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The dual-band emissions, multicolor continuous mechanochromisms, and application based on a single luminogen

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Keywords: Dual-band fluorescence emissions Solvent inclusions Mechanochromism Carbazole derivatives Imidazopyridine derivatives	Currently, the high contrast and multicolor continuous mechanochromic materials still face a great challenge. Here, a novel D- π -A type luminogen named as CzIPCN, was successfully constructed. By solvent diffusion method, crystals Y _C , B _T , R _E , and R _A were obtained, not only covering a large-span emission from blue to red, but also showing scare dual band emission. Interesting, the blue B _T and yellow Y _C have similar intermolecular π - π stacking interactions and significantly different emission maxima, while two emission maxima of the R _E and R _A appear at the similar frequency but with different intensity ratios. More interesting, emission maxima of B _T present tiny shifts before/after grinding, but R _E and R _A show very low mechanical force thresholds in mecha- nochromism, and yield significant color contrasts and wavelength shifts (>100 nm). Under both light&hard crushing and grinding, Y _C presents multicolor continuous mechanochromism. Additionally, CzIPCN not only shows pH-dependent fluorescence emission but also white light emission in a DCM-TFA mixture. Finally, high-

1. Introduction

The chameleon can rapidly adjust its skin color with the change of the background color, while mimosa will immediately close its leaves under slight environmental vibration [1–4]. To hunt prey or deal with environmental threats, many organisms in nature show various defensive behaviors. Inspired by these elegant and complex natural systems, researchers have designed and created a variety of stimulus-responsive smart materials in recent years, presenting great potentials in sensors [5–7], actuators [8–10], anti-counterfeiting [11–13], and other fields [14–17]. Of note, mechanochromic material has received extensive attention, whose emission wavelength or intensity can produce significant changes under the stimulation of external mechanical force (such as grinding, shearing, stretching, crushing, or compressing) [18–23]. However, it still faces a great challenge for luminogens to perform high-contrast and multicolor continuous mechanochromisms like the intelligent creatures.

The multicolor continuous mechanochromism is that mechanochromic materials show continuous color changes under multiple mechanical forces. By mechano-induced conformation transformation, phase-transition, and energy transfer from crystal to amorphous powders, Chi et al. achieved multicolor mechanochromism from light blue to bright yellow, across white color, along mechanical grinding [24]. Zhu et al. realized multicolor luminescence from blue to white, yellow and green by using a pure organic molecule with fluorescence (FL) and room temperature phosphorescence (RTP), whose dual-emission were regulated by molecular self-assembly and mechanochromism [25]. The dual-emission provide an effcient platform for the development of high-contrast and mechanochromisms, but multicolor continuous mechanochromisms were rarely reported due to sensitivity of triplet excitons to oxygen and environment. Furthermore, solvents can regulate the intermolecular stacking modes and porosity of solvent inclusions [26,27]. By inclusion, release, and rearrangement of solvent molecules under external mechanical forces, the consequent changes including environmental polarity, stacking mode, and molecular conformation will result in adjustable fluorescence emission [28-33]. For solvent-mediated crystallization, the so-called solvent inclusion refers that the solvent molecules are included in the crystal lattice by intermolecular interactions between solvents and solutes or filling channels/voids within the crystal lattice [34-36]. The solvent inclusion

level anti-counterfeiting patterns controlled by different mechanical forces were successfully constructed. It is worth mentioning that this is the first report on multiple anti-counterfeiting patterns using a single luminogen.

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phenomenon provides a possibility to tune product properties (mechanics, solubility, stability, bioavailability) without changing the molecular chemical structure [37–41]. Solvent inclusions have become a feasible method to develop mechanochromic materials, but without any relevant reports in terms of multicolor continuous mechanochromism [42–45].

