

# Versatile Method of Generating Triboluminescence in Polymer Films Blended with Common Luminophores

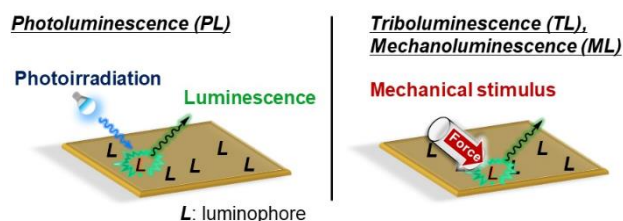
Ayumu Karimata,<sup>\*†</sup> Robert R. Fayzullin,<sup>‡</sup> and Julia R. Khusnutdinova<sup>\*†</sup>

<sup>†</sup>Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan.

<sup>‡</sup>Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, 8 Arbuzov Street, Kazan 420088, Russian Federation.

**ABSTRACT.** Herein we report a versatile method for the preparation of triboluminescent polymer films by physical blending with common luminophores. This method does not require the presence of a crystalline phase, or the use of materials known to be triboluminescent. Emission is generated in response to friction of the polymer surface via triboelectrification, either by rubbing directly or through an inert coating layer, even with low applied stress (< 0.1 MPa). Our findings offer a convenient and practical method of preparation of triboluminescent, amorphous polymer films with easily tunable emission properties.

Triboluminescence (TL), or mechanoluminescence (ML), is an emission of light generated in response to mechanical action. In contrast to photoluminescence (PL), TL does not require light irradiation to produce the excited state (Figure 1), which offers great advantages for the development of mechanoresponsive materials capable of visualizing applied mechanical force or as components for self-powered light-emitting devices. A variety of materials have been discovered to show TL, including photoluminescent as well as non-photoluminescent compounds such as sugars, inorganic salts, rare-earth doped ceramics, and semiconducting particles.<sup>1-10</sup> The most widely studied TL materials are crystalline solids that show emission upon their fracture. In practical terms, the utilization of crystalline materials to observe TL imposes serious limitations to reliable preparation and repeatable use, as the observed effect is usually a function of a crystal size and it tends to diminish after mechanical damage.<sup>12-13</sup>



**Figure 1.** Schematic concept of photoluminescence and triboluminescence of luminophores in a polymer film.

Considering widespread practical applications of synthetic polymers across all sectors in industry as components of consumer products, electronic devices, flexible displays, etc., the

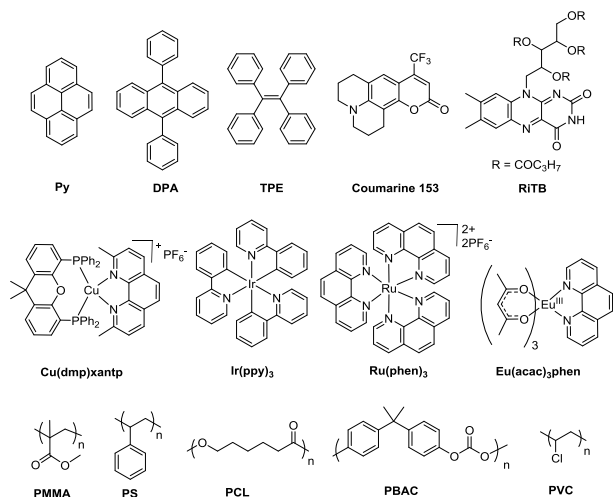
development of a general method to fabricate triboluminescent polymer films is of great practical importance. The most commonly adopted approach to fabricate TL polymer films is through the doping of polymers with additives of compounds known to show TL in the solid (crystalline) state. However, this leads to a limited choice of TL additives and often requires the presence of a crystalline phase within the polymer. For example, Demir et al. found that a known triboluminescent europium and copper complex blended with polymer matrix does not produce TL by impact of a steel ball when it is amorphous, while the films containing microcrystalline material are triboluminescent.<sup>12-13</sup> Although examples when polymers are blended with triboluminescent europium complexes were known, the presence of crystalline phase has not always been confirmed experimentally.<sup>14-16</sup> A different class of triboluminescent materials are based on rare-earth doped ceramics and semiconducting particles.<sup>2, 5-6, 8-9</sup> However, the limitations to their practical include limited dispersion in polymers, which in turn affects film transparency, homogeneity, and mechanical properties. Developing a simple and general method to fabricate triboluminescent amorphous polymer films and coatings with tunable emission is thus an important milestone for the practical use of the TL phenomenon.

