Interaction of TbCl₃ and lanthanide complexes with poly(*N*-vinylpyrrolidone)

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Abstract: The interaction of TbCl₃ and lanthanide(III) β-diketonate complexes with poly(*N*-vinylpyrrolidone) (PVP) polymer was studied using fluorescence spectroscopy. In the presence of PVP the emission of Tb^{3+} in ethanolic solution of TbCl₃ significantly increased owing to the excitation energy transfer from PVP to Tb^{3+} ions, which was more efficient as compared to a direct excitation of the Tb^{3+} $4f^7 5d^1$ levels. In contrast, emission of NEt₄Tb(hfa)₄ and NEt₄Eu(hfa)₄ complexes was almost completely quenched in solution containing PVP. The PVP bound both Ln^{3+} ions and hfa ligands which caused decomposition of Ln-hfa complexes and switched off the excitation energy transfer from the ligand to the emitting Ln^{3+} ion. The important role of hydrogen bonds in stabilization of interaction of hfa ligands with PVP was indicated.

Keywords: poly(*N*-vinylpyrrolidone); PVP; lanthanide(III); TbCl₃; emission quenching; rare earths

In recent years an increasing interest in hybride materials has been observed[1]. Due to the poor processability and mechanical properties the lanthanide(III) complexes must be incorporated into various hosts, such as zeolites, silica sol-gels or polymers, to profit from their excellent luminescence properties[2]. The most popular polymeric host for Ln(III) complexes is probably PMMA. Among other polymers PVP presents interesting properties as a host matrix for Ln^{3+} ions. PVP is an ampliphilic non-ionic polymer soluble in water and organic solvents and possesses film forming ability. The properties of Ln(III)-complexes embedded into PVP matrix are often different from analogous complexes in PMMA host[3].

The photoluminescence of PVP polymer films doped with TbCl₃ and EuCl₃ has been studied in Ref. [4]. In the excitation spectra of Tb^{3+} emission a broad and intense band was observed at about 311 nm. This band was assigned as a spin-allowed (4f-5d) transition, although it was also suggested that it can be due to the energy transfer from carbonyl groups of PVP to Tb^{3+} ions[4]. This conclusion was drawn from analysis of the spectra recorded for PVP:TbCl₃ films. Then, even assuming that the energy transfer is indeed observed, it still remains an open question whether the Tb^{3+} ions are bound to PVP or merely the distance between PVP molecules and Tb^{3+} ions is short enough for energy transfer to occur in films. Moreover, it remains unclear whether the appearance of PVP bands in excitation spectrum of Tb^{3+} has any effect on its emission intensity. Although in the region of PVP absorption the strong f-d transitions of Tb^{3+} are expected, no distinction between those two bands was attempted in Ref. [4].

Recently, we have investigated the emission properties of PMMA and PVP films doped with different Ln(III)-β-diketonate complexes[3]. The significant enhancement of Tb^{3+} emission was observed for PVP films doped with Tb-hfa complexes, whereas such effect was not observed for the same complex in PMMA host nor for the Tb-complexes with other ligands in PVP matrix.

Therefore, the main purpose of this paper was to investigate in more detail the interactions of TbCl₃ and Ln(III)-complexes with PVP in solution. We showed that Tb^{3+} ions were bound to PVP and that excitation energy absorbed by PVP was transferred effectively to the emitting Tb^{3+} ions. Moreover, analysis of the excitation spectra recorded for solution of NEt₄Tb(hfa)₄ and NEt₄Eu(btfac)₄ complexes in the presence of PVP provided a direct proof that PVP might coordinate not only Ln^{3+} cations, but also hfa anions. This caused the shift of the Ln(III)-hfa(complex)/Ln(III) equilibrium towards dissociated form and a relatively stable Ln(III)-hfa complexes underwent decomposition in PVP solution. On the other hand PVP practically did not interact with btfac ligand. This observation revealed the important role of terminal R_1 and R_2 substituents of R_1–(C=O)–CH_2–(C=O)–R_2 ligands in formation of hydrogen bonds with PVP.

1 Experimental

1.1 Synthesis

Polyvinylpyrrolidone (PVP) K15 (Fluka), MW ~10000 and polymerization number *n*=90, was used in the study. The stock solutions of different concentration (1×10^{-3} mmol/L–1 mol/L) were obtained by dissolving appropriate amount of PVP in spectroscopic grade ethanol.

