Photoinduced processes in dendrimers

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Chapter 1

Shining Light on Dendrimers

1.1 Introduction

Dendrimers (δένδρον = tree; μέρος = part) are highly branched macromolecules with a well-defined molecular structure. Flory was one of the first theoreticians who examined half a century ago the potential role of branched units in macromolecular architectures. It was only in 1978 that Vögtle et al. published for the first time an iterative synthetic method, the so-called “cascade synthesis”, via which well-defined branched amines of low molecular weight could be successfully produced. In the early 1980's Denkewalter et al. patented the synthesis of L-lysine-based dendrimers. However, despite size exclusion chromatography data, no detailed information about the structural characteristics of these dendrimers was given. In 1984-1985 Tomalia et al. synthesized and characterized the first family of poly(aminoamido) (PAMAM) dendrimers, which was subsequently produced on a commercial scale after optimization of the synthetic procedure. Shortly after that, in 1985, Newkome et al. reported the synthesis of tris branched polyamide dendrimers, the so-called “arborol” systems. Until that time all dendrimers were synthesized according to a divergent synthetic method, implying that the synthesis is started from a multifunctional core and elaborated to the periphery. In 1989-1990 Hawker and Fréchet introduced the convergent approach for the synthesis of the aromatic polyether dendrimers (Fréchet-type dendrimers). In the convergent procedure, first the dendritic wedges are synthesized and subsequently attached to a multifunctional core. Although the yields obtained using the convergent procedure are in general lower than for the divergent procedure, the purity (monodispersity) of the dendrimers is higher. After that Moore et al. reported the convergent synthesis of phenylacetylene dendrimers. In 1993, on the basis of the original work of Vögtle et al., Mülhaupt et al. and Meijer and de Brabander-van den Berg developed independently a synthetic procedure that enabled the production of poly(propylene imine) (PPI) dendrimers. In the same year van der Made and van Leeuwen et al. Zhou and Roovers, and Muzafarov et al. published the synthesis of carbosilane dendrimers. Because of their thermal and kinetical stability this class of dendrimers is particularly interesting for application in the field of catalysis.
Chapter 1

Even though many other types of dendritic systems have been synthesized, the dendrimers described above are the most frequently used and well-studied. The large variety of dendritic scaffolds and the different synthetic approaches available, make it possible to introduce functional groups in the core, in the branches and at the periphery. Many of the fascinating properties as well as their synthesis and possible applications have been described in excellent books and reviews by various experts in the field. \(^{15,27-47}\)

In the following sections we will give an overview of the photophysical processes known in dendrimers and focus on the unique properties of the dendritic systems as compared to monochromophoric systems and (hyperbranched) polymers. The possibility to implement a large number of chromophores, multiple binding sites, different functionalities at well-defined positions within the same macromolecular structure, are few of the very interesting and unique features of dendrimers. This chapter will conclude with a detailed scope and content of this thesis.

1.1.1 The Purposes behind the Development of Photoactive Dendrimers

After millions of years of evolution nature has reached such a high level of complexity and efficiency, that it is a great challenge, if not a dream, for many scientists to develop artificial systems, that are able to perform similar functions with an efficiency evenly high as nature. For example, the photosynthesis as it occurs in plants and trees converts the energy of sunlight in “chemical energy” with 95% efficiency. Light from the sun is efficiently absorbed by light-harvesting complexes (LHCs). These complexes consist of arrays of membrane-bound hydrophobic proteins containing photosynthetic pigments called chlorophylls, and in most cases accessory pigments, such as carotenoids, to ensure an efficient absorption of the sunlight. These pigments together cover with their absorption spectra the complete spectrum of the sun.

The energy gained by the light-harvesting system due to the absorption of sunlight is transferred to the photosynthetic reaction centers, which is also a chlorophyll, within 10^{-10} s with an efficiency of > 90%. A huge amount of chlorophyll molecules (approximately 300 in the green algae Chlorella) is required per reaction center and the orientation and spacing of all these chlorophyll molecules is responsible for the high efficiency of the energy transfer to the reaction center. Electrons of the excited reaction center are passed through a series of electron acceptors that convert electronic energy to chemical energy. The cyclic electron transport chain provides a proton gradient across the membrane of the cell, which drives the synthesis of ATP. The light reactions take place in two reaction centers (PSI and PSII) that are electrically connected in series. H\textsubscript{2}O is oxidized to O\textsubscript{2} and 4H\textsuperscript{+} in PSII via four single electron steps. These electrons are transferred to PSI, where they can be used to reduce NADP\textsuperscript{+} and H\textsuperscript{+} to NADPH. Both NADPH and ATP are necessary to drive the synthesis of carbohydrates from CO\textsubscript{2} and H\textsubscript{2}O in the dark reactions. The high efficiency of the electron transfer processes is, just like in case of the energy transfer processes, the result of a highly organized array of specific chromophores.

Due to their highly branched, well-defined structure in the nanoscale dimension, dendrimers provide a good scaffold for the preparation of mimics for the photosynthetic system on a
molecular scale. The periphery, the branches, and the core of the dendrimer can be functionalized with multiple chromophores to obtain a light-harvesting system. The energy gained by the light-harvesting units via absorption of light can be used for electron transfer processes to a central chromophore located in the core representing the reaction center. In order to make these electrons available for further reactions an efficient electron transfer through the dendritic system is necessary. The forward electron transfer has to be several orders of magnitude faster than the back electron transfer. In other words the charge separation has to be so fast that charge recombination is barely possible. To establish this, not only the choice of the electron donor-electron acceptor couple is crucial, but also the arrangement and connection of these components within a large structure, such as a dendrimer, is of great importance. The ultimate goal would be to use the light energy harvested at the periphery of the dendrimer to induce the "release" of electrons in the core for chemical reactions, as nature does within her photosynthetic system. Until now, only very few systems are known, in which the four crucial steps of the photosynthetic cycle are mimicked: (i) absorption of light, (ii) energy transfer to a reaction center, (iii) electron transfer, (iv) chemical conversion. Finally, the whole system should recover to its original state, in order to have a continuous process. In practise these are essential features in the development of solar cells, where a light-harvesting system provides via absorption of sunlight the energy to induce electron transfer to a semiconducting layer, transporting the electrons further away for storage. In this way the energy of the sun is used as a source to generate electricity.

Currently, dendrimer research is developing swiftly in the direction of highly functional materials. Also in the field of photoactive dendrimers the complexity of the systems has increased enormously. The investigation of dendritic structures functionalized with luminescent groups, photoswitchable units, energy and/or electron donor-acceptor components and the implementation of such functionalized dendrimers in devices, provide insight in the fundamental processes occurring in such complex systems and in their potential for future applications. In view of the development of new photoactive materials a very important question to be answered is: "why should dendrimers be used as photoactive materials, instead of small molecules or (hyperbranched) polymers?" Although the synthesis of chromophore-functionalized dendrimers is often more complex and time consuming than the synthesis of the single chromophore or polymeric materials containing the chromophore, for some applications dendritic systems are preferred.

Since dendrimers can be functionalized with multiple chromophoric groups, that are in very close proximity of each other, novel properties can arise compared to the single chromophoric system. Due to the stepwise synthesis, either divergent or convergent, chromophores can be implemented in the dendritic structure with high precision. The number of chromophores and the size of the dendrimer are very well controlled, which is of great importance for some biomedical applications. With (hyperbranched) polymers it is impossible to obtain such highly defined materials. In addition, the detectability of a dendritic molecule containing multiple chromophores is high, due to the "amplification" of the absorption and emission properties of the single
chromophore. This enables the detection of single dendrimers via single molecule spectroscopy (SMS), which is particularly interesting for nanotechnology. Furthermore, an increased sensitivity with respect to specific classes of molecules can be established, enabling the detection of very low concentrations of these molecules. This is of great interest for the field of molecular recognition, e. g. for the development of biosensors (immuno-diagnostics).

A specific advantage of the dendritic framework is that a microenvironment can be created around a single chromophore. By placing such a protective environment around a chromophore its luminescence properties can be dramatically improved. Such an environment can also be created by (hyperbranched) polymeric substituents, although in that case the structure will be less defined. Dendritic substituents can also promote supramolecular organization of chromophores, e. g. inducing the formation of fibers or doughnut-like structures.

The possibility to functionalize chromophores with large dendritic substituents is particularly interesting for the development of light emitting diodes (LEDs). The dendritic wedges do not only prevent the aggregation of chromophores, thereby reducing the amount of self quenching, but they also provide a way to improve the solubility of the chromophores in polymers, rendering a more homogeneous blend.

The introduction of photoisomerizable groups, such as azobenzene derivatives, in dendrimers enables the controlled induction of a structural change, especially when those units are attached to the core or implemented in the branches. If attached to the periphery, photoisomerizable groups, such as azobenzene derivatives, can be used to “close” the surface of a dendrimer by means of a photoinduced increase of steric hindrance at the periphery. For example, excitation with light results in the isomerization of azobenzene from the extended trans-form to the more compact cis-form. This type of dendrimers can be used as carriers for small molecules, while a controlled release of those guest molecules is possible using light, which induced the isomerization from cis to trans. In addition, azobenzene-functionalized materials are widely used in the field of datastorage.

