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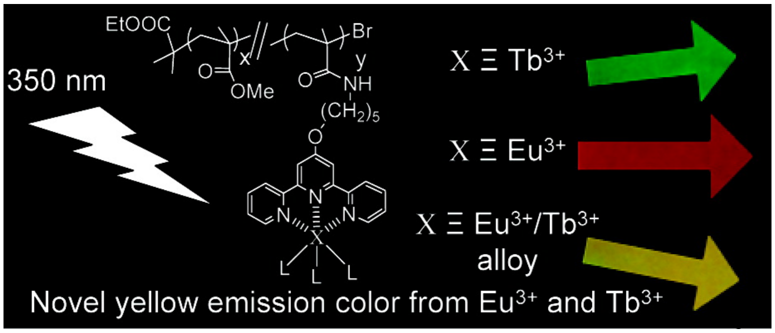

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Unique Emission from Polymer Based Lanthanide Alloys

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Abstract: The incorporation of metal−ligand interactions into macromolecules imparts them with unique and potentially useful properties. We report novel macromolecules prepared via ATRP that contain activated esters for subsequent incorporation of terpyridine. The addition of lanthanide ions ($Eu^{3+}$and Tb^{3+}) gave metal functionalized polymers that exhibited excellent emission of either pink (Eu^{3+}) or green (Tb^{3+}) light. A unique yellow luminescence was generated when these two different metal ions were incorporated into the same molecular backbone at a 1:1 ratio, producing an alloy. Upon heating above 50 °C, selective thermochromism, from yellow to orange/pink, was observed.

Introduction

Integration of organic and inorganic components into the same material can lead to a wide variety of advanced materials with unique properties.[1] In some cases, this increase in structural complexity gives rise to new properties, which cannot be foreseen on the basis of the single constituting moieties.[2] The incorporation of metal−ligands into organic polymers represents an ideal and extremely versatile approach to generate such hybrid materials.[1h] Metal−ligands such as bipyridine and terpyridine (terpy) impart many properties including luminescence, electro- and photochemistry, catalysis, charge, magnetism, and thermochromism.[3] Several groups, including our own, have been active in this area recently.[4] A significant focus of this work has been the incorporation of ligands at the chain end[5] leading to novel gels[6] and block copolymers.[7] More recently the incorporation of terpy into the side chain of random[4e,8] and block copolymers[9] has been reported.

Overall the number of studies on macromolecules containing bipyridine[4c,10] in the side chain has significantly outnumbered those incorporating terpy due, in general, to the lack of emission properties from terpy-transition metal complexes and limited commercial availability of functionalized terpy units. In contrast, terpy binds a range of lanthanide ions resulting in excellent luminescence. Europium(III) and terbium(III) are attractive

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Table 1. Conditions and Results for the Copolymerization of Active Ester Monomer with MMA and nBMA in Anisole[a]

no.	polymer	**1**:R:EiBBr:Cu:L	ratio (^{1}HNMR)	T [°C]	time (h)	yield (%)	M_n obsd	MWD
1	P(OSu-*r*-MMA)	50:50:1:1:2	47:53	90	0.17	69	11 300	1.23
2	P(OSu-*r*-MMA)	35:65:1:1:2	35:65	90	2	75	10 000	1.23
3	P(OSu-*r*-nBMA)	50:50:1:1:2	42:58	90	2	67	9700	1.12

[a] R = MMA or nBMA, L = PMDETA.

luminescent materials with many important applications including laser, phosphor, and optical communication amplifiers.[11] The advantages of rare earth complexes are high photoluminescence (PL) efficiency and sharp emission spectrum.[12] Renewed interest in metal−ligand complexes as the active component in LEDs was recently reported but required a polymer host, PMMA in this case, to assist device fabrication.[13] Therefore it would be ideal to create hybrid materials which have the advantages of both systems including the solubility of polymers along with the emission properties of lanthanide complexes.

