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Bright NUV mechanofluorescence from a terpyridine-based pure organic crystal

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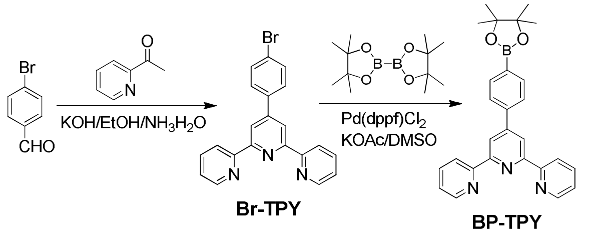
A bright NUV mechanofluorescent *terpyridine*-based material with piezoelectric space group was obtained. The single crystal analysis and quantum chemical calculation indicated the existence of enhanced intermolecular and intramolecular interactions and intersystem crossing, but which did not facilitate the room temperature phosphorescence.

Mechanoluminescence (ML) was first pointed out by Francis Bacon in 1605 based on his attentive observation on hard sugar fracture.[1] This type of luminescence could be excited by various external mechanical actions, such as stretching, cleaving, cutting, rubbing, grinding, shaking or scratching, sonication, etc.[2] It was predicted that nearly half of all solids probably showed ML phenomenon.[3] However, for centuries, inorganic salts and metal-organic complex have been the mainstay of ML materials, and only about 400 papers were published before the 21st century.[2–4] Recently, an increasing interest in ML has emerged as evidenced by more 400 papers published within the past 17 years, owing to the re-recognition of its potential applications in display, lighting, bioimaging, and stress sensing[5] and its academic significance in understanding fundamental photo-physical process.

Conjugated organic luminophores might be promising ML candidates because of their structure diversity, intrinsic luminescence, easy accessibility and modification. However, Their ML properties started to draw serious research attention only within the past few years,[6] Generally, the crystals with piezoelectric space groups (dipolar structures and noncentro-symmetric molecular arrangements), strong intermolecular and intramolecular interactions and crystalline fluorescence were expected to be promising ML candidates. For example, recently, some aggregation-induced emission (AIE) molecules have been found to be ML-active materials emitting blue and green light.[7-8] However, bright organic ML luminogens were still limited in number and kind, and the understanding on the crystal structure–ML activity and the luminescence mechanism were not comprehensive and clear. Moreover, there have been few reports on organic ML luminogens with bight NUV emission and no AIE effect at present.[8] We considered that NUV organic ML emitters could not only help ones to further understand ML process but also serve as the energy donor (host) to generate various visible ML and expand the color gamut. Therefore, to broaden the ML family and deepen the understanding on ML mechanism, it was necessary to exploit other kinds of bright ML organic materials with non-AIE effect and NUV emission.

Based on the above considerations, in the current work, we have designed and synthesized a *terpyridine* derivative (BP-TPY Scheme 1) to investigate its mechanoluminescence (ML), photoluminescence (PL), and crystal structure. The details for synthesis and characterization were depicted in the Supporting Information. As BP-TPY has a short conjugation and a branched configuration, the efficient NUV emission could be expected. The polar boric acid ester and lone pair electron-containing pyridyl units should render the crystal strong intermolecular and intramolecular interactions. Moreover, this noncentro-symmetric tapered molecule could be prone to stack in the piezoelectric space group. Thus, a bright NUV emission could be expected under light and mechanical stimuli.



Scheme 1. Structure and synthetic route of BP-TPY

Figure S1 showed the absorption and PL spectra of BP-TPY in THF solution and solid states. The light absorption for both

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† Electronic Supplementary Information (ESI) available: Details for synthesis and characterization Figure S1–Figure S6, crystallographic data and CCDC code and others. See DOI: 10.1039/x0xx00000x

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solution and solid film mainly appeared before 330 nm with the peak at 300 nm. Under 300 nm light excitation, BP-TPY emitted NUV light with the emission peaks at 358 and 368 nm for the solution and the solid, respectively, and a good color purity evidenced by the narrow full width at half-maximum of 35 nm. The corresponding fluorescence efficiency were 15%, 13%, respectively, which was commendable in view of its large band gap,small size, and low conjugation degree. BP-TPY could be regarded as a non-AIE but multi-state emission organic dye although its fluorescence efficiency was decreased by 50% in the aqueous media (Figure S2).

