

Synergy between Twisted Conformation and Effective Intermolecular Interactions: Strategy for Efficient Mechanochromic Luminogens with High Contrast

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Luminescent materials which show dynamically switchable solid-state emission in respect to mechanical stimuli such as shearing, grinding or rubbing have attracted increasing interest owing to their academic importance and promising applications in optical storage, mechanical sensors, displacement or deformation detectors, security papers, optical memories, optoelectronic devices and display devices.^[1–10] Despite their importance for the advancement in technology, comprehensive understanding on the mechanism and universal design principle of such luminogens is less well studied.^[1,2,8] On the one hand, compared with the intense exploration in pH, chemical, voltage and temperature responsive luminescent materials, investigation on mechanochromic luminogens remains in the preliminary stage with quite limited

examples available in the literature. Further in-depth understanding of the underlying mechanism in molecular level is still in demand to be established.^[1,8] On the other hand, most luminogens suffer from the problem of aggregation-caused quenching (ACQ) in the condensed phase,^[11] making efficient mechanochromic luminogens difficult to achieve. Moreover, such materials generally show low contrast ratio in luminescence, which significantly limits their real-world applications.^[1–10] Therefore, development of new mechanochromic luminogens with efficient solid-state emission and high contrast is strikingly desirable.

In 2001, our group discovered a new phenomenon of aggregation-induced emission (AIE), which is exact opposite to the ACQ effect.^[12] AIE luminogens are weak or practically non-luminescent in solutions, but become strong emitters when aggregated as powders or nanoparticles or fabricated as solid thin films.^[12,13,14] It would be nice if the AIE dyes exhibit also mechanochromic property. Scattered examples of such AIE-active mechanochromic luminogens has been reported by us,^[10] Park^[9b] and Chi.^[6c,15] However, the general design principles of these luminogens, particularly those with high efficiency and remarkably tunable emission wavelength and intensity, are rarely found. Up to date, only a few mechanochromic compounds with switchable on-off luminescence have been reported.^[7c,10a] To create mechanochromic luminogens with high contrast and useful application, it is necessary to decipher general design strategies.

According to our previous study, specific C–H··· π , C–H···O and C–H···N contacts help lock and rigidify the propeller-like conformations of AIE molecules, which effectively restrict their intramolecular rotations and thus dramatically enhance their crystalline-state emissions.^[16,17] Meanwhile, as supported by the spectroscopic and XRD analyses,^[1] mechano-fluorochromism is normally ascribed to the perturbation of molecular packing and intermolecular interaction, both of which play important roles on the optical properties of the luminogens.^[18] Thereby, it is crucial to introduce multiple adjustable interactions in the fabrication of ideal mechanochromic materials. Necessarily, these interactions should be strong enough to maintain the orientation and arrangement of the chromophores but mutable to external forces. It is rational to envision that AIE crystals with propeller-like conformations and multiple mutable interactions might be ideal candidates for efficient mechanochromic luminogens with remarkable contrast, whose solid-state fluorescence color and intensity can

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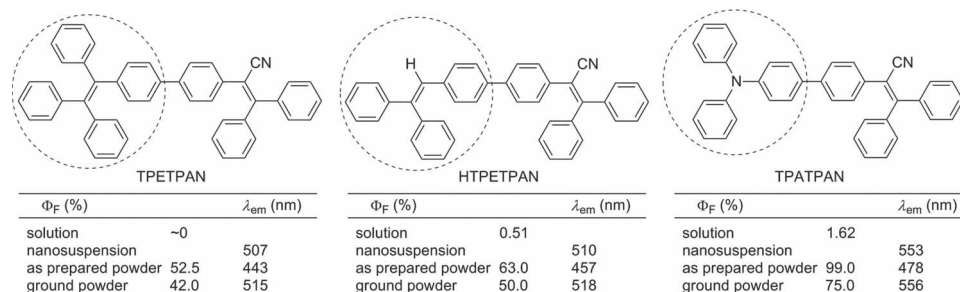


Figure 1. Chemical structures of TPETPAN, HTPETPAN and TPATPAN and their emission maxima (λ_{em}) and fluorescence quantum yields (Φ_F) in different states as indicated.

be simultaneously tuned by conformational change and intermolecular interaction variation.

