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# A new method to extend the stress response of triboluminescent crystals by using hydrogels



Anıl İncel<sup>a</sup>, Subrayal M. Reddy<sup>b,\*</sup>, Mustafa M. Demir<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, İzmir Institute of Technology, Gülbahçe, Urla, 35430 İzmir, Turkey

<sup>b</sup> Chemistry Division, School of Physical Sciences & Computing, University of Central Lancashire, Preston PR1 2HE, UK

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## ABSTRACT

Polyacrylamide hydrogel entrapment of  $\text{EuD}_4\text{TEA}$  or  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  radically extends the emission time of the triboluminescent (TL) crystalline particles by a factor of  $10^3$ , 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.

## 1. Introduction

TL is defined as light emission resulting from the breaking of chemical bonds within crystalline particles after the 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  $\text{ZnS:Mn}$ /polymer composite [9],  $\text{ZnO}$  tetrapod filled elastomers [10],  $\text{EuD}_4\text{TEA}$  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. The main advantage of polymer/TL composites is the

potential to transfer and accentuate TL response within host polymeric systems such films, fibers or any complex-shaped polymeric materials. In this work, two organometallic crystals (europium tetrakis (dibenzon-lymethide) triethylammonium,  $\text{EuD}_4\text{TEA}$  and copper (I) thiocyanate bipyridine triphenyl phosphine  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$ ) 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.

## 2. Experimental

Synthesis of  $\text{EuD}_4\text{TEA}$  [13] and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  [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 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  $\text{EuD}_4\text{TEA}$  or  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$ . Solutions were vortexed and purged with nitro-

\* Corresponding authors.

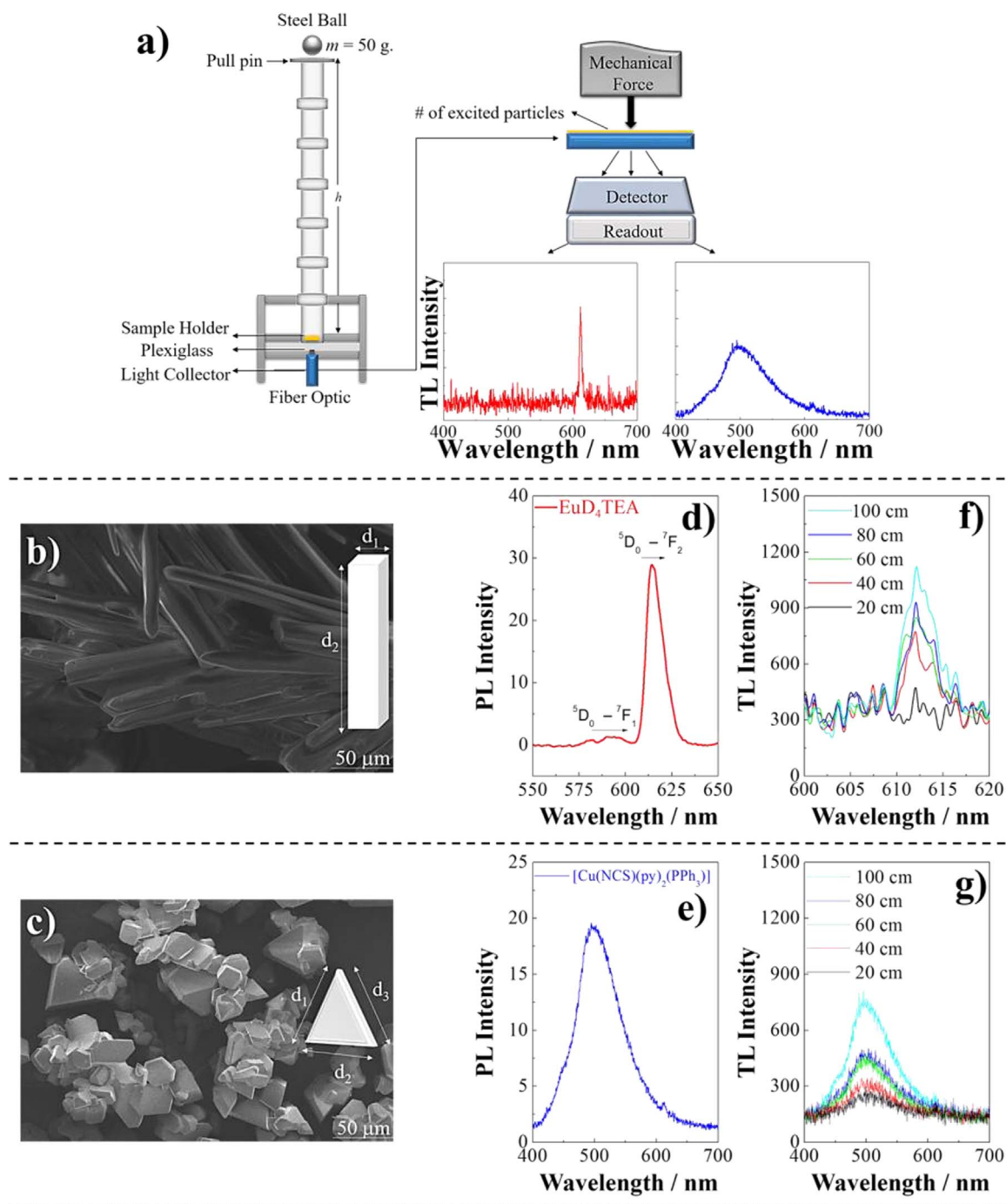
E-mail addresses: [smreddy@uclan.ac.uk](mailto:smreddy@uclan.ac.uk) (S.M. Reddy), [mdemir@iyte.edu.tr](mailto:mdemir@iyte.edu.tr) (M.M. Demir).

