Real-Time and *In Situ* Viscosity Monitoring in Industrial Adhesives Using Luminescent Cu(I) Phenanthroline Molecular Sensors

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geometry from tetrahedral in the ground state to square planar in the excited state. The real-time viscosity was also monitored reversibly by emission lifetime during polymer swelling (viscosity and lifetime decrease) and unswelling (viscosity and lifetime increase). Monitoring emission lifetime, unlike measuring the excited-state lifetime *via* transient absorption measurements in our previous study, allowed us to measure viscosity in opaque samples which scatter light. The optical probe $[Cu(diptmp)_2]^+$ in Gorilla Glue adhesive showed a clear correlation of the emission intensity or lifetime to viscosity during the curing process. We have also compared these lifetime changes using $[Ru(bpy)_3]^{2+}$ (bpy = bipyridine) as a control. $[Cu(diptmp)_2]^+$ showed not only a higher emission lifetime but also more ubiquity as a real-time viscosity sensor.

KEYWORDS: viscosity sensing, materials sensing, real-time monitoring, Cu(1) sensors, mechanical property sensing

INTRODUCTION

A variety of optical methods to sense viscosity have been developed that rely on changes in the molecular motion of rotors, and these have been used primarily to determine viscosity inside cellular and membrane environments.¹⁻⁷ The viscosities measured in these systems were typically in the range of $1-10^2$ centipoise (cP); however, these molecular rotors had limited the sensitivity for sensing beyond that range. This limits these sensors for applications of viscosity sensing in devices and coatings, which have much higher viscosities than the biological systems ($\sim 10^5 - 10^{10}$ cP).^{8,9} In addition, determining the viscosity of polymers and adhesives in real time remains a challenge, especially in confined environments where the small sample size limits measurement with traditional rheological methods. For these confined samples, an optical method to determine viscosity provides advantages since light can be used in these environments. Recently, we showed that Cu(I) 2,9-dimethyl-1,10-phenanthroline [Cu- $(dmp)_2$ can be used as an optical probe for viscosity sensing at the high viscosity range (10^2-10^8 cP) inside polymer films.¹⁰ This optical sensing was enabled by a known distortion

in the $[Cu(dmp)_2]$ geometry from tetrahedral in the ground state to square-planar like geometry in the excited state.¹¹ This rotational distortion, restricted in higher viscosity materials, shows an increase in the lifetime of the excited state as viscosity increases.¹⁰ There are a variety of reported Cu(I)phenanthroline complexes that showed an excited state Jahn– Teller distortion after excitation into the relatively low-energy MLCT absorbance band. We previously showed that we could take advantage of this excited-state rotatory motion in $[Cu(dmp)_2]^+$ and use this to calibrate the viscosity of a surrounding polymer matrix, as the lifetime of the ³MLCT (triplet metal-to-ligand charge transfer) excited state increased in higher viscosity supramolecular hydrogen bonding polyurethanes.¹⁰ We used transient absorbance (TA) to determine

