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Multicolor Organometallic Mechanophores for Polymer Imaging Driven by Exciplex Level Interactions

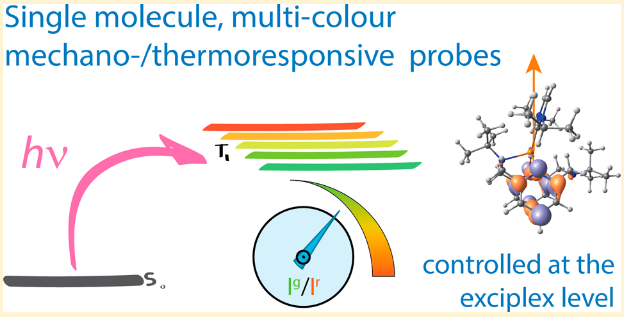
Georgy A. Filonenko,*[†] Dapeng Sun,[†] Manuela Weber,[‡] Christian Müller,[‡] and Evgeny A. Pidko[†,§]

[†]Inorganic Systems Engineering Group, Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The Netherlands

[‡]Institut für Chemie und Biochemie, Freie Universität Berlin, D-14195 Berlin, Germany

[§]TheoMAT Group, Chemistry and Biology Cluster, ITMO University, Lomonosova 9, St. Petersburg 191002, Russia

Supporting Information



ABSTRACT: Photoluminescent compounds can undergo various structural changes upon interaction with light. When these changes manifest themselves in the excited state, the resulting emitters can obtain a sensory function. In this work, we designed coordination compounds that can vary their emission color in response to thermal and mechanical stimuli. When embedded in a polymer matrix, Cu−NHC sensors act as mechanophores, and their color-based response can readily describe mechanical stress and phase transition phenomena. A strong practical advantage of new mechanophores over previous generations of organometallic stress sensors stems from their reliance on emission color variations that are easy to detect. In a broad context, our work implies that emission color variations that we often view as thermally governed can also be triggered mechanically and used to generate sensory information.

INTRODUCTION

Characterization of soft matter poses a grand fundamental challenge. In large part, it stems from the vast structural complexity and heterogeneity inherent to soft matter. As a result, we often cannot rely on conventional characterization techniques like rheology, thermal analysis, and scattering as they fall short of describing soft matter on the molecular level. In response to this challenge, researchers turned to the use of small molecule sensors that can respond to macroscopic mechanical stimuli and describe them from prescribed locations within the material. Termed as "mechanophores", these sensors add valuable molecular level information to a conventional global characterization foreground. The development of new mechanophores was the primary motivation for this work.

Modern mechanophores take many forms depending on their application and the type of response they generate.[1] The most common mechanism of sensory response involves the alternations of probe absorption or emission resulting in a detectable change of the material coloration. The direct advantage of such color-based mechanophores is the ease of signal detection that relies on simple, noninvasive optical measurements of emission, absorbance, or reflectance. Remarkable materials responding to various stimuli can be generated using such optically responsive probes especially when they are used in combinations to provide several independent response sources each having a specific color-based signal.[2,3]

The operation of most common mechanophores is based on the structural rearrangement or breakdown of the probe in response to external force. One of the earliest classes of mechanophores developed by Weder and co-workers[4,5] relied on aggregation-induced changes of the probe emission color. Many organic mechanophores can also require partly or nonreversible bond scission or isomerization events to produce a sensory response. Such chemical transformations can be accompanied by luminescence[6] or strong changes in fluorescence or absorbance between pristine and mechanically activated materials.[7−9] Finally, the latest reports described mechanophores that do not require any probe degradation. Instead, they utilize purely noncovalent interactions between emitter and quencher[10] or rely on variations of the intramolecular isomerization dynamics induced in organometallic emitters by external force.[11] These events impact the photoluminescence (PL) intensity output that is used as a main feedback channel. Having a clear advantage of being intrinsically reversible, such mechanophores do not show any color variations and require very accurate measurements of emission intensity. The latter requires a complex experimental setup to be performed accurately and represents a crucial practical limitation of sensors based on intensity measurements. In this respect, the measurement of emission color offers a more practical alternative. In conceiving this work, we

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sought to overcome this heavy practical limitation and create mechanophores that provide multicolor feedback while being intrinsically reversible.

