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Color-Based Optical Detection of Glass Transitions on Microsecond Timescales Enabled by Exciplex Dynamics

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Every measurement technique operates on a given timescale and measurements using emissive small molecule sensors are no exception. A family of luminescent sensors providing first optical characterization of dynamic phenomena in polymers at a timescale of several microseconds is described. This performance originates from the dynamics manifested in the excited state of the sensor molecules where diffusioncontrolled events select the emission color while radiative phenomena define the global operation timescale. Since the mechanism responsible for signal generation is confined to the short lived excited state of emissive probe, it is possible observe an unprecedented link between the timescale of sensory action and that of photoluminescence. An application of this new methodology is demonstrated by performing general, short timescale detection of glass transitions in a temperature ranges precluding the informative range of conventional techniques by tens of degrees.

The use of responsive small molecules and sensors is becoming increasingly common in polymer science. The last decade saw the development of molecular sensors that report material damage[1] and mechanical stress[2] or allow the creation of new mechanoresponsive materials with eye-readable color-based feedback.[3] A large portion of small molecule sensors is photoluminescent (PL) and utilizes light emission as the means for providing sensory response. Historically the use of PL probes to study soft matter is very diverse as the former have been used to study free volume,[4] polarity,[5] viscosity,[6] and micellization[7] in soft matter.[8] Subsequent works of several groups have extended the use of PL probes to visualizing mechanical impact[9,10] in a continuous time-resolved fashion.[10,11] Recent developments in the field are gradually transforming the role of small molecule sensors from indicative to analytical, e.g. to probe mobility[12] and dynamic heterogeneity in polymer glasses,[13] describe dynamics of individual polymer chains,[14] and probe local polymer viscosity.[15] In this work we aim at advancing the performance of luminescent sensors to analytical applications by enabling them to operate in the sensory setting at defined experimental timescales.

Every sensor responds to specific events that occur on a given timescale. In the context of soft matter and polymer science, one can fully appreciate the importance of detection timescale when materials under study can undergo glass transition—a main focal point of this study. Typically associated with the loss of chain mobility, formation of polymer glasses leads to a drastic change in material properties as they become brittle, lose elasticity, and differ significantly from their parent fluid. A crucial feature of a glass transition is its kinetic nature. As opposed to thermodynamic transitions like melting or crystallization, glass transition does not have a defined transition temperature.[16] Instead, any value of glass transition temperature (T_g) observed experimentally, depends on the observation timescale. For example, differential scanning calorimetry (DSC) reports T_g at the timescales of 10–100 s, while dynamic mechanical analysis can access shorter timescales down to fractions of a second. The widest range of timescales among common characterization techniques is provided by dielectric spectroscopy that can access sampling frequencies ranging from mHz to MHz when assessing relaxation timescales.[17,18] Shorter detection timescales can probe faster phenomena and typically provide higher T_g values that can increase by up to 10 K per decade of experimental timescale.[19]

In practice, the knowledge of glass transition temperatures is necessary for defining the operational limits of any polymer. The timescales of T_g analysis become important when materials are intended to withstand shock, dynamic impact or fast deformations. To predict whether material would behave as a glass or a fluid one should ideally match T_g detection technique timescale to that of the impact.

Among numerous applications in polymer characterization,[20] luminescent small molecules have also been used to detect glass transition. Unlike those of calorimetry and mechanical analysis, operation timescales of PL sensors for T_g detection are not strictly defined. For example, known luminescent sensors like pyrenes,[21] aggregate dyes,[22] and various polar aromatic emitters[18,23] appear to work on the same timescale as mechanical and thermal methods since their reported T_g values