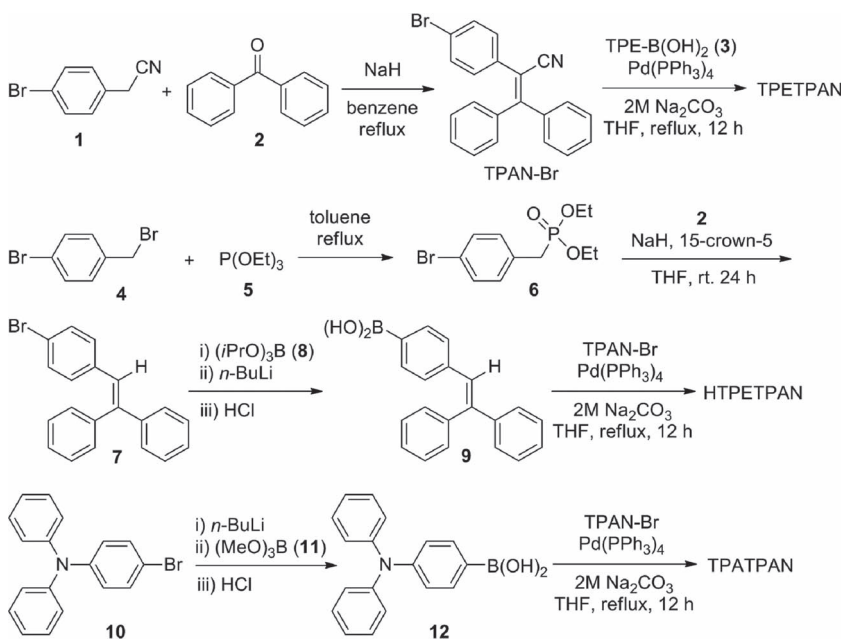
To verify it, we endeavored to create such systems. It is known that cyano groups can interact with aromatic hydrogen atoms to constitute C–H...N contact.^[9b] Recently, cyano-containing triphenylacrylonitrile (TPAN) was found to exhibit unique crystallization-induced emission characteristics.^[19] Decoration of traditional ACQ chromophores with TPAN can facilely generate new AIE-active molecules.^[19] Consequently, it is conjectured that compounds constructed from TPAN with highly twisted conformations may exhibit novel mechanochromic properties.

In this communication, a group of TPAN-containing luminophores, namely TPETPAN, HTPETPAN and TPATPAN (**Figure 1**), were rationally designed and synthesized. They are practically non-luminescent in solutions due to the active intramolecular rotations. Such rotations, however, are restricted in the crystalline state due to the van de Waals forces and effective C–H...N, C–H... π , C–H...H–C intermolecular interactions, turning them into highly efficient blue emitters with high fluorescent

quantum yields up to 99%. Grinding of such crystalline solids induces remarkable emission color change from blue to yellow and spectrum shift up to 78 nm as well as noticeable decrease in emission efficiency by 10.5–24%, which are rarely observed in traditional mechanochromic materials.^[1] Such changes are reversible aided by heating or solvent fuming process. The contrasts in emission color and intensity are so high that can be readily detectable by naked eyes, thus rendering such multi-stimuli-responsive solid emitters promising as smart materials. Moreover, the synergy interplay between the twisted conformation and intermolecular interactions demonstrates a novel design principle for the synthesis of mechanochromic luminogens with high contrast for high-technological applications.

