

White-Light-Emitting Lanthanide Metallogels with Tunable Luminescence and Reversible Stimuli-Responsive Properties

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S Supporting Information

ABSTRACT: We have developed model light-emitting metallogels functionalized with lanthanide metal–ligand coordination complexes via a terpyridyl-end-capped four-arm poly(ethylene glycol) polymer. The optical properties of these highly luminescent polymer networks are readily modulated over a wide spectrum, including white-light emission, simply by tuning of the lanthanide metal ion stoichiometry. Furthermore, the dynamic nature of the Ln–N coordination bonding leads to a broad variety of reversible stimuli-responsive properties (mechano-, vapo-, thermo-, and chemochromism) of both sol–gel systems and solid thin films. The versatile functional performance combined with the ease of assembly suggests that this lanthanide coordination polymer design approach offers a robust pathway for future engineering of multi-stimuli-responsive polymer materials.

Dynamic metal–ligand (M–L) coordination has recently emerged as a powerful strategy in the design of various types of stimuli-responsive material properties. This development parallels the pursuit of purely organic-based stimuli-responsive mechanisms that commonly utilize either reversible covalent chemistry or supramolecular interactions.¹ In the particular subset of stimuli-responsive properties labeled self-healing, several M–L systems have been reported to demonstrate remarkable self-healing responses after various types of damage stimuli.^{2–8} In addition to self-healing, self-reporting damage detection is a rapidly growing research area in which mechanophore-based strategies^{9–13} and luminescent materials are being explored in potential applications where color changes in response to various stimuli are of particular interest.¹⁴ These and other efforts in stimuli-responsive materials design promise to improve the overall performance, safety, lifetime, and environmental sustainability of a variety of materials in the future.^{15–19}

Among the stimuli-responsive light-emitting materials, lanthanide (Ln³⁺) M–L coordination polymers are being increasingly explored in the design of advanced functional materials because of their unique metal-controlled photoluminescence (4f–4f transitions).^{20,21} Using light-emitting lanthanide metal coordination complex probes, we recently demonstrated how a simple red, green, and blue (RGB) mixing approach offers remarkable versatility in the design of multi-stimuli-responsive white-luminescent fluids.²² Additional demonstrations by others of white-light-emitting supramolecular

gels²³ and lanthanide-doped emissive metallogels^{8,24} confirm that dynamic Ln–N interactions can indeed dominate stimuli-responsive material behaviors.^{7,22} However, little work has been done to characterize the fundamental stimuli-responsive coupling mechanisms between the reversible nature of light-emitting lanthanide metal coordination complex mechanics and the resulting stimuli-responsive optical dynamics. We have therefore developed model light-emitting metallogels functionalized with lanthanide metal ion–ligand (M–L) coordination complexes via a terpyridyl (Terpy)-end-capped four-arm poly(ethylene glycol) (4-Arm-PEG) polymer. Here we demonstrate (1) how the optical properties of these highly luminescent polymer networks are readily modulated by the lanthanide metal ion stoichiometry and (2) how the dynamic nature of the Ln–N coordination bonding offers reversible stimuli-responsive properties of sol–gel systems and solid thin films.

Our synthesis of the Terpy-end-capped 4-Arm-PEG polymer (1) starts with the alkoxylation of 4'-chloro-2,2':6',2''-terpyridine by 6-amino-1-hexanol in anhydrous dimethyl sulfoxide (DMSO) under basic conditions (Scheme S1). After standard purification, the chelating terpyridyl ligands are subsequently coupled via the quantitative amidation reaction between an active 4-Arm-PEG *N*-hydroxysuccinimidyl (NHS) ester (MS = 5269 Da) and the primary amine substituents (–NH₂) in dry DMSO at 60 °C. The purified polymer 1 is soluble in polar organic solvents such as CH₃CN, dimethylformamide (DMF), DMSO, and CH₃OH.

