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Photochemical study of the zinc *cis*-3-(4-imidazolylphenyl)-1-(pyridin-2-yl)[60]fullereno[1,2-*c*]pyrrolidine—*meso*-tetraphenylporphyrinate dyad

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Axial coordination of fullerenopyrrolidine bearing the donor imidazolyl group, *cis*-3-(4-imidazolylphenyl)-1-(pyridin-2-yl)[60]fullereno[1,2-*c*]pyrrolidine (C_{60}~Im), with zinc *meso*-tetraphenylporphyrinate (ZnTPP) in an *o*-dichlorobenzene solution affords a non-covalently bonded donor-acceptor dyad ZnTPP—C_{60}~Im. The photochemical behavior of the ZnTPP—C_{60}~Im complex was studied by fluorescence (excitation at $\lambda = 420$ nm) and laser kinetic spectroscopy (excitation at $\lambda = 532$ nm, 12 ns). The formation constant of the 1 : 1 porphyrin—fullerenopyrrolidine complex determined from quenching of ZnTPP fluorescence assuming static intracomplex quenching is $1.6 \cdot 10^4$ L mol^{-1}. Absorption spectra of the excited states in the system consisting of ZnTPP and Im~C_{60} (ZnTPP/C_{60}~Im) were measured in solution from 380 to 1000 nm. The quenching constant of the triplet-excited ZnTPP with fullerenopyrrolidine C_{60}~Im was determined. The results obtained indicate the formation of the triplet exciplex $\{PL\}^* \rightleftharpoons \{P^{\delta+}\cdots L^{\delta-}\}$ in the ZnTPP/C_{60}~Im system upon laser photolysis.

Key words: zinc tetraphenylporphyrinate, fullerenopyrrolidine, dyad, donor-acceptor complex, fluorescence, laser kinetic spectroscopy, excited states, exciplex.

The creation of systems for efficient charge photo-separation based on supramolecules is of unambiguous interest for understanding processes that occur in the photosynthetic reaction center and for development of molecular electronic devices.

Fullerenes and their derivatives possess unique properties. They absorb solar light in a rather wide spectral range and have a low first reduction potential; their molecules are electron acceptors (up to six electrons can be accepted during reduction to form the corresponding anionic particles), *etc.* Due to this they are suitable "building" materials for multicomponent systems capable of photoinduced energy and electron transferring. For instance, donor-acceptor dyads consisting of fullerene derivatives and porphyrin are used as models for studying photoinduced charge separation.[1—3]

In the present work, we studied the behavior of the noncovalently bonded donor-acceptor dyad formed by the axial coordination of *cis*-3-(4-imidazolylphenyl)-1-(pyridin-2-yl)[60]fullereno[1,2-*c*]pyrrolidine (C_{60}~Im, **1**), whose structure is shown in Fig. 1, with zinc *meso*-tetraphenylporphyrinate (ZnTPP) by fluorescence and laser kinetic spectroscopy.
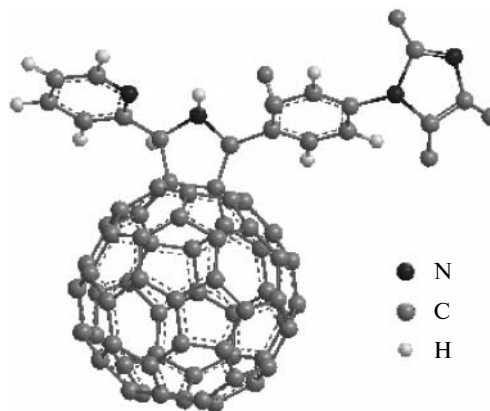

Fig. 1. Structure of compound **1**.

Experimental

Compound **1** was synthesized according to an earlier described procedure.[4] The obtained spectroscopic data (^{1}H NMR, electronic spectra, and other) for fullerenopyrrolidine **1** correspond to published data.[4] *o*-Dichlorobenzene used as solvent was purified and dried according to standard procedures and distilled before use.

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Absorption spectra were obtained on Specord UV-VIS and Specord M-40 spectrophotometers (quartz cell, thickness 1 cm).

Fluorescence emission was detected with a luminescence technique.[5] The spectra were recorded at room temperature in quartz cells (1 cm) equipped with a vessel for operation *in vacuo*. To determine the formation constant of the ZnTPP—**1** dyad from fluorescence quenching, solutions with a constant concentration of ZnTPP ($0.8 \cdot 10^{-6}$ mol L^{-1}) and a variable concentration of **1** ($0.4 \cdot 10^{-5}$—$6.0 \cdot 10^{-5}$ mol L^{-1}) were prepared in *o*-dichlorobenzene. We measured the intensity of fluorescence of ZnTPP upon excitation at $\lambda = 420$ nm. The instrumental measurement error was ~5%. The K_a value for the formation of the ZnTPP—**1** dyad was calculated by the equation[6,7]

$$I_0/(I_0 - I) = 1/A + 1/K_a A[\mathbf{1}],$$

where I_0 is the intensity of fluorescence of ZnTPP; I is the intensity of fluorescence of ZnTPP in a solution containing **1**; [**1**] is the molar concentration of fullerenopyrrolidine; A is the constant (difference in the quantum yields of emission of bonded and free ZnTPP).