The target luminogens were synthesized according to the routes shown in **Scheme 1**. Detailed procedures are described in the Experimental Section and Supporting Information. Briefly, taking TPETPAN as example, coupling of 4-bromophenylacetonitrile (**1**) with benzophenone (**2**) generated 2-(4-bromophenyl)-3,3-diphenylacrylonitrile (TPAN-Br). TPAN-Br, which underwent palladium-catalyzed Suzuki-coupling with TPE-substituted boronic acid (**3**), to furnish the resulting TPETPAN in 88% yield. All the reaction intermediates and final products were characterized spectroscopically with satisfactory results (see Experimental Section, and the Supporting Information, Figure S1–S7). TPETPAN, HTPETPAN and TPATPAN show good solubility in common organic solvents, exhibiting absorption maxima at 244/347, 243/353 and 243/304/370 nm in THF with molar absorptivities of $3.34 \times 10^4/2.91 \times 10^4$, $2.72 \times 10^4/3.40 \times 10^4$ and $3.66 \times 10^4/4.07 \times 10^4/3.61 \times 10^4$ L mol⁻¹ cm⁻¹, respectively (Supporting Information, Figure S8). While the absorption peak centered at 370 nm is associated with intramolecular charge transfer (ICT) transition in TPATPAN, others are attributable to π - π^* transitions.

When illuminated under a UV lamp, the dilute THF solutions of the luminogens emit almost no light. However, strong blue light was observed from their as prepared powders, revealing their AIE feature. Further photoluminescence (PL) spectra of TPETPAN in THF and THF/water aqueous mixtures



Scheme 1. Synthetic routes to TPETPAN, HTPETPAN and TPATPAN.

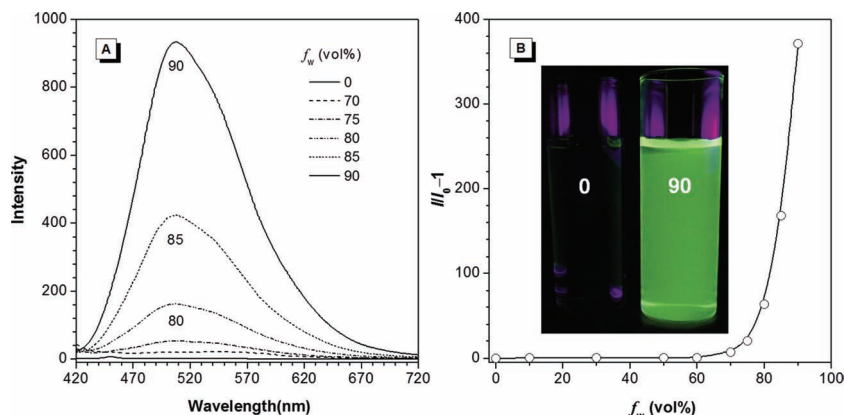


Figure 2. A) Emission spectra of TPETPAN in THF and THF/water mixtures with different water fractions (f_w). B) Plot of relative emission intensity ($I/I_0 - 1$) at 507 nm vs. the composition of the aqueous mixture. Concentration = 20 μM ; excitation wavelength = 400 nm. The inset in (B) is the fluorescent photos of TPETPAN in THF and 10/90 THF/water taken under 365 nm UV light illumination.

were also measured. As depicted in **Figure 2**, TPETPAN is practically non-luminescent in THF and the PL spectrum is almost a flat line parallel to the abscissa. The spectral pattern alters little even at a water fraction (f_w) of 75%, as the solvating power of the solvent mixture is still high enough to dissolve the luminogenic molecules. Afterwards, a greenish-yellow light was observed, whose intensity increases with increasing the

water content. At $f_w = 90\%$, the PL intensity is ≈ 372 -fold higher than that in THF, testifying that TPETPAN is AIE-active. Similar behaviors are also found in HTPETPAN and TPATPAN with maximum emission enhancement (I_{90}/I_0) of ≈ 50 - and 132-fold (Supporting Information, Figure S9,S10), respectively. The non-emissive nature of the luminogens in THF and aqueous mixtures with low f_w values should be ascribed to their molecular dispersion and active intramolecular rotations, which effectively consume the energy of the excitons non-radiatively.^[13,14] However, at high water content, such intramolecular rotations are restricted, which blocks the non-radiative relaxation channels and thus makes the aqueous mixture highly emissive.^[13,14] The PL of solutions of the luminogens was “turn on” at cryogenic temperatures (e.g. 77 K) because at such low temperatures, the solvent molecules as well as the dye molecules were frozen and thus largely restricts the intramolecular rotations of the dye molecules (Supporting Information, Figure S11).

