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Interligand electron transfer as a reason of very weak red luminescence of Eu((*i*-Bu)$_2$PS$_2$)$_3$Phen and Eu(C$_4$H$_8$NCS$_2$)$_3$Phen complexes

Arkady S. Kupryakov [a,b], Victor F. Plyusnin [a,b,*], Vyacheslav P. Grivin [a,b], Julia A. Bryleva [c], Stanislav V. Larionov [c]

[a] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, 630090 Novosibirsk, Russian Federation*
[b] *Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[c] *Nikolaev Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russian Federation*

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ABSTRACT

Nanosecond laser flash photolysis and time resolved luminescence were used to study the photophysical processes for Eu((*i*-Bu)$_2$PS$_2$)$_3$Phen (**1**) and Eu(C$_4$H$_8$NCS$_2$)$_3$Phen (**2**) complexes in acetonitrile. These complexes show a very weak red Eu^{3+} luminescence in spite of the fact that the phenanthroline molecule in triplet state is a good antenna to excite the red luminescence of many Eu(III)-Phen complexes. To determine the reasons of this effect the photoprocesses in solutions, containing the (*i*-Bu)$_2$PS$_2^-$ or C$_4$H$_8$NCS$_2^-$ ions and free phenanthroline molecule, have been studied with the use of laser flash photolysis (266 nm). It was shown that the phenanthroline in triplet excited state (^{T}Phen*) deprives the electron from these dithiolate ions with a high rate constants close to 10^9 M^{-1} s^{-1}. The transient spectra of phenanthroline anion-radical and dithiolate radicals were recorded which are in a good agreement with literature data. Since the effective concentration of dithiolate ions (L$^-$) in the coordination sphere of **1** and **2** complexes is close to 10 M the time of electron transfer between L$^-$ and ^{T}Phen* is in the range of 100 ps or less. As the laser flash photolysis of solutions of **1** and **2** complexes with a 10 ns time resolution failed to detect the spectra of phenanthroline anion-radical and dithiolate radicals, it indicates that the time of back electron transfer is less than 10^{-8} s. Thus, the very weak red luminescence of **1** and **2** complexes is due to the electron transfer between ligands in the coordination sphere which successfully suppresses the energy transfer from the phenanthroline triplet state to Eu^{3+} ion.

1. Introduction

In last decade the interest to light emitting systems dramatically grows in connection with the development of new technologies using light radiation. The such promising systems are the complexes of trivalent lanthanide ions, and especially europium and terbium ions. The Eu(III) and Tb(III) ions attract a great attention due to its unique luminescence properties such as hypersensitivity to coordination environment, narrow bandwidth and a millisecond lifetime [1,2]. However, the lanthanide ions have a very small absorption coefficient, and for the appearance of a bright luminescence of these ions the ligands-sensitizer are required. The sensitizing ligand transfers energy, as usual, from a triplet excited state to the Eu^{3+} and Tb^{3+} ions enhances the luminescence. Typical ligands mostly used due to availability are the carboxylate ions, β-diketonate ions, 1,10-phenanthroline (Phen) and their combination.

Very little has been reported on the luminescence of sulfur-coordinated lanthanide chelates. The photoluminescence of Eu (III)-dithiocarbamate complex at room temperature for the first time was detected in Ref. [3]. However, it was shown that the red luminescence of Eu(R$_2$NCS$_2$)$_3$Phen complex is very weak in spite of fact that the Phen molecule is an excellent sensitizer in other Eu-Phen complexes. Later it was also confirmed that the red luminescence of Eu(Et$_2$NCS$_2$)$_3$Phen complex is practically absent [4]. And it can be pointed that even for the Sm(R$_2$NCS$_2$)$_3$Phen and Pr (R$_2$NCS$_2$)$_3$Phen complexes, the main objects of studies in Ref. [4], the quantum yield does not exceed a few percents.

The 1,10-phenanthroline molecule is characterized by a weak fluorescence quantum yield (Φ_{fl}=0.0087) and a short singlet lifetime (< 1 ns in CH$_2$Cl$_2$ solution at room temperature) [5]. At 77 K an intense luminescence, related to the decay of the triplet excited state, is also recorded (458 nm), so the quantum yield of the triplet state may be very high. This is confirmed by the registration of intensive transient triplet–triplet absorption in the

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[*] Corresponding author at: Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, 630090 Novosibirsk, Russian Federation. Tel.: +7 383 3332385; fax: +7 383 3307350.
E-mail address: plyusnin@kinetics.nsc.ru (V.F. Plyusnin).

