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Synthetic molecular systems based on porphyrins as models for the study of energy transfer in photosynthesis

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Abstract. The published data on the synthesis and photochemical properties of porphyrin-based molecular ensembles which represent models of natural photosynthetic light-harvesting complexes are generalised and systematised. The dependence of the transfer of excitation energy on the distance between donor and acceptor components, their mutual arrangement, electronic and environmental factors are discussed. Two mechanisms of energy transfer reactions, *viz*., 'through space' and 'through bond', are considered. The bibliography includes 96 references.

I. Introduction

Absorption of solar energy and its subsequent transformation by cells in the course of photosynthesis is the basis for the energy supply for vital activities of all living organisms. It is therefore not surprising that this problem arouses considerable theoretical and practical interest from investigators.[1–6] Spectroscopic and theoretical studies of photosynthetic processes are mainly focused on the fundamental analysis of photophysical and photochemical characteristics of biological energy-transforming systems and the construction of supramolecular ensembles for molecular photonics and optoelectronics.[7–10]

Chlorophylls and related pigments as well as quinones and carotenoid polyenes are the major components of natural photosynthetic systems. Their interactions are reduced to three basic photochemical processes, *viz*., singlet – singlet energy transfer, triplet – triplet energy transfer and photoinduced electron transfer. For example, antenna systems, which contain chlorophylls, carotenoids and other accessory pigments, collect light and transfer excitation energy to the reaction centres *via* a singlet – singlet energy transfer mechanism.[11,12] Carotenoids are responsible for photoprotection of living organisms from destructive effects of highly reactive singlet oxygen by rapid quenching of the triplet state of chlorophylls *via* a triplet – triplet energy transfer mechanism.[13] The excitation energy derived from antenna complexes is transformed into chemical energy in the course of photoinduced electron transfer mediated by chlorophylls and quinones, which, in turn, generates long-living states with transmembrane separation of charges.[14–16]

Recent studies have led to the synthesis of molecular systems which successfully simulate certain stages of natural conversion of solar energy, particularly, the above-mentioned singlet and triplet energy transfer reactions. The choice of pigments, donors and acceptors for such model systems is based of their spectral properties, which determine the energy characteristics of various excited states. Chromophores related to pigments involved in natural photosynthetic processes are the most promising components for such systems.

The choice of the working principle, which regulates interactions between the individual fragments of a system, is no less important. These interactions, which are controlled by the spatial arrangement of the photosynthetic components and the nature of the separating medium, strongly affect the rates and quantum yields of photochemical processes. The spatial arrangement of pigments, donors and acceptors in natural photosynthetic systems is provided by their interactions with protein subunits. One of the strategies in the construction of artificial photosynthetic systems consists of the substitution of covalent bonds for pigment – protein interactions.[1–3,6] An alternative strategy involves noncovalent assembly of supramolecular complexes, mostly by virtue of the formation of hydrogen and coordination bonds.[17] The construction, in the past few years, of models in which amino acids and peptides are used as connecting bridges (spacers) permitted one to study different regularities of energy and electron transfer in a protein matrix.[18]

The majority of supramolecular model systems described in the literature reproduce the photoinduced electron transfer step. Spectroscopic studies of donor – acceptor model systems have made it possible to establish the dependence of rates of photochemical charge separation reactions on structural factors, such as the distance between the system components and their orientation, on the interactions between the electronic systems of the donor and the acceptor, thermodynamic driving force of the electron transfer and environmental factors.[1–3,6]

Until very recently, much less attention was given to the development of model systems mimicking certain functional steps of light-harvesting antenna complexes.

Light-harvesting antenna complexes inherent in natural photosynthetic systems absorb low-intensity sunlight at wavelengths ~280 – 900 nm (up to 1040 nm in the case of some bacterial complexes) eventually resulting in the transfer of energy to the reaction centres. These complexes contain a large number of chlorophyll or bacteriochlorophyll molecules, carotenoid poly-

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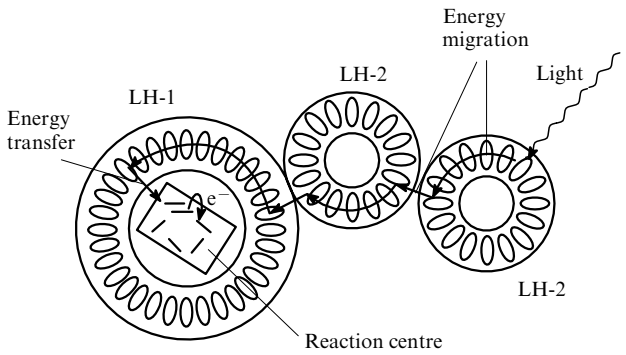


Figure 1. The structures of the bacterial light-harvesting complexes LH-1 and LH-2 responsible for the transfer of absorbed light energy to the reaction centres.[11]

enes and some other accessory pigments held at a small distance from one another by virtue of noncovalent interactions with the protein environment. Absorption of photons by pigments of antenna complexes is followed by migration of excited state energy generated by pigment ensembles until excitation reaches the reaction centre (Fig. 1). The energy can be transferred over sufficiently large distances at record-breaking high speed and with nearly quantitative quantum efficiency (quantum yields).[11, 12]

The complexity of supramolecular pigment–protein structures of natural antenna complexes hinders detailed investigations of light-harvesting reactions at the molecular level and does not provide unambiguous answers to the following questions. How do electronic, photophysical and photochemical properties of pigments influence the efficiency of light-harvesting processes? How does energy migration depend on the three-dimensional configuration of pigments (*viz.*, the distance between the components, their orientation, spatial packing, *etc.*)? What are the mechanisms of electronic interactions between pigments and the role of local environment? What are the effects of these interactions on the synthetic ensembles after substitution of covalent bonds for pigment–protein interactions between the components? What is the mechanism of functioning of the pigments as integral antenna systems within the ensembles and at what distances does energy migrate? Is it possible to increase the efficiency of energy migration in artificial systems by varying the system structure or energy gradients and what are the structural limitations for directional migration of energy? These questions are of crucial importance for the correct understanding of light-harvesting processes occurring in photosynthesising organisms and purposeful utilisation of solar energy. In this context, artificial model systems offer convenient subjects for the study of regularities of energy transfer in natural antenna complexes.

In this review, we consider the main principles of the construction of porphyrin-based model photosynthetic systems and the methods of their synthesis. The applications of these systems in the study of energy transfer in photosynthesis are also discussed.

II. Porphyrin dimers

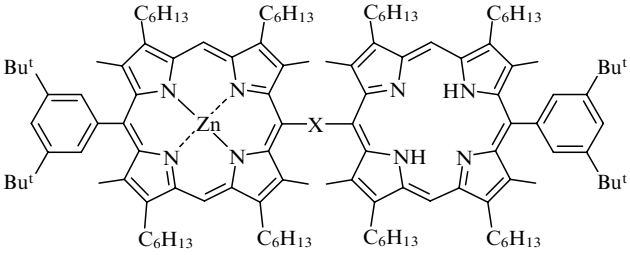
Porphyrin dimers present special interest for investigation of pairwise interactions between pigments in larger ensembles as the simplest models for energy transfer studies. According to the type of their binding, these compounds can be divided into three groups, *viz.*, covalently bound molecules with hydrocarbon spacers, complexes with amino acid and peptide spacers and systems linked by non-covalent bonds.

1. Porphyrin dimers with hydrocarbon spacers

a. Synthesis

The synthesis of covalently bound pigment ensembles is the most popular approach to the design of bisporphyrin model systems.

Covalently bound π-conjugated donor–acceptor systems are convenient models for the study of regularities of energy transfer at large distances. The polyyne- and polyene-bound bisporphyrins **1a–d** and **2a–d** are examples of such systems.[19] The strength of electron-exchange reactions between the donors and the acceptors in these compounds is largely determined by the 'centre-to-centre' distance between two porphyrin macrocycles. This, in turn, is strictly correlated with the number of unsaturated bonds in polyyne-bound systems and can be measured, with a high degree of precision, for polyene-bound molecules taking account of rotation of porphyrin rings around the single bonds.



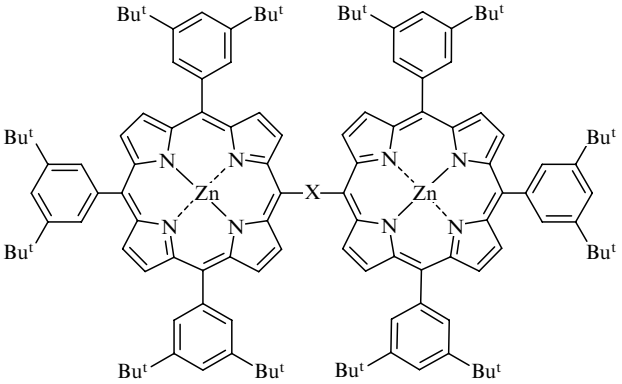
1a–d, **2a–d**, **3a–c**

1: X = *p*-C_6H_4–(–C≡C–)$_n$–C_6H_4-*p*; *n* = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**);

2: X = *p*-C_6H_4–(–CH=CH–)$_n$–C_6H_4-*p*; *n* = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**);

3: X = *p*-$C_6H_4C{\equiv}C{-}Ar{-}C{\equiv}C\,C_6H_4$-*p*; Ar = 1,2-$C_6H_4$ (**a**), 1,3-C_6H_4 (**b**), 1,4-C_6H_4 (**c**).

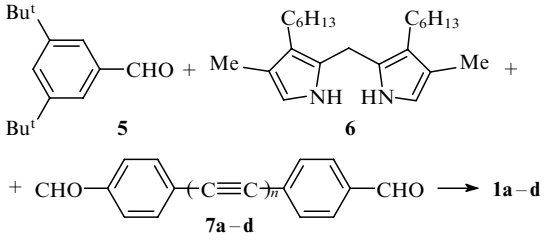
The efficiency of intramolecular singlet energy transfer in the dimeric porphyrins **3a–c** and **4a–c** containing bis(phenylethynyl)phenylene bridges is determined by both the distance and mutual arrangement of the pigments.[20, 21]



4a–c

X = *p*-$C_6H_4C{\equiv}C-Ar-C{\equiv}CC_6H_4$-*p*; Ar = 1,2-$C_6H_4$ (**a**), 1,3-C_6H_4 (**b**), 1,4-C_6H_4 (**c**).

The polyyne-bound bisporphyrins **1a–d** were obtained by trichloroacetic acid-catalysed condensation of 3,5-di-*tert*-butylbenzaldehyde (**5**), dipyrrolylmethane **6** and dialdehydes **7a–d**

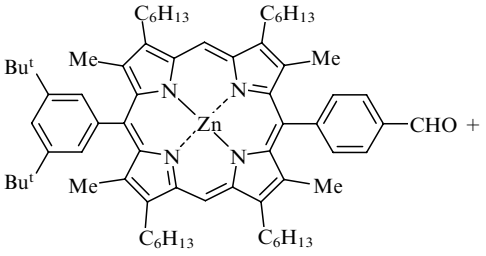


n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**).

with subsequent oxidation with *p*-chloranil [22, 23] and metallation of one of the porphyrin rings. The yields of bisporphyrins ranged from 13% to 46%.[19] Similarly, the dimers **2a**,**b** and **3a**,**b** were synthesised by condensation of dialdehydes with compounds **5** and **6**.[19, 20]

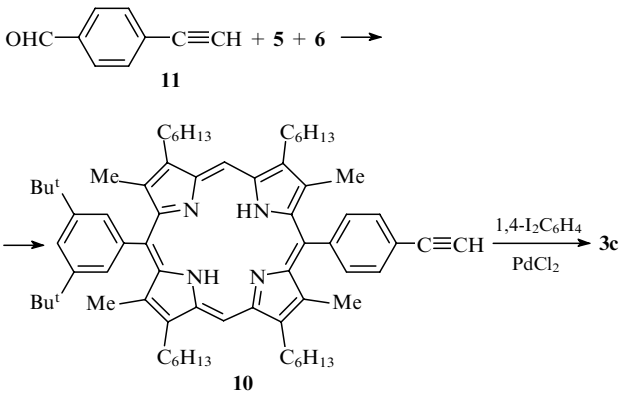
This one-pot synthesis of bisporphyrins is both convenient and efficient. The formation of polymeric side products in the condensation is suppressed by a large excess of the terminal monoaldehyde; the polyyne and polyene groups, which are especially acid-sensitive, are not affected, since the reaction is carried out under mild conditions.[22, 23]

An alternative approach, which includes condensation of the formyl-substituted zinc-porphyrin monomer **8** with bisphosphonates **9a**,**b**, was used in the synthesis of bisporphyrins **2c**,**d**.[19]



n = 1 (**a**), 2 (**b**).

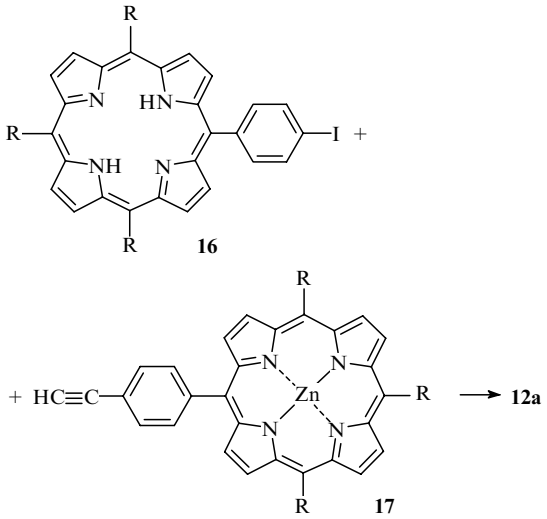
Bisporphyrin **3c** was synthesised by palladium-catalysed condensation of ethynylporphyrin **10** [the latter was prepared by the reaction of 4-ethynylbenzaldehyde (**11**) with compounds **5** and **6** with subsequent oxidation by *p*-chloranil] with 1,4-diiodobenzene.[24, 25] The yield of the dimer **3c** was 35%.[20]



Similarly, bisporphyrins **4a**–**c** were synthesised in 49%, 55% and 84% yields, respectively, by the reaction of ethynyl-substituted tetraarylporphyrins with 1,2-, 1,3- and 1,4-diiodobenzene in the presence of tris(dibenzylideneacetone)dipalladium(0) and triphenylarsine.[21]

An approach to the construction of model light-harvesting systems has been developed, which makes use of porphyrin building blocks. Firstly, *meso*-substituted porphyrins are synthesised from aldehyde precursors (containing iodine atoms and ethynyl groups) and pyrrole (or dipyrrolylmethanes) with subsequent palladium-catalysed condensation optimised for mild coupling of the porphyrin building blocks. In this case, spacers between porphyrins are formed directly in the condensation step.[25–27] This block synthesis was used to prepare the dimeric ensembles **12a**–**i**,[27–31] **13a**–**c** [32] and **14a**,**b**.[33] These model systems were employed for the systematic analysis of structural and electronic factors and their effects on the degree of electronic interactions between tetrapyrrole macrocycles as well as for the synthesis of the amphiphilic porphyrin dimers **15a**,**b**.[34] The latter can be incorporated into lipid bilayer membranes for transmembrane energy transfer studies.

Condensation of the iodoporphyrin **16** free base and the zinc ethynylporphyrin complex **17** in the presence of tris(dibenzylideneacetone)dipalladium(0) and triphenylarsine in a 5 : 1 toluene–triethylamine mixture (35 °C) afforded the dimer **12a** with a diphenylethyne linker (yield > 70%).



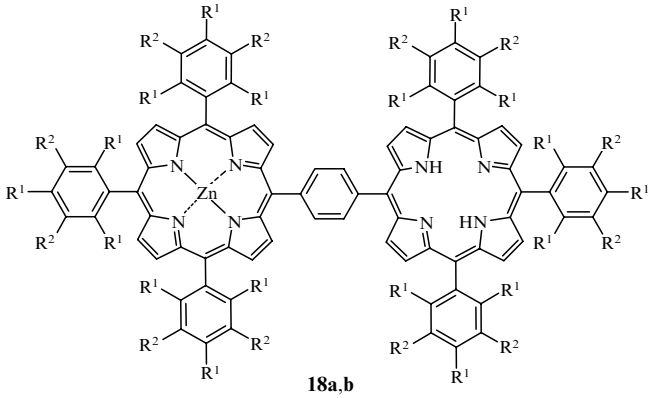
R = 2,4,6-$Me_3C_6H_2$.

Bisporphyrins **12b**–**h** were synthesised analogously in 70%–80% yields.[27–31]

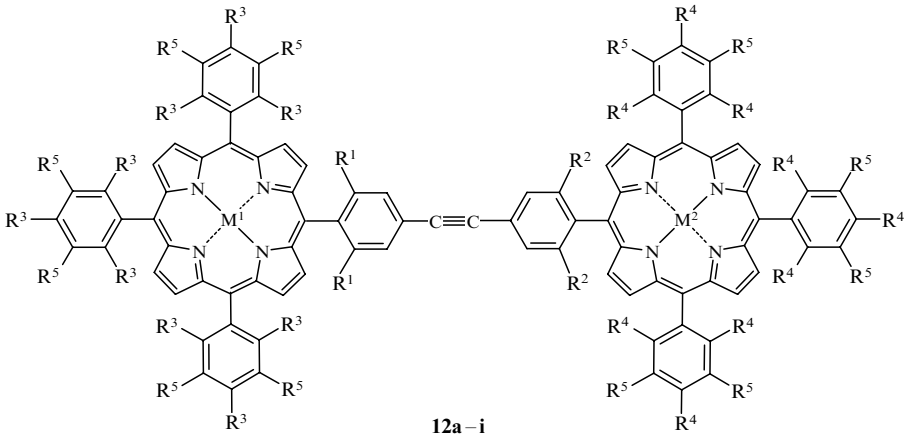
Since the palladium catalyst present in the reaction mixture is not involved in undesirable metallation reactions, free porphyrin bases can be used. If the reaction is carried out in neutral and weakly basic solvents at moderate temperatures, neither demetallation of zinc complexes nor oligomerisation of ethynyl-substituted porphyrins take place.[25, 27]

The diphenylethyne linkers in the systems **12a**–**i** ensure a sufficiently large (~20 Å) distance and relatively weak electronic interactions between the pigments, which excludes quenching of the excited state owing to the electron transfer, which competes with the energy transfer. However, in this case it is desirable to reduce the distance between the porphyrin chromophores in order to increase the rate of the energy transfer.

It was shown [35] that the distance between the porphyrin components of a dimer can be reduced to 13 Å if a *para*-phenylene linker is used, which significantly enhances their electronic interactions. Compounds **18a**,**b** were obtained by one-pot condensation of the corresponding aldehyde with terephthalaldehyde and pyrrole using boron trifluoride etherate as a catalyst and oxidation of the resulting product by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

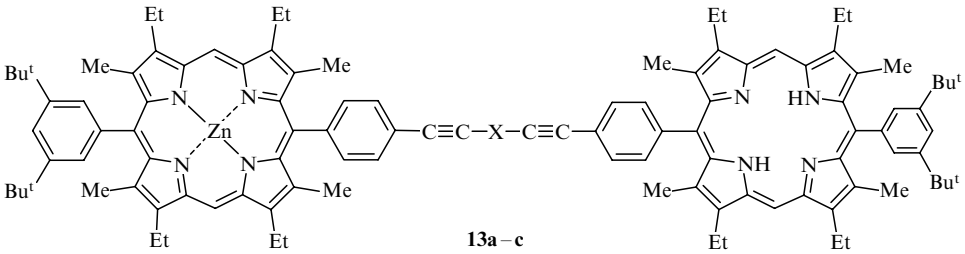


R^1 = Me, R^2 = H (**a**), R^1 = R^2 = F (**b**).



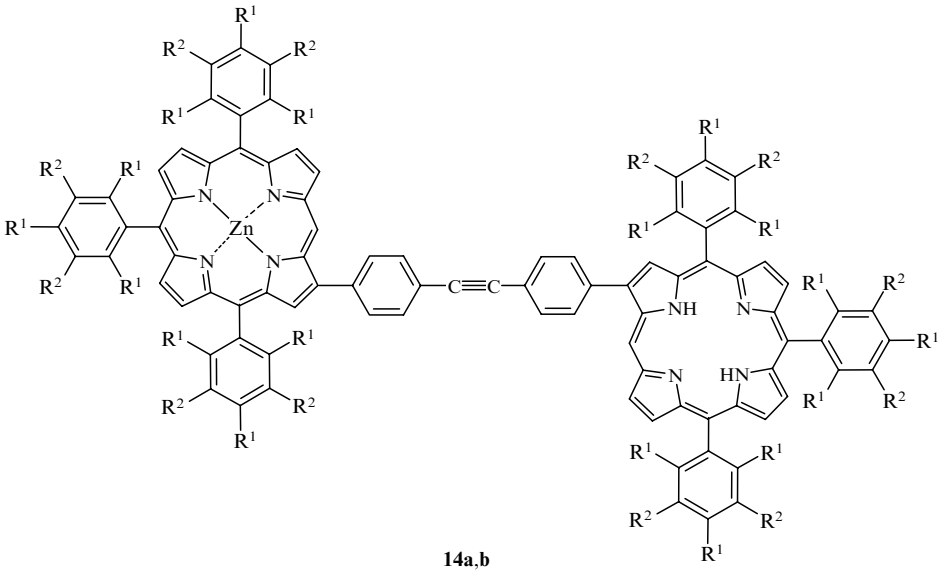
12a–i

Compound **12**	R^1	R^2	R^3	R^4	R^5	M^1	M^2
a	H	H	Me	Me	H	Zn	2 H
b	H	Me	Me	H	H	Zn	2 H
c	Me	H	H	Me	H	Zn	2 H
d	Me	Me	H	H	H	Zn	2 H
e	Cl	Cl	H	H	H	Zn	2 H
f	H	H	F	F	F	Zn	2 H
g	H	H	Me	Me	H	Mg	2 H
h	H	H	Me	Me	H	Cd	2 H
i	H	H	Me	Me	H	Zn	Mg



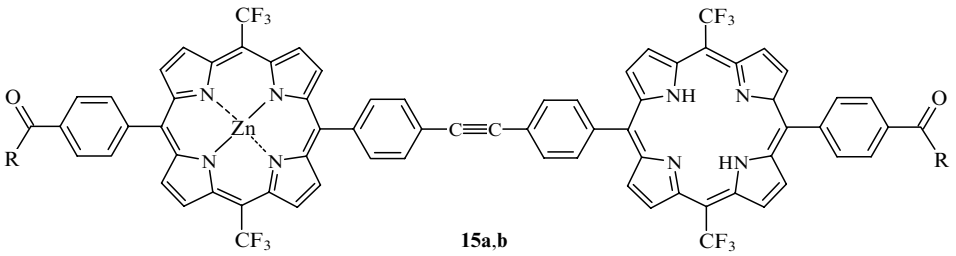
13a–c

X = 1,4-C_6H_4 (**a**), 1,4-naphthylene (**b**), 9,10-anthracenylene (**c**).



