Synthesis and Characterization of Linear Luminescent Schiff-Base Polyelectrolytes with Europium(III) in the Backbone[1a]

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ABSTRACT: The first luminescent linear europium(III) Schiff-base polyelectrolytes with europium in the polymer backbone have been synthesized and characterized. Europium-containing polyelectrolytes with ligand triplet states at or above the $^5D_0$ state of europium luminesce with high quantum yields, consistent with the intramolecular energy-transfer mechanism established for europium(III) complexes. New $[NaY(tstm)]_n$ polyelectrolytes, where $tstm^{4-}$ is the anionic ligand derived from *N*,*N*′,*N*″,*N*‴-**t**etra**s**alicylidene-3,4,3′,4′-**t**etraaminodiphenyl**m**ethane, were synthesized with $\overline{M}_n$ values (up to 21 600) based on NMR end-group analysis. Intrinsic viscosities provide Mark−Houwink constants of $a = 0.52$ and $K = 0.066$ cm^3/g for $[NaY(tstm)]_n$. Mixed-metal $[NaY_xEu_{1-x}(tstm)]_n$ polyelectrolytes provide enhanced emission over $[NaEu(tstm)]_n$. The intensity is most enhanced for polyelectrolytes with Y:Eu ratios between 1:2.5 and 1:9, probably by intrachain energy transfer from the yttrium units of the polyelectrolytes to the Eu^{III} ions. $[NaY_{0.2}Eu_{0.8}(tstm)]_n$ (Y:Eu = 1:4) luminesces more strongly than any other compound investigated and has a quantum yield of 0.74 at 77 K.

Introduction

Reports of lanthanide ions in polymeric systems generally involve either polymers used as matrices for lanthanide ions or complexes[2−6] or lanthanide ions or complexes bonded to branches of the polymer chains.[7−13] The use of lanthanide ions in the polymer backbones normally results in insoluble materials, in species which come apart upon dissolution, in species which are not well characterized, or in species that are simply held together by excess bridging ligands in solution.[14−18] However, by choosing the proper bis(tetradentate) Schiff-base ligands, lanthanide Schiff-base polymers[19,20] or polyelectrolytes with lanthanide ions in the polymer backbones can be synthesized.[21] The lanthanide ions in the polyelectrolytes are 8-coordinate *without* solvent coordination.

With appropriate ions, such as europium(III), these totally chelated species should have high luminescent intensities[22,23] and the chelating ligands should shield the luminescent ions from the solvent, which should overcome the solvent-quenching problem that exists in polymers containing solvated lanthanide ions.[12,24] The luminescence of lanthanide or rare-earth coordination compounds,[25−33] especially β-diketone complexes, and more recently, supramolecules,[34−36] has been widely investigated. The strong line emission from lanthanide ions in coordination compounds has generated a long-standing interest in finding new luminescent and laser materials involving such complexes,[32,37−42] including lanthanide-containing polymers.[4,7,9,11,13,24,43−46]

Because of their special structures, lanthanide Schiff-base polyelectrolytes have some advantages for luminescence research. The tetradentate Schiff-base ligands greatly stabilize the lanthanide ions in solution. Second, the high extinction coefficients of Schiff-base ligands in the near-ultraviolet−visible region allow efficient energy transfer to the coordinated lanthanide ion centers. An energy-transfer mechanism has been well documented for lanthanide β-diketone complexes.[32,41,42,47]

Eu^{III} and Y^{III} Schiff-base polyelectrolytes have been synthesized with *N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′-diaminobenzidine (H_4tsdb) and *N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′,4,4′-tetraaminodiphenylmethane (H_4tstm). $\overline{M}_n$ values have been analyzed by Fourier transform nuclear magnetic resonance of end-capped Y^{III} polyelectrolytes and by viscosity measurements. Triplet-state energies of the polyelectrolytes have been determined from the corresponding Y^{III} species. Nine mixed-metal $[NaY_xEu_{1-x}(tstm)]_n$ polyelectrolytes have been prepared in order to investigate their luminescence properties. Results show that the luminescence of the polyelectrolytes at 77 K reaches a maximum for $[NaY_xEu_{1-x}(tstm)]_n$ (Y:Eu = 1:4 at 1 mM Eu^{III}) and is even more intense than that of the most intense monomer, $Na[Eu(dsp)_2]$,[1] under analogous conditions. The enhanced luminescence of the mixed-metal polyelectrolytes is analogous to the so-called antenna or photon-harvesting effect observed for polymers,[48,49] lanthanide supramolecular compounds,[34,35] and mixed lanthanide complexes in solution[15] or in sol−gels.[50] Luminescence sensitization of europium(III) by terbium(III)[51] is a slightly different twist on this energy transfer situation.

Experimental Section

Reagents. Reagent grade and HPLC grade solvents and chemicals were used throughout. Prior to use, dimethyl sulfoxide (DMSO) was stirred for 2 days with barium oxide and fractionally distilled over calcium hydride under reduced pressure. NMP and DMF were further purified following literature procedures.[52] Salicylaldehyde (Hsal) was distilled under reduced pressure. 3,3′-Diaminobenzidine (db) was purified just prior to use by using the method of Vogel and Marvel.[53,54] The aromatic amine compounds were kept under an inert atmosphere of N_2 or Ar to avoid oxidation of the amine groups.