The implementation of chromophores in dendritic structures can also provide more insight in the structural features of dendrimers. Dyes can be used as internal probes to investigate the microenvironment created by dendritic branches. At the same time the influence of external factors, e. g. the solvent or ions, on the microenvironment can be studied. This may concern a change in the conformation of the dendritic structure, but also the accessibility of the dendritic structure by other molecules. The implementation of multiple chromophores within one dendrimer allows the investigation of internal interactions between the chromophores, such as the formation of excimers and energy and electron transfer processes. To what extent these interactions take place will depend on the flexibility of the dendritic framework and the position of the chromophores within the dendritic structure.
1.2 Dendrimers as Luminescent Materials

1.2.1 Interchromophoric Interactions in Periphery-Functionalized Dendrimers

The functionalization of dendrimers with chromophoric units at the periphery is a very straight-forward approach to gain more insight in the conformation of dendritic structures. Interactions between chromophores at the periphery of dendrimers are inevitable, especially for the higher generations, where a large number of chromophores are concentrated along the periphery of the dendrimer. Interchromophoric interactions in the ground state within dendrimers depend on the flexibility of the dendritic structure and on the properties of the chromophores themselves, i.e. their ability to stack (π-π interactions), to form hydrogen bonds or to undergo electrostatic interactions.

Fluorescent chromophores, that are known to form excimers at higher concentrations, such as pyrene and naphtalene, are particularly suitable to study in detail π-stacking interactions within dendrimers (Figure 1-1). Once attached to the periphery, the extend of excimer formation among the chromophoric groups depends strongly on the flexibility of the dendrimer structure. Upon excitation of the chromophores both an emission from monomers and from excimers can be detected. The higher the excimer fluorescence the greater the interactions along the periphery of the dendrimer. Cooperativity between functional groups, which can lead to new functions is directly related to the proximity of the chromophores within the dendritic structure.

Crooks et al. studied pyrene-terminated poly(propylene imine) dendrimers as a model for more complex systems, to demonstrate the relationship between structure and function. They observed an increase in excimer emission going to higher generations. The pyrene units were found to be preaggregated (prior to excitation) and interactions between the pyrene pending groups and the dendrimer backbone became evident on the basis of the relative quenching of the pyrene excited state by the dendritic core as a function of pH. Slomkowski et al. concluded that pyrene moieties implemented in the branches of phosphorus-containing dendrimers were not

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Figure 1-1. Schematic representation of the formation of excimers at the periphery of a dendrimer.
hindered in their mobility due to interactions between the branches and that no pyrene-pyrene dimers were formed in the ground-state, while in the excited state besides the monomer emission, also excimer emission was observed.\textsuperscript{49}

Excimers and exciplexes are known to act as energy traps in some polymeric materials. A high degree of entanglement of polymeric chains is responsible for the formation of excimers. Fox \textit{et al.} developed Fréchet-type dendrimers bearing naphthyl peripheral groups to investigate to what extend the branched structure of dendrimers can reduce the excimer formation.\textsuperscript{50} In line with Crooks \textit{et al.}, they suggested that the preaggregation of the chromophores is responsible for an enhanced excimer emission.

In order to gain more insight in the photophysical behavior of \(\pi\)-conjugated materials, which are widely applied in light-emitting diodes (LEDs), Bässler \textit{et al.} investigated the interchromophoric coupling in oligo(\(p\)-phenylenevinylene) (OPV)-substituted poly(propylene imine) dendrimers. This coupling was found to be sufficient to induce delocalization over more than one chromophoric group. A delayed emission component was attributed to the formation of excimers/exciplexes within the dendrimer.\textsuperscript{51} In a similar fashion, Müllen and De Schryver \textit{et al.} observed excimer-like behavior for peryleneimide-functionalized polyphenylene dendrimers.\textsuperscript{52-55}

\subsection*{1.2.2 Core-Functionalized Dendrimers}

Site isolation effects can be used to prevent intermolecular interactions between chromophores, in particular the self-aggregation of chromophores in the solid state, or interactions between a chromophore and the environment, that could cause a quenching of the emission. In order to “protect” the chromophore from external interactions, a dendritic structure can be built around it (Figure 1-2).\textsuperscript{56-84}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{dendritic_structure.png}
\caption{Site isolation effect of dendritic branches around a chromophore.}
\end{figure}

By the introduction of branched substituents (i) a microenvironment is created around the chromophore, making the chromophore inaccessible to certain molecules or ions because of their great difference in polarity with the dendritic wedges, and (ii) a barrier is created based on steric
crowding, which makes the core unreachable for large molecules. As will be demonstrated later on, this does not imply that the core is completely inaccessible to all molecules. Due to the flexibility of the dendritic structure, the cavities between the branches may still be accessible. In some cases the dendritic wedges will act as hosts for small molecules that are attracted by the microenvironment created by the branches and fit into the dendritic cavities. In other cases the periphery of the dendritic wedges may interact in such a way with specific molecules, that there is to some extend electronic coupling between a substrate molecule and the core via the branches. In both examples, interactions with the core cannot be prevented.

In particular, the isolation of the core is an approach to prevent aggregation of the central chromophore.57-59 Dendritic substituents, but also branched star polymers can be used to establish site isolation as demonstrated by Fréchet et al..60,61 In that case the degree of polymerization of the polymer chains and the solvent, in which the molecule may have an extended or a collapsed structure, determine the success of site isolation.

To determine the extent of shielding by the dendritic structure, Hawker, Wooley and Fréchet employed solvatochromic dyes implemented in the core of a dendrimer or attached to the focal point of a dendritic wedge.62 The dye shows a shift in the absorption and emission going from lower to higher generations. In fact, due to the change in conformation of the dendrimer, e. g. from an extended to a more globular structure, a different environment with different polarity is created around the dye. Moore et al. measured the emission of phenylacetylene dendrimers with an electron donor at the focal point as a probe to observe a similar effect.63 An abrupt change in the trend was observed going from the fourth to the fifth generation, suggesting the occurrence of dendritic encapsulation of the focal point.

Several groups investigated the accessibility of the core of functionalized dendrimers for fluorescence quenchers as well as the influence of the size, charge, and hydrophobicity of the quencher on its ability to penetrate the dendrimer. Both Aida et al.64 and Fréchet et al.65 investigated the ability of quenchers, such as Vitamin K₃,64 small generation free base porphyrin dendrimer,64 and benzylviologen,65 to quench the excited state of a zinc porphyrin protected by Fréchet-type dendritic wedges. Surprisingly, the emission of the higher generation zinc porphyrin-cored dendrimers was more efficiently quenched by a small quencher molecule, such as Vitamin K₃. This is due to the fact that in case of the higher generations zinc porphyrin-cored dendrimers, the wedges act as a host for the small quencher molecules resulting in an efficient quenching of the zinc porphyrin emission. On the other hand the branches cooperatively provide a barrier for large quencher molecules preventing in that case the quenching of the zinc porphyrin emission.

Aida et al. demonstrated the direct relationship between the size of the dendritic substituents and the accessibility of the functional group in the core, by measuring the binding interaction between dendritic imidazoles with zinc porphyrin-cored dendrimers. The accessibility of the core is largely reduced for the imidazole ligand using higher generations of the zinc porphyrin due to steric hindrance (Figure 1-3).66
Zinc porphyrins form stable complexes with imidazoles (left). By placing large dendritic branches around the zinc porphyrin, a site isolation effect is introduced, preventing coordination of a dendritic imidazole ligand (right).

Besides Aida et al. several other groups studied the site isolation effect for porphyrin-cored dendrimers using various types of dendritic wedges.

Bright et al. developed pyrene-cored Newkome-type dendrimers bearing carboxylate groups at the periphery in order to study the accessibility of the pyrene core for both neutral (nitromethane, acrylamide, \(N,N'\)-dimethylaniline, methyl iodide) and ionic (I\(^-\) and Cu\(^{2+}\) ions) quenchers. The role of size and charge was investigated and again it was found that the higher the dendrimer generation, the lower the quenching rates became. For the anionic quencher I\(^-\), this shielding effect was found to be even larger because of the electrostatic repulsion with the carboxylic acid groups at the periphery. On the other hand the cationic quencher was found to bind to the negatively charged dendrimer due to ion pair formation. In this way there is still some electronic coupling between the cationic quencher at the periphery and the core, so that in this case quenching rates are reduced as a result of the increase distance between the two components.