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the lifetime of the $[Cu(dmp)_2]^+$ in solid polymer films. By using TA, we were limited to using only transparent polymers, as scattering and absorbance of the matrix would create an error in the lifetime measurements for opaque samples. Using a more substituted phenanthroline ligand, diptmp (diptmp = 2,9-diisopropyl-3,4,7,8-tetramethyl-1,10-phenanthroline) is advantageous for addressing this limitation as it possesses more quantum yield. Moreover, being sterically congested increases the scope of restricting the rotation phenomenon, as proposed in our previous study. Thus, enhancing its sensitivity beyond just using $[Cu(dmp)_2]^+$. Various coordination complexes have been reported as effective viscosity sensors in liquid phases such as biological systems.^{3,7,12-16} However, these chromophores are limited by their inability to sense viscosity beyond the liquid phase. They possess low quantum yields and often use expensive ruthenium or lanthanide-based complexes. In addition, sensing in the excited state could be more sensitive because the excited state could potentially be more susceptible to alterations in dipolar interactions with the surrounding matrix media.¹⁷ Our approach was to use an optical probe with a high emission quantum yield that undergoes a rotational transformation in the excited state, which allows for determination of luminescence lifetime even in opaque samples in confined environments. $[Cu(diptmp)_2]^+$ complexes showed a higher luminescence quantum yield (Φ_{p}) of 4.7% (in deaerated CH₂Cl₂),¹⁸ with long ³MLCT excited-state lifetimes (~2900 ns). This high $\Phi_{\rm p}$ allowed us to look at changes in ³MLCT excited-state lifetimes using time-resolved emission (TE). In this work, we utilized a sterically congested Cu(I)phenanthroline-based probe $[Cu(diptmp)_2]^+$ (diptmp = 2,9diisopropyl-3,4,7,8-tetramethyl-1,10-phenanthroline).¹⁸ This Cu(I) complex is made from more earth-abundant elements compared to other M-L (metal-ligand) probes used (e.g., Ruor Ir-based probes) and provides a much higher emission quantum yield than our previously reported $[Cu(dmp)_2]^+$. We hypothesize that with this highly luminescent sensor, we will be able to sense viscosity changes in real-time and in situ in a variety of materials using luminescence, including in opaque or highly scattering solids. In order to perform real-time sensing, we utilized industrial epoxy adhesives and monitored the $[Cu(diptmp)_2]^+$ emission lifetime *in situ* as the adhesive experienced mechanical property changes during the curing process.¹⁸ (Scheme 1).

We also show that this probe was able to detect small changes in viscosity microenvironments in polymer films that were swollen in organic solvents. Such viscosity change measurements during swelling cannot be detected using traditional rheology, which highlights the advantages of this $[Cu(diptmp)_2]^+$ sensor.

MATERIALS AND METHODS

$$\begin{split} & [Cu(diptmp)_2]^+ \ (diptmp = 2,9\text{-}diisopropyl-3,4,7,8\text{-}tetramethyl-1,10-phenanthroline) was synthesized according to published proce$$
 $dures.^{18} [Ru(bpy)_3]^{2+} was purchased from Sigma-Aldrich. Quartz$ microscope slides (75 × 25 × 1 mm) were purchased from StarnaCells. Hardman Double/Bubble regular setting epoxy black (epoxy),Gorilla Glue (GG), and Liquid Fusion urethane (LF) adhesives werepurchased from All-Spec.

Rheology of Polymers. The mechanical property characterization was performed on TA Instruments Discovery hybrid HR-2 oscillatory rheometer. The samples were measured using a 50 mm diameter crosshatch lower Peltier plate with and an 8 mm crosshatch upper plate geometry. Oscillatory time-sweep rheology for the adhesives were carried out at 0.1% strain at 20 °C. To prepare the Scheme 1. Overall Scheme for Using $[Cu(diptmp)_2]^+$ as a Sensor to Monitor the Mechanical Property Changes Due to Viscosity^{*a*}



 ${}^{a}R_{1}$ and R_{2} represents bisphenol A derivate and aliphatic chain. (the complete structure is protected by trade secret).

samples, $\sim 1-2$ mg of $[Cu(diptmp)_2]^+$ was mixed with 400 mg of total adhesive (200 mg for each component for the two-component epoxy adhesive) for a total of 10 min using a glass-rod on a Teflon mold and drop-casted on the crosshatch geometry, with care taken to ensure covering the whole 8 mm area of the top plate. Initial conditions were optimized such as the mixing time of the metal complex and adhesives (two-component) was found to be 10 min for all 3 trials in each adhesive and amount of time taken to drop cast the sample onto the lower plate to be 5 min. This ensured we begin the oscillatory time-sweep experiments at the same point for all our measurements as the curing (polymerization) starts to happen in real-time.

UV–Vis Spectroscopy. UV–vis spectra of the $[Cu(diptmp)_2]^+$ films on quartz slides were recorded on a Shimadzu UV-2600 Spectrophotometer with a resolution of 0.5 nm. All samples were prepared such that the absorbance was less than 1 O.D.