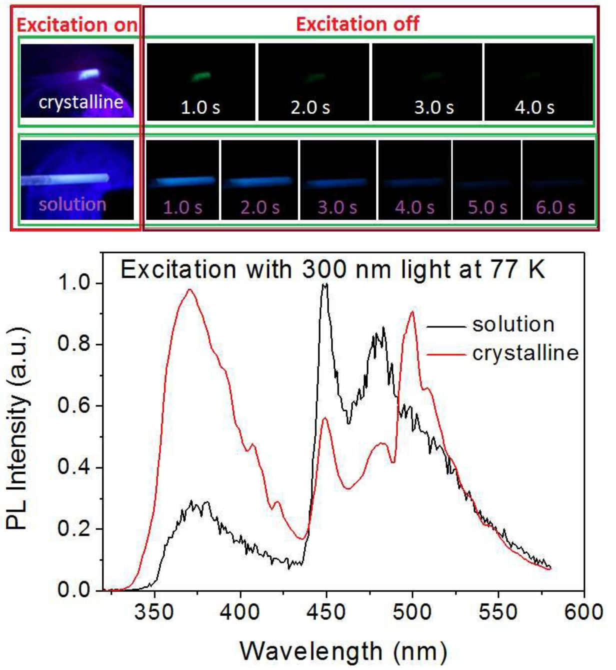

Figure 1. PL images of BP-TPY in solid state and THF solution taken at different times before and after turn-off of 254 nm excitation light (upper) and the PL spectra (down) under 300 nm excitation at 77K.

Under UV light excitation, BP-TPY crystal and solution all exhibited the remarkable fluorescence–phosphorescence dual emission at 77 K (Figure 1), but only fluorescence emission was observed at room temperature (Figure S1). BP-TPY crystal had a short (2.4 ns) and a long (1.53 s) luminescence lifetimes at 77 K but only a short fluorescence lifetime of 1.9 ns at room temperature (Figure S3). When the crystalline powder of BP-TPY was ground in a glass bottle using metal or plastic spade in dark room, a NUV light emission could be observed by naked eye and video recorded by digital camera (iPhone 7, Figure 2 and Figure S4). Unfortunately, the emission spectrum was not able to analyzed by a CCD spectrometer, probably due to that the light signal was not enough strong. In order to enhance the brightness, the bulky crystal grain was prepared by slowly evaporating its chloroform/methanol solution and ground as described for the crystalline powder. As expected, a bright deep blue light could be saw and well analyzed by a CCD spectrometer, which afforded a UV emission spectrum with the peak at 372 nm. Since ML spectrum matched very well with the room-temperature photofluorescence spectra (Figure 2), these light emissions should occur from the same excited states, regardless of the mode of excitation.

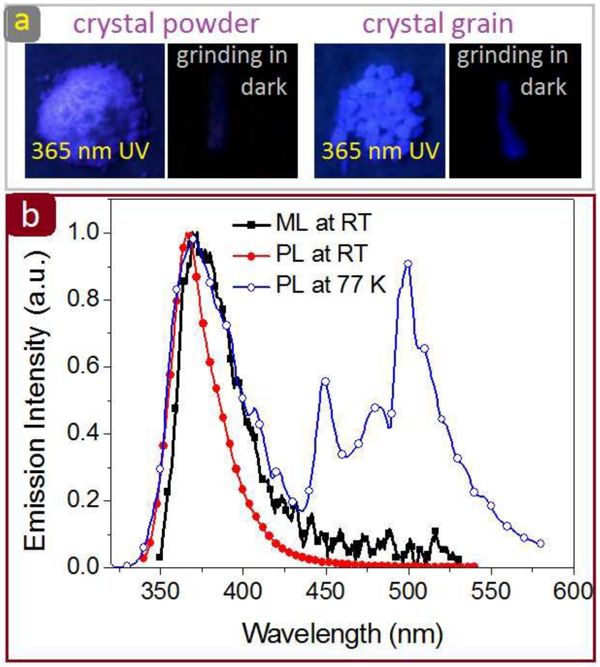

Figure 2. (a) PL and ML images of crystalline BP-TPY powder and grain at 298 K in dark room. (b) ML spectrum of BP-TPY crystal grain upon grinding with a spatula in dark room at room temperature and the comparison with its PL spectra recorded at 77 k and 298 K under 300 nm excitation.

