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İncel, A, Reddy, SM and Demir, MM (2017) A new method to extend the stress response of triboluminescent crystals by using hydrogels. Materials Letters, 186 . pp. 210-213. ISSN 0167-577X

It is advisable to refer to the publisher’s version if you intend to cite from the work.
http://dx.doi.org/10.1016/j.matlet.2016.10.007

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A New Method to Extend the Stress Response of
Triboluminescent Crystals by Using Hydrogels

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Keywords: damage sensor, luminescence, mechanosensor, optical composites, piezoelectricity, polymeric 
composites.

ABSTRACT
Polyacrylamide hydrogel entrapment of EuD₄TEA or Cu(NCS)(py)₂(PPh₃) radically extends the emission time of 
the triboluminescent (TL) crystalline particles by a factor of 10³, optimized when matching the 
hydrophilic/hydrophobic characteristics of the TL/gel components. Triboluminescence intensity improves with 
hydration of the TL/hydrogel composite. The composites may be used in impact-related sensor applications.

INTRODUCTION
Triboluminescence (TL) is defined as light emission resulting from the piezoelectric response of crystalline 
materials upon application of mechanical force [1, 2]. TL research is an emerging field for the potential development 
of self-responsive materials in mechano-sensing technology. However, TL materials currently have limitations to be 
applied as a sensing platform because of powder nature of the bulk crystal form. Additionally, the time of TL 
emission is on the order of microseconds [3, 4]. The integration of TL materials into solid matrices is critically 
important to enhance the applicability of these materials in a variety of force-induced sensor platform. The control 
over emission time (i.e. until any emission could be measured upon mechanical action) of TL signals can potentially 
increase the application of TL materials for example, in the chemical sensing of impact related damage to fragile and 
metastable components such as electronics and packaged foods. The synthesis of TL materials under different 
solvents can directly affect the size of crystals, and accordingly TL emission time of compounds [5-8]. Moreover, 
some materials like piperine [5], uranium [6], dimethyl methylphosphate (DMMP) [7], and caffeine [8] can enhance 
the emission when they are associated with TL systems. In terms of polymer-based TL composites, there are some
studies such as ZnS:Mn/polymer composite [9], ZnO tetrapod filled elastomers [10], EuD₄TEA incorporated within polymer films [11], diblock copolymers integrated inorganic TL materials [12] that have been carried out to understand the concept of TL materials within solid matrices. Main advantage of polymer/TL composites is to transfer TL response to any polymeric systems such as films, fibers or any complex-shaped materials for different end-use. In this work, two organometallic crystals (europium tetrakis (dibezonlymethide) triethylammonium, EuD₄TEA and copper (I) thiocyanate bipyridine triphenyl phosphine Cu(NCS)(py)₂(PPh₃)) with different emission wavelengths were obtained and integrated within hydrogel systems resulting in (previously unreported) extended TL emission. The emission of the TL materials of the two crystals was examined particularly in N-hydroxymethylacrylamide (NHMA), N-isopropylacrylamide (NIPAM) and acrylamide (AA) hydrogel matrices.

**EXPERIMENTAL**

Synthesis of EuD₄TEA [13] and Cu(NCS)(py)₂(PPh₃) [14] were carried out using modified methods described elsewhere. The fabrication of TL integrated hydrogels (NIPAM, NHMA, and AA) is described as follows. AA, 48% (w/v) NHMA, NIPAM, N,N'-methylenebisacrylamide (MBA), ammonium persulphate (APS), N,N,N',N'-tetramethylethyldiamine (TEMED) were all purchased from Sigma-Aldrich, Poole, Dorset, UK. Hydrogels were synthesised using a family of acrylamide-based monomers, namely AA, NHMA and NIPAM to form individual respective polymer hydrogels along with MBA as a cross-linker as previously reported [15]. In the preparation of a 1 mL hydrogel each of functional monomer was used individually along with MBA, APS as an initiator, and TEMED as a cross-linker for each of the hydrogels. Each solution was then immediately added to 50 mg of either EuD₄TEA or Cu(NCS)(py)₂(PPh₃). Solutions were purged with nitrogen. Each solution was then separately poured into a glass Petri dish (5 cm inner diameter) and onto a pre-layered cutting of Parafilm® tape to fit the glass surface. The polymerising solution (containing TL material) was then covered with a second layer of Parafilm® tape to sandwich the solution. The sandwiched solution was left to polymerise overnight at room temperature. The dishes containing TL material-entrapped gels were then stored at 4° C prior to use. Specifically designed drop tower system (Fig. 1a) was used for the measurement of TL emission. The material was placed into sample holder, within a black box (to exclude ambient light interference). A 50 gram steel ball with a diameter of 1 cm was positioned on a pullable pin at a set distance of 27 inches (70 cm) above the material. When the pin is pulled, then the ball falls and hits the material. As a result, TL emission occurs. A fiber optic cable pre-inserted directly through a small hole inside the black box, can capture and transfer the impact radiation through to Ocean optics USB2000+ spectrophotometer. The
detector type is a high-sensitivity 2048-element CCD array and the integration time is from 3 to 30000 ms. By using LabVIEW program, the spectra was recorded by quick view fluorescence mode as a graph of TL emission with respect to wavelength.

