Russian Chemical Reviews **62** (10) 963–979 (1993)
©1993 Russian Academy of Sciences and Turpion Ltd

UDC 54.07:547.567.2.655.741.577.3

Synthesis of molecular complexes based on porphyrins for the investigation of the energy transfer and primary charge separation in photosynthesis

S E Gribkova, R P Evstigneeva, V N Luzgina

Contents

I. Introduction 963
II. Methods of synthesis and photochemical properties of the model compounds 963
III. *Conclusion* 978

Abstract. Data on the synthesis, steric structures, and photochemical properties of molecular diad systems based on porphyrins as synthetic models of the reaction centre in photosynthesis are considered and treated systematically. The bibliography includes 102 references.

I. Introduction

The conversion of light energy into chemical energy has at present aroused much interest among investigators. Molecular photosynthetic systems, reproducing at a simpler level the individual stages of natural photosynthesis, are being created for the solution of this problem. The donor–acceptor systems based on porphyrin structures may serve as an example of such models.[1–3]

The most important stage in the transformation of light energy into chemical energy is the photochemical charge separation in the photosynthesis system. In nature, this problem has been solved by the creation during the evolutionary process of photosynthetic reaction centres in which charge separation takes place at a record speed. Studies in recent years have shown that synthetic molecular systems of the type D–P–Q, i.e. models containing a photosensitive pigment (P), an electron donor (D), and an electron acceptor (Q), are also capable of giving rise to the structure D^+-P-Q^- with separated charges simulating the primary charge separation in photosynthesis, where the singlet-excited porphyrin reduces the acceptor and is itself reduced by the donor. Such model systems make it possible to investigate in detail the dependence of the process itself on the distance between the donor and the acceptor, on their mutual orientation, on the free energy of the reaction, on the electronic interaction, and on the rates of electron transfer.[4–6]

All the compounds described, containing bound chromophores, are based on systems of two types: molecular diads and multicomponent structures—triads, tetrads, and pentads.

The synthetic methods for the creation of molecular assemblies[7] are discussed in the present review and the possibility of investigating the energy transfer and the primary charge separation in the photosynthesis on diad models is considered. Such models are the simplest systems for the photosynthetetic electron transfer, consisting of chromophores bound covalently to a donor or acceptor.

S E Gribkova, R P Evstigneeva, V N Luzgina Department of the Chemistry and Technology of Fine Organic Synthesis, M V Lomonosov Moscow Institute of Fine Organic Technology, prosp. Vernadskogo 86, 117571 Moscow, Fax (7-095) 430 79 83.

Received 3 May 1993
Uspekhi Khimii **62** (10) 1020–1036 (1993); translated by A K Grzybowski

II. Methods of synthesis and photochemical properties of the model compounds

1. Porphyrin dimers

Studies on the structure of the reaction centres in photosynthetic bacteria and of the mechanism of the electron transfer have shown that the reaction centre consists of six interacting tetrapyrrole pigments. It has also been established that the primary electron donor is a 'special pair' consisting of two aggregated chlorophyll molecules. The problem of current interest in the study of the primary photosynthetic process is therefore that of the creation of covalently bound conformationally-restricted structures containing two and more porphyrin units, i.e. molecular assemblies capable of participating very effectively in specific energy and electron transfer reactions.[4,8–10]

a. Methods of synthesis of porphyrin dimers

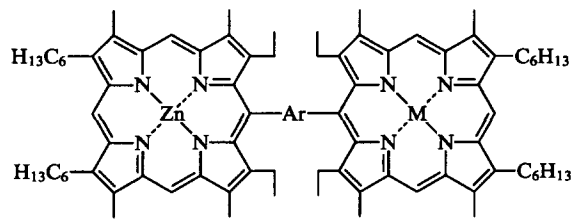
The synthesis of primary porphyrin dimers was described as early as the 1970s.[1] Since then, various multicomponent tetrapyrrole compounds have been obtained and investigated.[11–14]

It was shown that octaalkylporphyrin dimers **1a–q**,[8,9,15] **2a–o**,[16] **3a–i**,[17] and **4a–h**,[18] linked by aromatic spacers, are interesting models.

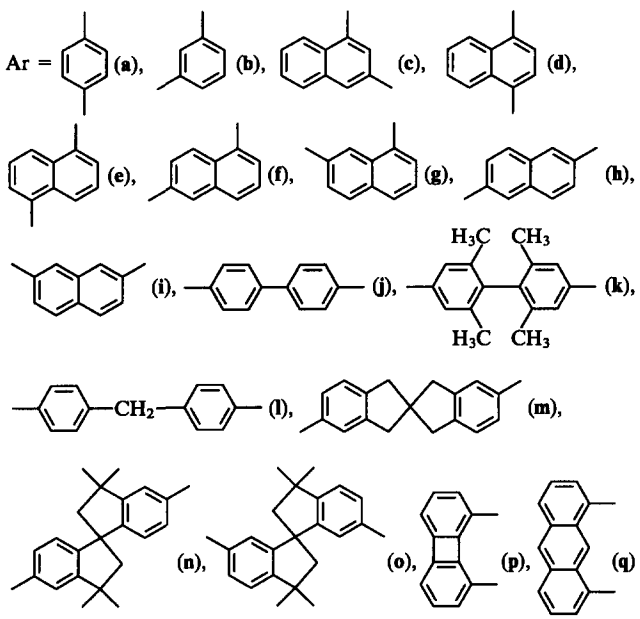
In these dimers, two porphyrin rings are held rigidly in a definite conformation as a result of steric hindrance. The aromatic spacer is perpendicular to the mean plane of the porphyrin, reducing to a minimum the direct $\pi-\pi$ interaction between the porphyrin and the connecting bridge.

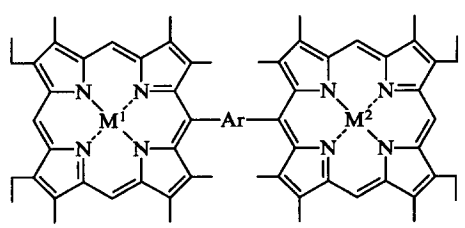
The spacer used in compounds **1m** and **1n** simulates the chromophores with a 'twist' type of conformation such as the haems and chlorophylls in natural systems, while compound **1o** serves as a model of the chromophore with the 'twist' conformation, which has partly the same geometry as the 'special pair' in the bacterial photosynthetic reaction centre. All these symmetrical porphyrins **1a–q**, **2a–o**, **3a–i**, and **4a–h** have been synthesised from the corresponding arenedialdehyde by Chang's method.[19,20]

An alternative approach has been used to synthesise the asymmetric dimer **5** (Scheme 1). Condensation of 1,19-dideoxybiladiene-ac dihydrobromide **6** with isophthalic aldehyde afforded the porphyrin **7a** with a formyl group, which was converted by the reaction with ethyl 4-ethyl-3-methyl-pyrrole-

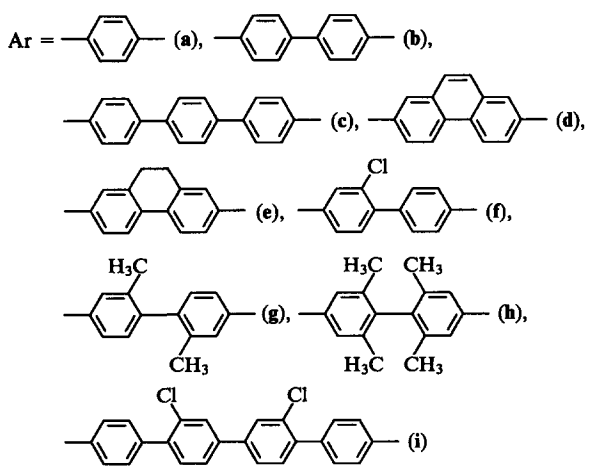


1a–q: M = 2H
2a–o: M = Fe^{III}





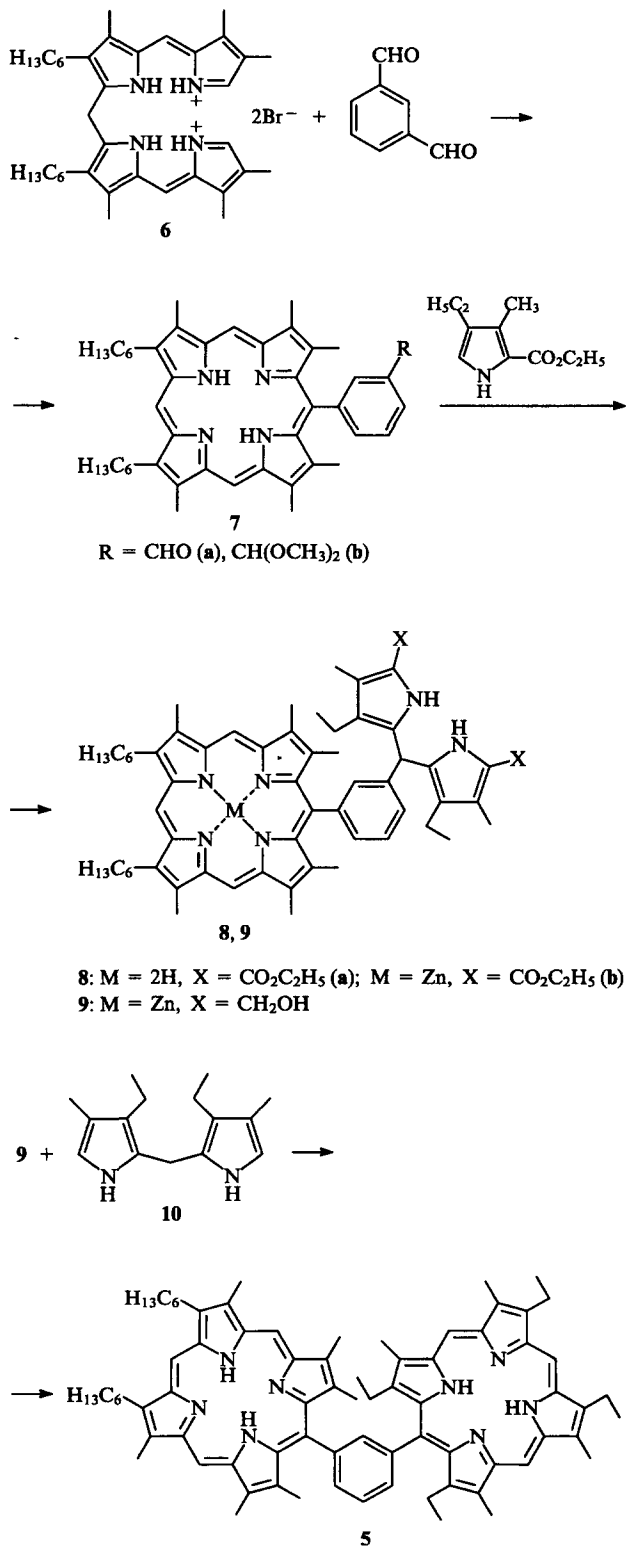
3a–i: $M^1 = M^2 = 2H$
4a–h: M^1 = Zn; $M^2 = Fe^{III}$

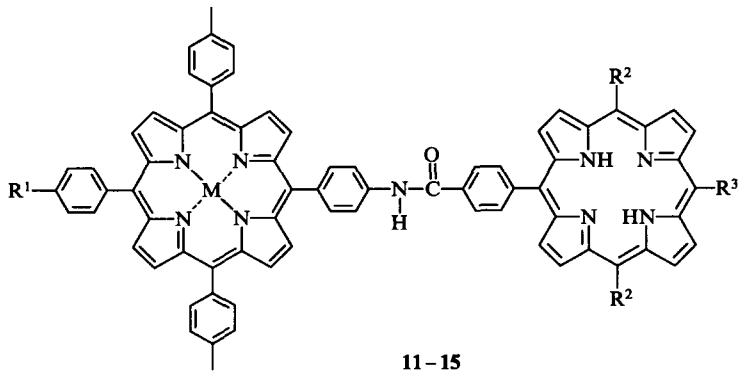


2-carboxylate into the porphyrin-dipyrrolylmethane **8a**. The latter was initially converted into the zinc complex **8b** and was then treated with $LiAlH_4$ in order to obtain the corresponding diol **9**, the interaction of which with 5,5′-unsubstituted dipyrrolmethane **10** afforded the dimer **5** in 9% yield.[9]

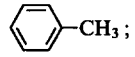
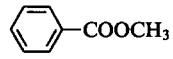
The principal task solved in relation to the given structures was the elucidation of the nature and degree of the interaction of the porphyrin components of these assemblies.

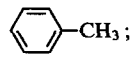
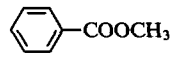
Scheme 1

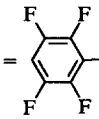


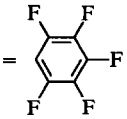


11-15

11: M = 2H; R^1 = $NHCOCH_3$;
R^2 =  ; R^3 = ;

12: M = Zn; R^1 = $NHCOCH_3$;
R^2 =  ; R^3 = ;

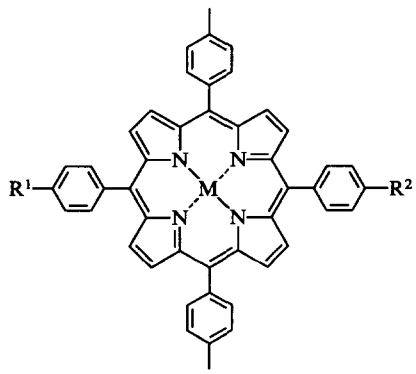
13: M = 2H; R^1 = $NHCOCH_3$; R^2 = R^3 = ;

14: M = 2H; R^1 = CH_3; R^2 = R^3 = ;

15: M = Zn; R^1 = CH_3; R^2 = R^3 = .