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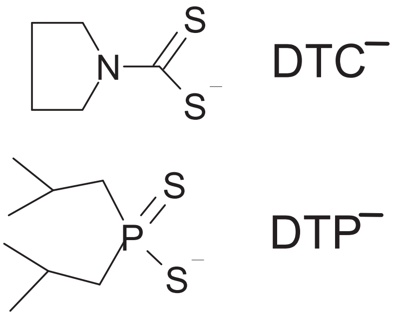
experiments using laser flash photolysis [6]. For a free Phen molecule the energy of triplet state is 21,834 cm^{-1}, and in the coordination state with the trivalent rare earth ions it changes little to 21,882 cm^{-1} [3].

It has been previously reported that the maximum quantum yield of the red Eu^{3+} ion luminescence can be achieved when the triplet state of the ligand is in between the $^5D_2$ and $^5D_1$ levels of Eu^{3+} (in the range of 21,500–22,500 cm^{-1}) [7]. This explains why phenanthroline ($E(T_1)=21{,}882$ cm^{-1} [3]) is known to be a strong sensitizer to the Eu^{3+} ion [8,9]. In Ref. [3] it was suggested that a very weak red luminescence of the $Eu(Et_2NCS_2)_3Phen$ complex is due to the formation of a ligand-to-metal charge transfer (LMCT) state induced by the electron transfer from the dithiocarbamate ligand to the Eu^{3+} ion. This process can lead to the appearance of the Eu^{2+} ion and thus, to the decrease of population of Eu(III) emissive levels.

Analysis of published data, however, showed that almost all complexes of rare earth ions containing dithiolate ligands and phenanthroline have a low quantum yield of luminescence. Thus, it could be assumed that for these complexes the interaction of dithiolate ligand and phenanthroline molecule plays a major role. So, in this paper, we tried to find out the reasons for which the phenanthroline molecule stops the work as an antenna to sensitize the luminescence of europium in the $Eu((i\text{-}Bu)_2PS_2)_3Phen$ and $Eu(C_4H_8NCS_2)_3Phen$ complexes. This problem was solved by the analyzing the spectra of transient absorption occurring during the laser flash photolysis of solutions containing the $(i\text{-}Bu)_2PS_2^-$ or $C_4H_8NCS_2^-$ ions and free Phen molecule.

2. Experimental section

The EuL_3Phen complexes ($L^-=C_4H_8NCS_2^-$, $(i\text{-}Bu)_2PS_2^-$) were synthesized, purified and analyzed according to techniques presented in Refs. [10,11]. The $Eu(NO_3)_3Phen$ complex was prepared by dissolving the $Eu(NO_3)_3$ and phenanthroline in equal concentrations. The formation of the $Eu(NO_3)_3Phen$ complex was confirmed by the optical spectra. Laser flash photolysis was carried out using a YAG:Nd laser (the 3rd harmonic, 355 nm, 7 ns, 5–30 mJ) [12]. The excitation and probe light beams entered in a 1 cm quartz cuvette with solution at a small angle (~2°). In numeric kinetic simulations the appropriate differential equations were solved using proprietary software (SPARK) based on the fourth-order Runge–Kutta method. The UV/vis absorption spectra were recorded using HP 8453 spectrophotometer (Agilent Technologies). Solutions were prepared in spectrally pure acetonitrile manufactured by Merck. Oxygen was removed by blowing argon through solution for 15–20 min. Spectra and kinetic curves of luminescence were recorded with a FLS920 spectrofluorometer ("Edinburg Instrument"). As the light sources the Xe900 lamp and laser diodes EPLED ($\lambda_{ex}=280$, 300, 320 nm, pulse duration 0.6 ns) were used. Luminescence quantum yields were measured relative to that of anthracene, using the value for the fluorescence quantum yield of anthracene in acetonitrile (0.28) [13]. The structures of $(i\text{-}Bu)_2PS_2^-$ and $C_4H_8NCS_2^-$ ions are shown in Scheme 1.



Scheme 1. Structures of $C_4H_8NCS_2^-$ (DTC^-) and $(i\text{-}Bu)_2PS_2^-$ (DTP^-) ligands.

