UNIVERSITY OF JYVÄSKYLÄ
DEPARTMENT OF CHEMISTRY

RESEARCH REPORT NO. 148

JUKKA AUMANEN

PHOTOPHYSICAL PROPERTIES OF DANSYLATED POLY(PROPYLENE AMINE) DENDRIMERS

Academic Dissertation for
the Degree of Doctor of Philosophy

UNIVERSITY OF JYVÄSKYLÄ
2011

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 148

PHOTOPHYSICAL PROPERTIES OF DANSYLATED POLY(PROPYLENE AMINE) DENDRIMERS

BY

JUKKA AUMANEN

Academic Dissertation
for the degree of
Doctor of Philosophy

To be presented, by permission of the Faculty of Mathematics and Science of the University of Jyväskylä for public examination in Auditorium FYS1, on November 4th 2011, at 12 noon

UNIVERSITY OF JYVÄSKYLÄ

ISBN 978-951-39-4477-3
ISSN 0357-346X

URN:ISBN:978-951-39-9977-3
ISBN 978-951-39-9977-3 (PDF)
ISSN 0357-346X

Jyväskylän yliopisto, 2024

ABSTRACT

Aumanen, Jukka
Photophysical properties of dansylated poly(propylene amine) dendrimers
Jyväskylä: University of Jyväskylä, 2011, 55 p.
(Department of Chemistry, University of Jyväskylä Research Report
ISSN 0357-346X; 148)
ISBN 978-951-39-4477-3
Diss.

Dendrimers are branched macromolecules having a treelike structural shape. Their symmetrical compact structure gives them unique properties as compared to irregularly branched polymers. In this thesis four generations of dansylated poly(propylene amine) (POPAM) dendrimers and their host-guest complexes with xanthene dyes are studied in order to obtain new experimental information on photophysical properties of dendrimers.

The internal dynamics of the dendrimers were investigated by time-resolved fluorescence anisotropy measurements at various temperatures. The time scales of the overall rotation and the local motions of the studied dendrimers were resolved and the volumes of the dendrimers were evaluated from the rotational correlation times. Surprisingly the volume of generation three and four dendrimers were observed to shrink when the temperature was increased. With the support of the results from molecular dynamics simulations the contraction was concluded to originate from the balance of intra- and intermolecular interactions.

The study of host-guest complexes concentrated to the intermolecular excitation energy transfer process from a dendrimer host to a xanthene dye guest. Femtosecond transient absorption spectroscopy was used to obtain EET rates for various host-guest combinations. EET rates were found to be practically independent on the dendrimer generation and the guest dye. The insensitivity of the EET rates to involved molecules was concluded to originate from almost identical average donor-acceptor distances. Further, guest to guest EET was observed in complexes having multiple guests.

New experimental information on dendrimers may help to develop novel dendrimer based applications in the future. Applications developed for artificial light harvesting or host-guest applications, e.g. drug delivery, may benefit from the studies presented in this thesis.

Keywords: dendrimers, internal dynamics, rotational correlation, excitation energy transfer (EET), light harvesting, host-guest complexes, time-resolved spectroscopy, transient absorption, fluorescence, time-correlated single photon counting, streak camera, anisotropy

Author's address

Jukka Aumanen
Department of Chemistry
P.O. Box 35
FI-40014 University of Jyväskylä
Finland
jukka.aumanen@jyu.fi

Supervisors

Professor Jouko Korppi-Tommola
Department of Chemistry
University of Jyväskylä

Reviewers

Professor Matti Hotokka
Fysikalisk kemi
Åbo Akademi
Finland

Professor Aatto Laaksonen
Department of Materials and
Environmental Chemistry
Stockholms Universitet
Sweden

Opponents

Professor Paola Ceroni
Dipartimento di Chimica "G. Ciamician"
Università di Bologna
Italy

PREFACE

The work of this thesis has been carried out in the Department of Chemistry at the University of Jyväskylä. The financial support from the graduate school LASKEMO is acknowledged.

First I would like to thank Professor Jouko Korppi-Tommola for offering me the opportunity to work in the interesting field of time-resolved spectroscopy, and always trusting me and the project.

The work of this thesis would not have been possible without collaboration with other research groups. First of all, spectroscopic measurements require samples, and the group of Professor Fritz Vögtle at the University of Bonn is gratefully acknowledged for the synthesis and purification of the dansylated POPAM dendrimers during the year 2005. Professor Villy Sundström is thanked for giving me an opportunity to carry out streak camera experiments in the University of Lund and Dr. Tero Kesti is thanked for practical help during the visit to Lund. The experimental results concerning the dynamics of dendrimers would have been rather difficult to interpret without the help of the molecular dynamics simulations by Dr. Gilberto Teobaldi and Professor Francesco Zerbetto. Especially, I would like to thank Gilberto for the comprehensive reports and prompt responses to my e-mails. You have been a great help to me.

Though being a solitary worker in this project at Jyväskylä, I have never felt alone at work, as I have the honour of being surrounded by such magnificent colleagues. In the beginning of my career I was also lucky to experience the great spirit of the tight Physical Chemistry community in "old building" and its tiny coffee room. Nowadays physical chemists are somewhat split up and the sense of community is perhaps partly lost, but at the same time it has given an opportunity to get to know many nice people working in Nanoscience Center.

In addition to colleagues I would like to thank all nice chemistry students I have been allowed to teach in the physical chemistry student lab and in exercise groups. To get students learn and understand chemistry, and sometimes to overcome their groundless fears of physical chemistry, has been highly rewarding and a good counterbalance to the research. It has been pleasure to teach you.

The success never comes without support. My deepest gratitude goes to my immediate family for all the care and love I have received through my life. Life may not be easy at every turn, nor has been, but with the support and love from the closest ones you can always carry on.

At last I would like to thank my nearest and dearest – Viivi: my wife, my beloved and my soul mate, and our children Vilppu and Valma - for being in my life. You make me feel myself extraordinary and precious like you are to me:

"In your eyes the light the heat, in your eyes I am complete, in your eyes…"

Jyväskylä, October 2011
Jukka Aumanen

LIST OF ORIGINAL PUBLICATIONS

This thesis is a review based on the original publications and the manuscript listed below and they are herein referred to by their Roman numerals.

I **Ultrafast energy transfer in dansylated POPAM–eosin complexes.**
J. Aumanen, V. Lehtovuori, N. Werner, G. Richardt, J. van Heyst, F. Vögtle and J. Korppi-Tommola,
Chem. Phys. Lett. **2006**, *433*, 75-79.
https://doi.org/10.1016/j.cplett.2006.11.034

II **Internal Dynamics and Energy Transfer in Dansylated POPAM Dendrimers and Their Eosin Complexes.**
J. Aumanen, T. Kesti, V. Sundström, G. Teobaldi, F. Zerbetto, N. Werner, G. Richardt, J. van Heyst, F. Vögtle, and J. Korppi-Tommola *J. Phys. Chem. B.,* **2010,** *114,* 1548-1558.
https://doi.org/10.1021/jp902906q

III **The effect of temperature on the internal dynamics of dansylated POPAM dendrimers.**
J. Aumanen, G. Teobaldi, F. Zerbetto and J. Korppi-Tommola
RSC Adv., **2011,** *In press,* DOI: 10.1039/c1ra00625h
https://doi.org/10.1039/C1RA00625H

IV **Energy transfer to xanthene dyes in dansylated POPAM dendrimers.**
J. Aumanen and J. Korppi-Tommola,
Manuscript submitted to Chem. Phys. Lett.
https://doi.org/10.1016/j.cplett.2011.10.061

The Author has carried out all spectroscopic measurements and analyzed the experimental results. All papers are written by the Author, excluding the parts in Papers II and III that concern MD simulations and the introduction section of Paper II.

OTHER PUBLICATIONS

List of the Author's other publications that are not included in this thesis.

1. **Study of Light Induced Dissociation Reaction of Ru(dcbpy)$(CO)_2I_2$ in Solution.**
   V. Lehtovuori, J. Aumanen, P. Myllyperkiö, M. Rini, E. Nibbering, J. Korppi-Tommola
   J. Phys. Chem. A., **2004**, *108*, 1644-1649.

2. **Characterization of used mineral oil condition by spectroscopic techniques.**
   J. Vanhanen, M. Rinkiö, J. Aumanen, J. Korppi-Tommola, E. Kolehmainen, T. Kerkkänen, P. Törmä
   Appl. Opt., **2004,** *43*, 4718-4722.

3. **Time-resolved coherent anti-Stokes Raman-scattering measurements of I_2 in solid Kr: Vibrational dephasing on the ground electronic state at 2.6-32 K.**
   T. Kiviniemi, J. Aumanen, P. Myllyperkiö, V. Apkarian, M. Pettersson
   J. Chem. Phys., **2005,** *123*, 064509.

4. **Dansylated Resorcinarenes.**
   N. K. Beyeh, J. Aumanen, A. Åhman, M. Luostarinen, H. Mansikkamäki, M. Nissinen, J. Korppi-Tommola, K. Rissanen.
   New J. Chem., **2007,** *31*, 370 – 376.

ABBREVIATIONS

CCD	charge coupled device
EET	excitation energy transfer
G	generation
MCP-PMT	microchannel plate photomultiplier tube
MD	molecular dynamics
NOPA	non-collinear optical parametric amplifier
POPAM	poly(propylene amine)
TCSPC	time-correlated single photon counting
TICT	twisted intramolecular charge transfer
UV	ultraviolet

CONTENTS

1 INTRODUCTION

Symmetrically branched macromolecules, dendrimers, are a relative new group of organic molecules with their history reaching back to the end of the 1970's. The beginning of the synthesis of dendrimers was a cascade method to produce hyperbranched molecules developed by Vögtle et al.[1] The first synthesis and characterization of dendrimers was introduced by Tomalia et al.[2] followed by another type of dendrimer by Newkome et al.[3] Since these pioneering works set the beginning of the dendrimer era, the research of the dendrimers has exploded and thousands of scientific articles on the subject have been published to date. At first the focus was on the synthesis to produce these structurally beautiful and fascinating molecules. Later the unique properties of the novel molecules attracted more attention and the ideas of the possible applications saw the light of the day. As dendrimers can be functionalized by attaching various molecular groups to a dendrimer core or periphery, dendrimers with desired properties have been designed. A high number of light absorbing chromophores in a single dendrimer form an effective light harvesting unit and a dendrimer hosting smaller molecules in its interior can function as a molecular drug delivery system. Producing molecular applications requires, however, basic knowledge of the properties of the molecules in question. The aim of this thesis is to study the dynamics of dendrimers in a timescale of molecular motions and to investigate dendritic light harvesting system that is effectively transferring harvested light energy to an encapsulated guest molecule.

1.1 Properties of dendrimers

The name "dendrimer" derives from the Greek word for tree, "dendron", owing to their symmetrical branched structure that is suggestive of trees. The anatomy of a dendrimer is presented in Figure 1.1. Dendrimer is composed of monomer units that are branched symmetrically from the centre of a dendrimer "the core". The number of branching points before an end group defines

the generation of the dendrimer. Each fragment from the core to the end groups is called "a dendron" and the pack of end groups "the periphery".

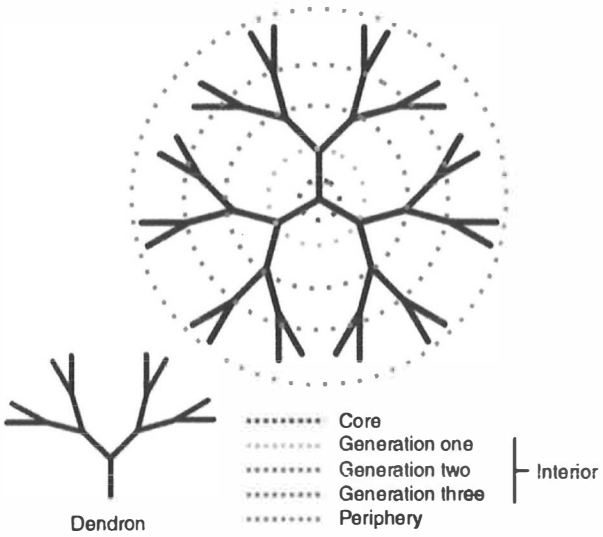

Figure 1.1: Anatomy of a dendrimer.[4] Reprinted by permission from Macmillan Publishers Ltd: *Nat. Biotechnol.*,23, 1517 © 2005

The symmetric structure gives dendrimers unique properties as compared to traditional polymers. Unlike polydisperse polymers, the molecular weight and structure of dendrimers are well-defined. The symmetrical branching from the core compress end groups close to each other isolating interior parts from the surroundings. The consequence is that the chemical and physical properties of dendrimers are mostly determined by the periphery.[5] The higher the generation of dendrimer the higher is the number of end groups and the tighter they are packed allowing multiplication of the features of the end groups in a single molecule. Besides to the periphery, functional units can be attached to the branching points or to the core making dendrimers versatile platform to develop potential applications. On top of that, dendrimers' versatility is increased even more by the ability to encapsulate smaller molecules into their interior to form host-guest complexes.

