Chemistry of Heterocyclic Compounds, Vol. 31, No. 3, 1995

SYNTHESIS OF A TRIAD MOLECULAR SYSTEM CONTAINING THE PHOTOSENSITIZER MESOPORPHYRIN II AND A SECONDARY ELECTRON DONOR AND ACCEPTOR FOR MODELING THE PHOTOSYNTHESIS PROCESS

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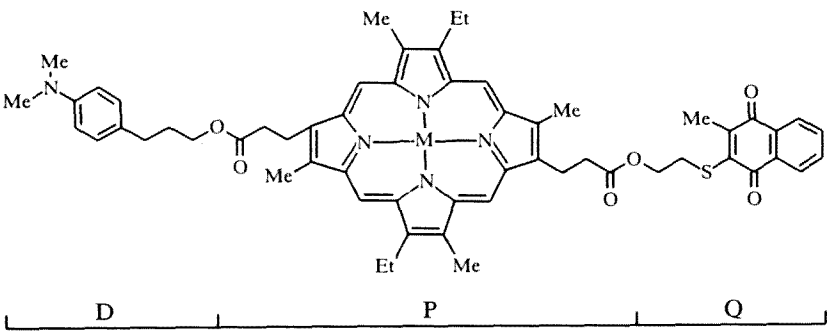
We describe two methods for synthesis of a triad molecular system based on mesoporphyrin II with electron-donor and electron-acceptor moieties for modeling the primary stage of charge separation in photosynthesis, differing in the order of addition of the donor and the acceptor. Using fluorescent spectroscopy, we have demonstrated quenching-containing compounds. Investigation of the triad and its zinc complex by kinetic fluorescent spectroscopy allowed us to determine the electron transfer rate constants for the triad and for its zinc complex.

A great deal of the attention has been paid to problems in the study of the photosynthesis process because of both the basic research aspect of the investigations and the possibility of creating molecular photocatalytic systems capable of reproducing natural photosynthesis schemes at a simpler level. One promising direction in this area has been modeling of the stage of electron transfer from the photoexcited pigment molecules to the primary acceptor using porphyrin–quinone compounds [1, 2], in which the electron acceptors (quinones) are covalently bonded to the electron donors (porphyrins, molecules having a structure similar to the structure of chlorophyll). However, the lifetime of the charges separated by the action of light in such structures is very short [(3-4) $\times 10^{-10}$ sec] [3, 4], which is due to rigid recombination. Introduction of an additional donor into the porphyrin–quinone compound makes it possible to significantly slow down charge recombination via electron transfer to the oxidized porphyrin [5, 6].

We synthesized the triad molecular system I (D–P–Q) based on mesoporphyrin II (VII) and is Zn complex, including an electron acceptor (a sulfur-containing quinone) and a secondary electron donor (a dimethylaniline derivative). Earlier it was shown that along with a branched polyene structure [5, 6], dimethylaniline also effectively plays the role of electron donor and is capable of reducing the porphyrin radical cation [7, 8].



I M=2H, Ia M=Zn

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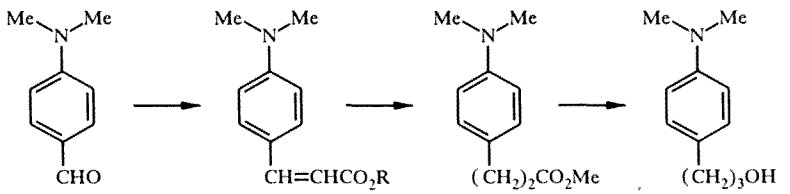
 0009-3122/95/3103-0296$12.50

The use of p-dimethylaminobenzyl alcohol (the product of reduction of p-dimethylaminobenzaldehyde (II) by sodium borohydride) as the potential donor was hindered by its extreme lability. In order to prevent the dimethylaminophenyl ring from affecting formation of the ester bond between the donor and the porphyrin, we increased the length of the covalent bridge. With this goal, the corresponding aldehyde II was condensed with malonic acid under the conditions of the Knoevenagel–Döbner reaction [9] (Scheme 1). The p-dimethylaminocinnamic acid (III) obtained in this way was methylated by diazomethane with formation of the corresponding methyl ester IV. Both derivatives of cinnamic acid III and IV contain a trans double bond, which was confirmed by the IR and PMR spectroscopy data. In the IR spectrum of these compounds, there is a band for the bending vibrations of the trans double bond at 986 and 980 cm^{-1} respectively, while in the PMR spectrum the spin–spin coupling constant of the doublets from the protons of the $-HC{=}CH-$ group is 16 Hz, which is also characteristic for the trans isomer.