TbCl₃·6H₂O was prepared by dissolving of Tb₂O₃ (99.99%) in concentrated HCl and evaporating of obtained clear solution to a dryness under continuous flow of N₂ gas.

The $(N(C_2H_5)_4)[Ln(hfa)_4]$ (Ln=Eu or Tb), denoted as NEt₄Ln(hfa)₄, and the $(N(C_2H_5)_4)[Eu(btfac)_4]$, denoted as NEt₄Ln(btfac)₄, compounds were prepared by reaction of lanthanide trichloride hexahydrate, LnCl₃·6H₂O, with hexafluoroacetylacetone (hfac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) or benzoyltrifluoroacetone (hbtfac, 4,4,4-trifluoro-1-phenyl-1,3-butanedione) and N(C₂H₅)₄Cl monohydrate in ethanol, using analogous procedure as described in Refs. [5, 6].

1.2 Characterization

Corrected emission and excitation spectra and luminescence decay times were recorded on an Edinburgh Instruments FLSP 920 spectrofluorimeter, equipped with a 400 W xenon lamp, 60 W microsecond flashlamp and a red-sensitive photomultiplier (Hamamatsu R-928).

2 Results and discussion

2.1 Spectral properties of PVP

Due to the presence of the carbonyl (>C=O) groups the PVP polymer possesses photoluminescent properties. Fig. 1 presents fluorescence and fluorescence excitation spectra recorded for different concentrations of PVP in ethanol. A red shift of fluorescence and excitation bands is observed as the concentration of PVP increases. For PVP concentration of 0.01, 0.2 and 1 mol/L the maxima of excitation bands are observed at 310, 324 and 338 nm, and of fluorescence bands at 385, 392 and 399 nm, respectively. For the lowest PVP concentration additional band appears in the excitation spectrum at 248 nm. In the spectra recorded for the PVP powder (inset in Fig. 1) the broad excitation and emission bands are observed with maxima at 331 and 389 nm, respectively. The PVP excitation bands observed
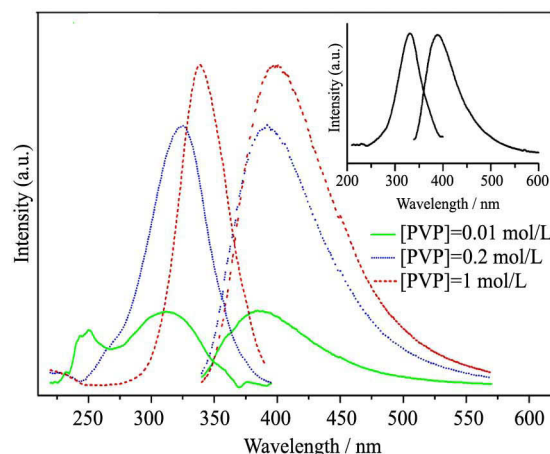

Fig. 1 Fluorescence (λ_{ex}=325 nm) and fluorescence excitation (λ_{em}=400 nm) spectra recorded for ethanolic solutions of PVP (The inset presents the spectra of the solid PVP (λ_{em}=330 nm, λ_{ex}= 410 nm))

in the 220–400 nm range can be attributed to the π-π* and n-π* electronic transitions between delocalised molecular orbitals involving the C=O groups[3].

2.2 Interaction of PVP with TbCl₃ in solution

Addition of saturated solution of TbCl₃ in ethanol to the ethanolic solution of PVP (1 mol/L) results in formation of a gelous precipitate, which after filtration and drying in air yields a white fine powder, hereafter denoted as TbCl₃-PVP.

