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Structure and properties of photosynthetic antennas: natural and artificial complexes

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Abstract. Key types of natural and artificial light-harvesting antennas, *i.e.*, supramolecular complexes that absorb light energy and transmit it to the receiver for electronic excitation, are considered. Attention is focused on the architecture of these complexes, the principles of the connection of individual units to a common system and structure – property relationships.The bibliography includes 122 references.

I. Introduction

Photosynthesis is the most efficient and energy-consuming way of light energy utilization on the Earth. The solar energy stored annually by photosynthesis is estimated at 10^{17} kcal, which corresponds to the conversion of 10 billion tonnes of carbon into carbohydrates.[1] Natural photosynthetic systems have complex structures and several levels of organization and are characterized by a great structural diversity. However, all these systems contain a number of common structural units that absorb light energy and convert it into other forms of energy.[2]

The primary light energy absorption in all photosynthetic organisms is performed by light-harvesting antennas (photo antennas), which are supramolecular complexes containing a large number of biological pigments (coloured molecules acting as chromophores in the complexes) in the protein surrounding.[3] Upon absorption of visible or near-infrared light, one of chromophores undergoes a transition into an electronically excited state, and then the electronic excitation energy is transferred through an antenna from one chromophore to another until it reaches the reaction centre – another supramolecular complex, where the charge separation followed by dark reactions take place.[4–8] An aggregate consisting of the reaction centre and its associated light-harvesting antennas is called a photosynthetic unit or a photosynthetic apparatus.[9]

The amount of solar energy absorbed by an antenna is determined by the number of chromophores and their absorption spectrum. In green plants, the light is absorbed by chlorophylls; in bacteria, by bacteriochlorophylls and carotenoids. All these molecules include an extensive π-electron system and absorb well in the visible region. As a rule, antennas contain several types of chromophores, whose absorption spectra cover the whole visible and near-infrared region, where the solar light has the maximum intensity.

The absorption cross-section of the solar energy, as well as its conversion efficiency and rate, are the key parameters characterizing light-harvesting antennas. The efficiency is determined by the fraction of the absorbed energy that reaches the reaction centre and is, in essence, the quantum yield. The rate of the energy conversion by an antenna is related to the time during which the electronic excitation reaches the reaction centre. To a certain extent, these parameters compete with each other. To achieve the maximum absorption, the antenna should contain a large number of pigments and, consequently, should occupy a large volume in space. However, a too large number of light-harvesting units will lead to a decrease in the rate of the energy transfer to the reaction centre and an increase in the fraction of competing energy dissipation processes, which will cause a decrease in the efficiency of the antenna. Therefore, there is a certain optimal structure of the antenna (for each particular organism) providing the best combination of the rates of energy absorption and conversion. Natural light-harvesting antennas are characterized by very high (not lower than 95%) quantum yields.[10, 11]

Another aspect of structure – property relationships is associated with the characteristic times of elementary events in light-harvesting antennas. These times are determined by the nature of electronic and electron – nucleus interactions

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between chromophores, as well as by their spatial arrangement with respect to each other.[12,13] The fast energy transfer between individual chromophores (characteristic times vary from 100 to 1000 fs [14,15]) should be combined with the relatively slow (tens of picoseconds) energy transfer from the antenna to the reaction centre to prevent the overloading of the latter.

Therefore, the energy transfer in natural photosystems is determined by a large number of correlated factors, including structural (sizes, the mutual arrangement and orientation of the molecules), electronic (energy levels of the ground and excited electronic states, transition dipole moments) and dynamic (migration times, lifetimes and transition probabilities) factors. The present review covers main types of the already synthesized artificial photosystems, attention being focused on their spatial arrangement, principles of the connection of individual units into a common system and structure–property relationships.

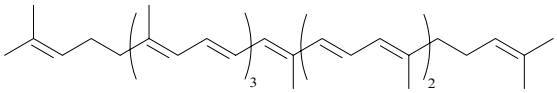
The review first describes main structural types of natural light-harvesting antennas, starting with the simplest purple bacteria and finishing with cyanobacteria, which are similar in the complexity of the photosynthetic organization to higher plants. Artificial light-harvesting antennas are discussed in the same fashion, starting with the simplest complexes (dyads and triads) and finishing with complex covalently and non-covalently bonded molecular and supramolecular systems.

II. Natural light-harvesting antennas

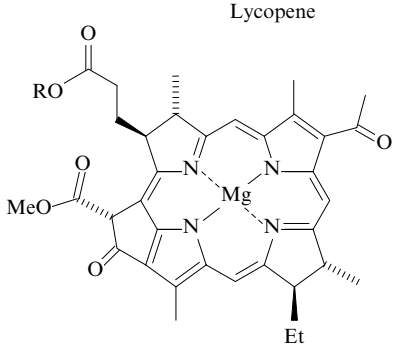
Researchers engaged in designing light-harvesting antennas are guided primarily by the properties of natural systems. A large number of various structural types of natural antennas are known.[3] All these antennas are membrane proteins containing a network of interacting chromophores. Reliable data on the structures of photosynthetic units are available for a relatively small number of living organisms. For this purpose, researchers use electron and atomic force spectroscopy, X-ray diffraction analysis and single-molecule spectroscopy[16] combined with molecular design methods. Selected key types of natural light-harvesting antennas are considered below in the order of increasing complexity.

1. Purple bacteria

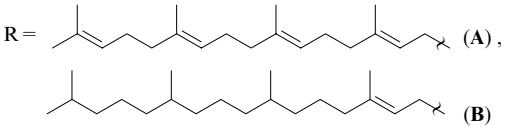
Purple bacteria are the simplest photosynthetic organisms grown in anaerobic environments.[17] Purple bacteria absorb in the green and near-infrared regions. In these bacteria, carotenoids (for example, lycopene) and bacteriochlorophylls [for example, bacteriochlorophyll *a* containing fragments of geranylgeraniol (**A**) or phytol (**B**)] act as pigments. In most bacteria, the photosynthetic apparatus comprises several types of antenna, which differ in the pigment absorption spectrum and the number of pigments in the antenna.[18–22] The LH1 antenna directly surrounds the reaction centre and includes B875 bacteriochlorophylls (the number indicates the wavelength at which the absorption maximum is observed), whereas the LH2 antennas containing two types of bacteriochlorophylls, B800 and B850, do not interact with the reaction centre (due to which they are referred to as peripheral) but serve to transfer the energy to the reaction centre through LH1 antennas. Some bacteria contain also accessory LH3 and LH4 antennas.[16,23]



Lycopene



Bacteriochlorophyll *a*



Due to the relative simplicity, antennas of purple bacteria are much better known and were studied in more detail than antennas of other organisms. All antennas of photosynthetic purple bacteria are structurally similar.[21] The key structural unit is a so-called αβ-heterodimer consisting of two low-molecular-weight hydrophobic peptides. The common motif in the secondary structure of each peptide is an α-helix. Most of pigments are located between two helices to form a sandwich structure through hydrogen bonds and coordination bonds between bacteriochlorophylls and certain amino acid residues. The heterodimers in the antennas are linked *via* interactions between the N- and C-termini of α- and β-peptides to form oligomers, *viz*., symmetric ring-shaped structures of different size.