Building upon our previous work on luminescent small-molecule-based fluids,²² we sought to incorporate the Ln(III)–Terpy coordination complexes into polymer networks. We found that incremental addition of Tb(ClO₄)₃ to a solution of polymer 1 (both in DMF/CH₃CN, 1:1 v/v) up to a Terpy:Ln ratio of 2:1 under gentle shaking gave rise to a transparent green-emissive gel, GLGel ($\tau = 0.38$ ms, $\Phi = 5.0\%$, CIE coordinates (0.28, 0.54)), in 2 min (Figures 1 and S1). A similar procedure resulted in a red-luminescent Eu(III)-coordinated metallogel, RLGel ($\tau = 1.36$ ms, $\Phi = 14.8\%$, CIE coordinates (0.54, 0.32)), but with a longer gelation time of approximately 10 min (see Figure S4). Detailed investigations of the coupling between metallogel assembly (and disassembly as described below) and the Tb(III) and Eu(III) coordination bond dynamics are underway, and insights from those studies will be reported in a future publication.

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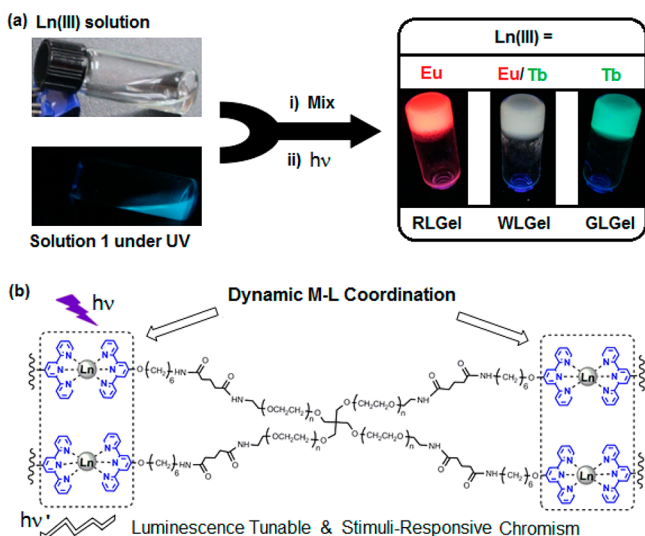


Figure 1. (a) Schematic preparation of Ln(III) coordination-based luminescent metallogels under UV light ($\lambda_{\text{ex}} = 365$ nm, 3.5 wt % polymer 1, DMF/CH₃CN = 1:1 v/v). (b) Chemical structure of polymer 1 cross-linked via Ln–Terpy coordination.

Next we investigated how to modulate the metallogel emission by tuning the stoichiometry of the two lanthanide chromophores (green and red). Titration of the Eu:Tb molar ratio led to a series of soft gels with a broad spectrum of emission (including white light) under UV irradiation (Figures 2a and S2a). Emission spectroscopy studies revealed that the

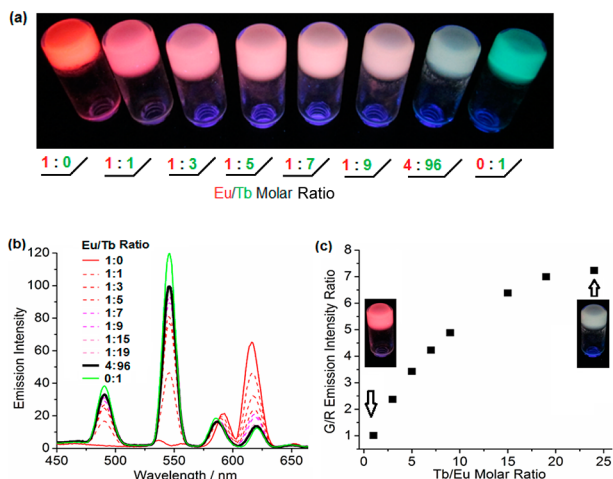


Figure 2. Luminescence tuning: (a) selected photographs of Ln(III)-based metallogels under UV irradiation; (b) emission spectra ($\lambda_{\text{ex}} = 345$ nm) of metallogels and (c) Job's plot of the green/red (G/R) emission intensity ratio as a function of the Tb:Eu molar ratio (1:1, 3:1, 5:1, 7:1, 9:1, 15:1, 19:1, and 96:4).

intensity of the green band at 545 nm increased gradually at the expense of the intensity of the red band at 616 nm as a function of Tb:Eu molar ratio (Figures 2b,c and S2b). Of particular interest is the observation that an intense white-light metallogel, **WLGel** (CIE coordinates (0.30, 0.49)), is established at the Eu:Tb molar ratio of 4:96. The straightforward luminescence control demonstrated here offers a simple design approach to broad-spectrum color tuning of light-emitting polymer materials.