The porphyrin dimers **11**–**15** were used to investigate the photoinduced electron transfer and the transfer of the energy of the excited state between the porphyrins.[21]

As an example, the synthesis of the porphyrin dimer **11** is described below. The diester **16** was hydrolysed to the corresponding monoester, from which the acid chloride was obtained by treatment with thionyl chloride. The condensation of the latter with 15-(4-acetamidophenyl)-5-(4-aminophenyl)-10,20-bis(4-methylphenyl)porphyrin, which had been obtained in its turn by the partial hydrolysis of compound **17**, leads to the amide **11** in 93% yield.



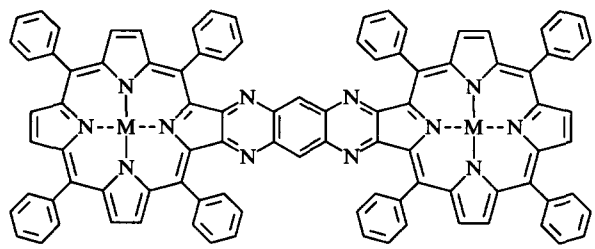
16, 17

16: R^1 = R^2 = $COOCH_3$; M = 2H;
17: R^1 = R^2 = $NHCOCH_3$; M = 2H.

The porphyrin dimer **12** was synthesised similarly in 63% yield. In this case, the acid chloride of the monocarboxyporphyrin was condensed with the zinc complex of 15-(4-acetamidophenyl)-5-(4-aminophenyl)-10,20-bis(4-methylphenyl)porphyrin.

5-(4-Methoxycarbonylphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin was obtained by Lindsay's method involving the condensation of pyrrole, pentafluorobenzaldehyde, and methyl 4-formylbenzoate with trifluoroacetic acid and subsequent oxidation of the resulting product with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, after which the ester was hydrolysed and the acid made to react with thionyl chloride. Interaction of the resulting porphyrin acid chloride with an excess of 5,15-bis(4-aminophenyl)-10,20-bis(4-methylphenyl)-porphyrin led to the diad **13**. The dimers **14** and **15** were synthesised via the same mechanism in 95% and 54% yields respectively.[21]

The steric disposition of the porphyrins in the system **18** and the distance between them (7.5 Å) are very similar to those for the central haems in the cytochrome units of the photosynthetic reaction centre of the bacterium *Rhodopseudomonas viridis*,[22] where the tetrapyrrole macrocycles are almost coplanar and are linked in such a way that the distance between the porphyrins is 7.5–8.5 Å.



18a, b

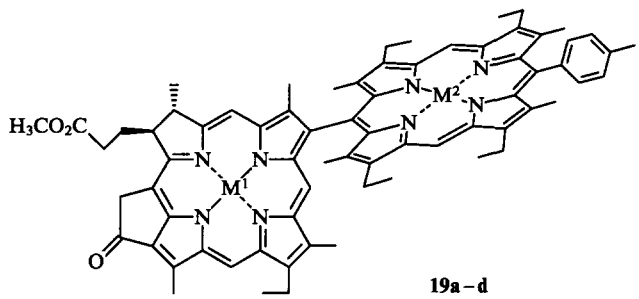
M = 2H (**a**), Zn (**b**)

The strategy used in the synthesis of such a rigidly linked bisporphyrin system involves the condensation of the α-dione (17,18-dioxo-5,10,15,20-tetraphenylchlorin) with the tetrahydrochloride of 1,2,4,5-benzotetraamine, taken in proportions of 2 : 1, in pyridine. The yield of the dimer **18** was 71%.

As already stated above, the electron donors and acceptors in the photosynthetic reaction centres are located at a fixed separation with a definite orientation relative to one another, which ensures an effective photoinduced separation of the charges and retards their recombination. However, it is believed that the intervening component located between the donor and acceptor exerts a major influence on the rate of electron transfer.

For example, in the bacterial photosynthetic reaction centre, the bacteriochlorophyll (BChl) molecule is located between the dimeric bacteriochlorophyll donor ($BChl_2$) and the bacteriopheophytin acceptor (BPh). It is believed that the 'super exchange' process, which involves the mixing of the low-energy ionic and virtual states of the intervening bacteriochlorophyll and of the selectivity excited donor, may lead to an appreciable increase in the rate of charge separation.[24]

For a better understanding of the influence of the low-energy states, formed during charge transfer, on the photophysical characteristics of the donor–acceptor systems, a series of chlorophyll-porphyrin molecules with a fixed distance between these two macrocycles were synthesised.[24]



19a–d

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

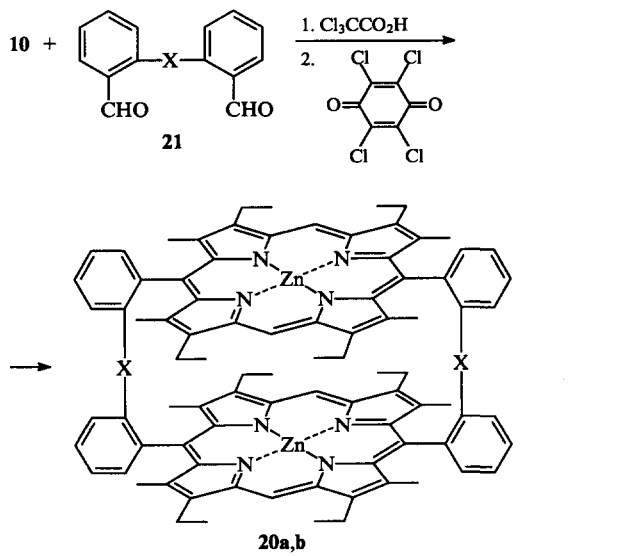
The dimer **19a** was obtained from methylpyropheophorbide *d* and *p*-toluic aldehyde by their condensation with the corresponding dipyrrolylmethane and subsequent oxidation of the resulting porphyrinogen with chloranil.

It was found that[24] the reaction of the dimer **19a** with zinc acetate at room temperature leads to the product **19d**, while compound **19b** is obtained on refluxing. After treatment of compound **19b** with a small amount of dichloroacetic acid, it loses the zinc atom more readily than the chlorin macrocycle, so that compound **19c** can be more effectively obtained from compound **19b**.

The structures of compounds **19a–d** contain a chlorophyll molecule bound rigidly to the porphyrin and the π-systems of the two macrocycles, restricted by steric interactions, are perpendicular to one another. Such orientation is preferred for the simulation of the geometrical relation between the bacteriochlorophyll donor and the spacer ($BChl_2$ and BChl) in the photosynthetic reaction centres.[23,24]

The porphyrin dimers, the macrocycles of which are in the 'face-to-face' configuration, are of interest. Compounds **20a,b** of this type have been synthesised from 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolylmethane **10** and the dialdehyde **21** (Scheme 2).[25,26]

Scheme 2



20a,b

X = $O(CH_2)_4O$ (**a**), $O(CH_2)_3O$ (**b**).

Although the yields of compounds **20a,b** are low (5% and 2% respectively), the reaction merits attention from the standpoint of its simplicity and the ease with which the starting materials can be obtained.[26]

The chemistry of porphyrin dimers and their metal complexes is at present in the stage of its establishment and a wide range of problems in this field still await solution. However, the accumulated experimental data indicate the importance of this field.[12]

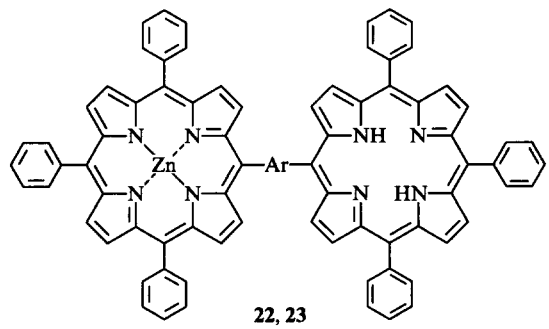
b. Photochemistry of porphyrin dimers

Considerable advances have been achieved hitherto in the study of the photochemical properties of the model compounds. Among the questions arising in the investigation of the photochemistry of such molecular structures, the most important involves the discovery of the characteristic features of the organisation of the photosynthetic apparatus ensuring a high efficiency of the charge separation.

In spectroscopic studies on the system **1a–q**, it was shown that the rates of the direct electron transfer diminish with increase in the 'centre-to-centre' distance between two porphyrins, whereas the rates of the reverse electron transfer remain almost constant [the rate constant is $k = (4$ to $6) \times 10^8\ s^{-1}$] for a series of 'centre-to-centre' distances from 8 to 22 Å and are independent of the orientation and structure of the spacer.[15]

It has also been noted that the intensity of the fluorescence of the metal-containing porphyrin is appreciably weakened, whereas the intensity of the fluorescence of the second porphyrin component is intensified, which indicates an effective transfer of excitation energy from the singlet state.[27]

Results agreeing with the data described by Osuka et al.[27] have been obtained for the dimers **22** and **23**.[28] Although Rempel et al.[28] used other porphyrin subunits, the models which they presented are similar to compounds **1b** and **11** in terms of geometrical parameters.



22, 23

22: Ar =

23: Ar =

The role of the intermediate linker in determining the electronic bonding between the electron donor and acceptor, which makes the electron transfer reaction possible, has attracted the attention of investigators in recent years. It has been found that, when the donor and acceptor are covalently bound via a rigid spacer, the rates of electron transfer increase. It has also been noted that, when aromatic spacers are employed, the rate constant depends on the distance between the chromophores to a much lesser extent than in the case where aliphatic linkers are used. Thus an increase in the length of the aromatic spacer by 4 Å leads to a decrease in the rate by a factor of 20, while in the case of an aliphatic bridge the rate falls by a factor of 100. Such an enormous difference can be explained by the fact that the electron transfer in the case of an aromatic linker proceeds via a 'super exchange' mechanism. Furthermore, it has been found that the rate constant for electron transfer depends on the electronic structure of the spacer.

All these data show that the electron transfer reactions between the spacer-bound chromophores are determined by the donor–acceptor interaction.[17]

Osuka et al.[16] described diporphyrins consisting of the hybrid metal complexes **2a–o** with different mutual orientations and a series of aromatic spacers including benzene, naphthalene, and spirobiindan fragments.

It has been demonstrated for these rigidly bound compounds that the reactions involving the separation and recombination of charges exhibit different dependences on distance. The rate constant for charge separation is related mainly to the distance and does not exhibit any dependence on orientation, whereas the rate constant for the recombination of charges is hardly influenced by either the distance or the mutual orientation.

In contrast to the well established dependence on distance, the data concerning the relation between the rate of electron transfer and the angle between the donor and acceptor are virtually lacking,[18] although Osuka et al.[16] believe that the recent studies have a bearing on precisely this problem.

The first results indicating the dependence on orientation were obtained using a series of bisporphyrins **4a–h**, in which the angle between the donor and acceptor varies systematically.

In these molecules the rate of intramolecular electron transfer changes by an order of magnitude when the angle between the porphyrin units is varied.[17,18]

In the dimers **4a–c**, the 'edge-to-edge' distances were measured and were found to be respectively 5.8, 10.1, and 14.4 Å. Studies showed that, with increase in the length of the spacer, the electron transfer rate constant diminishes: $(4 \pm 1) \times 10^{10}$, $(7 \pm 1) \times 10^{9}$, and $(1.1 \pm 1) \times 10^{9}$ s^{-1} for compounds **4a–c** respectively. However, Helms et al.[17] attribute this decrease in the rate not to the increase in the distance between the chromophores but to the break in the conjugation of the spacer owing to the biphenyl 'twist' angle (50°) for each junction between two benzene rings. The inadequate overlap of the chromophores for this value of the angle leads to an approximately sixfold decrease in the rate of electron transfer to the benzene ring, which is confirmed by the results.[17]

Much work has been done in the study of the photochemical characteristics of the dimers **11–15**.[21] The results clearly demonstrated the occurrence of the singlet–singlet energy transfer between the porphyrin components of the dimers **11–13** and **15**. The photoinduced electron transfer in compounds **13** and **15** was also observed, confirming the occurrence of electronic exchange interactions in these compounds, which probably lead to an increase in the rate constant for the singlet–singlet energy transfer. The fact that the quenching of the fluorescence is observed only in the diads where the charge-separated state is located at a lower energy level than the primary excited singlet state confirms the assignment of the fluorescence quenching process to electron transfer and not to other photophysical or photochemical processes.[21,24]

The photophysical properties of compounds **19b** and **19c** can be compared directly with the characteristics of the dimer $BChl_2$ in natural reaction centres. Spectroscopic studies of the natural reaction centre did not yield evidence for the formation of the ion pair $BChl^+-BChl^-$ in the bacteriochlorophyll dimer but made it possible to postulate that the low-energy state of the dimer with separated charges overlaps the singlet state of the dimer located at an even lower energy level. The results of the study of compound **19b** showed that the low-lying charge-separated state is located 0.1 eV above the excited singlet state and this influences strongly the rate of decomposition of compound **19b** without the formation of an ion pair. It may be that the dimer $BChl_2$ in the natural reaction centres also decomposes rapidly, like compound **19b**.