The structures of LH2 antennas were determined for the first time by X-ray diffraction analysis in the mid-1990s for the purple bacteria *Rhodopseudomonas acidophila*[24] and *Rhodospirillum molischianum*.[25] In the bacterium *R. acidophila*, the LH2 antenna consists of 9 heterodimers, each heterodimer containing one B800 bacteriochlorophyll and two B850 bacteriochlorophylls. Therefore, the pigments in the antenna are arranged in two concentric rings (Fig. 1): the B800 ring consists of 9 pigments, whereas the B850 ring consists of 18 pigments. The porphyrin rings of B800 and B850 are mutually perpendicular. The pigments of different rings are linked together through phytol side chains of pigments. In addition, each heterodimer includes one carotenoid, which is non-covalently bonded to all bacteriochlorophylls. The carotenoid not only absorbs green light and transfers the excitation energy to bacteriochlorophylls but also plays an important structural role by linking the helices of α- and β-peptides.

The LH2 antenna from *R. molischianum* has a similar structure, but it contains 8 rather than 9 heterodimers. Their composition is similar to that of the heterodimers from *R. acidophila*, but they differ from the latter by the type of carotenoid and the character of the binding of B800 to the protein surrounding.

The LH1 antennas, like LH2, have a ring-shaped structure, but their size is larger because they should contain a cavity for the reaction centre. For instance, the LH1

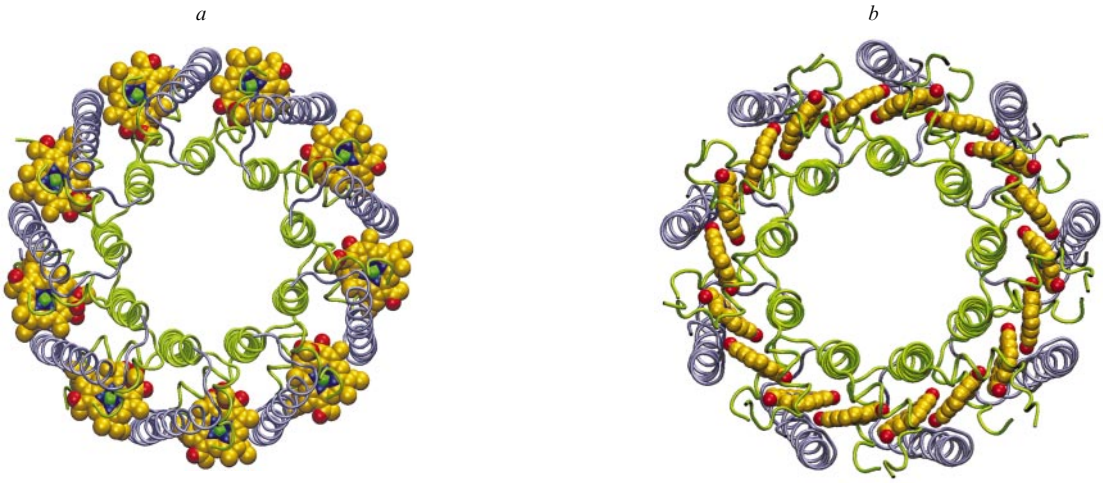


Figure 1. The ring-shaped arrangement of pigments in the LH2 antenna of *R. acidophila*: the B800 ring (*a*), the B850 ring (*b*).
The inner and outer helices indicate α- and β-peptides, respectively; van der Waals models represent bacteriochlorophylls, and their side chains are omitted.
The model is drawn based on the structure 2FKW [26] provided at the RCSB PDB website with the use of the VMD software.[27]

antenna in *Rhodospirillum rubrum* consists of 16 heterodimers [28] and, in the absence of the reaction centre, has a distinct symmetry. In the presence of the reaction centre (RC), the ring-shaped structure can be distorted. Thus, it becomes open and has an elliptical shape (Fig. 2).[30–32] In some bacteria, LH1–RC dimeric complexes can be formed.[33] In the discussion of the structures, one should take into account that the *in vivo* structure of the complex in the photosynthetic membrane can differ from that of the complex in the crystal. In spite of possible distortions of the structure, the ring shape of LH1 is, on the whole, characteristic of all purple bacteria.

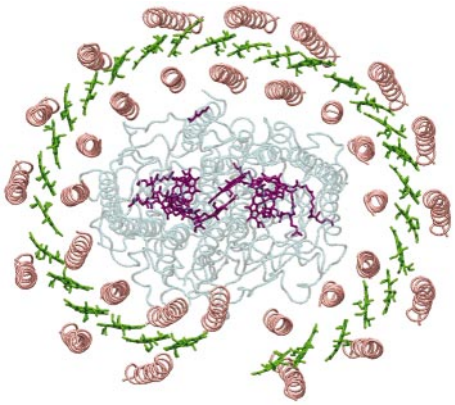


Figure 2. Structure of the LH1–RC complex of the bacterium *Rhodopseudomonas palustris*.
The model is constructed based on low-resolution data (4.8 Å). The peripheral helices represent the polypeptide chains of the LH1 antenna, bacteriochlorophylls of the antenna are located between these helices, pigments of the reaction centre in the protein surrounding are shown in the centre of the structure. The model is drawn based on the structure 1PYH [29] provided at the RCSB PDB website with the use of the VMD software.[27]

Under extreme conditions (for example, at low temperature or at low illumination), some bacteria form accessory LH3 and LH4 antennas, which are structurally similar to LH2 but differ from the latter in the type of carotenoid and the protein surrounding of bacteriochlorophylls.[34–37] These changes lead to a blue shift in the absorption spectrum of the chromophore: B850 → B830 or B850 → B820.

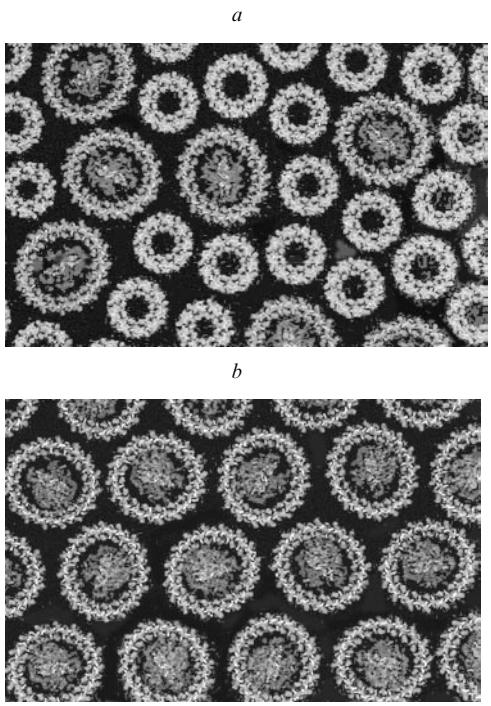


Figure 3. Models of photosynthetic membranes based on atomic force microscopy data: *Rhodospirillium photometricum* (*a*) and *Blastochloris viridis* (*b*).[40]
Large circles represent the LH1–RC complexes; small circles are the LH2 antennas.

