

LUMINESCENT TERBIUM COMPLEXES WITH POLYMER LIGANDS

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Alternating and statistical copolymers of 9-vinylcarbazole with diethyl fumarate (**1**), diethyl maleate (**2**), methacrylic acid (**3**), maleic anhydride (**4**), or maleic acid (**5**) were synthesized and characterized. These copolymers were tested as polymer ligands, that might be able to suppress the environmental vibronic quenching of a lanthanide ion and, simultaneously, to function as energy donors in the ligand-to-metal energy transfer processes. Time-resolved luminescence of a series of [Tb(III)-ligand] complexes in common and deuterated solvents revealed that the complexing properties of copolymers **3** or **5** are stronger than those of **1** or **2**. Consequently, the strong binding affinity decreases the ligand-metal (donor-acceptor) distance and gives rise to an efficient ligand-to-metal energy transfer. Thus, the intensities of the long-lived emission ($^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$) of the [Tb(III)-**3**], [Tb(III)-**5**], and [Tb(III)-**1**] or [Tb(III)-**2**] complexes were found to be eight times, five times, and less than twice that of uncomplexed Tb³⁺, respectively.

Keywords: Luminescence; Terbium complex; Polymer ligand; Carbazole energy donor; Time-resolved fluorescence spectroscopy; Lanthanoids; Lanthanide ions; Copolymers.

The design of complexes of lanthanide ions with encapsulating ligands is an important topic in the field of supramolecular chemistry, affording the possibility to obtain stable luminescent compounds suitable as fluorescence labels in fluoroimmunoassay¹, emitters in organic electroluminescent devices², or for plastic fiber lasers and optical amplifiers³. The luminescent properties of the metal ion can be optimized by a proper choice of the ligand. The importance of the luminescence of lanthanide ions is related to its peculiar characteristics, *viz.* a long lifetime and line-like emission bands, which are due to the fact that the emitting excited state and ground state have the same *fⁿ* electronic configuration and that the *f* orbitals are shielded from the environment by the outer *s* and *p* orbitals. Transitions between states of the *fⁿ* configuration are strictly parity-forbidden. The probability of such transitions is so low that the molar absorption coefficients are

of the order of 1 and the radiation lifetimes are in the millisecond time domain. There are two principal ways of increasing the weak luminescence of lanthanide metal ions. First, it is necessary to suppress the environmental vibronic quenching by a suitable encapsulating ligand. Second, we have to overcome the low molar absorption coefficients of lanthanide metal ions. In complexes of lanthanide ions with some strongly absorbing ligands, an intense luminescence of the ion may be obtained by the antenna effect^{4,5}, which is a light conversion process *via* absorption – energy transfer – emission, involving distinct absorbing (ligand) and emitting (metal ion) components. In such a process, the quantities contributing to the luminescence intensity are: (i) the intensity of the ligand absorption, (ii) the efficiency of the ligand-to-metal energy transfer and (iii) the efficiency of the lanthanide metal luminescence. The synthesis of strongly fluorescent lanthanide complexes with encapsulating ligands is based, for example, on 2,2'-bipyridine, 2,2'-biquinoline cryptands, or on their *N*-oxide derivatives. The 2,2'-bipyridine group has also been used as a building block in the syntheses of branched macrocyclic, tripode and tetrapode ligands⁵.

Recently^{6,7}, we replaced the low-molecular-weight pyridine cryptands with poly(2- and 4-vinylpyridine) or poly(2- and 4-vinylpyridine *N*-oxide). UV absorption of these polymeric ligands worked like “antenna” in the light conversion process. The fluorescence of the polymeric ligand (donor) overlapped with the absorption of the lanthanide metal ion (acceptor) and a ligand-to-metal energy transfer was observed. The increase in Tb³⁺ luminescence intensity was due to both the replacement of the inner-coordinated solvent (water or methanol) molecules and ligand-to-metal energy transfer. Approximately four molecules of water or methanol were

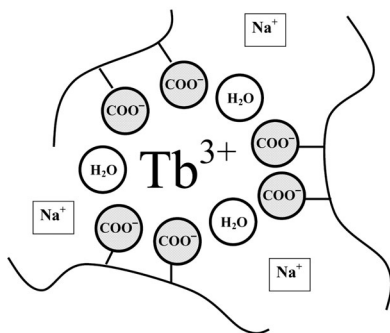


FIG. 1

Scheme of a terbium(III) complex with a polymer ligand containing carboxy groups in water (e.g. [Tb(III)-6])

displaced by the ligands. The luminescence intensity of the terbium ion was greatly enhanced upon binding to polycarboxylates like acrylic or methacrylic acids^{8,9}. The Tb³⁺ ions are strongly bound to polyanions in aqueous solution and some of their inner-coordinated water molecules were displaced upon binding (Fig. 1). In the case of the above homopolymers, a polymer coil formed a steric "cage" around the central lanthanide ion.