Scheme 1



II III, IV V VI

III R=H, IV R=Me

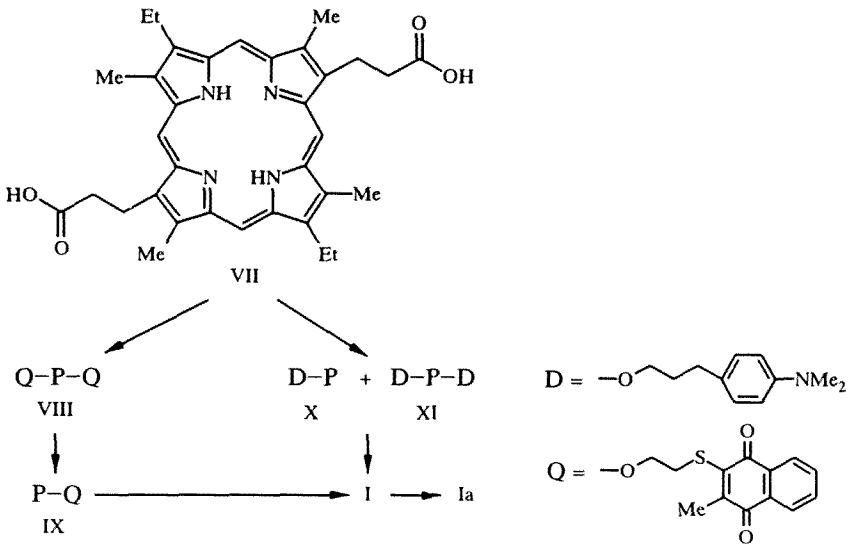
Attempts at direct reduction of the substituted cinnamic acid IV lithium aluminum hydride did not lead to the desired result due to the nonselectivity of the process. However, by consecutive reduction first of the double bond of compound IV by hydrogen on Pd/C with formation of the ester of dihydrocinnamic acid V, and then of the ester group by lithium aluminum hydride, we could obtain the desired compound VI.

The completeness of reduction was monitored by TLC and IR spectroscopy. In the IR spectrum, the band from the bending vibrations of the trans double bond at 980 cm^{-1} disappeared (for compound V), and the band for the stretching vibrations of the OH group appeared (for compound VI). The total yield of the alcohol VI after chromatographic purification was 50-57% (based on the starting aldehyde). The structure of the donor moiety of VI and compound V was confirmed by IR and PMR spectroscopy data and by elemental analysis. Due to the nonequivalence of the α- and β-methylene groups of the propionyl chain of compound VI, the signal from the protons of the β-methylene group in the PMR spectrum appears in the form of a triplet of triplets with the corresponding values of the spin–spin coupling constants. In the case of the precursor V, the nonequivalence of the protons in the α- and β-methylene groups leads to the appearance of two complex multiplets in the PMR spectrum.

An important step in obtaining the triad system I according to the first method was development of a technique for synthesis of the corresponding monoquinone derivative IX (Scheme 2). The starting mesoporphyrin II (VII) was obtained by acid hydrolysis of its dimethyl ester, which turn was synthesized by the Fischer method [10, 11] from the corresponding pyrroles. The use of pivaloyl chloride as the activating agent for mesoporphyrin II (VII) did not lead, as in the case of natural porphyrins [12], to preferential synthesis of monoesters; this is probably connected with the lack of steric hindrance in the formation of the intermediate mixed anhydride. After condensation of mesoporphyrin II (VII) with the hydroxyl-containing quinone obtained by addition of 2-mercaptoethanol of 2-methylnaphthoquinone [13, 14], under conditions of activation by pivaloyl chloride and after double chromatographic purification using preparative TLC on the support Kieselgel 60 F_{254} (Merck), we isolated two major products: the di- and monoquinone derivatives (compounds VIII and IX) in 41% and 25% yields. In this case, the mole ratio of the pivaloyl chloride and mesoporphyrin II was 2.3. When the mole ratio was decreased down to 1.8-1.2, the monosubstituted porphyrin was practically not formed. We found the following synthesis scheme to be optimal for the first synthesis method. The mesoporphyrin II (VII) was condensed with the corresponding quinone under conditions of activation by the system tert-butyl pyrocarbonate-4-dimethylaminopyridine (Boc_2O–DMAP) [13-15]. In this case, we obtained the diester VIII in 59% yield. Then porphyrin VIII was subjected to partial hydrolysis by 4 N hydrochloric acid [16]. The yield of the monoester IX after purification using preparative TLC was 40-43% after one hydrolysis cycle. In the last step, by the mixed anhydride method using the system Boc_2O–DMAP [13-15], we carried out condensation of the donor

component VI with the monoquinone derivative IX. After chromatographic purification on Kieselgel 60 F_{254} plates (Merck), we obtained the triad system I in 75% yield. We also obtained the zinc complex of triad Ia by treatment of triad I with a methanol solution of zinc acetate.

