Photochemical and photophysical properties of *meso*-tetraferrocenylporphyrin. Quenching of *meso*-tetraphenylporphyrin by ferrocene

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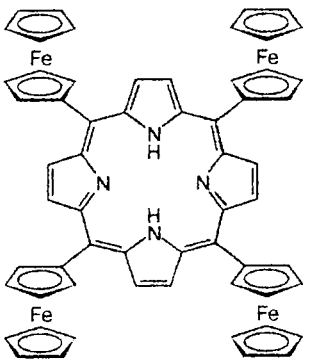
It was found that the quantum yield of the fluorescence of *meso*-tetraferrocenylporphyrin (TFcP) is at most $3.0 \cdot 10^{-5}$, and that of the triplet state of FTcP is at least 200 times lower than the quantum yield of *meso*-tetraphenylporphyrin (TPP). Excitation of TFcP in CCl_4 by light with $\lambda > 410$ nm results in the oxidation of TFcP. The singlet and triplet excited states of TPP in toluene and acetonitrile are quenched by ferrocene with rate constants of $1.2 \cdot 10^{10}$ and $1.7 \cdot 10^{10}$, $(4.6 \pm 0.5) \cdot 10^{8}$ and $(1.37 \pm 0.21) \cdot 10^{9}$ L mol^{-1} s^{-1}, respectively. The quenching mechanisms are discussed.

Key words: *meso*-tetraferrocenylporphyrin, *meso*-tetraphenylporphyrin, ferrocene, fluorescence, nanosecond laser photolysis.

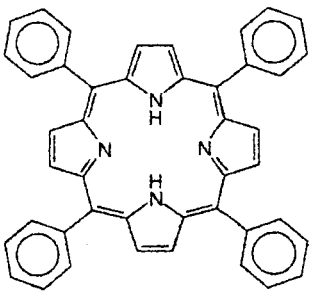
The photochemical and photophysical properties of porphyrins have been studied in detail in development of photocatalytic processes and studies of electron transfer reactions in biological and artificial systems.[1—6] Great attention was paid to porphyrin dyads and triads, molecular systems in which the tetrapyrrole cycle is covalently linked through a molecular bridge or without it with electron donors or acceptors such as viologen, quinones, C_{60}, *etc.*[7—18] These molecularly organized systems imitate directed electron transfer in biological objects and are of interest for photocatalysis and devices that convert light energy into electric energy.

New porphyrin molecules that can be considered as porphyrin dyads in which the tetrapyrrole cycle is covalently linked in the *meso*-position with metallocenes, in particular, with ferrocene (FcH), directly[19,20] or through various bridges, $CH_2—CH_2$,[21] *trans*-CH=CH [21] and *cis*-CH=CH,[21] and —⟨⟩—O— were recently synthesized.[22,23] A high quantum yield of charge separation and efficient light conversion in photogalvanic cells were observed for the porphyrin linked with Fc through the phenoxyl bridge.[23]

In this work, we studied the photochemical and photophysical properties of porphine covalently linked in *meso*-positions with four Fc groups, *meso*-tetraferrocenylporphyrin (TFcP). Quenching of singlet- and triplet-excited *meso*-tetraphenylporphyrin (TPP) by FcH was also studied to reveal the character of the interaction of excited porphine with Fc groups.



TFcP



TPP

Experimental

The following reagents were used: acetonitrile and toluene (Fluka, for HPLC analysis) as solvents, TPP (Fluka, without additional purification), and ferrocene (Fluka). The latter was recrystallized four times from methanol followed by vacuum sublimation. Synthesis of TFcP has been described in detail in previous works.[19,20]

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Spectrophotometric and fluorometric measurements were carried out on Specord M-40 and Specord UV-VIS spectrophotometers. Fluorescence spectra were recorded on Perkin—Elmer and Elumin fluorimeters.

Continuous photolysis was performed by a medium-pressure mercury lamp. A thermal filter (a 10-cm cell filled with water) and a ZhS-11 light filter with transmission $\lambda > 400$ nm were used.