A review of all research concerning dendrimers, their properties and applications would be, if not impossible, at least impractical in the introduction of this thesis. Therefore the focus of the following chapters is to briefly introduce the dendrimer properties appropriate to this particular research, such as light harvesting, energy transfer and host-guest complexation. Further viewpoints to dendrimers can be found from many extensive review articles that have been published.[4-18]

1.1.1 Structure and dynamics

The beautiful symmetrical two-dimensional structures of dendrimers, as presented by their structural formulae, may evoke a thought of highly ordered circular molecules in solution. However, in reality the planar structures are completely insufficient to describe the shape of dendrimers in solution. A few reasonably stiff dendrimers, in which bending of the branches is restricted, have been synthesized,[19, 20] but most of the dendrimers are flexible and form complicated three dimensional structures, like generation four dansylated POPAM dendrimer shown in Figure 1.2. The freedom of the inner motions raises a question whether the end groups really lie in the periphery of a dendrimer or are the

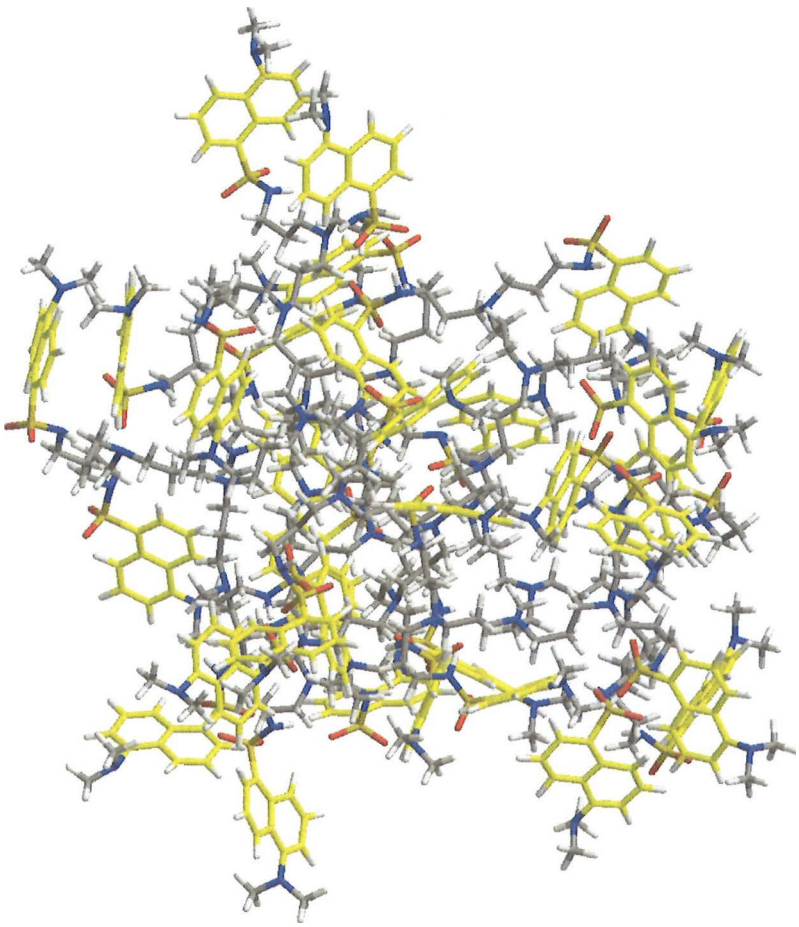

Figure 1.2: Three dimensional structure of generation four dansylated POPAM dendrimer in solution. The naphthalene rings of dansyls are coloured in yellow to illustrate the distribution of the end groups. The structure is obtained from MD simulations performed for Paper II.

branches folded back towards the centre. The first theoretical work on the subject by de Gennes and Hervet[21] predicted a "dense shell" model with all the end groups located at the periphery. Later the work by Lescanec and Muthukumar[22] stated a contradictory opinion and after that most of the theoretical studies have supported the "dense core" model, which predicts that the branches of flexible dendrimers tend to fold back and the atom density increases towards the centre of a molecule.[23] The underlying reason for back-folding is entropy that drives dendrimer branches to fill all the available space whenever the mobility of dendrons is sufficient.[23, 24] Therefore back-folding of the end groups is also generation dependent, as the short branches of the low generations do not have the required flexibility to fold back towards centre. On the other hand, the molecular weight increases exponentially with generation and without back-folding the lack of space for the end groups at the periphery would prevent the existence of the higher dendrimer generations.[25] Consequently the shape of dendrimers is usually generation dependent and higher generations take more spherical shape in solution than the lower ones.[26-29] Effective back-folding notably diminishes the size of the molecule and the growth of the volume of a dendrimer with the generation is clearly smaller than could be expected on the basis of the molecular masses.

Switching the dendrimer conformation from "dense shell" to "dense core" structure and vice versa have been suggested to be possible by altering solvent properties such as pH.[30, 31] Changing pH affects the strength of intradendrimer and dendrimer-solvent hydrogen bonding, and electrostatic repulsion and dendrimer is pushed to find the most energetically favourable conformation under new solvent conditions.[32] Though some early theoretical studies[33-35] predicted remarkable changes in size and shape of dendrimers with varying properties of solvent, most experimental[36, 37] and theoretical[30-32] studies have found only small changes in the volume or the sphericity of a dendrimer as a function of pH. Variation in pH has been discovered to change mostly the mass distribution and also the number of solvent molecules inside the dendrimer,[31, 32] but not the overall volume. The volume of dendrimer may, however, be affected by the choice of solvent. A collapse of the volume in poor solvents has been observed in experimental[38, 39] and in theoretical[40-42] studies. The studies showed only minor changes of a volume in good or medium solvents, but a poor solvent induced significant shrinking of a dendrimer minimizing the amount of unfavourable solute-solvent interactions.

In solution dendrimers, like all solutes, are in continuous motion. Various motions of the dendrimers in solution can be divided to three categories: 1) overall rotation of the whole dendrimer 2) bendings of the dendrimer branches (dendrons) 3) local motions of the end groups.[43] Rotational motion of the whole dendrimer is comparable to rotation of spherical particles in solution, since the size of a dendrimer is usually order of magnitude bigger than the size of solvent molecules. The latter two are the inner motions of dendrimers that give rise to conformational changes. Freedom of the motions of the dendrons depends on the stiffness of the structure and the length of the branch. In other words, high

generation and flexible spacer units allow greater mobility for dendrons. End groups may rotate locally depending on their size, and location within dendrimer. The mobility of the terminal units that are back-folded towards centre may be restricted by the spatial limitations. As a result of a different type of mobility the motion of the core of a dendrimer may differ largely from the peripheral motions, because the former is experiencing only the rotation of the whole molecule, whereas the latter is strongly affected by the bends of the branches and the rotation of the terminal units.

Dynamics of dendrimers has been most often studied by theoretical approaches and computational simulations, while experimental methods have been used less frequently. In such complicated systems as dendrimers the experimental results consist of ensemble averages of many different processes and hence are anything but straightforward to interpret. In this thesis time-resolved fluorescence anisotropy measurements have been performed to provide new experimental information on internal dynamics of dendrimers. In addition the results from molecular dynamics simulations have been used to interpret the experimental findings.

1.1.2 Host-guest complexes

One of the most fascinating properties of dendrimers is their ability to encapsulate guests to their interiors. The first host-guest systems of dendrimers were the "unimolecular micelles" by Newkome et al.[44] and Frechet et al.[45] followed by the "dendritic box" concept by Meijer et al.[46, 47] After that various different host-guest systems involving dendrimers have been prepared. Although the branches of dendrimers tend to fold back towards the core and fill all the available space of the interior, guest molecules can be complexed inside a dendrimer. The flexibility of dendrimers can provide space for guests by forming "cavities" that a guest can enter when the host-guest interactions, mainly hydrogen and ionic bonding, and van der Waals interactions, are energetically favourable. Apart from binding small organic molecules,[48-52] dendrimers can coordinate to metal ions[53-55] and metal nanoparticles[56, 57] or have metals attached to the core, the branching points or the periphery of a dendrimer.[58] Dendrimers containing metals have potential applications as e.g. light harvesting units,[59] catalysts[7, 60] and sensors, but as metallodendrimers are not the focus of this thesis they are not discussed further herein.

The encapsulation of molecules inside a dendrimer enables guests to be transported to environments that they are otherwise unwelcome,[61] because the solubility of the dendrimer, not the guest, determines the environment where a host-guest complex can enter. The solubility of dendrimers can be tuned by modifying end groups and therefore it is possible to carry smaller molecules inside dendrimer to different environments. This is one of the reasons why dendrimers can be potentially used in drug delivery applications.[62] To effectively transport a guest to a desired goal, a trigger to control encapsulation and release processes would be needed. As the three dimensional structure of the dendrimer affects to its ability to carry guests in the interior, the control over

the structure would be useful for the purpose. Possible ways to control the structure of a dendrimer have been proposed to be, for example, pH of the solution[30, 63] and an excitation with light.[64, 65]

1.1.3 Light harvesting and excitation energy transfer

The ability to collect the energy of the sunlight is one of the main factors that have made the life on earth such versatile and flourishing. Photosynthetic organisms have developed during millions of years to collect photons from sun and transfer them to the reaction centre. Photosynthetic organisms have, at least so far, been superior to artificial systems in light harvesting. Hence mimicking Nature could help to develop molecular devices to harvest solar energy. Topology of the dendrimers with peripheral antenna system around the centre suggests the possibility to form effective light harvesting units.[66] In similar fashion like in natural photosynthesis energy is collected by the light harvesting complex and transferred to the reaction centre, in dendrimers energy absorbed by the periphery can be transferred to an acceptor chromophore.

Excitation energy is transferred through space by long range dipole-dipole interactions without involving a photon to supply the energy to an acceptor. The rate of EET is defined by the Förster equation

$$k_{ET}(r) = \frac{8.8*10^{-5}\kappa^2\Phi_D J}{\tau_D n^4 r^6} \qquad (1.1)$$

where κ is the orientation factor, Φ_D and τ_D are the quantum yield and the lifetime of the donor at the absence of the acceptor, respectively, n is the refractive index of the solvent, J is the overlap integral of the donor emission and the acceptor absorption spectrum, and r is the distance between the donor and the acceptor. Energy transfer between the donor and the acceptor chromophores requires thus certain conditions to be fulfilled: The overlap between the fluorescence spectrum of a donor and the absorption spectrum of an acceptor has to be sufficient, and the two chromophores have to be close enough each other that the rate of EET is competitive with other excitation relaxation mechanisms. Given that in dendritic light harvesting systems a donor and an acceptor are located in a same dendrimer their separation cannot exceed the size of the dendrimer. For this reason EET in dendrimers is usually very effective in case donor and acceptor molecules are chosen to have a reasonable spectral overlap and no other faster excitation relaxation channels exist. As dendrimers are usually possessing multiple identical light absorbing chromophores the excitation energy may also migrate among them in case the spectral overlap of the absorption and emission bands is sufficient. Excitation energy hopping has been observed, for instance, in dendrimers having porphyrin,[67-69] peryleneimide[70, 71] and aminopyrene[72] chromophores in their periphery. In dendrimers with different acceptor and donor units energy may be transferred through several donors before arriving to the acceptor. The route of EET depends always on the

relative rates of the different processes and the fastest route is the most probable.

A large number of dendritic light harvesting systems with efficient EET to the energy sink have been designed to date.[66, 73] Dendrimers can be designed to possess chromophores in various locations to form desired functionality as illustrated in Figure 1.3.[74] The most common structure of light harvesting dendrimers is a peripheral antenna system and an acceptor unit at the core.[75, 76] Peripheral location allows high number of chromophores in a single molecule, as the number of end groups increases exponentially with growing dendrimer generation. This multiplies efficiently the absorption coefficient of the chromophore in a single dendrimer molecule.[66] Central location of the acceptor in the core of a dendrimer ensures effective EET from the antenna system. Nevertheless an acceptor does not have to be covalently attached to the dendrimer backbone, but it can be the guest molecule of a host-guest complex.[50, 77] Excitation energy can also be transferred to opposite direction from a guest molecule to the fluorescent labelled dendrimer depending on the chromophores in question.[78] All dendrimers do not require additional functionalization with chromophores in order to absorb light, as certain dendrimers are capable to collect light energy by their chromophoric backbone.[79-82] Two-photon absorbing dendrimers have also been synthesized and studied.[83, 84]

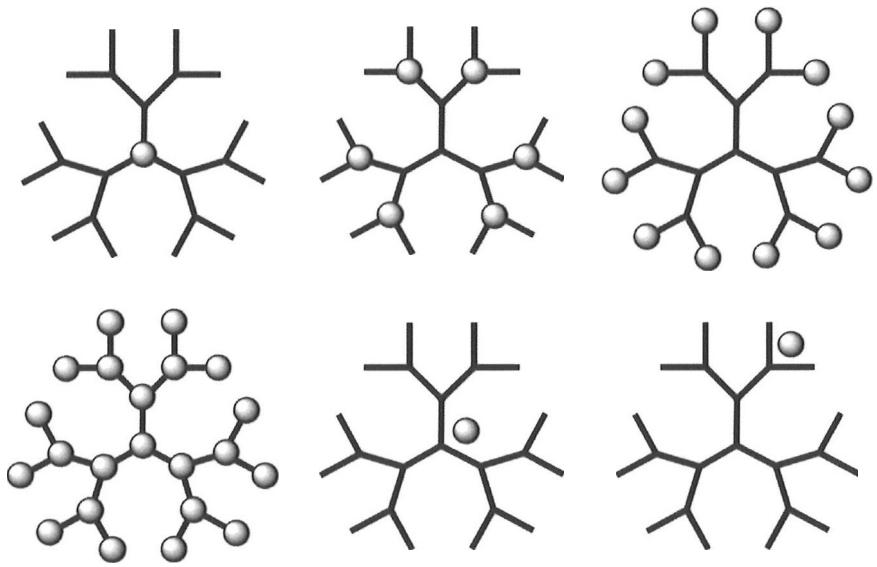

Figure 1.3: Possible location of the functional units in a dendrimer.

Light harvesting and EET properties of dendrimers can be utilized for sensing purposes, as the presence of external species can be indicated by the quenching of dendrimer fluorescence.[9] One advantage of dendrimers as sensors is the selectivity brought about by host-guest properties, and another is the amplification of the signal, as a single receptor can quench the fluorescence of all

chromophores of the host dendrimer.[84, 85] One reported example of a potential real life application, based on the fluorescence properties of dendrimers, is the detection of explosives.[84, 86] Water soluble fluorescent dendrimers can be potentially used in various biological applications.[87] Apart from opening the way to functional applications, light absorption and emission provide a possibility to study the properties of dendrimers by spectroscopic methods. They offer an indirect way to obtain information on the dynamics of a dendrimer and the presence of the guest molecules. One of the main themes of this thesis is to study intermolecular energy transfer process from a dendritic antenna to a fluorescent guest molecule hosted by a dendrimer.

