Triboluminescent Electrospun Mats with Blue-Green Emission under Mechanical Force

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ABSTRACT: Fibrous mechanosensing elements can provide information about the direction of crack propagation and the mechanism of material failure when they are homogeneously dispersed into the bulk volume of materials. A fabrication strategy of fibrous systems showing triboluminescent (TL) responses is in high demand for such applications. In this work, micrometer-sized Cu(NCS)(py)2(PPh3) crystals were synthesized, and polymeric fibrous mats containing the TL crystals were obtained via electrospinning as a stress probe for the determination of mechanical impact. Four different polymeric systems have been employed (PMMA, PS, PU, and PVDF), and the mechanophotonic sensing performance of electrospun mats of the polymer-crystal composites was measured. Photophysical properties (quantum yield, band gap, and broadness of the emission) of the TL crystal/electrospun mat composites were also studied. TL and PL emission maxima of the PU-based composite mat show identical behavior due to the chemical affinity between the two structures and the smallest fiber diameter. Moreover, the PU fiber mats exhibit long-lived bluish-green emission persisting over a large number of drops.

INTRODUCTION

Stability and stress-sensing elements are highly desirable in a variety of applications in materials engineering. In particular, monitoring the direction of failure in materials can provide information about the mechanism of failure. The key challenge is to develop and control reproducible signals from the sensing elements upon mechanical action. Recent advances in materials science have produced advances in such mechanophotonic sensor materials. One mechanism studied is triboluminescence (TL), where light emission is produced from materials under mechanical impact. 1−5 The triboluminescence of TL crystalline particles into a substrate offers significant potential in the development of impact-sensing technology. 1−15 In recent years, various TL materials such as ZnS/Mn, Y2O3, and Y2O3/Eu; EuD3,TEA, MgD3,TEA, ZnO microsized particles, CaAl2O4, and MgAl2O4; SrAl2O4; Ln/SrAl2O4; BaAl2SiO4; 3,6-dibromocarbazole, N-isopropylcarbazole; ester derivatives of 9-anthracencarboxylic acid; and N-phenyl imide compounds were introduced in the literature. Among these TL materials, organometallic compounds are particularly attractive, allowing the development of noncentrosymmetric structures with accompanying intense triboluminescence, a long-lived quantum yield, and good chemical stability.

The Cu(I)-based TL material, Cu(NCS)(py)2(PPh3), is a useful blue-green-emitting luminescent material. The organometallic complex consists of copper(I) thiocyanate and two ligands, pyridine and triphenylphosphine, behaving as both electron-donating and ancillary linkages to neutralize and stabilize the coordination. The synthesis procedure for this compound is well known, and the system is suitable for obtaining triangular crystalline particles. 15 During a typical TL process, the materials are fractured; therefore, for a possible sensor application, the amount of TL material in the medium gains importance. In the current literature, new TL materials are typically reported with only their solid-state TL responses. However, for practical applications the advantages of polymer composites are incontrovertible, and it is known that the PL properties of the molecule/crystal in a polymer composite can differ depending on the chemical nature of the bare polymer matrix. Although PL and TL follow two different mechanisms, the host polymer matrix would alter the amount of molecule/crystal and consequently influence the TL properties.

Furthermore, because TL performance is associated with the crystalline form of a material, the dissolution of the crystals destroys the TL signal. 16 A rough substrate that can hold the maximum number of TL crystals is needed to optimize the practical applications. A number of approaches have been explored, and polymer-based composites containing crystalline particles have consequently attracted a great deal of interest in the field of light-emitting materials. 16−29 Polymeric films composed of particles are recognized to have excellent physical,

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mechanical, optical, and electrical properties that are necessary for applications in sensor systems.\textsuperscript{36-35}

Electrospun fiber mats are a flexible and easily prepared substrate for functional nanomaterials such as catalytic nanoparticles,\textsuperscript{36-38} surface functional species,\textsuperscript{39} optical elements,\textsuperscript{40} and so forth. In this approach, a high potential difference is applied to a viscous polymer solution. When the applied electrical force overcomes the surface tension of the solution, a charged jet is developed, and the evaporation of solvent leaves behind a nonwoven mat of continuous fibers having submicrometer thickness.\textsuperscript{41}

In this study, Cu(NCS)(py)$_2$(PPh$_3$) crystals were used to impregnate the surface of nonwoven electrospun mats prepared from different polymers, including poly(methyl methacrylate), PMMA; polystyrene, PS; polyurethane, PU; and poly(vinylidene fluoride), PVDF. The polymers employed vary in terms of their morphology and mechanical and electrical properties. For instance, the first two polymers are amorphous, and the last two polymers have a semicrystalline nature. PU is an elastic polymer. PVDF has piezoelectric properties. The TL emission performance of the resulting fibrous composite system was measured with a homemade drop tower system. The triboluminescent performance of the composites was studied under mechanical impact over the range of 0.98–4.98 N.

