

University of Groningen

Localization and transport of excitation energy in inhomogeneous supramolecular arrays

Vlaming, Sebastiaan Maarten

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:

2010

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Vlaming, S. M. (2010). *Localization and transport of excitation energy in inhomogeneous supramolecular arrays*. s.n.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Chapter 1

Introduction

1.1 Introduction

Feynman was right: there indeed is plenty of room at the bottom [1]. Throughout the years, it has been possible to manipulate matter at ever decreasing length scales. This has led to the rise of nanoscience, where materials are being engineered on molecular length scales. The promise of further miniaturization of all kinds of devices is not only scientifically, but also economically of great interest. However, when one arrives at the nanoscale, one also enters the realm of quantum physics. This necessitates a whole new way of looking at such miniature devices, and not only poses problems, but also allows one to consider all kinds of novel functionalities. One example that is of great interest is the quantum computer [2, 3], which in principle allows for extremely efficient algorithms for certain problems that conventional computers have a hard time with [4, 5]. However, quantum computers are difficult to realize in practice. A large variety of different physical systems has been proposed, but each so far fails on a number of criteria that must be fulfilled to create a working quantum computer [6].

There are two fundamentally different approaches to obtaining nano-structured materials. In the top-down approach, one starts out from macroscopic structures and subsequently reduces certain dimensions of the device in question to the nanoscale. We will be more concerned with the alternative: the bottom-up approach, where one builds up the nanostructure by arranging molecules and atoms in a particular fashion. It is clear that the bottom-up approach to nanoscience is intimately linked with synthetic chemistry; one wants to be able to manipulate the behavior of molecules so that certain predefined patterns or structures are produced. A very promising strategy to produce structured supramolecular systems

is self-assembly, where under the right circumstances non-covalent interactions between the molecules will lead to an ordered arrangement of the molecules [7–10]. Self-assembly plays a crucial role in creating supramolecular structures in biological systems and, likewise, allows for the creation of synthetic structures such as aggregates or nanotubes. By manipulating the circumstances under which self-assembly takes place, such as the structure of the monomer molecule, the solvent, temperature or external forces, it is possible to influence the assembling process and thus the end product.

In order to create truly useful nano-engineered applications, one first requires a toolbox of nano-devices with certain specific, simple functionalities. Over the last decade(s), a number of such crucial devices have been created on the nanoscale; examples are the molecular motor [11–13], single molecule transistors [14, 15], single molecule rectifiers [14, 16, 17], and single molecule optical switches [18, 19]. An important ingredient to successfully create useful nanodevices is the ability to transport energy in an efficient way from point A to point B. A structure that can perform this task is often referred to as a nanowire. We are interested in molecular wires that guide energy from a donor site to the acceptor site through strongly interacting molecules that are in close proximity. Such systems allow for excitation of the donor site by incoming light. Strong interactions between the molecules lead to the transport of energy, through transfer of the electronic excited states, from the donor to the acceptor site.

1.2 Molecular nanowires

We distinguish two types of molecular wires on the basis of the strength of their interactions. First of all, for chains with a relatively large distance between chromophores, the excited states can be considered to be located at only one chromophore at the time. As a result, the optical absorption of such a system can be considered as the sum of the absorptions due to its components. The interaction between the chromophores is mediated by Coulomb interactions, and the energy transport consists of hops from one chromophore to the other. This is referred to as incoherent transport. This is well described by Förster theory [20, 21], and its recent generalizations that go beyond simple dipole-dipole interactions and can account for solvent screening effects and correlations between the baths of the donor and acceptor [22, 23]. Examples of such chains have been realized over the past 15 years. In 1994, Wagner and Lindsey reported on a molecular wire, consisting of a boron-dipyrromethene dye as the donor site, a free base porphyrin as the acceptor site, while three covalently linked zinc porphyrin molecules functioned as the wire [24]. The total transport efficiency was measured to be 76 percent. More

recently, Sauer and co-workers realized a different type of molecular photonic wire, based on a number of different chromophores attached to a DNA scaffold, in such a way that a downward gradient in energy is realized [25,26]. However, the reported efficiency was only around 15 percent, where around 70 percent was expected from theoretical arguments. This loss in energy might be explained by suboptimal orientations of the various chromophores or additional interactions with the DNA backbone. The results of both these studies confirm that efficient transport over longer distances requires a directionality in the energy transfer.

