

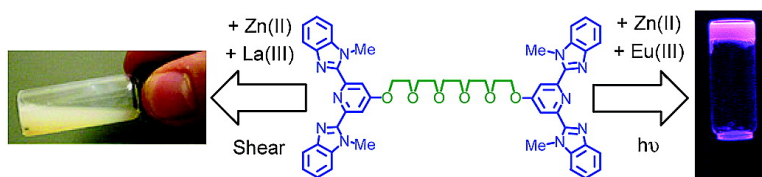
Communication

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## Multistimuli, Multiresponsive Metallo-Supramolecular Polymers

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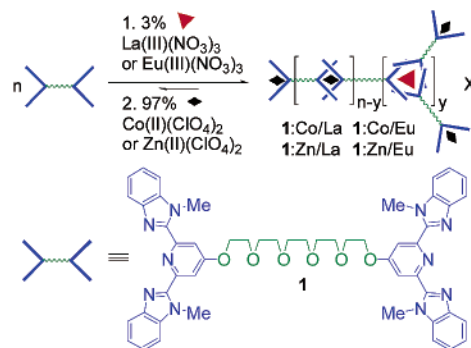
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Stimuli-responsive polymers<sup>1</sup> are polymers that show dramatic property changes in response to an environmental stimulus. Such materials can be classified according to the kind of stimuli that they respond to, such as photo-, chemo-, electro-, mechano-, etc., and offer potential applications in such fields as surface science<sup>2</sup> and separation science, as well as a growing number of bioapplications.<sup>3</sup> Gels are an important subclass of this field<sup>4</sup> and can be tailored to respond to different stimuli. Another area which holds promise for stimuli-responsive materials is that of supramolecular chemistry, where the environment can have a large effect on the degree of interaction (binding constant) between the individual components in the material. Such an alteration in the strength of the intermolecular noncovalent bonds can result in dramatic modification of the supramolecular structure and thus drive significant changes in the properties of the material. In this paper, we introduce the use of reversible metal–ligand interactions to build metallo-supramolecular gellike systems which are responsive to a number of different stimuli. An additional advantage of using metal ions as one of the supramolecular motifs is the ability to bestow the functional properties of these metals to the self-assembled materials, for example, light-emitting capabilities.

Recently, the use of metal–ligand interactions has been shown to be a viable method in the construction of polymeric materials.<sup>5</sup> We have focused on the tridentate ligand, bis(2,6-bis(1'-methylbenzimidazolyl)-4-hydroxypyridine) (**HO-BIP**), as a potential ligand for the construction of larger polymeric aggregates. It has been shown in the literature that similar 2,6-bis(benzimidazolyl)pyridine ligands not only bind transition metal ions in a ratio of 2:1 but can also bind the larger lanthanide ions in a ratio of 3:1.<sup>6</sup> We reasoned that it, therefore, should be possible to prepare metallo-supramolecular gels by simply mixing transition metal ions (>95%) and lanthanoid metal ions (<5%) with an appropriate bis-BIP functionalized monomer (Scheme 1).

Our initial studies have focused on the use of the bis-ligand functionalized compound **1** as the monomer unit in conjunction with either Co(II) or Zn(II) ions as the linear chain extension binding units, and La(III) or Eu(III) ions as the cross-linking components. Monomer **1** was prepared by simply reacting **HO-BIP**<sup>7</sup> with diiodopentaethylene glycol under basic conditions. The self-assembly of the gellike materials occurred spontaneously upon addition of the lanthanoid(III) nitrate (3 mol % based on the total number of **BIP** ligands) followed by the transition metal ion perchlorate (97 mol % based on the total number of **BIP** ligands) to a solution of **1** in CHCl<sub>3</sub>/CH<sub>3</sub>CN. The four possible metallo-supramolecular gellike materials **1:Co/La**, **1:Zn/La**, **1:Co/Eu**, and **1:Zn/Eu** were prepared in this way, and upon removal of the solvent all four could be reswollen with pure CH<sub>3</sub>CN (800% by wt.). At these concentrations, the 1:1 mixture of **1:Zn(II)** will slowly precipitate from a CH<sub>3</sub>CN solution but does not gel, while addition of >10% Ln(III) results in an intractable solid. Both Co materials are orange in color,

