DESIGN, SYNTHESIS, AND CHARACTERIZATION OF PHOTORESPONSIVE MATERIALS USING COORDINATION BONDS AND OTHER SUPRAMOLECULAR INTERACTIONS

Anton O. Razgoniaev

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Committee:
Alexis D. Ostrowski, Advisor
Scott O. Rogers
Graduate Faculty Representative
Alexander Tarnovsky
R. Marshall Wilson
ABSTRACT

Alexis D. Ostrowski, Advisor

When designing light-responsive, healable materials and adhesives, these materials need to include controllable reversible, bonding interactions. Such dynamic interactions are difficult to control, however. In this work, we present how these interactions can be controlled by incorporating photoactive metal ions into supramolecular polymer network what allow the tuning of optical and mechanical properties of the polymers with light.

Utilizing this approach, we created a series of supramolecular polymer melts and studied their mechanical and photo physical properties. We have shown that the photochemistry and photophysical properties of the metal center can be used to control the mechanical properties of the materials, and introduce new optical and mechanical properties not seen in the traditional covalent polymers. In particular, photo-induced metal-ligand bond labilization led to partial depolymerization of the supramolecular assembly, and softening of the materials. When the light stimulus was removed, the material recovered the initial stiffness back. We also investigated structure-property relationships in such systems where mechanical properties of the supramolecular polymers are controlled by coordination environment around metal cross-linking center.

We also considered how polymer host matrix impacts on the photophysical and photochemical properties of chromophores that undergo molecular motion in the exited state. In particular, change in excited state dynamics of \([\text{Cu(dmp)}_2]^+\) can be used to sense viscosity of various polymers. A linear dependence of excited state lifetime and emission wavelength on
viscosity was correlated with restricted photoinduced structural distortion of Cu(I) complex in more flow-resistance media.
To my parents, Natalia and Oleg

To my soul-mate, Evgeniia

For your endless support and love
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CHAPTER I. INTRODUCTION

1.1. General introduction

Supramolecular chemistry – the chemistry beyond the molecules – studies high order molecular organization between two or more molecules driven by intermolecular forces. Supramolecules are well defined discrete oligomeric associates formed due to intermolecular interactions based on principles of molecular recognition. Investigation of new synthetic routes to obtain artificial supramolecular assemblies with well-defined hierarchy is crucial for understanding of self-assembly processes in nature and development new materials with properties not seen in traditional materials. The possibility of building new complex structures via non-covalent synthesis depends on our knowledge how individual components of the assembly are bound together, how these interaction can be controlled based on molecular recognition principles and external stimulus.

In supramolecular chemistry, the molecules are held together by non-covalent interactions resulting into supramolecular assemblies that exhibit unique physical and chemical properties. These interaction may differ in nature, energy, and direction of the interaction. Among those non-covalent interactions one can name ion-ion, ion-dipole, dipole-dipole, π-π staking, coordination bonds, hydrogen bonds, Van-der-Waals interactions.\(^1\)\(^-\)\(^9\) Metal-ligand coordination interactions between organic Lewis-base type molecules and metal ion are one of the strongest non-covalent interactions. If the ligand has multiple metal-binding centers, it may participate in formation of repeating supramolecular structure with multiple metal centers (Scheme 1.1)
Repetition of such metal-ligand (M-L) fragments in one or multiple directions leads to formation of coordination polymers – high molecular weight compounds consist of organic molecules and metal-ion centers bound tighter via intermolecular interactions. Coordination polymers have shown to possess interesting mechanical properties due to dynamic nature of the metal-ligand interactions.

Organic part of the coordination polymer should not only serve as a building block in the complex supramolecular architecture but also contribute in integrated properties of a hybrid material. Hence, the current trend in design of new supramolecular polymers is investigation and exploration of new molecules that consist of two parts – the central binding unit (e.g. metal ion) and coordination sites. The later ones tailor relatively short organic molecules into complex supramolecular structures with well-defined architecture based on the nature of the non-covalent interactions. The central binding unit coordinate these small organic molecules and direct them into space giving a rise to new remarkable properties not seen in two separate building blocks of the supramolecular network. The hybrid materials can be designed that respond to a variety of different stimuli such as pH, electrical signals, or even electro-magnetic radiation. External light irradiation is advantageous because the timing, location, and
intensity of light can be controlled, thus allowing one to control the timing and location of the stimulus applied. The interaction of the supramolecular polymers with light, however, is the least explored at the moment.

1.2 Self-assembly

As it was mentioned in the Introduction section, supramolecular chemistry is chemistry beyond one molecules, namely, chemistry of the associates which can exist as individuals. The components of the associate are held together via non-covalent interactions. Each fragment participating into formation of the associate is a molecular building block “glued” to another building block by revisable dynamic intermolecular interactions. The original work of Pedersen,29 Cram,30–32 and Lehn33–37 led to a new paradigm in organic synthesis – supramolecular synthesis.

Deoxyribonucleic acid (DNA) is one of the most well-known natural supramolecular biopolymer. The unique properties of DNA is its double helix structure arises from cooperative multiple hydrogen bonding interactions between nucleobases as well as hydrophobic interactions. DNA can respond to an external stimulus to drive equilibrium of the relatively weak dynamic hydrogen-bonding interactions and accommodate different forms. Other biological systems utilize supramolecular chemistry for peptide folding, ion-transport function, receptor-ligand interactions, etc.38–42 For example, a cuticle of mussel byssal threads protects against physical damage. The cuticle is an outer proteinaceous coating that possesses unusual mechanical properties. During strain, the coticule limits bulk crack propagation to the microscale failure.43,44 This unique defensive mechanism against severe physical damage of the mussel threads is due to supramolecular interactions between catechol-like amino acid dihydroxy-
phenylalanine (dopa) in the cuticle protein and small amount of Fe(III)-ions.\textsuperscript{45,46} The Fe\textsuperscript{3+} cation strongly binds to large protein molecules to form transient (dynamic) supramolecular network. Despite large stability constant of a Fe-dopa associate ($\log K_\text{s} \approx 40$)\textsuperscript{47–49}, it is the metal-dopa bond requires lower force to rapture with respect to a typical C-C covalent bond under identical loading conditions.\textsuperscript{50} In contrast to covalent bonds, the Fe-catechol binding motif can spontaneously reform after breaking (Figure 1.1).

![Figure 1.1. Reversible Fe(III)-dopa cross-linking in mussel treads upon mechanical load](image)

Secondary interaction are also utilized in synthetic man-made polymers to benefit in unique mechanical properties of the materials. Namely, mechanical strength of Kevlar, Aramid, and Nomex and high extensibility of nylon result of dynamic hydrogen bonding interaction between the polymer chains.\textsuperscript{51}

### 1.3 Non-covalent interactions

Non-covalent interaction can be considered as the building blocks that are utilized to construct the host-guest interactions in the self-assembly network. These interactions can be classified by the origin of the interactions, strength of the non-covalent pair (bond energy), and the angle of the interaction. The bond energy of the non-covalent interactions may be as weak as
4-5 kJ/mol for Van de Waals forces and as strong as 350 kJ/mol for ion-ion pairs. The binding energies of some non-covalent pairs are listed in the

Table 1.1. Types of non-covalent interactions

<table>
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<tr>
<th>Non-covalent bonds</th>
<th>Bond energy (kJ/mol)</th>
<th>Example</th>
</tr>
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<tbody>
<tr>
<td>Ion-Ion Interactions</td>
<td>100-350</td>
<td>KBr</td>
</tr>
<tr>
<td>Metal Coordination</td>
<td>50-250</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Bonding</td>
<td>5-100</td>
<td></td>
</tr>
<tr>
<td>Ion-dipole Interactions</td>
<td>50-210</td>
<td></td>
</tr>
<tr>
<td>II-π stacking</td>
<td>5-60</td>
<td></td>
</tr>
<tr>
<td>Van der Waals Forces</td>
<td>&lt;5</td>
<td>Noble Gases, Inclusion complexes</td>
</tr>
</tbody>
</table>

As seen from the Table 1.1, there is a wide range of energies of intermolecular interactions, what allows for variety of combinations between non-covalent pairs to construct a supramolecular network. Although, the energy of these interactions are highly dependent on
pressure, solvent, or temperature, they still can be generalized on two groups based on the bond energy in the non-covalent pair.\textsuperscript{6} For instance, $\pi$-$\pi$ stacking,\textsuperscript{52} Van der Waals forces,\textsuperscript{6} and some hydrogen bonding interactions can be considered as weak\textsuperscript{3,53} while metal coordination complexes\textsuperscript{54} and ion-ion interaction\textsuperscript{55} can be classified as strong.

### 1.4. Supramolecular polymers

Chemistry and physics of supramolecular polymers area relatively new areas of research originated from biochemistry. Supramolecular polymers are defined as polymeric arrays of monomeric units that are linked together by reversible and directional non-covalent interactions, resulting in polymeric properties in dilute and concentrated solution as well as in the bulk material.\textsuperscript{6,8,9} Such replacement of covalent bonds with non-covalent reversible linkers provide unique properties in the bulk material not seen in the traditional polymers. Reversibility of secondary dynamic non-covalent interactions makes these polymers responsive to external stimulus as pH,\textsuperscript{22,23} electrical signals,\textsuperscript{24,15,25} and light.\textsuperscript{26,16,21,27,28}

Degree of polymerization in supramolecular polymers formed due to reversible association of multifunctional monomers strongly depends on the association constant ($K_a$) between end-capping groups and concentration of monomers\textsuperscript{9} (eq. 1.1).

\[
C \sim \left( \frac{M_0}{4K_aN_c} \right) \times \left( [(Dp^2) - 1] \right)
\]

(1.1)

Equation 1.1 Dependence of concentration of monomers in solution on association constant and degree of polymerization (DP)
Based on Equation 1.1, one can derive that DP is proportional to the product of association constant and square root of the monomer concentration (eq 1.2)

\[ DP \sim 2K_a[C]^{1/2} \]

(1.2)

Equation 1.2 Dependence of degree of polymerization (DP) in solution on association constant and concentration of monomers

This correlation can be graphically represented (Figure 1.2).

![Figure 1.2. Theoretical relationship between the association constant Ka and DP(degree of polymerization)](image)

As seen from the Figure 1.2, in order to achieve high DP values in diluted solution a \( K_a \) of at least \( 10^3 \) M\(^{-1} \) is required. In the bulk, however, the concentration term significantly grows and even at low \( K_a \) values sufficient DP of polymerization can be archived. Thus, even relatively
weak pi-pi stacking\textsuperscript{56,57} and hydrogen bonding\textsuperscript{58–64} associates provide mechanically robust bulk materials.

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CHAPTER II. EXPERIMENTAL

2.1. Reagents

2.1.1. Reagents

Krasol HLBH-P 3000 polymer was purchased from Cray Valley SA. Diisopropylethylamine (DIPEA, 98%), 2,4,6-trichlorotriazine (TCT, 99%), 2-picolylamine (99%), di-(2-picolyl)amine (98%), and 2,2′-dipyridylamine were obtained from TCI and stored under inert atmosphere. Ethanolamine (99%), N-methylethanolamine (98%), phenylisocyanate (98%), oxalyl chloride (99%), benzoyl chloride (99%), tetrakis(acetonitrile)copper(I) hexafluorophosphate (97%), chromium(III) chloride tetrahydrofuran complex (CrCl$_3$·3THF, 97%), and molecular sieves 4 Å were purchased from Sigma-Aldrich and stored under inert atmosphere. Celite 545, sodium sulfate anhydrous (Na$_2$SO$_4$, 99%), 2,2,6,6-tetramethyl-3,5-heptanедione (TMHD, 98%), potassium tetrachloroaurate (III) (KAuCl$_4$, 99%), metanil yellow (dye content 70%), Celite 545, CDCl$_3$ (99.5%), 1,10-Phenanthrolin-5-amine, oleylamine (technical grade, 70%), iron(II) trifluoromethanesulfonate (> 85%), diethylamine (>99.5%), 1,4-phenylene diisocyanate (98%), and 2,9-dimethyl-1,10-phenanthroline (>98%) were purchased from Aldrich and used as obtained. tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) sulfate was received from ICN pharmaceuticals. bis(2,2′-bipyridine)-(5-bromophenanthroline)ruthenium bis(hexafluorophosphate) was a gift from Dr. Ogawa which has been used in his previous work.1

All gases were purchased from PRAXAIR Inc. and used as received unless further specified.
2.1.2. **Solvents**

Dichloromethane (DCM) for spectroscopic studies was obtained from Alfa Aesar (spectroscopic grade) and was used as received. Chloroform (CHCl₃), diethyl ether (Et₂O), acetonitrile (CH₃CN), hexane (all purchased from EMD) were dried over molecular sieves 4 Å for 24 h prior use and stored under argon protection.²

2.2. **Experimental methods**

2.2.1. **UV-Vis absorption spectroscopy**

UV-Vis absorption spectra were reordered at Shimadzu UV-2600 spectrophotometer with 0.5 nm resolution. IR-Vis spectra of chromium-based metallopolymers were carried out at Shimadzu UV-3600 UV-vis-NIR spectrophotometer in the range of 1100-400 nm.

All liquid state spectra were recorded in high quality UV-vis quartz cells (Starna Cells) having a 1 cm pathlength. To measure absorbance spectra of the polymers, the thin films were prepared by deposition of solutions of the polymers on a glass substrate. The obtained films were air dried overnight and kept under high vacuum for additional 10 h to ensure complete solvent removal.

2.2.2. **Infrared spectroscopy**

FT-IR analysis was performed on JASCO FTIR-4000 equipped with a pellet sample holder. The polymer samples were air dried from chloroform solution on a CaF₂ window to form a thin film, and transmittance spectra were collected.
2.2.3. NMR characterization

$^1$H-NMR was recorded at room temperature on a Bruker AVANCE III spectrometer operating at 500 MHz in deuterated chloroform (Sigma Aldrich) using a chloroform residual signal as an internal standard (7.26 ppm).³

2.2.4. Mass-spectroscopy

Matrix assisted laser desorption/ionization (MALDI) was performed on a Bruker-Daltonix Omniflex mass spectrometer operated in linear, positive ion mode equipped with a microchannel plate detector. Dithranol was used as a matrix.

2.2.5. X-Ray diffraction

Powder X-Ray diffraction (PXRD) of the supramolecular polymers was done on a Bruker D8 Advance Davinci powder X-Ray diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) within 20 range from 2 to 50° with total irradiation time of 40 minutes. The polymers samples were air dried on a glass substrate and kept under high vacuum for 10 h prior the measurements.

