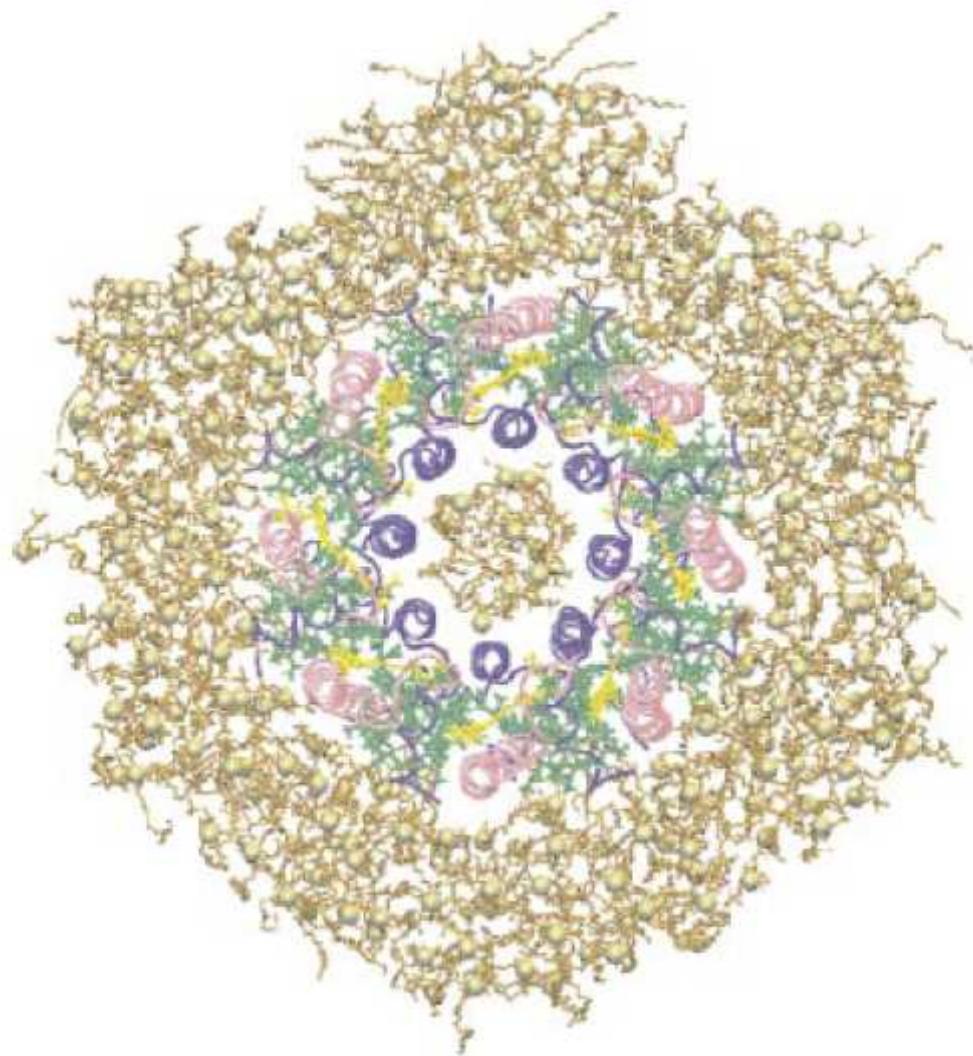


Light Harvesting and Energy Transfer



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Abstract

Resonance energy transfer is a crucial process in light harvesting. We consider three examples of energy harvesting systems: purple bacteria, dendritic molecules and zeolite L crystals filled with organic dyes. Practical applications of light harvesting are described. The role of the resonance energy transfer is emphasized. We discuss drawbacks of the light harvesting applications.

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Introduction

The concept of light harvesting is inspired by the process of photosynthesis. In early 1932 Emerson and Arnold showed in their experiments on chlorophyll that under the saturation condition of the intensity of illuminating light, hundreds of chlorophyll species are needed in order to reduce one carbon dioxide molecule [1]. It turned out that most of the chlorophyll molecules absorb light and then transfer it to a single reaction centre. The mechanism of the excitation funnelling has been proven to be resonance energy transfer (RET) [2]. During this process, an excited molecule (donor) transfers its energy very rapidly to adjacent molecule (acceptor) in a non-radiative way, such that lifetime of the donor excited state is shortened. Several conditions for the donor-acceptor distance and their spectral properties should be fulfilled in order to get an efficient energy transfer.

In the field of electronics, devices are operating on the principle of the charge flow because the latter can be simply governed. Molecular electronics implies the process of energy transfer to be used in applications, in addition to the charge transfer. Thus, new applications, which are conceptually different from the conventional devices, can be tailored.

In the present paper, the role of the energy transfer in light harvesting applications is reviewed. In the next chapter, we focus on the physics of the phenomenon of RET and consider the theoretical models of RET developed by Förster and Dexter. In the chapter 2, the light harvesting concept is discussed. This concept is then illustrated on the example of dendrimers (chapter 3). Chapter 4 focuses on the light harvesting applications of zeolite L channels. In chapter 5 we summarize.

1. Resonance energy transfer (RET)

1.1 Definition of RET

Consider an excited molecule. Various mechanisms of its relaxation are possible. The most important ones are photon emission (fluorescence), radiationless decay and intersystem crossing, following by radiative (phosphorescence) or non-radiative decay (see Fig. 1). If another molecule is located close enough and it has the appropriate excitation energy, an additional relaxation path is possible. The excited molecule (donor) can transfer its energy to the acceptor molecule non-radiatively. The process is called resonance energy transfer (RET) or electronic energy transfer (EET). The excitation energy is not simply transmitted by uncorrelated donor emission – acceptor absorption event. Instead, a nontrivial mechanism takes place such that the lifetime of the donor's excited state is diminished [3].

The phenomenon of energy transfer first was demonstrated in careful fluorescence quenching experiments. This is why RET sometimes called Fluorescent Resonance Energy Transfer or simply FRET. Sometimes this abbreviation stands for Förster Resonance Energy Transfer when one refers to a RET mechanism suggested by Theodor Förster [4].

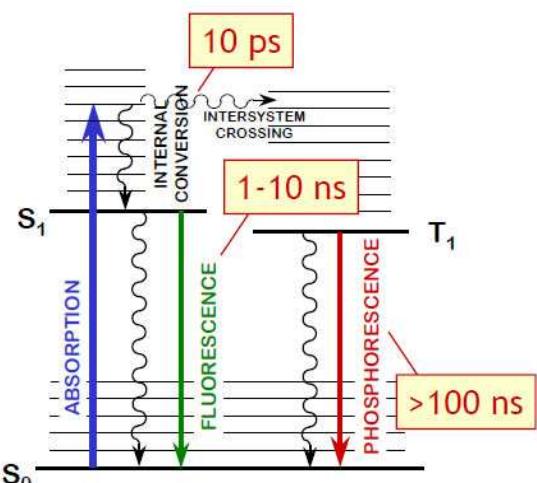


Fig. 1. Relaxation pathways in the excited molecule. Ground state is denoted as S_0 . Radiationless transitions are illustrated as waved lines. Typical relaxation times are indicated. Image is taken from [5].

The energy transfer is widely exploited by various biological systems in life nature. For instance, in the process of photosynthesis it is important to harvest light on the wide area and bring the energy to a reaction center. It has been demonstrated that a large number of chlorophyll molecules are involved in the capture of light to initiate the first steps in photosynthesis [1]. It has been shown that almost all molecules of chlorophyll act as an antenna, harvesting light and delivering the absorbed energy by means of energy transfer [2].

1.2 Strong versus weak electronic coupling

For the energy transfer, at least, two molecules are needed, an excited donor (D) and an acceptor (A) in its ground state. Since excitations are usually activated in the visible spectral region they are often called as chromophores more generally. An important for RET characteristics of such a duet is its interaction or, in other words, coupling. If coupling is absent, obviously no transfer is possible. Assume that for excitation energies (difference between HOMO and LUMO, bandgap) of the donor ΔE_D and the acceptor ΔE_A holds

$$\Delta = \Delta E_D - \Delta E_A > 0. \quad (1.1)$$

Then condition of the strong D-A coupling is $V \gg \Delta$, where V is the D-A interaction energy. In the case of Coulomb coupling between chromophores, it can be shown that excitation will oscillate between donor and acceptor with a frequency [6]:

$$\Omega = \frac{\sqrt{\Delta^2 + |V|^2}}{\hbar}, \quad (1.2)$$

where \hbar is the Plank constant. In other words, the energy of the electronic excitation is delocalized between donor and acceptor. Such a case is not really useful for practical applications in devices, where a directional energy transfer is preferred. The complementary case is the weak coupling limit $V \ll \Delta$. Here, a direct RET from the donor to the acceptor is possible. Famous Förster's theory of RET follows this approximation.