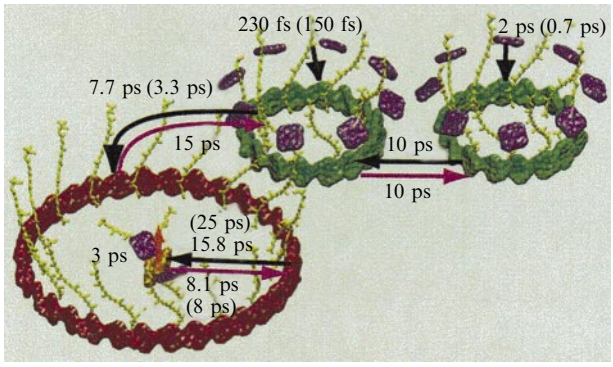


Figure 4. Key steps and characteristic times of the energy transfer in the minimal photosynthetic apparatus of the purple bacterium. For each step, the calculated and experimental (in parentheses) values are given.[14] Only pigments without the protein surrounding are shown. The LH1 antenna is shown as a large circle with the reaction centre inside, and the LH2 antennas are shown as small circles with pigments arranged around the circles. Carotenoids in both types of the antennas are represented by pale curved lines.

The number of antennas of different type in a photosynthetic apparatus and their mutual arrangement depend on the type of bacteria (Fig. 3) and the illumination at which they were grown.[38,39] In some bacteria, for example, in *B. viridis*, LH2 antennas are absent at all.[40]

Therefore, even in the simplest photosynthetic organisms, such as purple bacteria, light-harvesting antennas have a complex hierarchical structure. Due to this fact, the excitation energy transfer from chromophores to the reaction centre is also a complex multistep process[21] and is described by a set of characteristic times (Fig. 4), which can be divided into three groups. The energy transfer from carotenoids to bacteriochlorophylls and between strongly coupled bacteriochlorophylls in the B850 ring occurs very rapidly (in hundreds of femtoseconds). In the latter case, the excitation has an exciton character and extends over several pigments, up to the whole ring.[41] The B800 → B850 energy transfer takes about one picosecond, and the excitation energy transfer between different antennas and from the LH1 antenna to the reaction centre requires an order of magnitude longer time. In this organization, carotenoids and B800 bacteriochlorophylls act as energy acceptors, whereas other bacteriochlorophylls in LH2 and LH1 comprise an energy storage reservoir from which it can be transferred to the reaction centre of the photosynthesis when required.

2. Green bacteria

Since green bacteria exist under low light illumination, their photosynthetic apparatus comprises a very large (up to 250 000) number of pigments, which are primarily various bacteriochlorophylls and some part of them are carotenoids. Chromophores are arranged to form large antenna complexes, so-called chlorosomes of an ellipsoidal shape whose sizes in different directions vary from 10 to 200 nm. Unlike pigments of purple bacteria, pigments in chlorosomes do not have a protein surrounding. Since each chlorosome has an individual structure and composition, data on their detailed three-dimensional structures are lacking, although several large-scale models of their organization were proposed based on electron microscopy data.[42–46]

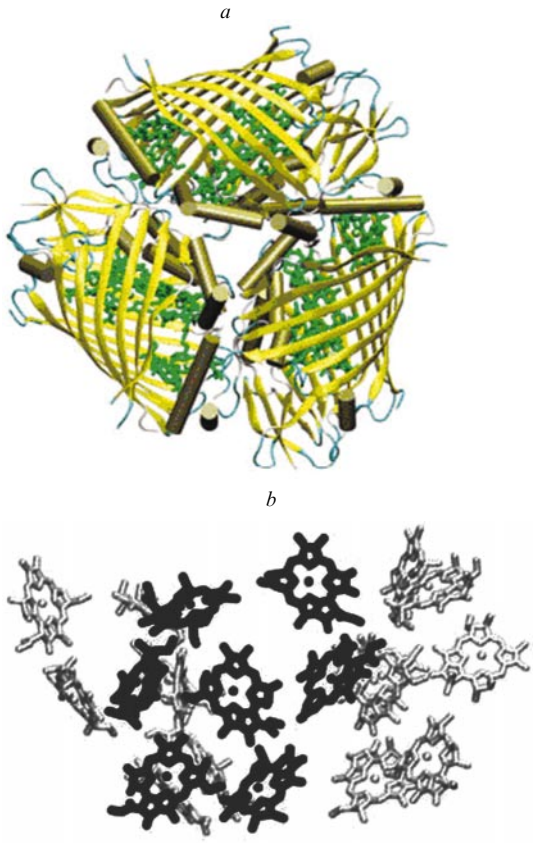


Figure 5. Structure of the FMO-complex of the bacterium *P. aestuarii*:[52] pigments in the protein surrounding (represented by β-sheets) (*a*); the relative arrangement of pigments in the complex (solid lines show pigments of one of the three subunits) (*b*).

In green sulfur bacteria, the energy transfer from chlorosomes to the reaction centre occurs through a special pigment–protein complex, the so-called Fenna–Matthews–Olson complex (FMO-complex).[47] As opposed to chlorosomes, the structures of these complexes for certain bacteria were determined at high resolution.[48–51] The FMO-complex of the bacterium *Prosthecochloris aestuarii* exists as a trimer. It contains three identical fragments, each of them consisting of 7 bacteriochlorophylls *a* enclosed in protein β-sheets (Fig. 5). The close packing of the pigments (the distance between the centres of adjacent pigments is 1.1 nm) mediated by the protein ensures the strong coupling between the pigments and assists in the rapid and efficient electronic excitation energy transfer through the complex. Some researchers state that the energy transfer in this system is a coherent process.[52] In our opinion, this statement is doubtful because the solar radiation is incoherent and, consequently, natural photosystems are not tuned to the coherence of the absorbed light.

3. Cyanobacteria

Blue-green algae, also known as cyanobacteria, perform photosynthesis producing oxygen. Cyanobacteria appeared later than purple bacteria in the course of the evolution of photosynthetic organisms and, consequently, they have a more complex structure of the photosynthetic apparatus.[53]

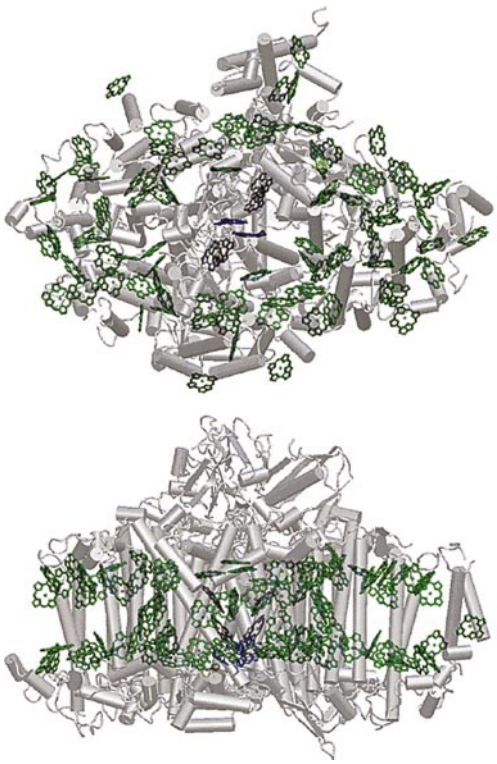


Figure 6. Structure of photosystem I of the cyanobacterium *S. elongatus* (views from two sides).[57]
Chlorophylls and the reaction centre are shown in dark gray, and the protein backbones are pale-gray. The cofactors and side chains of the chlorophylls are not shown.

