Reviews

Synthesis and photochemical properties of porphyrin-quinone compounds

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The results of studies on the synthesis of porphyrin-quinone compounds and investigation of their photochemical properties are summarized. Effects of various factors (the redox potential, the distance between donor and acceptor moieties, their spatial orientation, the free energy of the reaction, and solvents) on the photoinduced electron transfer in these model systems are discussed. The dyad and triad model systems have been compared. The possibility of using these systems for modeling the primary steps of photosynthesis is discussed.

Key words: porphyrins, quinones, porphyrin-quinones; dyads, triads, electron transfer, energy transfer; modeling of photosynthesis.

It is known that photosynthesis involves a stage of energy conversion of the singlet excited state of the "special pair" into the energy of the chemical potential realized in the form of the long-lived state with transmembrane separated charges. The transmembrane charge separation is realized with a quantum yield close to unity due to multistep electron transfer from the photoexcited "special pair" to an acceptor of quinone nature.[1–3] A considerable portion of the energy of the primarily excited state of the chlorophyll dimeric pair is stored in this state.

Several photosynthetic bacterial reaction centers have been studied recently by X-ray diffraction analysis.[3–5] Information about the structures of the reaction centers are widely used for designing model systems.

The conversion of light energy into the chemical energy of model systems based on porphyrins reproduces particular stages of photosynthesis at a simpler level. Examples of these systems are porphyrin-quinone compounds in which electron acceptors (quinones) are covalently linked with photoinduced electron donors (porphyrins).[1–3]

In this review, the results of our works on the preparation of various porphyrin-quinone compounds based on both natural and synthetic porphyrins and our study of their photochemical properties are generalized.

Porphyrin-quinones are the unique family of the compounds, which make it possible to study purposefully and model the primary stages of photosynthesis and to create in the future systems of solar energy conversion based on these compounds. The special selection of such parameters as redox potentials of components, the distance between chromophores, and solvent provides a high efficiency of the spatial charge separation and storage of a considerable portion of the photon energy. In order to perform these studies, one should synthesize porphyrin-quinone compounds containing covalent bridges of various types between components of model

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systems, which determine both spatial and structural organization of molecules.

All compounds obtained in our works can be divided into two main types: dyads and triads. Dyads (P—Q) are covalently linked porphyrin and quinone. Triads contain an additional electron donor (D—P—Q) or acceptor (P—Q—Q) along with porphyrin and quinone.

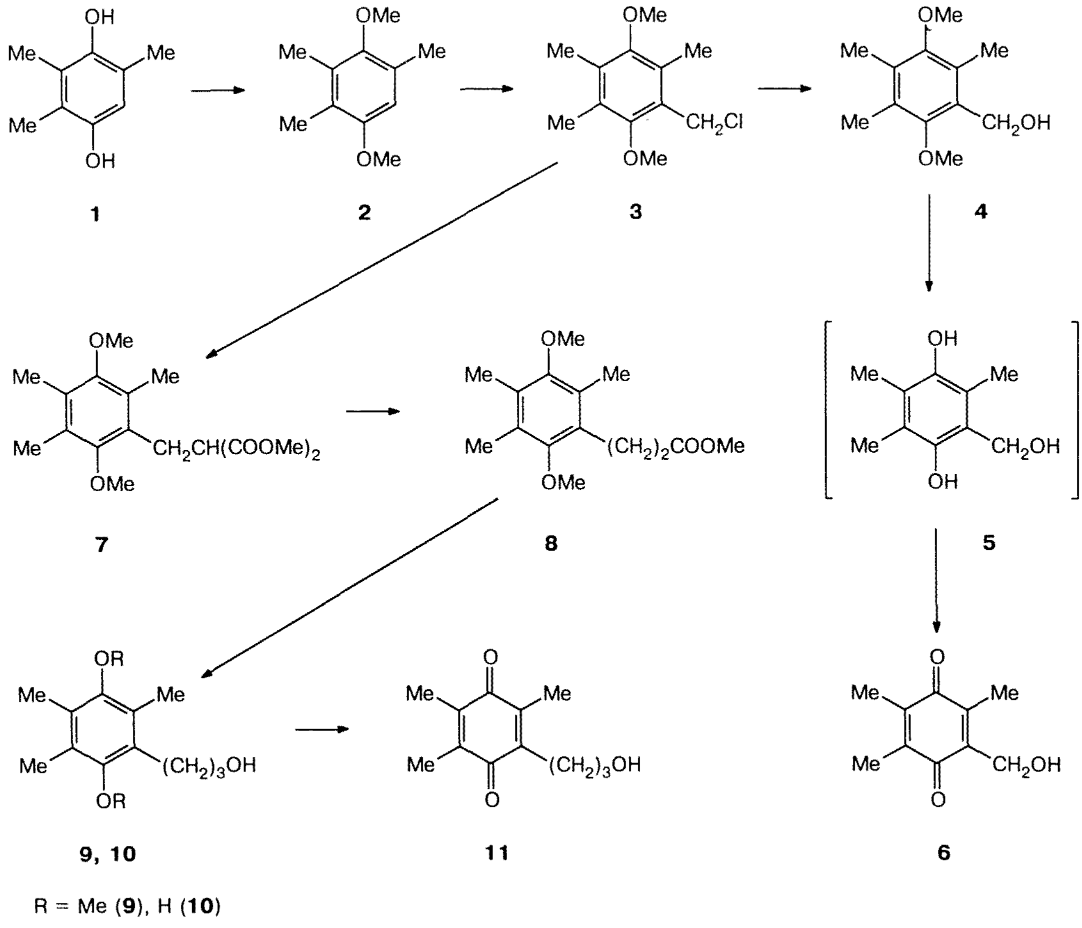
Synthesis of porphyrin-quinones with a flexible covalent bridge between porphyrin and quinone

At first we synthesized the simplest structures of porphyrin-quinones with a flexible covalent bridge based on natural porphyrin, deuteroporphyrin IX (DP IX).[6—8] The photosensitizer and the electron acceptor in these model systems are linked by the residues of propionic acid of porphyrins with the corresponding hydroxyl-containing quinones (Schemes 1 and 2, compounds **6**, **11**, **14a—c**, and **17a—c**).

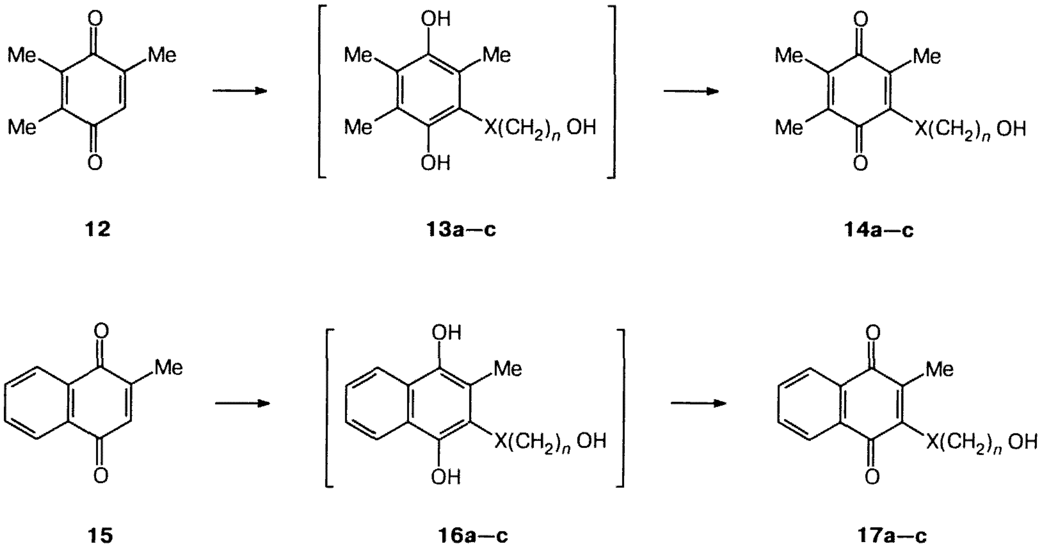
Synthesis of hydroxyl-containing quinones. Quinone components[8] **6** and **11** (see Scheme 1) were prepared from trimethylhydroquinone **1**. The total yields of compounds **6** and **11** were 25 and 7 %, respectively, calculated per hydroquinone.

One of the possible methods for controlling the intramolecular electron transfer is the change of the redox potential of an acceptor. This determines the significance of the synthesis of quinones **14a—c** with a heteroatom, nitrogen or sulfur (see Scheme 2). In addition, there is a possibility to change the benzoquinone structure for the naphthoquinone one and to prepare the corresponding compounds **17a—c**. It is known that quinones react readily with various derivatives containing mercapto or amino groups *via* the mechanism of nucleophilic substitution.[11,12] We used this property for introducing the hydroxyl group into the quinone structure accompanied by the change in the redox potential (see Scheme 2).[6,7] The addition of 2-mercaptoethanol, 2-aminoethanol, and 3-aminopropanol to the initial quinones **12** and **15** results in the formation of intermediate hydroquinones **13a—c** and **16a—c**, which oxidize *in situ* to substituted quinones **14a—c** and **17a—c**, respectively. The yields of products **14a** and **17a** are 91 and 55 %, respectively. The addition of amino alcohols under similar conditions occurs in low yields (8—25 %).

Scheme 1



Scheme 2



a: X = S, n = 2
b: X = NH, n = 2
c: X = NH, n = 3

In fact, values of the redox potentials of the quinones synthesized, measured as polarographic potentials of half-waves ($E_{1/2}$) in DMF and characterizing the electron-accepting activity of the quinones, differ substantially. They increase in the series **17b** < **14b** < **11** = **6** < **17a** < **14a** and equal −0.99, −0.96, −0.84, −0.74, and −0.70 V (relative to SCE), respectively.