1.3 Förster resonance energy transfer

Historically, RET was referred to as "transfer by inductive resonance". This term describes energy transfer as coupling of the multipolar transition moments of the donor and acceptor molecules via the Coulombic (electrostatic) interaction, conceptually analogous to coupled oscillators. In Förster's theory this coupling is restricted to the electric dipole-dipole interactions between donor and acceptor. This implies that the distance between chromophores is larger than the size of chromophores. The typical distance between chromophores for Förster's RET to occur is about 30-100 Å.

The process of the Förster RET is illustrated schematically in Fig. 2. Donor and acceptor molecules are labeled as D and A. Energy transfer steps are numbered from 1 to 6 and the resulting spectral densities of absorption (left) and emission (right) are shown. First, the donor is activated by absorption of a photon 1. Due to the Franck-Condon principle, the molecule is promoted to an excited vibrational level following by a rapid vibrational relaxation 2. The process of RET is represented in Fig. 2b by processes 3 and 4. The energy conservation law is guaranteed by the overlap of the donor's emission spectrum and the acceptor's absorption spectrum (d). Actually, the RET rate is proportional to it. A rapid relaxation 5 of both D and A takes place after the energy transfer. This strongly reduces back transfer to D. The final step of the overall process is photon emission 6 or radiation-less relaxation of the acceptor, usually followed by a rapid vibrational relaxation 7. It is possible to measure timing of RET by detecting the outgoing photon by means of time resolved spectroscopy.

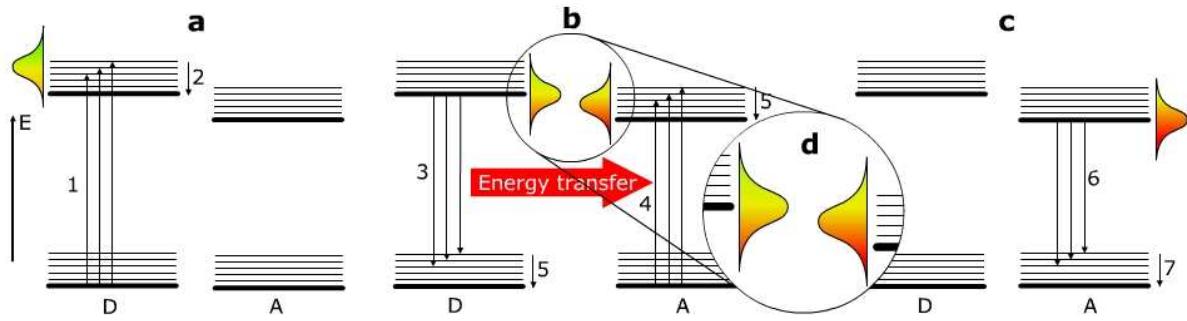


Fig. 2. Energy diagrams demonstrate the sequence of the steps in Förster energy transfer process. The arrows demonstrate transitions; the spectral densities are added to stress relative energies. Spectral overlap of the donor emission (left) and acceptor absorption (right) is zoomed (d). Idea of the figure is taken from [6].

Quantum mechanical model

In the Förster theory the donor-acceptor pair is considered as an isolated system which can be described by the ground state $\psi_{DA} = |D\rangle|A\rangle$, two singly excited states $\psi_{D^*A} = |D^*\rangle|A\rangle$ and $\psi_{DA^*} = |D\rangle|A^*\rangle$, and one doubly excited state $\psi_{D^*A^*} = |D^*\rangle|A^*\rangle$. In this theory, only the Coulomb coupling between donor and acceptor is taken into account, while their exchange interaction is neglected. This comes from an assumption that the wave functions of the donor and acceptor do not overlap at sufficiently large distances between chromophores.

We are interested in the rate of transition $\psi_{D^*A} \rightarrow \psi_{DA^*}$. Treating the D-A interaction V perturbatively, it can be obtained by applying the Fermi Golden Rule [7]:

$$k_{D^*A \rightarrow DA^*} = \frac{2\pi}{\hbar} |\langle \psi_{D^*A} | V | \psi_{DA^*} \rangle|^2 \rho. \quad (1.3)$$

Here, ρ is the density of the final states. Working out expression (1.3), Förster got his famous formula for the RET rate [3,4]:

$$k^{Förster} = \frac{\phi_D R_0^6}{\tau_D} \frac{1}{R^6}, \quad (1.4)$$

where ϕ_D is the fluorescence quantum yield, τ_D is the lifetime of the donor, R is the distance between donor and acceptor, and R_0 is the so-called Förster radii given by

$$R_0^6 = \frac{9000 \ln(10) \kappa^2 I}{128 \pi^5 N n^4}. \quad (1.5)$$

In this formula, I is Förster's spectral overlap of the normalized donor emission spectrum and the absorption spectrum of acceptor (see Fig. 2d); N is Avogadro's number; n is the refractive index of the surrounding medium; κ is the orientation factor associated with the dipole-dipole interaction. The fact that Förster's formula expresses the RET rate in terms of measured quantities, optical spectra of the donor and the acceptor made it of great utility.

The key feature of equation (1.4) is that it correctly describes that energy transfer rate decay as one over the sixth power of the distance between chromophores. Such a strong dependence is exploited in measurements of distances between fluorescent tags, proteins, in particular, by means of fluorescent resonance energy transfer.

Förster's formula (1.4) is accurate if four conditions are satisfied [3]: (a) the dipole-dipole approximation can be employed appropriately for the donor-acceptor interaction; (b) neither the

donor fluorescence lifetime, emission line shape, acceptor absorption line shape, nor oscillator strength is perturbed because of interactions among donors or acceptors respectively. (c) Static disorder (inhomogeneous line broadening) is absent in the donor and the acceptor optical spectra; (d) the energy transfer dynamics is incoherent. The last condition follows from the weak D-A interaction, assuming that the coupling to the bath is considerably stronger than the coupling between chromophores.

Finally, note Förster's theory of resonant energy transfer is based on the equilibrium Fermi Golden Rule approach [7] which is a perturbative treatment. Thus, it is valid only in the weak coupling limit with respect to the D-A interaction.

1.4 Dexter model of RET

When the distance between donor and acceptor becomes comparable with the size of chromophores, the dipole-dipole approximation fails. The high multipolar inter-chromophore interactions should be taken into account. In addition, molecular orbitals of the chromophores can overlap significantly, so that the exchange interaction becomes important. The size of chromophores becomes important. In such a case, Dexter's model of the energy transfer is used. The typical distance when one applies this model is about 6-20 Å.

When wave functions (molecular orbitals) of the chromophores (molecules) overlap, the donor-acceptor pair should be considered as a single quantum mechanical system that is described by a common wave function. Let's denote the state when the donor (acceptor) is excited and acceptor (donor) is in its ground state as $\psi_{DA} = |D^*A\rangle$ ($\psi_{DA^*} = |DA^*\rangle$). The difference from the previous case is that here, donor and acceptor are considered as correlated in terms of wave function overlap. At this point electron spin starts to play an important role. Due to the Pauli exclusion principle, the common wave function should be antisymmetric against the electron permutation. This implies the appearance of the exchange correlation term in the calculation of expression (1.3), in addition to the Coulomb part. The exchange term is proportional to the overlap integral of the wave functions of the chromophores. If the distance between them is short enough, this term can become dominant. The main result of that is that, after working out Fermi's Golden Rule (1.3), the one gets the energy transfer rate decaying exponentially with the distance R between donor and acceptor:

$$k^{Dexter} = K I \exp[-2R/L]. \quad (1.6)$$

Here, K is determined by the specific orbital interactions, I is the spectral overlap integral (see Fig. 2d), L is van der Walls's radii of chromophores.

Triplet-triplet transition

The Förster model of RET accounts only for the electric dipole allowed transitions. In nature, however, it turns out that energy transfer occurs even when such transitions are forbidden. For example, consider triplet-triplet energy transfer, that is proven experimentally to exist (see, e.g., [9,10]):



This transition is dipole forbidden. Working out the matrix element in the expression (1.3), one gets only the exchange term while the Coulombic one vanishes [11]. In this case, the only possibility for such a transport is the exchange interaction between chromophores (Fig. 3b).