14a,**b**

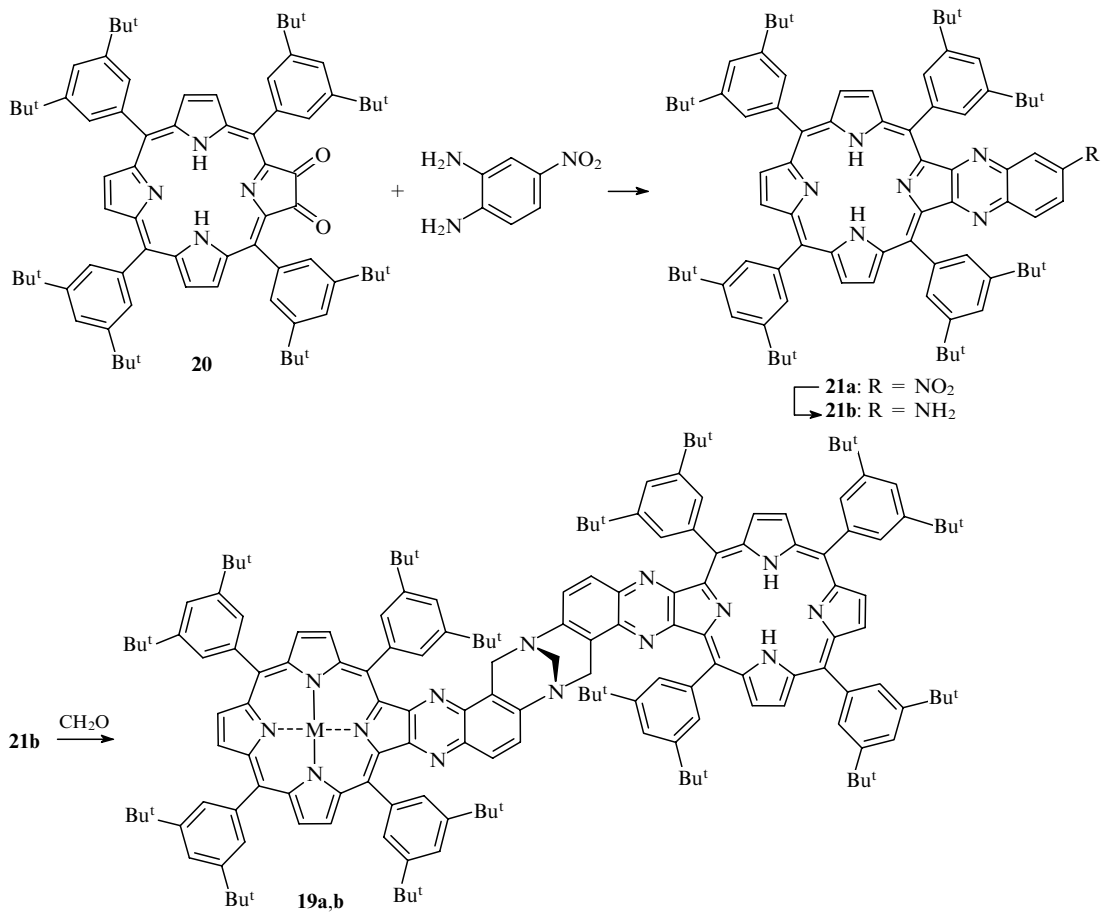
R^1 = Me, R^2 = H (**a**); R^1 = R^2 = F (**b**).



15a,**b**

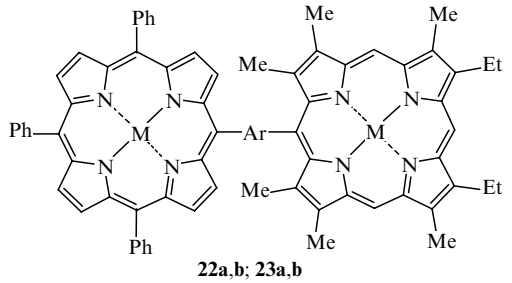
R = OH (**a**), $N(CH_2)_2SO_3^-Et_3NH^+$ (**b**).

Scheme 1



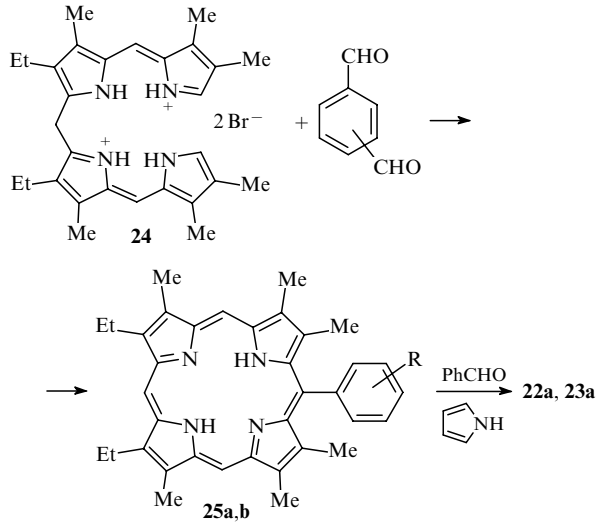
The 'centre-to-centre' distance between two porphyrin fragments in the dimers **19a**,**b** (Scheme 1) is equal to 16.5 Å, whereas their spatial configuration is fixed by two-point addition of each macrocycle to a rigid bridge in such a way that the angle between the planes is 96°. The synthesis of this system includes condensation of porphyrin-2,3-dione **20** with 1,2-diamino-4-nitrobenzene resulting in nitroquinoxalinoporphyrin **21a.** The latter is reduced by tin chloride in hydrochloric acid and the aminoquinoxalinoporpyrin **21b** formed reacts with formaldehyde. The yield of the dimer **19a** is 88%. Compound **19b** was obtained by metallation of bisporphyrin **19a** in 73% yield.[36]

Non-symmetrical porphyrin dimers containing two different macrocycles are promising models for the study of photosynthetic energy transfer. Studies into these compounds provide valuable information about the effects of electronic properties of porphyrin fragments on the yields and the direction of the energy transfer. For example, the covalently linked dimers **22a**,**b** and **23a**,**b** contain tetraphenylporphyrin and octaalkylporphyrin components; their π-systems possess different electronic properties. This allows their selective irradiation and elucidation of pathways of energy transfer following photoexcitation by light with an appropriate wavelength.



22: Ar = 1,4-C_6H_4; **23**: Ar = 1,3-C_6H_4; M = 2 H (**a**), Zn (**b**).

The non-symmetrical dimers **22a**,**b** and **23a**,**b** were synthesised in the following way. The condensation of 8,12-diethyl-2,3,7,13,17,18-hexamethylbiladiene-*a*,*c* dihydrobromide (**24**) with terephthalaldehyde resulted in porphyrin **25a** with the formyl group in the *para*-position. The reaction of the latter with pyrrole and benzaldehyde gave the dimer **22a**. Similarly, bisporphyrin **23a** was synthesised using isophthalaldehyde in the first step.[37]

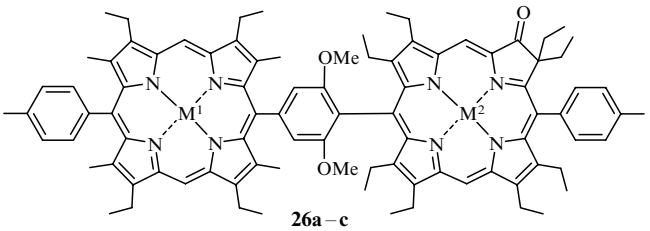


25: R = CHO (**a**), $CH(OEt)_2$ (**b**).

Despite the similarity of many structural, chemical and photophysical characteristics of synthetic porphyrins and natural chlor-

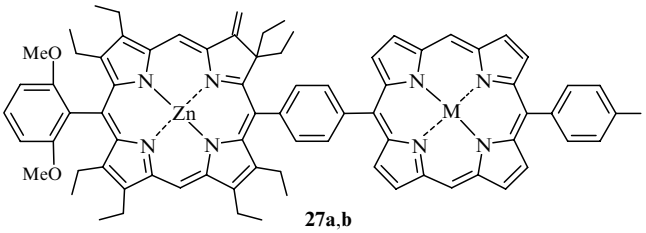
ins, their electronic properties differ considerably because of changes in the symmetry and conjugation pattern in chlorin due to the presence of a reduced pyrrole ring. The main difference between porphyrins and chlorophylls (or bacteriochlorophylls) constituting natural photosynthetic antenna complexes is in that the former absorb light strongly only in the blue region of the solar spectrum, whereas the latter absorb light in both blue and red regions. The orthogonal axes N–N in metalloporphyrins are degenerate (planar oscillator), whereas the dipole moment of the longwave transition in the metal complexes of hydroporphyrins is polarised along one of the N–N axes (linear oscillator), which favours directed transfer of energy. Therefore, the design of chlorin-containing donor–acceptor systems is a promising approach for the modelling of natural light-harvesting complexes.

In the ensembles **26a–c** and **27a,b**, the porphyrin and chlorin macrocycles are linked through rigid aromatic spacers, which fix the macrocycles in parallel planes at a fixed 'centre-to-centre' distance equal to ~12.8 Å.[38,39]



26a–c

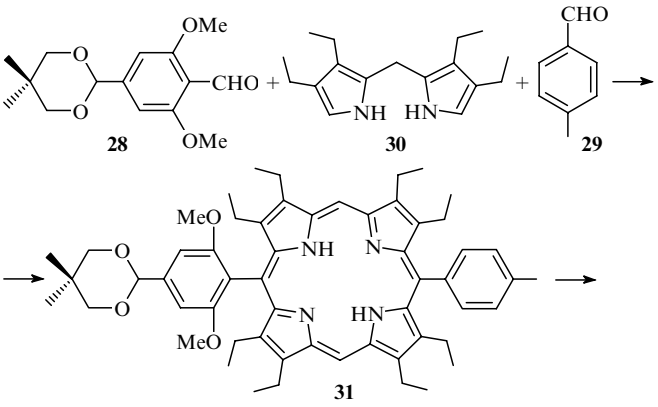
$M^1 = M^2 = 2H$ (**a**); M^1 = Zn, $M^2 = 2H$ (**b**); $M^1 = M^2$ = Zn (**c**).



27a,b

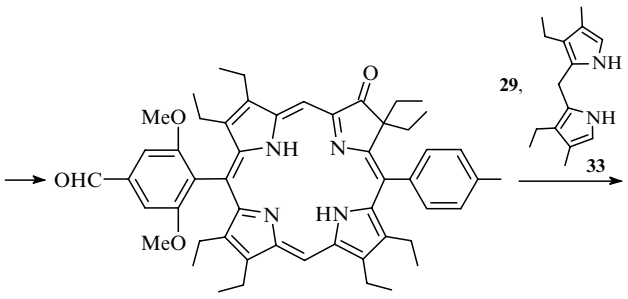
M = 2H (**a**), Zn (**b**).

The macrocyclic ensembles **26a–c** were synthesised in the following way. Condensation of the aldehydes **28** and **29** with 3,3′,4,4′-tetraethyldipyrrolylmethane (**30**) resulted in the porphyrin **31**; its hydroxylation with osmium tetroxide and treatment with trifluoroacetic acid gave the oxochlorin **32**. Condensation of compound **32** with *p*-tolualdehyde (**29**) and dipyrrolylmethane (**33**) and subsequent incorporation of zinc resulted in compound **26c** (yield 18%); demetallation of the latter by hydrochloric acid afforded the product **26a** in a quantitative yield. Treatment of the metal-free dimer **26a** with an equimolar amount of zinc acetate resulted in the selectively metallated bisporphyrin **26b** in quantitative yield.[38]



28 **30** **29**

31

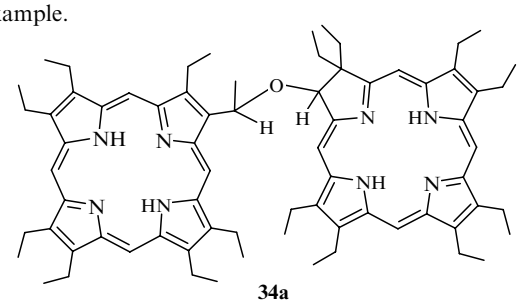


32

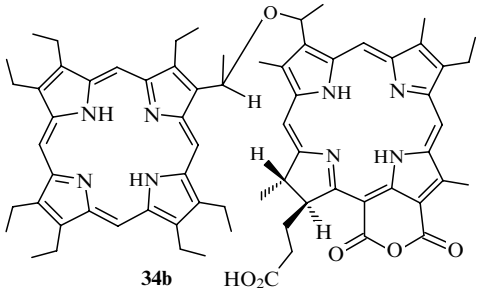
26c → **26a** → **26b**

The dimeric ensembles **27a,b** were synthesised in a similar way. The chlorin component was obtained by condensation of tetraethyldipyrrolylmethane **30** with 2,6-dimethoxybenzaldehyde and 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde. The resulting porphyrin was oxidised to oxochlorin, which was further converted into hydroxychlorin by treatment with methyllithium in ether according to Chang. Subsequent dehydration by boiling with trifluoroacetic acid in the presence of 2,2-dimethylpropane-1,3-diol gave methylenechlorin, which was condensed with dipyrrolylmethane and *p*-tolualdehyde following hydrolysis of the protective acetal group. The resulting metal-free dyad reacted with zinc acetate to give a mixture of mono- and dizinc-containing complexes **27a,b** (yields 15% and 30%, respectively).[39]

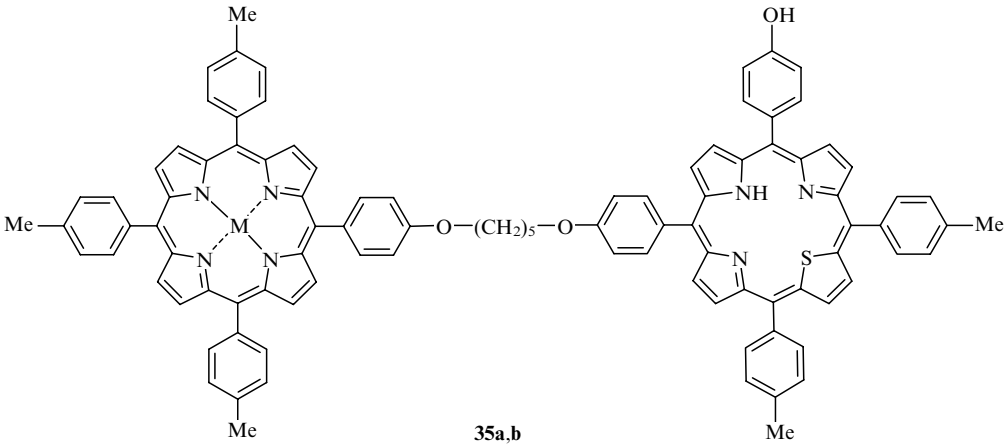
The porphyrin–chlorin heterodimers **34a,b** containing ether bonds between the macrocycles have also been synthesised. The dimer **34a** was prepared from 2-hydroxy-3,3,7,8,12,13,17,18-octaethyl-22*H*,24*H*-chlorin. This was treated with trifluoroacetic anhydride and the resulting trifluoroacetate reacted with 2-(1-hydroxyethyl)-3,7,8,12,13,17,18-heptaethylporphyrin.[40] The heterodimer **34b** was synthesised by condensation of the trifluoroacetylated porphyrin component with the corresponding hydroxychlorin in the presence of catalytic amounts of 4-dimethylaminopyridine.[41] Data from thin-layer chromatography, ^{1}H NMR spectroscopy and computer modelling studies suggest that these compounds exist as two stable isomers. One of them has a sterically hindered structure due to the spatial proximity of the porphyrin and chlorin macrocycles, while the tetrapyrrole fragments of the other isomer do not virtually overlap.[40–42] The effects of conformational mobility on spectroscopic and photophysical properties of the donor–acceptor systems were studied using the porphyrin–chlorin heterodimer **34a** as an example.



34a



34b HO_2C



35a,**b**

M = 2 H (**a**), Zn (**b**).

The dimeric ensembles **35a**,**b**, which contain an ordinary porphyrin and thiaporphyrin, have been synthesised.[43] The sulfur atom in one of their macrocycles changes the electronic structure of the porphyrin backbone; therefore, the properties of the tetrapyrrole fragments in the ground and excited states of these systems differ considerably.

The synthesis of the bisporphyrins **35a**,**b** included the preparation of a monomeric thiaporphyrin precursor by condensation of pyrrole and 2,5-bis(*p*-tolylhydroxymethyl)thiophene with *p*-hydroxybenzaldehyde and subsequent reaction of the resulting product with 5-[4-(5-bromopentyloxy)phenyl]-10,15,20-tritolylporphyrin.[43]

The ensembles in which the chromophores are linked through ethylene, ethyne or butadiyne linkers introduced directly into *meso*- or β-positions of the porphyrin macrocycles manifest interesting properties. These systems, in contrast to the above-described systems, are characterised by extraordinarily strong exciton and electronic interactions between the chromophores as can be evidenced from the significant changes in the electronic absorption spectra (splitting of the Soret band, pronounced bathochromic shifts, *etc*.).[8,44–49] As regards photosynthesis, these compounds can serve as spectral models of antenna pigments possessing absorption in the red spectral region.[44] However, dimers with conjugated ethylene, ethyne and butadiyne units between the chromophores are not used for the modelling of energy transfer; therefore, their synthesis and spectroscopic properties are not considered in this review.

b. Photochemical properties

Studies of photochemical properties of model compounds have shed light on the dependences of the rates and efficiencies of energy transfer reactions on the distance between donor and acceptor components,[19–21,35] their mutual arrangement[20,21,37] and extent of electronic interactions.[21,28,29]

Quenching of singlet excited states of porphyrin donors in the absence of acceptors can be effected in several ways (Fig. 2), *viz*., by radiative quenching through fluorescence emission with the rate constant k_F and by non-fluorescent quenching including intersystem transition to the triplet state, inradiative quenching to the ground energy state, *etc*., with the rate constant k_{NF}. For dilution commonly employed in photochemical studies ($\sim 10^{-6}$ mol litre^{-1}), intermolecular quenching can be neglected. Attachment of an acceptor to the porphyrin donor provides an additional route of quenching of its excited state, *viz*., intramolecular singlet energy transfer with the rate constant k_{EN}.[19]

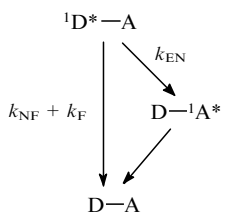


Figure 2. Possible ways of quenching of the singlet excited state of the donor (D, donor, A, acceptor).[19]

Emission spectra provide essential information about photoprocesses occurring in model systems. Quenching of fluorescence of a porphyrin donor concomitant with enhanced fluorescence of the acceptor implies an intramolecular transfer of singlet excitation energy.[19,50,51]

High efficiency of energy transfer is a prerequisite for the normal functioning of natural light-harvesting antenna complexes. The quantum yields (Φ) of the energy transfer can be correctly determined by several methods. One of them includes detailed comparison of steady-state absorption and fluorescence excitation spectra. However, high quantum fluorescence yields, significant overlap of the donor and acceptor fluorescence spectra and the presence of residual amounts of the original monomers do not allow reliable estimation of energy transfer efficiency in molecular ensembles by static measurements alone. An alternative approach consists in comparison of the rates of the energy transfer and competing quenching channels of the donor excitation (see Fig. 2).

The use of this method for the determination of quantum yields of the energy transfer from the zinc-containing porphyrin to the free base in the dimeric ensembles **12a**–**i** has demonstrated extremely high efficiency of this reaction (Φ = 87%–99%)[28–31,51] despite of the large distance (20 Å) and weak interactions between the chromophores. Similar results were obtained in the study of the model systems **18a**,**b** where the quantum yields of the energy transfer were $\geqslant$ 99%.[35] Efficient energy transfer from the octaalkylporphyrin to the tetraphenylporphyrin component was observed for the dimers **22** and **23** (Φ = 79%–99%).[37] Analysis of these systems did not reveal any competitive electron transfer reactions. Thus, the energy transfer is a predominant channel of decay of the excited states of porphyrin donors in these ensembles.

Energy transfer reactions follow two basic mechanisms. The first of them is the Förster 'through-space' mechanism, which is determined by the interactions between transient dipole moments. In this case, the reaction rate depends on the mutual donor and acceptor arrangement, the 'centre-to-centre' distance between them and the integral of spectral overlap of the donor emission and the acceptor absorption. The second route, *viz*., the Dexter 'through-bond' mechanism, is realised in the presence of strong electron-exchange interactions in the case of close contacts between the donor and the acceptor or the presence of a π-conjugated bridge between them.[52]

It was shown that linear π-conjugated polyyne and polyene spacers enhance the 'through-bond' electron-exchange interactions between two porphyrin macrocycles in donor–acceptor bisporphyrin systems.[19]

The values of rate constants for the intramolecular energy transfer in the systems **3b**,**c** containing porphyrin macrocycles in the *meta*- and *para*-positions of the aryl ring, are virtually identical despite the differences in the 'centre-to-centre' distances between the chromophores, which is a clear evidence of electronic 'through-bond' interactions in these compounds. Comparison of the energy transfer rates in the linear dimer **3c** ($k_{EN} = 5.7 \times 10^8$ s^{-1} for the 'centre-to-centre' distance of 26.2 Å) and the diphenylpolyyne-bound bisporphyrin **1d** ($k_{EN} = 1.9 \times 10^9$ s^{-1} for the 'centre-to-centre' distance of 27.0 Å) has demonstrated that the 1,4-bis(phenylethynyl)phenylene bridge is less active in 'through-bond' electronic interactions than diphenylpolyyne spacers of analogous lengths.[19,20]

At the same time, the rates of the energy transfer in the bisporphyrins **13a**,**b**, in which the arrangement of the porphyrin rings and the structures of spacers are similar to those in the dimer **3c**, are comparable with that calculated in the framework of the Förster approximation ($k_{EN} = 4.9 \times 10^8$ s^{-1}). This suggests that the electron energy transfer in these compounds follows the 'through-space' mechanism.[32] Probably, in this case both mechanisms contribute to the interactions between the electronic systems of these pigments.

The energy transfer in the diarylethyne-linked ensembles **12a**–**e** predominantly occurs by the 'through-bond' mechanism mediated by the π-electron system of the linker. This is supported by the fact that the rate constants for the energy transfer for all the dimers of this series (7.5×10^9 s$^{-1} < k < 4.2 \times 10^{10}$ s^{-1}) exceed markedly that predicted by the Förster theory for the 'through-space' mechanism (1.4×10^9 s^{-1}).

In terms of the Lindsey hypothesis, the dihedral angle between the porphyrin ring and the aryl rings of the linker is a critical structural parameter, which determines the possibility of the 'through-bond' energy transfer. Thus steric hindrances created by the introduction of *ortho*-substituents into the linker unit preclude coplanar arrangement of the aryl rings of the linker and the porphyrin rings. This diminishes orbital overlap and decreases fivefold the rate of the 'through-bond' energy transfer. In the dimer **12e**, this effect is predominant over other effects, such as withdrawal of the electron density and interactions of the π-orbitals of *ortho*-chloro-substituents with the *meso*- carbon atoms of porphyrins.[28,51]

Comparison of the rates of singlet–singlet energy transfer in two series of bis(phenylethynyl)phenylene-linked bisporphyrins **3a**–**c** and **4a**–**c** gave similar results. The β-alkyl groups in the dimers **3a**–**c** adjacent to the bridge attachment site hold the bridge in the virtually perpendicular position relative to the porphyrin planes, which minimises the electronic interactions between the porphyrins and the bridge. This conformational restriction is not so severe in the dimers **4a**–**c**, which is a reason for enhanced electronic interactions between porphyrins and increased rates of the 'through-bond' energy transfer in these systems in comparison with the bisporphyrins **3a**–**c**.[21]

The superexchange mechanism, which involves the binding chromophore, is also responsible for increased energy transfer rates in the systems **19a**,**b** characterised by strictly fixed mutual spatial arrangement of the porphyrin macrocycles and the bridge.[53]

At the same time, the decrease in the degree of conjugation between the π-electron systems of the linker and the porphyrins is accompanied by somewhat enhanced contribution of the 'through-space' energy transfer to the overall process. Thus the contribution of this mechanism to the energy transfer in the dimers **12d,e** where the rotation of the linker's aromatic rings is restricted by the substituents, exceeds 10%.[28,51]

The experimental values of the rate constants for the energy transfer for the dimers **22a** (2.4×10^8 s^{-1}), **23a** (8.5×10^8 s^{-1}) and **23b** (2.5×10^{10} s^{-1}) are in good accord with those predicted by the Förster theory. This can apparently be explained by the fact that the macrocycles in the above models cannot lie in the same plane with the binding phenylene groups due to steric hindrances; therefore, direct conjugation between the π-systems of the porphyrins and the linker is excluded while the contribution of the 'through-space' mechanism to the overal energy transfer process increases in accordance with the Lindsey hypothesis.[37]

Energy transfer in natural photosynthetic systems occurs at very fast rates. One of the ways to accelerate this process in synthetic ensembles is to reduce the distance between the porphyrins. Thus the rate constant for the energy transfer in the bisporphyrin **3a** exceeds by about an order of magnitude that in the dimer **3c**, which has an identical spacer, but the distance between chromophores is twice as long.[20] In the case of the dimer **4a** with closely located porphyrin fragments, the energy transfer rate is higher than in the system **4c**, but the effect is far less pronounced.[21]

The rates of the energy transfer in the *p*-phenylene-linked dimers **18a** (2.9×10^{11} s^{-1}) and **18b** (1×10^{11} s^{-1}) are much higher than in structurally similar ensembles containing the diphenylethyne linker, *viz*,. 4.2×10^{11} s^{-1} for **12a** and 4.2×10^9 s^{-1} for **12f**. The observed increase in the reaction rate is mainly due to enhancement of the electronic interactions between the porphyrin components which, in turn, is due to shortening of the distance between the chromophores in the former case.[35]

Analysis of spectral properties of the heterodimer **34a** revealed that the efficiency of the energy transfer in the 'folded' conformer characterised by spatial closeness of the two macrocycles (the 'centre-to-centre' distance determined by computer simulation studies is ~6 Å) is close to 100%. At the same time, the quantum yield of the energy transfer for the isomer having an 'open' conformation of the macrocycles (the distance between the chromophores is > 10 Å) is lower (74%) (see Ref. 54).

