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Restricted Photoinduced Conformational Change in the Cu(I) Complex for Sensing Mechanical Properties

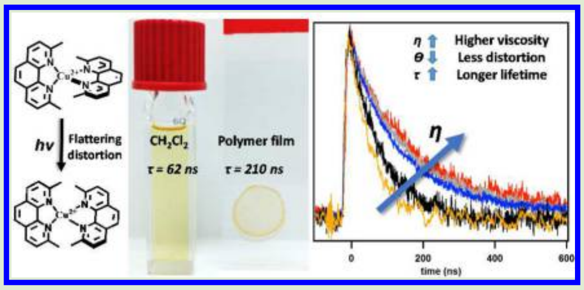
Anton O. Razgoniaev,*[†] Catherine E. McCusker,[‡,§] Felix N. Castellano,[‡] and Alexis D. Ostrowski*[†]

[†]Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States

[‡]Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States

Supporting Information

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 $[Cu(dmp)_2]^+$, where dmp = 2,9-dimethyl-1,10-phenanthroline, are 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 $[Cu(dmp)_2]^+$. 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.



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.[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.[7−9] In low viscosity environments, the twisted excited state conformation emits near 710 nm which converts into a lower-energy excited planar conformer with a maximum at ∼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.[10−12] We anticipated that the unique excited state dynamics of copper(I) bisphenanthroline metal-to-ligand charge transfer (MLCT) complexes may circumvent this limitation. Upon excitation, the ground state pseudotetrahedral geometry undergoes fast (<1 ps) distortion to achieve more flattened conformation and preserves this distorted geometry until relaxation back to the ground state occurs.[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.[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 $[Cu(dmp)_2]PF_6$ (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.

To prepare the materials, four different hydrogen bonding supramolecular polymers with end-capping urethane-based H-bonding "stickers" (Scheme 1b) were synthesized with variable viscosity due to the changes in the H-bonding motif (Figure

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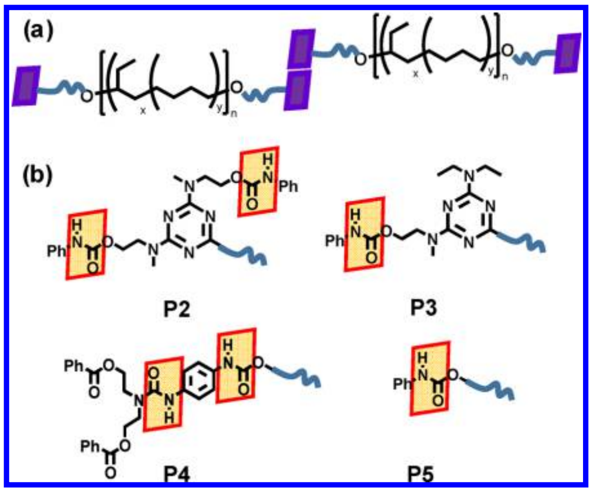
Scheme 1. (A) Schematic Depiction of Supramolecular Polyurethane (PU) Assembly[a] and (B) End-Capping Groups of Supramolecular PU[b]



[a]End-capping groups shown as purple boxes. [b]H-bonding motifs are highlighted in orange boxes.