Schiff Bases. The tetradentate Schiff-base ligand end-capping reagent and the bis(tetradentate) polyelectrolyte bridging ligands were prepared according to previously published procedures.[19,20]

Lanthanide(III) Schiff-Base Polyelectrolytes, $[NaY(tsdb)]_n$ and $[NaEu(tsdb)]_n$. H_4tsdb (0.500 g, 0.794 mmol)

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Table 1. Fractionated [NaY(tstm)]$_n$ Polyelectrolyte

fraction	yield	$\overline{M}_n$[a]	viscosity[b]
1	17%	21600	14.2
2	10%	18700	10.8
3	17%	17200	10.5
4	24%	13600	9.1

[a] $\overline{M}_n$ based on the results from the end-group analysis. [b] Intrinsic viscosity (cm^3/g) in NMP at 30.00 ± 0.02 °C.

Table 2. Preparation of [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ Polyelectrolytes

Y:Eu	mass of repeating unit	% Eu	viscosity[a]	$\overline{M}_n$[b]
0:1	815	18.7	6.69	7100
1:9	809	16.9	6.52	6800
1:4	802	15.2	6.80	7300
1:2.5	797	13.6	7.95	9900
1:1.5	790	11.5	7.97	9900
1:1	784	9.70	7.90	9800
1.5:1	777	7.82	8.08	10200
2.5:1	770	5.64	7.47	8800
4:1	765	3.98	7.00	7700
6:1	761	2.85	6.59	6900
1:0	752	0.00	8.05	10100

[a] Intrinsic viscosity (cm^3/g) in NMP at 30.00 ± 0.02 °C. [b] $\overline{M}_n$ calculated using the Mark–Houwink constants for [NaY(tstm)]$_n$.

and 0.794 mmol of Eu(NO$_3$)$_3$·3DMSO or Y(NO$_3$)$_3$·3DMSO were dissolved in 25 mL of DMSO at 75 °C. Then 0.152 g (3.81 mmol) of NaOH in 5 mL of methanol was added to the solution. The resulting solution was kept at 75 °C under N$_2$ for 16 h with magnetic stirring, and then 100 mL of methanol was added to the solution. The yellow precipitate was obtained after the solution was stirred for about 45 min at 75 °C. The product was filtered, washed with methanol and ether, and dried at 100 °C *in vacuo*. Yield: 55–60%. Anal. Calcd for NaYC$_{40}$H$_{26}$O$_4$N$_4$·1.2C$_2$H$_6$SO: Y, 10.7; DMSO, 11.3. Found: Y, 10.4; C, 61.0; DMSO, 11.5. Anal. Calcd for NaEuC$_{40}$H$_{26}$N$_4$O$_4$·0.8C$_2$H$_6$SO: Eu, 17.6; DMSO, 7.23. Found: Eu, 17.8; DMSO, 7.33.

[NaY(tstm)]$_n$. H$_4$tstm (0.9050 g, 1.405 mmol) was dissolved in 45 mL of DMSO with 0.7153 g (1.405 mmol) of Y(NO$_3$)$_3$·3DMSO at 75 °C under N$_2$. NaOH (0.2698 g, 6.744 mmol) in 10 mL of methanol was added to the solution. The resulting solution was allowed to react at 75 °C under N$_2$ for 16 h before 0.2000 g (0.467 mmol) of H$_2$bsp and 0.0374 g (0.934 mmol) of NaOH were added to the solution for a 45 min end-capping reaction. The solution was filtered and products with different $\overline{M}_n$ were obtained by slowly adding an ether and toluene (3:1) mixed solvent under stirring to a DMSO solution of [NaY(tstm)]$_n$ until the solution became turbid; then another 20 mL of the mixed solvent was added to the solution. After several minutes, an oil sank to the bottom of the flask to form a film. The solution was decanted from the oil, and the oil film was transformed to a precipitate by washing with methanol. The decanted solution was treated with another 30 mL of the mixed solvent, and another product was separated as above. The procedures were repeated several times to obtain different $\overline{M}_n$ products. The products was dried *in vacuo* at 100 °C. Results are given in Table 1. Anal. Calcd for NaYC$_{41}$H$_{28}$N$_4$O$_4$·0.7C$_2$H$_6$SO: Y, 11.0; C, 63.1; H, 3.99; N, 6.94; DMSO, 6.77. Found: Y, 11.2; C, 62.4; H, 3.95; N, 6.91; DMSO, 6.65.

[NaY$_x$Eu$_{1-x}$(tstm)]$_n$. H$_4$tstm (0.500 g, 0.776 mmol) was dissolved in 25 mL of DMSO with a total of 0.776 mmol of Eu(NO$_3$)$_3$·3DMSO and Y(NO$_3$)$_3$·3DMSO at 75 °C under N$_2$. The mole ratio of Y^{III} to Eu^{III} was varied from 1:9 to 6:1 as well as 0:1 and 1:0 (see Table 2). NaOH (0.149 g, 3.73 mmol) in 5 mL of methanol was added to each solution, which was then allowed to react for 16 h at 75 °C under N$_2$ with stirring. Spontaneous precipitation occurred during the reaction in some trials. The products were obtained by adding 100 mL of a 1:1 (v/v) methanol and water mixed precipitant containing 5 g of NaNO$_3$ to each solution. The products were filtered, washed with distilled water, and dried *in vacuo* at 100 °C. Yield: >97%.