In this paper we report on the syntheses and characterization of statistical or alternating copolymers having both complexing (carboxy or ester groups) and energy donor (carbazole fluorophore) properties. These polymers were studied as ligands for the terbium ion in solution, using steady-state and time-resolved fluorescence spectroscopies.

EXPERIMENTAL

Materials

Poly(ethene-*alt*-maleic anhydride), $M_w = 100\ 000$, was purchased from Polysciences, Inc., U.S.A. Terbium trichloride hexahydrate was purchased from Rhone-Poulenc Basic Chemicals Co. and anhydrous terbium trichloride from Aldrich; both were used as received. 9-Vinylcarbazole, diethyl fumarate, diethyl maleate, methacrylic acid, maleic acid, maleic anhydride, deuterium oxide, and 2,2'-azobis(isobutyronitrile) (AIBN) were commercial chemicals (Aldrich, Fluka). Methacrylic acid was vacuum-distilled and AIBN was crystallized from methanol. Toluene was refluxed (24 h) with sodium metal and distilled. The solvents for fluorescence measurements were of UV-spectroscopic quality (Fluka).

Polymer Syntheses and Characterization

*Poly(9-vinylcarbazole-*alt*-diethyl fumarate)* (1). 9-Vinylcarbazole (7.73 g, 0.04 mol), diethyl fumarate (6.89 g, 0.04 mol), AIBN (0.05 g) and toluene (50 ml) were sealed in an ampoule under argon and polymerized at 65 °C for 76 h. The content of the ampoule was precipitated into methanol (700 ml). Yield 11.41 g (78%). The copolymer was reprecipitated from toluene into methanol and characterized by GPC ($M_w = 39\ 400$, $M_n = 24\ 300$, $p = 1.62$), UV-VIS spectroscopy (Fig. 2), and elemental analysis (calculated: 72.31% C, 6.34% H, 3.83% N; found: 72.04% C, 6.15% H, 3.75% N).

*Poly(9-vinylcarbazole-*alt*-diethyl maleate)* (2) was prepared by the same procedure as copolymer 1, using diethyl maleate instead of diethyl fumarate. Yield 10.74 g (73%). The copolymer was characterized by GPC ($M_w = 46\ 900$, $M_n = 29\ 400$, $p = 1.60$), UV-VIS spectroscopy (Fig. 2), and elemental analysis (calculated: 72.31% C, 6.34% H, 3.83% N; found: 73.15% C, 6.05% H, 3.88% N).

*Poly(9-vinylcarbazole-*co*-methacrylic acid)* (3). 9-Vinylcarbazole (7.73 g, 0.04 mol), methacrylic acid (6.89 g, 0.08 mol), AIBN (0.05 g) and 1,4-dioxane (60 ml) were sealed in an ampoule under argon and polymerized at 70 °C for 15 h. The content of the ampoule was diluted with 1,4-dioxane (1:1) and precipitated into water (3000 ml). Yield 12.80 g (87%). The copolymer was reprecipitated from 1,4-dioxane into water and characterized by GPC ($M_w =$

10 400, $M_n = 8\ 000$, $p = 1.30$), UV-VIS spectroscopy (Fig. 2), elemental analysis (calculated: 72.31% C, 6.34% H, 3.83% N; found: 69.40% C, 6.44% H, 3.59% N), and alkalimetric titration.

