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Energy Transfer and its Regulation in Supramolecular Systems

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Hania, P. R. (2005). *Energy Transfer and its Regulation in Supramolecular Systems*. s.n.

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CHAPTER 1

Introduction: Energy Transfer Systems and Molecular-Scale Devices

> *Q: It's an unknown — isn't that enough?*
> *Picard: If you'd earned that uniform you're wearing, you know it's the unknown that brings us out here*
>
> Star Trek: TNG

In the last few years the first realizations of single-molecule transistors have started to appear,[1–4] following the theoretical description of organic electronic devices in the seventies.[5] Other recent examples of single-molecule devices are molecular wires (see for instance)[6–9] and the bisthienylcyclopentene-based photoswitchable resistor investigated by Dulic et al.[10] and He et al.[11] Although molecular-scale devices are still 'proofs of principle' rather than practical appliances, their study drives advancements in the fields of organic synthesis, solid-state physics and most of all the investigation and manipulation of matter at the molecular level.

Such devices, in particular the ones that produce specific (nonrandom) motion or perform logical operations, usually consume energy. Therefore in building functional molecular systems an important task is the efficient and site-specific delivery of the energy needed to perform these tasks.

Many functions at the (supra)molecular level have been effectively realized in nature, and energy delivery is no exception. Clear examples are therefore available to developers of synthetic energy transport systems.

In plants and animals, the energy consumed by cellular functions and growth is stored chemically. Green plants and some bacteria 'harvest' this energy from sunlight by means of their photosynthetic systems.[12–14] The light harvesting process starts with the absorption of sunlight by an extensive antenna system consisting of many chromophores, usually a combination of chlorophylls and carotenes with matching absorption bands. The collected energy is transferred to the so-called reaction center and used there to drive an electron transfer reaction. This in turn initiates a series of slower chemical reactions that store the solar energy.

In order to drive the electron transfer reaction in the reaction center continually, the total absorption cross section of the antenna system surrounding it needs to be large, and delivery of the absorbed energy should be efficient. One way in which the first requirement can be met is to pack hydrocarbon chromophores at a high density. This is realized in nature by binding to immobilized proteins, for instance in the LH2/LH1 system of purple photosynthetic bacteria, or via the formation of large aggregates (in the chlorosomes of green photosynthetic bacteria). Efficient delivery is ensured in both cases by a so-called 'energy funnel', which consists of a series of chromophores arranged in order of decreasing excitation energy. The resulting energy gradient directs the absorbed energy to the chromophore of lowest energy, which is located at the reaction center itself.

Naturally, synthetic light harvesting antennas are built on the same principles of high chromophore density and energy funneling, but the resulting structures are necessarily more simple. One important class of accessible architectures is formed by dendrimers, large treelike molecules consisting of many arms that branch out from a central point.[15,16] A high local density of chromophores can be realized by attaching them to the terminal points of the dendrimer branches, while an energy funnel can be created by placing a low-energy chromophore at the central point. An advantage of these structures is that they are completely chemically synthesized, which makes them easier to design compared to self-assembled supramolecular systems.

However, synthesized dendritic systems are of limited size. When energy has to be transferred over longer distances, self-assembly of large structures from many smaller constituents as seen in green bacteria becomes the most viable construction method. Moreover, reversible aggregation offers the possibility to replace photodamaged components without the need to replace a complete antenna system. Aggregation in such systems is based on hydrogen bonding, π-stacking and hydrophobic interactions.[17,18]

In this thesis, two relatively simple synthetic energy collecting systems are investigated using steady-state and time-resolved electronic spectroscopy. The first tool yields insight into the nature of the excited states on the systems, the latter into the nature of the energy transfer processes and interactions among excitations. The same methods are used to study the dynamics of a molecular photochromic switch, with the goal in mind of incorporating them into energy collecting systems to regulate energy transfer.

The thesis is organized as follows. Chapter 2 covers the main experimental methods: time-resolved pump-probe and fluorescence spectroscopy, which are used to probe the ultrafast dynamics of the investigated systems, and steady-state linear dichroism. Technical details of the experimental setups are given, as well as an overview of the experimental concepts. A description of energy transfer processes (not our work), needed to interpret our experimental results, is then provided in chapter 3. Here we focus on the assumptions that lead to expressions for the Förster energy transfer rate and Frenkel exciton states.