In this paper, we describe optimized ATRP polymerization conditions to create copolymers containing active ester units (OSu) with a narrow molecular weight distribution (MWD) that are easily functionalized with terpy to give side chain containing metal−ligand polymers. The functionalized random copolymer, poly(MMA)-r-(MA_{terpy}) was complexed with lanthanide ions resulting in luminescent solutions and thin films with pink or green light depending on the metal ion. For the first time, incorporation of Eu^{3+} and Tb^{3+} into the same polymer backbone changed the luminescence spectrum, yielding a yellow colored emission as the result of the newly created alloy. Model compounds support the necessity of including both lanthanide ions in the same molecular backbone and the critical importance of the 1:1 metal ratio. This unique yellow color enabled reversible thermochromism (yellow to orange/pink) upon heating above 50 °C from these novel macromolecules.

Results and Discussion

Copolymer Synthesis: ATRP is a convenient method for generating copolymers with narrow MWD. In addition, because of the living nature of the polymerization, minimal compositional differences in each copolymer chain are expected within a single sample.[14] Using optimized ATRP conditions, copolymers of the OSu monomer and MMA were synthesized successfully as shown in Table 1. All conditions generated copolymers with a final composition similar to the feed ratios. Although we have yet to determine reactivity ratios for the two monomers, we have performed preliminary experiments to check the randomness of the copolymer. A series of polymerizations were initiated and terminated prematurely, as described in the Supporting Information, so that copolymer content could be monitored as a function of time. These experiments showed that copolymerization of the two monomers generated copolymers that were initially rich in activated ester.

Terpyridine Modification of Active Ester Polymers: Following successful polymerization of the copolymers, the active ester functions were converted to amides containing the terpy groups. The conversion was easily accomplished by reacting an amine functionalized terpy, **1**, with the polymer in anhydrous DMSO and triethylamine at 60 °C for 2 h as shown in Scheme 1 for poly(MMA-*r*-OSu). By ^{1}H NMR and IR spectroscopy, the reaction proceeds to greater than 95% conversion. Key signals in the aromatic region of the ^{1}H NMR at 8.6, 7.9, 7.8, and 7.3 ppm are essentially identical in both the small molecule, **1**, and copolymer. Covalent attachment of **1** to the polymer backbone is further supported by the shift in the methylene protons adjacent to the amine. In **1**, these protons come at 2.6 ppm but shift to 3.4 ppm when bound to the polymer backbone. The excellent conversion was further confirmed by the complete disappearance of the signal at 2.8 ppm corresponding to the methylene protons of the succinamide ring. The active ester has very characteristic IR stretches at 1808, 1781, and 1672 cm^{-1} which are particularly diagnostic and upon polymer modification disappear completely suggesting high conversion of the active esters.

Lanthanide Incorporation and Emission: Initially, copolymer **2** was complexed with either Eu^{3+} or Tb^{3+} ions, and the characteristic emission bands were observed. The polymer−Eu^{3+} complex gave the expected pink color,[15a] while the polymer−Tb^{3+} complex emitted green light. Figure 1a and 1b show the emission from polymer−Eu^{3+} and polymer−Tb^{3+} materials, respectively.

Interestingly, when Eu^{3+} and Tb^{3+} were incorporated into the same polymer backbone in equimolar ratio a novel yellow color was observed as shown in Figure 1d. In contrast, when the two polymer−metal complexes, polymer−Eu^{3+} and polymer−Tb^{3+}, were formed first and then mixed together in a 1:1 ratio, the expected green color was observed (Figure 1c) since Tb^{3+} is more emissive. In addition, the emission curve for this sample reported in Figure 1c shows the simple addition spectra from the two metal centers as one would expect. The only difference between the two films in Figure 1c and 1d is their method of preparation. The film that generates Figure 1c was prepared from a solution of a 1:1 mixture of preformed polymer−metal complexes (polymer−Eu^{3+}/polymer−Tb^{3+}), while the spectra in Figure 1d was obtained from a sample prepared by the addition of 1:1 metal salts to a solution of metal free polymer generating an alloy, polymer−Eu^{3+}/Tb^{3+}. The comparison of all four solid sample emission spectra (Figure 1) shows several