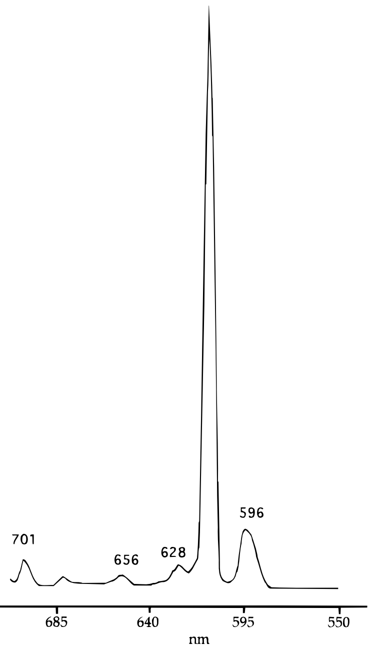


Figure 1. Emission spectrum of a typical europium(III) polyelectrolyte with the main peak at 613 nm.

Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)europium(III) Dihydrate {Eu(hfa)$_3$·2H$_2$O}. A literature method for preparing Ln(acac)$_3$ (where acac$^-$ is the anion of 2,4-pentanedione) compounds was used.[55] Yield, 95%; m p 130–131 °C (lit.[56] mp 125 °C) Anal. Calcd for EuC$_{15}$H$_3$F$_{18}$O$_6$·2H$_2$O: Eu, 18.8. Found: Eu, 18.7. When the product was further heated *in vacuo* at 100 °C, anhydrous Eu(hfa)$_3$ was obtained with a melting point of 202–204 °C (lit.[56] mp 196 °C). Anal. Calcd for EuC$_{15}$H$_3$F$_{18}$O$_6$: Eu, 19.7. Found: Eu, 19.7.

Analysis. C, H, and N were analyzed by standard microanalysis methods in the University of Massachusetts Microanalysis Laboratory. Ln^{3+} percentages were analyzed by EDTA titration by using Eriochrome Black T as an indicator and DMSO as a solvent. Percent of DMSO in the compounds was estimated from the weight loss obtained by heating 0.2000 g of the samples at 230 °C to a constant weight.

Characterization. Infrared spectra were obtained as KBr pellets with a Mattsen Cygnus 100 Fourier-transform infrared (FT-IR) spectrometer.

Ultraviolet–visible spectra were obtained with a Perkin-Elmer Model 3840 Lambda array spectrophotometer coupled with an IBM personal computer using software supplied by Perkin-Elmer.

Viscosity measurements were conducted in an Ubbelohde type viscometer in NMP solution at 30.00 ± 0.02 °C.

Thermal analyses were conducted with Perkin-Elmer TGS-2 and DSC-7 thermal analyzers under nitrogen gas with a heating rate of 20 °C/min. Both systems include Perkin-Elmer thermal analysis data stations and system 4 and 7 microprocessors, respectively.

Proton Fourier-transform nuclear magnetic resonance (FT-NMR) measurements were taken with Varian Models XL 80 and XL 200. The bsp-end-capped-polymer *tert*-butyl protons (average of 18 per chain) were integrated against the aromatic and aldehydic protons in the tstm^{4-} ligands (26 protons per tstm^{4-} unit). The average number of monomeric units (n_{mer}) *vs* the average number of bsp end groups (n_e) was obtained from the ratio of intensities adjusted for the number of protons in each. The average degree of polymerization was calculated by $\overline{DP} = 2(n_{\text{mer}}/n_e)$.[57] Several thousand acquisitions were acquired in order to obtain reliable results with the high-$\overline{M}_n$ polymers.

Table 3. Triplet-State Energy *vs* Quantum Yields of Eu(III) Schiff-Base Polymers

compound	triplet-state energy[a] (cm^{-1})	quantum yield
Eu(III)	19020 ($^5D_1$)[b]	
$[NaY_{0.2}Eu_{0.8}(tstm)]_n$ (Y:Eu = 1:4)	17270	0.74
$[NaEu(tstm)]_n$	17270	0.44
Eu(III)	17250 ($^5D_0$)[b]	
$[NaEu(tsdb)]_n$	16890	0.02

[a] The triplet-state energy obtained from the corresponding Y(III) Schiff-base polymers at 77 K in DMF–methanol–ether solvent. [b] Resonance levels of the Eu(III) ion.[42]

Luminescence and phosphorescence spectra were obtained with a Perkin-Elmer Model MPF-44 spectrometer with an R100A recorder. All emission spectra were obtained as soon as possible after the solutions were prepared. Liquid N_2 cooling was used to obtain the luminescence and phosphorescence spectra at low temperature (77 K). A mixed solvent (DMF:methanol:ether = 4:3:3 by volume) was used to obtain clear rigid glasses at 77 K as follows: First, the compounds were dissolved in hot DMF and cooled to room temperature. Then methanol and ether were added and the solution was carefully cooled in a quartz NMR tube in liquid nitrogen to make a glass suitable for emission spectral evaluation. [*Caution:* Rapid cooling in liquid nitrogen *or* rapid heating while part of the sample is still a glass can cause cracking of the quartz tube in which the rigid mixed-solvent sample is housed.] For solid-state luminescence measurements, a powdered compound was put in the tube and measured at 77 K.

Measurement slit values on the MPF-44 were as follows: emission/excitation slits = 2/2 nm for room temperature investigations, and emission/excitation = 6/10 nm for 77 K studies.

The triplet-state energies of the yttrium(III) Schiff-base polyelectrolytes at 77 K were obtained with the instrument slits set at emission/excitation = 20/20 nm. The triplet states of the europium species were estimated to be at the same energies obtained for the yttrium species.

The quantum yields of the Eu^{III} compounds were measured with $Eu(hfa)_3{\cdot}2H_2O$ as the standard. Its quantum yield is 43.6% in DMF at room temperature[58] and is 39% in EPA (ethanol:isopentane:ether = 2:5:5) solution at 77 K.[59] Eu^{III} concentrations of 1 mM were used in these experiments.

