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## Mechano-Responsive Room Temperature Luminescence Variations of Boron Conjugated Pyrene in Air

Received 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

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Stimuli responsive tunable luminescence is a promising field of research. Even though mechanofluoroscence is widely studied, mechanophosphorescence stays unexplored. Here we report the mechano-driven fluorescence and phosphorescence variations of a pyrene tetraboronic ester derivative. The fluorochromic and room temperature phosphorescence features are supported by theoretical studies and single crystal analysis. The mechanically ground fluorescence active but phosphorescence inactive pyrene tetraboronic ester exhibits room temperature phosphorescence in air with mechanical force. The efficient intermolecular electronic coupling in the dimer formed upon scratching enables a good communication between singlet and triplet states, hence results in room temperature mechanophosphorescence.

Phosphorescent materials known for their long-lived luminescence and high quantum yield find applications in displays, sensors, photovoltaic devices, photocatalysis etc.<sup>1-3</sup> Recently, organic phosphorescent materials are of prime interest due to their easier solution processibility and available opportunities in flexible light emitting devices.4-6 Many examples have been demonstrated in this direction to promote organic phosphorescent materials as efficient triplet emitters.<sup>5,6</sup> In this way, organic room temperature (RT) phosphors are emerging as potential alternatives to the existing phosphors. In order to allow the spin-forbidden transitions at ambient conditions, many strategies, namely, increased intermolecular interactions, heavy atom substitution, halogen bonding, crystallization, host-guest interactions, immobilization of the emitter in polymeric or micellar medium etc. have been employed.<sup>6</sup> Crystallization of organic phosphors found to be an effective and simple strategy to minimize the nonradiative deactivation and thereby to improve the triplet quantum yield.6b Display of phosphorescence from organic molecules is still guided by

serendipity rather than accurate molecular designs. A systematic synthetic approach by introducing more functional moieties enhanced intersystem crossing in organic phosphors. Arylboronic esters are one such class of molecules reported for tunable optical, especially, phosphorescence properties.<sup>7</sup> However, due to various limitations of organic molecules to exhibit stable phosphorescence, more focused research is needed in this direction.

Another area that has witnessed drastic innovations in the recent past is organic mechanofluorescent (MF) materials. MF materials have attained a great deal of appreciation due to promising applications in memory, display, and sensor devices.<sup>8</sup> Even though many MF molecules exhibit RT phosphorescence,<sup>9,10</sup> mechanical grinding mostly results in the disappearance of phosphorescence due to collapse of crystalline ordering.<sup>10c</sup> Recently, Li et al. reported phosphorescence variations of two RT phosphors.7d,11 Even mechanofluorescence widely though is studied. mechanophosphorescence (MP) is yet to be explored. Here we report the mechano-responsive luminescence variations of a boron conjugated pyrene, 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene derivative 1 (Fig 1a).<sup>12</sup>



Fig 1. a) Chemical structure of boron conjugated pyrenes 1 and 2. b) Normalized absorption spectra of 1 in DCM solution and thin film.

Absorption spectrum of **1** recorded in dichloromethane (DCM) solution exhibits characteristic pyrene peaks, but a slightly broad red shifted absorption is observed in thin film (Fig 1b). Emission spectrum of **1** shows sharp peaks in the UV region with blue emission colour both in solution and solid (Fig 2a, S1, ESI<sup>†</sup>). We accidently found that solid **1** exhibits mechanodriven fluorescence colour change (Fig 2a-d and Movie S1, ESI<sup>†</sup>). A gentle smearing on solid **1** with a metallic spatula

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<sup>\*</sup>Electronic Supplementary Information (ESI) available: Detailed experimental procedures, and additional tables and figures. See DOI: 10.1039/x0xx00000x

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results in colour change from blue to yellow indicating the MF features (Fig 2a, 2c). The reversible fluorescence colour change is achieved by adding solvents such as DCM or *n*-hexane (Movie S1) and found consistent for many cycles (>100). Thin film of **1** on Whatman filter paper also exhibited similar observation upon scratching with a needle/spatula (Fig 2b, 2d). In contrast to solid **1**, thin film has an enhanced excimer emission centred at ca. 530 nm due to amorphous aggregates formed upon evaporation on filter paper.