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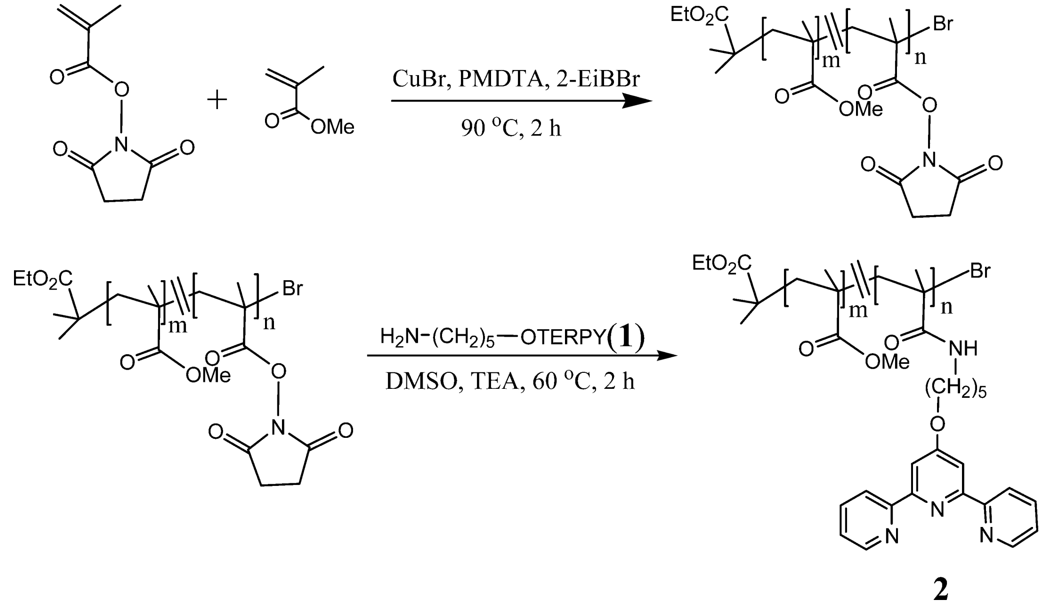
Scheme 1. Synthetic Conversion of the Active Esters in a Poly(OSu-r-MMA) Copolymer to Incorporate Terpy Pendant Groups[a]



[a] The copolymer used contains a 35:65 OSu to MMA ratio (Table 1, entry 2).

significant differences between the polymer−Eu^{3+}/polymer−Tb^{3+} sample (Figure 1c) and the polymer−Eu^{3+}/Tb^{3+} alloy (Figure 1d). The polymer−Eu^{3+}/polymer−Tb^{3+} sample gives the expected addition spectra of the two metal complexes. In sharp contrast, the polymer−Eu^{3+}/Tb^{3+} alloy emission spectra contains a large uncharacteristically broad emission band centered at 533 nm in addition to the peaks associated with Tb^{3+} emission at 485 and 546 nm. At the same time, the expected bands from Eu^{3+} emission at 590 and 613 nm are significantly diminished and broadened compared to those in Figure 1c. The presence of a new band at 533 nm with significant intensity and simultaneous decrease in Eu^{3+} emission indicate the presence of another species which is only present in the polymer−Eu^{3+}/Tb^{3+} alloy sample. This species is most likely a 1:1 Eu^{3+}/Tb^{3+} bimetallic complex, or alloy, formed by placing these two metal ions into the same polymer backbone. The formation of this 1:1 complex is strongly supported by further experimental evidence discussed below.

