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Time-Resolved Luminescence of Terbium Complexes with Poly(2- and 4-vinylpyridine *N*-oxide)s in Aqueous Solution

Drahomír Výprachticky,[1] Věra Cimrová,[1] Yoshi Okamoto,[2] Rudolf Kotva[1]*

[1] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
E-mail: vyprach@imc.cas.cz,
E-mail: cimrova@imc.cas.cz
[2] Polymer Research Institute, Polytechnic University, Six MetroTech Center, Brooklyn,
New York 11201, USA
E-mail: yokamoto@duke.poly.edu

Summary: Terbium complexes with polymer ligands of poly(2- and 4-vinylpyridine *N*-oxide)s (P2VPNO, P4VPNO) in aqueous solution were prepared and characterized. Multi-exponential decays of the $^5D_4 \rightarrow {}^7F_5$ terbium transition at 545 nm of [P2VPNO-Tb^{3+}] and [P4VPNO-Tb^{3+}] complexes were measured. The non-linearity of semi-logarithmic plots of time-resolved luminescence was more pronounced in [P4VPNO-Tb^{3+}] than in [P2VPNO-Tb^{3+}], being reduced by addition of salts such as sodium formate or acetate. We assume that multi-exponential decays of Tb^{3+} in the complexes are caused by a back metal-to-ligand energy transfer via triplet state of *N*-oxide polymer ligand. By carrying out separate experiments in water and deuterium oxide, the number of coordinated water molecules in the [P4VPNO-Tb^{3+}] complex was estimated as 4–5, assuming that the Tb^{3+} aqua complex contains nine water molecules.

Keywords: lanthanide complexes; poly(vinylpyridine N-oxide); terbium metal; time-resolved luminescence

Introduction

Lanthanide metal ions such as Tb^{3+} and Eu^{3+} exist as stable trivalent ions exhibiting characteristic luminescence in aqueous solution, which is known to be strongly influenced by their immediate coordinated environment [1]. The luminescence intensity of the ions is normally quite weak in aqueous solution since the coordinated water molecules serve as efficient quenchers of the emission [2]. Recently we have observed that luminescence intensities of the Tb^{3+} ion are greatly enhanced upon binding to polycarboxylates,[3] poly(vinylpyridine)s,[4] or poly(vinylpyridine *N*-oxide)s.[5] The results indicated that Tb^{3+} ions were strongly bound to the polymer ligands and

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that some of their inner-coordinated solvent molecules (water, methanol) were displaced upon binding. The luminescence decays were measured and the number of coordinated water (polycarboxylates) or methanol (polyvinylpyridines) molecules was determined using the deuterium isotope effect.[6] Here we investigated the Tb^{3+} complexes with poly(2-vinylpyridine *N*-oxide) (P2VPNO) and poly(4-vinylpyridine *N*-oxide) (P4VPNO) in aqueous or deuterium oxide solutions by time-resolved fluorescence technique.

Experimental

Materials and Synthesis. Terbium chloride hexahydrate was purchased from Rhone-Poulenc Basic Chemicals Co. and anhydrous terbium chloride from Aldrich; both were used as received. Syntheses and characterization of poly(2- and 4-vinylpyridine *N*-oxide)s were reported.[5]

Ultraviolet spectra. A Carry 2300 UV-vis-near IR spectrometer was used to determine the absorption spectra in water. The spectra of both polymers have a maximum at 255 nm; the molar absorption coefficients of P2VPNO and P4VPNO, ε_{255}, are 6 550 and 10 200 $\mathrm{L\,mol^{-1}cm^{-1}}$, respectively.

Steady-state fluorescence spectra. A Perkin Elmer LS50B fluorescence spectrometer was used for steady-state fluorescence measurements. The slit width was 5 nm for both excitation and emission monochromators and the fluorescence intensity was reported in arbitrary units. The samples in a quartz cuvette (1 x 1 x 4 cm) were measured in the L-format arrangement.

Time-resolved luminescence. The time-resolved luminescence decays in the millisecond time scale were measured with a Perkin Elmer LS50B instrument in the phosphorescence mode. The Tb^{3+} luminescence intensity was measured at twenty different delay points following the excitation (xenon lamp equipped with a chopper). The luminescence decay, $F(t)$, was analyzed by triple-exponential fit ($i = 3$) given by

$$F(t) = C + \sum_i B_i \exp(-t/\tau_i), \qquad (1)$$

where B_i is a preexponential factor representing the fractional contribution to the time-resolved decay of the component with a lifetime τ_i [rel $B_i = (B_i\ \tau_i/\Sigma\ B_i\ \tau_i) \times 100\ \%$], C is background and t is time. Least-square analysis of luminescence decay curves was used for evaluation of τ_{1-3}.

Results and Discussion

For [P4VPNO-Tb^{3+}] complexes, the multi-exponential decays (Eq. 1) in water or deuterium oxide were measured (Figure 1a).

