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ORIGINAL ARTICLE

Fluorescent Properties and Kinetic Rate Constants of some Zn-Tetraarylporphyrins Formation in Acetonitrile

Yulia B. Ivanova[1] · **Nugzar Z. Mamardashvili**[1]

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Abstract The fluorescence quantum yield of the 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetra(4-OH-phenyl)porphyrin, 5,10,15,20-tetra(4-Cl-phenyl)porphyrin, 5,10,15,20-tetra(4-NH_2-phenyl)porphyrin and their complexes with Zn^{2+} have been determined and the kinetic rate constants of the porphyrins ligands complexation with Zn^{2+} in acetonitrile have been estimated. It was shown that the substituents on the tetrapyrrolic macrocycle periphery have a strong influence on the fluorescent and coordination properties of the investigated porphyrins.

Keywords Porphyrin ligand · Metalloporphyrin · Fluorescence quantum yield · Kinetic rate constants

Porphyrins are typical amphoteric compounds (NH- acid and N- base) which are able to form metallocomplexes having important biological, photochemical, catalytic and fermentative functions [1–10]. These functions are mainly determined by the coordination properties of a porphyrin macrocycle and a metal cation in the reactionary center of the metalloporphyrin. Chemical modification of the macrocycle pyrrolic and meso-positions allows creating new polyfunctional materials with the desired properties [11, 12]. The electronic and steric effects of the substituents are the tools for the directed change of the porphyrins physicochemical properties. A special interest is the study of the effect of the peripheral substituents on the optical and coordination properties of the porphyrins and metalloporphyrins.

In the present study the fluorescence quantum yield of the 5,10,15,20-tetraphenylporphyrin (I, H_2TPhP), 5,10,15,20-tetra(4-OH-phenyl)porphyrin (II, H_2T(4-OH-Ph)P), 5,10,15,20-tetra(4-Cl-phenyl)porphyrin (III,H_2T(4-Cl-Ph)P), 5,10,15,20-tetra(4-NH_2-phenyl)porphyrin (IV,H_2T(4-NH_2-Ph)P) and their complexes with Zn^{2+} [Zn-5,10,15,20-tetraphenylporphyrin (V, ZnTPhP), Zn-5,10,15,20-tetra(4-OH-phenyl)porphyrin (VI, ZnT(4-OH-Ph)P), Zn-5,10,15,20-tetra(4-Cl-phenyl)porphyrin (VII, ZnT(4-Cl-Ph)P), Zn-5,10,15,20-tetra(4-NH_2-phenyl)porphyrin (VIII, ZnT(4-NH_2-Ph)P)] have been determined and the kinetic rate constants of the porphyrins ligands complexation with Zn^{2+} in acetonitrile have been estimated. It was shown that the substituents on the tetrapyrrolic macrocycle periphery have a strong influence on the fluorescent and coordination properties of the investigated porphyrins.

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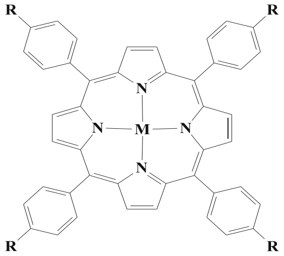
✉ Yulia B. Ivanova
jjiv@yandex.ru

Nugzar Z. Mamardashvili
ngm@isc-ras.ru

[1] G. A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Academicheskaya str. 1, Ivanovo, Russian Federation 153045



M:H, R: H (I, H_2TPhP), **-OH**(II, H_2T(4-OH-Ph)P), **- Cl** (H_2T(III, 4-Cl-Ph)P),

- NH_2, (IV, H_2T(4-NH_2-Ph)P)

M:Zn, R: H (V, ZnTPhP), **-OH**(VI, ZnT(4-OH-Ph)P), **- Cl** (VII, ZnT(4-Cl-Ph)P),

- NH_2, (VIII, ZnT(4-NH_2-Ph)P)

Experimental

UV-Vis spectra of the compounds (I-VIII) in acetonitrile were recorded by the spectrometer Cary 100 (Varian). The fluorimetric measurements of the acetonitrile solutions of the compounds (I-VIII) were recorded by the spectrofluorometer Shimadzu RF-5301. The methods of the procedure and protocols of the experimental data analysis were described in our previous papers [1, 13–15]. The studied compounds were prepared according to the synthetic procedures [16–18]. Dry acetonitrile (the amount of water is less then 0.03 %) was used in the experiment. Commercially available $Zn(OAc)_2$ was purified by recrystallization with acetic acid followed by dehydration at 380–390 K according to the method described in the work [19].