2.2.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry traces were obtained using DSC Q2000 system at a heating rate of 10°C min⁻¹ from -85°C to 155°C using sample of approximately 2 mg.

2.2.7. Nanosecond transient absorption pump-probe spectroscopy

Nanosecond transient absorption measurements were collected with a LP980 laser flash photolysis system (Edinburgh Instruments) using Vibrant 355 Nd:YAG/OPO system (OPOTEK) as the excitation source. Liquid samples as well as polymer films were prepared with an optical density of 0.2–0.4 at the excitation wavelength (420 nm, ~2-3 mJ/pulse). To prepare the $[\text{Cu(dmp)}_2]\text{PF}_6$ in polymer film sample, 30 mg of a corresponding polymer was dissolved in 1
mL spectrophotometric grade DCM and 30 μL of 5 mM DCM stock solution of [Cu(dmp)2]PF6 was added. Then final solution was placed on a microscope slide and the solvent was evaporated to form a film. Kinetic traces were collected with a PMT, and transient absorption spectra and gate delayed emission spectra (typically 20 ns delay) were collected with an iStar ICCD camera (Andor Technology). All kinetic traces were fit with single exponential functions using IGOR Pro. All flash photolysis experiments were performed at ambient temperatures. The reported kinetics are average of 500 and emission spectra are average of 200 measurements. All experiments were performed twice on the same sample irradiating the same spot to verify sample stability during photolysis.

Liquid samples were bubbled degassed with argon for 30 minutes in 1 cm path length quartz optical cells prior the measurements to prepare deaerated samples. To perform lifetime measurements on polymer films under argon protection, the previously prepared glass slides covered with polymer/[Cu(dmp)2]PF6 composites were places under high vacuum overnight and kept under argon atmosphere inside a glovebox. The samples were placed into a glass chamber, covered with a cap, and sealed with a layer of parafilm to prevent argon leakage.

2.2.8. Scanning transmission electron microscopy of nanoparticles

The size of gold nanoparticles was studied on Hitachi S-4800 STEM operating at 200 keV. The sample (a 10 μL drop) was spotted on holey carbon 400 mesh copper grid, washed with two drops of hexane, and precipitated with one drop of ethanol. Size distribution histograms of nanocrystals were obtained based on STEM images. Briefly, the sizes of one hundred randomly chosen nanoparticles for each synthesis were measured in two dimensions using ImageJ software.
2.2.9. Density Functional Theory (DFT) calculations

First, molecular mechanics calculations were performed to permit rapid and extensive conformational searching on molecules of interest. In order to describe the ligand and receptor properly when bound and to avoid modeling of the wrong conformer of the ligand Merck molecular force field (MMFF) was utilized.4 After locating the conformational minima Molecular properties such as geometries, energies and electron density distribution were calculated by the Density Functional Theory (DFT) using the hybrid of Becke’s non-local three parameter exchange and correlation functional with the Lee-Yang-Parr functional (B3LYP)5-7 using Spartan 14 (Wavefunction, Inc) software. The 6-31*+ basis set was used in optimization of metal complexes.8 The choice of density functional theory functional was made based on the performance of the method on big systems and direct inclusion of the correlation effects which is crucial in the presence of transition metal atoms.

2.2.10. Rheological characterization

a. General

All experiments were performed on a TA Instruments Discovery HR-2 rheometer with 8 mm parallel plates. About 100-150 mg of a metallopolymer was placed into 0.5-1 mm gap between the plates and trimmed if needed. Strain sweeps were carried out in 0.1% – 5% stain range at constant 1 Hz frequency and 25°C temperature in order to determine the linear viscoelastic region. All experiments were performed three times to ensure repeatability.

The sample preparation for supramolecular thermoplastics is of the great importance for good data reproducibility. First, H-bonded polymer P1 was heated at 110°C in the oven for 30 min into a Teflon mold to erase presence of any crystalline domains. Rapid cooling of the polymer mass with liquid nitrogen provided polymer P1 in the melt state (P1-M). The polymer
was placed between the plates of the rheometer and sheared at 1 Hz oscillation frequency for 30 mins at 5°C for better adhesion. To recover the crystalline state (P1-X), the viscoelastic polymer mass P1-M was heated at 60°C for 12h between the plates of the rheometer.

b. Time-temperature master curves

Time-temperature superposition (TTS) master curves were generated based on a set of frequency sweep tests performed on each sample. The frequency sweep experiments were carried out at 0.5% strain and 0.1-10 rad/s frequency range within 5-50°C temperature range with 15°C increment. The reference temperature was 20°C for all TTS master curves.

c. Step relaxation test

Relaxation tests were performed by applying a 0.5% step strain \( \gamma \), and then the stress \( \sigma \) and relaxation modulus \( G(t) = \sigma/\gamma \) were monitored over time at 15°C.

d. Dynamic mechanical response upon light activation

To measure change in mechanical properties upon light activation, we have performed time sweep test at 1 Hz oscillation frequency, 0.5% strain, and 25°C. The samples were irradiated using either a 450 nm, 655 nm or 980 CW laser equipped with focusing lens and optical filter (800 mW cm\(^{-2}\)) for 2 minutes and allowed for “dark” relaxation for another 3 minutes between the radiations. The experiments were repeated three times to get average values and standard deviations for storage (\(G'\)), loss moduli (\(G''\)), and \(\tan(\delta)\). The percent change of the parameters before and after radiations were calculated according to the formula:

\[
\frac{X_{dark} - X_{light}}{X_{light}} \times 100\% \tag{2.1}
\]
Equation 2.1 Percent change of storage (G') and loss (G'\″) moduli values upon light radiation

where X is G' or G'\″; light and dark correspond to a parameter measured upon or in absence of light radiation, respectively.

2.2.11. Light-induced self-healing in polymer films

A scoop (~1-5 mg) of metanil yellow, \textit{tris}(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) sulfate, or \textit{bis}(2,2′-bipyridine)-(5-phenanthroline)ruthenium bis(hexafluorophosphate) was dissolved in methanol. The amount of solvent was adjusted such that 50-75 \(\mu\)L of the prepared stock solution diluted in 3 mL of methanol has absorbance equal to 0.5 at the maximum absorbance peak in the UV-Vis spectrum (Figure 4.SF4). 1200 mg of the \textbf{P1}, \textbf{P2}, or \textbf{P3} polymers were dissolved in 10 mL chloroform. For the self-healing tests, amounts of the chromophore stock solutions corresponding to Abs = 0.5 were taken and concentrated to \~20 \(\mu\)L and diluted with extra 200 \(\mu\)L of CHCl\(_3\). 330 \(\mu\)L (40mg) of the polymer stock solution was added to the chromophore MeOH/CHCl\(_3\) solution and well mixed. Then final solution was placed on a microscope slide and the solvent was evaporated to form solid film. The procedure was repeated until the absorbance of the solid film matched the required value. Prior to self-healing tests, the polymer films were dried in air overnight. The polymer films were cut with a razor blade and the cut area was irradiated with 455 nm CW laser equipped with the 455 nm filter and collimating lens at 100-350 mW radiation power with 50 mW increment. The diameter of the laser beam is 2.2 mm. Radiation time is 30 seconds

The temperature of the irradiation spot of the polymers was determined using a Flir C2 Compact Thermal Imaging System. To account for inhomogeneity of the chromophore distribution along the polymer films the temperature was determined at three different spots on
the material, and recorded temperatures are averages. The microscope images were taken on OMAX optical microscope equipped with A35140U3 digital camera operating in 4X magnification mode.

2.3. Synthesis

2.3.1. Synthesis of 2,4-dichlorotriazine terminated hydrogenated poly(ethylene-co-butylene) (I)

Under nitrogen atmosphere, a solution of 50 mL anhydrous chloroform with hydroxyl terminated Krasol HLBH-P 3000 (9 g, 3 mmol) and diisopropylethylamine (1.94 g, 15 mmol) was added dropwise to 20 mL of chloroform solution of sym-trichlorotriazine (922 mg, 15 mmol) in a 100 mL round-bottom flask equipped with a magnetic stirrer. The reaction mixture was stirred for 12 h at room temperature under N2. The solvent was removed under reduced pressure, and 100 mL of hexane was added to precipitate both the hydrochloride salt of diisopropylethylamine and cyanuric chloride. The solution was filtered through Celite 545 to separate the product from the solid impurities. The hexane solution was extracted 3 times with 50 mL of acetonitrile, 2 times with 100 mL of water, and washed with brine. The organic layer was dried over Na2SO4 and filtered through a silica plug to eliminate colored impurities from the product. Removal of hexane under reduced pressure afforded the clear, viscous liquid dichlorotriazine terminated hydrogenated poly(ethylene-co-butylene) product in 92% yield (2.76 mmol, 9.09 g). 1H NMR (500 MHz, CDCl3) δ = 4.50 (m, –CH2–O–), 1.5-0.7 (m, CH2 and CH3 backbone).
Scheme 2.1. Synthesis of 2,4-dichlorotriazine terminated hydrogenated poly(ethylene-co-butylene) (1)

2.3.2. Synthesis of 2-chloro-4-(2-picolylamino)-triazine terminated hydrogenated poly(ethylene-co-butylene) (L1)

2-picolylamine (324 mg, 3 mmol) and DIPEA (388 mg, 3 mmol) were dissolved in chloroform (15 mL) and added within 15-20 minutes to a 50 mL chloroform solution of dichlorotriazine terminated Krasol HLBH-P (4.9 g, 1.256 mmol). The reaction mixture was stirred at room temperature for 4 h and then the solvent was removed in vacuo. The product was redissolved in hexane, filtered through Celite, washed with acetonitrile, then water, and brine, dried over Na2SO4 in the similar fashion as for compound (1). The product was filtered through a silica plug using hexane/ethyl acetate as an eluent (10:1) to obtain pale yellow liquid product in 83% yield (3.59 g, 1.04 mmol). 1H NMR (500 MHz, CDCl3) δ = 8.56 (2H, m, CHPy), 7.69 (2H, m, CHPy), 7.24 (4H, m, CHPy), 5.05 (4H, m, N–CH2–Py), 4.74 (4H, m, –CH2–O–), 1.5-0.7 (m, CH2 and CH3 backbone).

Scheme 2.2. Synthesis of 2-chloro-4-(2-picolylamino)-triazine terminated hydrogenated poly(ethylene-co-butylene) (L1)
2.3.3. Synthesis of 2-chloro-4-di-(2-picolyl)amine-triazine terminated hydrogenated poly(ethylene-co-butylene) (L2)

Di-(2-picolyl)amine (DPA, 598 mg, 3 mmol), DIPEA (388 mg, 3 mmol), and dichlorotriazine terminated Krasol HLBH-P (4.9 g, 1.256 mmol) were mixed according to the synthesis procedure of L1. The reaction mixture was stirred at room temperature for 4 h and then the solvent was removed in vacuo. The product was isolated in the same manner as L1 to obtain pale yellow viscous liquid in 84% yield (3.8 g, 1.05 mmol). $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 8.54$ (4H, m, CHPy), 7.63 (4H, m, CHPy), 7.30 (2H, m, CHPy), 7.18 (6H, m, CHPy), 5.05 (8H, m, N–CH$_2$–Py), 4.24 (4H, m, –CH$_2$–O–), 1.5-0.7 (m, CH$_2$ and CH$_3$ backbone).

Scheme 2.3. Synthesis of 2-chloro-4-di-(2-picolyl)amine-triazine terminated hydrogenated poly(ethylene-co-butylene) (L2)

2.3.4. Synthesis of 2-chloro-4-(2,2’-dipyridylamino)-triazine terminated hydrogenated poly(ethylene-co-butylene) (L3)

2,2’-Dipyridylamine (514 mg, 3 mmol), DIPEA (388 mg, 3 mmol), and dichlorotriazine terminated Krasol HLBH-P (4.9 g, 1.256 mmol) were mixed according to the synthesis procedure of L1. The reaction mixture was stirred at room temperature for 4 h and then the solvent was removed in vacuo. The product was isolated according to purification procedure of L1 to obtain pale yellow viscous liquid in 82% yield (3.8 g, 1.05 mmol). $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 8.46$ (4H, m, CHPy), 7.81 (4H, m, CHPy), 7.57 (2H, m, CHPy), 7.22 (6H, m, CHPy), 4.21 (4H, m, –CH$_2$–O–), 1.5-0.7 (m, CH$_2$ and CH$_3$ backbone).
Scheme 2.4. Synthesis of 2-chloro-4-(2,2′-dipyridylamino)-triazine terminated hydrogenated poly(ethylene-co-butylene) (L3)

2.3.5. Preparation of Cr(III)-metallopolymers

CrCl₃·3THF 0.44 mmol (165 mg) were dissolved in 10 mL of anhydrous methanol under inert atmosphere. 2 mL aliquot of this Cr(III) solution (0.088 mmol, 33 mg) was added to 8 mL anhydrous chloroform solution of either L₁ (0.135 mmol, 465 mg), L₂ (0.135 mmol, 489 mg), or L₃ (0.135 mmol, 482 mg). An immediate color change from purple to green was observed indicating ligand substitution, however the solution was left at room temperature under N₂ protection for at least 24 hours and as long as 3 months to ensure complete ligand substitution. The solvent was partially air-dried, and the rest part of the metallopolymer solution was casted on a Teflon mold and air-dried for 2 days. The polymers were kept under high vacuum for 24 h to remove residual solvent and then stored in dark, ambient conditions before rheological testing.

2.3.6. Synthesis of 2,4-bis((2-hydroxyethyl)amino)triazine terminated hydrogenated poly(ethylene-co-butylene) (2)

To a stirring solution of ethanolamine (2.73 g, 45.5 mmol) in 30 mL of chloroform a solution of 2,4-dichlorotriazine terminated hydrogenated poly(ethylene-co-butylene) (5.00 g, 1.51 mmol) in 50 mL of chloroform was added dropwise over 20 minutes. The reaction mixture was stirred at ambient temperature for 1 hour and then was refluxed for additional 12 hours. The precipitate was filtered off through Celite 545, and chloroform was evaporated under reduced pressure. The residue was redisolved in 150 mL of hexane and washed with acetonitrile (5x30 mL). If needed, the separatory funnel was heated for better hexane/acetonitrile separation. The
hexane layer was evaporated under reduced pressure and the residue was left under high vacuum for 24 h in a warm oil bath giving 4.65 g (92%) of soft elastic polymer (2). $^1$H NMR (500 MHz, CDCl$_3$) δ = 4.24 (m, 4H; –CH$_2$–O–Tr), 3.78 (m, 8H; NH–CH$_2$), 3.56 (m, 8H; –CH$_2$–OH), 2.3-0.5 (m, 518H; CH$_2$ and CH$_3$ backbone).