Time-Resolved Optical Spectroscopy. To investigate timeresolved emission and transient absorption in our materials, we utilized nanosecond time-resolved spectroscopic techniques. An LP-980 laser flash photolysis system by Edinburgh Instruments with a Vibrant 355 nm Nd:YAG/OPO system (OPOTEK) as the excitation source was used. The pulse width of the laser source was \sim 5–7 nm. Samples for time-resolved emission spectroscopy were prepared by drop-casting of 400 mg of the polymer adhesive mixed with $\sim 1-2$ mg $[Cu(diptmp)_2]^+$ probe onto a quartz slide. Kinetic traces were collected with a PMT detector, and all kinetic traces were fit with single exponential functions using Igor Pro. Spectra were collected with 5 nm resolution. Also, transient absorption spectra and gatedelayed emission spectra (typically 40 ns delay) were collected with an iStar ICCD camera (Andor Technology). All experiments were performed at ambient temperatures. The reported kinetics and emission spectra are averages of 20 measurements. The reported lifetime and emission values are averages of 3 different samples (N =3), and errors are \pm standard deviation.

Swelling Studies. Samples (~400 mg) were cast on a quartz slide through a Teflon mold $(15 \times 5 \times 3.5 \text{ mm})$, which was placed on top of the quartz slide. When completely cured, the Teflon mold was removed to get films on a quartz slide which would all have an

identical volume. The quartz slide was mounted on a holder (Figure S13), and cross-section microscopic images were recorded using STEMI 2000-C (ZEISS, White plains, NY, USA) optical microscope. ZEISS software was used to analyze the images by drawing the region of interest (ROI) with the polygon tool (Figure 4). Samples were swollen inside a diffusion chamber with DCM and ethyl ether (100 mL) added inside the closed chamber to create an atmosphere saturated with solvent vapor. The diffusion time was the time interval that the sample on the quartz slide remained inside the diffusion chamber (it is not the consecutive amount of time the sample was inside). For the effusion experiments, samples were deswollen in a dry desiccator under vacuum (1.5 mTorr) for specific effusion time intervals where this effusion time was the time spent inside the desiccator under the 1.5 mTorr vacuum (Figure S14). After drawing the ROI for cross-section images at different solvent diffusion/ effusion intervals, the cross-section area was obtained for all and then multiplied by 15 mm (Teflon mold length dimension) to determine the volume of the sample at each different time (diffusion or effusion) for 3 different trials (T). From the obtained volume values, in order to calculate the % change in volume upon diffusion/effusion (swelling/ deswelling) we normalized the percentage with respect to the absolute maximum volume value V_{max} (after diffusion of 100 min or ~1.7 h) using the following equation

% change in volume (normalized w. r. t V_{max}) = $V_x/V_{\text{max}} \times 100$

where x = volume obtained at diffusion time of x hours.

Although there is some variation in the sample volume due to small differences in each ample volume, care was taken to ensure consistency, with the same amount of $[Cu(diptmp)_2]^+$ (~1.2) in 400 mg of adhesive. This amount was used as it completely filled up the Teflon mold. We utilized the mold to have better microscopic pictures as the % change in volume can be quantified properly when using a mold with known dimensions.

RESULTS AND DISCUSSION

In our previous study, we showed that we could use Cu(I)based complexes as sensors to determine the viscosity of



Figure 1. Steady-state UV–vis absorption and emission spectrum of $[Cu(diptmp)_2]^+$ in CH_2Cl_2 , epoxy, and LF urethane adhesives with the blank epoxy and LF urethane absorption spectrum.

polymers using transient absorption, where the lifetime of the excited state increased in more highly viscous media. This technique was limited to clear samples, however, since it is difficult (or impossible) to accurately measure transient absorbance in highly scattering or opaque solid materials. For this study, we set out to use a similar Cu(I) complex, $[Cu(diptmp)_2]^+$, which has a high phosphorescent quantum yield to investigate not only clear samples but also the opaque samples with high scattering since we hypothesized that we would be able to monitor these samples using transient



Figure 2. (a) Time-resolved emission lifetime traces measured over time as the epoxy adhesive cured. ($\lambda_{ex} = 465 \text{ nm}$ for $[Cu(diptmp)_2]^+$), ($\lambda_{probe} = 605 \text{ nm}$). The inset image shows a sample of ~ 1–2 mg of $[Cu(diptmp)_2]^+$ mixed with 400 mg of epoxy on a quartz slide. (b) Real-time, *in situ* viscosity monitoring of the epoxy adhesive polymerization *via* $[Cu(diptmp)_2]^+$ emission lifetime in both air (orange triangles) and under N₂ (black triangles) compared to the viscosity measured using a rheometer as the epoxy cured (blue circles).