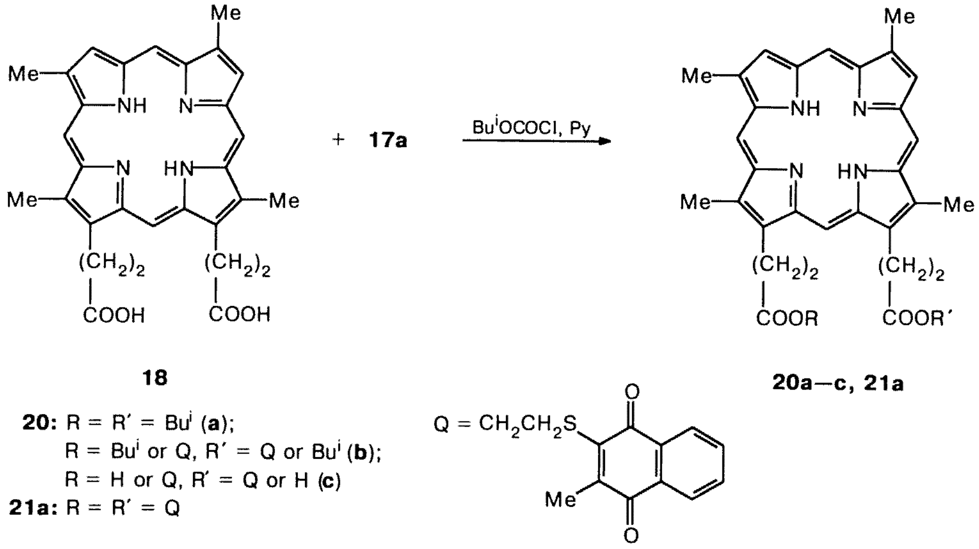
Synthesis of porphyrin-quinone compounds. The main problem at the next stage of the synthesis was the condensation of porphyrins and quinones to form the ester bond[6—8] (Scheme 3). DP IX (**18**) obtained from protohemin IX (**19**) by the Fischer method[13] was chosen as the carboxyl component. The condensation was performed by the method of mixed anhydrides using one of three reagents: (1) di-*tert*-butylpyrocarbonate (Boc_2O), (2) pivaloyl chloride (PivCl), and (3) isobutylchloroformate (Bu^iOCOCl) (Schemes 3 and 4).[6—8] The direction of the reaction depends strongly on the method of activation. The action of PivCl in anhydrous THF in the presence of pyridine at −10 °C results in the formation of a mixture of mono- and disubstituted derivatives **20c** (68 %) and **21a** (5 %). Despite a fourfold excess of quinone **17a**, the main reaction product was monosubstituted porphyrin-quinone **20c**. This can be likely explained by steric factors. When Bu^iOCOCl was used under similar conditions (see Scheme 3), diisobutyl ester **20a** (6 %), a mixture of the isomers of positions 6 and 7 of isobutylquinone diester **20b** (11 %), monosubstituted derivative **20c** (9 %), and target product **21a** (53 %) were isolated and identified.[6]

According to the data of TLC, the synthesis of diquinone derivatives **21a—h** using Boc_2O (see Scheme 4) in the presence of 4-*N*,*N*′-dimethylaminopyridine (DMAP) and pyridine occurs *via* the following scheme: monoester is formed mainly at the beginning of the reaction, and disubstituted compounds **21a—h** are formed in 1 h. The yields of products **21a—h** are 60—90 %, which are considerably higher than those obtained using other activating agents.[6—8]

Of the three considered methods for activation of the carboxyl group, the activation by Boc_2O is most promising, because it provides a high selectivity of the process and high yields of target products, and the reaction occurs under milder conditions and with a sufficiently high rate.

The data of ^1H NMR spectroscopy confirm completely the structure of the compounds synthesized and allow one to draw a preliminary conclusion about the relative orientation of the porphyrin and quinone moieties of products **21a—h**. The positions of the signals of the protons of the porphyrin ring and its nearest substituents in the ^1H NMR spectra of compounds **21a—h** are almost the same compared to those of the corresponding signals of dimethyl ester of DP IX. At the same time, porphyrin-quinones are characterized by considerable upfield shifts of the signals of protons of the quinone moieties relative to the signals of initial quinones **6**, **11**, **14a—c**, and **17a—c** (*cf.* Refs. 6—8, 14). This effect is caused by the influence of the magnetic anisotropy of the porphyrin macrocycle and depends substantially on the distance between chromophores.[1,2,6—8,14] The singlets of methyl groups of the quinone moieties in porphyrin-quinones **21a—h** demonstrate the upfield shifts by 0.27—1.52 ppm. Shortening of the bond by two

Scheme 3

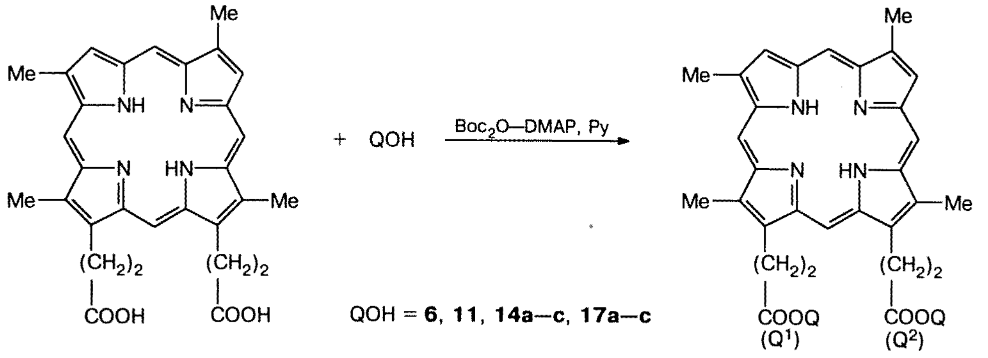


18

20a—c, 21a

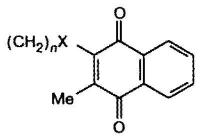
20: R = R' = Bu^i (**a**);
R = Bu^i or Q, R' = Q or Bu^i (**b**);
R = H or Q, R' = Q or H (**c**)
21a: R = R' = Q

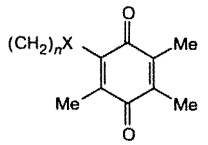
Scheme 4



18

21a—h

21	Q	X	*n*
a		S	2
c		NH	2
e		NH	3

21	Q	X	*n*
b		S	2
d		NH	2
f		NH	3
g		CH$_2$	0
h		CH$_2$	2

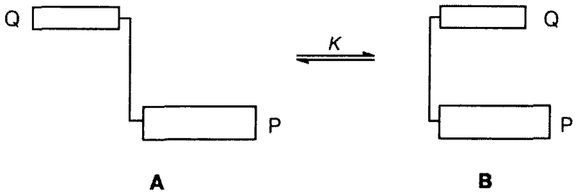
methylene groups in compound **21g** results in a decrease in the effect of magnetic anisotropy of the porphyrin cycle on the change in the chemical shifts (Δδ) of protons of the quinone moiety. It is likely that the longer chain allows the quinone moiety to approach closer the center of the porphyrin ring. In addition, the mutual orientation of the moieties changes, which also affects the Δδ value of the signals of the quinone moiety and enlarges the range of shifting the signals of methyl groups as the spacer chain lengthens.

The comparison of the ^{1}H NMR spectra of compounds **21a—h** makes it possible to follow the changes in the spatial structure caused by the existence of the heteroatom. The degree of the influence of the heteroatom on the distance between the quinone moiety and the porphyrin plane can be estimated by the Δδ value. The degree of overlapping decreases in the following series of porphyrin-quinones: **21h** (contains no heteroatom) → **21d** (nitrogen-containing) → **21b** (sulfur-containing).

The ^{1}H NMR spectra of compound **21e** have been studied to elucidate the spatial organization of porphyrin-quinones.[14] The two naphthoquinone moieties in a molecule of compound **21e** (Q^1 and Q^2) are nonequivalent due to the asymmetry of porphyrin. Therefore, the signals of methyl protons are manifested as two singlets with substantial upfield shifts compared to the spectrum of initial quinone **17c**. The signals of aromatic protons of the quinone moieties are the complex unresolved multiplet in the range of 7.3—7.8 ppm.

On the one hand, the changes in the chemical shifts observed ($\Delta\delta_{obs}$) are sufficiently high, which proves unambiguously the existence of the interaction between the porphyrin and quinone moieties. On the other hand, their values are considerably lower than the $\Delta\delta$ values for protons of quinone moieties in "capped" porphyrin-quinones in which quinone is linked by two or more covalent bridges with the porphyrin macrocycle and is arranged above its center.[15,16]

Two explanations for the difference observed have been suggested. First, porphyrin-quinone can exist in the conformation in which quinone moieties are arranged considerably farther from the porphyrin center than in "capped" porphyrin-quinones. Second, two equilibrium conformations, "open" (**A**) and "closed" (**B**), that rapidly transform into one another can exist:



In this case, the chemical shifts in the ^{1}H NMR spectrum of compound **21e** are the weighted-means of the shifts in each of the conformations:

$$\delta_{obs} = p_A\delta_A + p_B\delta_B,$$

where p is the relative population of the corresponding conformation.

When the second situation is realized, the δ_{obs} values should depend on the temperature, because its change results in the change in relative populations of the conformations. It can be seen from the temperature dependence of $\Delta\delta_{obs}$ presented in Fig. 1 that the decrease in the temperature results in the substantial increase in $\Delta\delta_{obs}$. The limiting changes in the chemical shifts of methyl groups are close to the $\Delta\delta$ values of quinone moieties in "capped" porphyrin-quinones.[15,16] This allowed one to draw a conclusion that the geometry of "closed" conformer **B** is close to that of "capped" porphyrin-quinones. It is reasonable to expect that two quinone moieties in the "closed" conformation of molecule **21e** are localized at the different sides of the plane of the porphyrin cycle due to steric reasons.