Experimental observations indicated that the alloy system also gave yellow emission in solution.[16] To quantify this emission, the luminescence spectrum for the solution used to prepare the films of the polymer−Eu^{3+}/Tb^{3+} alloy shown in Figure 1d was collected.[16] From this spectrum, it is clear that the species responsible for the yellow emission color is also present in solution before film preparation. It is also apparent that the ratio of the two bands at 533 and 546 nm is decreased compared to that of the film which is most likely due to less intensity at 533 nm since the ratio of 546 nm to 485 nm is similar between the two samples. Because the species responsible for the yellow emission is present in solution, we were able to perform solution titration experiments to probe the influence of metal ion ratio on the 533 nm band intensity.[16] For this titration experiment, one metal salt, $Eu(NO_3)_3$, was added to the polymer solution in $CHCl_3$/MeOH so that the molar ratio between metal and terpy is below 50 mol %. To this sample, $Tb(NO_3)_3$, also dissolved in $CHCl_3$/MeOH, was titrated, and the emission spectra were collected. These experiments showed that the maximum in 533 nm emission occurred at a metal ratio of 1:1.[16] If the order of metal ion addition is reversed so that Tb^{3+} ions are incorporated first and Eu^{3+} ions are titrated, the maximum for 533 nm emission is still observed at the 1:1 metal ratio.

The use of small model compounds is often helpful for deconvoluting the behavior of polymeric materials. We examined the lanthanide complexes of two model systems.[16] The first molecule is a simple analogue of the terpy ligand containing a 4′ butyloxy but without the polymeric backbone. Under no circumstances could we get this small molecule model complex to yield the yellow colored emission or band at 533 nm. Instead, mixed systems always showed emission bands from both Eu^{3+} and Tb^{3+} complexes consistent with the addition spectra and very similar to Figure 1c; this is true whether the samples were examined in solution or in the solid state. When small model complexes were prepared and cast into films using polystyrene as a host matrix, emission spectra over a range of concentrations and metal complex stiochiometries always gave the simple addition spectra of the two individual complexes. By mixing the appropriate combination of pink and green light, yellow colored emission could be observed, but again, *and of critical importance to our discussion*, the emission spectra always showed the addition spectra of the two chromophores and never any new emission bands responsible for the yellow color.[16,17] These observations supported our hypothesis that incorporation of Eu^{3+} and Tb^{3+} into the same macromolecular backbone, resulting in very intimate spatial arrangement, is essential for generating this unique alloy which produces a new emission band at 533 nm and the yellow color reported here. This idea is further supported by the second model compound shown in Figure 2.

This model compound is an excellent analogue of a polymeric diad and allows the incorporation of two metal ions which are held locally in 3-D space. When both metal salts were added

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(16) See Supporting Information.