Results and Discussion

In order to study the effect of chemical modification of the tetrapyrrolic macrocycle on its photophysical properties the fluorescence quantum yield of the porphyrin ligands (I-IV) and their complexes with Zn^{2+} (V-VIII) in acetonitrile have been determined. Fluorimetric measurements were conducted as follows:

1. In the optical quartz cell with an optical pathway of 1 sm the acetonitrile solution of the investigated sample (optical density of the solution A < 0.1) was placed.
2. In order to avoid the error in determination of the sample fluorescence intensity the correction on the «dark» current (output current of the photomultiplier, not irradiated by the light) was curried out.
3. To take into account an effect of the solvent on the investigated sample fluorescence intensity, the fluorescence intensity of the clean solvent was subtracted from the fluorescence intensity of the solution.
4. Account of the Rayleigh scattering was carried out by variation in the wide interval of the excitation wavelengths (±40 nm), before the stable indications of the corresponding sample fluorescence peak coordinates (position of the fluorescence peaks must not change in the dependence on the excitation wavelength [21]).
5. The obtained fluorescence spectrum of sample was compared with the literary standard values [20]. The intensity of fluorescence was calculated.
6. The fluorescence quantum yield of the compounds (I-IV) solutions of in acetonitrile was calculated by standard procedure [22], using the formula (1):

$$Q_x = \frac{I_x A_{st}}{I_{st} A_x} Q_{st} \qquad (1)$$

where Q_x and Q_{st} - the quantum yields of the sample and standard respectively, A_x and A_{st} - their optical density at the wavelength of excitation, I_x and I_{st} – integrated intensities.

The fluorescence spectra for the ligands and their Zn-complexes in the acetonitrile are shown on the Fig.1 (spectra are calibrated regarding to a maximum of the fluorescence intensity). The values of the quantum yields for the investigated compounds are depicted in the Table 1. It was determined that the fluorescence quantum yield of the ZnTPhP and H_2TPhP in acetonitrile are two times lower in compare with corresponding values for these compounds in toluene ([20], Table 1). Probably, unlike to a non-polar toluene, a dipolar acetonitrile contributes to the extinguishing of the solutions fluorescence.

A similar effect is described in the literature [23] on the example of the tetraazaporphyrin photo-physical parameters in isobutanol, isopropanol and toluene solutions.

Analyzing obtained data, it could be concluded that the quantum yields of the ligands H_2T(4-NH_2-Ph)P, H_2T(4-Cl-Ph)P and their Zn-complexes (ZnT(4-NH_2-Ph)P, ZnT(4-Cl-Ph)P) are practically identical. That is, the metal-complexes formation does not significantly affect on the fluorescence properties of starting tetrapyrrolic macrocycles. In the same time, in case of the ligands H_2TPhP, H_2T(4-OH-Ph)P, the Zn-complexes formation is accompanied by a significant (almost three times) extinguishing of their fluorescence (Table 1).

Significant changes in the fluorescence quantum yield depending on the nature of the substituents are observed among the porphyrin ligands H_2TPhP, H_2T(4-NH_2-Ph)P and H_2T(4-Cl-Ph)P. The Cl-substitution of the macrocycle phenyl groups leads to the extinguishing of its fluorescence (the quantum yield is decreasing about 1.6 times