Scheme 2



According to the second synthesis method or triad I, the mesoporphyrin II (VII) was condensed with the donor component VI under conditions of activation by the system Boc_2O–DMAP. In the investigations of this reaction, we could establish the optimal ratio between the reacting components for obtaining the monosubstituted compound X. Thus, for a mole ratio of mesoporphyrin II (VII) and the dimethylaniline derivative (VI) of 1:0.8, the yield of the monoester X after chromatographic purification was 42%. Under these conditions, in addition to the monoester X, the disubstituted porphyrin XI was also formed in 2% yield. The mono derivative X obtained was condensed under analogous conditions with the corresponding quinone; and after purification using preparative TLC, we isolated the triad molecule I. During chromatographic purification on Kieselgel or silica gel of porphyrin I, X, XI, containing a dimethylaniline moiety, we observed that the porphyrin ring is easily metalated by the zinc ions contained in the sorbent, with formation of the corresponding zinc complexes. However, such high reactivity was not observed for the starting dimethyl ester of mesoporphyrin II and the porphyrin–quinones VIII and IX. This is probably connected with the presence in compounds I, X, XI of an electron-donor component, facilitating incorporation of zinc ions into the porphyrin. The content of zinc complex in the compounds obtained was no greater than 5-10%, which was established using electronic spectra and fluorescence spectra. In the fluorescence spectrum, there are bands characteristic for the free base of triad I (620, 680 nm) and its zinc complex (580, 620 nm), with practically identical intensity. In the case of porphyrin X and XI, we observed analogous changes in the spectra. Subsequent treatment of compounds I, X, XI with solutions of hydrochloric acid and ammonia led to removal of the zinc and reversion to the original spectrum of the free base.

In order to prove the structure of the triad molecule I and the porphyrins VIII-XI, we used UV, IR, PMR, and fluorescent spectroscopy and also mass spectrometry (the method of bombardment by fast atoms in the case of triad I and elemental analysis in the case of compounds VIII, IX).

For the synthesized porphyrins VIII, IX and the triad molecule I, in the PMR spectra we observed upfield shifts of the signals from protons of the quinone residues compared with the starting quinone and dimethylaniline derivative. Such changes, characteristic for porphyrin–quinones with flexible covalent bridges between the chromophores [2, 3, 8, 13, 14], are a consequence of the effect of the magnetic anisotropy of the porphyrin ring and suggest the quinone moiety is located above the plane of the porphyrin. In the case, $\Delta\delta$ is 0.38-0.50 ppm for protons of the quinone ring, 0.66-0.96 ppm for protons of the methyl group of the quinone, and 0.24-0.47 ppm for protons of the methylene group of the covalent chain closest to the quinone. These data suggest that the methyl group is closest to the plane of the macrocycle. For the dimethylaniline part of the porphyrins X, XI, the values of $\Delta\delta$ are 0.35-0.40 ppm for protons of the phenyl ring, 0.20 for protons of the methyl group, 0.27 ppm for protons of the methylene group of the covalent bridge closest to the phenyl ring. The value of $\Delta\delta$ decreases as

the distance to the porphyrin decreases, which is connected with the corresponding protons moving further away from the plane of the porphyrin ring. Thus for the β-methylene group of the propionyl residue, $\Delta\delta$ is 0.14 ppm. From this it follows that the phenyl ring is closest to the plane of the porphyrin.

The triad molecule I and its zinc complex Ia have poorly resolved spectra in deuterochloroform, which is explained by the intramolecular interaction of the different moieties. In the case of triad I, we can avoid this by adding 1% trifluoroacetic acid to the sample, as a result of which protonation of the amines in the system and breakdown of the intramolecular associates occur in the system, which ultimately improves the resolution of the PMR spectrum. However, we found that under analogous conditions, breakdown of the metal complex of triad Ia occurs. Therefore in this case, we could clearly assign only the signals corresponding to the meso protons, the protons of the aromatic ring of the quinone part of the molecule, and the protons of the phenyl group of the donor component. The remaining signals are complex multiplets and difficult to decipher.