In the emission spectra of the solid TbCl₃-PVP (Fig. 2(a)) one may observe the narrow lines corresponding to the f-f transitions of Tb³⁺ and a broad band with maximum at about 400 nm attributed to PVP fluorescence. This broad band is very similar to that observed for solid PVP (inset in Fig. 1). Similarly, the broad band observed in excitation spectra recorded while monitoring fluorescence at 410 nm (Fig. 2(b), curve (3)) corresponds to that observed for solid PVP. The Tb³⁺ emission decay times measured for solid TbCl₃·6H₂O are τ_1=450 μs (51%) and
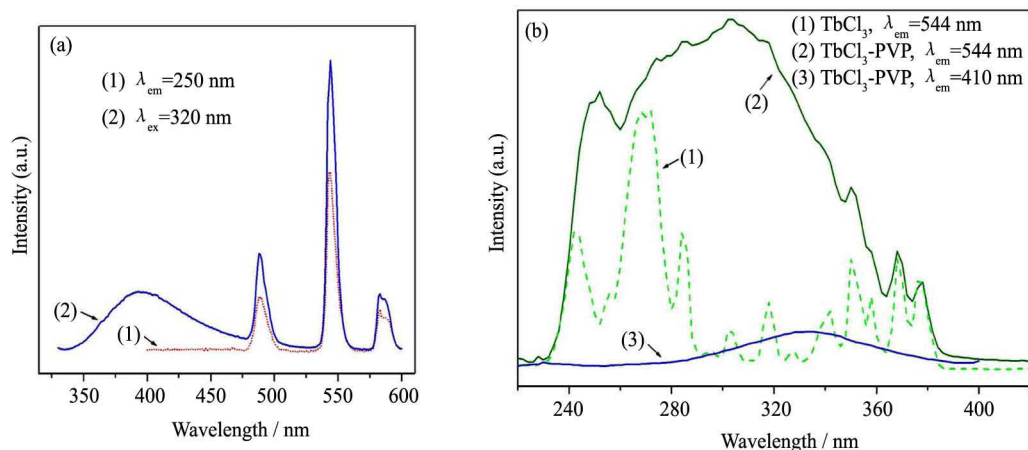

Fig. 2 Emission spectra recorded for TbCl₃-PVP powder under excitation at λ_{ex}=250 nm (1) and λ_{ex}=320 nm (2) (a) and comparison of excitation spectra recorded while monitoring the Tb³⁺ emission at λ_{em}=544 nm for solid TbCl₃·6H₂O (1) and TbCl₃-PVP (2) as well as the PVP fluorescence at λ_{em}=410 nm for TbCl₃-PVP (3) (b)

τ_2=700 µs (49%). The emission decay time of Tb^{3+} in $TbCl_3$-PVP is dominated by a longer component of τ_2= 700 µs (88%).

Much more significant differences are observed between excitation spectra recorded while monitoring Tb^{3+} emission (544 nm) in solid $TbCl_3 \cdot 6H_2O$ and $TbCl_3$-PVP (Fig. 2(b)). Apart from the numerous f-f transitions, two strong bands assigned as f-d transitions appear at 243 and 270 nm in the spectrum of $TbCl_3 \cdot 6H_2O$. In the spectrum of $TbCl_3$-PVP the f-f transitions are also present, but on the slope of the broad and strong band with the maximum at about 305 nm. This broad excitation band should be assigned to PVP absorption. Hence, appearance of this band in excitation spectrum of Tb^{3+} emission indicates occurrence of excitation energy transfer from PVP polymer to Tb^{3+} ions. Note, that this energy transfer affords much more efficient excitation of Tb^{3+} emission as compared to a direct excitation through the $4f^7 5d^1$ levels. Moreover, the broad absorption band of PVP enables efficient excitation in more extended wavelength range.