Poly(9-vinylcarbazole-alt-maleic anhydride) (4). 9-Vinylcarbazole (5.80 g, 0.03 mol), maleic anhydride (2.95 g, 0.03 mol), AIBN (0.04 g) and toluene (40 ml) were sealed in an ampoule under argon and polymerized at 65 °C for 4 days. The content of the ampoule was poured into toluene (300 ml) and chloroform (200 ml) was added. The volume was reduced approximately to one half (first precipitate) and *n*-heptane (20 ml) was added. The precipitated material was filtered off. Yield 1.07 g (12%). The copolymer was characterized by GPC ($M_w = 16\ 900$, $M_n = 11\ 950$, $p = 1.41$) and FTIR spectroscopy [3410, 3058 (arom. C–H, stretching); 2935 (aliph. C–H, stretching); 1858 (asym. C=O, stretching); 1781 (sym. C=O, stretching); 1483 (ring stretching); 1453 (CH₂, scissoring); 1265 (C–O–C, stretching); 1158 (CH₂, wagging); 949 (C–O–C, stretching); 749 (arom. C–H, out-of-plane); 723 (CH₂, rocking) cm⁻¹].

Poly(9-vinylcarbazole-alt-maleic acid) (5) was prepared by hydrolysis of copolymer **4** (0.58 g) with aqueous 2×10^{-1} M NaOH (50 ml) in tetrahydrofuran (50 ml) at room temperature. The reaction mixture was stirred for 24 h and then acidified with concentrated HCl to pH 1–2. The precipitate was filtered off, washed with water and dried. Yield 0.34 g (55%). The copolymer was characterized by GPC ($M_w = 17\ 500$, $M_n = 11\ 800$, $p = 1.48$), UV-VIS spectroscopy (Fig. 2), FTIR spectroscopy [3416, 3054 (arom. C–H, stretching); 2971, 2877 (aliph. C–H, stretching); 1726 (C=O, stretching); 1482 (ring stretching); 1452 (CH₂, scissoring); 1408 (O–H, in-plane bending); 1158 (CH₂, wagging); 924 (O–H, out-of-plane bending); 747 (arom. C–H, out-of-plane); 722 (CH₂, rocking) cm⁻¹], elemental analysis (calculated: 69.90% C, 4.89% H, 4.53% N; found: 66.49% C, 4.69% H, 3.97% N), and alkalimetric titration.

Poly(ethene-alt-maleic acid) (6). Poly(ethene-*alt*-maleic anhydride) (5.04 g, 0.04 mol of anhydride groups) was hydrolyzed with 1 M sodium hydroxide (100 ml) for 12 h. The reaction mixture was acidified with concentrated HCl to pH 1–2, dialyzed against water and freeze-dried. Yield 4.83 g (84%). Titration with aqueous NaOH confirmed the 1:1 molar composition of the prepared copolymer **6**.

Methods and Procedures

Molecular weights of the polymers were determined using a GPC chromatograph (Laboratory Instruments, Czech Republic) equipped with RI and UV 254 nm detectors, 8 × 600 mm column (PSS 10 000, PSS, Germany) column and data collection and treatment (Data Monitor, Watrex, Czech Republic). Polystyrene standards (PL Laboratories, U.K.) were used for calibration. The samples were measured in tetrahydrofuran (THF), which was dried over a 4A molecular sieve and distilled.

Alkalimetric titrations of copolymers **3** and **5** (0.1 g) were performed in dioxane (20 ml) with methanolic 5.0×10^{-2} M sodium hydroxide, using phenolphthalein as pH-indicator. Titration of water-soluble copolymer **6** was performed in water with aqueous sodium hydroxide.

UV-VIS spectra were recorded on a Perkin–Elmer Lambda 20 spectrophotometer in THF in a quartz cuvette (0.1 or 1.0 cm). Molar absorption coefficients (ϵ) and molar concentration of polymers are expressed per monomer unit.

FTIR spectra were measured using a Perkin–Elmer Paragon 1000 PC spectrometer, in KBr pellets or as a film on a KBr pellet.

Steady-state fluorescence spectra were measured in 1:1 (v/v) 1,4-dioxane/methanol with a Hitachi Perkin-Elmer MPF-2A (without delay) or Perkin-Elmer LS 50B (with a delay of 0.05 ms) spectrofluorimeters in L-format using a quartz cuvette ($1 \times 1 \times 4$ cm). The concentrations of terbium ($[\text{Tb}^{3+}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$) and ligands ($[\text{ligand}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$) were tuned taking into account the corresponding molar absorption coefficients (Figs 2 and 3) and L-format arrangement.