\section*{EXPERIMENTAL DESIGN}

\textbf{Materials and Methods.} Copper(I) thiocyanate (99%), triphenylphosphine (99%), pyridine (anhydrous, 99.8%), poly(methyl methacrylate) (PMMA) (350 kDa), polystyrene (PS) (350 kDa), polyurethane (PU), and poly(vinylidene fluoride) (PVDF) (280 kDa) ethanol (≥99.8%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other reagents and solvents are available in analytical grade and were used as received. Scanning electron microscopy (SEM) performed with an FEI Quanta 250 FEG (Hillsboro, OR, USA) was used to characterize surface morphologies. The parameters for imaging were 2.0 kV, 2.0 nm, secondary electrons, and 6.5 mm for the accelerating voltage, spot size, detector type, and working distance, respectively. Fluorescent images under a blue filter (435–480 nm) were recorded using an Olympus IX2-ILL100 fluorescence microscope (Lambertville, NJ, USA). Photoluminescence emission spectra were recorded using a Varian Cary fluorescence spectrophotometer (Palo Alto, CA, USA). A homemade drop tower system was designed and prepared consisting of a USB2000+ preconfigured 200–850 nm UV–vis spectrophotometer and fiber optic cable (Ocean Optics, Winter Park, FL, USA). Single crystal X-ray diffraction data was collected at 100(2) K on a Bruker D8 Venture diffractometer using Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and a Photon 100 detector. A total of 29 970 reflections were measured, of which 5319 were independent ($R_{int} = 0.0298$). Cu(NCS)(py)$_2$(PPh$_3$) was found to crystallize in the monoclinic crystal system with $a = 9.4006(4)$ Å, $b = 15.1492(7)$ Å, $c = 10.2153(4)$ Å, and $\beta = 116.9660(10)^\circ$. The systematic absences in the data were indicative of space group $P2_1$. The structure was solved by intrinsic phasing (SHELXT) and subsequently refined by full matrix least-squares techniques (SHELXL) on $P2_1$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically, using appropriate riding models. Final $R$ values of $R1 = 0.0185$ and $wR2 = 0.0509$ were obtained on the basis of the observed data.

\textbf{Preparation of the Composites.} In the preparation of the composite materials, electrospun mats were used as the substrates and crystalline particles were used to impregnate their surfaces. Cu(NCS)(py)$_2$(PPh$_3$) crystalline particles were used to impregnate four different polymeric mats, which are PMMA, PS, PU, and PVDF. Each polymer was first dissolved in N,N-dimethylformamide (DMF). Then, each film was prepared by electrospinning the dissolved polymer solution. Electrospinning conditions were fixed as 18 kV, 25 cm, 4 mL/h, and 50% for the applied voltage, spinning distance, pumping rate, and humidity of air, respectively. Crystalline particles of Cu(NCS)(py)$_2$(PPh$_3$) were dispersed in distilled water. The electrospun films were cut to approximately 1 cm in size, and each film was treated with the crystalline dispersion to fabricate the composite film. Finally, the same set of samples with similar Cu(NCS)(py)$_2$(PPh$_3$) content was prepared by an alternative method called blending. In this approach, TL crystals were first dissolved in the polymer solution, and then the homogeneous solution was subjected to electrospinning.

\textbf{Measurement of Triboluminescence.} The triboluminescence (TL) performance of the Cu(NCS)(py)$_2$(PPh$_3$) crystalline particles and electrospun mat-based composites was measured by using a drop tower mechanism specifically designed for TL testing. The material was placed in a sample holder within a black box. A 50 g steel ball with a diameter of 1 cm was positioned on a pullable pin at a set distance of 40 in. (100 cm) above the material. When the pin is pulled, the ball falls and hits the material, and TL emission occurs. A fiber optic cable preinserted directly through a small hole inside the black box can capture and transfer the resulting impact radiation to the spectrophotometer. TL intensity versus wavelength curves are obtained in quick view fluorescence mode. For the impact from a falling object, potential energy is assumed to convert to kinetic energy without dissipation so that a drop from 50.0 cm height causes 2.45 N of mechanical impact for the measurement of the composite’s TL response.