In the mass spectrum of the triad molecule I, there are ion peaks with m/z 955-959, characterizing the molecular ion. The maximum intensity in this group of signals is exhibited by the ion peaks with m/z 957 (M^+) and 958 ($M + H^+$). The presence of a number of signals in the molecular ion region also is explained by possible protonation and deprotonation of compound I.

For porphyrin–quinones VIII, IX, and triad I, the electronic spectrum is the superposition of the spectra of the porphyrin and the quinone without a change in the shape and position of the absorption bands, which indicates the absence of interaction between the covalently bonded chromophores in the ground state. This is consistent with literature data [13, 14] for model systems of this type.

The fluorescence spectrum of the porphyrin-quinones VIII, IX, and triad I is analogous to the spectrum of the dimethyl ester of mesoporphyrin II, but for quinone-containing porphyrins we observed strong quenching of the fluorescence of the porphyrin by the quinone [17, 18], which is a consequence of the photoinduced electron transfer from the porphyrin to the quinone [2-4]. Thus for compound IX, the fluorescent yield was 13% relative to the fluorescence of the dimethyl ester of mesoporphyrin II.

Using the method of kinetic fluorescent spectroscopy with picosecond time resolution, we established the rate constants for electron transfer in the triad molecule I and its zinc complex Ia [17, 18]. Thus the value of K is 1.5×10^9 sec^{-1} for triad I and 5×10^{10} sec^{-1} for its zinc complex Ia (in acetone). The value of the rate constant for electron transfer in the triad molecule I, measured using picosecond laser and absorption spectroscopy, is 1.25×10^9 sec^{-1} (in THF). For compound IX, the value of the rate constant for electron transfer, measured using kinetic fluorescent spectroscopy with picosecond time resolution, is equal to 2.53×10^9 sec^{-1} (in methanol).

Thus our investigations allow us to suggest a high degree of photochemical activity for the triad molecular system, which is of interest for further more detailed study of this system.

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu IR-435 spectrometer for vaseline oil mulls or KBr pellets. The electronic spectra were recorded on Shimadzu UV-240 and Beckman DU-8 spectrophotometers. The ^1H NMR spectra were recorded on a Brucker WM-250 spectrometer at the operating frequency 250 MHz in deuterochloroform; internal standard, hexamethyldisiloxane. The fluorescence spectra were obtained on Shimadzu RF-540, Hitachi-650, and Hitachi-850 spectrofluorimeters. The mass spectra were recorded on a Kratos MS-50 spectrometer by bombardment with accelerated xenon atoms with energy 6-8 keV. We used glycerin as the matrix.

The condensations were carried out in anhydrous solvents. The purity of the compounds by TLC in the following systems: Silufol UV-254, 10:1 chloroform–methanol (A); 5:1 chloroform–methane (B); Kieselgel F_{254} (Merck), 15:1 chloroform–methanol (C); 5:1 chloroform–methanol (D); 2:1 chloroform–hexane (E); Alufol, 10:1 chloroform–methanol (F).

The elemental analysis data for C, H, N, and S correspond to the calculated values.

4-Dimethylaminocinnamic Acid (III). Obtained according to the technique in [9] from 30 g (0.2 moles) 4-dimethylaminobenzaldehyde (II). Yield, 30 g (78%). T_{mp} 223-224°C (decomp.). Let.: 225° (decomp.) [9] IR spectrum: 1660 (CO in COOH conjug. with C=C), 1585 C=C Ph, 1330 (tert-$N(CH_3)_2$, 986 (trans-CH=CH–), 812 cm^{-1} (1,4-subst. on the arom. ring). PMR spectrum, 7.72 (1H, d, J = 16 Hz, CH=CHCO), 7.46 (2H), 6.68 (2H, all d, J = 9 Hz, H arom.), 6.23 (1H, d, J = 16 Hz, CH=CHCO), 3.04 ppm (6H, s, CH_3).