The luminescence lifetimes (τ_{OH} , τ_{OD}) of Tb(III) complexes with polymer ligands **1**, **2**, **3**, and **5** were measured in 1:1 (v/v) 1,4-dioxane/MeOH or 1:1 (v/v) 1,4-dioxane/MeOD with a time-resolved spectrofluorimeter FL 900 CDT (Edinburgh Analytical Instruments, U.K.). Mea-

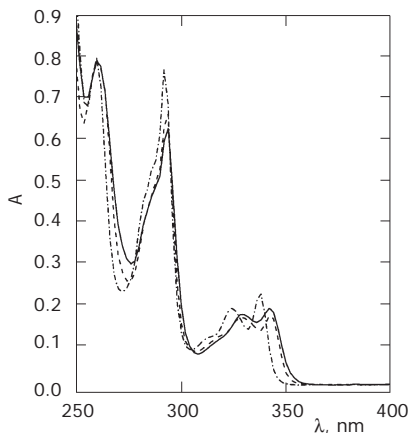


FIG. 2

Electronic absorption spectra of polymer ligands **1** or **2** (dash-and-dot line same for both, $c = 0.1827 \text{ g dm}^{-3}$), **3** (dashed line, $c = 0.1827 \text{ g dm}^{-3}$), and **5** (solid line, $c = 0.162 \text{ g dm}^{-3}$) in 1,4-dioxane (1 mm cuvette)

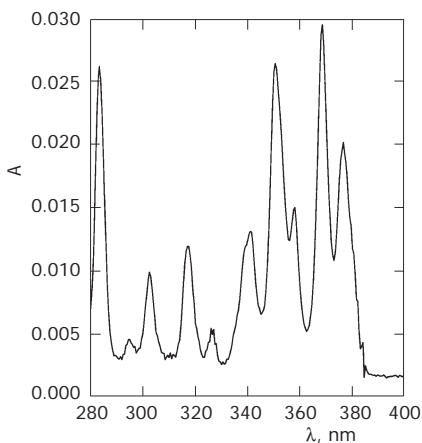


FIG. 3

Electronic absorption spectrum of aqueous $1 \times 10^{-1} \text{ M TbCl}_3$ (1.0 cm cuvette)

measurements were performed on a microsecond (μs) time scale, using a computer-controlled μF900 xenon flashlamp for excitation. The [Tb(III)-1] and [Tb(III)-2] complexes were excited at 372 nm, the [Tb(III)-3] and [Tb(III)-5] complexes at 340 nm, and emissions of all of them were recorded at 545 nm. The concentrations of the terbium metal and the ligands were the same as for steady-state measurements.

The luminescence lifetimes (τ_{H} , τ_{D}) of Tb(III) complexes with copolymer **6** were determined in water (H_2O) or deuterium oxide (D_2O) with a Perkin-Elmer LS 50B instrument. In the determination of the emission lifetimes, the luminescence intensity (I) at 20 delay-time points after excitation with a xenon lamp equipped with a chopper was measured within the time interval of 0–7 ms. The luminescence lifetime for a single-exponential decay was obtained as the slope of the $\ln I$ vs time (t) dependence by means of a linear regression. The [Tb(III)-6] complex was excited at 353 nm and its emission was recorded at 545 nm. Copolymer **6** was neutralized with sodium hydroxide to pH 9.0 before mixing with aqueous terbium trichloride ($[\text{COONa}] = 1.25 \times 10^{-1} \text{ mol dm}^{-3}$, $[\text{Tb}^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$).

RESULTS AND DISCUSSION

Syntheses of Polymer Ligands

Radical copolymerization of 9-vinylcarbazole with electron-acceptor monomers like diethyl fumarate or diethyl maleate was studied in connection with the preparation of 1:1 alternating copolymers¹⁰. A generalized mechanism for the alternating radical polymerization, involving participation of both the monomer charge-transfer complex and the free monomers in the propagation process of the polymerization, was proposed. The 1:1 composition was obtained with the fumarate¹¹ regardless of feed composition, whereas with the maleate¹² (copolymerization parameters: $r_1 = 0.27$, $r_2 = 0$), the strict 1:1 incorporation of monomer took place when the mole ratio of 9-vinylcarbazole was less than 0.5. In the syntheses of polymer ligands **1** and **2**, equimolar amounts of comonomers in the feed were used. The carbazole content in copolymers was determined by UV-VIS spectroscopy in 1,4-dioxane (Fig. 2), assuming that the molar absorption coefficient of the carbazole structure unit in the copolymer is the same as that of 9-vinylcarbazole¹³ ($\epsilon_{292} = 16\,500$ and $\epsilon_{340} = 4\,400 \text{ l mol}^{-1} \text{ cm}^{-1}$). We have determined the same value, 50 mole % of carbazole units, in copolymers **1** or **2**. The alternating character of the copolymers was confirmed also by elemental analyses (ex N) of **1** and **2**.

