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An initial attempt to reveal the excited state of mechanoluminescence from purely organic luminogens with room temperature phosphorescence

Jie Yang, Xuming Gao, Zongliang Xie, Yanbin Gong, Manman Fang, Qian Peng, Zhenguo Chi, Zhen Li*

Abstract: For the first time, two stable purely organic luminogens were reported to exhibit both mechanoluminescence (ML) and photoluminescence (PL) with dual fluorescence-phosphorescence emissions at room temperature. Careful analyses of the crystal structures coupled with theoretical calculations, demonstrated that the room temperature phosphorescence (RTP) and ML properties are both heavily related to the molecular packing. Particularly, the formation and fracture of molecular dimers with intermolecular charge transfer have great effect on the ISC transitions as well as excited triplet state emissions, in both PL and ML processes.

Mechanoluminescence (ML), as a special light-emitting process induced by mechanical stimulation such as grinding, rubbing, or shaking, has attracted extensive attention for its potential applications in the displays, lighting, bioimaging, and stress sensing.[1] Regardless of its long history, with the first report of sugar by Francis Bacon in 1605, organic ML luminogens remain limited in number, partially due to the lack of reliable guidance and unclear inherent mechanism. On the other hand, as the most investigated light-emitting process, photoluminescence (PL) has been well understood, which made great contribution to promote the researches on other kinds of emitting processes, including electroluminescence (EL) and chemiluminescence (CL).[2] Based on these success stories and the previous reported ML luminogens, we would like to explore the unknown excited process of mechanoluminescence with the well understood photoluminescence (PL) acting as template.

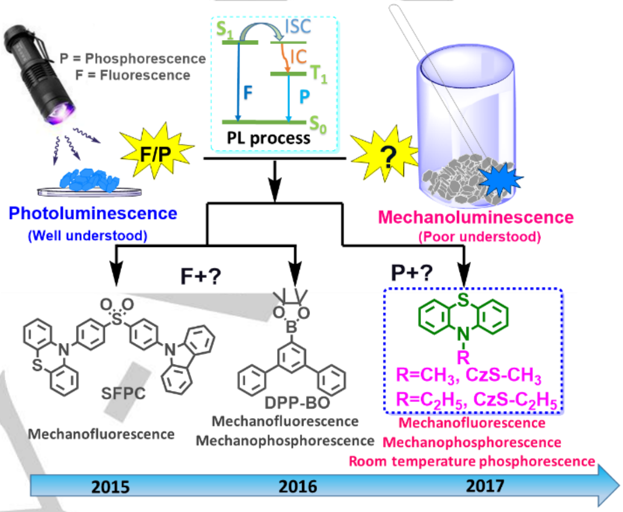

Figure 1 The development process to explore the unknown excited state of mechanoluminescence with the well understood photoluminescence (PL) process acting as template.

Thanks to the enthusiasm of scientists, some bright ML luminogens have been developed by combining the concept of aggregation-induced emission (AIE) since 2015 (Figure 1).[3] However, they mainly concerned on the fluorophores with emissions from excited singlet state, while the luminogens with mechanophosphorescence have seldom been reported, although in principle there should be. In 2016, our group was lucky to obtain a mechanophosphorescence from DPP-BO at room temperature, which demonstrated the existence of excited triplet state in the ML process.[4] For the PL emissions of DPP-BO, it was a little pity that no phosphorescence was observed at room temperature, although strong and long lifetime phosphorescence could be achieved under low temperature (i.e. 77 K). The much different emitting behaviors between PL and ML process at room temperature left a patch of dark cloud on the understanding of ML process and internal mechanism. Thus, this urged us to develop some bright ML luminogens with room temperature phosphorescence in PL process. Hopefully, through the comprehensive comparison between their PL and ML behaviors, more clear understanding on ML could be achieved.