Laser photolysis of a ZnTPP—C_{60}~Im mixture in *o*-dichlorobenzene was carried out with the second harmonic of an Nd^{3+}:YAG laser ($\lambda = 532$ nm, pulse duration 12 ns, pulse energy ~1.0 mJ). The detection system was described in detail in Ref. 8. Experiments were carried out in evacuated quartz cells 1 cm thick at [ZnTPP] $= 0.2 \cdot 10^{-4}$ mol L^{-1} and [**1**] $= (0.28—4.76) \cdot 10^{-4}$ mol L^{-1} using *o*-dichlorobenzene as solvent.

Results and Discussion

The formation of the zinc(II) tetraphenylporphyrinate complex with **1** when mixing solutions of C_{60}~Im and ZnTPP in *o*-$C_6H_4Cl_2$ is accompanied by a decrease in the Soret band intensity, the shift of the metal porphyrin absorption bands to the long-wavelength region, and the appearance of isosbestic points. It has been shown previously,[9] no spectral changes were observed on mixing solutions of ZnTPP and *cis*-1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine in *o*-$C_6H_4Cl_2$, *i.e.*, neither the nitrogen atom of the 2-pyridyl group, nor the pyrrolidinic nitrogen atom coordinated with ZnTPP. Hence, we concluded that the formation of the donor-acceptor dyad ZnTPP—**1** is due to the axial coordination of the nitrogen atom of the imidazolyl group with the central zinc atom of metal porphyrin similarly to the earlier observation.[10]

Quenching of fluorescence of ZnTPP with fullerenopyrrolidine 1. The absorption spectrum of ZnTPP contains two intense bands: the B or Soret (423 nm) and Q (549 nm) bands identified as the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions and lower-intensity bands at 402, 510, and 589 nm. The both transitions $S_1 \rightarrow S_0$ (596 and 645 nm) and $S_2 \rightarrow S_0$ were identified in the fluorescence spectra of ZnTPP ($\lambda_{exc} = 397$ nm).[11] In the spectra of highly dilute solutions of ZnTPP in benzene, the S_2 peak appears at 428.3 nm, and its intensity and position are strongly affected by the metal porphyrin concentration in the solution. The change in the
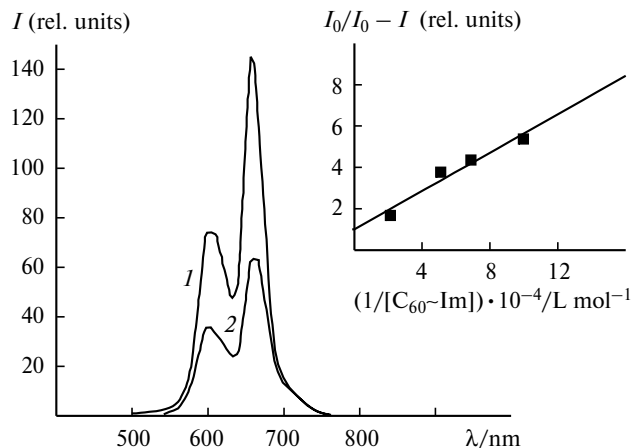

Fig. 2. Fluorescence spectra of ZnTPP ($8 \cdot 10^{-7}$ mol L^{-1}) in *o*-dichlorobenzene in the absence (*1*) and presence of C_{60}~Im ($4.79 \cdot 10^{-5}$ mol L^{-1}) (*2*). The plot of $I_0/(I_0 - I)$ *vs.* $1/C_{60}$~Im is presented in inset.

ZnTPP concentration exerts an insignificant effect on the intensity and structure of the fluorescence Q(0,1) band.[11]

The present study of quenching of ZnTPP fluorescence ($\lambda_{exc} = 420$ nm) with fullerenopyrrolidine **1** showed that the addition of excess **1** to the solution containing $0.8 \cdot 10^{-6}$ mol L^{-1} ZnTPP results (in inert atmosphere) in a decrease in the fluorescence intensity (*I*) of ZnTPP by ~50% (Fig. 2). The high ε_{ZnTPP} value in the visible spectral region (Soret band) makes it possible to excite predominantly metal porphyrin, although its concentration is much lower than the fullerenopyrrolidine concentration. The quantum yield of fluorescence of fullerenes is substantially lower than the quantum yield of the excited state ZnTPP* (see Ref. 12).