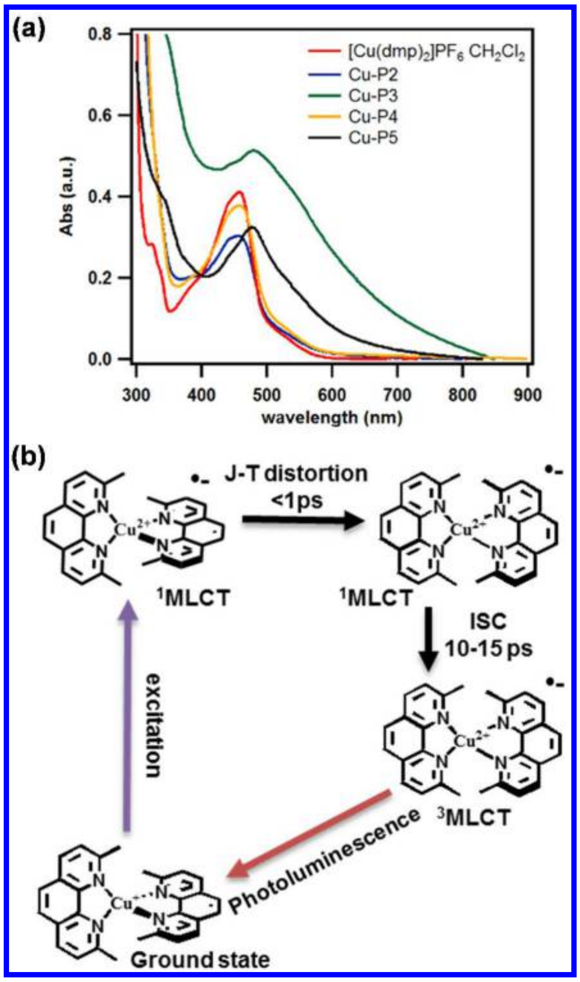


Figure 1. (a) Steady-state absorption spectra of the $[Cu(dmp)_2]PF_6$ complex in CH_2Cl_2 solution (red) and Cu−P2 (blue), Cu−P3 (green), Cu−P4 (orange), and Cu−P5 (black) polymer films. (b) Simplified excited state dynamics diagram of a Cu(I) diimine-based complex.

S15). 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 1a). H-bonding polymers P2 and P4 were viscoelastic materials with crossover frequencies at 3×10^{-2} rad s^{-1} and 10 rad s^{-1}, respectively (Figure S10). Polymers P3 and P5 containing only one urethane sticker per terminus, however, were viscous liquids providing no significant contribution to overall elastic properties (Figure S10). 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 wt % (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 (η^*) from 5×10^7 to 2×10^4 Pa s, while the P4/P5 mixture covered the range of 3×10^4 to 2×10^2 Pa s (Figures 3a and S10).

The $[Cu(dmp)_2]PF_6$ 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−P*X* (where X is 2−5) is presented in Figure 1a. Ground state spectra of Cu−P2 and Cu−P4 films revealed a metal to ligand charge transfer (MLCT) band with a maximum that corresponded to the absorption of $[Cu(dmp)_2]PF_6$ in CH_2Cl_2 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 and a decrease in the observed scattering in the absorbance spectra (Figure S11). 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 S16). 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. These changes in solubility, together with the shifts in absorbance, indicated that it is the hydrogen bonding moieties that maintained the inorganic complex solublility in the polymers.

In solution, the dynamics of the $[Cu(dmp)_2]^+$ after photoexcitation have been well characterized. The ground state d^{10} electronic configuration of the Cu(I)-bis(diimine) motif prefers a pseudotetrahedral coordination environment. Upon excitation to the MLCT excited state (Figure 1b), the Cu(I) metal center formally oxidizes to a Cu(II) d^9 configuration that favors a tetragonally distorted environment and transiently reduces the phenanthroline-based ligand to a radical-anion species (Figure 1b).[16] On subpicosecond time scales 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).[13,14]

Due to the structural rearrangements that occur during photoexcitation and relaxation of the excited state, it is expected that incorporation of the $Cu(dmp)_2^+$ 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 $[Cu(dmp)_2]^+$ incorporated into different P2−P5 materials featuring notable changes in mechanical properties (Figure S15).

The transient absorption difference spectra of $[Cu(dmp)_2]PF_6$ 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 2a and 2b). The difference spectrum revealed the MLCT ground state bleach centered around 450 nm[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 $[Cu(dmp)_2]^+$ 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 $[Cu(dmp)_2]^+$ 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. 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-anion transients indicated that these decay processes originated from the same MLCT excited state (Table S1).

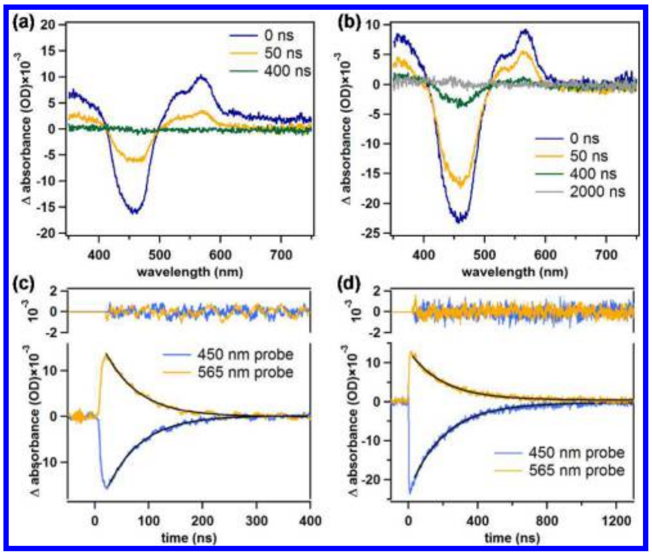


Figure 2. Transient absoprtion difference spectra of $[Cu(dmp)_2]PF_6$ in (a) areated DCM solution and (b) supramolecular polymer P2 film after 420 nm pulsed excitation. Delayed times provided in the legend. Panels (c) and (d) represent transient absorption kinetic traces of $[Cu(dmp)_2]PF_6$ in aerated DCM and polymer P2, respectively.

