 50% (corresponding values of p=1 and 0.5 respectively) were calculated.



Results

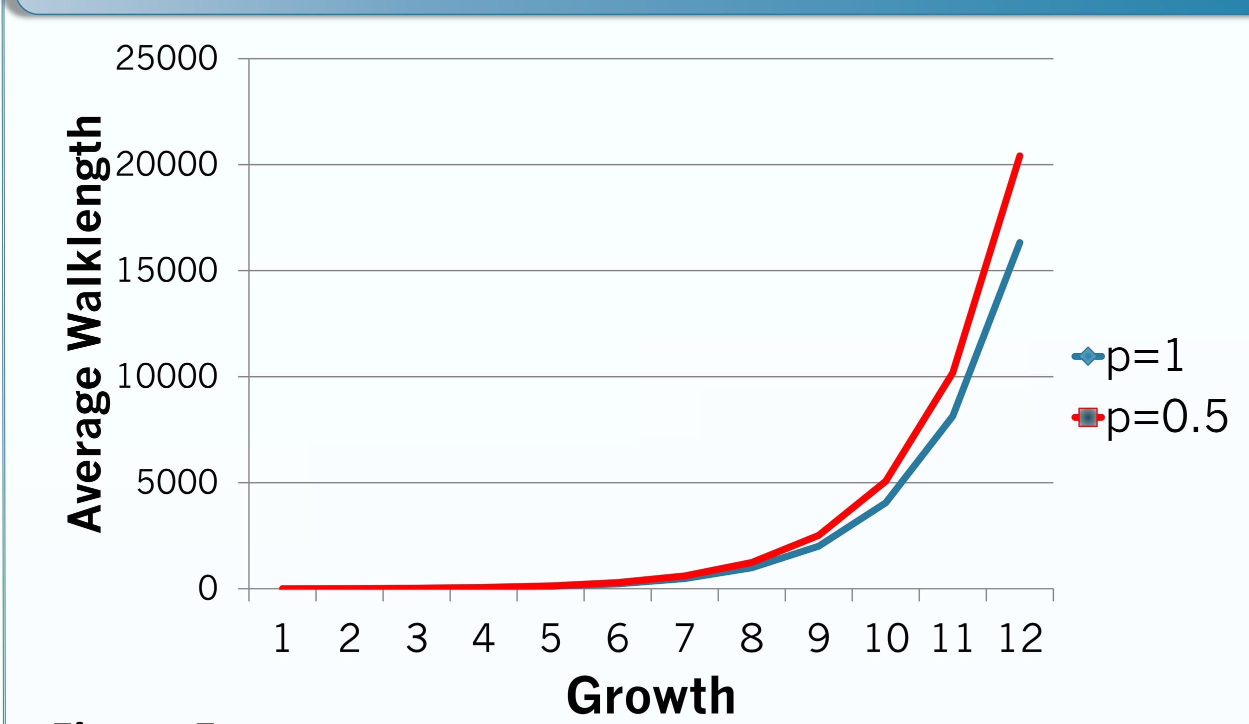


Figure 5. Average Walklengths of Compact Dendrimer (b=3). When transmittance of terminal site is reduced average walkengths increase.