**Fig 2.** a), b) Normalized emission spectral changes and c), d) corresponding photographs showing reversible emission colour change of solid **1** and thin film on Whatman filter paper, respectively, before and after grinding/scratching for 2 min ( $\lambda_{ex}$  = 365 nm). e) XRD spectra of **1** before and after ball milling followed by manual grinding. f) Variation of the (normalized) emission spectra of mechanically ground **1** upon mixing with increasing amount of KBr ( $\lambda_{ex}$  = 365 nm) and g) corresponding photographs under 365 nm UV light.

The sharp and intense peaks observed in X-ray diffraction (XRD) of solid 1 prove that strong intermolecular interactions in the crystals heavily contribute towards MF. A considerable decrease in crystallinity of 1 is observed after ball milling (1 hour) followed by manual grinding (20 min) using a mortar and pestle (Fig 2e). The number of peaks and corresponding peak intensity are decreased upon grinding the sample. The red shifted broad emission from the ground sample is due to the excimer-type emission of pyrene in the loosely aggregated state13 and this is confirmed by the excitation spectra (Fig S2, ESI<sup>+</sup>) and fluorescence lifetime measurements (Fig S3, S4 and Table S1, S2, ESI<sup>+</sup>). No new band in the excitation spectrum and the longer fluorescence lifetime attribute the MF colour change to excimer formation. The absolute fluorescence quantum yield of 1 (46.5%) has decreased to 35.4% with mechanical force and which is supported with the corresponding emission spectra (Fig S5). In addition, MF experiment with mixtures of 1 and varying amounts of potassium bromide (KBr) showed the disappearance of 550 nm excimer peak (Fig 1f) with a significant change in fluorescence colour from yellow to blue (Fig 2g). It indicates that excimer formation upon mechanical grinding is concentration dependent and dilution with KBr retains the monomer emission (Fig 1f, 1g). In contrary, molecule 2 is not MF active due to fluorescence quenching via two-dimensional sheet assembly formation (Fig S6, S7, ESI<sup>+</sup>).<sup>14</sup> DOI: 10.1039/C8CC03494J In general, rigidification of molecules in the crystalline state controls the non-radiative deactivation pathways to facilitate efficient phosphorescent emission.<sup>15</sup> Hence we compared the fluorescence and phosphorescence of 1 in both solid and solution states at RT and 77 K (Fig 3). As shown in Fig 3a, fluorescence peak of 1 shifted from 421 nm at RT to 441 nm at 77 K in 2-methyltetrahydrofuran (MTHF) solution. However, no phosphorescence was observed for MTHF solution of 1 at RT. When the temperature is changed to 77 K, phosphorescence peaks located at 547, 590 and 656 nm becomes visible (Fig 3a). Photographs and videos of frozen MTHF solution of 1 after excitation with 365 nm UV light for 3 sec show that the phosphorescence is long lived even up to 1-2 sec (Fig 3c, Movie S2, ESI<sup>+</sup>). Solid sample fluorescence also shows a red shift at low temperature along with two additional peaks at around 550 and 590 nm (Fig 3b). Besides phosphorescence, solid 1 exhibits a residue of delayed pyrene fluorescence located between 400-500 nm at RT and 77 K (Fig 3b).  $^{\rm 16}$  Since mechanically ground 1 (Fig 3d) is not RT phosphorescent, we consider that the two additional structured peaks at 550 and 590 nm in fluorescence spectra are due to phosphorescence (Fig 3b) and it disappears upon grinding. Phosphorescence lifetime of 1 varied as 34 µs, 1.7 sec for solid at RT in air (Fig S9, ESI<sup>+</sup>) and MTHF solution at 77K in air (Fig 3e), respectively.<sup>7e</sup> Phosphorescence quantum yield of 1 was found to be 2.9 % at RT in air.