Balzani and Vögtle et al. demonstrated that dendritic wedges are capable of protecting a \([\text{Ru(bpy)}_3]^{2+}\) core to a very large extend from \(^1\text{O}_2\) (singlet oxygen), which is commonly known as an efficient triplet quencher. Both Newkome-type poly(ether amide) wedges and Fréchet-type poly(benzyl ether) wedges were successfully used to protect the \([\text{Ru(bpy)}_3]^{2+}\) core (Figure 1-4).
Going to higher generation dendrimers, the excited-state lifetime and the quantum yield of emission increased as a result of the shielding effect of the dendritic wedges. In case of a second generation Newkome-type dendrimer the lifetime was found to be twice as long and the emission red-shifted with 30 nm compared to a third generation Fréchet-type dendrimer in aerated acetonitrile. This indicates that the more polar Newkome-type dendrimers stabilize the triplet metal-to-ligand charge transfer excited state (³MLCT) of the [Ru(bpy)₃]²⁺ core.

Similar results were obtained by Vinogradov et al. with their palladium porphyrin-dendrimers. Functionalization of a palladium porphyrin with Fréchet-type, Newkome-type, or polyglutamate dendritic wedges resulted in all cases in a decrease in the quenching rates with ¹⁰O₂. Very remarkable is the extreme decline in quenching rate observed for the Fréchet-type dendrimers by a factor 30. Also in this case, the Newkome-type dendrimers are

Figure 1-4. Second generations of the Fréchet-type (1 and 2) and the Newkome-type (3) [Ru(bpy)₃]²⁺ complexes.\textsuperscript{74,75}
successfully applied to shield the core from $^{1}\text{O}_2$ in various solvents, such as DMF and THF. They concluded that the bulkiness of the dendritic wedges does not necessarily play a large role in the shielding effect with respect to $^{1}\text{O}_2$, but rather the composition of the dendritic matrix (by means of polarity and its ability to “solubilize” $^{1}\text{O}_2$) and the solvent used.

It is for example known that the shielding effect with respect to $^{1}\text{O}_2$ is extremely pronounced for carboxylate terminated dendrimers. The carboxylate groups create an unfavorable environment for $^{1}\text{O}_2$, as reported also by Turro et al.. They demonstrated that the oxygen concentration is significantly lower at the periphery of carboxylate-terminated PAMAM dendrimers in water, by probing the emission of $[\text{Ru(phen)}_3]^{2+}$, which was electrostatically bound to the periphery. Castellano et al. came to the same conclusion investigating the quenching reactions between a $[\text{Ru(bpy)}_3]^{2+}$-cored dendrimer bearing coumarin-450 groups at the periphery and a series of quencher molecules, such as PTZ and MV$^{2+}$, and also $^{1}\text{O}_2$.  

Komatsu et al. did not measure a significant effect on the lifetimes of the singlet and the triplet excited states of fullerene-cored Fréchet-type dendrimers (Figure 1-5) compared to fullerene itself in o-dichlorobenzene. The rates of bimolecular quenching processes are significantly reduced due to the protection of the bulky higher generation dendritic substituents.

![Figure 1-5. The structure of a 3rd generation fullerene-cored Fréchet-type dendrimer, investigated by Komatsu et al.](image)

In contrast with the results of Komatsu et al. and in accordance with the results of Vögtle et al. and Balzani et al., Nierengarten et al. and Armaroli et al. do observe an increase in the lifetime of fullerene in toluene, dichloromethane, and acetonitrile as a result of its substitution with Fréchet-type dendritic wedges of increasing generation, shielding the fullerene core from triplet quenchers, such as $^{1}\text{O}_2$ (Figure 1-6).
Bright \textit{et al.} investigated the ability of $\beta$-cycloextrin ($\beta$-CD) and antidansyl-antibody residues to bind to a dansyl moiety substituted with Newkome-type wedges in water (Figure 1-7).\textsuperscript{82} The binding of $\beta$-CD could be completely impeded by using high generation dendritic wedges. Surprisingly, this was not the case for the anti-dansyl antibodies, which have a 100-fold higher molecular mass than $\beta$-CD. This suggests that the dendritic structure can be altered to allow access to the dansyl moiety at the focal point if the binding affinity is large enough.

In a similar fashion, Raymo \textit{et al.} and Credi \textit{et al.} concluded, based on electrochemical experiments and a quenching study with $[\text{Ru(bpy)}_3]^{2+}$, that the binding of $\beta$-CD to ferrocene-containing carbohydrate dendrimers is strongly dependent on the number (1 or 2) of substituents on the ferrocene moiety and on the number (1 or 3) of carbohydrate branches present in the substituents.\textsuperscript{83}
More recently, Houston et al. and Abruña et al. underlined once more the influence of steric crowding at the periphery, the conformation of the dendrimer and electrostatic interactions between charged dendrimers and charged quencher molecules, on the quenching dynamics studying the interactions between \([\text{Ru(bpy)}_3]^{2+}\)-functionalized PAMAM dendrimers and several quencher molecules, such as nitroaromatics.\(^8\)

### 1.2.3 Self-Organized Fluorescent Dendritic Materials

The hierarchical self-assembly of dendritic macromolecules or dendrons via non-covalent interactions, such as hydrogen bonding and van der Waals interactions, has attracted great attention for the design of well-defined mesoscopic materials. Furthermore, the self-organization of macromolecules can be used as a model for the self-organization events in natural systems. Percec et al. reported the cylindrical columnar assembly of carboxylic acid-anchored poly(benzyl ether) dendrons having long alkyl chains at the periphery.\(^8\) Implementation of fluorescent chromophoric groups in such assemblies leads to novel types of well-organized fluorescent materials.

Aida et al. used metal-metal interactions among group 11 metal ions (Cu(I), Ag(I), Au(I)) for the hierarchical self-organization of dendritic macromolecules. Upon complexation of the metal ion to a first generation dendritic pyrazole-anchored poly(benzyl ether) dendrons super-helical luminescent fibers were formed (Figure 1-8).\(^8\)

![Figure 1-8. Luminescent fibers formed from metallacycles (\(M^I = \text{Cu(I)}, \text{Ag(I)}, \text{or Au(I)}\)) containing first generation pyrazole ligands.\(^8\)](image)

The higher generations of the dendritic wedges were also successfully employed as ligands for the metallacycles. In that case glassy aggregates were formed instead of fibers, demonstrating that the formation of highly organized supramolecular structures depends strongly on the size of the dendritic wedges.
Masuhara et al. and Aida et al. showed that fluorescent doughnut-like assemblies could be obtained using wire-type dendrimers, consisting of a fully conjugated poly(phenyleneethynylene) backbone (25 DP (DP = degree of polymerization)) wrapped with flexible first generation poly(benzyl ether) dendritic wedges (Figure 1-9).  

![Figure 1-9](image)

**Figure 1-9.** Wire-type first generation dendrimer with a fully conjugated poly(phenyleneethynylene) backbone (DP = 25), which forms doughnut-like assemblies.

Changing the DP of the backbone or the generation of the wedge resulted in differently shaped structures, such as yarn-like structures and particles. Furthermore, repetitive contraction and swelling was observed for these gel-like wire-type dendrimer assemblies applying photon pressure of a near-infrared laser beam. Recently, Masuhara et al. reported the photophysical properties of the aggregates consisting of this type of π-conjugated wire-type dendrimers. They found that the fourth generation dendritic wedges were bulky enough to prevent aggregation of the conjugated backbone, while in case of the smaller generations aggregation was observed. The aggregate formation could be probed via the changes in the spectral properties.

Meijer et al. and De Schryver et al. demonstrated that third generation oligo(p-phenylenevinylene) (OPV)-terminated poly(propylene imine) dendrimers form vesicles in protic polar solvents. These vesicles could be trapped and manipulated using optical tweezers (micromanipulation), resulting in novel structures. They showed that micromanipulation is a new and promising tool to control shape and dimension in π-conjugated assemblies.
1.3 Photoisomerization of Azobenzene-Containing Dendrimers

Azobenzene derivatives are potential interesting materials for application in optical datastorage and optical switching systems due to their facile and reversible photoisomerization properties. In general small systems containing azobenzene are well understood and their response to light is predictable and can be easily controlled. In several examples the azobenzene moieties are implemented in polymeric structures and due to the length, shape and size of the polymer, their photobehavior is hard to control. In contrast, the use of a defined unimolecular structure, such as a dendrimer, as a skeleton for multichromophoric units could lead to a more predictable control of the photoinduced configurational changes and even to a better stability of the system. Several groups studied dendrimers having azobenzene moieties implemented in the core, at the periphery, or throughout the dendritic structure pursuing different goals.

Aida et al. showed that benzyl aryl ether dendritic branches can be used to harvest low-energy photons (infra-red (IR) light). The energy is channelled to the core, where the photoisomerization of the azobenzene moiety can occur. The dendritic matrix protects against collisional de-excitation and defines the directionality of energy transfer process (Figure 1-10). The surprising finding of Aida et al. was further supported by calculations performed by Tanaka et al. However, until now this remains the only example of a molecule in which a chemical transformation can be performed with IR (low energy) light.