This conclusion is further supported by results presented in Fig. 3. In this experiment PVP was incrementally added to ethanolic solution of $TbCl_3$. The increase of intensity of Tb^{3+} emission was expected, as is indeed observed in the spectra shown in Fig. 3(a). The inset in Fig. 3(a) presents the changes in relative emission intensity, F/F^0 (F^0 – intensity for initial $TbCl_3$ solution in the absence of PVP), as a function of lg n_{PVP} (n_{PVP} - µmoles of PVP). Initially, the intensity of Tb^{3+} emission monitored at 544 nm remains almost unchanged. After addition of 0.056 µmol of PVP to $TbCl_3$ solution (2 µmol) the increase of intensity is clearly observed, accompanied by changes in a shape of Tb^{3+} emission band (Fig. 3(a)). This indicates that Tb^{3+} ions interact with PVP polymer in solution. In the presence of 2.2 µmol of PVP, which corresponds approximately to the PVP:Tb stoichiometry of 1:1, emission is 3.3 times more intense than for $TbCl_3$ solution without PVP.
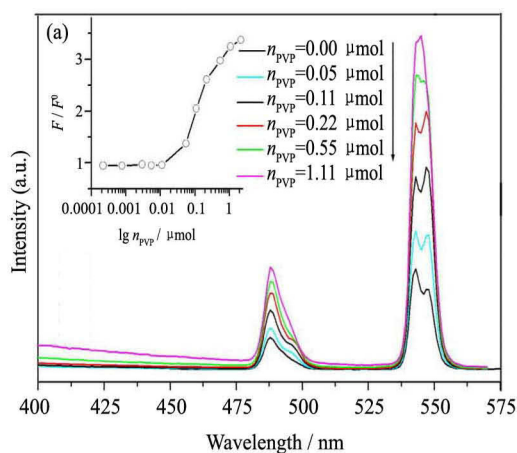
Fig. 3(b) presents excitation spectra recorded while monitoring Tb^{3+} emission (544 nm) in ethanolic solution of $TbCl_3$ (2 µmol) containing different amounts of PVP. At low PVP concentration one my observe the drop of intensity of the excitation band at 235 nm, whereas the band at 267 nm remains practically unchanged. If the PVP content is in 2.78×10^{-3}–0.011 µmol range the intensity of both bands is nearly constant. If PVP content exceeds 0.055 µmol the intensity of both f-d excitation bands increases, reaching the maximum values for n_{PVP}=0.11 µmol. At the same time the higher energy band shifts towards longer wavelengths, from 235 to 238 nm for n_{PVP}=0.11 µmol and even to 244 nm for larger contents of PVP, whereas the lower energy band shifts by the same amounts in the opposite direction, from 267 to 258 nm. Starting from PVP contents of about 0.11 µmol a broad band extending from 350 nm towards UV region became visible in the spectrum. As concentration of PVP further increases the intensity of the f-d bands strongly decreases and for n_{PVP}=2.2 µmol the band at 244 nm is observed barely as a shoulder on the slope of the dominating broad band attributed to PVP.

As the concentration of PVP increases, the energy difference between the spin-allowed and spin-forbidden f-d transition of Tb^{3+} decreases. This implies the increased covalency of interaction of 5d electrons with ligands[7], which indicates that PVP substitutes for Cl^- and H_2O ligands coordinated to Tb^{3+} ions. The observed changes in the shape of excitation bands of Tb^{3+} emission monitored at 544 nm also point unambiguously to the occurrence of interaction between PVP polymer and Tb^{3+} ions and provide evidence that excitation energy is transferred from PVP to Tb^{3+} ions.

The Tb^{3+} emission decay curve recorded for ethanolic solution of $TbCl_3$ is single exponential with a time constant of 1.2 ms. As the concentration of PVP increases the second component appears on the decay curve, with significantly longer time constants of 2.5 ms.
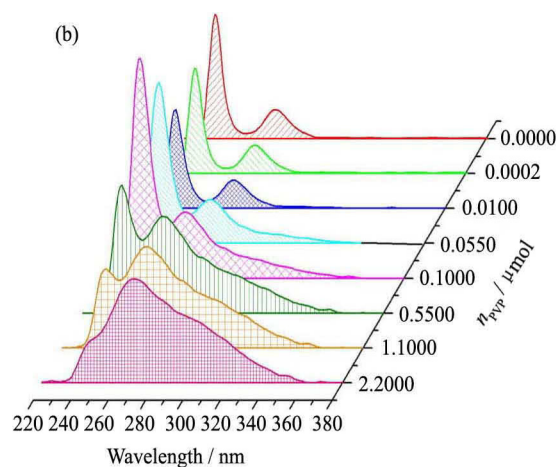

Fig. 3 Changes in Tb^{3+} emission spectra (λ_{ex}=270 nm) upon incremental addition of PVP (from 0 to 1.11 µmol) to ethanolic solution of $TbCl_3$ (2 mL, 2.0 µmol) (The inset presents the relative intensity F/F^0 (F^0 – intensity for n_{PVP}=0) as a function of added µmoles of PVP (a); Excitation spectra recorded while monitoring Tb^{3+} emission (λ_{em}=544 nm) in $TbCl_3$ ethanolic solution (2 mL, 2.0 µmol) containing different amounts of PVP (from 0 to 2.2 µmol) (the vertical axis - not shown - presents emission intensity in a.u.) (b)

2.3 Interaction of PVP with Ln(III) complexes in solution

In the previous section we have shown that Tb^{3+} ions interact with PVP in solution. It is well established now, that PVP can interact not only with cations, but also with inorganic anions[8]. Then, an interesting question is if PVP can interact with ligands coordinated to Ln(III). If this is a case then binding of both Ln^{3+} ions and ligands to PVP could strongly decrease the stability or even cause decomposition of Ln(III) complexes.