We have recently reported a family of copper(I) complexes supported by macrocyclic pyridinophane ligands (<sup>R</sup>N<sub>4</sub>) and N-heterocyclic carbene (NHC) that were used as cross-linkers in polyacrylate films that showed repeatable changes in PL intensity in response to elastic deformation.<sup>17</sup> Interestingly, the same complexes were also found to exhibit TL in their crystalline state, and even when physically blended into amorphous polymer films.<sup>18</sup> We have shown that TL in amorphous blended polymethylmethacrylate (PMMA) films likely originates from triboelectrification of the polymer matrix.

Considering that excitation via triboelectrification is likely to be a general phenomenon, we sought to develop a simple and convenient method of generating TL in polymer films. Herein we report a versatile and simple method to fabricate triboluminescent polymer films containing a wide range of common luminophores and polymer matrices, which simplifies the preparation of triboluminescent polymers without the need for presence of a crystalline phase. Moreover, the luminophores may be selected from a wide range of common organic and organometallic photoluminescent compounds, which are not limited only to TL materials.

To investigate the versatility of this method, we selected nine representative organic compounds or metal complexes that were reported to show fluorescence, thermally activated delayed fluorescence (TADF),<sup>19-20</sup> or phosphorescence in the literature (Chart 1): Before testing them as additives for luminophore-blended polymers, we examined whether these compounds show TL properties in the crystalline state.

**Chart 1. Common luminophores and polymers selected for this study.**



The TL of crystalline samples was confirmed by grinding the crystals using a glass tube under Ar. The generated emission was detected using a fiber optic probe. The summary of PL and TL properties in Table 1 show that five of the selected compounds show no detectable or very weak TL in the crystalline state (see SI and supporting movie 6 for details). Previous studies also confirm that **Py** shows no TL in crystalline state.<sup>21-22</sup> Only the crystals of **TPE**, **RiTB**, **Ir(ppy)<sub>3</sub>**, and **Eu(acac)<sub>3</sub>phen** showed visible TL under argon.

Although currently there is no unifying theory to explain the origin of TL in solids, it has often been attributed to the formation of oppositely charged planes upon crystal fracture, generating a sufficiently strong electric field to cause discharge through the surrounding gas, which is manifested by the presence of gas-specific sharp emission lines in TL spectrum of non-photoluminescent materials. If the materials are tribophotoluminescent (emit PL when fractured), this may result in excitation of the luminophore via absorption of the UV emission from the excited gas or directly by electron bombardment.<sup>1-2, 5-6, 9, 23-24</sup> While many earlier studies reported that this phenomenon is most commonly observed in non-centrosymmetric (piezoelectric) crystals,<sup>22</sup> several other studies showed that TL may also be present in centrosymmetric crystals (as well as achiral polymers and metals), and no full correlation is present between lack of centrosymmetry and TL.<sup>10-11</sup> To establish whether non-centrosymmetric crystals were required to observe TL among our selected compounds, we (re)examined their crystal structures by single crystal X-ray diffraction (SC-XRD) (Table S1) and powder X-ray diffraction (PXRD), which confirmed the absence of polymorphs in the studied samples and that the PXRD patterns were consistent with patterns simulated based on the SC XRD structures (Figure S10, 11). No correlation was observed between TL properties and the crystal space group, with both non-centrosymmetric **TPE** (*P2<sub>1</sub>*), **RiTB** (*P1*) and centrosymmetric **Ir(ppy)<sub>3</sub>** (*P*),

and **Eu(acac)<sub>3</sub>phen** (*P2<sub>1</sub>/c*) crystalline samples showing TL in the crystalline state. This is also consistent with our previous results<sup>8</sup> and many recent examples showing TL in centrosymmetric crystals.<sup>6, 9-10</sup>