Like the apparatus of green plants, it contains two pigment–protein complexes, the so-called photosystems I and II (PSI and PSII, respectively). Only photosystem I operates under anaerobic conditions (in the absence of oxygen). In photosystem I, the energy is absorbed by the antenna followed by the energy transfer to the reaction centre, the charge separation in the reaction centre and the transmembrane electron transfer. All units of photosystem I are present in the same protein. Chlorophylls and accessory pigments, the so-called phycocyanins, act as chromophores in cyanobacteria. Carotenoids that are also present in PSI perform a photoprotective function.[54]

The structures of only a few photosystems I were determined by X-ray diffraction analysis,† among which is PSI of the cyanobacterium *Synechococcus elongatus*.[56] This PSI contains 96 chlorophylls (almost all of them are of the type *a*), six of which belong to the reaction centre and the other to the light-harvesting antenna. As opposed to purple bacteria, the arrangement of chlorophylls in the antenna is almost nonsymmetric (pseudosymmetry C_2) and looks quite chaotic (Fig. 6). Nevertheless, the results of the computer simulation showed that these arrangements and the mutual orientation of pigments are, first, stable to structural damages and, second, lead to the optimal quantum yield ($>96\%$).[57]

† Recently, a new method was proposed for structural investigations based on the use of femtosecond X-ray pulses; this method allows one to obtain structural data from nanometer-sized crystals.[55]

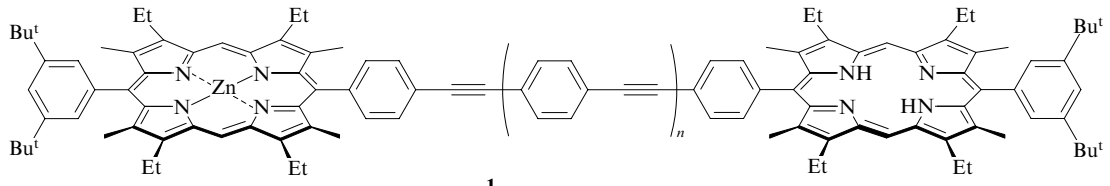
Photosystems of higher plants have a more complex organization.[58–60] A comparison of photosystems I of cyanobacteria and higher plants was reported.[60]

To summarize the brief consideration of natural photosystems, let us note firstly the rather evident fact that their supramolecular structure became more complex in the course of the evolution. The ways of this complication are still debated. It was found that in photosystems I of cyanobacteria and higher plants, pigments near the reaction centre are arranged in an optimal fashion from the standpoint of the efficiency of the energy transfer, whereas the arrangement of peripheral chlorophylls does not meet this condition.[60] Hence, it can be concluded that the energy transfer from the antenna to the reaction centre is not a rate-limiting step in the overall process of the light energy conversion. Other factors, such as the coordination of chlorophylls and associated shifts of the signals in the absorption spectrum, the characteristics of the electron transfer, the conditions of the photosystem assembly from individual components and the photoprotection against excessive radiation, can also play a key role. Meanwhile, the efficiency of the light energy conversion is one of the most important factors for artificial light-converting systems, due to which their properties and structure may be substantially different from those of natural photosystems.

III. Simplest artificial light-harvesting antennas

The electronic excitation energy transfer in molecular systems is complicated by competitive processes, such as fluorescence, radiationless transitions and charge transfer, which lead to a decrease in the quantum yield. Donor–acceptor and donor–bridge–acceptor systems are the simplest objects for investigations of their properties and characteristic features of the processes that occur in light-conversion devices.

One of the main approaches to the design of supramolecular light-harvesting systems is based on the mimicking of natural patterns and the use of components structurally similar to natural systems. For instance, two molecular dyads, which are the carotenoids peridinin and fucoxanthin linked to the porphyn pyropheophorbide were studied.[61] These dyads are similar to the structural units of natural photosystems. Unlike LH2 antenna of purple bacteria, in which the energy transfer from carotenoid to bacteriochlorophyll occurs in hundreds of femtoseconds, the dyads are characterized by a substantially slower dynamics: the characteristic times are tens and hundreds of picoseconds, *i.e.*, they are two to three orders of magnitude larger than in natural antenna, and they strongly depend on the polarity of the solvent due to the presence of polar groups in the above-mentioned carotenoids. The quantum yield of the energy transfer also depends on the nature of the solvent. Thus, the use of benzene instead of acetonitrile leads to an increase in the quantum yield by a factor of four (from 22% to 80%). On the contrary, the rate of the transfer in another similar dyad[62] consisting of purpurin and carotene is higher (the time of transfer is ~ 50 fs) due to the conjugation of the fragments of the dyad. However, the quantum yield deviates from the unity due to the fast internal conversion and is 70%. The energy transfer following the fast (tens of femtoseconds) relaxation to low-lying singlet states of carotenoid is observed in carotenoid–phthalocyanine dyads, in which the carotenoid is covalently



$n = 0-3$

1

bonded to the central atom of silicon phthalocyanine.[63] The quantum yield of the energy transfer in these systems strongly depends on the positions of the low-lying singlet energy levels of carotenoid with respect to the energy levels of phthalocyanine and decreases from 92% to 30% as the length of the conjugated system of double bonds in the carotenoid increases by one unit.

Porphyrins are widely used as structural units due both to the relative ease of synthesis (from pyrrolecarbaldehyde derivatives) and the flexibility of their molecular properties, which can be varied by introducing particular substituents or by selecting the central atom. Another advantage is that porphyrins can be linked to other components of the light-harvesting system through the coordination of ligands to the central atom of the porphyrin, which also can have a substantial effect on the photophysical properties of the porphyrin-containing systems.[64]

As in the case of carotenoid–porphyrin dyads, rate and quantum yield of the energy transfer are to a large extent determined by the fashion in which the porphyrin units are linked together. The energy transfer dominates over competing side processes if a system of bonds between molecular fragments is conjugated or partially conjugated, in particular, consists of phenylene[65] or phenylene ethynylene units (as for example, in structure **1**).[66] It is interesting that in the latter case, the energy transfer occurs between two triplet rather than singlet states; the quantum yield of the energy transfer remains unchanged to a certain extent as the length of the bridge increases and it is virtually equal to the unity. The relationship between the rate of the energy transfer and the length of the bridge between the porphyrin units is well described by an exponential function:[66]

$$k = k_0 \cdot \exp(-\beta R),$$

where k is the rate of the energy transfer, k_0 is the coefficient, R is the distance between the porphyrin units (in Å), β is the decay coefficient, which is equal to 0.45 $Å^{-1}$ for the zinc porphyrin–bridge–porphyrin system and, according to the calculations, varies for different dyads from 0.19 to 0.99 $Å^{-1}$ depending on the type of the porphyrin units and the angle between them.