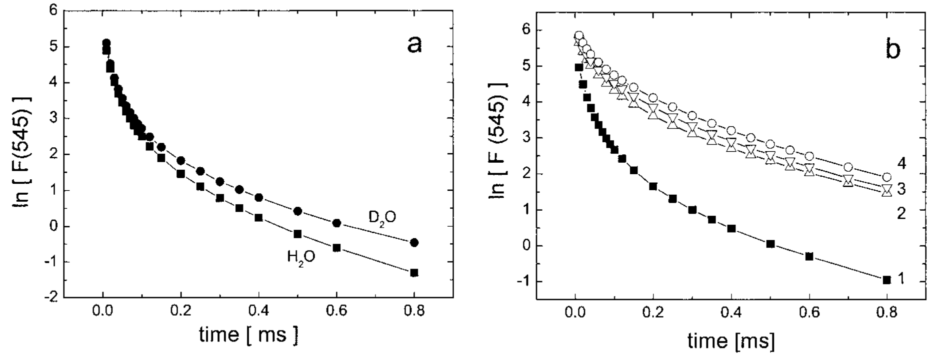

Figure 1: Time-resolved luminescence of the [P4VPNO-Tb^{3+}] complex at 545 nm ($\lambda_{ex} = 320$ nm) in (a) water (■) or deuterium oxide (●); (b) in water (■) and after addition of 0.0244 M (Δ) or 0.134 M (∇) of sodium acetate or 0.153 M (○) of sodium formate. [P4VPNO] = 1.16×10^{-2} M, [$TbCl_3$] = 1.0×10^{-3} M.

When solvents containing O-H groups are coordinated to lanthanide ions, efficient non-radiative deactivations take place via vibronic coupling with the vibrational states of the O-H oscillators (3500 cm^{-1}). If the O-H oscillators are replaced by the low-frequency O-D oscillators (2800 cm^{-1}), the vibronic deactivation pathway becomes much less efficient. By carrying out separate experiments in H_2O and D_2O solutions, the number of coordinated water molecules (n) in lanthanide – ligand complexes can be calculated [6] from the experimental excited-state lifetimes measured (in ms) in water (τ_{OH}) or deuterated water (τ_{OD}) using the equation: $n = q\ (1/\tau_{OH} - 1/\tau_{OD})$, where q = 4.2 was determined for Tb^{3+}. For single-exponential decays, the n could be evaluated; we determined the values 3.6, 3.4, and 2.4 for poly(acrylic acid), syndiotactic poly(methacrylic acid), and isotactic poly(methacrylic acid) ligands, respectively.[3,7] This approach to calculation of n was not directly applicable in the case of multi-exponential decays. Nevertheless, skipping the coinciding strongly nonlinear points for $t < 0.1$ ms, the linear regression of the points with $t > 0.1$ ms gave $\tau_{OH} = 0.18$ ms and $\tau_{OD} = 0.22$ ms (regression coefficient ~ 0.98). From these values we can roughly estimate *n* = 4-5. If it is assumed that the Tb^{3+} aqua complex contains nine water molecules[8], then about 4-5 water molecules were displaced upon the [P4VPNO-Tb^{3+}] complex formation and the coordination increased the luminescence intensity of Tb^{3+} (Figure 2).

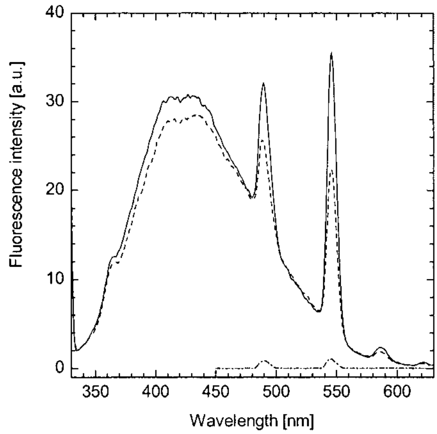

Figure 2: Emission luminescence spectra of $TbCl_3$ (λ_{ex} = 353 nm, dash-and-dott line) in water and of the [P4VPNO-Tb^{3+}] complex (λ_{ex} = 320 nm) in water in the presence (solid line) or absence (dashed line) of sodium formate; [P4VPNO] = 1.16×10^{-2} M, [$TbCl_3$] = 1.0×10^{-3} M, [HCOONa] = 0.153 M.