Fluorescence titration of ZnTPP with fullerenopyrrolidine C_{60}~Im was carried out. The formation constant $K_a = 1.6 \cdot 10^4$ L mol^{-1} was calculated from the slope of the plot of $I_0/(I_0 - I)$ *vs.* $1/[C_{60}$~Im] (see Fig. 2, inset) assuming the static mechanism of quenching inside the complex. This value agrees with the K_a value for the dyad of ZnTPP with {1-(4-imidazolylphenyl)[60]fullereno[1,2-*c*]pyrrolidine} (**2**) in *o*-$C_6H_4Cl_2$ (see Refs 1 and 10). At [C_{60}~Im] $= 4.79 \cdot 10^{-5}$ mol L^{-1} the amount of metal porphyrin bound in the ZnTPP—**1** donor-acceptor
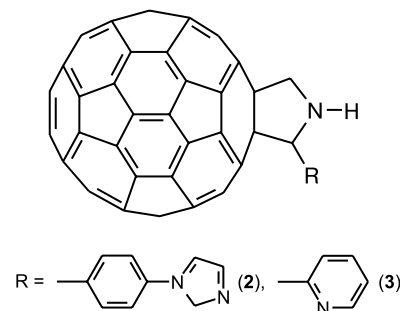
complex is ~44%. Thus, in the system under study the intramolecular contribution (due to complexation forming the ZnTPP—**1** dyad) to fluorescence quenching should be significant. It was shown[10] for compound **2** and some other fullerene derivatives that the energy transfer from singlet-excited ZnTPP to fullerenopyrrolidine is not necessary for fluorescence quenching.

The bimolecular quenching constant (k_q) calculated from the linear region of the plot* $I_0/I = 1 + K_s[\text{L}]$, where $K_s = k_q\tau_0$, and τ_0 is the lifetime of fluorescence of ZnTPP**, assuming the dynamic mechanism of fluorescence quenching of ZnTPP with compound **1**, is approximately three orders of magnitude higher than the quenching constant of the diffusion-controlled process. These results assume both types of the photochemical process: dynamic and static (inside the complex). It was shown[10] that in the absence of axial coordination of the ligand with ZnTPP, as in the case of compound **3**, the dependence in the Stern—Volmer coordinates is linear with a small slope, while in the case of pyridine as extraligand, the dependence is almost parallel to the abscissa, indicating the dynamic route of quenching of ZnTPP fluorescence. Note that, when mixing compounds **1** and ZnTPP in solvents (S) capable of strong coordination bonding with the zinc ion in ZnTPP, no spectral changes (for the ZnTPP—S system) were observed. Thus, the data obtained suggest the static (intramolecular) quenching of fluorescence of ZnTPP in the ZnTPP—**1** noncovalently bonded donor-acceptor dyad.

Nanosecond laser photolysis of a mixture of ZnTPP and C_{60}~Im. In the ground state ZnTPP and C_{60}—Im exhibit noticeable absorption at 532 nm ($\varepsilon_{532} = 3400$ L mol^{-1} cm^{-1} and 1630 L mol^{-1} cm^{-1}, respectively), which prevents selective excitation of the components of the system. The absorption bands of triplet ZnTPP lie at 400, 470, 745, and 845 nm (toluene, $\varepsilon_{400} = 42\,000$ L mol^{-1} cm^{-1}, $\varepsilon_{470} = 74\,000$ L mol^{-1} cm^{-1}, $\varepsilon_{740} = 5300$ L mol^{-1} cm^{-1} and $\varepsilon_{845} = 8200$ L mol^{-1} cm^{-1}).[13] For pulse excitation in deaerated PhCN, absorption bands for ^{3}ZnTPP* appear at 750 and 850 nm (see Ref. 12), and in MeCN they are observed at 470 and 840 nm (see Ref. 14). The ZnTPP radical cation absorbs at 630 and 650 nm (see Ref. 15), and absorption bands of the C_{60}~Im radical anion lie at 1000 nm (see Refs 4 and 10), which is close to the absorption of $C_{60}^{\bullet-}$ at 1060 nm (see Ref. 16).

