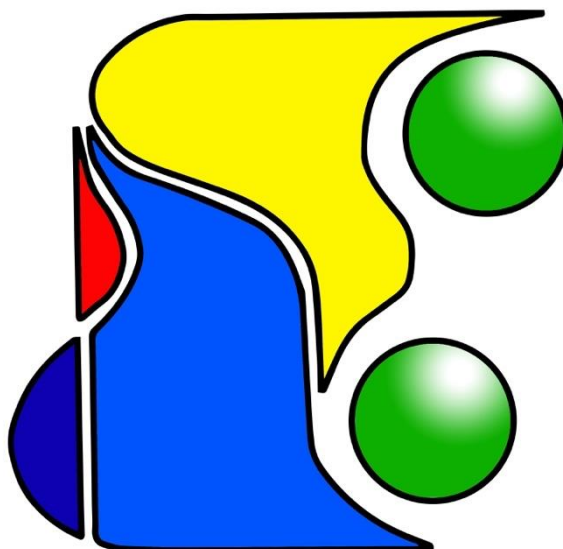


SPACC
先端錯体工学研究会

The Society of Pure and Applied Coordination Chemistry

News Letter

(October, 2021)



SPACC ニュースレター
(2021 年 10 月号)

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Triboluminescence of pyridinophane Cu^I (NHC) complexes in crystals and polymers

Okinawa Institute of Science and Technology
Coordination Chemistry and Catalysis Unit
Ayumu Karimata, Julia R. Khusnutdinova

- ✓ First observation of triboluminescence of transition metal complex in amorphous polymer film.

Triboluminescence (TL), which is also called mechanoluminescence (ML) or fractroluminescence (FL), is a phenomenon in which light emission is caused by crushing, grinding, or rubbing materials¹⁻⁴. In more general terms, triboluminescence is a way of converting mechanical energy directly to light. Currently, triboluminescent materials attract attention as components for damage sensors^{1,2}, self-powered displays³, pressure-sensitive devices. etc. Despite its long history (first example of TL was recorded by Bacon in 1605), the detailed mechanism of this fascinating phenomenon remains a subject of debate until now, and search for new TL materials and their applications remains an active area of research. Among many types of TL materials, europium and terbium complexes have been widely studied, however, the use of rare earth metal-based materials has certain disadvantages due to their high cost and low availability. At the same time, there are only a few reports of inexpensive transition metal complexes that show TL in the crystalline state, however, no examples of transition metal-based amorphous materials (such as amorphous polymer films) were known until recently¹⁻⁵.

Photoluminescent Cu^I complexes have been studied extensively for OLED, photo-catalysis, and chemical sensors because copper is a cheap and abundant metal. Although there are many reports on mechanochromic behavior of photoluminescent Cu^I complexes in crystalline state, examples of triboluminescent Cu^I complexes are extremely limited and it is difficult to single out a particular family of copper complexes where this phenomenon could be systematically studied by variation of substituents or counteranions⁶.

Our research group has synthesized and studied a new series of Cu^I complexes bearing a flexible macrocyclic ligand, pyridinophane (^RN4) in order to create new stimuli-responsive polymer materials⁷. During these studies, we found that [^RN4Cu^I(NHC)]X complexes (NHC = N-heterocyclic carbene) show good air stability and high photoluminescence quantum yield (PLQY). Furthermore, we demonstrated earlier that when such complexes are covalently incorporated as cross-linkers into an elastic polymer chain, the photoluminescence intensity changes in response to simple film mechanical stretching/release in a sensitive and repeatable manner (< 0.1 MPa and < 100% in strain). Thus, these systems showed potential in the visualization of mechanical stress distribution in the polymer by observing changes in photoluminescence

intensity using simple imaging method in real time using a CCD camera⁸. However, this approach required (i) covalent attachment of the metal complex to the polymer and (ii) using external excitation source (e.g. commercial “blacklight” UV lamp) to observe emission via photoluminescence.

Serendipitously, during these studies we noticed that the entire family of six [(^RN4)Cu^I(NHC)]X complexes **Cu1–6** with variable ligands and counteranions (Scheme 1) also show intense TL simply by grinding the crystals with a spatula or glass rod, which can be visible even by a naked eye in air. Detailed investigation of the photophysical properties of these complexes showed that they have good PLQY of 0.66–0.83 in crystals and 0.51–0.79 in poly(methylmethacrylate) (PMMA) films. Interestingly, **Cu1–4** with different counteranions (PF₆⁻, CF₃SO₃⁻, CF₃COO⁻, BPh₄⁻) show

similar PLQY, indicating the effect of counter anion in the crystals is not significant. The photographs of the crystals **Cu1–6** producing light emission by grinding them under air are shown in Figure 1. We then attempted to capture the moment of generation of light from the crystal by using high speed camera. The crystal of **Cu5** was compressed by the two glass plates under air and the photographs show light emission on

the cracks in the crystal during the fracture (Fig 2).