Figure 3. Real-time *in situ* monitoring of swelling of cured epoxy adhesive by diffusion of DCM and unswelling *via* vacuum.

emission (TE) For the TE studies, we chose to investigate how the $[Cu(diptmp)_2]^+$ emission lifetime would change in three different industrial adhesives: Hardman Double/Bubble regular setting epoxy black (epoxy), Gorilla Glue, and Liquid Fusion urethane (LF). In order to do TE, we need to know the wavelength of light at which $[Cu(diptmp)_2]^+$ absorbs. The epoxy and LF adhesives are sufficiently transparent such that UV-vis spectra were recorded, and the 420 nm band shown in the UV-vis absorption spectra corresponds to the ³MLCT band of $[Cu(diptmp)_2]^+$ (Figure 1).



Figure 4. Region of interest's cross-section image processing area analysis for microscopic images using Zeiss software.



Figure 5. (a) Time-resolved emission lifetimes measured as the GG adhesive (opaque) cured ($\lambda_{ex} = 465 \text{ nm}$ for $[Cu(diptmp)_2]^+$, $\lambda_{probe} = 605 \text{ nm}$). The inset image shows a sample of $\sim 1-2 \text{ mg}$ of $[Cu(diptmp)_2]^+$ mixed with 400 mg of GG adhesive on a quartz slide. (b) *In situ* viscosity monitoring of the GG adhesive polymerization *via* $[Cu(diptmp)_2]^+$ emission (orange triangles) compared to the viscosity of the GG sample measured with a rheometer (blue circles).

Therefore, the wavelength value of 465 nm was utilized as a pump pulse (pulse width ~ 5-7 nm) to excite the sample, and emission was monitored at 605 nm (emission maxima; Figure 1) to monitor the temporal resolution of the excited state dynamics. TE for [Cu(diptmp)₂]⁺ was performed in epoxy adhesive, and the lifetime traces for the ³MLCT excited state showed clearly longer lifetimes as the adhesive cured over time (Figure 2a). The epoxy adhesive was a two-component adhesive comprised of epoxy resin and aliphatic amine. As soon as the sample is prepared, the 2 components are mixed together, and it starts to cure, initiating the polymerization reaction, which results in macroscopic changes in the viscosity of the adhesive (Scheme 1).

The changes in the lifetime of emission from $[Cu-(diptmp)_2]^+$ showed an increase and then plateau that mirrors



Figure 6. (a) In situ viscosity monitoring of the LF adhesive polymerization via $[Cu(diptmp)_2]^+$ emission. (b) In situ viscosity monitoring of the LF adhesive polymerization via $[Ru(bpy)_3]^{2+}$ emission vs $[Ru(bpy)_3]^{2+}$ constant emission in epoxy and GG adhesive.

the trend seen for the changes in viscosity as measured with traditional Rheological methods (Figure 2b). To confirm that this increase in lifetime was not due to changes in oxygen permeability over time as the adhesive cures, we performed the experiment under an inert N₂ atmosphere. We saw a similar increase in lifetime under inert atmosphere ruling out the possibility of lifetime increase due to less oxygen permeability as the sample cures and becomes stiff (Figure 2b). Triplet (³MLCT) states are known to be quenched by ³O₂;¹⁹ therefore, lifetime values under nitrogen were slightly higher though this quenching by ³O₂ later became less prominent as the adhesive completely cured.