Scheme 2.5. Synthesis of 2,4-bis((2-hydroxyethyl)amino)triazine terminated hydrogenated poly(ethylene-co-butylene) (2)

2.3.7. Synthesis of 2,4-bis((2-hydroxyethyl)(N-methylamino))triazine terminated hydrogenated poly(ethylene-co-butylene) (3)

The reaction between N-methylethanolamine (3.42 g, 45.5 mmol) and 4,6-dichlorotriazine terminated HLBH-P (5.00 g, 1.51 mmol) was accomplished according to the procedure described for polymer (2) yielding 4.55 g (90%) viscous liquid (3). $^1$H NMR (500 MHz, CDCl$_3$, δ = 4.30 (m, 4H; –CH$_2$–O–Tr), 3.66 (m, 8H; –CH$_2$–OH), 3.14 (s, 12H CH$_3$–NH), 2.92 (m, 8H; NH–CH$_2$), 2.3-0.5 (m, 539H; CH$_2$ and CH$_3$ backbone).

Scheme 2.6. Synthesis of 2,4-bis((2-hydroxyethyl)(N-methylamino))triazine terminated hydrogenated poly(ethylene-co-butylene) (3)

2.3.8. Synthesis of 4,6-bis((2-(3-phenylureido)ethyl)amino)-1,3,5-triazine terminated hydrogenated poly(ethylene-co-butylene) (P1)

To the stirring solution of 2.51 g (0.75 mmol) polymer (2) in 40 mL of anhydrous chloroform, a 20 mL CHCl$_3$ solution of 381 mg (3.2 mmol) phenyl isocyanate was added under
inert atmosphere. The mixture was refluxed for 22 hours under nitrogen followed by a purification procedure as reported for polymer (2) to yield 2.92 g (89%) of stiff white polymer P1. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$ = 7.6-7.25 (m, 16H; Ar H), 7.06 (t, 4H; Ar H), 4.30 (m, 12H; $-\text{CH}_2\text{O-Tr} + \text{CH}_2\text{O-C(O)-NH}$), 3.78 (m, 8H; NH$-\text{CH}_2$), 2.3-0.5 (m, 515H; CH$_2$ and CH$_3$ backbone).

Scheme 2.7 Synthesis of 2,4-bis((2-(3-phenylureido)ethyl)amino)-1,3,5-triazine terminated hydrogenated poly(ethylene-co-butylene) (P1)

2.3.9. Synthesis of 2,4-bis((2-(3-phenylureido)ethyl)(N-methylamino))-1,3,5-triazine terminated hydrogenated poly(ethylene-co-butylene) (P2)

The reaction between 2.53 g polymer (3) (0.75 mmol) and 381 mg phenyl isocyanate (3.2 mmol) was accomplished according to the procedure described for polymer P1 yielding 3.06 g (92%) colorless viscoelastic material P2. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$ = 7.51-7.33 (m, 4H; Ar H), 7.23-6.85 (t, 16H; Ar H), 4.23 (m, 4H; $-\text{CH}_2\text{O-Tr}$), 3.76 (m, 8H; CH$_2$O-C(O)-NH), 3.46 (m, 8H; NH$-\text{CH}_2$), 3.12 (s, 12H CH$_3$-NH), 2.3-0.5 (m, 540H; CH$_2$ and CH$_3$ backbone).

Scheme 2.8. Synthesis of 2,4-bis((2-(3-phenylureido)ethyl)(N-methylamino))-1,3,5-triazine terminated hydrogenated poly(ethylene-co-butylene) (P2)
2.3.10. Synthesis of oxalyl monochloride terminated hydrogenated poly(ethylene-co-butylene) (4)

To the cold 40 mL hexane solution of 2.54 g (20 mmol) oxalyl chloride was added dropwise 40 mL cold hexane solution of 260 mg (2 mmol) DIPEA and 3 g (1 mmol) HLBH-P 3000 under nitrogen protection. The reaction mixture was stirred for 1 h at 0°C and then for an additional hour at room temperature. The hexane solution of the product was washed with 4 portions of acetonitrile (10 mL). Hexane was removed under reduced pressure to yield 3.06 g (97%) of the polymer (4). This product is stable in air during the purification process, but if not used immediately for further reactions, it should be stored under N₂ protection. ¹H NMR (500 MHz, CDCl₃, δ = 4.38 (m, 4H; –CH₂–O–), 2.3-0.5 (m, 509H; CH₂ and CH₃ backbone).

Scheme 2.9. Synthesis of oxalyl monochloride terminated hydrogenated poly(ethylene-co-butylene) (4)

2.3.11. Synthesis of 1,10-phenanthroline terminated hydrogenated poly(ethylene-co-butylene) polymer (L₄).

To the suspension of 300 mg (1.536 mmol) of 1,10-phenanthroline-5-amine and 200 mg (1.536 mmol) DIPEA in 30 mL of dry CHCl₃ add 30 mL CHCl₃ (dry) solution of 2.32 g (0.732 mmol) polymer (4) under nitrogen protection. The reaction mixture was vigorously stirred for 3 h. Chloroform was evaporated under reduced pressure, the polymer was redissolved in 90 mL hexane with addition of 20 mL of acetonitrile. The hexane layer was washed with acetonitrile (3×30 mL). For better separation, the separatory funnel was gently heated with a heat gun. Removal of hexane under reduced pressure resulted in 2.18 g (85%) of the yellowish polymer (L₄). ¹H NMR (500 MHz, CDCl₃, δ = 9.51 (s, 2H, NH-phen), 9.28 (m, 2H, Ar H), 9.18 (m, 2H,
Scheme 2.10. Synthesis of 1,10-phenanthroline terminated hydrogenated poly(ethylene-co-butylene) polymer ($L4$)

2.3.12. Preparation of supramolecular metallopolymer $Fe-L4$

To the 10 mL chloroform solution of 1.4 g (0.4 mmol) polymer ($5$) was added 1 mL of a methanol solution of 23.6 mg (0.067 mmol) of iron(II) trifluoromethanesulfonate. The solvent was partially air-dried and the residue of the metallopolymer solution was casted on a Teflon mold and air-dried for 2 days. The polymer was kept under high vacuum for 24 h to remove residual solvent.

2.3.13. Synthesis of 2-chloro-4-(2-hydroxyethyl)(N-methylamino)triazine terminated hydrogenated poly(ethylene-co-butylene) ($5$)

To a stirring solution of 2-(methylamino)ethanol (260 mg, 3.42 mmol) and DIPEA (442 mg, 3.42 mmol) in 30 mL of chloroform a solution of 2,4-dichlorotriazine terminated HLBH-P (5.5g, 1.66 mmol) in 50 mL of chloroform was added dropwise over 20 minutes. The reaction mixture was stirred at ambient temperature for 1 hour, and then the solvent was evaporated under reduced pressure. The residue was redisolved in 75 mL of hexane and washed with acetonitrile (3x30 mL). The hexane layer was evaporated under reduced pressure and the residue was left under high vacuum for 24 h giving 5.24 g (93%) of a viscous liquid. $^1$H NMR (500 MHz,
CDCl$_3$) $\delta = 4.34$ (4H, m, CH$_2$-triazine), 3.89 (4H, m, CH$_2$-OH), 3.80 (4H, m, CH$_2$-N), 3.25 (6H, m, CH$_3$-N), 1.5-0.7 (m, 506H, CH$_2$ and CH$_3$ backbone).

Scheme 2.11. Synthesis of 2-chloro-4-(2-hydroxyethyl)(N-methylamino)triazine terminated hydrogenated poly(ethylene-co-butylene) (5)


The mixture of 3 g (0.9 mmol) of polymer (5), 150 mg (1.95 mmol) of diethylamine, and 252 mg (1.95 mmol) of DIPEA was reflux in 40 mL of chloroform for 10 h. The product was isolated in the similar fashion as described for polymer (5) giving 2.83 g (93%) of viscous polymer (6). $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 4.28$ (4H, m, CH$_2$-triazine, 1H, b, OH), 3.84 (4H, m, CH$_2$-OH), 3.73 (4H, m, CH$_2$-N), 3.56 (8H, m, CH$_2$-N), 3.17 (6H, m, CH$_3$-N), 1.5-0.7 (m, 584H, CH$_2$ and CH$_3$ backbone).


### 2.3.15. Synthesis of 2-diethylamino-4-(2-(3-phenylureido)ethyl)(N-methylamino)triazine terminated hydrogenated poly(ethylene-co-butylene) (P3)

To a stirred solution of 2.51 g (0.75 mmol) polymer (6) in 30 mL of anhydrous chloroform, a 10 mL CHCl$_3$ solution of 381 mg (3.2 mmol) phenyl isocyanate was added under an inert atmosphere. The mixture was refluxed for 12 hours under nitrogen and purified according to the procedure reported for polymer (5) to yield 2.92 g (92%) of viscous a polymer
P3. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.35$ (8H, m, CH Ar), 7.06 (4H, m, CH Ar), 6.54 (2H, b, NH-Ar), 4.37 (4H, m, CH$_2$-O-C(O)), 4.29 (4H, m, CH$_2$-O-triazine), 3.87 (4H, m, CH$_2$-N), 3.56 (8H, m, CH$_2$-N), 3.18 (6H, m, CH$_3$-N), 1.5-0.7 (m, 520H, CH$_2$ and CH$_3$ backbone).

Scheme 2.13. Synthesis of 2-diethylamino-4-(2-(3-phenylureido)ethyl)(N-methylamino)triazine terminated hydrogenated poly(ethylene-co-butylene) (P3)

2.3.16. Synthesis of polymer (7)

To the stirring CHCl$_3$ solution of 1.6 g (10 mmol) of 1,4-phenylene diisocyanate was added dropwise 40 mL of CHCl$_3$ solution of 3 g (1 mmol) HLBH-P 3000 under nitrogen protection. The reaction mixture was refluxed overnight, and chloroform was removed under reduced pressure. The product was redisolved in 30 mL of hexane followed by filtration of 1,4-phenylene diisocyanate excess through Celite. Hexane was washed with CH$_3$CN 3 times (30 mL), and evaporated under reduced pressure to yield 3.13 g (94%) of the polymer (7). This product was stable in air during the purification process, but if not used immediately for the next step, it should be stored under inert atmosphere. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.33$ (4H, m, CH Ar), 7.04 (4H, m, CH Ar), 6.54 (2H, b, NH-Ar), 4.18 (4H, m, CH$_2$-O-), 1.5-0.7 (m, 553H, CH$_2$ and CH$_3$ backbone).

Scheme 2.14. Synthesis of polymer (7)
2.3.17. Synthesis of polymer (8)

Diethanolamine (210 mg, 2 mmol) was dissolved in 20 mL of dichloromethane and added quickly to the vigorously stirring CH₂Cl₂ solution of polymer (7). The reaction mixture immediately turned turbid. After additional 15 minutes of stirring, the amount solvent was concentrated to 5 mL under reduced pressure, and the product was precipitated with 35 mL of MeOH. The solid was centrifuged at 8000 rpm for 10 minutes. The solvent was discarded, and the formed solid was re-dispersed in 5 mL DCM. The methanol precipitation cycle was repeated two more times, and the final product was placed under high vacuum with mild heating to result in 2.94 g (92%) of white stiff polymer mass. ¹H NMR (500 MHz, CDCl₃) δ = 8.40 (2H, b, NH-Ar), 7.23 (overlaps with CHCl₃, m, CH Ar), 6.51 (2H, b, NH-Ar), 4.16 (4H, m, CH₂-O-), 3.79 (8H, m, CH₂-OH), 3.47 (8H, m, CH₂-N), 1.5-0.7 (m, 50H, CH₂ and CH₃ backbone).

Scheme 2.15. Synthesis of polymer (8)

2.3.18. Synthesis of polymer P4

Polymer (8) 1.75 g (0.5 mmol), benzoyl chloride 350 mg (2.5 mmol), and DIPEA 322 mg (2.5 mmol) were mixed together in chloroform under an inert atmosphere and refluxed for 8 h. The product was isolated in the similar fashion as for polymer (8) to result in 1.68 g (85%) of viscoelastic polymer P4. ¹H NMR (500 MHz, CDCl₃) δ = 8.06 (8H, m, CH Ar), 7.72 (2H, b,
NH-Ar), 7.61 (4H, m, CH Ar), 7.47 (12H, m, CH Ar), 7.33 (4H, m, CH Ar), 6.51 (2H, b, NH-Ar), 4.57 (8H, m, CH2-O-C(O)), 4.20 (4H, m, CH2-O-), 3.81 (8H, m, CH2-N), 1.5-0.7 (m, 54H, CH2 and CH3 backbone).