Phenothiazine is a well-known heterocyclic compound with electron-rich nitrogen and sulfur heteroatoms, which favors the n-π* transition and good communication between excited singlet state and triplet state, as partially confirmed by some phenothiazine-based luminogens with the TADF (thermally activated delayed fluorescence) property.[5] Meanwhile, its non-planar "butterfly" structure could hinder the possible intermolecular π-π stacking as well as the non-radiative transition, to some extent.[6] In this communication, the phenothiazine group was selected as the main building block to construct two purely organic luminogens of CzS-CH$_3$ and CzS-C$_2$H$_5$ with ultra-simple molecular structures, in which, the RTP and ML properties have been successfully integrated. Careful analyses of the crystal structures, coupled with theoretical calculations, demonstrate that the RTP and ML properties are both heavily related to the

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molecular packing, especially for the formation and fracture of molecular dimers with intermolecular charge transfer in the light-emitting process. Herein, we present the synthesis, PL and ML characterizations, crystal structures, and theoretical calculations of CzS-CH_3 and CzS-C_2H_5 in detail, to understand their unique ML process and internal mechanism.

Both of CzS-CH_3 and CzS-C_2H_5 could be conveniently synthesized through only one step（Scheme S1). Their UV-visible absorption spectra were measured in THF solution, in which, CzS-C_2H_5 gave a little violet-shifted absorption at 254, 310 nm in comparison with CzS-CH_3 (256, 312 nm), indicating their minor different electronic structures (Figure S1). Similar phenomenon occurred for their PL spectra measured in THF solutions with deep blue emissions at room temperature (Figure S2). Under a low temperature of 77K, the PL emissions of CzS-CH_3 and CzS-C_2H_5 changed to the bright green ones with two emission peaks around 484, 511 nm (Figure S3), which could last about 1 s even after stopping the UV-irradiation (Figure 2E). The green emissions with such long lifetimes could well certify that they were phosphorescence from the excited triplet state.

CzS-C_2H_5 crystal presented two much different emission peaks (426, 497 nm) at room temperature (Figure 2A), and the emission lifetime of the peak at 497 nm could be up to 4.59 ms (Figure 2B, Figure S4), exhibiting the typical RTP effect.[7] Furthermore, bright blue emission was observed by scraping its solid samples at room temperature, showing remarkable ML character. In the ML spectrum of CzS-C_2H_5 crystal (Figure 2A, the ML spectrum of as prepared CzS-C_2H_5 powder was shown in Figure S5), there were one main emission peak at about 430 nm and another peak tail in the long wave region. Through fitting multi-peaks in Origin 8.0, two emission peaks could be separated: a strong one peaked at about 430 nm and another weak one at about 490 nm (Figure S5), which were in good accordance with its fluorescence and phosphorescence in PL process. Then why CzS-C_2H_5 gave much different PL and ML emissions, especially for the phosphorescence at the longer wavelength?

In consideration of the destruction effect on crystal under scraping in the ML process, the PL emission of the sample after grinding should show more close relationship with ML. Thus, the CzS-C_2H_5 crystal was ground heavily using a mortar and pestle, highly-contrast mechanochromism effect could be observed,[8] and its PL emission changed from green to blue (Figure 2C, Figure S6), accompanying with the destruction of crystal. The changes of CzS-C_2H_5 crystal under grinding were further confirmed by powder X-ray diffraction (PXRD) patterns (Figure 2D). There were many sharp peaks for the CzS-C_2H_5 crystal, however much weakened along with some peaks missing after grinding heavily, indicating the destruction of crystal to some extent. Through careful analyses on the PL spectrum of ground CzS-C_2H_5, it was found that there was only one main emission peak at about 426 nm and another peak tail in the long wave region, much similar to that of the ML one. At the same time, the phosphorescence lifetime shortened to 1.59 ms and the PL quantum yield decreased from 8.1% to 3.6% after grinding for the weakened RTP effect, partially demonstrating the crystallization-induced phosphorescence. Thus, the different PL behaviors in different states could prove the significant influence of molecular packing on the emissive property.