The considerable similarity of the photophysical characteristics of the dimers of the reaction centre and the heterodimers **19b,c** suggests that further studies should be carried out on these lines.[24]

2. Porphyrin-carotenoid compounds

Studies on the synthesis and properties of molecular diads consisting of a porphyrin or a chlorophyll derivative and a carotenoid polyene are of considerable interest.

Carotenoids (Car) simulate the functions of an antenna, absorbing light in the region of the solar spectrum where chlorophyll is ineffective, and transfer the energy of the excited singlet state to chlorophyll.[1,6,29–35]

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

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

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

Furthermore, they play the role of photoprotectors. On irradiation of chlorophylls, long-lived excited triplet states are generated. The chlorophyll triplets react with oxygen, forming singlet oxygen ($O_2^{*1}\Delta_g$), which is very reactive and is therefore dangerous to plant tissues.

$$\mathrm{Chl\,(BChl)} + h\nu \longrightarrow {}^1\mathrm{Chl}^*\ ,$$

$${}^1\mathrm{Chl}^* \longrightarrow {}^3\mathrm{Chl}^*\ ,$$

$${}^3\mathrm{Chl}^* + O_2 \longrightarrow \mathrm{Chl} + O_2^{*1}\Delta_g\ .$$

Carotenoid polyenes prevent the decomposition of plant tissues by singlet oxygen by 'extinguishing' the triplet state of chlorophyll before its interaction with oxygen. This energy transfer from the triplet state of chlorophyll leads to the triplet carotenoid (a harmless state) and the initial state of chlorophyll.

$$\mathrm{Chl\,(BChl)} + h\nu \longrightarrow {}^1\mathrm{Chl}^*\ ,$$

$${}^1\mathrm{Chl}^* \longrightarrow {}^3\mathrm{Chl}^*\ ,$$

$${}^3\mathrm{Chl}^* + \mathrm{Car} \longrightarrow \mathrm{Chl} + {}^3\mathrm{Car}^*\ ,$$

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

Carotenoids can also fulfil the function of photoprotectors by 'extinguishing' singlet oxygen.

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

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

It has been established that under certain conditions carotenoid polyenes can act as electron donors in photosynthetic systems, although their importance as electron donors is not known.[1,6,29–35]

In order to investigate the photochemical characteristics of carotenoids, namely their functions as photoprotectors and antennae, a series of porphyrin-polyene compounds **24–37** were synthesised.[36–41] (see over)

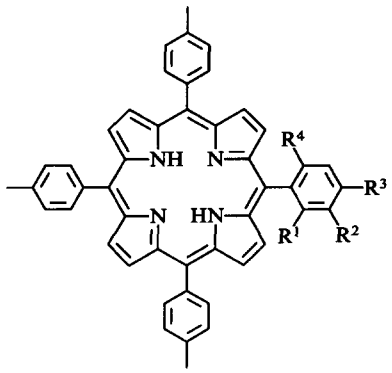
a. Methods of synthesis of porphyrin-carotenoid compounds

Compounds **24–36** have been obtained by condensing the corresponding 5-aminophenyl-10,15,20-tris(4-methylphenyl)porphyrins with the acid chloride of 7′-apo-7′-(4-carboxyphenyl)-β-carotene.

Compounds **27** and **28** were synthesised using 7′-apo-7′-(4-aminophenyl)-β-carotene and the acid chloride of the porphyrin obtained by treating 5-carboxyphenyl-10,15,20-tris(4-methylphenyl)porphyrin with oxalyl chloride.[36]

The reaction of 5-hydroxyphenyl-10,15,20-tris(4-methylphenyl)porphyrins with 7′-apo-7′-(4-iodomethylphenyl)-β-carotene leads to the model systems **29–31**.

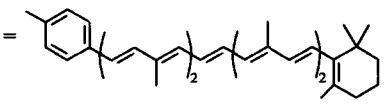
The porphyrin-carotenoid compounds **32** and **33** were obtained respectively by the interaction of dihydroxyphenyl derivatives of tetraphenylporphyrin with 7′-apo-7′-(4-iodomethylphenyl)-β-carotene.



24–37

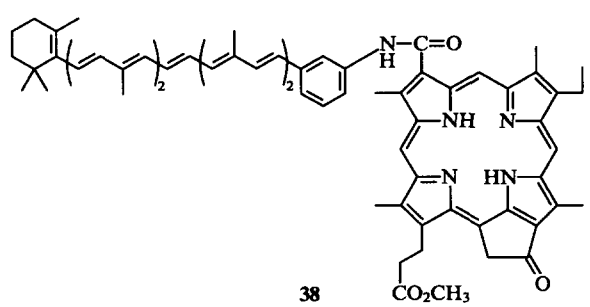
24: $R^1 = R^2 = R^4 = H$; $R^3 = NHCOX$;
25: $R^1 = R^3 = R^4 = H$; $R^2 = NHCOX$;
26: $R^2 = R^3 = R^4 = H$; $R^1 = NHCOX$;
27: $R^1 = R^2 = R^4 = H$; $R^3 = CONHX$;
28: $R^2 = R^3 = R^4 = H$; $R^1 = CONHX$;
29: $R^1 = R^2 = R^4 = H$; $R^3 = O$–X;
30: $R^1 = R^3 = R^4 = H$; $R^2 = O$–X;
31: $R^2 = R^3 = R^4 = H$; $R^1 = O$–X;
32: $R^2 = R^3 = H$; $R^1 = R^4 = O$–X;
33: $R^3 = R^4 = H$; $R^1 = R^2 = O$–X;
34: $R^1 = R^2 = R^4 = H$; $R^3 = O(CH_2)_3OCOX$;
35: $R^1 = R^2 = R^4 = H$; $R^3 = O(CH_2)_2OCOX$;
36: $R^1 = R^2 = R^4 = H$; $R^3 = COO$–X;
37: $R^2 = R^3 = R^4 = H$; $R^1 = COO$–X.

X =



Compound **34** was synthesised using the phosphonium salt of 5-[4-(3-hydroxypropoxy)phenyl]-10,15,20-tris(4-methylphenyl)-porphyrin and β-apo-8′-carotenal, while compound **35** was obtained in its turn by condensing 5-[5-(2-hydroxyethoxy)-phenyl]-10,15,20-tris(4-methylphenyl)porphyrin with 7′-apo-7′-(4-carboxyphenyl)-β-carotene in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCC).[37–39]

Carotenal, which is necessary for the synthesis of compounds **36** and **37**, was itself synthesised from α-bromo-*p*-toluic aldehyde with the aid of the corresponding phosphonium salt. The aldehyde group was protected in the form of an acetal by means of ethylene glycol. The Wittig reaction of this salt and β-apo-8′-carotenal was accompanied by the hydrolysis of the protecting group with formation of an aromatic aldehyde, which was converted into an alcohol by reduction with KBH_4. Condensation of the polyene alcohol with the acid chloride of the corresponding porphyrin afforded the molecular systems **36** and **37**.

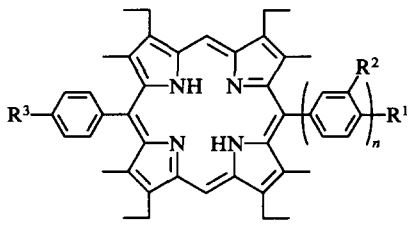


38

The synthesis of the diad **38**, in which the cartenoid is bound to a chlorophyll precursor—pyropheophorbide *a*, has been described.[42] Compound **38** was obtained from derivatives of the aminocarotenoid and pyropheophorbide *a* by the acid chloride method.

Compounds **24–38** described above are porphyrin-carotenoids with a flexible covalent bond. The appreciable conformational mobility of such systems gives rise to certain complications in photochemical studies and investigators have therefore endeavoured to create rigidly bound structures.

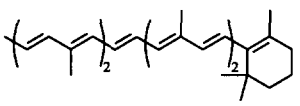
Model compounds in which the carotenoid is bound to the porphyrin by a rigid aromatic spacer have been described.[43,44]



39–42

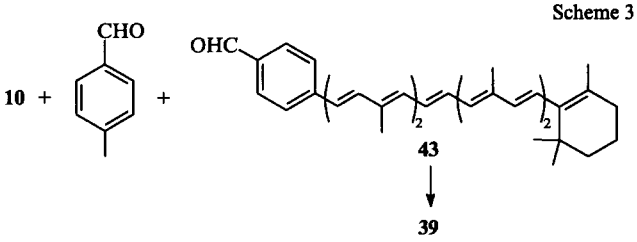
39: $R^1 = X$; $R^2 = R^3 = H$; $n = 1$;
40: $R^1 = X$; $R^2 = H$; $R^3 = CH_3$; $n = 2$;
41: $R^1 = H$; $R^2 = X$; $R^3 = CH_3$; $n = 1$;
42: $R^1 = R^3 = X$; $R^2 = H$; $n = 1$.

X =



Compounds **39–42** have been synthesised in accordance with Scheme 3. Condensation of 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolylmethane **10**, 7′-apo-7′-(4-formylphenyl)-β-carotene **43**, and 4-methylbenzaldehyde with dichloroacetic acid and subsequent oxidation of the reaction mass with *p*-chloranil led to the porphyrin-carotenoid **39** in 95% yield.

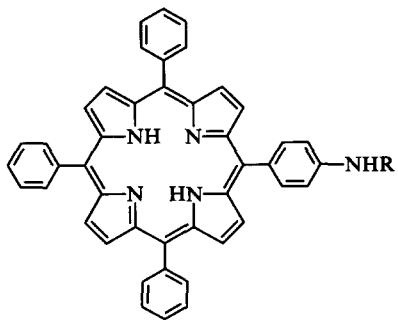
Scheme 3



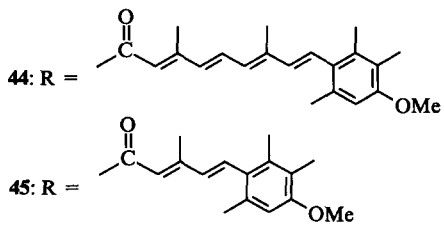
Compounds **40** and **41** were synthesised similarly in 50% and 15% yields respectively. The biscarotene-porphyrin **42** was obtained in 67% yield by condensing compounds **10** and **43**.[43]

The study of the properties of porphyrin-carotenoids has been continued[45] using the aromatic derivatives of retinoic acid, differing in the length of the conjugated bonds, as the polyenes.

The porphyrin-carotenoids **44** and **45** (see following page) were synthesised in 51% and 68% yields respectively from 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and aromatic derivatives of retenoic acid by the mixed anhydride method using ethyl chloroformate as the activating agent.[45]



44, 45



b. Photochemical studies

Not only the porphyrin but also the carotenoid is excited by light. One of the functions of the carotenoid—that of an antenna—consists in the absorption of light and the singlet–singlet energy transfer to the porphyrin.

Such intramolecular energy transfer has been detected[43] for compounds **39** and **40** from fluorescence spectra. It was noted that in tetrahydrofuran (THF) ~30% of the excitation energy absorbed by the carotenoid is transferred to the porphyrin. In the porphyrin-carotenoid diad, the fluorescence lifetime (840 ps) is appreciably reduced compared with the porphyrin H_2P (10^4 ps), indicating the existence of an additional path to the decomposition of the singlet-excited state (^1P_e) in the carotenoid-containing system. A possible explanation of this effect may be electron transfer from the carotenoid to the excited state of the porphyrin with the appearance of a short-lived charge-separated state in the form $Car^{\cdot+}-P^{\cdot-}$. If this is so, then the charge-separated state should return very rapidly to the initial state, since the spectrum of the carotenoid radical-cation is not observed even over a time interval ranging from several picoseconds to several nanoseconds.[43,46,47]

A similar phenomenon has been noted in the covalently bound porphyrin-carotenoid compounds **24**–**37**. Thus the main manifestation of the decomposition of compound **24** accompanied by fluorescence is a decrease in the fluorescence lifetime to 3.4 ns. The study of compound **24** showed that the transfer of the energy of the singlet state takes place within the limits of 10%. This relatively small amount of energy is indeed quite appreciable, since the lifetime of the excited singlet state of the carotenoid is usually several picoseconds owing to the rapid internal conversion. The successful simulation of the function of the carotenoid antenna in compound **24** is due to the interaction between the chromophores as a result of the partial overlap of the π-electron systems of the carotenoid and the porphyrin through the amide bond and the aromatic ring. In other carotenoid-porphyrin systems, a high efficiency of the energy transfer was found. For example, in compound **37** the efficiency of the singlet–singlet energy transfer is about 25%. Such high efficiency is due to the disposition of the carotenoid chain over the porphyrin in such a way that the two π-electron systems can interact with one another (within the limits of ~4 Å).[6]

The reaction centre in the photosynthetic process may be protected against decomposition by singlet oxygen, which is generated by the triplet states of chlorophylls or porphyrins. The energy transfer from the triplet state may be investigated with the aid of laser flash spectroscopy: the maximum of the porphyrin triplet absorption is at ~440 nm, whereas the absorption maximum for the carotenoid is in the region of ~540 nm. The rapid and effective transfer of the energy of the triplet state from the porphyrin to the carotenoid requires an electron exchange mechanism. In the case of compound **24** the transfer is facilitated further by the partial conjugation between the chromophores. In the porphyrin-carotenoid systems, where there is a deficiency of such conjugations, a rapid triplet transfer can nevertheless occur through a series of conformations where the π-electron systems are in contact (compound **37**).[6]

There exist two different paths for the triplet–triplet energy transfer, which probably occurs via an electron exchange mechanism: a static transfer which does not require appreciable intramolecular motion, and dynamic transfer associated with intra-molecular changes. The relative importance of the triplet energy transfer via these pathways depends on the molecular structure. The photochemical and photophysical conditions for the protection of the reaction centre against damage by singlet oxygen both in photosynthetic systems and biological organisms are determined by them.[37]

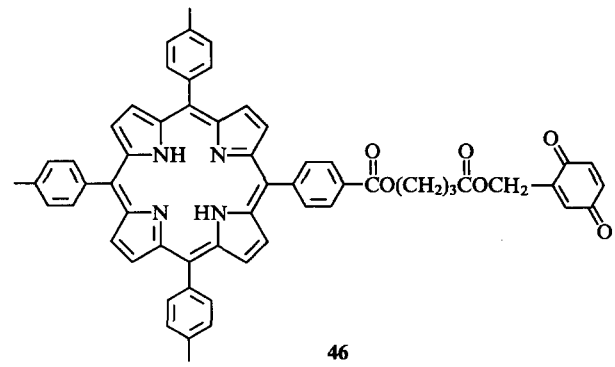
The energy transfer process has also been detected in the model compounds **44** and **45**. It was noted that the efficiency of the energy transfer increases with the length of the polyene chain from 33% to 55% on passing from system **45** to system **44**.[48,49]

Finally, most of the molecular diads obtained to simulate the photosynthesis electron transfer process are covalently bound porphyrin-quinone systems.