Scheme 2.16. Synthesis of polymer P4

2.3.19. Synthesis of polymer P5

To the stirring solute of 1.5 g (0.5 mmol) hydroxyl terminated hydrogenated poly(ethylene-co-butylene) in 20 mL of anhydrous chloroform, a 10 mL CHCl3 solution of 131 mg (1.1 mmol) phenyl isocyanate was added under an inert atmosphere, and the mixture was refluxed for 20 hours under nitrogen. Chloroform was evaporated under reduced pressure, and the residue was redisolved in 50 mL of hexane and washed with acetonitrile (3x15 mL). The hexane layer was evaporated under reduced pressure giving 1.58 g (97%) of a viscous sticky liquid P5. 1H NMR (500 MHz, CDCl3) δ = 7.40 (4H, m, CH Ar), 7.33 (4H, m, CH Ar), 7.08 (2H, m, CH Ar), 6.55 (2H, b, NH-Ar), 4.21 (4H, m, CH2-O-), 1.5-0.7 (m, 484H, CH2 and CH3 backbone).
2.3.20. Gold nanoparticle synthesis

Oleylamine-capped Au nanocrystals were synthesized based on previously reported procedures.\textsuperscript{9,10} Briefly, 14 mg of KAuCl\textsubscript{4} and 5 mL oleylamine were sonicated until a clear yellow solution was obtained. The reaction mixture was heated at 100°C for 30 minutes under nitrogen protection. The reaction was cooled down to room temperature and transported into centrifuge tube. The Au-NPs were precipitated via addition of 15 mL of ethanol and centrifuged for 8 min at 7500 rpm. The solvent was discarded, and the formed solid was re-dispersed in 5 mL of hexane. The cleaning cycle was repeated two more times. The final product was stored in chloroform. The Au nanoparticles were characterized via STEM (Figure 4.SF5) and show average size of synthesized gold nanoparticles to be 6.4±1.2 nm.
2.4. NMR spectra of polymers

Figure 2.1. 500 MHz $^1$H NMR spectrum of polymer (1) in CDCl$_3$ at 298 K

Figure 2.2. 500 MHz $^1$H NMR spectrum of polymer L1 in CDCl$_3$ at 298 K
Figure 2.3. 500 MHz $^1$H NMR spectrum of polymer L2 in CDCl$_3$ at 298 K

Figure 2.4. 500 MHz $^1$H NMR of polymer L3 in CDCl$_3$ at 298 K
Figure 2.5. 500 MHz $^1$H NMR of polymer (2) in CDCl$_3$ at 298 K

Figure 2.6. 500 MHz $^1$H NMR of polymer (3) in CDCl$_3$ at 298 K
Figure 2.7. 500 MHz $^1$H NMR of polymer P1 in CDCl$_3$ at 298 K

Figure 2.8. 500 MHz $^1$H NMR of polymer P2 in CDCl$_3$ at 298 K
Figure 2.9. 500 MHz $^1$H NMR of polymer (4) in CDCl$_3$ at 298 K

Figure 2.10. 500 MHz $^1$H NMR of polymer L4 in CDCl$_3$ at 298 K
Figure 2.11. $^1$H NMR of polymer (5) in CDCl₃ at 298 K

Figure 2.12. $^1$H NMR of polymer (6) in CDCl₃ at 298 K
Figure 2.13. $^1$H NMR of polymer P3 in CDCl$_3$ at 298 K

Figure 2.14. 500 MHz $^1$H NMR of polymer (7) in CDCl$_3$ at 298 K
Figure 2.15. 500 MHz $^1$H NMR of polymer (8) in CDCl$_3$ at 298 K

Figure 2.16. 500 MHz $^1$H NMR of polymer P4 in CDCl$_3$ at 298 K
2.5. References


3.1. Abstract

We have demonstrated the ability to control the mechanical properties of metallosupramolecular materials via choice of ligand binding group, as well as with external light irradiation. These photoresponsive Cr(III)-based materials were prepared from a series of modified hydrogenated poly(ethylene-co-butylene) polymers linked through metal-ligand interactions between a Cr(III) metal center and pyridyl ligand termini of the polymers. The introduction of these Cr(III)-pyridine bonds gave rise to new mechanical and optical properties of the polymer materials. Depending on the type of pyridyl ligand, DFT calculations revealed changes in coordination to the Cr(III), which ultimately led to materials with significantly different mechanical properties. Electronic excitation of the Cr(III)-materials with 450 and 655 nm CW lasers (800 mW cm\(^{-2}\)) resulted in generation of excited state photophysical processes which led to temporary softening of the materials up to 143 kPa (41.5%) in storage modulus (G') magnitude. The initial mechanical strength of the materials was recovered when the light stimulus was removed, and no change in mechanical properties was observed with light irradiation where there was no absorbance by the Cr(III) moiety. These materials demonstrate that introduction of metal-ligand bonding interactions into polymers enables the design and synthesis of photoresponsive materials with tunable optical-mechanical properties not seen in traditional polymeric materials.
3.2. Introduction

Traditional supramolecular polymer synthesis paradigms rely on the creation of materials with specific mechanical properties based on the amount of hydrogen bonding interactions, hydrophobic interactions, and other van der Waals forces. New materials, including self-healing materials with dynamic bonding interactions have been creating using these kind of interactions.1–3 In an alternative approach, our group4 and others5–24 have designed materials with such dynamic bonding interactions that rely on coordination of transition metal ions with polymers. These metal coordination bonds have intermediate bond strengths (100-300 kJ/mol) compared to hydrogen bonds (1-40 kJ/mol) or C-C covalent bonds (~330 kJ/mol). In addition, the strength of the metal coordination bonds changes depending on the type of metal ion and coordinating ligand. The metal coordination bonding interactions have been shown to change the properties of polymers, specifically giving rise to materials with unique mechanical properties.5,8,12,16,19–21,25–29

Responsive metallosupramolecular materials can be designed that respond to a variety of different stimuli such as pH,30,31 electrical signals,18,20,23 or even light.4,21,29,32,33 We describe here the design, synthesis, and characterization of metallosupramolecular polymers that respond to light stimulus. We used a modular synthetic method to create a suite of pyridyl-modified polymers (Scheme 3.2). This allowed us to systematically investigate how small changes in ligands affected the overall properties of the materials. Simply by changing the ligand coordination moiety, we showed changes in the mechanical properties of the bulk metallopolymer material. In addition, such metallopolymer coordinated to Cr(III) ions showed reversible photo-responsive behavior, with light-induced changes in mechanical properties due to the photophysics of the Cr(III)-ligand bonds (Scheme 3.1). This shows that integrating metal
ions into polymers can be used to tune the mechanical and optical properties of materials depending on the dynamics and photoreactivity of the metal-coordination bonding interactions for a chosen ligand and metal.

![Scheme 3.1. Light-induced changes in mechanical properties of Cr(III)-metallopolymer](image)

3.3. Results

3.3.1. Synthesis of supramolecular polymers

For the synthesis of a suite of metallosupramolecular polymers, we used hydrogenated poly(ethylene-co-butylene) (HLBH-P 3000) as the polymer backbone, and terminated this polymer with different pyridine ligands to coordinate to metal ions according to Scheme 3.2. The polymers $L_1$, $L_2$, and $L_3$ were synthesized utilizing temperature controlled stepwise nucleophilic aromatic substitution of $sym$-trichlorotriazine.$^{34-36}$ A single substitution of a chlorine atom by –OH nucleophiles occurs at room temperature. Triazine-terminated hydrogenated poly(ethylene-co-butylene) (1) formed from this reaction was active for further nucleophilic substitution at room temperature only with primary and secondary amines.$^{34}$ The ligand-modified polymers ($L_1$-$L_3$) were created after a $2^{nd}$ substitution with different pyridine-based ligands. The polymers were characterized by $^1$H NMR (Figure 2.1-4), UV-vis absorption (Figure 3.SF1), FT-IR (Figure 3.SF2), and MS-MALDI (Figure 3.SF3) which indicated
successful, sequential substitution to create the ligand-modified polymers. Such modular approach allows for simple modification of polymers containing nucleophilic termini with a linker that has two open reactive sites for further modification. With this method, we were able to easily prepare gram scale quantities of metallopolymer materials, and simply change the ligand binding group.

Scheme 3.2. Modular synthesis of the metallopolymers using trichlorotriazine as a linker

### 3.3.2. Spectroscopic properties of the metallopolymers

After synthesis of the ligand-modified polymers (L1-L3), metallosupramolecular materials were formed from their reaction with CrCl₃·3THF. The clear chloroform solutions of the original polymers developed green color within 10-15 minutes after mixing with the lavender colored Cr(III) methanol solution. This color change and blue shift in the absorbance indicated formation of pyridine-Cr(III) coordination bonds. UV-vis and UV-vis-NIR of solutions and thin films of the materials revealed peaks consistent with the typical octahedral Cr(III) absorption profile 37,38 assigned as two weak (molar absorptivity ε~10² M⁻¹cm⁻¹) spin-allowed quartet transitions (⁴A₂g → ⁴T₂g and ⁴A₂g → ⁴T₁g) (Figure 3.1 and Figure 3.SF4). Due to the inert nature of the Cr(III) ion and the slow ligand substitution kinetics, further time was needed to ensure complete ligand substitution by the pyridyl groups. Complete substitution was determined by electronic absorption spectra of the metallopolymer. Samples tested after 3 months of mixing CrCl₃·3THF and L1, L2, and L3 ligands showed a blue shift in the absorbance spectra of
solution (Figure 3.SF4) and thin films (Figure 3.1) with respect to the ones reacted for 4 days (Figure 3.SF8). This reaction may be accelerated if the polymer solution and chromium salt are refluxed overnight to obtain the final product (Figure 3.SF10), and we attributed the red-shifted spectra to those with Cr(III) only partially coordinated to the more π-accepting pyridine-based polymers, with some remaining weaker field π-donor Cl ligands.

For the final materials, UV-vis revealed two spin-allowed quartet bands at 604 nm and 431 nm (16.6 and 23.2×10^3 cm⁻¹, respectively) for Cr-L₁, one band at 574 nm (17.4×10^3 cm⁻¹) for Cr-L₂, and two bands at 630 nm and 447 nm, (15.9 and 22.4×10^3 cm⁻¹ respectively) for Cr-L₃. The energies of these d-d transition are too low to be fully-substituted Cr(III)-pyridine-based polymers with [Cr(Lx)₃]³⁺ motifs. After comparison of electronic spectra of the formed Cr(III)-metallopolymer with the published spectra of Cr(III) complexes of 2,2'-bipyridine,³⁷,³⁹ we assigned predominate formation of cis-[Cr(Lx)₂Cl₂]^⁺ (where Lx is L₁, L₂, or L₃) complexes.

![Figure 3.1. Absorption spectra of Cr(III) metallosupramolecular polymers formed from L₁ (blue), L₂ (red), and L₃ (orange) in thin film 3 months after mixing](image)

3.3.3. Coordination environment around Cr(III)-center

The prepared Cr-based metallopolymers consist of non-polar hydrogenated poly(ethylene-co-butylene) backbone polymer chain and charged polypyridine-chromium termini. These so different in polarity fragments tend to phase separate to form supramolecular system which account for unique viscoelastic properties of the bulk material.\(^4^3\) The supramolecular metallopolymers form semi-regular pattern rather than random “spaghetti”-like polymer as it would be if the polymer backbone chains were linked through regular covalent carbon-carbon bonds. In the supramolecular metallopolymers, the non-polar polymer backbone follows the projection govern by coordination environment of the metal-ligand center at least in the close vicinity to the metal center.

Coordination of Cr(III) by the polymers not only changed the optical properties of the obtained materials, but also altered the mechanical properties. The starting pale yellow, viscous liquid of the ligand-modified polymers L1-L3, became viscoelastic (Cr-L1 and Cr-L2) or brittle (Cr-L3) materials after formation of Cr(III)-based metallosupramolecular polymers (Figure 3.2a). This showed how coordination of the Cr(III) ions can dramatically change the relatively low molecular weight amorphous polymers into a supramolecular assembly with specific mechanical properties, depending on the metal coordination. As it was discussed previously by Rowan and coworkers,\(^4^3\) the structural changes in the coordination environment around metal center impact on viscoelastic properties of the metallopolymers. They found that the linear (coplanar) segment of the supramolecular assembly accounts for high elasticity of the metallopolymers while addition of the branching points into the supramolecular network reduces the molecular weight of the linear component and results in more viscous materials.
In the absence of crystallographic data for the Cr(III)-metallopolymer melts, we have performed density functional theory (DFT) calculations to find the optimal geometries for a Cr(III) metal center and pyridyl ligand termini of the polymers. As seen from the Figure 3.2b and Figure 3.SF5, the presence of methylene bridge between the triazine linker and the pyridine-metal binding moiety led to orthogonal arrangement of the triazine linkers with respect to each other in cis-[Cr(L1)2Cl2]+ and cis-[Cr(L2)2Cl2]+. In the case of Cr-L3, however, the triazine rings tended to be more coplanar in the cis-[Cr(L3)2Cl2]+ complex. This can be seen in the dihedral angle ($\theta$) value between the planes of the two triazine linkers. The dihedral angle was governed by the coordination environment around Cr(III) metal center and the angle determines the directionality of how the polymer chains were projected in space in the metallosupramolecular polymers. This change in the directionality of the polymer projections ultimately acts as a way to predict the structure–properties relationships where changes in the projection angle correlated to overall material properties.
Figure 3.2. a) Pictures of prepared Cr(III)-based metallopolymer Cr-L1, Cr-L2, and Cr-L3 from the top to bottom. b) The optimized complexes using DFT (B3LYP/6-31*+) geometries of cis-[Cr(Lx)2Cl2]+ metal-ligand center of the metallopolymer where Lx is 1) L1, 2) L2, and 3) L3. The long polymer chain was replaced with ethyl substituent to decrease computational time. Chlorine is shown in green, oxygen in red, nitrogen in blue colors. Hydrogen atoms are omitted for clarity. The angles between the 2 triazine polymers are shown in each and indicated with the 2 shaded planes.

3.3.4 Mechanical properties

Despite changes in the mechanical properties of Cr-L1 and Cr-L2 compared to Cr-L3, we observed formation of amorphous solvent-free elastic melts with glass transition temperatures (T_g) below room temperature, which is dictated by the soft nature of the poly(ethylene-co-butylene) polymer backbone. The amorphous nature of the materials was also confirmed by an
absence of crystalline domains on PXRD patterns (Figure 3.SF5). This was consistent with other metallosupramolecular systems,\textsuperscript{16,40–43} where, a broad peak around $2\theta=20^\circ$ ($d=4.4$ Å) was attributed to the amorphous halo.

The frequency-dependent moduli $G'$, $G''$ and tangent $\delta$ curves at 25°C for both the \textbf{Cr-L1} and \textbf{Cr-L2} metallosupramolecular materials were similar (Figure 3.3). Over the higher frequency range the storage modulus was greater than the loss modulus in both \textbf{Cr-L1} and \textbf{Cr-L2} metallopolymers indicating that the elastic properties of the Cr(III)-based materials dominate over the viscous losses. When approaching the lower frequency range (longer relaxation time), the plateau region transferred to the terminal region. This transition was accompanied by a crossover in the storage and loss modulus, where now the loss modulus was greater than the storage modulus. The crossover point – the frequency where $\tan(\delta) = 1$ – indicates the relaxation time ($\tau_{\text{relax}}$) of the supramolecular metallopolymer materials. It should be noted that $\tau_{\text{relax}}$ is not the actual lifetime of the Cr-N coordination bonds but it is the characteristic time indicates when material properties are governed by the middle segment (polymer backbone) and when by permanent cross-linked supramolecular network.
Figure 3.3. Frequency dependence of mechanical properties of metallopolymers a) Cr-L1 and b) Cr-L2 reveal the similar bond relaxation times

For the Cr-L1 polymer, the crossover frequency was 0.001 Hz and for the Cr-L2 polymer it was 0.0009 Hz, corresponding to 1000 s and 1100 s bond relaxation times, respectively (Figure 3.3). Such similar dynamics suggest that the Cr-L1 and Cr-L2 metallosupramolecular polymers have the same molecular weight, the same bond strength between the chromium metal center and ligand-modified polymer, and the same coordination geometry around Cr(III) ions. These are all parameters that are known to tune the bond dynamics and mechanical properties in metallopolymer materials.\textsuperscript{41,43,44} It should be noted that incomplete ligand substitution resulted in decreased molecular weight of the Cr(III)-based metallopolymers which altered the crossover frequency towards shorter relaxation times. For Cr-L1 and Cr-L2 materials reacted for 3 months the bond relaxation time was observed on the order of $10^3$ seconds
range (Figure 3.3), however the samples reacted for 4 days still showed similar mechanical properties but the bond relaxation time was on the order of $10^1$ seconds (Figure 3.SF9).