1.2 Dansylated POPAM dendrimers

The dendrimers used in this study belong to poly(propylene amine) (usually called POPAM or PPI) family. The dendrimer backbone is built of propylene amine blocks. In the beginning of the 1990's de Brabander-van den Berg and Meijer[88] developed the large scale synthesis of these dendrimers that brought POPAM dendrimers up to generation five commercially available. The periphery of this commercial dendrimer can be functionalized with dansyl chromophores by a reaction with dansyl chloride.[89, 90] The schematic structures of the resulting dansylated POPAM dendrimers of generations one to four (G1-G4) are presented in Figure 1.4. Dansyl chloride, or 5-(dimethylamino)naphthalene-1-sulfonyl chloride, is a widely used fluorescent label in biological research for its ability to react with the free amino groups of proteins.[91] The resulting dansyl sulphonamide is highly fluorescent and has a large Stokes shift absorbing in UV-region and emitting in visible region around 500 nm. Dansyl fluorescence wavelength and quantum yield are sensitive to local environment[92] making it a popular molecular probe. Besides dansylated POPAM's, various other dendrimers containing dansyl chromophores have been designed and studied.[77, 93-101]

Dansylated POPAM dendrimers suit well as a model system for dendrimer studies as they hold many of the fascinating properties of dendrimers: 1) they have a flexible structure that allow them change their shape and volume in solution 2) they absorb effectively UV light with multiple dansyl chromophores 3) they form host-guest complexes with xanthene dyes and transfer excitation energy from dendrimer to the encapsulated dye[50] Despite the sensitivity of dansyl chromophore to its environment, it has been observed to retain its absorption and emission properties when attached to POPAM dendrimers and the absorption coefficient depends almost linearly on the number of dansyls of the dendrimer.[50, 90] The presence of the dansyl chromophores is also very important from the practical point of view, as they make the spectroscopic studies possible by absorbing and emitting visible and UV light. Without chromophores POPAM dendrimers could be spectroscopically studied only in the vacuum UV or infrared regions, which would require additional experimental efforts.

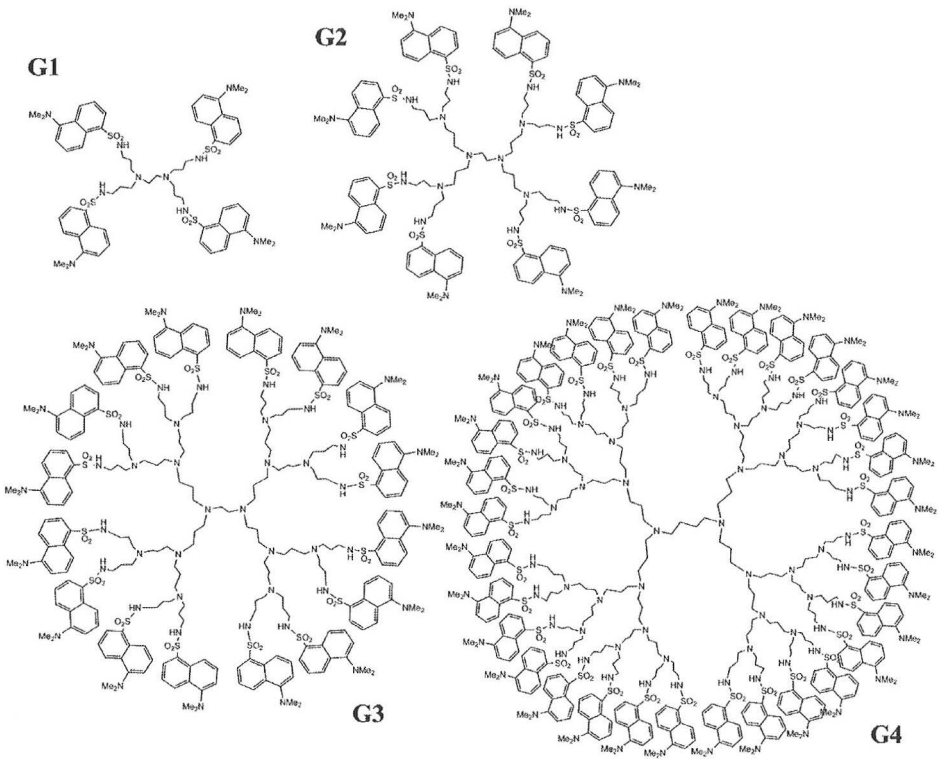

Figure 1.4: Schematic 2D structures of the dansylated G1-G4 POPAM dendrimers

1.3 Motivation and aims of the study

The motivation of the work presented in this thesis is to achieve new dynamic information on dendrimers in solution by using time-resolved spectroscopic methods. The study has focused on several aspects of the dendrimers. First was to get new insights to the structure and the internal dynamics of flexible dendrimers in solution. Experiments provide information on the time scales of the motions of the dendrimers, and this information can be used to make conclusions about the structure and the size of dendrimers in solution. Repeating the measurements at various temperatures enable estimation of the temperature effects to the structure and dynamics, and a systematic study of four different dendrimer generations reveal the size dependencies of the properties.

Another point of interest was host-guest complexes that POPAM dendrimers from a second to higher generations form with xanthene dyes. In these complexes effective EET from a dendrimer to an encapsulated dye have been reported,[50] but time scales of the EET processes from host to guest have not been studied before. Most of the time-resolved spectroscopic studies of EET in dendrimers published so far have been related to intradendrimer EET, and the host-guest aspect gives a new viewpoint to EET. Besides host-guest EET, also

other EET processes, such as energy migration in dendrimers and EET between the guest molecules in multiguest complexes, were examined. From the several xanthene dyes eosin was studied most detailed, and lesser attention was given to rose bengal and fluorescein complexes. The reasons for the preference of eosin are 1) higher fluorescence intensity than that of rose bengal, 2) better complexation to dendrimers as compared to fluorescein, 3) better background information for time-resolved spectroscopy studies, as steady state spectroscopy[50] and MD simulations[102] studies of POPAM-eosin complexes have been reported previously.

Broadly speaking the main goal of this work is to broaden knowledge of the fundamental nature of dendrimers. Deeper understanding of these molecules may help to produce possible applications in the future. Potential applications that may benefit from these studies include all devices based on light harvesting and EET processes, and host-guest properties of the dendrimers. An example of a potential host-guest application is drug delivery where dendrimers can be used to transport drug molecules to a desired location, where they are released in a controlled way.

2 EXPERIMENTAL

In this chapter the spectroscopic methods that were employed in this work are introduced. First the main principles of the ultrafast spectroscopy are shortly presented followed by the sections that describe the time-resolved experimental methods that were used in this work. Finally, at the end of the chapter the specifications of the laser systems are given as well as the description of the sample preparation.

2.1 Femtosecond spectroscopy

At molecular level many chemical events take place in time domain from femto- to picoseconds. The periods of various motions of the molecules, such as rotations and vibrations, are typically in the ultrafast region. Similar time scales apply to many chemical reactions and, in particular, transition states and reaction intermediates.[103, 104] Without methods to observe ultrafast events understanding of chemistry at molecular level would be limited. To detect these fast processes experimentally the time resolution of the experiment needs to be shorter than the investigated phenomena. The impulse to manipulate or measure the state of molecules should be short enough that the nuclei of the atoms can be considered to be practically motionless during the measurement. Otherwise all the obtained information would be more or less a time average of the event, preventing observation of the details of the processes involved. Such short impulses to manipulate molecules can be produced most conveniently by using femtosecond lasers. Historically femtosecond laser pulses were first generated with dye-lasers and a lot of effort has been devoted in the past to even produce the pulses for femtosecond experiments. Nowadays the development of the titanium sapphire lasers has brought commercial ready-to-use femtosecond lasers available and opened up the opportunities to take full advantage of short laser pulses in chemistry research.

Though titanium sapphire lasers can provide laser pulses shorter than 100 fs, which is short enough for most of the experiments, the wavelength range of the pulses is limited around 800 nm, restricting their use to the study of samples absorbing in this particular spectral region. To influence the sample, the wavelength of the excitation pulse has to match the energy of a transition in the molecule under study. The wavelength of laser pulses can be tuned by using nonlinear optical effects in birefringent crystals. Nonlinear optical effects allow generation of sum and difference frequencies of two photons as well as transfer of the energy from high energy pulse to the weaker one. In the simplest process, second harmonic generation, two original photons are combined to a single photon, when they propagate through a birefringent crystal.[105] Since energy of the photons is conserved, the frequency of a new photon is twice that of the original photons, allowing generation of 400 nm pulses from the 800 nm fundamental. To really tune the wavelength of the pulses over broad range, parametric amplifiers can be utilized, as was done in the transient absorption experiments of this thesis. With a non-collinear parametric amplifier (NOPA) the wavelength of femtosecond pulses can be tuned in the range between 460 nm and 1600 nm.[106] In a NOPA an energetic pump pulse and a weaker seed pulse are guided to have a spatial and temporal overlap in a birefringent crystal. A photon from the pump pulse is divided to two photons, signal and idler, with total energy and momentum conserved. If the frequencies of the created signal photon and the seed photon are equivalent, the seed pulse is amplified. This requires that the phase matching conditions are fulfilled, i.e. momentum is conserved. Phase matching can be adjusted for different frequencies by turning the crystal relative to incoming laser beams. As in non-collinear configuration signal and idler are travelling to different directions, the signal beam of NOPA can be separated spatially from pump and idler beams.

The wavelength range can be expanded to UV-region below 400 nm by sum-frequency generation of NOPA output and 800 nm fundamental, or by frequency doubling the output of NOPA. Sum-frequency generation provides higher UV pulse energies as energy can be taken from the fundamental, whereas frequency doubling is simpler to use. The choice of the method depends on the pulse energy that is needed to excite the sample. Also the pulse durations affect the usability of the two methods, as the conversion efficiency in the nonlinear processes is proportional to the energy density of the pulses, i.e. pulse duration. In this study both methods to produce UV pulses were used.

Besides wavelength also the duration of the pulses has to be manipulated before they are guided to the sample in an experiment. Different frequencies have a different velocity as they propagate through a transparent medium such as glass, causing temporal lengthening of the pulse as it travels through the optics needed to guide the laser beams. Femtosecond pulses have fairly wide spectrum, which increases the effect of the group velocity dispersion. To achieve the best possible time resolution and to avoid harmful incoherent effects, the group velocity dispersion has to be compensated. This can be done with a prism com-

pressor that induces negative group velocity dispersion to the pulse by making different frequencies to travel different distances through the compressor.

2.2 Transient absorption

In transient absorption spectroscopy the changes of absorption in time after excitation are investigated. A sample is excited with a pump pulse and the absorption is measured with a probe pulse overlapping spatially the excitation spot. The excitation of the sample can either increase or decrease the initial absorption at a specific wavelength. When part of the molecules in the excitation volume is excited, the population on the molecular ground state decreases leading to bleaching of the absorption band. Another source for a negative transient absorption signal is stimulated emission, which amplifies the intensity of the probe beam. The increase of the optical density, i.e. a positive signal, can originate from excited state absorption or from the absorption of a photoproduct. When time evolutions of these signals are followed, the rates of the changes of populations of electronic states can be observed. However, in practise, various signals may overlap each other making the interpretation of the data often complicated.

The relative time separation of the pump and the probe pulse is adjusted by an optical delay line, which changes the path distance that a pulse travels before reaching the sample. The intensity of the probe pulse after the sample is then monitored step by step with a photodiode. If accurate spectral resolution is desired then the probe pulse can be guided through a monochromator to select only a part of the spectral bandwidth of the pulse to be monitored. Usually the data is not presented as absolute absorption values, but as a change of absorption compared to that without excitation. This can be done by opening and blocking the pump beam periodically with an optical chopper. As the intensity of the probe pulse is sensitive to fluctuations of the laser system, an additional probe pulse, so called reference pulse that passes the sample next to the excitation volume, is used to improve the sensitivity of the measurement. The transient absorption at each time delay is then calculated from recorded probe (P) and reference (R) intensities as[105]

$$\Delta A(\upsilon, \Delta t) = \log \frac{I_R(\upsilon)}{I_P(\upsilon,\Delta t)}_{\text{with excitation}} - \log \frac{I_R(\upsilon)}{I_P(\upsilon,\Delta t)}_{\text{without excitation}} \quad (2.1)$$

Transient absorption method allows the study of phenomena that are faster than 100 fs. On the other hand the method is much more demanding than fluorescence methods that have been used in this study. For instance changing of the wavelength of the beams requires a significant amount of adjusting before the setup is optimized. The length of the optical delay line also restricts extending the measurements beyond nanosecond time scales. In this work tran-

sient absorption was the main tool to study the energy transfer processes of the host-guest complexes.

2.3 Streak camera

A streak camera is an efficient device to measure the time evolution of fluorescence spectra. The fluorescence induced by a short laser pulse is collected to a spectrograph where wavelengths are spatially separated. Photons are guided to a photocathode, where electrons are released proportionally to the intensity of the light. Formed electrons are accelerated and guided between a pair of sweep electrodes with a high speed sweeping voltage. The sweeping voltage deflects the electrons according to their arrival time converting temporal separation into spatial separation. This deflection is recorded in perpendicular direction with respect to wavelength dispersion produced by the spectrograph. The electrons are then multiplied in a microchannel plate before hitting a phosphor screen. When hitting the phosphor screen the electrons create a visible image which is recorded with a CCD camera. Consequently, the location of an electron on the screen is determined by the wavelength and the arrival time of the original photon. The intensity of light signal at each CCD pixel is thus proportional to the amount of fluorescence photons with same wavelength and time separation after excitation pulse.

