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A simple and versatile strategy for realizing bright multicolor mechanoluminescence

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Multicolor mechanoluminescence(ML) is first realized by using the stable organic blue ML emitter N-henylcarbazole as host matrix. It is claimed that a good ML host should have a moderate melting point and can dissolve or disperse organic dyes but maintain high ML activity and crystallinity. This strategy is versatile and can avoid unknown molecular design and trouble chemical synthesis.

Mechanoluminescence (ML, or tribo- and fracto-luminescence) is a kind of old but not rare light-emitting phenomenon. In 1605, Francis Bacon observantly noted a sparkling light from the scraped lumps of sugar at night.[1] This attentive observation can be regarded as the first public report on ML and has triggered the subsequent appearance of a number of ML active materials. It is ever surmised that nearly half of all solids probably show ML property, however, ML investigations fail to attract one's much attention, as evidenced by only about 400 papers published before 2000.[2] Moreover, among them, bright ML materials are limited, and their mainstay are inorganic and organometallic solids.[3] Recently, the researches on ML effect and materials have attracted an increasing interest due to the re-recognition of their potential applications in lighting, display, bio-imaging, and stress sensors and their academic value in understanding photo-physical process,[4] In comparison with the conventional ML materials, conjugated organic solids have the advantages of structure diversity, intrinsic luminescence, easy accessibility and processability as well as readily chemical modification, which enables them to be promising candidates for new ML materials.[5] Generally, ML is related to piezoelectric effect of crystals with piezoelectric space groups,[6] and special intermolecular interactions and packing modes can endow the aggregates with interesting functions.[7] However, organic ML crystals start to draw serious research attention only within the past few years and are currently in the initial stage of investigation.[8] It is still impossible to predict in advance whether new organic luminescent crystals can exhibit ML activity even if they belong to piezoelectric space groups, and thus the each identified ML compound is still an isolated event.[9] At present, bright organic ML materials are scarce, and their color gamuts are rather limited. Therefore, it is important to develop a new and simple strategy for realizing bright and multicolor ML materials.

We have been interested in developing bright organic blue ML emitters, especially those have high thermal stability, easy to crystallization and low melting point, because they might serve as the host matrix to generate other color ML by doping various fluorescent dyes. At first glance, this doping strategy seems to be undramatic but actually challenging because some special requests are needed for producing bright ML blends. It is conceivable that the vacuum co-deposition method used in the organic electroluminescence device is not only tedious but also unworkable since many organic dyes can not be vacuum-deposited. Moreover, the amorphous solids are non ML active. Alternatively, the feasible approaches should be the solution mixing and melt blending, and latter is the best because of the simplicity and solvent-free. Such ML materials should at least have the characteristics of high thermal stability, bright blue emission, ease of crystallization, and moderate melting point. Not only that, a good ML matrix should easily form ML active crystals regardless of fluorescent dopants and crystallization methods. The moderately low melting points for ML crystals can enable both the melt matrix and the doping dye to be thermally stable during dissolution and dispersion of organic fluorescent dyes. To the best of our knowledge, there have been no reports on such ML crystals and doping strategy to date. If this attempt works well, it should open up a new and versatile avenue for bright multicolor organic ML materials.

We recently find that our previously reported a blue organic ML material, *N*-phenylcarbazole (NPC) can be used as such a