In the synthesis of copolymer **3**, we used the 2:1 molar ratio of methacrylic acid to 9-vinylcarbazole, *i.e.*, 33 mole % of 9-vinylcarbazole in the polymerization feed. From UV-VIS spectra, elemental analysis (ex N), and alkalimetric titration we determined 27, 30, and 33 mole % of carbazole structure units in copolymer **3**, respectively. Using Q - e values¹⁴ of

9-vinylcarbazole ($Q = 0.26$, $e = -1.29$) and methacrylic acid ($Q = 0.98$, $e = 0.65$), the copolymerization parameters were calculated¹⁵ as $r_1 = 0.02$, $r_2 = 1.15$. According to these results, we assume that in a statistical copolymer two methacrylic acid units follow after one carbazole structure unit on average. Two adjacent carbazole units are improbable ($r_1 \ll 1$). This was further confirmed by fluorescence measurements where the excimer emission was not observed.

Copolymerization of 9-vinylcarbazole and 1:1 (mol/mol) maleic acid in 1,4-dioxane (AIBN, 60 °C) gave an oligomer having molecular weight less than 1500 (GPC). Such oligomer was found to be quite inefficient as a ligand for terbium. Consequently, poly(9-vinylcarbazole-*alt*-maleic acid) (**5**) was prepared by hydrolysis of poly(9-vinylcarbazole-*alt*-maleic anhydride) (**4**). Using Q - e values of 9-vinylcarbazole (above) and maleic anhydride¹⁴ ($Q = 0.86$, $e = 3.69$), we calculated the copolymerization parameters $r_1 = 0.0005$, $r_2 \approx 0$, which predicted an alternating character of copolymer **4**. It has been reported¹⁶ that copolymerization of 9-vinylcarbazole with maleic anhydride in benzene (AIBN) led to the simultaneous formation of poly(9-vinylcarbazole) homopolymer and a roughly alternating copolymer poly(9-vinylcarbazole-*alt*-maleic anhydride). The former was extracted from the mixture with chloroform in a Soxhlet extractor. We performed the copolymerization in toluene (1:1 (mol/mol) in the feed) and then chloroform was added as a solvent for the homopolymer. Addition of *n*-heptane precipitated the more polar copolymer **4**. The hydrolysis of **4** with aqueous sodium hydroxide gave copolymer **5**. Analyses of FTIR spectra of **4** and **5** have revealed that anhydride group bands [1858 (asym. C=O); 1781 (sym. C=O); 1265, 949 (C–O–C) cm^{-1}] disappeared, giving rise to those of COOH groups [1726 (C=O); 1408, 924 (O–H) cm^{-1}]. From the elemental analysis (ex N), UV-VIS spectra (Fig. 2), and alkalimetric titration of COOH, we determined 42, 33, and 36 mole % of carbazole units in copolymer **5**, respectively. Similar results, *i.e.* a moderate excess of maleic anhydride in copolymer with respect to the 1:1 mole ratio of monomer feed, were reported for copolymerization of 1-vinylindole with maleic anhydride¹⁷.

