Mechanochromic Materials

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Linearly Tunable Emission Colors Obtained from a Fluorescent–Phosphorescent Dual-Emission Compound by Mechanical Stimuli**

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Abstract: *Organic mechanoluminochromic materials are mechano/piezo-responsive and promising for applications in sensors, displays, and data storage devices. However, their switching range of emission is seriously impeded by only one kind of emission (either a fluorescent or phosphorescent peak) in the spectrum of single organic compounds. This study presents a design strategy for pure organic compounds with excellent room-temperature fluorescent–phosphorescent dual-emission (rFPDE) properties, which combines the effective factors of dipenylsulfone group, crystalline state, and heavy atom effect. Following the principle of color mixing, myriad emission colors with a wide range from orange to purple and across white zone in a straight line in the chromaticity diagram of the Commission Internationale de l'Eclairage (CIE) can be obtained by simply mechanical grinding the compound. The unique properties could be concentrated on a pure organic compound through this design strategy, which provides a new efficient channel for the discovery of efficient mechano-responsive organic materials.*

Controlling and tuning the solid-state luminescence of organic materials continues to be an attractive topic in both theoretical research and practical applications in the fields of sensing,[1] color displays,[2] and data storage.[3] The relationship in the molecular level between the emission properties of organic luminescent materials and the external pressure or mechanical stimuli has recently gained considerable attention because the knowledge of such a relationship is essential to real-world applications of the "smart" materials.[4–11] Many studies have been conducted on mechano/piezo-responsive organic luminescent materials, also known as mechanoluminochromic materials. However, studies focusing on the switching range of the emission of such materials remain limited.[11,12] On the other hand, although the compounds are constructed with complex molecular structures, these single organic compounds generally exhibit only one kind of emission, either fluorescent or phosphorescent, in the solid state.[13] This limitation seriously impedes the extent of the switching range of such compounds. Thus, pure organic molecules with room-temperature fluorescent–phosphorescent dual-emission (rFPDE) properties are essentially superior to the above-mentioned luminophores for mechanoluminochromic materials. Given the difference between the radiative processes of fluorescence and phosphorescence, the separate dual emissions in rFPDE materials exhibit respectively tunable luminescent characteristics under external stimuli,[14] which significantly enrich their emission switching. We present in this communication a successful strategy to obtain new rFPDE materials with a large separation in their dual emissions from a single organic compound (Figure 1A). When the crystals of the rFPDE organic compound were converted into the amorphous powder by mechanical stimulus, the compound exhibits an unusually wide range of blue shift in its emission from orange to purple. Furthermore, the emission color can be controlled and tuned to a white light by simply grinding the compound, following the linear shift in the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates, according to the principle of color mixing (Figure 2B).

To date, only few examples of rFPDE organic materials have been described, which commonly utilize a complex host–guest doping system.[14,15] In such doping systems, the guest luminophore is dispersed into a glassy host matrix, amorphous polymer, or small molecule to restrict the competitive thermal non-radiative decay pathways and facilitate the strong room-temperature phosphorescence (RTP). The obvious disadvantage of these complex bi-phase systems is the inevitable phase separation, which results in unstable luminescence because of the inherent difference between the molecular structure of the host and the guest molecules. Moreover, these systems exhibit dual emission only under a nitrogen atmosphere (that is, in an oxygen-free atmosphere)[14] or through the use of deuterated organic compounds as the guests,[15a] which further limits their practical applications. Nevertheless, some reports have shown that the rigid surrounding of the crystalline state can also effectively

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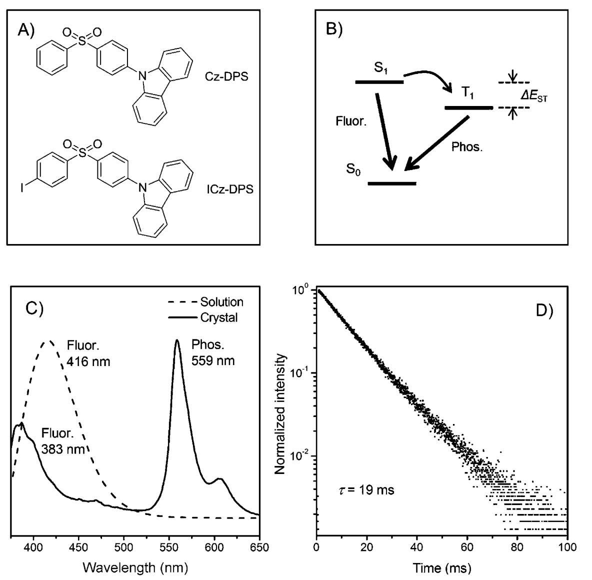