3. Porphyrin-quinone systems

a. Methods of synthesis

One of the first compounds of this type described was the porphyrin-quinone **46** obtained by condensing *meso*-(*p*-carboxylphenyl)tritolylporphyrin with substituted dimethoxybenzene and subsequent dimethylation and oxidation of the hydroquinone.[50]



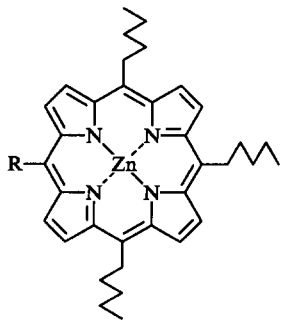
46

Data obtained by laser flash photolysis and EPR spectroscopy showed this compound can assume a conformation in which electron transfer from the porphyrin to the quinone occurs.[1,50]

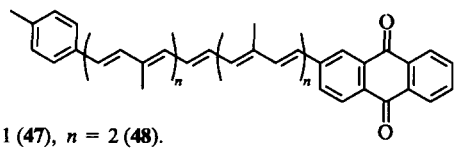
Data have been published[51] concerning two zinc complexes of the porphyrin-polyene-anthraquinone compounds **47** and **48** having five and nine double bonds between the donor and the acceptor (see over). The 'centre-to-centre' distance between the porphyrin and the quinone in these molecules is 25 Å for compound **47** and 35 Å for compound **48**.

Recent experiments have shown[6] that carotenoids usually act only as energy transfer agents in photosynthesis, although under unusual conditions there may be electron transfer from the carotenoids. However, it is believed[51] that the low electronic energy state of the polyenes can be used to create artificial photosynthetic systems which use the polyene as molecular 'conductors' to facilitate the electron transfer between the donor and the acceptor.

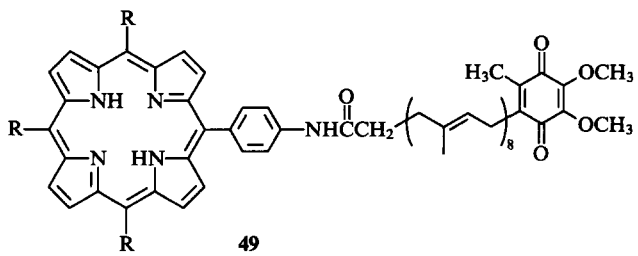
Compound **49**, containing a ubiquinone derivative, has been synthesised from 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin in order to study the photoinduced electron transfer.[52]



47, 48

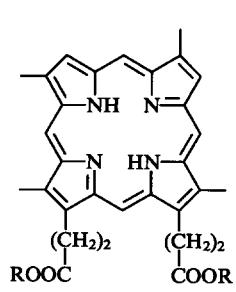
R = 

n = 1 (**47**), n = 2 (**48**).

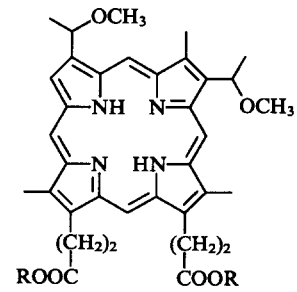


49

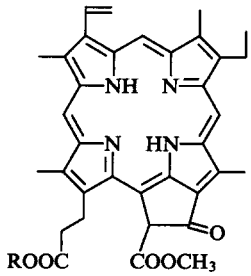
R = C_6H_5.



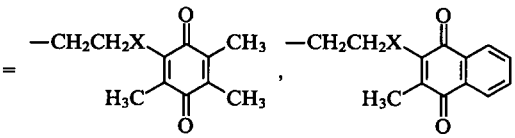
50



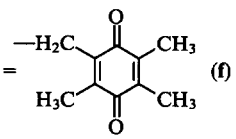
51



52

R = 

X = CH_2 (**a**), S (**b**), NH (**c**). X = S (**d**), NH (**e**).

R =  (**f**)

Ubiquinones — 2,3-dimethoxy-5-methyl-6-polyprenylbenzoquinones — are most important factors in cell metabolism; they play a significant role in the cell bioenergetics and also in the photosynthetic process.[4, 53, 54]

The addition of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin to the ubiquinone acid Q_8 has been achieved by the mixed anhydride method using ethyl chloroformate (yield 5%).[52]

The natural porphyrins **50**–**52** — deuterioporphyrin IX, haematoporphyrin IX, and pheophorbide *a* linked to a quinone by an ester bond — have been used to synthesise porphyrin-quinone compounds.[55–57] An interesting feature of these systems consists in the fact that the quinone structure in them is linked directly to the heteroatom (nitrogen and sulfur). This is due to the strategy used in the synthesis. At the same time, there is a possibility of elucidating the influence of the heteroatom on the photochemical electron transfer reaction and the dark charge recombination.

The length of the covalent chain between the quinone and porphyrin components corresponds to 5 or 7 atoms. The change in the distance between the chromophores makes it possible to determine the dependence of the degree of interaction between donor and acceptor and of the efficiency of the photoinduced charge separation on the distance: an increase in the length of the covalent chain under these conditions increases the lifetime of the separated charges, hindering their recombination.[6, 58]

Hydroxylated quinone derivatives have been obtained by adding 2-mercaptoethanol, 2-aminoethanol, and 3-aminopropanol to 2-methylnaphthoquinone and 2,3,5-trimethylbenzoquinone.

An advantage of this method of synthesis lies in the fact that the conditions in the modification of the quinone component and in its condensation with the porphyrin structure make it possible to employ unsubstituted quinones, reducing the total number of stages and simplifying the synthesis of the porphyrin-quinone derivatives.

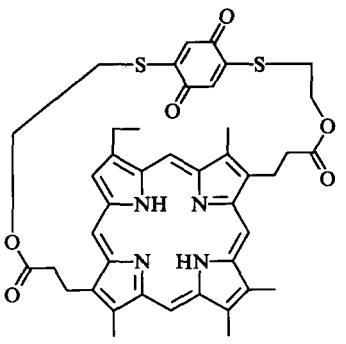
Condensation of hydroxylated quinones with porphyrins using di-*tert*-butyl pyrocarbonate (Boc_2O) and 4-dimethylaminopyridine (4-DMAP) leads to the formation of the diquinone derivatives **50**–**52** in satisfactory yields.[55–57]

However, the presence of a flexible covalent bridge in compounds **50**–**52** is responsible for their considerable conformational lability on exposure to external factors, which makes it difficult to explain the experimental data on electron phototransfer in such systems. The creation and study of model structures with a molecular geometry known beforehand therefore becomes important.[7, 59, 60]

One of the aspects of studies in this field involved the construction of models in which the quinone was strictly oriented over the centre of the porphyrin ring — the so called 'covered' porphyrins. The advantage of such model compounds arises from the possibility of monitoring during the synthetic process the relative oxidation-reduction potentials of the fragments, the distance between them, and their mutual orientation.[7]

Such a 'covered' porphyrin-quinone has been obtained from the symmetrical mesoporphyrin II and a quinone with two hydroxy-groups.[61]

In order to synthesise the 'covered' porphyrin-quinone **53**, a method was developed to obtain the bifunctional sulfur-containing electron-accepting component – 2,5-di-(2-hydroxyethylthio)-1,4-benzoquinone (DHEP). Condensation of the acid chloride formed when the mesoporphyrin II is treated with oxalyl chloride with DHEP affords the required compound **53**.

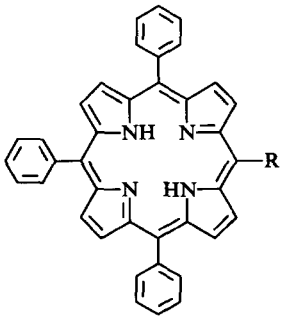


53

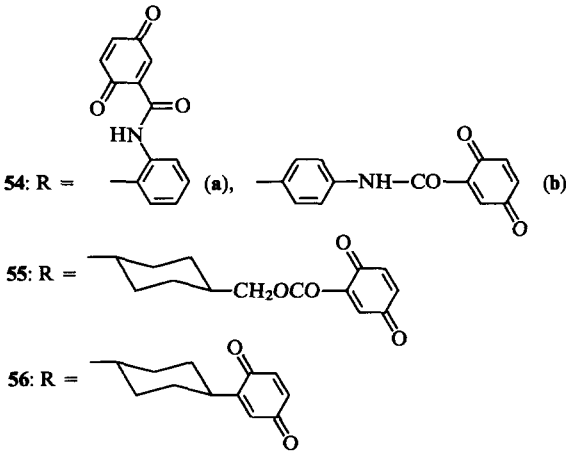
Compound **53** differs from the porphyrin-quinones known in the literature [7,59,60,62–65] by the presence of a sulfur atom linked directly to the quinone structure, which influences significantly the efficiency of the photoinduced transfer process.[61]

Another aspect ensuring the rigidity of the structure is the creation of models with a fixed distance between the porphyrin and the quinone. The synthesis of a compound meeting this requirement has been described.[66]

The mono-*o*-aminotetraphenylporphyrin, obtained by the Rothenmund reaction using pyrrole, benzaldehyde, and *o*-nitrobenzaldehyde with subsequent reduction of the nitro-group to the amino-group, was condensed with the chloride of 2,5-diethoxybenzoic acid. After selective hydrolysis and oxidation of the hydroquinone to the quinone with lead dioxide, the porphyrin-quinone **54a** was isolated.



54–56



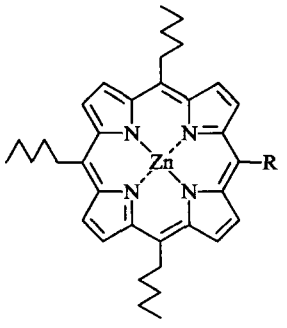
Another approach to the synthesis of a similar compound **54b** has been proposed.[67,68] Mono-*p*-aminotetraphenylporphyrin was made to react with acetylated gentisic acid in the presence of the ethyl ester of 2-ethoxy-1,2-dihydroxyquinoline. The protecting groups were then removed in a methanol solution of hydrochloric acid and the hydroquinone system was oxidised with lead dioxide to the quinone system (compound **54b**).

The porphyrin-quinone model compounds **55** and **56** have also been described.[67]

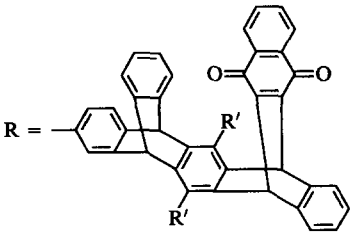
The Rothenmund condensation of pyrrole, benzaldehyde, and *trans*-4-(hydroxymethyl)cyclohexanaldehyde affords a hydroxylated porphyrin, the esterification of which with acetylated gentisyl chloride and subsequent removal of the protecting groups from the quinone component and oxidation of the hydroquinone system with lead dioxide lead to compound **55**.

In the synthesis of the porphyrin-quinone **56**, the monoester of cyclohexane-1,4-dicarboxylic acid was bound to *p*-benzoquinone by oxidative decarboxylation. After the substitution of the corresponding hydroquinone by treatment with sodium dithionite and reduction of the ester group with diisobutylaluminium hydride, the aldehyde was obtained. The latter reacts with pyrrole and benzaldehyde in the presence of atmospheric oxygen to form the required compound **56**, in which the porphyrin and quinone halves of the compound are connected by a rigid spacer.

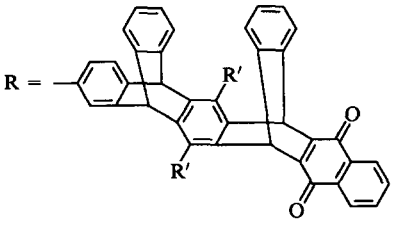
The four porphyrin-quinone compounds *syn*- and *anti*-**57** and *syn*- and *anti*-**58** with a fixed distance between the donor and the acceptor were synthesised to obtain information about the dependence of the electron transfer between the chromophores on the orientation of the quinone component.[69]



57, 58



R′ = H (*anti*-**57**), OCH_3 (*anti*-**58**).



R′ = H (*syn*-**57**), OCH_3 (*syn*-**58**).