\section*{RESULTS AND DISCUSSION}

\textbf{Characterization and Structure of Cu(NCS)(py)$_2$(PPh$_3$).} The morphology of the as-synthesized Cu(NCS)(py)$_2$(PPh$_3$)

\begin{center}
\textbf{Scheme 1. Synthesis of the Cu(NCS)(py)$_2$(PPh$_3$) Complex}
\end{center}

\begin{center}
\includegraphics[width=0.5\textwidth]{Scheme1.png}
\end{center}

\begin{center}
\textbf{data were measured using Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and a Photon 100 detector.} A total of 29 970 reflections were measured, of which 5319 were independent ($R_{int} = 0.0298$). Cu(NCS)(py)$_2$(PPh$_3$) was found to crystallize in the monoclinic crystal system with $a = 9.4006(4)$ Å, $b = 15.1492(7)$ Å, $c = 10.2153(4)$ Å, and $\beta = 116.9660(10)^\circ$. The systematic absences in the data were indicative of space group $P2_1$. The structure was solved by intrinsic phasing (SHELXT) and subsequently refined by full matrix least-squares techniques (SHELXL) on $P2_1$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically, using appropriate riding models. Final $R$ values of $R1 = 0.0185$ and $wR2 = 0.0509$ were obtained on the basis of the observed data.

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crystalline particles was determined by using SEM. Figure 1a shows a representative electron micrograph of the crystalline powder. There are a number of larger individual crystals in powder assembled into a triangular shape, and the overall particle size distribution is presented in Figure 1b. Each length of individual crystal was measured with the ImageJ program. Three lengths show a Gaussian distribution with average sizes of $100 \pm 25$, $15 \pm 10$, and $40 \pm 20 \mu m$. The photoluminescence of Cu(NCS)(py)$_2$(PPh$_3$) (87 $\mu M$) was measured in DMF, and the spectrum is given in Figure 1c. The complex gives bluish-green luminescence with a peak maximum of 496 nm that is classically observed for the transitions of d orbitals of Cu and $\pi-\pi^*$ transitions of aromatic ligands. The TL spectrum of the as-prepared Cu(NCS)(py)$_2$(PPh$_3$) (25 mg) particles was obtained using the drop tower system, and the TL spectra as a function of height are given in Figure 1d. The TL signals occur at 496 nm, having the same maximum as the PL spectrum. The taller height is translated to a larger applied compression force on the crystalline particles; therefore, greater emission was observed from the 100 cm height. This TL emission is also characterized with respect to applied force and is shown in Figure 1e. Regardless of the impact velocity (developed from the drops from different heights), the wavelength and the shape of the spectra remain unchanged. Not surprisingly, increasing the impact velocity increases the intensity of the signal. When mechanical force is applied, the TL emission might originate from the breaking of copper–nitrogen bonds. The physical deformation of the molecular structure causes charge separation between positively (Cu cations) and negatively (N anions) charged species. This charge separation may produce an electrical field, leading to TL emission.

**Triboluminescence of the Composite.** Crystalline Cu(NCS)(py)$_2$(PPh$_3$) particles were incorporated onto the surfaces of electrospun mats of four polymers. The TL performance of the composite was measured by the drop tower system (Figure 3a) in a fashion similar to the measurement on the as-prepared crystalline powder above. Figure 3bc presents the TL spectra of Cu(NCS)(py)$_2$(PPh$_3$) associated on electrospun mats of PMMA, PS, PU, and PVDF as a function of the number of drops. The TL emission shows a different response with respect to the chemistry of the polymer in terms of the TL intensity from the first impact. The first TL intensities of the composites are 1200, 2500, 4000, and 2750 counts/s for PMMA, PS, PU, and PVDF, respectively. Moreover, the TL response of composite mats (Figure 3b) is quenched after 3, 5, and 6 drops for PMMA, PS, and PVDF, respectively. The TL response of the same crystals can withstand 8 drops for the PU-based composite. We note that the wavelength and profile of the TL emission remain unchanged over consecutive drops, and there is a gradual loss in intensity as the composite becomes quenched (Figure 3c). For comparison, a composite prepared by the blending method exhibited no TL response upon application of mechanical force (Figure S1). In the dissolution process, Cu(NCS)(py)$_2$(PPh$_3$) crystalline particles were molecularly dispersed and the long-range crystalline structure was lost, leading to the loss of the TL properties.

