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Spectroscopic study of the reaction of *cis*-1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine and 2-(2-pyridylmethyl)-1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine with zinc *meso*-tetraphenylporphyrinate

A. N. Lapshin, V. A. Smirnov, R. N. Lyubovskaya, and N. F. Gol´dshleger★

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: gold@cat.icp.ac.ru

Axial coordination of the pyrrolidine nitrogen atom in *cis*-1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine to zinc *meso*-tetraphenylporphyrinate in cyclohexane gives rise to a donor-acceptor complex. The formation constant of the 1 : 1 porphyrin—fullerenopyrrolidine complex was determined by spectrophotometric and fluorescence titration. The values of the constant estimated by spectrophotometric and fluorescence methods are $1.2 \cdot 10^4$ and $9.7 \cdot 10^3$ L mol^{-1}, respectively.

Key words: fullerene, donor-acceptor dyad, 1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine, 2-(2-pyridylmethyl)-1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine, zinc *meso*-tetraphenylporphyrinate, fluorescence titration, formation constant.

Fullerenes and their derivatives have unique properties, such as absorption in a wide spectral range, the electron-donating properties and ability to accept up to six electrons upon reduction giving rise to the corresponding anionic species, low first reduction potential, *etc*. As a consequence, these compounds are suitable building blocks for multicomponent systems showing the ability to be involved in photoinduced energy and electron transfer processes. For example, donor-acceptor dyads consisting of fullerenes and metalloporphyrins serve as interesting models for studying photoinduced charge separation processes.[1—3] Photoactive and catalytically active molecular and supramolecular assemblies based on new polyfunctional fullerene derivatives are also of interest from the point of view of the construction of electronic devices capable of absorbing solar energy and converting it into other forms.

In the present study, the reactions of 2-pyridyl-substituted fullerenopyrrolidines, *viz*., *cis*-1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine (**1**) and 2-(2-pyridylmethyl)-1,3-di(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine (**2**), were investigated by spectrophotometric and fluorescence methods as possible components of noncovalently bound donor-acceptor dyads with zinc *meso*-tetraphenylporphyrinate (ZnTPP). The distinguishing feature of these molecules is the presence of the secondary and tertiary nitrogen atoms in the pyrrolidine ring fused to fullerene C_{60} in compounds **1** and **2**, respectively.

Experimental

The absorption spectra were measured on Specord UV—VIS and Specord M-40 spectrophotometers in 1-cm quartz cells at 293 K. To determine the formation constant of the donor-acceptor substituted fullerenopyrrolidine—metalloporphyrin complex, we prepared a series of solutions with a constant concentration of zinc(II) tetraphenylporphyrinate and a variable concentration of ligand **1** and an analogous series of solutions of the free ligand. The formation constant *K* for the ZnTPP—**1** complex was calculated from the spectroscopic data at $\lambda = 416$ nm according to a known method[4] by the equation[5]

$$\Delta A/[\mathrm{X}] = K\Delta\varepsilon \mathrm{P}_{\mathrm{tot}} - K\Delta A,$$

where X is ligand **1**, $\Delta A = A - A_0$ (A is the absorbance of the solution for the *i*th mixture and A_0 is the initial absorbance), $\mathrm{P}_{\mathrm{tot}}$ is the total concentration of ZnTPP, and $\Delta\varepsilon = \varepsilon_{\mathrm{PX}} - \varepsilon_{\mathrm{X}}$ ($\varepsilon_{\mathrm{PX}}$ and ε_{X} are the molar extinction coefficients for the ZnTPP—**1** complex and ligand **1**, respectively).