Fig. 4 presents the plot of $\lg((F^0-F)/F)$ against $\lg[PVP]$ for $NEt_4Tb(hfa)_4$ complex in ethanolic solution containing different amounts of PVP. In the presence of PVP the emission of Tb^{3+} is efficiently quenched. A very similar plot is obtained for $NEt_4Eu(hfa)_4$ complex. However, the quenching effect is practically unobserved in the case of $NEt_4Eu(btfac)_4$ complex.

The difference may result from the specific interaction of PVP with Ln-hfa complexes or from different values of stability constants of $NEt_4Eu(hfa)_4$ and $NEt_4Eu(btfac)_4$ complexes. The exact values of stability constants have not been determined yet, however, the simple experiment has been performed showing that the values are similar for both complexes - Fig. S3 in Ref. [3]. It has been shown that for low concentration of $NEt_4Eu(btfac)_4$ (1.0×10^{-6} mol/L) in solution containing also the $NEt_4Tb(hfa)_4$ (1.0×10^{-5} mol/L) complex, the btfac ligand in Eu-complex is entirely substituted with hfa ligand from Tb-complex. On the other hand at higher concentration of Eu-complex (1.6×10^{-5} mol/L) the btfac ligand substitutes for hfa ligand in $NEt_4Tb(hfa)_4$ complex (1.0×10^{-5} mol/L). The possibility of the reversible shifting of the $NEt_4Tb(hfa)_{4-x}(btfac)_x \leftrightarrow NEt_4Eu(btfac)_{4-x}(hfa)_x$ equilibrium by changing the concentration of both complexes in relatively narrow range ($1.0 \times 10^{-6} - 1.6 \times 10^{-5}$ mol/L) proves that their stability constants must be comparable.
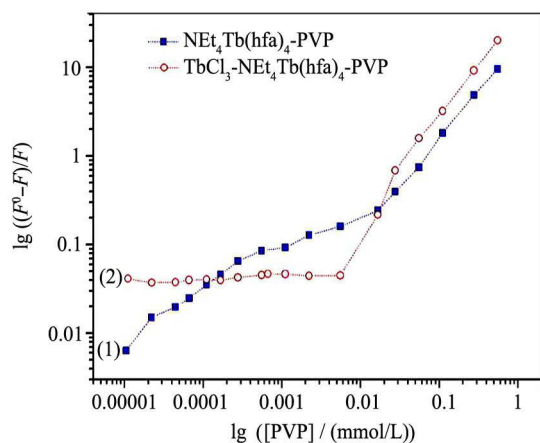
Therefore, the differences in quenching efficiency observed between $NEt_4Eu(hfa)_4$ and $NEt_4Eu(btfac)_4$ complexes must result from specific interaction of PVP with hfa ligand, whereas such interaction does not occur, or is significantly less effective, for btfac ligand. In order to prove this assumption different amounts of PVP were added to the ethanolic solution (2 mL) containing $NEt_4Eu(hfa)_4$ (0.02 μmol) and $NEt_4Eu(btfac)_4$ (0.003 μmol). Fig. 5 shows that excitation spectra of Tb^{3+} (λ_{em}=544 nm) and Eu^{3+} (λ_{em}=614 nm,) emission recorded for solution of $NEt_4Tb(hfa)_4$ and $NEt_4Eu(btfac)_4$ complexes without PVP, are the same (curves (1) and (2)) and correspond to that of Ln-hfa complexes (curve (7)). Such results indicate that for this composition of solution the btfac ligand in $NEt_4Eu(btfac)_4$ complex is substituted with hfa ligand (btfac is not a good sensitizer of Tb^{3+} emission, so substitution of hfa for btfac in $NEt_4Tb(hfa)_4$ complex decreases the Tb^{3+} emission intensity, but does not influence the shape of excitation bands). As the concentration of PVP in solution increases, the band characteristic for hfa ligand gradually disappears, whereas the band of btfac ligand becomes more and more noticeable in excitation spectra (curves (3) and (4)). Finally, if concentration of PVP in solution reaches the value of 1.1 mmol/L, the excitation spectra obtained while monitoring Tb^{3+} (curve (5)) or Eu^{3+} (curve (6)) emission, are very similar to the spectrum of $NEt_4Eu(btfac)_4$ complex in the presence of PVP (curve (8)). Such evolution of the spectra upon increasing amount of PVP in solution signifies that the concentration of btfac ligand must increase relative to that of hfa ligand.