The photophysical properties of porphyrin dyads substantially depend on their mutual orientation, which can be controlled by the complexation.[64] The geometry and photophysical properties of porphyrin dyads are also influenced by the central atom, which has a certain stabilizing effect on the skeleton of the molecule.[67]

Molecular systems with zinc porphyrins, in which the nitrogen atoms of the porphyrin system of one of the units are replaced by sulfur or oxygen atoms, were synthesized.[68] This replacement leads to the directed electronic excitation energy transfer from usual zinc porphyrin to modified porphyrin. The energy transfer in zinc porphyrin–Si-phthalocyanine systems occurs in the same direction.[69] In this case, the process is complicated by the electron transfer to phthalocyanine, the contribution of this process to the overall pattern of the dynamics of excited states being dependent on the polarity of the solvent.

Simple systems, such as dyads and triads of chromophores, are convenient objects for investigations of the characteristic features of photophysical processes that take place in light-harvesting antennas; however, these systems have virtually no prospects for practical application because of the low quantum yield of the energy transfer. When dealing with dyads and triads consisting of different components, one should take into account competing processes, in particular, the charge transfer, which often takes place if the molecule contains molecular fragments with a high electron affinity (for example, fullerene).[70, 71]

IV. Covalently bonded systems

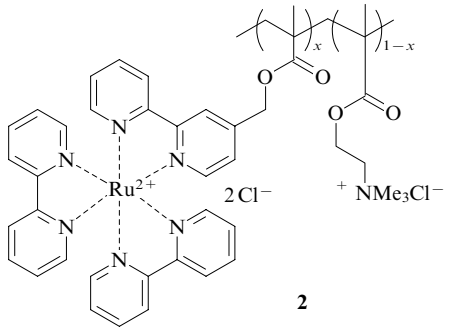
In light-harvesting systems consisting of a large number of chromophore molecules, the fashion in which individual structural units are joined together and the type of their spatial organization play an important role. There are several main modes of the binding responsible for the principal differences both in the method of assembling light-harvesting antennas from building blocks and the regime of their operation.

Covalent ensembles of chromophore molecules belong to the frequently occurring structural type of artificial light-harvesting antennas. These systems are often used to investigate the dynamics of the excitation propagation in ensembles of identical molecules.

The ring-shaped structure of the light-harvesting apparatus is one of the employed structural patterns rising from antennas of purple bacteria. Unlike natural light-harvesting antennas, chromophore molecules comprising artificial systems are covalently bonded, resulting in an increase in the rate of the excitation energy transfer.[72] These systems cannot be treated in terms of the Förster theory, which considers the incoherent energy transfer between weakly coupled components. In this case, the theory underestimates the rates of the energy transfer. Similar results were obtained in the study of a guest–host system based on zinc porphyrins linked to diphenylacetylene units:[73] the energy transfer through space (according to the Förster theory) occurs with a quantum yield of 65% in approximately 1 ns, as opposed to the energy transfer through bonds, which occurs in 40 ps with virtually quantitative yield. The investigation of the dynamics of the excitation migration in a series of ring-shaped antennas consisting of fused porphyrins shows that the structural flexibility of light-harvesting systems leads to a substantial decrease in the efficiency of energy transfer.[74] Thus, the flexibility of the molecule results in a gradual localization of the initially delocalized electronically excited state induced by the vibrational motion of the carbon atoms of the C≡C bond.[75]

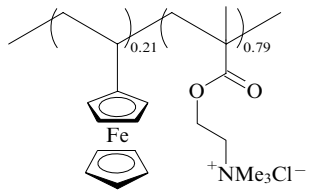
Light-harvesting antennas having a polymer or dendritic structure are interesting models for investigating the dynamics of the excitation energy transfer. The close packing of pigments in such antennas favours the through-space energy transfer due to $\pi-\pi$ interactions and, consequently, the creation of a common conjugation chain is not necessary.

Antennas having a polymer (chain) structure are attractive from the synthetic viewpoint. These antennas can be prepared by the one-pot synthesis using the chemical (see, for example, Ref. 76) or electrochemical initiation.[77] Moreover, photophysically active molecules can be attached to the polymer matrix.[78, 79] Examples are structures **2** and **3**.[79]



2

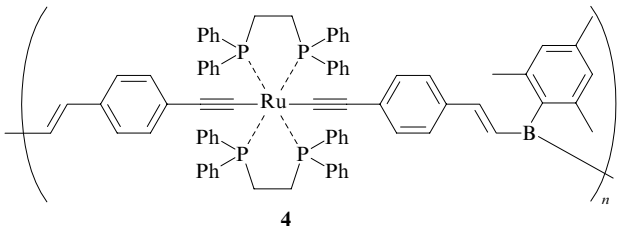
x = 0.04, 0.12, 0.18



3

The sequential arrangement of structural units becomes unfavourable due to the inevitability of dissipative processes, if the excitation energy or charge trap is in contact only with the ends of the antenna. The elimination of these processes is possible only in the absence of structural defects that disconcert the transport chain. For instance, it was found[76] that the quantum yield of the exciton transfer to one of the ends of the chain in the acenaphthylene–maleic acid copolymer greatly increases with decreasing pH due to the formation of the rigid helical structure in an acidic medium. Noteworthy is the formation of a conjugated bond chain along the whole polymer backbone, as for example, in organoboron complex of ruthenium **4**.[80]

Due to high charge mobility and high intensity of the $d\pi-p\pi^*$ transition, this system is suitable for the use in photovoltaics. A layered structure of two such conjugated polymers was tested[81] as a solar cell, and the energy efficiency was 4.6% and 62% for white and monochromated light, respectively.



4

As examples of polymer antennas, let us refer to polystyrene photosensitized by ruthenium and osmium polypyridine complexes[82, 83] and polymers composed of zinc porphyrins.[84] The properties of the former polymer depend on the pH of the medium, and the near-unity quantum yield of the energy transfer can be achieved in an acidic medium due to changes in the conformation of the chain. A system based on perylene bisimide and platinum porphyrin with a poly-isocyanopeptide backbone is a specific reaction centre having a polymer structure.[85] In this system, the electronic excitation transfer is accompanied by the electron transfer.

The close packing of chromophore units in polymers, even in the absence of the conjugation between these units, promotes fast excitation energy transfer. Thus, the energy transfer between adjacent chromophores in poly(dimethylvinylfluorene)[86] takes, on the average, 0.8–0.9 ps, although a substantial scatter in the values is observed due to the disorder of the units.

Dendritic antennas belong to another common type of light-harvesting antennas. The popularity of this class of compounds is, in particular, determined by the possibility of varying the structure of the antenna, thus controlling the number of the dendrimer generation and the composition of each layer. The synthesis of each subsequent dendrimer generation is a multistep chemical process, whose yield depends on the type of the dendrimer. In the case of aryl ethers, the facile convergent synthetic method providing a high yield can be used.[87] For polyphenylene[88] and polyphenylacetylene[89] dendrimers, the yield in each step varies from 60 to 90%, resulting in a decrease in the purity of high-generation dendrimers.