![Figure 1-10. Light-harvesting of IR-light by the benzyl aryl ether dendritic branches (left) induces the E to Z isomerization of the azobenzene core (right).](image)

McGrath et al. reported benzyl aryl ether dendrimers with azobenzene cores and benzyl aryl ether dendrimers with azobenzene moieties at the periphery, in all cases consisting of exactly three azobenzene units per dendrimer. He studied the effect of the photoisomerization of the azobenzene units on the polarity and on the size of the dendrimer in relation to the position of the
azobenzene moieties within the dendritic structure. Four discrete states could be prepared upon irradiation, depending on the $E/Z$ configuration of the individual azobenzene moieties, namely $EEE$, $EEZ$, $EZ$ and $ZZZ$ (Figure 1-11).

![Diagram of azobenzene-core dendrimers and dendrimers with azobenzene peripheral groups](image)

**Figure 1-11.** A schematic representation of the azobenzene-functionalized dendrimers studied by McGrath et al.\textsuperscript{111,112}

These macromolecular isomers\textsuperscript{117} could be separated using thin-layer chromatography (TLC) based on the difference in polarity between the $Z$ and the $E$ isomer. The photomodulation of the dendrimer polarity was found to be relatively insensitive to the position of the responsive groups within the structure. This was demonstrated by a small difference in both the absolute $R_F$ values and the range of $R_F$ values on TLC, comparing dendrimers of the same generation, one with the interior azobenzene units and the other with the exterior azobenzene units. In contrast, the photomodulation of the dendrimer hydrodynamic volume was found to be extremely sensitive to the position of the photoresponsive groups within the dendritic structure.

Majoral et al. prepared for phosphorus containing dendrimers with azobenzene moieties precisely placed within their framework. The ratio between $E$ and $Z$ isomers in the photostationary state varied greatly depending on the location of the azobenzene units within the dendritic framework.\textsuperscript{113} Progressive implementation of azobenzene units inside the dendrimer induces a progressive reluctance to isomerize. Furthermore, the rate of the $E$ to $Z$ isomerization was found to depend on the location of the azobenzene moiety. This appeared to be more likely due to a substituent effect than to the position of the azobenzene.

To introduce shape-persistency to photoswitchable systems and to create the possibility to develop nanoparticles (dendrimers) with a well-defined number of chromophores within a confined volume, De Schryver et al. and Mullen et al. synthesized and studied polyphenylene dendrimers with an azobenzene core (Figure 1-12).\textsuperscript{114} They found only a slight steric effect on the $E$ to $Z$ isomerization of an azobenzene unit implemented in the core of polyphenylene dendrimers. At the same time, gel permease chromatography revealed a decrease in the hydrodynamic volume (24% for generation 4 up to 38% for generation 2), corresponding to a dramatic change in the dendritic structure upon isomerization of the azobenzene moiety.
The structure of a first generation water-soluble azobenzene-functionalized dendrimer developed by Moroder et al.  

Figure 1-12. Azobenzene substituted with 3rd generation rigid polyphenylene dendritic wedges developed by De Schryver et al. and Mullen et al. as a shape-persistent photoswitchable system.  

Moroder et al. developed water-soluble dendritic azobenzene peptides, creating the possibility to use azobenzene dendrimers for the photomodulation of molecular recognition processes in aqueous media (Figure 1-13). They found that the photoisomerization in a buffered aqueous solution is strongly affected both by intra- and intermolecular interactions, such as hydrophobic interactions, \( \pi \)-stacking and interactions between ammonium salt from the buffer solution and the aromatic groups. However, at high dilution the photoisomerization still occurs in such an extend, that photomodulation of molecular recognition processes between ligands grafted to the dendrimer and receptor molecules can be exploited.
Meijer et al. and De Schryver et al. studied the merging of giant vesicles, consisting of fifth generation (64 end groups) alkyl-modified, azobenzene-functionalized PPI dendrimers (containing on average 32 azobenzene groups and 32 palmitoyl groups) (Figure 1-14).  

![Diagram of dendrimer structure](image)

**Figure 1-14. The azobenzene-functionalized fifth generation PPI dendrimer employed by Meijer et al. in giant vesicles** and Langmuir and Langmuir-Blodgett films.  

They demonstrated that in this particular case the combination of the photoisomerization of the azobenzene units, bearing sufficient free space to isomerize, and local heating using an IR-beam, is essential for the merging process. Giant vesicles consisting of PPI dendrimers lacking the photoswitchable azobenzene units could not be merged, showing that the presence of the photoswitchable units is necessary for the merging process. In addition, the merging of giant vesicles consisting of dendrimers completely substituted with azobenzene moieties failed as well. In that case the free volume necessary for the azobenzenes to isomerize is reduced and the photoswitching is hampered. This is an example of covalent synthesis (of the dendrimer) and supramolecular organization (formation of giant vesicles) followed by micromanipulation (IR irradiation and photoisomerization upon excitation with UV light) leads to the bottom-up synthesis of micrometer-sized objects.

The same dendrimer has been investigated in Langmuir and Langmuir-Blodgett films and it has been shown that stable photoresponsive films can be formed. Microphase separation of the
azobenzene moieties within the monolayers is prevented, since the azobenzene units are anchored to the dendrimer and "diluted" in the matrix of palmitoyl alkyl chains. As a result Z to E isomerizations is facilitated.

Shibaev et al. demonstrated that it is possible to form a smectic A (SmA) liquid crystalline phase with a first generation carbosilane dendrimer substituted with azobenzene units. The E to Z isomerization upon UV irradiation resulted in the break-down of the smectic order and a transition to an isotropic melt.

Balzani and Vögtle et al. utilized azobenzene-functionalized poly(propyleneamine) dendrimers as photoswitchable dendritic hosts for the dye eosin Y (Figure 1-15). The encapsulation of eosin Y has been monitored by the decrease in the fluorescence quantum yields due to the quenching of the eosin Y excited state by the amines present in the dendrimer core. The degree of quenching depends on the geometry of the azobenzene units and it was found that the Z isomer is more efficient host than the E isomer. Further proof of eosin Y being encapsulated in the dendrimer comes from the photoinduced E to Z isomerization of the azobenzene moieties upon excitation of eosin Y. In addition, the meta-azobenzene-functionalized poly(propyleneamine) dendrimers were, in contrast to the para-azobenzene-functionalized analogue found to be suitable for application in holographic materials.

Figure 1-15. A fourth generation para-azobenzene-functionalized dendrimer employed as a photoisomerizable guest for eosin Y.

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1.4 Energy Transfer

1.4.1 Excitation Energy Transfer among Chromophores at the Periphery

Energy transfer among identical chromophores at the periphery of dendrimers upon excitation with light is a generally observed phenomenon (Figure 1-16).

![Schematic representation of energy transfer among chromophores along the periphery of a dendrimer.](image)

Both the distance between the chromophores and the orientation of the chromophores along the periphery influence the efficiency of this energy transfer process.

Interactions between peryleneimide chromophores in the excited state at the periphery of polyphenylene dendrimers have been extensively studied by De Schryver et al. and Müllen et al. Processes such as energy hopping and singlet-singlet annihilation were studied using time-resolved fluorescence techniques and fluorescence upconversion. These processes were found to be strongly related to the three dimensional structure of the dendrimer and in particular to the spatial orientation of the chromophores at the periphery.

Electronic energy transfer among free base porphyrin moieties at the periphery of poly(propylene imine) dendrimers was studied using time-resolved anisotropy measurements (TRAMS) by Ghiggin et al. The position and the orientation of the porphyrin moieties, which depends on the generation, was found to influence strongly the efficiency of the energy transfer process among the porphyrin units. For example, in case of a third generation dendrimer interdendron porphyrin energy transfer was suggested to be unfavorable due to dendron segregation.

Röder et al. showed that energy transfer among pheophorbide-a chromophores at the periphery of poly(propylene imine) dendrimers takes place efficiently, while the photosensitized production of singlet oxygen is dramatically reduced due to interchromosphoric interactions at the periphery. They used basically the amount of singlet oxygen produced upon excitation of the pheophorbide-a units as an indirect measure for the interchromosphoric interactions. However, the
small amount of photosensitized produced singlet oxygen produced was in all cases destructive for the pheophorbide-α-substituted dendrimers.

1.4.2 Light-Harvesting (Antenna Effect)

Several systems have been employed in order to mimic the photosynthesis. Among the artificial systems, dendrimers are particularly interesting for light-harvesting processes, since their branched structure offers the possibility to attach multiple chromophores at the periphery, which are able to collect light (antenna molecules). The advantage to use a large number of chromophores resides in the large absorption cross section and thus an efficient collection of the incident light. Once the light is absorbed the energy gained has to be transferred to an energy relay system (reaction center), which is preferentially located in the core in case of dendrimers or at the focal point in case of dendrons, in order to make it available for chemical conversion (Figure 1-17). A wide range of dendrimers containing a large variety of chromophores has been synthesized for light-harvesting.\textsuperscript{75,124-161}

![Figure 1-17. A schematic representation of a light-harvesting system.](image-url)

Poly(benzyl ether) dendrons have been used in several cases to harvest light and to transfer the energy to a light-emitting core. Poly(benzyl ether) dendrons with a carboxylate group at the focal point were employed as ligands for lanthanides by Fréchet et al.\textsuperscript{125,126} The efficiency of energy transfer was found to be much higher in case of the Tb\textsuperscript{3+}-complexes. In relation to the Förster mechanism for energy transfer, this is attributed to the larger spectral overlap between the dendrimer emission and the lanthanide absorption in case of the Tb\textsuperscript{3+}-complexes compared to the Er\textsuperscript{3+}-complexes. In addition the substitution pattern within the dendrons determines to what extend site isolation of the lanthanide complex is established.