Functionalization of C_{60} by the [2+3]cycloaddition of azomethine ylides to form fullerenopyrrolidines changes the electronic and spectral properties of the excited state of fullerene. For instance, if the absorption band of $^3C_{60}$* lies at 740 nm (see Ref. 12), then triplet substituted

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* The observed dependence in the Stern—Volmer coordinates I_0/I—[L], where L is the quencher, is a linear region transformed into a descending branch at high ligand concentrations.
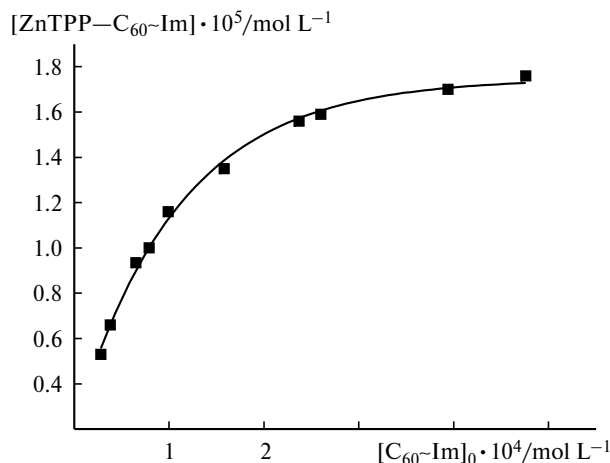** In o-C$_6$H$_4$Cl$_2$ τ is 2.1 ns.[10]

Fig. 3. Plot of the equilibrium concentration of the ZnTPP—**1** dyad *vs.* initial concentration of **1** ([ZnTPP]$_0 = 0.2 \cdot 10^{-4}$ mol L^{-1}, o-C$_6$H$_4$Cl$_2$).
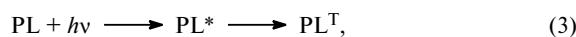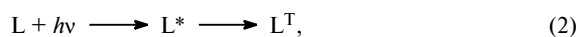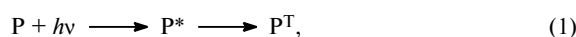
fullerenopyrrolidines absorb at 700 nm (see Ref. 17), and their lifetimes are much shorter than the lifetime of $^3C_{60}$*.

The equilibrium concentrations of the ZnTPP—**1** donor-acceptor dyad were calculated using the K_a formation constant found from the fluorescence quenching. As can be seen from the data in Fig. 3, the most part of ZnTPP in the ground state at high concentrations of **1** are bound into the ZnTPP—**1** complex, which is seen from the absorption spectra (see above).

The dependence of the differential absorption spectra of a ZnTPP/**1** mixture, obtained by mixing the components ZnTPP and **1**, on the concentration of **1** was studied in the spectral range from 400 to 1000 nm. Pulse photolysis experiments show substantial changes in the differential absorption spectra of the system under study in o-C$_6$H$_4$Cl$_2$ (Fig. 4). Note that the laser pulse energy (1.0 mJ) suggests the stability of the ZnTPP—**1** dyad upon excitation.

Just after a laser pulse, bands at 480, 740, and 850 nm appear in the absorption spectrum. According to published data,[12,13] these bands were assigned to ^{3}ZnTPP*, whose concentration in the solution containing [**1**] = $0.38 \cdot 10^{-4}$ mol L^{-1} with a delay time of $1.5 \cdot 10^{-5}$ s was estimated as ~$0.7 \cdot 10^{-6}$ mol L^{-1} (see Fig. 4).

The main processes in the system containing ZnTPP (P) and **1** (L) during nanosecond laser photolysis can be described by Eqs (0)—(17):
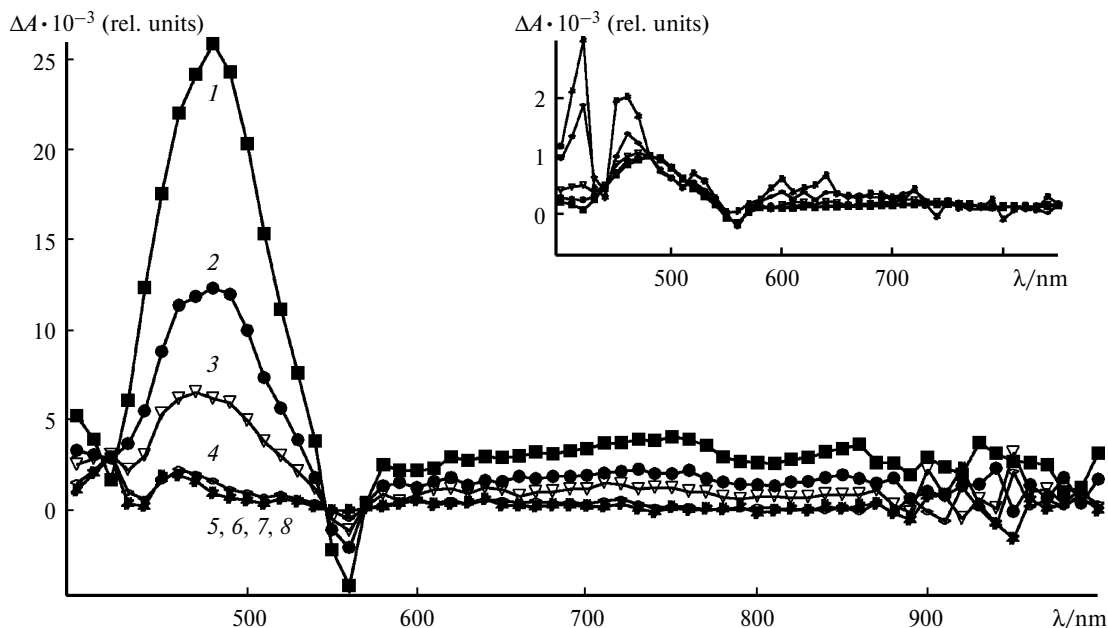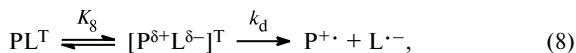
$$P + L \underset{}{\overset{K}{\rightleftharpoons}} PL, \tag{0}$$