Laser photolysis. Two types of lasers were used for the excitation of the sample: (1) a ruby laser, second harmonic, $\lambda = 347$ nm, pulse energy to 15 mJ, pulse duration 30 ns, diameter of the beam ~1 cm; (2) an Nd^{3+}:YAG laser, second harmonic, $\lambda = 532$ nm, pulse energy to 5 mJ, pulse duration 12 ns, diameter of the beam 7 mm. In experiments with a ruby laser, detection was performed by a Techtronix memorizing oscillograph (the transmission band to 1 GHz) followed by PC processing of the curves using the IGOR PRO 3.1 program package. In experiments with an Nd^{3+}:YAG laser, spectra were recorded on an ATsP—KAMAK analog-to-digital converter with a time resolution of 10 ns per point. A ruby laser allows one to excite both porphyrin and ferrocene; the latter has weak absorption at $\lambda = 347$ nm. In experiments with Nd^{3+}:YAG, only porphyrin is excited. Since the intensity of its absorption at 532 nm is lower than that at 347 nm, it was necessary to use higher concentrations of porphyrin and monitor dimer formation.

Experiments were carried out in 2-mm and 1-cm quartz cells. In experiments with laser photolysis, anaerobic conditions were created by evacuation, and in experiments with continuous photolysis, argon bubbling was used.

Results and Discussion

Absorption spectra of TFcP and TPP (Fig. 1). The spectrum of TFcP consists of the *B* band at 22960 cm^{-1}, $\varepsilon = 2.34 \cdot 10^4$ L mol cm^{-1} and *Q* bands at 15035 cm^{-1}, $\varepsilon = 1.45 \cdot 10^4$ L mol cm^{-1}; 13730 cm^{-1}, $\varepsilon = 1.07 \cdot 10^4$ L mol cm^{-1}. H_2TPP has *B* bands at 23580 cm^{-1} and *Q* bands at 19424, 18260, 16850, and 15400 cm^{-1}.

Quenching of fluorescence of TPP by ferrocene. Quantum yield of fluorescence of TFcP. The fluorescence spectrum of TPP consists of two bands: *Q*(0.0) 653 nm and *Q*(0.1) 715 nm.[24] Ferrocene quenches fluorescence of TPP. The dependence of the fluorescence intensity of the concentration of FcH (0.2—1.4 mmol L^{-1}) is linear in Stern—Volmer coordinates with slopes of $(0.19 \pm 0.01) \cdot 10^3$ and $(0.13 \pm 0.01) \cdot 10^3$ L mol^{-1} in acetonitrile and toluene, respectively.

No bands that could be attributed to the formation of molecular complexes between TPP and FcH in the ground or excited states were observed in either absorption or fluorescence spectra. This indicates the dynamic character of quenching. Under the condition that the lifetime of TPP fluorescence is equal to 10.8 ns,[26,24] estimation of the quenching rate constants (k_q^S) gives $1.7 \cdot 10^{10}$ and $1.2 \cdot 10^{10}$ L mol s^{-1} in acetonitrile and toluene, respectively. The k_q^S values are close to that of the rate constant of the diffusionally-controlled reaction ($k_{dif} \approx 8RT/3000\eta$)[26]: $1.0 \cdot 10^{10}$ and $1.7 \cdot 10^{10}$ L mol s^{-1} in toluene and acetonitrile, respectively.

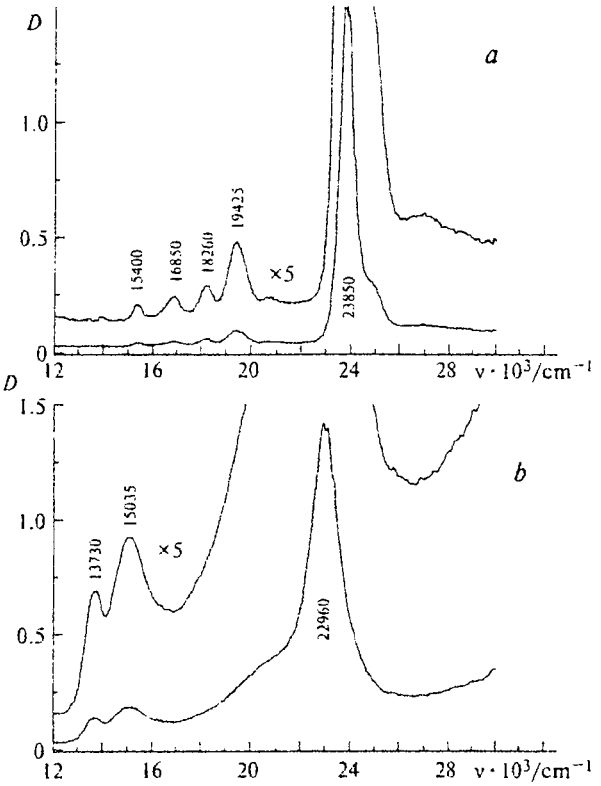
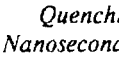