Fluorescence emission was recorded on a luminescence apparatus described earlier[6] with the use of a 1-cm quartz cell equipped with a vessel for performing operations *in vacuo*. To determine the formation constant of the ZnTPP—**1** complex from fluorescence quenching, six solutions with a constant concentration of ZnTPP ($0.8 \cdot 10^{-6}$ mol L^{-1}) and an increasing concentration of compound **1** ($0.4 \cdot 10^{-5}$—$6.0 \cdot 10^{-5}$ mol L^{-1}) were prepared; and analogous series of solutions was prepared for compound **2**. The measured signal was the fluorescence intensity of ZnTPP, $\lambda_{\mathrm{ex}} = 420$ nm. Fluorescence measurements were carried out by comparing two compounds, which made it

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possible to exclude the absolute error. The measurement error for the fluorescence intensity was ~5%. The constant K_a for the ZnTPP—**1** complex was calculated by the equation[7,8]

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

where I_0 is the fluorescence intensity of ZnTPP in a reference solution containing compound **2,** I is the fluorescence intensity of ZnTPP in a solution containing compound **1**, [**1**] is the molar concentration of fullerenopyrrolidine **1**, and a is the constant characterizing the difference in the quantum yields of coordinated and free ZnTPP.

Cyclohexane was purified and dried according to standard procedures and distilled before use. The reactions were performed with the use of commercial ZnTPP.

Fullerenopyrrolidine 1 was synthesized according to a known procedure.[9] A mixture of 2-picolylamine and 2-pyridinealdehyde (1 : 1, 0.35—0.37 mmol) was dissolved in *o*-dichlorobenzene (2—5 mL), and the solution was added to a saturated solution of C_{60} (250 mg, 0.35 mmol) in *o*-dichlorobenzene (10 mL). The reaction mixture was refluxed for 20 min. The course of the reaction was monitored by TLC. After cooling to room temperature, the reaction mixture was diluted with a tenfold volume of toluene and purified by chromatography on a column (15 cm × 1.5 cm) packed with SiO_2 (40—100 μm). Unconsumed fullerene was eluted with toluene, and the reaction product, fullerenopyrrolidine **1**, was eluted with a methanol—toluene mixture (0.4—0.5 : 99.6—99.5). The yield was 0.15 g (~65% based on consumed fullerene C_{60}). Found (%): C, 93.89; H, 1.55; N, 4.73. $C_{72}H_{11}N_3$. Calculated (%): C, 94.22; H, 1.20; N, 4.58. The spectroscopic data for compound **1** are consistent with the published data.[9]

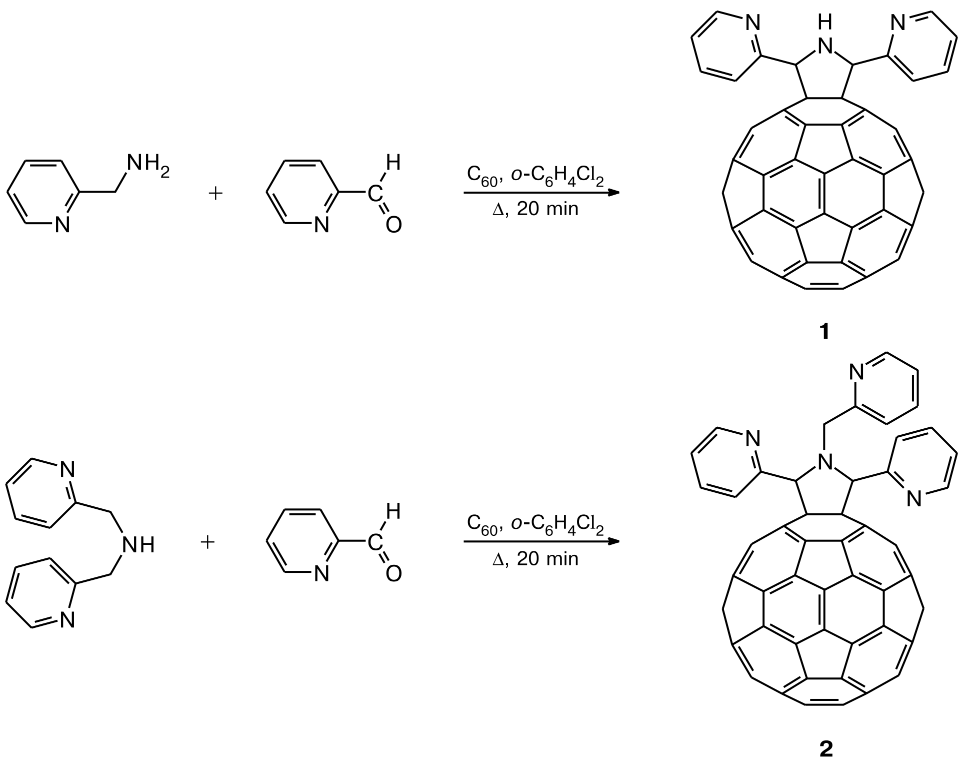
Compound **2** was synthesized by P. A. Troshin according to a known procedure.[9]