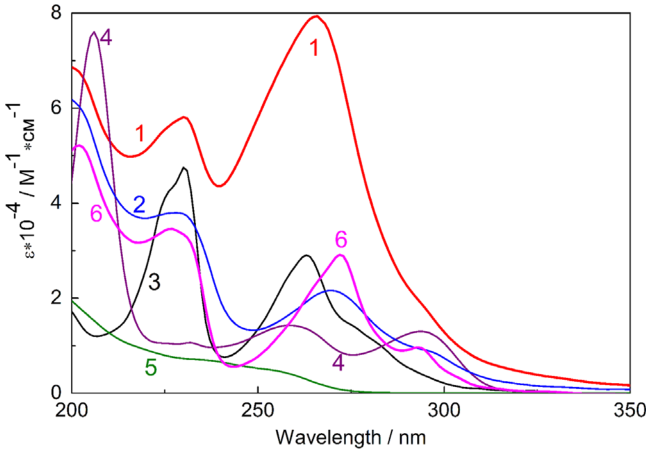


Fig. 1. UV/vis absorption spectra of $Eu(C_4H_8NCS_2)_3Phen$ (**1**), $Eu((i\text{-}Bu)_2PS_2)_3Phen$ (**2**), Phen (**3**), $(i\text{-}Bu)_2PS_2Na$ (**4**), $C_4H_8NCS_2NH_4$ (**5**), and $Eu(NO_3)_3Phen$ (**6**) in CH_3CN.

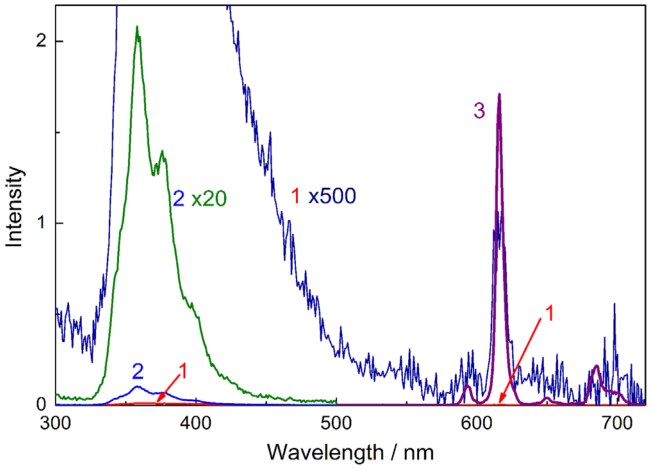


Fig. 2. Luminescence spectra of $Eu((i\text{-}Bu)_2PS_2)_3Phen$ (**1**) complex, free Phenanthroline (**2**) and $Eu(NO_3)_3Phen$ (**3**) complex in CH_3CN, the excitation at 266 nm. In all cases the absorbance at 266 nm is 0.35. The spectra (**1**) and (**2**) enlarged 500 and 20 times, respectively, are also shown.

3. Results and discussion

3.1. Absorption spectra and luminescence properties of Eu^{3+} complexes, free Phen and dithiolate ligands

Fig. 1 shows the absorption spectra of free 1,10-phenanthroline, free ligands $(i\text{-}Bu)_2PS_2^-$, $C_4H_8NCS_2^-$, $Eu((i\text{-}Bu)_2PS_2)_3Phen$ and $Eu(C_4H_8NCS_2)_3Phen$ complexes in acetonitrile. The spectra of Eu(III) complexes are determined by the superposition of absorption of ligands (phenanthroline and dithiolate ions) which show some changes because of the embedding of these ligands into the coordination sphere of the Eu(III) ion.

The solutions of both EuL_3Phen complexes practically exhibit no luminescence. Fig. 2 shows the low-intensity luminescence spectra of the $Eu((i\text{-}Bu)_2PS_2)_3Phen$ complex and free phenanthroline. It can be seen from the spectrum 1 × 500 in Fig. 2 that only at a strong enlargement the traces of red Eu^{3+} luminescence (line 615 nm) are appreciable. The estimates show that the quantum yield of luminescence in this case is less than 4×10^{-4}. The spectra in Fig. 2 shows that the introduction of Phen molecule in the coordination sphere of europium ion containing dithiolate ions results in a further decrease of Phen luminescence intensity fourfold (thus, the quantum yield of Phen luminescence is reduced from 0.0087 to 0.0023). The luminescence behavior of $Eu(C_4H_8NCS_2)_3Phen$ complex is similar to the