Figure 1. A) Chemical structures of compounds Cz-DPS and ICz-DPS. B) Energy-level diagram of the relevant photophysical processes in initiating rFPDE (ΔE_{ST} = energy gap, S_0 = ground state, S_1 = singlet excited state, T_1 = triplet excited state, Fluor = fluorescence; Phos = phosphorescence). C) Photoluminescence (PL) spectra of ICz-DPS in chloroform solution (10^{-5} mol L^{-1}, -----) and crystal state (——). Excitation wavelength: 350 nm. D) Time-resolved emission decay curve of 559 nm emission from the crystal of ICz-DPS. Phosphorescent lifetime (τ) is indicated.

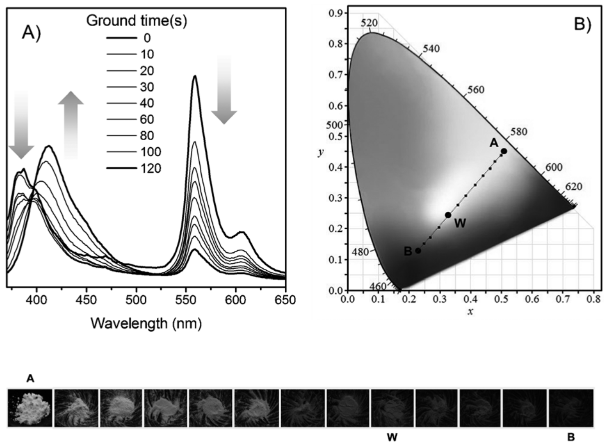

Figure 2. A) PL spectra of ICz-DPS at different grinding times. Excitation wavelength: 350 nm. B) Corresponding CIE chromaticity coordinates in CIE-1931 chromaticity diagram of the ICz-DPS samples at different ground time. C) Corresponding photos of the ICz-DPS samples at different ground time under 365 nm UV irradiation. CIE chromaticity coordinates of three samples are indicated in (B): the original crystal (sample A), the sample after grinding for 120 s (sample B), and the ground sample with white emission (sample W).

shut down the thermal non-radiative deactivation and prevent quenching by oxygen in the air, thereby resulting in efficient RTP emission. Some studies have been conducted on RTP in the air, but not on the dual emission of special organic crystals, including host–guest co-crystals[16] and aromatic ketone crystals.[17] Given that their conversion from the crystalline into an amorphous state is one of the important mechanisms of the mechanoluminochromic materials, designing organic crystals with rFPDE feature is a suitable strategy involving novel mechano-responsive materials. A large separation of the fluorescent and phosphorescent peaks in the designed compound is also indispensable for exhibiting increasingly wide and colorful emission switching under the external stimuli. However, increasing the separation of the emission peaks consequently implies a large energy gap (ΔE_{ST}) between the singlet (S_1) and triplet (T_1) excited states (Figure 1 B). When the organic compounds have a large ΔE_{ST}, the electron transition from the S_1 to T_1 excited states through the spin-forbidden intersystem crossing to initiate phosphorescence becomes difficult.[13] Thus, obtaining RTP or even rFPDE in common organic compounds with a large ΔE_{ST} is extremely difficult. Nevertheless, some organic groups with lone electron pairs, such as aromatic carbonyls[16a,17] and sulfones,[18] facilitate electronic coupling between their S_1 and T_1 excited states, which in turn promotes intrinsic triplet generation through intersystem crossing to exhibit phosphorescence. Dias et al.[18] have recently shown that sulfone derivatives containing electron donor (D) and acceptor (A) units can exhibit strong phosphorescence at low temperatures despite their large ΔE_{ST}. It is thus suggested that large ΔE_{ST} might not be an insuperable impediment to obtain novel organic compounds that exhibit rFPDE feature with large separation in their dual emissions in the air.