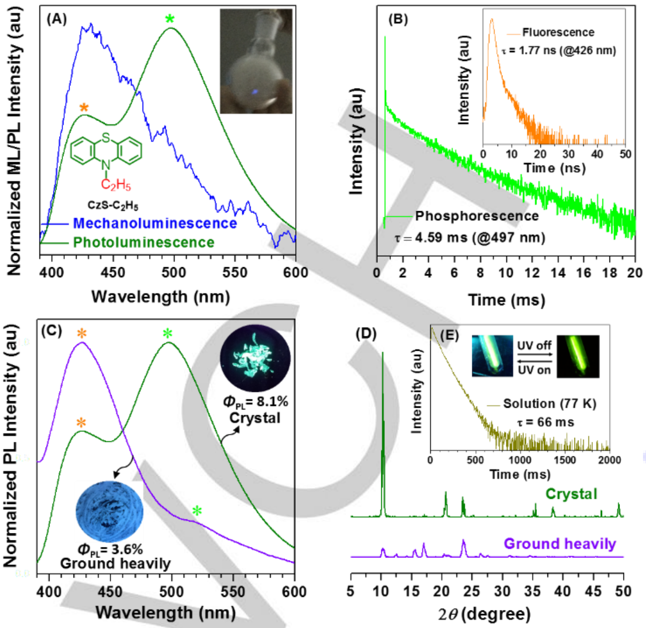

Figure 2 **(A)** The mechanoluminescence (ML) and photoluminescence (PL) spectra of CzS-C_2H_5 crystal (Inset: ML image of CzS-C_2H_5 sample upon scrapping with a glass rod in daylight); **(B)** The time-resolved PL-decay curves for phosphorescence at 497 nm and fluorescence at 426 nm of CzS-C_2H_5 crystal at room temperature; **(C)** the prompt PL spectra and the photos under 365 nm UV–irradiation of CzS-C_2H_5 in crystal and after grinding heavily; **(D)** The PXRD patterns of CzS-C_2H_5 in crystal and after grinding heavily; **(E)** The time-resolved PL-decay curves for low temperature phosphorescence of CzS-C_2H_5 in solution at 77K (Inset: the pictures taking at different times, before and after turning off the 365 nm UV-lamp).

Furthermore, the CzS-C_2H_5 was doped in polymethyl methacrylate (PMMA) with mass fraction about 5% to eliminate the molecular packing effect as well as restrict the non-radiative motion. There was just one emission peak at about 440 nm and no delayed component, namely phosphorescence, could be detected (Figure S4 and Figure S7). Also, no ML emission could be observed upon scraping. This control experiment could further demonstrate the great effect of molecular packing on RTP and ML properties from another side.

As for CzS-CH_3, similar phenomena were observed (Figure S8-S12). It also showed crystallization-induced phosphorescence and mechanochromism effects (green to blue).[9] However, its ML emission was much weaker and only visual in dark for its lower PL efficiencies (Φ_{PL} = 3.0% in crystal, 2.1% after grinding heavily).

To explore the possible mechanisms of the emissive property for CzS-CH_3 and CzS-C_2H_5, we cultured their single crystals, which corresponded to the C1n1 and Pna21 space groups respectively, and were both non-centrosymmetric (Table S1). As shown in Figure 3 and Figure S13, efficient intermolecular hydrogen bonds could be observed in crystals, while no π-π interaction was found. This status could contribute much to their relatively high PL efficiencies.[10] Particularly, molecular dimers were formed with multiple C-H…π and C-H…N bonds.[11] With this packing mode, the efficient intermolecular electronic coupling effect should exist, thus making significant influence on their light emissions, including PL and ML. For CzS-CH_3, six C-H…π (ranging from 2.90 to 3.90 Å) and three C-H…N bonds (3.07 to 3.90 Å) were present in the molecular dimers. Interestingly, these dimers were connected by some relatively weaker hydrogen bonds, including one C-H…π (2.56 Å) and two C-H…N (3.55 to 3.77 Å). Same phenomena were observed in CzS-C_2H_5 crystal: two molecules interacted with each other through six C-H…π (ranging from 3.00 to 3.90 Å) and two C-H…N bonds (3.34 and 3.36 Å) to form a dimer. Then, each of two CzS-C_2H_5 dimers were