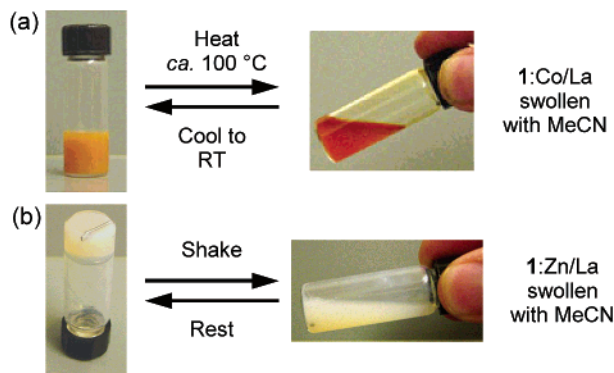
**Scheme 1.** Schematic Representation of the Formation of a Metallo-Supramolecular Gellike Material Using a Combination of Lanthanoid and Transition Metal Ions Mixed with Monomer **1**



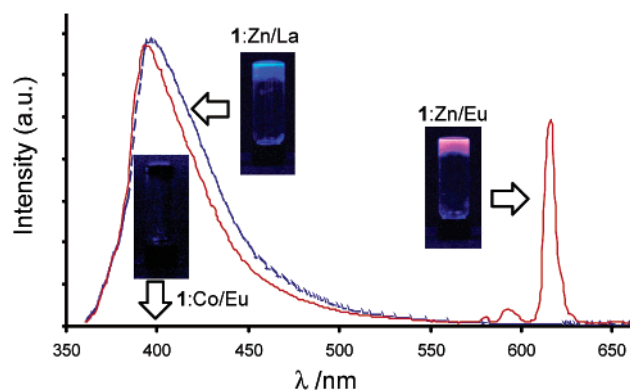
indicative of the binding of the ligand to the Co(II), while the Zn(II) systems are slightly off-white in color.

All four gels show thermoresponsive behavior. For example, heating **1:Co/La** to ca. 100 °C results in a reversible gel–sol transition (Figure 1a). At these higher temperatures, the orange color of these Co-materials persists in solution, suggesting that it is the La/ligand interactions which are being thermally broken. Furthermore, these materials are also mechanoresponsive, exhibiting a thixotropic (shear-thinning) behavior. Figure 1b shows how the shaking of **1:Zn/La** can result in the formation of a free-flowing liquid, which upon standing for ca. 20 s results in the reformation of the gellike material. Initial rheological studies<sup>8</sup> on this system demonstrate that this material has a yield stress of approximately 1600 ± 200 dynes/cm<sup>2</sup>. The recovery time is very dependent on the amount of CH<sub>3</sub>CN present in the system (material with less solvent recovers more quickly).