The emission imaging of the TL taken by high speed camera from the side view clearly confirmed that TL is generated inside crystal, not from the contact surface (Fig 3).

One of discussed mechanism of TL is that strong electric field is generated on the cracked surface of a piezoelectric (non-centrosymmetric) crystal when the crystal is

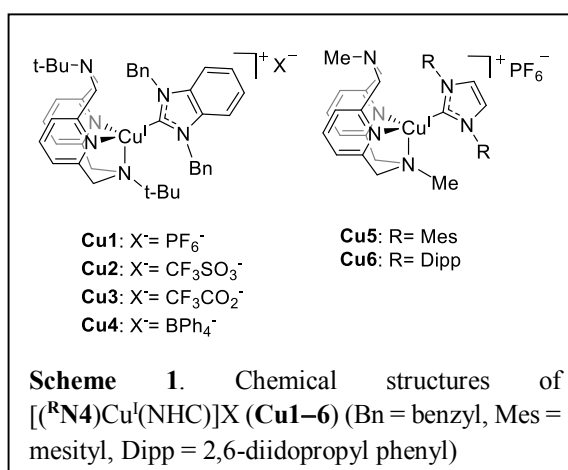


Table 1. TL properties and space group for crystalline and PMMA (1 wt%) of **Cu1–6** under a nitrogen.

Cu	Anion	λ_{\max} in crystal	λ_{\max} in PMMA	Space group ^a
Cu1	PF ₆	544	526	<i>Pca</i> 2 ₁ , NC
Cu2	OTf	539	530	<i>Pca</i> 2 ₁ , NC
Cu3	CF ₃ Ac	536	536	<i>Pca</i> 2 ₁ , NC
Cu4	BPh ₄	540	527	<i>Pbca</i> , C
Cu5	PF ₆	536	552	<i>P2</i> ₁ / <i>n</i> , C
Cu6	PF ₆	527	543	<i>P2</i> ₁ 2 ₁ 2 ₁ , NC

^a C: Centrosymmetric, NC: Non-centrosymmetric

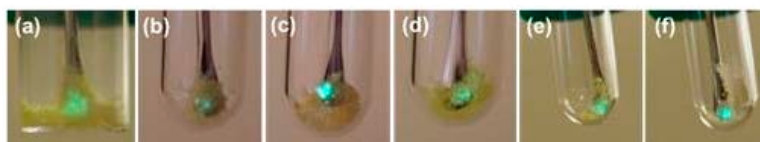


Figure 1. Photographs of TL in crystal of (a) **Cu1**, (b) **Cu2**, (c) **Cu3**, (d) **Cu4**, (e) **Cu5**, and (f) **Cu6**. The crystals in glass tube were ground under air.

broken, which leads to excitation of a molecule in the crystal^{1–5}. However, there are many reports on TL in non-piezoelectric crystals thus consistent with the idea that TL may be generated via various mechanisms. Our study with crystals of **Cu1–6** show that both centrosymmetric and non-centrosymmetric crystals show

intense TL (Table 1). Powder X-ray diffraction patterns of ground crystals were consistent with the simulated patterns obtained from single crystal of **Cu1–6**, indicating that packing structure does not change by mechanical grinding. Strong molecular interactions such as π - π stacking or dipole interaction are not present in the crystals.



Figure 2. Photographs of TL of crystal of **Cu5** taken by high speed camera (view from top). The crystal (size: ca. 2 mm) was compressed between two glass plates under air.

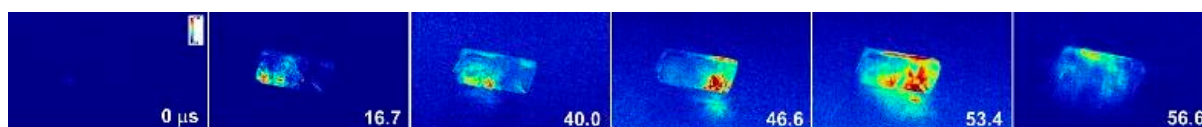


Figure 3. Emission imaging for TL of the crystal of **Cu5** (size: ca. 2 mm) that was compressed between two glass plates under air (view from side).