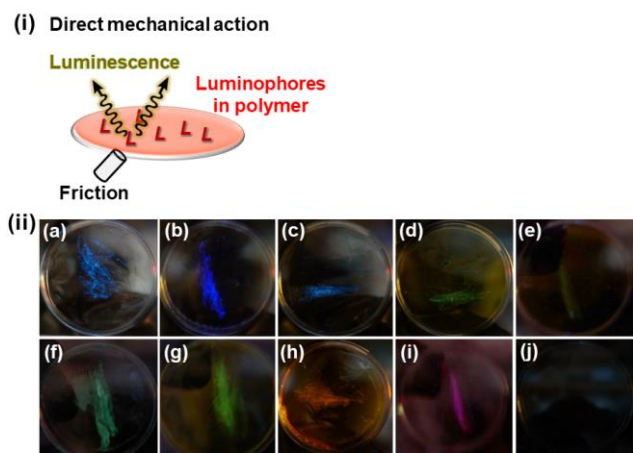
**Table 1. Summary of PL and TL properties in crystal and PMMA film (1 wt%).<sup>a</sup>**

Luminophore	In crystalline state			In PMMA film		
	$\phi^b$	PL $\lambda_{\max}^c$	TL $\lambda_{\max}^c$	$\phi$	PL $\lambda_{\max}^c$	TL $\lambda_{\max}^c$
Py	0.25	473	n.d. <sup>d</sup>	0.58	393	393
DPA	0.73	452	n.d.	0.88	433	432
TPE	0.23	442	456	0.35	464	471
Coumarine153	0.17	527	n.d.	0.59	516	508
RiTB	0.06	601	610	0.24	530	521
Cu(dmp)xantp	0.61	524	550 <sup>e</sup>	0.60	523	535
Ir(ppy) <sub>3</sub>	0.34	540	548	0.74	537	534
Ru(phen) <sub>3</sub>	0.03	620	n.d.	0.17	598	595
Eu(acac) <sub>3</sub> phen	0.08	611	613	0.07	611	613

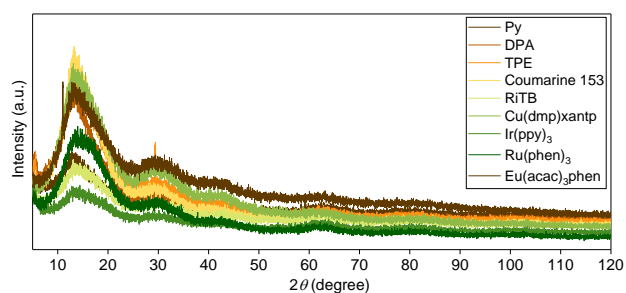
<sup>a</sup>PL properties were measured under N<sub>2</sub> gas flow. TL were measured under Ar gas atmosphere. <sup>b</sup>Photoluminescence quantum yield (PLQY). <sup>c</sup>nm. <sup>d</sup>Not detected or extremely weak. <sup>e</sup>Very weak emission detected spectroscopically.

Next, we prepared luminophore-blended polymethylmethacrylate (PMMA) films by dissolving the luminophores and the polymers in dichloromethane solution, followed by casting on glass and drying under vacuum. Transparent films were obtained, with film thickness of ca. 50-80  $\mu\text{m}$  (Figure S7).

Notably, all of these nine luminophores showed TL when blended in PMMA and rubbed directly with a glass rod under an inert atmosphere (Figure 2). PXRD and emission microscopy images of the films confirmed the absence of crystal and nano/micro particles (Figure 3 and Figure S14), confirming that a crystalline phase is not necessary to observe TL in blended polymer. The TL spectra in PMMA containing 1 wt% of each luminophore are shown in Figure S22. The film thickness was not an essential factor and TL under argon was observed when the film thickness was varied in 50-300  $\mu\text{m}$  range. Emission maxima of PL and TL in PMMA are summarized in Table 1 and the PL spectra of the luminophores in PMMA films, solutions and solid are summarized in Figure S5. TL maxima of **Coumarin 153**, **RiTB**, and **Ru(phen)<sub>3</sub>** show a blue-shift compared to PL, while that of **TPE** and **Cu(dmp)xantp** are red-shifted. Such emission shifts are likely due to the different environment on the surface of PMMA compared to bulk PMMA.<sup>25-28</sup> The slight shift of the PL and TL maxima in PMMA films as compared to crystalline state is likely due to different environment in PMMA and lack of intermolecular interactions.