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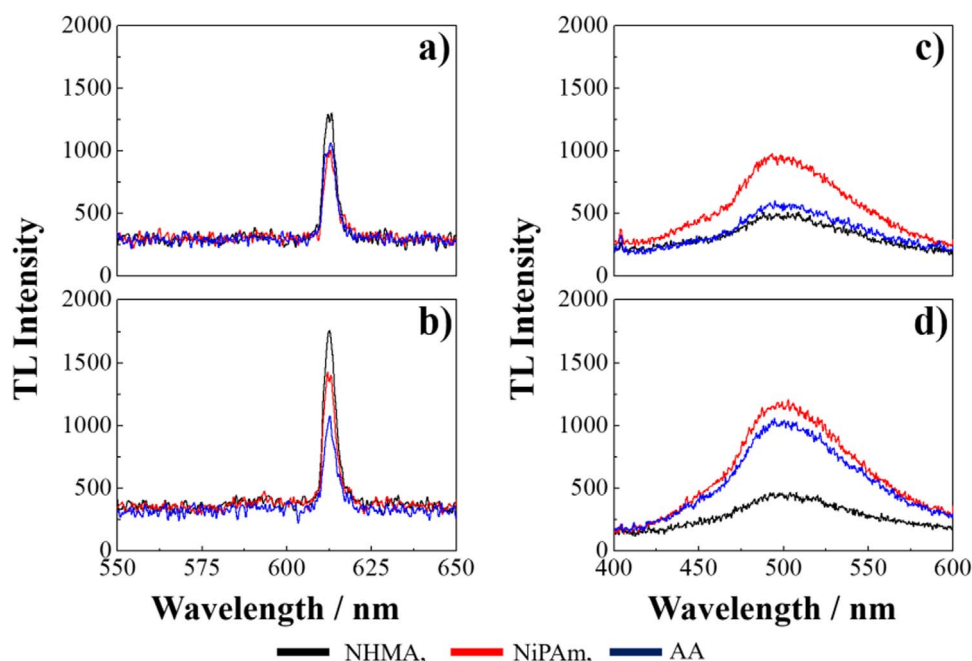
**Fig. 1.** Drop tower system (a), SEM images of  $\text{EuD}_4\text{TEA}$  (b) and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  (c), PL emissions of  $\text{EuD}_4\text{TEA}$  (d) and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  (e), TL emissions of  $\text{EuD}_4\text{TEA}$  (f) and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  (g) from different heights.

gen. 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 g steel ball with a diameter of 1 cm was positioned on a pullable pin at a set distance of 27 in. (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

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 30,000 ms. By using LabVIEW program, the spectrum was recorded by quick view fluorescence mode as a graph of TL emission with respect to wavelength.

### 3. Results and discussion

Fig. 1 presents morphology and optical feature of the both TL crystals. Based on scanning electron microscopy (SEM) images,  $\text{Eu}(\text{III})$ -based crystals (Fig. 1b) are rectangular, while the  $\text{Cu}(\text{I})$ -based



**Fig. 2.** TL emission spectra of composite materials by  $\text{EuD}_4\text{TEA}$  (a,b) and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  (c,d) for before water treatment (a,c) and after water treatment (b,d).

