

A New Triboluminescent Material

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Triboluminescent (or mechanoluminescent) materials emit light when they are crushed, scratched, or rubbed in solid state.¹⁻¹⁵ Owing to the fracture-induced light emission, triboluminescent materials have been investigated as sensor materials for monitoring structural damage in solid substrate.^{16,17} Although the triboluminescent phenomenon is related to electric discharge, the exact light emission mechanism is still unknown. Various types of triboluminescence materials including resorcinol,¹⁸ coumarin,¹⁹ sucrose²⁰ have been reported. Most of triboluminescent materials are also photoluminescent.²¹

Among numerous triboluminescent compounds reported to date, certain compounds such as europium tetrakis (dibenzoylmethide) triethylammonium (EuD₄TEA)²² and salicylic acid salicylate (SAS)¹⁸ shown in Figure 1 emit strong red and blue light, respectively, when they are rubbed (*vide infra*). The light emitted from these materials can be seen even under room light. Considering the significance of the triboluminescent materials in the field of solid state chemosensor, the development of new triboluminescent compounds that display a strong visible light is still an important task. In this communication, we report a new triboluminescent material 1,2-bis(4-(4-*tert*-butylphenoxy)phenyl)ethane-1,2-dione (BBPE) (Figure 1). The substituted benzil derivative BBPE was found to emit an intense green light upon scratching.

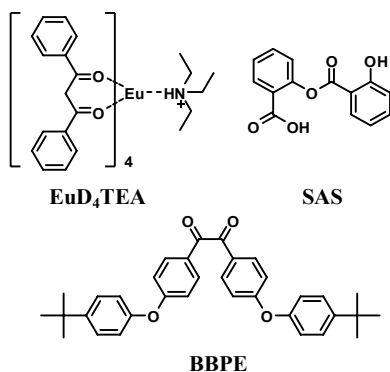
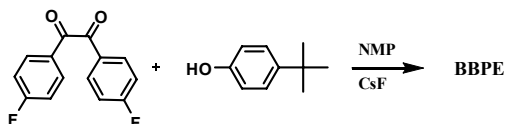


Figure 1. Structure of triboluminescence materials.



Scheme 1. Synthesis of BBPE.

The triboluminescent BBPE was readily prepared from commercially available 4,4'-difluorobenzil and 4-*tert*-butylphenol in the presence of CsF (Scheme 1).²³

Structure of the benzil derivative BBPE was confirmed by ¹H NMR and X-ray crystallographic analysis (Figure 2).

In order to investigate if the benzil derivative BBPE is photoluminescent, the pale yellow solid powder BBPE is placed in a Petri dish and is irradiated with 365 nm UV light. As displayed in Figure 3, green fluorescence can be observed with BBPE.

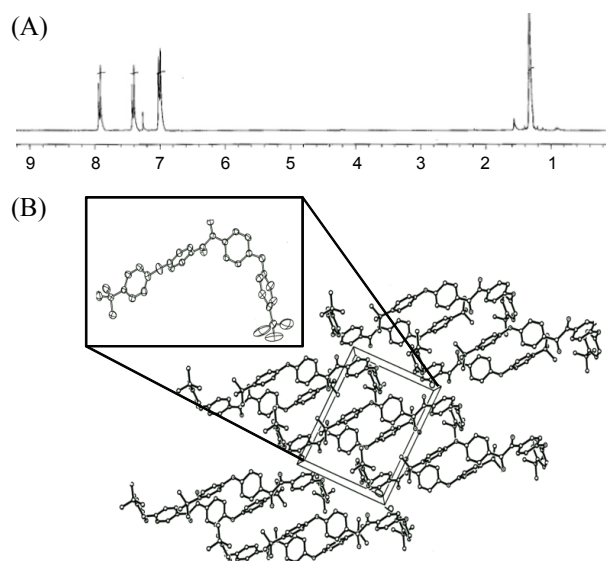


Figure 2. ¹H NMR spectrum (A) and molecular structure (B) of BBPE.