As was indicated above, the PVP polymer binds Ln^{3+} ions. The spectra in Fig. 5 show additionally, that PVP can interact also with some ligands. In our case only hfa ligand is bound to PVP. This causes that the relative concentration of btfac ligand in solution increases, and
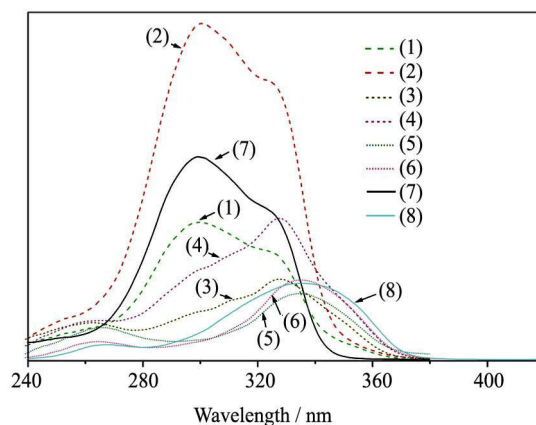
Fig. 4 Logarithmic plot of emission quenching of Tb^{3+} in $NEt_4Tb(hfa)_4$ (1) and $NEt_4Tb(hfa)_4$-$TbCl_3$ (2) ethanolic solutions treated with different concentrations (from 1×10^{-5} to 0.55 mmol/L) of PVP (λ_{ex}=320 nm, λ_{em}=540 nm)

Fig. 5 Excitation spectra of Eu^{3+} (614 nm) and Tb^{3+} (543 nm) emission recorded for ethanolic solutions (V=2 mL) containing $NEt_4Tb(hfa)_4$ (0.02 μmol) and $NEt_4Eu(btfac)_4$ (0.003 μmol) complexes (1, 2) in the presence of 0.3 (3, 4) and 2.2 (5, 6) μmol of PVP; the excitation spectra obtained for pure solution of $NEt_4Tb(hfa)_4$ complex (7) and solution of $NEt_4Eu(btfac)_4$ complex in the presence of 3.7 μmol of PVP (8) are also shown for comparison

consequently the equilibrium between $NEt_4Tb(Eu)(hfa)_4$ and $NEt_4Tb(Eu)(btfac)_4$ forms is shifted towards complexes with btfac ligand. In the case if the btfac ligand was also bound to PVP, or the hfa ligand was not bound, the ratio of hfa/btfac ligands would remain constant and no changes in excitation spectra of Tb^{3+} and Eu^{3+} emissions would be observed.

The analogous experiment was carried out for solution containing $TbCl_3$ and $NEt_4Tb(hfa)_4$ complex. Additions of $TbCl_3$ to ethanolic solution (2 mL) of $NEt_4Tb(hfa)_4$ (0.02 μmol) causes the increase of emission intensity, which reaches the maximum after addition of 0.03 μmol of $TbCl_3$. In Fig. 4(2) the changes in emission intensity, expressed as $lg((F^0–F)/F)$, are presented as a function of $lg[PVP]$ for ethanolic solution composed of $NEt_4Tb(hfa)_4$ (0.02 μmol) and $TbCl_3$ (0.03 μmol). For higher concentration of PVP the emission of $NEt_4Tb(hfa)_4$-$TbCl_3$ solution (Fig. 4, curve (2)) is quenched analogously as observed for $NEt_4Tb(hfa)_4$ solution (Fig. 4, curve (1)). However, a significant difference can be seen between presented curves at region of lower PVP concentration. In the case of $NEt_4Tb(hfa)_4$ solution the emission intensity decreases with the very first amounts of PVP added. In contrast, the emission intensity of solution containing both $NEt_4Tb(hfa)_4$ and $TbCl_3$ is insensitive to the presence of PVP, until its concentration reaches about 6×10^{-3} mmol/L.

The emission of Tb^{3+} in solution of $NEt_4Tb(hfa)_4$ complex decays with the time constant of 14 μs. Addition of $TbCl_3$ to this solution increases the decay time of Tb^{3+} emission, and in the presence of 0.03 μmol of $TbCl_3$ the decay curve is single-exponential with τ=44 μs. Upon addition of PVP the decay curve converts into double-exponential and then into triple-exponential; the contribution of the component with the shorter time constant (44 μs) gradually decreases at the expense of a longer component (250–300 μs). At the same time, for PVP concentration larger than 1×10^{-3} mmol/L, the short component with τ=14 μs, characteristic for the $NEt_4Tb(hfa)_4$, became again visible in the decay curve, with its contribution increasing as the amount of PVP increases. This is an important finding since when correlated with observed evolution of excitation spectra it enables one to propose the interpretation of processes occurring in solution.