The comparison of the complex viscosity monitored by traditional rheological techniques (in this case, oscillatory time sweeps) and the lifetime values (time-resolved emission) showed that this $[Cu(diptmp)_2]^+$ can be used to qualitatively probe the viscosity and use it as a real-time in situ sensor. In order to determine a quantitative relationship and create a sort of standard curve of the correlation of the ³MLCT lifetime and viscosity, the ³MLCT lifetime and $log(\eta^*)$ at the same curing times for the epoxy polymerization in air and nitrogen was plotted (Figure S8). In this case, this relationship can be used to determine η^* (complex viscosity) from lifetime values. However, in order for $[Cu(diptmp)_2]^+$ to be a ubiquitous quantitative sensor, it should yield back η^* from lifetime values independent of the environment. While small, the differences in the values and linear slope between air and N2 show that these small changes can limit this as a ubiquitous, quantitative viscosity sensor. It should be noted that this lifetime increase

Scheme 2. Proposed Potential Energy Surface Jablonski Diagram for Increment in Lifetime for (a) Our $[Cu(diptmp)_2]^+$ Viscosity Probe and (b) Control $[Ru(bpy)_3]^{2+}$ Probe



was also accompanied by a slight (<7 nm) blueshift in the steady-state emission maxima (Figure S2). These blueshifts in electronic triplet state were partially attributed to changes in polarizability during the epoxy polymerization due to changes in the relative permittivity/dielectric constant (κ) of the surrounding media. Moreover, the diffusion coefficient of the chromophore is inversely proportional to the viscosity of the surrounding media [Stokes–Einstein equation ($D \sim 1/\eta$)]. Therefore, any nonradiative bimolecular quenching pathways that contribute to the overall lifetime are more suppressed, as the excited state [Cu(diptmp)₂]⁺ was less likely to diffuse in more viscous surrounding media.

To rule out the hypothesis that the lifetime changes could be due to quenching of the optical probe by the initiator, which would decrease over time as less initiator was present as the adhesive was cured, we performed sensing studies on fully cured samples so that all initiator was consumed. For these studies, identical sized samples of epoxy with $[Cu(diptmp)_2]^+$ sensor were prepared (Teflon mold; $15 \times 5 \times 3.5$ mm, Figure S14). Then, we used a diffusion chamber saturated with a solvent (dichloromethane, DCM) to swell the samples, which we hypothesized would lead to an increase in volume and thus a decrease in viscosity at the surface where the material was swollen (Figure S14). When we performed these swelling studies, the idea was that swelling does not break the cross-linking in the polymer network, but the DCM solvent diffused into the polymer network, disrupting the intermolecular

interactions, thereby decreasing microviscosity while still maintaining the polymeric assembly.

As expected, $[Cu(diptmp)_2]^+$ in epoxy adhesive showed increasingly shorter lifetimes as the polymer was allowed to swell with solvent for longer times in the diffusion chamber (Figures 3, S9). This was attributed to a decrease in microviscosity as the solvent penetrated the polymer surface.²⁴ Ethyl ether was also used as a swelling solvent, and changes in the lifetime of $[Cu(diptmp)_2]^+$ in epoxy were observed but with a significantly longer time to diffuse (Figure S13). To show the reversibility of this sensor, the swollen adhesive was unswelled by vacuum to facilitate the effusion of the solvent out of the epoxy material, and as a result, the lifetime of the $[Cu(diptmp)_2]^+$ chromophore increased as the sample spent longer time under vacuum, approaching back to the initial value for a completely unswollen material (Figures 3, S9).

To correlate the lifetime changes with actual volume changes during swelling of the material, the samples were monitored by optical microscopy. Cross-section images were taken as the polymer both before and during each time point that the material was allowed to swell or placed under vacuum. To determine the volume of the sample, an ROI was drawn in ZEISS software with the polygon tool for post-image processing to calculate the area (Figure 4). Utilizing the area value, it was multiplied by the length of the Teflon mold (15 mm) to get the corresponding volume values (Figure 4, Tables S2, S3). Then, the swelling/deswelling of the film was quantified by the percent volume (normalized w.r.t the maximum swollen volume) changes. As the volume of the film increased from solvent swelling, the ³MLCT emission lifetime decreased (Figure 3). These results demonstrate that $[Cu(diptmp)_2]^+$ could be used as a reversible sensor for swelling in solid films. In order to highlight the sensitivity of using this optical method to sense swelling compared to traditional rheological measurements, viscosity studies were also performed on the epoxy materials after swelling of the cured adhesive with a solvent or similar times as done for the optical measurements.