The other two thorny issues faced by mechanochromic materials are insensitive to weak mechanical forces, and generally present single fluorescence signal, which affect detection limits of piezo-luminescence sensors on the one hand, on the other hand obstruct high-level anticounterfeiting and data encryption. Provided a luminogen has weak intermolecular interactions and a side to face arrangement mode, intermolecular arrangement and stacking mode of luminogen will be easily damaged under weak external force stimulation, and accompanied by fluorescence response [46,47]. In solution or solid state, some luminogens can simultaneously present local (LE) and intramolecular charge transfer (ICT) states, or singlet and triplet states, or single molecule and aggregated states emission, which combined with mechanochromism, is expected to yield high-level anti-counterfeiting. However, solving the above-mentioned problems still faces great challenges due to difficulty in predicting intermolecular arrangement and stacking mode in advance [48–50]. Under different thermodynamic conditions (temperature, pressure, pH, etc.), the phenomenon of crystallizing into two or more crystals is called polymorphism [51–53], such as basic copper chloride (α and β), and copper phthalocyanine with eight different crystal forms, etc. Unfortunately, only a very few polymorphs exhibit a wavelength shift above 100 nm under external mechanical stimuli [54-56]. To combat the increasingly rampant counterfeit and shoddy goods, the demand for high-level and multi-scale anti-counterfeiting trademark is becoming more urgent. Based on dual band emission, high contrast and multicolor continuous mechanochromism of a single luminogen, the above problems are expected to be successfully resolved.

Here, a novel luminogen named as CzIPCN, was designed, and synthesized with D (electron donor)-π-A (electron acceptor) architecture using benzene ring as a conjugate bridge by furnishing carbazole units and p-cyanophenyl imidazopyridine (Scheme 1). Owing to rotatable C-N and C-C bonds, twisted D-π-A luminogen easily forms different molecular conformations in different microenvironments and undergoes adjustable molecular conformation to response different external mechanical forces, yielding multicolor continuous luminescence signals. Meanwhile, the twisted molecular conformation results in loose molecular stacking, large voids, or channels, facilitating the entry of solvent molecules into the rigid crystal matrix, while strong ICT effect and twisted molecular conformation will boost rapid generation of triplet excitons, which is conducive to endow luminogens with RTP properties. Of note, flexible control of intramolecular distortion is expected to yield multiple luminous expressions such as fluorescence, thermal delayed fluorescence, and RTP. By finely adjusting the crystal cultivation environment, CzIPCN may present various intermolecular arrangement and stacking modes via intermolecular hydrogen bonding, π - π stacking and dipole-dipole interactions. Interesting, CzIPCN not only forms solvent inclusions with CH₂Cl₂ (DCM) and THF by intermolecular interactions, but also forms polymorphs in acetone (ACE) and ethyl acetate (EtOAc). By crushing and grinding with different strength, the vellow solvent inclusion can show multicolor continuous mechanochromism from yellow to yellow-green, to white, to blue-green, to blue. For polymorphs, both have two similar emission bands but different apparent colors due to variant intensity ratios between two emission bands. By applying a weak external mechanical force, the pink crystals rapidly transform into blue crystals. The acidchromism of CzIPCN was also investigated in THF solution, producing almost pure white light by fine adjustment. Besides, CzIPCN is also a phosphor in nature, emitting a bright yellow afterglow at 77 K when UV lamp is switched off. Noteworthy, it is rare that a single compound can show rainbow and dual-band emissions, as well as yield high contrast and multicolor continuous mechanochromisms. To deeply



Scheme 1. (a) Solvent inclusions and polymorphs of CZIPCN under natural light radiation. (b) Dual-band emissions and extremely sensitive mechanochromism of polymorphs R_E and R_A . (c) Multicolor continuous mechanochromism of Y_C .

explore the internal mechanism of the above phenomena, a series of photophysical performance tests, crystal analysis and theoretical calculation were completed.