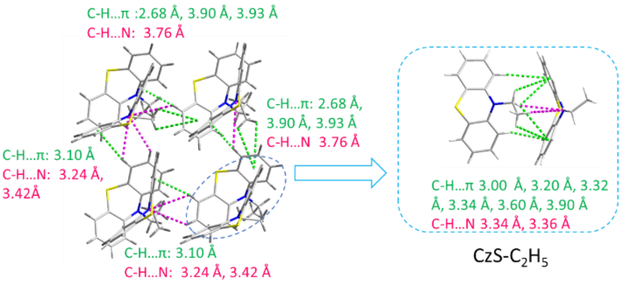

Figure 3 The entire (left) and local (right) packing modes of the CzS-C_2H_5 crystal (The local packing picture, namely dimer, was selected from the part in cycle of corresponding entire one).

linked with three C-H…π (ranging from 2.68 to 3.93 Å) and one C-H…N bonds (3.76 Å) or one C-H…π (3.10 Å) and two C-H…N bonds (3.24 and 3.42 Å). Finally, these strong intermolecular interactions in crystals of CzS-CH_3 and CzS-C_2H_5 could largely reduce the possible energy loss via non-radiative relaxation channels by decreasing the molecular slippage, under the stimulus of mechanical force, just as demonstrated in our previous work.[3d,4]

In order to further evaluate the strength of intermolecular interactions, their powder X-ray diffraction (PXRD) spectra in different states were measured (Figure S14-S15). As easily seen, the as-prepared samples exhibited non-negligible peaks, which partially disclosed their good crystallinity. On the other hand, their crystals presented the good mechanical stability, that is, they could retain sharp and high diffraction peaks after grinding lightly. Only upon heavy grinding, could these crystals be destructed to some extent without obvious PXRD peaks. These results proved the strong intermolecular interactions present in crystals, which could contribute much to PL and ML properties by restricting the non-radiative transitions in these two processes.

To explore the origin of the big difference between ML and PL spectra, and look more closely into the influence of molecular packing, TD-DFT calculations were carried out on the isolated molecules and relevant dimers (derived from their single-crystal structures). First, the theoretic analyses on their $S_0 \rightarrow S_1$ transitions were carried out.[12] As shown in Figure S16, the isolated molecules of CzS-CH_3 and CzS-C_2H_5 were both π-π* transitions because of the involved HOMO, LUMO and LUMO+1 electron clouds spreading on the phenothiazine moiety. This would not favor the ISC transition, neither for the RTP effect. Besides, the oscillator strength (*f*) of CzS-C_2H_3 (0.0011) was much larger than that of CzS-CH_3 (0.0002), and this should be mainly responsible for its higher PL efficiency (8.1%) than that of CzS-CH_3 (3.0%). Accordingly, increasing the overlap between HOMO and LUMO and expanding the π conjugation could lead to the enhanced oscillator strength (*f*), then improve the PL as well as ML efficiencies.[12] Interestingly, obvious CT transitions were revealed in the dimers for both of them from an occupied orbital of one molecule to the vacant orbital of another. Also, the red shifted absorptions from solution to aggregation state could well prove the formation of intermolecular CT states for CzS-CH_3 and CzS-C_2H_5 aggregates (Figure S17).[11] Then the intermolecular charge transfer states could result in an enhanced ISC process. On the other hand, the increased dipole moments from 2.43 and 2.40 debye in isolated CzS-CH_3 and CzS-C_2H_5 to 3.74 and 3.45 debye in the relevant dimers, could further certify the formation of intermolecular charge transfer states in the molecular dimers. The formed charge transfer states, thus, served as bridge to realize the good communication between excited singlet state and triplet state and lead to the efficient phosphorescence in crystals upon UV-irradiation.[11a,11b,13] However, the molecular dimers would be destructed under scraping, then resulting in the inefficient ISC transition as well as weak mechanophosphorescence in the ML process. Thus, the formation and fracture of molecular dimers with intermolecular charge transfer in the light-emitting process would be mainly responsible for the big difference between PL and ML process.