$$P + h\nu \longrightarrow P^* \longrightarrow P^T, \tag{1}$$

$$L + h\nu \longrightarrow L^* \longrightarrow L^T, \tag{2}$$

$$PL + h\nu \longrightarrow PL^* \longrightarrow PL^T, \tag{3}$$

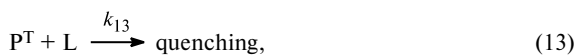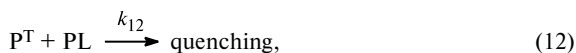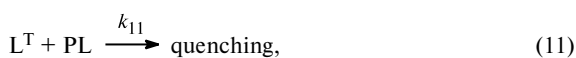$$P^T \xrightarrow{1/\tau_0^{P(T)}} P, \tag{4}$$

Fig. 4. Differential absorption spectra of the ZnTPP/**1** system in o-$C_6H_4Cl_2$ upon pulse excitation ($\lambda = 532$ nm, $[ZnTPP]_0 = 2 \cdot 10^{-5}$ mol L^{-1}, $[\mathbf{1}]_0 = 3.8 \cdot 10^{-5}$ mol L^{-1}). Delay time: $1.5 \cdot 10^{-5}$ (*1*), $2.5 \cdot 10^{-5}$ (*2*), $3.5 \cdot 10^{-5}$ (*3*), $6.5 \cdot 10^{-5}$ (*4*), $1 \cdot 10^{-4}$ (*5*), $2 \cdot 10^{-4}$ (*6*), $4 \cdot 10^{-4}$ (*7*), and $9 \cdot 10^{-4}$ s (*8*). The normed absorption spectra are presented in inset.

$$L^T \xrightarrow{1/\tau_0^{L(T)}} L, \tag{5}$$

$$P^T + L \xrightarrow{k_q^P} PL^T, \tag{6}$$

$$L^T + P \xrightarrow{k_q^L} PL^T, \tag{7}$$

$$PL^T \underset{}{\overset{K_8}{\rightleftharpoons}} [P^{\delta+}L^{\delta-}]^T \xrightarrow{k_d} P^{+\cdot} + L^{\cdot-}, \tag{8}$$

$$K_8 = k_8/k_{-8};$$

balance equation $K = PL/P \cdot L$, where $P + PL = P_0$, $L + PL = L_0$;

$$P^T + PL \xrightarrow{k_q} PL^T, \tag{9}$$

$$L^T + PL \xrightarrow{k_{10}} PL^T, \tag{10}$$

$$L^T + PL \xrightarrow{k_{11}} \text{quenching}, \tag{11}$$

$$P^T + PL \xrightarrow{k_{12}} \text{quenching}, \tag{12}$$

$$P^T + L \xrightarrow{k_{13}} \text{quenching}, \tag{13}$$

$$L^T + P \xrightarrow{k_{14}} \text{quenching}, \tag{14}$$

$$PL^T \longrightarrow PL, \tag{15}$$

$$P^{+\cdot} + L^{-\cdot} \longrightarrow \text{decay}, \tag{16}$$

$$\{P^{\delta+}\cdots L^{\delta-}\} \longrightarrow \text{decay}. \tag{17}$$

Here K is the equilibrium constant of the complexation of ZnTPP with **1** in the ground state; k_q is the bimolecular fluorescence quenching constant including both contributions: dynamic and static quenching; k_q^P and k_q^L are the bimolecular rate constants of dynamic quenching of free triplet porphyrin and ligand by the ligand and porphyrin, respectively; $\tau_0^{P(T)}$ and $\tau_0^{L(T)}$ are the fluorescence lifetime of triplet porphyrin and the ligand, respectively; k_d is the dissociation constant of the triplet radical ion pair.