**Figure 2.** (i) The schematic illustration of TL generation by direct friction of a polymer film surface. (ii) Photographs of TL generated by direct friction of PMMA films containing 10 wt% of (a) Py (b) DPA (c) TPE (d) Coumarine 153 (e) RiTB (f) Cu(dmp)xantp, and (g) 3 wt% of Ir(ppy)<sub>3</sub> (h) 5 wt% of Ru(phen)<sub>3</sub> (i) 15 wt% of Eu(acac)<sub>3</sub>phen (j) no luminophore. The films were placed on a glass Petri dish and rubbed with a glass rod under Ar. Exposure time of the camera is 5 or 10 s.



**Figure 3.** PXRD patterns of PMMA films including 2 or 3 wt% of luminophores.

Next, to examine if TL can be observed in other polymer films, we prepared luminophore-blended films in other commercially available polymers including polystyrene (PS), poly( $\epsilon$ -caprolactone) (PCL), poly(bisphenol A)carbonate (PBAC), poly(vinyl chloride) (PVC). All of these polymers showed TL, with PCL samples prone to exhibit less intense TL (Figures S23). Interestingly, visible TL was also observed in the films prepared by blending RiTB and PCL, which may be useful for preparation of biocompatible triboluminescent materials. When the luminophores were blended in PBAC, visible TL was observed even under humid air (relative humidity 40%) (Figure S28, S29 and supporting movie 3), which may be convenient for practical application of TL films under ambient atmosphere.

Although TL in polymers has not been studied to the same extent as TL in crystalline materials, relevant studies indicate that closely related phenomena occur upon friction being generated on a polymer surface, resulting in electric field generation through tribocharging.<sup>24, 29-31</sup> Similar to TL in crystals, this may result in surrounding gas discharge and triboemission of particles (electrons, ions, photons), which may be experimentally detected by observation of gas-specific emission lines in the TL spectrum. In addition, if gas discharge is involved, the TL intensity may be dependent on the gas dielectric strength,

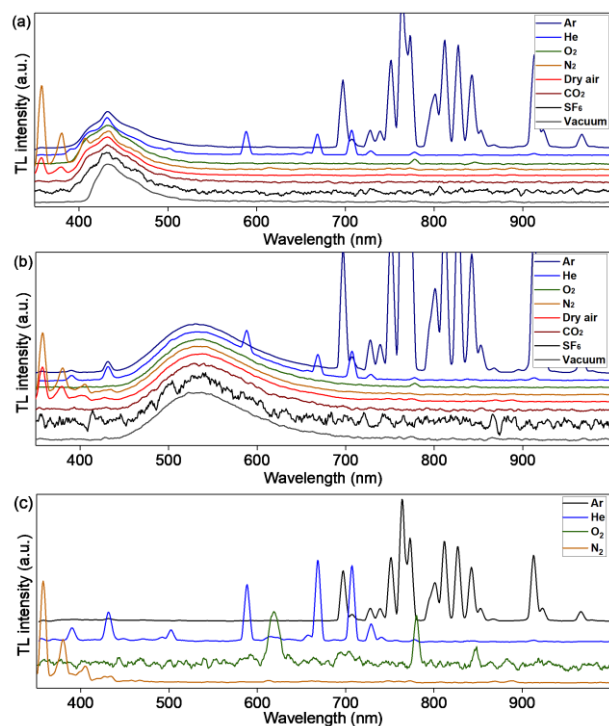
with helium and argon being more likely to undergo dielectric breakdown, followed by CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and air, and with SF<sub>6</sub> showing highest resistance to discharge.<sup>23</sup>

To determine if triboelectrification-induced gas discharge occurs in luminophore-blended films, TL spectra were measured in PMMA films under an atmosphere of different gases: argon, nitrogen, oxygen, helium, and dry air. The full range of TL spectra of PMMA films containing DPA and Cu(dmp)xantp, which exhibit good PLQY (0.88 and 0.69, respectively), clearly show the presence of a broad intense emission peak of a luminophore and sharp peaks (Figure 4), which can be ascribed to the emission from the corresponding gas discharge. These peaks are in good accordance with emission spectra of gas discharge tubes obtained independently (Figure S17) or reported in the literature.<sup>29</sup> The gas discharge spectra were observed even in PMMA films in the absence of luminophore additives (Figure 4c), however, the weak emission could only be detected effectively by spectroscopic measurements, showing that polymer blending with luminophores is essential to observe clearly discernible visible emission. Consistent with the order of relative dielectric strengths of gases, the TL intensity increases under He, while it is extremely weak or absent under an SF<sub>6</sub> atmosphere, with intermediate intensity observed under an N<sub>2</sub> or Ar atmosphere.