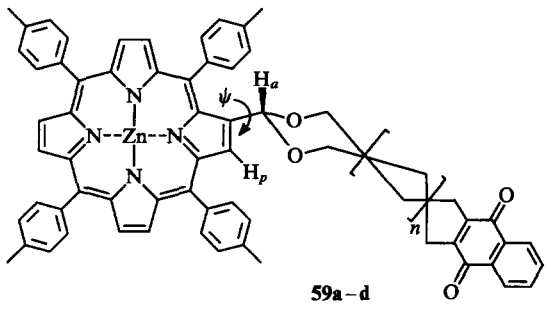
A hydrocarbon spacer—pentiptycene—was used to maintain a fixed distance and to restrict the spatial mobility between the porphyrin and the quinone in compounds **57** and **58**. The reasons for using this rigid system as a spacer are as follows: firstly, it is related to the thoroughly investigated triptycene spacer;[60,70,71] secondly, the presence of two

positional isomers, in which the porphyrin and the quinone are in the '*syn*'- or '*anti*'-positions relative to one another, makes it possible to investigate the dependence of the photoinduced electron transfer over a fixed distance on the orientation; thirdly, the presence of the central benzene ring, rigidly bound to two triptycene bridges, makes it possible to introduce substituents into the remaining free positions in this ring and to alter the influence of the ionic states of the spacer on the 'superexchange' electron transfer process.[69]

The Diels-Alder condensation of the reduced anthraquinone with the quinone and formylation of the naphthoquinone-pentiptycene derivative obtained afford a mixture of '*syn*'- and '*anti*'-aldehydes, which enter into the Lindsay reaction with 1-hexanal and pyrrole to form *syn*- and *anti*-**57** in an overall yield of 2.9%.

In order to obtain *syn*- and *anti*-**58**, anthracene was made to undergo the diene condensation with *p*-benzoquinone followed by hydrogenation of the diketone, the reaction of which with *o*-phthalaldehyde afforded 1,4-anthraquinone. The subsequent stages in the reduction of 1,4-anthraquinone to the hydroquinone and treatment with an excess of dimethyl sulfate led to the formation of the 1,4-dimethoxyanthracene derivative in 75% yield. Condensation of the latter with naphthoquinone and subsequent formylation gave rise to a mixture of the corresponding aldehydes required for the synthesis of *syn*- and *anti*-**58**. The yield of the isomers is 4.8%. The *syn*- and *anti*-isomers were separated as the corresponding zinc complexes by preparative thin-layer chromatography on silica gel.[69]

The rigid spirocyclic spacer[72] in the models **59a–d** controls the 'edge-to-edge' distance between the porphyrin and the quinone and reduces to a minimum the complications in the interpretation of the experimental data induced by the rotational degree of freedom of the porphyrin-acetal linkage (the angle ψ).

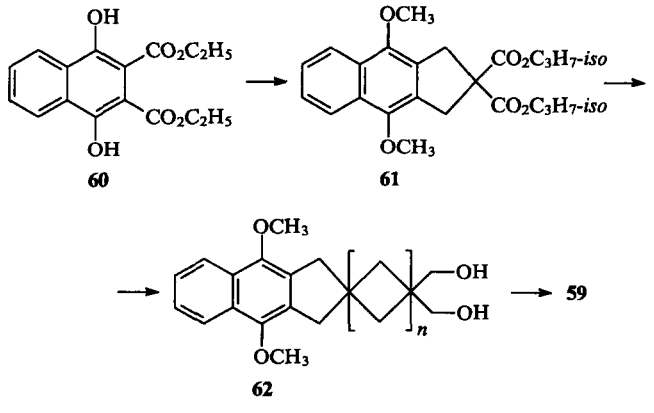


59a–d

n = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**).

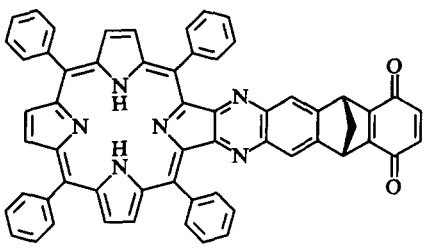
Compounds **59a–d** were synthesised in accordance with Scheme 4.

Scheme 4

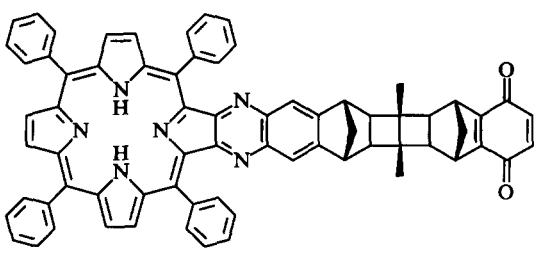


The diester **60** was treated with methyl iodide, reduced to the diol, and converted into the dichloro-derivative, which was cyclised and the resulting diisopropyl diester **61** was converted into compound **62**. The 1,4-dimethoxynaphthalene derivative **62** was oxidised to the corresponding naphthoquinone diol and condensation of the latter with 1-(dimethoxymethyl)tetra-tolylporphyrin afforded compound **59**.

The porphyrin-quinones **63** and **64**, in which the connecting bridge not only fixes rigidly the 'centre-to-centre' distance between the chromophores, amounting to 11.6 Å for compound **63** and 16.2 Å for compound **64**, but also, in contrast to other spacers, excludes the rotational degree of freedom of the quinone component, have been described.[73]



63



64

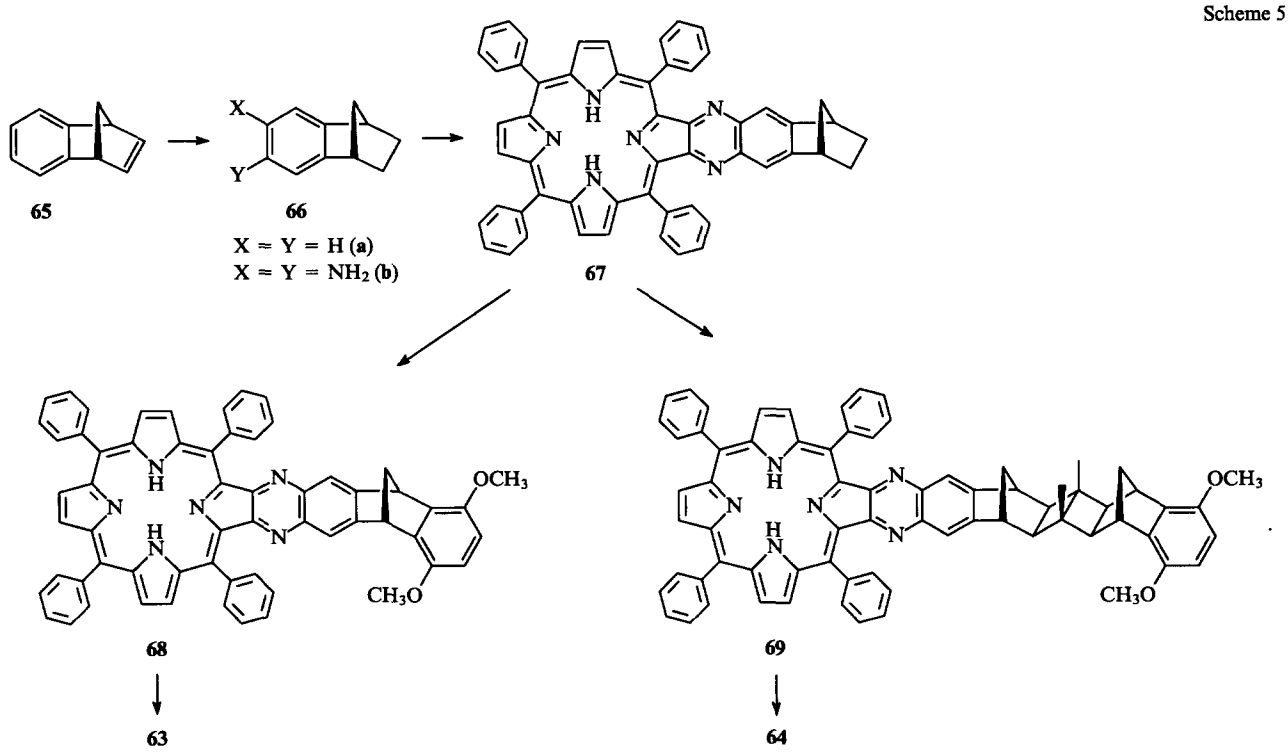
Two methods of synthesis of compounds **63** and **64**, differing in the sequence of operations, have been developed.[74]

The synthesis was begun with benzonorbornadiene **65** to which the porphyrin group was attached through the series of stages presented in Scheme 5.

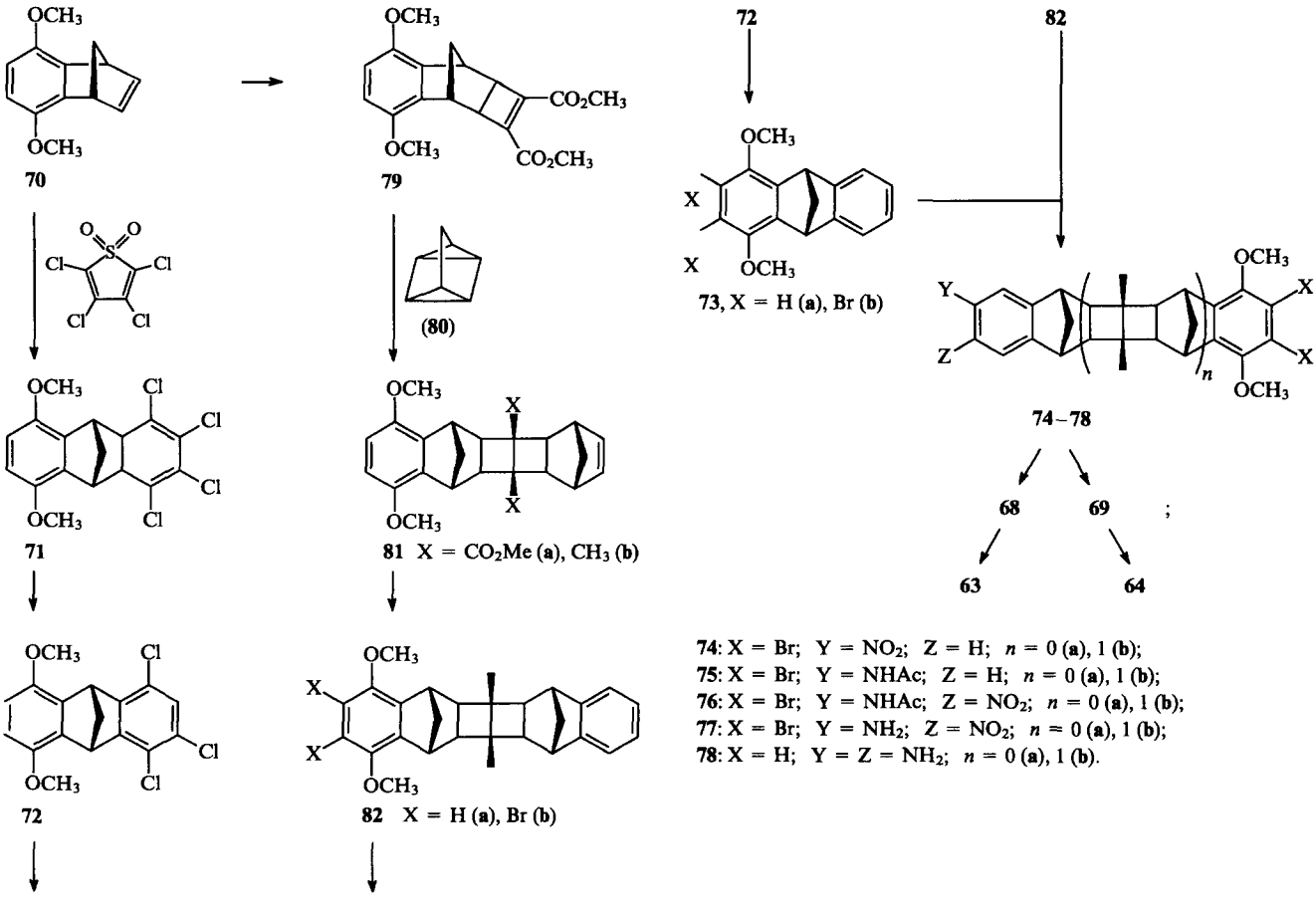
Compound **65** was initially reduced to compound **66a**, the nitration and subsequent reduction of which afforded the unstable diamino-compound **66b**. The latter was immediately treated with 17,18-dihydroxy-5,10,15,20-tetraphenylchlorin and compound **67** was obtained. The subsequent transformation of compound **67** led to the dimethoxybenzene derivatives **68** and **69**, from which the required porphyrin-quinones **63** and **64** were synthesised.

The other approach to the synthesis of such porphyrin-quinones is illustrated in Scheme 6. The key compound in this synthesis is 5,8-dimethoxybenzonorbornadiene **70**, the treatment of which with tetrachlorothiophene dioxide led to compound **71**. The dehydrohalogenation of the latter under standard conditions afforded compound **72**, the subsequent reductive dechlorination of which gave rise to the product **73a**. The protecting groups were introduced into the dimethoxybenzene ring of compound **73a** by bromination, which yielded compound **73b**. The subsequent synthetic stages presented no problems. Nitration of compound **73b** with copper nitrate led to compound **74a**, the reduction of which with zinc acetate afforded compound **75a**. The latter was subjected in its turn to nitration ($HNO_3-AcOH-Ac_2O$) with formation of compound **76a**, the treatment of which with hydrazine hydrate yielded compound **77a**. Compound **77a** was converted into compound **78a** in one stage using hydrazine hydrate and Pd/C in ethanol. The reaction of compound **78a** with the α-dione (17,18-dioxo-5,10,15,20-tetraphenylchlorin) led to compound **68** in 82% yield.