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ML matrix.[10] NPC crystals show a melting point of 91 °C and can be readily sublimated, and the sublimate and the cooled melt are all in the form of large blue crystals exhibiting bright blue ML with the peak wavelength of 420 nm. Moreover, both the natural volatilization and the rotary evaporation, the volatile residues are large flakes of blue crystals. When shoveling the crystals into a glass bottle, the sparkling blue light can be seen under soft light, and it became showier in the dark (Figure 1). The crystals in the bottle are stirred with a magnetic bar or shaken quickly with hand, the blue light is still visible by the naked eye and recordable by iPhone 6 (Videos in the ESI), emphasizing the high ML activity and brightness. These results indicate that NPC readily forms ML active crystals no matter how crystallization methods probably due to the piezoelectric space group (Fdd2)[6b] and the simple molecular structure. To demonstrate the accessibility of this doping strategy, here we have employed several polar organic fluorescent dyes with different fluorescent colors as the dopants to prepare the multicolor ML blends by simple melt blending.
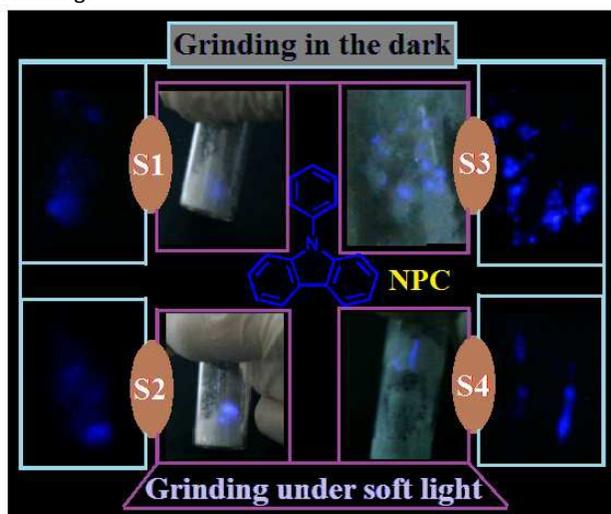

Figure 1. The photos of NPC crystals and ML prepared by the different crystallization conditions (S1: rotary evaporation, S2: natural volatilization, S3: sublimate, and S4: cooled melt) at room temperature.

Inspired by bright blue ML, easy crystallization and low melting point of NPC crystal, we consider that NPC has the potential as the ML matrix for producing various visible ML by doping (blending) different fluorescence color dyes. In fact, the melted NPC liquid can be regarded as a non-polar organic solvent, which should well dissolve or disperse various organic fluorescent dyes. Here we employ four polar dyes with green, yellow, orange and red emission as the dopants (column A in Figure 2), and they have high melting points (≥ 160 °C, Figure S1). The blends are prepared by adding a given amount of dopant (4~5 W%) into the stirring NPC melt at 110 °C and then cooled to the room temperature. It can be expected that, upon cooling the mixture melt to the crystalline state of NPC matrix, the dopants would aggregate into very small nanoparticles or molecularly dissolve in NPC matrix. Since the blends show the same fluorescence colors (column B in Figure 2) and emission

spectra (Figure 3a,b) as the dopant solids, rather than the dopant solutions (Figure 3c), the dopants have self-aggregated and crystallized in the NPC matrix upon cooling process, which can be ascribed to the different polarity between dopants and NPC and the reduced solubility induced by cooling and crystal-lization as well as the high melting points of four organic dopants. Overall, the polar dopants should be dispersed in NPC matrix in the form of small nanocrystals. Moreover, there are commendable overlaps between ML spectrum of NPC crystals and absorption spectra of the dopants (Figure 3d). These can contribute much to the energy transfer.
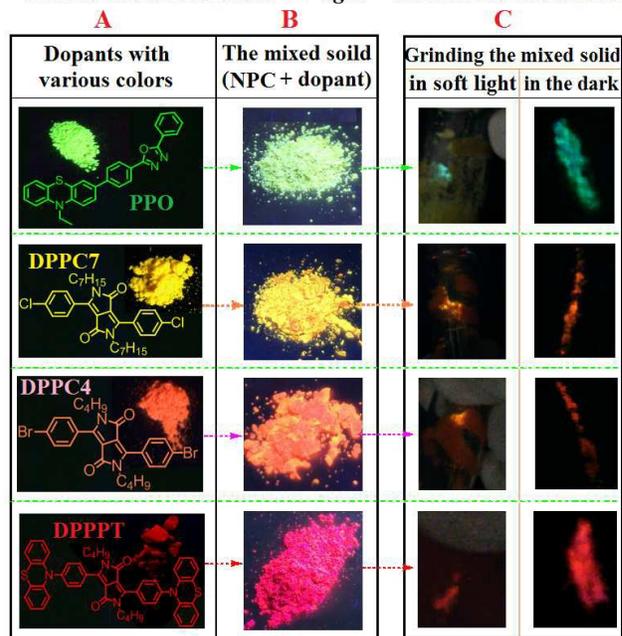

Figure 2. The apparent state and photofluorescence images of the different colors doped solids (column A) of the dopant (4~5 W%) in NPC matrix (column B) solids upon mechanical grinding in soft light and in the dark without external excitation (column C).