The quantum yields of the Eu^{III} polymers were calculated using the equation[60]

$$\frac{\Phi_{\mathrm{sta}}}{\Phi_{\mathrm{x}}} = \frac{I_{\mathrm{sta}}}{I_{\mathrm{x}}} \times \frac{A_{\mathrm{x}}}{A_{\mathrm{sta}}}\left[\frac{n_{\mathrm{sta}}}{n_{\mathrm{x}}}\right]^2 \qquad (1)$$

where Φ is the quantum yield, I is the intensity of the luminescence, A is the absorbance, and n is the refractive index of the "*sta*" (standard) and "x" (unknown) solutions. When eq 1 was used to calculate the quantum yields, the absorption values, A_{sta} and A_{x}, were based on room temperature measurements. The quantum yield results are provided in Table 3.

Results

Synthesis of Polyelectrolytes. $[NaY(tsdb)]_n$ had been prepared previously.[21] The analogous $[NaEu(tsdb)]_n$ has been prepared by one of the same methods (Scheme 1). Controlling the amount of NaOH and the exact stoichiometry of the reagents is key to successful polyelectrolyte formation. For the new $tstm^{4-}$ ligand polyelectrolytes $\{[NaEu(tstm)]_n$, $[NaY(tstm)]_n$, and $[NaY_xEu_{1-x}(tstm)_n]\}$, both (1) the amount of NaOH and (2) the use of a methanol and water mixed solvent (1:1) were found to be important. Some of these new polyelectrolytes could not be precipitated with methanol alone. $NaNO_3$ in the methanol/water precipitant was used to salt out high yields of the products and prevent colloidal materials from forming. Without $NaNO_3$, unfilterable colloidal solutions were obtained in the mixed solvent precipitation attempts.

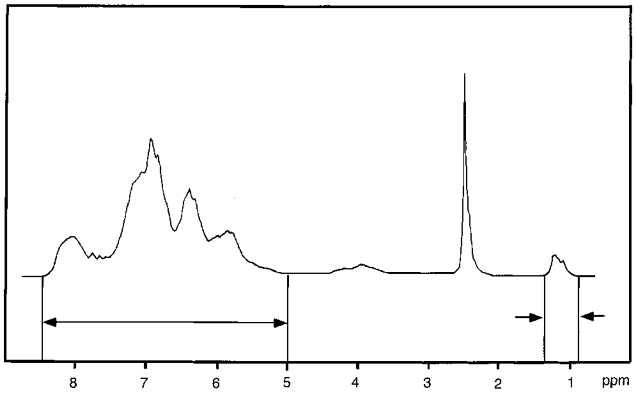
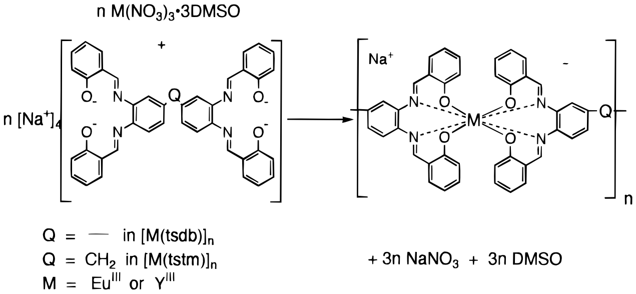
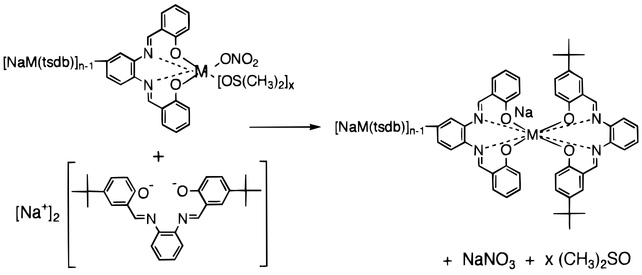


Figure 2. ^1H NMR spectrum for an end-capped $[NaY(tstm)]_n$ polyelectrolyte ($\overline{M}_n$ = 18 700) in DMSO-d_6 showing the polymer aromatic and the bsp^{2-} end cap *tert*-butyl regions that are integrated to determined $\overline{M}_n$.

Scheme 1



Scheme 2



The $\overline{M}_n$ values of the $[NaY(tstm)]_n$ polyelectrolytes were carefully measured by FT-NMR spectroscopy end-group analysis of the intensity of the *tert*-butyl proton signal of the end-capping bsp^{2-} ligand (Scheme 2) at about 1.2 ppm (18 protons per bsp^{2-}) *vs* the signals from aldimine and aromatic Schiff-base protons ranging from 5.0 to 8.5 ppm (26 protons per repeating unit) as shown in Figure 2. The highest $\overline{M}_n$ found for $[NaY(tstm)]_n$ after fractionation is 21 500 with a $\overline{DP}$ of 53.

The decomposition temperatures found for the polyelectrolytes are 474 °C for $[NaEu(tstm)]_n$, 461 °C for $[NaY(tstm)]_n$, 519 °C for $[NaEu(tsdb)]_n$, and 477 °C for $[NaEu_{0.5}Y_{0.5}(tstm)]_n$. From DSC measurements of $[NaY(tstm)]_n$, the glass transition temperature (T_g) has been determined to be 147 °C with an onset temperature of 142 °C.