Scheme 5



Scheme 6



The following synthetic transformations were carried out in order to obtain compound **82a** from compound **70**. The ruthenium-catalysed cyclisation reaction between compound **70** and dimethyl acetylenedicarboxylate (DMAD) afforded the adduct **79**, which was subjected to a further cyclisation reaction with the quadricyclane **80**. The product **81a** was subsequently converted into compound **81b**. Further transformations were similar to those described above for the synthesis of compound **78a**. In the concluding stage, the dimethoxy-derivative **69**, synthesised from compound **78b**, was converted into the required porphyrin-quinone **64** in 62% yield.[74]

During the subsequent several years, it was shown that the rigidly bound polynorbornylenebicyclo[2.2.0]hexyl systems have a series of exceptional advantages over other hydrocarbon bridges usually employed. Firstly, the norbornyl spacer is extremely effective, which was demonstrated by numerous photoelectron and picosecond absorption spectroscopic studies. It was predicted that the intramolecular electron transfer in these systems should be especially rapid. This was subsequently confirmed. Secondly, the overall rigidity of the polynorbornylenebicyclo[2.2.0]hexyl spacers completely rules out any conformational uncertainties between the chromophores. Consequently, these spacers make it possible to achieve specific orientations and distances between the porphyrin and the quinone. Thirdly, and this is the most important advantage, there is a possibility of adding a series of chromophore rings, including benzenes, naphthalenes, anthracenes, pyrimidines, and pyrazoles, to both ends of the spacers.[73]

As already mentioned above, much attention is being devoted nowadays to the study of the role of the spacer connecting the donor and the acceptor.[23,24,69] It has been shown[73–75] that saturated hydrocarbon spacers effect electron transfer at a high rate between the oxidation-reduction sections similar to those found in the photosynthetic unit.

It has been suggested[69] that aromatic aminoacids, such as tyrosine, phenylalanine, and tryptophan, located between the electron donor and acceptor in proteins, can also accelerate the electron transfer reactions.

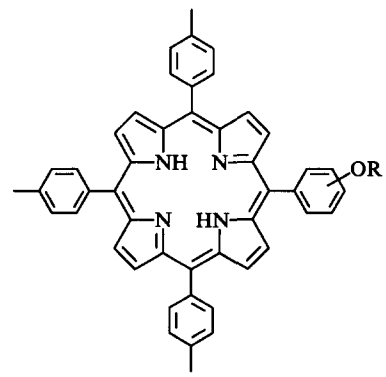
Osuka and Maruyama's study[76] is part of a research program designed to investigate the role of the aminoacid residues in biological electron transfer reactions in model compounds incorporating a porphyrin. Tyrosine was chosen among the aminoacids because it has been postulated that it performs the functions of both an electron and a proton donor.

The porphyrin-tyrosine **83** was obtained by condensing the acid chloride of the monomethyl ester of mesoporphyrin II with the ethyl ester of L-tyrosine (yield 96%). Irradiation of the porphyrin-tyrosine **83** in the presence of benzoquinone **84** in benzene by light at a wavelength > 590 nm under an argon atmosphere led to the formation of the adduct **85** in 75% yield (Scheme 7).[76]

Quinone-substituted porphyrins have been generally recognised recently as models of the primary electron transfer in the photosynthetic process. However, despite the vigorous investigation of the photoinduced electron transfer reactions between the porphyrin and the quinone, there have been only a few studies of synthetic interest.[77]

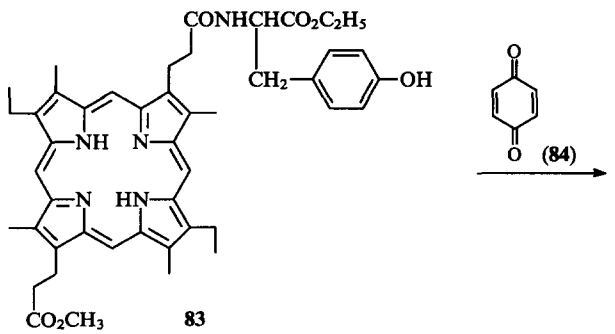
A highly effective synthesis of porphyrin-quinones, based on the self-photosensitisation of the porphyrin, has been reported.[64,76,77] The proposed method of synthesis has a number of advantages: firstly, it does not require the protection of the quinone groups and, secondly, different quinones, with a wide range of electrochemical and stereochemical properties, may be used.

Irradiation of hydroxyphenylporphyrin in the presence of benzoquinone or naphthoquinone ($\lambda > 590$ nm, Ar) in chloroform affords the quinone-substituted porphyrins **86a,b** or **87a,b** respectively.[77] The wavelength $\lambda > 590$ nm and the absence of air in the reaction solution are decisive factors for the high yield of the porphyrin-quinone compounds. Compounds **88a–c** and **89a–c** have been obtained similarly.[64]

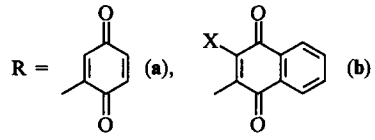


86 (*p*-OR)
87 (*o*-OR)

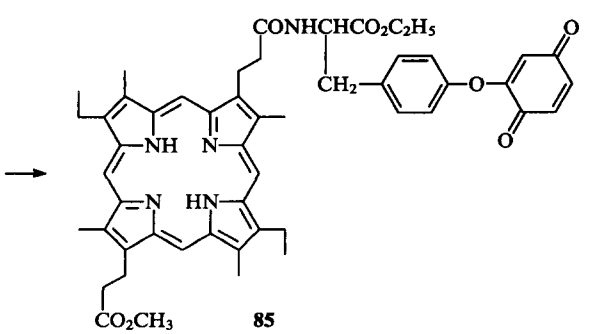
Scheme 7



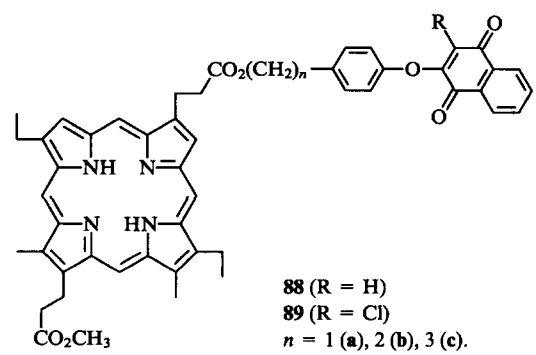
83



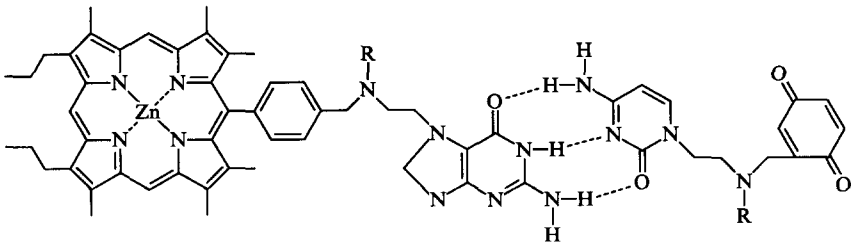
X = H, Cl, Br, CH_3



85



88 (R = H)
89 (R = Cl)
n = 1 (**a**), 2 (**b**), 3 (**c**).



90 91

R = $CH_2C_6H_4O(CH_2)_2O(CH_2)_2OCH_3$.

A multiplicity of covalently bound porphyrin-quinone derivatives have been synthesised to be used as models of the photoinduced electron transfer.

An alternative approach to the photosynthetic modelling includes the synthesis of supermolecular aggregates which are not covalently bound. The multichromophore structures of the photosynthetic reaction centres or light-absorbing antenna aggregates may serve as examples of such non-covalent binding in natural systems.

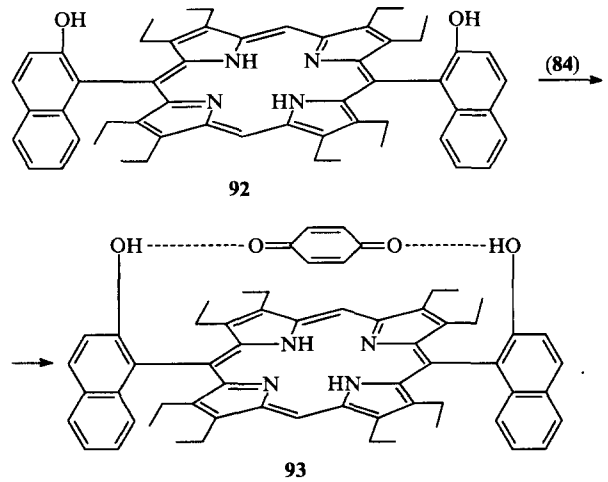
This new approach to the construction of photochemically active systems is simpler than that described above and based on the formation of covalent bonds between the chromophores.[78] The synthesis of the new noncovalently bound photosynthetic system **90**–**91** has been described recently.[79]

When the guanine and cytosine derivatives are mixed in methylene chloride, the formation of hydrogen bonds between the complementary bases is observed. The subunits of the assemblies formed in this way assume different conformations and the 'edge-to-edge' distance between them does not exceed 20 Å.

The rate constants for the binding of the guanine and cytosine derivatives in methylene chloride have been determined by ^{1}H NMR spectroscopy (k = 3100 ± 470 mol^{-1}). The 'coated' porphyrin-quinones, obtained as a result of the non-covalent binding, have been described by Aoyama et al.[80]

5,15-*cis*-Bis-(2-hydroxy-1-naphthyl)octaethylporphyrin **92** in chloroform binds selectively benzoquinone **84** with formation of the symmetrical adduct **93** of the 'face-to-face' type via hydrogen bonds (Scheme 8).

Scheme 8



92 93

The noncovalent binding used to construct porphyrin-quinones of the 'face-to-face' type is free from synthetic difficulties and the yield of complex **93** can reach 100% when a large excess of the quinone and a low temperature are used. It is noteworthy that the four free positions in the initial benzoquinone make it possible to obtain a whole series of derivatives with functional group substituents, which permits the modification of the electronic and steric structures of the quinones.[80]

Scheme 8 constitutes an extremely simple procedure for the synthesis of porphyrin-quinone compounds. On the basis of these results, one can postulate that the combination of the individual components into a single system via hydrogen bonds constitute a new and important strategy for the construction of biologically important structures[78] and in general of molecular aggregates with functional group substituents.[79,80]

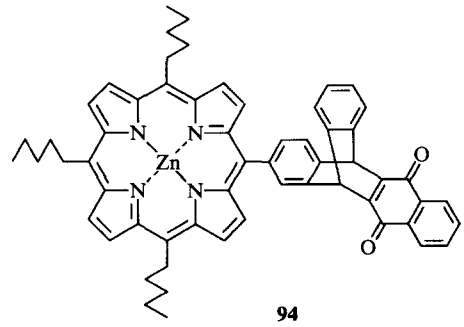
b. Photochemistry of the porphyrin-quinone compounds

In the first studies on the synthesis of porphyrin-quinone compounds, attempts were made to investigate their photochemical properties.

In the system **46** described, tetraphenylporphyrin plays the role of chlorophyll (an electron donor), while the quinone plays the role of the electron acceptor.

Important information about the photochemical processes occuring in porphyrin-quinone compounds can be obtained from the emission spectra. The fluorescence spectra of the derivatives **50a**–**f** and **51a**–**f** do not differ from the spectra of the initial porphyrins, but in their case an intense quenching of the fluorescence of the porphyrin is observed. The relative fluorescence quantum yield of the diquinone derivatives is 4%–5%. Such quenching of the fluorescence, which is characteristic of covalently bound porphyrin-quinone compounds, is a consequence of the photoinduced electron transfer from the porphyrin to the quinone.[55,56]

The introduction of the pentiptycene spacer between the porphyrin and the quinone in compounds **57** and **58** diminishes both the charge separation and charge recombination rate constants by a factor of ~10 compared with those observed for compound **94**.



94

The 'edge-to-edge' distance between the π-systems of the porphyrin and the naphthoquinone in compounds **57** and **58** is ~6 Å, while the corresponding distance in the porphyrin-quinone **94** is ~2.4 Å and, although the donor–acceptor distance has increased by 3.6 Å on passing from compounds **94** to compounds **57** and **58**, the presence of the benzene ring and of the unsaturated carbon atoms in the peptiptycene spacer in compounds **57** and **58** reduces the rate of electron transfer in these systems by more than an order of magnitude, which was in

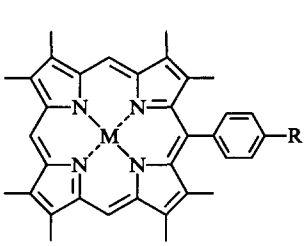
fact expected on passing from the spacer with one saturated carbon atom (compound **94**) to a spacer with two such atoms (compounds **57** and **58**).