To evaluate the mechanochromic behaviors of these compounds, their solid-state emissions were investigated. As shown in **Figure 3**, the as prepared solid powders of TPETPAN, HTPETPAN and TPATPAN emit intense blue or sky blue

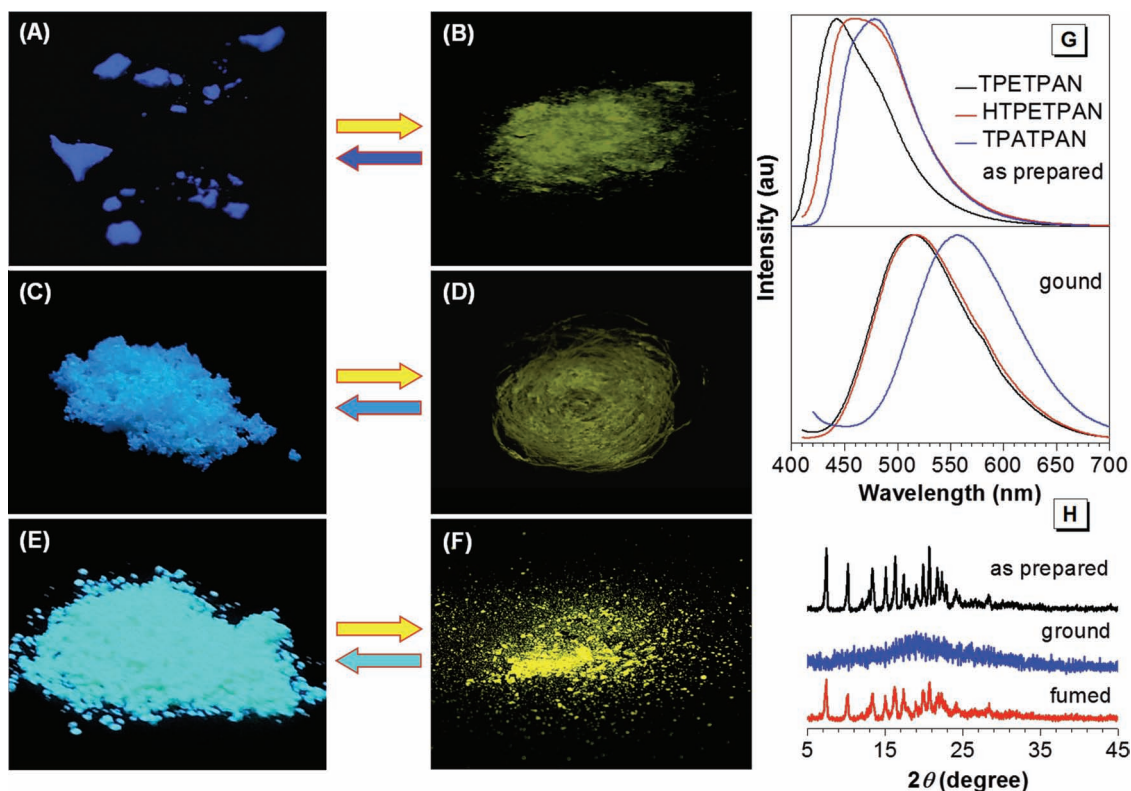


Figure 3. Fluorescent photographs of: A,C,E) as prepared and B,D,F) ground samples of: A,B) TPETPAN, C,D) HTPETPAN (C,D), and E,F) TPATPAN taken under UV illumination. G) PL spectra of as prepared and ground powders of TPETPAN, HTPETPAN and TPATPAN. H) XRD diffractograms of as prepared, ground and solvent fumed powders of TPATPAN.