Similarly, Aida et al. studied the energy transfer from the poly(benzyl ether) wedges to a free base porphyrin core.\textsuperscript{127} In that case the efficiency of the energy transfer was found to be strongly related to the number of dendritic wedges attached to the porphyrin core. It was postulated that cooperativity between the wedges is necessary for an efficient energy transfer. This cooperativity
seemed to decrease with increasing conformational mobility of the wedges. Polyion complex (PIC) micelles were obtained by mixing zinc porphyrin-cored poly(benzyl ether) dendrimers bearing primary amine moieties at the periphery and PEG-b-poly(α,β-aspartic acid).\textsuperscript{128} The possibility to use these micelle encapsulated dendrimer porphyrins as tumor environment-sensitive delivery systems of photosensitizers for photodynamic therapy (PDT), \textit{i.e.} a method for the localized treatment of solid tumors, looks promising and is still under current investigation.\textsuperscript{129}

In other work Aida \textit{et al.} reported that the blue luminescence of a dendritic rod consisting of a rigid poly(phenyleneethylene) backbone substituted with poly(benzyl ether) wedges, could be strongly enhanced due to the steric effect and the antenna function of the dendritic envelope.\textsuperscript{130}

Finally, as discussed in §1.3, Aida \textit{et al.} demonstrated that poly(benzyl ether) dendrons can be used to harvest IR-light, which induced the photoisomerization of an azobenzene moiety implemented in the core.\textsuperscript{94}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure18.png}
\caption{A schematic representation of the light-harvesting systems developed by Aida \textit{et al.}, consisting of 2\textsuperscript{nd} generation Fréchet-type dendrons and zinc porphyrin ($P_{Zn}$) units as light-harvesting antennae and a free base porphyrin ($P_{FB}$) as an energy acceptor in the core or at the focal point.\textsuperscript{131,132}}
\end{figure}

Based on the wheel-like arrays of bacteriochlorophyll found in the X-ray structure of the light-harvesting antenna complex (LH2) from the purple photosynthetic bacterium \textit{Rhodopseudomonas acidophila} strain 10050,\textsuperscript{162} Aida \textit{et al.} synthesized both dendritic wedges
and dendrimers containing a free base porphyrin (PFB) unit at the focal point or in the core respectively and zinc porphyrin (PZn) units through the branches (Figure 1-18).  

Energy transfer was observed from the PZn to PFB in all compounds reported. Interestingly, the morphology was found to be of great influence on the energy transfer efficiency. The decrease in the rate of energy transfer going to larger generations is a consequence of the increasing distance between the energy donors and the energy acceptor. However, the large decrease in the energy transfer efficiency observed in the case of the cone-shaped dendrons must be related to the morphology of the molecule. Indeed, fluorescence depolarization measurements showed that the energy migration among the PZn moieties in the star-shaped dendrimers is much more efficient, confirming that the morphology of the light-harvesting antenna plays a crucial role.

Balzani et al. synthesized via the so-called "complexes as metals/complexes as ligands" strategy various dendrimers consisting exclusively of Ru(II)- and Os(II)-polypyridine moieties, with 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) as bridging ligands and 2,2'-bipyridine (bpy) and 2,2'-biquinoline (biq) as terminal ligands. A schematic representation of these metallo-dendrimers and the structures of the bridging and terminal ligands are given in Figure 1-19.

Within this type of dendrimers, energy transfer is observed from the higher $^3\text{MLCT}$ levels to the lower $^3\text{MLCT}$ levels. The energy of the $^3\text{MLCT}$ level of each unit depends on the metal ion (the $^3\text{MLCT}$ state of Ru(II) polypyridine complexes is higher in energy than the $^3\text{MLCT}$ state of the corresponding Os(II) polypyridine complexes) and the ligands attached. The energy transfer occurs according to the Dexter electron exchange mechanism, precluding long-range interactions between the periphery and the core.

The synthetic control on the composition of these polynuclear dendrimers allows a high degree of control on the direction of the energy transfer processes within the dendrimer, i.e.
center-to-periphery or periphery-to-center energy transfer. Campagna et al. introduced a third type of metal ion, namely Pt(II), in the polynuclear polypyridine dendrimers. The introduction of the third metal was necessary to establish a periphery-to-center energy gradient, with the highest energy levels located at the periphery and the lowest energy level positioned in the core, resulting in an efficient antenna effect (Figure 1-20).

![Energy transfer diagram](image)

**Figure 1-20.** Optimal organization of the energy levels of the metal complexes from the periphery ($M_p$) along the branches ($M_b$) to the core ($M_c$) in order to achieve an efficient antenna effect.

Fréchet et al. developed poly(aryl ether) dendrimers with coumarin-2 chromophores at the periphery as light-harvesting moieties and a coumarin-343 in the core as an energy trap. The energy absorbed by the coumarin-2 dyes is for all generation quantitatively transferred to the central coumarin-343 dye. Only a slight decrease in the efficiency (~93%) was observed for generation 4. After that, Fréchet et al. and Righini et al. studied in more detail the energy transfer occurring within the poly(aryl ether) dendrimers with coumarin-2 as light-harvesting peripheral units and either coumarin-343 or heptapolythiophene as energy traps implemented in the core (Figure 1-21).

![Dendrimer structure](image)

**Figure 1-21.** The second generation of the light-harvesting dendrimers developed by Fréchet et al., consisting of coumarin-2 peripheral groups and a coumarin-343 or heptathiophene energy acceptor at the focal point.
The polythiophene unit was investigated, since it is possible to tune the absorption and emission properties of this unit by changing the degree of oligomerization. With increasing generation the rate of the energy transfer went down in accordance with the Förster theory. Very recently, Fréchet et al. and Saykally et al. studied the coumarin-2/coumarin-343 dendrimers in films using photoluminescence near-field scanning optical microscopy.\textsuperscript{143} The photoluminescence was shifted more to the red going to the smaller generations, because of the formation of coumarin-343 excimers. For generation 4 complete site isolation of the coumarin-343 dye was observed, since the photoluminescence spectrum resembled the solution photoluminescence spectrum. In addition, a more spatially homogeneous film could be obtained based on the high generation.

Dendrimers bearing coumarin-2 units as energy donors at the periphery and a phenylenebis(dicarboximide) unit implemented in the core could be employed as fluorescence resonance (FRET)-based ultraviolet (UV) to near-infrared (NIR) converters.\textsuperscript{144} This also accounts for the same dendrimers, bearing in addition Fluorol 7GA moieties at the periphery.\textsuperscript{145} In other words, these molecules can be used to transform UV radiation directly into near-IR radiation, due to the energy transfer from the coumarin-2 units, eventually \textit{via} an intermediate dye, such as Fluorol 7GA (Figure 1-22), to the perylenebis(dicarboximide) moiety in the core.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1_22.png}
\caption{The three component dendritic FRET-based UV to NIR converter, consisting of coumarin-2 (light-harvesting moiety) and Fluorol 7GA (intermediate energy acceptor moiety) peripheral groups and a perylenebis(dicarboximide) unit (NIR emitter) in the core, developed by Fréchet et al.\textsuperscript{145}}
\end{figure}

The overall efficiency in the three component system (coumarin-2, Fluorol 7GA and perylenebis(dicarboximide)), where the energy transfer occurs \textit{via} a cascade route, was found to
be 76% (upper limit),\textsuperscript{145} while a quantitative conversion (99%) of the absorbed UV light in the NIR emission of the perylene dye is observed in the two component system (coumarin-2, perylenebis(dicarboximide)).\textsuperscript{144}

Vögtle \textit{et al.} and Balzani \textit{et al.} investigated energy transfer processes within dansyl-substituted poly(propyleneamine) dendrimers. They found that upon partial protonation of the dansyl moieties, energy transfer occurs from the non-protonated dansyl units to the protonated ones.\textsuperscript{146} Furthermore, coordination of a single Co(II) ion to the poly(propyleneamine) core results in the quenching of the emission of all dansyl units, rendering a very large signal amplification and thus a much larger sensitivity for Co(II) ions.\textsuperscript{147,148} The true mechanism (electron or energy transfer) could not be revealed, since the excited dansyl units are both good energy- and electron donors, while Co(II) amine complexes have several low-energy excited states and are easily to oxidize.