*Poly(9-vinylcarbazole-*alt*-diethyl fumarate) and
Poly(9-vinylcarbazole-*alt*-diethyl maleate) as Ligands in Tb(III) Complexes*

Luminescence properties of the [Tb(III)–ligand] complexes were investigated in solution using steady-state fluorescence spectroscopy. Excitation spectra of copolymers **1** and **2** are similar to their absorption spectra (Fig. 2) and their short-lived fluorescence emission spectra exhibited a maximum at

360 nm. There was a good overlap between the emission spectrum of the ligand and absorption spectrum of the terbium ion (Fig. 3), which is demanded for efficient energy transfer. We compared the long-lived luminescence emission intensity of the Tb^{3+} ion in the absence or presence of the ligand (**1** or **2**). The excitation spectra of $[\text{Tb}(\text{III})\text{-1}]$ and $[\text{Tb}(\text{III})\text{-2}]$ complexes for emission at 545 nm follow the metal absorption spectrum with typical maxima at 280, 320, 353, and 372 nm. In the emission spectra ($\lambda_{\text{exc}} = 372$ nm), we distinguished typical long-lived emission bands at 490, 545, 585, and 620 nm corresponding to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$, and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$ transitions of terbium, respectively. The short-lived complementary emission of the ligand at 360 nm was measured if the spectra were recorded without a delay between excitation and emission. For comparison of the long-lived emission, the spectra were recorded with a delay of 0.05 ms to avoid the interfering emission of the complementary ligand. Comparing the emission intensities of $[\text{Tb}(\text{III})\text{-1}]$ or $[\text{Tb}(\text{III})\text{-2}]$ complexes with those measured in the absence of the ligand (Fig. 4), a moderate increase (ca 25%) in the luminescence intensity was observed. As the spectral characteristics for efficient ligand-to-metal energy transfer are favorable (overlap), the binding affinity of the ligand is a problem. Binding properties of the ester groups are weak (see the time-resolved study below) and, consequently, the distance for efficient ligand-to-metal energy transfer is too large. That is why the excitation spectra of $[\text{Tb}(\text{III})\text{-1}]$ or $[\text{Tb}(\text{III})\text{-2}]$ complexes follow

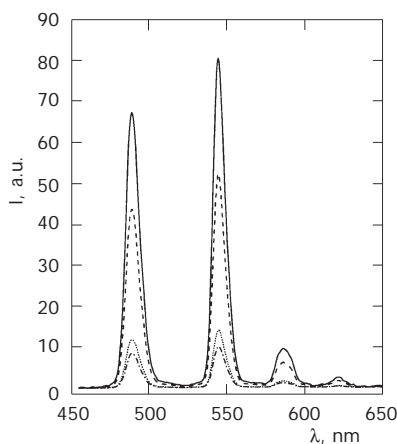


FIG. 4

Luminescence emission spectra of Tb^{3+} in the absence (dash-and-dot line) and presence of the ligands; **1** or **2** (dotted line for both), **3** (solid line), and **5** (dashed line) taken with the 0.05 ms delay. $[\text{Tb}^{3+}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{ligand}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$

that of Tb^{3+} and the emission intensities increased only moderately. No difference in luminescence properties of trans (fumarate) and cis (maleate) stereoisomers was found (Fig. 4).

*Poly(9-vinylcarbazole-co-methacrylic acid) and
Poly(9-vinylcarbazole-alt-maleic acid) as Ligands in Tb(III) Complexes*

To improve the binding properties of the ligand, the ester groups in the copolymer were replaced with carboxy groups. Polycarboxylates generally were found to have good binding properties^{8,9,18}. Copolymers **3** and **5** were synthesized and their fluorescence and binding properties were evaluated. Excitation spectra of copolymers **3** and **5** are similar to the absorption spectra (Fig. 2) and their emission spectra exhibited a maximum at 360 nm. The emission intensities of Tb^{3+} in the absence or presence of the ligand were investigated similarly as above. Compared with polymer ligands **1** and **2**, we have observed a different luminescence behavior of [Tb(III)-**3**] and [Tb(III)-**5**] complexes. The excitation spectra ($\lambda_{\text{em}} = 545 \text{ nm}$) of [Tb(III)-**3**] and [Tb(III)-**5**] exhibit a large emission band at 340 nm and two smaller bands at 280 and 372 nm. The emission intensities of the [Tb(III)-**3**] complex were found eight times and for the [Tb(III)-**5**] complex five times higher than that of Tb^{3+} (Fig. 4). We assume that nonradiative energy transfer from the carbazole fluorophore to the terbium central ion is responsible for the observed increase in luminescence intensities of Tb(III) complexes. The binding properties of carboxy groups in copolymers **3** and **5** are stronger than those of ester groups of **1** and **2**, giving rise to an efficient ligand-to-metal energy transfer. The excitation energy was trapped by carbazole fluorophore and nonradiatively transferred to the metal. Consequently, the band at 340 nm in excitation spectra coincides with absorption bands of copolymers **3** and **5** (Fig. 2). Stronger binding properties of **3** and **5** in comparison with **1** and **2** were revealed by time-resolved spectroscopy.