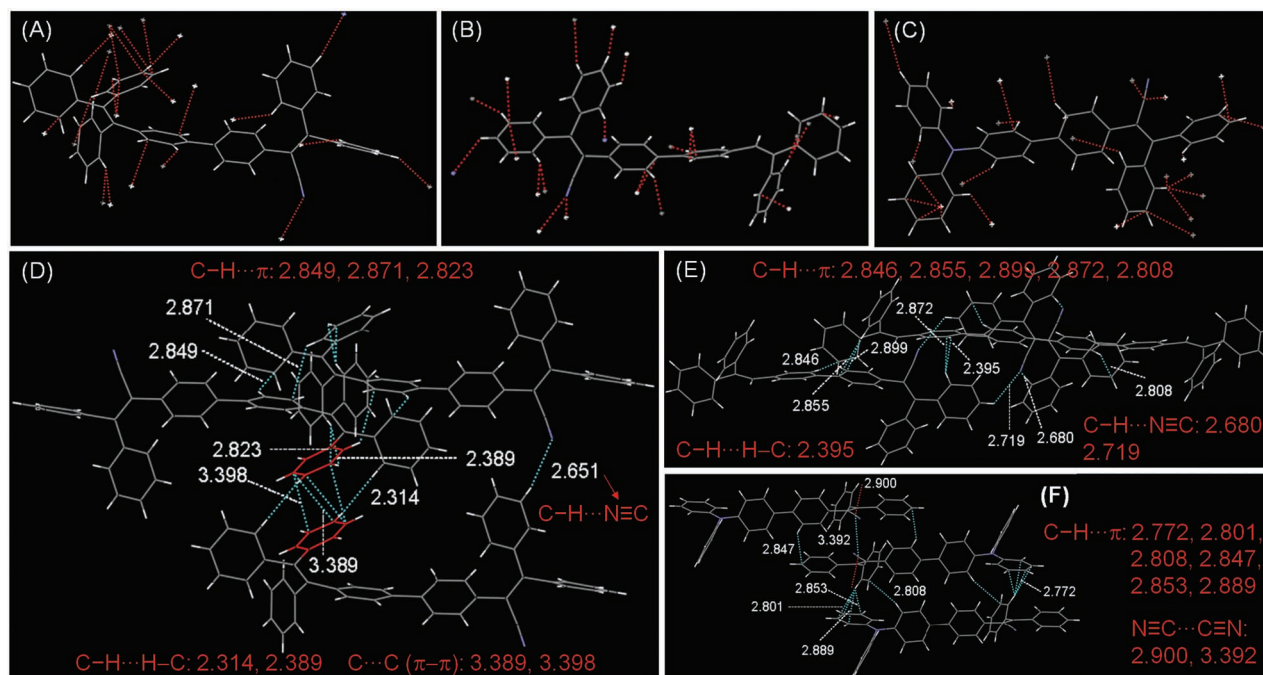


Figure 4. Crystal structure of: A) TPETPAN, B) HTPETPAN and C) TPATPAN, and multiple C-H... π , π - π , C-H...N, C-H...H-C and N≡C...C≡N intermolecular interactions in crystals of: D) TPETPAN, E) HTPETPAN and F) TPATPAN.

light at 443, 457 and 478 nm, with full width at half maxima (FWHM) of 77, 90 and 78 nm, respectively. After grinding with a pestle or shearing with a spatula, the PL spectra of TPETPAN, HTPETPAN and TPATPAN are broadened and shift to 515, 518 and 556 nm, showing remarkable FWHM and emission wavelength changes of 37, 20 and 34 nm, and 72, 61 and 78 nm, respectively. Meanwhile, as visualized by the naked eyes, the emission of ground TPETPAN and HTPETPAN is much weaker than the untreated ones. On the contrary, both as prepared and ground solids of TPATPAN exhibit bright emissions. The emission color and intensity of ground samples can be fully restored upon heating or solvent fuming, suggesting the reversibility of the mechanochromic fluorescence process.