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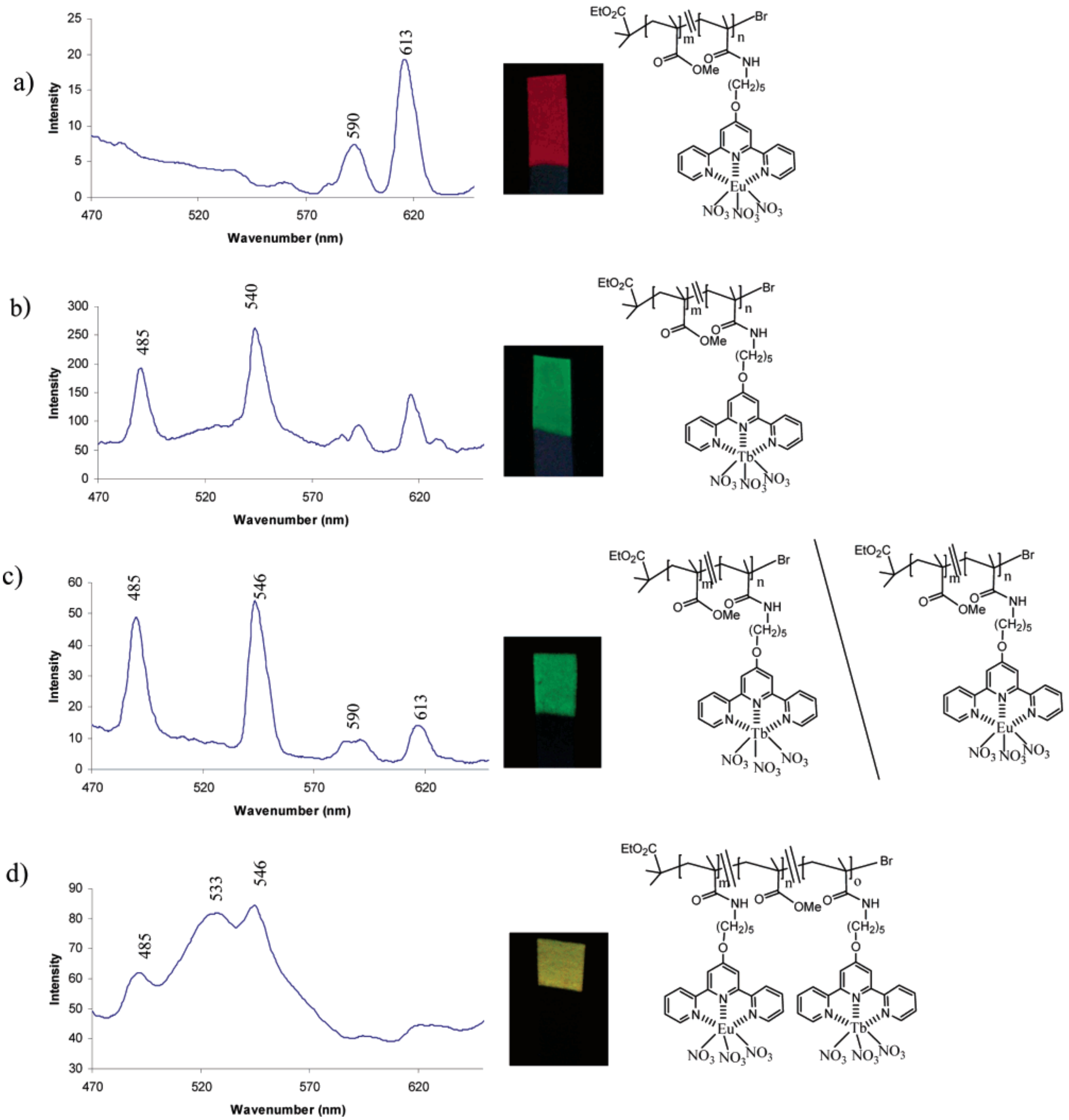

Figure 1. Solid-state fluorescence spectrum of (a) polymer−Eu^{3+}, (b) polymer−Tb^{3+}, (c) a 1:1 mixture of polymer−Eu^{3+} and polymer−Tb^{3+}, (d) polymer−Eu^{3+}/Tb^{3+} alloy. Only the alloy shown in spectrum d has the new emission band at 533 nm. Excitation wavelength is 350 nm.

to a solution of this model compound, yellow emission was observed. An emission spectrum from a solid sample is shown in Figure 2, and the novel emission band at 533 nm is clearly present. Titration experiments, like those performed on the polymer sample discussed above, showed similar observations; the maximum in yellow emission was reached at a 1:1 molar ratio of the two lanthanide salts regardless of the addition order. Interestingly, the ratio of emission at 533 to 546 nm for these solutions is lower than those for the polymeric samples, consistent with expectations since the model compound solution likely contains three molecular species: those with either two Eu^{3+} ions or two Tb^{3+} ions bound to the terpys and one mixed metal species (Eu^{3+} and Tb^{3+}) while the polymeric structures will always have both metal salts incorporated on the backbone. This model compound also supports the critical importance of 1:1 metal ion stiochiometry since this is the *only* mixed metal system that can be formed.