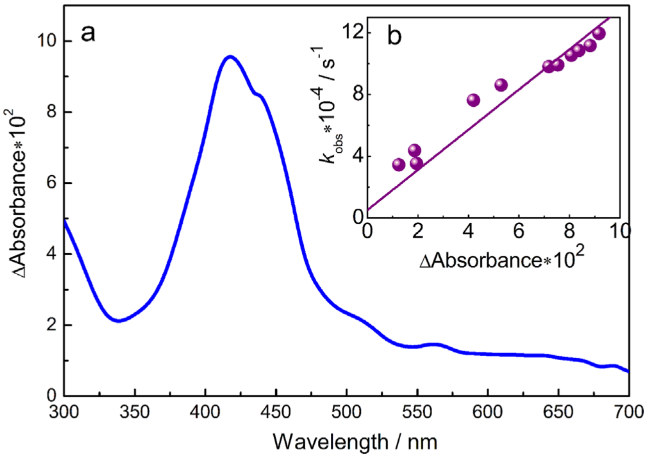


Fig. 3. Laser flash photolysis of Phen (2×10^{-5} M) in acetonitrile. (a) – T–T absorption spectrum after laser pulse (266 nm); (b) – the dependence of k_{obs} of T–T absorption decay on the initial absorption value (ΔA) at 420 nm.

Eu((i-Bu)$_2$PS$_2$)$_3$Phen complex. If the dithiolate ligands are absent in coordination sphere (the Eu(NO$_3$)$_3$Phen complex) the quantum yield of red luminescence of Eu^{3+} ion increases from $\sim 4 \times 10^{-4}$ to 0.086.

So, to study the processes that lead to the quenching of Phen triplet state and the absence of red Eu(III) luminescence the laser flash photolysis of solutions of EuL$_3$Phen complexes and solutions containing both the free phenanthroline and free dithiolate ligand have been used.

3.2. *Laser flash photolysis of EuL$_3$Phen complexes, phenanthroline and Eu(NO$_3$)$_3$Phen complex*

Upon the excitation of EuL$_3$Phen complexes in acetonitrile by a nanosecond laser pulse (266 nm, 5 ns) the transient absorption within 300–700 nm is absent. For the solution of free Phen in acetonitrile a laser pulse leads to the appearance of intense band of triplet–triplet (T–T) absorption with the maximum at 420 nm (Fig. 3a). The dependence observed rate constant (k_{obs}) of the absorption decay at 420 nm on the initial absorption (ΔA) is shown in Fig. 3b. Due to the second-order reaction of triplet–triplet annihilation the k_{obs} should be the linear function of ΔA:

$$k_{obs} = k_1 + 2k_2 \times \Delta C = k_1 + (2k_2/\varepsilon l)\Delta A \tag{1}$$

where $k_1 = 5.2 \times 10^3$ s^{-1} – the first order rate constant and $(2k_2/\varepsilon l) = 1.3 \times 10^6$ cm × s^{-1} in which $2k_2$ – the rate constant of triplet–triplet annihilation, ε – the absorption coefficient of triplet state at 420 nm and l – cuvette length.

The absorption coefficient of Phen in triplet state at 420 nm and its quantum yield were determined by carrying out the experiments on energy transfer from the Phen triplet state to anthracene. This process is possible due to the low energy of anthracene triplet state in comparison with triplet state of phenanthroline, 1.82 [14] vs. 2.34 eV [15]. Assuming that the Phen in triplet state transfers energy completely to anthracene and using absorption coefficient of anthracene at 420 nm – 45,500 M^{-1} cm^{-1} [16] and its quantum yield – 0.58 [17] for the Phen were obtained the values – 5900 ± 200 M^{-1} cm^{-1} and 0.76, accordingly. It allows us to determine the rate constant of triplet–triplet annihilation, $2k_2 = 7.7 \times 10^9$ M^{-1} s^{-1}.

So, the absence of a T–T absorption of Phen in the case of flash photolysis of EuL$_3$Phen complexes can be determined by the joint coordination of Phen and dithiolate ions and the fast disappearance of Phen triplet state.