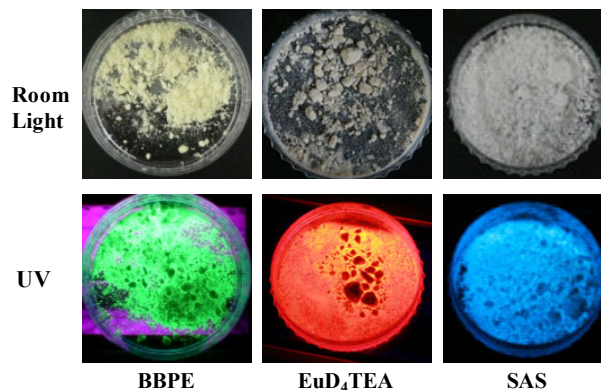


Figure 3. Photographs of Petri dishes containing BBPE, EuD₄TEA, and SAS under room light and 365 nm UV light.

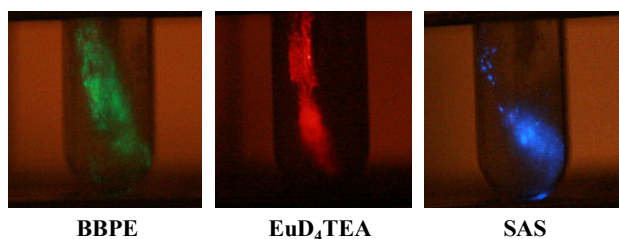


Figure 4. The triboluminescence observed from BBPE, EuD₄TEA, and SAS. Solid sample was placed in a test tube and was stirred vigorously with a spatula to induce the triboluminescence.

The europium complex EuD₄TEA²⁴ and salicylic acid derivative SAS²⁰ are found to emit red and blue fluorescence, respectively, under 365 nm UV light.

It is well known that the europium complex EuD₄TEA is one of the brightest triboluminescent materials.²⁴ We are curious if BBPE is also triboluminescent and if BBPE emits light upon grinding, we are eager to know the intensity of the light generated from BBPE. In order to test this feasibility, BBPE powder was placed in a glass test tube. The solid powder was vigorously stirred with a spatula and the light emission was monitored. To our surprise, BBPE-containing test tube was found to emit a very strong green light upon grinding the powder sample (Figure 4). The intensity of light generated was slightly weaker than that of EuD₄TEA and stronger than that of SAS. The colors of light emitted from grinding of solid samples are almost identical with those from UV irradiation (compare Figure 3 with Figure 4). We observed much stronger emission of green light with freshly prepared BBPE crystals than with amorphous powder sample of BBPE. This is reasonable since the triboluminescence effect is maximized when good crystals of a triboluminescent compound are fractured. Recrystallization of the sample usually results in the recovery of intense triboluminescence when the effect of the triboluminescence becomes weak.

In conclusion, we have developed a new triboluminescent compound based on a substituted benzil derivative. The green light emitting triboluminescent BBPE was readily prepared from commercial sources in one step. Crystals of BBPE was found to emit an intense green light upon grinding the crystals. In addition, BBPE is also photoluminescent and emits green fluorescence upon 365 nm UV irradiation. The new triboluminescent material described above should be considered as an important addition to the fracture-induced light emission area.

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- 4-*tert*-Butylphenol (15.0 g, 0.1 mol), 4, 4'-difluorobenzil (9.8 g, 0.04 mol) and CsF (13.8 g, 0.09 mol) were placed in a flask containing 90 mL of anhydrous NMP. The mixture was stirred at 110 °C for 24 h under nitrogen atmosphere. After cooling, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in ethyl acetate and washed with water. The organic layer was collected and concentrated *in vacuo*. The desired product was obtained by silica gel column chromatography (10% ethylacetate-hexane). yield: 75%; mp 122 °C; ¹H NMR (300 MHz, in CDCl₃) δ 1.32 (s, 18H), 6.85 (m, 8H), 7.40 (m, 4H), 7.91 (m, 4H).
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