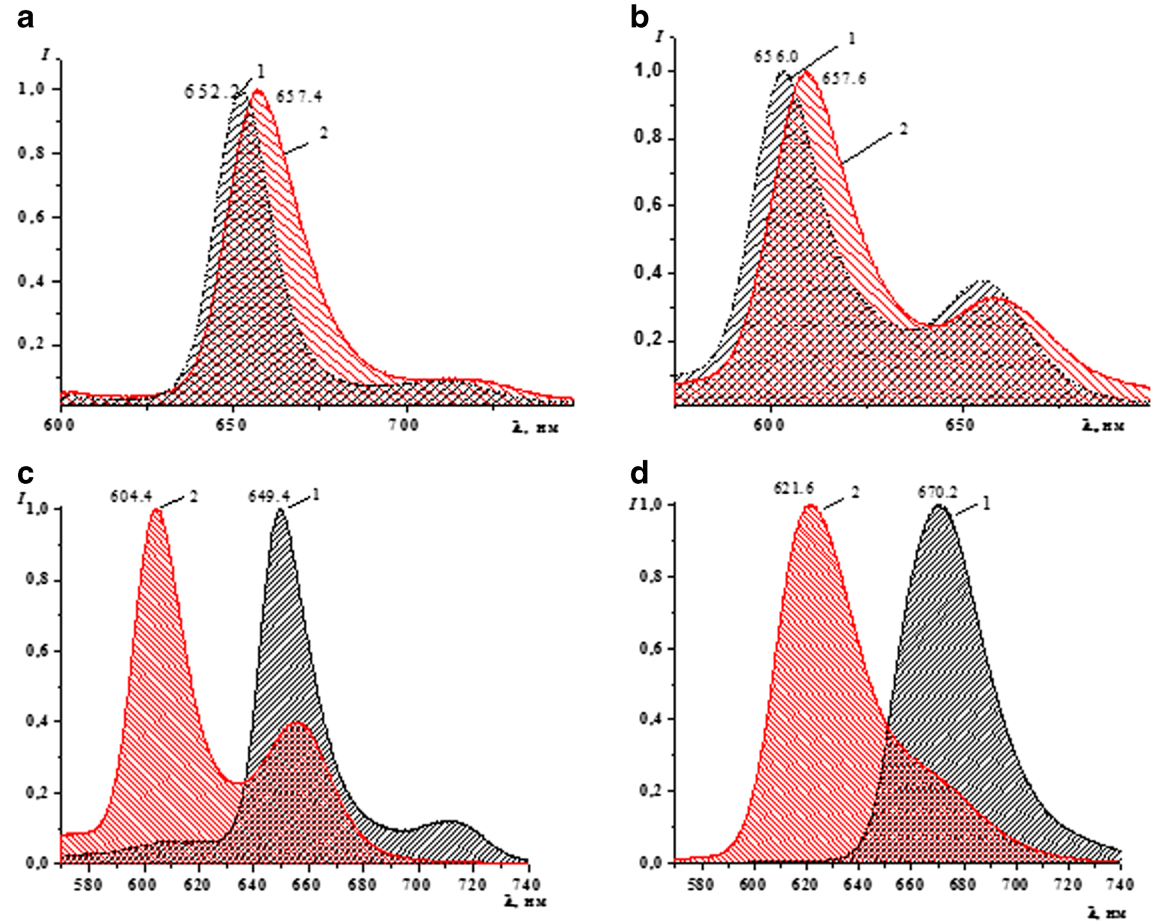


Fig. 1 Fluorescence spectra in the acetonitrile at 298 K: **a** H_2TPhP (*1*) ($1.01{\cdot}10^{-5}$ M) and $H_2T(4\text{-}OH\text{-}Ph)P$ (*2*) ($1.50{\cdot}10^{-5}$ M), λ_{ex} = 555 nm; **b** ZnTPhP (*1*) ($1.76{\cdot}10^{-6}$ M) and ZnT(4-OH-Ph)P (*2*) ($1.86{\cdot}10^{-6}$ M), λ_{ex} = 555 nm; **c** $H_2T(4\text{-}Cl\text{-}Ph)P$ (*1*) ($1.5{\cdot}10^{-6}$ M) and ZnT(4-Cl-Ph)P (*2*) ($1.5{\cdot}10^{-6}$ M), λ_{ex} = 555 nm; **d** $H_2T(4\text{-}NH_2\text{-}Ph)P$ (*1*) ($1.5{\cdot}10^{-6}$ M) and ZnT(4- NH_2-Ph)P (*2*) ($1.5{\cdot}10^{-6}$ M), λ_{ex} = 555 nm

in compare with the corresponding value for the H_2TPhP). In case of the NH_2-substitution occurs increasing of the fluorescence intensity (the quantum yield is increasing about 3.4 times in compare with the corresponding value for the H_2TPhP).

Table 1 Quantum fluorescence efficiency and kinetic parameters of the Zn-porphyrins formation in acetonitrile in the system (2) at 298 K*

Porphyrin	Qx	kv^{298}, l·mol/s	E_a, kJ/mol	$\Delta S^{\neq}$,J/(mol·K)
H_2TPhP [6] ZnTPhP [6]	0.059 0.017	0.302 ± 0.029	70 ± 2	-46 ± 2
$H_2T(4\text{-}OH\text{-}Ph)P$ [6] ZnT(4-OH-Ph)P [6]	0.048 0.0169	0.875 ± 0.018	60 ± 3	-53 ± 2
$H_2T(4\text{- }Cl\text{ -}Ph)P$ ZnT(4- Cl -Ph)P	0.038 0.033	0.212 ± 0.011	95 ± 3	38 ± 2
$H_2T(4\text{-}NH_2\text{ -}Ph)P$ ZnT(4-NH_2 -Ph)P	0.2 0.18	3.405 ± 0.092	22 ± 2	-154 ± 5