The goal that we set implied that a fundamentally different mechanism would be necessary for the mechanophore to change color in response to external force. As a main design motif, we explored a **CuN_4** complex family containing a pyridinophane macrocyclic ligand and a copper N-heterocyclic carbene (NHC) core (Figure 1A) that we recently utilized for imaging deformation dynamics in polyurethanes.[12] Coincidentally, we discovered that complexes **2** and **3** (Figure 1A) can drastically change their emission color when cooled to liquid nitrogen temperatures. As the mechanism behind this thermochromic behavior was unclear, we investigated its origin and potential in sensory applications. We found a particularly strong inspiration in an elegant precedent recently reported by Steffen and co-workers[13] who described a family of copper N-heterocyclic carbene (NHC) complexes showing PL color variations in response to grinding in the crystalline state. Authors proposed that variations in ion pairing in the excited state of the phosphor were in fact responsible for the observed mechanochromism. In this work, we found that a similar phenomenon governs the thermochromic behavior of complexes **1**−**3** and enables their remarkable performance in a sensory role.

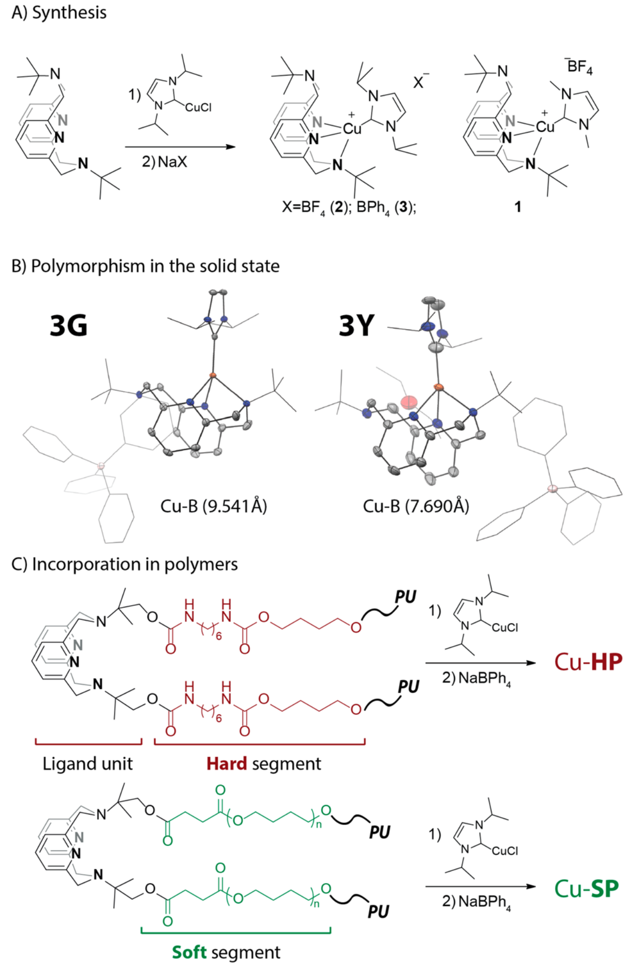

Figure 1. Structures and synthesis of new compounds used in this work (A). Selected solid-state structures of polymorphs of complex **3** and Cu−B distances (B) and selective polymer phase labeling pathway (C). For structural data for compounds **2** and **3**, see Supporting Information.

■ RESULTS AND DISCUSSION

The new coordination compounds **2** and **3** were prepared by the direct complexation of a macrocyclic ligand and a Cu−NHC precursor followed by an ion exchange with the corresponding sodium salt (Figure 1A). Similar to the known complex **1**, **2** and **3** are cationic species containing a noncoordinating BF_4 or BPh_4 anion. Isolated as crystalline solids, **2** and **3** were characterized by NMR spectroscopy and single crystal X-ray diffraction (Figure 1B and Supporting Information). Similar to complex **1**, the new complexes in the solid state featured a Cu center bound to three N-donor atoms of the macrocyclic ligand with a tetrahedral environment around the metal site. Interestingly, both **2** and **3** crystallized as two polymorphs, denoted **Y** and **G**, having different packing and ion pair arrangement in the crystal (Figure 1B; for polymorphs of **2**, see Supporting Information).