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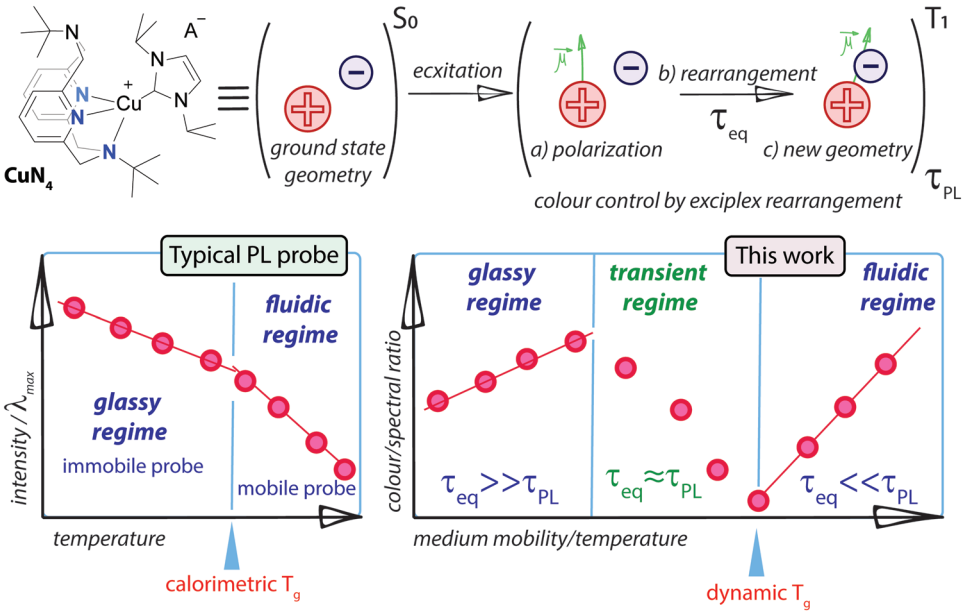

Figure 1. Illustration of emission and color variation mechanisms exploited in this work and typical response curves for conventional T_g sensors and probes developed in this work.

are similar. This highlights a lack of link between emission and T_g sensing timescales in these sensors and the absence of analytical framework describing their operation at large. Recognizing this mismatch, we aimed this work at designing emissive sensors for T_g detection that operate on defined timescales. Particularly, we aimed at linking their T_g detection timescale to that of photoluminescence. Being essential for turning emissive probes into actual measurement instruments, this task required a novel approach to the sensor design.

The premise for this work came after recent discoveries of luminescent complexes that exhibit strong color variations driven by their excited state dynamics.[24,25] For example, our group disclosed a family of Cu-based emitters (CuN_4, **Figure 1**)[24] that produce luminescence with varied color through the sequence of events depicted in Figure 1. According to these findings, in the ground state CuN_4 exists as an ion pair—a cationic complex and the weakly coordinating anion. Excitation leads to strong polarization of the cation due to the metal-to-ligand charge transfer process and associated intramolecular charge transfer.[24] This initiates a structural rearrangement within a short lived exciplex leading to contraction of an ion pair distance. This distance, affected by the medium temperature, reflects the strength of ion paring, which in turn controls the exciplex stability and emission color.[24]

Altogether, the emission in CuN_4 can be viewed as a combination of two independent processes—fast exciplex rearrangement with a timescale τ_{eq} followed by phosphorescence with timescale τ_{PL} (Figure 1). While τ_{PL} is generally temperature independent in the absence of nonradiative recombination, the exciplex rearrangement involves anion diffusion—a process with timescale defined entirely by the type of host medium and its temperature. Based on our previous observations[24] we assumed that the relative rates of emission and diffusion can reflect the state of the polymer environment and allow for distinguishing between fluidic and glassy states.

We first investigated the behavior of our sensors in purely fluidic environments that do not readily form glasses. The two complexes used as PL probes were Cu-based emitters **1** and **2** depicted in **Figure 2**A. In addition to the known complex **1**[24] containing a bulky tetraphenylborate anion we prepared a new complex **2** with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion (BArF) that exhibits excellent solubility and withstands temperatures up to 250 °C in the solid state (Figure S4.1, Supporting Information).