*Binding Properties of Polymer Ligands 1, 2, 3, 5, and 6
in Tb(III) Complexes Followed by Time-Resolved Luminescence*

The $4f^n$ electronic configuration of a lanthanide ion gives rise to several spectroscopic terms whose energies are determined by mutual electronic repulsion, spin-orbital coupling and, in a coordination environment, the ligand field. The electrostatic interaction yields terms with separations of the order of 10^4 cm^{-1} and the spin-orbital interaction splits these terms into J states, with typical splitting of 10^3 cm^{-1} . The J degeneracy of the free-ion

states is partially or fully removed in coordination compounds by the ligand field, the splitting being of the order of 10^2 cm^{-1} . According to the theory of nonradiative transitions in lanthanide complexes¹⁹, the non-radiative relaxation between various J states occurs by interaction of the electronic levels of the lanthanide ion with suitable vibrational modes of the environment. The efficiency of these processes depends on the energy gap between the ground and excited states and the vibrational energy of the oscillators²⁰. When solvents containing O–H groups are coordinated to lanthanide ions, efficient nonradiative deactivations take place *via* vibronic coupling with the vibrational states of the O–H oscillators²¹. If the O–H oscillators are replaced by the low-frequency O–D oscillators, the vibronic deactivation pathway becomes much less efficient. Copolymer **6** is soluble in water; by carrying out separate experiments in H_2O and D_2O , we determined the number of coordinated water molecules (w) in the Tb(III) complex by means of

$$w = q(1/\tau_{\text{H}} - 1/\tau_{\text{D}}) , \quad (1)$$

where τ_{H} and τ_{D} are the experimental luminescence lifetimes (in ms) in H_2O and D_2O , respectively, and q is 4.2 for Tb(III) complexes²². We have measured the luminescence lifetimes τ_{H} and τ_{D} of [Tb(III)–**6**] to be 0.95 and 3.05 ms, respectively (Fig. 5). The corresponding number of coordinated

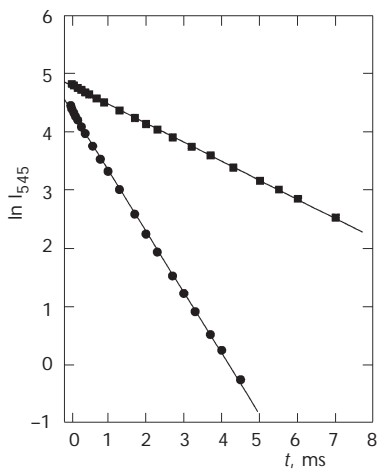


FIG. 5

The decays of luminescence emission intensity (I) at 545 nm (semilogarithmic plot, $\lambda_{\text{exc}} = 353 \text{ nm}$) of [Tb(III)–**6**] complex measured in H_2O (●) or D_2O (■); $\tau_{\text{D}} = 3.05 \text{ ms}$, $\tau_{\text{H}} = 0.95 \text{ ms}$. $[\text{Tb}^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\mathbf{6}] = 6.25 \times 10^{-2} \text{ mol dm}^{-3}$

water molecules in the [Tb(III)-**6**] complex was calculated from Eq. (1) as $w = 3$. Since 8–9 water molecules are coordinated to terbium ion in aqueous solution^{5,23}, ca 5–6 hydrate water molecules of [Tb(H₂O)₈₋₉]³⁺ are replaced with the ligand carboxy groups (Fig. 1). The result indicates that alternating copolymer **6** exhibits strong binding properties, which can be expected also for copolymers **3** and **5**, having similar structure with alternating carboxy groups. Unfortunately, carbazole-containing ligands **1**, **2**, **3**, and **5** are insoluble in water to measure their binding properties as above (w), but they are soluble in 1:1 (v/v) 1,4-dioxane/methanol. We would like to evaluate the binding properties of these ligands in such mixed solvent. We have measured the luminescence lifetimes τ_{OH} and τ_{OD} in 1:1 (v/v) 1,4-dioxane/MeOH and 1:1 (v/v) 1,4-dioxane/MeOD, respectively. Typical experimental decays are shown in Fig. 6 and the luminescence lifetimes are summarized in Table I. On the assumption that methanol behaves like a half water molecule, it was proposed²⁴ to determine the number of coordinated methanol molecules (m) from the luminescence lifetimes (in ms) determined in methanol (τ_{MeOH}) and deuterated methanol (τ_{MeOD}) by