However, with the traditional oscillatory rheology, no significant changes in viscosity values were observed during swelling (Figure S12). We expect this is because the changes in viscosity were likely only very small and more isolated on the surface during swelling, and rheological measurements take place between two plates, making the task of determining any of these small changes in viscosity during swelling beyond the sensitivity of this technique. This comparison showcases that the $[Cu(diptmp)_2]^+$ probe can be used to detect even small changes in polymer cross-linking and dynamics that are unable to be measured using typical rheology. It also demonstrates the noninvasive method and sensitivity of probing *in situ* microviscosity in real-time using optical spectroscopic methods.

To demonstrate the utility of this optical sensing method, we chose an opaque adhesive to determine if $[Cu(diptmp)_2]^+$ could be used as a viscosity probe for opaque samples. $[Cu(diptmp)_2]^+$ was incorporated in Gorilla Glue (GG) adhesive, and results showed that the emission lifetime lengthened as the adhesive cured and increased in viscosity, similar to what was observed in the LF adhesive (Figure 5a). This lifetime change was accompanied by a slight blueshift in emission maxima (Table S1). The error for lifetime measurements was higher, and the correlation with viscosity changes was less accurate in the opaque GG compared to epoxy

(Figure 5b). The GG adhesive expands in volume as it undergoes curing, and the curing rate is dependent on moisture (since water is the curing initiator), which leads to less reproducible curing rates for all three trials. Therefore, the error in the lifetime measurements was higher due to these differences in curing and expansion of volume from changes in humidity, temperature, and any bubbles that formed during curing. By comparison, in the epoxy adhesive, there was a negligible expansion over time during curing, and errors were only due to minor factors such as temperature. Regardless, the optical method using the $[Cu(diptmp)_2]^+$ was still able to sense the viscosity changes during the curing of the opaque GG adhesive (Figure 5b).

Unlike in the epoxy adhesive, when looking to create a sort of calibration correlation between ³MLCT lifetime and log η^* for GG adhesive, they did not show a linear relationship (Figure S10). This is because (1) the GG adhesive expands as it cures, and (2) the curing rate depends on moisture. When we perform rheological measurements, the sample is between two parallel plates. The curing expansion affects the rheology studies as they tend to show a higher viscosity at a lower curing time due to the additional force from expansion. Moreover, since the curing rate for this adhesive is affected by changes in humidity, the availability of water vapor changes as the polymer cures, which changes the curing rate during the measurements, so they are not the same between when measuring the samples between two plates in rheology vs on the quartz slide in the optical measurements. As such, the correlation is more of an exponential relationship. Regardless, $[Cu(diptmp)_2]^+$ is able to sense the viscosity changes in the GG adhesive, however, with a different correlation due to the changing rates of polymerization and expansion.

In order to design a quantitative optical viscosity probe, it is critical to understand the fundamental photophysical mechanism for these mechanosensitive probes to be more fully utilized. In our previous work, we attributed the lifetime changes to changes in the ability of the $[Cu(diptmp)_2]^+$ ³MLCT excited state to undergo the Jahn–Teller distortion depending on the rigidity of the surrounding media.¹⁰ While we expect this to certainly be a factor in the lifetime changes, other contributions cannot be ignored, most notably suppression of nonradiative relaxation processes in more rigid media could lead to longer excited state lifetimes without any contribution from the Jahn–Teller distortion.

To determine the mechanism responsible for the lifetime changes and confirm the increased sensitivity in sensing due to the contribution of the restricted rotation behavior of the [Cu(diptmp)₂]⁺ Jahn–Teller distorted ³MLCT state, we chose $[Ru(bpy)_3]^{2+}$ as a control sensor since it is emissive without having any analogous Jahn-Teller distortion in the excited state. No increase in the emission lifetime of $[Ru(bpy)_3]^{2+}$ was observed for epoxy and GG adhesive as they were curing; however, there was emission present (Figures 6b, S3, S5). This shows that $[Ru(bpy)_3]^{2+}$ could not be used as an effective sensor in those materials where $[Cu(diptmp)_2]^+$ showed clear sensing of viscosity during curing. Of note is that there was an immediate large blueshift (>30 nm) in the emission from $[Ru(bpy)_3]^{2+}$ prior to curing, with both the initial and final emission maxima peak at ~583 nm with a distinct difference in the spectral shape. We attributed these large emission peak shifts to a reaction of $[Ru(bpy)_3]^{2+}$ with components in both epoxy and GG adhesive; therefore, essentially, the emission lifetime is not from the same triplet MLCT state (Figures S3,