Another important application of the Dexter theory is the case when the orientation factor K is close zero in (1.5) that happens at the magic angle. Then the only exchange term contributes to the transfer rate (1.3).

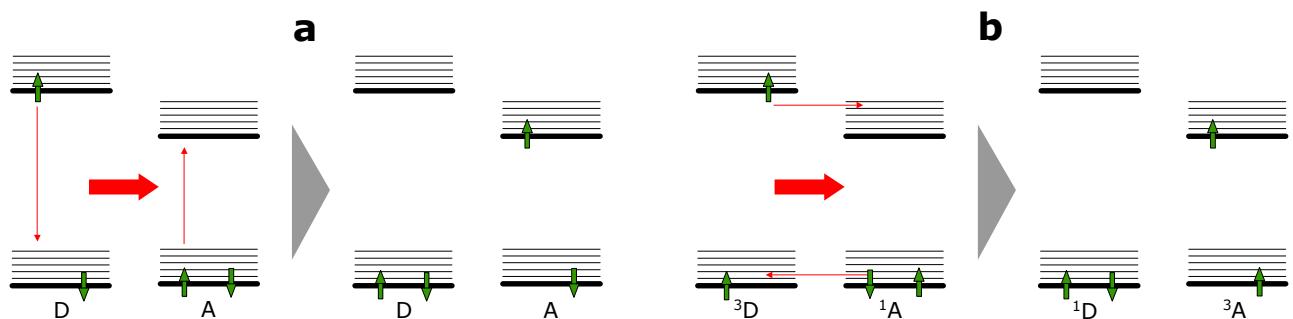


Fig 3. Energy levels diagrams for the two RET processes. Förster's resonance energy transfer (a) occurs if dipole transitions are allowed. The singlet-singlet transfer is only possible. Dexter's energy transfer is illustrated for the triplet-triplet transition (b). The exchange of electrons occurs between donor and acceptor. Green arrows denote electron spin schematically.

The considered above theories describe the weak electronic coupling limit for point chromophores in extreme distance ranges under equilibrium conditions. However, there exist situations when the Förster-Dexter approach is not applicable. This concerns, in particular, the energy transfer between molecular aggregates [12], in the case of a nonequilibrium bath, etc. Plenty of references to these works can be found in [3].

2. Light harvesting

2.1 Inspired by nature

All the energy that mankind consumes comes from the Sun (except of small part of it that is produced by nuclear plants). It is amazing that most of this energy is first captured by photosynthetic bacteria or higher organisms by means of photosynthesis and converted into the energy of chemical bonds. These organisms have created sophisticated and extremely efficient mechanisms for the sunlight transduction. Then a lot of transformations of this energy are made, before it, for instance, finally is consumed by your body playing soccer or while just thinking on this stuff. From this point of view photosynthesis is one of the most important processes that supply life by energy. Nevertheless, amount of solar energy consumed yearly by the entire planet is several orders of magnitude less than that of coming from the Sun. This is why it is so attractive to find efficient ways of converting the solar energy into its useful forms. Why don't use the ideas that survived for ages and embodied in the process of photosynthesis!

2.2 Purple bacteria

In early 1932 Emerson and Arnold showed in their experiments on chlorophyll that, under the saturation condition of the intensity of illuminated light, hundreds of chlorophyll species are needed in order to reduce one carbon dioxide molecule [1]. To explain the cooperative action of the chlorophylls, it was postulated that only very few chlorophylls in the primary reaction site, termed the photosynthetic reaction centre (RC), directly take part in the photochemical reaction. Most chlorophylls serve as light-harvesting antenna by capturing the sunlight and funnelling the electronic excitation toward the RC. At this point, a term of photosynthetic unit (PSU) was introduced as a union of RC with the associated light harvesting antenna, consisting of an ensemble of light capturing chlorophylls. It was later revealed by Duysens that the process of funnelling of

the electronic excitation that occurred in the photosynthetic process is the resonance energy transfer [2,14]. The discovered principle of light harvesting turned out to be common for all the photosynthetic systems, starting from bacteria ending higher plants.

Among the all known photosynthetic systems, the purple bacteria are probably the most studied and best characterized [14]. All of them contain two types of light harvesting complexes which are usually called as LH1 and LH2. The first light harvesting complex, forming a ring, surrounds the reaction center (Fig. 4). The second complex also composed of a ring-shaped aggregate that usually is non-covalently bonded to the LH1. Also, the third light harvesting complex (LH3) exists for some types of bacteria. Usually such PSUs have one LH1 ring and many of LH2 or LH3 complexes. Its number is determined by the growth conditions, such as light intensity and temperature. The planar organization of the bacteria is optimal for the transfer of electronic excitation to the reaction center.

Spectroscopic analysis revealed the key features of such bacteria [16]. First, there is an excitation energy gradient from the periphery to the center, i.e., $E_{LH_2} > E_{LH_1} > E_{RC}$. Second, there exists a significant overlap of emission and absorption spectra of the pairs LH2-LH1, LH1-RC. In other words, a cascade-like system of the excited levels is furnished. This allows energy to be transferred from the peripheral LH2 through LH1 to RC (Fig. 4). The efficiency of transfer was found to be surprisingly high (near 95%).

The mechanism of energy transfer that occurs in the bacteria has been extensively debating. Because of strong van der Waals interactions between aggregates, it was assumed that their wave functions overlap strongly. Thus, Dexter's theory should be applied. However, it was shown through calculations [17] that a generalized Förster mechanism governs energy transfer, resulting in a transfer time on the order of 200 fs.

There is a model of the top view of LH2 complex embedded in lipid bilayer (brown) on the cover taken from [18].

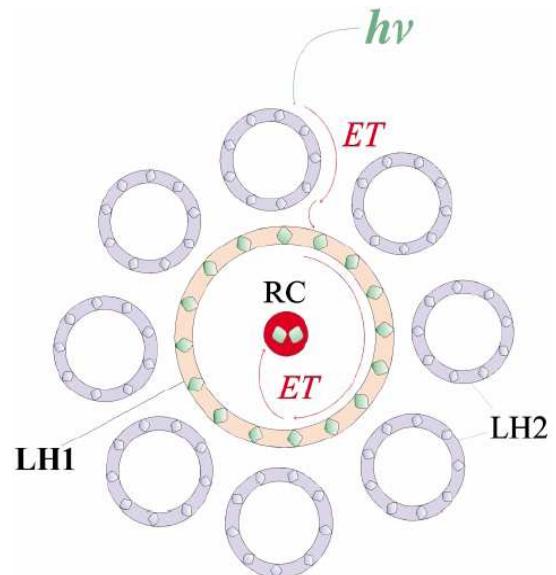


Fig. 4. Schematic topology of the purple bacterium. A coplanar arrangement of ring-like aggregates is shown. Light harvesting complexes are denoted as LH1 and LH2. The absorbed energy is transferred from the outer complex LH2 to the reaction center (RC) through LH1. The figure is taken from [15].

3. Dendrimers

3.1 Dendrimers is a natural structure for the light harvesting

Dendritic architecture is perhaps one of the most pervasive topologies observed in our planet. Examples of these patterns can be found in different fields. In abiotic systems, for instance, lightning patterns, snow crystals, erosion fractals exhibit such a structure. In the biological world, they are roots and branches of the trees, plant/animal circulatory system, corals, neurons, etc. Dendritic architectures penetrated even to artificial systems. Thus, in computer science, they are used for data storage/search, routing internet traffic etc. In the material world, such structures can be found at different length scale (from kilometres to nanometres). The reason for such extensive abundance of these dendritic topologies at virtually all dimensional length scales is not entirely clear. However, one might speculate that these are evolutionary architectures that have been

optimized over the past several billions years to provide structures manifesting maximum interfaces for optimum energy extraction/distribution, nutrient extraction/distribution, and information storage/retrieval [19].

Such topological objects can also be exploited in artificial light harvesting applications. Special molecules – dendrimers – are used for this purpose. The macromolecule constituents are organized in a branching form from a central core, creating a sphere of end groups at the periphery (Fig. 5). The total number of the basic elements increases exponentially with every generation and the number of end groups is on the order of that of elements in the bulk (Fig. 6). This is why peripheral end groups are of high importance and usually bear functionality that can be tailored according to the requirements. So, dendrimers are characterized by the combination of high number of functional groups and a compact molecular structure.