The energy level diagrams and excited state transition configurations of isolated molecules and dimers, were calculated to explore how the molecular dimer affecting ISC transition (Figure S18-S20, Table S2-S5).[14] As shown in Figure S18, there was just one minor ISC channel for the isolated CzS-CH_3, while one main and two minor channels could be observed in the isolated CzS-C_2H_5, indicating its more efficient ISC transitions for the little different molecular structure. When it turned to the molecular dimers, much increased number of ISC channels were obtained for the efficient intermolecular interactions and formed intermolecular charge transfer states. For CzS-CH_3 dimer, one main and four minor channels were found. In the meantime, the ISC channels increased to one main and six minor ones for the CzS-C_2H_5 dimer. On the other hand, the decreased energy gaps between S_1 and T_1 states, $\Delta(S_1\text{-}T_1)$, could also be found from the isolated molecules to dimers—0.68 to 0.57 eV for CzS-CH_3 and 0.66 to 0.58 eV for CzS-C_2H_5 (Figure S21-S22). The decreased energy gaps of $\Delta(S_1\text{-}T_1)$ in the dimers could surely contribute much to the spin-orbit coupling between S_1 and T_1 states. Accordingly, the increased ISC channels between S_1 and T_n states, as well as the small energy gaps of $\Delta(S_1\text{-}T_1)$ could both improve the RTP efficiency.[14] Thus, these calculated results could well certify the great promotion of RTP effect for the formed molecular dimers, further proving the important role of molecular packing on their light-emitting process.

As revealed by our experimental results coupled with the theory calculations, the molecular packing played a significant role in the light-emitting process, including PL and ML (Figure 4). In crystal, the formed molecular dimers through the strong intermolecular hydrogen bonds, could lead to the intermolecular charge transfer (CT) states, thus serving as bridge to realize the good communication between the excited singlet and triplet states. On one hand, it could increase the ISC channels for the orbital

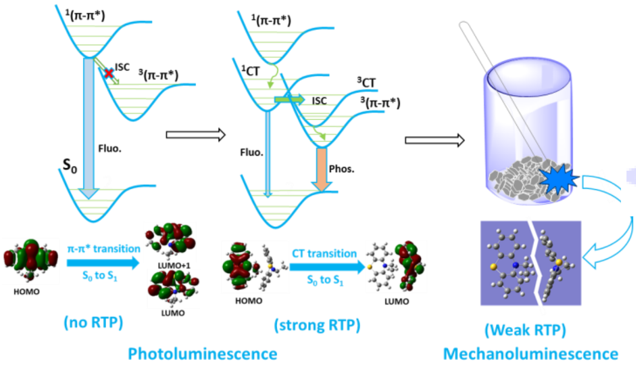

Figure 4 A proposed mechanism for PL and ML process in CzS-CH_3 and CzS-C_2H_5—in the isolated molecules with π-π* transition from S_0 to S_1 state, ISC transition would be hard to happen, while the formed CT transition in dimers could serve as bridge to realize the good communication between excited singlet state and triplet state, thus realizing the RTP effect; As for the ML process, the destructed dimers upon scraping would lead to the inefficient ISC transition as well as the weak mechanophosphorescence in ML process.

degeneracy of two molecules;[14a] on the other hand, the energy gaps between S_1 and T_1 states could be largely shortened for the strong electron coupling effect in dimers.[14b] Thus, these two factors could both facilitate their RTP effect of crystals in PL process. If their crystals were ground heavily, the molecular dimer would be destroyed, then leading to the weak RTP property and mechanochromism effect. Furthermore, when they were doped into PMMA without the intermolecular coupling effect, no RTP effect could be achieved. On the other hand, the destructed dimers under scraping would lead to the inefficient ISC transition as well as the weak mechanophosphorescence in ML process.