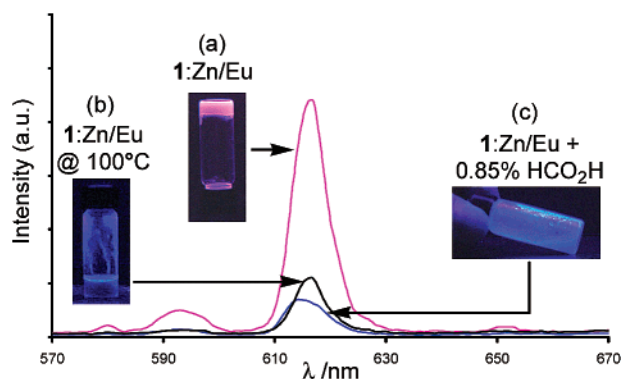
The Eu(III)-containing materials offer the possibility of utilizing the interesting spectroscopic properties of this lanthanide ion.<sup>9</sup> For example, Eu(III) ions can show an intense metal-centered luminescence in the presence of an appropriate UV absorbing ligand via the so-called “antenna effect”.<sup>10</sup> This is in effect a light conversion process which occurs by absorption of the light by the ligand, followed by a ligand-to-metal energy-transfer process finally resulting in the metal ion-based emission. BIP ligands have been shown<sup>11</sup> to act as “antenna” for Eu(III) ions, and as such this opens up the possibility of these material to be utilized as photo- or electroluminescent materials.<sup>12</sup> **1:Zn/Eu** was indeed photoluminescent, showing the emission bands indicative of the lanthanide metal centered emission (581, 594, 616, 652 nm) as well as a ligand centered emission at 397 nm (Figure 2). Note the emission of the unbound ligand is at 365 nm, indicating that the ligand emission is sensitive to metal binding. While, not surprisingly, **1:Zn/La** displayed only the metal-bound ligand-based emission (397 nm), **1:Co/Eu** did not show any fluorescent behavior, probably on account of the presence of low energy metal centered levels which facilitate radiationless decay processes.<sup>13</sup> As such, the photoresponsive nature



**Figure 1.** (a) The thermo-responsive nature of 1:Co/La and (b) the mechano-responsive nature of the thixotropic 1:Zn/La system. Both materials are swollen in acetonitrile (800% by wt.).



**Figure 2.** Photoluminescent spectra of the acetonitrile swollen 1:Zn/La, 1:Zn/Eu, and 1:Co/Eu (excited at 340 nm). 1:Co/Eu shows no photoluminescence and lies essentially along the baseline. The insets show the gels under UV light (365 nm). The PL spectra have been normalized.



**Figure 3.** A section of the photoluminescent spectra of the acetonitrile swollen 1:Zn/Eu materials after being excited at 340 nm. (a) As prepared, (b) at 100 °C, and (c) after addition of 0.85% HCO<sub>2</sub>H. The insets show pictures of the materials under UV light (365 nm).

of these materials can be controlled by the nature of transition metal ion as well as lanthanide ion. The luminescence of 1:Zn/Eu can also be used as a tool to examine the nature of metal binding in this system. For example, heating 1:Zn/Eu shows a substantial reduction in the lanthanide-based emission (Figure 3) but no significant shift of the ligand emission, further supporting the fact that it is mainly the Ln(III)/ligand bonds that are thermally broken and not the transition metal ion/ligand interactions.

Lanthanides are known to bind well to carboxylic acids.<sup>14</sup> Therefore, we reasoned that these lanthanide-containing systems should also be chemoresponsive to such molecules; that is, breakdown of the gellike material should occur upon addition of a small amount of formic acid. Addition of 0.85 wt % of formic acid to 1:Zn/Eu results not only in the loss of the mechanical stability of the material but also quenching of the Eu(III) emission (Figure 3). This is consistent with the formate anion displacing the BIP ligand on the Eu(III) cation, resulting in a “switching off” of the aromatic ligands antenna effect. This process can be reversed by drying out the material in a vacuum oven for 8 h at 40 °C. Upon reswelling the material with acetonitrile, an increased Eu(III) emission is observed.

In summary, we have used a combination of metal ions in conjunction with the bis-ligand monomer **1** to produce supramolecular polyelectrolyte gellike materials which can exhibit thermo-, chemo-, mechano-responses, as well as light-emitting properties. The nature of the response exhibited by these systems depends on the metal ion and the amount of swelling solvent. Given the wide variety of metal ions (with different metal/ligand kinetic stabilities and functional properties), counterions, and possible cores of the ligand-terminated monomer, a wide variety of environmentally responsive metallo-supramolecular materials can be envisaged.

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**Supporting Information Available:** The synthesis and characterization of **1** and the PL and UV data of the polymeric systems (S1–S7) (PDF), as well as a movie of the mechanoresponse of 1:Zn/La (MPG). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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