The analogous measurements performed in other inert solvents ($CDCl_3$, toluene-d_8) have shown that the geometry of the "closed" conformation and the thermodynamics of the $\mathbf{A} \rightleftharpoons \mathbf{B}$ equilibrium are almost independent of solvent.[14]

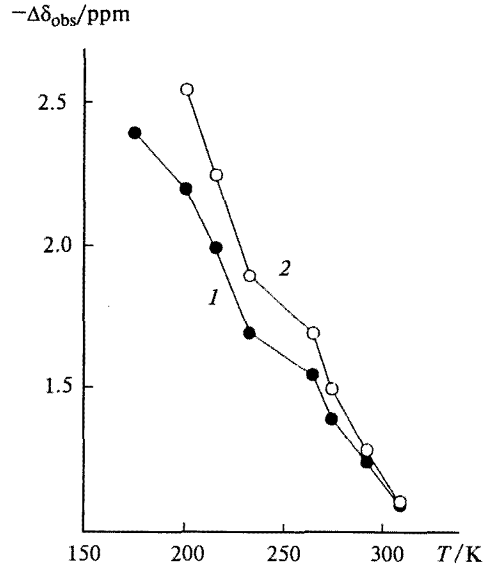


Fig. 1. Temperature dependence of the difference in the observed chemical shifts ($\Delta\delta_{obs}$) of methyl protons in the ^{1}H NMR spectra of compounds **21e** and **17c**: *1*, Q^1; *2*, Q^2.

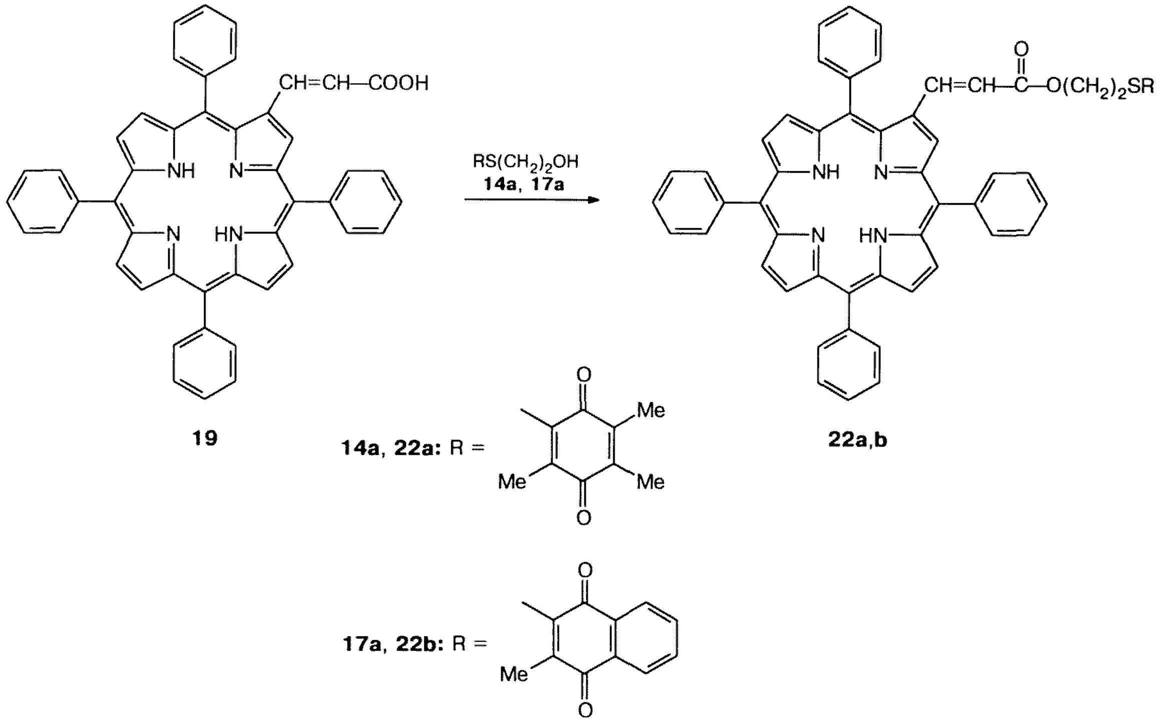
The results of the studies testify that there is a conformational equilibrium in porphyrin-quinones with flexible covalent bridges. It is of interest that the preferable conformation in the system studied depends on the temperature: at 20 °C, as follows from the comparison of the observed and limiting changes in the chemical shifts ($\Delta\delta_{obs}$ and $\Delta\delta^\circ$), the "open" conformation predominates, while the "closed" conformation becomes more populated at low temperatures.[14]

Quinone derivatives[9] **22a,b** were synthesized from 2-(2-carboxy)vinyl-5,10,15,20-tetraphenylporphyrin (**19**) obtained by the procedure described previously[10] (Scheme 5) in order to estimate the effect of the arrangement of quinone in the porphyrin ring of tetraphenylporphyrin on its physicochemical and photochemical properties. In order to form the covalent bond between porphyrin and quinone, the carboxyl group of the residue of acrylic acid at the β-position of the pyrrole ring of porphyrin was esterified by thio-substituted derivatives of benzo- and naphthoquinones (**14a** and **17a**, respectively) by the method of mixed anhydrides using Boc_2O (see Scheme 5).

As in the ^{1}H NMR spectra of porphyrin-quinones **21a—h**, the signals of protons of the quinone moiety of compounds **22a,b** shift upfield relative to the signals of the initial quinones, which is caused by the effect of magnetic anisotropy of the porphyrin ring and testifies that the quinone moiety is localized near the porphyrin plane.[6—9,14]

Porphyrin-quinones **24a—f** (Scheme 6)[17] were synthesized in order to elucidate the effect of substituents in the porphyrin ring on the spatial organization of porphyrin-quinones and on the photoinduced electron trans-

Scheme 5



19

22a,b

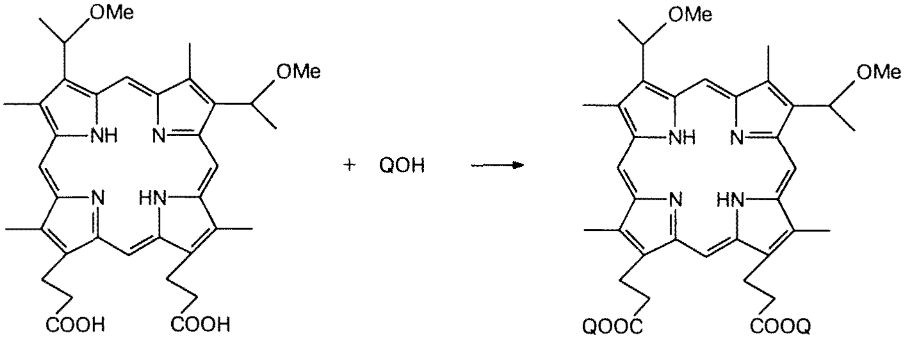
14a, 22a: R =

17a, 22b: R =

fer in the system. Dimethyl ether of hematoporphyrin IX (**23**) was chosen as a carboxyl component, because it contains methoxyethyl groups at positions 2 and 4 of porphyrin, its oxidation potential is higher, and, hence, its electron-donating properties are more efficient than those of DP IX.

The method of mixed anhydrides using Boc$_2$O as an activating agent was used for the formation of the ester bond (see Scheme 6). It has been shown by TLC that the reaction is considerably (by 4—6 times) faster than in the case of DP IX and is totally complete after 15—30 min. After purification, the yields of products **24a—e**

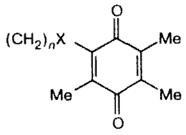
Scheme 6

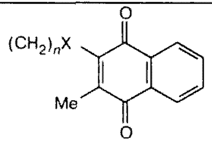


23

QOH = **6**, **11**, **14a,b**, **17a,b**

24a—f

24	Q	X	*n*
a	 	S	2
b		CH$_2$	2
e		NH	2
f		CH$_2$	0

24	Q	X	*n*
c	 	S	2
d		NH	2

are 67—76 %. The only exception is compound **24f** (34 %), which is likely related to its lability.

In the ^1H NMR spectra of compounds **24a—f**, the signals of protons of the porphyrin cycle are characterized by almost the same chemical shifts as in the spectrum of the initial porphyrin, while the signals of protons of the quinone moiety shift upfield relative to the signals of the initial quinones, which testifies that the quinone moiety of the molecule approaches the porphyrin plane.[6—9,14,17] The $\Delta\delta$ value is maximum for the signals of protons of the quinone moiety in the spectrum of compound **24b** that contains no heteroatoms in the side chain of quinone. The existence of the heteroatom results in a decrease in $\Delta\delta$ associated with the removal of quinone moieties from the porphyrin plane. Sulfur-containing porphyrin-quinones **24a,c** have lower $\Delta\delta$ values than nitrogen-containing compounds **24d,e**. Considering compounds **24a—d**, including benzoquinone and naphthoquinone structures, it should be emphasized that naphthoquinone derivatives **24c,d** are characterized by higher $\Delta\delta$ values than benzoquinone derivatives **24a,b**.

The comparison of the ^1H NMR spectra of derivatives **24a—f** and their analogs based on DP IX shows that the $\Delta\delta$ values of protons of the quinone moiety of derivatives **24a—f** are lower than those of derivatives of DP IX.[7,17] It is likely caused by steric hindrances appeared when quinones approach to the porphyrin plane, because the porphyrin cycle contains methoxyethyl groups at positions 2 and 4.

Of numerous donor-acceptor systems used for modeling photosynthetic processes, only several models containing natural chlorins, including pheophorbide *a*, are described.[1—3] The use of pheophorbide *a* as a photoinduced electron donor makes it possible to compare parameters of electron transfer in porphyrin- and pheophorbide-quinones for better understanding the process of charge separation in photosynthesis and to choose more efficient chromophores for using in photosynthetic model systems.

