Light Harvesting and Energy Transfer in Dendrimers

I. Introduction

Dendrimers, a special class of tree-like, hyperbranched, three-dimensional macromolecules, have attracted considerable attention recently.\(^1\)\(^2\) Controlled synthesis of dendrimers through either divergent or convergent methods results in their size and structure being both regular and well-defined. The unique physical properties of dendrimers have given rise to several important applications. In particular, dendrimers are now recognized to have important roles in catalysis, host-guest chemistry, optical electronics, biology and drug delivery.\(^3\)\(^4\)

In nature, the light harvesting and energy transfer processes involve transferring the energy of photons absorbed by a light-absorbing antenna moiety to a nearby secondary energy acceptor species. Thus, artificial light-harvesting systems capable of converting solar radiation into a useful source of energy with similar efficiencies would be extremely beneficial. Recognizing this fact, the interest in molecules and molecular assemblies capable of light harvesting and energy transfer has expanded greatly. In this seminar, light absorption followed by nearly quantitative energy transfer through the dendritic backbone to a core or an encapsulated chromophore will be discussed.
II. Principles of Energy Transfer

When a cuvette containing donor and acceptor molecules is illuminated by light at a certain wavelength, the donor molecules adsorb photons and become excited. The donor excited state then decays by two competitive pathways, energy transfer to the acceptor and donor fluorescence. The scheme illustrating these processes is shown below:\(^5\)

\[
\begin{align*}
D + A \xrightarrow{h} & \quad D + A \\
\uparrow \nu_E & \quad \uparrow \nu_A \\
D + A + h\nu_E \rightarrow D^* + A & \rightarrow D + A^* \\
\downarrow \nu_E & \quad \downarrow \nu_A \\
A + D + h\nu_D & \quad A + D + h\nu_A
\end{align*}
\]

where \(K_D\) is the radiative decay rate of the donor without energy transfer, \(K_T\) is the rate of energy transfer to the acceptor, \(K_A\) is the radiative decay rate of the acceptor, \(h\) is Planck’s constant, \(K_{Di}\) and \(K_{Ai}\) are radiationless decay constants, and \(\nu_E\), \(\nu_D\), and \(\nu_A\), are the frequencies of donor excitation, donor fluorescence and acceptor fluorescence, respectively. The fraction of absorbed photons that are transferred, without radiation, to the acceptor is called the efficiency of energy transfer, \(E\):

\[
E = \frac{K_T}{K_T + K_D + K_{Di}}
\]

To observe energy transfer clearly, the following conditions must be met: (1) the donor and acceptor chromophores must have strong electronic transitions in the near ultraviolet to near infrared spectral range; (2) there must be considerable overlap of the excited donor emission spectrum with the absorption spectrum of the acceptor; (3) the donor and acceptor should be spatially close (~10-100 Å).\(^5\) Thus, to achieve high quantum yield during energy transfer, careful structural design of dendrimers is important.
III. Energy Transfer by “Hopping” and Funneling Processes in Dendrimers

Two basic characteristics of dendrimers make them promising candidates for light harvesting: (1) exponential growth of the number of peripheral absorbing units with their generation number; and (2) the relative short distance between the periphery and the center, where a photochemical sensor or a trap can be located. In the hopping process in dendrimers, an energy funnel is created by the monotonic decrease in electronic excitation energy for each generation toward the locus. When the dendrimer is illuminated by light, excitations initially localized at the molecular periphery are influenced by thermodynamic bias, and preferentially “hop” inward toward the center.

“Compact” and “extended” Bethe dendrimers have been synthesized and characterized by Moore et al. The compact dendrimers do not act as energy funnels due to their energetically degenerate nature. In contrast to the compact dendrimers, with increasing length legs toward the center of the molecules, the extended Bethe dendrimers show very efficient energy transfer due to the energetic bias (Fig. 1A).

In the associated perylenic derivatives of both compact and extended Bethe dendrimers, perylene acts as an exciton trap that collects absorbed photonic energy at the base of the energetic funnel (Fig. 1B). The energy gradient inherent in the extended nanostar molecule is sufficiently larger than the entropic hopping bias toward the...
periphery. Thus rapid and efficient funnelling of the absorbed light energy toward the locus occurs with nearly 100% energy transfer efficiencies.

IV. Dendrimers as Scaffolds for Energy Transfer

Unlike hopping energy transfer process, dendrimers can act as scaffolds for energy transfer and do not play a role in energy transfer. In considering the concept of resonance energy transfer and to maintain high energy-transfer efficiency in dendrimers, it is essential to maintain a good spectral overlap between the emission spectrum of the donor dye and the absorption spectrum of the acceptor dye and to select moieties with high transition dipole moments. Fréchet et al. synthesized a series of dye labeled poly(arylether) dendrimers using the laser dye coumarin 2 as the terminal donor chromophore and coumarin 343 as the focal acceptor dye (Fig. 2). The terminal chromophores collectively act as an antenna for light harvesting, while the focal dye plays the role of a fluorescent probe. In these dye-labeled dendrimers, light is absorbed by the numerous peripheral chromophores followed by quickly funneled to a fluorescent core with a remarkably high efficiency (Fig. 3). Since the whole transfer process is independent of the dendritic architecture, the role of the dendrimers backbone is a structural rather than functional one. This approach provides exceptional flexibility in

Fig. 2. Structure of the G-4 dye-labeled dendrimer.11

Fig. 3. Absorption and emission spectra of the model donor and acceptor fragments.11
that additional features, such as affinity towards a cell, or a drug, can be easily introduced by simply changing the components of the dendrimer.

V. Energy Transfer in Host-guest Systems

Meijer and coworkers demonstrated another type of energy transfer—the transfer occurred in host-guest complexes, from the arms of dendrimers to the encapsulated dye molecules. Poly(propylene imine) dendrimers were functionalized with conjugated oligo(p-phenylene vinylene) (OPV) groups through an amide linkage. Water-soluble anionic dyes can be extracted into organic phases with high efficiency by these functionalized dendrimers. Based on acid-base interactions between the tertiary amines and the anionic units of the guest, G3 can trap 7 Sulforhodamine B molecules while G5 can load 26. The energy transfer efficiency of the host-guest assemblies is only about 40% and lower than the covalently linked donor and acceptor systems. Fig. 4 shows the schematic energy transfer process in the G3/Sulforhodamine B complex. However, drop-cast thin films of the host-guest systems show almost complete quenching of the OPV fluorescence with higher than 90% transfer efficiency. Thin films constructed from OPV dendrimers with Rhodamine 6G, Rhodamines 101, and Sulforhodamine 101 as the acceptor also show very efficient energy transfer.

Furthermore, these dendrimer/dye systems mix very well with organic semiconducting poly(p-phenylene vinylene) (PPV) polymers. Energy transfer is observed from the organic PPV polymer to the Sulforhodamine B dye with the OPV units acting as

Fig. 4. Schematic representation of the energy transfer process taken in the G3/Sulforhodamine B (Black Bars) complex.
a compatibilizer in these systems. A promising property of this type of system is the
ability to adjust the emission wavelength of semiconducting polymers.

VI. Conclusion

Several examples of nanoscale photonic molecular assemblies in which light
absorption is followed by nearly quantitative energy transfer through “hopping” and
funneling processes in dendrimer to a core chromophore, using dendrimers as scaffolds,
and energy transfer in host-guest systems have been described. With the characteristics of
high quantum yields, good solubility and a large range of versatility, these molecules may
find future applications in photonic devices such as light-emitting diodes, fluorescent
sensors, and as fluorescent labels for biological molecules.

VII. References

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