In light harvesting applications, functional groups are chromophores. They can be accurately positioned on the periphery, focal point, and/or even at each branching point of the dendritic structure. In this case periphery (and sometimes branching points) plays the role of the light harvesting antenna, which gather the energy and transfer it to the focal point (reaction centre, core) by means of RET. Such a light harvesting structure naturally resembles that one occurring in the nature.

Despite the dendrimers are large macromolecules, it is possible to synthesise them with a high level of accuracy. The modern synthesis procedure allows creation of species with the uniform molecular weights. So, they do not suffer from the problem of polymer synthesis – polydispersity [20]. Essential thing in the process of the synthesis is implementation of correct chromophores in order to achieve efficient energy transfer. Spectral overlap and distance between chromophores should be considered.

3.2 Energy transfer pathways in dendrimers

In light harvesting applications, energy is transferred from the periphery, where chromophores are mainly located, to the focal point of a dendrimer. Thus peripheral functional groups act as donors and the core acts as an acceptor in the RET process. The energy conservation law and the Franck-Condon principle require the excitation energy of the acceptor to be smaller than that of the donor. Since we expect all the excitations to be transferred to the core, its excitation energy is required to be the smallest among all the chromophores in the macromolecule.

Discovering a general pathway of the excitation is important in discussion of the energy transfer mechanism in dendrimers. Two options are possible. One is the direct excitation transfer from the distant functional element to the reaction center (Fig. 7a). Another one is the successive

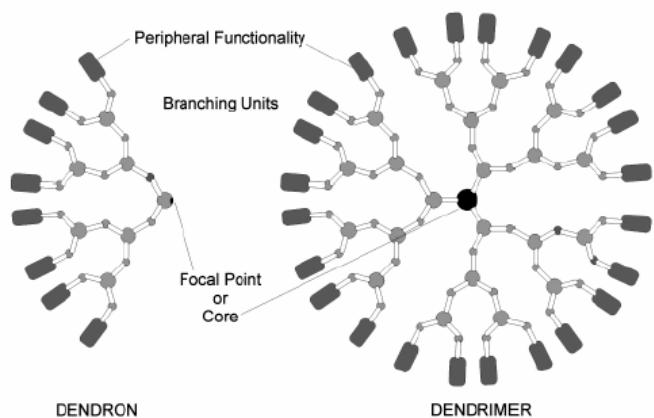


Fig. 5. Schematic representation of the structure of a dendron and a dendrimer. The third generation is illustrated. Figure is taken from [15].

why peripheral end groups are of high importance and usually bear functionality that can be tailored according to the requirements. So, dendrimers are characterized by the combination of high number of functional groups and a compact molecular structure.

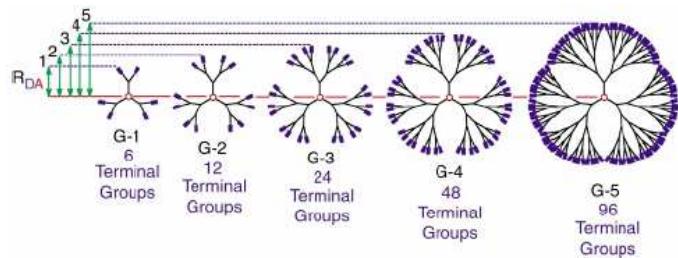


Fig. 6. Five generations of a dendrimer is shown schematically. The number of the terminal groups is counted. Distance R_{DA} between the core and peripheral elements is compared. Figure is taken from [15].

transfer through the dendrimeric framework using a special structure of the molecule (Fig. 7b). In this discussion, excitation localization and brakes in conjugation of organic backbone are important issues

Direct transfer

Dendrimers are large molecules. In order to keep them stable at least stable basic elements should be used. For this reason, aromaticity is usually exploited, which introduces the resonance energy to the stability. Thus, dendrimers usually have large number of the benzene rings. Branching of the elements is preferably at the *meta* positions. This is because the *para* branching causes linear structures and the *ortho* one leads to quick termination of a dendrimer due to steric hindrance. The *Meta* branching is responsible for breaks in conjugation (subsequent alteration single-double bonds) between the basic elements. This leads to fragmentation of the resonant electronic π -system of the macromolecule and thus to localization of the excitations within a fragment, which is usually a basic element [21].

If the fragments are of the same structure and size (Fig. 8a), the excitation energy and absorption spectra would be then more or less uniform for all of it within the entire molecule. Donor-acceptor pairs are not desired to be composed of the same fragments; the resonance energy migration is not efficient among them. Since in light harvesting applications the core has the smallest excitation energy and its absorption spectrum overlaps nicely with emission spectrum of the light harvesting chromophores, only the direct RET is possible from the periphery to the focal point.

With each generation, the number of terminal groups is doubled (in binary dendrimers), but the distance between the terminal groups and the core also increases (Fig. 6). Longer distances make the direct resonance energy transfer to be less efficient. Thus, a kind of compromise with number of the functional groups and their separation from the reaction centre must be acquired designing such dendrimers.

Successive transfer

An effective funnelling the excitation from the periphery to the core through fragments of the dendritic framework is possible if excitation energy gradient is present towards the periphery. In such a case, the framework can be designed in such a way that the excited peripheral functional group has a good emission spectral overlap with absorption spectra of an adjacent fragment (see Fig. 2d). This makes RET between them of high efficiency. Such

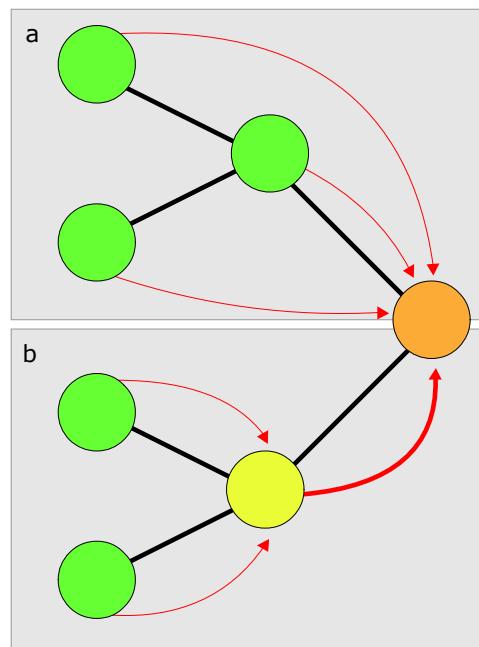


Fig. 7. Schematic representation of the general RET pathways in the dendrimers. Direct (a) and successive (b) transfers are shown. Colors of the basic elements are used to emphasize their excitation energies.

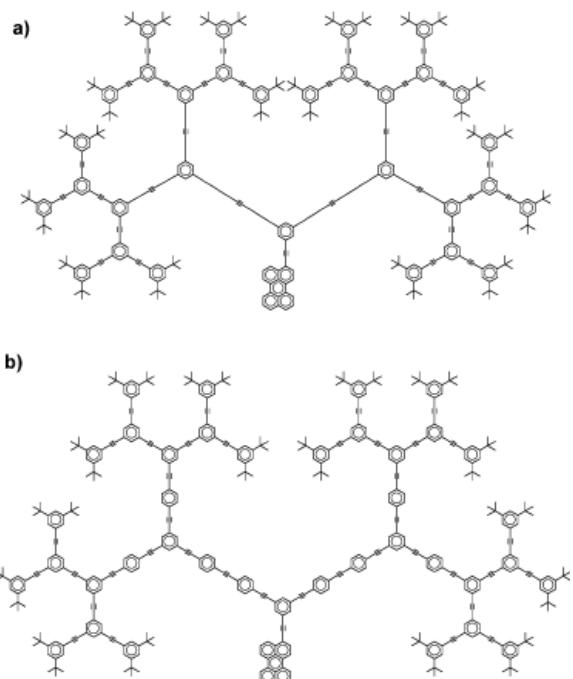


Fig. 8. Chemical structure of perylene-functionalized phenylacetylene dendrimers with (a) and without (b) energy gradient. Figure is taken from [15].

an energy gradient can be realized by varying sizes of the fragments. There is a nice analogy with the well-known quantum-mechanical example of a particle in a box potential. The bigger the box size is, the smaller excitation energy it has [7]. In our case, a fragment plays the role of the box. One wishes to make bigger boxes (longer fragments) closer to the core. An example of such structure is presented in the Figure 8b. It is shown in [21] that in this case excitations are transferred successively through the framework of the dendrimer with efficiency close to 100%.