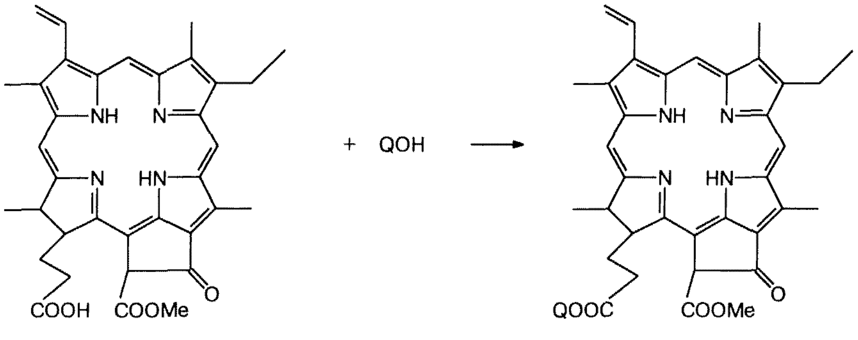
Pheophorbide-quinones **26a—e** were prepared from pheophorbide *a* (**25**) and hydroxyl-containing quinones **11**, **14a,b**, and **17a,b** (Scheme 7).[18] In order to form the covalent bond between chlorin and quinone, the carboxyl group of the residue of propionic acid of pheophorbide *a* was esterified by hydroxyl-containing quinones **11**, **14a,b**, and **17a,b** by the method of mixed anhydrides using Boc_2O.

The yields of products **26a—e** after chromatographic purification were 15—26 %.[18] The lower yields of pheophorbide-quinones **26a—e** compared to those obtained for the corresponding porphyrin-quinones **24a—e** are likely caused by the lability of **26a—e** during the chromatographic purification, because, according to the data of TLC, these were the main products in the reaction mixture.

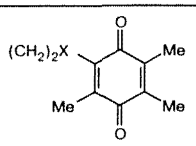
The positions of the signals of protons of the chlorin cycle in the ^1H NMR spectra of compounds **26a—e** are almost the same as those in the spectrum of the initial pheophorbide *a* ($\Delta\delta$ = −0.01 to +0.18 ppm), while the signals of protons of the quinone moiety shift upfield relative to the signals of the initial quinones.[6—8,14,17]

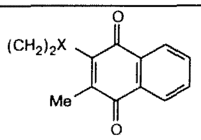
Analysis of the ^1H NMR spectra of derivatives **26a—e** and their analogs **24a—e** based on hematoporphyrin IX shows that the $\Delta\delta$ values of protons of the quinone moiety of pheophorbide-quinones **26a—e** are lower than those of the corresponding protons in the spectra of compounds **24a—e**.[17,18] This can be caused by both the lower ring current of the chlorin system compared to that of the porphyrin system and an increase in the distance between the chlorin and quinone

Scheme 7

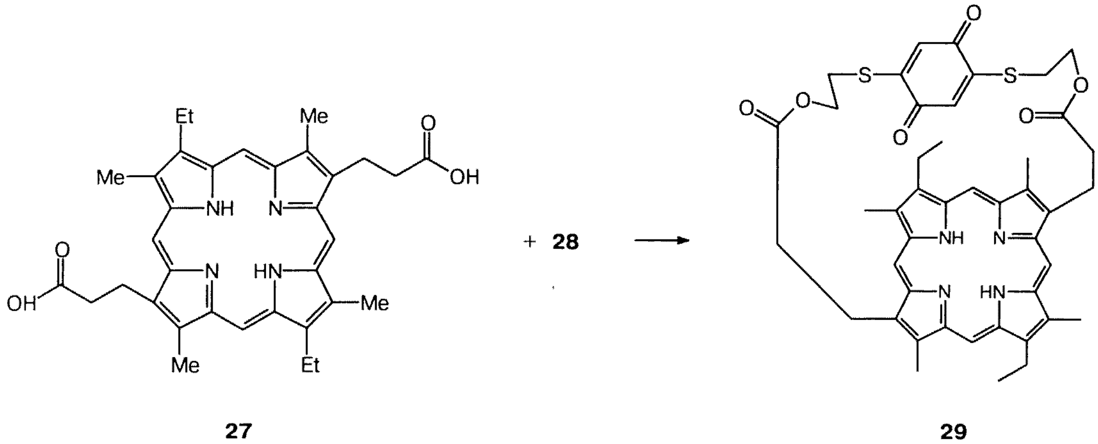


25 QOH = **11**, **14a,b**, **17a,b** **26a—e**

26	Q	X
a		S
b		NH
e		CH_2

26	Q	X
c		S
d		NH

Scheme 8



moieties due to steric hindrances created by the distortion of the macrocycle plane by the reduced double bond and the cyclopentanone ring of pheophorbide.[17,18]

Synthesis of porphyrin-quinones with fixed arrangement of a donor and an acceptor

Dyad systems **24a—f** and **26a—e** mimic well the primary processes of photoinduced charge separation in the natural reaction center. The study and interpretation of the results of investigation of these systems allow one to understand better the mechanism of photoinduced electron transfer and the effects of various factors on this mechanism.

However, the conformational mobility of various moieties of a molecule is a substantial disadvantage of similar dyad systems, because it makes difficult to interpret experimental data on the photoinduced electron transfer. In this connection, it was necessary to create the systems with the structure known beforehand (the conformation, the distance between a donor and an acceptor).[1—3] Therefore, porphyrin-quinone derivatives, in which quinone is rigidly oriented above the center of the porphyrin macrocycles, so-called "capped" compounds, are of great interest.

"Capped" porphyrin-quinone **29** was synthesized on the basis of symmetric mesoporphyrin II (**27**) and quinone **28** with two hydroxyl groups (Scheme 8). Compound **29** differs from porphyrin-quinones of similar types described in Refs. 19—21 by the existence of the S atom directly attached to the quinone structure. This allows one to elucidate the effect of heteroatom on the efficiency of charge separation in "capped" model systems and to select the acceptor with the most appropriate redox potential.

The method developed allows one to obtain sulfur-containing quinone **28** with two hydroxyl groups at positions 2 and 5 (Scheme 9). The attempts to synthesize the target product *via* one stage by the addition of 2-mercaptoethanol to 1,4-benzoquinone (**30**) were unsuccessful. The reaction *via* two stages increased the selectivity of the process. At the first stage, initial quinone **30** was added to a 5—10-fold excess of 2-mercaptoethanol in an alcohol medium. This resulted in the formation of substituted hydroquinone **31**, whose oxidation gave the corresponding quinone **32**. The addition of the second molecule of 2-mercaptoethanol followed by the formation of disubstituted hydroquinone **33** occurred under similar conditions at the next stage. Quinone **28** containing two hydroxyl groups was isolated after the oxidation of the reaction mass by air oxygen. The directed 2,5-addition to quinone was proved by the data of ^{13}C NMR spectroscopy.

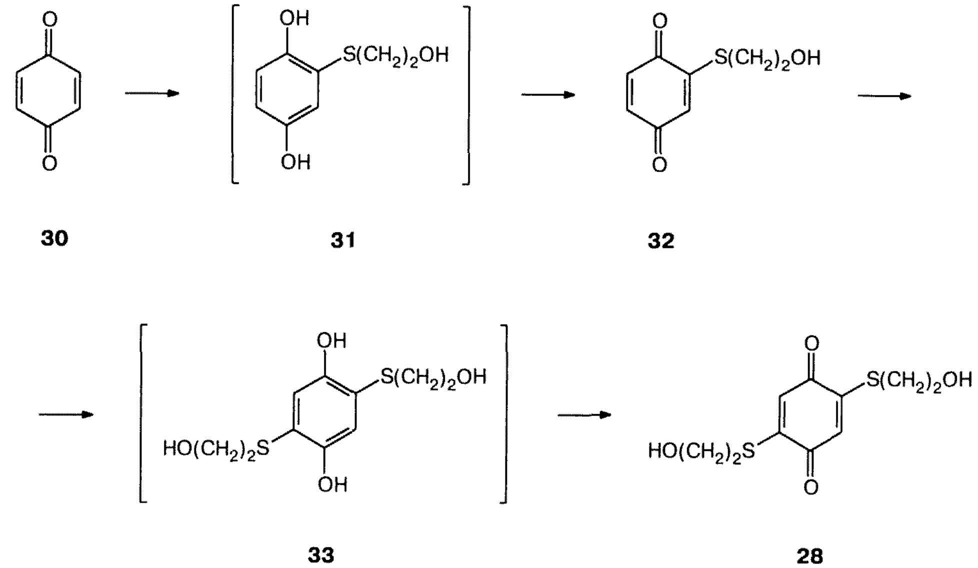
The carboxyl component, mesoporphyrin II, was synthesized by the Fischer method[22,23] followed by hydrolysis of its dimethyl ester.

The acid chloride obtained by treatment of mesoporphyrin II with oxalyl chloride was condensed with hydroxyl-containing quinone **28** under conditions of high dilution in CH_2Cl_2, which are typical of the similar type reactions.[19—21] Both components were added simultaneously with equal rates to a solution of triethylamine. The target product was isolated in a 6.4 % yield.