### 3.3.5. Ligand labialization studies in solution

To demonstrate photoreactivity of the Cr-pyridine coordination bond in the prepared metallopolymers, we studied the photointiated ligand substitution in the Cr-based polymers since Cr(III) complexes are known to undergo ligand substitution reactions in solution.$^{45,46}$ As a competing ligand, 2,2,6,6-tetramethyl-3,5-heptanediene (TMHD) was added to the solution of Cr-L1 or Cr-L2 in a 2:1 molar ratio. As a hard Lewis-base, the enol-form of TMHD has greater affinity to the hard Lewis-acid Cr(III) center rather than the nitrogen-based pyridine polymers. Addition of TMHD in the dark revealed no significant change in the steady-state absorption spectra of Cr-L1 and Cr-L2 over 1 hour, suggesting no ligand substitution occurred. However, upon 15 min of excitation we observed a red-shift in the absorbance spectra of the metallopolymers (Figure 3.4a and 3.4b). This indicated substitution of the higher field pyridine ligand to the lower field oxygen-based TMHD ligand. Assuming this photochemistry is analogous to that observed in $O_h$ Cr(III) complexes, after excitation from the $^4A_{2g}$ state to the $^4T_{2g}$ and $^4T_{1g}$ states by light absorption (Figure 3.SF11), we expect either complete dissociation of the Cr-pyridine bond and formation of pentacoordinated intermediate$^{47}$ which readily reacted with competing ligand, or significant Cr-pyridine bond elongation, followed by ligand substitution through hepta-coordinated species.$^{46}$
It is clear, from TD-DFT analysis (Figure 3.4c), that the excitation occurs from a mostly nonbonding Cr(III) d-singly occupied orbital into a combination of LUMO and LUMO+1 orbitals, that are antibonding with respect to the Cr-N bond and have clear localization on the ligand as well. The Cr-nitrogen bond is weakening upon excitation and the ligand substitution occurs. The weakening of the coordination bond should reflect in dynamic changes in mechanical properties of the metallopolymers when irradiated.
3.3.6. Ligand labialization studies in bulk material

The dynamic response of the **Cr-L1** and **Cr-L2** materials was measured during external light irradiation (Figure 3.5). Upon 455 nm and 650 continuous wave (CW) irradiation (flux density 800 mW cm\(^{-2}\)) both the storage (G') and loss (G'\(^{\prime\prime}\)) moduli of both metallopolymer materials dropped and plateaued, remaining lower until the external light stimulus was turned off. This observed drop in G' and G'' values indicates light controlled, reversible changes in mechanical strength of Cr(III)-based metallopolymer materials.

![Figure 3.5.](image)

**Figure 3.5.** Reversible change in mechanical properties of **Cr-L1** (blue) and **Cr-L2** (red) metallopolymer upon a) 450 nm and b) 655 nm CW radiation (120 s, 800 mW cm\(^{-2}\)). Irradiation of starting hydroxyl terminated hydrogenated poly(ethylene-co-butylene) has no visible change in loss modulus (G'\(^{\prime\prime}\)) represented by black empty circles.
The elastic melts Cr-L1 and Cr-L2 possessed not only good reversibility with no significant hysteresis in moduli change upon 450 nm and 655 nm exposure, but also exhibited considerable softening during light irradiation (Table 3.1). No such photoresponsive behavior was seen in the starting polymer (Figure 3.5). This shows that it was the addition of the Cr(III) ions that created such unique optical-mechanical properties in the material. It should be noted that excitation of the materials with 980 nm light where Cr(III) has no absorption showed no change in the mechanical properties of the polymers (Figure 3.6a).

Table 3.1. Measured change in absolute storage $G'$ and loss $G''$ moduli values before and after 450 nm and 655 nm CW irradiation (800 mW cm$^{-2}$). Relative percent change is shown in parentheses.

<table>
<thead>
<tr>
<th>Metallopolymers</th>
<th>$\Delta G'$±SD,450 nm</th>
<th>$\Delta G''$±SD,450 nm</th>
<th>$\Delta G'$±SD,655 nm</th>
<th>$\Delta G''$±SD,655 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-L1</td>
<td>132 (±4) kPa</td>
<td>61±1 kPa</td>
<td>143±6 kPa</td>
<td>68±3 kPa</td>
</tr>
<tr>
<td></td>
<td>(37.7±1.1%)</td>
<td>(39.5±0.9%)</td>
<td>(41.5±1.7%)</td>
<td>(44.3±1.7%)</td>
</tr>
<tr>
<td>Cr-L2</td>
<td>54±2 kPa</td>
<td>24±1 kPa</td>
<td>71±1 kPa</td>
<td>30±1 kPa</td>
</tr>
<tr>
<td></td>
<td>(29.1±0.9%)</td>
<td>(30.4±1.1%)</td>
<td>(37.9±0.8%)</td>
<td>(37.2±1.8%)</td>
</tr>
</tbody>
</table>

The photoresponsive behavior of the Cr(III) supramolecular materials is attributed to the photolabilization of the Cr(III)-pyridine coordination bonds. Excitation to the first or second excited quartet state of the Cr(III) center ($^4A_{2g} \rightarrow ^4T_{2g}$ or $^4A_{2g} \rightarrow ^4T_{1g}$, respectively) triggered the decrease in mechanical strength of the metallopolymers. This is presumably due to lengthening of the metal-ligand bonding interactions as discussed previously (Figure 3.4c). To show that we are indeed seeing an enhanced softening of these materials, we have prepared the same polymers with Zn(II) and included a visible-absorbing dye methylene blue in these polymers to match the absorbance at 655 nm to that of the Cr-metallopolymers (Figure 3.6F7). There is some softening of the material with the dye, due to either the light to heat conversion, or vibronic cooling to heat...
conversion after relaxation of the dye excited state. This change is quite significantly less than what we observed in the Cr(III) metallopolymers (Figure 3.6b), showing that there is enhanced softening due to the photolabilization mechanism.

Figure 3.6. a) No changes in mechanical strength of Cr-L1 (blue) and Cr-L2 (red) metallopolymers upon 980 nm (120 s, 800 mW cm\(^{-2}\)) CW radiation. b) Zn-L1 with visible light absorbing dye methylene blue (MB) shows low 655 nm CW radiation (800 mW cm\(^{-2}\)) responsiveness.

The light to heat conversion that Rowan and coworkers observed in their Zn(II)-based polymers may also be happening\(^{16}\), but there is also a new ligand exchange mechanism that leads to the softer material due to breaking of the Cr(III)-N bonds. Alternatively, once excited, one of the possible channels for Cr(III) complexes to relax is non-radiative decay associated with heat generation (Figure 3.6F11).\(^{37,48}\) Heat generated from light absorption still may lower the storage and loss moduli which reflects as softening of the materials. Similar phenomena were observed in previously reported Zn(II)-based metallopolymers.\(^{16}\) It is more likely that two processes take place in the Cr(III)-based metallopolymers to alter mechanical stiffness of the materials upon light activation.

### 3.4 Conclusions

In summary, we have demonstrated an effective synthetic route utilizing step-wise nucleophilic substitution in sym-trichlorotriazine to create polymers with different ligands for
metal binding. Mixing these polymers with Cr(III) ions resulted in materials with tunable mechanical properties, depending on how the choice in ligand changed the coordination around the Cr(III) center which dictated different angles of the polymer projection in space.

In addition, these photoresponsive materials showed reversible change in mechanical stiffness upon light activation. This change was observed only when the excitation wavelength overlaps with the absorbance profile of the Cr(III) moiety, which excludes any infra-red heating of the material and confirms the changes in the mechanical properties were due to the photochemistry and photophysics of the Cr(III) excited state. These results show how different metal – ligand coordination geometries can direct and tune the mechanical properties of polymeric materials, depending on the specific coordination chemistry. By using the photochemistry and photophysics of coordination complexes as inspiration, we can also create materials that respond to light in specific ways. This work provides a foundation for elucidating how tuning the metal-ligand bonding dynamics and photoreactivity can be used to create materials for advanced coatings with unique optical and mechanical properties.

3.5. Supporting information

Figure 3.SF1. UV-Vis absorbance spectra of 2,4-dichlorotriazine terminated HLBH-P (gray), polymer L1 (blue), polymer L2, and polymer L3 (orange). No absorption detected in the visible part of the spectrum
Figure 3.SF2. FT-IR spectra of 2,4-dichlorotriazine terminated HLBH-P (gray), polymer L₁ (blue), polymer L₂, and polymer L₃ (orange). No absorption detected in the visible part of the spectrum.

Figure 3.SF3. Matrix assisted laser desorption-ionization mass spectra of a) polymer L₂ and b) polymer L₃. Any attempts to obtain mass-spectra of starting HLBH-P 3000, triazine-terminated HLBH-P (1), and polymer L₁ were unsuccessful.

Figure 3.SF4. Absorption spectra of mixture CrCl₃·3THF and L₁ (blue), L₂ (red), and L₃ (orange) in CHCl₃ solution after 3 months after mixing.
Figure 3.SF5. Powder X-Ray diffraction patterns of a) Cr-L1 (blue), b) Cr-L2 (red), and c) Cr-L3 (orange) supramolecular polymers suggest amorphous nature of the materials.

Figure 3.SF6. Cartoon schematic of how the different ligands (L1, L2, and L3) lead to orthogonal projections for Cr-L1 and Cr-L2, and more coplanar projection for Cr-L3 metallopolymer.

Figure 3.SF7. a) Frequency dependence of mechanical properties of Zn-L1 metallopolymer. b) UV-Vis spectra of chloroform solutions of Zn-L1 and Zn-L1 with methylene blue (MB) dye metallopolymers.
Figure 3.SF8. Absorption spectra of mixture CrCl$_3$·3THF and L1 (blue), L2 (red), and L3 (orange) in a) solution (CHCl$_3$) and b) thin film of the prepared metallopolymers after 4 days of the reaction.

Figure 3.SF9. Frequency dependence of mechanical properties of metallopolymers a) Cr-L1 and b) Cr-L2 still reveal the similar bond relaxation times even after 4 days of the reaction.

Figure 3.SF10. Absorbance spectra of chromium (III) chloride tetrahydrofuran complex (CrCl$_3$·3THF, black solid line), CrCl$_3$·3THF and L1 reacted for 4 days (Cr-L1 4 days, grey solid line), CrCl$_3$·3THF and L1 reacted for 3 months (Cr-L1 3 months, blue dashed line), and Cr-L1 refluxed overnight (Cr-L1 24h reflux, blue solid line) show that complete ligand substitution in Cr-L1 metallopolymer can be achieved under reflux for 24h.
Figure 3. SF11. Simplified Jablonsky diagram for octahedral Cr(III) complexes

3.6. References


CHAPTER IV. SUPRAMOLECULAR THERMOPLASTIC ELASTOMERS: SWITCHABLE MECHANICAL PROPERTIES AND PHOTOHEALABLE EFFECT

4.1. Abstract

We report the synthesis and characterization of supramolecular thermoplastic elastomers with mechanical properties that can be reversibly modulated with temperature due to changes in supramolecular architecture. Detailed characterization of this material revealed dramatically different supramolecular assemblies that form two states: a semi-crystalline state showed essentially no response to oscillatory shear deformations while the melt state behaved as a typical energy dissipative material with clear crossover between storage and loss moduli. This study also presents insights into how to engineer these supramolecular materials to be light responsive. The low capacity of H-bonding polymers to respond to visible light stimulus was overcome by incorporation of various chromophores into the supramolecular polymer. IR thermography was utilized to estimate temperature generation upon 455 nm laser irradiation (2.6-9.2 W cm⁻²) of polymer films. We found differences in heat generation in materials with gold nanoparticles as the chromophore compared to those with molecular dyes. Comparison studies on heat generation revealed no differences in light response whether an Fe(II)-phenanthroline based chromophore was either physically blended into a H-bonding polymer or acted as both supramolecular cross-linker and light absorbing center. These materials showed healing of defects and scratches with light-irradiation (Scheme 4.1), as long as the overlap of material absorbance and laser excitation was sufficient. Such results provide a baseline understanding of how materials can be designed with specific chromophores and supramolecular bonding interactions to tune the healing efficiency of the materials after light irradiation.
4.2. Introduction

To create next-generation materials it is necessary to design specific bonding interactions into the material to control the material properties.\textsuperscript{1–19} Stimuli-responsive materials are promising, since this allows for precise control of the bonding interactions in the polymer using an external change. One of the possible designs of such materials is a low molecular weight amorphous polymer backbone with dynamic bonds such as hydrogen (H-bonding) or metal coordination. These interactions link short polymer molecules together to create a supramolecular network that provides toughness and elasticity to the bulk material, but allow for a dynamic response to the external stimulus.

In the past decade, there have been several reports on supramolecular thermoplastics – materials with both an amorphous polymer backbone chain and a well-ordered supramolecular network – that create crystalline segments or clusters in the material. One approach to create these ordered crystalline domains in the supramolecular thermoplastics is based on the
modification of end-groups of low molecular weight telechelic polymers with multiple hydrogen bonding dynamic motifs that “stick” together and assemble into a supramolecular network in the solid state.\textsuperscript{20–29} Another technique to design a more sophisticated supramolecular architecture in the polymer matrix utilizes dynamic-bonding interactions between the polymer end-group\textsuperscript{30,31} or side chain of block copolymers\textsuperscript{32–36} and small molecules. It is a challenge to make these materials have stimuli-responsive properties, however, since the key design feature of this class of supramolecular materials is based on complex interactions of multiple hydrogen-bonding “stickers”, whose photochemical properties suffer from lack of visible light absorption. This limits them as stimulus-responsive materials, significantly reducing the capacity to respond to light stimuli.\textsuperscript{4,8,37–45} Alternatively, in supramolecular materials using metal coordination motifs, the metal coordination center can also serve as chromophore so that visible light irradiation can be used to control the metal-ligand interactions.