RESULTS and DISCUSSION

Figure 1 presents morphology and optical feature of the both TL crystals. Based on scanning electron microscopy (SEM) images, Eu(III)-based crystals (Fig. 1b) show rectangular, while the Cu(I)-based crystals (Fig. 1c) possess triangular prisms. Fluorescence spectrophotometry measurements were conducted in polar aprotic solvent, N,N-dimethyl formamide and photoluminescence (PL) emission of EuD₄TEA and Cu(NCS)(py)₂(PPh₃) are given in Fig. 1d and 1e, respectively. PL signal of the former crystal is centered on 614 nm, and the latter one is at 496 nm. TL spectra of EuD₄TEA and Cu(NCS)(py)₂(PPh₃) are given in Fig. 1f and 1g, respectively. In both cases, the higher height translates to a larger compression force onto crystals; therefore, higher intensity in TL emission.

Figure 2 shows TL emission spectra of TL/gel composites. Fig. 2a and 2b depicts TL spectra of the composites consisting of EuD₄TEA before and after water treatment, respectively. TL intensity increases after water soaking of the hydrogels. TL spectra of Cu(NCS)(py)₂(PPh₃) consisting of gel composite before and after treatment are shown in Fig. 2c and 2d, respectively. Even though, the incorporation of EuD₄TEA within an NHMA gel shows a better TL response, NIPAM shows the same tendency when integrated with Cu(NCS)(py)₂(PPh₃). The percentage change of TL emissions can be ordered as 37%, 40%, and 2% for NHMA, NIPAM, and AA composites integrated with EuD₄TEA, respectively. With Cu(I) based composites this order was found to be 5%, 22%, and 75% respectively.

Figure 3 illustrates TL intensity vs emission time of the water soaked composites. Eu(III) based composites were at 150, 200 and 250 seconds for AA, NIPAM, and NHMA, respectively. The most hydrophilic hydrogels, eg NHMA, exhibited the longest emission time with the Eu(III) system. Hydrogen bonding interaction between the hydroxyl functional group of NHMA and the amine groups within TEA of the complex could be stabilizing the structure of the complex and enhancing the TL emission times. On the other hand, the quench times are reduced for Cu(I) based composites at 100 seconds being the maximum. The emission changes were 10, 60, and 90 seconds for NHMA, AA, and NIPAM, respectively. In the latter case, the total emission time apparently increased with increasing hydrophobicity of the hydrogel. The Cu(NCS)(py)₂(PPh₃) compound comprises of hydrophobic ligands. A similar effect has been reported using cyclotriveratrylenes as fluorescent markers, which have their emission enhanced with binding of similarly hydrophobic quaternary ammonium molecules but not with hydrophilic (or charged) species.
Therefore, it is possible that preferential non-polar interactions between the ligands and hydrophobic NIPAM could be stabilizing the complex and enhancing the emission time. In both cases, the TL materials demonstrate optimum TL when the gels are fully hydrated.

The medium in which the light propagates plays a significant role on the photo-physical properties of the TL crystals. The propagation of light through the gel volume depends on the optical density of the solvent in addition to polymeric crosslinking points, where the scattering is induced. Hydrogels provide a dense and viscous medium compared to air. Not surprisingly, TL emission time increases at high viscosity medium. High intensity emission within hydrogels may originate from the better dispersion of TL crystalline particles throughout the hydrogel volume. It is well established that within a cross-linked polymer chain architecture the crystalline particles would be physically entrapped and have less chance to diffuse and/or undergo agglomeration. Figure 4 presents SEM images of TL composites in dry gel (panel a) and in hydrated gel states (panel b), respectively. In the dry state, TL crystals are dispersed into particles as large domains in aggregated and agglomerated form. On the other hand, upon soaking with water, the particle domains are separated and become dispersed due to gel swelling. Thus, TL crystals may individually emit light, resulting in higher overall emission from the assembly of individual crystals.

CONCLUSION

In summary, two TL crystals (red: EuD₄TEA and blue: Cu(NCS)(py)₂(PPh₃)) were incorporated within hydrogels via in situ radical polymerization. The hydrogel matrix was found to have no effect on spectral shape of the TL emission; however, it plays a significant role on the luminescence efficiency and emission time of the TL crystals. The luminescence intensity is improved presumably due to the better particle dispersion. Moreover, sharp TL response of the crystalline particles can be extended to the order of minutes in an appropriate gel matrix. The control over TL response can be achieved by the adjustment of the hydrophilicity/hydrophobicity of the surrounding gel medium.

ACKNOWLEDGEMENT

Thanks to The Scientific and Technological Research Council of Turkey, Turkey encoded with KBAG-114Z292 and joint funding from the Royal Society of Chemistry, UK (Analytical Chemistry Trust Fund) and Natural Environment Research Council, UK (NE/J01/7671) for supporting this work. SMR wishes to thank H. EL-Sharif for useful discussions regarding thin layer hydrogel preparation.
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FIGURE CAPTIONS

Figure 1: Drop tower system (a), SEM images of EuD4TEA (b) and Cu(NCS)(py)2(PPh3) (c), PL emissions of EuD4TEA (d) and Cu(NCS)(py)2(PPh3) (e), TL emissions of EuD4TEA (f) and Cu(NCS)(py)2(PPh3) (g) from different heights.

Figure 2: TL emission spectra of composite materials by EuD4TEA (a,b) and Cu(NCS)(py)2(PPh3) (c,d) for before water treatment (a,c) and after water treatment (b,d).

Figure 3: TL emission of the composites composite after water treatment for EuD4TEA (a) and Cu(NCS)(py)2(PPh3) (b) based composites.

Figure 4: SEM images of NHMA/EuD4TEA composite before (a) and after (b) water treatment.
Figure 1