Fig. 1. Absorption spectra of TFcP (*a*) ([TFcP] = $2.63 \cdot 10^{-5}$ mol L^{-1}) and TPP (*b*) ([TPP] = $2.63 \cdot 10^{-5}$ mol L^{-1}) in toluene.

No fluorescence of TFcP solutions was observed in our experiments. The estimations show that the quantum yield of TFcP fluorescence is 300 times lower than that of TPP (0.11—0.13),[2,25] *i.e.*, it does not exceed 10^{-4}. Note that the quantum yield of fluorescence of porphyrin linked with FcH through the  bridge decreases by 100 times only as compared to that of unsubstituted porphyrin.[22]

Quenching of the triplet state of TPP by ferrocene. Nanosecond laser photolysis of TFcP. Ferrocene quenches the triplet state of TPP, and the absorption of possible products of the reaction of triplet TPP with FcH in the 350—1000 nm region was not observed. Note that the radical anion of TPP has an absorption band at $\lambda = 730$ nm,[1] and the FcH^+ cation has it at $\lambda = 615$ nm.[31]

The dependence of the inverse lifetime of the triplet state of TPP on the concentration of FcH is linear in a wide range from $2 \cdot 10^{-8}$ to $2 \cdot 10^{-4}$ s. The quenching rate constant is $(4.6 \pm 0.5) \cdot 10^8$ and $(1.37 \pm 0.21) \cdot 10^9$ L mol s^{-1} in toluene and acetonitrile, respectively, which is substantially lower than the diffusion limit. The efficiency of quenching increases noticeably as the polarity of the medium increases.

The yield of the triplet state of TFcP is at least 200 times lower than that in the case of TPP.

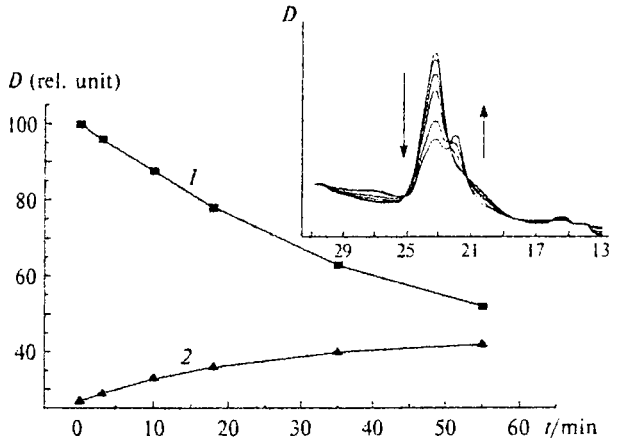


Fig. 2. Kinetics of a decrease in intensity of the B band of TFcP (*1*) and accumulation of the product (*2*) with λ_{max} = 461 nm in a toluene—CCl_4 (60 : 40) mixture. The change in the absorption spectrum of TFcP during phototransformation is shown in insertion.