Excitedly, after cooling, these blends all become the clumpy crystals with different fluorescence colors, and they are found to be still high ML activity and emit bright green, orange, and red light upon mechanical grinding (column C and D in Figure 2). In the dark room, ML is very bright and clear, and even in the room without direct light (soft light), these ML are all visible. Since NPC crystals emit blue light upon UV light and mechanical excitation and these dopants are all non ML active, the ML emissions with green, yellow, and red colors for the blends must be from the dopants excited by ML of NPC crystals. We have not seen blue fluorescence from the blends upon mechanical grinding, implying the quite complete energy transfer in the ML process. This signifies the uniform and fine dispersion of dopants in NPC matrix. Figure 4a depicts the ML spectra of the blends recorded by a CCD spectrometer. For the sake of comparison, the ML spectrum of pure NPC crystal is also included. Overall, the obtained ML spectra by a CCD spectrometer are well consistent with their solid PL spectra (Figure 3a), excepting that the NPC/ClDPP blend shows a

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moderately red-shifted ML emission relative to the PL one, which will be investigated further (vide infra). Since there are no detectable blue emissions, the ML energy of NPC crystals has been well transferred to the dopants, which once again signifies that dopants are well dispersed in NPC matrix.
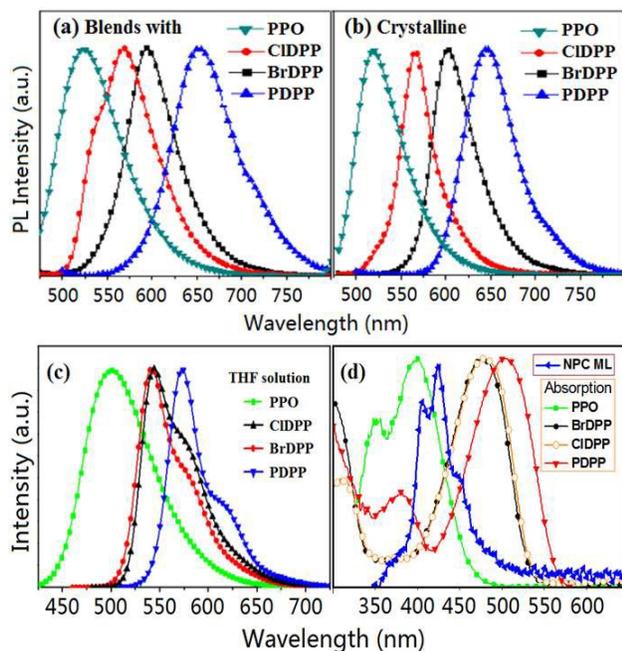

Figure 3. The photoluminescence (PL) spectra of NPC blends with the doped solids (4~5 W%) (a), and PPO, ClDPP, BrDPP and PDPP in crystalline state (b) and in THF solution (c); The absorption spectra of PPO, ClDPP, BrDPP and PDPP and Mechanoluminescence (ML) spectra of NPC (d).