The hydroxymethyl derivative of resorcinol is a commonly used basis for synthetic dendritic antennas. Since such antennas do not absorb visible light (but absorb in the UV region), their combination with a chromophore giving fluorescence in the visible region (for example, with polythiophene)[90] makes it possible to reveal characteristic features of the energy transfer dynamics. A similar system with azobenzene as a excitation acceptor (a reaction centre) was reported.[91]

The mechanism of the electronic excitation energy transfer through a dendritic antenna substantially depends on the mode of the binding of the units. In the presence of a system of conjugated bonds, as for example, in azaborine[92] or thiophene[93, 94] derivatives, the excitation energy transfer occurs along the bonds of the molecule. In the case of non-conjugated dendrimers, for example, based on aromatic ethers, the excitation energy transfer can occur only through space, due to which the character of dynamic processes in light-harvesting antennas may vary depending on the conformation of the macromolecule, which can be influenced by the nature of the solvent, the temperature and other external factors. Thus, the rate of the excitation energy transfer in the dendrimer based on benzyl ether containing aminopyrene as a fluorophore[95] substantially changes even after the replacement of a nonpolar solvent by another one due to the difference in the density of the packing of dendrimer molecules. In the case of small conjugated systems, for instance, the phenyl ethynylene dendrimer with perylene as the energy trap,[96] a mixed mechanism of energy transfer is observed; the through-space energy transfer accounts for 46%.

The morphology of polymeric molecules is intermediate between a coil and a rod depending on their rigidity,

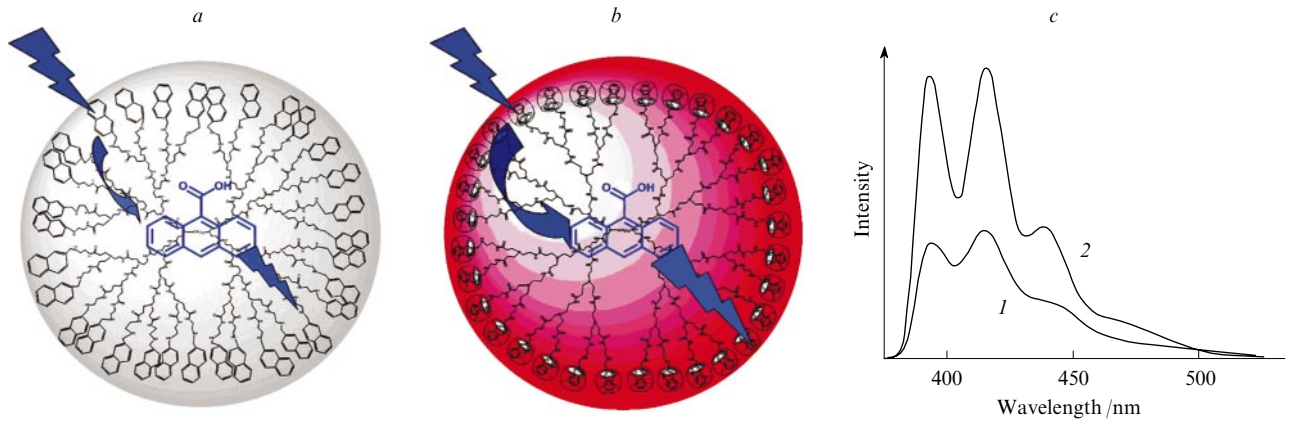


Figure 7. PAMAM dendrimer with attached peripheral naphthalene units and anthracene-9-carboxylic acid retained by PAMAM through acid-base interactions: without cucurbit[7]uril (*a*), with cucurbit[7]uril that forms a guest–host complex with naphthalene units (*b*), fluorescence spectra of the dendrimer in the absence (*1*) and in the presence (*2*) of cucurbit[7]uril (*c*).[98]

whereas the three-dimensional structure of one dendrimer branch is cone-like or hemispheric, where generations of molecules form layers. Since the number of molecules belonging to one dendrimer generation increases with the number of the generation, the steric repulsion between molecules is observed in high-generation dendrimers, resulting in various photophysical effects.

The influence of the structure of the dendrimer on its properties can be exemplified by the study of the fluorescence quantum yield of the systems Porph(Ar-dendr-5)$_n$Tol$_{4-n}$ ($n = 1-4$), where Porph is the porphyrin core, Ar-dendr-5 is the fifth-generation arene dendrimer and Tol is *p*-tolyl.[97] The increase in the number of substituents on the porphyrin macrocycle directly correlates with an increase in the quantum yield (from 10% for $n = 1$ to 80% for $n = 4$ at 20 °C; it decreases with increasing temperature). The authors believe that this fact is associated with a decrease in the distance between the benzene moieties and the rigid arrangement of these moieties due to increasing steric repulsion as the number of dendrimer branches increases, which favours the excitation energy transfer.

The opposite effect was observed for the polyamidoamine (PAMAM) dendrimer, in which peripheral naphthalene units serve as chromophores of the light-harvesting antenna.[98] In these systems, the fluorescence quantum yield of naphthalene varies from 6 to 12% and decreases with the number of generations in PAMAM due to the formation of naphthalene excimers (which also can give fluorescence but at a higher wavelength). The encapsulation of peripheral chromophores by cucurbit[7]uril (macrocyclic cavitand) led to an increase in the quantum yield to 18%–20% due to the elimination of the possibility of the excimer formation by adjacent naphthalene molecules. Experiments with the insertion of anthracene-9-carboxylic acid as the energy acceptor into the dendrimer (Fig. 7) revealed an increase in its fluorescence intensity with increasing amount of the introduced cucurbit[7]uril. This is also due to the loss of excimer fluorescence of naphthalene and the associated increase in the quantum yield of excitation energy transfer from naphthalene units to the acid. It is interesting that in photosystems of the same type, which consist of the fluorophore core and a dendrimer as the light-harvesting antenna but which are built based on structurally rigid polythiophene or polyphenylene dendrimers, the fluorescence quantum yields depends only slightly on structural variations and ranges from 20% to 29%.[94, 99, 100]

Light-harvesting antennas consisting of covalently bonded chromophore units are promising components of solar cells and artificial photosystems due to the possibility of varying photophysical properties. Drawbacks of these antenna are the complexity of the synthesis and the inhomogeneity of the composition (heterogeneity), which is due to the fact that the steps in the synthesis are not completed.