To gain an insight into the effect of crystal structure on ML effect, the single crystal of BP-TPY was cultured and analyzed. The result revealed that BP-TPY adopted two different twisted conformations to pack each other and form a monoclinic crystal system with the noncentrosymmetric and piezoelectric space group Pc (Figure S5, Table S1). The twisted backbone and small-size conjugation without any electron donor moiety contributed to the NUV emission. As expected, there were indeed strong intermolecular and intramolecular interactions in BP-TPY crystal (Figure 3), which should largely reduce the possible energy loss through non-radiative relaxation under the mechanical stimulus. These results could explain bright mechanoluminescence of BP-TPY crystal. On the other hand, it was known that the crystal fracture could separate electrical charges and ionize air (such as nitrogen), and the discharge of the ionized nitrogen could emit a multiple-peak spectrum in the range of 310–430 nm with fine six-finger structure.[4a] Since the strong absorption of BP-TPY was before 310 nm, together with the spectral identity between light and mechanical excitation, the structure-less ML should result from the direct excitation of crystal fracture-induced piezoelectric field, rather than the secondary excitation of nitrogen discharge emission on BP-TPY crystal. It was noticed that the intermediate Br-TPY crystal exhibited unique photoluminescence but no ML activity (Figure S6), which was not surprising since the present each identified ML compound is still an isolated event and its ML activity was impossibly predicted in advance.

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Recently, Li et al. have found an unique example of the fluorescence–phosphorescence dual mechanoluminescence at room temperature from a *m*-terphenyl boric acid ester (DPP-BO)[6f]. By comparing the optical properties of BP-TPY and DPP-BO, we could find that they had the same photoluminescence behaviors, such as fluorescence–phosphorescence dual photoluminescence at low temperature and only photofluorescence at room temperature. However, why BP-TPY only exhibited the mechanofluorescence, which required further investigations.

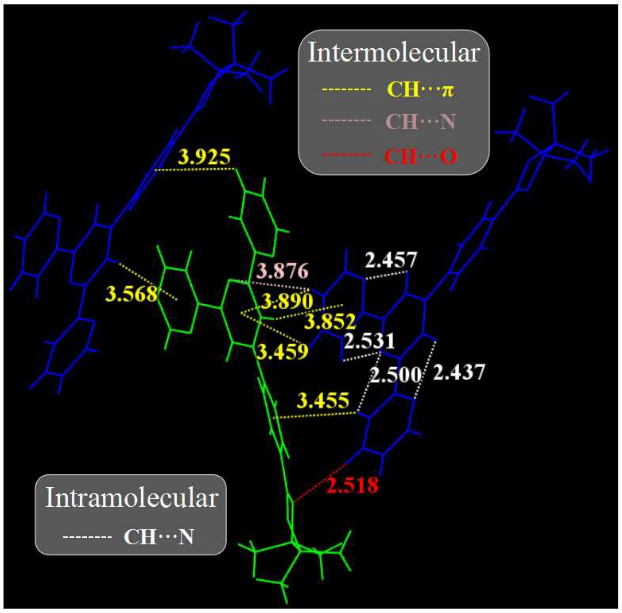

Figure 3. The intermolecular and intramolecular interactions in BP-TPY single crystal. There were four strong intramolecular CH···N interactions for each molecule, and intermolecular four CH···π, one CH···N, and one CH···O interactions between the two closely coupled molecules.