The second type of molecular wire, and the one we are mostly interested in in this thesis, consists of strongly interacting chromophores. In that case, the electronic excited states will be coherently shared by many chromophores along the chains, leading to what are referred to as exciton states. The collective properties of the exciton states strongly differ from those of the individual chromophoric excited states; we will soon go into some more detail with regards to this. In principle, the fact that the excited states are collectively shared by portions of the chain should lead to rapid energy transfer within such domains. This is referred to as coherent transport. Strongly coupled molecular nanowires have been experimentally realized by creating structures with, for example, zinc porphyrins [27] or perylene polyisocyanides [28] in close proximity to each other. However, there are still practical problems that strongly limit the efficiency of strongly coupled nanowires. The strongly coupled systems realized so far are rather sensitive to heterogeneities in the environment, what is referred to as disorder in the exciton literature. Disorder will lead to local minima in energy on certain segments of the chain, which will tend to trap the excitation energy and prevent it from reaching the designated acceptor unit. In addition, no directed energy transport has so far been realized. Such problems might be overcome by adding an excitation energy gradient, i.e. a bias.

Of course, not all transport is purely incoherent or coherent. When the electronic interaction energies are comparable in magnitude to the couplings to vibrational modes, one enters a cross-over regime. It is possible to use a stochastic Liouville equation approach to describe these systems, such as the well-known Haken-Strobl-Reineker model [29–31].

1.3 Excitons and molecular aggregates

We will now briefly discuss the nature of collective electronic excited states, and some of the systems they typically occur in. Already in the 1930's, the existence of such excitations was suggested by Frenkel [32] and Peierls [33]. The general concept is introduced most easily by approximating each molecule by a two-level system,

consisting of the ground state and the optically dominant excited state. In case N such molecules are decoupled, there will be an N -fold degenerate lowest excited state, corresponding to the direct product of one molecule being in the excited state, while all others are in the ground state. This is referred to as a molecular exciton, where the electron and hole are located on the same molecule. Interactions between different molecules in the system will tend to delocalize the exciton wave function over a number of unit cells; such a shared excitation is known as a Frenkel exciton. In the molecular systems we consider, these interactions are mediated by the optical transition dipoles of the molecules. The delocalization does not alter the fact that the electron and hole will still be located in very close proximity; this kind of exciton is commonly found in systems with a small dielectric constant, so the charges of the electron and hole are hardly screened. Consequently, their binding energy is typically high, on the order of an electron volt.

In solid-state physics, another type of exciton is also commonly encountered, particularly in systems with a large dielectric constant. In that case, the electron and hole charges are screened to a large extent and thus only weakly feel each other's presence. This is the Wannier exciton [34,35], where the electron and hole are typically separated by a large number of lattice spacings. The weak electron-hole interaction implies a low binding energy, which may be of the order of 0.1 eV. The intermediate regime, where the electron-hole separation corresponds to a small number of lattice spacings and the exciton movement is thus accompanied by local charge redistributions, is usually referred to as a charge transfer (CT) exciton.

After introducing interactions between the molecules, the degeneracy of the excited states is broken, and the new eigenstates correspond to excitations that are coherently shared by a number of molecules. The splitting in energy of the various exciton states leads to a band of exciton states. Additional splitting can occur when there are multiple molecules or transitions per unit cell, this is referred to as Davydov splitting [36]. The delocalized nature of the electronic excited states has important consequences for the optical and transport properties, as the system will collectively interact with incoming light or its surroundings. The theory of these exciton states and their dynamics has been developed in more detail in later years [36–40].

In general, it is also crucial to include interactions with the environment. Inhomogeneities in the environment will lead to excitation energies and couplings that will vary from molecule to molecule; this is commonly referred to as disorder. In modeling this, one often takes the excitation energies (and sometimes also the couplings) as stochastic variables, described by some probability density which is often taken as a Gaussian distribution. This leads to localization of the Frenkel excitons, where the wave functions are no longer extended over the entire system, but only over some smaller region. The spatial extent of such a region is known as

the localization length.

An excellent example of a system where Frenkel excitons occur are molecular aggregates, which are systems where molecules are clustered in certain geometries, usually by self-assembly, and stabilized by non-covalent bonds (such as hydrogen bonds, Van der Waals forces, electrostatic forces, hydrophobic interactions, $\pi-\pi$ interactions). These systems have a long history. In 1937, Jelley [41] and Scheibe [42] independently observed strong spectral changes upon changing the concentration of the dye pseudo-isocyanine (PIC); the typical monomer band disappeared, while a narrow, red shifted absorption band appeared. These changes were attributed to the self assembly of molecular aggregates, where the monomers form semi-regular structures leading to collective optical properties. Aggregates where the exciton absorption peak is red shifted are nowadays referred to as J aggregates. Depending on the relative orientation of the molecules within the aggregate, it is also possible to obtain a blue shifted absorption peak; such systems are known as H aggregates. An important application for aggregates over the years are photosensitizers, in particular cyanine dyes [43].