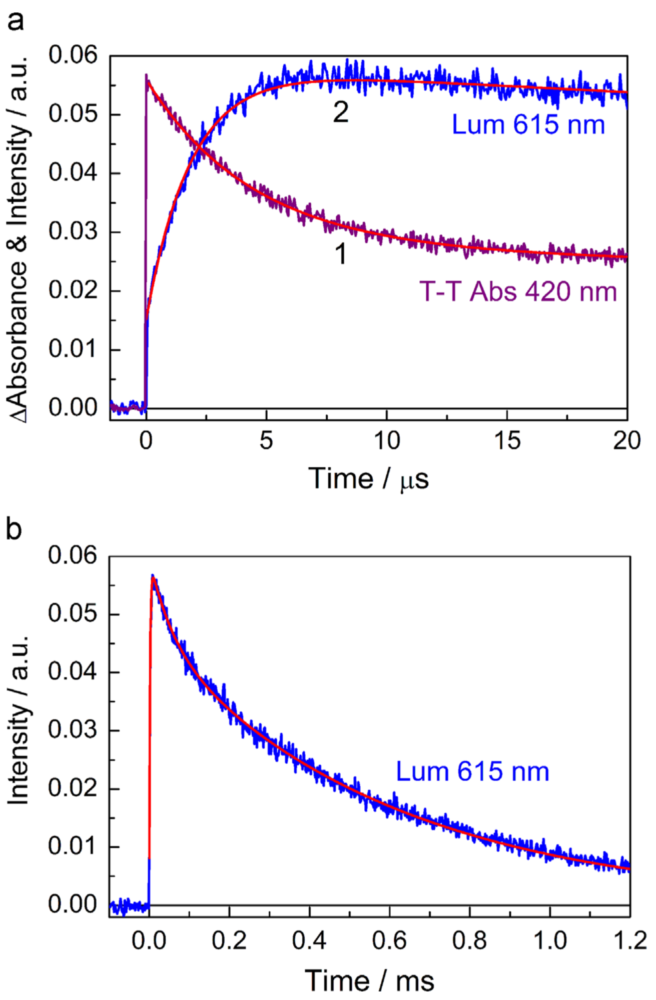


Fig. 4. Laser flash photolysis and luminescence of Eu(NO$_3$)$_3$Phen (1.9×10^{-5} M) in acetonitrile. (a) – The T–T absorption of coordinated Phen at 420 nm (**1**) and luminescence at 615 nm (**2**); (b) – kinetics of luminescence of Eu(NO$_3$)$_3$Phen complex at 615 nm in millisecond time domain.

When the coordination sphere of Eu^{3+} ion has no dithiolate ligands (the example is Eu(NO$_3$)$_3$Phen complex) the Phen molecule begins to play the role of active antenna. Fig. 4 shows the kinetics of red Eu^{3+} luminescence at 615 nm in a different time intervals (Fig. 4a and b) with quantum yield 0.086. Of course, the quantum yield of Eu(NO$_3$)$_3$Phen red luminescence is not large, however, more than 200 times higher than the quantum yield for the EuL$_3$Phen complexes. Traces (2) in Fig. 4a clearly display the formation of Eu(NO$_3$)$_3$Phen red luminescence (615 nm) due to energy transfer (ET) from the triplet level of phenanthroline to europium ion ($\tau_{ET} = 1.9 \pm 0.1$ μs). The kinetics of T–T absorption decay at 420 nm in Fig. 4a (trace (1)) confirm this energy transfer in the case of Eu(NO$_3$)$_3$Phen complex.

It should be noted that the some fraction of Eu(NO$_3$)$_3$Phen red emission appears immediately after the laser pulse (see the initial step on kinetic curve, trace (2) in Fig. 4a). Since the direct excitation of Eu(III) must be insignificant or completely absent, this emission originates from a process that is fast compared to the time resolution of our experiment which is limited by the duration of laser pulse (5 ns). The Eu-based emission immediately after the photoexcitation of coordinated Phen molecule could arise due to a fast ET process from the singlet excited state of the Phen ligand to Eu(III) ($S_1 \rightarrow {}^5D_0$ transition), which occurs in parallel with the $S_1 \rightarrow T_1$ intersystem crossing (ISC) [18,19].

Thus, it can be concluded that in laser flash photolysis experiments the coordination cannot lead to the fast decay of triplet–triplet absorption of Phen in the EuL$_3$Phen complexes. The point likely is that in the coordination sphere of Eu^{3+} ion the Phen molecule and dithiolate ligands are in direct contact. Therefore,