S5, Table S1). Moreover, this lifetime is altogether from a different species, as $[Ru(bpy)_3]^{2+}$ turned pink, and the emission is not at the usual ~615 nm signal. However, in another adhesive that we tested, Liquid Fusion (LF), both $[Ru(bpy)_3]^{2+}$ and $[Cu(diptmp)_2]^+$ sensors showed changes in lifetime during curing (Figure 6). In addition, while the $[Cu(diptmp)_2]^+$ showed just small shifts in the emission spectra (2 nm, 53 cm⁻¹), the $[Ru(bpy)_3]^{2+}$ showed a more significant blueshift in the emission spectra (17 nm, 462 cm⁻¹) during the LF polymerization.

These results challenged our previously proposed mechanism that the lifetime changes for the Cu(I) probes were due solely to restricted Jahn–Teller rotation. There have been reports of shifts in lifetime for $[Ru(bpy)_3]^{2+}$ due to rigidochromism in silica gel matrixes.²⁵ Therefore, it is likely that in the Liquid Fusion adhesive, the changes in lifetime are also due to rigidochromism.^{25–28} In this case the blueshifted, higher energy, the ³MLCT excited state gives rise to slower nonradiative relaxation to the ground state, which, in turn, gives a longer emission lifetime (Scheme 2a).

We propose then that the mechanism for the emission lifetime changes in $[Ru(bpy)_3]^{2+}$ is due to suppression of these nonradiative relaxation pathways, as there is no known excited state Jahn-Teller distortion in $[Ru(bpy)_3]^{2+}$ (Scheme 2a). The $[Cu(diptmp)_2]^+$ emission also shows a slight shift of 2 nm (53 cm⁻¹) in Liquid Fusion adhesive, however, much less pronounced compared to the shift seen with $[Ru(bpy)_3]^{2+}$ (Figure S6). Both shifts are accompanied by changes in the ³MLCT lifetime, but the sensitivity to the viscosity of the environment is much more pronounced in the Cu(I) probe due to an additional pathway of restricted rotation of the Jahn-Teller distortion in the excited state when in a more rigid environment (Figure S11, Scheme 2b). In addition, the $[Cu(diptmp)_2]^+$ is able to sense viscosity changes in all 3 different adhesives, whereas the control $[Ru(bpy)_3]^{2+}$ sensor has a limited range, showing sensing only in the LF adhesive.

CONCLUSIONS

In conclusion, we have shown that $[Cu(diptmp)_2]^+$ is an effective viscosity sensor using the emission lifetime for solid films which cover a broad range of viscosities $(10^2 - 10^7 \text{ Pa s or})$ $10^{5}-10^{10}$ cP). In addition, this sensor can be used in a variety of different polymer adhesives to track the curing in situ in real time. The mechanism for this behavior is attributed to the suppression of the nonradiative relaxation process accompanied by the restricted rotation of the Jahn-Teller-distorted excited state from the Cu(I) chromophore in the confined environment of the polymer adhesive (Scheme 2). It can also be used to effectively monitor swelling in polymer films due to the diffusion of different solvent vapor (DCM vs ether) into the material (Figure S13). The use of this optical probe could be impactful in thin-film electronic devices, such as polymer solar cells and thin-film transistors, where the device performance relies heavily on ordered layering of materials in order to replicate the optimum performance of these devices. The molecular sensor works effectively to sense the swelling/ deswelling (microviscosity changes) and also for opaque samples. Therefore, the ability of the molecular sensor to be able to sense the microviscosity changes at the interface susceptible to the vapor would allow researchers to address this inconsistency in replicability of the performance. These changes could be utilized to quantify the performance of devices by making a calibration curve not only at different

vacuum flows but also at different amounts of solvent vapor diffusion conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c06554.

Spectral shifts in emission, graphs for lifetime *versus* log of viscosity and % change in volume, spectral data analysis, analysis of microscopic imaging data for swelling, and schematic images with more details on how various experiments were performed (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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