Results and Discussion

The donor-acceptor noncovalently bound substituted fullerenopyrrolidine—metalloporphyrin dyads are formed through coordination of a fullerene-based nitrogen-containing ligand with metalloporphyrin.[1] We studied the reaction of zinc(II) *meso*-tetraphenylporphyrinate with fullerenopyrrolidines **1** and **2** containing two and three substituents, respectively, in the pyrrolidine ring. Pyridyl-substituted derivatives of fullerenopyrrolidines **1** and **2** were synthesized[9] by [2+3]-cycloaddition of azomethine ylides, which were generated from picolylamines (2-(picolyl)amine for **1** and di(2-picolyl)amine for **2**) and carbonyl compounds (2-pyridinealdehyde), to fullerene C_{60} (Scheme 1).

Spectroscopic study of complexation in the ZnTPP—fullerenopyrrolidine system was carried out with the use of cyclohexane as a solvent, which is not coordinated to metalloporphyrin. This provides favorable conditions for the reaction of the latter with the ligand. It should be emphasized that the concentrations of the components (**1**, **2**, and ZnTPP) required for spectroscopic

Scheme 1



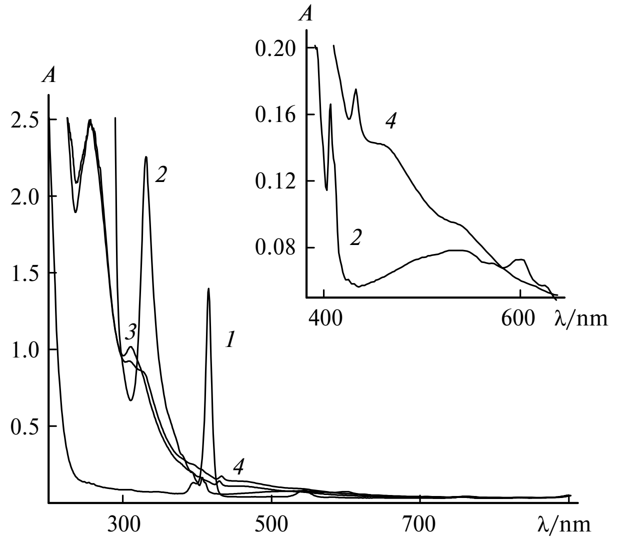


Fig. 1. Absorption spectra of ZnTPP (*1*), C_{60} (*2*), and fullerenopyrrolidines **1** (*3*) and **2** (*4*) (in cyclohexane). The absorption spectra of C_{60} (*2*) and fullerenopyrrolidine **2** (*4*) in the region of 400—600 nm are shown in the inset.

studies can be achieved in cyclohexane. In addition, the systems under study were found to be sufficiently photostable in this solvent.

The absorption spectrum of ZnTPP in the ground state (Fig. 1) has a very intense band (the Soret band) at λ_{max} = 416 nm (ε = 700000 L mol^{-1} cm^{-1}; *cf.* lit. data[10]: ε = 752000 L mol^{-1} cm^{-1}), which corresponds to the transition into the second singlet excited state S_2, and weaker Q bands at 550 nm assigned to a series of vibronic transitions to the lower-lying excited singlet level S_1.