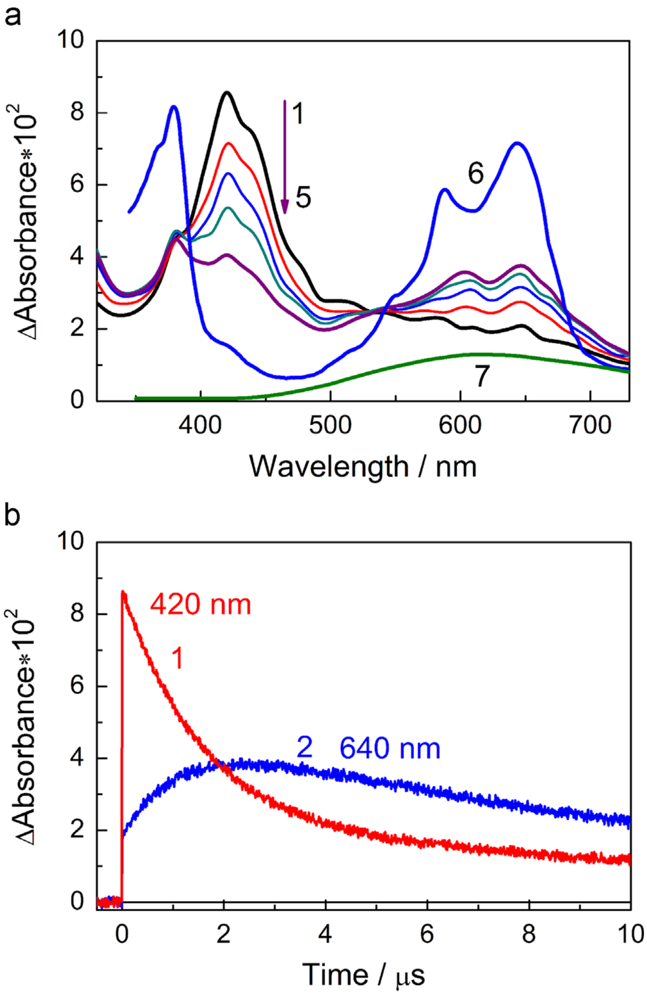


Fig. 5. Laser flash photolysis of Phen (2.4×10^{-5} M) and (i-Bu)$_2$PS$_2$Na (2.6×10^{-4} M) solution in CH$_3$CN. (a) – (**1–5**) – spectra at 0, 0.4, 0.8, 1.2, 2.0 μs after laser pulse, (**6**) – spectrum of Phen$^{\bullet-}$ anion-radical [19], (**7**) – spectrum of (i-Bu)$_2$PS$_2^-$ radical [20]; (b) – kinetics at 420 nm (**1**) and 640 nm (**2**).

the data on laser flash photolysis of free Phen solution containing dithiolate ion are presented below.

3.3. *Laser flash photolysis of phenanthroline in presence of dithiolate ion*

In solution containing the Phen and dithiolate ion the decay of Phen T–T absorption is accompanied by the appearance during some microseconds of a new absorption in 350–450 and 550–700 nm region (Fig. 5a). The initial band at 420 nm of Phen T–T absorption decays faster than in absent of dithiolate ion. It means that the decay of Phen excited triplet state is determined by the electron transfer reaction:

$$^{T}(\text{Phen})*+(i-\text{Bu})_2\text{PS}_2^{-}\rightarrow\text{Phen}^{\bullet-}+(i-\text{Bu})_2\text{PS}_2^{\bullet}\qquad(2)$$

The spectrum of Phen$^{\bullet-}$ anion radical is presented in Refs. [18,19] and it is characterized by the bands with maxima at 380, 590 and 643 nm (Fig. 5a, spectrum 6). These peaks coincide with the bands shown in Fig. 5a (maxima at 388, 593 and 646 nm). The spectrum of Phen$^{\bullet-}$ radical anion overlaps with the wide band of i-Bu$_2$PS$_2^{\bullet}$ radical with a maximum at 616 nm (ε=2580 M^{-1} cm^{-1}) [20] (Fig. 5a, spectrum 7). Dithiocarbamate radicals have almost a similar absorption band with maximum at 580 nm (ε=3100 M^{-1} cm^{-1}) [12].

The ΔG_{et} for electron transfer from the dithiolate ion to an electron acceptor Phen can be expressed as following:

$$\Delta G_{\text{et}}=e(E_{\text{ox}}{}^{0}-\text{E}_{\text{red}}{}^{0})-E_{\text{T}}\qquad(3)$$

where $E_{\text{ox}}{}^0$ and $E_{\text{red}}{}^0$ are oxidation and reduction potentials for dithiolate (0.30 V for H$_2$NCS$_2^-$ in DMSO (vs SHE) [21]) and phenanthroline (−2.18 V (vs SCE) [15,22], −1.94 (vs SHE) (0.24 V SCE vs SHE [23])), respectively, e is the elemental charge and E_{T} indicates the energy of Phen in triplet state (2.34 eV [15]). Thus, ΔG_{et} can be estimated as –0.1 eV and the process of electron transfer is thermodynamically possible with the rate constant close to the diffusion-controlled limit.