2. Results and discussion

2.1. Photo-physical properties in solution

Recently, luminogens with aggregation-induced emission (AIE) activity exhibit mechanochromic behavior due to the loose molecular stacking, while high-contrast mechanochromism is usually achieved by controlling intramolecular charge transfer (ICT) effect. Thereby, the UV-Vis absorption and fluorescence emission spectra of CzIPCN were tested in various solvents. Fig. S1a indicates that with the increase of solvent polarity, absorption maxima of CzIPCN show only 4 nm red shifts, while its emission maxima are highly solvent dependent, which confirms ICT characteristic of CzIPCN (Fig. S1b). Owing to poor solubility, two fluorescence emission peaks (410 nm and 425 nm) can be observed in nhexane solution, which should come from single molecule and aggregates respectively. In THF-H₂O solution system (Fig. S1c), emission intensity of CzIPCN continues to decline with the increase of water fraction (f_w), except for a slight fluctuation of $f_w = 80$ %, outlining an obvious aggregation-caused quenching (ACQ) scene. For comparison, CzIP without p-cyanobenzene shows aggregation-induced enhanced emission (AIEE) activity [57]. As a speculation, p-cvanobenzene in CzIPCN reduces the electron density of imidazolopyridine unit, easily resulting in intermolecular π - π stacking and the resulting ACO due to reduced electronic repulsion.

2.2. Mechanochromism of CzIPCN

Various crystal forms are expected to be obtained by slow solvent diffusion of n-hexane into a CH₂Cl₂/THF/EtOAc/ACE solution of CzIPCN at room temperature. Luckily, four different crystals were obtained, which were named respectively as Y_C (CCDC 2270670), B_T (CCDC 2270671), R_E (CCDC 2270672) and R_A according to different colors and solvents (Fig. 1a). More specifically, yellow Y_C appear in the mixed solution of n-hexane-DCM, while blue B_T , red R_E and R_A come from n-hexane-THF, n-hexane-EtOAc, n-hexane-ACE solution in turn. It is worth mentioning that these crystals are still stable after being placed for several months. Furthermore, B_T (460 nm) present a single emission peak, but Y_C (467 nm and 535 nm), R_E (442 nm and 575 nm) and R_A (450 nm and 575 nm) show dual band emissions (Fig. 1b). To investigate luminescence lifetimes were measured (Fig. S6). The emission peaks at 535 nm and 575 nm should belong to phosphorescence

radiation based on luminescence lifetimes of 840 μ s-3.51 ms, while the emission peaks at 442 nm, 445 nm, and 465 nm come from fluorescence radiation, with luminescence lifetimes of ns levels. Furthermore, the excitation spectra show that dual band emissions of Y_C, R_E and R_A have the same excitation maxima (Figs. S2–5). Moreover, Y_C and B_T are DCM-containing and THF-containing crystals in sequence, while R_E does not contain solvent molecules, which are further confirmed by the following crystal analysis. Unfortunately, we are unable to complete the single crystal diffraction of R_A due to poor crystal quality. Amazing, CzIPCN achieved a large-span multicolour emission from blue to red based on the different crystals.

By "on-off" switching of ultraviolet lamp, the crystals cannot present visible afterglow, which should be due to short phosphorescence lifetimes. Crystal analyses indicate dihedral angles of ring A-B, B-C and C-D are 55.01°, 2.58° and 37.50° in $Y_{\rm C}$ respectively, indicating twisted molecular configuration (Fig. 2a). By C-H…Cl (2.902 Å), C-H…C (2.725 Å), C-H…N (2.569 Å) and C-H…C (2.899 Å) bonds, each CzIPCN molecule forms hydrogen bonds with three CH₂Cl₂. Crystal analyses further show two CzIPCN molecules in one cell unit adopt antiparallel stacking mode, moreover, between aminopyridine units exist intermolecular π - π stacking interactions, whose plane-plane (Cp-Cp) and centroid-centroid (Cg- C_{g}) distances are 3.298 Å and 3.541 Å respectively. Compared with $Y_{C_{g}}$ B_T shows similar antiparallel stacking and more distorted molecular conformation (Fig. 2b), whose dihedral angles are 59.99°, 14.59° and 36.54° respectively, which promote the blue shift of emission maxima. Besides, each CzIPCN molecule interacts with two THF molecules by C-H…O (2.468 Å and 2.648 Å) and C-H…C (2.884 Å and 2.842 Å) bonds in B_T. Based on the crystal analysis of B_T and Y_C, the ACQ mechanism of CzIPCN should be attributed to π - π stacking between aminopyridine units in the AIE test. Different from B_T and Y_C, there are four CzIPCN molecules instead of two in one cell unit of R_E, without any solvent molecules (Fig. S7). The two adjacent molecules are arranged by adopting head (carbazole unit) to head and side to face arrangement modes. More interesting, they have different molecular conformations (Fig. S8). For one of both molecules, dihedral angles of ring A-B, B-C and C-D are 49.59° , 36.70° and 31.67° respectively. For the other one, the corresponding dihedral angles are reduced to 46.32°, 35.32° and 27.22°. Even so, different molecular conformations cannot take responsible for the dual-band fluorescence emission of R_E based on theoretical calculation. Weak interactions or intermolecular hydrogen bonds are concentrated on the carbazole unit and CN- of CzIPCN, rather than between aminopyridine units and solvent molecules, which should be due to D-\pi-A CzIPCN promotes electron transfer from carbazole unit to pcyanobenzene unit, leading to electron deficient carbazole unit and electron rich cyan. We know that twisted D-π-A type molecular conjugation contributes to reduce the energy gap between S_1 and T_1 (ΔE_{ST}),