The dansyl-functionalized dendrimers could also be employed for the extraction of fluorescent dyes, such as eosin Y,\textsuperscript{149,150} fluorescein,\textsuperscript{150} and rose bengal\textsuperscript{150} from H\textsubscript{2}O to CH\textsubscript{2}Cl\textsubscript{2}. Once hosted in the dansyl-functionalized dendrimer, one molecule of eosin Y was found to be capable of quenching the fluorescence of all dansyl moieties at the periphery via energy transfer (Figure 1-23).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure123.png}
\caption{Quenching of all dansyl peripheral groups by one single molecule eosin Y hosted in the dendrimer via energy transfer.\textsuperscript{149,150}}
\end{figure}

The bi-exponential lifetime of the emission of eosin Y hosted by the dendrimer was attributed to the possibility for eosin Y to occupy two different sites within the dendritic structure. Fluorescein and rose bengal show (qualitatively) similar behavior as eosin Y. In addition, eosin Y was found to sensitize dioxygen emission via its triplet state. The sensitization process was four
times more efficient in the case of free eosin Y compared to eosin Y hosted in the dendrimer, confirming once more the protection of the branches against $^1$O$_2$ as discussed in §1.2.2.

Continuing the development of light-harvesting systems, Vögtle et al. and Balzani et al. developed a dendrimer containing three different types of chromophores, namely 8 dansyl-, 24 dimethoxybenzene-, and 32 naphtalen units (Figure 1-24). The introduction of multiple dyes in one dendrimer provides a way to collect efficiently a relatively large amount of light per molecule. As the dansyl dendrimers described above, also these dendrimers are able to host eosin Y. Upon excitation of the dendrimer with light the energy is almost quantitatively ($> 95\%$) transferred to the eosin Y guest. The exact position of the eosin Y guest within the dendrimer is unknown.

Figure 1-24. Intramolecular, i.e. within the dendrimer, and intermolecular (dendrimer host to eosin Y guest) energy transfer processes in a multicomponent light-harvesting system.$^{151}$

In a similar fashion, Balzani et al. and Vögtle et al. developed a dansyl-functionalized dendrimer (24 dansyl groups in total at the periphery) bearing 21 amide moieties for the complexation of lanthanide ions (Nd$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Er$^{3+}$, and Yb$^{3+}$). The complexation of the lanthanide ions to the amide units in the dendrimer is accompanied by the quenching of the fluorescent excited state of the dansyl moieties and the sensitized emission in the near-infrared (NIR) from the lanthanide complex in case of Nd$^{3+}$, Er$^{3+}$, and Yb$^{3+}$. For the Nd$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, and Er$^{3+}$ complexes the quenching process proceeds via energy transfer. Sensitized emission from Eu$^{3+}$ and Tb$^{3+}$ is only observed at 77 K when all dansyl units are protonated. In case of Yb$^{3+}$ the sensitized NIR emission takes place via the intermediate formation of an electron-transfer excited state. In case of Gd$^{3+}$ both energy transfer and electron transfer are not
allowed. The small quenching observed is attributed to a charge perturbation on the fluorescent dansyl excited state.

Balzani et al. and Vögtle et al. demonstrated for naphtyl-functionalized poly(benzyl ether) dendrimers, bearing a \([\text{Ru(bpy)}]\)\(^{2+}\) moiety in the core, that the fluorescence of the aromatic branches is efficiently quenched by energy transfer to the central \([\text{Ru(bpy)}]\)\(^{2+}\) unit. Furthermore, the dendritic wedges were found to protect the \([\text{Ru(bpy)}]\)\(^{2+}\)-based core from \(^1\text{O}_2\) quenching.\(^{154}\)

Goodson III et al. found for the nitrogen-core distyrylbenzene dendrimers, which were earlier described as potential materials for OLEDs (vide infra), an efficient energy transfer from the distyryl branches to the nitrogen core according to the Förster mechanism (energy hopping dynamics), while the interbranch interactions were found to be very strong.\(^{155}\)

Both Nierengarten and Armaroli et al.,\(^{75,156,157}\) Guldi et al.\(^{158,159}\) and Langa et al.\(^{160}\) synthesized fullerenes functionalized with phenylenevinylene dendrons. The phenylenevinylene dendrons were successfully employed as light-harvesting antennae. Upon excitation of the dendritic wedges, an efficient (nearly quantitative) energy transfer is observed from the wedges to the fullerene core. When the periphery is functionalized with dibutylaniline or dodecyloxynaphthalene donor units (Figure 1-25), an electron transfer is observed from the dendrons to the fullerene core, rendering the charge separated state, \(\text{C}_{60}^-\)-dendron\(^{+}\).\(^{159}\)

![Figure 1-25. Energy and electron transfer in fullerene-containing phenylenevinylene dendrons developed by Guldi et al.\(^{159}\)](image)

The charge separated state is stabilized by the dendrons. The overall efficiency for funnelling the light from the dendritic wedges to the core and the subsequent electron transfer from the wedges to the fullerene core is 76%, which gives a good starting point for the preparation of integrated photosynthetic systems and photovoltaic cells.

De Schryver et al. and Müllem et al. describe the energy hopping process between peryleneimide chromophores at the periphery of polyphenylene dendrons followed by an energy transfer to a terpyleneimide chromophore at the focal point of the dendrimer (Figure 1-26).\(^{161}\)
The possibility for the teryleneimide acceptor group to rotate towards one of the peryleneimide donor groups, resulted in two different energy transfer rates, namely $k_1 > 20 \text{ ns}^{-1}$ and $k_2 = 5.5 \text{ ns}^{-1}$. The first one was found to be comparable with the rate of energy hopping ($k_{\text{hopping}} = 4.6 \text{ ns}^{-1}$) and corresponds to energy transfer over the greater distance from the two peryleneimide groups to the teryleneimide moiety. The other component is at least four times faster and corresponds to the energy transfer over a small distance from the single peryleneimide group to the terylene moiety, which are in close proximity of each other.

![Energy trapping pathways in a peryleneimide functionalized polyphenylene dendron bearing a teryleneimide energy trap at its focal point](image)

**Figure 1-26.** Energy trapping pathways in a peryleneimide functionalized polyphenylene dendron bearing a teryleneimide energy trap at its focal point.

1.4.3 Single Molecule Spectroscopy (SMS)

The detection of single molecules is a great step forward in the field of nanotechnology. Due to their well-defined size dendrimers are excellent candidates for single molecule spectroscopy (SMS). Implementation of fluorescent units in the dendritic structure renders the possibility to correlate fluorescence mapping and topography. In 1998 De Schryver *et al.* reported for the first time the detection of single dendrimer macromolecules, consisting of Fréchet-type dendrons attached to a dihydropyrroledione (DPP) core, embedded in a thin polystyrene polymer film. The dendrimer served as a probe to get highly local information about the topology and microviscosity of polymer films. The on/off behavior and the sudden photobleaching showed that single molecules were detected, which could be discriminated from clusters of dendrimers.

Subsequently, dendrimers containing multiple chromophores, namely polyphenylene dendrimers bearing perylenecarboximide chromophores at the periphery, were investigated upon.
immobilization in a polyvinylbutyral film on their on/off behavior typical of single molecules.\textsuperscript{52,164} Non-interacting and dimer-like interacting chromophoric sites could be distinguished, while the transitions between the different spectral forms and decay times reflected the dynamic character of the interchromophoric interactions. Using SMS the different structural isomers of polyphenylene dendrimers bearing two perylenecarboximid units at the periphery could be distinguished.\textsuperscript{165}

After having successfully demonstrated the light-harvesting ability of a polyphenylene dendrimer bearing three peryleneimide energy donors and one terylene energy acceptor at the periphery,\textsuperscript{166} the intramolecular Förster energy transfer within a dendrimer consisting of four peryleneimide energy donors at the periphery and a teryleneimide as an energy sink implemented in the core embedded in a film of Zeonex (a polynorbornene) was studied using SMS (Figure 1-27).\textsuperscript{167}

Three key-role photophysical processes in light-harvesting complexes could be achieved using this system: (i) large absorption cross-section of the complex due to a large number of chromophores with high extinction coefficients and varying spatial orientation, (ii) energy hopping of the exciton along the chromophores at the periphery of the light-harvesting complex until eventually (iii) efficient and uni-directional energy transfer of an exciton from a chromophore at the periphery to a chromophore at the center of the complex.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-27.png}
\caption{The light-harvesting system studied by de Schryver et al. with SMS, based on peryleneimide peripheral groups, that collect the light, and a teryleneimide moiety in the core as an energy sink.\textsuperscript{167}}
\end{figure}

Several other examples of SMS on dendrimers have been and are currently reported, but this discussion is beyond the scope of this thesis.
1.5 Photoinduced Electron Transfer (PET)

Until now, photoinduced electron transfer (PET) processes have been mainly employed in dendrimer chemistry to investigate the conformation and accessibility of the dendritic structure and the role of the dendritic scaffold in electron transfer processes.

Turro et al. and Tomalia et al. investigated the electron transfer processes between cationic quenchers adsorbed on the periphery of carboxylate-terminated PAMAM dendrimers containing a \([\text{Ru(bpy)}_3]^{2+}\) unit in the core, in order to gain more insight in the structural features and in particular in the relationship between structural changes and electron transfer rates going to higher generations of PAMAM dendrimers.\(^{168}\) In accordance with earlier theoretical calculations,\(^{169}\) they found a structural transition occurring at about generation 3.5 by probing the excited state lifetime of the \([\text{Ru(bpy)}_3]^{2+}\) moiety.