Importance of the Macromolecular Architecture for Alloy Formation and Yellow Emission: Taken together these three different experiments suggest that the species responsible for the yellow emission involves a 1:1 Eu^{3+}/Tb^{3+} stiochiometry. This complex could form metastable Eu^{2+} species which have been reported to give a broad yellow emission,[18a−c] but this is unlikely since Eu^{2+} emission is typically centered around 570 nm.[18] Alternatively, the complex could involve a bridging ligand, like nitrate or one pyridine ring of the terpy, to form a bimetallic complex, or it is also possible that the terpy units of the metal complexes associate through $\pi-\pi$ stacking[18d] when

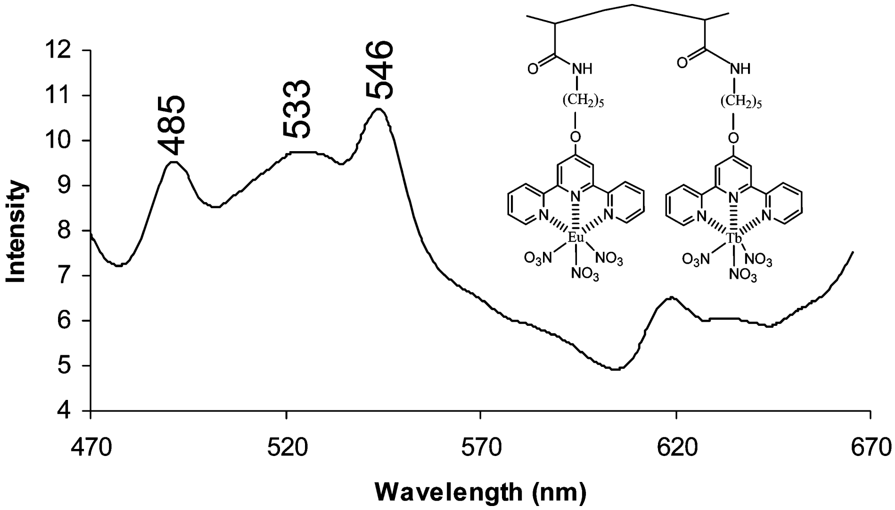

Figure 2. Solid-state emission spectrum of a film prepared from a solution containing a 1:1 Eu^{3+}/Tb^{3+} metal ratio and the model compound shown. Excitation wavelength is 350 nm.

both metals are present, leading to the new yellow emission. This emission at 533 nm is much broader than typical lanthanide emissions bands and more characteristic of organic-like emission. At the same time, addition of an excess ligand, like triphenylphosphine, to the yellow emitting solution reduces the amount of emission at 533 nm compared to 546 nm. Increasing the amount of excess triphenylphosphine further reduces the emission at 533 nm. This experiment appears to favor the presence of a bridging bimetallic complex. In either of these latter two cases, bridging or $\pi-\pi$ stacking, this associating complex is only formed when both metals are present in the same polymeric backbone, consistent with a weakly associating system where confinement of these two metal ions into one macromolecular backbone generates a high local concentration of the two species. This idea of effective molarity, in which the local concentration is different from the bulk, would explain the observations reported here. Further support for this hypothesis comes from two other observations. When the solution sample is concentrated into a film, the intensity of the yellow band increases suggesting more bimetallic complex is formed when the sample is concentrated. Additionally, the association constant between the two species to give the yellow band must be quite small since no precipitation from cross-linking is ever observed in the solution containing both polymer$-Eu^{3+}$ and polymer$-Tb^{3+}$. If the association between the heterometal systems was large, one would expect cross-linking and precipitation as we have reported previously for bis-Cu(II) terpy containing polymers.[4e] Although the exact origin of the yellow emission band is still under investigation, what is clear from these studies is the *importance* of the metal ratio and the intimate spatial arrangement provided by the macromolecular architecture.