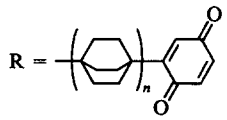
The electron transfer reactions involving the excited state and the recombination of the ion pair in the porphyrin-quinone compounds **57** and **58** exhibit an appreciable dependence on the orientation: the ion pair recombines twice as fast in the *anti*-isomers as in the *syn*-isomers. Such dependence on the orientation has also been observed for the fluorescence lifetimes of these compounds. Taking into account the nature of these dependences, one can postulate that the electron transfer is effected through the bonds of the rigid hydrocarbon spacer.[69]

A similar conclusion has also been reached by Antolovich et al.[73] The observed and theoretically predicted ability of the spacers to promote the electron transfer diminishes in the sequence spirocycles > bicyclo[2.2.2]octanes > alkanes. This result confirms the fact that the electron transfer over large distances in the porphyrin-quinone systems takes place through the hydrocarbon bonds of the spacer.[60,72]

As already stated above, the natural chromophores participating in the main stages of the photosynthetic electron transfer are represented by the special pair $BChl_2$, the excited electronic state of which transfers an electron to pheophytin in the first stage of the process at a rate of $\sim 3 \times 10^{11}$ s^{-1}, while in the second stage the charge is transferred from pheophytin to the quinone at a rate of $\sim 4 \times 10^9$ s^{-1}. It is assumed that this natural donor–acceptor pair is simulated in the second stage of the photosynthesis process by the porphyrin-quinone molecules connected by the spacer.[73] However, in only a few of the model compounds are the distance between the chromophores and the orientation of the latter similar to those in the natural photosynthetic unit.

One of the model compounds in which the spacer ensures a suitable 'centre-to-centre' distance is system **95**.[75]





95, 96

n = 1 (**95**), 2 (**96**)
M = 2H (**a**), Zn (**b**)

Compounds **95a,b** with a strong octaalkylporphyrin donor exhibit[73] high rates of charge separation in different solvents, reaching 1.25×10^{10} s^{-1}.

It is of interest to note that the rates of the photoinduced intramolecular electron transfer in the model system **95b** can exceed the rate of electron transfer from pheophytin to the quinone (4×10^9 s^{-1}) in the photosynthetic unit. Investigators attribute this to the fact that the spacer in compound **95** contains the *p*-phenylene π-system conjugated with the porphyrin. The degree of this conjugation is compensated by the marked rotation about the bond connecting these halves, which hinders the determination of the 'edge-to-edge' distance between the donor and the acceptor systems.[73] The increase in this distance and in the 'centre-to-centre' distance in compound **95** as a result of the introduction of a second bicyclooctane unit into the spacer[75] led to compound **96** in which the rate of electron transfer was found to be $< 10^7$ s^{-1}.

The results of a study of the porphyrin-quinone systems **63** and **64** have been reported.[73] This is yet another part of the studies of electron transfer over long distances. The distance (16.2 Å) between the chromophores attained in compound **64** and its zinc complex greatly exceeds the 'centre-to-centre' distances in compound **95** and **96** and in the photosynthetic BChl unit between the pheophytin and quinone halves (13–14 Å), whereas the angle between the normals to the chromophores is 40°–45° (established from extrapolated crystal structure data), which is comparable to the values for the natural systems (35° ± 6°). The rates of electron transfer in compound **95** are comparable with those obtained for compound **64** despite the greater number of saturated bonds and the greater distance in space between the chromophores, which is probably associated with the structures and configurations of the hydrocarbon spacers employed.[73] Thus the rate of charge separation in system **95** was found to be 3.7×10^7 s^{-1} in propionitrile,[75] which is comparable with the rate 3.6×10^7 s^{-1} for compound **64** in acetonitrile.[73]

The results obtained by Antolovich et al.[73], confirm and expand the data of Joran et al.,[75] who demonstrated the possibility of attaining high rates of charge separation ($> 10^9$ s^{-1}) between the porphyrin and quinone components with the aid of saturated bonds.

The system **90–91**, in which the effective specific electron transfer over long distances takes place through hydrogen bonds, has been considered.[79] In methylene chloride, the fluorescence of the porphyrin **90** is quenched following the addition of large amounts of compound **91**. The fluorescence quantum yield of compound **90** falls with increase in the concentration of compound **91** to 35%.

The binding constant for compounds **90** and **91** is 1290 ± 230 mol^{-1}, while the electron transfer rate constant is $k = (4.2 \pm 0.7) \times 10^8$ s^{-1}. These values correspond to electron transfer through bonds over a distance of 12 Å, which follows from the interpolation of data for porphyrin-quinone compounds bound covalently via a spacer.[74]

The porphyrin-quinone compound **93**, described by Harriman et al.,[79] has a 3 Å separation of the 'face-to-face' type and, as shown by UV spectroscopy, exhibits the porphyrin-quinone π–π-interaction. It was found that the fluorescence of the porphyrin-quinone **93** is fully quenched by effective electron transfer with the complex. The authors concluded that the ability of quinones to quench the fluorescence of the porphyrin **92** is determined not by their oxidation-reduction properties but by the degree of binding of the quinone to compound **92**.

4. Porphyrin compounds bound covalently to aminoacid residues — tyrosine and tryptophan

Much attention is being devoted nowadays to the study of the role of aromatic aminoacids, especially tyrosine (Tyr) and tryptophan (Trp), in the photosynthetic process. It was established previously that, together with other aromatic aminoacids, tyrosine influences the conformation of the protein component of the photosynthetic pigment,[81,82] but tyrosine began to be considered as an electron donor only in recent years.[34,82–86]

It has been shown that in the case of the photosystem II a further two cofactors, called Z* and D*, participate in the photosynthetic process in addition to chlorophyll. A series of studies[83,84,87,88] showed that the tyrosine radicals participating in electron transfer from the water-cleaving manganese-protein complex to the photochemically oxidised radical-cation P_{680}^+ are the Z* and D* cofactors. The spectroscopic characteristics of the tyrosine radicals Z* and D* of the photosystem II are being widely investigated at the present time.[89–94]

The study of the tyrosine radicals helped to discover the location of L-Tyr[162] in *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides*—it was found to be located between the special pair and the nearest cytochrome subunit.[84,85,87,95]

As already mentioned above,[69,76] aromatic aminoacids such as Tyr and Trp accelerate the electron transfer reaction between the donor and the acceptor separated by a fairly long distance—via electron binding through the corresponding orbitals.[84]

The study of the mechanism of the photocatalytic decomposition of water made it possible to discover the

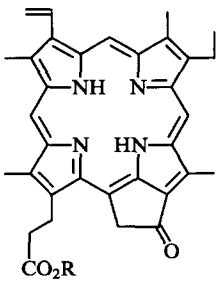
participation in this process of the manganese ion[96] located in the proteins of the photosystem II.

It is believed that tyrosine is an electron transfer agent between clusters made up of four manganese atoms in the oxygen complex formed and in the chlorophyll radical-cation P_{680}^{+} of the photosystem II of the green bacteria.[87,88,97,98] Furthermore, tyrosine-containing porphyrins exhibit a biological activity — they have a carcinostatic effect.[85,99]

The zinc complexes of pyrochlorophyllide *a* and bacteriochlorophyllide *a*, containing the methyl esters of the aminoacids Trp and Tyr in the side chain of the macrocycle and capable of being coordinated to the metal and of $\pi-\pi$ interaction with the macrocycle, have been synthesised in order to investigate the chlorophyll–protein interactions. It was shown by ^{1}H NMR spectroscopy that, as a result of the above interactions, the aminoacid residues participate in the formation of the dimeric compounds in which the methoxycarbonyl group of the aminoacid is coordinated to the metal. The planes of the macrocycles are parallel and overlap in the rings IV.[82]

Such compounds can also serve as models of the reaction centre of the chlorophyll molecule.[82,100]

The condensation of the activated ester of pyropheophorbide *a* with a fivefold excess of the methyl esters of L-Tyr or L-Trp leads to the formation of the covalently bound complexes **97a** and **98** containing aminoacid residues (2-chloro-*N*-methylpyridinium iodide in a mixture of methylene chloride and triethylamine was used as the activating agent in the synthesis of the activated ester of pyropheophorbide *a*).[82]



97–99

97: R = NH–CH(CH$_2$–C$_6$H$_4$–OH)–CO$_2$X

X = CH_3 (**a**), C_2H_5 (**b**)

98: R = NH–CH(CH$_2$–indol-3-yl)–CO$_2$CH$_3$

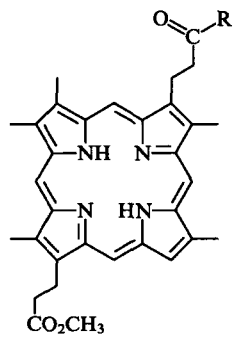
99: R = NH–CH(CH$_2$–C$_6$H$_4$–O–C$_6$H$_3$(=O)$_2$)–CO$_2$C$_2$H$_5$

Compounds **97b** and **98** were synthesised by the method described[83] (59% and 55% yields respectively) in order to carry out further investigations.[87,101]

Irradiation of compound **97b** in the benzene–acetonitrile solvent mixture in the presence of benzoquinone by light at a wavelength in excess of 590 nm under an inert gas atmosphere affords compound **99** in 56% yield, the yield depending on the quinone concentration. This concentration dependence clearly indicates that compound **99** is formed as a result of the quenching of the triplet state of pyropheophorbide-tyrosine **97b** by benzoquinone **84**. This reaction is similar to the photochemical reaction of tyrosine-mesoporphyrin II **83** with benzoquinone.[76,87,95]

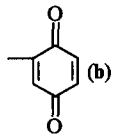
Irradiation of compounds **98** and **84** under identical conditions did not yield a photochemical product.[87]

On the other hand, pulsed irradiation (0.3 s) of a solution of compounds **100a** and **84** in deuteriobenzene at 514 nm from an argon laser in the tube of a ^{1}H NMR spectrometer (400 MHz) under an inert gas atmosphere affords compound **100b** in 8% yield.[101]



100

R = NH–CH(CH$_2$–indol-3-yl)–CO$_2$CH$_3$

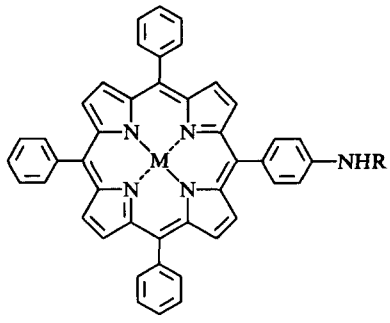
X = H (**a**),  (**b**)

Tyrosine-containing porphyrins have been synthesised from 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and di-(*tert*-butoxycarbonyl)-protected tyrosine in order to create subsequently photosynthetic model systems and to investigate their biological activity.[102]

In this case tyrosine adds to the amino-group of the porphyrin and not to the carboxy-group, as described in other studies.[76,82,87,95,101]

Two methods were used to synthesise compound **101**. The mixed anhydride method using isobutyl chloroformate as the anhydride-forming agent (the yield of tyrosylporphyrin was 26.6%) and the *N*,*N*′-dicyclohexylcarbodiimide method (yield 80%).

Trifluoroacetic acid was used to remove the protecting groups from tyrosylporphyrin **101** and compound **102a** was obtained in 92.5% yield.



101, 102

101: R = NH–CH(CH$_2$–C$_6$H$_4$–OBoc)–CO–NH–Boc

M = 2H

102: R = NH$_2$–CH(CH$_2$–C$_6$H$_4$–OH)–CO–

M = 2H (**a**), Mn (**b**)

Manganese ions were introduced by heating the porphyrin **102a** with manganese acetate and the yield of compound **102b** was 42.8%.[102]

It follows from the foregoing that the porphyrins bound to tyrosine can serve as model compounds for the investigation of the photosynthetic process and, in particular, of the mechanism of the catalytic decomposition of water and also for the elucidation of the role of tyrosine in the natural photosynthetic process, which is at present the subject of scientific discussions.

III. Conclusion

The model compounds presented above have found extensive application in the study of the primary photosynthetic process. Furthermore, they are ideal models for the determination of the main principles of the photoinduced electron transfer.[1,4,7]

Only a small proportion of the enormous amount of work carried out on the study of the natural photosynthetic process is described in the present review. Such research has become possible as a result of the development of methods for the synthesis of complex molecules, for the determination of their structures, and for the investigation of their spectroscopic, photochemical, and photoelectric properties.