The photoluminescence of both complexes was studied in dichloromethane (DCM) and 1,2-dichloroethane (DCE) solvents that remain liquid in a combined temperature range of −90 to 80 °C. Together with PL spectra, we analyzed a spectral intensity ratio ($R(I_{530}/I_{610})$, Figure 2B) as a color descriptor. The ratiometry data collected for both complexes in solution follows a linear trend as function of solution temperature regardless of solvent or complex type (Figure 2B). This is in line with our previous observations[24] suggesting that PL color would vary monotonically in fluids where anion diffusion is fast. The long PL lifetimes that vary from 8.96 µs (30 °C) to 24.28 µs (−90 °C) for complex **1** in DCE (Figure S3.1, Supporting Information) allow assuming that $\tau_{PL} >> \tau_{eq}$ and an equilibrium exciplex structure characterized by specific color is formed within the lifetime of the excited state. Combined with our previous observations of a monotonic ratiometry curve behavior for **1** and its analogues in DCM[24] our data confirms that a linear monotonic trend of ratiometry curve is indeed indicative of fluidic nature of the environment hosting the emitter molecule.

Unlike small molecule organic solvents that abruptly crystallize below their melting points, glass-forming polymers undergo a gradual transition when cooled. This transition is

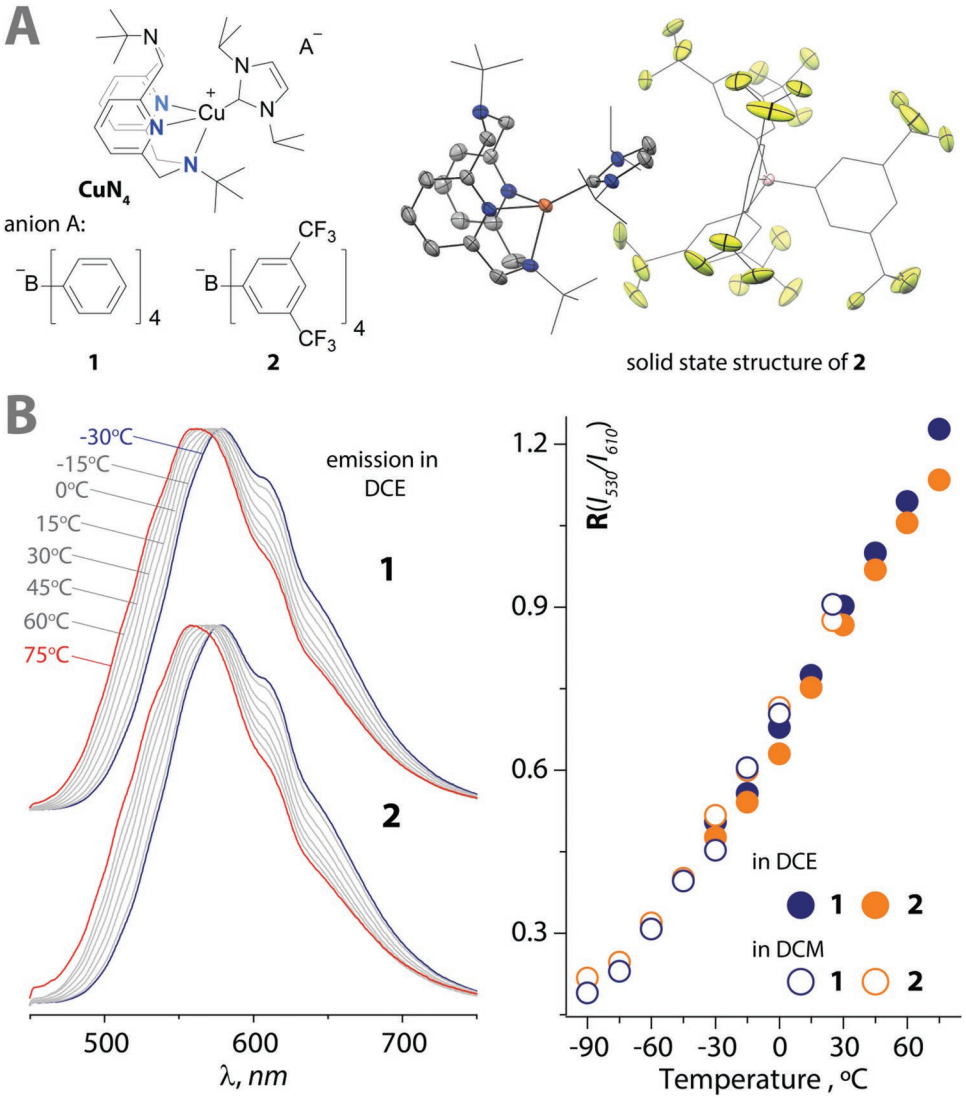

Figure 2. A) Structures of complexes **1** and **2** used in this work with solid state structure of the new complex **2** and B) photoluminescence and ratiometry data for these complexes in dichloromethane and 1,2-dichloroethane solutions as a function of temperature. Excitation at 405 nm, complexes used at 1.2×10^{-3} M concentrations. DCM ratiometry data for **1** (1.6×10^{-3} M) is taken from ref. [24].

characterized by the slow change of polymer viscosity, chain mobility, and diffusion rates within the material[26] suggesting that ion pair rearrangement rate for sensors **1** and **2** would gradually slow down at lower temperatures as a consequence of slower anion diffusion.