The electronic absorption spectra of fullerenopyrrolidines **1** and **2** are presented in Fig. 1, where the spectrum of C_{60} is also shown for comparison. Both compounds are characterized by intense bands in the UV region at 260 and 314 nm (ε_{314} = 38700 L mol^{-1} cm^{-1}) typical of fullerene derivatives. The visible region of the spectra of compounds **1** and **2** has a band at about 430 nm (ε = 3000 L mol^{-1} cm^{-1}) characteristic of 1,2-dihydro derivatives of C_{60} [11] and a series of broad long-wavelength bands. The almost identical UV-Vis absorption spectra are indicative of the similar electronic nature of compounds **1** and **2**. The spectra of these compounds differ from the spectrum of the starting C_{60}, which is evidence for strong perturbation of electron levels upon the formation of the pyrrolidine ring fused to fullerene C_{60}.

The spectral changes observed upon the reaction of ZnTPP with fullerenopyrrolidine **1** in cyclohexane are shown in Fig. 2. An increase in the concentration of ligand **1** causes a decrease in the intensity of the Soret band, shifts of absorption bands of metalloporphyrin to longer wavelengths (from 416 to 430 nm), and the appearance of an isosbestic point at 423 nm. This is indicative of the formation of a 1 : 1 complex of ZnTPP with fullerenopyrrolidine **1** in solution. The spectral changes in the ZnTPP—**1** system were not observed when toluene, CH_2Cl_2, or *o*-dichlorobenzene were used as the solvent. It was demonstrated[12] that 1-(2-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine, unlike the 4-pyridyl derivative (C_{60}-4-py), does not react with ZnTPP in *o*-dichlorobenzene. Based on the absence of spectral changes during spectrophotometric titration of zinc(II) *meso*-tetraphenylporphyrinate with 1-phenyl[60]fullereno[1,2-*c*]pyrrolidine in *o*-dichlorobenzene, the authors of the cited publication[12] concluded that the pyrrolidine nitrogen atom in the compounds under study is not involved in the formation of a donor-acceptor dyad. However, studies in cyclohexane were not carried out in the cited work. It is also known[13] that 1,3-di(4-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine forms a rather stable 1 : 1 complex with ZnTPP in cyclohexane due to coordination of the nitrogen atom of the pyridyl substituent to zinc, analogously to that described in the study.[12]

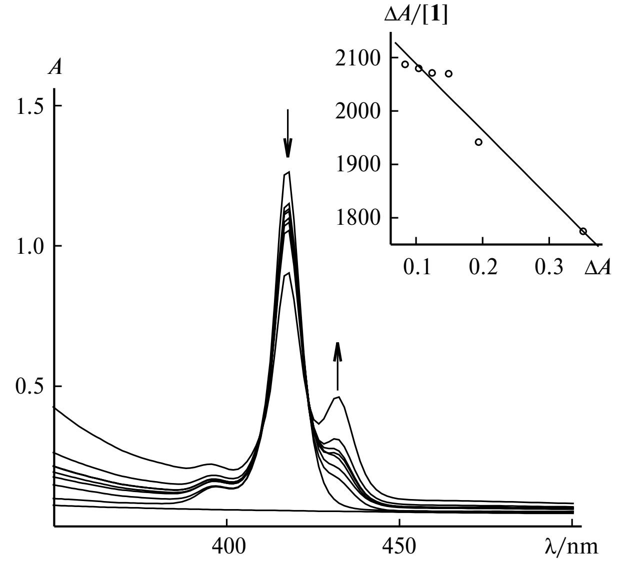


Fig. 2. Spectral changes upon complexation of ZnTPP ($2 \cdot 10^{-6}$ mol L^{-1}) with fullerenopyrrolidine **1** in cyclohexane. Changes in the absorption of the solution at λ = 416 nm on the Δ*A*/[**1**]—Δ*A* coordinates are shown in the inset.