This provides the background for the three main chapters covering the experimental results obtained by us. First, a study of cylindrical J-aggregates is presented in chapter 4. As indicated, these huge (10^4–10^5 monomers) structures resemble the light harvesting antennas found in green photosynthetic bacteria.[19] The strong coupling between the molecules that make up these aggregates results in excitonic states that are delocalized over a few to tens of molecules. The cylindrical geometry of the system then produces a multiple-band excitonic spectrum, which is analyzed in section 4.2.3 using a Frenkel exciton model developed by Didraga et al.[20–22] Subpicosecond energy transfer is found to occur from the outer to the inner wall, which explains the observed fluorescence spectrum. In addition, annihilation-assisted backtransfer is observed at high irradiation doses.

Then an example of a dendritic light harvesting system is studied in chapter 5. One reason for selecting such a multiple-donor/single acceptor architecture is that it allows to investigate interactions between multiple excitations on a single system. The studied molecule is a typical example of a weakly coupled system, in which the energy transfer process can be described using the Förster equation. The energy transfer rate is determined at low excitation power, and the effects of multiple-donor excitation on the transfer behavior are extensively investigated.

Finally, chapter 6 details the reaction pathways and ultrafast reaction dynamics of a bisthienylcyclopentene-based photochromic switch, which closely resembles the systems that were used as single-molecule resistor.[10,11] *Perfluoro* and *perhydro*cyclopentene analogs are compared in order to establish the effects of electronegative groups at the bridging unit.

These three studies will each be introduced further at the beginnings of the respective chapters.

References

[1] Piva, P. G.; DiLabio, G. A.; Pitters, J. L.; Zikovsky, J.; Rezeq, M.; Vogel, S.; Hofer, W. A.; Wolkow, R. A. *Nature* **2005**, *435*, 658.

[2] Kubatkin, S. *Nature* **2003**, *425*, 698–701.

[3] Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruna, H. D.; McEuen, P. L.; Ralph, D. C. *Nature* **2002**, *417*, 722–725.

[4] Liang, W. J.; Shores, M. P.; Bockrath, M.; Long, J. R.; Park, H. K. *Nature* **2002**, *417*, 725.

[5] Aviram, A.; Rathner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277–283.

[6] Xu, B.; Xiao, X.; Tao, N. J. *JACS* **2003**, *125*, 16164.

[7] Xu, B.; Tao, N. J. *Science* **2003**, *301*, 1221–1223.

[8] Dekker, C. *Physics Today* **1999**, *52*, 22.

[9] Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones II, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705–1707.

[10] Dulic, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402.

[11] He, J.; Chen, F.; Liddell, P. A.; Andreasson, J.; Straight, S. D.; Gust, D.; Moore, T. A.; Li, J.; Sankey, O. F.; Lindsay, S. M. *Nanotechnology* **2005**, *16*, 695–702.

[12] van Grondelle, R.; Dekker, J.; Gillbro, T.; Sundstrom, V. *Biochim. Biophys. Acta* **1994**, *1187*, 1.

[13] Crofts, A. R. *http://www.life.uiuc.edu/crofts/bioph354* **2000**.

[14] van Amerongen, H.; van Grondelle, R.; Valkunas, L. *Photosynthetic excitons;* World Scientific Pub Co: Singapore, 2000.

[15] Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688.

[16] Tomalia, D. A.; Naylor, A. M.; Goddard III, W. A. *Angew. Chem. Int. Ed.* **1990**, *29*, 138–175.

[17] Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chemical Reviews* **2005**, *105*, 1491–1546.

[18] Shimizu, T.; Masuda, M.; Minamikawa, H. *Chemical Reviews* **2005**, *105*, 1401–1444.

[19] Didraga, C. *Optical properties of Frenkel excitons in cylindrical molecular aggregates;* Ph.d. thesis Rijksuniversiteit Groningen: Groningen, 2004.

[20] Didraga, C.; Klugkist, J.; Knoester, J. *J. Phys. Chem. B* **2002**, *106*, 11474.

[21] Didraga, C.; Knoester, J. *J. Lum.* **2003**, *102*, 60–66.

[22] Didraga, C.; Knoester, J. *J. Chem. Phys.* **2004**, *121*, 946.