It was shown that direct dipole–dipole 'through-space' interactions become predominant in the energy transfer in the ensembles **3a**,[20] **18a**,**b** [35] and **34a** [54,55] with decreased distances between the donor and acceptor components.

Whereas the effects of steric factors on the rates and mechanisms of energy transfer have been studied in sufficiently great detail, the contribution of spacers to the electronic structure of the excited state has been studied to lesser extent. It is known, however, that the strength of the electronic interaction depends not only on structural parameters, such as the distance between the chromophores constituting the system and their mutual arrangement, but also on the relative orbital energies of the donor, the acceptor and the spacer group.

Investigation into the effect of the electronic structures of bridges on the rate of energy transfer has been carried out [32] with the systems **13a**–**c** with identical distances between the macrocycles, well-defined mutual arrangements of two porphyrin ring planes and minimum degree of conjugation between the donor, the bridge and the acceptor, which allowed consideration of the system components as individual chromophores.

Spectral studies of the model bisporphyrins **13a**–**c** revealed the strongest quenching of donor emission in the case of the anthracenylene-linked dimer **13c**, which suggests the higher efficiency of the energy transfer in this compound. Moreover, the rate constant for the energy transfer for the dimer **13c** ($k = 10^9$ s^{-1}) exceeds approximately twofold those for the bisporphyrins **13a**,**b** (5.8×10^8 and 5.4×10^8 s^{-1}, respectively) with phenylene- and naphthylene-containing spacers. These results indicate stronger electronic interactions in the dimer with anthracene-containing spacer, apparently due to the proximity of the energy levels of the lower singlet excited states of the donor, the acceptor and the anthracene chromophore (17 500, 16 000 and 21 600 cm^{-1}, respectively). However, splitting of the energy levels between the donor and the bridge as well as between the bridge and the acceptor is large enough to prevent stepwise energy transfer with the involvement of the intermediate excited state of the binding chromophore.[32]

Comparison of photochemical properties of the dimeric ensemble **12f** containing pentafluorophenyl groups in all the non-binding *meso*-positions of the tetrapyrrole macrocycle and its non-fluorinated analogue **12a** was carried out in order to elucidate the effects of electronic factors on the extent of interactions of the porphyrin components in the ground and excited states. The rate of the energy transfer in the bisporphyrin **12f** was 10 times lower than that in the dimer **12a** despite identical diphenylethyne linker in both compounds. The lower rate of the energy transfer in the former dimer is attributed to weakened electronic interactions between Zn-porphyrin and the free base in the S_1 excited state.

The degree of the 'through-bond' energy transfer between components of dimeric ensembles depends on the electronic and oscillation matrix elements. In the dimers **12a**,**f** possessing identical linkers, oscillator contributions are the same and interactions between the porphyrin components are predominantly determined by electronic factors. Their magnitude depends on the nature and distribution of the electron density of molecular orbitals involved in bonding. In compound **12a**, as in most *meso*-substituted porphyrins, HOMO has the a_{2u} symmetry characterised by considerable electron densities on *meso*-carbon atoms including those attached to the linker. In contrast, the pentafluorophenyl groups in the dimer **12f** stabilise the orbital with the a_{2u} symmetry, which changes the HOMO symmetry to a_{1u}. Such a change in the orbital ordering diminishes the electron density on the peripheral *meso*-atoms of the macrocycle where the linker is attached, and thus reduces the electronic matrix element. Thus, the rate of the energy transfer between the zinc-containing porphyrin and the free base of the dimer decreases. Redistribution of the electron density from the *meso*-carbon atoms of the a_{2u} orbital to the strongly electron-withdrawing pentafluorophenyl rings is yet another factor inducing appreciable decrease in the rate of the energy transfer in the dimer **12f**.[29]

In the case of the fluorine-containing dimer **18b**, a threefold decrease in the rate of the energy transfer was observed in comparison with the non-fluorinated analogue **18a** (1×10^{11} and 2.9×10^{11} s^{-1}, respectively). This effect correlates with the above-described fluorine-induced changes in the orbital characteristics of porphyrin components in the case of *meso*-diarylethyne-linked dimers.[35]

An opposite effect was observed for the β-linked dimers **14a**,**b** in which the presence of pentafluorophenyl groups in the non-binding *meso*-positions promotes stronger electronic interactions. As a result, the rate of the energy transfer in the dimer **14b** ($k = 4.2 \times 10^{10}$ s^{-1}) exceeds more than twofold that in the mesityl-substituted ensemble **14a** ($k = 1.8 \times 10^{10}$ s^{-1}). This, too, is due to enhanced contribution of the a_{1u} orbital characterised by higher electron density on the β-pyrrole atoms, where the linker is attached, to the wave function of the excited electronic state in pentafluorophenyl-substituted dimers.[33]

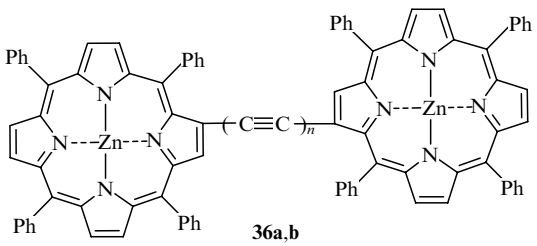
A 17-fold decrease in the rate of the energy transfer in the *meso*-diphenylethyne-linked β-alkyl-substituted dimer **1a** (see Ref. 19) in comparison with the *meso*-aryl-substituted bisporphyrin **12a** possessing the identical linker is mainly due to the electronic factors determined by the differences in the orbital ordering.[29] In particular, eight β-alkyl substituents and two aryl groups in the *meso*-positions of each porphyrin fragment in the dimer **1a** determined the a_{1u} HOMO symmetry characterised by the absence of electron density on the *meso*-carbon atoms to which the linker is attached. In addition, the steric hindrance due to the β-methyl groups in the pyrrole rings of the porphyrin macrocycle limit the rotation of the aromatic rings of the linker and prevent their coplanarity with the porphyrin macrocycles. This diminishes the conjugation of their π-electron systems and thus makes an additional contribution to the weakening of the electronic interactions between the dimer components.

The enhancement of 'through-bond' electronic interactions and the increase in the rate of singlet energy transfer upon substitution of the tetraarylporphyrin component in the systems **4a**–**c** for the 10,20-diaryloctaalkylporphyrin component in the dimers **3a**–**c** are explained in a similar way.[21]

Thus, the site of attachment of the linker should be chosen with due regard to the general pattern of substitution in the tetrapyrrole macrocycle in order to ensure optimum electronic interactions. For porphyrins with the a_{2u} HOMO symmetry, the strongest electronic interactions are provided by linkers attached to the *meso*-positions of the macrocycles, whereas stronger electronic interactions between the pigments with the a_{1u} HOMO symmetry are provided by spacers introduced into β-pyrrole positions. It should also be considered that the electron densities of the eight β-pyrrole carbon atoms with the a_{1u} orbital symmetry are much lower than those of the four *meso*-atoms with the a_{2u} orbital symmetry. Consequently, the electronic interactions through spacers connecting β-positions of the porphyrin macrocycles should be less efficient than those through spacers connecting *meso*-carbon atoms.[29, 33]

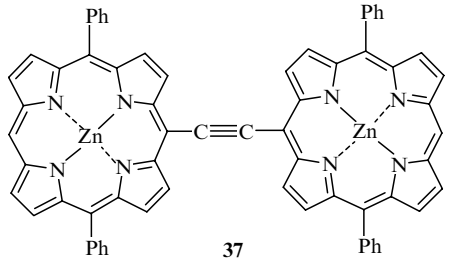
The LUMO characteristics also contribute to linker-mediated electronic interactions between chromophores. The electronic factor is determined by the overlap of the e_g orbitals of porphyrin with the d_π-orbitals of the metal. Thus an increase in the rate of the energy transfer in the cadmium-containing ensemble **12h** ($k = 6.7 \times 10^{10}$ s^{-1}) in comparison with the magnesium-containing dimer **12g** ($k = 3.2 \times 10^{10}$ s^{-1}) reflects the putative role of cadmium *d*-orbitals in the electronic interactions.[31] Stronger 'through-bond' interactions in the zinc-containing diporphyrin **19b** in comparison with its non-metallated analogue **19a** is thought[53] to be due to the interaction of the metal d_π-orbitals with the porphyrin ring, which increases the electron density on the pyrrole carbon atoms bearing the spacer group.[53]

The effect of the bridge topology on the electronic interactions between porphyrins in the ground and excited states was studied in the example of the conjugated dimers **36** and **37**. The energies of absorption maxima in the region of the Q-bands of the β,β-linked ensembles **36a**,**b** are essentially the same as those of the isolated zinc-containing tetraphenylporphyrin complex, which points to weak electronic interactions between the chromophores in the ground and the lowest singlet electron-excited states. Contrariwise, a pronounced bathochromic shift and enhanced low-energy absorption in the region of the Q-bands in the *meso*,*meso*-linked dimer **37** suggest the presence of strong electronic interactions between the porphyrin macrocycles. These data are in good agreement with the order of changes in the strength of the electronic interaction (*meso*,*meso* > *meso*,β > β,β) for *meso*-substituted porphyrins at a fixed twist angle between the tetrapyrrole planes predicted on the basis of the above-described analysis of the electronic structure. Moreover, the rotation barrier around the ethyne linker in the *meso*,*meso*-linked ensemble **37** is a minimum in comparison with β,β-linked dimers. This suggests that the conformers in which the components of the *meso*,*meso*-linked dimer have planar structures and maximum conjugation predominate in solutions at room temperature.[44, 45]



36a,**b**

$n = 1$ (**a**), 2 (**b**).



37

These data suggest that the electronic structure together with steric factors are essential for efficient electronic interactions and high rates of the energy transfer in dimeric ensembles.

Zinc-containing porphyrin complexes analogous in structural, chemical and photophysical characteristics to those of chlorophylls and bacteriochlorophylls are widely employed in photosynthetic model systems. However, natural photosynthetic pigments contain magnesium atoms in their chlorin rings. Spectral properties of the ensembles **12a**,**g**,**h**, which contain zinc, magnesium and cadmium in one of their macrocycles, were compared in order to examine the effects of metal substitution on the photodynamic behaviour of bisporphyrins. The rates of the energy transfer for the three dimers were very close, which can be attributed to the similarity of electronic interactions between the chromophores in the magnesium-, zinc- and cadmium-containing bisporphyrins. However, the quantum yield of the energy transfer for the Mg-containing dimer (Φ = 99.7%) is higher than that for the Zn-containing dimer (Φ = 99%) due to the longer lifetime of the excited state of the Mg-porphyrin (10 ns) in comparison with that of the Zn-porphyrin (2 ns). Although this difference is insignificant in the case of the isolated dimer, this may be multiplied in multiporphyrin ensembles, which perform more energy transfer steps.[30] A more significant decrease in the efficiency of the energy transfer in the case of the cadmium-containing dimer (Φ = 87%) is almost exclusively due to the very short ($\sim$ 100 ps) lifetime of the Cd-porphyrin excited state, which, in turn, may be a result of acceleration of the singlet–triplet intersystem transition, which competes with the energy transfer due to the presence of a heavy metal.[31] Moreover, magnesium- and especially cadmium-containing bisporphyrins are more labile with respect to demetallation and photochemical oxidation and are more prone to electron transfer, whereas zinc-containing dimers are rather stable against these side reactions.

These data suggest that synthetic ensembles capable of highly efficient energy transfer may contain both Mg- and Zn-porphyrins; the choice of a metal should be made with due regard to all the factors mentioned above.[30] Moreover, the extremely high rate ($k = 1.1 \times 10^{11}$ s^{-1}) and the nearly quantitative efficiency of the energy transfer in the dimer **12i**, which contains Zn- and Mg-tetraarylporphyrin complexes, confer attractive properties on the combination of these complexes within a single ensemble. At the same time, the use of cadmium complexes in artificial energy-transforming systems is limited due to reduced efficiency of the energy transfer and lability of these compounds.[31]

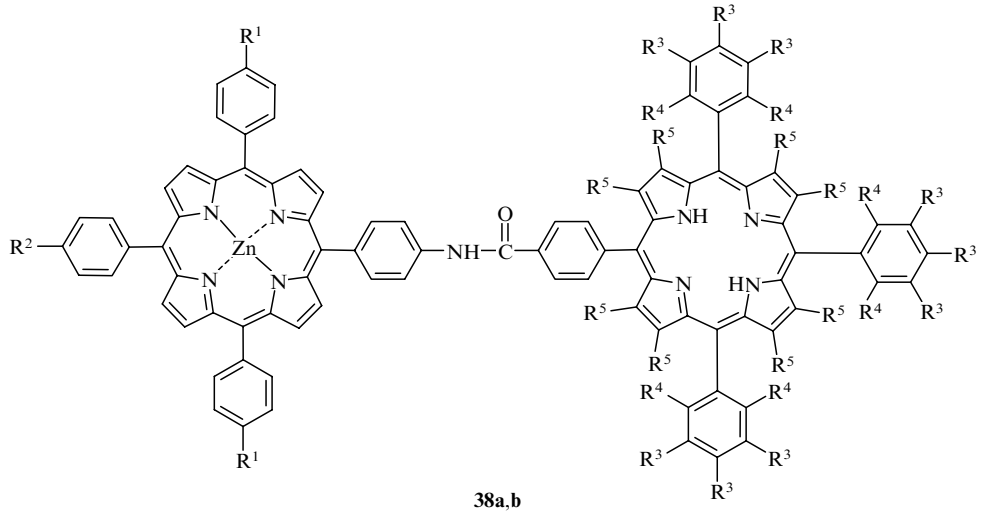
The effects of environmental factors, such as viscosity, solvent polarity and temperature, on the photodynamic behaviour of the diarylethyne-linked ensembles **12a**–**d** have been discussed.[51] These studies have shown that the rates of energy transfer in viscous media (*e.g.*, castor oil) are 1.3–1.9 times lower than in toluene. This can be explained by the fact that higher viscosity of the medium impedes probably the rotation of the aromatic rings of the linker around a single bond, which prevents their coplanarity with the porphyrins and thus weakens electronic 'through-bond' interactions between the porphyrin macrocycles.

With a decrease in temperature to 150 K, the rates of the energy transfer in these dimers show a slight decrease. Presumably, the mobility of the aromatic group and a concomitant change in the average dihedral angle between the linker and the porphyrin are also decreased due to freezing of the solvent. The degree of thermoinduced conformational changes depends on rotational restrictions of the linker. Therefore, the most appreciable (2.5-fold) decrease in the rate of the energy transfer is observed for the dimer **12a** where a broad range of dihedral angles is possible due to the lack of torsional restrictions. No such changes were observed for the ensemble **12d**.[51]

The dynamics of singlet–singlet energy transfer in the porphyrin–chlorin system **34a** containing ether bond between the macrocycles changes with temperature. At 293 K, the excitation energy migrates repeatedly between the interacting donor and acceptor components over the lifetime of acceptor fluorescence, since the rates of forward and reverse energy transfer reactions exceed the deactivation rates of S_1 states of porphyrin and chlorin by more than an order of magnitude. In contrast, the transfer of excitation energy from porphyrin to chlorin at 77 K is irreversible, for in this case the calculated rate of the reverse transfer is much lower than the deactivation rate of the acceptor S_1 state.[55]

It was shown that the polarity of the solvent affects only slightly the efficiency and rate of energy transfer in diarylethyne-linked dimers. However, significant quenching of fluorescence of the porphyrin free base in the dimers **12a**,**b** observed in polar solvents (*e.g.*, dimethyl sulfoxide) is ascribed to the charge transfer from the neighbouring metal complex.[51] Magnesium-containing ensembles are even more sensitive to this process due to increase in the driving force of the electron transfer process.[30]

Similar photoinduced electron transfer to the excited singlet state has also been observed in the hybrid porphyrin–chlorin dimer **26b** (see Ref. 38) and the bisporphyrins **38a**,**b** (see Ref. 56).



38a,**b**

R^1 = Me, R^2 = NHCOMe, R^3 = H, R^4 = R^5 = Cl (**a**); R^1 = R^2 = NMe_2, R^3 = R^4 = F, R^5 = H (**b**).

It should be emphasised that the charge transfer occurs after the excitation has reached the acceptor and has no appreciable influence on the energy transfer between the donor and acceptor components in the above-described ensembles.[51]

The fluorescence spectra of bisporphyrins linked by flexible hydrocarbon chains can be interpreted by the existence of two conformations, *viz*., the 'open' conformation where quenching of the donor fluorescence is fairly ineffective and the 'folded' conformation characterised by effective quenching of donor emission owing to the transfer of singlet energy to the acceptor.[57–59] Changes in the solvent polarity bring about transition of one form into another. Thus the 'open' conformation is predominant for solutions of bisporphyrins **35** in toluene, whereas in dimethylformamide the 'folded' conformation is preferable in which the 'centre-to-centre' distance between two porphyrin components is 18.7 Å. Such conformational transition results in the enhancement of the efficiencies and rates of energy transfer in polar solvents.[59]

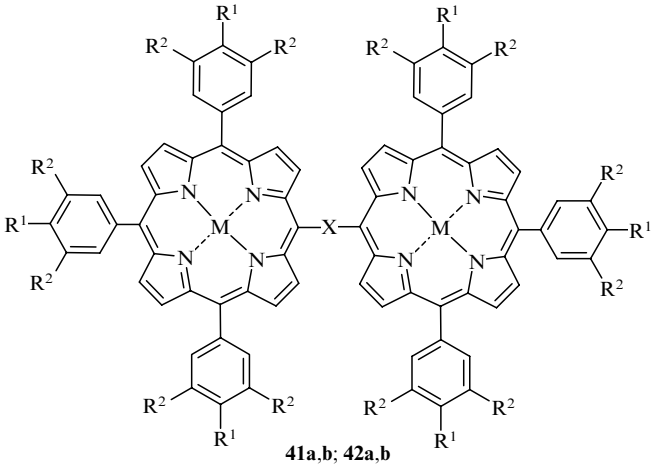
The knowledge of regularities of the energy transfer depending on structural, electronic and environmental factors is useful for the design of more complex model donor–acceptor systems.

2. Porphyrin dimers with peptide spacers

All the bisporphyrins described above contain hydrocarbon spacers. However, chlorophyll and bacteriochlorophyll in photosynthetic antenna systems exist in a protein environment, which affects the photophysical properties.[11, 12, 60] Synthetic porphyrin dimers with the macrocycles linked through amino acid or peptide spacers represent convenient model subjects for the study of intramolecular interactions and energy transfer between tetrapyrrole chromophores within natural pigment–protein complexes.

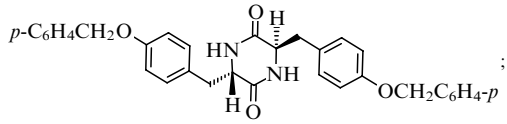
a. Synthesis

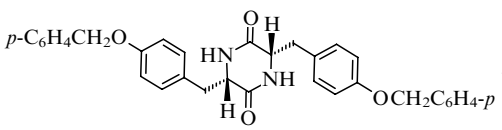
The porphyrin dimers **39a**,**b** and **40a**,**b** linked through amino acid bridges served as models for the studies of spectral properties of chromophores in biological photosynthetic systems.[61] These compounds were synthesised in 10%–15% yields by condensation of 5-*o*-(2-bromoethoxy)phenyl-10,15,20-triphenylporphyrin with glycine or racemic phenylalanine in dimethylformamide in the presence of a phase-transfer catalyst.

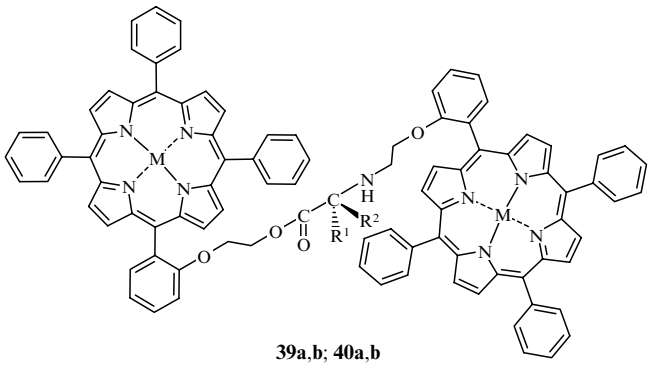


41a,**b**; **42a**,**b**

41: R^1 = Me, R^2 = H; **42**: R^1 = H, R^2 = Bu^t; M = 2H (**a**), Zn (**b**).

D,L-**41**, D,L-**42**: X = ;

L,L-**41**, L,L-**42**: X = .



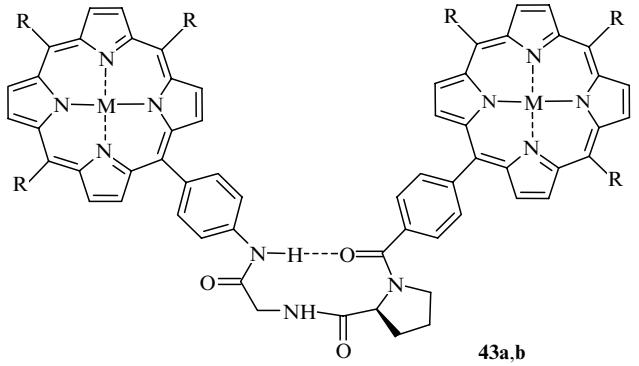
39a,**b**; **40a**,**b**

39: R^1 = R^2 = H; **40**: R^1 = Bn (H), R^2 = H (Bn); M = 2H (**a**), Zn (**b**).

The porphyrin dimers with macrocycles covalently linked through cyclic dipeptides, *viz*., piperazine2,5-diones (compounds **41a**,**b** and **42a**,**b**),[62] β-folded oligopeptides (dimers **43a**,**b**, **44a**–**d**, **45a**,**b**)[63] and the oligo-L-proline spacers **46a**–**i** and **47a**–**i**,[64] were synthesised for studies of intramolecular interactions and energy transfer between the porphyrin components.