Methyl Ester of 4-Dimethylaminocinnamic Acid (IV). A solution of diazomethane in ether (120 ml) (obtained from 12 g nitromethylurea) was added to a solution of 1.4 g (7.3 mmoles) acid III in 110 ml of a 10:1 methanol–water mixture at 0°C with stirring. The reaction mixture was stirred for 1 h and the solvent was removed; the residue was crystallized from hexane and dried under vacuum over paraffin and phosphorus pentoxide. Yield, 1.5 g (quant.). T_{mp} 132-133°C (Lit.: 134-136°C [18]). IR spectrum: 2989, 2793 (C–H), 1685 (CO in COOH conjug. with C=C), 1625, 1595 (C=C of Ph), 1331 (tert-$N(CH_3)_2$), 980 (trans-CH=CH–), 814 cm^{-1} (1,4-subst. on arom. ring). PMR spectrum: 7.63 (1H, d, J = 16 Hz, $\underline{CH}$=CHCO), 7.42 (2H), 6.66 (2H, all d, J = 9 Hz, CH atom.), 6.22 (1H, d, J = 16 Hz, CH=$\underline{CH}$CO), 3.78 (3H, s, OCH_3), 3.01 ppm (6H, s, NCH_3).

Methyl Ester of 3-(4-Dimethylaminophenyl)propionic Acid (V). A solution of 987 g (4.82 mmoles) compound IV in 75 ml THF was hydrogenated over 522 mg 10% Pd/C by passing hydrogen through it for 36 h with stirring. The reaction mass was filtered, the catalyst was washed with 150 ml THF, the solvent was removed, and the residue was extracted with pentane. The pentane was removed, the residue was chromatographed on a column (1 × 15 cm) with silica gel L 40/100, eluting with the system 1:1 chloroform–hexane. The fraction with R_f 0.81 was collected (A). The oil was dried under vacuum over paraffin and phosphorus pentoxide. Yield, 192 mg (56%). IR spectrum (in a film, KBr): 2900 (C–H), 1730 (CO in ester), 1610 (Ph), 1340 (tert-$N(CH_3)_2$), 807 cm^{-1} (1, 4-subst. on arom. ring). PMR spectrum: 7.07 (2H), 6.70 (2H, all d, J = 8.5 Hz, CH arom.), 3.69 (3H, s, OCH_3), 2.95 (6H, s, NCH_3), 2.94-2.84 (2H, m, $\underline{CH_2}CH_2CO$), 2.66-2.56 ppm (2H, m, $CH_2\underline{CH_2}CO$).

3-(4-Dimethylaminophenyl)propan-1-ol (VI). A solution of 856 mg (4.11 mmoles) compound IV in 50 ml ether was added gradually with stirring to a suspension of 154 mg (4.04 mmoles) lithium aluminum hydrate in 100 ml ether. The reaction mass was stirred for 1 h, poured into 400 ml water, extracted with ether (3 × 300 ml), and dried over anhydrous sodium sulfate, and the solvent was removed. The residue was chromatographed on a column (1 × 20 cm) with silica gel L 100/160, eluting with the system 1:1 chloroform–hexane. The fraction with R_f 0.45 was collected (A) and the solvent was removed. The oil was dried under vacuum over paraffin and phosphorus pentoxide. Yield, 41 mg (38%). IR spectrum (in a film, KBr): 3300 (OH), 2898 (C–H), 1610, 1514 (Ph), 1340 (tert-$N(CH_3)_2$), 810 cm^{-1} (1,4-subst. on arom. ring). PMR spectrum: 7.10 (2H), 6.73 (2H, all d, J = 8.5 Hz, CH arom.), 3.70 (2H, t, J = 6.5 Hz, $CH_2CH_2\underline{CH_2}O$), 2.93 (6H, s, NCH_3), 2.64 (2H, t, J = 7.5 Hz, $\underline{CH_2}CH_2CH_2O$), 1.88 ppm (2H, t.t, J_1 = 6.5 Hz, J_2 = 7.5 Hz $CH_2\underline{CH_2}CH_2O$).