Compared with single-color-emissive materials, white-luminescent materials offer the potential for more sensitive stimuli-responsive properties given their multispectrum chromism. We therefore specifically focused on characterizing the stimuli-responsive properties of the white-emissive metallogel **WLGel** described above. First we sought to demonstrate direct coupling between reversible color changes and gel–sol phase transitions since the Ln–N_{Terpy} bond dynamics dictates not only the emission color but also the stability of the gel network. As illustrated in Figure 3a, reversible gel–sol transitions are

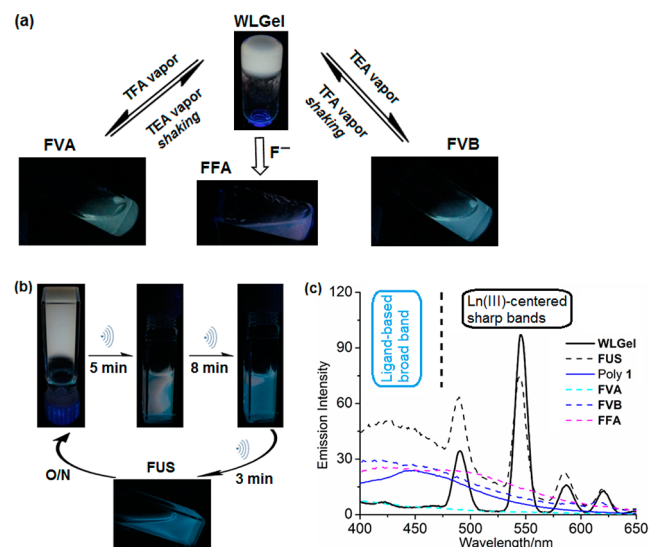


Figure 3. (a, b) Stimuli-responsive emission color changes and phase transitions of **WLGel**: (a) pH-triggered vapochromism and F[−]-induced chemochromism; (b) sonication-induced mechanochromism. (c) Emission spectra of **WLGel**, “free” polymer 1 in solution, and fluids generated after gel–sol transitions (FVA, FVB, FFA, and FUS) induced by various stimuli. All of the photographs were taken under a UV lamp ($\lambda_{\text{ex}} = 365$ nm).

indeed correlated with color changes when **WLGel** is exposed to the vapor of either trifluoroacetic acid (TFA) or triethylamine (TEA). The change in the emission spectrum across the gel–sol transition confirms the disappearance of the characteristic sharp white-emissive bands of the gel phase (see Figure 3c). Similarly, addition of up to 3 equiv of tetra-*n*-butylammonium fluoride relative to Ln ions also triggered a color change coupled with a gel–sol transition as a consequence of the competing interaction between Ln(III) cations as Lewis acids and fluoride anions (F[−]) as Lewis bases. The F[−]-induced **WLGel** network disassembly was likewise spectroscopically confirmed by emission quenching of the Ln-centered sharp bands (see Figure 3c), but in contrast to the above, this gel–sol transition is irreversible because of the generation of LnF₃ precipitates (see Figure 3a).

The dynamic Ln–N_{Terpy} bonds further enabled us to explore mechano-optically coupled stimuli-responsive properties of **WLGel**. We exposed **WLGel** to sonication in an ultrasonic bath at 25 °C, and upon sonication for 5 min a gel–sol transition was observed by a gradual breakdown of **WLGel** accompanied by generation of a fluid phase (Figures 3b and S3). In contrast to the white luminescence of the remaining gel, the fluid was observed to emit blue light. Continued sonication of the **WLGel**/fluid mixture led to complete phase transition into a blue fluid, **FUS** (CIE coordinates (0.21, 0.26)). Similar to

the chemically induced gel–sol transitions described above, the mechanically induced fluid reveals a new broad emission band at around 430 nm similar to the blue emission of the “free” polymer **1** observed in Figure 1a (see Figure 3c). However, in contrast to emission changes observed upon chemically induced gel–sol transitions (see the FVA, FVB, and FFA spectra in Figure 3c), the sharp emission bands of the WLGel were observed to partially remain in the FUS fluid state, indicative of incomplete cleavage of all of the M–L cross-links in the polymer network. Gel reformation of FUS occurred overnight at room temperature with no external triggers. Comparative studies with single-metal RLGel and GLGel are shown in Figure S3.