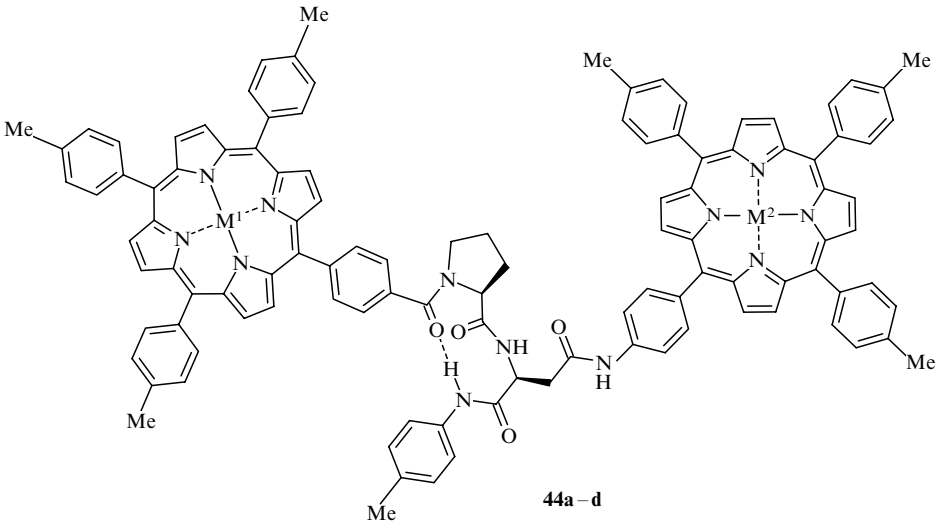
In these dimers, two porphyrin rings are held in specific conformations by rigid peptide spacers. Thus rigid β-folded structures of the dipeptides in the molecules **43a**,**b**, **44a**–**d** and **45a**,**b** are determined by the formation of hydrogen bonds between the carbonyl groups of the porphyrins and amino groups of amino acid residues of the peptides.[63] Due to the cyclic side chain, the oligo-L-proline spacers in the dimers **46a**–**i** and **47a**–**i** acquire fairly stable helical conformations provided the number of amino acid residues is no less than four.[18, 64]

The general strategy of the preparation of these compounds is based on the use of standard protocols of the peptide synthesis. The symmetrical bisporphyrins **41a**,**b** and **42a**,**b**, which are covalently linked to tyrosine residues by ether bonds to form piperazine-2,5-dione, were obtained from the zinc-containing porphyrins **48a**,**b**, which in turn were synthesised by the condensation of the corresponding aromatic aldehydes with methoxycarbonylbenzaldehyde and pyrrole followed by reduction of the ester groups to hydroxy groups, substitution of bromine for



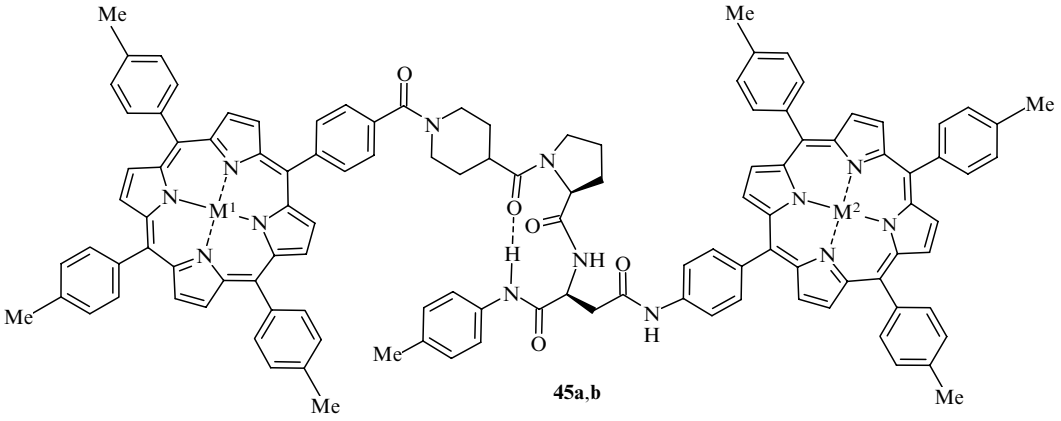
43a,**b**

R = *p*-MeC$_6$H$_4$; M = 2H (**a**), Zn (**b**).



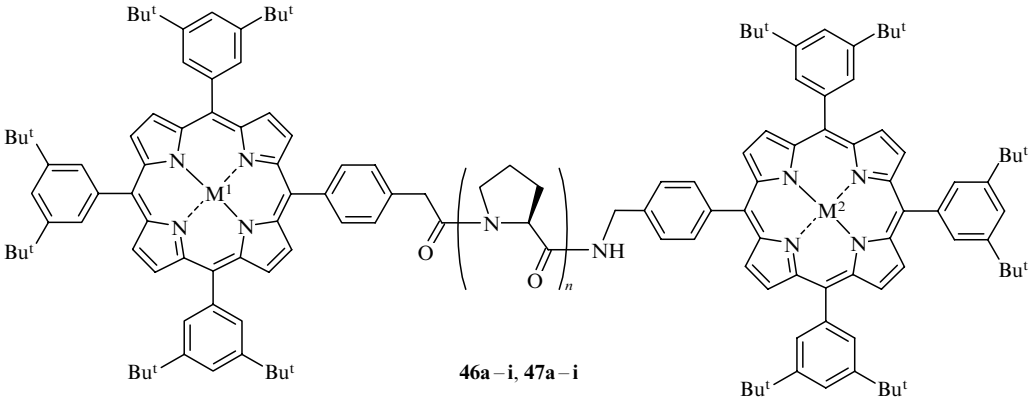
44a–d

$M^1 = M^2 = 2H$ (**a**), Zn (**b**); M^1 = Zn, $M^2 = 2H$ (**c**); $M^1 = 2H$, M^2 = Zn (**d**).



45a,b

$M^1 = 2H$, M^2 = Zn (**a**); M^1 = Zn, $M^2 = 2H$ (**b**).



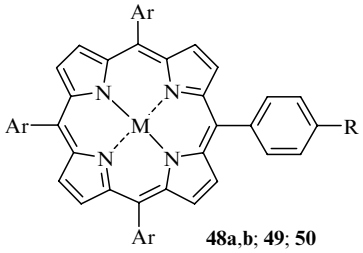
46a–i, 47a–i

46: M^1 = Zn, $M^2 = 2H$; **47**: $M^1 = 2H$, M^2 = Zn; n = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**), 4 (**e**), 5 (**f**), 6 (**g**), 7 (**h**), 8 (**i**).

hydroxy groups and introduction of zinc into the porphyrin rings.[62]

Condensation of benzyloxycarbonyl-protected L- or D-tyrosine with L-tyrosine methyl ether afforded dipeptides, which were converted into piperazine-2,5-diones following deprotection. Reactions of the latter with the porphyrins **48a**,**b** afforded the diastereomerically pure zinc-containing dimers **41b** and **42b**; their demetallation resulted in compounds **41a** and **42a**.[62]

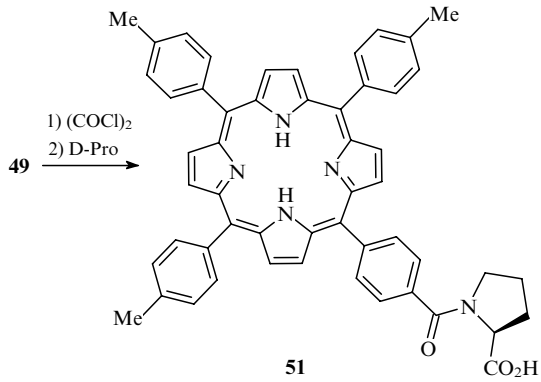
An alternative approach was used in the synthesis of the porphyrin dimers **43a**,**b**, **44a–d** and **45a**,**b** linked through β-folded peptides. In this synthesis, 5-(*p*-carboxyphenyl)-10,15,20-tri-*p*-tolylporphyrin (**49**) and 5-(*p*-aminophenyl)-10,15,20-tri-*p*-tolylporphyrin (**50**) were used as the porphyrin components, while



48a,b; **49**; **50**

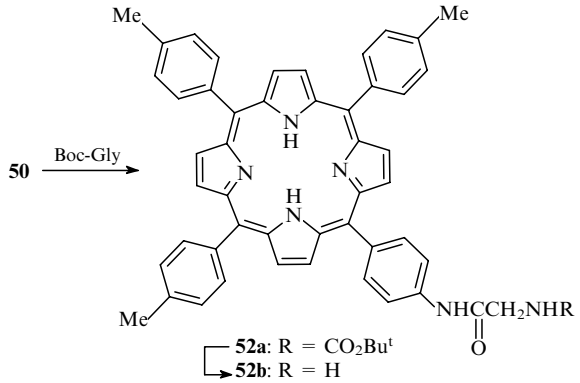
48: R = CH_2Br, M = Zn, Ar = 4-MeC_6H_4 (**a**), 3,5-$Bu^t_2C_6H_3$ (**b**);
49: R = CO_2H, M = 2H, Ar = 4-MeC_6H_4;
50: R = NH_2, M = 2H, Ar = 4-MeC_6H_4.

the amino acid sequences D-Pro-Gly and D-Pro-L-Asp were used as the β-folded peptide spacers. The acid **49** was converted into its acid chloride, which reacted with D-proline to yield compound **51**.



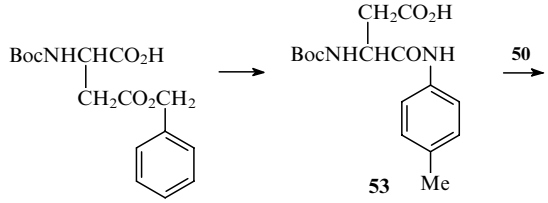
51

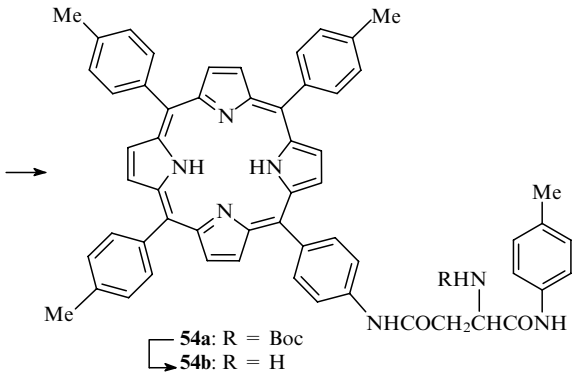
The reaction of the amine **50** with *tert*-butoxycarbonylglycine (Boc-Gly) using dicyclohexylcarbodiimide (DCC) as a coupling reagent resulted in the derivative **52a**. The last step included condensation of the acid **51** with the amine **52b** under the action of DCC in the presence of 1-hydroxybenzotriazole. This reaction afforded the porphyrin dimer **43a** linked through a β-folded dipeptide (yield 76%). The bisporphyrin **43a** was easily converted into the dizinc complex **43b** by treatment with an excess of zinc acetate.[63]



51 + **52b** ⟶ **43a** ⟶ **43b**

The dimers in which both porphyrin residues are linked to aspartic acid were synthesised in the following way. First, the β-carboxy group of Boc-L-Asp(OH)-OH was selectively protected followed by protection of the α-carboxy group. Subsequent hydrolysis of benzyl ester afforded the amino acid derivative **53** with a free β-carboxy group; its reaction with the amino acid component **50** yielded the derivative **54a**. Condensation of the acid **51** with the amine **54b** (obtained in 66% yield by deprotection of compound **54a**) gave the dimer **44a**, which gave further the complex **44b** (yield 58%).

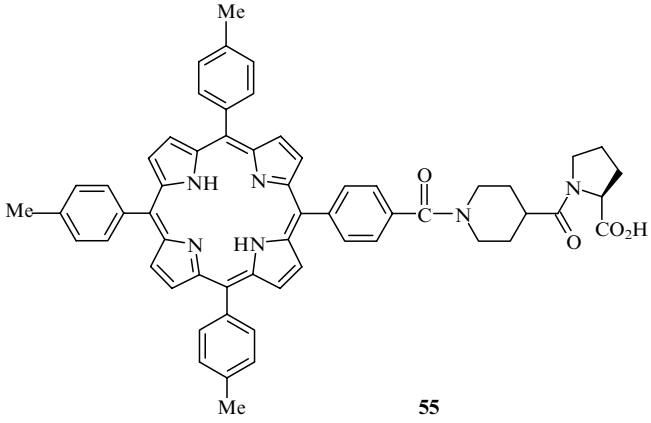




54b + **51** ⟶ **44a** ⟶ **44b**

The selectively metallated dimers **44c**,**d** were synthesised by the condensation of the zinc-containing porphyrin component with the porphyrin free base.[63]

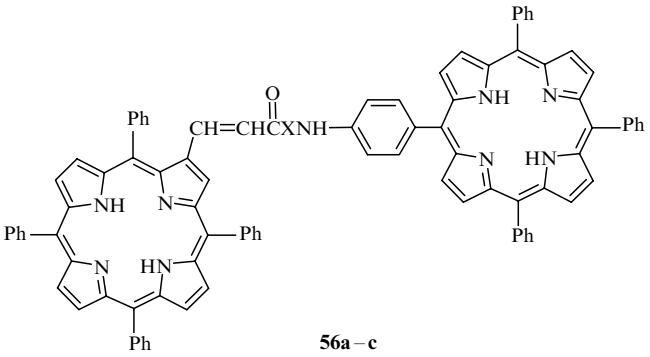
The synthesis of the dimer **45a** included condensation of 5-(*p*-carboxyphenyl)-10,15,20-tri-*p*-tolylporphyrin (**49**) with piperidine-4-carboxylic acid, reaction of the product with D-proline to yield the amino acid derivative **55** and condensation of the latter with the zinc – porphyrin complex **54b** in the presence of DCC.[63]



55

The bisporphyrin **45b** was synthesised from the zinc complex of compound **55** and the porphyrin free base **54b** in a similar way.[63] This strategy was also used in the synthesis of the bisporphyrin donor – acceptor model systems **46a** – **i** and **47a** – **i** linked by oligoproline spacers.

Porphyrin components differing in the positions of their functional groups used in the synthesis of peptide-linked bisporphyrins made it possible to obtain *meso*-β-linked ensembles **56a** – **c**.[65,66] An interesting feature of these systems is that their spacers contain an aromatic amino acid, *viz*., phenylalanine. Incorporation of aromatic amino acids into model photosynthetic systems is an important issue, since it was found that such aromatic amino acids as tyrosine and tryptophan mediate interactions between tetrapyrrole chromophores by virtue of electronic coupling of their molecular orbitals. Substitution of aliphatic amino acids for aromatic ones enables one to establish the dependence of the strength of interchromophore interactions and the efficiencies of photoinduced processes on the nature of the amino acid components of the spacers. The bisporphyrins **56a** – **c** were synthesised from the amino acid derivatives of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and 2-(2-carboxy)-vinyl-5,10,15,20-tetraphenylporphyrin using the dicyclohexylcarbodiimide method.

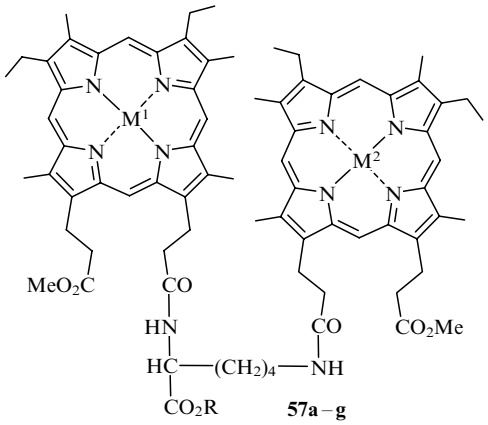


56a–c

X = NHCHCNHCH$_2$CO (**a**), NHCHCNHCH$_2$CO (**b**),
CHMe$_2$ CH$_2$Ph

NHCH$_2$CNHCHCNHCH$_2$CO (**c**).
CH$_2$Ph

The covalently linked mesoporphyrin dimers **57a-g** containing a lysine residue as the spacer were synthesised to study chlorophyll–protein interactions. UV-Vis and circular dichroism spectroscopic studies revealed that these dimers form complexes with polypeptides of natural light-harvesting systems owing to axial coordination of zinc and nickel atoms with histidine and the formation of hydrogen bonds between the ester groups of the dimer and the polar amino acid residues of the peptides. In the synthesis of the dimers **57a–g**, the mesoporphyrin IX monomethyl ester was condensed with Boc-L- or Boc-D-lysine using *N*-hydroxysuccinimide–DCC as the activating reagents. The product formed reacted with the second molecule of the mesoporphyrin monomethyl ester under identical conditions.[67]



57a–g

Compound **57**	M^1	M^2	R
a	2 H	2 H	H
b	Zn	2 H	H
c	Zn	Zn	H
d	Zn	Zn	H (D-isomer)
e	2 H	2 H	Me
f	Zn	Zn	Me
g	Zn	Ni	H

b. Photochemical properties

Photochemical studies of the piperazine-2,5-dione-linked systems **41a**,**b** and **42a**,**b** revealed that the chromophores of the L,L-dimers **41a**,**b** having *p*-tolyl substituents interact more efficiently than the chromophores of the L,L-dimers **42a**,**b** with 3,5-di-*tert*-butylphenyl substituents. This difference is due to the fact that the bulkier 3,5-di-*tert*-butyl groups in the molecules **42a**,**b** disturb interactions of the porphyrin rings.

It was also found that the porphyrin components in the L,L-dimers **41a**,**b** and **42a**,**b** interact more efficiently in comparison with the D,L-dimers. This can be attributed to the localisation of both tyrosine phenylene groups in L,L-isomers on one side of the piperazine-2,5-dione plane, whereas in D,L-isomers these groups are localised on different sides of this plane. Thus the porphyrin components of the L,L-dimers are closer to each other than in the D,L-dimers. It thus follows that the strength of intramolecular interaction depends on the 'centre-to-centre' distance between the porphyrin rings.[62]

Evidence for the dependence of interactions between chromophores on the 'centre-to-centre' distance was also obtained for the dimers **43a**,**b** and **44a–d**.[63]

The efficiency of intramolecular energy transfer from zinc complexes to porphyrin free bases in the asymmetrical dimers **44c**,**d** (Φ = 86%) and **45a**,**b** (Φ = 76%) depends on the distance between tetrapyrrole components rather than on the nature of the spacer. The efficiency of quenching of the excited states of zinc-containing porphyrin complexes in compounds **46** and **47** decreases with an increase in the number of proline residues, *i.e.*, the average distance between the chromophores, in the course of energy transfer irrespective of its direction. These findings prompted a conclusion that singlet energy transfer in dimers linked by peptide spacers occurs predominantly 'through-space'.[63,64]

The dipole–dipole 'through-space' interaction described by the Förster approximation is the most probable mechanism of energy transfer from the zinc complex to the nickel-containing porphyrin in the dimer **57g**. The most efficient energy transfer was noted between the porphyrin rings that form coordination and hydrogen bonds with polypeptides of natural light-harvesting complexes. This suggests that polypeptides induce efficient intramolecular energy transfer between pigments in model photosynthetic compounds.[67]

3. Non-covalently linked bisporphyrin systems

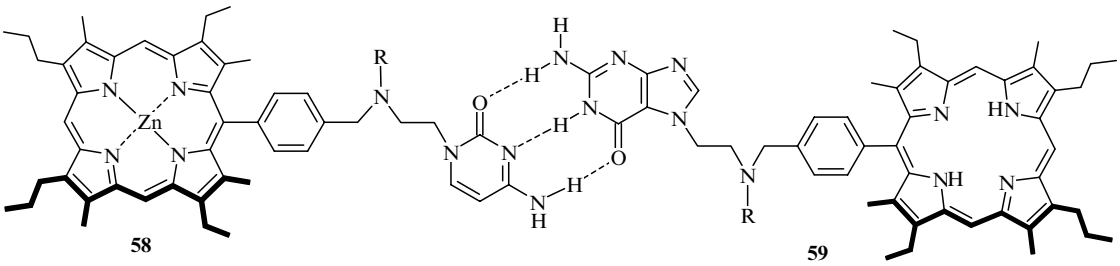
The above-described methods for the construction of model photosynthetic systems are based on the formation of covalent bonds between chromophores, but they are not always suitable for the synthesis of muticomponent ensembles. An alternative approach consists in the assembly of supramolecular aggregates due to non-covalent interactions, such as the formation of hydrogen bonds, salt bridges and coordination bonds between metals and ligands.[17]

The strategy of synthesis of non-covalently linked ensembles consists first in the synthesis of chromophores possessing specific recognition sites and their subsequent self-assembly into highly ordered multicomponent structures. According to the type of their binding, these model systems resemble those discovered in the light-harvesting antennae.

The design of non-covalently linked supramolecular complexes can be based on pairwise interactions between complementary heterocyclic bases. The complex **58–59**, which is stabilised by hydrogen bonds between guanine and cytosine residues, was among the first ensembles of this kind described in the literature.[68]

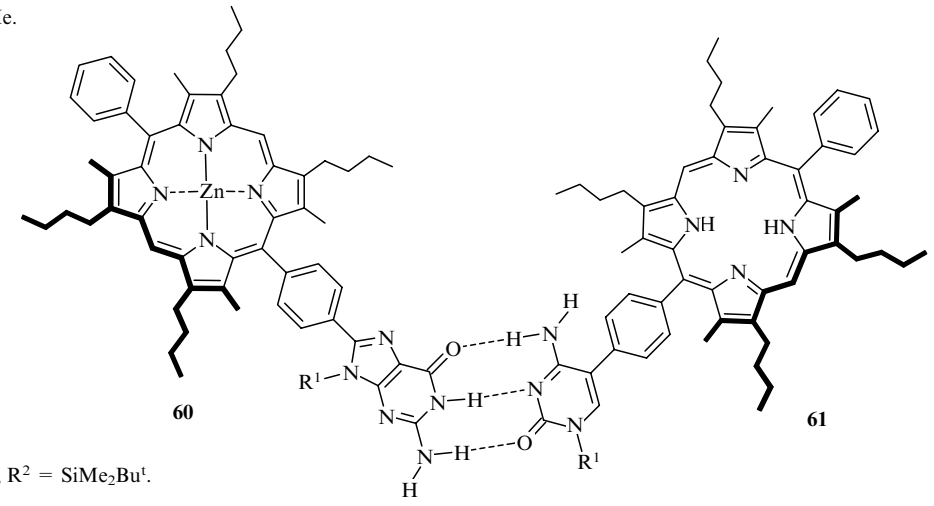
However, high flexibility of this first-generation system prevented detailed studies of the energy transfer mechanism observed. The synthesis of the rigid dimeric porphyrin ensemble **60–61** in which the donor and the acceptor are linked directly to guanosine and cytidine residues through phenyl groups has been described.[69] The arrangement of its two porphyrin residues is such that the angle between the planes of their macrocycles is $\sim 90^\circ$ and the 'centre-to-centre' distance was estimated[69] to be ~ 22.5 Å. The porphyrin fragments can rotate by $\sim 45^\circ$ around the C–C bond linking the phenyl ring to the heterocyclic base.

The nucleoside-substituted porphyrin **60** was prepared by the Lindsey condensation of the guanosine-containing benzaldehyde **62** with benzaldehyde and 3,3′-dibutyl-4,4′-dimethyldipyrrolyl-

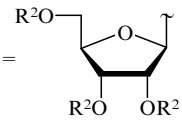


58 **59**

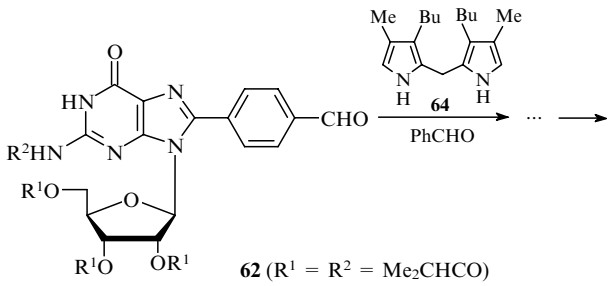
R = $(CH_2)_2O(CH_2)_2OMe$.



