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Multifunctional molecular siblings

The interaction of light with matter always ignited the curiosity of researchers and has been a driving force for the discovery and development of new theories, niche technology and novel functional materials. Light emission from an electronically excited system is called luminescence. Depending on the excitation source, luminescence may be termed as electroluminescence, photoluminescence, bioluminescence, chemiluminescence or triboluminescence. Among these processes, triboluminescence (TL) is a rare phenomenon and can be produced by external stimuli such as grinding, shearing, rubbing, scratching of the materials crystallized in non-centro symmetric space groups (piezoelectric space groups). Such materials have promising practical applications in display technology, light sources, real-time sensors of mechanical stress and structural damage. TL materials are very limited in literature and are mostly contain heavy metal oxides or organometallic complexes of Mn, Eu, Dy and Sr. By considering cost, modulation and tunability, organic materials are superior to the inorganic materials. Even though TL has a very long history, very few purely organic materials are known with TL characteristics. There is no thumb rule for the design and development of TL materials. Therefore, developing organic TL materials is a challenging task.

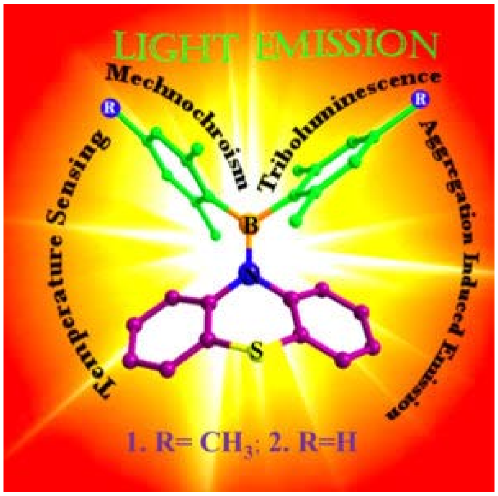

Fig. 1. Chemical structures of phenothiazinyl boranes 1 and 2 and the schematic representation of various multi-functional properties obtained by simple structural modulation.

Polar hetero-diatomic B-N unit is isoelectronic analogue of nonpolar homo-diatomic C=C bond. Recently, we exploited the concept of BN/CC isosterism for the design and development of novel materials that exhibit interesting properties including aggregation-induced emission, bright solid state emission and mechanochromism. In this work, we were able to produce TL material by minute structural perturbation. We synthesized the molecular siblings, diarylborane phenothiazines, **1** and **2** which contain electron deficient boryl and electron rich phenothiazine moiety (Fig. 1), keeping in view that phenothiazine is a strong electron donor with a cyclic amine moiety and its non-planar geometry combined with a sterically demanding diarylboryl unit would inhibit the π-stacking interactions which eventually would lead to strong luminescence in the solid state. The only difference between **1** and **2** is the absence of an additional *para*-methyl group in the diarylboryl unit of **2**. Both the compounds showed strong emission in the condensed state owing to the restricted intramolecular motions. Even though compounds **1** and **2** possess similar structures, their solid state and stimuli responsive luminescence characteristics were entirely different from one another. Compound **1** showed a bluish green color emission in the solid state while **2** showed a greenish yellow color emission; also the solid state luminescence quantum yield of **2** was twice as that of **1** (Fig. 2, top left). The nano-aggregates of **1** showed a temperature dependent emission, a reddish orange color emission at 298 K and greenish yellow color emission at 273K, while nano-aggregates of **2** was insensitive to the changes in temperature (Fig. 2, top right). The highly distinct luminescence change within a small temperature window is highly appealing for practical applications. The solid state luminescence properties of **1** were dependent on the mechanical grinding, and a reversible luminescence color change was observed with consecutive mechanical grinding and annealing (Fig. 2, bottom right). However, no significant luminescence color changes were observed in the solid state for compound **2** with mechanical grinding. From the detailed analysis of the molecular structural parameters of **1** and **2**, it was inferred that the difference in their solid state interactions and crystal packing plays a major role in their stimuli responsive luminescence properties. Compound **2** features a densely packed structure with strong intermolecular interactions in the solid state compared to compound **1**, which is responsible for the intense solid state emission and insensitivity to external stimuli such as mechanical grinding and temperature.

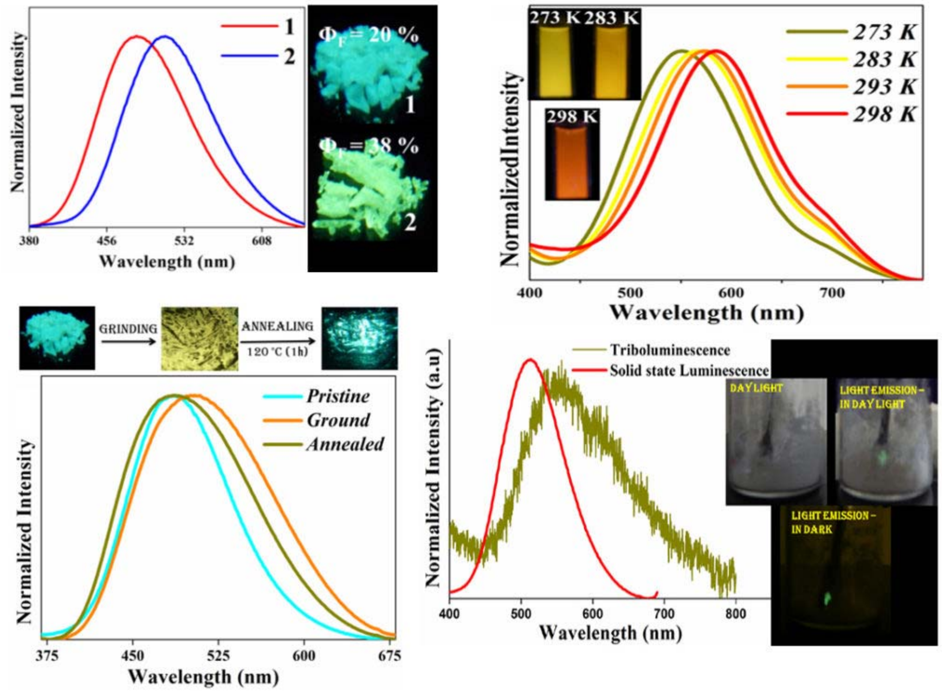

Fig. 2. Luminescence spectra (λex= 350 nm) and images of solid samples of 1 and 2 under UV-light (top left, λex= 365nm). Emission spectra and photographs of nano-aggregates of 1 at different temperatures under UV light (top right). Solid state emission spectra and photographs of pristine, ground and annealed samples of 1 (bottom left). Solid state emission and TL spectra of compound 2 and the images of compound 2 taken under day light, light emission under day light and under dark light while crushing the crystals with a stainless spatula without any external excitation source of light (bottom right).

The crystals and microcrystallines samples of compound **2** showed triboluminescence characteristics (Fig. 2, bottom right). A green color light emission was observed upon crushing the samples with a stainless steel spatula or a glass rod. This could be reversed by recrystallization from different organic solvents. Compound **2** crystallized in trigonal crystal system with the non-centerosymmetric *R*3c space group, which is classified as a piezoelectric space group. A crush or crack on the surface of such kind of materials creates a separation of charges at the surfaces, the recombination of these charges will produce excitons and the radiative decay of excitons will generate light.

Compounds **1** and **2** represent rare examples of small molecules with multifunctional properties obtained by minute structural perturbation. By exploiting these properties, these materials may find potential applications in displays, light emitting devices and security markers. In particular, intense green triboluminescence of the compound **2** can find applications in damage detection in polymer objects and generation of X-rays.

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