NMR end-group analysis has not been obtained for the $[NaY_xEu_{1-x}(tstm)]_n$ and $[NaEu(tstm)]_n$ polymers, because the paramagnetism of the Eu(III) ion makes assignment of the spectra less reliable. Therefore, inherent viscosity has been used to estimate approximate $\overline{M}_n$ values for the polyelectrolytes containing

Table 4. Spectroscopic Data for Bis(tetradentate) Schiff Bases and the New Polymers

compound	UV−vis[a] (nm)	assignment	IR[b] (cm^{-1})	assignment
H_4tsdb	374 (4.70, sh)	$n \rightarrow \pi^*$	1615	C=N
	350 (4.73); 275 (4.73)	$\pi \rightarrow \pi^*$	1278	Ph−O
H_4tstm	360 (4.56, sh)	$n \rightarrow \pi^*$	1613	C=N
	342 (4.63, sh); 276 (4.64)	$\pi \rightarrow \pi^*$	1278	Ph−O
[NaEu(tsdb)]$_n$	408 (4.68)	$n \rightarrow \pi^*$	1612	C=N
	302 (4.48); 258 (4.48)	$\pi \rightarrow \pi^*$	1342, 1326	Ph−O
[NaEu(tstm)]$_n$	380 (4.45)	$n \rightarrow \pi^*$	1613	C=N
	334 (4.47); 289 (4.53)	$\pi \rightarrow \pi^*$	1341, 1321	Ph−O
[NaY(tstm)]$_n$	382 (4.45)	$n \rightarrow \pi^*$	1613	C=N
	334 (4.45); 291 (4.53)	$\pi \rightarrow \pi^*$	1342, 1323	Ph−O
[NaY$_{0.5}$Eu$_{0.5}$(tstm)]$_n$	382 (4.40)	$n \rightarrow \pi^*$	1613	C=N
	333 (4.40); 291 (4.48)	$\pi \rightarrow \pi^*$	1340, 1323	Ph−O
[NaY$_{0.2}$Eu$_{0.8}$(tstm)]$_n$	376 (4.46)	$n \rightarrow \pi^*$	1614	C=N
	334 (4.45); 289 (4.50)	$\pi \rightarrow \pi^*$	1342, 1323	Ph−O

[a] DMSO solvent; log ϵ in parentheses; sh = shoulder. [b] KBr pellet.

europium. The intrinsic viscosities for [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ are around 6.5−8.1 cm^3/g (Table 2) and the $\overline{M}_n$ values estimated from the Mark−Houwink equation range from about 7 000 to 10 000.

UV−visible and infrared spectra data for the ligands and the polyelectrolytes are given in Table 4. Only the important peaks in the IR spectra that shift upon complexation are reported here along with their assignments. Assignments for the UV absorption are based on the results obtained for the Ln$_2$(dsp)$_3$ and M[Ln-(dsp)$_2$] complexes.[61] The UV peaks of the Schiff-base polyelectrolytes exhibit high extinction coefficients ($\epsilon >$ 10 000 M^{-1}cm^{-1}).

Phosphorescence and Triplet-State Energy. The triplet-state energies of the europium(III) Schiff-base polyelectrolytes have been estimated from the analogous yttrium(III) polyelectrolytes by measuring the phosphorescence spectra of the yttrium species. The phosphorescence band emission of yttrium complexes is strong, and two or three clearly defined bands were observed for the polyelectrolytes. The shortest wavelength phosphorescence band was assumed to be the 0−0 transition,[62] and the position of this band is reported in Table 3. Because the yttrium ions have no accessible f-electron levels, ligand triplet-state phosphorescence is observed. Because the two ions are very similar in size and equal in charge, the effect of the metal ions on the ligands should also be similar. Previously, for these reasons others have used complexes of La^{III}, Gd^{III}, Y^{III}, or Lu^{III} to obtain complex ion triplet-state energies.[42,63−65] On the other hand, since energy transfer occurs to the f-electron states of europium, no phosphorescence ligand peaks can be observed in the europium complexes with accessible energy-transfer possibilities. Table 3 shows that the [NaLn(tstm)]$_n$ polymers, where Ln = Y, Eu, or a copolymer of the two ions, have higher triplet-state energies than the [NaLn(tsdb)]$_n$ polymers, where Ln = Y or Eu. Given the greater conjugation of the tsdb^{4-} ligand, the lower triplet-state energy is as expected.

Luminescence. Quantum yields were determined for the europium Schiff-base polyelectrolytes both in DMSO solutions at room temperature and in DMF−methanol−ether mixed solvent glasses at 77 K. The luminescence of the [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polyelectrolytes is significant only at 77 K and shows several features:

i. The luminescence intensities of the [NaEu(tstm)]$_n$ polyelectrolyte glasses reach a maximum at about 1 mM Eu^{III} (Figure 3) .

ii. The luminescence intensities relative to the weight percent of Eu^{III} in the [Na$_x$Eu$_{1-x}$(tstm)]$_n$ polyelectrolyte glasses exhibit maximum emission intensities at Eu:Y = 9:1 in [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ for both 0.50 and 1.00 mM glass concentrations (Figure 4).

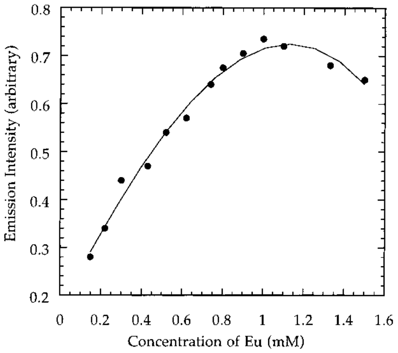


Figure 3. Emission intensities at 613 nm for [NaEu(tstm)]$_n$ at 77 K *vs* the Eu(III) concentrations.