To have a quantitative picture, the PL yields of the luminogens in solutions ($\Phi_{f,s}$) and as prepared ($\Phi_{f,aps}$) and ground ($\Phi_{f,gs}$) solid states were determined. While the $\Phi_{f,s}$ values of TPETPAN, HTPETPAN and TPATPAN are all low in THF ($\leq 1.62\%$), their $\Phi_{f,aps}$ values are much higher (52.5–99.0%), giving AIE factors ($a_{AIE} = \Phi_{f,aps}/\Phi_{f,s}$) of ∞ , 123.5 and 61.1, respectively (Figure 1). The $\Phi_{f,gs}$ values are calculated to be 42.0%, 50.0% and 75.0%, and are lower than those of the as prepared samples (Figure 1), which are in consistent with the results from the naked eye observation.

Emission behaviors of solid emitters are strongly dependent on the molecular packings.^[1,18,20] To decipher the different spectroscopic properties between the luminogens, we analyzed their structures by powder X-ray diffraction (XRD). The as prepared TPATPAN powders are crystalline in nature, as suggested by the appearance of many sharp and intense reflection peaks in their X-ray diffractogram (Figure 3H). On the contrary, a diffuse, broad halo was observed only in the ground solids,

suggesting that they are amorphous with poorly organized structure. However, upon solvent fuming, peaks coincided with those in the as prepared powders emerge, revealing the recovery of the ordered crystalline lattice. Clearly, the reversible transition between the ordered stable crystalline state and disordered metastable amorphous state is crucial to the switchable emission color and intensity of the luminogens. Similar features are also observed in TPETPAN and HTPETPAN (Supporting Information, Figure S12).

To further explore the mechanochromic mechanism, we analyzed their single crystal structures. As illustrated in Figure 4 and Supporting Information, Figure S13, all the molecules adopt a highly twisted conformation. When genuinely dissolved in solutions, their multiple phenyl blades undergo active intramolecular rotations, which have quenched their emission. However, in the aggregated state, such intramolecular rotations are impeded. Moreover, their propeller-like conformations prevent the formation of detrimental species such as excimers or exciplexes. All these collective factors make the luminogens highly emissive in the solid state. In the crystalline state, the luminogens may adopt a more twisted conformation in order to fit into the crystalline lattice. This shortens their effective conjugation length and hence makes them to emit bluer light. On the other hand, once the crystalline lattice collapses by external stimuli, the dye molecules may relax to a more planar conformation and thus emit redder PL. Besides van de Waals forces, numerous intermolecular C-H... π , C-H...H-C and C-H...N contacts, and even local π - π interactions are observed in the crystals (Figure 4 and Supporting Information, Figure S14). These multiple interactions have locked and rigidified the molecular conformation, largely reducing the energy