The (i-Bu)$_2$PS$_2^{\bullet}$ band (616 nm [20]) does not overlap with the T–T absorption of Phen (420 nm), so the kinetics of absorption at 420 nm decay allow to determine the observed rate constant (k_{obs}) (Fig. 6a) and then due to the cutoff on ordinate axis to calculate the

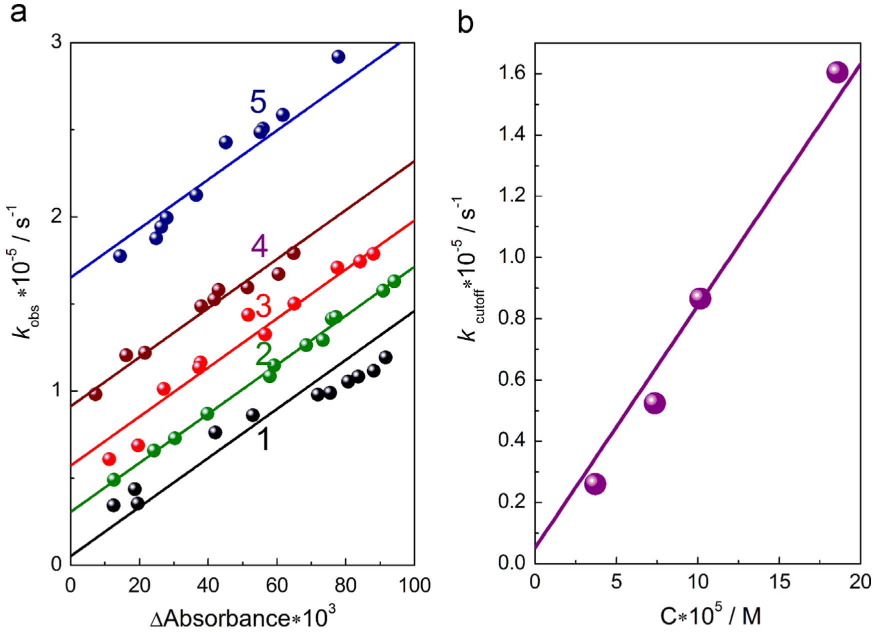


Fig. 6. Flash photolysis of Phen (2.4×10^{-5} M) at different concentrations of (i-Bu)$_2$PS$_2$Na in CH$_3$CN. (a) – Dependence of k_{obs} of T–T absorption decay on initial absorption ΔA at 420 nm, (**1–5**) – correspond to (i-Bu)$_2$PS$_2$Na concentrations 0, 3.7, 7.4, 10.2, 18.6×10^{-5} M, respectively; (b) – dependence of k_{cutoff} on the ordinate in (a) on (i-Bu)$_2$PS$_2$Na concentration.

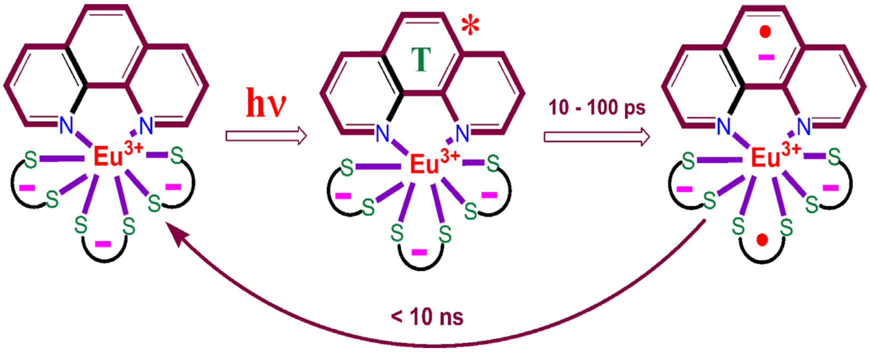


Fig. 7. The scheme of photophysical processes in coordination sphere of EuL_3Phen complexes. First step is the excitation of Phen molecule into triplet state ($^{T}Phen^{*}$). Next process is the electron transfer from dithiolate (L^{-}) ion to $^{T}Phen^{*}$ with the formation $Phen^{\bullet -}$anion-radical and $L^{\bullet}$ radical. The back electron transfer and return to initial ground state of EuL_3Phen complexes is during some nanoseconds.

bimolecular rate constant (k_{bimol}) of electron transfer between the Phen in triplet excite state and dithiolate ion. The k_{obs} in these case is a function of the amplitude of initial T–T absorbance (ΔA) and concentration of $i\text{-}Bu_2PS_2^-$ ion (C) and k_{obs} can be described as

$$k_{obs} = k_1 + (2k_2/\epsilon l) \times \Delta A + k_{bimol} \times C \quad (4)$$

where k_{bimol} – the bimolecular rate constant of electron transfer. From slope of the straight line in Fig. 6b the $k_{bimol} = (7.9 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$. The $(i\text{-}Bu)_2PS_2^{\bullet}$ radical which can be generated by the flash photolysis of disulfide ($(i\text{-}Bu_2PS_2)_2$) solutions decay due to the recombination with the rate constant $2k_{rec} = 7.6 \times 10^9\ M^{-1}\ s^{-1}$ [20].