It has been demonstrated that the TL emission depends on the size of the crystalline particles.43,44 When the number of drops increases, i.e., the crystals are beaten many times, the size of the Cu(I) center (Figure 2a) in distorted tetrahedral geometry (N–Cu–N = 99.59 to 106.88°; N–Cu–P = 115.38° to 116.23°) for the N-bonded thiocyanate, triphenylphosphine, and two pyridine ligands. An important feature enabling TL is the lack of a center of symmetry characteristic of space group $P2_1$, and the proper absolute structure was confirmed by a Flack parameter of 0.010(11). The molecules pack in a manner by which the Cu(I) centers maintain a polar directionality along the b axis throughout the structure (Figure 2b). When any mechanical force is applied, the TL emission might originate from the breaking of copper–nitrogen bonds. The physical deformation of the molecular structure causes charge separation between positively (Cu cations) and negatively (N anions) charged species. This charge separation may produce an electrical field, leading to TL emission.
of the crystalline particles becomes smaller. SEM images of crystalline particles were periodically captured after each drop. Figure 4 shows the images of initial crystals and after the first, third, fifth, and eighth drops. All distributions show Gaussian behavior with mean diameters as follows: 120 ± 20, 100 ± 15, 80 ± 12, 50 ± 10, and 30 ± 8 μm, respectively. It is inevitable that the particle size of crystals decreases with the increasing number of drops, and this is likely a source of decreasing TL intensity with consecutive drops.

The physical properties of the solid substrate also play an important role in influencing the TL performance of the composites. The electrospun mat prepared using PU exhibits representative fiber morphology. Figure 5a shows an SEM image of a PU-based composite prepared by surface impregnation. A uniform distribution of crystalline particles is observed on the surface of the PU electrospun mat. In the case of the PU electrospun mat prepared by blending (Figure 5b), there are no crystals embedded in the surface (rather, the Cu(I)
Photophysical Properties of Cu(NCS)(py)$_2$(PPh$_3$) and Composites. Room-temperature excitation, photoluminescence (PL), and triboluminescence (TL) spectra of the Cu(NCS)(py)$_2$(PPh$_3$) complex in the solid state and its composite with various polymeric fiber mats are shown in Figures 6 and 7, respectively. Table 1 summarizes some of the data extracted from those curves. The complex presented higher optical band gaps ($E_{\text{opt}}$) as a result of blue-shifted excitation spectra in all of the polymeric fiber mats. This shift was at a negligible level in the surface-impregnated films. However, in blended composites more than a 0.5 eV blue shift is accompanied by a broadening of the PL emission spectra ($\lambda_{\text{ex}} = 307$ nm), which reveals the possibility of H-type aggregate formation as a result of face-to-face interactions of the complex in those polymeric fiber mats. This situation is further confirmed by the reduced absolute fluorescence quantum yield ($\Phi_f$) measured in those composites. The $\Phi_f$ value of the solid complex is 98%, and the highest $\Phi_f$ value that is achieved with the blended polymer mats is 1.75% (in the PU matrix). Surface-impregnated polymer mats exhibited higher fluorescence quantum yields.

The TL emission spectrum of the bare complex was red-shifted 10 nm and displayed a narrower distribution compared to the PL emission with a peak centered at 300 nm (Figure 6). The full width at half-maximum (fwhm) difference between the PL and TL emissions was more than 20 nm (Table 1). As stated above, no TL response could be detected from blended films, and no significant difference in the maximum TL emission wavelength is observed between the surface-impregnated composite mats. The main TL emission band of the composite occurs at 497, 496, 498, and 496 nm in the order of PMMA, PS, PU, and PVDF, whereas these values are 490, 490, 497, and 490 nm, respectively, for the PL curves. Except for the PU matrix, a red shift in TL responses, compared to the PL maxima, is detected for all of the surface-impregnated polymer mats. The spectral differences between TL and PL emissions have been explained by self-absorption possibilities, pressure-induced changes in the Franck–Condon factors, the fracture-induced formation of different excited states, and the scattering of photons. In terms of excitation and PL emission spectra of the complex, independent from the matrix, the self-absorption possibility plays a minor role when the integral of overlapped regions is taken into consideration. The red shift in TL emission spectra may arise from the pressure-induced changes, which is defined as altering the spectral feature due to the generation of different excited energy states by mechanical

Table 1: Summary of the photophysical properties of the Cu(NCS)(py)$_2$(PPh$_3$) complex in the solid state and its composite with various polymeric fiber mats.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>Full Width at Half-Maximum (fwhm) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>3.65</td>
<td>20</td>
</tr>
<tr>
<td>PS</td>
<td>3.65</td>
<td>20</td>
</tr>
<tr>
<td>PU</td>
<td>3.65</td>
<td>20</td>
</tr>
<tr>
<td>PVDF</td>
<td>3.65</td>
<td>20</td>
</tr>
</tbody>
</table>

Overlapped regions are taken into consideration.  