Although absorption of emission in UV region from excited gas was proposed as one of the mechanisms of TL generation in PL solids,<sup>2-3, 6, 23</sup> this does not appear to be the main factor in luminophore-blended PMMA films, as TL was also observed under CO<sub>2</sub> gas, in which no clearly observed gas discharge emission lines were present (Figure 4a, 4b, and supporting movie 2). Under vacuum (>0.1 Torr), a slight increase in the TL intensity was observed (See supporting movie), however detectable gas discharge emission peaks were not present in the TL spectra (Figure 4a, b and Figure S24 and S25). Interestingly, although O<sub>2</sub> is usually expected to quench TL of Cu complexes, TL of Cu(dmp)xantp in PMMA was spectroscopically detected even under O<sub>2</sub>, presumably due to steric prevention from contact with O<sub>2</sub> in a rigid polymer matrix.

Furthermore, following the hypothesis that triboelectric charging may be involved in electric field generation, we examined whether TL intensity depends on the relative position of the two materials in the triboelectric series, which rank the materials according to the ability to acquire positive or negative charge. In general terms, if two materials are further away in the triboelectric series, greater charge may be accumulated, and less efficient charge separation should occur by friction between two identical materials, although reported studies indicate that several factors such as surface roughness and generation of polymer fragments may also be responsible for triboelectrification by rubbing two chemically identical materials. When the surface of the PMMA films containing the luminophore was rubbed by a rod made of polyethylene or PMMA instead of glass, negligible TL is observed, while rubbing with PTFE (poly(tetrafluoroethylene) or PVC, both of which are positioned as more negatively charged compared to PMMA and PE in the triboelectric series (Table S2), produced visible TL, consistent with the hypothesis that triboelectrification is involved in generating the TL. Overall, triboelectrification in polymers and other materials occur via complex mechanisms and this phenomenon remains poorly understood at the molecular level.<sup>32-35</sup>

Based on these observations and previously reported studies,<sup>29-31</sup> we propose that tribocharging in luminophore-blended polymer films leads to electric field generation, which causes surrounding gas discharge and luminophore excitation by energy transfer from excited gas and electron bombardment.



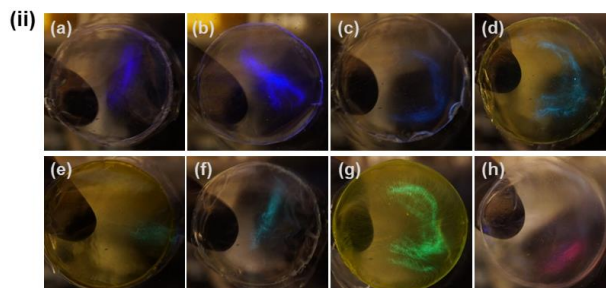
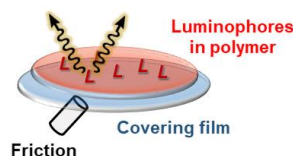
**Figure 4.** Observation of gas-specific emission lines in TL spectra of PMMA films containing (a) **DPA** (2 wt%) and (b) **Cu(dmp)xantp** (3 wt%) and (c) PMMA without luminophores under different gases.

Considering the idea that electric charge buildup via triboelectrification likely plays a major role here,<sup>30-31</sup> we then explored the possibility of generating TL in the absence of a direct physical damage to the sample which contained the luminophore, via mechanical force applied through a layer of another, inert material not containing luminophores (Figure 5i). This was demonstrated in two experimental setups described below.