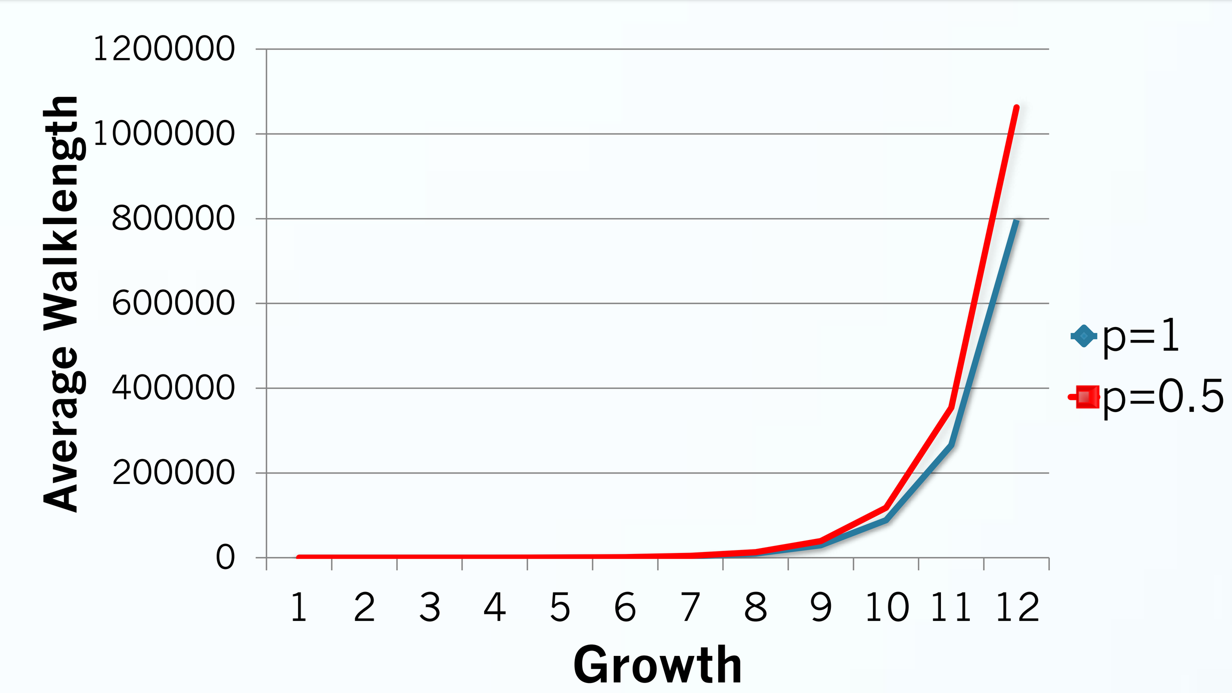


Figure 6. Average Walklengths of Compact Dendrimer (b=4). When transmittance of terminal site is reduced average walkengths increase.

Table 1. Average Walklengths of Compact Dendrimer (b=3).

	Walklengths		
Growth	p=1	p=0.5	% p=1/p=0.5
1	1	2	50.0
2	5.666666665	8.333333331	68.0
3	17.85714285	24.14285714	74.0
4	45.66666666	59.53333332	76.7
5	105.1935484	134.6129032	78.1
6	228.5238095	289.4761904	78.9
7	479.7244094	604.1968503	79.4
8	986.8431371	1238.827451	79.7
9	2005.911937	2513.403131	79.8
10	4048.951124	5067.946236	79.9
11	8139.97313	10182.47044	79.9
12	16326.98534	20416.98387	80.0

Table 2. Average Walklengths of Extended Dendrimer (b=3).

	Walklengths		
Growth	p=1	p=0.5	% p=1/p=0.5
1	3.5	5	70.0
2	20.83333333	25.5	81.7
3	68.07142857	79.78571429	85.3
4	177.6333333	204.3	86.9
5	413.9516129	471.5	87.8
6	905.4047619	1025.785714	88.3
7	1908.287402	2155.468504	88.5
8	3934.809804	4436.770588	88.7
9	8009.112524	9021.840509	88.8
10	16179.28495	18214.77273	88.8
11	32541.38178	36623.62506	88.9
12	65287.43553	73464.43187	88.9

Discussion

The results indicate that walklengths on the system are dependent primarily on the growth or extension of the the active sites from the central trap at the core. Affinity of the the active sites for the energy or particle traveling in the system also effects walklengths. If the affinity is increased in the endpoints, as it would be in light harvesting dendrimers with chromophores attached at the endpoint, the walklength or mean travel time to the reaction center is increased. Although growth or expansion leads to higher walklengths, the percentage of similarity in average walklengths between dendrimers with particle attracting terminal sites and those with no relatively greater affinity is greater in extended dendrimers.

Future Directions

We are extending our study by placing different types of acceptors at the terminal sites and donors within the dendrimer and study the energy transfer by solving the system of stochastic equations for the lattice. This will allow us to compare the transfer efficiency as a function of size, nature and number of the donors and acceptors

References

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