Fig. 1. (a) Fluorescent photographs of four crystals and their ground samples under 365 nm UV light. (b) Fluorescence emission spectra of crystals Y_C , R_E , B_T and R_A ($\lambda_{ex} = 360$ nm).



Fig. 2. (a) Single crystal structures, intermolecular interactions and intermolecular π - π stacking of Y_C and (b) B_T.

which can boost intersystem transition and the resulting yield RTP. Thereby, phosphorescence spectra and afterglow of CzIPCN were recorded in DCM solution at 77 K (Fig. S9). The results indicate CzIPCN is a phosphor in nature, and the corresponding phosphor emission peaks are 550 nm and 606 nm, which confirms the absence of visible afterglow is due to crystals PtzIPCN cannot suppress non-radiative deactivation of triplet excitons.

The ICT characteristic and twisted molecular conformation reminds us to examine the mechanochromism of CzIPCN. Before/after grinding, emission maxima of B_T remain constant, while R_E and R_A present significant color contrast, whose emission maxima shift to 450 nm from initial dual-band emission (Fig. S10). Mechanochromism of R_E and R_A only need a very weak mechanical force, even a light touch on the sample is enough to trigger off this mechanochromism (Fig. 3a). Crystal



Fig. 3. (a) Photographs of Y_C , R_E and R_A subjected to different mechanical forces under 365 nm ultraviolet light radiation. (b) Fluorescence spectra of Y_C before/after the actions of different mechanical forces, and (c) the corresponding CIE coordinate diagram, (d) XRD and (e) DSC patterns.