In CH_2Cl_2 solutions, new complexes **2** and **3** were moderately efficient emitters with complex **3** having a quantum yield (QY) of 42% and complex **2** showing a 21% QY. Regardless of composition, all compounds exhibited pronounced thermochromism in CH_2Cl_2 solutions; namely, the emission color gradually changed from green-yellow to dark orange upon cooling to −90 °C. This change was characterized by a ca. 50 nm red-shift of emission maxima and a marked change in PL spectrum profile (Figure 2A for complex **2** and Section S3 of Supporting Information). Several emission bands were present in all emission spectra, and the position of the main emission feature at ca. 560 nm was highly dependent on sample temperature. For all complexes in this work, cooling led to the red-shift of PL spectrum. The degree of color change in **1**−**3** can readily be described in ratiometric terms using the spectral intensity ratio as a descriptor. We found that the ratiometric data expressed as *R*(530/610) correlated linearly with the sample temperature for solutions, films, and crystals of the representative complex **2** (Figure 2A) and its analogues (Section 3 of Supporting Information).

Similar to their solutions, crystalline **2** and **3** also showed thermochromic behavior. The emission spectrum in all cases underwent a pronounced red-shift upon cooling (Figure 2A and Section 3 of Supporting Information). We noted that the initial emission color of these crystals depended heavily on the arrangement of ion pairs in them. The emission of **Y** polymorphs at low temperature was significantly red-shifted compared to that of **G** polymorphs (Figure 2A for complex **2**, Figure S3.6 for complex **3**). Examining the solid-state structures of all polymorphs, we found no particularly strong interactions or short contacts that could contribute to thermochromic behavior. Apart from the presence of cocrystallized solvent molecules, noted for both **3Y** and **2G**, the **Y** and **G** polymorphs differ only in the packing of ion pairs with respect to each other with the Cu−anion distances being on average shorter in **Y** polymorphs indicating a tighter ion pairing compared to the **G** subset. Yet again, color ratios in both polymorphs of **2** and **3** scaled linearly with temperature of the sample evidencing a common mechanism of the thermochromism regardless of the polymorph examined.

We noted that the color variations among all environments considered here were observed to the largest extent in dichloromethane solutions, a fluxional environment that allows for unhindered anion diffusion around the cationic complex.