Generally, luminophores containing multiple heteroatoms like N, P, and O were prone to phosphorescence emission since the lone pair electrons should favour the n–π* transition and populate triplet excitons through facilitating the spin-forbidden transition of singlet-to-triplet excited states (intersystem crossing, ISC). Moreover, by analyzing the packing structure of BP-TPY crystal, we found that the intermolecular and intramolecular interactions in BP-TPY crystal were significantly stronger than those in DPP-BO one, in which the additional C-H···N interactions were observed besides of shorter C-H···O interaction distance (2.518 Å versus 3.184 Å) for former. These interactions were considered to be much beneficial to the n–π* transition and the ISC enhancement. To further understand the ISC feature, TD-DFT calculation was carried out based on a pair of strong interacted BP-TPY derived from the single crystal structure (Figure 4). It was found that there were 9 T_n states containing 19 possible channels for ISC based on the same transition orbital compositions between T_n and S_1 within ± 0.3 eV energy level[9] (Table S2 in the Supporting Information). The much increased number of ISC transitions for BP-TPY than DPP-BO should be much more favourable for populating triplet excitons. Thus, the absence of room-temperature phosphorescence in BP-TPY crystal should result from the energy loss possibly through non-radiative relaxation channels from T_1 to S_0 as well as the endothermicity of ISC process from S_1 to T_n, which could significantly decrease the phosphorescence emission probability. In other words, ML features and mechanisms still remained complicated and ambiguous and were dependent on the studied compound structures. Enhancing the ISC transitions was only necessary but not sufficient conditions for the spin-forbidden triplet-to-singlet phosphorescence emission.

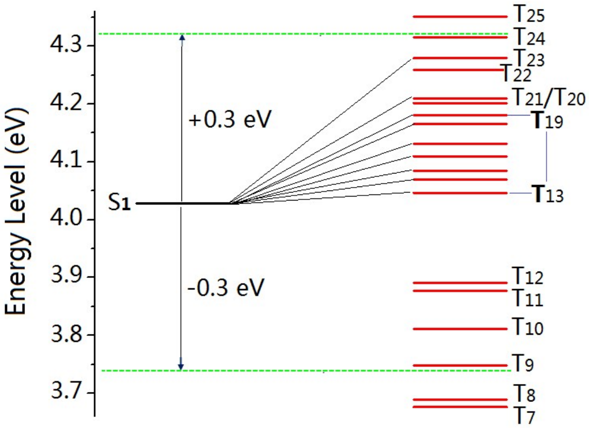

Figure 4. Energy level diagram of the two closely coupled BP-TPY molecules and the possible channels for the intersystem crossing from singlet S_1 to triplet T_n. There were 9 T_n states containing 19 possible channels for ISC based on the same transition orbital compositions between T_n and S_1 within ± 0.3 eV energy level (S_0 = 0 eV).

In summary, a new *terpyridine*-based ML material (BP-TPY) with bright NUV emission has been obtained. BP-TPY is a multi-state emission and non-AIE-active luminophore, and the ML spectrum is almost the same as its PL spectra. There are strong intermolecular and intramolecular interactions and much increased number of ISC transitions in BP-TPY crystals with multiple heteroatoms, but room-temperature photo- and mechano-phosphorescence are not observed. Therefore, for spin-forbidden phosphorescence emission, enhancing the ISC transitions was only necessary but not sufficient conditions, and ML features and mechanisms still remain ambiguous and seem to be dependent on the studied molecular structures. NUV ML emissions are very meaningful because they could not only help to understand the ML process but also serve as the energy donor to generate various visible ML emissions by in-situ exciting other fluorescent dopants. The investigation on the "BP-TPY as host function" is another interesting subject and is underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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Bright NUV mechanofluorescence from a terpyridine-based pure organic crystal

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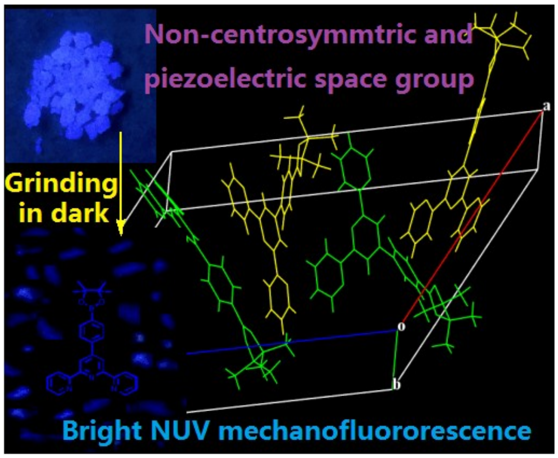

Bright NUV mechanofluorescence from a terpyridine-based pure organic crystal with non-centrosymmtric packing and piezoelectric space group.