The similar experiments for Phen and $C_4H_8NCS_2^-$ ion solutions showed that for the reactions of electron transfer in this system

$$^{T}(Phen)_{*} + C_4H_8NCS_2^- \rightarrow Phen^{\bullet -} + C_4H_8NCS_2^{\bullet} \quad (5)$$

the rate constant is equal to $k_{bimol} = (3.6 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$.

3.4. *The explanation of absence of the EuL_3Phen complexes luminescence*

Beyond doubt, the very weak red luminescence of Eu^{3+}-dithiocarbamate complexes in spite of the presence of Phen molecules in coordination sphere is quite intriguing fact. The mechanism of infrared luminescence of Yb^{3+}-Tryptophan system due to the electron transfer in LMCT states is discussed in Ref. [24]. In conclusions it was supposed that a similar effect is the reason of a low quantum yield of Eu^{3+}-Tryptophan luminescence. The theoretical analysis of LMCT involvement in the photochemical processes for Ln^{3+} complexes is represented in Ref. [25]. Later, in work of Faustino et al. [3] on the study of $Eu(R_2NCS_2)_3Phen$ luminescence it was also suggested that the quenching of red Eu^{3+} emission is due to LMCT states. Moreover, in the excitation spectra these LMCT bands were indicated. However, the LMCT bands for three $Eu(R_2NCS_2)_3Phen$ complexes have significantly different energy. And the question remains as the authors identified these LMCT bands. In addition, the studies of $Eu(R_2NCS_2)_3Phen$ luminescence were done in the solid phase, where a number of new processes are of importance that do not exist for the isolated molecules in solutions.

Thus, we consider that the existence of fast electron transfer from the dithiolate ions to excited Phen molecule in triplet state can explain the absence of the red luminescence of EuL_3Phen complexes. The presence of three L^- ligands in the coordination sphere of Eu^{3+} ion corresponds to very high local concentration of L^-, more than 10 M. The rate constants of electron transfer $\sim 10^9\ M^{-1}\ s^{-1}$ provide the decay of Phen triplet state in the range of 10–100 ps. The absence of transient absorption of $Phen^{\bullet -}$ ion radical and $L^{\bullet}$ radical (both located in coordination sphere) upon nanosecond laser flash photolysis of EuL_3Phen solutions in acetonitrile means that the back reaction of electron transfer

$$(Phen^{\bullet -})Eu(L^{\bullet})L_2 \rightarrow (Phen)EuL_3 \quad (6)$$

is faster than the laser pulse duration (less than 5–10 ns). Thus, the presence of Phen and three dithiolate ligands in the coordination sphere of europium ion leads to the opening of new photoprocesses related to the fast interligand electron transfer. Under these conditions, the process of energy transfer from the excited Phen molecule in triplet state to the Eu^{3+} ion cannot compete with these new channels of interligand electron transfer. Really, above on the $Eu(NO_3)_3Phen$ example it was shown that the energy transfer is very slow process and takes some microseconds.

Thus, on the basis of time-resolved spectroscopic data and the information available in the literature, we have proposed the scheme of processes in EuL_3Phen complexes after the excitation of Phen (Fig. 7). First step is the excitation of Phen molecule to triplet state ($^{T}Phen^{*}$). Next process is the electron transfer from dithiolate L^- ion to $^{T}Phen$ with the formation of $Phen^{\bullet -}$anion-radical and $L^{\bullet}$ radical. The back electron transfer and return to initial ground state of EuL_3Phen is during some nanoseconds. Thus, to study the photophysical processes for LnL_3Phen (L^- = different dithiolate or dithiolene ligands), it is necessary to take into account the possibility of electron transfer from L^- ligand to excited Phen molecule in triplet state.

4. Conclusions

The study of transient spectra and kinetics of free Phen solutions, containing dithiolate ions, by a laser flash photolysis (266 nm) allowed to show that the rate constants of electron transfer from the dithiolate anions (L^-) to the excited Phen molecule in triplet state ($^{T}Phen^{*}$) lie in the range $10^9\ M^{-1}\ s^{-1}$, close to diffusion limit. The high local concentration of L^- ions in the coordination sphere of EuL_3Phen complex leads to a fast and reversible electron transfer between L^- and $^{T}Phen^{*}$. This process completely suppresses the energy transfer from the $^{T}Phen^{*}$ to Eu^{3+} ion, and Phen molecule stops to work as an effective antenna. As result of these processes, the red luminescence of EuL_3Phen complexes practically disappears.

Acknowledgments

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