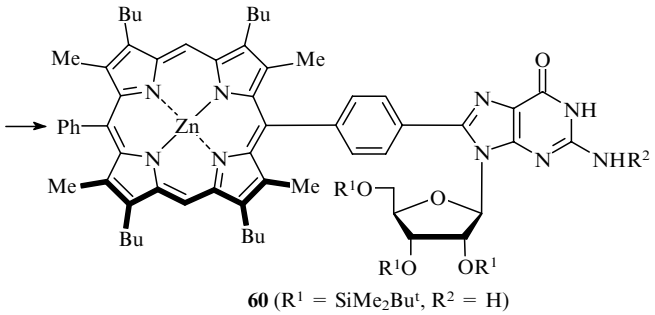
60 **61**

R^1 =  , $R^2 = SiMe_2Bu^t$.

methane (**64**) with subsequent removal of the isobutyryl group, introduction of the *tert*-butyldimethylsilyl group and metallation.



62 ($R^1 = R^2 = Me_2CHCO$)

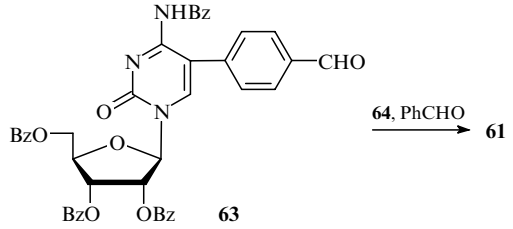


60 ($R^1 = SiMe_2Bu^t$, $R^2 = H$)

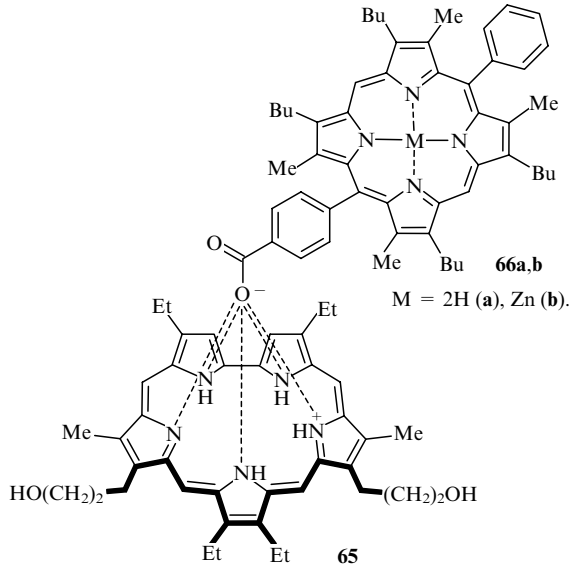
The nucleoside-substituted metal-free porphyrin **61** was synthesised in a similar way from the cytidine-containing benzaldehyde **63**.

The reaction of the cytidineporphyrin **61** with the guanosine-containing zinc complex **60** in dichloromethane results in the formation of a three-point hydrogen bond between the complementary bases. According to ^1H NMR spectroscopic data, the binding constants of the guanosine and cytidine derivatives in the ensemble **60**–**61** are equal to $22\,000 \pm 2000$ litre mol^{-1} (see Ref. 69).

The photoactive non-covalent complexes **65**–**66a** and **65**–**66b** (see Ref. 70) were assembled from carboxylate-containing porphyrins and the monoprotonated pentapyrrole chromophore sapphirine through the salt bridge formed. These systems are prepared by mixing porphyrin and sapphirine (in the form of a free acid and a free base) in dichloromethane; their binding constants determined by ^1H NMR spectroscopy are $\sim 10^3$ litre mol^{-1}. The two chromophores in these ensembles are oriented perpendicularly to each other in such a way that porphyrin is localised above the plane of sapphirine, while the 'centre-to-centre' distance between the chromophores is equal to 12.5 Å.



63 **61**



66a,**b**

M = 2H (**a**), Zn (**b**).

65

It was shown [69, 70] that the non-covalently linked bisporphyrin systems described above can be used as models in studies of photoinduced energy transfer between pigments.

The singlet–singlet energy transfer from the zinc complex to the porphyrin free base in the ensemble **60**–**61** is effected to a distance of ~ 22.5 Å and is characterised by the rate constant $k \approx 9.1 \times 10^8$ s^{-1} and 60% efficiency, which is consistent with the parameters calculated on the basis of the Förster approximation. These results suggest that dipole–dipole 'through-space' interactions are the most probable mechanism of singlet energy transfer. In this case, the role of hydrogen bonds between complementary bases is solely to bind chromophores and not to promote singlet energy transfer.

On the other hand, the triplet energy transfer in the ensemble **60**–**61,** which follows from the appearance of an absorption band at 545 nm characteristic of triplet states of metal-free porphyrins, seems to be effected through hydrogen bonds which play in this case a more active mediatory role.[69]

Irradiation of porphyrin subunits in the ensembles **65**–**66a** and **65**–**66b** induces singlet–singlet energy transfer from porphyrin to sapphirine within the complexes; this process is characterised by lower energy of the first excited singlet state. The calculated rate constants for the energy transfer in systems, which utilise metal-free bases and zinc–porphyrin complexes as donors, were equal to 4.3×10^{10} and 1.1×10^{11} s^{-1}, respectively, which is consistent with the Förster mechanism. Rapid energy transfer in the ensembles **65**–**66a** and **65**–**66b** is due to higher values of spectral overlap integrals of porphyrin emission and sapphirine absorption.[70]

The donor–acceptor ensembles described in this Section can be incorporated into more complex multicomponent systems mimicking natural light-harvesting complexes.

III. Multiporphyrin ensembles

Natural photosynthetic light-harvesting complexes contain several hundreds of pigments responsible for the migration and transfer of excitation energy to the reaction centres. Therefore, an ideal model system should include a great and strictly defined number of chromophores with known photophysical properties. The molecular organisation of such a system should allow accurate control over the mutual arrangement of pigments in the integral ensemble. This, in turn, will ensure efficient transfer of excited state energy.

Limited solubility of multiporphyrin ensembles is one of the main difficulties in their design. The approaches to the solution of this problem include incorporation of long alkyl groups into β-pyrrole positions and of alkyl, 3,5-di-*tert*-butylphenyl or *ortho*-disubstituted phenyl groups into more accessible *meso*-positions of terrapyrrole macrocycles. The porphyrins thus substituted are less susceptible to aggregation and, correspondingly, are more readily soluble in organic solvents, which facilitates the synthesis, chemical and spectroscopic analysis of the multiporphyrin ensembles based on them.[27]

Yet another problem is related to the quenching of excited states by photoinduced electron transfer which competes with the energy transfer. One of the ways to limit the energy transfer envisages the design of porphyrin ensembles with sufficiently long fixed 'centre-to-centre' distances where electronic interactions between the pigments are relatively weak.

1. Synthesis

Two promising approaches to the synthesis of multiporphyrin ensembles include building block synthesis of covalently linked systems and self-assembly of pigments possessing special recognition sites. Building block synthesis, which consists in condensation of substituted iodoaryl- and ethynylarylporphyrins under mild conditions in the presence of a palladium catalyst, was used for the preparation of linear trimers **67**[25] and **68**,[27] the linear amphiphilic ensemble **69**[34] and the star-like five-porphyrin ensemble **70**[30, 71] in which the macrocycles were linked through diarylethyne spacers.

The synthesis of a dithiaporphyrin (N_2S_2) block and its further use in the construction of the model light-harvesting system **71** have been reported.[72] The preparation of the N_2S_2-porphyrin includes the reaction of 4-(trimethylsilylethynyl)benzaldehyde (2 equiv.) with dilithiothiophene (1 equiv.), condensation of 2,5-bis[4-(trimethylsilylethynyl)phenyl(hydroxy)methyl]thiophene with pyrrole in the presence of boron trifluoride etherate and removal of trimethylsilyl protective groups. The reaction of the dithiaporphyrin formed with 5-(4-iodophenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin in the presence of a palladium catalyst and triphenylarsine affords the pentamer **71** in 37% yield.

As mentioned previously, one of the main tasks in photosynthetic modelling is the construction of molecular ensembles which, like natural antenna complexes, are characterised by high molar absorption coefficients in both blue and red regions of the visible spectrum and significant overlap of absorption spectra of the acceptor and emission spectra of the donor. These properties are inherent in systems containing porphyrins and phthalocyanines, which differ in their electronic characteristics. Yet another attractive feature of the combination of porphyrin and phthalocyanine chromophores within a single ensemble is that the energy of the first singlet excited state of phthalocyanine is lower than that for porphyrin.

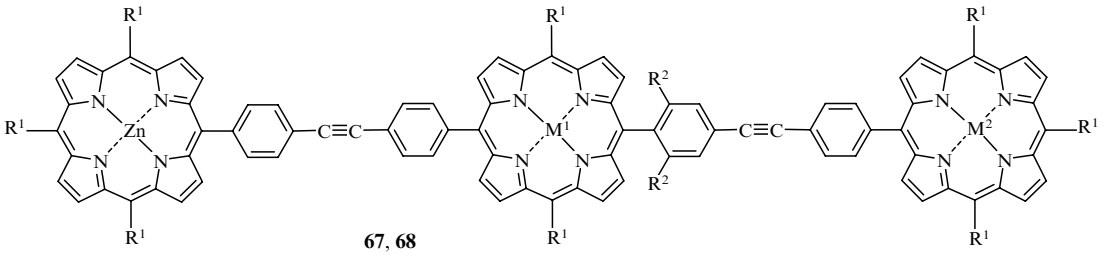
The light-harvesting complexes **72** and **73** contain four and eight porphyrin components, respectively, which are covalently linked to phthalocyanine to form a star-like structure. The use of a phenylethyne linker between the porphyrin and phthalocyanine components makes it possible to reduce the distance and to enhance interchromophore electronic interactions in the above systems in comparison with their structural analogues, *viz*., the diphenylethyne-linked pentamers **70** and **71**.

The ensembles **72a**,**b** were synthesised in 45% and 15% yields by cyclotetramerisation of ethyne-linked porphyrin–phthalonitrile in pentan-1-ol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene and $MgCl_2$ or $Zn(OAc)_2$, respectively. Subsequent selective demetallation and metallation reactions afforded the pentads **72c**–**e**, which contain different metals in their tetrapyrrole macrocycles.[73]

A similar approach was used for the synthesis of the ensembles **73a**–**c**. In this case, cyclotetramerisation was preceded by palladium-catalysed preparation of the porphyrin dimer containing a phthalonitrile fragment.[74]

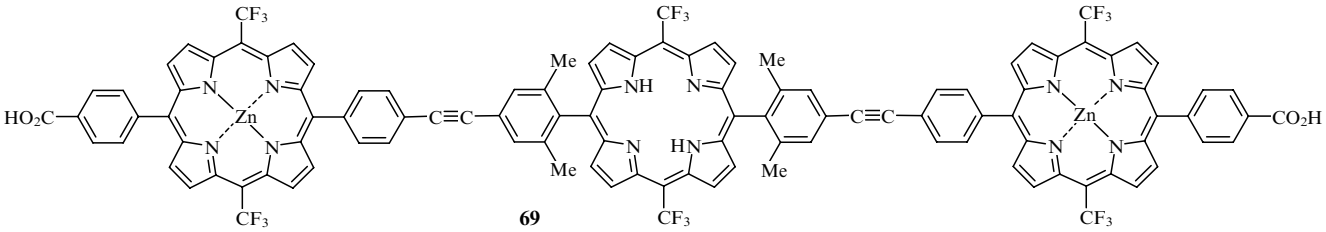
Miller *et al*.[75] have carried out the synthesis of the linear chromophore ensemble **74**, containing perylene, bisporphyrin and phthalocyanine components, which manifests enhanced light-harvesting properties owing to strong absorption in all the visible region of the spectrum. This system can function as a cascade transferring excitation energy towards the acceptor. The ensemble **74** was synthesised in four steps: (1) synthesis of *trans*-substituted AB_2C-porphyrin building blocks, each possessing only one non-substituted *meso*-position; (2) oxidative *meso,meso*-condensation of the porphyrin monomers to yield the bisporphyrin containing the phthalonitrile and iodophenyl fragments; (3) synthesis of bisporphyrinphthalocyanine ensembles by mixed cyclisation of the bisporphyrin and 4-*tert*-butylphthalonitrile and (4) palladium-catalysed condensation of the resulting product with ethynylperylene.

X-Ray diffraction analysis of antenna complexes of photosynthesising bacteria revealed that these consist of two concentric circular ensembles of bacteriochlorophyll molecules non-covalently bound to apoproteins (see Fig. 1).[11] The planes of overlapping bacteriochlorophyll *a* molecules in the inner ring containing two thirds of all chromophores are perpendicular to the plane of the tylakoid membrane, whereas the planes of chromophores in the outer ring are almost parallel to the membrane surface. Such spatial arrangement ensures the most efficient energy transfer through dipole–dipole resonance interactions between pigments in the photosynthetic subunit.

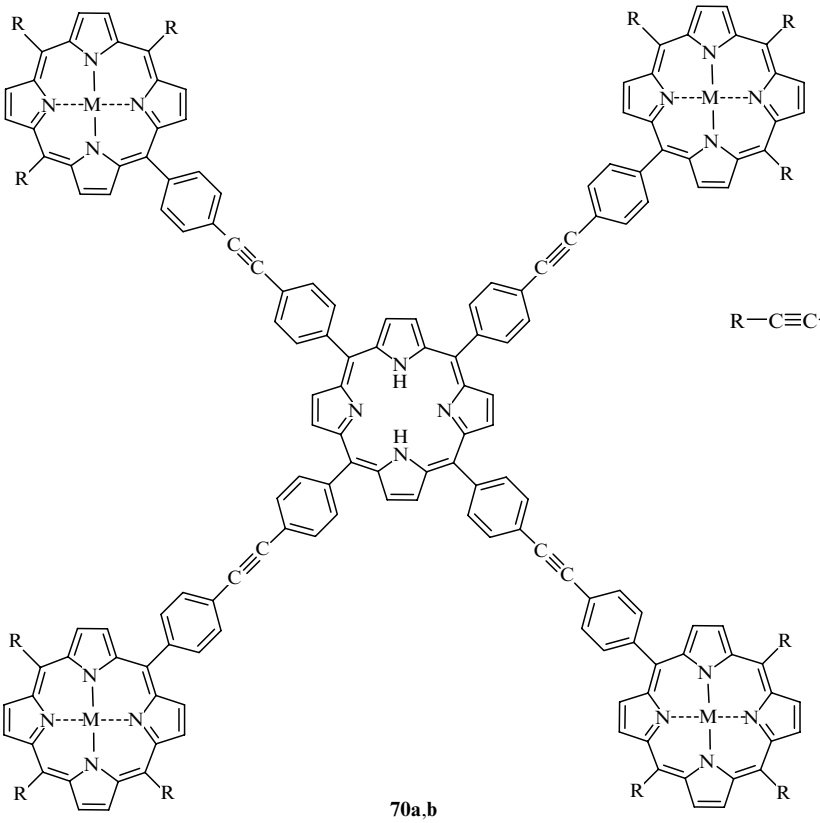


67, **68**

67: R^1 = 2,4,6-$Me_3C_6H_2$, R^2 = H, M^1 = 2 H, M^2 = Zn; **68**: R^1 = 2,4,6-$Me_3C_6H_2$, R^2 = Me, M^1 = Zn, M^2 = 2 H.

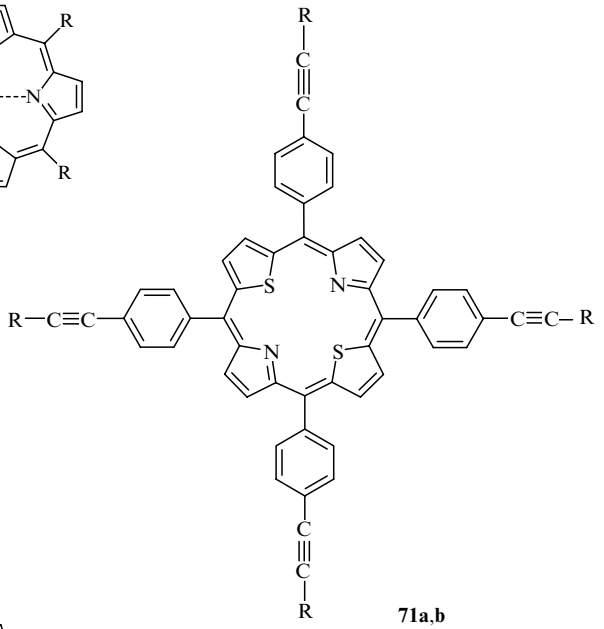


69

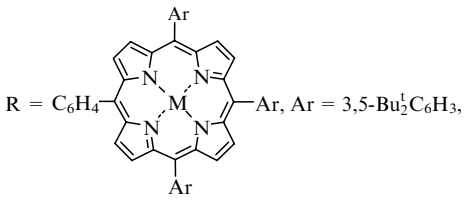


70a,**b**

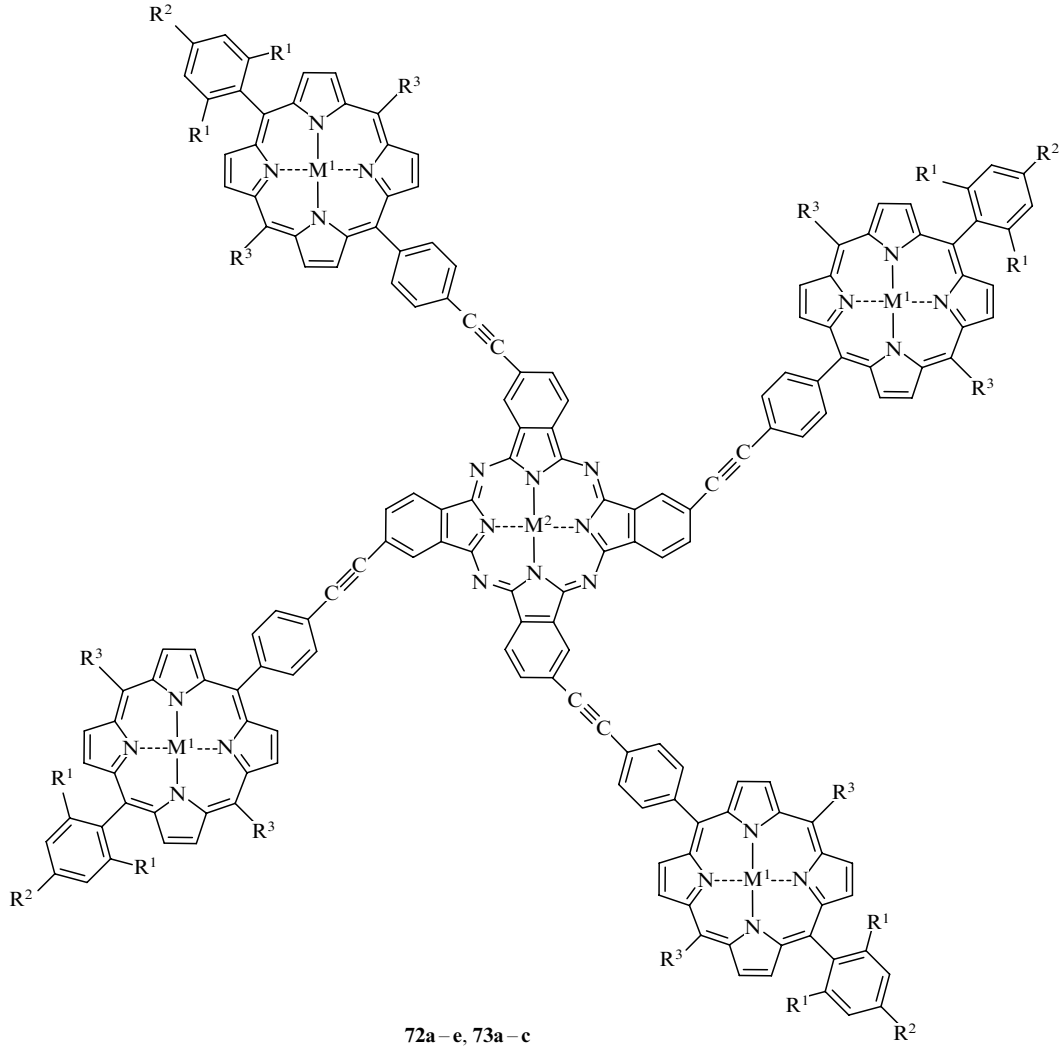
R = 2,4,6-$Me_3C_6H_2$; M = Zn (**a**), Mg (**b**).



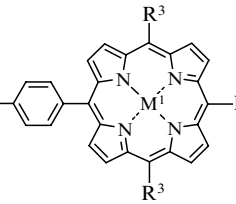
71a,**b**



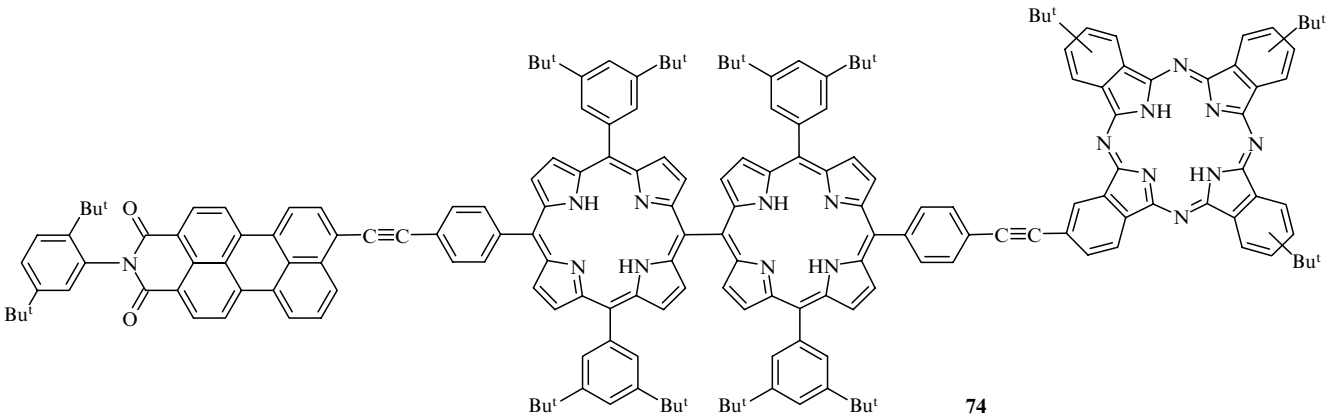
M = 2 H (**a**), Zn (**b**).