1,3,5,7-Tetramethyl-4,8-diethyl-2,6-di(2-(2-(3-methyl-1,4-naphthoquinon-2-yl)thioethyl)oxycarbonylethyl)porphyrin (VIII). 2-(2-hydroxyethyl)thio-3-methyl-1,4-naphthoquinone (99.3 mg, 0.40 mmoles) was added to a solution of 100 mg (0.17 mmoles) mesoporphyrin II (VII) in a mixture of 20 ml chloroform and 3 ml pyridine. Then 88 mg (0.40 mmoles) tert-butyl pyrocarbonate was added at 0°C, and then after 10 min 5 mg (0.4 mmoles) 4-dimethylaminopyridine was added and this was stirred for 2 h at 20°C. The reaction mass was poured into 300 ml of 2% hydrochloric acid, extracted with chloroform (3 × 30 ml), and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on plates (20 × 20 cm) with Kieselgel 60 F_{254} (Merck), eluting with the system 2:1 chloroform–hexane. The major fraction was collected, the solvent was removed, and the residue was crystallized in pentane. The crystals were dried under vacuum over paraffin and phosphorus pentoxide. Yield, 104 mg (59%). R_f 0.42 (C). Electronic spectrum (chloroform), λ_{max} (lg ε): 621.3 (3.60), 567.9 (3.83), 535.3 (3.95), 499.1 (4.17), 399.7 nm (5.19). IR spectrum: 3301 (NH), 1730 (CO in ester), 1655 (CO of quinone), 1589, 1555 cm^{-1} (C=C of quinone). PMR spectrum: 9.98 (2H), 9.94 (2H, all s, meso-H), 7.75-7.71 (4H), 7.27-7.23 (4H, all m, CH arom.), 4.31 (4H, t, J = 7.75 Hz, $\underline{CH_2}CH_2CO$), 4.24 (4H, t, J = 6.25 Hz, $CH_2\underline{CH_2}O$), 4.06 (4H, q, J = 7.5 Hz, $\underline{CH_2}CH_3$), 3.63 (6H), 3.56 (6H, all s, CH_3 of porph.), 3.14 (4H, t, J = 7.75 Hz, $CH_2\underline{CH_2}CO$), 3.13 (4H, t, J = 6.25 Hz, $\underline{CH_2}CH_2O$), 1.87 (6H, t, J = 7.5 Hz, $CH_2\underline{CH_3}$), 1.78 (6H, s, CH_3 of quin.).

1,3,5,7-Tetramethyl-4,8-diethyl-6-(2-carboxyethyl)-2-(2-(2-(3-methyl-1,4-naphthoquinon-2-yl)thioethyl)oxycarbonylethyl)porphyrin (IX). Hydrochloric acid (25 ml, 4N) was added to a solution of 40 mg (0.04 mmoles) porphyrin VIII in 2 ml dioxane and stirred for 1 h at 20°C. The reaction mixture was poured into 300 ml water and extracted with chloroform (3 × 30 ml), the extract was washed with water (3 × 300 ml) and dried by sodium sulfate, and the solvent was removed. The residue was subjected to preparative TLC on plates (15 × 15 cm) with silica gel L 5/40, eluting with the system 10:1 chloroform–methanol. The fraction with R_f 0.39 was collected (B), crystallized in pentane, and dried under vacuum over paraffin and phosphorus pentoxide. Yield, 19 mg (43%). Electronic spectrum (chloroform), λ_{max} (lg ε): 620.5 (3.61), 566.9 (3.75), 533.5 (3.92), 499.1 (4.07), 399.7 nm (5.16). IR spectrum (vaseline oil, KBr): 3306 (NH), 1735 (CO in ester), 1700 (CO in COOH), 1660 (CO of quinone), 1585, 1550 cm^{-1} (C=C of quinone). PMR spectrum: 9.98 (3H), 9.93 (1H, all s, meso-H), 7.71-7.66 (2H), 7.24-7.19 (2H, all m, CH arom.), 4.34 (2H, t, J = 8 Hz, $\underline{CH_2}CH_2COOH$), 4.28 (2H, t, J = 7.75 Hz, $\underline{CH_2}CH_2CO$), 4.20 (2H, t, J = 6.25 Hz, $CH_2\underline{CH_2}O$), 4.06 (2H), 4.01 (2H, all q, J = 7.5 Hz, $\underline{CH_2}CH_3$), 3.63 (3H), 3.59

(3H), 3.58 (3H), 3.54 (3H, all s, CH_3 porph.), 3.31 (2H, t, J = 8 Hz, $CH_2\underline{CH_2}COOH$), 3.12 (2H, t, J = 7.75 Hz, $CH_2\underline{C}H_2CO$), 3.04 (2H, t, J = 6.25 Hz, $\underline{C}H_2CH_2O$), 1.87 (3H), 1.83 (3H, all t, J = 7.5 Hz, $CH_2\underline{CH_3}$), 1.48 (3H, s, CH_3 quin.).