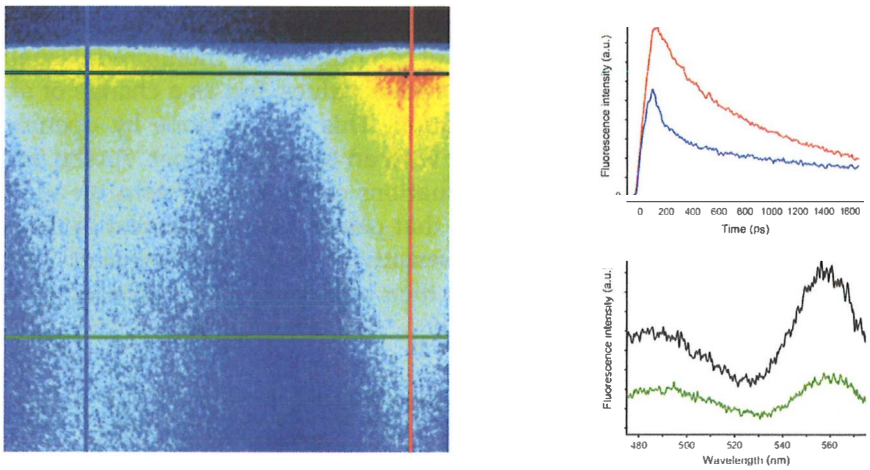

Figure 2.1: Streak camera image of fluorescence of dansylated G4 POPAM-eosin complex (left panel). Panels on the right show vertical (kinetics, top) and horizontal (spectra, bottom) cross-sections taken from the image at the positions marked with correspondingly coloured lines.

An example of a streak image is shown in Figure 2.1 together with the cross-sections taken from the image. As seen in the figure, streak camera can

collect the time evolution of the fluorescence spectrum, and kinetic traces at each wavelength at a same time. This ability to collect a large amount of data in a single measurement is a real strength of streak camera techniques. Time resolution of a streak camera is reasonably good, with the best models reaching subpicosecond resolutions. The drawback is a limited signal-to-noise ratio, a limited streak length and a poor sensitivity as compared to single photon counting methods.

2.4 Time-correlated single photon counting

Time-correlated single photon counting (TCSPC) is an experimental method to observe fluorescence decay times. The method is based on a measurement of the time separation between the excitation of a sample and the first emitted photon observed by a detector. A sample is excited repeatedly with laser pulses and each time the photon is observed, one count is registered to a multichannel analyzer to a channel that corresponds the time delay between the excitation and the photon observation. This is repeated usually until the peak channel has collected 10000 counts. The number of counted photons at each channel form a histogram that represents the decay of the fluorescence, since the probability to collect an emitted photon is proportional to emitting state population. However, to get the histogram to represent the true fluorescence decay, observing several photons after a single excitation pulse has to be avoided by keeping the photon counting rate relatively low. Every time when two photons are collected from the same excitation pulse, only the first one is counted and the histogram becomes distorted to shorter times. Therefore the photon collection rate has to be kept around one hundredth of the rate of the excitation pulses. Then the probability of more than one registered photons after a single excitation pulse is statistically low enough and the histogram can be considered to be undistorted. The disadvantage of the lowering of a collection rate is longer measurement times as 99 out of hundred excitation pulses do not add counts to the histogram.

The time resolution of TCSPC is typically from tens to hundreds of picoseconds depending on the response time of the detector and the timing electronics, and the pulse duration of the excitation laser. The time resolution falls short of that of streak camera, not to mention that of transient absorption spectroscopy, but on the other hand longer lifetimes up to the microseconds can be easily reached. Another advantage of TCSPC is the relative easiness of use, as complicated optical setups are unnecessary and almost ready to use commercial systems are available. In this thesis TCSPC showed its strengths in studies related to rotation of the dendrimers, especially at lower temperatures where longer fluorescence times had to be recorded.

2.5 Anisotropy

The concept of anisotropy can be exploited to obtain information about depolarization of excited molecules. Excitation of molecules with polarized light is selective, preferring the molecules that have their transition moment aligned parallel to the electric vector of the excitation photon. Therefore immediately after excitation of an isotropic sample, the excited molecules are not randomly oriented and signals measured parallel and perpendicular to excitation polarization are different. Monitoring time-dependent changes in orientations of molecular transition moments gives information about depolarization processes in the sample. Anisotropy is calculated from the parallel and perpendicular signal intensities as follows[107]

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \tag{2.2}$$

The orientational probability distribution gives rise to an initial anisotropy value of 0.4 in an isotropic sample, providing that the orientation of the transition moment is retained in the molecule. After excitation the anisotropy may diminish by depolarization processes, such as rotational motions or excitation energy transfer. Rotation times of relatively small molecules are usually clearly faster than fluorescence decay times preventing the observation of anisotropy in steady state fluorescence measurements, as orientations of the molecules are almost randomized before light is emitted. Though steady state anisotropies can be observed for large molecules and solid samples, the real connection to molecular dynamics can be obtained only by time-resolved measurements. By following the anisotropy decay in time the progress of the depolarization processes can be observed. An example of formation of the anisotropy signal is presented in Figure 2.2, where parallel and perpendicular TCSPC signals are shown together with the calculated anisotropy decay signal.

If the rotational motion of a molecule can be extracted from the time-resolved anisotropy decay information, the volume of the molecule in solution can be estimated by using Stokes-Einstein-Debye equation

$$\theta = \frac{\eta V}{RT} \tag{2.3}$$

The equation states that the rotation correlation time (θ) depends on the volume of the molecule (V), the viscosity of the solvent (η) and the temperature (T). In this form the equation is valid for spherical particles larger than the solvent molecules, whereas modified versions of this equation are needed to describe the rotation of non-spherical or small molecules.[107] In addition to rotational motions, depolarization can be a consequence of excitation energy transfer to randomly oriented acceptors.

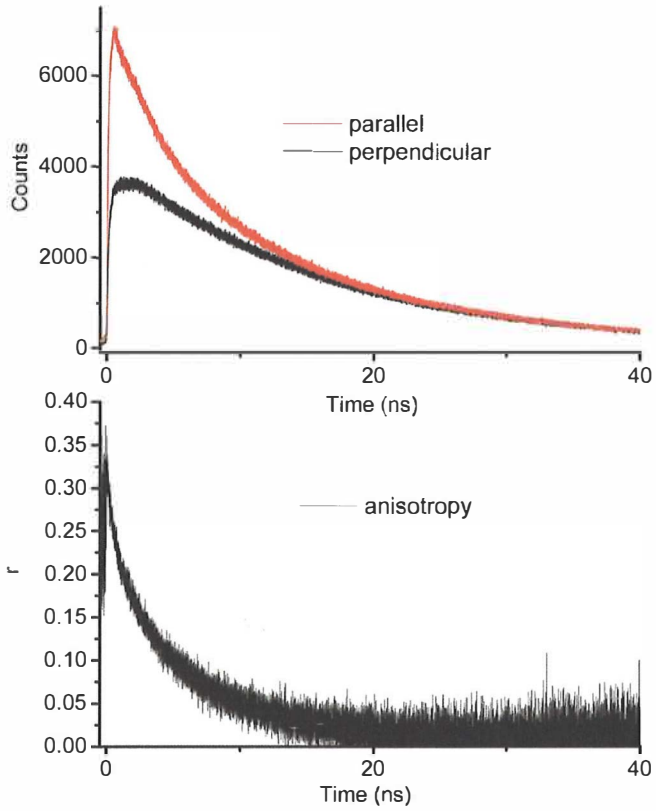

Figure 2.2: Time evolution of fluorescence of dansylated G4 POPAM dendrimer detected in parallel and perpendicular polarization with respect to excitation polarization (upper panel). The corresponding anisotropy signal is shown in the lower panel.

In this work anisotropy measurements were carried out by making use of the three spectroscopic methods introduced in the previous sections. Anisotropy decay proved to be helpful in determining the various motions of the dendrimers and provided a way to estimate the volumes of the dendrimers by Stokes-Einstein-Debye equation, as well as excitation energy transfer rates in the host-guest complexes.

2.6 Experimental setups used in this work

Home-built transient absorption setups were used in the experiments of Papers I and IV. In Paper I amplified femtosecond laser pulses were obtained from Quantronix Odin multipass amplifier, which was seeded with pulses from Coherent Mira 900 Ti:Sapphire oscillator pumped with Coherent Verdi Nd:YVO_4 laser. In paper IV femtosecond pulses were provided by Coherent Libra integrated one-box femtosecond laser. Both femtosecond setups provided pulses at ~800 nm wavelength with 1 kHz repetition rate and pulse energies around 0.9

mJ. Two home-built NOPA's were used to tune the wavelength of the pump and probe pulses. Streak camera measurements reported in Paper II were performed in co-operation with Professor Villy Sundstöm's group in the department of Chemical Physics at the University of Lund, Sweden. Excitation pulses were provided by a Spectra-Physics Tsunami Ti:Sapphire oscillator. The output pulses of the oscillator were frequency doubled and the pulse repetition rate was decreased from 82 MHz to 4 MHz by a pulse picker. Time-resolved fluorescence spectra were recorded by Hamamatsu C 4742-95 streak camera. Time-correlated single photon counting measurements presented in Papers III and IV were performed with PicoQuant HydraHarp 400 data acquisition system using pulsed picosecond diode lasers with 10 MHz repetition rate from the same manufacturer as excitation sources, and MCP-PMT detector to observe fluorescence photons.

2.7 Sample preparation

POPAM dendrimers were functionalized with dansyl chromophores by Professor Fritz Vögtle's group of the University of Bonn. Synthesis and purification along with the spectroscopic methods to control the purity of the prepared dendrimers have been described previously.[90] For the spectroscopic measurements dendrimers were dissolved in chloroform. Due to small amount of dendrimers available, the samples were not made by weighing and diluting, but the concentration was controlled mainly by recording the absorption spectra of the prepared solutions. For fluorescence measurements optical density was set to about 0.1 at the excitation wavelength. For transient absorption measurements higher absorbance of the sample is needed and the optical density of the sample was set between 0.5 - 0.7 at the excitation wavelength.

The dendrimer-dye complexes were formed by adding a droplet of highly concentrated ethanolic dye solution into the prepared dendrimer chloroform solution and mixed vigorously. As xanthene dyes are not soluble in chloroform, ethanol was used as solvent. This procedure adds ethanol impurity to chloroform solution, but as the concentration of the dye in ethanol was almost saturated, only very small amounts of ethanol were left in chloroform solutions of the complexes.

2.8 Molecular dynamics simulations

Molecular dynamics simulations were used to help to interpret the experimental results. MD simulations were performed in cooperation with Dr. Gilberto Teobaldi (Univ. of Bologna and Univ. of Liverpool) and Prof. Francesco Zerbetto (Univ. of Bologna) and the details of the simulations can be found in the original papers (Papers II and III)

3 RESULTS AND DISCUSSION

This chapter summarizes the central results of the studies included in this thesis. The chapter is divided in two main sections; the first section sums up the results related to dansylated POPAM dendrimers in solution, while the second section discusses photophysical properties of the host–guest complexes of the dendrimers studied. The discussion of pristine dendrimers is focused on their dynamics, and size and shape aspects, while the results from the complexes are mostly handling the intermolecular energy transfer processes. The details of the studies are presented in the original Papers I-IV.

3.1 Internal dynamics in dansylated POPAM dendrimers

The dynamics of dansylated POPAM dendrimers were experimentally studied by observing the time-resolved anisotropies of dansyl fluorescence. In Paper II a streak camera and in Paper III TCSPC method was used for time-resolved fluorescence detection. In both papers MD simulations were combined with the experiments to help to interpret the experimental results.

3.1.1 Fluorescence properties of dansylated POPAM's

Several studies on basic steady state absorption and fluorescence properties of dansylated POPAM dendrimers have been published[50, 53, 85, 90] and therefore these properties were not the focus of this thesis. All the measured spectra and the observed fluorescence lifetimes were in agreement with previous studies and practically independent of the dendrimer generation (Paper III).

Time-resolved fluorescence spectra revealed that for all dendrimer generations fluorescence maximum shifts towards red in time (Paper II), as is illustrated in Figure 3.1. The spectral shift was concluded to be induced by excited state solvation process. The 15-30 ps solvation component resolved for the solvation correlation function was considered to be the reorganization of the first

solvent layer around dansyl chromophores, whereas the interpretation for the longer, around 400 ps, solvation component remained slightly uncertain. Such long solvation component is commonly met in proteins or micelles where solvent molecules are trapped inside larger molecules.[91, 108] It can be speculated that the solvent molecules "frozen" inside the dendrimer would be the origin of the slow solvation. On the other hand the independency of the solvation component on a dendrimer generation and the high mobility of the solvent inside the dendrimer, as predicted by MD simulations, are against this suggestion. The true character of this slow solvation remained therefore more or less an open question.

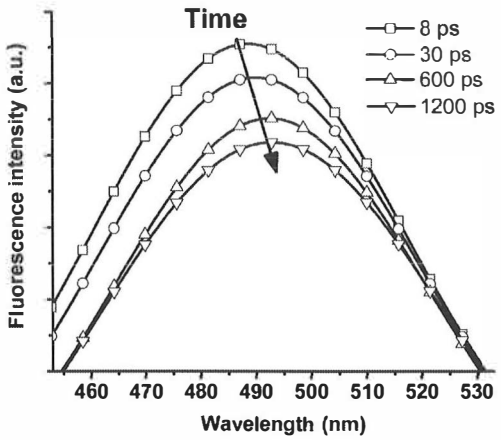

Figure 3.1: Time evolution of the fluorescence spectra of the G1 dansylated POPAM dendrimer

3.1.2 The dynamics of dansylated POPAM dendrimers

Fluorescence anisotropy decay was found to be strongly dependent on the dendrimer generation, as can be expected if it was to be connected to the rotational motions of the molecule. An example of the generation dependency observed in streak camera measurements is displayed in the left panel of Figure 3.2. However, the observed anisotropy decay was not just lengthening with increasing size of the molecule, but the resolved fast decay component became shorter for larger dendrimers going from 140 ps of G1 to 60 ps of G4. This component was concluded to be connected to the local motions of the peripheral dansyl chromophores and is thus not directly dependent on a size of a molecule. In large dendrimers simultaneous motions of the dendrons are likely to affect the observed decay times.