Figure 5. SEM (a, b) and FM (c, d) images (scale bar = 200 μm) of the composite mats prepared by both surface impregnation and blending.

Figure 6. Excitation, PL, and TL emission spectra of the Cu(NCS)(py)$_2$(PPh$_3$) complex in the solid state.
action. This explanation is further supported by the lifetime measurements that were all on the nanosecond scale (data not shown here), short enough to allow the effects of pressure-induced changes.46

The TL emission intensities and \( \Phi_f \) values of the polymer mats increase in the order of PMMA < PS < PVDF < PU (inverse order of fiber diameters). Among the studied polymers, PU exhibited the highest \( \Phi_f \) values and the minimum spectral difference between the TL and PL emissions. This situation is attributed to the chemical composition of PU, which contains phenyl rings and carbonyl groups that may provide a medium for van der Waals, \( \pi-\pi \), and dipole–dipole interactions between the complex and the polymer matrix. Additionally, these interactions may be motivated by the lower fiber diameter of PU polymer mats.

## CONCLUSIONS

Organometallic-based triboluminescent complex Cu(NCS)\(_2\)(py)\(_2\)(PPh\(_3\)) was synthesized and utilized as a mechanosensing platform using electropsun fiber mats of four different polymer matrices: PMMA, PS, PU, and PVDF. The newly designed composite system by the surface impregnation of crystalline particles on the electrospun mats leads to potential applications in the development of smart optical probes. Notably, the PU-based composite also exhibits an impressive TL response with extended mechanical action due to an electrospun mat with the thinnest fiber network formation. Additionally, the photophysical properties of the composite, such as solid-state PL and TL, show compatible spectral characteristics. This result implies that the PU with chemical affinity wraps the Cu(I) complex and keeps the luminescence transitions at the same level. This system offers a high quantum yield, long-lived detectable TL response, and higher PL efficiency.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b02875.

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**Table 1. Photophysical Data for the Cu(NCS)\(_2\)(py)\(_2\)(PPh\(_3\)) Complex and Its Composite with Polymeric Mats**

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{\text{PLmax}} ) (nm)</th>
<th>fwhm(_{\text{PL}} )</th>
<th>( \lambda_{\text{TLmax}} ) (nm)</th>
<th>fwhm(_{\text{TL}} )</th>
<th>( E_{\text{opt}} ) (eV)</th>
<th>( \Phi_f ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>solid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bare</td>
<td>490</td>
<td>113</td>
<td>500</td>
<td>90</td>
<td>2.92</td>
<td>98</td>
</tr>
<tr>
<td>surface-impregnated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>490</td>
<td>113</td>
<td>497</td>
<td>87</td>
<td>3.06</td>
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</tr>
<tr>
<td>PS</td>
<td>490</td>
<td>107</td>
<td>496</td>
<td>85</td>
<td>3.05</td>
<td>34.7</td>
</tr>
<tr>
<td>PU</td>
<td>497</td>
<td>116</td>
<td>498</td>
<td>86</td>
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</tr>
<tr>
<td>PVDF</td>
<td>490</td>
<td>112</td>
<td>496</td>
<td>85</td>
<td>3.00</td>
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</tr>
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<tr>
<td>PMMA</td>
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<td>130</td>
<td>NA</td>
<td>NA</td>
<td>3.44</td>
<td>0.285</td>
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<tr>
<td>PS</td>
<td>519</td>
<td>127</td>
<td>NA</td>
<td>NA</td>
<td>3.53</td>
<td>0.503</td>
</tr>
<tr>
<td>PU</td>
<td>525</td>
<td>140</td>
<td>NA</td>
<td>NA</td>
<td>3.57</td>
<td>1.75</td>
</tr>
<tr>
<td>PVDF</td>
<td>519</td>
<td>143</td>
<td>NA</td>
<td>NA</td>
<td>3.55</td>
<td>0.863</td>
</tr>
</tbody>
</table>

\( E_{\text{opt}} \) and PL data of blended composite mats are extracted from Figure S3. Calculated from the offset of the excitation spectra.

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**Figure 7.** Excitation, PL, and TL emission spectra of the composite fiber mats [PMMA (a), PS (b), PU (c), and PVDF (d)] prepared by surface impregnation with respect to the chemistry of the polymer.
TL response of a PU composite fiber prepared by blending, the fiber diameter of electrospun films, and the excitation and PL emission spectra of the composites prepared by blending

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Notes
The authors declare no competing financial interest.

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