

Investigation of Molecular Structures for Soft Matters with Mechanoresponsive Colors

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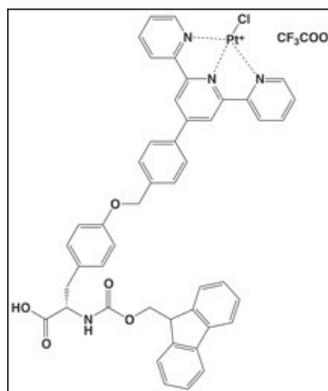
Abstract:

Materials with mechanoresponses are a new discipline in organic soft matter synthesis. One mechanoresponse, thixotropy, is the tendency of a material to become less viscous upon the addition of mechanical stress such as shaking. Separately in other gels, a visible color change during the gel-to-solution transition has been observed. While gels with either thixotropic or color-change qualities have been reported, the molecular structure of a thixotropic gel with mechanoresponsive colors has not yet been confirmed. In this work, we investigate molecular structures of gels. Synthesized platinum-terpyridine (Pt-terpy) complexes bearing an amino acid moiety were manipulated by changing solvent, counter anion and molecular structure. Pt-terpy gels and corresponding solution samples were analyzed through stable-by-inversion tests and emission spectroscopy. A thixotropic Pt-terpy gel without (fluoro-9-yl)methoxycarbonyl (Fmoc) moiety exhibited a 648 nm emission peak, which indicated the presence of Pt-Pt interactions. Thixotropic gels that display mechanoresponsive colors may be applicable as oscillation sensors for buildings and earthquakes.

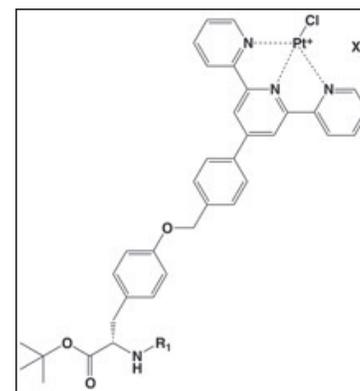
Introduction:

Polymers with mechanoresponsive colors display a change in color when stretched due to the presence of mechanically sensitive chemical groups in the polymer linkages [1]. However, other soft matters may be able to exhibit responses to mechanical stimuli. Thixotropy is the property of a material to become less viscous upon added shear stress. By shaking a thixotropic gel, the inherent network structure will break down, and the gel will undergo a phase change from gel to solution [2]. After standing, the material will return to its original state as the gel network reforms. In a separate phenomenon, some gels visibly change color during the gel-to-solution transition [3]. The color modification is related to the different metal interactions of the metal centers in the gel phase relative to the solution phase.

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Scheme 1:
Molecular structure
of Pt-terpy thixotropic gel.



Scheme 2: Basic molecular structure
for synthesized Pt-terpy
complex analogs.

Reticular Materials Group has previously synthesized a Pt-terpy thixotropic gel. The monomer for the thixotropic gel incorporates the Pt-terpy moiety and a functionalized tyrosine, shown in Scheme 1. The hydrogen bonding between the amino acid units are thought to cause the gelation capabilities of this complex. In addition, Pt-terpy possesses many spectral properties; specifically, emission at approximately 650 nm indicates Pt-Pt interactions [4]. However, the previously synthesized Pt-terpy thixotropic gel showed no absorption or emission that indicated the presence of Pt-Pt interactions.

A gel that exhibits both properties of thixotropy and color change upon phase transition has yet to be reported. In this study, we employed traditional organic synthesis procedures to manipulate the Pt-terpy complex structure in order to create a thixotropic gel with mechanoresponsive colors.

Experimental Procedure:

A series of Pt-terpy complexes of analogous forms were synthesized and tested for their gelation potential and color change ability. The basic structure is shown in Scheme 2. Counter anion salts in 10x molar excess were dissolved in Pt-terpy solutions for anion exchange. Alteration to the

original Pt-terpy complex was accomplished primarily through the metalation of Pt to a functionalized multidentate ligand followed by deprotection of Fmoc. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was completed to ensure successful synthesis.