The number of generations, i.e. distance from the core to periphery, is not a limiting factor for the process of RET in successive funnelling an excitation. The presence of the energy gradient toward periphery and the spectral overlap (see Fig. 2d) in donor-acceptor pairs are sufficient conditions for the energy transfer in dendrimers. This implies that the excitation energy of the peripheral chromophore is the biggest in the macromolecule, and band gap of the core is the smallest one. So, the periphery absorbs the shortest wavelengths and the core absorbs the longest ones. Another important thing is that intermediate fragments usually can also absorb light. Since its absorption spectra is in the middle between that of the core and periphery, increasing of the generation broadens absorption spectrum of the entire dendrimer.

3.3 Mechanism of RET in dendrimers

Describing the energy transfer mechanism in dendrimers is a big challenge. All the chromophores are covalently bounded and share common molecular orbitals. Under these conditions, the exchange interaction part (Dexter's model) to the overall energy transfer might be important. On the other hand, usually, every basic element is separated from each other by cross-conjugation of the organic backbone. This implies localization of their π -electron systems from each other, thus reducing exchange contribution and providing Förster's mechanism of RET. Also special dendrimer-like effects appear. For example, in dendrimers there exist a large number of donors that are spatially close to each other, so that the interactions between them sometimes should be considered. Summarizing, there is no general approach for the theoretical description of the energy transfer in such systems. Each particular dendrimer should be considered separately.

Phenylacetylene

Consider perylene-functionalized phenylacetylene. Förster's model is the only possible mechanism in the case of the direct RET (Fig. 8a). However, the application simply of the Förster theory does not give the experimentally measured energy transfer rate. Ultra fast spectroscopy was used to investigate different generations of this dendrimer [22]. It was found that discrepancy between the theory and the experiment is more pronounced in dendrimers of higher generations, where the energy transfer efficiency goes down. The absence of good correlation with the predicted and measured rates of the energy transfer is not surprising when one considers the many factors which change with generation. They are a distribution of the interchromophore distances, the overlap integral, the fluorescence quantum yield, and the fluorescence lifetime of the donor in the absence of the acceptor etc. An important issue is that the interchromophore distance is not a constant here but is better described by the statistical distribution.

It was found [22] that in the case of energy gradient (Fig. 8b) the excitation transfer rate to the core is of two orders of magnitude bigger than in the gradientless counterpart (Fig. 8a). This phenomenon can not be described by simply taking into account a better spectral overlap between chromophores in Förster's theory. Here, discrepancy with Förster's model is even larger than in the previous example. An explanation of this phenomenon can be based on the special fractal structure of the dendrimer [21].

Dexter vs. Förster model of RET in dendrimers

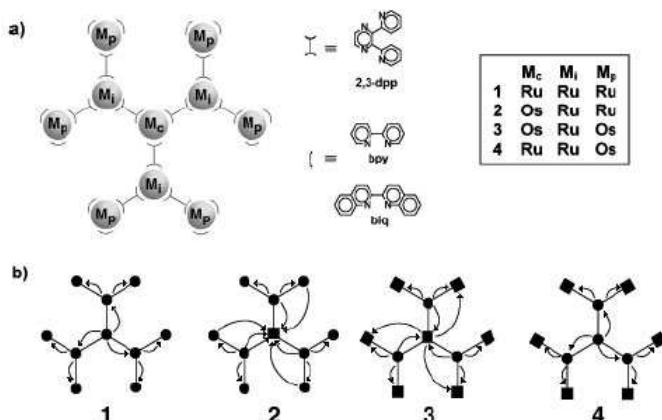
In this section, two examples of dendrimers are presented in order to demonstrate the energy transfer mechanism that is mostly caught by Dexter's and Förster's models of RET.

Historically, the energy transfer in dendrimers was first demonstrated in 1992 by Balzani and co-workers [15,23]. They studied metal-coordinated compounds. Ru and Os where the metals of the choice in this work, and polypyridine organic complexes where acting as ligands (Fig. 9a). The energy gradient was created due to the fact that metal excitation energy depends not only on the nature of the metal itself, but also on the ligands surrounding it. Direction of the energy transfer is shown in the Figure 9b for different combinations of metals. The arrows indicate also the excitation energy differences between complexes ligands. Despite this type of the energy transfer is not applicable in light harvesting applications, the example is shown to present a dendrimer with the primary Dexter mechanism of RET. This example is characterized by a small size of the system with a strong orbital overlap between chromophores.

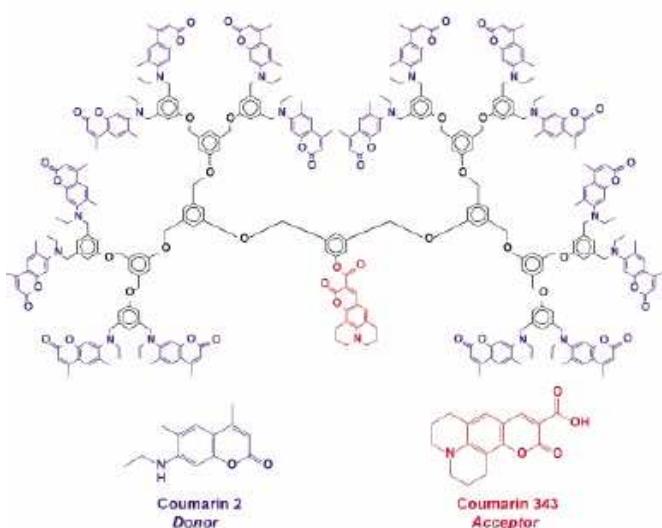
In order to illustrate purely Förster's mechanism of energy transfer in dendrimers, the system should obey special requirements. First, functional groups (donors) and the core (acceptor) should have large dipole moments and a large spectral overlap between donor's emission and acceptor's absorption spectra. They should be well enough separated from each other and posses a high quantum yield of fluorescence. The dendritic backbone should be photocemically silent to prevent fractal-specific energy transfer mechanisms. In addition to these photophysical requirements, there are "wishes" of processability of the dendrimer. This requires solubility of the end group chromophores which are attached through a functional "handle" to the dendritic structure. Amino-functionalized Coumarin-2 and acid-functionalized Coumarin-343 as the donor and the acceptor (Fig. 10) satisfy these requirements.

Morphology dependence

Porphyrin cored dendrimers are interesting examples of the light harvesting systems because the coordination number of the porphyrin is 4. This allows spatial separation of the connected dendrons from each other especially in the anti- position. As it will be demonstrated below, this results in a high energy transfer efficiency.



Pig. 9. An example of Dexter energy transfer mechanism in denritic structures. (a) Schematic representation of metaldendrimers having branching ligands and different combinations and positions of Ru and Os metals. (b) Directions of energy transfer is indicated by arrows in the different structures 1-4. Ru is denoted by circles, Os – by squares. Figure is taken from [15]



Pig. 10. An example of a dendrimer with the primary Förster type energy transfer. Figure is taken from [15]

A series of the 5th generation porphyrin cored dendrimer (see Fig. 11), having different number n ($n=1..4$) of dendron subunits, is considered. Let's denote them as $(G5)_n P$. A dendrimer solution was illuminated by light of the wavelength resonant to the absorption band of the branched dendrons [24]. The excitation energy is partially transferred to the porphyrin core, followed by the subsequent radiative deactivation of the latter, and partially is emitted by the dendrons themselves, without energy funneling to the dendrimer core.

Since the emission spectra of porphyrin and dendrons are different, efficiency of the energy transfer (light-harvesting) can be measured. It was shown that the most efficient one (>80%) appears to be in the fully substituted $(G5)_4 P$. In sharp contrast, the compound $(G5)_3 P$ showed dramatic decrease of the energy transfer efficiency (31%). That of the anti- $(G5)_2 P$ appeared to be the same as of the singly substituted $(G5)_1 P$ (10%). In addition, syn- $(G5)_2 P$ showed a somewhat increase of the efficiency to 20% compared to its anti- counterpart. The efficiency is increased proportionally to the number of substituents n in the series: $(G5)_1 P < \text{syn-}(G5)_2 P < (G5)_3 P < (G5)_4 P$. The tetrasubstituted dendrimer $(G5)_4 P$ turned out to be the best one, allowing a highly efficient energy transfer.