*Qx - quantum yield of fluorescence; kv^{298} - kinetic rate constant; E_a-energy activation; $\Delta S^{\neq}$ entropy activation

In the investigated Zn-porphyrins a strong influence of the substituents on the fluorescence properties of the macrocycle also was established. Acetonitrile solutions of the ZnT(4-NH_2-Ph)P and ZnT(4-Cl-Ph)P showed increasing of the fluorescence quantum yield in 2 and 10 times correspondingly, in comparison with analogous values of the ZnTPhP and ZnT(4-OH-Ph)P. These experimental findings are in good agreement with the literature and testify that the heteroatom may be included in the conjugated system of a compound, significantly changing its fluorescence properties [21–27].

The studies of the porphyrin ligands (I-IV) coordination properties towards Zn^{2+} in the system (2) was carried out by the spectrophotometric method [1] at 298-318 K. The fluctuation of the temperature in the course of the experiment did not exceed ±0.1 K. In all cases, the clear isosbestic points were observed in the UV-Vis spectra of the reacting systems (Fig. 2, Fig.SI.1–3, Table 2).

$$H_2P\text{–}Zn(OAc)_2\text{–}CH_3CN, \qquad (2)$$

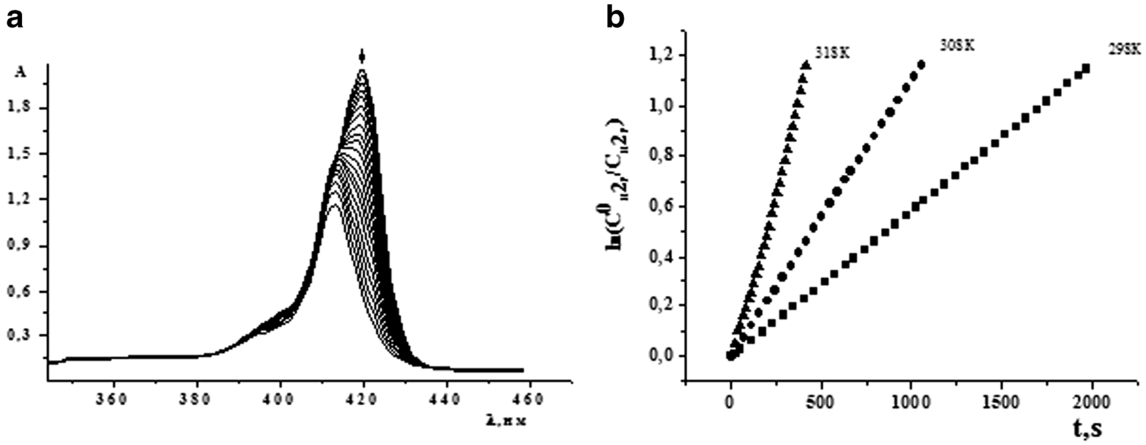


Fig. 2 Changes in the UV-Vis spectra of the system (2) at 298 K, ($C_{H2TPhP} = 9.45 \cdot 10^{-5}$ M; $C_{Zn(OAc)2} = 8.84 \cdot 10^{-3}$ M) **a**, and the dependence of the $\ln(C^0_{H2P}/C_{H2P})$ on the τ at 298, 308 and 318 K ($C_{H2TPhP} = 1.85 \cdot 10^{-5}$; $C_{Zn(OAc)2} = 1.84 \cdot 10^{-3}$ M)

where $H_2P = H_2TPhP$, $H_2T(4\text{-}OH\text{-}Ph)P$, $H_2T(4\text{-}Cl\text{-}Ph)P$, $H_2T(4\text{-}NH_2\text{-}Ph)P$.

The reaction of the metalloporphyrins (V-VIII) formation has the first kinetic order on the porphyrin ligand and on the salt (Figs.2, 3, Fig.SI. 1–6).

The reaction of formation of the porphyrin ligands complexes with the divalent metal cations in nonaqueous solutions takes place according with the equation (3)

$$H_2P + \left[MX_2(Solv)_{n-2}\right] \rightarrow MP + 2HX + (n-2)Solv \qquad (3)$$

where X – acido ligand, Solv – molecule of a solvent, n – coordination number of the metal cation, H_2P – porphyrin ligand, M – metal cation. The kinetic parameters were calculated according to [13].