First, to demonstrate this method, PMMA or PS films containing a luminophore (1 wt%) were covered with a PVC film containing no additives (thickness: ca. 20  $\mu\text{m}$ ), as illustrated in Figure 5i. The surface of the PVC cover was then rubbed with a glass tube under dry air allowing us to detect TL spectroscopically. We observed the same spectrum as upon direct contact, although with much weaker intensity (Figure S30). Rubbing the surface of PVC covering film with silicone rubber provides stronger TL than with a glass rod. To the best of our knowledge, this is the first demonstration of TL of common luminophores blended in polymers by friction through the layer of another inert, additive-free polymer not containing luminophores. The photographs of TL generated by rubbing the PVC cover with a silicone rubber under Ar are shown in Figure 5. TL was observed by gentle rubbing of the outer coating surface while keeping the mechanical stress at less than 0.1 MPa. The versatility and simplicity of this method can be fur-

ther extended to use commonly available materials and additives. When PS film was painted with permanent fluorescent markers and covered with PVC film, rubbing of the PVC covering film with a silicone rod in an argon atmosphere produced clearly visible TL (Figure S31-S32, supporting movie 4).

(i) Rubbing through a layer not containing luminophores



**Figure 5.** (i) The schematic illustration of TL generation by indirect friction through a layer of inert dielectric material. (ii) Photographs of the TL generated by this method using PVC outer layer and luminophore blended PS inner layer containing: (a) **Py** (b) **DPA** (c) **TPE** (d) **Coumarine 153** (e) **RiTB** (f) **Cu(dmp)xantp** (g) **Ir(ppy)<sub>3</sub>** (h) **Eu(acac)<sub>3</sub>phen** blended in PS (1 wt%). The PS/PVC layers are held by a finger against the glove box window and rubbed by a silicone rubber. Exposure time of the camera is 5 s.

In another experiment, PMMA blended with luminophores (**DPA** or **Cu(dmp)xantp**) was placed inside the glass flask under vacuum, then simple rubbing of the outer surface of the glass flask with a latex rubber glove also produces clearly discernible emission, showing that TL may be obtained via contactless method (Figure S33, supporting movie 5). This demonstrates potential and great variability of the discovered method for a convenient fabrication of triboluminescent materials by using commonly available items.

In summary, we disclosed a general and simple method for the preparation of triboluminescent, amorphous polymer films based on a wide range of blended luminophores and polymer matrices. We demonstrated that TL amorphous polymer films can be prepared using a wide range of common luminophore additives, which do not exhibit TL properties in the crystalline state. Although the exact mechanism of TL generation in solids remains poorly understood, our studies show that tribocharging of the polymer matrix is likely involved in generating the electric field, eventually resulting in luminophore excitation by energy transfer from excited gas and electron bombardment. A significant finding resulting from these conclusions is that TL can also be generated by friction through an outer layer of another inert dielectric material which does not contain any luminophores. These findings offer a new, convenient, and broadly applicable method for producing light by applying mechanical stimuli on polymer films with commonly available luminophores. A range of materials

made up of polymer matrices with variable properties, including biocompatible materials, and luminophores with a tunable emission range, can be created via this method.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details and characterization data (PDF).

## AUTHOR INFORMATION

### Corresponding Authors

**Julia R. Khusnutdinova** – Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan; orcid.org/0000-0002-5911-4382; Email: juliak@oist.jp

**Ayumu Karimata** – Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan; orcid.org/0000-0003-0323-2256; Email: ayumu.karimata@oist.jp

### Author

**Robert R. Fayzullin** – Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, 8 Arbuzov Street, Kazan 420088, Russian Federation; orcid.org/0000-0002-3740-9833

### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

This work was supported by JSPS KAKENHI Grant Number JP18K05247. We thank Dr Hyung Been Kang (MEMS, OIST), Dr. Paolo Barzaghi and Dr. Shinya Komoto (Imaging Section), Engineering section and Instrumental Analysis section for technical support and OIST POC grant for funding. R. R. F. performed crystal structure determination within the statements for Kazan Scientific Center of RAS.