Light-responsive materials that utilize a variety of different metal-coordination bonding interactions – classic metal-coordination interactions and metal nanoparticles – have been designed.\textsuperscript{38,46–49} In these materials, healing was observed due to local heat generation from the light irradiation – usually because of the high absorbance of the UV light used – which led to breaking of the supramolecular interactions in the local irradiation volume.\textsuperscript{38,46} In contrast, our group has recently shown that materials can be designed with light-induced bond labilization, where visible light irradiation can be used to reversibly soften materials, beyond that of any light to heat generation.\textsuperscript{45} These results evoke a question: is it necessary to include the chromophore as part of the supramolecular structure and break the metal coordination bonds, or is it sufficient to just generate heat from chromophore being dispersed into the polymer matrix? Understanding the photophysics and photochemistry of the chromophores in supramolecular materials is critical
then, to elucidate how light irradiation can be used to control the bonding interactions in the polymers, and ultimately the mechanical properties of materials.

In order to fully characterize how light stimulus can be used to control mechanical properties in supramolecular materials, we prepared new supramolecular polymers with both H-bonding and metal coordination bonding motifs, and measured the heat generation and self-healing of these materials using different chromophores. By changing the type of chromophore, and type of bonding interactions in the polymers, we investigated how light irradiation controlled the heat generation, and ultimately light-induced self-healing in the materials. Specifically, we created a hydrogen-bonding supramolecular polymer with multiple “stickers” whose thermoplastic mechanical properties can be reversibly modulated through changing the hierarchy of the supramolecular architecture from crystalline to disordered. These two disordered and crystalline materials had the same chemical composition of the building units, and can act as a supramolecular thermoplastic as well as viscoelastic polymer melt based on assembly of the H-bonding network. We measured the heat generation and self-healing of polymers with different bonding interactions using different chromophores. We used IR thermography to determine the heat generated in the materials during light irradiation, and showed that regardless of whether the absorber is a part of the supramolecular assembly or dispersed in the H-bonding polymer, it generates about the same amount of heat. Comparison studies on light to heat conversion in different types of chromophores revealed differences in heat generation in gold nanoparticles with respect to molecular dyes. All the materials showed self-healing after sufficient light irradiation.
4.3. Results

4.3.1. Synthesis of supramolecular polymers

We used our previously reported modular synthetic approach to modify polymer termini groups via nucleophilic aromatic substitution of the sym-trichlorotrizine ring to create a series of hydrogenated poly(ethylene-co-butylene) polymers (HLBH-P 3000). These polymers all had dynamic bonding motifs that enhanced the elastic properties of the materials via supramolecular interactions. The introduction of H-bonding motifs was accomplished in two steps upon heating of polymer (1) in excess of 2-ethanolamine to obtain polymer (2). Further reaction of the free hydroxyl-groups of polymer (2) with phenyl isocyanate yielded a supramolecular H-bonded polymer P1 (Figure 4.1b) with three H-bonding stickers – one triazine-triazine (Tr-Tr) and two urethane-urethane (UT-UT) stickers per polymer termini (Figure 4.1c and 4.1d). The H-bonded polymer P2 (Figure 4.1b) was synthesized in the similar fashion as P1: triazine-terminated HLBH-P 3000 (1) was sequentially reacted with N-methylethanolamine and phenyl isocyanate to obtain polymer (3) and supramolecular polymer P2 with only two UT-UT stickers per termini, respectively. With the goal of specifically comparing how light irradiation affects the properties of materials with either hydrogen bonding or metal-coordination bonding interactions, a polymer with metal-coordination binding (polymer Fe-L4, Figure 4.1b), was obtained from first synthesis of a precursor oxalyl monochloride terminated HLBH-P 3000 polymer (4) by reaction of HLBH-P 3000 and excess of oxalyl chloride. Polymer Fe-L4 was then synthesized by reaction of polymer (4) and 5-amino-1,10-phenanthroline, with subsequent addition of 25% stoichiometric required amounts of Fe(OTf)2 in methanol/chloroform solvent mixture. The ratio of Fe(II) ions to phenanthroline terminated HLBH-P (5) was chosen to decrease the optical density of the material and make the polymer film thick enough for self-healing studies. The starting HLBH-P
3000 was a viscous liquid whereas, in contrast, supramolecular polymer \( P1 \) was a solid material (after solution or thermal annealing) and \( P2 \) was a viscoelastic melt. Metallopolymer \( \text{Fe-L4} \) was a dark orange/reddish viscoelastic material due to the absorbance of the Fe(II)-phenanthroline moieties with an expected absorbance peak at 515 nm (Figure 4.SF1).

![Chemical structures and hydrogen-bonding interactions](image)

**Figure 4.1.** a) General synthetic scheme to create supramolecular polymers using sim-trichlorotriazine chemistry b) Chemical structures of H-bonded supramolecular polymers \( P1, P2 \), and metallopolymer \( \text{Fe-L4} \). c) Triazine-triazine (Tr-Tr) and d) urethane-urethane (UT-UT) hydrogen-bonding interactions

### 4.3.2. Mechanical properties of supramolecular polymers

The mechanical properties of the supramolecular polymers \( P1, P2 \), and \( \text{Fe-L4} \) were studied by means of oscillatory rheology. The time-temperature superposition (TTS) master curve for a reference temperature of 20°C of the solution cast polymer \( P1 \) (Figure 4.2a) revealed that elastic properties dominated over viscous losses (storage modulus \( G' > \) loss modulus \( G'' \) ) over a wide range of oscillation frequencies. However, if the same polymer \( P1 \) was heated to 100°C and rapidly cooled down to room temperature with liquid nitrogen, the TTS master curve
displayed a liquid-like behavior of H-bonded polymer P1 at low frequencies where loss modulus $G''$ exceeded storage modulus $G'$ (Figure 4.2b). The fact that the polymer P1 with the same chemical composition had temperature controlled response to oscillatory shear stress is indicative of an essentially different hierarchy of the supramolecular architecture. We assigned these architectures as crystalline (P1-X) and melt (P1-M) states of polymer P1 (Figure 4.2a and 4.2b).

![Figure 4.2. Time-temperature superposition (TTS) curves (T_{ref} = 20°C) of a) crystalline state of polymer P1-X, b) melt state of polymer P1-M, c) P2, and d) metallopolymer Fe-L4. Storage modulus is shown as full blue circles, loss modulus as empty green circles, and complex viscosity as red triangles](image)

To better understand the influence of the multiple hydrogen-bonding stickers on the formation of these two different states in polymer P1, the additional H-bonded supramolecular polymer P2 with the same urethane stickers, but without possibility to form Tr-Tr H-bonding
interactions (Figure 4.1c) was prepared for comparison. The TTS master curve of P2 (Figure 4.2c) displayed oscillatory shear response similar to P1-M rather than P1-X. Thus, both P1-M and P2 revealed TTS curves consistent with viscoelastic polymer melts with a clear crossover between G' and G'' in accordance with their transient hydrogen-bonding cross-links, whereas the P1-X state behaved as a permanently cross-linked covalent network despite being supramolecular polymer.

The metallopolymer Fe-L4 with Fe(II)-phenanthroline metal-coordination bonding revealed typical oscillatory shear response (TTS master curve) for energy dissipative materials (Figure 4.2d) with a crossover point at \((3 \pm 1)10^{-3} \text{ rad s}^{-1}\).

### 4.3.3 Detailed characterization of supramolecular thermoplastic P1

For a better understanding how differences in the assembly of hydrogen bonding motifs in the supramolecular polymers govern the mechanical properties, we carried out FT-IR measurements on the polymer films. The FT-IR spectrum of the polymer P2 with only UT-UT interactions possible revealed broad signals centered at 3332 cm\(^{-1}\) and 1709 cm\(^{-1}\) assigned to H-bonded N-H stretching and H-bonded C=O stretching modes of the urethane fragment, respectively (Figure 4.3). The infrared spectrum of P1-X showed a much sharper N-H stretching mode at 3332 cm\(^{-1}\) compared to the one in P2 spectrum and a sharp C=O stretching signal centered at 1700 cm\(^{-1}\). This \(\sim 10 \text{ cm}^{-1}\) energy difference between the C=O stretching of P1-X and P2 is indicative of the formation of regular well-ordered hydrogen bonding network in P1-X state.\(^{50-52}\) Two new signals centered at 3435 cm\(^{-1}\) and 3258 cm\(^{-1}\) in the P1-X state correspond to vibration of free and hydrogen bonded N-H of the \textit{sym}-triazine respectively.\(^{53-55}\) Analysis of the infrared absorption profile of the P1-M state showed non-ordered urethane and \textit{sym}-triazine
hydrogen bonding motifs as well as a significant contribution of free urethane fragments (1738 cm\(^{-1}\) C=O vibration).

Figure 4.3. FT-IR spectra of P1-X (blue), P1-M (red), and P2 (orange)

In order to support FT-IR and rheology data that suggested the presence of a well-ordered hydrogen bonding network in the P1-X polymer, we performed differential scanning calorimetry (DSC) and powder x-ray diffraction (PXRD) measurements. The DSC trace of the solution cast polymer P1 (Figure 4.4a) showed an endothermic peak centered at 85°C, which was assigned to a phase transition between the well-ordered crystalline hydrogen-bonding network (P1-X) and the melt state (P1-M). The second heating cycle of the P1 polymer as well as P2 polymer, however, did not reveal such a characteristic signal at the DSC curve what correlates with viscoelastic nature of both P1-M and P2 polymer and solid-like behavior of the P1-X polymer. It should be noted that both P1 and P2 H-bonding polymers displayed a glass transition temperature at -49°C on the DSC traces, which corresponds to the soft phase formed by the poly(ethylene-co-butylene) segments. Powder X-ray diffraction (PXRD) measurements also supported the presence of the crystalline domains in the P1-X state (Figure 4.4b).
**P1-X** polymer at 110°C and rapid cooling with liquid nitrogen, however, erased these small features on the PXRD pattern centered at $2\theta=19.2^\circ$ and $2\theta=21.5^\circ$ and left only amorphous halo.

![Figure 4.4](image.png)

Figure 4.4. a) Differential scanning calorimetry traces of **P1-X** (blue), **P1-M** (red), and **P2** (orange) polymers. b) Powder X-ray diffraction patterns of **P1-X** (blue) and **P1-M** (red) supramolecular polymers

To further investigate the influence of supramolecular network architecture on the mechanical properties of the materials, step-stress relaxation experiments were performed. After stress was applied, both **P1-M** and **P2** polymer melts relaxed over time since their reversible hydrogen bonding cross-links can be separated, followed by diffusion in the polymer matrix, and finally locating a new associative partner (Figure 4.5a). This leads to a stress-induced relaxation, and a detailed discussion of the theoretical insights of such results is available in the literature.56–58

In comparison, **P1-X** with totally different hierarchy of the supramolecular architecture (ordered hydrogen bonding network in **P1-X** versus disorder in **P1-M** and **P2**) inhibits the stickers to diffuse away and forces them to reconnect back with the old associative partner, which prevents formation of a new supramolecular network. Because this hydrogen-bonding pair breaks and re-forms many times without possibility to be separated in the **P1-X** polymer, the
strain energy cannot dissipate, and the observed relaxation time becomes extremely long (Figure 4.5a). Remarkably, such a long relaxation time is more characteristic for permanent covalent networks rather than for supramolecular polymer assemblies.

![Diagram](image)

Figure 4.5. a) Step strain relaxation curves at 15°C of P1-X (blue), P1-M (red), and P2 (orange) polymers. b) Tan(delta) (yellow triangles), storage G’ (blue solid circles) and loss G’’ (green empty circles) moduli recovery curves from P1-M to P1-X state over time upon heating at 60°C.

The transition between the semi-crystalline P1-X and melt P1-M states is reversible and can be achieved in both directions. As previously described, melting and rapid cooling of the P1-X polymer resulted in the viscoelastic material P1-M. The P1-X state, however, can be recovered back upon slow heating of the melt state at 60°C for 3-4 hours (Figure 4.5b). At this temperature, the spontaneously formed hydrogen bonding network undergoes continuous rearrangement, allowing the urethane and triazine stickers to find their self-complementary associative partners and reform a well-organized supramolecular network. In other words, the P1-X can be assigned as a thermodynamic and P1-M as a kinetic “product”.

4.3.4. Interaction of polymers and light

In order to investigate interaction of polymers with light, we prepared a number of P1-X films with different dyes dispersed. The samples were damaged with well-defined, intersecting
cuts with a razor blade, and then irradiated with 455 nm continuous wave (CW) laser radiation (OEM laser system with 455 nm band pass notch filter) for 30 sec at different laser powers. The output powers and corresponding laser flux densities are listed in Table 4.1.

Table 4.1. Correlation between 455 CW laser output power and its flux density. The laser beam diameter \( d = 2.2 \) mm

<table>
<thead>
<tr>
<th>Output power [mW]</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux [W cm(^{-2})]</td>
<td>2.63</td>
<td>3.95</td>
<td>5.26</td>
<td>6.58</td>
<td>7.89</td>
<td>9.21</td>
</tr>
</tbody>
</table>

Once excited, the chromophores relax back to the ground state via non-radiative mechanisms that generate heat. The heat generated in the polymers increases the temperature of the material at the irradiation spot, which was measured using a FLIR C2 Compact Thermal Imaging System. We used optical healing as a visualization tool to observe when the stimulus (light) caused changes in the material. Specifically, the photo-thermal heating of the P1-X polymer molt the material when the certain temperature threshold of \( \sim 70-75^\circ\text{C} \) was reached, which correlated to the DSC curve of P1-X. The melting of the P1-X polymer occurred only at the radiation area creating a “well” with some invagination involved (see Figure 4.6c), which shows how precise spatial control of the material melting could be achieved when using light as an external stimulus.

For more accurate estimates of the amount of photons absorbed by each polymer film with a dispersed chromophore, we used a modified formula for spectral overlap (S.O.) which depends on the area overlap between the chromophore absorbance and laser excitation profiles (equation 4.1).
Equation 4.1 Spectral overlap integral between chromophore and laser excitation profiles

\[ J(\lambda) = \int_{0}^{\infty} A_p(\lambda) \lambda^4 F_{\text{laser}}(\lambda) d\lambda \]  

where \( J(\lambda) \) is a spectral overlap, \( A_p \) is absorbance of the polymer film, \( \lambda \) is wavelength, \( F_{\text{laser}} \) is the laser output spectrum normalized to an area of 1.