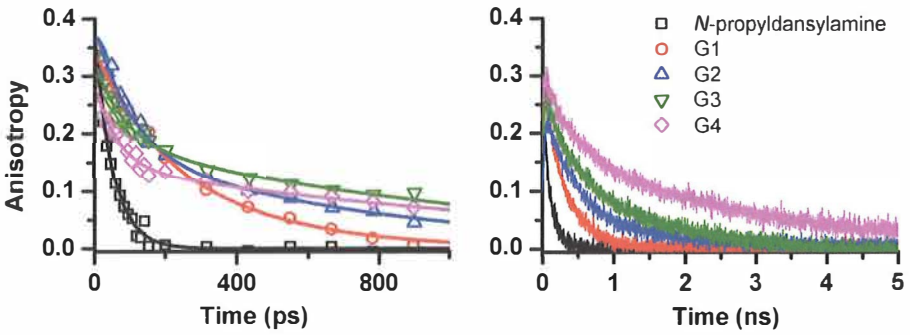

Figure 3.2: Fluorescence anisotropy decays of G1-G4 dansylated POPAM dendrimers and monodansyl reference compound N-propyldansylamine. The left panel shows subnanosecond decays obtained by streak camera measurements and the right panel nanosecond decays from TCSPC studies.

Whereas the relatively short time window (< 2 ns) of the streak camera limited accurate determination of the overall rotation times of the dendrimers, a TCSPC method provided reliable time constants. As dominated by the overall rotation, the anisotropy decays obtained by TCSPC showed beautiful dependency on the size of the dendrimer (Figure 3.2, right panel). The rotation times 1.5 ns for G3 and 2.6 ns for G4 from the TCSPC experiment do not match with the values obtained from the streak camera measurements, but this is mainly a consequence of the limited time-window of the streak camera experiment. Actually the streak data can be adequately fitted by using the values obtained from the TCSPC experiments. On the other hand TCSPC confronted its limitations when studying the local motions, which are too fast to be observed with the method. With both methods accurate fit of the data requires also an intermediate decay component of several hundred picoseconds. This is connected to the motions of the dendrons. A first generation dendrimer (G1) makes an exception as its branches are too short to provide for distinguishable dendron motions. Local motions and overall rotation are the only notable motions for the G1 to be considered and therefore the anisotropy decay of G1 was well fitted with just one decay component as local motions were not resolved in TCSPC. For this generation both streak camera and TCSPC gave the same overall rotation time of 300 ps.

For the dendrimer generations higher than one the interpretation of anisotropy decays becomes more complicated. An additional challenge is that the observed signals are always averages from many different species. Each individual dendrimer in solution is instantly slightly differently shaped; a phenomenon brought about by the flexible nature of dendrimers. And not only the shape of the molecules, but the location of the excited dansyls in a molecule, contains a great deal of variety. Electronic excitation lands on a dansyl of a dendrimer randomly and it is impossible to know whether fluorescence originates from a dansyl located at the outer parts of the dendrimer or from a backfolded dansyl near the centre of the molecule. Hence the anisotropy decay components are averages of rotational relaxation of variously located and ori-

ented dansyls within the dendrimer. Molecular dynamics simulations in Paper II demonstrated the variety of the dansyl rotation times in G4 dendrimer (Figure 3.3).

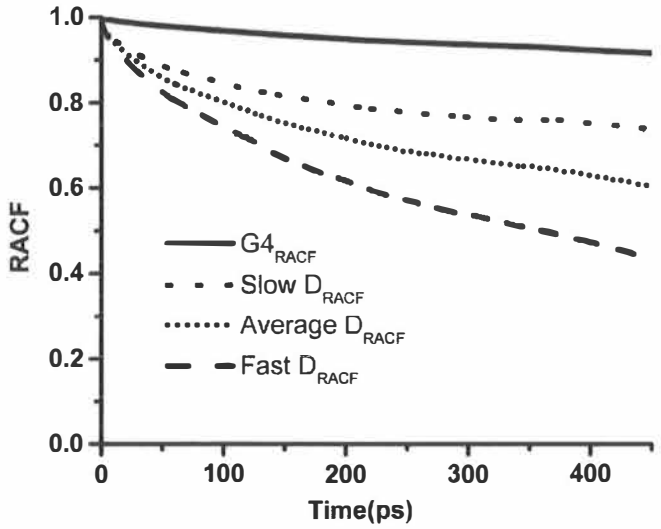

Figure 3.3: Rotational autocorrelation function of the dansyls in dansylated G4 POPAM from MD simulations. Fast and slow components are averaged from dansyl that have lower and higher D_{RACF} than the average of all 32 dansyls (dotted line). The calculated rotation of the whole G4 dendrimer is shown for comparison (solid line).

To sum up, the observed anisotropy decays originate from the three different category motions of dansyl chromophores: local motions, dendron bendings and dendrimer overall rotation. Furthermore the location of an individual dansyl within the dendrimer affects its rate of orientational relaxation. Due to the average nature of the signals the determined time constants should not be taken literally, but more as time scales. On the other hand the overall rotation is present in relaxation of each dansyl, given that for "free" peripheral dansyls overall rotation is always a part of the total rotational relaxation and for the back-folded dansyls that are almost "frozen" inside the dendrimer it is the only rotational relaxation process. Rotation correlation time constant of 51 ps resolved for monodansyl reference compound N-propyldansylamine in chloroform solution can be considered as a limit of the time scale of unrestricted local motions of dansyls. In dendrimers dansyl motions are, however, partially restricted via spatial crowding, and bonding to the dendritic arms, which slows down the motions as can be observed from the resolved time constants from 60 to 140 ps. The obtained results for dynamical processes give a full support to a "dense core" model of the soft dendrimer as they systematically refer to back-folding of some of the dendrons of the dendrimers.

3.1.3 Temperature effects to the dynamics and the structure

Besides finding the generation dependency of the dynamics of POPAM dendrimers, the motivation for Paper III was to study the effect of temperature to the structure and motions.

Lowering the temperature reduces the thermal energy of a molecule and increases the viscosity of the solvent, which predicts considerable slowing of the motions of dendrimers, even if the structure of the molecule remains unchanged. As predicted, the observed fluorescence anisotropy decays became longer for all dendrimer generations as temperature was decreased. For G1 rotational correlation time lengthened from 0.3 ns at 293 K to 1.58 ns at 213 K. The analogous values for higher generations were from 1.17 ns to 4.26 ns for G2, from 1.48 ns to 9.24 ns for G3 and from 2.61 ns to 19.1 ns for G4. In addition a clear change of the relative amplitudes of the two decay components was observed. The lower the temperature the higher was the proportion of the longer anisotropy component indicating stiffening of the dendrimer structure. This is not a particularly surprising result considering that thermal energy is needed to overcome potential barriers to change the shape of a molecule. Although the experiment confirmed the expected stiffening, more interesting question was to inspect the temperature driven changes to the shape and the volume of dendrimers.

The volumes of the dendrimers at various temperatures were calculated by using Stokes-Einstein-Debye model (Equation 2.3). The measured anisotropy decays were fitted by two exponentials and the longer component was assumed

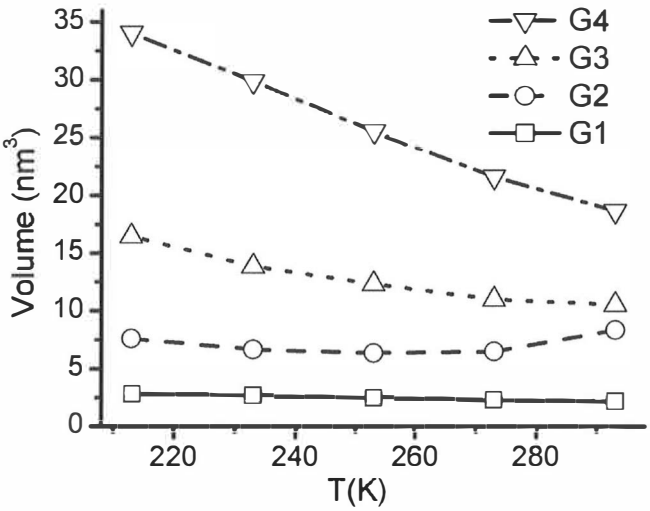

Figure 3.4: The volume of the G1-G4 dansylated POPAM dendrimers as a function of temperature. The volumes were calculated from the experimental rotation correlation times obtained by TCSPC measurements

to describe the overall rotation. The volumes of the G3 and G4 POPAM dendrimers were observed to shrink with rising temperature from 213 K to 293 K, but the change in the G1 and G2 dendrimers was rather small or negligible (Figure 3.4). Almost constant volume of the small G1 and G2 dendrimers is an expected result considering the shorter dendrons of the molecules. Lower generation dendrimers are stiffer than the higher generations and short branches do not allow considerable back-folding towards centre that would be needed to alter the volume in a large extent. It has to be also noted that Equation 2.3 is valid only for the spherical molecules and generation one and two dendrimers are considered to be less spherical than the larger ones.[27, 28] Therefore the estimated volumes of the G1 and G2 should be taken as first approximations.

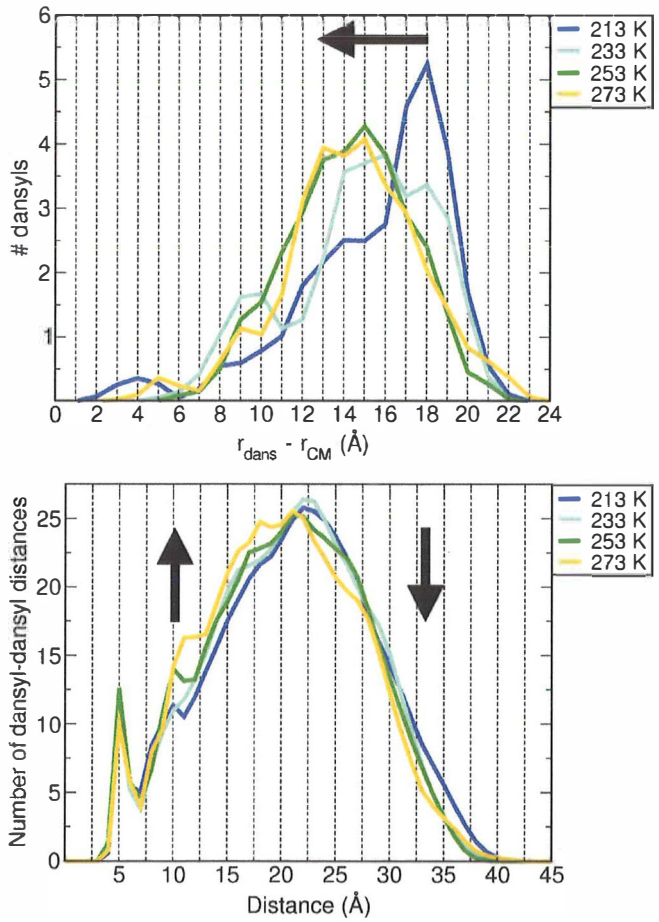

Figure 3.5: Histograms of the time-averaged distances between the dansyls and the centre of mass (CM) of the G4 dansylated POPAM dendrimer at several temperatures (upper panel). The lower panel presents similar information for time-averaged dansyl-dansyl distances.

The volumes of the generations three and four decreased gradually with the rising temperature, which may be opposite to what would intuitively be expected. Spectroscopic measurements revealed the behaviour of the molecule, but they offered little to explain the reasons behind the phenomenon. In that point molecular dynamic simulations for the G4 dansylated POPAM dendrimer proved to be helpful. Simulations supported the experimental findings by predicting the volume shrinking, though the predicted change in volume was clearly smaller than the experimental results indicated. Nevertheless qualitatively there was an agreement with the experiments and the simulations, and the shrinking of the dendrimer can be observed also from the changes in distance distribution of the dansyl groups as presented in Figure 3.5. Simulations predicted that the higher the temperature the closer to the centre of mass of the dendrimer the dansyls are located, and at the same time dansyls pack also a bit closer to each other. The direction of the changes in histograms as temperature rises is illustrated with black arrows in Figure 3.5.

Simulations gave a possibility to estimate the shape of the G4 POPAM dendrimer in chloroform. Calculated asphericity values (0.009-0.019) did not suggest significant deviation from spherical shape anywhere in the studied temperature range, which for its part justifies the use of the Equation 2.3 for volume calculations of G4 dendrimer. The unchanged overall shape of the dendrimer as a function of temperature can be considered to be an expected result, on account of the symmetrical structure of the dendrimers. Even if the degree of back-folding of the end groups changed, it would affect similarly to identical dendrons on the opposite site of the molecule and thus not reduce the overall sphericity.

In addition to giving qualitative support for the experimental findings, MD simulations helped to find the explanations to the experimental observations. The shape of a dendrimer is largely determined by the balance of the intra-dendrimer and dendrimer-solvent interactions that are temperature dependent. The changes of the two interaction energies as a function of temperature are shown in Figure 3.6. The net result is that as temperature rises it becomes energetically favourable to increase intra-dendrimer interactions and decrease dendrimer-solvent interactions leading to stronger back-folding and thus smaller volume of the molecule. Besides the interaction energies the final shape and volume are affected by steric hindrance that may prevent back-folding, and the temperature dependent properties of the solvent. The entropy gain that is achieved, when solvent molecules transfer from the interior of the dendrimer to the bulk solvent, was concluded to be only a marginal factor in volume shrinking.