The regions of triplet-triplet absorption of ZnTPP (P*) at 485 nm, absorption at 600—720 nm (see Fig. 4), and absorption at 420 nm (see Fig. 4, inset) can be distinguished in the differential spectra from the times of absorption decay. Broad structureless bands at 600—720 nm can be considered as the absorption of the ZnTPP$^{+\cdot}$ radical cation and triplet state of **1** (Eqs (8) and (2)), according to published data,[14,17] and as the absorption $\{PL\}^* \rightleftharpoons \{P^{\delta+}\cdots L^{\delta-}\}$ (Eq. (8)). A weak band at 630 nm can be distinguished in the normed spectra (see Fig. 4, inset), which indicates, most likely, the formation of the ZnTPP$^{+\cdot}$ radical cation upon a laser pulse in the presence of C_{60}~Im. However, at delay times of $1.5 \cdot 10^{-5}$—$9 \cdot 10^{-4}$ s the absorption spectrum contains no pronounced absorption band of the $\mathbf{1}^{-\cdot}$ radical cation at 900—1000 nm (see Fig. 4). This can be caused by both the low yield of the state of charge separation $P^{+\cdot} + L^{-\cdot}$,
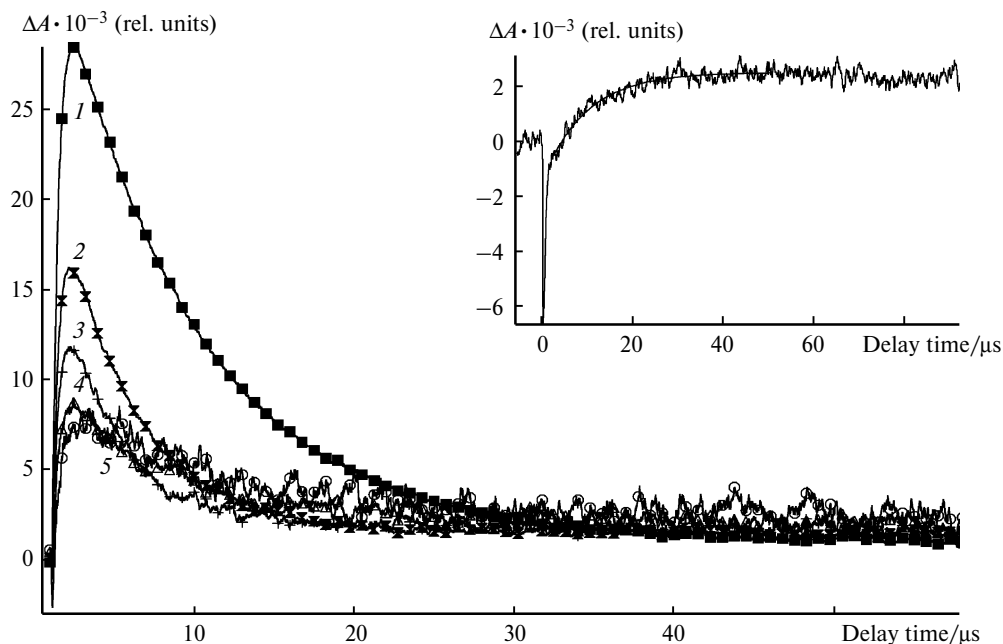
Fig. 5. Kinetics of the absorption decay at 453 nm after laser excitation at $\lambda = 532$ nm for the ZnTPP/C$_{60}$~Im system ([ZnTPP] = $2 \cdot 10^{-5}$ mol L^{-1}) in o-C$_6$H$_4$Cl$_2$ at the C$_{60}$~Im concentration: $7.9 \cdot 10^{-5}$ (*1*), $15.8 \cdot 10^{-5}$ (*2*), $23.7 \cdot 10^{-5}$ (*3*), $39.4 \cdot 10^{-5}$ (*4*), and $47.6 \cdot 10^{-5}$ mol L^{-1} (*5*). The kinetics of the absorption increase at $\lambda = 420$ nm in the ZnTPP ($2 \cdot 10^{-5}$ mol L^{-1})/C$_{60}$~Im system ($3.8 \cdot 10^{-5}$ mol L^{-1}) in o-C$_6$H$_4$Cl$_2$ is presented in inset.

which is indicated by the weak band of ZnTPP$^{+\bullet}$ at 630 nm, and the high rate of ion recombination in the system under study. Charge separation in the ZnTPP—**2** noncovalently bonded donor-acceptor dyad in o-dichlorobenzene with formation of the **2**$^{-\bullet}$ and ZnTPP$^{+\bullet}$ radical ions occurred[10] within ~0.01 µs and was interpreted as the participation of singlet-excited metal porphyrin in the photoinduced intramolecular charge transfer.