For gelation, the Pt-terpy complex was completely dissolved in solvent. Water was added to the solution to trigger gelation, followed by mixing of the reaction vial and standing. The presence of gel qualities was analyzed through the stable-by-inversion test.

Emission spectroscopy was employed on gel and solution samples of the synthesized Pt-terpy forms. Absorption spectroscopy was used to determine the necessary wavelength of excitation for emission measurements. Emission peaks were examined to determine the presence of Pt-Pt interactions.

Results and Conclusions:

The Pt-terpy complexes showed limited solubility in the water-miscible solvents (i.e. MeOH, CH₃CN), and dimethyl sulfoxide was selected as the best solvent for the water-triggered gelation protocol. Pt-terpy complexes with a trifluoroacetate (CF₃COO⁻) counter anion increased the solubility of the complexes and formed gels. The Pt-terpy complex must be reasonably soluble in the solvent in order for the gelation test to be valid. The Pt-terpy complex with X = CF₃COO⁻ and R₁ = H was successfully synthesized (Scheme 2), and a thixotropic gel formed. Comparison of emission spectra between gel and solution samples of Pt-terpy complex (X = CF₃COO⁻, R₁ = H) showed that only the gel state emitted at 648 nm, as seen in Figure 1. Comparison of emission spectra between complexes where R₁ = H or Fmoc demonstrated that only Fmoc deprotected Pt-terpy complexes emitted at 650 nm, as seen in Figure 2. It is hypothesized that deprotection of Fmoc reduced π -stacking and emphasized interaction between metal centers. Therefore, we synthesized a Pt-terpy thixotropic gel that contained Pt-Pt interactions.

Future Work:

Future work will analyze the gel characteristics and emission spectral properties of a Pt-terpy complex capped with a phenylacetylene ligand. It is thought that the presence of the phenylacetylene ligand will emphasize Pt-Pt interactions through π -orbital stacking of the ligand near the metal center. Later studies will synthetically alter the Pt-terpy structure further in order to achieve mechanoresponsive colors.

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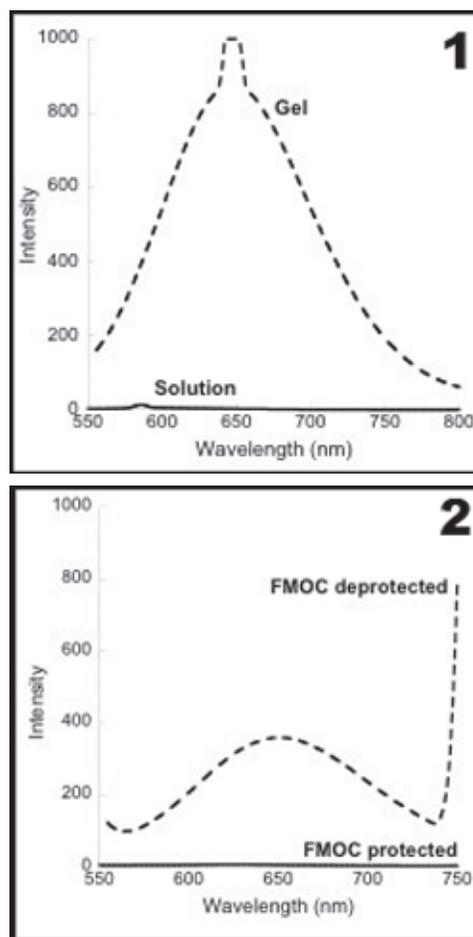


Figure 1, top: Emission spectra of [tBuO₂C-Pt-NH₂][Cl][CF₃COO] gel and solution in DMSO/H₂O.

Figure 2, bottom: Emission spectra of [tBuO₂C-Pt-NH₂][Cl][CF₃COO] and [tBuO₂C-Pt-NHFmoc][Cl][CF₃COO] gels in DMSO/H₂O.

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