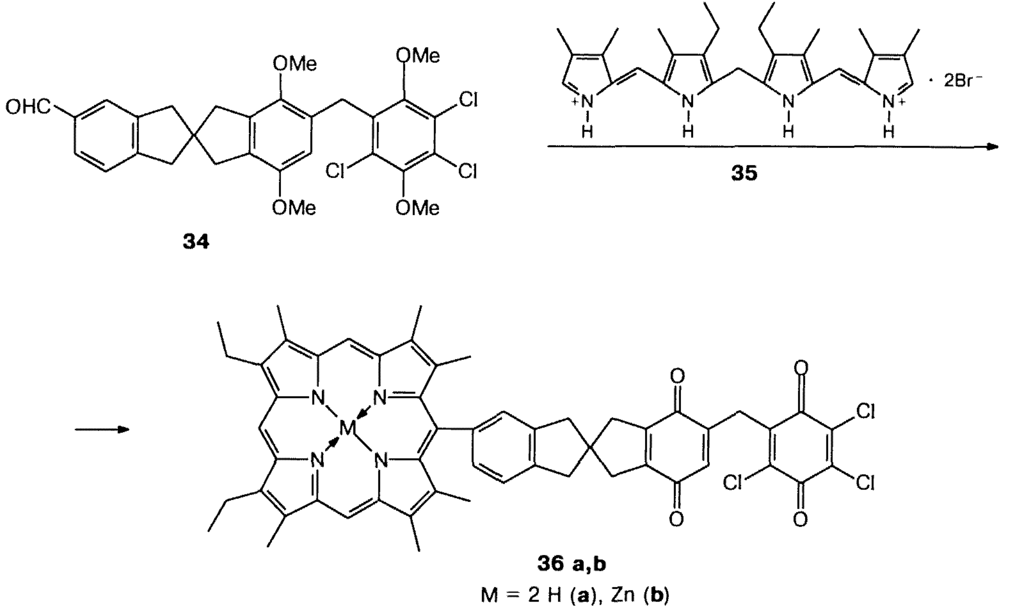
In the ^1H NMR spectrum of compound **29**, the signal of protons of the quinone ring is considerably shifted upfield (by 4.88 ppm) relative to the signal of the initial quinone **28**. This testifies that the quinone moiety is localized above the plane of the porphyrin macrocycle and agrees well with the literature data.[19—21]

However, the highly efficient photoinduced charge separation at large distances in the photosynthetic reaction center is achieved due to the multistep electron transfer *via* several donor and acceptor components, if the gradient of redox potential exists in the system. The use of the same principles in triad and tetrad photosynthetic models makes it possible to generate a long-lived state with separated charges in a high quantum yield.[1—5]

For more detailed study of the electron transfer, triad **36a** and its zinc complex **36b** were synthesized (Scheme 10), in which the primary donor is fixed toward porphyrin by the rigid spiro[4,4]nonane spacer, Scheme 9



Scheme 10



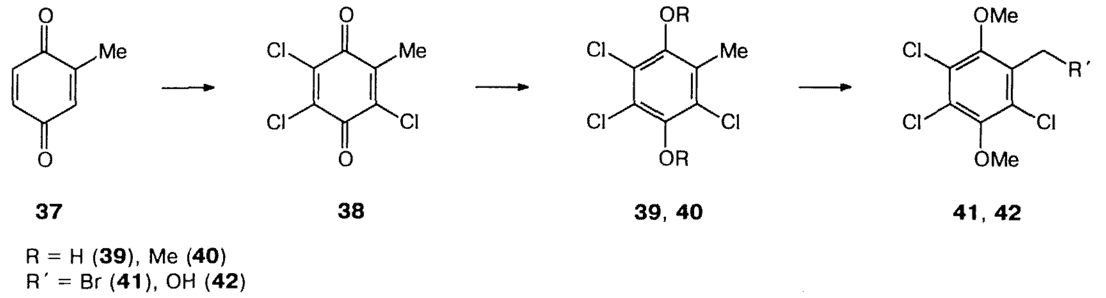
and the secondary acceptor is fixed by the methylene bridge that provides the almost unchanged removal from the other parts of the system.[24] The distance between the centers of porphyrin and the primary acceptor in these systems is 12.6 Å, the secondary acceptor is removed from porphyrin at 16.6—17.4 Å, while the distance between the centers of quinones is equal to 5.0 Å (all distances were determined by the CHEM 3D PLUS 3.0 program).

Trichlorobenzoquinone as a secondary acceptor is necessary for the creation of the gradient of the redox potential, which provides efficient multistep electron transfer in triad systems **36a,b**.

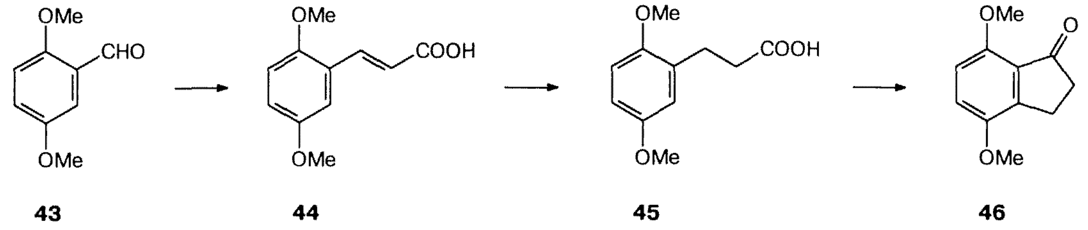
Compound **36** was obtained by acid-catalyzed cyclization of 4,5-diethyl-1,2,3,6,7,8-hexamethylbiladiene-*a*,*c* (**35**) with aromatic aldehyde **34** (see Scheme 10).

Aromatic aldehyde **34** was synthesized *via* several stages (Schemes 11—13). Hydroxy-substituted derivative **42** was synthesized by the procedures described previously[24,25] (see Scheme 11). Then dimethoxyindanone (**46**) was synthesized from 2,5-dimethoxybenzaldehyde (**43**) (see Scheme 12).[26] Unlike the procedures published previously (Ref. 27), we used polyphosphoric acid, which served as both the solvent and Lewis acid, for intramolecular cyclization according to Friedel—Crafts.[28]

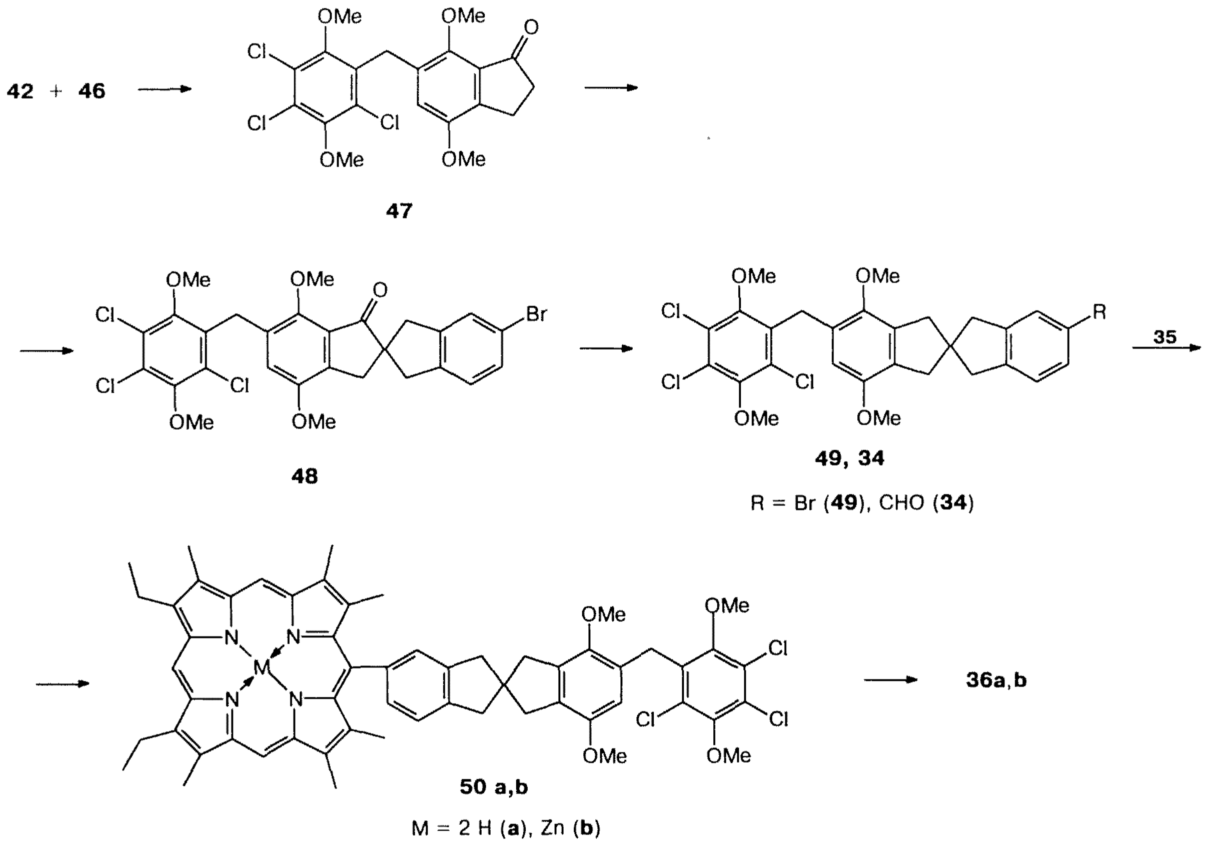
Scheme 11



Scheme 12



Scheme 13



At the next stage of the synthesis, derivatives **42** and **46** were condensed in polyphosphoric acid to form product **47** (see Scheme 13) in a 85 % yield as a mixture of isomers of positions 5 and 6 of indanone. To prepare the spirocycle, compound **47** was condensed with 3,4-bis(bromomethyl)bromobenzene by boiling in anhydrous THF in the presence of sodium hydride. The removal of the keto group accompanied by the reduction of ketone **48** was performed by the treatment by triethylsilane in trifluoroacetic acid, but this resulted in the formation of compound **49** in a 94 % yield. To substitute Br for CHO, the latter compound was treated by *n*-butyllithium and DMF in anhydrous THF at −78 °C, and the yield of aldehyde **34** was 65 %.

The porphyrin macrocycle was based on biladiene-*a,c* (**35**).[29] Porphyrin **50a** was obtained in a 8 % yield by the condensation of aldehyde **34** and biladiene-*a,c* **35** under reflux in methanol in the presence of catalytic amounts of HBr (see Scheme 13). The demethylation of compound **50a** by boron tribromide followed by the oxidation by lead dioxide resulted in the formation of triad **36a** in a total yield of 22 % (after chromatographic purification). Zinc porphyrin complexes **50b** and **36b** were prepared in quantitative yields by the treatment of compounds **50a** and **36a**, respectively, by zinc acetate in CH_2Cl_2.