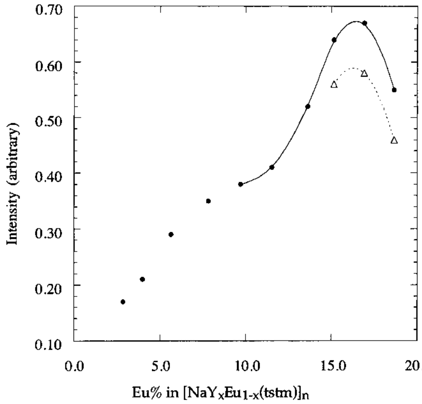


Figure 4. Emission intensities at 613 nm at 77 K for 0.50 (•) and 1.00 mM (Δ) [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ glasses plotted *vs* weight percent Eu as *x* varies.

iii. At a constant 1 mM Eu^{III} concentration, the luminescence intensity at 613 nm of [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ glasses changes appreciably with composition. The polyelectrolyte with a Y:Eu mole ratio of 1:4 has the highest intensity (quantum yield = 0.74), and the polyelectrolytes with Y:Eu ratios of from 1:9 to 1:1.5 (or 2:3) all have higher intensities than pure [NaEu(tstm)]$_n$, but the mixed-metal polyelectrolyte with a Y:Eu ratio of 1:1 has a lower emission intensity than pure [NaEu-(tstm)]$_n$ (Figure 5). The quantum yield of 0.74 is higher than that of any of the monomeric or dimeric Schiff-base complexes as well, either at 77 K or at room temperature.[1]

DMF−methanol−ether mixed solvent glasses (4:3:3 by volume) were also prepared that contained the separate [NaY(tstm)]$_n$ and [NaEu(tstm)]$_n$ polymers with

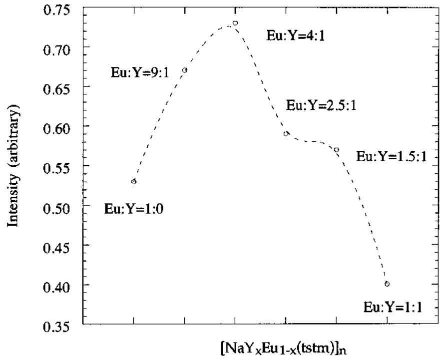


Figure 5. Emission intensities at 613 nm for [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ at 77 K and 1 mM Eu(III).

the same Y:Eu ratios used in the [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ mixed-metal polymers. The mixtures of separate yttrium and europium polymers exhibit less intense excitation spectra than the corresponding [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ mixed-metal polymers; in fact, the luminescence intensities at 613 nm at 77 K are approximately the same as those of glasses containing only the same amount of [NaEu(tstm)]$_n$ (without any added yttrium polymer). Thus the emission intensities of the separate polymers are much weaker than those of the corresponding [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ glasses for $x = 0.1-0.4$.

Discussion

Polyelectrolyte Characterization. The preparation and characterization of analogous [NaLn(tstb)]$_n$ polyelectrolytes, where Ln = Y, La, Gd, and Yb, have been reported previously.[21] To form linear coordination polyelectrolytes with these Schiff-base ligands, the metal ions must coordinate with two tetradentate ligands forming 8-coordinate metal centers. The new polyelectrolytes prepared here appear to have such structures based on their infrared spectra, which are similar to the Na[Ln(L)$_2$] monomers,[1] and other properties delineated below.

Fractionation of the polymers by gradually adding an ether–toluene mixed precipitant (or nonsolvent) to the solution makes it possible to separate different $\overline{M}_n$ polyelectrolytes. Further evidence for the formation of soluble polyelectrolytes includes the films formed in the bottom of the flasks after adding the organic precipitants and the colloidal precipitates formed by adding water and methanol as a precipitant when no inorganic electrolytes (salts) are added.

The $\overline{M}_n$ values of [NaY(tstm)]$_n$ were carefully measured by an NMR end-group analysis technique that has been successfully used with other coordination polymers previously.[19–21] In order to determine the approximate Eu^{III} polyelectrolyte $\overline{M}_n$ values, which cannot be obtained by using the same NMR end-group analytical method because of the Eu^{III} paramagnetism, the Mark–Houwink equation ($\eta = K\overline{M}^a$) constants for the analogous [NaY(tstm)]$_n$ polyelectrolytes were established. A plot of the logarithms of the $\overline{M}_n$values from the NMR end-group analysis of a series of fractionated [NaY(tstm)]$_n$ polyelectrolytes *vs* the logarithms of their intrinsic viscosities (in cm^3/g) in Figure 6 gives the constants $a = 0.52$ and $K = 0.066$ cm^3/g in the equation after linear regression with $R^2 = 0.992$. These data are similar to those found for the polyelectrolyte that has no methylene bridges [NaY(tsdb)]$_n$ ($a = 0.51$ and $K = 0.081$ cm^3/g). The virtually unchanged a value for [NaY(tstm)]$_n$ indicates that the introduction of a single methylene group per repeating unit of the polymer chain does not appreciably modify the solvent–polyelectrolyte interactions, even though an increase in polymer solubility is observed.

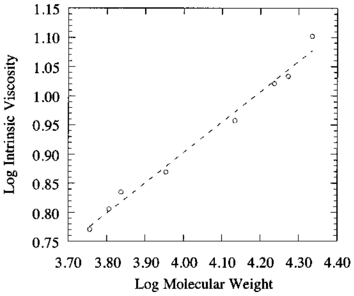


Figure 6. Composite Mark–Houwink plot for the [NaY(tstm)]$_n$ polyelectrolytes.