Thus, the ZnTPP—**1** complex can be prepared in a solution in cyclohexane, like in the solid state,[9] only through the axial coordination of the pyrrolidine nitrogen atom to the central atom of metalloporphyrin (zinc). The constant *K* (~$1.2 \cdot 10^4$ L mol^{-1}) was determined from the slope of the plot of Δ*A*/[X] *vs.* Δ*A* (see Fig. 2). However, under the same conditions, the constant *K* for the formation of the ZnTPP—**1** complex through the axial coordination of the pyrrolidine nitrogen atom should be smaller than *K* for the formation of the dyad through coordination of the pyridine nitrogen atom of the ligand to the zinc atom.[13] For example, the Zn—N(pyrrolidine) distance in the ZnTPP—**1** complex (2.29(1) Å) is substantially longer[9] than the Zn—N(pyridyl) distance in the ZnTPP—1-(4-pyridyl)[60]fullereno[1,2-*c*]pyrrolidine dyad (2.158(5) Å).[14] It should be noted that intense absorption of fullerenopyrrolidine **1** ($\varepsilon^{1}_{416} \approx$ 3000 L mol^{-1} cm^{-1}) in the spectral region chosen for investigation decreases the accuracy of the determination of the formation constant for the donor-acceptor dyad from the spectrophotometric data* (see also Ref. 7).

Fluorescence quenching of ZnTPP was studied in parallel for the ZnTPP—**1** and ZnTPP—**2** systems. Due to high $\varepsilon_{\mathrm{ZnTPP}}$ in the visible spectral region (the Soret band), metalloporphyrin can be predominantly excited in spite of the fact that its concentration is substantially lower than that of fullerenopyrrolidine. The fluorescence quantum yields of fullerenes are much lower than that of ZnTPP,[15] and the emission band is outside the detection range of a fluorescence detector, due to which fluorescence of ZnTPP can be measured without interference with the band of fullerene. The formation constant of the ZnTPP—**1** dyad was determined from the fluorescence quenching with the use of compound **2** as a reference sample, because the spectroscopic properties of the latter are similar to those of compound **1**.

The addition of a large excess of compound **1** to a solution containing ZnTPP ($0.8 \cdot 10^{-6}$ mol L^{-1}) led to a decrease in the fluorescence intensity of ZnTPP by ~50% compared to that of the ZnTPP—**2** system (Fig. 3). It should be noted that the absorption spectra of a mixture containing equivalent amounts of ZnTPP and **2** are the sums of the spectra of both components in cyclohexane. In this case, the red shift of the Soret band is absent as opposed to a mixture of ZnTPP and **1**. The use of fullerenopyrrolidine **2** as a reference compound allows one to ignore luminescence absorption of metalloporphyrin by rather concentrated solutions of compound **1**, because high concentrations of a quencher are required for the determination of the complexation constants from fluorescence quenching.[16] Fluorescence titration of ZnTPP with fullerenopyrrolidine **1** was performed. The constant $K_a = 9.7 \cdot 10^3$ L mol^{-1} was determined from the plot of $I_0/(I_0 - I)$ *vs.* 1/[**1**].

Therefore, the above-considered spectrophotometric data are indicative of the formation of the ZnTPP—**1** complex in cyclohexane. The main difference of compound **1** from compound **2** is that the pyrrolidine ring of fullerenopyrrolidine **1** contains the secondary nitrogen atom accessible to complexation. To our opinion, a comparative study of the ZnTPP—**1** and ZnTPP—**2** systems made it possible to reveal the intramolecular contribution (due to complexation) to the fluorescence quenching in the ZnTPP—**1** dyad. Other possible contributions[17] can be taken into account by performing measurements relative to compound **2**.