**Fig 3.** Comparison of the normalized fluorescence and phosphorescence spectra of **1** in a) MTHF solution (C = 1 mM) and b) solid at RT and 77K ( $\lambda_{ex} = 365$  nm). c) Phosphorescence images of **1** glassy MTHF solution (at 77 K for 1 min) in a quartz tube (3 mm) recorded at different time interval upon turning off of the excitation source (365 nm) after 3 sec exposure. d) Phosphorescence spectra of solid **1** at RT before and after grinding. e) Phosphorescence lifetime decay profile of MTHF solution of **1** (C = 1 mM) at 77 K ( $\lambda_{ex} = 365$  nm and  $\lambda_{mon} = 550$  nm).

Crystal structure analysis shows that crystals of **1** (CCDC 1541247) belong to monoclinic P21/n space group (Fig 4a). The intramolecular geometry of the molecule reveals planar pyrene moiety to which pinacolboronate (BPin) substituents are adhered, whereas the tetramethyl groups occupy positions

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above and below the pyrene plane. Molecular packing in the crystals is solely governed by the weak interactions such as, C-H...B, C-H...π. The closely linked molecules generate the zig-zag chain structure along the a-axis through dimeric association engaging BPin groups via weak C-H...B contact (Fig 4b and 4c). These neighbouring chains are linked loosely through offcentred C-H... $\pi$  interactions between the methyl C-H and benzene ring of the pyrene (Fig 4c). Notably, no molecular stacking pattern through  $\pi$ ... $\pi$  association of pyrene moieties is found, perhaps due to the presence of four BPin groups, which precludes the pyrene...pyrene association. The lack of  $\pi$ ... $\pi$ interaction between the pyrenes leads to a strong blue emission from the crystals (Fig 4d). The closest distance of ~6.96 Å between pyrene rings is found along the chain structure (Fig 4b). The pyrene moieties of neighbouring molecules within the chain are parallelly displaced and separated by BPin moieties, which are loosely associated through C-H...B contact (Fig 4c). However, it is possible that by shearing, scratching or pressing of solid 1, the weak interactions such as C-H...B, and C-H... $\pi$  contacts, which connects the adjacent molecules may break and allow the 'close in' of pyrene moieties along the chain to establish the  $\pi ... \pi$  interactions between them along the chain structure.

Intriguingly, a golden yellow glow is observed when mechanically ground phosphorescence inactive 1 is scratched with a metal spatula at RT in air (Fig 4e). This scratch induced phosphorescence colour is similar to that of normal one observed at 77 K (Fig 3c and Movie S3, S4, ESI<sup>+</sup>). Supplementary movie files show the mechano-driven phosphorescence activation in 1. We repeated the scratching experiment in multiple times (>100 times) and consistent results were obtained at ambient condition. We have followed the important measures described below to confirm the MP. The ball milled and mechanically ground 1 samples without sharp peaks in XRD spectrum was used for MP experiments to nullify the contribution from crystalline assembly and thereby triboluminescence.<sup>17</sup> The observed MP colour is drastically different from the anticipated blue triboluminescence emission colour of the micro-crystalline assembly, if any, present in the ground sample. Hence it can be ascertained that the golden yellow glow is truly due to MP and not from triboluminescence or thermally activated delayed fluorescence upon scratching. In addition, it is undoubtful that the scratch induced phosphorescence colour of 1 is matching with phosphorescence in solution at low temperature (77 K). A spin forbidden singlet-triplet intersystem crossing made possible upon scratching in our demonstration.<sup>11</sup> However, the short lifetime of triplet emission limits further detailed understanding of the process. The use of other stimuli such as ultra sound or heat to induce intersystem crossing found unsuccessful. The absence of MP from the ground mixture of 1 and KBr (Fig 2f) points that the observed phenomenon is concentration dependent and the probable origin of MP is from the dimeric association of 1 in the ground state. 4e,4f,7d,11 In addition, the ground sample gradually failed to exhibit MP upon exposure to oxygen, indicating the involvement of triplet state in yellow glow. MP is completely disappeared after ~30

min exposure to oxygen and regained after degassing the sample. DOI: 10.1039/C8CC03494J



Fig 4. A deep analysis of the crystal cell of 1 showing a) single molecule b) dimer and c) stacking mode in crystal using C-H···B and C-H···T interactions. d) Photograph of the crystal (left) showing deep blue emission (right). e) Schematic showing the mechanophosphorescence of 1 upon scratching with metal spatula at ambient condition in dark. f) Overall mechanoresponsive luminescence tuning of 1 with corresponding energy levels obtained from DFT calculations. I, mechanical grinding, II, crystallisation, III, scratching.