It can be assumed that the structureless absorption at 600—720 nm belongs, to a great extent, to the {PL}* $\rightleftharpoons$ {P$^{\delta+}$···L$^{\delta-}$} complex in the triplet state.

The bands of triplet ZnTPP were identified in the absorption spectra of the system under study. No noticeable presence of triplet C$_{60}$~Im (see Fig. 4) was observed at these time delays.

The characteristic kinetic curves of absorbance changes in the system containing ZnTPP and C$_{60}$~Im (ZnTPP/C$_{60}$~Im) after a laser pulse are shown in Figs 5 and 6. The kinetics of absorption decay at $\lambda = 453$ nm (^{3}ZnTPP*) and 700 nm (possibly, ^{T}{P···L}*) indicates that fullerenopyrrolidine **1** is involved in quenching during laser photolysis (Eqs (11) and (13)). The lifetimes of the intermediate states were estimated from the decay in the exponential dependences, which agrees well with the experimental results.

At higher ligand concentrations, the most part of ZnTPP exists as a ZnTPP—C$_{60}$~Im complex (see Fig. 3). Just this determines, most likely, the shape of the plots of the pseudofirst rate constant of absorption decay at 700 nm
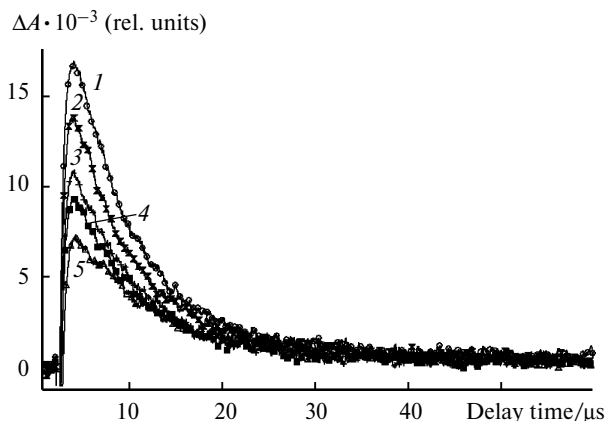

Fig. 6. Kinetics of the absorption decay at 700 nm after laser excitation at $\lambda = 532$ nm for the ZnTPP/C$_{60}$~Im system ([ZnTPP] = ($2 \cdot 10^{-5}$ mol L^{-1}) at the C$_{60}$~Im concentration: $39.4 \cdot 10^{-5}$ (*1*), $23.7 \cdot 10^{-5}$ (*2*), $47.6 \cdot 10^{-5}$ (*3*), $15.8 \cdot 10^{-5}$ (*4*), and $7.9 \cdot 10^{-5}$ mol L^{-1} (*5*).

(Fig. 7) and decay of ^{3}ZnTPP* at 453 nm (Fig. 8) in the Stern—Volmer coordinates.

At low C$_{60}$~Im concentrations, dynamic quenching of triplet ^{3}ZnTPP* unbound into the complex with the ligand is observed. The bimolecular quenching constants determined from the linear regions of the Stern—Volmer dependence (see Figs 7 and 8) are $1.3 \cdot 10^9$ and $1.15 \cdot 10^9$ L mol^{-1} s^{-1} for $\lambda = 453$ and 700 nm, respectively. The bimolecular quenching constant of ZnTPP fluorescence
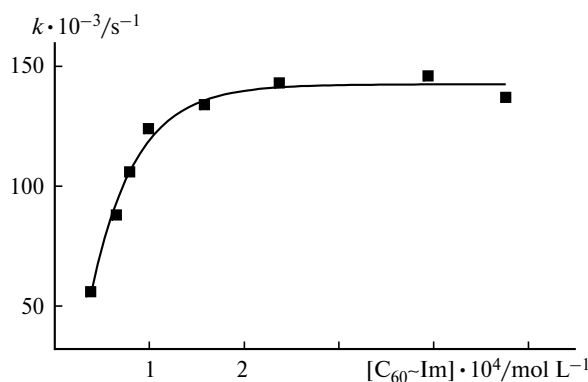
Fig. 7. Plot of the pseudofirst rate constant of the absorbance decrease at 700 nm *vs*. initial concentration of $C_{60}\text{~Im}$ at $[\text{ZnTPP}]_0 = 0.2 \cdot 10^{-4}$ mol L^{-1}.
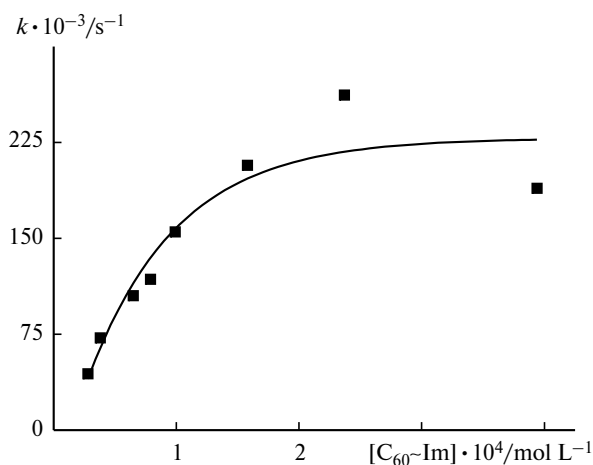
Fig. 8. Plot of the pseudofirst rate constant of $^3\text{ZnTPP}$ decay ($\lambda = 453$ nm) *vs*. initial concentration of **1** at $[\text{ZnTPP}]_0 = 0.2 \cdot 10^{-4}$ mol L^{-1}.