analysis indicate that the quantity and intensity of intermolecular hydrogen bonds and weak interactions are insufficient for R_E than Y_C (Figs. S8 and 2a). More importantly, π - π stacking combined with more intermolecular hydrogen bonds and weak interactions contribute to enhance resistance to destruction of external mechanical forces for Y_C, while the dimer of R_E adopts orthogonal arrangement only with a weak interaction between two molecules (Fig. S8). Obviously, the latter should be more susceptible to external mechanical forces according to intermolecular stacking and weak interactions. Interestingly, Y_C shows continuous mechanochromism by using different external forces. By light crushing, hard crushing, light grinding, and hard grinding (Fig. 3a), Y_C presents multicolor variation from yellow, yellow-green, white, green to blue, and their CIE (CIE: Commission International de l'Eclairage) values are (0.26, 0.32), (0.29, 0.40), (0.30, 0.42), (0.25, 0.36) and (0.15, 0.18) in turn (Fig. 3c). Moreover, a closer examination reveals the intensity ratio between 535 nm and 467 nm increase significantly by light crushing (Fig. 3b), and further heighten with the increase of crushing strength. To understand the above mechanochromism, X-ray diffraction (XRD) spectra of CzIPCN were examined under different solid forms (Fig. 3d and Fig. S14). The XRD data indicate the position of diffraction peaks do not shift after light/hard crushing, but diffraction peaks become sharper, especially for the diffraction peak at 26°, which illustrates that light crushing and hard crushing do not alter intermolecular arrangement and stacking. Differential scanning calorimetry (DSC) tests show Y_C has two melting peaks (Fig. 3e), one at around 236.1 °C and the second one at 247.1 °C (main melting peak), but crushed samples only give a melting peak at 242.1 °C. More importantly, heavy crushed Y_C presents enhanced absorption at 450-700 nm compared with that of lightly crushed Y_C, while absorption spectrum of heavy ground Y_C relative to crushed Y_C gives significant hypsochromic shift (Fig. S11). Therefore, mechanochromism induced by crushing may derive from planarized molecular conformation and homogenization of crystalline grain. By contrast, diffraction peaks of hard ground Y_C become narrower and sharper, accompanied by the appearance of new peaks at 5°, 19° and $23^\circ.$ Meanwhile, DSC curve shows the corresponding melting peak shift to 236.5 °C and becomes no longer sharp. XRD and DSC tests demonstrate that mechanochromism of ground sample is due to phase transition from crystalline to crystalline. Subsequently, the mechanochromic reversibility is investigated by heating and DCM fuming (Fig. S12). The results indicate that ground sample cannot go back to the original state, confirming irreversibility of the mechanochromism, but ground sample can go back to the original state by crystal growth. Although there were several precedents where the emission color gradually changed in response to the intensity of mechanical stimuli, they could not present a

color span as large as the current research, nor did they exhibit the dual band fluorescence emission [58–61].

2.3. White light emission induced by pH

Conventionally, white light emission (WLE) is realized by combining three primary-color emitters or two complementary color emitters, which often face several challenges such as complicated fabrication methods, energy transfer between different emitters, and the difference in photo-stability of emitters [62]. Single-component white light emitters (SWLEs) can eliminate the mentioned problems, and show a rapid increasing trend in recent years [63], but they are still very rare. The imidazopyridine unit in CzIPCN can be used as a proton acceptor, whose protonation will red-shift emission maxima due to enhanced intramolecular push-pull electron effects, thereby SWLEs is expected to be achieved by complementary neutral and protonated form of CzIPCN. As shown in Fig. 4a, fluorescence emission spectra of CzIPCN were investigated in DCM-TFA solution. With the decrease of pH from 7 to 3, emission maxima at 445 nm presents an obvious descending trend, while a new should peak at 540 nm gradually forms, accompanied by the changes of fluorescent hue from blue to white. When the pH is 2, CzIPCN showed a warm white fluorescence, and the corresponding CIE value, color rendering index and correlated color temperature were (0.28, 0.34), 77.56, and 8812.14 K in turn, which stemmed from almost identical emission intensity of neutral and protonated CzIPCN. The color of the solution changes from warm white to yellow at pH = l, and only single fluorescence emission peak can be observed, indicating that CzIPCN is completely protonated. Overall, CzIPCN showed pH-dependent fluorescence emission and produced WLE in an DCM-TFA mixture under excitation at 365 nm.

2.4. Theoretical calculation

To further explain the fluorescence emission of CzIPCN at different crystal states, the lowest singlet excited state (S_1) structure of CzIPCN molecule constructed from the single crystal structure was optimized by using the ORCA5 program package at the def2-svp/PBE level of theory. Firstly, eleven initial conformations of B_T containing single THF molecule are constructed by altering the position of THF (Fig. S15), whose S_1 state are calculated and optimized to obtain the most stable molecular conformation based on the minimum energy (Fig. S16a). The results indicate that the THF molecule was adsorbed at the joint of the ring B-C, and the ring B-C showed slight twist, but rings B, C and D are almost in the same plane, which forms a dihedral angle of near 90° with ring A,



Fig. 4. (a) Emission spectra of CzIPCN in DCM at a concentration of 10^{-5} M upon changes of pH from 1 to 7 by TFA. Inset: Photo of the solution under 365 nm UV light radiation. (b) Corresponding CIE color coordinates for solutions at different pH values.