$$m = k (1/\tau_{\text{MeOH}} - 1/\tau_{\text{MeOD}}), \quad (2)$$

where k is 8.4 for Tb(III) complexes. The 1,4-dioxane molecule does not contain an O–H oscillator and if there is any quenching caused by this solvent, it is equal in both mixtures containing the same amount of 1,4-di-

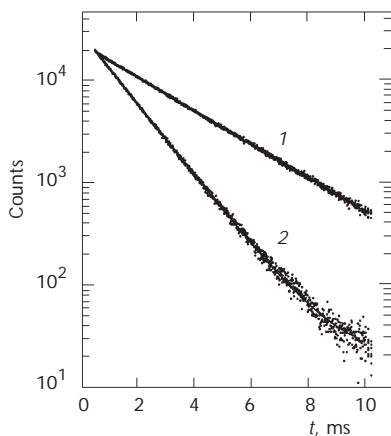


FIG. 6

Time-resolved luminescence ($\lambda_{\text{exc}} = 340$ nm, $\lambda_{\text{em}} = 545$ nm) of [Tb(III)-**5**] complex measured in 1,4-dioxane/MeOD (1) or 1,4-dioxane/MeOH (2); $\tau_{\text{OD}} = 2.62$ ms, $\tau_{\text{OH}} = 1.245$ ms. [Tb³⁺] = 2.5×10^{-2} mol dm⁻³, [5] = 2.5×10^{-4} mol dm⁻³

oxane. Nevertheless, we do not know the k value for the mixed solvent 1,4-dioxane/methanol in Eq. (2) and, consequently, we cannot determine the number of coordinated methanol molecules in this solvent explicitly. That is why we used the ratio m/k for evaluation of binding properties of ligands **1**, **2**, **3**, and **5** in [Tb(III)–ligand] complexes (Table I). With decreasing the m/k ratio, the binding properties of a ligand increase and more quenching methanol molecules are displaced from the terbium coordination sphere by the ligand. The binding properties of the ligands decrease in the order of **3** > **5** > **1** \cong **2**. Thus the results obtained from the time-resolved experiments supported the order of emission intensities of the [Tb(III)–ligand] complexes found out using the steady-state approach. In conclusion, the increase in the long-lived luminescence intensity of the [Tb(III)–ligand] complexes is due to both effects, *i.e.*, (i) replacement of some methanol molecules inner-coordinated to Tb³⁺ by complex formation and (ii) the nonradiative energy transfer from the ligand to Tb³⁺.

TABLE I

Luminescence lifetimes of the [Tb(III)–ligand] complexes in 1,4-dioxane/MeOH (τ_{OH}) and 1,4-dioxane/MeOD (τ_{OD}) and m/k ratio calculated according to Eq. (2) ($\lambda_{\text{em}} = 545 \text{ nm}$)

Ligand	λ_{exc} , nm	τ_{OH} , ms	τ_{OD} , ms	m/k
1	340	1.060	2.570	0.55
2	340	1.045	2.600	0.57
3	372	1.520	2.690	0.29
5	372	1.245	2.620	0.42

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SYMBOLS

A	absorbance
c	weight concentration, g dm^{-3}
e	Alfrey–Price copolymerization parameter
I	luminescence intensity, a.u.
J	energy states, eV
k	experimental constant for Tb ³⁺ in methanol complexes
m	number of coordinated methanol molecules in a complex
M_n	number-average molecular weight

M_w	weight-average molecular weight
p	polydispersity index ($p = M_w/M_n$)
q	experimental constant for Tb ³⁺ in water complexes
Q	Alfrey-Price copolymerization parameter
r	copolymerization parameter
t	time, s
w	number of coordinated water molecules in a complex
ε	molar absorption coefficient, l mol ⁻¹ cm ⁻¹
λ	wavelength, nm
λ_{em}	emission wavelength, nm
λ_{exc}	excitation wavelength, nm
τ	luminescence lifetime, ms

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