1,3,5,7-Tetramethyl-4,8-diethyl-2-(2-carboxyethyl)-6-(2-(3-(4-dimethylaminophen-yl)propyl)oxycarbonylethyl)porphyrin (X) and 1,3,5,7-Tetramethyl-4,8-diethyl-2,6-di-(2-(3-(4-dimethylamino-phenyl)propyl)-oxycarbonylethyl)porphyrin (XI). Di-tert-butyl pyrocarbonate (37 mg, 0.17 mmoles) was added to a solution of 35 mg (0.2 mmoles) compound VI and 143 mg (0.24 mmoles) mesoporphyrin II (VII) in a mixture of 20 ml chloroform and 3 ml pyridine at 0°C, and after 10 min 2.2 mg (0.02 mmoles) 4-dimethylaminopyridine was added and this was stirred for 2 h at 20°C. The reaction mass was poured into 300 ml 2% hydrochloric acid, extracted with chloroform (3 × 50 ml), and dried with sodium sulfate. The solvent was removed, the residue was chromatographed on a column (3 × 15 cm) with silica gel L 100/160. This was eluted by the system 2:1 chloroform–hexane, isolating 1,3,5,7-tetramethyl-4,8-diethyl-2-6-di-(2-(3-(4-dimethylaminophenyl)propyl)oxycarbonylethyl)porphyrin (XI); then eluting with the system 25:2 chloroform–methanol, we isolated compound X. The porphyrin X was chromatographed on plates (20 × 20 cm) with silica gel, eluting with the system 25:1 chloroform–methanol. Compounds X and XI were treated with hydrochloric acid and an ammonia solution, as for triad I.

PMR spectrum of compound X ($CDCl_3$ + 1% CF_3COOH): 10.90 (3H), 10.68 (1H, all s, meso-H), 7.24 (2H), 7.17 (2H, all d, J = 8 Hz, CH arom. Ph), 4.47 (4H, t, J = 7 Hz, $\underline{CH_2}CH_2CO$), 4.11 (4H, q, J = 7.5 Hz, $\underline{CH_2}CH_3$), 4.04 (2H, t, J = 6.5 Hz, $CH_2CH_2\underline{C}H_2O$), 3.67 (6H), 3.63 (6H, all s, CH_3 porph.), 3.22 (4H, t, J = 7 Hz, $CH_2\underline{CH_2}CO$), 3.14 (6H, s, NCH_3), 2.59 (2H, t, J = 7.5 Hz, $\underline{CH_2}CH_2CH_2O$), 1.83 (2H, t. t, J_1 = 6.5 Hz, J_2 = 7.5 Hz, $CH_2\underline{C}H_2CH_2O$), 1.72 (6H, t, 7.5 Hz, $CH_2\underline{CH_3}$), −3.97 (1H), −4.05 ppm (1H, all s, NH).

PMR spectrum of compound XI ($CDCl_3$ + 1% CF_3COOH): 10.05 (4H, s, meso-H), 6.69 (4H), 6.37 (4H, all d, J = 8 Hz, CH arom. Ph), 4.38 (4H, t, J = 7 Hz, $\underline{CH_2}CH_2CO$), 4.10 (4H, t, J = 6.5 Hz, $CH_2CH_2\underline{CH_2}O$), 4.09 (4H, q, J = 7.5 Hz, $\underline{CH_2}CH_3$), 3.64 (6H), 3.62 (6H, all s, CH_3 porph.), 3.26 (4H, t, J = 7.5 Hz, $CH_2\underline{CH_2}CO$), 2.74 (12H, s, NCH_3), 2.37 (4H, t, J = 7.5 Hz, $\underline{CH_2}CH_2CH_2O$), 1.83 (6H, t, J = 7.5 Hz, $CH_2\underline{CH_3}$), 1.74 ppm (4H, t.t, J_1 = 6.5 Hz, J_2 = 7.5 Hz, $\underline{C}H_2CH_2CH_2O$).