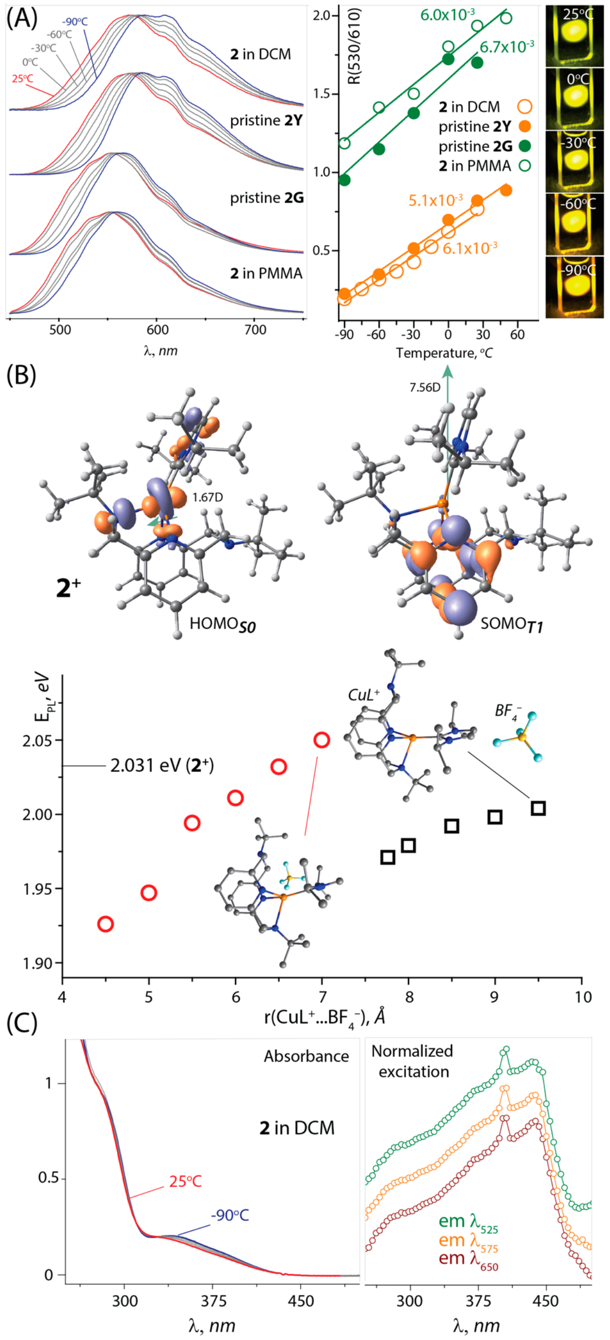

Figure 2. Thermochromism of **2** in different environments: (A) normalized PL spectra and ratiometric data recorded with excitation at 405 nm; (B) DFT analysis of emission color variations, frontier orbitals of the cationic core $\mathbf{2}^+$ and emission energy variations upon ion pair contraction illustrated for two selected stable T_1 configurations; and (C) characterization of the ground state of complex **2** by absorbance and excitation spectroscopy.

Given the purely electrostatic interaction between the weakly coordinating anion and the cationic Cu complex, we proposed that their thermochromic behavior can be directly related to the anion mobility in the system. Therefore, we studied the emission of **2** and **3** in poly(methylmethacrylate) (PMMA) films where the complexes can be finely dispersed and anion mobility should be largely suppressed. The emission of **1**−**3** in rigid PMMA medium was significantly blue-shifted compared to the corresponding solutions. The red bands observed in cold dichloromethane were nearly absent in PL spectra of PMMA films that, however, remained strongly thermochromic (Figure 2A and Figure S3.2). An important observation that we drew from emission data collected for complex **2** in all forms was the monotonic nature of the emission color change in the analyzed temperature range. Such linearity implies that thermally induced phase transitions and conformational changes are not the likely cause for the thermochromic behavior as they would induce abrupt, nonmonotonous color variations.

In line with our suggestion, temperature variations do not appear to alter the ground states of **1**−**3**. Transmittance spectra of **1**−**3** in dichloromethane solutions and PMMA films do not reveal any new features between 25 and −90 °C confirming the identical structure of the ground state present at each temperature (Figure 2C and Figure S3.3). Excitation spectroscopy studies on solutions of **2** indicate identical ground state absorption features regardless of the emission band investigated (Figure 2C) or solution temperature (Figure S3.5a) with all bands in the PL spectrum of **2** showing identical phosphorescence lifetimes (Figure S3.5b) further supporting the message above.

Ruling out the involvement of the ground state transformations, we analyzed the photophysical events leading to emission using DFT calculations. With complex **2** as a model, we found that formation of the triplet excited state is associated with significant geometry distortion at the Cu center that is common for Cu-based phosphors.[14,15] Such distortion, seen in Figure 2B, brings the NHC ligand in the same plane with pyridine N-donor atoms thus breaking the symmetry of the S_0 state. Unlike the S_0 state, the excited state of cationic **2** shown in Figure 2B is highly polarized due to the electron transfer associated with the excitation. This polarization is the underlying reason for the structural sensitivity of emission color in **2**. A dipole formed in the T_1 state due to charge separation can interact with the weakly coordinating anion and alter the T_1 stability and emission color. The extent of this interaction is governed by two independent factors: the location of the anion with respect to the dipole and its proximity to the complex. As for location variations, we found that **2** can adopt several excited state configurations that are distinguished exclusively by the position of the BF_4 anion relative to the Cu center (Figure S5.2). The predicted PL maxima in these species differ by 20−30 nm and can account for discrete emission bands that we observed experimentally. A much stronger effect on the predicted PL energy is inflicted by variations of anion−cation distance. As shown in Figure 2B, several configurations of **2** were highly sensitive to the increase of ion pair separation that led to a strong blue-shift of predicted emission energy. Coincidentally, this distance dependent polychromism is strongly pronounced in the most stable configuration of **2** that is predicted to constitute ca. 90% of total population in solution of **2** (Figure S5.1).