Photolysis of TFcP under conditions of continuous irradiation. Irradiation of TFcP in toluene by visible light for 1 h virtually does not decompose TFcP. The intensity of the *B* band slightly decreases in acetonitrile (8% during 1 h of irradiation). However, a substantial conversion of TFcP to the reaction product is observed in a toluene—CCl_4 (6 : 4, v/v) mixture. The kinetics of decrease in the intensity of the *B* band of TFcP and that of an accumulation of the product at λ_{max} = 461 nm (21680 cm^{-1}) are shown in Fig. 2: at least four isosbestic points are observed due to the phototransformation of TFcP (405, 452, 477, and 546 nm). It is most likely that the photooxidation of TFcP occurs. During dark oxidation of TFcP by tetracyanoethylene in acetonitrile ([TFcP] = $1.5 \cdot 10^{-5}$ mol L^{-1}, [TCNE] = $4 \cdot 10^{-4}$ mol L^{-1}), the B band of TFcP disappears, and the same band appears at λ = 461 nm. For comparison, we carried out experiments with the TPP—ferrocene system under similar conditions: the intensity of the B band decreases substantially more slowly (1—1.5% in the absence of FcH and 3% at [FcH] = 3 mmol L^{-1}) than in the case of TFcP.

Mechanism of quenching of excited states of porphyrins by ferrocene. The following mechanisms of quenching of the excited states of organic molecules by ferrocenes have previously been discussed: (1) energy transfer,[18,21,22,26—30] (2) effect of heavy atom metal,[21,22] and (3) redox mechanism.[21,26—30]

Intramolecular energy transfer in TFcP seems improbable, because the energies of the lowest singlet and triplet states of FcH are 2.46 and 1.65—1.78 eV, respectively.[27,31] These are much higher than those of the lowest excited states of porphyrins ($E(S_1)$ = 1.86 eV, $E(T_1)$ = 1.43 eV for TPP).[2]

Quenching of fluorescence due to the heavy atom effect is also improbable, because the quantum yield of the triplet state of TFcP is low. This conclusion agrees with the data[21] that indicates that the yields of the triplet state of porphyrin are almost the same for 5,15-bis(4-tolyl)-2,3,7,8,12,13,17,18-octamethylporphine and its Fc derivative. However, for several porphyrins (TPP)$GePh_2$, (TPP)GePh(Fc), and (TPP)$Ge(Fc)_2$ in which Fc forms the σ-bond with Ge,[30] the quantum yield of the triplet state increases with increase in the number of Fc substituents, which is related to the heavy atom effect.

Quenching of TPP fluorescence by ferrocene is thermodynamically favored: the oxidative potential of singlet-excited TPP is +1.05 eV,[2] and the Fc^{II}/Fc^{III} potential is equal to +0.315 eV in acetonitrile (SCE).[33] The possibility of redox quenching of fluorescence is favored by the photooxidation of TFcP in CCl_4 during excitation in the *B* band. As is known, irradiation of solutions of FcH in CCl_4 at $\lambda \geq 400$ nm does not lead to its photochemical transformation, whereas at λ = 366, 344, 313, or 280 nm, *i.e.*, in the charge transfer band, the reaction of FcH with CCl_4 occurs with a quantum yield of 0.13, 0.8, 1.1, or 1.2, respectively[34]:

$$Fe(C_5H_5)_2 \cdot CCl_4 \xrightarrow{h\nu < 380\ nm} [Fe^+(C_5H_5)_2^-]^{*CT} \cdot CCl_4 \longrightarrow Fe^+(C_5H_5)_2 \cdot Cl^- + CCl_3.$$

The photoreaction of TFcP with CCl_4 occurs during irradiation in the spectral range in which the direct excitation of Fc does not result in transformation, but the formation of a state with charge transfer from Fc to the porphyrin fragment is possible, and this state reacts with CCl_4. The low quantum yields of fluorescence and the triplet state of TFcP can be due to the fast back electron transfer in the corresponding excited state of TFcP.

Redox quenching of the porphyrin triplet state by ferrocene is also thermodynamically favored, because the oxidation potential of triplet TPP is equal to +0.62 eV. [2] The redox mechanism is indicated by the dependence of the quenching rate constant on the polarity of the medium. Quenching does not produce free radical ions, and this indicates that the lifetime of the triplet state with charge transfer is short.

Thus, the low quantum yields of fluorescence and the triplet state of TFcP, as compared to those of other Fc-substituted porphyrins, are due to the fast nonradiative deactivation of the state with intramolecular charge transfer. The reaction of this state with a CCl_4 molecule competes with the relaxation process and results in the formation of the product.

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