To figure out why the NPC/ClDPP blend exhibits the red-shifted ML relative to the PL, we investigate the fluorescence behavior of pure ClDPP crystals upon mechanical grinding. It is found that, the yellow ClDPP solid becomes an orange one, and the corresponding emission peak is red shifted by 32 nm from 563 to 595 nm. Thus, ClDPP is a mechanofluorochromic (MFC) dye. Interestingly, the fluorescence emission of ground ClDPP solid is consistent with the ML of NPC/ClDPP blend, and this consistency has two aspects of meanings. One was that the present ClDPP is dispersed in NPC matrix in the form of crystalline state, and the dispersed crystalline grains have already produced MFC behavior upon mechanical grinding, and another was that the MFC behavior happens before ML of NPC matrix. We think that this result should intrigue ones to exploit organic luminophores with both ML and MFC behaviors to investigate the interesting photophysical properties.
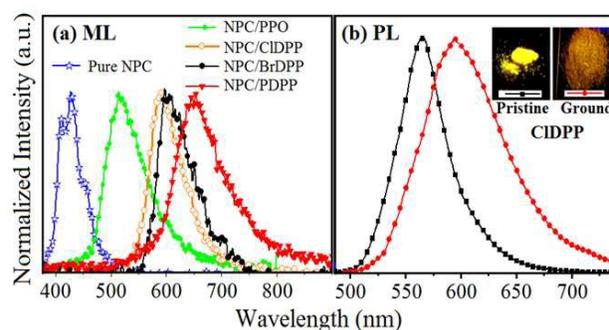

Figure 4. (a) Mechanoluminescence (ML) spectra of pure NPC crystal and its doped solids with different organic fluorescent dyes in the dark at room temperature, which are collected by Acton SP2750 spectrometer with a liquid-nitrogen-cooled CCD (SPEC-10, Princeton) as a power detector; (b) The PL spectra and fluorescence images of ClDPP power before (left) and after grinding (right).

Finally, to further understand the potential of NPC as ML matrix and the effect of dopant concentration on ML emission, we have prepared two other NPC/BrDPP blends with lower (2 W%) and higher (10 W%) concentration of BrDPP, respectively. The fluorescence photos and emission spectra of the cooled blends are showed in Figure 6a. The solution and crystalline states of BrDPP emit green (540 nm) and orange (602 nm), respectively, but the blend containing 2 W% of BrDPP is a yellow-emitting solid (576 nm), and its ML also exhibits yellow emission (578 nm). This implies that the present BrDPP is in a new and unknown dispersed state in NPC matrix. When the concentration of BrDPP in NPC matrix is increased to 10 W%, the resulting blend emits orange PL (600 nm) and ML (598 nm), which is the same as that of the above blend with 4 W% of BrDPP and corresponds to the emission of the crystalline BrDPP. This experiment demonstrates that NPC still acts as an excellent ML matrix even if the dopant concentration is as high as 10 W%. ML colors of NPC/dyes blends mainly depend on the fluorescence colors and the dispersion states of dopants.
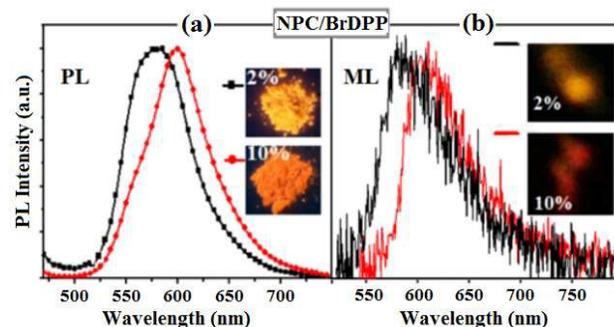

Figure 5. The Photoluminescence (PL) (a), Mechanoluminescence (ML) spectra and fluorescence images (b) of two NPC/BrDPP blends with BrDPP concentration of 2 W% and 10 W%, respectively .

Conclusions

In summary, we have demonstrated that bright organic blue ML materials with good thermal stability, easy crystallization and moderately low melting point can act as ML matrix to produce multicolor ML by doping organic dyes with various

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colors, and NPC is exploited as the first ML matrix. NPC can always form ML crystals no matter how crystallization methods and still retain the high ML activity even under high dopant concentrations. The ML colors of the blends mainly depend on the fluorescence colors and the dispersion states of dopants. We also demonstrate that the MFC behavior of the organic dopants happens before the ML behavior of ML matrix, indicating an intriguing optical phenomenon and a worth studying photophysical process. Overall, we have first realized the multicolor ML through simple melt blending and broaden ML family and color gamut. This simple strategy has opened up a feasible and versatile avenue for bright multicolor organic ML materials without need for difficult molecular design and tedious chemical synthesis.

Conflicts of interest

There are no conflicts to declare.

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