The glass transition temperature, T_g, found at about 147 °C for [NaY(tstm)]$_n$, is a little lower than that of the [NaY(tsdb)]$_n$ polyelectrolyte (*ca* 162 °C).[21] The methylene groups in the polymer chains apparently increase the flexibility and/or decrease the interchain attractions, thereby reducing the T_g of the polyelectrolytes.

The preparation of mixed-metal [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polyelectrolytes provides a way to adjust the percentage of Eu^{III} ions in the polyelectrolyte systems. Yttrium(III) was chosen based on the fact that its d^0 electronic configuration precludes the absorption of photon energy from either the ligands or the europium ions; furthermore, it has been widely used as a matrix for europium compounds in luminescent and laser materials.[38,66] The structure of [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ was confirmed by infrared spectra (Table 4) to be the same as that of [NaY(tstm)]$_n$. The results in Table 2 show that the [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polyelectrolytes have $\overline{M}_n$ values between about 7 000 and 10 000 based on the intrinsic viscosities of the polyelectrolytes and the Mark–Houwink equation for [NaY(tstm)]$_n$. Low $\overline{M}_n$ values are expected for these polyelectrolytes because the water–methanol precipitant used to obtain a high yield of products precipitated oligomers as well as the longer chain polymers. The high yield of products ensures the same ratio of Y:Eu in the polyelectrolytes as that in starting materials, which is important in the investigation of luminescence properties of these compounds and provides a reliable comparison among them. Spontaneous precipitation during the syntheses in some trials is logical because the solubility of the polyelectrolytes in solution becomes smaller as the molecular weight increases during the polymerization reaction. The same thing happens in the synthesis of [NaGd(tsdb)]$_n$.[21]

Triplet-State Energy of the Polyelectrolytes. As expected from their structures, the triplet-state energy of the europium and yttrium polyelectrolytes is affected by two factors. First, increased conjugation in a Schiff base reduces the triplet-state energy. The triplet-state energy of the [NaEu(tstm)]$_n$ polyelectrolyte with methylene groups separating the benzene rings is appreciably higher than that of [NaEu(tsdb)]$_n$ with adjacent conjugated aromatic rings. Obviously and not unexpectedly, the introduction of the methylene groups breaks down the conjugated system.

Proposed Intramolecular Energy-Transfer Mechanism for the Eu(III) Schiff-Base Polyelectrolytes. Whereas several different paths have been suggested

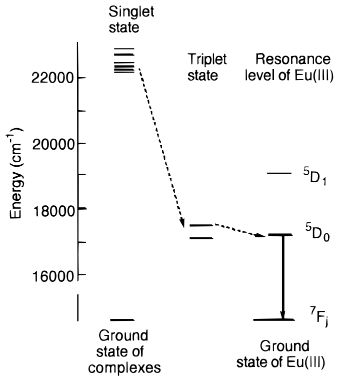


Figure 7. A logical mechanism of intramolecular energy transfer for europium(III) Schiff-base complexes. The triplet states for the polyelectrolytes are shown in the middle of the figure.

for the energy transfer from ligand excited states to the resonance states of Ln^{III} in lanthanide β-diketone complexes,[32] the favored mechanism (somewhat simplified) involves ligand excitation by the absorption of ultraviolet energy to an excited singlet (S_1) state, followed by energy migration via nonradiative intersystem crossing to a ligand triplet (T) state and energy transfer from the triplet state to a resonance state of a Ln^{III} ion, from which the emission occurs. In order to luminesce, the lowest triplet-state energy level of the complex must be nearly equal to, or lie above, the resonance energy level of the lanthanide ion.[30,34,42] The luminescence results for our Eu^{III} Schiff-base polyelectrolytes are consistent with this mechanism. Strong evidence comes from the triplet-state energies of the polyelectrolytes shown in Table 3. For [NaEu(tsdb)]$_n$, whose triplet-state energy is lower than the lowest resonance-state energy of Eu^{III}, a very low quantum yield has been obtained, which indicates that very little energy transfer takes place in this species. For [NaEu(tstm)]$_n$, with a triplet-state energy higher than the lowest resonance state of Eu^{III}, a high quantum yield has been obtained under suitable conditions (77 K glass). The reason that a low temperature is required for luminescence in these polyelectrolytes comes from the fact that the triplet-state energies of these polyelectrolytes are so close to the resonance state of the Eu^{III} ions that the quenching of the emitting level via thermal excitation back to the lowest triplet state of the ligand takes place at room temperature.[63] The higher rates of collision between the complexes and the solvent molecules at room temperature provides further quenching.[67−69] When the triplet-state energy is as high as that in europium salen (salicylideneethylenediamine) and its derivatives (*ca* 20 000 cm^{-1}), room temperature luminescence is observed[1] because energy transfer back to the ligand is negligible for these complexes, even at room temperature. Another possible temperature-dependent quenching mechanism that involves the population of LMCT excited states from the $^5D_0$ emitting state of Eu^{3+} followed by efficient nonradiative decay to the ground state[34,70] seems unlikely for these complexes because no apparent LMCT band has been observed, nor are they expected at a low enough energy to be operative in these systems.