V. Non-covalently bonded supramolecular systems

The supramolecular chemistry offers great possibilities for the design of artificial light-harvesting antennas. The assembly of molecules to complex structures *via* coordination bonds and non-covalent interactions extends the range of structural types of light-harvesting apparatus and simplifies the synthesis. Natural photosystems are supramolecular, both relatively small systems and systems composed of hundreds and thousands of molecules (for example, chlorosomes of green bacteria and thylakoids of plants and cyanobacteria) being observed. Since such structures are very extended at least along one direction, their photophysical properties are substantially different from the properties of molecules and, in some aspects, are similar to the properties of crystals. Thus, the electronic excitation energy transfer in these structures can be represented as the migration of exciton quasiparticles. Due to the low dielectric permeability of supramolecular systems, primary optical excitations in the latter are Frenkel excitons.[101] The exciton delocalization length is an important characteristic of supramolecular systems.[101] The formation of J- and H-aggregates is detected based on the shift of the absorption maximum (relative to dilute dye solutions).[101]

J-Aggregates and H-aggregates, which are one-dimensional arrays of molecules (*i.e.*, stacks), are examples of the supramolecular organization of chromophore molecules.[101] These structures can be stabilized by both interactions between the chromophore molecules (electrostatic interactions, hydrogen bonds, $\pi-\pi$ interactions) and by means of surfactants.[102, 103] If the chromophore is amphiphilic, the self-organization to J-micelles (for example, tubular

micelles) is observed.[104] The aggregation of molecular dyads [102] results in the virtually 100% quantum yield of the energy transfer due to the large volume concentration of energy donor and acceptors and their close arrangement. The aggregation of molecules can give more complex structures, for example, of cylindrical shape in the case of porphin tetrasulfonic acid.[105]

The exciton delocalization length in crystals can be as large as 15 nm.[106] In aggregates of natural bacteriochlorophylls in the absence of the protein surrounding, the exciton delocalization length is smaller and equals about three molecule lengths.[107] The sizes of molecular aggregates can be controlled by adding foreign substances. Thus, the addition of polyethylene glycols to carboxy derivatives of porphyrins affects the size of the resulting particles and the mode of the arrangement of molecules in the particles,[108] the latter being responsible, to a substantial extent, for photophysical properties.

The formation of supramolecular systems of the type 'shell–chromophores' can be referred to as the 'forced aggregation'. Cyanine dyes encapsulated in the cavity of helical carboxymethyl cellulose molecules [109] or pyronin in cavities of zeolite (Fig. 8) [110] are examples of such systems. To obtain extended J-aggregates, the concentration of the pigment in the shell should be relatively high (20% in the case of the pyronin–zeolite system). Otherwise, only small clusters of molecules are formed in the channels of a framework substance. The voids in the crystal framework can be filled by complex systems. It was shown [111] that the insertion of LH2 antennas into the cavities of mesoporous silicon dioxide does not change their structure and the absorption spectrum. Therefore, SiO_2 serves as a convenient matrix for investigations of such systems outside biological membranes.

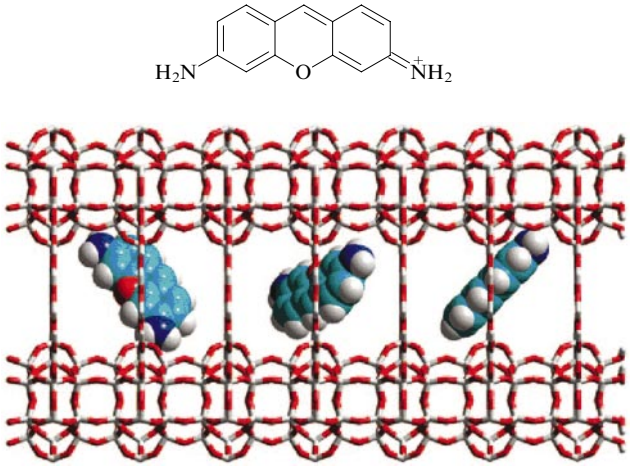
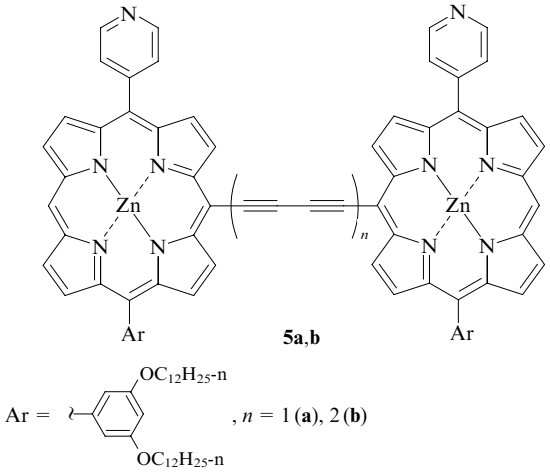


Figure 8. Structural formula of the pyronin dye and its J-aggregate in channels of zeolite.[110]

Two-component molecular crystals, in which the efficient electronic excitation energy transfer between components can occur, are of great interest. In this case, if the enegy acceptor can give efficient fluorescence, (for example, perylene, anthracene derivatives [112] and perylene bisimide derivatives [113]), light absorption–emission with a quantum yield up to the unity is observed,[113] the transfer occurring within a few picoseconds or faster. It should be emphasized that the fluorescence quantum yield decreases with increasing disorder (the concentration of defects) in the crystal.[112] Hence, the best results can be obtained with the use of structurally similar molecules as the energy donor and acceptor. The high quantum yield of the energy transfer (up to 97%) was observed also in the case of the coprecipitation of several organic dyes onto an inactive material, *viz*., silica gel.[114]

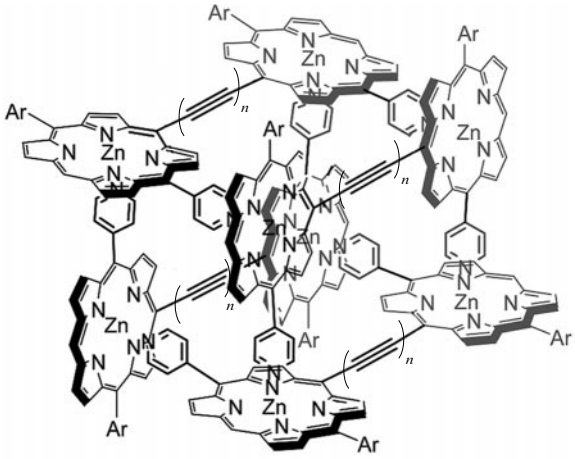
The bis(nickel porphyrin)–fullerene system described in the study [115] is an interesting example. Due to the presence of pyridyl substituents on the porphyrin rings, dimeric molecules, in which two nickel porphyrin moieties are linked by two butadiyne bridges, form a framework structure and its cavities are occupied by C_{60} molecules. This system is characterized by a small (<1 ps) time of the transition from the singlet to triplet state and the possibility of the formation of exiplexes from components of the system. In addition, the electron transfer (fullerene as the acceptor) takes place in this system, the charge mobility being very high. Although the quantum yield of the generation of charge carriers is low (6.2%), such systems can be used in photovoltaics.

The coordination of various ligands to the central atoms of porphyrins allows the preparation of rather complex ordered structures: prismatic [116,117] and ring-shaped,[118] which resemble light-harvesting antennas of purple bacteria. For example, tetrameric associates **6** and **7** are formed from linear dimers **5a**,**b** in noncoordinating solvents.