We compared the differences in photo-thermal effect between physically blended Fe-phen chromophore into the hydrogen-bonded polymer (P1-Fe-phen) versus the metallopolymers Fe-L4, where the Fe-phenanthroline moiety was covalently attached to the supramolecular system (Figure 4.6c and 4.6d). Despite some differences in the absorption profiles of P1-Fe-phen and Fe-L4 (Figure 4.6a), the spectral overlap with the CW laser excitation profile is similar for both polymer films (Table 4.2). As seen from Figures 4.6b, both P1-Fe-phen and Fe-L4 films show linear increase in temperature generated with increase in laser radiation power. Moreover, regardless of the chromophore being part of the supramolecular system or not, both polymers P1-Fe-phen and Fe-L4 generated about the same amount of heat at each laser excitation power. This shows that the chromophore does not have to be chemically incorporated into the material; simply physical blending would give the same photo-thermal effect. Despite no differences in the heat generated between the two Fe-phen systems (either physically blended chromophore or covalently attached to the supramolecular network), some differences in the healing were observed (Figure 4.6c and 4.6d). Supramolecular metallopolymers Fe-L4 partially depolymerizes upon heating which was observed as a gradual disappearance of the scratched area with accordance to its viscoelastic behavior, instead of the “well” seen when the chromophore was not part of the network (Figure 4.6c and 4.6d). The supramolecular network of
the hydrogen-bonded polymer $\mathbf{P1-X}$ resists moderate heating until melting region of $\sim$70-75°C is reached causing the whole H-bonded network to collapse, and polymer flows and fills the damaged area.

Table 4.2. Absolute spectral overlap (S.O.) values for the set of polymers with different dyes and metallopolymer $\mathbf{Fe-L4}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>P1-Fe-phen</th>
<th>P1-MY</th>
<th>P1-Ru-bpy</th>
<th>P1-Au-NPs</th>
<th>Fe-L4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute S.O.</td>
<td>$2.25\times10^{10}$</td>
<td>$1.97\times10^{10}$</td>
<td>$2.38\times10^{10}$</td>
<td>$1.90\times10^{10}$</td>
<td>$2.27\times10^{10}$</td>
</tr>
</tbody>
</table>
Figure 4.6. a) Absorbance of the P1-Fe-phen and Fe-L4 films. b) Temperature generated at the 455 nm CW laser radiation as a function of excitation power. Error bars are omitted for clarity. Standard deviation for each point on the graph vary within 2-3°C. Optical images of c) P1-Fe-phen and d) Fe-L4 mechanically damaged film irradiated at various excitation powers. The black scale bar is 400 μm.
We also tested the nature of the chromophore on the optical healing (Figure 4.8), where the optical densities of the films at the maximum absorbance wavelength of the chromophores were approximately equal to each other (Figure 4.7a). We chose different chromophores to cover the major classes of dyes. Namely, Au-NPs which absorb light due to localized surface plasmon resonance, metanil yellow (MY) which is an organic dye with a S₀→S₁ electronic transition, and tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) sulfate (Fe-phen) and bis(2,2'-bipyridine)-(5-bromophenanthroline)ruthenium bis(hexafluorophosphate) (Ru-bpy) which are both inorganic dyes with a metal-to-ligand charge transfer (MLCT) excited state transition. As shown in Figure 4.7c, we measured the temperature changes with different light excitation powers for these different chromophores. All of these showed a linear relationship between laser power and temperature generated, regardless of the type of chromophore. It should be noted that Ru-bpy showed some leveling off with the temperature increase at higher excitation powers, and this was attributed to the visible photo-bleaching of the materials (Figure 4.SF2).

![Figure 4.7](image-url)  
Figure 4.7. a) Absorbance of the P1-X films with different chromophores. b) Temperature generated at 100 mW radiation power vs % of S.O. c) Temperature generated at the 455 nm CW laser radiation as a function of excitation power. Error bars are omitted for clarity. Standard deviation for each point on the graph vary within 2-3°C.
Figure 4.8. A set of optical microscope images of P1- a) metanil yellow, b) Fe-phen, c) Ru-bpy), d) Au-NPs, and e) Fe-L4 mechanically damaged polymer films irradiated at 100, 150, 200, 250, 300, 300, and 350 mW. The black scale bar is 400 μm. The last image in the series shown as an example of IR-camera image taken at the highest radiation power.
Control experiments without chromophore incorporated into the either of polymers showed no temperature increase upon light irradiation even at 9.2 W cm\(^{-2}\) excitation power (Figure 4.SF3). In addition, we calculated the spectral overlap of the chromophore absorbance in the different materials according to Equation (4.1) (Table 4.2).

![Graphs showing absorbance and temperature generation](image)

**Figure 4.9.** a) Absorbance of the P1-X-Au films with different film thickness. b) Temperature generated at 100 mW radiation power vs % of S.O for molecular chromophores and the set of Au-NPs films. Error bars are omitted for clarity. Standard deviation for each point on the graph vary within 2-3°C.

Plotting the temperature changes with spectral overlap at 100 mW excitation power (before the Ru-bpy is photo-bleached), we observed a linear correlation, where those chromophores with a larger spectral overlap showed more heat generation (Figure 4.7b), with the exception for Au-NPs. Au-NPs, at the first glance, showed larger heat generation than the MY despite lower spectral overlap with the laser irradiation profile. However, when the temperature-spectral overlap correlation for Au-NPs was expanded, the molecular dyes revealed much steeper slope and greater temperature build-up with the spectral overlap increase (Figure 4.9). This observation is still unclear and will be thoroughly investigated in the future publications.
Figure 4.10. a) Absorbance of the P1-X-Au films. b) Temperature generated at 100 mW radiation power vs % of S.O. c) Temperature generated at the 455 nm CW laser radiation as a function of excitation power. Error bars are omitted for clarity. Standard deviation for each point on the graph vary within 2-3°C
To correlate optically induced healing with film thickness and, as a result, different optical densities of the samples, we prepared a series of P1-X supramolecular polymer films with dispersed Au-NPs as a chromophore (Figure 4.10a and 4.11). To investigate the heat generated during the irradiation process at different excitation powers (Figure 4.10c), we used the IR camera to image the polymer films. As shown in Figure 4.10b, there are two regimes for temperature recorded on the materials upon light radiation. First, a linear correlation of heat generation and spectral overlap was observed for the absorbance less than unity at the excitation wavelength (Figure 4.10b). In the second regime, the dependence of absorbance vs spectral overlap was reaching a plateau. The calculated spectral overlap values are available in Table 4.3.

Table 4.3. Absolute spectral overlap (S.O.) values for the set of P1-X-Au polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>(P1\text{-}\text{Au Abs}=0.16)</th>
<th>(P1\text{-}\text{Au Abs}=0.39)</th>
<th>(P1\text{-}\text{Au Abs}=0.62)</th>
<th>(P1\text{-}\text{Au Abs}=0.76)</th>
<th>(P1\text{-}\text{Au Abs}=1.24)</th>
<th>(P1\text{-}\text{Au Abs}=1.68)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute S.O.</td>
<td>(7.02\times10^9)</td>
<td>(1.71\times10^{10})</td>
<td>(2.74\times10^{10})</td>
<td>(3.36\times10^{10})</td>
<td>(5.65\times10^{10})</td>
<td>(7.52\times10^{10})</td>
</tr>
</tbody>
</table>
Figure 4.11. A set of optical microscope images of P1-X-Au mechanically damaged polymer films with different optical densities irradiated at 100, 150, 200, 250, 300, 300, and 350 mW. The black scale bar is 400 μm. The last image in the series shown as an example of IR-camera image taken at the highest radiation power.
4.4. Conclusions

Using a modular synthetic method, we were able to create H-bonded and metal coordination supramolecular materials with unique mechanical properties. Particular interesting is the polymer whose mechanical properties can be modified though temperature control of supramolecular assembly. The amorphous state, where urethane and triazine hydrogen bonding units are randomly bound together or even have no associative partner at all, revealed characteristic for energy dissipative materials oscillatory shear stress response. In the semi-crystalline state, most of the hydrogen bonding motifs are bound to their corresponding self-complementary associative partner to form well-ordered supramolecular network. This polymer was used as a platform for detailed investigation of photohealing effect.

Comparison of the photo-self-healing and photo-thermo-dynamics of these supramolecular materials provided some answers to our initial question: Is it necessary to include the chromophore as part of the supramolecular structure to create light-responsive materials? The answer: Not really. Our results showed that regardless of the type of chromophore (organic, inorganic, nanoparticle), with sufficient spectral overlap of the chromophore absorbance and laser output, enough heat can be generated to create local healing of the supramolecular network. As expected, there was a linear trend observed between the heat generated and the spectral overlap for most chromophores, even if it was part of the supramolecular network. There was one exception, however. Materials with Au nanoparticles showed more heat generated due to excitation in the plasmonic excited state as opposed to the electronic excited states of the other chromophores. This provides yet another example of the enhanced heat generation observed with Au nanoparticles, showing that when the chromophore has different photophysics compared to the typical electronic excited state photophysics, this translated to changes in the bonding
dynamics – and thus mechanical properties of the materials. In addition, the self-healing of the materials after light irradiation was affected by the nature of the chromophore. A more continuous healing was observed for materials with the chromophore integrated into the supramolecular network as opposed to the well-like healing observed for semi-crystalline materials with the chromophore just incorporated into the polymer.

These results provide important insights into how light irradiation and photophysics affect the bonding dynamics and mechanical properties of supramolecular materials. Specifically, these results show how one can tune the photo-response and self-healing of different materials simply by tuning the type of supramolecular bonding motifs, the amounts and types of chromophore, and controlling the laser irradiation timing and intensity.

4.5 Supporting Information

Figure 4.SF1. a) UV-Vis absorption spectra of polymer (3) in CHCl₃ over addition of Fe(OTf)₂ CH₃CN solution. b) Absorbance of 315 nm (violet) and 515 nm (green) bands versus equivalents of Fe(OTf)₂ added confirms formation of 3:2 Fe-L₄ metallopolymer.
Figure 4.SF2. Photo bleach of P1-Ru-bpy polymer after 250 mW 455 nm CW laser radiation.

Figure 4.SF3. Light radiation with 455 nm CW laser at 350 mW radiation power of P1-X, P1-M, and P2 alone show no photohealable effect and no temperature increase at the radiation area.
Figure 4.SF4. UV-Vis absorption spectra of 50-75 μL stock solutions of metanil yellow, [Fe(tmphen)₃]SO₄, [Ru(5-Br-phen)(bpy)₂](PF₆)₂ in 3mL methanol and Au-NPs in chloroform.

Figure 4.SF5 a) STEM image and b) size distribution histogram show average size of synthesized gold nanoparticles to be 6.4±1.2 nm. Scale bar: 20 nm.

4.6. References


(31) Balkenende, D. W. R.; Olson, R. A.; Balog, S.; Weder, C.; Montero de Espinosa, L.


5.1. Abstract

When designing photoresponsive materials, the impact of a polymer host matrix on the photophysical and photochemical properties of chromophores can be dramatic and advantageous for correlating macromolecular properties. Some compounds possess changes in their photophysical response with variation in the surrounding media (e.g. crystalline glass vs. solution). This study demonstrates how changes in the excited state dynamics of $[\text{Cu(dmp)}_2]^+$, where dmp = 2,9-dimethyl-1,10-phenanthroline, is used to quantitatively probe the viscosity of the surrounding polymer matrix. A correlation of both excited state lifetime and photoluminescence emission wavelength on viscosity was observed in different supramolecular materials containing $[\text{Cu(dmp)}_2]^+$. These effects were attributed to restricted photoinduced structural distortion of the Cu(I) complex as the polymer matrix hardened. This photoluminescence sensor features a greater dynamic range for viscosity sensing (6 orders of magnitude) and displayed larger changes in lifetime response with respect to typical organometallic mechanosensitive probes.

5.2. Introduction

With growing interest in developing light-responsive materials and mechanical stress responsive probes, a fundamental understanding of the photophysical properties of mechanoresponsive compounds in viscous environments of polymers is of significant importance. Luminescent mechanosensitive probes – those with photophysical and photochemical properties that depend on mechanical properties, e.g. viscosity, of the surrounding
media – can be used as real-time reporters of physical changes of the immediate environment. The main design principles of such molecules are based on their ability to accommodate two distinct states with dramatically different photophysical properties (such as emission spectrum and lifetime) via twisting or rotating along specific chemical bonds.\textsuperscript{1–6} A conjugated zinc-porphyrin dimer is one example of such molecular motors with restricted rotation along an ethyne bridge that leads to red-shifted emission of the planar conformation with respect to that detected for the twisted conformation.\textsuperscript{7–9} In low viscosity environments, the twisted excited state conformation emits near 710 nm that converts into lower-energy excited planar conformer with a maximum at \( \sim 790 \) nm. In high viscosity environments, however, this twisting process is inhibited and the photoluminescence spectrum becomes dominated by the twisted conformer. At relatively low viscosities (1-10 Pa s), this leads to saturation or leveling off of both excited state lifetime and ratio of emission maxima between the planar and twisted conformers.\textsuperscript{10–12} We anticipated that the unique excited state dynamics of copper(I) \textit{bis}-phenanthroline metal-to-ligand charge transfer (MLCT) complexes may circumvent this limitation. Upon excitation, the ground state pseudo-tetrahedral geometry undergoes fast (<1 ps) distortion to achieve more flattened conformation and preserves this distorted geometry until relaxation back to the ground state occurs.\textsuperscript{13,14} Previous studies on the photoluminescent properties of copper(I) MLCT complexes revealed excited state lifetime lengthening and blue-shifted photoluminescence with purposefully designed coordination environments inhibiting this distortion.\textsuperscript{15}

The photophysical properties of Cu(I) MLCT excited states have been studied both in solution and in the solid state, however their excited state dynamics in viscous polymer environments remain largely unexplored. Herein, we utilized time-resolved pump-probe techniques to investigate the photophysical properties of the \([\text{Cu(dmp)}_2]\text{PF}_6\) (dmp = 2,9-
dimethyl-1,10-phenanthroline) in numerous supramolecular hydrogen bonding polymers featuring a range of viscosities. The correlation between the excited state lifetimes and mechanical properties of the supramolecular polymers is discussed. The issues associated with excited state oxygen quenching and exciplex formation within the hydrogen bonding motifs of the supramolecular polymers are also considered.