Obviously, this effect originates from the cooperative influence of the dendrons on the process of the energy migration. Highly-branched 5th generations of the dendrons assemble a spherical environment around the porphyrin. In a tetrasubstituted dendrimer, the conformational freedom of the substituents is highly reduced. This introduces a better order to the 3-dimensional dendrimeric subunits, which results in a more efficient energy migration along the dendrons and, thus, in higher probability to be transferred to the while excitation lifetime. The conformational freedom is enhanced with temperature. Hence, one expects the decrease of the energy transfer efficiency on heating the sample. It was also shown in [24] that this effect indeed took place in such dendrimers.

Temperature dependence

In addition to the conformational issues, there is another interesting effect that influences the energy transfer in dendrimers under elevated temperatures. In [25], thermodynamic issues were considered. It was shown that, besides the energy gradient stems the excitation from the periphery to the core, a contrary (entropic) trend is possible, that stems the excitation backward the core to the periphery. The limiting factor of this additional trend is the energy loss that occurs while propagating through the energy gradient. This loss can be compensated by the thermal energy. The threshold temperature is determined by the following expression:

$$k_B T > U / \ln(Z - 1). \quad (3.1)$$

Here, k_B is the Boltzman constant, U is the energy bias, and Z is the coordination number of the dendrimer. For temperature that satisfies inequality (3.1), the excitation prefers to go to the periphery, so that the energy transfer to the core becomes inefficient. This effect is exclusively due

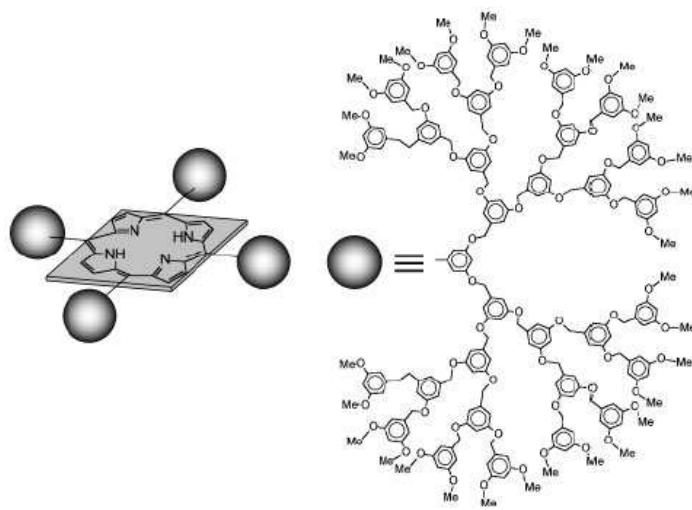


Fig. 11. Porphyrin encapsulated by the 5th generation of poly(benzyl ether) dendrons. Chemical structure of the dendron is shown. Figure is taken from [15].

to the geometrical structure of the dendrimer. It can act as a temperature sensor or can be used to drive, by temperature changes, the photochemical reaction at the core.

3.4 Applications of the light-harvesting

Signal amplification

In electronics, an idealized signal amplifier can be named "a piece of wire with gain", as the output is an exact replica of the input, but larger [28]. In dendrimers, this term means a different process. A signal here is the fluorescence of the core chromophore. Its intensity can be amplified by the dendrimer that acts as an antenna, harvesting light from a relatively large area and delivering it to the core. The dendrimer simply helps the core to gain in absorbing the light. As a result, the core fluorescence of a higher intensity is observed.

Let's consider the total fluorescence of the dendrimer that is presented in Fig. 10. The fluorescence of the peripheral groups is quenched by the energy transfer to the core (see Fig. 12a). The fluorescence intensity of the core is more than 3 times amplified when exciting the peripheral groups (b) compared to the direct excitation (c).

This example illustrates a dendrimer with only two types of chromophores (functional groups and the core). In the presence of the energy gradient (see Fig. 8b), the chromophores in the bulk also can absorb light. Since they have absorption spectra in between of the donor and acceptor ones, the overall absorption spectrum appears to be broad. All the energy absorbed is transferred to the core enhancing its fluorescence even more in such a dendrimer. In this case, the absorption spectra between maxima (b) and (c) in Figure 12 would be continuous.

Signal amplification is useful if the fluorescence of the core chromophore is weak under the direct excitation. In gradient dendrimers, a fluorescence band narrowing occurs with respect to the absorption spectrum. If the core can act as a host system for some kind of the guest molecules, such a system can be used for sensing applications

Sensors

Fluorescent chemical sensors are based on the change of fluorescence of the receptor species influenced by molecules what one wants to sense. A nice example of such a sensor is pH chemical indicator that is often demonstrated in school classes on Chemistry. When introduced into a solution, it may bind to hydrogen or hydroxide ions. Ions influence the electron configuration of the indicator changing its bandgap. As a consequence, the color changes.

It is also possible to design a fluorescent chemical sensor based on energy transfer. The receptor consists of two parts – donor and acceptor. The acceptor usually acts as a host system for

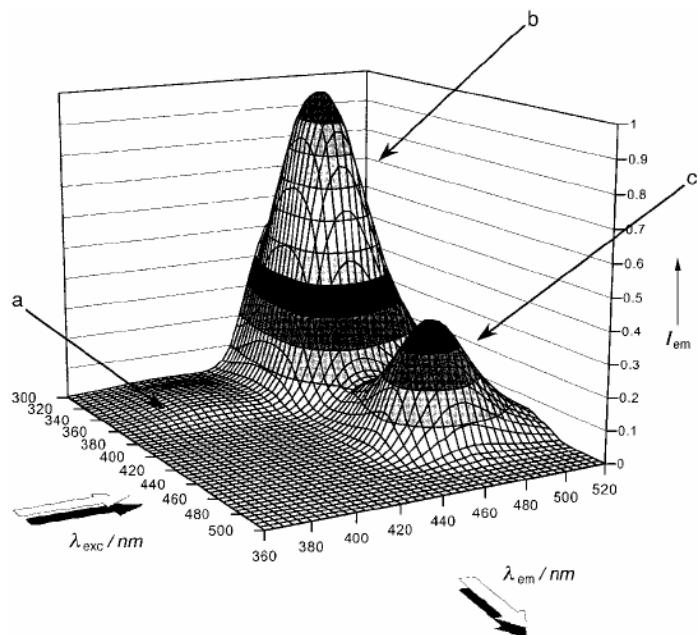


Fig. 12. The total fluorescence of the dendrimer shown in Figure 10. (a) Spontaneous emission of the donor dye; (b) emission of the core after the energy transfer from the periphery; (c) emission of the core upon the direct excitation. Figure is taken from [26].

sensing guest (target) species. When the host-guest system is bound, its excitation energy changes. This influences the spectral overlap of the donor's emission and the acceptor (host + guest) absorption spectra. Therefore, the energy transfer can be efficient in either bound or free states. The former case is illustrated schematically in Fig. 13a. In this example, the acceptor is designed such that the non-radiative decay is favorable. Here, the energy transfer leads to the fluorescence quenching of the receptor. The fluorescence is quenched if in the solution both guest species and sensor molecules are present. In such a way the fluorescent chemical sensor that is based on the energy transfer works. The efficient sensing here occurs if concentration of the target species is about or higher than of the receptors. Concentration of the receptors in solution is required to be high enough in order to observe fluorescence. This limits applications of such sensors for ultra low concentration detecting.

Using the concept of the signal (quenching) amplification, much lower concentrations can be detected (Fig 13b). A single host system is connected to a number of the chromophores. When a guest molecule binds to it, an efficient quenching of all the chromophores takes place. So, the ratio of quenched chromophores to a single target molecule is highly increased. In this way, ultra low concentrations can be detected.