Fig. 5. (a) Simulated conformation of CzIPCN with one DCM molecule in excited states. (b) Simulated conformation of CzIPCN with three DCM molecules in excited states.

and the corresponding fluorescence emission wavelength and oscillator intensity are 456.5 nm and 0.57 respectively, which is consistent with the experimental values (459 nm). By using a similar approach, S₁ state of B_T containing two THF molecules are calculated and optimized to explore solvent effects. Interestingly, the emission maxima, oscillator intensity and molecular conformation remain stable, outlining negligible solvent effects (Fig. S16b).

To in-depth discuss the inherent mechanism of dual band emission for Y_C, more than fifty molecular conformations were established and optimized by altering the position and orientation of DCM, and thereby two most stable S1 states were found. As shown in Fig. 5a, twist angle of ring B-C is 30° in the lowest stable one, and DCM is diagonally above ring B, whose H points to the N atom on ring B. There are two emission peaks in this S1 states, located at 445.7 nm and 548.4 nm, with corresponding f of 0.46 and 0.01 respectively. For the other one, DCM is located directly above ring B, but rings B, C and D maintain plane configuration. Only a single emission peak is observed, whose emission maxima and f are 441 nm and 0.69 in turn. From the above, we found that position and orientation of DCM affect fluorescence emission of crystals, but the theoretical calculations confirmed that the emission peak at 535 nm couldn't possibly come from fluorescence due to tiny f for the calculated emission peak at 548.4 nm. Subsequently, S1 state of Y_C containing three DCM molecules are calculated and optimized based on the corresponding single crystal data (Fig. 5b). For Y_C, molecular conformation of S1 state presents slight bending between rings B, C, and D, and gives two emission peaks at 467 nm and 539 nm with corresponding f of 0.43 and 0.001. It is worth noting that two emission peaks are basically consistent with the experimental value, but the f at 539 nm is still tiny compared to the experiment results. By using optimization methods like the above, emission maxima and f of R_E are 441 nm and 0.69 in turn, corresponding to the experimental result at 442 nm very well (Fig. S17a). However, fluorescence emission at 575 nm cannot be calculated by single molecule optimization. Therefore, S1 state of RE is further calculated and optimized based on bimolecular model (Fig. S17b). The results show that the right molecule has the same molecular configuration as single molecule model, whose rings B, C and D is located on the same plane, forming a twist angle 72° between ring A and rings B, C and D. Different from the right molecule, dihedral angles of rings A-B and C-D are 55° and 32° respectively, and their emission maxima and f are 443.9 nm, 0.59, 499.8 nm, 0.12 and 579.6 nm, 0.005 in turn. The emission maxima at 579.6 nm with tiny f still cannot match with experimental result, it can be inferred that the emission peak at 575 nm should come from the triplet state. Zhu et al. found that a hexathiobenzene molecule containing fully substituted acetamides could form crystallization driven self-assembly under mixed solvent conditions and solid film state [8]. With the fine-tuning of the environment and the improvement of crystallinity, luminescent behavior of the molecule gradually transitioned from aggregation induced phosphorescence to aggregation induced dual state emission (fluorescence and phosphorescence). Owing to the tunable ratios between fluorescence and room temperature phosphorescence, the molecule exhibited multi-color luminescence phenomena such as yellow, white, and blue. Thereby, the main reasons for multicolor crystals and tunable mechanochromisms of CzIPCN are that different intensity ratios between fluorescence and room temperature phosphorescence and molecular conformations. In our previous experiments, tunable pure organic room temperature phosphorescence was also achieved by crushing and grinding, which was attributed to monomer and aggregate emission, and the size of different crystal particles [64].