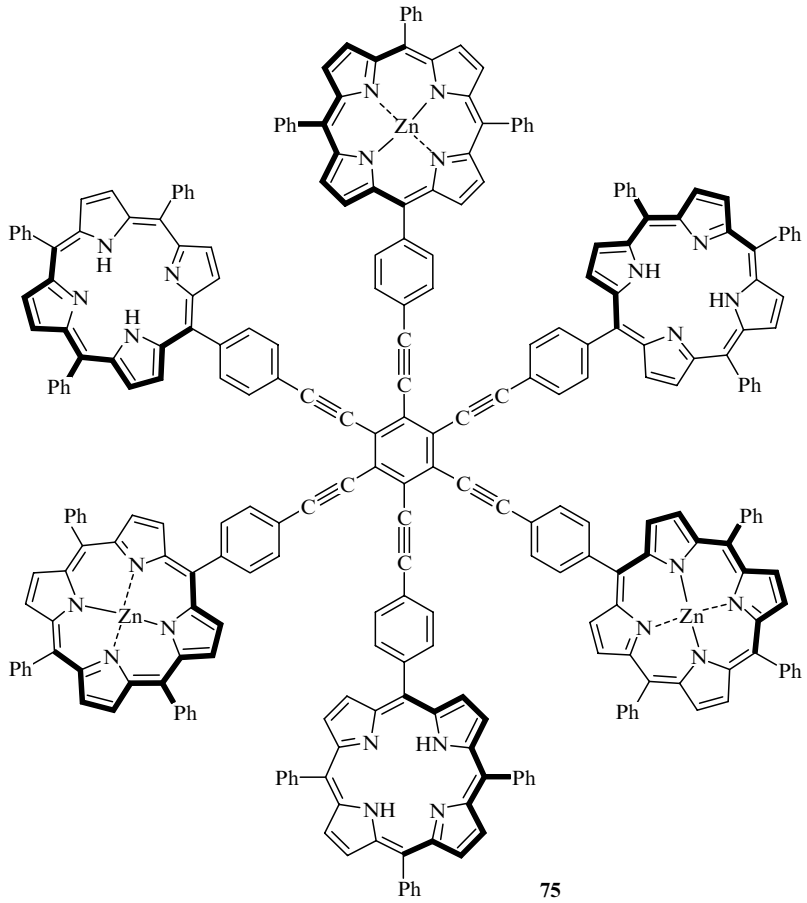
72a–**e**, **73a**–**c**

72: $R^1 = R^2 = Me$, $R^3 = 2,4,6\text{-}Me_3C_6H_2$; **73**: $R^1 = H$, $R^2 =$  R^3; $R^3 = 2,4,6\text{-}Me_3C_6H_2$;

$M^1 = M^2 = Mg$ (**a**), Zn (**b**), 2 H (**c**), $M^1 = 2\,H$, $M^2 = Mg$ (**d**), $M^1 = Zn$, $M^2 = Mg$ (**e**).



74



75

The multiporphyrin ensemble **75** was designed for simulation of spatial arrangements of chromophores in the inner rings of natural antenna complexes. In this model, six porphyrin rings are covalently linked through rigid ethynyl linkers to six positions of the benzene ring, which functionally replaces protein matrices of natural complexes. The diameter of the cyclic ensemble **75** is 46.7 Å and the 'centre-to-centre' distance between chromophores is 13.2 Å, *i.e.*, it is higher than the average distance (~9 Å) between magnesium ions of bacteriochlorophylls in natural systems.

The three-step synthesis of the hexaporphyrin ensemble **75** includes reaction of the zinc-containing complex of 5-(4-iodophenyl)-10,15,20-triphenylporphyrin with the 1,3,5-tris(trimethylsilyl) derivative of hexaethynylbenzene in the presence of a palladium catalyst under standard conditions, removal of protective groups and reaction of the star-like trimer formed with a large excess of the metal-free porphyrin. The total yield of the resulting ensemble **75** is 11%.[76]

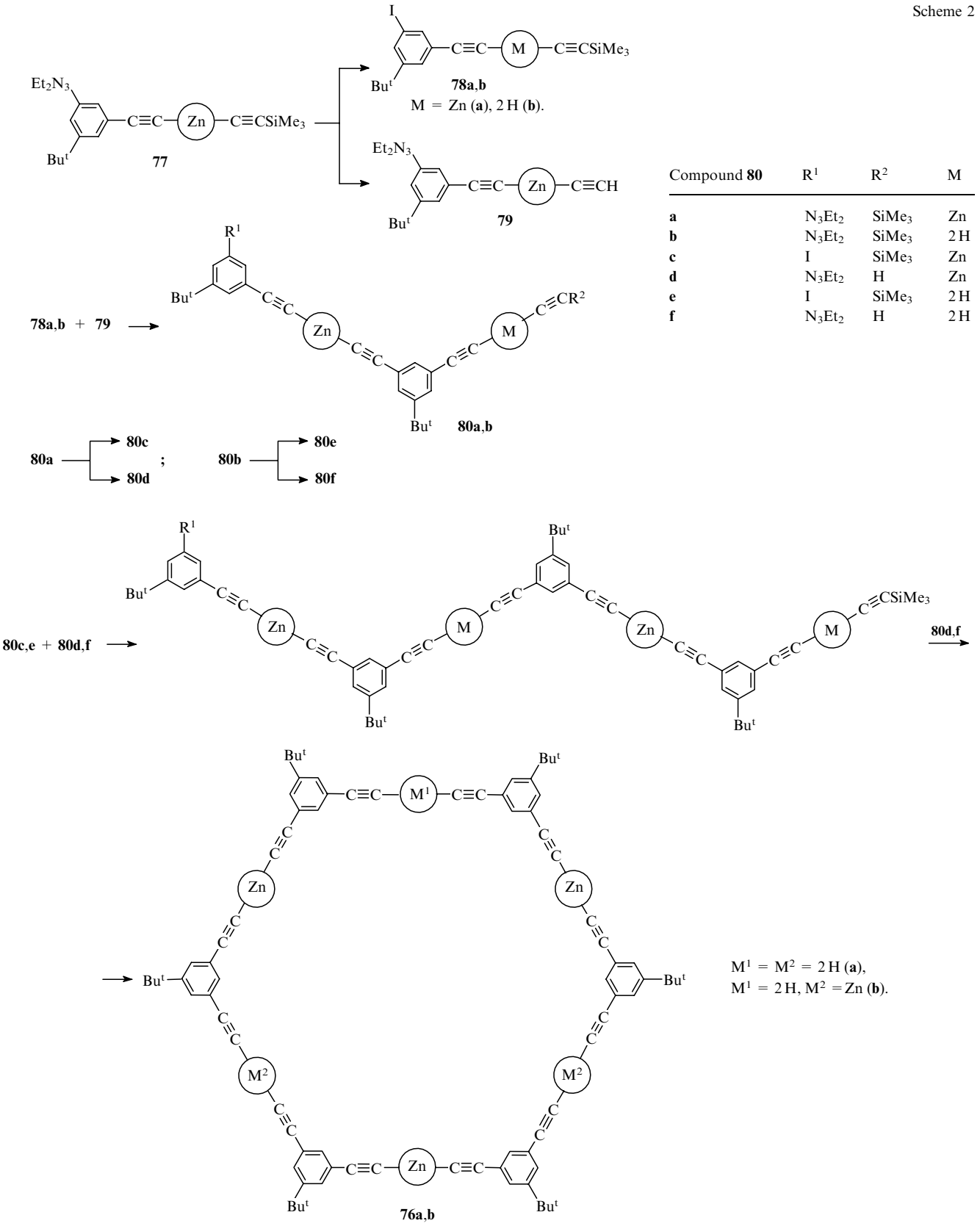
The hexagonal cyclic ensembles **76a**,**b** have been described[77] in which the six porphyrin rings are linked rigidly through six *meta*-diethynylphenyl bridges to form a cavity with an internal diameter of ~ 46 Å. A multistep synthesis of these ensembles is based on the use of only one building block (**77**) in which two protected, reactive positions, *viz.*, the ethynyl group and the carbon atom of the phenyl ring, can be activated selectively (Scheme 2). Cross-condensation of porphyrins **78a** and **79**, which are readily prepared from compound **77** by treatment with methyl iodide or sodium hydroxide, respectively, in the presence of a palladium catalyst results in the bisporphyrin **80a**. Iteration of this three-step reaction sequence yields porphyrin tetramers; their condensation with dimeric fragments and cyclisation result in the formation of the hexameric ensembles **76a**,**b**.

Eight chromophores in the system **81** are linked to the polypeptide chain, which may form a secondary α-helical structure after certain degree of oligomerisation. This conformation is determined by the natural trend of porphyrins for aggregation and is characterised by overlap of the chromophores, which ensures electronic interactions sufficient to enhance migration of excitation energy within the ensemble.

The synthesis of the octamer **81** is based on the use of the L-lysine-containing porphyrin **82**, which was prepared by condensation of carboxy and amino components in the presence of DCC and 1-hydroxybenzotriazole (HOBT) (yield 94%). The strategy of oligomer synthesis involves selective removal of protective *tert*-butoxycarbonyl and allyl groups under mild conditions (Scheme 3). Thus treatment of the porphyrinlysine **82** with a solution (1 mol litre^{-1}) of chlorotrimethylsilane and phenol in dichloromethane results in the removal of the protective Boc group (yield 91%). Removal of the allyl protection from the carboxy group of compound **82** was carried out in a dimethylacetamide–piperidine mixture in the presence of tetrakis(triphenylphosphine)palladium in 84% yield. The dimer **83** was synthesised by condensation of the amine and the acid in the presence of DCC and HOBT. Iteration of this three-step procedure affords the tetramer **84** and the octamer **81** in 86% and 80% yields, respectively.[78]

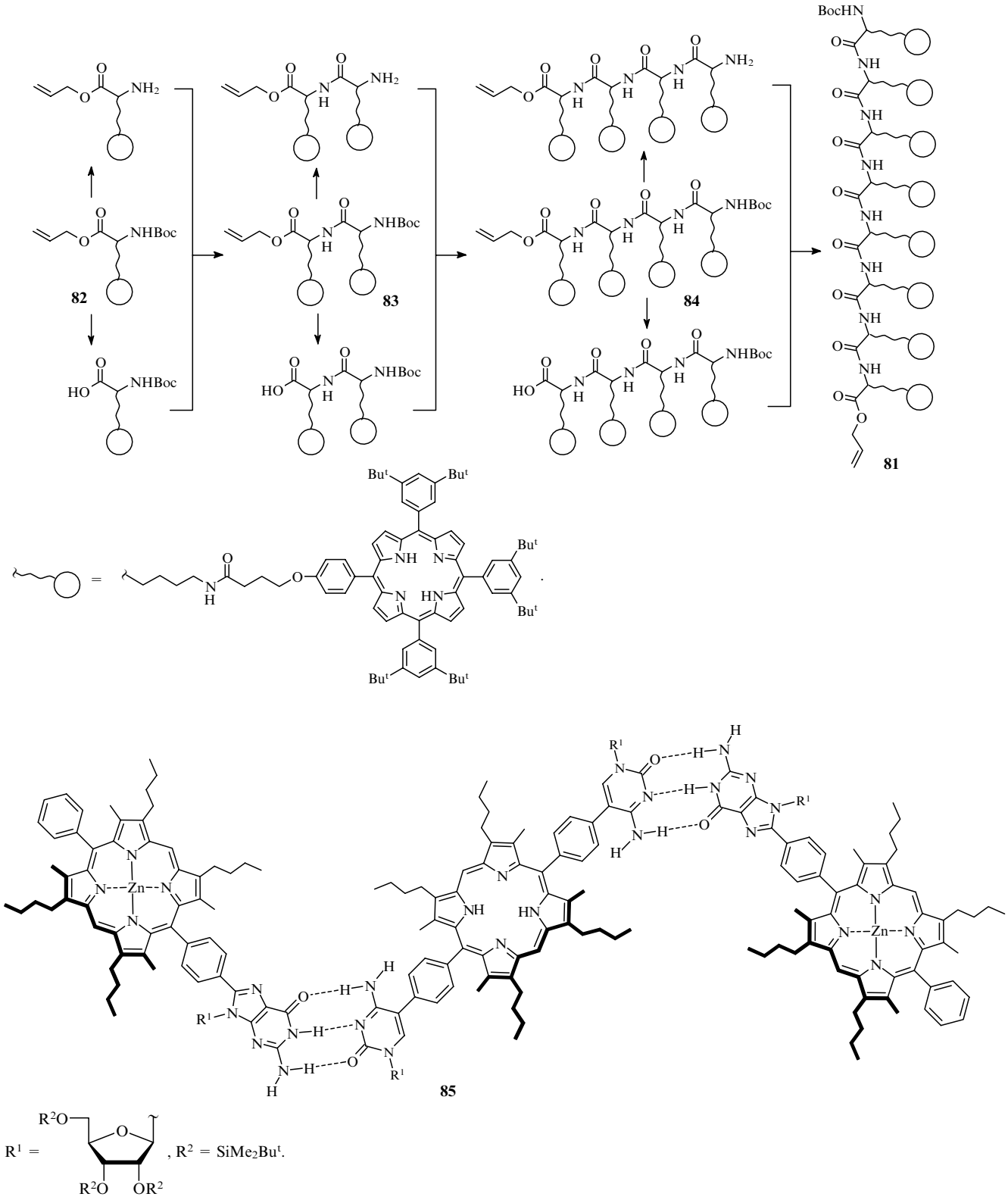
A strategy based on an ordered assembly of chromophores owing to specific non-covalent interactions, was used in the design of a model photosynthetic system **85**. This is formed as a result of pairwise interactions between complementary heterocyclic bases upon mixing of guanosine and cytidine porphyrin derivatives in dichloromethane.[69]

Scheme 2



Compound **80**	R^1	R^2	M
a	N_3Et_2	$SiMe_3$	Zn
b	N_3Et_2	$SiMe_3$	2 H
c	I	$SiMe_3$	Zn
d	N_3Et_2	H	Zn
e	I	$SiMe_3$	2 H
f	N_3Et_2	H	2 H

Scheme 3



2. Photochemical properties

Photochemical studies of the system **70a** have shown that the emission from the central porphyrin free base predominates in the fluorescence spectrum. The quantum yields of emission of zinc-containing complexes within the ensemble (Φ = 0.38%) were 12-fold smaller than that of the corresponding monomeric zinc-porphyrin complex. At the same time, the presence of four peripheral metal-containing porphyrin fragments virtually did not influence the emission yield of the central porphyrin free base (Φ = 12%). It was noted also that the whole fluorescence excitation spectrum coincided almost completely with the absorption spectrum. Based on these data, the yield of the energy transfer from the peripheral zinc complexes to the porphyrin free base was estimated to be equal to 90%. Thus, the pentamer **70a** can accumulate and concentrate the energy of photons in the centre of the ensemble.[71]

Similar results were obtained for the ensembles **71a**,**b** where the efficient energy transfer occurs from the peripheral porphyrin fragments to the central dithiaporphyrin subunit.[72]

The quantum yields of the energy transfer from the photoexcited porphyrin components to the central phthalocyanine in the model systems **72b**–**e** exceed 99%. However, the efficiency of energy transfer in the ensemble **72a** is decreased by 40%, which is attributed to the contribution of the charge transfer from the excited porphyrin to the ground state of phthalocyanine due to probable easier oxidation of magnesium-containing porphyrins in comparison with zinc-porphyrin complexes and free bases.[73]

An approach to the targeted transfer of energy to the terminal acceptor includes a cascade of energy transfers along the ensemble of pigments linked in succession. Studies of spectral properties of the linear molecular system **74** revealed an ultrafast ($k \geqslant 3.3 \times 10^{11}$ s^{-1}) and nearly quantitative cascade-like energy transfer from perylene to bisporphyrin and further to phthalocyanine. The directional energy transfer in this rigid structure is determined by the nature of the donor and acceptor chromophores, type of spacers and strong electronic interactions between the pigments in the bisporphyrin energy-transferring subunit. In addition, the ensemble **74** is characterised by significant overlap of absorptions of the components in the visible region of the spectrum, which determines its high light-harvesting capacity.[75]

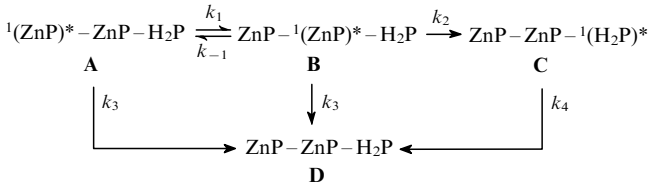
The effective transfer of singlet excitation energy from zinc-containing complexes to porphyrin free bases was observed in the ensembles **75** ($\Phi = 98\%$) and **76a** ($\Phi = 91\%$) in which the spatial configuration of the chromophores mimicks the mutual arrangement of pigments in light-harvesting complexes of natural photosynthesising organisms.[76,77] At the same time, the energy transfer from five zinc-containing chromophores to the single acceptor in the hexamer **76b** occurs with the quantum efficiency of 40%.[77] Such a significant difference is explained by the increase in the number of non-productive stages in the energy transfer between zinc-containing porphyrins in the ensemble **76b**.

In contrast with the above-described systems, the singlet energy transfer in the non-covalently linked ensemble **85** where two zinc complexes and one porphyrin free base are held at a distance of 22.5 Å from one another due to pairwise interactions between guanine and cytosine follows the Förster 'through-space' mechanism ($k \approx 9 \times 10^8$ s^{-1}) with a 60% efficiency. The quantum efficiency of the energy transfer in this system can be optimised by reducing the distance (by ~ 5 Å) between the porphyrin components.[69]

Fast migration of excitation energy between isoenergetic pigments takes place in natural light-harvesting complexes. It was of interest to determine the rate of this process. In an attempt to study the dynamics of this process and the feasibility of a reversible energy transfer, Hsiao *et al.*[51] have performed computer-assisted simulation of the photodynamic behaviour of the trimer **68** with some admissions. First, considering that absorption characteristics of two zinc-containing chromophores are identical, the authors admitted that primary excitation is distributed uniformly between these two porphyrins. Second, it was assumed that the two-photon absorption was negligible under the conditions used. Third, it was suggested that the rate of energy transfer from the terminal zinc porphyrin (ZnP) to the central one (k_1) is equal to that of the reverse process (k_{-1}). And, finally, the rate of the energy transfer between the central zinc-containing complex and the porphyrin free base (H_2P) (k_2) was taken to be equal to the rate measured for the analogous dimer **12c** (Scheme 4).

The temporal evolution of the energy transfer between the chromophores in the trimer is described by a system of differential equations which, for a fixed value of k_1 with a time interval of 0.5 ps, is solved with respect to the concentrations of singlet excited states for each of the three individual chromophores at a given moment of time. The decay curves constructed on the basis of the calculated values should correlate with the experimental monoexponential curves of absorption bleaching of the metal-free

Scheme 4



porphyrin in the ground energy state and of decay of the singlet state of zinc-containing porphyrins. The rate constant for the energy transfer between two isoenergetic zinc-containing porphyrins estimated in this way, $k_1 = k_{-1} = (2.2 \pm 0.8) \times 10^{10}$ s^{-1}, is comparable to that for the energy transfer between a zinc-containing complex and the free base.[51]

The total quantum yields of energy transfers in multicomponent porphyrin ensembles are difficult to predict, even if the efficiencies of individual steps of these processes are known. As the synthesis of such ensembles is very time and material consuming, rational design of efficient energy-transmitting molecular structures demands reliable prediction of their properties.

Van Patten *et al.*[79] have developed a general analytical technique for simulation of the kinetics of energy migration in weakly bound multipigment ensembles containing several donors but only one terminal acceptor. This approach is based on the system of differential equations which describe the temporal evolution of the energy transfer between the neighbouring chromophores. Thus in the case of the trimeric porphyrin ensemble **68**, these processes include energy migration between the donors (k_1, k_{-1}), energy transfer to the terminal acceptor (k_2), relaxation of the singlet state of the donors (k_3) and the terminal acceptor (k_4) (see Scheme 4). In this specific case, it is necessary to consider four configurations the interaction of which is described by the following system of differential equations:

$$dA/dt = (-k_1 - k_3)A + (k_{-1})B,$$

$$dB/dt = k_1 A + (-k_{-1} - k_2 - k_3)B,$$

$$dC/dt = k_2 B - k_4 C,$$

$$dD/dt = k_3 A + k_3 B + k_4 C,$$

where $A - D$ are the concentrations of states **A**–**D**, respectively.

In the general case, the energy transfer for a multiporphyrin ensemble $ZnP_{N-1}-H_2P$ can be regarded as an analogous first-order task for a series of reactions with N + 1 configurations. These equations are constructed with allowance for irreversibility of the energy transfer to the acceptor, whereas excitation energy migrates between isoenergetic donors in both directions (see Scheme 4).

By varying the initial conditions for excitation and the empirical data for the rates of energy transfer in all stages, it is possible to find solutions for the given system with respect to the concentrations of singlet excited states for each particular chromophore at a given moment of time. Their subsequent summation in time makes it possible to determine the general quantum efficiency of the energy transfer, *i.e.*, the percentage of ensembles in which the excitation reaches the terminal acceptor. This method allows prediction of the quantum efficiency depending on the rates, lifetimes of excited states and structures of ensembles.

The results of these calculations showed that the quantum efficiency of the energy transfer to the terminal acceptor in linear ensembles during random excitation of isoenergetic donor pigments with fixed rates of the energy transfer in each step decreases rapidly with an increase in the molecule length. The quantum efficiency strongly depends on the changes in the rates of the energy transfer between isoenergetic pigments. For example, the quantum efficiency of excitation capture for a linear twenty-porphyrin ensemble (the rate constant for the energy transfer between its isoenergetic pigments, k_1, is 2×10^{10} s^{-1}) is as low as 35%. However, with an increase in the transfer rate

($k_1 = 1 - 10^{12}\ s^{-1}$) the quantum yield of the energy transfer for this ensemble increases to 70%, whereas that for the linear fifty-porphyrin ensemble is 43%. Thus, the increase in the rate of the energy transfer results in a significant increase in the quantum efficiency.

The energy transfer becomes more efficient provided the migration of energy competes successfully with relaxation of the excited state. With this in mind, van Patten *et al.*[79] have studied the dependence of the efficiency of the energy migration in linear ensembles on the lifetime of the singlet excited states. A comparative study for different rates of competing deactivation has demonstrated that the quantum efficiency increases significantly with an increase in the lifetime (τ) of the excited singlet state of the donor. Calculations have shown that the quantum yields for ten-component linear ensembles containing zinc- and magnesium–porphyrin complexes as donors (τ = 2.4 and 9 ns, respectively) are 62% and 85%, respectively. Qualitatively similar results were obtained in simulation of linear ensembles where the excitation and energy capture occur at different ends of the molecule.