Since the relative populations in T_1 should not be significantly altered by temperature variations, we concluded that temperature itself is not responsible for emission color changes. Instead, we propose that variations of medium density, and thus molar and free volume, are driving the observed color changes by controlling the extent of ion pairing, e.g., separation between the dipole in T_1 and the nonbound anion. For example, as the solutions of **1**−**3** are cooled, the increase of density inflicts tighter ion pairing and triggers the red-shift of PL as predicted by the DFT calculations. As the medium density changes typically show linear dependence

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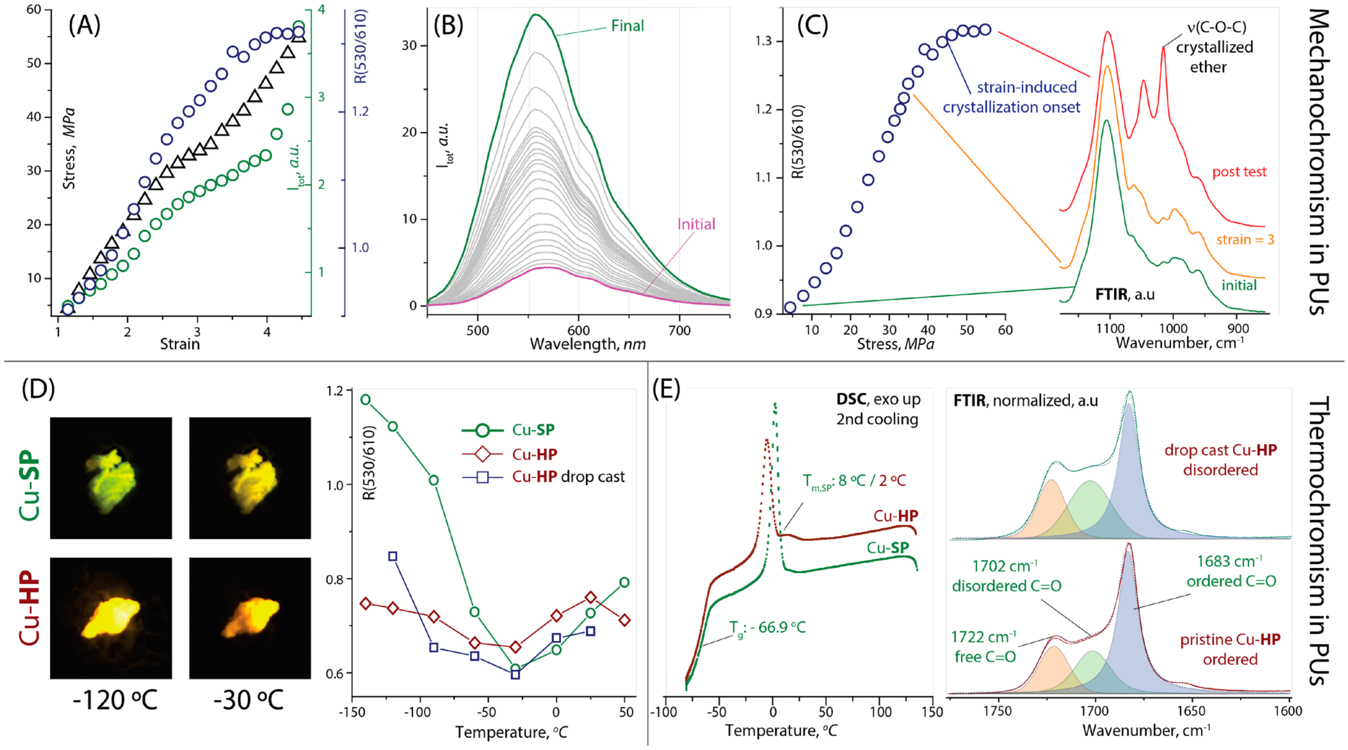

Figure 3. Behavior of CuN_4 mechanophores in the polymer environment. Mechanochromism of soft phase labeled **Cu-SP** polyurethane: (A) stress−strain curve plotted with total integral intensity and color ratiometry data (see tensile test methodology in the Supporting Information), (B) PL spectra, and (C) color ratiometry data with IR spectroscopy data for the soft phase crystallization. Thermochromism in hard and soft phases of PUs: (D) thermochromism of hard and soft phase labeled PUs and (E) thermal (DCS) and structural (FTIR) data underlying the observed color variations.

from temperature for dichloromethane[16] and PMMA,[17] they appear as a likely reason behind the monotonic nature of the PL color change that we observed for both environments.