with substituted fullerenopyrrolidine $C_{60}\text{~Im}$ is higher by approximately three orders of magnitude.

The kinetics of the increase in the absorbance of the product at $\lambda = 420$ nm (see Fig. 5, inset), which is observed at rather low concentration of **1**, in combination with the Stern—Volmer dependence of the pseudofirst rate constant (see Figs 7 and 8) can indicate in favor of the formation of a triplet exciplex ($^T\{\text{PL}\}^* \rightleftharpoons \{P^{\delta+}\cdots L^{\delta-}\}$), whose absorption spectrum and lifetime are close to the characteristics of the $^3\text{ZnTPP}^*$ triplet state, although other products of photochemical transformations are possible in this system.

A possible reason for the formation of the $\{\text{PL}\}^* \rightleftharpoons \{P^{\delta+}\cdots L^{\delta-}\}$ exciplex in the ZnTPP/**1** system can be the electronic properties of fullerenopyrrolidine $C_{60}\text{~Im}$ and polarity of the medium. It is known that the formal redox potentials E_f of substituted fullerenes are somewhat shifted to negative values compared to E_f of the

redox transitions for C_{60} (see, *e.g.*, Ref. 18) due to the violation of π-conjugation in a C_{60} molecule under the effect of the annelated pyrrolidine ring: the introduction of addends changes hybridization of the carbon atoms from sp^2 to sp^3.

The presence of the 2-pyridyl group in a molecule of fullerenopyrrolidine $C_{60}\text{~Im}$ can exert no effect on the complexation ability of the nitrogen atom of the imidazolyl group of the ligand and, therefore, the formation constant of the noncovalently bonded dyads ZnTPP—**1** and ZnTPP—**2** (see Refs 1 and 10) are close. At the same time, *cis*-arrangement of the substituents in the pyrrolidine ring of $C_{60}\text{~Im}$ favors the interaction of the lone electron pair of the nitrogen atom in the 2-pyridyl group with orbitals of the nearest carbon atoms of the fullerene sphere (*peri*-conjugation[19]) bearing spin density. This results in a greater shift of the reduction potentials of 2-pyridyl-substituted fullerenopyrrolidines to negative values, indicating a decrease in the acceptor properties of the fullerene fragment.[4,20] The enhancement of the donor ability of ligand **1** can decrease the probability of the formation of the state of charge separation for the ZnTPP—**1** donor-acceptor complex on its photoexcitation in a low-polarity medium.

Our conclusion about a possible existence of triplet exciplexes in the ZnTPP/**1** systems can be confirmed by the results of the study[21] of quenching of metal porphyrins in the triplet state with fullerenes C_{60} (C_{70}). For example, for laser irradiation of C_{70} in the presence of metal octaethylporphyrinate (MOEP, M = Zn^{II}, Mg^{II}, *etc*.) in toluene no formation of $\text{MOEP}^{\bullet+}$ and $C_{70}^{-\bullet}$ was found. In this case, the kinetics of the absorption decay of $^3C_{70}^*$ depends linearly on the MOEP concentration, and k_q for the $^3C_{70}^*$—MOEP system is $(4.8—5.3) \cdot 10^9$ L mol^{-1} s^{-1}. No energy transfer occurred from $^3C_{70}^*$ to MOEP, because the absorption band of $^3\text{MOEP}^*$ was not observed. This is caused by a difference in the redox potentials of the excited triplet states $^3C_{70}^*$ and $^3\text{MOEP}^*$. The authors[21] assumed that the triplet exciplex $^3\{C_{70}^{(\delta-)}—\text{MOEP}^{(\delta+)}\}^*$ is formed in a nonpolar solvent (toluene). A change in the polarity of the medium (variation of the $C_6H_5Me : C_6H_5CN$ ratio) resulted in the appearance of the $\text{MOEP}^{+\bullet}$ radical cations and $C_{70}^{-\bullet}$ radical anions, *i.e.*, dissociation of the triplet according to the known chemistry of exciplexes.[22]

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