Scheme 5.1 $^{3}$MLCT lifetime enchantment of [Cu(dmp)$_2$]$^+$ chromophore in viscous polymer matrix versus DCM solution

5.3. Results

5.3.1. Materials

To prepare the materials, four different hydrogen bonding supramolecular polymers with end-capping urethane-based H-bonding “stickers” (Scheme 5.2b) were synthesized with variable viscosity due to the changes in the H-bonding motif (Figure 5.SF1). The selected polymer backbone was low molecular weight (3000 Da) hydrogenated poly(ethylene-co-butylene) (HLBH-P 3000) to enhance phase segregation in the bulk and facilitate network assembly (Scheme 5.2a). H-bonding polymers P2 and P4 were viscoelastic materials with cross-over frequencies at $3\times10^{-2}$ rad s$^{-1}$ and 10 rad s$^{-1}$, respectively (Figure 5.1). Polymers P3 and P5 containing only one urethane sticker per terminus, however, were viscous liquids providing no significant contribution to overall elastic properties (Figure 5.1).
Using the obtained set of polymers and their various combinations, materials were generated with a wide spectrum of mechanical properties. Mixtures of P2/P3 and P4/P5 polymers with 70/30, 50/50, and 30/70 weight percent (wt%) ratios were prepared to vary the viscosity of the final supramolecular polymeric material. Mixtures of P2/P3 polymers at different ratios covered a range of zero-shear viscosities ($\eta^*$) from $5 \times 10^7$ to $2 \times 10^4$ Pa s, while P4/P5 mixture covered the range of $3 \times 10^4$ to $2 \times 10^2$ Pa s (Figure 5.7a).
Scheme 5.2 a) Schematic depiction of supramolecular polyurethane (PU) assembly. End-capping groups shown as purple boxes. b) End-capping groups of supramolecular PU. H-bonding motifs are highlighted in orange boxes.

The \([\text{Cu(dmp)}_2]^{PF_6}\) chromophore was encapsulated within the supramolecular polymers during the film casting process. Comparison of the UV-Vis absorption spectra of the Cu(I) complex-containing polymer films Cu-PX (where X is 2-5) is presented in Figure 5.2a. Ground state spectra of Cu-P2 and Cu-P4 films revealed metal to ligand charge transfer (MLCT) band with a maximum that corresponded to the absorption of \([\text{Cu(dmp)}_2]^{PF_6}\) in CH2Cl2 solution (λ_max = 458 nm). Both Cu-P2 and Cu-P4 composites were clear films with no significant background scattering. On the other hand, the Cu-P3 and Cu-P5 materials with one urethane binding group per terminus were opaque (high background scattering) with red-shifted absorption maxima centered at 480 nm. Such a red shift in the absorbance peak is indicative of the Cu(I) complex experiencing a change in the polarity of its environment (Figure 5.SF2). Addition of different amounts of P2 and P4 to these preformed materials (even at 30 wt%), however, significantly increased the solubility of the Cu(I) complex in these materials causing a blue-shift of the
absorption maximum back to 458 nm (Figure 5.2b). These changes in solubility, together with the shifts in absorbance, indicated that it is the hydrogen bonding moieties that maintained the inorganic complex soluble in the polymers.

Figure 5.2 a) Steady-state absorption spectra of [Cu(dmp)₂]⁺PF₆ complex in CH₂Cl₂ solution (red), Cu-P2 (blue), Cu-P3 (green), Cu-P4 (orange), and Cu-P5 (black) polymer films. b) UV-Vis spectra of [Cu(dmp)₂]⁺ in P2:P3 at different ratio (light blue), and P4:P5 different ratio (grey) films revealed absorption maximum that corresponded to the one in DCM solution

5.3.2. Excited state dynamics of [Cu(dmp)₂]⁺ in solution and polymer film

In solution, the dynamics of the [Cu(dmp)₂]⁺ after photoexcitation have been well characterized. The ground state d¹⁰ electronic configuration of the Cu(I)-bis(diimine) motif prefers a pseudotetrahedral coordination environment. Upon excitation to the MLCT excited state (Figure 5.3), the Cu(I) metal center formally oxidizes to a Cu(II) d⁹ configuration that favors a tetragonally distorted environment and transiently reduces the phenanthroline-based ligand to a radical-anion species (Figure 5.3). In sub-picosecond timescales after the excitation, the molecule undergoes a significant Jahn-Teller (J-T) structural distortion that involves flattening of the molecular geometry of this complex followed by singlet-triplet intersystem crossing (ISC).
Due to the structural rearrangements that occur during photoexcitation and relaxation of the excited state, it is expected that incorporation of the $\text{[Cu(dmp)$_2$]PF}_6$ complex into a material would lead to changes in the excited state dynamics. It is unknown, however, specifically how the polymer matrix affects the photophysics. In order to understand how the polymer mechanical properties play a role in the photophysics and photochemistry of this chromophore we investigated the excited state lifetime of the $\text{[Cu(dmp)$_2$]PF}_6$ incorporated into different P2-P5 materials featuring notable changes in mechanical properties.

The transient absorption difference spectra of $\text{[Cu(dmp)$_2$]PF}_6$ were collected using a LP980 laser flash photolysis system (Edinburgh Instruments) in aerated DCM solution and polymer P2 film at selected delay times following 420 nm excitation (Figure 5.4a and 5.4b).
The difference spectrum revealed the MLCT ground state bleach centered around 450 nm\textsuperscript{17–19} as well as characteristic positive absorption features of transiently formed phenanthroline radical-anion species with peaks at 350 nm and as a dual-peak band in the 490-640 nm spectrum region with maxima at ~530 and 565 nm in both DCM solution and the supramolecular polymer P2. Probing the transient absorbance (TA) difference spectra at a 400 ns delay revealed that all transient species in aerated DCM solution had already decayed, while there was signal detected in the polymer film, indicating a characteristic increase in excited state lifetime. In order to quantify the observed lifetime difference, kinetic traces were measured at 450 and 565 nm and
adequately modeled using single exponential functions. The \([\text{Cu(dmp)}_2]^+\) lifetimes in aerated DCM solution were 62 ± 2 ns at both probe wavelengths, implying that the ground state recovery 450 nm band and phenanthroline radical-anion 565 nm decay kinetic traces originated from the same MLCT excited state and returned to the ground state. The lifetimes of \([\text{Cu(dmp)}_2]^+\) determined in the H-bonding polymer P2 materials were 210 ± 4 ns, which was almost 3.5 times longer than that determined in aerated DCM solution (Figure 5.4c and 5.4d). Equivalent 450 and 565 nm decay kinetics suggested that even in the viscoelastic media of the polymer there were no competing excited state deactivation processes. Quantitatively, the matched MLCT photoluminescence lifetimes and transient absorption time constants of the phenanthroline radical-anon transients indicated that these decay processes originated from the same MLCT excited state (Table 5.1).
Table 5.1 Summarized transient excited state lifetimes under Argon protection ($\tau_{\text{Argon}}$), in air ($\tau_{\text{Air}}$), and emission lifetime in air ($\tau_{\text{em,Air}}$) for the complete set of the supramolecular polymers P2-P5 and their corresponding mixtures

<table>
<thead>
<tr>
<th>Sample</th>
<th>P2</th>
<th>P2/P3 70/30</th>
<th>P4</th>
<th>P2/P3 50/50</th>
<th>P2/P3 30/70</th>
<th>P4/P5 70/30</th>
<th>P4/P5 50/50</th>
<th>P4/P5 30/70</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{\text{Argon}}$ (ns)</td>
<td>227</td>
<td>202</td>
<td>197</td>
<td>190</td>
<td>184</td>
<td>183</td>
<td>169</td>
<td>149</td>
</tr>
<tr>
<td>$\tau_{\text{Air}}$ (ns)</td>
<td>210</td>
<td>185</td>
<td>179</td>
<td>175</td>
<td>169</td>
<td>164</td>
<td>153</td>
<td>135</td>
</tr>
<tr>
<td>$\tau_{\text{em,Air}}$ (ns)</td>
<td>207</td>
<td>187</td>
<td>182</td>
<td>175</td>
<td>172</td>
<td>167</td>
<td>149</td>
<td>137</td>
</tr>
</tbody>
</table>

The more planar excited state geometry of Cu(I)-diimine complexes is susceptible to energy-wasting exciplex formation with donor solvents or coordinating counterions.$^{16,20–22}$ Any formed five-coordinate copper-species undergo fast non-radiative decay and, as a consequence, significantly shorten the $^3\text{MLCT}$ excited state lifetime. In order to rule out the possibility that the urethane and triazine end-capped supramolecular polymers quench the excited state, we prepared a series of Cu-P2 polymer films with different loadings of $[\text{Cu(dmp)}_2]^+$. As shown in Figure 5.5, the MLCT lifetime and emission maximum are independent on the Cu(I) complex loading into Cu-P2 materials within the tested 0.5-4.5 wt% range. According to the Stokes-Einstein equation, the diffusion coefficient is inversely proportional to the viscosity of surrounding media ($D \sim 1/\eta$); thus, the viscous supramolecular polymer surrounding matrix significantly lowers the diffusion constant for coordinating urethane and triazine moieties with the excited Cu(I) complex and would help suppress any potential bimolecular quenching deactivation pathway.
The longest reported lifetime for \([\text{Cu(dmp)}_2]^+\) in organic solvent is 90 ns, observed in non-coordinating DCM argon saturated solution, where all possible bimolecular quenching mechanisms were suppressed (Figure 5.SF3). The observed 210 ns lifetime of Cu-P2, however, cannot be simply explained by only decreasing quenching rates in the viscous polymer environment. In general, the Cu(I) complexes most resistant to structural distortion feature the longest excited state lifetimes. Substitution at 2,9-positions of the phenanthroline ligand as well as methylation of 3,8-positions have been found to restrict the excited state J-T distortion and effectively lengthen the excited state lifetime. In order to evaluate if the viscous surrounding media of the supramolecular polymer P2 impacts the excited state geometrical changes in a similar fashion to steric congestion, the photoluminescence properties in materials with different mechanical properties were investigated. \([\text{Cu(dmp)}_2]^+\) exhibits weak (quantum yield $\phi = 0.04\%$ in degassed DCM), broad, structureless photoluminescence with a significant Stokes shift. The observed Stokes shift is proportional to the degree of the flattening distortion exhibited by the excited state. As presented in Figure 5.6, the \([\text{Cu(dmp)}_2]^+\) photoluminescence
maximum was blue-shifted from 705 nm in DCM solution to 665 nm in the polymer P2. Thus, minimization of the dihedral angle opening between two phenanthroline ligands in the excited state in the highly viscous (\(\eta = 5 \times 10^7\) Pa s) polymer P2 results in blue-shifted photoluminescence relative to DCM and, as a consequence, lengthens the MLCT excited state lifetime.

![Normalized time-gated (20 ns delay) emission spectra after 420 nm excitation of [Cu(dmp)2]PF6 in DCM solution and P2 (dark blue), P2:P3 at different ratio (light blue), P4 (orange), P4:P5 different ratio (grey). b) A linear correlation between phosphorescence maximum and logarithm viscosity of supramolecular polymers. More red-shifted emission is detected for less viscous surrounding media.](image)

In order to correlate excited state lifetimes with the bulk properties of the investigated materials, a series of hydrogen-bonding supramolecular polymers and their mixtures to cover almost 6 orders of magnitude range of zero-shear viscosities were prepared (Figure 5.7a). For all polymers, a linear relationship was observed between increasing MLCT excited state lifetime and logarithm of the viscosity of the surrounding polymer matrix (Figure 5.7b). This correlation suggested that with a 10 times increase in viscosity of the supramolecular polymer, the excited state lifetime (\(\tau\)) lengthens on average by 13 ns. There was also a relationship between the [Cu(dmp)2]^+ emission maximum and the mechanical properties of the supramolecular polymers (Figure 5.6). In general, the photoluminescence spectra were blue-shifted in the more viscous polymers, implying that there was less J-T structural distortion. The correlation between excited
state lifetime and the wavelength of the emission has been previously observed in similar charge-
transfer osmium(II) phenanthroline complexes in agreement with the energy gap law.31,32

Figure 5.7 a) Complex viscosities at different shear rates obtained from TTS curves. c) Linear
correlation of $^3$MLCT excited state lifetime and $\log(\eta^*)$

Oxygen is known to quench the $[\text{Cu(dmp)}_2]\text{PF}_6$ excited state via electron and energy
transfer mechanisms, which shortens the excited state lifetime. For instance, the $[\text{Cu(dmp)}_2]\text{PF}_6$
lifetime in aerated DCM solution is 62 ns (Figure 5.4c), while in inert gas protected media the
lifetime increases up to 90 ns (Figure 5.SF3). In order to investigate if the hydrogenated
poly(ethylene-co-butylene)-based supramolecular polymer protects the Cu(I) complex from
oxygen quenching, we have performed TA measurements on Cu-PX materials (where X is 2-5)
under Argon protection. On average, a 10-15% lifetime enhancement was observed for all tested
materials in the deaerated environment (Figure 5.7b). The linear increase of MLCT lifetime with
increases in viscosity of the supramolecular polymers was preserved in aerated environments as
well. This observation additionally supports that the lifetime of the $[\text{Cu(dmp)}_2]^+$ complex
lengthens due to tuning the excited state distortion by the viscous polymer surrounding, and not
simply due to changes in local oxygen concentration or quenching by the polymer side chains.
5.4 Conclusions

In summary, this work demonstrates how restricted photoinduced conformational changes in [Cu(dmp)$_2$]$^+$ can be utilized to report on mechanical properties of supramolecular polymers. A linear correlation between excited state lifetime and photoluminescence maxima of [Cu(dmp)$_2$]$^+$ as a function of the viscosity of surrounding media was found. The drawback of [Cu(dmp)$_2$]$^+$, is its low emission quantum yield, which significantly limits application of conventional fluorescence imaging techniques to detect changes in bulk materials. This limitation can be overcome by utilizing more sterically congested Cu(I) complexes featuring higher emission quantum yields. In addition, the [Cu(dmp)$_2$]$^+$ mechanophore showed a greater linear lifetime-viscosity regime and larger lifetime sensitivity per order of magnitude change in viscosity (13 ns vs 0.7 ps, respectively) compared to other organometallic mechanosensitive probes.$^{10-12}$

5.5 Supporting information

Figure 5.8 Pictures of supramolecular polymers P2 and P5. P2 forms self-standing film while P5 is viscous liquid.
Figure 5.SF2 Pictures of transparent Cu-P2 and opaque Cu-P5 composites with the same loading of $[\text{Cu(dmp)}_2]\text{PF}_6$ into the polymers

Figure 5.SF3 a) Transient absorption and b) emission kinetic traces of $[\text{Cu(dmp)}_2]\text{PF}_6$ in deaerated DCM. $\lambda_{\text{exc}} = 420$ nm

5.6 References


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