A rational explanation for phosphorescence in crystalline as well as in amorphous samples is given below. Single-crystal Xray structure of 1 reveals that sterically bulky BPin groups place pyrene rings at a distance of ~6.96 Å, which eventually prevents triplet quenching in the excited state. In addition, rigidification of molecules in the crystalline state limits the nonradiative decay processes. The presence of BPin units and crystalline ordering helps 1 to realise phosphorescence in solid state at RT, 77 K and in solution at 77 K. In order to probe the phosphorescence further, a series of TD-DFT computations were carried out at the B3LYP/6-31+G(d) level of theory and revealed that an energy gap ( $\Delta E_{ST}$ ) of 0.08 eV between the singlet (S1) and triplet (T2) excited states makes RT phosphorescence possible (Fig S10, S11, Table S3,4, ESI<sup>+</sup>). Crystalline assembly features of **1** are completely disappeared upon mechanical grinding and excitation of the amorphous sample leads to a broad red shifted excimer emission. The reversible fluorescence switching between blue and yellow colours is systematically characterized (Fig 2, 4f). As seen in most of the reported examples, the mechanically ground 1 is unable to show phosphorescence due to lack of molecular ordering (Fig 3e).<sup>9b,10c</sup> The amorphous **1** can easily adopt a different molecular ordering<sup>12</sup> with a slight variation such as mechanical force and scratching induces a favourable trigger to form ground state dimer, which showcase triplet emission (Fig S12, S13). Natural Bond Orbital charge analysis shows the possibility of significant charge transfer between the stacked upper and lower rings in the dimer (Fig S14, ESI<sup>†</sup>). The recent reports on MP variations4e,4f,7d,11 support the fact that an efficient intermolecular electronic coupling in dimers via  $\pi$ ... $\pi$ interactions realize a good communication between singlet

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and triplet states and hence lead to the efficient room temperature phosphorescence upon scratching.<sup>18</sup> The whole processes related to phosphorescence in crystalline and amorphous solids are schematically represented in Fig 4f. In order to get clarity on the formation of any metastable oxidation and/or oxygenation products during aerobic grinding, thermogravimetric analysis and X-ray photoelectron spectroscopy experiments have been conducted on pristine and sample ground under aerobic condition (Fig. S15, S16, ESI<sup>+</sup>). Absence of any anomalous observations in these two experiments and yellow glow appeared upon mechanical grinding under anaerobic condition in glove box (Ar) (Movie S5, ESI<sup>+</sup>) nullify such contributions and hence support MP.

In conclusion, an exciting example of MP in pure organic phosphors is introduced. A metal- and heavy atom-free organic molecule with mechano-driven RT phosphorescence and fluorescence variations are successfully achieved by a boron conjugated pyrene derivative. RT phosphorescence exhibited by the boronic ester derivative is completely disappeared with mechanical grinding. A mechano-triggered revamp of phosphorescence for the amorphous sample is promoted by a strong intermolecular electronic coupling and low singlet-triplet energy gap of the dimer assembly. We believe that this successful demonstration of MP will pave the way to develop next-generation stimuli responsive RT phosphorescent materials for smart applications.

VCW, KCR and Goudappagouda, acknowledge UGC, India for fellowship. This work is supported by SERB, Govt. of India EMR/2014/000987. We thank Dr. Retheesh Krishnan for helpful discussion, Dr. Pramod Pillai and Dr. Subi J. George for phosphorescence and phosphorescence lifetime facility, respectively.

## **Conflicts of interest**

"There are no conflicts to declare".

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