Since the quantum yields are determined by the competition between the energy migration and relaxation of the excited state, the efficiency of the energy transfer increases significantly in cyclic and branched ensembles with the minimum number of non-productive energy transfer steps. For example, the quantum efficiency for a tri-branched ten-component ensemble shown in Fig. 3 *c* (Φ = 91%) is similar to that for a linear tetramer, whereas that for a linear ensemble comprising nine zinc-containing porphyrins and one free base is as low as 63%.[79]

It should be noted that the quantum efficiency estimated for a cyclic porphyrin decamer with an integral acceptor (Φ = 84%, see Fig. 3 *b*) exceeds markedly the experimental value for the hexamer **76b** with an identical structure (Φ = 40%). There are several explanations for this phenomenon: (1) different sizes of the macrocyclic ensembles in theoretical and synthetic models; (2) decreased (in comparison with theoretical value) rate of intramolecular energy transfer in the synthetic ensemble where porphyrin subunits are linked through *meta*-positions of aromatic rings of the linkers; (3) predominant excitation, under the experimental conditions, of only one zinc-containing chromophore in each multiporphyrin ensemble with the resulting loss of excitation energy in the reversible energy transfer between neighbouring zinc porphyrins and (4) possible rotation of porphyrin chromophores in the synthetic hexamer.[77]

Introduction of different types of donors into model systems increases the ratio of rates of forward and reverse energy transfer processes between the donors ($k = k_1/k_{-1} > 1$), which, in turn, leads to a directed energy transfer (Fig. 4) and sharp increase in the quantum efficiency. Modelling of such cascade ensembles demonstrated that a twofold decrease in the rate of the reverse reaction (k = 2) results in an increase in the quantum efficiency which is commensurate with a 50-fold increase in the rate of direct energy transfer in the linear ensemble under conditions of random migration of the excitation energy.[79]

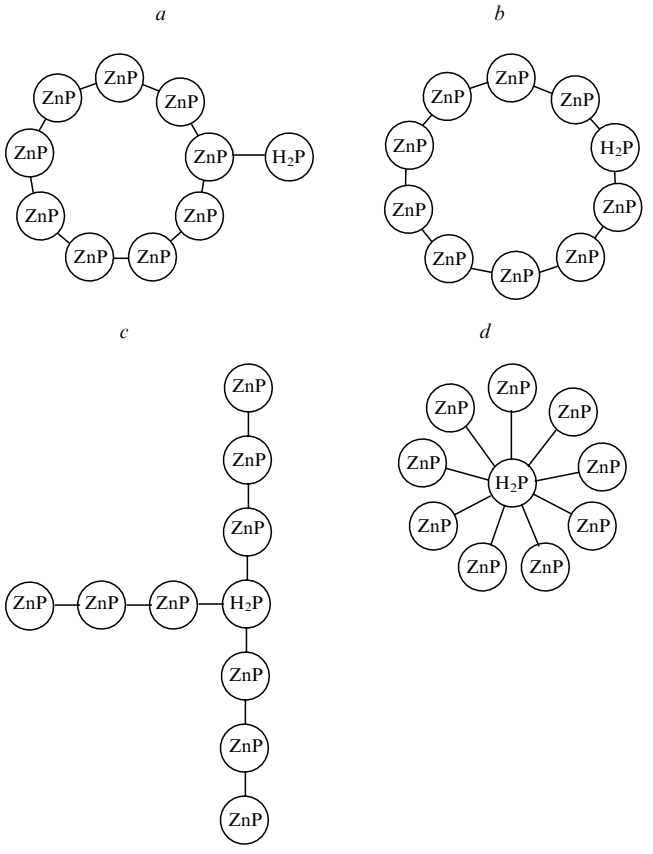


Figure 3. The effect of architecture on the quantum yields (Φ) of energy migration to a single acceptor in cyclic (*a*, *b*) and branched (*c*, *d*) ensembles containing nine donor pigments. All donor pigments have similar absorption patterns: $k_1 = k_{-1} = 2 \times 10^{10}\ s^{-1}$, $k_2 = 2.1 \times 10^{10}\ s^{-1}$, $k_3 = 4.2 \times 10^{8}\ s^{-1}$; Φ = 76% (*a*), 84% (*b*), 91% (*c*), 98% (*d*).[79]

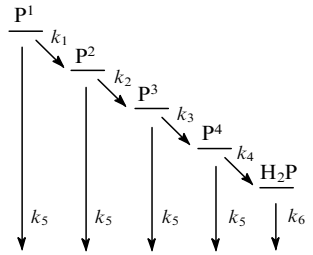


Figure 4. A five-membered cascade ensemble containing several types of donor pigments ($P^1 - P^4$) and an acceptor (H_2P).[79] (Here and in Figs 5 and 6 k_i are the rate constants of the corresponding energy transfer).

An important characteristics of light-harvesting model systems is their antenna effects, which represent products of the number of donor pigments in an ensemble with the quantum efficiency of the energy transfer. For example, the dimer **12a** and the corresponding star-like pentamer **70** have identical quantum efficiencies (98%),[51, 71] but the antenna effect of the former ensemble is 0.98, whereas that of the latter is 3.92, which points to a higher light-harvesting capacity of the pentamer.[79]

The antenna effect provides a possibility for the choice of strategies in the design of multicomponent ensembles. From the standpoint of energy capture by the acceptor, the most efficient architecture of the ensemble is the one which ensures maximum antenna effect. Thus the addition of three donors to a ten-component tri-branched ensemble (see Fig. 3 *c*), which manifests an antenna effect of 8.19 and a quantum efficiency of 91%, can be effected in two ways. Attachment of one zinc-containing porphyrin each to the ends of branches decreases the quantum efficiency to 87%, while the antenna effect increases to 10.44. An alternative route consists in direct addition of the fourth linear ensemble consisting of three zinc-containing porphyrins to a free base resulting in the formation of a symmetrical cross-shaped structure. This procedure does not influence the level of quantum efficiency, since all the four linear branches are independent structures, but enhances the antenna effect to 10.92. These calculations have shown that the appearance of a new individual route for the direct energy transfer from additional donors to the acceptor does not increase the number of non-productive energy transfers in the existing set of donors and is therefore the most efficient way to enhance the light-harvesting properties of the ensemble. Systems with star-like architecture (see Fig. 3 *d*) manifest the best light-harvesting properties, their quantum efficiencies are comparable with those of the corresponding dimer and the

antenna effect depends linearly on the number of the attached donors.

The results of theoretical modelling pave the way to the synthesis of multicomponent ensembles with anticipated high efficiency of the overall energy transfer process.[79]

IV. Porphyrin – carotenoid compounds

Carotenoids (Car) are present in the composition of antenna complexes and reaction centres of natural photosynthetic systems. They function as light-harvesting pigments by absorbing light in the spectral regions where the extinction coefficients of chlorophylls (Chl) and bacteriochlorophylls (BChl) are low and by supplying the excitation energy to these pigments through a fast singlet – singlet transfer.[12, 80–82]

$$Car + h\nu \longrightarrow {}^1Car^*,$$

$${}^1Car^* + Chl\,(BChl) \longrightarrow Car + {}^1Chl^*,$$

$${}^1Chl^* \longrightarrow Chl + h\nu\ (\text{fluorescence}).$$

Contrariwise, in the case of high light intensity carotenoids dissipate excesse energy through singlet energy transfer from chlorophyll to the carotenoid and thus control the intensity of singlet energy flow to photosynthetic reaction centres.[83]

In addition, carotenoids fulfil the photoprotective function. Upon irradiation of photosynthetic complexes with high-intensity light, primary electron donors (special pairs) obtain excitation energy from antenna systems and effect primary electron transfer prior to regeneration of the quinone component of the electron transport chain. Under these conditions, the primary charge-separated state, which involves the radical cation of the special pair and the radical anion of bacteriopheophytin (BPh), is not subject to ordinary conversions and undergoes recombination with the formation of the triplet state of the special pair. Triplet states of chlorophylls are usually long-living and are highly energetic. They can also react with other compounds, particularly, with molecular oxygen to generate singlet oxygen. Sensitisation of singlet oxygen represents an energy transfer from the triplet state of chlorophyll to the ground state of oxygen according to an electron-exchange mechanism.

$$BChl \xrightarrow{h\nu} {}^1BChl^*,$$

$${}^1BChl^* + BPh \longrightarrow BChl^{+\bullet} + BPh^{-\bullet},$$

$$BChl^{+\bullet} + BPh^{-\bullet} \longrightarrow {}^3BChl^* + BPh,$$

$${}^3BChl^* + O_2 \longrightarrow BChl + {}^1O_2^*.$$

Singlet oxygen is known to be extremely reactive and causes the destruction of plant tissues.

Carotenoid polyenes prevent the deleterious effects of singlet oxygen by quenching the triplet states of chlorophylls and bacteriochlorophylls prior to their reaction with oxygen. This represents a triplet – triplet energy transfer and results in the formation of a low-lying triplet state of a carotenoid, which is harmless for plant tissues.

Studies of the temperature dependences of the decay rate of the triplet state of the primary donor and the quantum yield of the triplet carotenoid have led to the discovery of a transient excited state which was attributed to the triplet state of the monomeric bacteriochlorophyll localised on the inactive side of the reaction centre. Thus, the triplet energy is transferred from the special pair to the neighbouring bacteriochlorophyll in a thermally activated step; the triplet state of bacteriochlorophyll generated in this process is rapidly quenched by the carotenoid.[84]

$${}^3(BChl_2)^* + BChl + Q \longrightarrow BChl_2 + {}^3BChl^*,$$

$${}^3BChl^* + Car \longrightarrow BChl + {}^3Car^*,$$

$${}^3Car^* \longrightarrow Car + Q,$$

where Q is heat.

Carotenoids behave also as photoprotectors by directly quenching singlet oxygen.[84, 85]

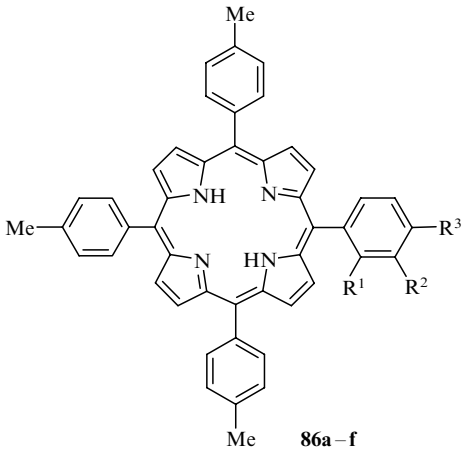
$$Car + {}^1O_2^* \longrightarrow {}^3Car^* + {}^3O_2,$$

$${}^3Car^* \longrightarrow Car + Q.$$

Biomimetic model compounds containing porphyrin or chlorophyll derivatives covalently linked to carotenoid polyenes have been developed for the study of photochemical characteristics of carotenoids, particularly, their photoprotective and antenna functions.

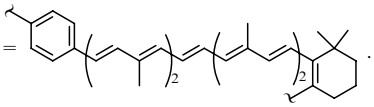
1. Synthesis

The carotenoid – tetraarylporphyrin dyads **86a**,**b** linked by the ester bond, were described in 1980. With these compounds it was shown for the first time that the efficient intramolecular singlet – singlet energy transfer from carotenoids to porphyrins requires that strict conformational demands be met.[86, 87] The models **86c** – **f** were subsequently prepared for the study of singlet – singlet and triplet – triplet energy transfer between carotenoids and porphyrins.[2, 85]



86a – **f**

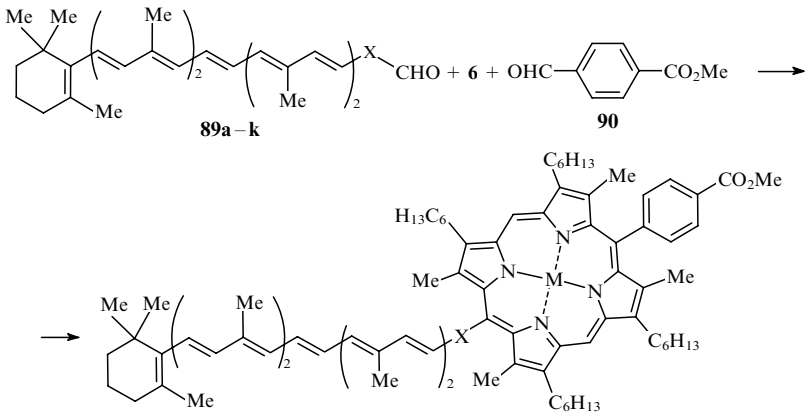
$R^1 = R^2 = H$, $R^3 = CO_2CH_2X$ (**a**), NHCOX (**c**), $O(CH_2)_3OCOX$ (**f**);
$R^2 = R^3 = H$, $R^1 = CO_2CH_2X$ (**b**), NHCOX (**e**); $R^1 = R^3 = H$,

R^2 = NHCOX (**d**); X = 

The synthesis and investigation into photodynamic behaviour of the dyads **87a** – **k** and **88a** – **k** in which the carotenoid and the porphyrin are linked through aromatic groups have been reported.[88] Owing to steric repulsion between the *meso*-aryl rings and methyl groups in the adjacent β-pyrrole positions, the aromatic bridge occupies an almost perpendicular position relative to the porphyrin plane and the 'centre-to-centre' distances between the pigments in the majority of models are fixed. These conformational restrictions permit one to establish the dependences of the rates of dynamic processes of the photoexcited state on geometric parameters of the molecules. Yet another essential feature of these models is conjugation of carotenoid and porphyrin π-electronic systems in the systems **87a** – **g** and **88a** – **g** containing phenylene, naphthylene and biphenylene spacers, which help realisation of considerable 'through-bond' electronic interactions between the chromophores.

The dyads **87a** – **k** were prepared by trichloroacetic acid-catalysed condensation of the carotenoid-substituted aromatic aldehydes **89a** – **k**, which in turn were synthesised by the Wittig reaction from the corresponding arylphosphonium salt and β-apo-8′-carotenal, with 4-methoxycarbonylbenzaldehyde (**90**) and dipyrrolylmethane **6** (Scheme 5). Despite the lability of the carotenoids in acidic media, this method afforded carotenoid-linked porphyrins in quite acceptable yields. Metallation of

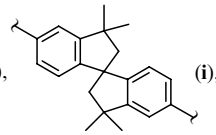
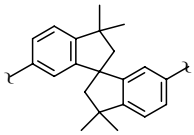
Scheme 5



89a–k **90**

87a–k: M = 2 H; **88a–k**: M = Zn

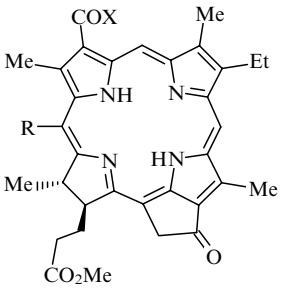
X = 1,4-C_6H_4 (**a**), 1,3-C_6H_4 (**b**), 2,6-naphthylene (**c**), 2,7-naphthylene (**d**), *p*-$C_6H_4-C_6H_4$-*p* (**e**), *m*-$C_6H_4-C_6H_4$-*p* (**f**), *p*-$C_6H_4-C_6H_4$-*m* (**g**),

p-$C_6H_4-CH_2-C_6H_4$-*p* (**h**),  (**i**),  (**j**), *p*-$C_6H_4-CONH-C_6H_4$-*p* (**k**).

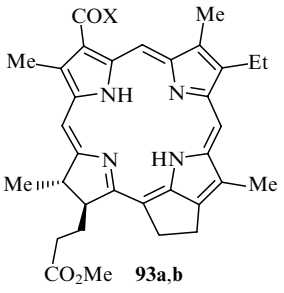
compounds **87a–k** by zinc acetate results in the model systems **88a–k**.[88]

The carotenoid–pyropheophorbide dyads **91–95** (see Refs 89–91) were prepared to study the interactions of the carotenoid and chlorophyll in the excited state. The natural carotenoids fucoxanthin and zeaxanthin used in these model studies fulfil different functions in the photosynthetic apparatus. It was found that fucoxanthin transfers energy to chlorophyll *a* in natural systems with high efficiency, whereas zeaxanthin, which is a member of the xanthophyll cycle, quenches excess energy during intense illumination. Studies of electronic interactions of these carotenoids with chlorin-type pigments are important for gaining insight into the mechanisms of photochemical processes underlying biological functions of natural carotenoids. The use of different pyropheophorbide components allows one to vary the energy levels of their S_1 states and the extent of 'through-bond' electronic interactions between the two pigments.

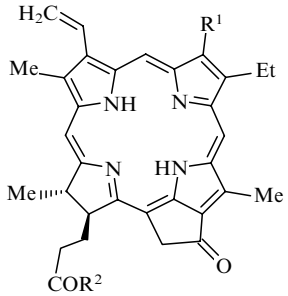
The dyads **91–95** were prepared by the reaction of chlorophyll *a* derivatives with fucoxanthin and zeaxanthin in the presence of 4-dimethylaminopyridine using 2-chloro-1-methylpyridinium iodide as a condensing reagent. These reactions occurred with acceptable yields (15%–30%) without formation of side products and *cis–trans*-isomerisation of the carotenoid component. According to ^{1}H NMR spectroscopic data, these dyad molecules have extended conformations in solution.



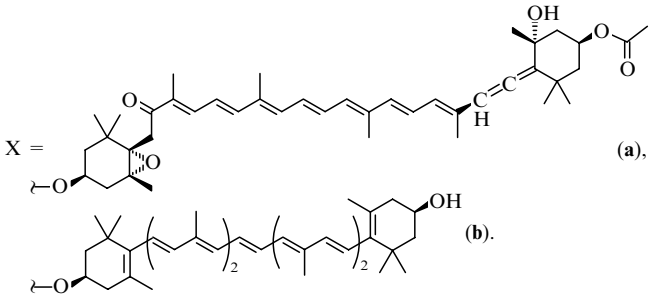
91a,**b**: R = H; **92a**,**b**: R = Cl



93a,**b**



94a,**b**: R^1 = Me, R^2 = X; **95a**,**b**: R^1 = COX, R^2 = OMe.



(**a**), (**b**).

2. Singlet–singlet energy transfer

Despite the large number of publications devoted to the studies of light-harvesting function of carotenoids in photosynthesising organisms, the detailed mechanism of the transfer of solar energy to chlorophylls is still obscure. Among a variety of factors hampering the understanding of singlet–singlet energy transfer mechanisms mediated by carotenoids, special mention should be made of the following: (1) experimental problems connected with determination of energy levels of the lowest excited singlet states of carotenoids; (2) fast time scale of the energy transfer; (3) difficulties in estimation of the energy transfer rate constants for individual chromophore pairs within multicomponent ensembles; (4) lack of detailed information about the structures of light-harvesting antenna complexes.

A characteristic feature of carotenoids is the presence of two low-lying singlet excited states. Intense colour of carotenoids, *e.g.*, β-carotene, is due to a strictly allowed electric dipole transition to the second excited singlet state S_2. The radiative rate constant for

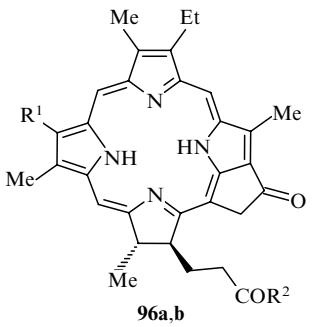
this state is rather high, but its lifetime is ~ 200 fs and, correspondingly, the quantum yield of fluorescence is very low. The first excited singlet state S_1 is characterised by a longer lifetime (~ 10 ps), but is strictly forbidden and is seldom detected in ordinary absorption spectra. The radiative rate constant for this state and quantum yield of fluorescence are usually very low.[80] As a consequence, spatial requirements for effective singlet–singlet energy transfer from carotenoids to chlorophylls or porphyrins are very strict, which imposes strong limitations on molecular structures of artificial photosynthetic systems.

The very first studies of energy transfer in porphyrin–carotenoid compounds revealed that sreric factors influence strongly the efficiency of this process. Thus the carotenoid unsaturated chain in the dyad **86a**, which contains tetraarylporphyrin linked to the carotenoid through the *para*-position of the *meso*-aryl ring, is removed from the tetrapyrrole macrocycle as a result of which singlet–singlet energy transfer does not take place. At the same time, the folded carotenoid chain in the *ortho*-isomer **86b** lies above the porphyrin macrocycle with an interchromophore distance of ~ 4 Å and the π-electron systems of the two chromophores are in contact with one another. In this case, the singlet–singlet energy transfer occurs with ~ 25% efficiency (see Refs 2, 86 and 87).

Singlet–singlet transfer of excitation energy from carotenoids to porphyrins can be studied by fluorescence excitation spectroscopy. In these studies, the fluorescence intensity of porphyrin depends on the excitation wavelength. If porphyrin fluorescence is induced by the light absorbed by the carotenoid, the energy transfer from the carotenoid to porphyrin follows the singlet–singlet mechanism.[2] The use of this technique has made it possible to detect this type of intramolecular energy transfer in compounds **87a**–**k**. The efficiency of this process was estimated from the ratio of excitation to absorption spectra and is equal to 9%–35% (see Ref. 88). The energy transfer from the carotenoid to pyropheophorbide in the fucoxanthin-containing compounds **91a**–**95a** occurs with the quantum efficiency of 12%–44% (see Ref. 91).

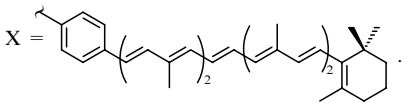
Elucidation of the mechanism of the singlet–singlet energy transfer from the carotenoid to chlorophyll in photosynthesising organisms is a topical problem in the study of the light-harvesting function of carotenoids. The existence of close orbital contact needed for the singlet–singlet energy transfer in the dyad **86b** calls into question the applicability of the Förster dipole–dipole approximation, which has been formulated for complexes where the distances between chromophores are larger than their sizes. Thus, the probability of energy transfer through electron-exchange interactions which demand orbital overlap becomes higher. In the carotenoid–porphyrin dyad **86c**, the chromophores are linked by a partially conjugated amide bond and the energy transfer yield is ~ 13%. This is rather high, especially with reference to a very short lifetime of the excited singlet state of the carotenoid. Electron-exchange interactions caused by partial overlap of π-electron systems of carotenoid and porphyrin through the amide bond appeared to play a crucial role in the energy transfer in this model system.

Similar results were obtained for the dyads **96a**,**b** in which the carotenoid is linked to the pyropheophorbide derivative. The quantum yield of the energy transfer in compound **96a** is < 5%; the lifetime of the corotenoid singlet state (16 ps) remains unchanged upon attachment of pyropheophorbide. In contrast, the lifetime of the carotenoid S_1 state in the dyad **96b** decreases to 7 ps due to energy transfer to pyropheophorbide which occurs with the quantum efficiency of ~ 50%. These results are interpreted by the fact that in the molecule **96a** saturated carbon atoms separate the π-orbitals of the two chromophores and thus prevent electron-exchange interactions required for effective singlet energy transfer. In the molecule **96b**, partial conjugation of the π-electron systems of the carotenoid and porphyrin through the amide bond ensures electron-exchange interactions; therefore, energy transfer occurs with high efficiency.[2,85]



96a,**b**

R^1 = CH=CH_2, R^2 = NHX (**a**), R^1 = CONHX, R^2 = OMe (**b**);

X = 

In the model compounds **87a**–**g**, the conjugation of the π-electron system of the carotenoid with the porphyrin macrocycle through the aryl bridge enhances electronic interactions between the chromophores. The rates of singlet–singlet intramolecular energy transfer in these dyads depend on the site of attachment of the carotenoid to the aromatic spacer. Thus comparison of the energy transfer rates in the dyads **87a**,**b** revealed that this process occurs faster in a *para*-linked structure than in the *meta*-isomer ($k = 5 \times 10^{10}$ and 3×10^{10} s^{-1}, respectively). This can be rationalised by stronger electronic interaction between chromophores in the former case due to much greater orbital density in the *para*-position. Analogously, distribution of the electron density on the molecular orbitals of spacers provides an explanation for the observed dependence of the rate of the energy transfer on the carotenoid-binding site in naphthylene- and biphenylene-bound systems. The results obtained suggest that 'through-bond' electronic interactions represent the most essential mechanism of intramolecular singlet–singlet energy transfer. This conclusion is consistent with the dipole-forbidden nature of the carotenoid S_1 state, since energy transfer involving such forbidden states can only be effective in the presence of electron-exchange interactions in the system.[88]

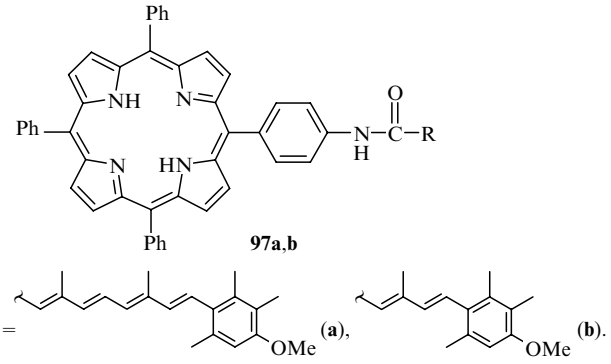
Effective orbital overlap, is possible where chromophores are in van-der-Waals contact. In the case of bound chromophores (see above), orbital overlap occurs in folded conformations, where the π-systems of the donor and the acceptor are in direct contact with one another. The orbitals of the linkers and the environment (*e.g.*, the solvent or a protein) also take part in electron-exchange interactions. Orbital contacts of non-bound pigments in solution require molecular collisions; therefore, the rates of electron-exchange interactions depend directly on the rate of diffusion. However, the lifetime of the S_1 state of carotenoids is so short (tens of picoseconds) that no collisions with the expected energy acceptors (*viz.*, porphyrins or chlorophylls) can take place. It thus follows that carotenoids are inefficient donors of the singlet state energy in non-bound systems in solution.[85]

The results illustrating the necessity of electron exchange for singlet energy transfer from carotenoid pigments are very important for the design of more complex photosynthetic model systems in which chlorophylls and carotenoids are bound to the protein. Functioning of carotenoids as antennae in the transfer of singlet excitation energy to chlorophylls requires that two protein-bound pigments were in a van-der-Waals contact with one another.