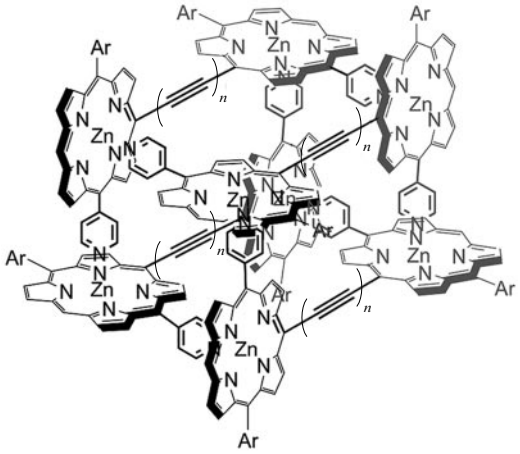


It should be noted that associates **6a**,**b** are built from planar conformers of dimers; associates **7a**,**b**, from orthogonal conformers. This mode of the binding, provided the conjugated structure of the ligands, allows the fast (at a rate of up to 10^{12} s^{-1}) excitation energy transfer between components of the system.[116]

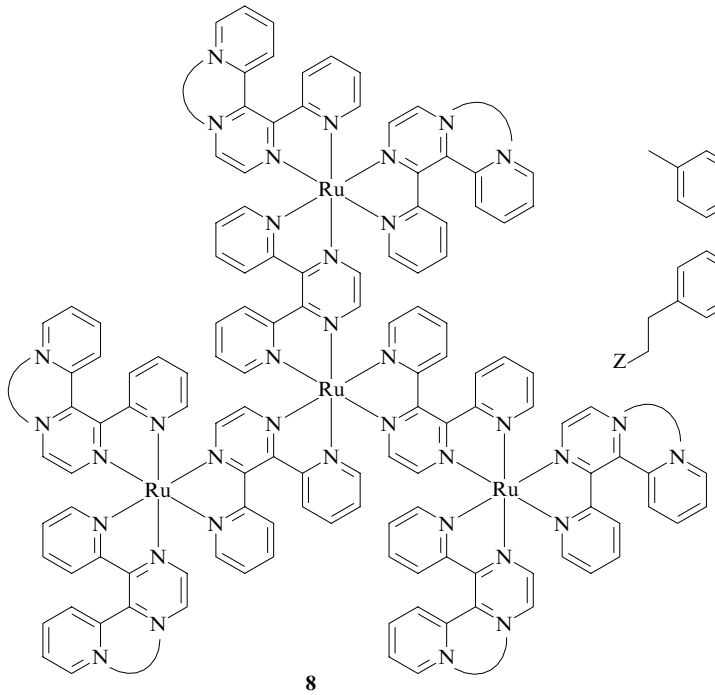
Noteworthy is the use of protein molecules as a basis for light-harvesting apparatus. A self-assembling large helical light-harvesting array, in which the excitation energy transfer to the acceptor occurs within 200 ps in 36% yield, was obtained based on chromophores templated by the tobacco mosaic virus coat protein.[119] The complex of porphyrin derivatives with a synthetic polypeptide containing posi-



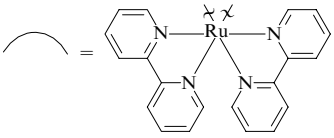
6a,**b**

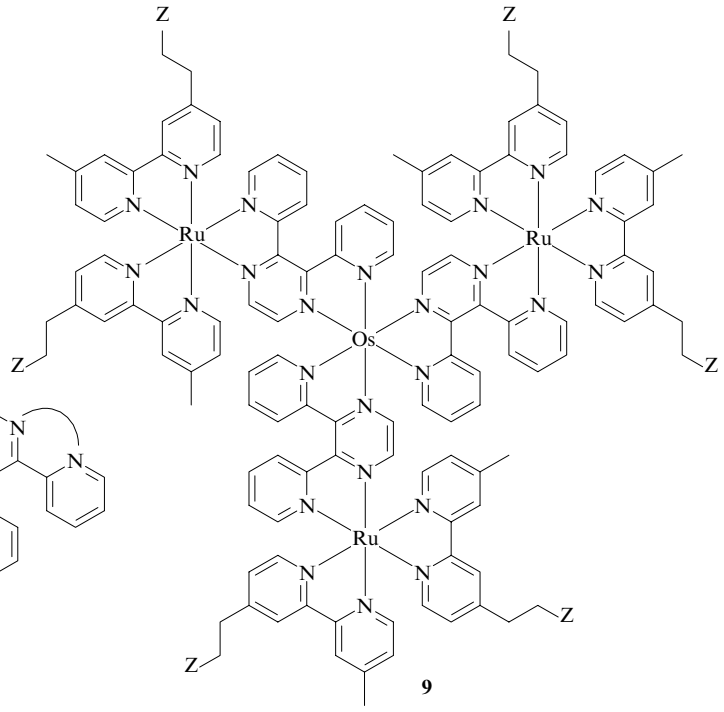


7a,**b**



8





9

Z is pyren-1-yl

tively charged lysine residues [120] is interesting in that the change in the pH of the medium from 7.6 to 3.6 leads to a decrease in the time of the energy transfer by one-and-a-half order of magnitude (from 279 to 9 ps).

Metal complex dendrimers, which are generated by the reaction of 2,3-bis(2-pyridyl)pyrazine with metal ions, in particular, with Ru^{II} and Os^{II} (structures **8** and **9**),[121, 122] are prominent examples of self-assembling systems.

Structure **9** contains a metal atom different from that in the light-harvesting antenna as the reaction centre, which favours the directed excitation energy transfer and allows its rate to be experimentally determined.

Supramolecular light-harvesting antennas are characterized by the ease of the preparation and the efficiency of the energy transfer. The large possible ratio of the number of energy donors to the number of energy acceptors is also responsible for good characteristics of light-harvesting antennas. Meanwhile, supramolecular light-harvesting antennas are formed due to specific intermolecular interactions, which imposes restrictions on the structure of the antennas consisting of specified components. The optimal route to the design of light-harvesting apparatus is, in our opinion, based on a combination of methods of supramolecular chemistry and the synthesis of complex (polymer and dendritic) antennas.

VI. Conclusion

The above-considered examples provide insight into the structural diversity of natural and artificial light-harvesting antennas. When comparing these systems, it should be emphasized that, in spite of the diversity, the organization of all natural light-harvesting antennas follows the same principle. Thus, they are supramolecular, in many cases hierarchical, structures based on pigments, such as porphyrins and carotenoids, in the protein surrounding. These structures were optimized during millions of years of the evolution for their efficient operation, primarily, for the light energy collection and its transfer to the reaction centre.

On the other hand, approaches applied to the design of artificial light-harvesting antennas are much more diverse. Researchers use various classes of light-absorbing molecules and various ways of their assembling, including covalent and noncovalent interactions. As opposed to natural photosystems, in which the protein surrounding plays an important role, emphasis is given to the composition and structure of the pigment complexes in artificial systems, whereas the influence of the surrounding seems to be of secondary importance; in some systems, the surrounding is absent at all.

In spite of a large number of methods of synthesis and the diversity of available artificial systems, their quantitative characteristics are far from those of natural analogues. The energy- and charge-transfer processes are accompanied by a large number of competing processes, such as the vibrational relaxation, luminescence and chemical side reactions. Hence, the aim of most studies is to investigate the transfer mechanisms and the influence of structural, electronic and energy factors on the quantum yield, *i.e.*, in fact, to elucidate the structure–property relationships. The available data suggest that the efficient system should combine the thoroughly selected chemical structure of pigments with a flexible, predominantly non-covalent, binding of the pigments to form a common system. Due to the latter feature, systems can respond to external effects, for example, to changes in the acidity of the medium or illumination, and, consequently, the properties of the complex are possible to control.

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