The kinetic parameters of the porphyrin ligands (I-IV) complexation with the Zn^{2+} in the system (2) are presented in the Table 1. With the confidence probability coefficient 0.90, an error in the determination of the constant k_v was ±0.03 un. According to [1] the basic contribution into the activation energy of the reaction introduces partial destruction and deformation of the salt solvate complex coordination sphere (detachment of two solvent molecules from the metal cation and tension of the remaining bonds M − Solv, M − X). The N-H bond length change occurring in the transient state of the reaction also influences on the activation energy of the complexation [1].

The electronic effects of the peripheral substituents have an influence on the rate of complexation. The electron-donor groups (−OH, $-NH_2$) increasing the electron density on the tertiary atoms of nitrogen promote to the complexes formation (Table 1). Accordingly, the electron-withdrawing group ($-Cl^-$) has an opposite action.

The energy of activation (E^a) of the zinc complexes (V-VIII) formation can be placed in the following sequence:

$$ZnT(4\text{–}NH_2\text{–}Ph)P < ZnT(4\text{–}OH\text{–}Ph)P < ZnTPhP < ZnT(4\text{–}Cl\text{–}Ph)P,$$

which is coherent with our previous data [5] regarding the summary influence of the induction and resonance effects of the substituents on the tetrapyrrolic macrocycle reactivity.

On the base of these findings we can conclude that the limiting factor, which determines the rate of the complexation in acetonitrile, is a coordinating interaction between having a lone pair of electrons tertiary nitrogen atoms of the macrocycle and the metal cation of the salt.

Thus, in this work the fluorescence quantum yield of the 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetra(4-OH-

Table 2 Spectral characteristics of the porphyrin ligands [H_2TPhP, $H_2(4\text{-}OH)TPhP$, $H_2T(4\text{-}Cl\text{-}Ph)P$, $H_2T(4\text{-}NH_2\text{-}Ph)P$] and their Zn-complexes in the system (2)*

Porphyrin	Soret band	$\lambda_4(\lg\varepsilon)$	$\lambda_3(\lg\varepsilon)$	$\lambda_2(\lg\varepsilon)$	$\lambda_1(\lg\varepsilon)$
H_2TPhP	413(4.09)	511(3.02)	545(2.87)	589(2.82)	646(2.83)
ZnTPhP	420(4.34)	-	555(3.42)	594(3.08)	-
$H_2(4\text{-}OH)TPhP$	417(4.73)	516 (3.72)	553 (3.60)	593(3.37)	649(4.41)
Zn (4-OH)TPhP	423(4.84)	-	556(3.75)	598(3.66)	-
$H_2T(4\text{-}Cl\text{-}Ph)P$	414(4.68)	512(3.76)	546(3.64)	588(3.58)	643(3.51)
ZnT(4-Cl-Ph)P	421(4.95)	-	554(3.79)	594(3.61)	-
$H_2T(4\text{-}NH_2\text{-}Ph)P$	426(4.80)	522 (3.60)	562 (3.73)	605_{sh}(3.42)	657 (3.47)
$ZnT(4\text{-}NH_2\text{-}Ph)P$	429(4.86)	-	561(3.88)	606(3.90)	-

*the error of definition makes 1–3 %

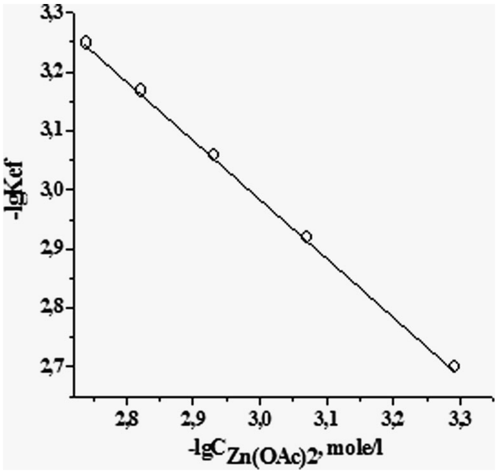


Fig. 3 The dependence of the lg$k_{эф}$ on the lg$c_{Zn(OAc)2}$ of the ZnTPhP formation in the system (2) at 298 K

phenyl)porphyrin, 5,10,15,20-tetra(4-Cl-phenyl)porphyrin, 5,10,15,20-tetra(4-NH_2-phenyl)porphyrin and their complexes with Zn^{2+} have been determined and the kinetic rate constants of the porphyrins ligands complexation with Zn^{2+} in acetonitrile have been estimated. It was shown that the substituents on the tetrapyrrolic macrocycle periphery have a strong influence on the fluorescent and coordination properties of the investigated porphyrins. These experimental results could be used in the development of new fluorescent molecular devices for determination and separation of ions and molecules of different nature in solutions.

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