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 nonradiative decay and, as a consequence, significantly shorten the ^{3}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 $[Cu(dmp)_2]^+$. As shown in Figure S12, the MLCT lifetime and emission maximum are independent of 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 the 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 $[Cu(dmp)_2]^+$ in organic solvent is 90 ns, observed in noncoordinating DCM argon-saturated solution, where all possible bimolecular quenching mechanisms were suppressed (Figure S14).[14,23] 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[23−27]

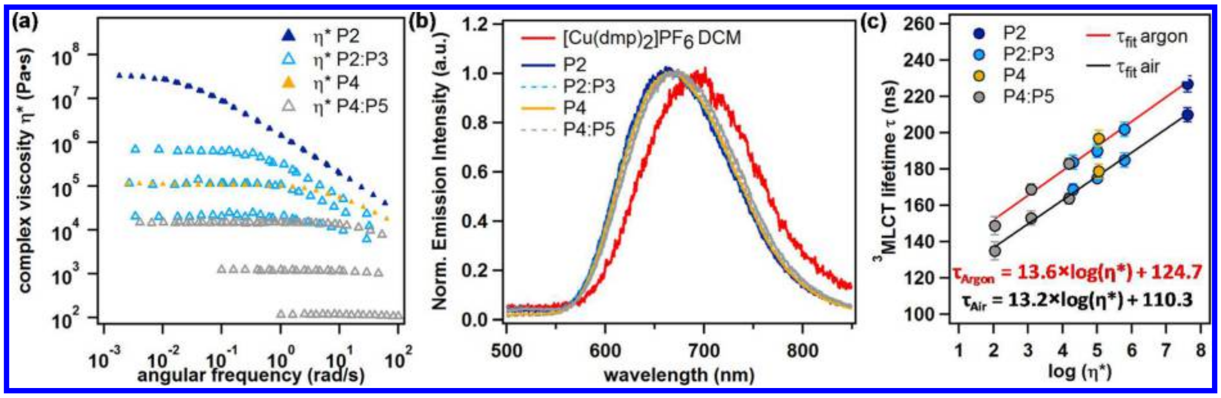


Figure 3. (a) Complex viscosities at different shear rates obtained from TTS curves. (b) Normalized time-gated (20 ns delay) emission spectra after 420 nm excitation of $[Cu(dmp)_2]PF_6$ in DCM solution and P2 (dark blue), P2:P3 at different ratio (light blue), P4 (orange), and P4:P5 different ratio (gray). (c) Linear correlation of ^{3}MLCT excited state lifetime and log(η*).

as well as methylation of 3,8-positions[14,28−30] 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. $[Cu(dmp)_2]^+$ exhibits weak (quantum yield ϕ = 0.04% in degassed DCM[23]), 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 3b, the $[Cu(dmp)_2]^+$ 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 (Figure S13).

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 3a). 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 3c). This correlation suggested that with a 10 times increase in viscosity of the supramolecular polymer the excited state lifetime (τ) 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 (Figures 3b and S13). 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]

Oxygen is known to quench the $[Cu(dmp)_2]PF_6$ excited state via electron and energy transfer mechanisms, which shortens the excited state lifetime. For instance, the $[Cu(dmp)_2]PF_6$ lifetime in aerated DCM solution is 62 ns (Figure 2c), while in inert gas protected media the lifetime increases up to 90 ns (Figure S14). 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 measurments on Cu−P*X* 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 3C).

The linear increase of MLCT lifetime with increases in viscosity of the supramolecular polymers was preserved as aerated environments as well. This observation additionally supports that the lifetime of the $[Cu(dmp)_2]^+$ 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.

In summary, this work demonstrates how restricted photo-induced 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]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.7b00465.

Detailed synthesis and characterization of the polymers are included (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: alexiso@bgsu.edu.
*E-mail: arazgon@bgsu.edu.

ORCID

Catherine E. McCusker: 0000-0002-0471-9034
Felix N. Castellano: 0000-0001-7546-8618
Alexis D. Ostrowski: 0000-0002-3207-1845

Present Address

[§]Department of Chemistry, East Tennessee State University, Johnson City, Tennessee 37614, United States.

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

The reported emission spectra were collected in a time-gated regime utilizing an iStar ICCD camera; therefore, the absolute value for the emission maximum could be different from the one obtained on a steady-state fluorimeter with a PMT detector. We start labels from “P2” instead of “P1” to be consistent with our upcoming publication[33] where the same P2 polymer was used and “P1” label was already assigned for the different polymer.

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