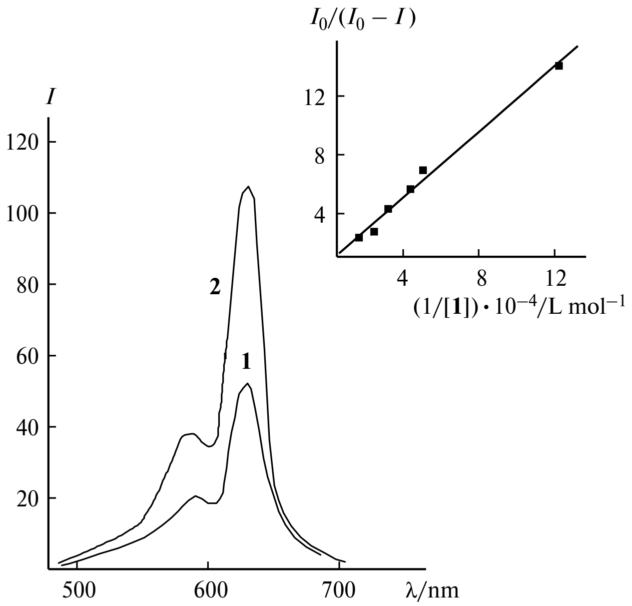


Fig. 3. Fluorescence spectra of ZnTPP ($0.8 \cdot 10^{-6}$ mol L^{-1}) in the presence of fullerenopyrrolidines **2** or **1** ($6.0 \cdot 10^{-5}$ mol L^{-1}). The determination of the formation constant for the ZnTPP—**1** dyad from the plot of $I_0/(I_0 - I)$ *vs.* 1/[**1**] is presented in the inset.

The crystal structure[9] of the noncovalently bound donor-acceptor ZnTPP—**1** dyad formed upon the axial coordination of the pyrrolidine nitrogen atom of the ligand to the central atom of metalloporphyrin (zinc) shows that the pyrrolidine ring in compound **1** adopts a *syn—cis* configuration. In our opinion, the high formation constant of the ZnTPP—**1** complex in cyclohexane can be explained in the context of the *peri*-conjugation mechanism (through-space orbital coupling), which has been proposed earlier[18—20] for the explanation of the reactivities of fullerene derivatives. The *cis*-arranged 2-pyridyl groups in compound **1** shield the fullerene sphere, thus hindering the interaction between the orbital of the lone pair of the pyrrolidine nitrogen atom and the π-system of fullerene.* At the same time, this configuration is favorable for the interaction between the orbitals of the nitrogen lone pairs of the 2-pyridyl groups and the p orbitals of the adjacent carbon atoms of the fullerene sphere bearing the spin density. This leads to a decrease in the acceptor ability (and, correspondingly, to an increase in the donor ability)

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* The absorbance A_0 includes also the absorption of fullerenopyrrolidine **1**. This gives the formation constant of $(1.2\pm0.1) \cdot 10^4$ L mol^{-1}.

* In polar media, delocalization of the nitrogen lone pair of the pyrrolidine ring fused to fullerene leads, due to interaction of this lone pair with the π system of fullerene, to an increase in the acidity by several orders of magnitude and a decrease in the reactivity of the pyrrolidine nitrogen atom, for example, in *N*-methyl-1-(*n*-alkyl)fullerenopyrrolidine.[19,20]

of the fullerene fragment, which is manifested in a larger shift of the first reduction peak of compound **1** to negative potentials compared to the 4-pyridyl derivative of fullerenopyrrolidine (C_{60}-4-py).[21] In addition, the electron-withdrawing properties of the substituent C_{60} are rather weak ($\sigma = 0.06$).[20] As a result, the presence of the fullerene structure can have a slight effect on the electron-donating properties of the second nitrogen atom of the pyrrolidine ring in compound **1** and, consequently, on its ability to form complexes with ZnTPP. The fact that the formation constant of the ZnTPP—py complex in *o*-dichlorobenzene is similar to that of ZnTPP—(C_{60}-4-py)[12] indirectly confirms this conclusion. Nevertheless, further investigations, including the determination of the formation constant of the complex of ZnTPP with 2,5-di(2-pyridyl)pyrrolidine (or its derivatives) as a model compound and a comparison of this constant with the formation constant of the ZnTPP—**1** dyad are required.

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