

Triboluminescence of pyridinophane copper complexes in crystals and polymers

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Triboluminescence (TL) is known as a light-emission caused by applying mechanical force on a material without photo-excitation. Many Eu and Tb complexes have been reported to show TL, while, there are extremely limited examples on triboluminescent Cu^I complexes. Our research group has studied luminescent pyridinophane (N4) Cu^I complexes¹ and their mechanoresponse in polymers². Recently new family of luminescent (N4)Cu^I(NHC)]X complexes **1**, **2**, and **3a–d** were prepared (Figure 1). The crystals show good photoluminescence efficiency (0.66–0.83) in the crystals and bright TL by grinding them even under air³. Piezoelectricity of crystal has been previously discussed in the literature as a factor to cause strong electric field that leads to excitation of molecule in crystal. However, TL of this luminescent Cu^I complex series is observed in both centrosymmetric and non-centrosymmetric crystals, as well as even in amorphous PMMA films. TL spectra of PMMA films containing 1 wt% of complex **1** were measured by rubbing the surface of the film using glass tube

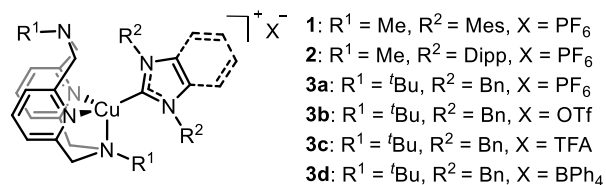


Figure 1. Chemical structure of N4Cu^I(NHC) **1**, **2**, and **3a–d**.

under atmosphere of various gases. In N₂, Ar, and He, intense gas discharge emission was observed (Fig. 2c), which was not observed in the crystal. TL is observed even under CO₂ and in vacuum, while emission is extremely weak or absent in SF₆ gas, implying that gas discharge mechanisms is involved in the excitation of the Cu^I complex in PMMA.

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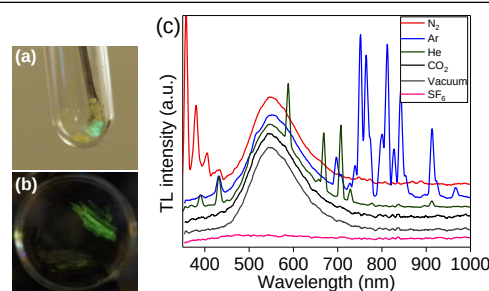


Figure 2. Images of TL of **1** (a) crystal and (b) PMMA film (10 wt%). (c) TL spectra of **1** in PMMA film under different gas (1 wt%).