Luminescent Polyelectrolytes. These new europium(III) polyelectrolytes have several advantages over the traditional lanthanide polymer systems in which lanthanide ions are attached to branched organic polymer chains. First, all Eu^{III} ions in the new polyelectrolytes are 8-coordinate with two tetradentate ligands. This provides completely filled coordination spheres for the chelated Eu^{III} ions, unlike the restrictions of most organic polymer chain ligands that incompletely fill the coordination spheres and thus include solvent molecules in the coordination spheres.[9−11,44] The fully chelated coordination spheres shield the europium ions from solvent deactivation and have greatly improved luminescence. Furthermore, the ligands have strong absorption in near-UV−visible spectral region, and polyelectrolytes with suitable triplet-state energies can be synthesized. Together these can lead to excellent luminescence properties for the polyelectrolytes. Whereas the highly conjugated [NaEu(tsdb)]$_n$ has a low triplet-state energy (*ca* 16 900 cm^{-1}) as noted above, placing the methylene spacer between the conjugated Schiff-base entities raises the triplet state to 17 270 cm^{-1} and the quantum yield to 0.44. Concentration quenching occurs only at concentrations higher than 1 mM for [NaEu(tstm)]$_n$ (Figure 3).

The most significant results come from the luminescence properties of the mixed-metal [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polyelectrolytes. The luminescence intensity of [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ reaches a maximum when the Y^{III} content in the polyelectrolytes is 10 mol % of the total lanthanide content (Y:Eu = 1:9) (when the total lanthanide concentration is maintained constant at 1 mM). The luminescence intensity of pure [NaEu(tstm)]$_n$ is lower than that of the [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polymers with Y:Eu ratios of either 1:9 *or* 1:4 (Figure 4). As pointed out above, concentration quenching for the Eu^{III} ions under these conditions is significant only when the Eu^{III} concentration surpasses 1 mM; therefore, the higher luminescence intensity found for [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ with Y:Eu = 1:9 and 1:4 is related to the presence of Y^{III} ions in the polyelectrolytes. The luminescence intensities of the [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polyelectrolyte series, for constant Eu^{III} concentrations of 1 mM, further confirm this suggestion. The highest intensity was observed for [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ with Y:Eu = 1:4, but the intensities of the [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ luminescence for all species with anywhere from 60 to 90% Eu metal content (Y:Eu ratios of 1:1.5 to 1:9) are higher than for pure [NaEu(tstm)]$_n$ (Figure 5). In fact, [NaY$_{0.2}$Eu$_{0.8}$(tstm)]$_n$ (Y:Eu = 1:4) luminesces more strongly than any other compound investigated and has a quantum yield of 0.74 at 77 K (Table 3).

In order to evaluate intramolecular *vs* intermolecular effects in the polyelectrolyte systems, glasses were prepared containing the same Y:Eu ratios noted above by mixing [NaY(tstm)]$_n$ and [NaEu(tstm)]$_n$ polymers together. These glasses give less intense excitation spectra from those of the corresponding [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ mixed-metal polymers; the luminescence intensity is approximately the same as those of glasses containing only the same amount of [NaEu(tstm)]$_n$ and is much weaker than those of the corresponding [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ glasses, when $x = 0.1-0.4$. These results with the mixed yttrium and europium homometallic polymers show (1) that the Eu^{III} and Y^{III} ions are distributed in the mixed-metal [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polyelectrolyte chains {although it is difficult to determine the randomness of the metal-ion distribution in [NaY$_x$Eu$_{1-x}$(tstm)]$_n$} and (2) that the enhanced luminescence intensity in the [NaY$_x$Eu$_{1-x}$(tstm)]$_n$ polymers apparently results from energy transfer from the yttrium units of the polyelectrolytes to Eu^{III} ions *i.e.*, the antenna effect[15,34,35,48] or luminescence resonance energy transfer (LRET),[71] although in this latter case, the energy transfer was *from* europium(III) *to* an organic dye over sizeable distances. On the other hand, some of the increased intensity in our complexes theoretically could result from decreases in Eu−Eu intrachain self-quenching because of the presence of Y^{III} ions between Eu^{III} ions, although the $Eu^{III}-Eu^{III}$ distances, even when adjacent in the same chain are quite large. Just as larger concentrations of complex ions in solution cause so-called self-quenching, the polymer chains can fold back upon themselves and provide the same situation. This would explain the decreasing slope observed for the polyelectrolyte (Figure 3) even below 1 mM Eu^{III}. In the mixed-metal species, the chance of a Eu^{III} center finding another Eu^{III} center to which it can transfer energy is diminished.

Finally, whereas solutions containing both Eu^{III} and La^{III} have been shown to undergo intermolecular energy transfer from an excited state of the La complex to a Eu complex at high concentrations,[72] such intermolecular transfer is insignificant at the 1 mM metal level of the current study.

Summary

The europium(III) N,N',N'',N'''-tetrasalicylidene-3,4,3′,4′-tetraaminodiphenylmethane Schiff-base polymer has excellent luminescence properties with high quantum yields because of the strong absorption in the near-UV−vis region by the Schiff-base ligands, the effective intramolecular energy transfer from the ligands to the europium(III) ions, and the supramolecular nature of the polymers. These factors, plus the good stability of the species in solution, make this class of Schiff-base polyelectrolyte a good candidate for luminescence and laser materials. The intramolecular energy transfer from the ligands to the europium ions seems to follow the well-established mechanism developed for lanthanide β-diketone complexes. The triplet-state energy plays an important role in the energy transfer—the analogous N,N',N'',N'''-tetrasalicylidene-3,4-diaminobenzidine polymer with a triplet state lower than the appropriate europium excited state shows negligible luminescence.

The introduction of yttrium(III) ions into the europium(III) polyelectrolyte system forming $[NaY_xEu_{1-x}(tstm)]_n$ enhances the luminescence intensity of the polymer system. The extra energy transfer in the polyelectrolytes is apparently intrachain transfer from the yttrium units, although a decrease in Eu−Eu self-quenching cannot be totally ruled out. The $[NaY_{0.2}Eu_{0.8}(tstm)]_n$ polyelectrolyte provides the best luminescence.

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