In comparison with previous cases, the unique point of CzS-CH_3 and CzS-C_2H_5 is the both existing RTP and ML effects. The RTP property demonstrated the presence of ISC and the corresponding stable T_1 state. However, the similarity of their ML and PL (after grinding heavily) spectra indicated that the excited energy of single molecules mainly accounted for the ML behavior because of the fracture effect under scraping in ML process, although the excited level of RTP mainly depended on the molecular dimer (the crystal samples with molecular dimers show stronger RTP than the grinding samples with cracked molecular dimers). Further on, the excited energy of single molecules transferred to adjacently uncracked molecular dimers partly, thus leading to the strong mechanofluorescence and weak mechanophosphorescence in CzS-CH_3 and CzS-C_2H_5. Actually, for most other ML luminogens, their ML spectra were also much similar to the PL emissions after grinding, certifying the accuracy of our understanding on the other hand.[5] As for DPP-BO with dual mechanofluorescnce and mechanophosphorescence in our previous report, no RTP effect was found.[4] Its excited energy should be also formed on the single molecules at the initial state. At the same time, some stronger coupled units for DPP-BO could be achieved under scrapping which favored efficient ISC transitions. Then, part of the excited energy on isolated molecules could transfer to the strong couple ones and lead to the dual mechanofluorescence and mechanophosphorescence.

Actually, more other bright ML luminogens with RTP effect should be developed, in order to make a more comprehensive understanding of the excited state for ML process. Possibly, three main issues should be taken into consideration.

First, the twisted conformation is required, to restrict the π-π interaction as well as the non-radiative transition,[3-6] for the realization of bright ML in aggregated state. Secondly, heteroatoms of N, O, S *et al.* with lone pair electrons should be introduced, which could contribute much to the n-π* transition and intersystem crossing, thus achieving the efficient RTP.[14] Thirdly, the charge transfer state with relatively large but suitable dipole moment plays a significant role in the ML and RTP effects.[3b,11a,11b,13] There are mainly two approaches to realize this point: one is to integrate electron donor and acceptor in a single molecule to assure the intramolecular charge transfer, while another is to construct the molecular dimer with efficient intermolecular charge transfer.

In summary, with the integrated RTP and ML properties, CzS-CH_3 and CzS-C_2H_5 could fill the gap for the ML luminogens concerning excited triplet state emission at room temperature in both PL and ML processes, and drift the last patch of dark cloud on the understanding of ML process and inherent mechanism heavily related to the molecular packing, especially for the formation of molecular dimers with the intermolecular charge transfer.

Acknowledgements

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Keywords: Mechanoluminescence, room temperature phosphorescence, multiple stimulus response

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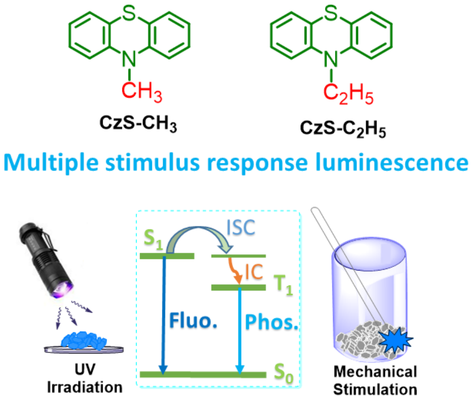

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An initial attempt to reveal the excited state of mechanoluminescence from purely organic luminogens with room temperature phosphorescence

For the first time, two stable purely organic luminogens were reported to exhibit both mechanoluminescence (ML) and photoluminescence (PL) with dual fluorescence-phosphorescence emissions at room temperature. With the help of well understood PL process acting as template, the unknown excited state of ML were revealed preliminarily.