One may expect that in solution containing $NEt_4Tb(hfa)_4$ and $TbCl_3$ a non-stoichiometric complex is formed, which can be presented as $(NEt_4)_xTb(hfa)_yCl_z$. The recurrence of the decay component characteristic for $NEt_4Tb(hfa)_4$ complex after addition of PVP points unambiguously to the binding of Tb^{3+} ions by PVP. The number of moles of hfa ligand increases in respect to that of Tb^{3+} ions, and the $NEt_4Tb(hfa)_4$ complex is reestablished in expense of the non-stoichiometric $(NEt_4)_xTb(hfa)_yCl_z$ complex. During this step the emis-

sion intensity remains almost unchanged. Then, when the excess of Tb^{3+} ions, in regard to the stoichiometry of the $NEt_4Tb(hfa)_4$ complex, was bound to PVP, the additional amounts of PVP cause quenching of the Tb^{3+} emission, analogously as is observed for solution of $NEt_4Tb(hfa)_4$ complex (without $TbCl_3$) treated with PVP (curve (1) in Fig. 4). Besides providing the hard prove for binding of Tb^{3+} ions by PVP, this experiment also shows that the Tb^{3+} cations interact with PVP polymer more efficiently than hfa anions, which is not unexpected.

3 Conclusions

The results presented in this paper provided direct evidences that Ln^{3+} ions as well as hfa ligands strongly interacted with PVP polymer in solution. This interactions led to the emission quenching of Ln-hfa complexes. Due to the binding of both Ln^{3+} ions and ligands to PVP, the $NEt_4Ln(hfa)_4$ complex decomposed and the energy transfer from the light harvesting ligand to the emitting Ln^{3+} ion was impeded. Although, owing to the energy transfer from PVP to Tb^{3+} ions the emission was more intense than for Tb^{3+} ions in solution without PVP (in fact at Tb^{3+} concentration of about 1×10^{-5} mol/L its emission was not detectable if excited directly through f-f or f-d bands), it was several dozen times less intense than in the cases where hfa ligand played a role of sensitizer.

The Ln^{3+} ions were most probably coordinated to the C=O group of PVP. The shift of electronic density towards oxygen atom of C=O group resulted in tautomeric structure of PVP with partial negative charge on oxygen atom and partial positive charge on nitrogen atom. Owing to this PVP attained ability for coordination of anions. Indeed binding of anions seemed to be prerequisite for shifting of the $Ln(hfa)_4^-\leftrightarrow$Ln-PVP+hfa-PVP equilibrium towards dissociated form of the Ln-hfa complex. If the interaction of ligand with PVP was not sufficiently strong, which was the case of btfac ligand, the complex (e.g. $NEt_4Eu(btfac)_4$) was stable in PVP solution and its emission was not quenched. Since the affinity of Tb^{3+} and Eu^{3+} ions towards PVP was expected to be similar, only interaction of ligands with PVP could account for the observed different stability of $NEt_4Tb(hfa)_4$ and $NEt_4Eu(btfac)_4$ complexes in PVP solutions, since their stability constants were comparable. The electrostatic interactions between anionic ligands and partial positive charge induced on PVP's nitrogen atom should be of similar strength for hfa and btfac, which suggested that formation of hydrygon bonds played an important role in binding of ligands to PVP. More specifically, we suggested that hydrogen bonds formed by terminal (–CF_3 or –C_6H_5) substituents of ligands were the most important factor influencing the strength of binding interactions of ligands with PVP. The CF_3 groups were known to be acceptors of proton in hydrogen bond, however the benzene ring of btfac ligand possessed only a

weak ability for formation of hydrogen bonds. Besides, the steric effect could additionally hinder binding of this ligand to PVP. Hence, the interaction of btfac with PVP was expected to be weaker than that of hfa, where two CF_3 groups could participate in formation of stabilizing hydrogen bonds. The more detailed study of mechanism of interaction of PVP with Ln(III)-complexes and ligands will appear in our forthcoming paper.

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