We assumed the existence of a temperature where anion diffusion is sufficiently slow to prevent the formation of the exciplex equilibrium structure within τ_{PL}. At this temperature, the ratiometry curve would deviate from linear fluid-like trend and one would effectively detect a dynamic T_g at τ_{PL} timescale.

To verify this hypothesis we prepared a series of polymer blends containing **1** dissolved in the polymer host. To eliminate the potential effects of polymer modifications on behavior of **1** we used the PL probe in free molecular state instead of synthetically incorporating it into the polymer backbone. In this way we could directly compare PL properties of **1** in glass forming polymers and organic fluids that do not readily form glasses.

We firstly studied the thermal behavior of **1** in polyurethane (PU) environment similar to that used in our previous work.[24] Namely, we used aliphatic PU containing polyether soft segments and hexamethylene diisocyanate-butanediol hard segments (see Section S2, Supporting Information). The **1/PU** blends prepared by solution casting showed pronounced thermochromism with its ratiometric curve comprised of three distinct regions (**Figure 3**). The part of the curve upwards of –15 °C has a positive slope as a function of temperature that mirrors a fluid-like behavior previously observed for solutions of **1** and **2** (Figure 2). Namely, we observed a blue shift of emission color at elevated temperatures which indicated a gradual increase of ion pair spacing typical for ion pairs in fluidic environment.[24]

DSC analysis (Section S4, Supporting Information) revealed no thermal transitions in **1/PU** above the calorimetric T_g of –65 °C, thus, we expected the linear ratiometry curve trend to continue into the low temperature region. On the contrary, ratiometric