In general, the proposed emission mechanism implies that the change of PL color can be triggered by any nonthermal stimulus as long as it affects ion pairing. Variations in solvent polarity and molar volume and associated changes in viscosity and density are known to affect ion pairing in solution.[18−20] Indeed, we found that solutions of **3** changed emission color in response to solvent polarity variations (Figure S3.4). Moreover, crystalline **3Y** polymorphs were mechanochromic (Figure S3.6) and responded to grinding with a notable PL color change. More importantly, due to the remarkable structural sensitivity of emission, the new copper complexes can readily be used for characterizing mechanically and thermally induced transformations in complex polymer environments that we demonstrate in the last section of this work.

As the proof of concept polymers, we selected segmented polyurethanes (PUs), structurally complex materials known to undergo both thermally and mechanically induced transformations. Using the synthetic strategy developed in our previous work,[12] we introduced emissive probes into the main chain of PUs to label "soft" and "hard" phases of the polymer. The soft phase was formed by long chain polytetrahydrofuran (pTHF, 650 Da) polyether while the hard phase was derived from hexamethylene diisocyanate (HDI) extended with 1,4-buthanediol loaded at a 1:4 ratio with respect to pTHF. The macrocyclic ligand was introduced into the PU phases at the polymer synthesis stage at $1.5\%_{mol}$ loading with respect to HDI and further converted to a Cu−NHC complex similar to complex **3** having the highest quantum efficiency of 42% among emitters in this work (Figure 1C).

Tensile elongation tests depicted in Figure 3A reveal a pronounced mechanochromism induced in PUs by mechanophore incorporation. First, upon loading, films of **Cu-SP** containing the probe in the soft PU phase showed a noticeable increase of the relative emission intensity that is fully in line with our previous observations disclosed for $\mathbf{CuN_4}$ mechanophores. Namely, an external mechanical force apparently led to suppression of mechanophore isomerization dynamics representing the nonradiative PL decay pathway. This, in turn, led to increase in emission intensity similar to that previously reported for $\mathbf{CuN_4}$ mechanophores embedded in similar polyurethanes.[11,12] In addition to the expected performance, **Cu-SP** films were strongly mechanochromic and underwent the blue-shift of the emission color in response to extension (Figure 3A−C). The original color of the sample was recovered immediately after the sample was allowed to relax with no external stress applied (Figure S3.8). The ratiometric analysis of the probe emission was found to correlate with mechanical stress. First, both ratiometric and total intensity data feature identical response onset occurring simultaneously at the stresses of ca. 5 MPa. The ratiometric response, thereafter, scales linearly with the applied stress and mimics the total intensity analysis until the stress values reach ca. 45 MPa. The proposed emission mechanism implies that the blue-shift of **Cu-SP** emission color upon extension is indicative of an increase of the anion−cation separation, and thus a weaker ion pairing. This observation is in good agreement with the literature precedents reporting an increase of the free volume in polymers as they undergo tensile elongation.[21,22]

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At the latest stages of deformation when the stresses are greater than 45 MPa, the integral intensity data deviated from the color-based analysis. Namely, while the integral intensity increased rapidly at stresses >45 MPa, the color of the PU film did not change any further (Figure 3C). Confronted with this discrepancy, we sought to explain such probe behavior and assign it to specific physical events in the deforming PU. First, the suppression of mechanochromism implied that at high stress and strain values the soft phase rearrangement is complete and further deformation of the PU does not involve the soft phase restructuring. This suggestion is in direct agreement with a large body of works suggesting that soft phase deformation reaches the full extent before the actual sample failure. More specifically, the soft phase in similar HDI/BDO/pTHF-based polyurethanes was shown to reach maximal extensibility at strains of 2.5−3 with no significant variations taking place thereafter.[23] Furthermore, suppression of mechanochromism in **Cu-SP** coincides with strain-induced crystallization of the soft phase common in polyether-based PUs.[24] According to IR spectroscopy analysis, soft segments in **Cu-SP** remained amorphous at low strains <3 while at higher stains an irreversible soft phase crystallization takes place as evidenced by increase of absorbance bands at 996, 1016, and 1048 cm^{-1} typical for crystalline pTHF (Figure 3C).[24] With these data we could dismiss the observed increase in the integral emission intensity as an artifact caused by the change in the sample crystallinity. The color-based analysis, however, provided a clear indication of a morphological change in PU highlighting our methodology as an operationally simple and highly informative technique to complement intensity analysis that can easily be misinterpreted.