Herein, a D-A type dipenylsulfone derivative (that is, 4-(*N*-carbazolyl)diphenylsulfone; Cz-DPS) with twisted conformations, which can lead to strong solid-state emission by preventing inter-molecular interactions,[4e] has been designed and synthesized. It has been found that this compound exhibited an emission spectrum of dual peaks (separated by about 150 nm), of which a very strong fluorescence peak together with a weak RTP peak was found for the crystalline state in the air (Supporting Information, Figure S1). In terms of practical usages in emission switching, the weak phosphorescence of Cz-DPS must be enhanced in addition to the large separation of the dual peaks. It is known that the massive nucleus of a heavy atom can enhance the spin–orbit coupling of the excited electrons of organic compounds, thereby increasing the intersystem crossing between the S_1 and T_1 states of the excited chromophore molecules and promoting strong phosphorescence, and such a heavy atom effect has been widely used in improving the phosphorescence.[16a] Thus, another new rFPDE molecule, 4-iodo-4′-(*N*-carbazolyl)diphenylsulfone (ICz-DPS), has been designed and synthesized in an attempt to enhance the phosphorescence of Cz-DPS through the internal heavy atom effect (Figure 1 A). It has been found that substituting only one iodine atom at the *para* position of the free phenyl group in Cz-DPS exerts only little effect on the molecular energy levels. This can be concluded from their similar absorption and photoluminescence (PL) spectra in solution state (Supporting Information, Figure S2). As expected, the crystals of ICz-DPS exhibit outstanding rFPDE characteristic with large separate dual emissions as well (ca. 170 nm). Its fluorescent and phosphorescent peaks are located at 383 and 559 nm with emission lifetimes of 0.37 ns and 19 ms, respectively (Figure 3 C and 1 D). The

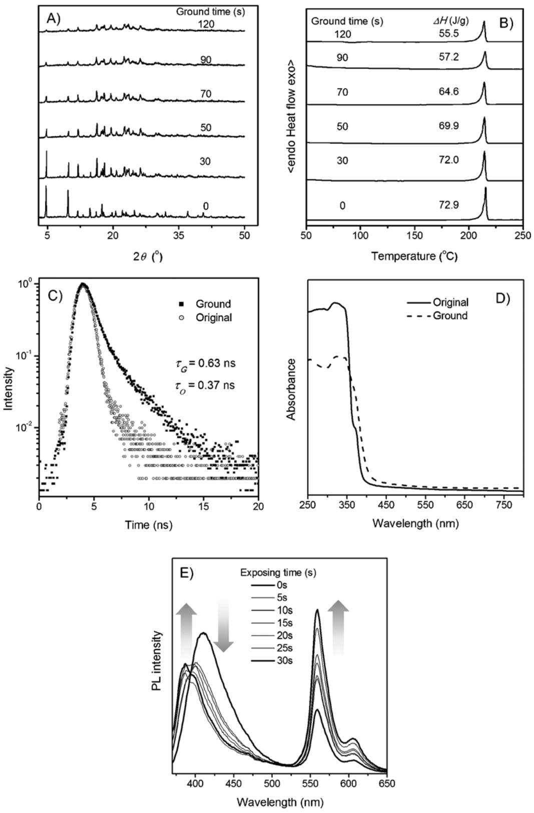

Figure 3. A) WAXD curves of the ICz-DPS samples with different grinding times. B) DSC curves of the ICz-DPS samples with different grinding times. The melting enthalpy of the crystalline in samples is indicated. C) Time-resolved emission decay curves of the original crystal and the sample after ground for 120 s. Fluorescence lifetimes are indicated: τ_G for the ground sample and τ_O for the original sample. D) UV/Vis absorption spectra of the original ICz-DPS crystal (——) and the sample after ground for 120 s (-----). E) PL spectra of the ground ICz-DPS sample during exposing to dichloromethane vapor for 30 s.

fluorescence emission is fit with a double-exponential decay, while the phosphorescent part can be fit with a single-exponential decay. Its fluorescent part is bluer than that of Cz-DPS crystal may be due to the different molecular stacking in their crystals. More importantly, the phosphorescent peak is indeed enhanced and even higher than its fluorescent peak, as a result of the heavy atom effect of iodine. The proper integration of the dipenylsulfone group, crystal state, and heavy-atom effect has thus resulted in a novel rFPDE pure organic compound.