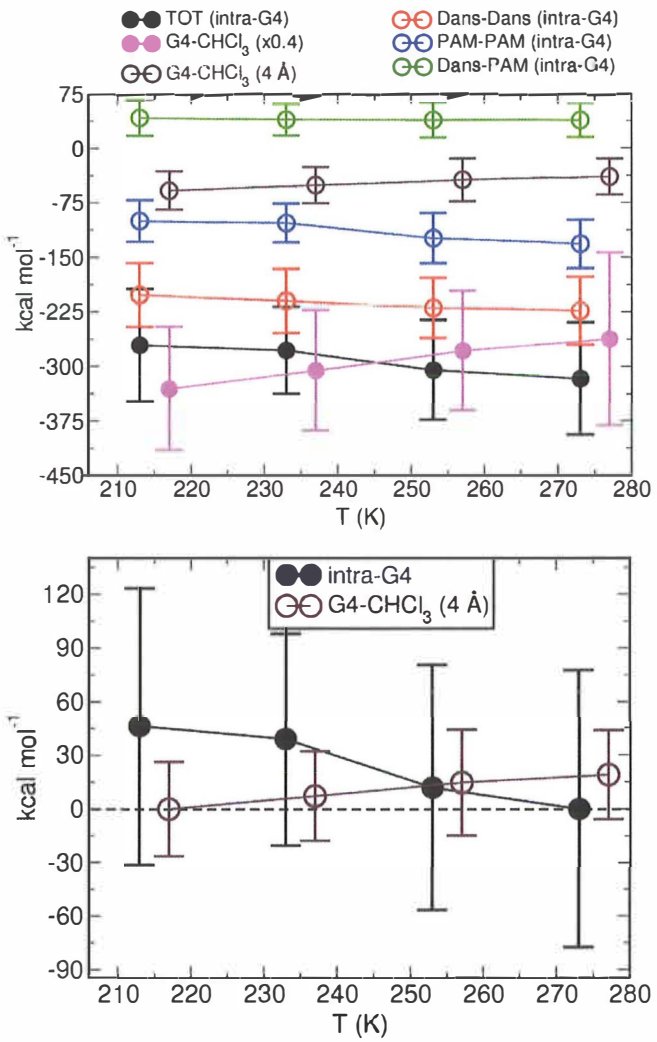

Figure 3.6: Total intra-dendrimer (intra-G4) and G4-$CHCl_3$ interaction energies (filled circles) are compared in upper panel. The dansyl (Dans)-Dans, propylene amine (PAM)-PAM and Dans-PAM contributions (open circles) to the total (TOT) intra-G4 energy, and the contribution of the solvent molecules less than 4 Å away from G4 to the total G4-$CHCl_3$ interaction energy are also shown. Lower panel compares the total intra-G4 energy to the contribution from the solvent molecules less than 4 Å away from G4.

From the view of applications, the observed temperature dependent volume shrinking is potentially promising. Particularly in host-guest applications controlling the volume of a dendrimer may open up the way to control the hosting capability of a dendrimer. Forcing guest molecules out from the interior of a dendrimer in a controlled way would potentially be very useful for instance in drug delivery applications. Though the relatively broad temperature range, i.e. tens of Kelvins, would definitely be impractical for most of the applications, the understanding of the factors behind the volume changes may allow

development of the dendrimers with stronger tendency to react to the temperature. However, as the simulations indicate, the structural changes result from the delicate balance of various interaction energies related to dendrimer and solvent, and therefore the prediction of the behaviour on the basis of a molecular structure is anything but straightforward.

3.1.4 Dansyl-dansyl energy transfer

Whenever the absorption and the fluorescence spectra have a reasonable overlap, excitation energy transfer between closely packed chromophores of a dendrimer becomes probable. It follows that the fluorescence anisotropy can decay not only by the motions of the chromophores, but also by EET between identical chromophores in the same dendrimer. However, in case of dansyl the spectral overlap of the absorption and fluorescence spectra is almost negligible due to large Stokes shift of the dansyl resulting from the formation of the TICT state.[109] In Paper II the possibility of the anisotropy loss to originate from dansyl-dansyl EET was speculated, but as the internal motions of the dansyl units (50 -140 ps) are supposed to be much faster than dansyl-dansyl EET (> 200 ps), the EET could not be observed with the anisotropy experiments, even if it existed. Strong energy hopping from dansyl to dansyl would also change the absorption and fluorescence spectra of dansylated dendrimers compared to those of a monomeric dansyl in solution. However, the shapes of the spectra are practically independent on the dendrimer generation and the absorption coefficient corresponds to the number of dansyls in a dendrimer,[90] which refers to an absence of strong interactions between dansyls units. Dansyl-dansyl EET was therefore concluded to be a negligible energy distribution pathway for dansylated POPAM dendrimers.

3.2 Excitation energy transfer in host-guest complexes

The host-guest complexes formed by dansylated POPAM's and xanthene dyes were studied in all four original papers. Paper I focused on the excitation energy transfer from dendrimer to eosin guest and in Paper IV eosin acceptor was replaced by rose bengal and fluorescein dyes. In addition fluorescence studies of POPAM-eosin complexes were performed in parallel with the corresponding studies of pristine dendrimers in Papers II and III.

3.2.1 Excitation energy transfer to encapsulated dye

Dansylated POPAM dendrimers are known to encapsulate xanthene dyes to their interior and efficient energy transfer from the excited dansyl to the guest dye(s) has been observed.[50] The main motivation for Paper I was to find out the time scales of the EET. Transient absorption experiments revealed a delayed rise of the bleach of the eosin absorption after selective excitation of the dansyls

in G2, G3 and G4 dendrimer-eosin complexes (Figure 3.7). Direct excitation of the eosin(s) led to an instant instrument limited rise, instead. The rise of the eosin signal after dansyl excitation was thus concluded to be connected to the EET from dansyl to eosin.

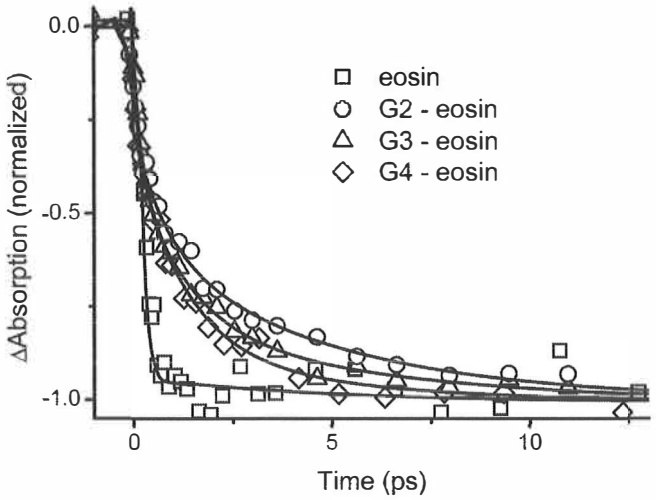

Figure 3.7: The rise of the transient absorption signals of G2-G4 dansylated POPAM-eosin complexes after UV excitation compared to the corresponding signal from eosin in solution.

The rise signals were found to be multiexponential, i.e. they required more than one exponential function to be fitted adequately. This is mainly a consequence of the arbitrary nature of the excitation process. Low excitation energy allows only a single dansyl in a dendrimer to be excited at a time and the excitation probability is not affected by the location of the guest dye(s), but rather the dansyl orientation in respect of the polarization of the excitation light. An acceptor may lie next to the excited dansyl or further away, hence a random excitation of dansyls results into a distribution of distances between the excited dansyl (donor) and the guest dye (acceptor). According to Förster model (Equation 1.1) this generates a variety of EET times that are observed in a measured signal. An average defined by only one time constant would therefore be insufficient to describe the wide range of EET rates. In Paper I three exponentials were used to fit the rise signals and the obtained rise times were between 100 fs and 7 ps for all dendrimer generations. For eosin as an acceptor, 100 fs component corresponds to the donor-acceptor distance of 6 Å and 7 ps to 13 Å distance. The distances sound reasonable separations for the excited dansyl and the closest eosin, in view of the size of the POPAM dendrimers. The streak camera measurements presented in Paper II allowed us to observe the dansyl-eosin EET, not only from the rise of eosin fluorescence, but also from the fast decay of dansyl fluorescence. The revealed 4-8 ps EET time constants can be concluded to match those obtained by femtosecond transient absorption ex-

periment, since the 3 ps time-resolution of the streak camera prevents the observation of the faster components.

Surprisingly the effect of the generation of a host dendrimer to EET rate was rather small as can be seen from Figure 3.7. Intuitively the energy transfer could have been expected to be somewhat faster in smaller dendrimers, as the distance between chromophores may be thought to be shorter. But on the other hand in the higher generations dansyls are more tightly packed and back-folded towards the centre. Hence the generation independency to average donor-acceptor distance can be explained by back-folding and the dye's desire to go to the interior of the dendrimer to avoid the contact with the solvent to which it is not soluble. In addition we have to remember that in presence of several guest dyes, as may be the case in G3 and G4 complexes, energy is transferred from excited dansyl to the closest guest dye and not to the one further away. This makes the average EET distance smaller than the average distance of all dansyls and guests. Furthermore no dansyl-dansyl hopping was observed to occur prior to arrival of excitation to the guest, because the effectiveness of the dansyl-eosin EET is superior to that between dansyls. The inefficiency of dansyl-dansyl EET is discussed in Section 3.1.4.

In Paper IV fluorescein and rose bengal dyes were used as guests. It turned out that host-guest EET for these acceptors did not vary much from the results obtained for eosin complexes. The closer look to the factors contributing to EET rate (Equation 1.1), in particular overlap integral and donor-acceptor distance, reveal that the observed insensitivity to acceptor is, in fact, predictable. The limits of donor-acceptor distances are basically set by the size of a host dendrimer, which, in turn, is unaffected by the choice of a guest. Therefore the distribution of donor-acceptor distances remains more or less constant regardless of a guest. The variation of overlap integral from $1.5*10^{15}$ $M^{-1}cm^{-1}(nm^4)$ of dansyl and rose bengal to $2.5*10^{15}$ $M^{-1}cm^{-1}(nm^4)$ of dansyl and eosin is not enough to expose any notable differences, in particular in many component fits, where the revealed time constants typically may vary depending on the given initial values for the fit and the noise level of the signal.

The efficiency of EET from dendrimer to guest was a drawback for the fluorescence studies of the complexes as EET quenches the dansyl fluorescence. It was concluded that dansyl fluorescence seen after time scale of EET (> 10 ps) originates almost exclusively from the dendrimers that do not possess any guests inside them. Therefore true effect of the complexation to the dynamics of the dendrimers could not be studied much further.

The photochemical properties of dansylated POPAM dendrimers make them efficient UV-light harvesters that can transfer absorbed energy effectively to a guest molecule. Hence POPAM-xanthene complexes can be used as UV to visible light converters, where the visible wavelength of the converter can be adjusted by changing the guest dye. EET can also be used for sensing purposes as the quenching of the donor fluorescence indicates the presence of an acceptor.

3.2.2 Relaxation of the excitation of the guest molecule

Transient absorption and time-resolved fluorescence experiments suggested that the higher the generation of the host dendrimer the shorter are the fluorescence and excited state lifetimes of the guest. This is consistent with the results obtained by Balzani et al.[50] Binding to a dendrimer, most likely via hydrogen bonding, opens up new non-radiative relaxation channels to depopulate excited states of the guest. The fluorescence lifetime of bound eosin was observed to shorten more than the lifetime of bound rose bengal. Though fluorescence intensity of dendrimers was quenched severely in complexes due to EET, their lifetimes nevertheless seemed to remain intact. But as discussed in the previous section, the observed dansyl fluorescence comes mainly from uncomplexed dendrimers and consequently this emission tells practically nothing about the behaviour of complexes.

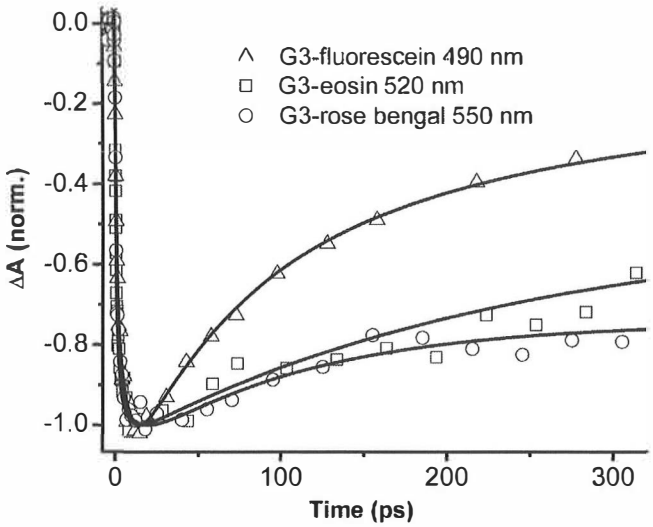

Figure 3.8: Normalized transient absorption signals of G3 dansylated POPAM complexes with three xanthene dyes. Probe wavelength was tuned to match the absorption band of each dye.

Surprisingly in complexes the transient absorption decay signal of eosin was insensitive to probe wavelength, despite whether the signal was measured from the ground state absorption region (bleach) or from the fluorescence band (stimulated emission). On the contrary in rose bengal complexes the stimulated emission decay seemed to be faster than the bleach of absorption (Paper IV). The difference was concluded to originate from the different probability of xanthene dyes to populate triplet states. Rose bengal that contains heavy iodine atoms is expected to have a rapid intersystem crossing channel, whereas for fluorescein the triplet quantum yield is negligible. Triplet populations were seen in transient absorption signals as the ground state bleach did not recover

to the initial level as shown in Figure 3.8. Part of the population is stuck at the long living triplet excited states, which have relaxation times too long to be determined in present experiments. When stimulated emission region was probed, triplet state population was not observed, because the signal measures only the population of the fluorescent singlet state.