Bossman et al. used the PET between \([\text{Co(phen)}_3]^{3+}\) and \([\text{Ru(phen)}_3]^{2+}\) complexes adsorbed on the periphery of carboxylate-terminated PAMAM dendrimers to study the deposition and clustering of electron donors and electron acceptors on a dendritic surface.\(^{170}\)

By introducing anionic groups at the periphery to pre-complex a cationic quencher such as methyl viologen to a zinc porphyrin-cored dendrimer Sadamoto et al. observed an electron-transfer reaction through the dendrimer backbone.\(^{171}\) Similarly, Aida et al. reported an efficient fluorescence quenching between oppositely charged free-base and zinc-porphyrin dendrimers.\(^{172}\) In both these cases, the electronic coupling through the dendritic wedges between the electron acceptor and the electron donor determines whether the electron transfer occurs.

In some studies PET was used to explore the accessibility of the core for quencher molecules. Vogtle et al. and De Cola and Balzani et al. investigated for this purpose the poly(benzyl ether) dendrimers containing a \([\text{Ru(bpy)}_3]^{2+}\) moiety in the core (§1.2.2. Figure 1-4: structure 2). The electron transfer reactions between the cationic quencher methyl viologen dication, the neutral quencher tetraphiafulvalene, and the anionic quencher anthraquinone-2,6-disulfonate anion and the different generations of \([\text{Ru(bpy)}_3]^{2+}\)-cored dendrimers were studied.\(^{69}\) A site isolation effect introduced by the dendritic branches was observed in all cases, implying a decrease in the quenching constants going to higher generations. However, the rate constants for the quenching reactions involving the different quencher molecules were not always predictable. Several factors were suggested to influence the charge transfer processes: (i) the dependence of the diffusion rate constants on the radius of the compound, (ii) the protection of the dendritic wedges towards diffusion of the quencher within the dendrimer, (iii) the competition between the solvent and the dendritic branches for the solvation of the core, (iv) Coulombic interactions between the positively charged core and the charged quenchers, and (v) the folding of the dendritic branches around the core.

Mihara et al. synthesized \(\alpha\)-helical peptide-functionalized PAMAM dendrimers in which one metalloporphyrin (Fe(III) or Zn(II)-mesoporphyrin) was coordinated to every two \(\alpha\)-helix peptides (Figure 1-28).\(^{173,174}\)
The electron transfer quenching reactions between either the negatively charged quencher naphtalene sulfonate (NS⁻), or the positively charged quencher methyl viologen (MV²⁺) and the Zn(II)-mesoporphyrins were investigated. In both cases the quenching was amplified going to higher generations. For NS⁻ this effect could be explained by the fact that the electrostatic binding of NS⁻ to the positively charged periphery of the dendrimer is stronger in case of the higher generation, which promotes a more efficient quenching of the Zn(II)-mesoporphyrin excited state via electron transfer. The more efficient electron transfer from the Zn(II)-mesoporphyrins to MV²⁺ could not be explained very satisfactorily and is attributed to a dynamic quenching process.

Subsequently, Mihara et al. implemented both positively and negatively charged peptide dendrimer-multi-Zn(II)-porphyrin ((Zn-MP)ₙ-PD) into a catalytic cycle together with MV²⁺, triethanolamine, and the enzyme hydrogenase for photoinduced hydrogen evolution (Figure 1-29).¹⁷⁵

![Figure 1-28. Schematic representation of the peptide PAMAM dendrimers developed by Mihara et al., hosting a metalloporphyrin between every two α-helix peptides.¹⁷³,¹⁷⁴](image)

![Figure 1-29. Photoinduced hydrogen evolution using (Zn-MP)ₙ-PD as an electron donor, MV²⁺ as an electron carrier, and hydrogenase as a hydrogen evolution catalyst; triethanolamine (D) was introduced to reduce again [(Zn-MP)ₙ-PD]_{ox}⁻¹⁷⁵](image)
This is one of the few examples where dendrimers and light have been employed in a catalytic application. The dynamic interaction between the positively charged dendrimers and MV$^{2+}$ was found to be the most efficient in this system for the photoreduction and the hydrogen evolution.

To demonstrate that long-range charge transfer reactions occur very efficiently within dendritic systems, several groups developed dendrimers containing either electron donor moieties at the periphery and an electron acceptor moiety in the core or vice versa.

Fox et al. showed that when a suitable electron donor, e.g., a 3-[dimethylamino]phenoxy group, is attached to the focal point of Fréchet-type dendrons with naphtyl or pyrenyl peripheral groups, the emission of the naphtyl or pyrenyl units is efficiently quenched via electron transfer.$^{176}$ Obviously, both a strong through-bond and through-space electronic coupling between the electron donor and the electron acceptor through the branches could be responsible for the mechanism of the PET. Furthermore, Fox et al. observed an efficient electron transfer from a singly reduced biphenyl unit placed at the periphery to the [Ru(bpy)$_3$]$^{2+}$ core of poly(benzyl ether) dendrimers.$^{177}$

**Figure 1-30.** Photoinduced electron transfer in a 3$^{rd}$ generation 4,4'-bipyridine-cored Fréchet-type dendrimers with either benzyl$^{178,179}$ or naphtyl$^{180}$ peripheral groups.

Vögtle et al. and Balzani et al. developed Fréchet-type dendrimers containing an electron accepting 4,4'-bipyridinium unit in the core (Figure 1-30).$^{178}$ This compound showed a charge transfer from the branches to the 4,4'-bipyridinium core, indicating that the branches serve in this case as light-harvesting antennae for electron transfer process. This could be particularly interesting for photochemical energy conversion and information processing. At the same time, Kaifer et al. published the electrochemical behavior of these 4,4'-bipyridine-cored dendrimers,
reporting fast heterogeneous electron transfer for generation 1 to generation 3.\textsuperscript{179} In line with the intentions of Vögtle \textit{et al.} and Balzani \textit{et al.}, Fox \textit{et al.} synthesized the same dendrimer, but this time substituted at the periphery with naphtyl moieties (Figure 1-30) and studied the PET processes within these dendrimers using flashphotolysis and transient absorption techniques.\textsuperscript{180} The multiple electron redox events occurring in this system were found to depend on the laser energy.

Modarelli \textit{et al.} developed anthraquinone-terminated Newkome-type dendrimers bearing a free base- or a zinc-porphyrin moiety in the core (Figure 1-31).\textsuperscript{181,182} The porphyrin emission was nearly completely (96 - 99.5\%) quenched \textit{via} a charge transfer reaction from the zinc porphyrin core to the anthraquinone moieties at the periphery. The rapid electron transfer observed was attributed to backfolding of the dendrimer branches, resulting in short porphyrin-anthraquinone distances and through-space electron transfer.

\textbf{Figure 1-31. Photoinduced electron transfer from the core to the periphery in a 2$^{\text{nd}}$ generation zinc porphyrin-cored Newkome-type dendrimer with anthraquinone peripheral groups, developed by Moradelli \textit{et al.}}\textsuperscript{181,182}

De Schryver \textit{et al.} described the electron transfer in a rigid first generation triphenylamine-cored polyparaphenylene dendrimer bearing a peryleneimide acceptor at the periphery.\textsuperscript{183} A long-lived charge separated state was formed in a moderately polar solvent. The charge transfer state undergoes thermally activated back electron transfer, resulting in the population of the locally excited state and as a consequence in a delayed fluorescence component.
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at room temperature. Such a process is uncommon for polyaryl bridges and long-distance through-space electron transfer. The two distinct sets of forward and back electron transfer rates refer to the existence of two different constitutional isomers. The electron transfer was found to occur via a trough-space mechanism.

1.5.1 (Organic) Light Emitting Diodes ((O)LEDs)

An emerging area of possible applications for dendrimers is in opto-electronic devices, such as (organic) light-emitting diodes ((O)LEDs). Dendritic macromolecules have been blended into OLEDs either as charge transporting components \(^{184-190}\) or as light-emitting materials \(^{191-196,203}\). With these dendritic OLEDs it is possible to obtain emission in the red, yellow-green and blue regions of the spectrum.

The working of OLEDs is based on the injection of oppositely charged carriers, which pair to form excitons. Blends of hole transporting components (p-type materials) and electron transporting components (n-type materials), usually consisting of a host matrix and a guest, can be sensitive to phase separation, leading to aggregation and luminescence quenching. One way to avoid this phase separation is to incorporate the guest chromophore within a dendritic structure, which is similar to the structure of the host. In addition, dendrimers do not form a crystalline phase and avoid the aggregation of the luminescent chromophores, inhibiting luminescence quenching (site isolation). Especially, π-conjugated dendritic wedges, such as stilbene-containing dendrons, are appealing candidates for implementation in OLEDs to ensure good charge mobility.\(^{155,184,187,196-204}\) Furthermore, variation of the dyes implemented in the core and a sufficient, but not complete, *i.e.* transparent to electrons and holes, site-isolation of these dyes by the dendritic wedges surrounding them, may in this way lead to color-tunable OLEDs.