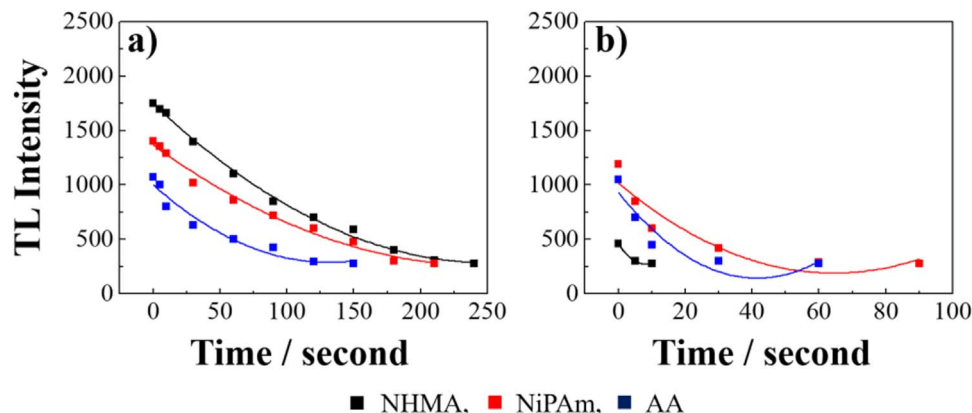
crystals (Fig. 1c) possess triangular prisms. Fluorescence spectrophotometry measurements were conducted in polar aprotic solvent, N,N-dimethyl formamide and photoluminescence (PL) emission of  $\text{EuD}_4\text{TEA}$  and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  are given in Fig. 1d and e, respectively. PL signal of the former crystal is centered on 614 nm, and the latter one is at 496 nm. TL spectra of  $\text{EuD}_4\text{TEA}$  and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  are given in Fig. 1f and g, respectively. In both cases, the higher height translates to a larger compression force onto crystals; therefore, higher intensity in TL emission.

Fig. 2 shows TL emission spectra of TL/gel composites. Fig. 2a and b depicts TL spectra of the composites consisting of  $\text{EuD}_4\text{TEA}$  before and after water treatment, respectively. TL intensity increases after water soaking of the hydrogels. TL spectra of  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  consisting of gel composite before and after treatment are shown in Fig. 2c and d, respectively. Even though, the incorporation of  $\text{EuD}_4\text{TEA}$  within an NHMA gel shows a better TL response, NIPAM shows the same tendency when integrated with  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$ . The percentage change of TL emissions can be ordered as 37%, 40%, and 2% for NHMA, NIPAM, and AA composites integrated with  $\text{EuD}_4\text{TEA}$ , respectively. With Cu(I) based composites this order was found to be 5%, 22%, and 75% respectively.

Fig. 3 illustrates TL intensity vs emission time of the water soaked

composites. Eu(III) based composites were at 150, 200 and 250 s 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 time. On the other hand, the quench times are reduced for Cu(I) based composites at 100 s being the maximum. The emission changes were 10, 60, and 90 s for NHMA, AA, and NIPAM, respectively. In the latter case, the total emission time apparently increased with increasing hydrophobicity of the hydrogel. The  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  compound comprises of hydrophobic ligands. A similar effect has been reported using cyclotrimeratrylenes as fluorescent markers, which have their emission enhanced with binding of similarly hydrophobic quaternary ammonium molecules but not with hydrophilic (or charged) species [16]. 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 [17]. The propagation of light through the gel volume depends on the optical density of



**Fig. 3.** The change in TL emission of composites after water treatment for  $\text{EuD}_4\text{TEA}$  (a) and  $\text{Cu}(\text{NCS})(\text{py})_2(\text{PPh}_3)$  (b) based composites.

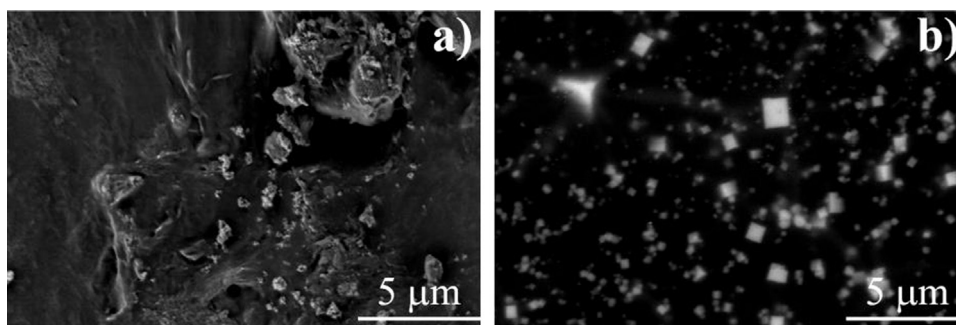


Fig. 4. SEM images of NHMA/EuD<sub>4</sub>TEA composite before (a) and after (b) water treatment (upon mechanical force).

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 [18].

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 [19]. Fig. 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.

#### 4. Conclusion

In summary, two TL crystals (red: EuD<sub>4</sub>TEA and blue: Cu(NCS)(py)<sub>2</sub>(PPh<sub>3</sub>) 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.

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