Based on clearly observed photoluminescence from polymer-blended complexes, we decided to examine if triboluminescence phenomenon will also be observed in the polymer films. Application of easily prepared polymer films that can be easily prepared by simple mixing and casted as coatings on the surface is significantly more attractive for possible practical applications of such materials in device fabrication as compared to using purely crystalline materials. Surprisingly, when small amounts of **Cu1–6** were physically blended into rigid polymer films (e.g. PMMA) simply by dissolving and casting from solution, such films also exhibit

visible TL when rubbed with a glass or plastic rod, even without tearing or rupturing the film. The photographs of TL of 10 wt% PMMA films are shown in Figure 4. Powder X-ray diffraction analysis as well as fluorescence microscopy images confirmed the absence of crystalline phase and nano/microparticles in the PMMAs with 1 wt% and 10 wt% of **Cu1–6**. Previous studies on TL of photoluminescent molecules in polymers have not revealed the generation of TL from amorphous state, or have shown TL from crystals dispersed in polymers^{6,9-12}. To the best of our knowledge, this is the first observation of TL of transition metal complex in amorphous polymer film. Red-shift of TL compared to photoluminescence was also confirmed, which can be ascribed to different environment on the rubbed surface of PMMA. To get insight into the origin

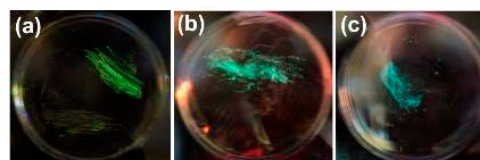


Figure 4. Photographs of TL of PMMA film (diameter: ca. 5.5 cm) containing 10 wt% of (a) **Cu1**, (b) **Cu5**, (c) **Cu6**. The films were rubbed with a glass rod under Ar gas.

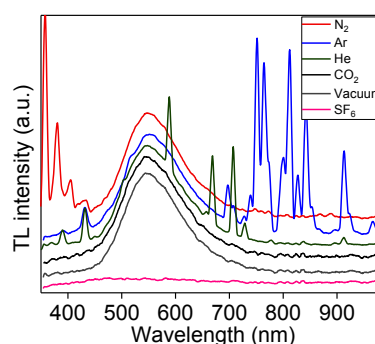


Figure 5. TL spectrum of **Cu5** in PMMA film (1 wt%) under different gas of Air, N₂, Ar, He, CO₂, SF₆, and vacuum (0.5 Torr).

of TL in PMMA film, TL spectra of **Cu5** in PMMA (1 wt%) were measured under different gas flow including nitrogen, argon, helium, carbon dioxide, sulfur hexafluoride, as well as under vacuum (0.5 Torr). TL of **Cu1–6** from PMMAs are not observed in air, which is probably due to quenching of excited state by oxygen or high humidity. A broad emission band of **Cu5** was observed along with sharp intense peaks that can be ascribed to gas plasma emission of nitrogen, argon, or helium (Figure 5). This is sharp contrast to TL in the crystals where no discernible gas discharge lines were observed. Unexpectedly, under CO₂ gas and under vacuum (0.5 Torr), the emission spectra showed only the TL peak of **Cu5** without the gas discharge peaks. Interestingly, emission was extremely weak in SF₆ gas. This result implies that triboelectrification is likely involved in the observed TL properties of Cu-containing polymer films leading to generation of the electric field and gas discharge, which eventually causes photoluminescence of the copper complex blended into the film. More importantly, we have shown that this may be observed in the absence of the crystalline phase using a simple Cu complex. Our discovery will provide new opportunity of organometallic compounds for a wide range of applications including mechanical sensors capable of visualizing mechanical actions on polymer materials via photoluminescence, and mechano-responsive materials such as self-glowing materials. Detailed studies including screening of various luminophores and polymers for effective TL in polymers as well as mechanistic investigation are ongoing.

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2020年度
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なお，2020年度の各賞の受賞年は2021年ですが，2020年度までの業績に対しての授賞となります。

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Hydrogen Production and CO₂ Utilization "

会期: 2021 年 12 月 15 日~20日

会場: Virtual (Online)

シンポジウム世話人:

Yutaka Amao, Yusuke Yamada, David E Herbert, Shi Zhang Qiao

編集後記

今年のノーベル化学賞は有機触媒が受賞テーマでしたね。2010 年にクロスカップリング触媒でノーベル化学賞をご受賞された根岸英一先生と本研究会は、工学院大学での本研究会の国際会議で御講演を賜った御縁があります。今年6月の先生の訃報にふれ、研究会としましては、次回号にて、根岸先生と関係の深い先生方にご寄稿いただき、追悼特集を掲載させていただきたいと思っております。(桑村)

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