To further investigate potential applications of light-emitting metallopolymers as stimuli-responsive materials, we examined the thermo- and vapochromisms of solid-state films generated via solvent evaporation from solutions in MeOH. The mechanically robust films likewise proved to be highly luminescent with red emission for Eu-coordinated, green for Tb-coordinated, and white for Eu/Tb-coordinated hybrid metallopolymers (Eu:Tb = 4:96) (Figure S5). Furthermore, the white-luminescent solid-state network was found to reversibly change colors from green through white to red when the temperature was cycled between $-196\text{ }^{\circ}\text{C}$ (frozen in liquid N_2) and $60\text{ }^{\circ}\text{C}$ (Figure 4b). This distinctive green-to-red

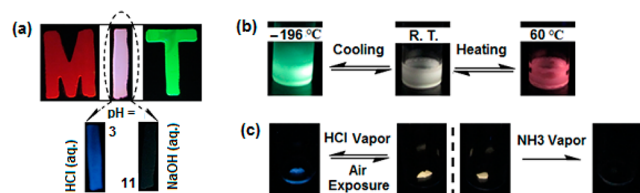


Figure 4. (a) Luminescent dip coatings from polymer **1** solutions with Eu (red letter “M”), Tb (green letter “T”), and Eu/Tb at 4:96 (white letter “I”) on a nonfluorescent neutral silica matrix on a TLC plate and pH-responsive color changes of the white letter “I”. (b) Thermo-chromism and (c) vapochromism of solvent-evaporated white-light-emitting metallopolymer films. All of the photographs were taken under a UV lamp ($\lambda_{\text{ex}} = 365\text{ nm}$).

thermo-chromism strongly suggests intrinsic energy transfer from Tb- to Eu-centered luminescent chromophores with increasing temperature.^{21c,23a} Finally, red-, green-, and white-emissive dip coatings could easily be generated from solutions of polymer **1** mixed with Eu, Tb and 4:96 Eu/Tb, respectively (Figure 4a). The white-luminescent coatings (Figure 4a) and films (Figure 4c) proved to be responsive to changing pH conditions as well: (1) a change to blue emission was observed upon exposure to aqueous HCl and HCl vapor as a result of protonation of N_{Teryp} and subsequent cleavage of Ln(III)–N coordination; (2) white-light emission was quenched upon exposure to aqueous NaOH and NH_3 vapor as a consequence of the hydrolysis of Ln(III) ions.

In conclusion, we have presented a model design strategy for the preparation of light-emitting polymer metallopolymers cross-linked via Ln–L interactions. The luminescence tuning enabled by Ln–L coordination bonding demonstrates a simple approach to the engineering of full-spectrum light emission of polymer gels, coatings, or films. Furthermore, by taking advantage of the dynamic nature of Ln(III)–N coordination bonds, we have demonstrated reversible stimuli-responsive properties including mechano-, vapo-, thermo-, and chemo-

chromism of the same set of materials (polymer gels, coatings, and films). Given the reversible multi-stimuli-responsive behavior of the simple model materials presented here, we envision that further study of the dynamic Ln–L coordination polymer concept will offer unique possibilities for the development of, for example, smart coatings or paints that allow real-time monitoring of environmental physical/chemical conditions in solvent or the gas phase. Finally, the optomechanically coupled reversible gel–sol transitions demonstrated here provide early evidence that Ln–L coordination bonding may afford in situ dynamic mechanophores that report not only local mechanical stimuli but also postfailure self-healing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07394.

Synthetic details, chemical characterization, and general procedures for metallopolymers (PDF)

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Notes

The authors declare no competing financial interest.

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