Returning to the film studies, it seemed reasonable that since metal$-$ligand complexes are reversible, heating the 1:1 mixture of polymer$-Eu^{3+}$/polymer$-Tb^{3+}$ shown in Figure 1c would scramble the metal centers resulting in a sample very similar to the one shown in Figure 1d that was generated by adding both Eu^{3+} and Tb^{3+} salts to the same polymer solution before film formation. When the film of a 1:1 mixture of polymer$-Eu^{3+}$/polymer$-Tb^{3+}$ was heating to 50 °C for several seconds, an irreversible transformation to the yellow polymer alloy was observed.[16] The emission spectra of this sample after heating are identical to those observed for the sample shown in Figure 1d and again suggest that only incorporation of Eu^{3+} and Tb^{3+} into the same molecular backbone generates the new emission spectra with a band at 533 nm giving the yellow color.

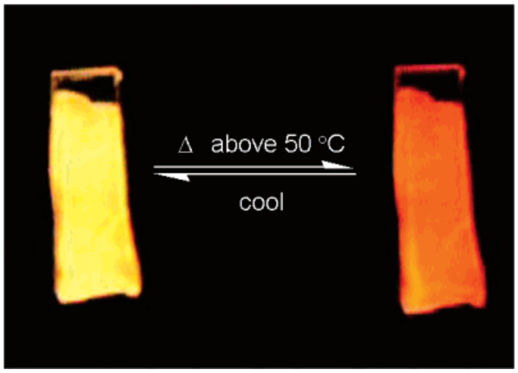

Figure 3. Reversible thermochromism from yellow to orange is observed by heating above 50 °C. Films are excited with a handheld short wavelength UV lamp.

Thermochromism: In addition to showing that the yellow color is only generated from samples in which the metal ions are distributed into the same molecular backbone, further support for a weakly associating bimetallic complex is found when the yellow emitting alloy sample, polymer$-Eu^{3+}/Tb^{3+}$, is heated. As shown in Figure 3, when a film of the polymer$-Eu^{3+}/Tb^{3+}$ alloy is heated from rt to 50 °C, the color changes from yellow to orange/pink, which is very similar in color to pure Eu^{3+} emission. The change in color is consistent with a weakly associating complex at rt that produces yellow emission; however, upon heating this complex dissociates to give emission from the individual metal centers. It might be expected that a green colored emission would be observed at 50 °C from Tb^{3+}, but it is known from control experiments on polymer$-Tb^{3+}$ complexes that quenching occurs in this system when heated to 50 °C. As a result, the color of the alloy film is dominated

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(18) (a) Diaz, A.; Keszler, D. A. *Chem. Mater.* **1997**, *9*, 2071−2077. (b) Nag, A.; Kutty, T. R. N. *J. Mater. Chem.* **2004**, *14*, 1598−1604. (c) Kim, J. S.; Jeon, P. E.; Park, Y. H.; Choi, J. C.; Park, H. L. *Appl. Phys. Lett.* **2004**, *85*, 3696−3698. (d) Hunter, C. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1584−1586.

by polymer−Eu^{3+} emission above 50 °C. When the film is cooled back to rt, the bimetallic complex is reformed and yellow emission is again observed. This color change was reversible for up to twenty cycles with no observable degradation which provides strong support for a weakly associating complex at rt. Therefore, the unique properties of this macromolecular-metal system allowed discovery of thermochromic properties and exemplifies the unique and interesting properties these materials can generate.

Conclusions

ATRP of the OSu monomer produced well-defined copolymers. These polymers with active ester moieties represent an extremely versatile platform to generate highly functional materials as demonstrated here by the incorporation of terpy. It enables easy access to polymers containing terpy in the side chain unlike other approaches reported in the literature. Lanthanide based polymeric alloys containing Eu^{3+} and Tb^{3+} were synthesized for the first time generating a novel yellow emission color. Model compounds and titrations studies confirmed the critical importance of the 1:1 metal ratio as well as the intimate spatial relationship. This bimetallic complex enabled reversible thermochromism from lanthanide ions covalently chelated to the polymeric backbone. These unique properties illustrate the importance of the macromolecular architecture and the critical need to develop improved synthetic routes to produce hybrid materials such as those described here.

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Supporting Information Available: Experimental details including synthetic methods, solution titrations, and other experimental findings are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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