References

1. D Gust, T A Moore *Science* **244** 35 (1989)
2. D Gust, T A Moore *Top. Curr. Chem.* **159** 103 (1991)
3. M R Wasielewski *Chem. Rev.* **92** 435 (1992)
4. R K Clayton *Photosynthesis: Physical Mechanisms and Chemical Patterns* (Translated into Russian; Moscow: Mir, 1984)
5. T A Moore, D Gust, P Matkis, J-C Mialocq, C Chachaty, R V Bensasson, E J Land, D Doizi, P A Liddell, W R Lehman, G A Nemeth, A L Moore *J. Am. Chem. Soc.* **109** 846 (1987)
6. D Gust, T A Moore *J. Photochem.* **29** 173 (1985)
7. V V Borovkov, R P Evstigneeva, L N Strekova, E I Filippovich, R F Khairutdinov *Usp. Khim.* **58** 1032 (1989) [*Russ. Chem. Rev.* **58** 602 (1989)]
8. A Osuka, K Maruyama *J. Am. Chem. Soc.* **110** 4454 (1988)
9. K Maruyama, T Nagata, N Ono, A Osuka *Bull. Chem. Soc. Jpn.* **62** 3167 (1989)
10. J L Sessler, M R Johnson, S E Creager, J C Fettinger, J A Ibers *J. Am. Chem. Soc.* **112** 9310 (1990)
11. D Dolphin, J Hiom, J B Paine III *Heterocycles* **16** 417 (1981)
12. V A Makarov, E I Filippovich, R P Evstigneeva, V I Bol'shakov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **29** 3 (1986)
13. V A Makarov, E I Filippovich, R P Evstigneeva *Khim. Geterosikl. Soedin.* 1190 (1987)
14. R Karaman, O Almarsson, T C Bruice *J. Org. Chem.* **57** 1555 (1992)
15. K Maruyama, A Osuka *Pure Appl. Chem.* **62** 1511 (1990)
16. A Osuka, K Maruyama, N Mataga, T Asahi, I Yamazaki, N Tamai *J. Am. Chem. Soc.* **112** 4958 (1990)
17. A Helms, D Heiler, G McLendon *J. Am. Chem. Soc.* **114** 6227 (1992)
18. A Helms, D Heiler, G McLendon *J. Am. Chem. Soc.* **113** 4325 (1991)
19. R Young, C K Chang *J. Am. Chem. Soc.* **107** 898 (1985)
20. C K Chang, I Abdalmuhdi *J. Org. Chem.* **48** 5388 (1983)
21. D Gust, T A Moore, A L Moore, F Gao, D Luttrull, J M De Graziano, X C Ma, L R Makings, S-J Lee, T T Trier, E Bittersmann, G R Seeley, M Rougee, F C De Schryver, M.Van der Auweraer *J. Am. Chem. Soc.* **113** 3638 (1991)
22. M J Crossley, P L Burn *J. Chem. Soc., Chem. Commun.* 39 (1987)
23. P Mathis *Pure Appl. Chem.* **62** 1521 (1990)
24. M R Wasielewski, D G Johnson, M P Niemczyk, G L Gaines III, M P O'Neil, W A Svec *J. Am. Chem. Soc.* **112** 6482 (1990)
25. A Osuka, F Kobayashi *Chem. Lett.* 1521 (1990)
26. A Osuka, F Kobayashi, T Nagata, K Maruyama *Chem. Lett.* 287 (1990)
27. A Osuka, K Maruyama, Y Yamazaki, N Tamai *Chem. Phys. Lett.* **165** 392 (1990)
28. U Rempel, B Von Maltzan, C Von Borczyckowski *J. Lumin.* **48** 415 (1991)
29. R J Cogdell, H A Frank *Biochim. Biophys. Acta* **895** 63 (1987)
30. D O Hall, K K Rao *Photosynthesis* (Translated into Russian; Moscow: Mir, 1983)
31. J Amesz *Prog. Bot.* **49** 87 (1987)
32. M Khaled, A Hadjipetrou, L D Kispert, R D Allendoerfer *J. Phys. Chem.* **95** 2438 (1991)
33. T Noguchi, H Hayashi, M Tasumi *Biochim. Biophys. Acta* **1017** 280 (1990)
34. B Demming-Adams *Biochim. Biophys. Acta.* **1020** 1 (1990)
35. H Hayashi, S V Kalaczkowski, T Noguchi, D Blanchard, G H Atkinson *J. Am. Chem. Soc.* **112** 4664 (1990)
36. D Gust, T A Moore, A L Moore, C Devadoss, P A Liddell, R Hermant, R A Nieman, L J Demanche, J M De Graziano, I Gouni *J. Am. Chem. Soc.* **114** 3590 (1992)
37. D Gust, T A Moore, R V Bensasson, P Mathis, E J Land, C Chachaty, A L Moore, P A Liddell, G A Nemeth *J. Am. Chem. Soc.* **107** 3631 (1985)
38. R V Bensasson, E J Land, A L Moore, R L Crouch, G Dirks, T A Moore, D Gust *Nature (London)* **290** 329 (1981)
39. A L Moore, A Joy, R Tom, D Gust, T A Moore, R V Bensasson, E J Land *Science* **216** 982 (1982)
40. G Dirks, A L Moore, T A Moore, D Gust *Photochem. Photobiol.* **32** 277 (1980)
41. A L Moore, G Dirks, D Gust, T A Moore *Photochem. Photobiol.* **32** 691 (1980)
42. P A Liddell, D Barrett, L R Makings, P J Pessiki, D Gust, T A Moore *J. Am. Chem. Soc.* **108** 5350 (1986)
43. A Osuka, H Yamada, K Maruyama *Chem. Lett.* 1905 (1990)
44. A Osuka, H Yamada, K Maruyama, N Mataga, T Asahi, I Yamazaki, Y Nishimura *Chem. Phys. Lett.* **181** 418 (1991)
45. E I Filippovich, R P Evstigneeva, V N Luzgina, T G Egorova, N R Kurdyumova, I E Mikerin, S M Makin *Zh. Obshch. Khim.* **60** 2511 (1990)
46. D Gust, T A Moore, P A Liddell, G A Nemeth, L R Makings, A L Moore, D Barrett, P J Pessiki, R V Bensasson, M Rougee, C Chachaty, F C De Schryver, M Van der Auweraer, A R Holzwarth, J S Connolly *J. Am. Chem. Soc.* **109** 846 (1987)
47. T A Moore, D Gust, G Dirks, G A Nemeth, A L Moore, P A Liddell, R V Bensasson *NATO ASI Ser. C, N 214 (Supramol. Photochem.)* 263
48. N A Sadovnikova, N D Gudkov, Yu M Stolovitskii, V N Luzgina, E I Filippovich, R P Evstigneeva *Dokl. Akad. Nauk SSSR* **312** 481 (1990)
49. V N Luzgina, S E Gribkova, R P Evstigneeva, N D Gudkov, N A Sadovnikova, G D Olovyanishnikova, Yu M Stolovitskii, N F Neznaiko, in *Tezisy Dokladov Mezhdunarodnoi Konferentsii po Fotosintezu i Fotobiologii, Pushchino, 1991* (Abstracts of Reports at the International Conference on Photosynthesis and Photobiology, Pushchino, 1991) p. 49
50. J L Y Kong, P A Loach *J. Heterocycl. Chem.* **17** 737 (1980)
51. M R Wasielewski, D G Johnson, W A Svec, K M Kersey, D E Cragg, D W Minsek, in *Photochemical Energy Conversion* (Eds J R Norris, D Meisel) (Amsterdam: Elsevier, 1989) p. 135
52. R P Evstigneeva, V N Lusgina, E I Filippovich, S E Konanykhina, in *The 15th International Symposium on Macrocyclic Chemistry, Odessa, 1990 (Abstracts of Reports)* p. 68
53. T Heinis, S L Chowdhury, S L Scott, P Kebarle *J. Am. Chem. Soc.* **110** 400 (1988)
54. A I Kozhukhova, E A Obol'nikova, G I Samokhvalov *Zh. Org. Khim.* **24** 1778 (1988)
55. V V Borovkov, E I Filippovich, R P Evstigneeva *Khim. Geterosikl. Soedin.* 608 (1988)
56. V V Borovkov, A A Gribkov, R P Evstigneeva, I A Struganova, G V Ponomarev, G V Kirillova, B V Rozynov, P V Bondarenko, R A Zuborev, A N Knysh *Khim. Geterosikl. Soedin.* 1324 (1991)
57. V V Borovkov, A A Gribkov, A N Kozyrev, A S Brandis, A Ishida, Y Sakata *Bull. Chem. Soc. Jpn.* **65** 1533 (1992)
58. M Migita, T Okada, N Mataga, S Nishitani, N Kurata, Y Sakata, S Misumi *Chem. Phys. Lett.* **84** 263 (1981)
59. B Morgan, D Dolphyn, in *Metal Complexes with Tetrapyrrole Ligands* (Berlin: Springer, 1987) Vol. 1, p. 115
60. M R Wasielewski, in *Photoinduced Electron Transfer, Part A* (Eds M A Fox, M Chanon) (Amsterdam: Elsevier, 1988) p. 161
61. V V Borovkov, R P Evstigneeva, E I Filippovich, B V Rozynov *Dokl. Akad. Nauk SSSR* **308** 871 (1988)
62. J S Lindsey, J K Delaney, D C Mauzerall, H Linschitz *J. Am. Chem. Soc.* **110** 3610 (1989)
63. D Mauzerall, J Weiser, H Staab *Tetrahedron* **45** 4807 (1989)
64. A Osuka, K Maruyama *Tetrahedron* **45** 4815 (1989)
65. J K Delaney, D C Mauzerall, J S Lindsey *J. Am. Chem. Soc.* **112** 957 (1990)
66. I Tabushi, N Koga, M Yanagita *Tetrahedron Lett.* **20** 257 (1979)
67. J Von Gersdorff, M Huber, H Schubert, D Niethammer, B Kirste, M Plato, K Mobius, H Kurreck, R Eichberger, R Kietzmann, F Willing *Angew. Chem.* **102** 690 (1990)

68. F Von Lehdzian, J Schlupmann, J Von Gersdorff, K Mobius, H Kurreck *Angew. Chem.* **103** 1536 (1991)
69. M R Wasielewski, M Niemczyk, D Johnos, W A Svec, D Minsek *Tetrahedron* **45** 4785 (1989)
70. M R Wasielewski, M P Niemczyk *J. Am. Chem. Soc.* **105** 5043 (1984)
71. M R Wasielewski, M P Niemczyk, W A Svec, E B Pewitt *J. Am. Chem. Soc.* **107** 1080 (1985)
72. S Knapp, T G M Dhar, J Albaneze, S Gentemann, J A Potenza, D Holten, H J Schugar *J. Am. Chem. Soc.* **113** 4010 (1991)
73. M Antolovich, P Keyte, A Oliver, M Paddon-Row, J Kroon, J Verhoeven, S Jonker, J Warman *J. Phys. Chem.* **95** 1933 (1991)
74. M Antolovich, A M Oliver, M N Paddon-Row *J. Chem. Soc., Perkin Trans. 2* 783 (1989)
75. A R Joran, B A Leland, G G Geller, J J Hopfield, P B Dervan *J. Am. Chem. Soc.* **106** 6090 (1984)
76. A Osuka, K Maruyama *J. Chem. Res. (S)* 286 (1987)
77. A Osuka, S Morikawa, K Maruyama, S Hirayama, T Minami *J. Chem. Soc., Chem. Commun.* 359 (1987)
78. P Tecilla, R Dixon, G Slobodkin, D Alavi, D Waldeck, A Hamilton *J. Am. Chem. Soc.* **112** 9408 (1990)
79. A Harriman, Y Kubo, J Sessler *J. Am. Chem. Soc.* **114** 388 (1992)
80. Y Aoyama, M Asakawa, Y Matsui *J. Am. Chem. Soc.* **113** 6233 (1991)
81. M F Perutz *Br. Med. Bull.* **32** 195 (1976)
82. S G Boxer, R R Bucks *Isr. J. Chem.* **21** 259 (1981)
83. B A Barry, G T Babcok *Proc. Natl. Acad. Sci. USA* **84** 7099 (1987)
84. R Huber *The EMBO J.* **8** 2125 (1983)
85. Jpn. Appl. 62-33 180; *Ref. Zh. Khim.* 9O153P (1988)
86. P J Nixon, X-S Tang, J T Trast, D A Chisholm, B A Diner *Photosynth. Res.* **34** 87 (1992)
87. K Maruyama, H Yamada, A Osuka *Photochem. Photobiol.* **53** 617 (1991)
88. C B Buser, B A Diner, G W Brudvig *Photosynth. Res.* **34** 87 (1992)
89. D Le Nouen, J Marko, G Vermeersch, N Febvay-Garot, A Lablache Combiner, M Persce-Fauvet, A Gaudermer *J. Phys. Org. Chem.* **3** 69 (1990)
90. S Shochat, J Schutrups, S Otte, B Vrieze, R Bos, P Gast, A J Hoff *Photosynth. Res.* **34** 124 (1992)
91. B Svensson, L Davidsson, C Tommos, J Smith, W Vermaas, S Styring *Photosynth. Res.* **34** 140 (1992)
92. Y Kodera, K Takura, H Mino, A Kawamori *Photosynth. Res.* **34** 136 (1992)
93. H Mino, Y Kodera, A Kawamori *Photosynth. Res.* **34** 136 (1992)
94. C W Hoganson, G T Babcock *Photosynth. Res.* **34** 148 (1992)
95. K Maruyama, H Yamada, A Osuka *Chem. Lett.* 833 (1989)
96. M A Shafiev, S I Allakhverdiev, V V Klimov, in *Tezisy Dokladov Vsesoyuznoi Konferentsii po Preobrazovaniyu Svetovoi Energii v Fotosinteziruyushchikh Sistemakh i Ikh Modelyakh, Pushchino, 1989* (Abstracts of Reports at the All-Union Conference on the Transformation of Light Energy in Photosynthesising Systems and Their Models, Pushchino, 1989) p. 114
97. P J Van Leeuwen, M H Vos, H J Van Gorkom *Biochim. Biophys. Acta* 173 (1990)
98. C Jegerschold, H Agren, S Styring *Photosynth. Res.* **34** 150 (1992)
99. Jpn. Appl. 64-61 481; *Ref. Zh. Khim.* 19O155P (1990)
100. V N Luzgina, E I Filippovich, R P Evstigneeva *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **30** 3 (1987)
101. A Osuka, K Maruyama *Chem. Lett.* 1853 (1986)
102. S E Gribkova, V N Luzgina, R P Evstigneeva *Zh. Org. Khim.* **24** 758 (1993)