## REFERENCES

- (1) Zink, J. I., Triboluminescence. *Acc. Chem. Res.* **1978**, *11* (8), 289-295.
- (2) Sage, I.; Bourhill, G., Triboluminescent materials for structural damage monitoring. *J. Mater. Chem.* **2001**, *11* (2), 231-245.
- (3) Jha, P.; Chandra, B. P., Survey of the literature on mechanoluminescence from 1605 to 2013. *Luminescence* **2014**, *29* (8), 977-993.
- (4) Mukherjee, S.; Thilagar, P., Renaissance of Organic Triboluminescent Materials. *Angew. Chem. Int. Ed.* **2019**, *58* (24), 7922-7932.
- (5) Bünzli, J.-C. G.; Wong, K.-L., Lanthanide mechanoluminescence. *J. Rare Earth* **2018**, *36* (1), 1-41.
- (6) Xie, Y.; Li, Z., Triboluminescence: Recalling Interest and New Aspects. *Chem* **2018**, *4* (5), 943-971.
- (7) Li, W.; Huang, Q.; Mao, Z.; Li, Q.; Jiang, L.; Xie, Z.; Xu, R.; Yang, Z.; Zhao, J.; Yu, T.; Zhang, Y.; Aldred, M. P.; Chi, Z., Alkyl Chain Introduction: In Situ Solar-Renewable Colorful Organic Mechanoluminescent Materials. *Angew. Chem. Int. Ed.* **2018**, *57* (39), 12727-12732.
- (8) Su, L.; Wang, H. J.; Zi, Y. L., Recent progress of triboelectrification-induced electroluminescence: from fundamentals to applications. *J Phys-Mater* **2021**, *4* (4), 042001.
- (9) Zhuang, Y.; Xie, R. J., Mechanoluminescence Rebrightening the Prospects of Stress Sensing: A Review. *Adv. Mater.* **2021**, *33* (50), e2005925.
- (10) Tu, L.; Xie, Y.; Li, Z., Advances in Pure Organic Mechanoluminescence Materials. *J. Phys. Chem. Lett.* **2022**, *13* (24), 5605-5617.
- (11) Chandra, B. P.; Zink, J. I., Triboluminescence of inorganic sulfates. *Inorg. Chem.* **1980**, *19* (10), 3098-3102.
- (12) İncel, A.; Emirdag-Eanes, M.; McMillen, C. D.; Demir, M. M., Integration of Triboluminescent EuD<sub>4</sub>TEA Crystals to Transparent Polymers: Impact Sensor Application. *ACS Appl. Mater. Interfaces* **2017**, *9* (7), 6488-6496.
- (13) İncel, A.; Varlikli, C.; McMillen, C. D.; Demir, M. M., Triboluminescent Electrospun Mats with Blue-Green Emission under Mechanical Force. *J. Phys. Chem. C* **2017**, *121* (21), 11709-11716.
- (14) Fontenot, R. S.; Hollerman, W. A.; Bhat, K. N.; Aggarwal, M. D.; Penn, B. G., Incorporating strongly triboluminescent europium dibenzoylmethide triethylammonium into simple polymers. *Polym. J.* **2014**, *46* (2), 111-116.
- (15) George, T. M.; Sajan, M. J.; Gopakumar, N.; Reddy, M. L. P., Bright red luminescence and triboluminescence from PMMA-doped polymer film materials supported by Eu<sup>3+</sup>-triphenylphosphine based  $\beta$ -diketonate and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene oxide. *J. Photochem. Photobiol.* **2016**, *317*, 88-99.
- (16) Takada, N.; Sugiyama, J.; Katoh, R.; Minami, N.; Hieda, S., Mechanoluminescent properties of europium complexes. *Synth. Met.* **1997**, *91* (1), 351-354.
- (17) Karimata, A.; Patil, P. H.; Khaskin, E.; Lapointe, S.; Fayzullin, R. R.; Stampoulis, P.; Khusnutdinova, J. R., Highly sensitive mechano-controlled luminescence in polymer films modified by dynamic CuI-based cross-linkers. *Chem. Commun.* **2020**, *56* (1), 50-53.
- (18) Karimata, A.; Patil, P. H.; Fayzullin, R. R.; Khaskin, E.; Lapointe, S.; Khusnutdinova, J. R., Triboluminescence of a new family of Cu(I)-NHC complexes in crystalline solid and in amorphous polymer films. *Chem. Sci.* **2020**, *11* (39), 10814-10820.
- (19) Yanagida, S.; Yoshida, M.; Sameera, W. M. C.; Kobayashi, A.; Kato, M., Insight into the Origin of Competitive Emission of Copper(I) Complexes Bearing Diimine and Diphosphine Ligands. *Bull. Chem. Soc. Jpn.* **2019**, *92* (10), 1684-1693.
- (20) Czerwieniec, R.; Leidl, M. J.; Homeier, H. H. H.; Yersin, H., Cu(I) complexes - Thermally activated delayed fluorescence. Photo-physical approach and material design. *Coord. Chem. Rev.* **2016**, *325*, 2-28.
- (21) Gong, Y.-B.; Zhang, P.; Gu, Y.-r.; Wang, J.-Q.; Han, M.-M.; Chen, C.; Zhan, X.-J.; Xie, Z.-L.; Zou, B.; Peng, Q.; Chi, Z.-G.; Li, Z., The Influence of Molecular Packing on the Emissive Behavior of Pyrene Derivatives: Mechanoluminescence and Mechanochromism. *Adv. Optical Mater.* **2018**, *6* (16), 1800198.
- (22) Hardy, G. E.; Kaska, W. C.; Chandra, B. P.; Zink, J. I., Triboluminescence-structure relationships in polymorphs of hexaphenyl-carbodiphosphorane and anthranilic acid, molecular crystals, and salts. *J. Am. Chem. Soc.* **1981**, *103* (5), 1074-1079.
- (23) Sweeting, L. M., Triboluminescence with and without Air. *Chem. Mater.* **2001**, *13* (3), 854-870.
- (24) Dickinson, J. T.; Jahan-Latibari, A.; Jensen, L. C., Fracture emission from single fibres of Kevlar. *J. Mater. Sci.* **1985**, *20* (5), 1835-1841.
- (25) Ellison, C. J.; Torkelson, J. M., The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nat. Mater.* **2003**, *2* (10), 695-700.
- (26) Priestley, R. D.; Ellison, C. J.; Broadbelt, L. J.; Torkelson, J. M., Structural Relaxation of Polymer Glasses at Surfaces, Interfaces, and In Between. *Science* **2005**, *309* (5733), 456-459.
- (27) Roth, C. B.; McNerny, K. L.; Jager, W. F.; Torkelson, J. M., Eliminating the Enhanced Mobility at the Free Surface of Polystyrene: Fluorescence Studies of the Glass Transition Temperature in Thin Bilayer Films of Immiscible Polymers. *Macromolecules* **2007**, *40* (7), 2568-2574.
- (28) Shundo, A.; Okada, Y.; Ito, F.; Tanaka, K., Fluorescence Behavior of Dyes in Thin Films of Various Polymers. *Macromolecules* **2012**, *45* (1), 329-335.
- (29) Nakayama, K.; Nevshupa, R. A., Characteristics and Pattern of Plasma Generated at Sliding Contact. *J. Tribol.* **2003**, *125* (4), 780-787.