Two photon absorption

The two photon absorption is a non-linear process and requires higher intensities. Such intensities can be achieved by focusing of relatively weak radiation. The easiness of manipulating the position of the focal point of optical system in three dimensions makes 2PA an attractive effect for various applications. It is very easy to apply the phenomenon in such fields as 3-D micro-fabrication, optical storage, photodynamic therapy etc. This effect is of highly interest in the biological community. The two photon laser scanning fluorescence microscopy (2P LSM) allows getting 3-D spatial resolution imagining of living tissues down to $500\mu\text{m}$ deep. In this technique, the distribution of the two photon absorbing dye is measured in a sample. The dye (2P chromophore) is usually introduced as a probe. The damage caused by the radiation and the background fluorescence is highly reduced in this technique [29]. Biological applications require usage of chromophores whose 2PA cross-sections are optimized for the reduced scattering and the minimal absorption in (bio)organic materials. This is the infrared spectral range of about 700-1200nm. Recently it was shown that semiconductor quantum dots satisfy these requirements. However, these inorganic systems are usually toxic for biological environment. One can prevent these unfavorable issues using organic chromophores. In order to increase the 2PA cross-section of organic chromophores, the concepts of light-harvesting is used. Functional groups of a dendrimer act as two photon absorption

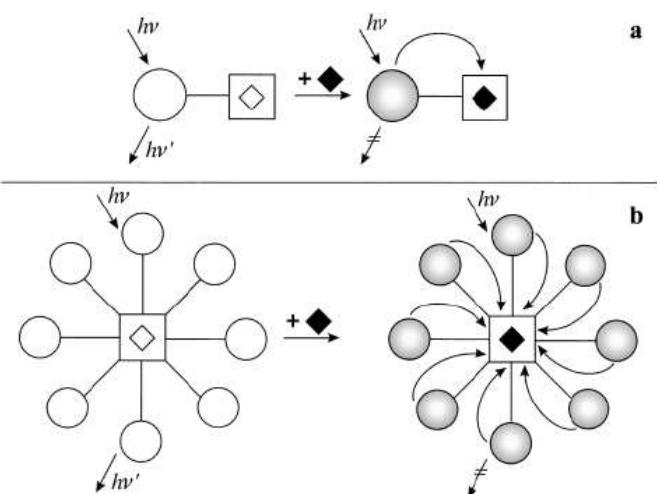


Fig. 13. Schematic representation of (a) a conventional fluorescent sensor and (b) a fluorescent sensor signal with amplification. The curved arrow indicate quenching process. Figure is taken form [27].

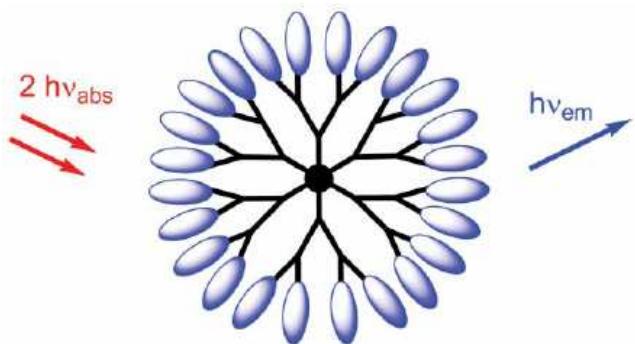


Fig. 14. Schematic representation of the two photon absorption in a dendrimer. Figure is taken from [29].

chromophores. They transfer the excitation to the core. As a result, the amplified fluorescent signal is detected. Magnitudes of the 2PA cross-section in the 4th generation dendrimer can be even bigger than that of inorganic quantum dots [29].

The all-organic approach introduces additional advantages as compared with semiconductor nanodots. They enable the molecular control of photophysical properties, modulation of solubility in various environments, and further covalent functionalization for additional functionality.

An example of the practical application of the 2PA is presented in the next section.

Triplet oxygen detection

An interesting combination of both phosphorescence quenching and two photon absorption was recently reported as an efficient oxygen sensor [30]. The oxygen concentration is a critical parameter in tissue pathologies such as retinal diseases, brain abnormalities and cancer. It is important to make 3-D imaging of it. The suggested method allows doing that with resolution of 2P LSM and high efficiency. The typical problem of using 2P LSM in combination with the phosphorescence quenching is designing the probe dye. This is a subject of our interest here.

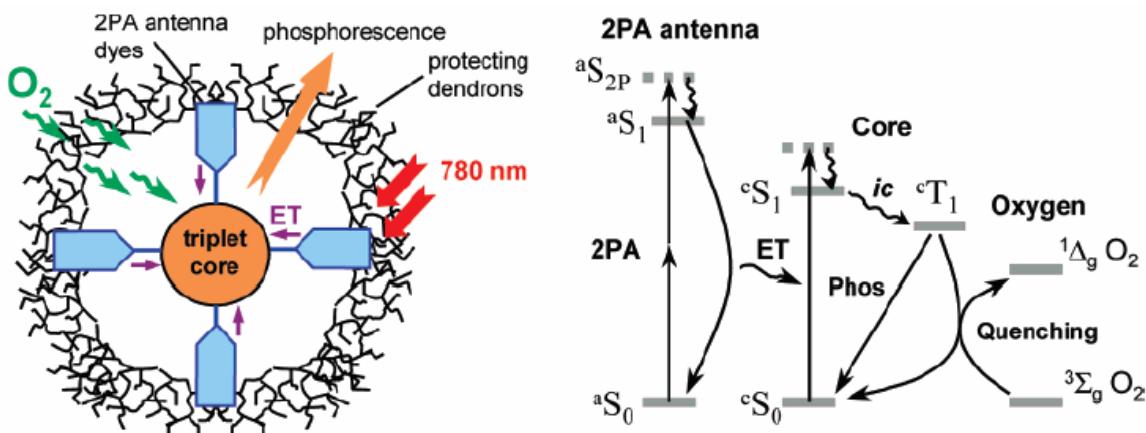


Fig. 15. Schematic representation of the triplet oxygen detection by means of two photon absorption (2PA) and phosphorescence quenching. The energy transfer mechanism from the core to oxygen is interesting. Both chromophores from the triplet state go to the singlet state. Figure is taken from [30].

The scheme of the triplet oxygen detection is presented in the Fig. 15. Let's concentrate on the phosphorescence quenching first. The oxygen molecule is a triplet in its ground state. The first excited state is a singlet. This transition is dipole forbidden. Hence, Dexter's mechanism of the energy transfer is relevant here. There are two possibilities for the donor electron configuration in order to get "spin-correct" energy transfer. One possibility implies the ground state to be a triplet and the excited state to be a singlet. The donor is usually excited optically or via Förster's energy transfer. The intersystem crossing from triplet to singlet should follow the donor excitation. Usually, a triplet state has a lower energy. Therefore, the probability of such a crossing is low. Another possibility is that the donor is excited from its singlet ground state followed by the intersystem crossing to the triplet state. Then electrons exchange between donor and oxygen molecules, such that both turn out in the singlet state. The mechanism is shown in Fig. 15 (right). This is the reason why we say "phosphorescence quenching" instead "fluorescence quenching".

It is clear that the donor should be strongly phosphorescent. For biological oxygen measurements Pt or Pd porphyrins are usually used. A problem here is that these species have very small 2PA cross-sections and are not efficient for practical applications in combination with 2P LSM. Therefore, 2PA antenna is used to enhance excitation of the porphyrin. As 2PA absorbers, coumarins were chosen.

In order to prevent self-aggregation, the phosphorescent dye is bound to the bio membranes in the live organism and to make 2P chromophore soluble it is protected by dendritic encapsulation. This almost does not affect the sensitivity of the dye, however, also introduces a supporting matrix for its components, keeping distances to be optimal for the efficient energy transfer.

Catalysis

Usage of light harvesting in the catalysis of chemical reactions is inspired by the photosynthesis. A lot of attempts have been made in this field. The main problem here is the mass transport from the focal point of the light harvesting system. One usually overcomes this problem by exciting one of the reagents in the core followed by its diffusion outside the light-harvesting system. Excitation usually enhances the reactivity. For example, in the previous section a mechanism of the oxygen activation is shown. It is highly reactive in the singlet state. Using the 2P LSM technique, the amount of produced oxygen singlets is negligible because of the exposure of a very small volume. But if one generates the oxygen singlet in the whole sample, efficient chemical reactions can occur. An example of such a reaction is given in [31]. The [4 + 2]cycloaddition of the photoproduced singlet oxygen to dienes with subsequent reduction to the allylicdiol was demonstrated.

4. Light harvesting in zeolite channels

Dendrimers are an elegant artificial realization of the concept of the energy transfer. They allow making applications that mimic that of evolved in the nature and are conceptually different from the conventional devices. The price paid for that is that conventional devices often cannot be made of dendrimers. For instance, it is still a challenge to design a photovoltaic cell based on dendrimers. The principal problem here is to separate electron-hole pairs which are produced in the core of the macromolecule. To overcome these difficulties and to find out new applications, the scientists developed other light-harvesting systems. In this section, some of them are briefly described.