2.5. Anti-counterfeiting patterns

Based on rainbow fluorescence emission and unique mechanochromic performance, CzIPCN can be used to construct advanced anticounterfeiting patterns. Firstly, B_T , Y_C , R_E , R_A and ground sample of CzIPCN were dispersed in Aloe vera gel. (Fig. 6) Then, the facial contour and features of a Winnie Bear was outlined by taking advantage of solvent inclusions, polymorphs, and ground sample of CzIPCN. The left and right eyebrows of Little Bear 1 were drawn using crystals R_E and R_A respectively, and the nose and mouth, eyes, and facial contour were J. Jiang et al.

Fig. 6. Anti-counterfeiting application by using different crystals and mechanical forces under UV light.

drawn by using B_T , Y_C and ground sample in turn. Under the irradiation of a 365 nm UV lamp, the facial contour and features of the Winnie Bear present a colorful pattern containing blue, yellow, and red. By gently crushing, Little Bear 1 with pink eyebrows and yellowish eyes transformed into Little Bear 2 with blue eyebrows and yellowish-green eyes due to sensitive Y_C , R_E and R_A , while facial contour, nose and mouth of Little Bear remained constant. Further increasing the crushing force, except for Little Bear 's eyes turning cyan, all other facial contour and features remained unchanged, which fully reflected continuous mechanochromic characteristic of Y_C . Finally, blue Little Bear was obtained by grinding, which provided a method for preparing dynamic anti-counterfeiting patterns. Subsequently, a blooming tulip was drawn by Y_C , R_A and Y_C , displaying pink petals, yellow stamens, as well cyan leaves, and stems, which completely turned a pure blue tulip after grinding.

3. Conclusions

In conclusion, CzIPCN was successfully prepared by furnishing Nphenylcarbazole and p-cyanophenyl imidazopyridine units. It showed highly solvent dependent fluorescence emission and obvious ACQ characteristic due to ICT and intermolecular π - π stacking. By solvent diffusion method from n-hexane to DCM, THF, EtOAc and AC solution of CzIPCN, two solvent inclusions (Y_C and B_T,) as well crystals R_E and R_A were obtained. The four crystals present a large-span fluorescence emission from blue to red, and Y_C, R_E and R_A yield scare dual band fluorescence and phosphorescence emission. Crystal analysis further confirm B_T and Y_C have similar intermolecular π - π stacking modes, while R_E shows intermolecular orthogonal stacking patterns. For Y_C and R_E , the short wavelength emission comes from fluorescence, while the long wavelength emission belongs to room temperature phosphorescence based on theoretical calculation and lifetime tests, optimization of S1 structure, and low temperature phosphorescence test. By light crushing, hard crushing, light grinding, and hard grinding, Y_C presents multicolor continuous mechanochromism due to the tunable ratios between fluorescence and room temperature phosphorescence, which are caused by planarization of molecular conformation, homogenization of crystalline grain and crystalline-to-crystalline phase transition. Owing to weak intermolecular hydrogen bonding and orthogonal stacking patterns, RE and RA are extremely sensitive to external mechanical forces, yielding significant color contrast only by light crushing. By comparison, B_T presents tiny shifts before/after grinding. Besides, CzIPCN shows pHdependent fluorescence emission and produces white light emission in an DCM-TFA mixture. The CIE value corresponding to white light emission is (0.28, 0.34), which stems from almost identical emission intensity of neural and protonated CzIPCN. Based on rainbow color and dual-band emission, and continuous mechanochromism of crystals and ground CzIPCN, two anti-counterfeiting patterns are successfully constructed. This work not only provides a novel and scare luminogen with large-span and dual band fluorescence emission, but more importantly provides a theoretical basis and experimental guidance for designing novel and high contrast mechanochromic materials, as well as achieving multiple anti-counterfeiting and encryption by a single luminogen.

Author statement

Jianfeng Jiang and Chenwei Hu contributed equally to this work. This paper is completed under the guidance of Professor Yongtao Wang, and theoretical calculation are provided by Professor Lei Ma.

CRediT authorship contribution statement

Lei Ma: Data curation. Yongtao Wang: Conceptualization. Jianmei Guo: Data curation. Jianfeng Jiang: Data curation. Chenwei Hu: Data curation. Jiaqi Liu: Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2024.176594.

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