- (30) Han, C. B.; Zhang, C.; Tian, J.; Li, X.; Zhang, L.; Li, Z.; Wang, Z. L., Triboelectrification induced UV emission from plasmon discharge. *Nano Res.* **2015**, *8* (1), 219-226.
- (31) Puhan, D.; Nevshupa, R.; Wong, J. S. S.; Reddyhoff, T., Transient aspects of plasma luminescence induced by triboelectrification of polymers. *Tribol. Int.* **2019**, *130*, 366-377.
- (32) Galembeck, F.; Burgo, T. A. L.; Balestrin, L. B. S.; Gouveia, R. F.; Silva, C. A.; Galembeck, A., Friction, tribochemistry and triboelectricity: recent progress and perspectives. *RSC Adv.* **2014**, *4* (109), 64280-64298.
- (33) Lacks, D. J.; Shinbrot, T., Long-standing and unresolved issues in triboelectric charging. *Nat. Rev. Chem.* **2019**, *3* (8), 465-476.
- (34) Zhang, J.; Su, C.; Rogers, F. J. M.; Darwish, N.; Coote, M. L.; Ciampi, S., Irreproducibility in the triboelectric charging of insulators: evidence of a non-monotonic charge versus contact time relationship. *PCCP* **2020**, *22* (20), 11671-11677.
- (35) Zhang, X.; Chen, L.; Jiang, Y.; Lim, W.; Soh, S., Rationalizing the Triboelectric Series of Polymers. *Chem. Mater.* **2019**, *31* (5), 1473-1478.

---

For Table of Contents Use Only