Zeolites are hydrated alumino-silicate minerals that have a regular porous structure. Such a structure implies the existence of a very large number of small channels in the bulk. A wide variety of molecules and positive ions can be accommodated inside the channels. Therefore zeolites are often used to absorb unwanted or harmful elements from soil, water or air. Over 150 structural types of zeolites have been identified. They occur in the nature and can be synthesized.

In light harvesting applications zeolites are used as channels for dye molecules in order to achieve directional energy transfer.

Zeolite L antenna

Galzaferri and co-workers suggested to use zeolite L as a backbone of light harvesting antenna because it is very versatile [33]. A zeolite crystal consists of extended one-dimensional tube systems (Fig. 16) and can be prepared in a large size range.

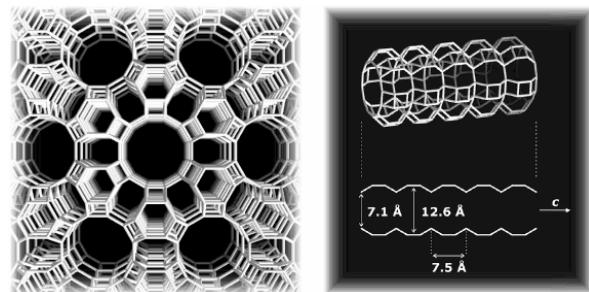


Fig. 16. Zeolite L framework. Seven large channels are shown (left). The structure of a channel is presented on the right. Figure is taken from [32].

Zeolite crystals are treated with dye molecules. Channels in such crystals are oriented along the cylinder axis. Dye molecules penetrate (diffuse) to the large channels. They do not aggregate with each other, rather, they are separated by distances that allow Forster's energy transfer. After molecules of one type penetrated the crystal, the latter is treated with molecules having smaller excitation energy. In such a way, a bidirectional molecular sandwich is made. The gradient of the excitation energy is directed from the periphery of the cylinder to its center. Finally, the energy absorbed in the bulk of such cylinder is transferred to its ends (see Fig. 17), where it is emitted as fluorescence. The data on crystals of size ranging from 30 nm to 3000 nm have been reported.

If one swaps the dye diffusion sequence then the energy transfer from the ends of the crystal to its central part is possible.

The stopcock principle

Communication between dye molecules inside the cylinder with molecules or a material outside it is needed for different application of the proposed zeolite L based light harvesting systems. For this purpose, specially designed molecules, called stopcocks, are attached to the interface. Such molecules also prevent penetration of small molecules, like oxygen and water, into the channels. Stopcock molecules can be either covalently bounded to the zeolite backbone (irreversible stopcocks) or electrostatically attracted by the negative zeolite channels (reversible stopcocks).

Since we are interested in the energy transfer from the inside to outside, stopcocks with strongly fluorescent units should be used. They also should have the absorption spectrum overlapping the emission spectrum of the edge dye.

Photovoltaic cell

The bidirectional antennae have been considered so far. The energy is transferred along one-dimensional channels in both directions. For practical applications of light harvesting the unidirectional energy transfer is usually desirable. The synthesis of such an antenna is now under investigation [34]. Here, we describe the idea of the photovoltaic cell.

Obviously, the unidirectional energy transfer can be realized by treating cylindrical zeolite crystals with different dyes only at one side. Hence, the other side should be closed for penetration of the dye molecules. For photovoltaic applications, we need to connect our antenna to a macroscopic device such as a semiconductor substrate. The substrate first is modified by preparing a monolayer of stopcocks. Then, the zeolite crystal is added in such a way, that the tail of the stopcocks penetrates into the channels. After that, the crystal can be filled in from the top with desired dyes. With this arrangement, the energy is transferred

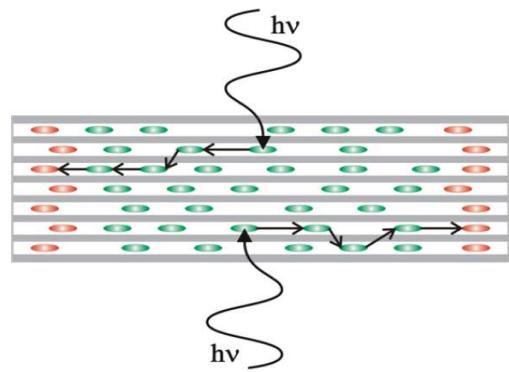


Fig. 17. Bidirectional energy transfer in the zeolite channels. Figure is taken from [32].

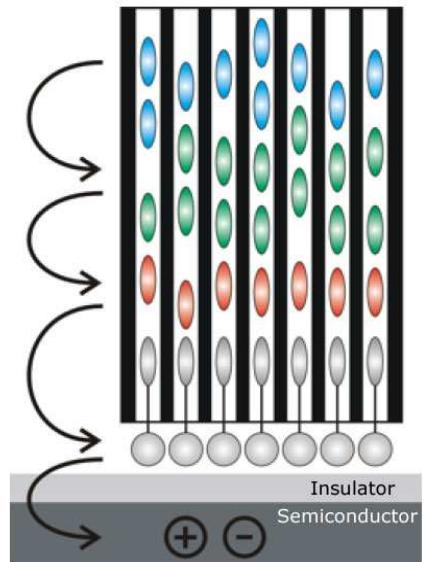


Fig. 18. Electron-hole pair creation in the semiconductor substrate induced by the energy transfer from the dye trough stopcock. Figure is taken from [32].

subsequently from the dyes in zeolite L to the stopcock and then to the semiconductor, creating electron-hole pairs (Fig. 18). To separate them probably p-n junction can be used. The energy transfer mechanism from the stopcock to the semiconductor substrate is claimed to be Dexter's type.

Unfortunately, there is no working device based on this idea, however, electron-hole pairs have been proven to create in the semiconductor [35].

5. Conclusions and perspectives

We discussed resonance energy transfer as a crucial process in light harvesting. Three examples were considered: purple bacteria, dendritic molecules and zeolite L crystals filled with organic dyes.

Purple bacteria take part in the process of photosynthesis. Antenna complexes LH1 and LH2, which are rings of chromophores, are common blocks of all of them. The light is gathered by LH2. After that, the excitation of LH2 is transferred to LH1, followed by the energy transfer from LH1 to the reaction center, surrounded by LH1. In this way, the sunlight energy is transformed into the chemical energy with the quantum yield almost equal to one.

Dendrimers are branched artificial macromolecules. It is possible to design them in order to mimic the structure of the natural purple bacteria. Peripheral functional groups harvest the light and transfer it to the core of the dendrimer. Dendrimer size and spectral overlap of the emission and absorption of dendrimer units should be considered here in the discussion of the type of RET. Dendrimers with both Forster's and Dexter's mechanisms of RET are illustrated. It is shown that resonance energy transfer is efficient if a gradient of excitation energy toward the periphery is present in the dendrimer. Under elevated temperatures, however, energy transfer can be favorable toward the periphery of the dendrimer; it is because of the entropic gradient. The efficiency of energy transfer in large dendrimers strongly depends on the morphology issues, namely the number and positions of core's substituents. Light harvesting in dendrimers allows conceptually new application. For example, dendrimers can be used in fluorescent signal amplification, detection of ultra low concentrations, catalysis, enhancement of the cross-section in two photon absorption etc. Unfortunately, conventional devices often can not be made of dendrimers. Thus, it is still a challenge to design a photovoltaic cell based on dendrimers.

Light harvesting in zeolite L crystals with channels filled with different organic dyes is considered. This material is considered as a potential candidate to achieve one dimensional directional energy transfer and to design a photovoltaic cell. The concept of this device based on zeolite L is discussed. However, no data have been reported in the literature so far concerning a working device.

There are several drawbacks in the considered light harvesting applications. Despite the synthesis of dendrimers almost excludes their polydispersivity, it remains a quite sophisticated process. The catalysis by the reaction center of dendrimer is often not applicable because of the problem of mass transport from the reaction center. This means that dendrimers can hardly be used so far to convert the solar energy to the energy of chemical bonds. Usually, applications of dendrimers as light harvesting complexes are performed in solutions. There is no solid state devices based on dendrimers. Attempts to make a photovoltaic cell based on zeolite L crystal, it is still far from making a working device. In zeolite L the energy migrates over identical dyes in a large volume where no excitation energy gradient is present. Hence, the energy transfer is not that efficient than, for example, in dendrimers. On the other hand, organic devices undergo degradation both on irradiation and on oxidation. In the live nature, a regeneration process is always present, and is not in artificial systems. To this end, studies of regeneration in organic systems seems to be an important problem in the future.

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