The ^1H NMR spectra of compounds **50a,b** and **36a,b** demonstrate well their characteristic features. For example, the signals of protons of the methyl groups at positions 3 and 7 of porphyrin are manifested in the range of strong field (2.5 ppm) due to the ring current of the phenyl ring, while the signals of the other methyl groups of porphyrin are observed in the range of 3.65—3.50 ppm as singlets of 6 H, which reflects the symmetry of porphyrins obtained relative to the axis intersecting positions 5 and 15 of porphyrin.

The values of redox potentials of trimethylbenzoquinone, trichlorotoluquinone, and diquinone **51** measured as polarographic potentials of half-waves ($E_{1/2}$) in acetonitrile characterize the electron-accepting activity of quinones and testify that no interactions between two moieties of the molecule exist in compound **51**. These data also indicate that triads **36a,b** have the gradient of redox potential necessary for the photoinduced multistep electron transfer. In the case of trimethylbenzoquinone and trichlorotoluquinone, the corresponding $E_{1/2}$ values are −0.73 and −0.13 V, while they are −0.75 and −0.20 V in the case of diquinone **51** (Fig. 2).

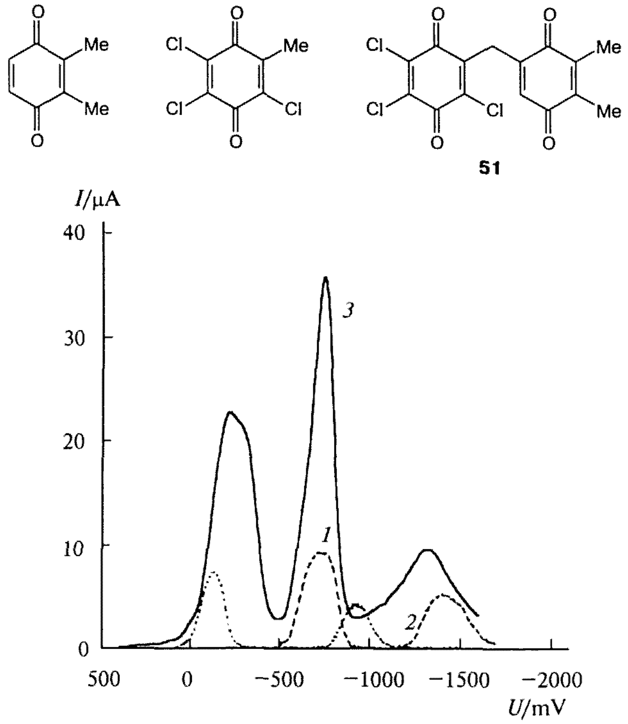


Fig. 2. Voltammograms of trimethylbenzoquinone (*1*), trichlorotoluquinone (*2*), and diquinone **51** (*3*) measured by differential pulse voltammetry (in MeCN). Scanning rate 20 mV s^{-1} (relative to an Ag/AgCl electrode, Bu_4NClO_4 as a supporting electrolyte).

Synthesis of porphyrin-quinones containing an additional electron donor

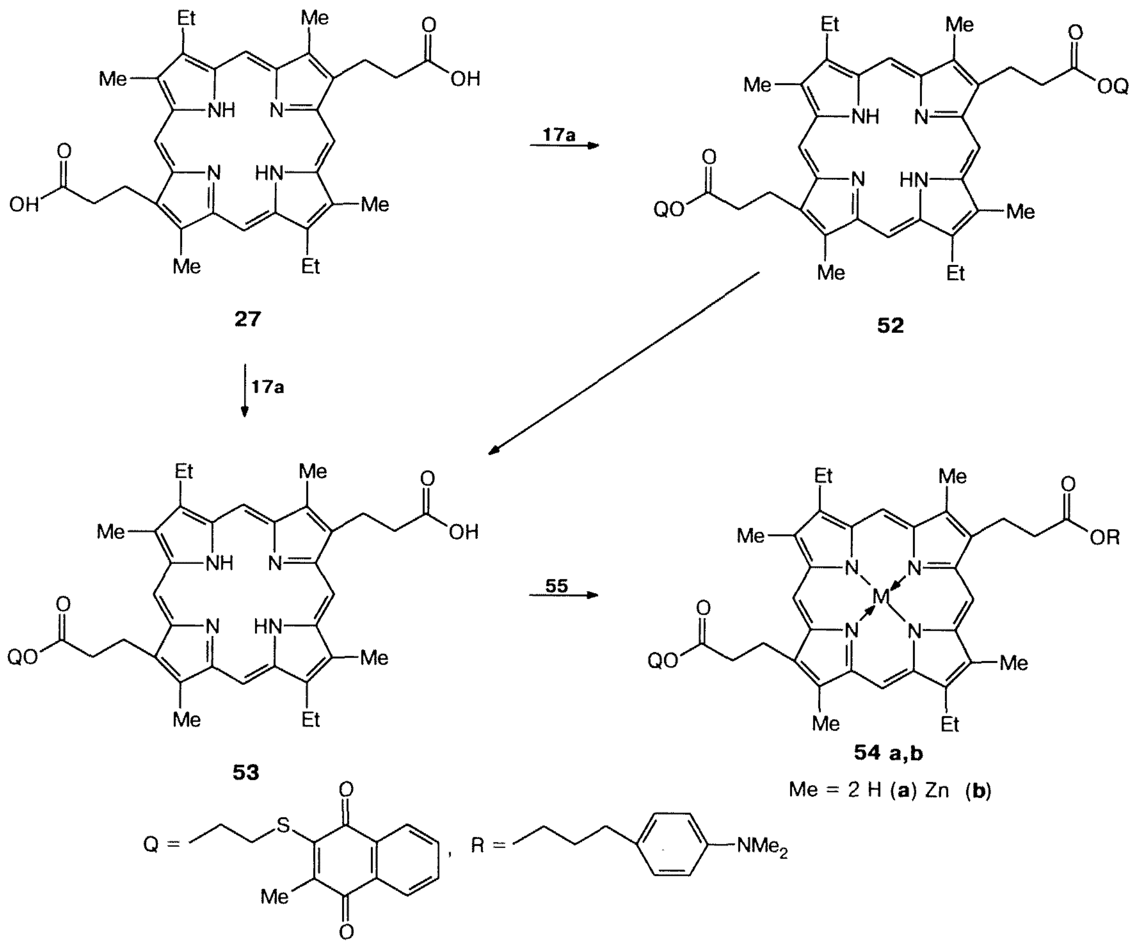
The creation of systems containing an additional donor moiety along with a photosensitizer and an acceptor was basically a new stage in the study of the primary process of photosynthesis using model compounds.[1—3] The introduction of an additional donor into the porphyrin-quinone compound makes it possible to increase the lifetime of charge separated state due to electron transfer from the donor to the oxidized porphyrin moiety. The synthesis of the similar triad system[30—32,37] (Scheme 14) was performed on the basis of mesoporphyrin II.

The development of the synthesis of the corresponding monoquinone derivative **53** (see Scheme 14) was an important stage in preparation of triad molecule **54**. It turned out that the use of pivaloyl chloride as an activating agent for mesoporphyrin II (**27**) did not result, as in the case of natural type porphyrins, in the predominant formation of monoester. This is likely caused by the absence of steric hindrances in the formation of intermediate mixed anhydride.

In our opinion, the procedure presented in Scheme 14 is optimum one. Mesoporphyrin II was condensed with quinone **17a** under the conditions of activation by Boc_2O. Diester **52** was obtained in a 59 % yield and then partially hydrolyzed by 4 *N* HCl. The yield of monoester **53** was 40—43 % (per one cycle of hydrolysis). Donor component **55** was condensed with monoquinone derivative **53** at the last stage by the method of mixed anhydrides using the Boc_2O—DMAP system. The yield of the triad after chromatographic purification was 75 %.[32]

The ^1H NMR spectra of porphyrins **52** and **53** and triad molecule **54** exhibit the upfield shifts of the signals of protons of the donor and acceptor moieties relative to the signals of the initial quinone and dimethylaniline. The similar changes typical of porphyrin-quinones with

Scheme 14



a flexible covalent bridge between chromophores are the result of the magnetic anisotropy of the porphyrin ring and indicate that the quinone moiety is localized above the porphyrin plane.

Under the real conditions of photosynthesis, amino acid residues from the protein surrounding of pigments can act as donor moieties, and the participation of lipid moieties in this processes also cannot be ruled out. For example, phospholipids contain residues of amino alcohols, aminoethanol and choline. In order to study donor properties of amino alcohols in the photoexcited system,[33] the triad containing the donor moiety (the residue of dimethylaminoethanol), photoexcited pigment (DP IX), and the acceptor moiety (2-(2-hydroxyethyl)thio-3-methylnaphthoquinone (**17a**)) was synthesized (Scheme 15, compound **59**). The electron-donating and electron-accepting moieties were connected *via* flexible covalent bridges.

The strategy of the synthesis of triad molecule **59** was in the subsequent condensation of DP IX (**18**) with the corresponding acceptor and donor components (see Scheme 15).