3.2.3 Energy transfer from guest to guest

Dendrimers can bind several guest dyes at a time, which raises a question about the possibility of EET between the guests. Each of the three xanthene dyes studied have a relatively large overlap of the absorption and fluorescence spectra allowing for efficient EET. As the location of the dyes is restricted to the interior of the host dendrimer, the intermolecular distances of the guests remain relatively small suggesting fast EET. The hint of EET between the guests was seen in the TCSPC studies of Paper III, where the instant anisotropy of eosin fluorescence after direct eosin excitation depended on the generation of a host dendrimer. This suggests that the process that reduces anisotropy is faster than the time resolution of the experiment and therefore the dynamics of the process could not be resolved. Such fast anisotropy decay was speculated to be induced by energy transfer between randomly oriented guest molecules, but experiments with better time resolution were needed to study the details of proposed guest-guest EET.

Transient absorption anisotropy measurements reported in Paper IV were performed to confirm the existence of guest to guest EET in complexes. Straight excitation of eosin led to 700 fs anisotropy decay in G3- and G4-eosin complexes (Figure 3.9). This corresponds, according the Förster equation (Equation 1.1), the donor-acceptor distance of 1.5 nm, which is within the dimensions of the dendrimers. Experiments clearly showed the dependence between the amplitude of the fast anisotropy decay and the relative amount of the dye and the dendrimer. The addition of guest dyes increases the number of dendrimers that host more than one guest at a time making guest-guest EET possible. In G2 complexes the fast anisotropy decay was missing, as G2 can act as a host only for one eosin guest at a time. Overload of the dye led to a collapse of signal-to-noise ratio in transient absorption measurements. This was concluded to be a consequence of eosin aggregation in solution, giving a strong background scattering and killing the transient absorption signal. Under overload conditions guest molecules travel in and out from the dendrimer and form a dynamic equilibrium in solution.[102]

The longer anisotropy decay component observed in Paper IV was concluded not to describe EET, but dynamics of the guest molecule inside a dendrimer. This component became slower in higher generation dendrimers suggesting that the guest is at least partly stuck to the dendrimer and rotating together with the host.

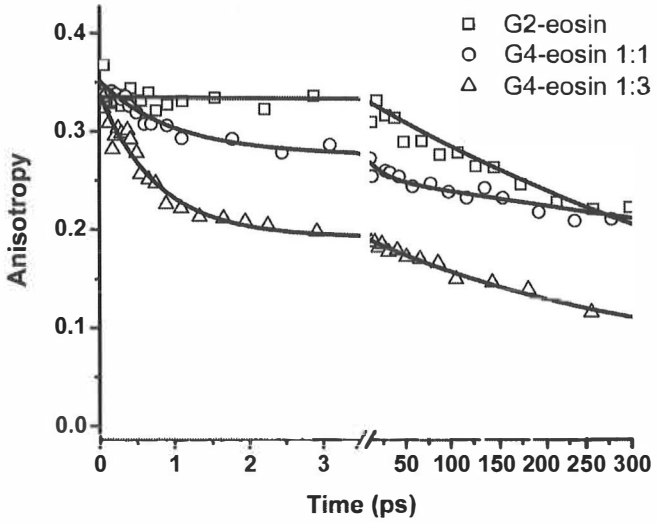

Figure 3.9: Anisotropy decay of the transient absorption signal of eosin in dendrimer-eosin complexes after selective excitation of eosin. Note the change of time scale after the break at 4 ps.

In light harvesting applications that base on chromophore containing dendrimers EET between the guests may appear as a harmful side effect that prevents collection of excitation energy to a single energy sink. Various amounts of guest molecules bound to dendrimers make the behaviour of individual complexes non-uniform because of differences in guest-guest interactions. However, as guests are not covalently bound the number of guests in each dendrimer cannot be controlled, and the host-guest solution consists always a distribution of different complexes.

3.3 Summary of the results

The time scales of dansylated POPAM dendrimer motions were found to vary from < 100 ps local motions of the end groups to a nanosecond scale of overall rotation. Dynamics were dependent on a dendrimer generation and temperature of the solution. EET processes in dendrimer-dye host-guest complexes were observed to be much faster than intra-dendritic dynamics and ranged from 100 fs to 8 ps. To sum up the main results from the time-resolved studies the observed time scales for the internal dynamics of dansylated POPAM dendrimers and the EET processes in POPAM-eosin complexes are collected to Figure 3.10. The presented time scales for the overall rotation of a dendrimer and local motions of the dansyl groups are determined only for uncomplexed dendrimers. The dynamical studies of the complexes were prevented by the efficient quenching of dansyl fluorescence due to EET to the guest dyes.

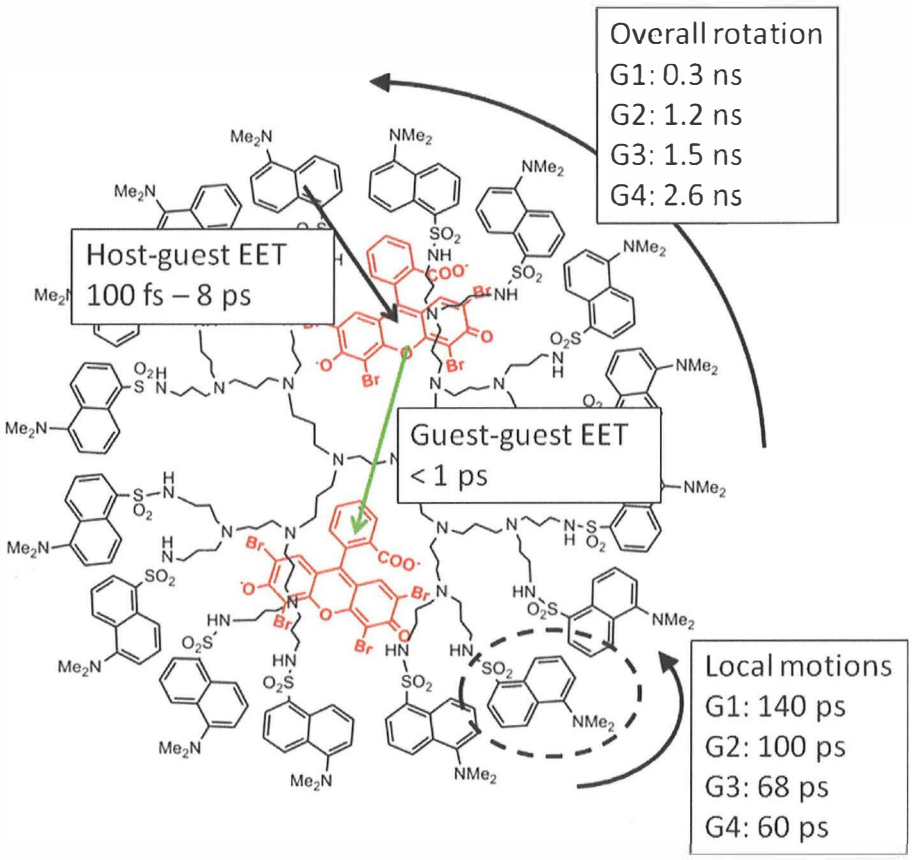

Figure 3.10: Schematic representation of the experimentally observed time scales of the internal dynamics of G1-G4 dansylated POPAM dendrimers at room temperature and the intramolecular EET processes in host-guest complexes formed by a dendrimer and xanthene dye(s). Two eosin guest molecules (red) are drawn inside the G3 dansylated POPAM dendrimer (black).

4 CONCLUSIONS

Dendrimers, a class of molecules with fascinating structural and functional properties, have been the focus of this thesis. Four generations of dansylated poly(propylene amine) dendrimers, and their host-guest complexes with xanthene dyes were studied primarily with various time-resolved spectroscopic methods. The results from molecular dynamics simulations were used to interpret experimental results.

The results offered new and quite general information on the dynamics of soft dendrimers in solutions. The typical time scales of the various motions were resolved for four dendrimer generations at various temperatures. One of the most interesting findings was the observation of the reduction of dendrimer volume with increasing temperature. This was shown to result from a delicate balance between intradendrimer and dendrimer-solvent interactions. Knowing the hydrodynamic volume of a dendrimer in solution would be important in host-guest applications, in order to control the amount of guest molecules in the dendrimer and release of the guest.

Dansyl chromophores in the periphery allow efficient UV-light harvesting and when a dendrimer hosts a xanthene dye in its interior, the excitation energy is effectively transferred to the guest. Such property has a potential to be used in light harvesting and conversion applications, and in molecular sensors. Besides a host-guest EET, a guest to guest EET was observed in this work. The time scales of the EET processes in host-guest complexes were determined and interpreted in view of Förster energy transfer.

Though studies were performed only with one particular family of dendrimers, POPAM's, many of the results are valid for all "soft" dendrimers in solution generally. The experimental results may serve as benchmarks to theoretical and computational studies, whereas theoretical and computational studies offer explanations to experimental results in atomistic scale. Several practical applications of dendrimers have been developed and due to their unique properties the dendrimers are promising platforms to new molecular applications that we may see in the future. The work presented in this thesis offered new information on the properties of soft dendrimers and in that sense the work has broadened the general knowledge of this interesting group of molecules.

REFERENCES

1. E. Buhleier, W. Wehner and F. Vögtle, *Synthesis.* **1978** 155-158.

2. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J.* **1985**, *17,* 117-132.

3. G. R. Newkome, Z. Yao, G. R. Baker and V. K. Gupta, *J. Org. Chem.* **1985**, *50,* 2003-2004.

4. C. C. Lee, J. A. MacKay, J. M. J. Fréchet and F. C. Szoka, *Nat. Biotechnol.* **2005**, *23,* 1517-1526.

5. W. Jang, K. M. Kamruzzaman Selim, C. Lee and I. Kang, *Prog. Polym. Sci.* **2009**, *34,* 1-23.

6. D. Astruc, E. Boisselier and C. Ornelas, *Chem. Rev.* **2010**, *110,* 1857-1959.

7. D. Astruc and F. Chardac, *Chem. Rev.* **2001**, *101,* 2991-3023.

8. A. W. Bosman, H. M. Janssen and E. W. Meijer, *Chem. Rev.* **1999**, *99,* 1665-1688.

9. P. Ceroni, G. Bergamini, F. Marchioni and V. Balzani, *Prog. Polym. Sci.* **2005**, *30,* 453-473.

10. M. J. Cho, D. H. Choi, P. A. Sullivan, A. J. P. Akelaitis and L. R. Dalton, *Prog. Polym. Sci.* **2008**, *33,* 1013-1058.

11. R. Esfand and D. A. Tomalia, *Drug Discov. Today.* **2001**, *6,* 427-436.

12. S. M. Grayson and J. M. J. Fréchet, *Chem. Rev.* **2001**, *101,* 3819-3868.

13. S. Lo and P. L. Burn, *Chem. Rev.* **2007**, *107,* 1097-1116.

14. O. A. Matthews, A. N. Shipway and J. F. Stoddart, *Prog. Polym. Sci.* **1998**, *23,* 1-56.

15. D. K. Smith, A. R. Hirst, C. S. Love, J. G. Hardy, S. V. Brignell and B. Q. Huang, *Prog. Polym. Sci.* **2005**, *30,* 220-293.

16. D. A. Tomalia and J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40,* 2719-2728.

17. D. A. Tomalia, *Prog. Polym. Sci.* **2005**, *30,* 294-324.

18. F. Zeng and S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681-1712.

19. M. Higuchi, S. Shiki, K. Ariga and K. Yamamoto, *J. Am. Chem. Soc.* **2001**, *123*, 4414-4420.

20. S. Rosenfeldt, N. Dingenouts, D. Potschke, M. Ballauff, A. J. Berresheim, K. Müllen, P. Lindner and K. Saalwachter, *J. Lumin.* **2005**, *111*, 225-238.

21. P. G. de Gennes and H. Hervet, *J. Phys. Lett.* **1983**, *44*, 351-360.

22. R. L. Lescanec and M. Muthukumar, *Macromolecules.* **1990**, *23*, 2280-2288.

23. M. Ballauff and C. N. Likos, *Angew. Chem., Int. Ed.* **2004**, *43*, 2998-3020.

24. D. Boris and M. Rubinstein, *Macromolecules.* **1996**, *29*, 7251-7260.

25. K. B. Sebby, E. D. Walter, R. J. Usselman, M. J. Cloninger and D. J. Singel, *J. Phys. Chem. B.* **2011**, *115*, 4613-4620.

26. K. Karatasos, D. B. Adolf and G. R. Davies, *J. Chem. Phys.* **2001**, *115*, 5310-5318.

27. J. S. Klos and J.-U. Sommer, *Macromolecules.* **2009**, *42*, 4878-4886.

28. P. K. Maiti, T. Cagin, G. Wang and W. A. Goddard, *Macromolecules.* **2004**, *37*, 6236-6254.

29. P. M. R. Paulo, J. N. C. Lopes and S. M. B. Costa, *J. Phys. Chem. B.* **2007**, *111*, 10651-10664.

30. Y. Liu, V. S. Bryantsev, M. S. Diallo and W. A. Goddard III, *J. Am. Chem. Soc.* **2009**, *131*, 2798-2799.

31. I. Tanis and K. Karatasos, *Phys. Chem. Chem. Phys.* **2009**, *11*, 10017-10028.

32. P. K. Maiti, T. Cagın, S. Lin and W. A. Goddard, *Macromolecules.* **2005**, *38*, 979-991.

33. P. Welch and M. Muthukumar, *Macromolecules.* **1998**, *31*, 5892-5897.

34. M. Murat and G. S. Grest, *Macromolecules.* **1996**, *29*, 1278-1285.

35. I. Lee, B. D. Athey, A. W. Wetzel, W. Meixner and J. R. Baker, *Macromolecules.* **2002**, *35*, 4510-4520.

36. W. Chen, L. Porcar, Y. Liu, P. D. Butler and L. J. Magid, *Macromolecules.* **2007**, *40*, 5887-5898.

37. G. Nisato, R. Ivkov and E. J. Amis, *Macromolecules.* **2000**, *33*, 4172-4176.

38. S. De Backer, Y. Prinzie, W. Verheijen, M. Smet, K. Desmedt, W. Dehaen and F. C. De Schryver, *J. Phys. Chem. A.* **1998**, *102*, 5451-5455.