1,3,5,7-Tetramethyl-4,8-diethyl-2-(2-(2-(3-methyl-1,4-naphthoquinon-2-yl)thioethyl)oxycarbonyl)ethyl-6-(2-(3-(4-dimethylaminophenyl)propyl)oxycarbonylethyl)porphyrin (I). A. Obtained according to the technique for compound VIII from 11 mg (0.014 mmoles) porphyrin IX. After chromatographic purification, the residue was dissolved in 30 ml chloroform. The extract was washed with 2% hydrochloric acid (2 × 300 ml), water (2 × 300 ml), and dried over anhydrous sodium sulfate. The solvent was removed, the residue was crystallized in pentane. The crystals were dried under vacuum over paraffin and phosphorus pentoxide. Yield, 10 mg (76%). R_f 0.33 (C). Electronic spectrum (chloroform), λ_{max} (lg ε): 621.1 (3.30), 568.1 (3.80), 534.7 (3.87), 499.1 (4.06), 400.3 nm (5.19). IR spectrum (vaseline oil, KBr): 3295 (NH), 1725 (CO in ester), 1650 (CO of quinone), 1610, 1510 (C=C Ph), 1574, 1550 cm^{-1} (C=C of quinone). PMR spectrum ($CDCl_3$ 1% CF_3COOH): 10.72 (1H), 10.68 (1H), 10.56 (2H, all s, meso-H), 8.12-8.04 (2H), 7.73-7.65 (2H, all m, CH arom. Ph), 7.30 (2H), 7.14 (2H, all d, J = 8 Hz, CH arom. Ph), 4.47 (2H), 4.43 (2H, all t, J = 7.5 Hz, $\underline{CH_2}CH_2CO$), 4.33 (2H, t, J = 6.25 Hz, $CH_2\underline{CH_2}O$), 4.15 (4H, q, J = 7.5 Hz, $\underline{CH_2}CH_3$), 4.05 (2H, t, J = 6.5 Hz, $CH_2CH_2\underline{C}H_2O$), 3.70 (3H), 3.68 (6H), 3.66 (3H, all s, CH_3 porph.), 3.42 (2H, t, J = 6.25 Hz, $C\underline{H_2}CH_2O$), 3.13 (4H, t, J = 7.5 Hz, $CH_2\underline{CH_2}CO$), 3.07 (6H, s, NCH_3), 2.59 (2H, t, J = 7.5 Hz, $CH_2CH_2CH_2O$), 2.36 (3H, s, CH_3 quin.), 1.83 (2H, t.t, J_1 = 6.5 Hz, J_2 = 7.5 Hz, $CH_2\underline{C}H_2CH_2O$), 1.76 ppm (6H, t, J = 7.5 Hz, $CH_2\underline{C}H_3$). Mass spectrum, m/z (relative intensity, %): 959 ($(M + 2H)^+$, 40), 958 ($(M + H)^+$ 70), 957 (M^+, 100), 956 ($(M-H)^+$, 30), 955 ($(M-2H)^+$, 20).

B. Obtained according to the technique for compound VIII from 26 mg (0.037 mmoles) porphyrin X and 21 mg (0.084 mmoles) 2-(2-hydroxyethyl)thio-3-methyl-1,4-naphthoquinone. The residue was chromatographed on a column with Sephadex LH-20, eluting with chloroform. The final purification was carried out by repeated chromatography on plates (20 × 20 cm) with Kieselgel in the system 4:1 chloroform–hexane. Yield, 9 mg (26.6%). R_f 0.33 (C). Mass spectrum, m/z (relative intensity, %): 959 ($(M + 2H)^+$, 40), 958 ($(M + H)^+$, 70), 957 (M^+, 100), 956 ($(M-H)^+$, 30), 955 ($(M-2H)^+$, 20).

Zinc Complex of 1,3,5,7-Tetramethyl-4,8-diethyl-2-(2-(2-(3-methyl-1,4-naphthoquinon-2-yl)thioethyl)oxycarbonyl)ethyl-6-(2-(3-(4-dimethylaminophenyl)propyl)oxycarbonylethyl)porphyrin (Ia). A saturated solution of zinc acetate in methanol (3 ml) was added to a solution of 5 mg (0.005 mmoles) compound I in 20 ml chloroform. The reaction mixture was stirred for 30 min at 20°C, washed with water (3 × 100 ml), dried with sodium sulfate, and passed through a bed (2.5 × 4.5 cm) of aluminum oxide (activity IV, neutral), and then the solvent was removed. The residue was crystallized in pentane and dried under vacuum over paraffin and phosphorus pentoxide. Yield, 5 mg (96%). R_f 0.34 (C). Electronic spec-

trum (chloroform), λ_{max} (lg ε): 570.9 (7.31), 535.1 (7.26), 405.1 nm (8.35). IR spectrum (in a film, KBr): 1730 (CO in ester), 1655 (CO of quinone). PMR spectrum ($CDCl_3$): 10.05-9.9 (4H, m, meso-H), 7.75 (2H, m, CH quin.), 7.42-7.21 (2H, m, CH quin.), 7.42-7.21 (2H, m, CH arom. Ph), 3.55 (3H, s, CH_3 porph.), 1.4 ppm (3H, s, CH_3 quin.).

We would like to thank B. V. Rozynov for recording the mass spectra of the triad molecule and T. Okada for determination of the rate constants for electron transfer in triad I and its zinc complex Ia using laser absorption spectroscopy.

This work was supported by the Russian Foundation for Basic Research (Grant 94-03-08070).

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