Although the predominance of electron-exchange interactions in 'through-bond' singlet energy transfer from the carotenoid to porphyrin has been confirmed experimentally, one should not rule out some contribution of dipole–dipole interactions. The two π-electron systems in the fucoxanthin–pyropheophorbide dyads **91a**–**95a** are separated by at least five saturated carbon atoms and there is no evidence of folded conformation. In this case, direct orbital overlap required for 'through-bond' electron-exchange interactions is insignificant and its contribution to the singlet–

singlet energy transfer observed is very low. However, in non-symmetrical carotenoids, such as fucoxanthin, the S_1 state can 'borrow' oscillating dipole energy from the S_2 state and thus become weakly dipole-allowed. The rate constants and the efficiencies of energy transfer in the dyads **91a**–**95a** estimated with the use of the Förster approximation are in good agreement with the experimental results. These studies suggest that dipole–dipole interactions play a crucial role in the intramolecular singlet–singlet energy transfer from fucoxanthin to pyropheophorbide in these compounds.[89, 91]

According to Sadovnikova *et al.*,[92] the energy transfer in model compounds **97a**,**b** is also described in terms of the Förster theory. The efficiency of energy transfer in these systems varies depending on the lengths of the conjugated bonds in the polyene and changes from 33% to 55% on going from compound **97b** to compound **97a**, apparently due to the increased spectral overlap integral of the donor fluorescence and the acceptor absorption in the latter case.



Elucidation of the role of two excited singlet carotenoid states in the energy transfer is yet another important problem, which attracts keen attention of investigators. An analysis of time resolved fluorescence spectra showed that the quenching time of the carotenoid S_1 state in compound **96b** (7 ps) coincides with the time of formation of the singlet state of the pyropheophorbide component.[85] A similar phenomenon was observed for the fucoxanthin-containing dyads **91a**–**95a**. Besides, the decrease in the efficiency of the energy transfer in the series **92a** > **91a** > **93a** is commensurate with the decrease in the spectral overlap between the fluorescence of the S_1 state of fucoxanthin and Q_y-absorption of pyropheophorbide.[88–90] The lifetime of the carotenoid S_2 state does not exceed several hundreds of femtoseconds and therefore cannot contribute to the energy transfer, which proceeds on a picosecond time scale. These findings point to the involvement of the carotenoid S_1 state as an energy donor in the singlet energy transfer.[80, 85, 89]

The energy transfer from the carotenoid S_2 state is also possible as was the case with the light-harvesting antenna complex B800-850 of the purple bacterium *Rhodobacter sphaeroides*; however, in this case the process proceeds on a femtosecond time scale.[80]

The S_1 state of zeaxanthin in the dyads **91b**–**95b** is energetically lower than the singlet state of pyropheophorbide and cannot therefore take part in the energy transfer to pyropheophorbide. An alternative route of the energy transfer from the singlet-excited state to pyropheophorbide is that from the S_2 state of zeaxanthin. This hypothesis is corroborated by the fact that the fluorescence spectrum from the S_2 state of zeaxanthin overlaps with the high-energy absorption Q_x-band of pyropheophorbide. The quantum yields of the energy transfer from the S_2 state of the carotenoid to the S_1 state of pyropheophorbide in compounds **91b**–**95b** do not exceed 15%. The strictly allowed nature of the $S_2 \rightarrow S_0$ transition permits the contribution of dipole–dipole interactions to this mechanism. However, the rate constants for the energy transfer estimated with the use of the Förster model correlate weakly with experimentally determined values. The Förster theory of dipole–dipole interactions assumes that the excitation is followed by oscillatory relaxation of the donor state prior to its deactivation through energy transfer. However, no complete oscillatory equilibrium can be reached in zeaxanthin-containing compounds in which the rapid energy transfer is effected from the short-lived S_2 state. Therefore, the use of the Förster model for the description of the energy transfer mechanism is not correct in this case. It should be noted, however, that the carotenoid and pyropheophorbide components of the dyads **91b**–**95b** are separated by fewer saturated carbon atoms in comparison with the components of the corresponding fucoxanthin-containing compounds **91a**–**95a**. This structural difference can favour somewhat stronger 'through-bond' electronic interactions in those cases where the energy is transferred from zeaxanthin to pyropheophorbide.[89–91]

Thus, highly efficient transfer of excitation energy from carotenoids to chlorophylls can follow several mechanisms. Their detailed study in each concrete case depends on the structures of the carotenoid and chlorophyll and their mutual arrangement in the protein environment.

Efficient singlet–singlet energy transfer is thermodynamically possible in those cases where the singlet state energy of the donor (carotenoid) exceeds that of the acceptor (chlorophyll or bacteriochlorophyll). In the case of partial degeneracy of excited singlet states of the carotenoid and chlorophyll, the overall efficiency of the energy transfer may depend on the lifetimes of their singlet states. The reduction of the lifetime of the S_1 state of chlorophyll in natural photosynthetic systems owing to the fast electron transfer to an additional acceptor, *e.g.*, accessory chlorophyll, can enhance the efficiency of the energy transfer from the carotenoid to chlorophyll. On the other hand, in the absence of additional fast photochemical processes, which quench the singlet state of chlorophyll, the efficiency of the energy transfer from the carotenoid to chlorophyll can be less than optimum.[85]

In addition to the key light-harvesting function discussed above, an opposite process, *viz.*, photochemical quenching of the first excited singlet state of porphyrin or chlorophyll by the carotenoid, was discovered in the studies of carotenoid-containing model compounds. This phenomenon is similar to energy dissipation after excessive irradiation of chlorophylls *in vivo*. A comprehensive analysis of mechanisms of quenching of porphyrin fluorescence by carotenoids will shed additional light on the ability of the latter to control the intensities of singlet energy fluxes to photosynthetic reaction centres.

Spectroscopic studies of the dyads **91b** and **94b** have demonstrated that zeaxanthin diminishes the intensity of pyropheophorbide fluorescence by 20% and 45%, respectively, and noticeably reduces the lifetime of the excited singlet state of pyropheophorbide (5.6 and 3.9 ns, respectively) in comparison with dimethyl esters of free pyropheophorbides (6.8 and 7.8 ns, respectively). This points to the existence of an additional pathway of quenching of the singlet excited state of pyropheophorbide in carotenoid-containing systems.[89] A possible explanation of this phenomenon is electron transfer from the carotenoid to the singlet excited state of pyropheophorbide with subsequent ultrafast recombination of charges.[93] An alternative mechanism of quenching of pyropheophorbide fluorescence consists in reverse singlet–singlet energy transfer from the excited S_1 state of pyropheophorbide to zeaxanthin. This route is thermodynamically allowed, since the S_1 state of zeaxanthin possesses lesser energy than that of pyropheophorbide. The ability of zeaxanthin to quench the singlet excited state of pyropheophorbide corresponds with the role played by this carotenoid in the quenching of excess energy of chlorophyll under conditions of the excess irradiation *in vivo*.[89, 90]

Similar quenching of porphyrin fluorescence by the carotenoid was observed in the dyads **87a**–**k** and **88a**–**k.** Thus the lifetime of porphyrin fluorescence in compound **87a** decreases to 850 ps, *i.e.*, becomes close to the time of formation of the carotenoid S_1 state (930 ps), which reflects the intramolecular energy transfer from the excited singlet state of porphyrin to the carotenoid. The carotenoid S_1 state generated is subjected to reversible energy transfer to porphyrin, which competes with its

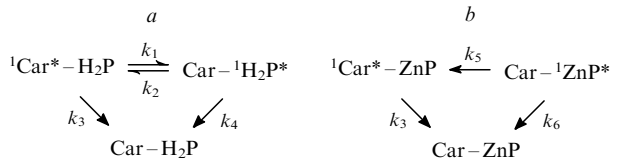


Figure 5. A scheme of singlet energy transfer in the porphyrin – carotenoid compounds **87a** – **k** (*a*) and **88a** – **k** (*b*).[88]

fast internal transition to the ground state. The singlet – singlet energy transfer between the carotenoid and the metal-free porphyrin in compounds **87a** – **k** is reversible (Fig. 5 *a*) assuming that the S_1 states of the two chromophores are nearly isoenergetic. At the same time, the unidirectional singlet – singlet energy transfer from zinc porphyrin to the carotenoid (Fig. 5 *b*) observed in systems **88a** – **k** indicates that the S_1 state of the carotenoid is energetically lower than that of the zinc – porphyrin complex.[88]

The above-described approach, which is based on the changes in positions of the S_1 energy level of porphyrin or chlorophyll induced by chemical modifications, *e.g.*, metallation, introduction of appropriate substituents and changes in the π-electron system, makes it possible to estimate the true localisation of the non-radiative S_1 state of carotenoids provided the lifetime of the singlet excited state is determined exclusively by the intramolecular energy transfer between the carotenoid and the tetrapyrrole pigment.[89]

3. Triplet – triplet energy transfer

Photoprotection of plant tissues from the destructive action of singlet oxygen is provided by quenching of triplet states of chlorophylls through the transfer of energy to carotenoids. In contrast to singlet – singlet energy transfer, triplet – triplet transfer is forbidden as regards the dipole – dipole mechanism and occurs exclusively in the presence of electron-exchange interactions, which demand orbital overlap of the donor and the acceptor.

The triplet – triplet energy transfer in porphyrin – carotenoid dyads can be studied by monitoring the quenching of transient absorption of the triplet state of porphyrin around ~ 440 nm and the concomitant increase in the carotenoid triplet absorption at ~ 550 nm.

The triplet – triplet energy transfer in the isomeric dyads **86c**,**d** in which the carotenoid is linked to porphyrin through the *para*- and *meta*-position of the *meso*-aryl group, respectively, was studied in order to determine structural and photophysical parameters of effective photoprotection. In these systems, electron-exchange interactions are mediated by π-electrons of the amide bonds. The rate constants for the triplet energy transfer in compounds **86d** and **86c** determined by laser-flash spectroscopy for solutions of these compounds in toluene were equal to 2×10^7 and 1×10^8 s^{-1}, respectively. The calculated yield of the singlet oxygen generated by the triplet state of porphyrin in the *meta*-linked dyad **86d** was 30%; singlet oxygen was not formed in the case of the *para*-isomer **86c**. These findings suggest that in the former case the carotenoid fails to entrap the bulk of the singlet oxygen sensitised by the attached porphyrin. As a result, singlet oxygen avoids direct contacts with the quencher even if the former is localised in immediate proximity to the latter. It thus follows that the triplet energy transfer from porphyrin to the carotenoid should proceed at a very fast rate in order to suppress completely the formation of singlet oxygen. Thus the triplet of the special pair of bacteriochlorophyll in the reaction centres of *Rhodobacter sphaeroides* is quenched by the energy transfer to the carotenoid with the rate constant $k > 10^8$ s^{-1}.

In the absence of conjugation between the chromophores, rapid triplet transfer takes place in a molecule with a folded conformation in which all the π-electron systems are in close contact with one another. Fast triplet – triplet energy transfer was observed in the porphyrin – carotenoid system **86b** characterised by good spatial orbital overlap of the two chromophores.[2,85]

The energy transfer from the triplet excited state of pyropheophorbide (Ppd) to the attached carotenoid was observed in model compounds **91a**,**b** and **94a**,**b**. It was found that the rates of energy transfer in these systems did not depend on the type of the carotenoid, but were determined by the flexibility of the bond linking the chromophores. In this case, 'through-bond' electron-exchange interactions are weak due to the presence of saturated carbon atoms between the π-systems of the chromophores and the orbital overlap required for such triplet transfer should be effected 'through-space'. However, according to ^{1}H NMR data the extended conformations of these dyads are the most stable where the carotenoids are spatially separated from pyropheophorbide. Folded conformations may appear exclusively in the case of intramolecular mobility of chromophores in solution. The molecular structures **91a**,**b** are little flexible. To some extent, this restricts their intramolecular movement, which would bring the π-systems of the two chromophores into close contact. Correspondingly, the rates of the triplet – triplet energy transfer in these compounds are lower than those in the more flexible molecules **94a**,**b**.[89]

The triplet – triplet energy transfer mediated by intramolecular movements was also observed in the porphyrin – carotenoid dyad **86f** containing flexible polymethylene spacer between the chromophores.[2] This dynamic process is similar to that observed between non-bound donors and acceptors upon collision in solution.

Fast quenching of the triplet state of the special pair in *Rhodobacter sphaeroides* is a two-step process, which includes a triplet energy transfer from the bacteriochlorophylls of the special pair to the auxiliary bacteriochlorophyll with its subsequent transport to the carotenoid.[84]

The photochemical properties of the molecular triads **98a**,**b** and **99**, which consist of a carotenoid covalently linked to porphyrin, which, in turn, is linked to a pyropheophorbide derivative (Car – P – Ppd) in the system **98** and the fullerene (Car – P – C_{60}) in the system **99**, were studied in order to elucidate the structural and dynamic parameters of multistep triplet energy transfer.[94,95]

The excitation of porphyrin or pyropheophorbide in compound **98a** dissolved in acetone results in the population of the first excited singlet state of pyropheophorbide, which accepts singlet energy from the excited porphyrin with ~ 100% efficiency (Fig. 6). Subsequent intersystem transition gives rise to the triplet state of pyropheophorbide (the quantum yield is ~ 1), which sensitises the formation of singlet oxygen in air ($k \approx 2.5 \times 10^9$ s^{-1}).

The quantum yield of the singlet oxygen in the triad **98a** (Φ = 36%) is much lower than that for the free pyropheophorbide (Φ = 80%), which reflects competitive quenching of the triplet state of pyropheophorbide in the triad by intramolecular energy

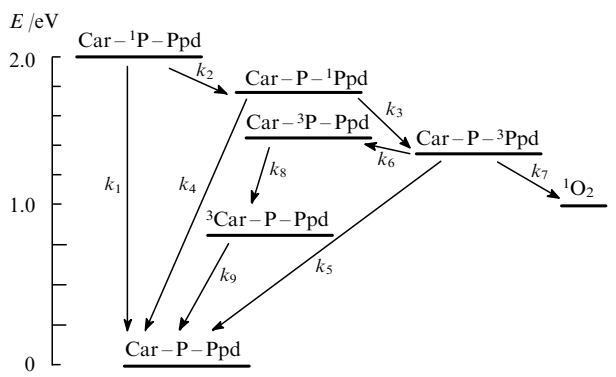
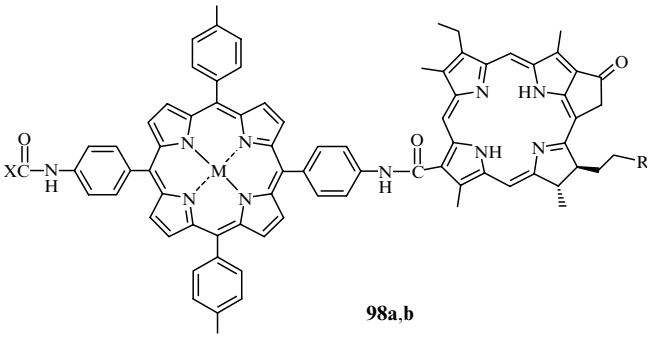


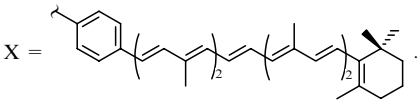
Figure 6. A scheme of energy transfer in the triad Car – P – Ppd.[94]

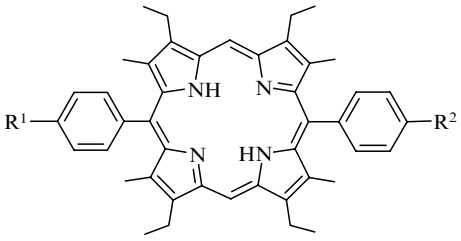


98a,b

M = 2 H (**a**), Zn (**b**); R = CO_2Me;

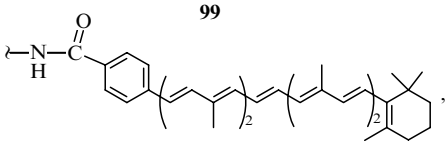
X =





99

R^1 =



R^2 = Me—N



transfer with the formation of a carotenoid triplet state. The rate constant for this triplet transfer, k_6, is equal to 2.9×10^6 s^{-1}. The linear structure of the triad prevents the appearance of conformations where orbital interactions of the carotenoid with pyropheophorbide required for the triplet–triplet energy transfer are possible. It was suggested[94] that intramolecular triplet energy transfer in compound **98a** is a two-step process. Its first step consists in the energy transfer from the triplet state of pyropheophorbide ($\sim$ 1.33 eV) to the attached porphyrin, while the second step includes fast quenching of the porphyrin triplet state formed (1.44 eV) by the carotenoid ($k_8 > 10^8$ s^{-1}) (see Fig. 6). The rate of the overall process is determined by the endoergic step of the triplet energy transfer from pyropheophorbide to porphyrin.

The temperature dependence of the formation of the carotenoid triplet state was studied in order to gain an insight into the two-step mechanism of triplet energy transfer. No triplet absorption of the carotenoid was observed upon excitation of cooled (to 77 K) solution of compound **98a** in butyronitrile, which points to the lack of the energy transfer. Consequently, this process requires sufficient activation energy for its realisation, which correlates with the putative two-step mechanism of the triplet energy transfer with the first endoergic step.

The height of the potential barrier in such endoergic transfer can be varied by chemical modification of the system. The presence of a zinc atom in the porphyrin macrocycle of the triad **98b** increases the triplet state energy of porphyrin from 1.44 to 1.59 eV with a concomitant increase in the activation energy by 0.15 eV. In this case, the transfer of triplet energy is too slow to compete with sensitisation of singlet oxygen. As a result, the carotenoid loses its ability to afford photoprotection by quenching the triplet state of pyropheophorbide.[85,94]

The quantum yield of singlet oxygen in the triad **98b** is commensurate with that obtained for the corresponding pyropheophorbide–porphyrin dyad. Consequently, in the absence of energy transfer the proximity of the carotenoid to the site of singlet oxygen generation does not provide effective photoprotection. This clearly demonstrates that rapid quenching of the triplet state of the sensitiser is a much more efficient means of photoprotection than deactivation of singlet oxygen that has already formed.[94]

The triplet excitation energy in the fullerene-containing triad **99** is transferred from the fullerene component (Car–P–$^3C_{60}$) to the carotenoid polyene resulting in the generation of state ^{3}Car–P–C_{60}. As in the previous case, the activation energy E_a = 0.17 eV is necessary for the energy transfer, which is consistent with the two-step mechanism where the energy migrates from the excited triplet state of fullerene to porphyrin with the formation of Car–^{3}P–C_{60} in a slow thermally activated step, fast transfer of energy from the porphyrin triplet to the carotenoid culminates in the generation of the terminal state.[95]

Thus, there are several strict structural and energetic limitations for the stepwise triplet energy transfer, *viz*., electronic interactions between the donor chromophore, the intermediate porphyrin and the carotenoid should be sufficiently strong; in addition, the thermodynamic barrier to migration of the triplet energy should not be too high.

In contrast to the triplet state of chlorophyll, the excited triplet state of the carotenoid does not sensitise singlet oxygen, which is a prerequisite for photoprotection. Thermodynamic analysis of this process suggests that the energy of the lower triplet state of a potential sensitiser should exceed that of the singlet oxygen (0.98 eV) for the latter could be formed. The published data on the energy of the triplet states of carotenoids are very scarce, which can be attributed to the difficulties in the detection of phosphorescence of the carotenoid chromophore.

Moore *et al*.[85] have carried out a series of photoacoustic laser-flash experiments using the dyad **86c** as an example and calculated the energy of the lowest triplet state of the carotenoid by measuring heat energy released upon relaxation of ^{3}Car–P into the ground state in solution. The triplet energy of the carotenoid determined in this way (0.64 $\pm$ 0.04 eV) is much lower than that of chlorophyll ($\sim$ 1.3 eV) and bacteriochlorophyll ($\sim$ 1 eV) in photosynthetic reaction centres. This allows directed transfer of triplet energy to the carotenoid trap, which makes the transfer fast and irreversible. Low triplet energy of carotenoids also explains the lack of sensitisation of singlet oxygen by the triplet state of the carotenoids needed for effective functioning of natural photoprotective systems.

V. Conclusion

The porphyrin-containing ensembles described in this review are convenient models for the study of photoinduced energy transfer. These data suggest that optimisation of efficiency of electronic interactions between pigments and the rates of energy transfer in these models should take into account structural characteristics altogether, such as mode and the character of substitution in macrocycles, the type of coordination metal ions, the nature and binding site of the linker, *etc*. By varying these features, it is possible to gain control over electronic and steric factors, which determine various parameters of photodynamic processes and to obtain compounds with predetermined spectral characteristics and energy levels of excited states of pigments. The data on the structure of natural light-harvesting antenna complexes combined with fundamental energy transfer theories provide a basis for the construction and fine tuning of model molecular photosynthetic systems.[2,29,35]

The use of the multistep energy transfer strategy is an efficient approach to the reproduction of natural photosynthetic processes.

The development of novel methods for the synthesis of covalently linked ensembles [27] and the principles of non-covalent self-assembly of pigments [17] has made possible the synthesis of a great variety of multicomponent structures. Preliminary reliable estimation of expected photochemical properties of each target structure allows the design of highly efficient model photosynthetic systems.[79]

The synthesis of multicomponent clusters with several isolated sets of donors which provide independent routes of energy transfer to the terminal acceptor is a promising approach to the modelling of energy transfer. Such systems possess the most efficient light-harvesting properties, although their application is limited for steric reasons. Yet another promising strategy consists in incorporation of several types of donor pigments into a single ensemble, which may lead to directed energy transfer and a sharp increase in the quantum efficiency of energy migration. The construction of such cascade ensembles has become possible owing to fine tuning of energy levels of excited states of pigments. For example, cascade ensembles may include linear compositions of porphyrin, chlorin and bacteriochlorin pigments; their longest wavelength absorption bands are shifted from 646 to 740 nm.[79]

Synthetic light-harvesting complexes reproduce only some of the structural and functional characteristics of natural objects, which opens up new possibilities for their investigation. Further approximation of artificial photosynthetic schemes to biological transmembrane energy-transducing processes is aimed at reaching a definite level of supramolecular organisation of cofactors, which is controlled by polypeptide subunits of natural photosystems. Elucidation of factors providing effective control over the rates and mechanisms of biological energy transfer occurring in the protein matrix still continues to be a central problem. Only a few synthetic models containing peptide-linked chromophores have been designed so far in order to elucidate the effects of protein components on interpigment interactions and regularities of energy transfer processes.[67, 78] However, the usefulness of this approach demands further investigations.

And, finally, it seems very tempting to use multiporphyrin ensembles in non-biological objects, such as molecular photonic and optoelectronic devices. The feasibility of incorporation of such systems into highly ordered structures, *e.g.*, liposomes, micelles, polymers and monolayers deposited onto conducting supports, significantly increases the efficiency of molecular devices due to limited intramolecular migrations of pigments. Multicomponent ensembles able to function as molecular photonic wires and optoelectronic switches have already been devised.[10, 96] Hence, the basic principles of photosynthesis can successfully be employed in the design of synthetic molecular devices. Their versatility and main characteristics are comparable to, and sometimes surpass, those of the natural systems.

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