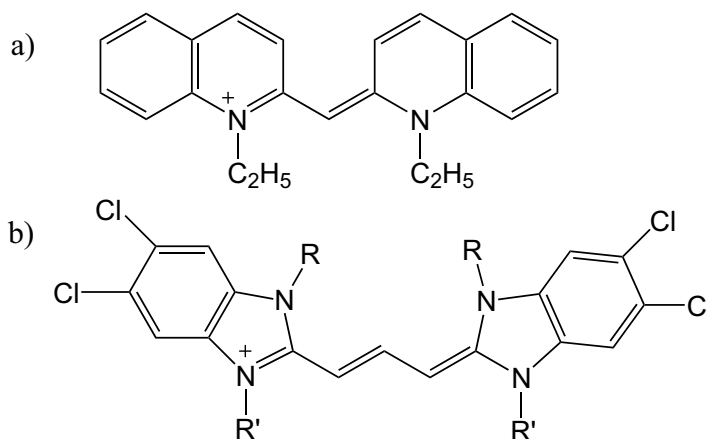


Figure 1.3.1: The chemical structure of several chromophores discussed in the text. Molecule a) is PIC. Molecule b) is the general structure of the 5,5',6,6'-tetrachlorobenzimidacarbocyanine dyes; depending on the sidegroups R and R' and the counterions, this chemical structure can amongst others correspond to TDBC or C8S3.

Many dyes are now known to spontaneously form aggregates under certain circumstances. Often, they tend to form regular structures of low dimensionality, such

as the linear aggregates formed by PIC [44], or the cylindrical aggregates formed by carbocyanines such as TDBC or C8S3 [45, 46].¹ Several porphyrin derivatives are also known to form cylindrical structures [47–51]. The chemical structure of several of these molecules is shown in Fig. 1.3.1.

1.4 Natural photosynthetic complexes

In fact, similar strongly interacting systems designed for capturing and transporting energy already exist in nature. The photosynthetic complex of many organisms functions by very similar principles [52–55]. In purple photosynthetic bacteria, such as *Rhodospseudomonas acidophila*, there are typically two light-harvesting (LH) complexes: the LH2 systems which initially collect the light surround the central LH1 complex, where in turn the reaction center is located [56]. As an example, we will briefly discuss the LH2 system in more detail.

The LH2 system consists of two rings: the B800 ring and the B850 ring [57]. The B800 ring consists of nine bacteriochlorophyll (BChl) molecules (see Fig. 1.4.1), which are weakly coupled. However, even in the B800 ring, excitonic effects are still observable and are important in correctly understanding the inner workings of the LH2 system [58]. These molecules collect the light, and subsequently transfer it to the B850 ring. The B850 ring consists of 18 BChl molecules, arranged in a ninefold symmetry. Here, the molecules are closer to each other which leads to excitonic excited states. Subsequently, rapid further transfer to the LH1 system and to the reaction center occurs on a timescale of 5–25 ps [59]. The transport efficiency in these photosynthetic systems is quite high; over 95 percent of the absorbed energy ends up at the reaction center [58]. This fact inspires us to consider similarly structured synthetic structures as candidates for efficient synthetic light-harvesting antennas.

The structure of this amazingly efficient natural photosynthetic system ties together many of the topics treated in this thesis. The first topic is light harvesting and the subsequent transfer of energy, which is made unidirectional because of a bias, i.e. a gradient in excitation energy. The B850 ring has excited states that are lower in energy than the B800 rings, while the subsequent energy transfer to the LH1 and the reaction center is also made more efficient due to the lower energy of each structure compared to the previous one. Secondly, it is crucial to consider the collective nature of the excited states in the B850 ring, which are well described by the Frenkel exciton Hamiltonian. Thirdly, the structure of the B800 and B850 rings, which have a cylindrical symmetry that also appears in the cylindrical aggregates

¹5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(4-sulfobutyl)-benzimidazolocarbo-cyanine and 3,3'-bis(3-sulfopropyl)5,5',6,6'-tetrachloro-1,1'-dioctylbenzimidazolocarbo-cyanine molecules, respectively.