39. S. Stechemesser and W. Eimer, *Macromolecules.* **1997**, *30,* 2204-2206.

40. G. Giupponi and D. Buzza, *J. Chem. Phys.* **2004**, *120,* 10290-10298.

41. E. Timoshenko, Y. Kuznetsov and R. Connolly, *J. Chem. Phys.* **2002**, *117,* 9050-9062.

42. J. T. Bosko and J. R. Prakash, *Macromolecules.* **2011**, *44,* 660-670.

43. D. A. Markelov, S. V. Lyulin, Y. Y. Gotlib, A. V. Lyulin, V. V. Matveev, E. Lähderanta and A. A. Darinskii, *J. Chem. Phys.* **2009**, *130,* 044907.

44. G. R. Newkome, C. N. Moorefield, G. R. Baker, M. J. Saunders and S. H. Grossman, *Angew. Chem., Int. Ed.* **1991**, *30,* 1178-1180.

45. C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Chem. Soc., Perkin Trans. 1.* **1993** 1287-1297.

46. J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg and E. W. Meijer, *Science.* **1994**, *266,* 1226-1229.

47. J. F. G. A. Jansen, E. W. Meijer and E. M. M. de Brabander-van den Berg, *J. Am. Chem. Soc.* **1995**, *117,* 4417-4418.

48. H. Namazi and M. Adeli, *Biomaterials.* **2005**, *26*, 1175-1183.

49. A. E. Beezer, A. S. H. King, I. K. Martin, J. C. Mitchel, L. J. Twyman and C. F. Wain, *Tetrahedron.* **2003**, *59,* 3873-3880.

50. V. Balzani, P. Ceroni, S. Gestermann, M. Gorka, C. Kauffmann and F. Vögtle, *Tetrahedron.* **2002**, *58,* 629-637.

51. M. T. Morgan, M. A. Carnahan, C. E. Immoos, A. A. Ribeiro, S. Finkelstein, S. J. Lee and M. W. Grinstaff, *J. Am. Chem. Soc.* **2003**, *125,* 15485-15489.

52. M. W. P. L. Baars, R. Kleppinger, M. H. J. Koch, S. Yeu and E. W. Meijer, *Angew. Chem., Int. Ed.* **2000**, *39,* 1285-1288.

53. F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli and V. Balzani, *J. Am. Chem. Soc.* **2000**, *122,* 10398-10404.

54. M. F. Ottaviani, F. Montalti, N. J. Turro and D. A. Tomalia, *J. Phys. Chem. B.* **1997**, *101*, 158-166.

55. K. Vassilev and W. T. Ford, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2727-2736.

56. R. W. J. Scott, O. M. Wilson and R. M. Crooks, *J. Phys. Chem. B.* **2005**, *109*, 692-704.

57. R. M. Crooks, M. Q. Zhao, L. Sun, V. Chechik and L. K. Yeung, *Acc. Chem. Res.* **2001**, *34*, 181-190.

58. S. Hwang, C. D. Shreiner, C. N. Moorefield and G. R. Newkome, *New J. Chem.* **2007**, *31*, 1192-1217.

59. V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26-34.

60. R. Andres, E. de Jesus and J. C. Flores, *New J. Chem.* **2007**, *31*, 1161-1191.

61. U. Gupta, H. B. Agashe, A. Asthana and N. K. Jain, *Biomacromolecules.* **2006**, *7*, 649-658.

62. C. Yiyun and X. Tongwen, *Eur. J. Med. Chem.* **2005**, *40*, 1188-1192.

63. K. Yang, L. Weng, Y. Cheng, H. Zhang, J. Zhang, Q. Wu and T. Xu, *J Phys Chem B.* **2011**, *115*, 2185-2195.

64. T. Nguyen, D. Türp, D. Wang, B. Nölscher, F. Laquai and K. Müllen, *J. Am. Chem. Soc.* **2011**, *133*, 11194-11204.

65. F. Puntoriero, P. Ceroni, V. Balzani, G. Bergamini and F. Vögtle, *J. Am. Chem. Soc.* **2007**, *129*, 10714-10719.

66. A. Adronov and J. M. J. Fréchet, *Chem. Commum.* **2000** 1701-1710.

67. J. Larsen, J. Andersson, T. Polívka, J. Sly, M. J. Crossley, V. Sundström and E. Åkesson, *Chem. Phys. Lett.* **2005**, *403*, 205-210.

68. J. Larsen, B. Brüggemann, J. Sly, M. J. Crossley, V. Sundström and E. Åkesson, *Chem. Phys. Lett.* **2006**, *433*, 159-164.

69. M. S. Choi, T. Aida, T. Yamazaki and I. Yamazaki, *Angew. Chem., Int. Ed.* **2001**, *40*, 3194-3198.

70. M. Maus, R. De, M. Lor, T. Weil, S. Mitra, U. Wiesler, A. Herrmann, J. Hofkens, T. Vosch, K. Müllen and F. C. De Schryver, *J. Am. Chem. Soc.* **2001**, *123*, 7668-7676.

71. M. Lor, R. De, S. Jordens, G. De Belder, G. Schweitzer, M. Cotlet, J. Hofkens, T. Weil, A. Herrmann, K. Müllen, M. Van Der Auweraer and F. C. De Schryver, *J. Phys. Chem. A.* **2002**, *106*, 2083-2090.

72. T. Ahn, A. Nantalaksakul, R. R. Dasari, R. O. Al-Kaysi, A. M. Müller, S. Thayumanavan and C. J. Bardeen, *J. Phys. Chem. B.* **2006**, *110*, 24331-24339.

73. A. Nantalaksakul, D. R. Reddy, C. J. Bardeen and S. Thayumanavan, *Photosynth. Res.* **2006**, *87*, 133-150.

74. V. Balzani, P. Ceroni, M. Maestri, C. Saudan and V. Vicinelli, *Top. Curr. Chem.* **2003**, *228*, 159-191.

75. P. R. Hania, D. J. Heijs, T. Bowden, A. Pugzlys, J. Van Esch, J. Knoester and K. Duppen, *J. Phys. Chem. B.* **2004**, *108*, 71-81.

76. F. V. R. Neuwahl, R. Righini, A. Adronov, P. R. L. Malenfant and J. M. J. Frechet, *J. Phys. Chem. B.* **2001**, *105*, 1307-1312.

77. U. Hahn, M. Gorka, F. Vögtle, V. Vicinelli, P. Ceroni, M. Maestri and V. Balzani, *Angew. Chem., Int. Ed.* **2002**, *41*, 3595-3598.

78. M. Lard, S. H. Kim, S. Lin, P. Bhattacharya, P. C. Ke and M. H. Lamm, *Phys. Chem. Chem. Phys.* **2010**, *12*, 9285-9291.

79. E. Atas, Z. Peng and V. D. Kleiman, *J. Phys. Chem. B.* **2005**, *109*, 13553-13560.

80. V. D. Kleiman, J. S. Melinger and D. McMorrow, *J. Phys. Chem. B.* **2001**, *105*, 5595-5598.

81. D. Liu, S. De Feyter, M. Cotlet, A. Stefan, U. Wiesler, A. Herrmann, D. Grebel-Koehler, J. Qu, K. Müllen and F. C. De Schryver, *Macromolecules.* **2003**, *36*, 5918-5925.

82. J. S. Melinger, Y. Pan, V. D. Kleiman, Z. Peng, B. L. Davis, D. McMorrow and M. Lu, *J. Am. Chem. Soc.* **2002**, *124*, 12002-12012.

83. D. W. Brousmiche, J. M. Serin, J. M. J. Fréchet, G. S. He, T. Lin, S. Chung, P. N. Prasad, R. Kannan and L. Tan, *J. Phys. Chem. B.* **2004**, *108*, 8592-8600.

84. M. Guo, O. Varnavski, A. Narayanan, O. Mongin, J. Majoral, M. Blanchard-Desce and T. Goodson, *J. Phys. Chem. A.* **2009**, *113*, 4763-4771.

85. V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka and F. Vögtle, *Chem. Commum.* **2000** 853-854.

86. H. Cavaye, P. E. Shaw, X. Wang, P. L. Burn, S. Lo and P. Meredith, *Macromolecules.* **2010**, *43*, 10253-10261.

87. A. Caminade, A. Hameau and J. Majoral, *Chem. --Eur. J.* **2009**, *15*, 9270-9285.

88. E. M. M. de Brabander-van den Berg and E. W. Meijer, *Angew. Chem., Int. Ed.* **1993**, *32*, 1308-1311.

89. A. Archut, S. Gestermann, R. Hesse, C. Kauffmann and F. Vögtle, *Synlett.* **1998** 546-548.

90. F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli, L. De Cola and V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 12161-12166.

91. R. Sarkar, M. Ghosh and S. K. Pal, *J. Photochem. Photobiol., B.* **2005**, *78*, 93-98.

92. Y. Li, L. Chan, L. Tyer, R. T. Moody, C. M. Himel and D. M. Hercules, *J. Am. Chem. Soc.* **1975**, *97*, 3118-3126.

93. C. M. Cardona, J. Alvarez, A. E. Kaifer, T. D. McCarley, S. Pandey, G. A. Baker, N. J. Bonzagni and F. V. Bright, *J. Am. Chem. Soc.* **2000**, *122*, 6139-6144.

94. V. Balzani, P. Ceroni, S. Gestermann, M. Gorka, C. Kauffmann and F. Vogtle, *Dalton Trans.* **2000** 3765-3771.

95. B. Branchi, P. Ceroni, V. Balzani, F. Klärner and F. Vögtle, *Chem. --Eur. J.* **2010**, *16*, 6048-6055.

96. C. Hartmann-Thompson, D. L. Keeley, J. R. Rousseau and P. R. Dvornic, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5101-5115.

97. T. Kapp, A. Dullin and R. Gust, *Bioconjug. Chem.* **2010**, *21*, 328-337.

98. P. Ortega, M. Jesus Serramia, R. Samaniego, F. Javier de la Mata, R. Gomez and M. Angeles Munoz-Fernandez, *Org. Biomol. Chem.* **2009**, *7*, 3079-3085.

99. B. Branchi, P. Ceroni, G. Bergamini, V. Balzani, M. Maestri, J. van Heyst, S. Lee, F. Luppertz and F. Vögtle, *Chem. --Eur. J.* **2006**, *12*, 8926-8934.

100. B. Wang, X. Zhang, X. Jia, Z. Li, Y. Ji, L. Yang and Y. Wei, *J. Am. Chem. Soc.* **2004**, *126*, 15180-15194.

101. S. Fuchs, A. Pla-Quintana, S. Mazeres, A. Caminade and J. Majoral, *Org. Lett.* **2008**, *10*, 4751-4754.

102. G. Teobaldi and F. Zerbetto, *J. Am. Chem. Soc.* **2003**, *125*, 7388-7393.

103. A. H. Zewail, *J. Phys. Chem. A*. **2000**, *104*, 5660-5694.

104. A. H. Zewail, *Science*. **1988**, *242*, 1645-1653.

105. Claude Rullière, Ed., *Femtosecond Laser Pulses - Principles and Experiments*, Springer Verlag, Berlin Heidelberg, **1998**.

106. E. Riedle, M. Beutter, S. Lochbrunner, J. Piel, S. Schenkl, S. Spörlein and W. Zinth, *Appl. Phy. B*. **2000**, *71*, 457-465.

107. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum Publishers, New York, **1999**.

108. D. Banerjee and S. K. Pal, *Chem. Phys. Lett*. **2008**, *451*, 237-242.

109. D. P. Zhong, S. K. Pal and A. H. Zewail, *ChemPhysChem*. **2001**, *2*, 219-227.

ORIGINAL PAPERS

I

Ultrafast energy transfer in dansylated POPAM–eosin complexes

by

Jukka Aumanen, Viivi Lehtovuori, Nicole Werner, Gabriele Richardt, Jeroen van Heyst, Fritz Vögtle and Jouko Korppi-Tommola, 2006

Chemical Physics Letters, **2006**, 433, 75-79

https://doi.org/10.1016/j.cplett.2006.11.034

II

Internal Dynamics and Energy Transfer in Dansylated POPAM Dendrimers and Their Eosin Complexes

by

Jukka Aumanen, Tero Kesti, Villy Sundström, Gilberto Teobaldi, Francesco Zerbetto, Nicole Werner, Gabriele Richardt, Jeroen van Heyst, Fritz Vögtle and Jouko Korppi-Tommola, 2010

Journal of Physical Chemistry B, **2010**, 114, 1548-1558

https://doi.org/10.1021/jp902906q

III

The effect of temperature on the internal dynamics of dansylated PO-PAM dendrimers

by

Jukka Aumanen, Gilberto Teobaldi, Francesco Zerbetto and Jouko Korppi-Tommola, 2011

RSC Advances, **2011**, in press, DOI: 10.1039/c1ra00625h

https://doi.org/10.1039/C1RA00625H

IV

Energy transfer to xanthene dyes in dansylated POPAM dendrimers

by

Jukka Aumanen and Jouko Korppi-Tommola, 2011

Manuscript, submitted to Chemical Physics Letters **2011**,

https://doi.org/10.1016/j.cplett.2011.10.061