The crystalline ICz-DPS with highly separate dual emissions is actually found to respond sensitively to the external mechanical grinding because of its unique rFPDE characteristic, as shown in Figure 2. During grinding, the fluorescent peak at 383 nm decreases gradually, and a new peak emerges at 412 nm. The phosphorescent peak at 559 nm exhibits a sustained reduction but is located at the same position. The PL quantum yield of the sample also decreased continusouly as the phlosphorescent part reduced rapidly (Supporting Information, Figure S3). After grinding for 120 s, both peaks at 383 and 559 nm decreased, whereas the new peak at 412 nm became the most intensive peak. That is to say, the ratios between the new peak and the two original peaks are reversed (Figure 2 A). The result of grinding process is quite similar to changing their ratios in mixing two colors together. Two highly different colors are observed, namely orange from the original peaks and purple from the new 412 nm peak. As a result, a wide-range emission switching of ICz-DPS may occur from orange to purple during grinding, contrary to the general red-shifts observed in the emission of common mechanoluminochromic materials (Figure 2 C). In addition, when the above emission changes are transferred to the CIE chromaticity coordinates, it can be clearly confirmed that the emission color of the ground sample comes from the color mixing of orange and purple with different ratios.[19] A straight line with a nearly perfect correlation coefficient (0.9999) can be drawn across all the points of CIE chromaticity coordinates, from point A (0.50, 0.45) (that is, orange color) to point B (0.23, 0.13) (purple color) in the CIE-1931 chromaticity diagram, as shown in Figure 2 B. It is worth noting that the above straight line also crosses the white region. Therefore, it is possible to tune the emission color into a white light by simply grinding the crystalline sample, as the point W (0.32, 0.24), following the principle of color mixing. This observation of the capability to be controlled and tuned the solid-state emission color to white by proper external mechanical stimuli for a single organic compound would represent the first report in the field of organic mechanoluminochromic materials.

The above changes in the emission of ICz-DPS during the grinding process are found to be attributed to the transition from the crystalline to the amorphous form in the solid state, as shown by the wide-angle X-ray diffraction (WAXD) measurements and differential scanning calorimetry (DSC) determinations. In Figure 3 A, the diffraction peaks in the WAXD curves confirm the crystalline form of the pristine sample decreased in either number or intensity after grinding. The melting enthalpy of the crystalline in samples, which were evaluated through DSC analysis, also decreased along with the grinding process (Figure 3 B). When grinding smashes the crystals, the rigid surrounding of the crystal state for RTP will be destroyed. Both the thermal non-radiative deactivation and the oxygen in the air efficiently quench the RTP emission (at 559 nm). At the same time, the ICz-DPS molecules adopt a relatively relaxed and planar conformation with a reduced band gap between the S_1 and ground (S_0) states in their amorphous powder state. This change would lead to intensity decrease in the fluorescent peak at 383 nm and a newly grown red-shifted peak at 412 nm, which is in agreement with the emission of relaxed ICz-DPS molecules in the diluted solution state (416 nm, Figure 1 C). The reduced band gap can also be proven through the red-shifted absorption onset of the ground sample in the UV/Vis absorption spectra (Figure 3 D). The prolonged fluorescence lifetime after grinding shown in Figure 3 C also indicates a relatively more relaxed state of the molecules in the amorphous powder. Furthermore, the obtained amorphous state of ICz-DPS can be completely converted back to the crystalline state by exposing to dichloromethane vapor (Figure 3 E), indicating that tuning of the emission of ICz-DPS is reversible, which is greatly conducive to the practical applications.

In summary, the present report demonstrates a design strategy for pure organic compounds with excellent rFPDE properties. The novel rFPDE compound ICz-DPS possesses the capability to control and tune the solid-state emission color to white, as well as wide range of color switching by proper external mechanical stimuli, fitting with the principle of color mixing. To the best of our knowledge, such results are unique in the sense that no single organic compound has yet been demonstrated to be capable of generating variant emission tones following the principle of color mixing. It is our belief that this strategy for the molecular design would open a new avenue in the development of efficient mechano-responsive organic luminescent materials.

Keywords: color mixing · dual emission · mechanochromic materials · phosphorescence · tunable emission

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