The terbium luminescence increase may be accounted for by two effects: the replacement of some of the water molecules inner-coordinated to Tb^{3+} ion upon complex formation and a possible energy transfer from the P4VPNO ligand to the Tb^{3+} ion. The ligand-to-metal energy transfer was proved by experiments in the presence and absence of terbium metal.[5] We assume that the multi-exponential decays at 545 nm are caused by back metal-to-ligand non-radiative energy transfer (quenching). The non-radiative deactivation of Tb^{3+} via the triplet state of *N*-oxide-containing branched macrocyclic ligands was described.[6] The *N*-oxide polymers have no ionizable groups, but charge separation in the N^+–O^- bond results in a large dipole moment. The quenching is likely associated with a too compact arrangement of N^+–O^- groups in the coordination sphere of the metal ion. We have found out that the curvature of multi-exponential decay of the [P4VPNO-Tb^{3+}] luminescence can be reduced by addition of salts such as sodium acetate or sodium formate

(Figure 1b). Addition of the salt increases the luminescence lifetime (Table 1) and intensities of terbium $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions at 490 and 545 nm, respectively (Figure 2). In a competitive process with the polymer ligand, formate or acetate anions probably optimize the ligand-metal distances in the energy transfer processes. Such explanation was further supported by time-resolved luminescence decays of the [P2VPNO-Tb^{3+}] and [P4VPNO-Tb^{3+}] complexes at 545 nm (Figure 3a).

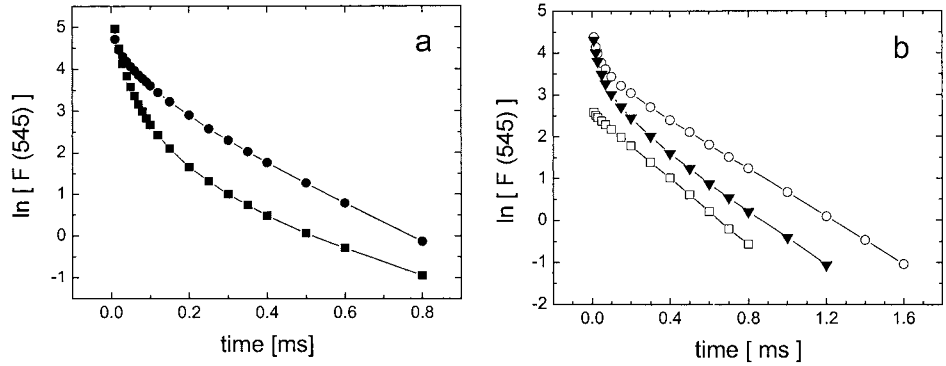

Figure 3: Time-resolved luminescence in aqueous solutions at 545 nm (λ_{ex} = 320 nm) of (a) [P2VPNO-Tb^{3+}] (●) and [P4VPNO-Tb^{3+}] (■), [ligand] = 1.16 x 10^{-2} M, [TbCl$_3$] = 1.0 x 10^{-3} M; (b) 1.0 x 10^{-2} M TbCl$_3$ (□), 1.0 x 10^{-2} M TbCl$_3$ + 1.16 x 10^{-3} M P4VPNO (○), 1.0 x 10^{-3} M TbCl$_3$ + 1.16 x 10^{-3} M P4VPNO (▼).

The complex with the P2VPNO ligand was quenched less, possessing a higher content of the longer-lifetime component (Table 1) than that with the P4VPNO ligand. Steric reasons seem to play an important role. In P2VPNO, the N^+–O^- group is more shielded by its polymer backbone and cannot occupy such tight arrangement in the metal sphere as that of P4VPNO. Finally, direct excitation of terbium leads to a single-exponential decay of its $^5D_4 \rightarrow {}^7F_5$ luminescence at 545 nm. In the [P4VPNO-Tb^{3+}] complex, because of absorption coefficients of the ligand and metal at the excitation wavelength, the overall terbium luminescence was acquired via ligand-to-metal energy transfer. With increasing ligand-to-metal ratio, the number of ligands in coordination sphere of the metal increases and a non-linearity (quenching) of time-resolved decays increases (Figure 3b). It was verified that the quenching was not caused by the chloride counterion after

$TbCl_3$ dissociation. Experiments of time-resolved luminescence of [P4VPNO-Tb^{3+}] and [P2VPNO-Tb^{3+}] performed with terbium triflate or nitrate provided similar results to those with terbium chloride.

In conclusion, with increasing ligand concentration, the ligand-to-metal energy transfer increases and one observes a higher emission intensity of Tb^{3+} ion at 490 and 545 nm; simultaneously, back metal-to-ligand quenching increases, which leads to multi-exponential decays of the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ emissions of terbium.

Table 1: Luminescence lifetimes ($\tau_{1\text{-}3}$ in triple-exponential fit; Eq. 1) calculated by least-square analysis from decay curves 1-5 shown in Figures 1b and 3a.

Luminescence decay	Luminescence lifetime τ_i (μs) and rel B_i (%)		
	τ_1 (rel B_1)	τ_2 (rel B_2)	τ_3 (rel B_3)
1	13 (18 %)	43 (41 %)	167 (41 %)
2	19 (8 %)	70 (33 %)	258 (59 %)
3	20 (7 %)	75 (28 %)	233 (65 %)
4	20 (5 %)	72 (25 %)	235 (70 %)
5	12 (3 %)	69 (27 %)	200 (70 %)

Acknowledgment

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