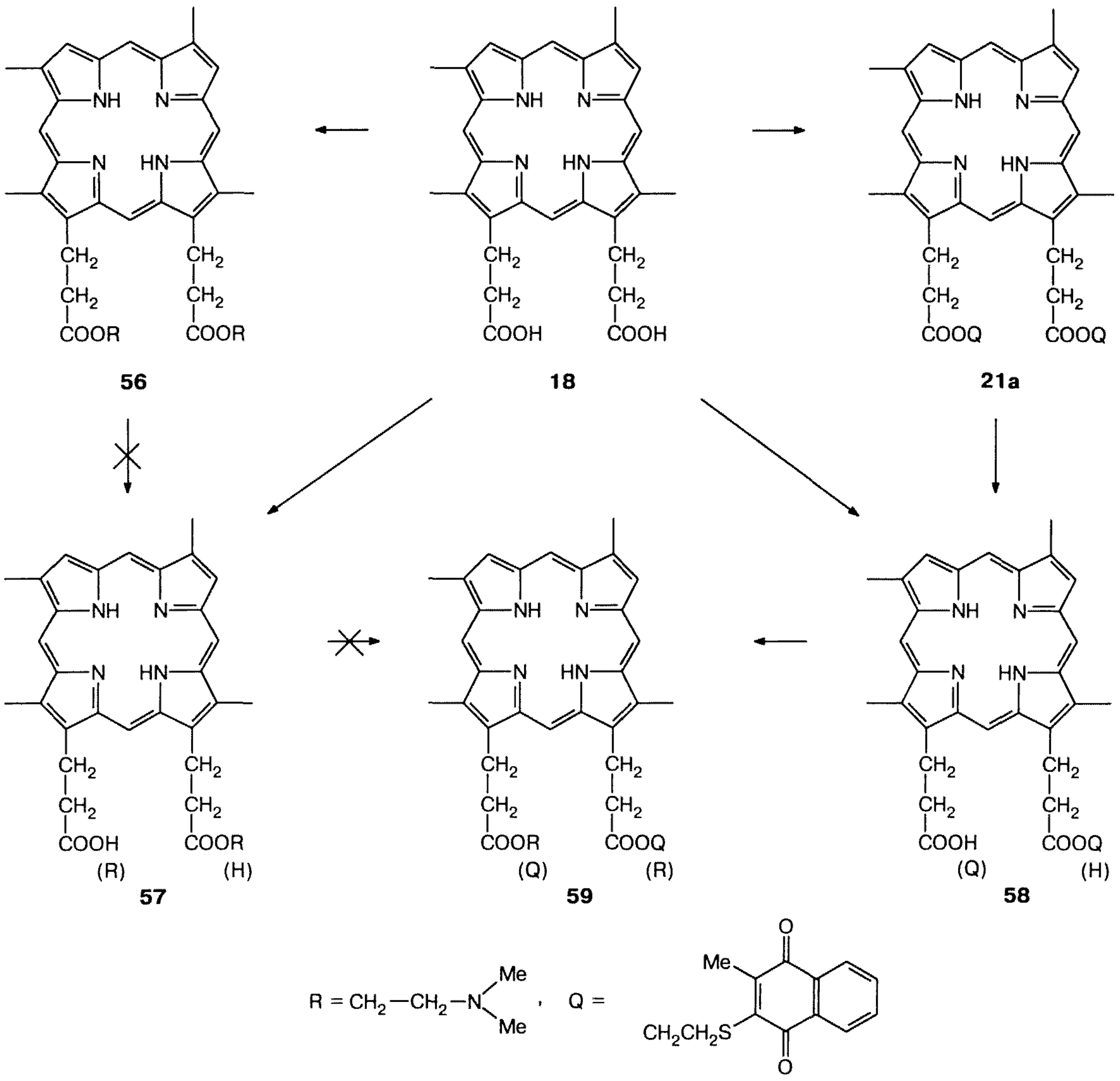
PivCl was used as an anhydride-forming agent for the preparation of monoquinone derivative **58**. The addition of porphyrin occurred at 20 °C (yield 40 %). As a result of the reaction, diquinone derivative **21a**, which was then hydrolyzed by 4 *N* HCl, was isolated along with compound **58**. The yield of monoester **58** after purification was 45—50 % (per cycle of hydrolysis).

Monoquinone derivative **58** was condensed with *N*,*N*'-dimethylaminoethanol by the method of mixed anhydrides using the Boc_2O—DMAP system.[6—8,17,18] Triad **59** was obtained in a 30 % yield.

The attempt to synthesize the triad *via* the different sequence, *i.e.*, to obtain first compound **57** and then to condense it with quinone, was unsuccessful. The use of PivCl as an activating agent did not result in the predominant formation of monoester **57** (the yield was 2 %). This is likely associated with the absence of steric hindrances in the formation of mixed anhydride. The hydrolysis of diester **56** under the action of 4 *N* HCl also did not give desired compound **57**: DP IX and initial ester **56** were isolated in the result of the reaction.

The ^1H NMR spectra of derivatives **56**, **57**, and **59** exhibit insignificant upfield shifts of the signals of protons of the donor moiety compared to the spectrum of

Scheme 15



the initial *N*,*N'*-dimethylaminoethanol, while the spectra of triad **59** demonstrates the upfield shifts of the signals of protons of the quinone moiety relative to the signals of the initial quinones. This is characteristic of porphyrin-quinones with a flexible covalent bridge between chromophores and is explained by the effect of magnetic anisotropy, which testifies that the quinone moiety is localized near the porphyrin plane.[6—8,14,17,18,33]

Photochemical properties of porphyrin-quinones

Recent intensive studies of the simplest covalently-linked model compounds made it possible to establish the main principles of the photoinduced electron and energy transfer.[1—3]

In the general case, the electron transfer in porphyrin-quinone compounds occurs as shown in Fig. 3. Irradiation of porphyrin results in its transition to the

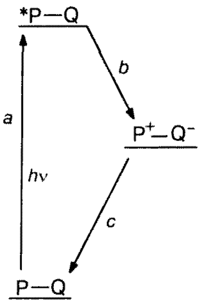


Fig. 3. Diagram of energy states of the typical porphyrin-quinone dyad and the routes of electron transfer (for explanations see text).

primary singlet excited state *P—Q (see Fig. 3, stage *a*). This state can decay due to usual photophysical processes, which compete with the photoinduced electron transfer from porphyrin to quinone, resulting in the formation of the system with separated charges $P^+—Q^-$ that stores a portion of the energy of the singlet excited state in a similar manner as the photosynthetic reaction center stores a portion of the excitation energy of the "special pair". The amount of the stored energy depends on redox properties of the dyad, and the quantum yield of the $P^+—Q^-$ state depends on components of the system.[1—3] As a result, the state of separated charges transits (see Fig. 3, stage *c*) into the ground P—Q state, and the stored energy is released as heat.

Compounds with a flexible covalent bond between porphyrin and quinone. The fluorescence spectra of porphyrin-quinone compounds **21a—h** obtained previously[6—8] do not differ from those of the initial porphyrins. However, they are characterized by strong quenching of the fluorescence of porphyrin moieties by quinone moieties. The relative quantum yield of fluorescence of diquinone derivatives is 4—5 % for compounds **21a—f**, 1.5 % for **21g,h**, and 30 % for **20b,c**. The similar quenching of fluorescence is typical of covalently linked porphyrin-quinones and is the result of photoinduced electron transfer from the porphyrin moiety to the quinone moiety. The data obtained by measuring the efficiency of fluorescence quenching in derivatives **21a—h** correlate with the electron-accepting activity of quinone substituents. The electron transfer rate constant is $2.37 \cdot 10^9$ s^{-1} for porphyrin-quinone **21b** (see Ref. 36).

The preliminary studies of photochemical properties of compounds **22a,b** show that the fluorescence of these porphyrin-quinones is decreased by 30 and 54 %, respectively, relative to the fluorescence of porphyrin **19** (Ref. 9).

The measurements of the fluorescence spectra of compounds **24a—f** allow one to establish that their intensities are considerably lower than those in the spectra of the initial porphyrins (Fig. 4). It is evident that the fluorescence quenching is associated with the intramolecular electron transfer from the porphyrin moiety of a molecule to quinone. For example, the quantum yield of fluorescence of porphyrin increases in the following series: **24a** < **24f** < **24e** < **24c** < **24b** < **24d** (see Fig. 4).[17] The electron-accepting activity of quinone substituents characterized by polarographic potentials of half-waves of reduction of initial quinones decreases in the series **24a** > **24c** > **24e** = **24f** > **24b** > **24d** (Refs. 17 and 18).

Thus, the data obtained by measuring the efficiency of fluorescence quenching in derivatives **24a—f** correlate with the electron-accepting activity of quinone substituents. A stronger quenching of fluorescence in the case of compounds **24e,f** can be explained by the fact that the efficiency of intramolecular charge separation depends on the energy parameters and the spatial arrangement of a donor and an acceptor, because, according to the data of ^{1}H NMR spectroscopy, quinone substituents in molecules **24e,f** that do not contain heteroatoms are considerably closer to the porphyrin plane than those in sulfur-containing compounds **24a,c** (see Ref. 17).

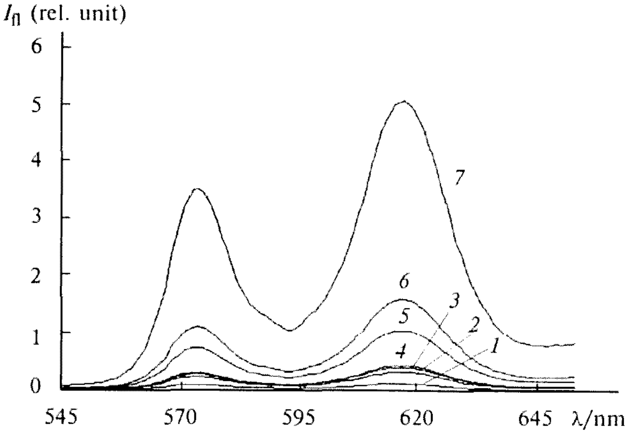


Fig. 4. Fluorescence spectra (in acetone) of compounds **24a** (*1*), **24f** (*2*), **24e** (*3*), **24c** (*4*), **24b** (*5*), **24d** (*6*), and **23** (*7*); λ_{ex} = 400 nm, $C = 10^{-5}$ mol L^{-1}.