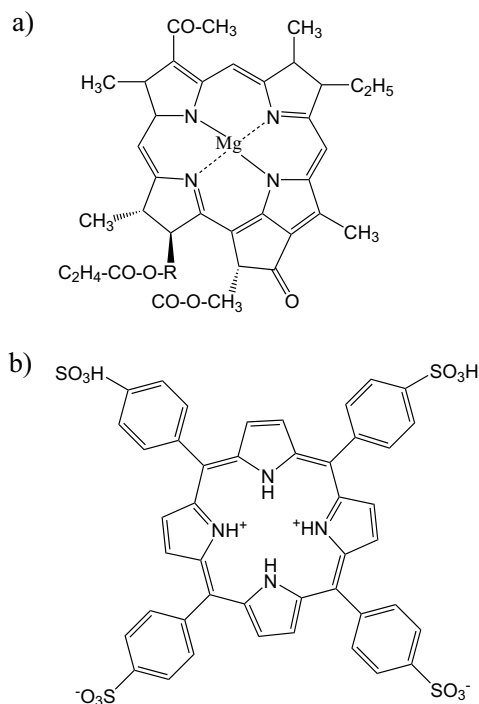


Figure 1.4.1: The chemical structure of two chromophores discussed in the text. Molecule a) is a bacteriochlorophyll present in the LH2 complex, discussed in Section 1.4; the side group R is a phytol group [60]. Molecule b) is the zwitterionic form of TPPS₄, a porphyrin derivative whose aggregates are studied in detail in Chapter 6. Note the common ringlike structure and the abundance of pyrrole rings.

studied in Chapter 6 and consist of monomers (BChl's) that have a comparable structure to the TPPS₄ monomers considered in Chapter 6 of this thesis (see also Fig. 1.4.1). Finally, disorder and deviations from a perfect, homogeneous structure are crucial in adequately understanding the LH2 system [61–63].

1.5 Outline

In Chapter 2, we will begin by providing the background to the formalism that we employ in the later chapters. Some basic results related to the Frenkel exciton model will be derived, with particular focus given to the optical and transport

properties and the role disorder plays in this.

Chapter 3 proceeds with studying the effect of a linear variation of the excitation energies of a chain, i.e. a bias, on the transport properties. One may naively think that such a bias will always enhance the transport efficiency, but it will be shown that this is incorrect. The localization induced by the bias, its effect on the excitation, transport, and trapping subprocesses, and the additional possible complications of disorder and nonzero temperatures are analyzed, where it is shown that in general there is some specific, nonzero bias value that optimizes the transport efficiency.

Chapter 4 revisits a number of classic topics in localization theory. Traditionally, box disorder or Gaussian disorder distributions are most commonly used in such studies. Lorentzian disorder is a special case in the study of disordered systems, in that it allows for analytical solutions for many quantities, such as the disorder-averaged Green's function. However, it turns out that many effects that commonly occur in disordered systems are completely different for Lorentzian disorder as compared to disorder distributions with a finite second moment. In particular, we show that exchange narrowing is absent, that the structure of the wave functions is modified considerably, while also the scaling of the localization length with disorder is quite different.

In Chapter 5, this study is extended to Lévy distributions, a class of heavy-tailed distributions that contains Gaussians and Lorentzians as special cases. Such disorder distributions can lead to the novel effect of exchange broadening. In addition, we observe strong alterations of the wave function structure, characterized by segmentation induced by sites with energies in the tails of the distribution. This induces a blue shift of the absorption spectrum upon increasing the amount of disorder, in contrast to the well known conventional red shift. Also the scaling of the localization length and the width of the exciton absorption peak with disorder are generalized, with considerable differences for the various possible choices for the disorder distribution.

Finally, Chapter 6 provides an analysis of the structure and the optical properties of meso-tetra(4-sulphonatophenyl)porphyrin (TPPS₄) aggregates. These molecules can aggregate into cylindrical structures, which have quite interesting optical properties. The similarity to naturally occurring photosynthetic systems is striking, in particular the cylindrical geometry they have in common and the similarity in chemical structure between the natural chlorophylls and the TPPS₄ molecules. We extend the exciton formalism for cylindrical geometries to multiple transitions per unit cell, and apply this to the TPPS₄ aggregates. This allows for a calculation of the polarization dependent absorption spectra that such a solution of aggregates will show. A comparison to the experimental spectra allows us to propose a microscopic structure of this system, which was hitherto unknown.