Thermochromism in PUs containing emissive probes also carries a diagnostic function. We observed that the thermally induced color variations in **Cu-SP** contrast those of the reference complex **3**. While solutions of **3** undergo a red PL shift upon cooling, emission of **Cu-SP** shifts toward the blue part of the spectrum in the same temperature range (Figure 3D). According to calorimetry data (Figure 3E), the abrupt color change in **Cu-SP** coincides with the glass transition of the soft phase. Consequently, as the PU approaches the T_g, the thermochromism direction changes and the blue-shift of PL upon cooling takes place. This observation highlights the sensory role of the new chromophores as their thermochromism is controlled by the behavior of the host material that can even contrast the behavior of the free probe in solution.

Thermochromism of the new sensors also allows distinguishing between soft and hard phases once they are labeled with corresponding chromophores. A pronounced difference in color can be observed between **Cu-SP** and its counterpart **Cu-HP** containing a mechanophore in the hard crystalline phase. Apart from the significantly red-shifted emission at room temperature, **Cu-HP** shows nearly no color changes upon cooling (Figure 3D). Color variations in **Cu-HP** were nearly 8-fold lower in magnitude than those of **Cu-SP** allowing for distinguishing the hard and soft phase labeled PUs with naked eye observations. Finally, thermochromism in **Cu-HP** was found to correlate with the hard phase disorder. Comparing the **Cu-HP** prepared by drop casting with the parent material prepared by precipitation from hot solutions, we saw the cast samples to be more responsive to temperature variations. Namely, drop cast samples had an increased magnitude of the blue-shift upon cooling, with the behavior resembling that of the glass forming **Cu-SP** (Figure 3D). Having examined the hard phase composition using IR spectroscopy (Figure 3E), we found that drop casting fabrication introduces significant disorder in the hard phase of **Cu-HP**. The amount of ordered (1683 cm^{-1}) carbonyl groups forming the hard phase crystallites in **Cu-HP** decreases by >20% with relative abundance of disordered H-bonded and free hard segments increasing. As a consequence, a large fraction of probe molecules becomes dispersed in the soft phase and engages in thermally induced transitions typical for the soft phase that was not intended to host a mechanophore in a first place.

CONCLUSION

In this work we set out a new principle for designing thermo- and mechanoresponsive molecules for soft matter characterization. Introducing structural sensitivity into organometallic phosphors on the exciplex level enables a new multicolor response pathway in these intrinsically reversible sensors. As a result, simple ratiometric analysis can be used to monitor polymer transformations that are induced thermally and mechanically. The color of the new probes was shown to be highly sensitive to the probe location that places our methodology on the front line for characterizing complex polymer systems where distinction between macroscopic material compartments is necessary. As an important outcome of our work, we anticipate that tunable photoluminescence induced at the exciplex level may very likely be a general phenomenon that is related to temperature variations indirectly. Furthermore, as it takes effect in various organometallic compounds and hands them a sensory function, we expect our findings to put a new spotlight on organometallic emitters and spur new applications in this diverse class of compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b04121.

Full synthesis and characterization data and testing methodology description (PDF)
XYZ coordinates (ZIP)
Crystal data for **3G** (CIF)
Crystal data for **2G** (CIF)
Crystal data for **3Y** (CIF)
Crystal data for **2Y** (CIF)

AUTHOR INFORMATION

Corresponding Author

*g.a.filonenko@tudelft.nl

ORCID

Georgy A. Filonenko: 0000-0001-8025-9968
Evgeny A. Pidko: 0000-0001-9242-9901

Notes

The authors declare no competing financial interest.

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