The comparison of quantum yields of fluorescence of derivatives **24a—f** and their analogs based on DP IX shows that the fluorescence of porphyrin is quenched stronger in the case of DP IX derivatives. This also agrees well with the ^{1}H NMR spectra.[17,18]

The strong quenching of the fluorescence of pheophorbide *a* is observed in the fluorescence spectra of compounds **26a—e**. It is likely related to the photoinduced intramolecular electron transfer from pheophorbide to the quinone acceptor.[1—3,17,18,36] The relative quantum yield of fluorescence increases in the series **26c** < **26a** < **26e** < **26d** < **26b** (see Table 1). It is necessary to mention that the efficiency of the fluorescence quenching in pheophorbide-quinones **26a—e** is lower than that in the corresponding porphyrin-quinones **24a—e** likely due to the larger removal of quinone to the pheophorbide plane and the existence of one (not two) channel of electron transfer.[7,17,18,36]

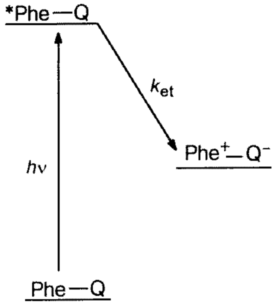
Table 1. Reduction potentials and parameters of fluorescence spectra for compounds **25** and **26a—e**

Compound	$-E_{1/2}/V^a$	I_{fl} (%)^b	τ_1/ns^c	τ_2/ns^c	k_{et} /10^8 s^{-1}
25	—	100	—	6.24	—
26a	0.70	13.6	1.27	6.45	6.3
26b	0.96	55	2.33	6.87	2.8
26c	0.74	5	1.03	6.45	8.2
26d	0.99	40	2.20	6.44	3.0
26e	0.84	18	2.08	6.54	3.3

[a] Measured for compounds **11**, **14a,b**, and **17a,b**.
[b] λ_{fl} = 668 nm, λ_{ex} = 410 nm, $C = 10^{-5}$ mol L^{-1}, acetone.
[c] λ_{fl} > 560 nm, λ_{ex} = 410 nm, $C = 10^{-5}$ mol L^{-1}, acetone.

The kinetics of fluorescence decay was measured on a picosecond pulse fluorimeter to determine in more detail the parameters of electron transfer in pheophorbide-quinones **26a—e**. All curves were two-component with short-lived (τ_1) and long-lived (τ_2) components, while only the component with a τ_2 lifetime was observed for initial pheophorbide **25** (see Table 1).[18]

It is evident that the first component is related to the quenching of fluorescence of pheophorbide (Phe) by the intramolecular electron transfer from pheophorbide to the quinone acceptor:



The τ_1 and τ_2 values made it possible to calculate the electron transfer rate constants (k_{et}, see Table 1) by the equation $k_{et} = 1/\tau_1 - 1/\tau_2$.

These data showed that the electron transfer rate constants for compounds **26a,c**, whose reduction potentials are maximum, are higher than those for **26b,d,e**. The changes in the fluorescence quenching of pheophorbide and in the electron transfer rate constants for pheophorbide-quinones **26a—e** are parallel (see Table 1).

It has been established that the electron transfer rate constants in compounds **26a—e** depend approximately linear on the reduction potentials of initial quinones **11**, **14a,b**, and **17a,b** (Fig. 5). The deviations from linearity are observed due to different spatial orientations of chlorin and quinone moieties of the molecule.[18]

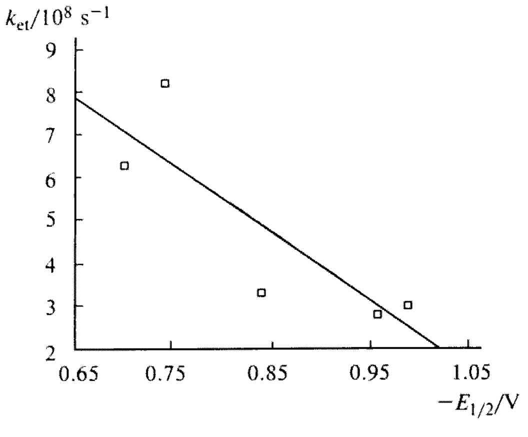


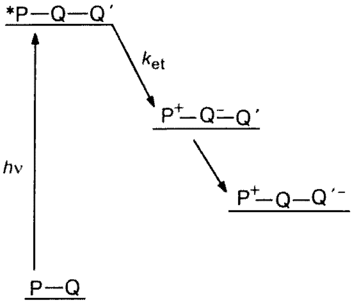
Fig. 5. Dependence of the electron transfer rate constant (k_{et}) in compounds **26a—e** on reduction potentials ($E_{1/2}$) of quinones **11**, **14a,b**, and **17a,b**.

It is noteworthy that the electron transfer rates in compounds **26a—e** depend on the redox potentials of quinones, *i.e.*, on the free energy of the reaction, despite the fact that the chromophores are not rigidly fixed in the molecule.

Porphyrin-quinones with fixed arrangement of a donor and an acceptor. Study of the fluorescence spectra of compounds **36a,b** has found a strong quenching of the fluorescence of the porphyrin moiety related to the photoinduced intramolecular electron transfer from porphyrin to quinone moiety. The relative quantum yields of fluorescence for compounds **36a,b** are 12 and 0.8 %, respectively.[24]

The kinetics of fluorescence decay was measured on a picosecond pulse fluorimeter for more detailed determination of the parameters of electron transfer in triad **36a**. The curve of fluorescence decay also was two-component with the short-lived (τ_1 = 2.42 ns) and long-lived (τ_2 = 13.7 ns) components.[24]

It is evident that the first component is related to the quenching of the fluorescence of porphyrin by the intramolecular electron transfer from the porphyrin moiety to the quinone acceptor:



The process of electron transfer in triad **36a** was studied in more detail by transient laser absorption spectroscopy. The decay of the singlet excited state of porphyrin (P*) (λ_{abs} = 445 nm) and the radical cation of porphyrin (P$^+$) (λ_{abs} = 697 nm) was observed upon irradiation of compound **36a** with visible light with λ_{ex} = 532 nm. The decay curve of the singlet excited state was monoexponential (Fig. 6). The rate constant of the electron transfer from the porphyrin moiety to quinone was calculated from the lifetime of the P* state (2.3 ns) and comprised $4.35 \cdot 10^8$ s^{-1}.

Porphyrin-quinones containing an additional electron donor. The fluorescence spectra of porphyrin-quinones **52—54** are similar to that of dimethyl ester of mesoporphyrin II, however, quinone-containing porphyrins are characterized by the strong quenching of the fluorescence of the porphyrin moiety by the quinone moiety[30—32] due to the photoinduced electron transfer from the porphyrin moiety to the quinone acceptor.[1—3,6—9,17,18] For example, for compound **53**, the quantum yield of fluorescence was 13 % of the yield of fluorescence of dimethyl ester of mesoporphyrin II.

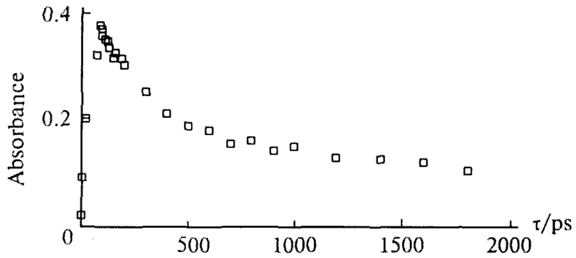


Fig. 6. Decay kinetics of the singlet excited state of porphyrin (P*) in triad **36a** (λ_{ex} = 532 nm, λ_{abs} = 445 nm, THF).

The kinetics of fluorescence decay in triad molecule **54a** and its zinc complex **54b** was measured by kinetic fluorescence spectroscopy with picosecond time resolution.[30—32] The electron transfer rate constant was $1.5 \cdot 10^9$ s^{-1} for triad **54a** and $5 \cdot 10^{10}$ s^{-1} for its zinc complex **54b** (in acetone). The value of the electron transfer rate constant in triad molecule **54a** measured by picosecond transient spectroscopy was equal to $1.25 \cdot 10^9$ s^{-1} (in THF). For compound **53**, the electron transfer rate constant measured by the same method was $2.53 \cdot 10^9$ s^{-1} (in methanol).[37]

The fluorescence spectra of porphyrin-quinones **21a**, **58**, and **59** are identical to that of the initial porphyrin.[33] The fluorescence spectrum of triad **59** exhibits an insignificant quenching of the fluorescence (10 %), while it is 30 % for porphyrin-quinone **58**, which corresponds to the electron transfer from the porphyrin moiety to quinone. In the case of compounds **57** and **56**, ignition of the fluorescence by 3 and 14 %, respectively, was observed, which testifies to the energy transfer from the additional donor to the porphyrin moiety. The introduction of two donor moieties into the porphyrin molecule results in a more than fourfold increase in the fluorescence of porphyrin compared to the ignition of the fluorescence for the compound with one donor moiety.

***

The data considered allow one to briefly formulate the main results of the studies on the photoinduced electron transfer in porphyrin-quinone compounds, which are convenient models of reaction centers of photosynthesis.

The synthesis of such compounds with a fixed distance between a donor and an acceptor and a certain mutual orientation makes it possible to study the effects of various factors on the efficiency of electron transport. As in photosynthesis, electron transfer in porphyrin-quinone compounds mainly involves singlet excited states of pigments at distances of up to 15—20 Å. The electron transfer is evidenced by the efficient quenching of fluorescence of the porphyrin moiety and the change in the decay kinetics of fluorescence of the singlet excited state of porphyrin. The electron transfer also results in the appearance of new absorption bands in optical spectra of solutions irradiated with visible light. According to the modern models of electron transfer, the rate of the process depends on the mutual orientation of porphyrin and quinone, decreases as the chain lengthens, and is determined by the value of the free energy of the reaction. The change in the length and the nature of the spacer and the mutual orientation of porphyrin and quinone by directed synthesis allows one to control the process of electron transport in porphyrin-quinone compounds.

Solvents also play an important role in charge transfer in porphyrin-quinone compounds. The data obtained to date testify that the medium affects the energy of the process.[38]

A considerable increase in the lifetime of separated charges is achieved on going from dyad systems to covalently linked triads. The stepped character of charge separation in these molecules provides a high rate of their separation and a low rate of their dark recombination.

The results of the studies of electron transfer processes in porphyrin-quinone compounds make it possible to correctly interpret the data on the electron transfer kinetics in photosynthesis. The synthesis and study of covalently linked triads with various donor moieties and spacers as well as other model systems containing porphyrin-quinone moieties will allow one to better understand the mechanisms of electron transport in biological structures and favor the development of artificial molecular systems for solar energy utilization.

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