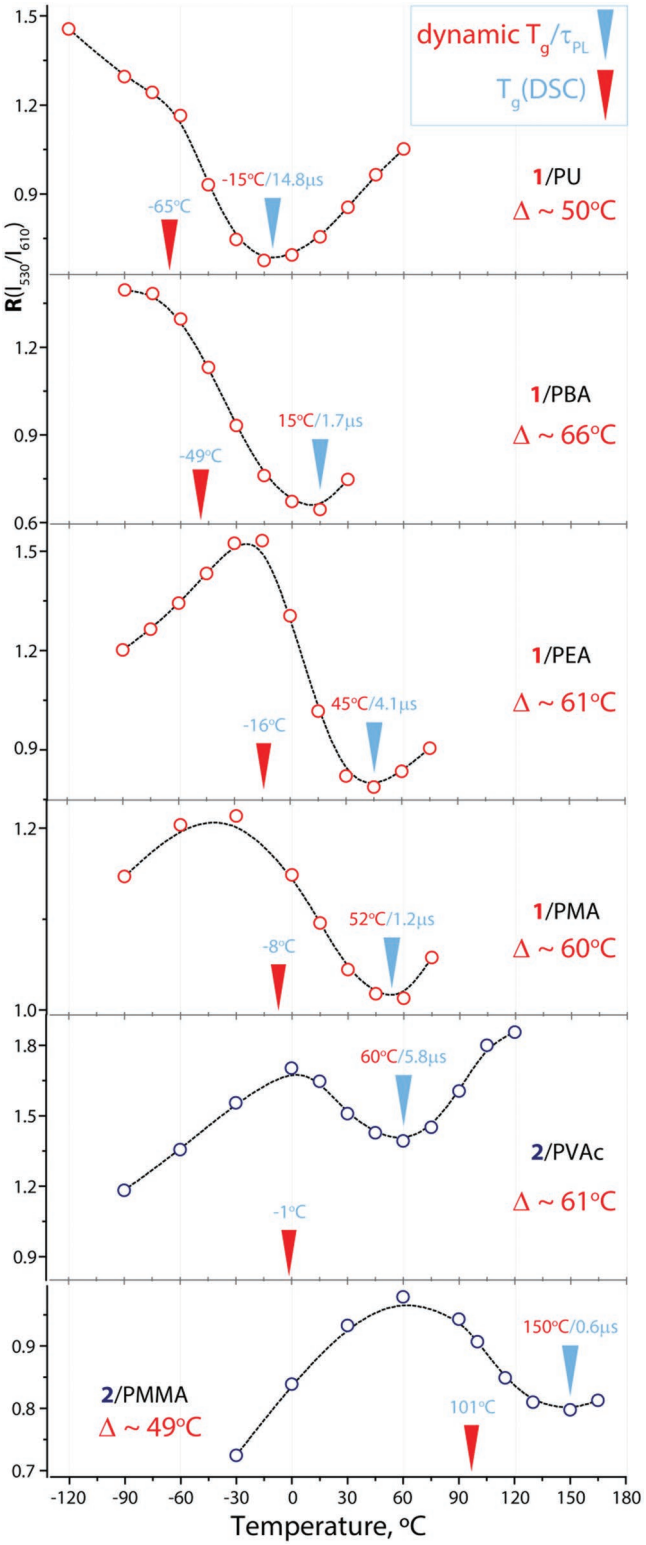

Figure 3. Color ratiometry data as a function of temperature in polymer blends containing complexes **1** and **2**. Emission lifetimes, dynamic, and calorimetric T_g are indicated on the graph. Calorimetric T_g determined at 10 K min^{-1} heating rate. Section S3 of the Supporting Information contains the relevant spectral data for all curves depicted.

curve has changed the slope sign at −15 °C that is ≈50° above the calorimetric T_g. We assumed that this point—a minimum on ratiometric curve—indicated the temperature where the exciplex rearrangement is sufficiently slow to affect the PL on the radiative timescale.

Since anion mobility in **1/PU** is defined by polymer viscosity the transition detected at the minimum of ratiometric curve is formally a glass transition that occurs on the PL timescale. At −15 °C the PL process lifetime was measured to be 14.8 μs—that is ≈7 decades, or orders of magnitude, faster than the timescale of DSC (Figure S3.2, Supporting Information). The difference of 50° between calorimetric and PL-based dynamic T_g is, therefore, a likely result of a short observation timescale. In support of this notion, the literature data for similar polyurethanes[27] and our DCS analysis of the glass transition kinetics estimate the shift of calorimetric T_g by up to 8 K per decade of observation timescale (Figure S4.2, Supporting Information). These results suggest that when registered at the timescale of microseconds, dynamic T_g would indeed be expected to occur at ≈−15 °C.