Building on the design of the perylene-terminated dendritic systems of Moore et al., who tried to develop suitable electroactive materials for fabricating LEDs,\(^{191,192}\) Fréchet et al. synthesized dendrimers with peripheral redox-active triarylamines as hole-transporting moieties and a fluorescent chromophore (coumarin-343 or pentathiophene) in the core as a component of a OLED, while 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole was added as an electron transporting material.\(^{193}\) Efficient energy transfer was observed from the periphery to the core, both in the photoluminescence and in the electroluminescence experiments.

Burn et al. demonstrated that the size of the dendritic branches indeed provides a way to control the interchromophoric interactions within a tris(distyrylbenzenyl)amine cored dendrimer.\(^{199}\) Excellent miscibility can be achieved by using the common dendrimer architecture of host and guest molecules.\(^{200}\) The dendrons were comprised of stilbene units that are joined in a *meta*-arrangement around the branching benzene unit, while a tert-butyl surface provided good solubility in organic solvents. Two different third generation hosts were employed for implementation in LEDs, namely a tris(distyrylbenzenyl)amine-cored dendrimer (emitting in the green) and a 1,3,5-tris(distyrylbenzenyl)benzene-cored dendrimer (emitting in the blue). A first generation platinum porphyrin dendrimer was used as a phosphorescent guest (Figure 1-32).\(^{200}\)
The long lifetime of the platinum porphyrin guest gives rise to a frequency dependent quenching process, which is independent of the host material. Overall they showed that the use of conjugated dendrimers provides an elegant way to control the phosphorescence, trapping, and quenching of excitations in LEDs.

![Figure 1-32](image_url)

**Figure 1-32.** Structures of the third generation distyrylbenzyl dendrimers with either an amine or a benzene core and the meso-substituted first generation platinum porphyrin dendrimer implemented in a LED by Burn et al.

Strohriegl et al. demonstrated that the introduction of electron-deficient units in dendrimers causes an improvement of the fluorescence quantum yield and the brightness of the OLED compared to PPV-monolayer LEDs.

![Figure 1-33](image_url)

**Figure 1-33.** The symmetrically and asymmetrically substituted DSBs with propoxy- (1) or oxadiazole-functionalized (2) poly(benzyl ether)-type wedges introduced in OLEDs by Wong et al.
Wong et al. synthesized both asymmetrically and symmetrically substituted highly luminescent distyrylbenzenes (DSBs) with propoxy- or oxadiazole-functionalized poly(benzyl ether)-type wedges (Figure 1-33).\textsuperscript{203} The oxadiazole units are introduced as electron-deficient substituents in order to improve the charge imbalance.

The asymmetrically substituted DSBs rendered higher energy transfer efficiencies than the symmetrically substituted DSBs. On the other hand, the fluorescence lifetimes and the quantum yields of emission were reduced as compared to the symmetrically substituted DSBs due to a less effective shielding of the DSB-unit. A remarkable device performance was found for the oxadiazole-functionalized asymmetrically substituted DSB-based OLEDs when the emissive layer is blended with diphenylamine. It was found that a large excess of oxadiazole moieties implicates a large number of electron traps, which reduces the electron transport through the device. This could be overcome by the addition of an electron donor, in this case diphenylamine.

Meijer et al. demonstrated that the dyes do not necessarily have to be part of the dendritic structure in order to produce potentially color tunable OLEDs. Homogeneous films of oligo(p-phenylene vinylene) (OPV)-terminated poly(propylene imine) dendrimers hosting different dyes, such as sulforhodamine B, rhodamine B, rhodamine 6G, and sulforhodamine 101, in their dendritic cavities could be obtained in which energy transfer from the OPV units to the dye is observed.\textsuperscript{194}

1.6 Summary and Outlook

With this overview we intended to show the major developments in the field of photoactive dendrimers. The implementation of chromophores in dendrimers is an excellent tool to gain more insight in the structural features of dendrimers, such as the accessibility of the core (site isolation), structural changes due to external factors, and intradendritic interactions. Although not all structural aspects are fully understood, see e. g. the discussion around site isolation, the increasing number of dendritic systems available will certainly contribute to a better understanding of dendrimers in general.

At the same time, the introduction of chromophores in dendrimers also comprises the introduction of functionality. The attachment of luminescent units, photoswitchable groups, and energy and/or electron donor-acceptor couples resulted in a broad scope of photoactive dendrimers. Some of them demonstrate very elegantly the possibilities for application, e. g. as light-harvesting systems, in (O)LEDs, as (photoswitchable) drug carriers, or as supramolecular sensors. Since the price to produce highly functionalized dendritic materials is high, the performance, the possibility to recycle the material, and its stability are crucial for application.

A more futuristic, but certainly not unreachable, aim is the development of a true artificial photosynthetic system. Dendrimers have proven to be suitable light-harvesting systems. The light absorbed can be used to induce an electron transfer reaction to a well defined position within the dendritic framework. The final step would be to make these electrons available for chemical
conversion and to find the conditions in which the system can be recovered to its original state, so that the cycle can be started over again.

Other challenges and opportunities to use photoactive dendrimers can be found in the field of nanotechnology (SMS), surface chemistry, and photocatalysis. Also, the use of dendrimers as template molecules for the formation of supramolecular assemblies based on non-covalent interactions provides a way to compose a library of novel photoactive dendritic materials.

1.7 Scope and Contents of this Thesis

Initially, dendrimer chemistry mainly focussed on the synthesis and characterization of new dendritic molecules. Nowadays, the challenges have changed to the development of functional dendritic materials, including numerous photoactive dendrimers, as outlined in the previous paragraphs of this Chapter. Over the past few years, the complexity of photoactive dendritic materials has increased enormously. Multifunctionality is introduced, either by the implementation of units, that respond not only to light, but also to other external factors, such as pH, or by the introduction of different units among which photoinduced processes, such as electron and energy transfer, occur. An even higher degree of complexity can be reached when the dendrimer is used as a template molecule to which different chromophoric guests can bind. Currently, the field of self-assembled functional supramolecular structures is rapidly expanding, also in dendrimer chemistry.

The work described in this Thesis is a contribution to the field of multifunctional photoactive dendrimers. The Thesis starts from a system in which a chromophore, responsive towards light and pH, is covalently linked to the periphery of a dendrimer, and develops towards a self-assembled supramolecular photoactive dendritic system containing two different (selective) binding sites, to which different chromophoric guests can bind simultaneously in a non-competitive fashion.

Chapter 2 describes the photophysical properties of methyl orange-functionalized dendrimers. The E/Z isomerization has been investigated as well as the responsiveness of the methyl orange moieties towards pH. The isomerization proceeds extremely fast as compared to azobenzene, while the properties of the methyl orange units as a pH indicator are lost.

The three following chapters show the development of a self-assembled dendritic structure, in which photoinduced electron and energy transfer processes can occur. Directionality and selectivity are introduced to this supramolecular system by using two different binding motifs within the dendrimer.

Chapter 3 describes the synthesis of an electron donor - electron acceptor dyad, in which the donor ([Re(Br)(CO)3(bpy)]) and the acceptor (methyl viologen) are assembled via hydrogen bonds. The binding motif exists of the “Hamilton” receptor and a barbiturate as complementary units. An ultrafast photoinduced electron transfer process is observed within the dyad and its kinetics in relation to the conformation of the dyad are discussed. This “simple” model system
served to give more insight in the electron transfer kinetics between [Re(Br)(CO)₃(bpy)] and an
electron acceptor in a hydrogen-bonded assembly, as a similar donor-acceptor pair will be used
later on in the far more complicated dendritic systems.

Chapter 4 describes the formation of a supramolecular assembly consisting of “Hamilton”
receptor-functionalized dendrimers with barbiturates. The photophysical properties of the
“Hamilton” receptor are used to probe the formation of the assembly. Energy transfer is observed
between the “Hamilton” receptors at the periphery and a photoactive
[Re(Br)(CO)₃(bpy)]-barbiturate. The presence of the basic poly(propyleneamine) core is crucial
for the energy transfer process to occur.

In Chapter 5 a second guest is introduced to the assembly described in Chapter 4, which can bind
to the second binding site present in the core. The difference in binding motif between the guest
molecules is such, that they do not compete for each others binding site. Photoinduced electron
transfer between two different photoactive guests, namely a [Re(Br)(CO)₃(bpy)]-barbiturate guest
(electron donor) and an anthraquinone-urea guest (electron acceptor), within the supramolecular
assembly is investigated. This is the first example of a dendrimer in which two different guest can
be bound selectively via hydrogen bonds.

In the Appendix a more detailed description is given of the different spectroscopic techniques
used to study the photoinduced processes within the systems presented in this Thesis.
1.8 References

Chapter 1


Shining Light on Dendrimers


Shining Light on Dendrimers