Demonstrating the further use of our methodology, we extended it to several common elastomers. Making use of the fact that chemical incorporation was not necessary for **1** to report T_g we prepared corresponding blends with poly methyl (**1/PMA**), ethyl-(**1/PEA**), and butyl-(**1/PBA**) acrylate elastomers that have distinctly different values of calorimetric T_g (Figure 3). All three blends were thermochromic and showed nonmonotonic behavior of ratiometric curves similar to that of **1/PU**. Shown in Figure 3, the curve minima for all tested polyacrylates were registered at temperatures 60°–66° above their calorimetric T_g. Emission lifetimes of 1.2–4.1 μs were detected for these poly acrylates at their dynamic T_g (Figure 3; Figures S3.3–S3.5, Supporting Information). With previous reports on polyacrylates suggesting that T_g in these polymers scales by ≈7 K per decade we could confirm that our dynamic T_g observation timescale appears to be close to that of PL process as well.[28]

Molecular sensors described in this work can also be used to characterize commercial of-the-shelf polymers with relatively high T_g values. To avoid probe thermolysis that for complex **1** typically involves the elimination of benzene from tetraphenylborate ion we used a more stable complex **2** where BPh_4^- is replaced with a fluorinated BArF anion. Complex **2** reveals no signs of degradation up to 250 °C by thermogravimetric analysis (Figure S4.1, Supporting Information) and withstands treatment in air at 180 °C with no detectible decomposition detected by ^1H and ^{19}F NMR.

Poly(vinylacetate) and poly(methyl methacrylate) can be readily blended with **2** (**2/PVAc**, **2/PMMA**, Figure 3) and subjected to the same testing protocol. While **2/PVAc** has a calorimetric T_g of −1 °C the PL-based analysis reveals a ratiometric curve minima at ≈60 °C—a value corresponding to ΔT = 61° with respect to the calorimetric T_g. The dynamic nature of this T_g is in line with the reference data[29] reporting the 8 K per decade scaling factor for T_g in PVAc. Investigation of the PMMA blend containing **2** similarly reveals a dynamic T_g at 150 °C—a value ≈49° above calorimetric T_g.

A notable feature of all ratiometry curves in Figure 3 is a characteristic transient regime between dynamic and

calorimetric T_g that is typically absent in response curves of conventional PL dyes (Figure 1). We concluded that the presence of transient regime is a direct consequence of the dynamic nature of T_g values that were detected. Anion diffusion rate is a smooth function with respect to temperature,[26] therefore, detected dynamic T_g marks the onset of the diffusion and emission timescale mismatch that develops further until the condition of $\tau_{eq} >> \tau_{PL}$ is met. Remarkably, conventional PL probes[18,21–23] that operate in no connection with their luminescence timescale do not exhibit this broad transient feature taking up to 50° range to develop. This suggests that observed transient is a useful indicator of the link between polymer and exciplex dynamics.

To summarize, in this work we have put forward the first example of organometallic small molecule sensor that utilizes its short lived excited state domain for setting the experimental measurement timescale of T_g detection. Color-based T_g detection using our methodology is a direct consequence of the exciplex dynamics involved in emission wherein two independent processes coexist. First, the fast exciplex rearrangement process selects the emission color and provides the sensitivity to variations in polymer dynamics. Second, the radiative relaxation process sets the limits on detection timescale that can be unambiguously quantified. With dynamic organometallic emitters becoming more common[25,30] and virtually unlimited number of ligand, metal, and counterion combinations available for further synthesis, we anticipate the methodology described in this work to be readily tunable and applicable in general. Having introduced the timescale terms into the operation of emissive polymer sensors, we hope to bring these compounds one step closer to becoming quantitative characterization instruments.

Experimental Section

Full synthesis, characterization data, and methodology description can be found in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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