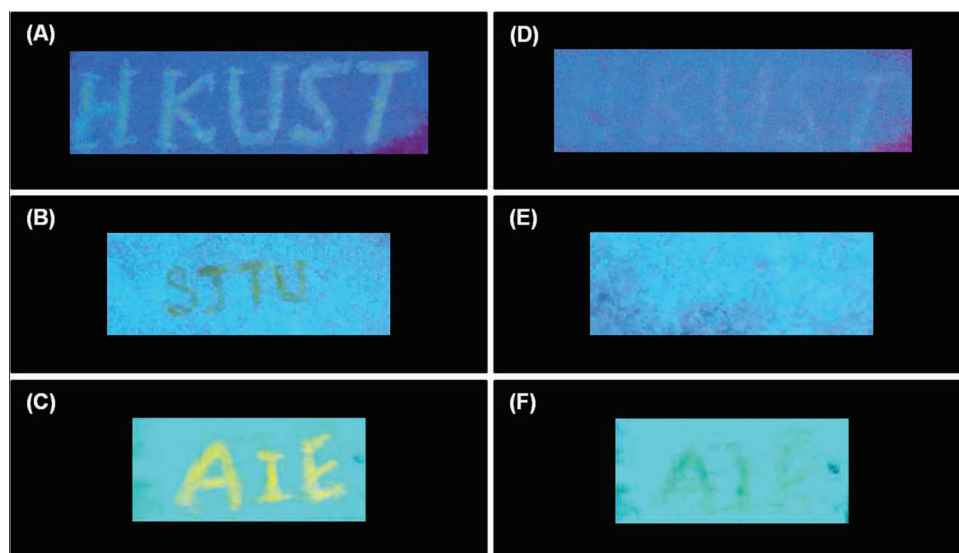


Figure 5. Fluorescent images of: A,D) TPETPAN, B,E) HTPETPAN, and C,F) TPATPAN spray-coated on filter papers with letters of (A–C) “HKUST”, “SJTU” and “AIE” written using a spatula. D–F) The letters became invisible or erased after treated the coating papers in (A–C) by vapor fuming.

loss via non-radiative relaxation channels. Upon amorphization by mechanical force, some of these interactions are lost. That explains why the crystals show stronger emission even they possess a low conjugation.

Generally, the emission color change in such mechano-chromic systems as transition-metal complexes,^[8,21] liquid-crystalline^[4c,20a] and crystalline solids,^[1] D-A conjugates,^[7] and dye-doped polymeric materials^[5] are associated with monomer-excimer transformation, dipole-dipole interaction or conformational planarization, in which crystal-crystal, crystal-amorphous, or crystal-liquid crystal mutual interconversions are involved. However, few reports are concerned with the efficiency change. Herein, significant emission wavelength change (up to 78 nm), as well as noticeable efficiency variation (up to 24%) was observed in the present luminogens caused by the conformational change and intermolecular interaction variation in the crystalline and amorphous states.

Such dynamically switchable fluorescence color and efficiency make the present luminogens promising to be used in optical storage, deformation, pressure and volatile organic compound (VOC) sensors, security papers, etc. For example, the luminogens spray-coated on filter papers emit bright blue light after solvent fuming. Letters of “HKUST”, “SJTU” and “AIE” are written on the paper using a spatula, which induces obvious

emission change. When observed under UV light, these letters emit vague or intense yellow light, which can be distinguished easily from the bright blue background (Figure 5). The contrast is even more obvious than in the grounding case. The letters can be erased upon heating or solvent fuming, demonstrating a reproducible recording-erasing process. Such intriguing properties render such materials promisingly applicable in optical recording, security inks and latent image developers.^[1] Meanwhile, when dotted their solutions on filter papers, these molecules become emissive after solvent evaporation. However, upon exposure to solvent vapors, the dots turn to dark but emit again when the vapors evaporate, thus validating their capacity as sensors for volatile organic compounds (Supporting Information, Figure S15).

Due to their AIE characteristics and relatively high solid-state efficiency, we studied the electroluminescence (EL) of the present luminogens by formation of organic light-emitting diodes (OLEDs) with a device configuration of indium tin oxide (ITO)/NPB/X/TPBi/LiF/Al, where X = TPETPAN, HTPETPAN or TPATPAN, TPBi is 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (the electron-transport layer) and NPB is 1,4-bis[(1-naphthylphenyl)amino]biphenyl (the hole-transport layer). All the devices emit yellow EL at ≈ 546 nm (Supporting Information, Figure S16, Table 1). Among the luminogens, TPETPAN

Table 1. Performances of EL devices of TPETPAN, HTPETPAN and TPATPAN.^{a)}

| Device | λ_{\max} [nm] | V_{on} [V] | L_{\max} [cd m ⁻²] | PE_{\max} [lm W ⁻¹] | CE_{\max} [cd A ⁻¹] | EQE [%] |
|--------|--------------------------|------------------------|-------------------------------------|--------------------------------------|--------------------------------------|--------------|
| I | 404, 546 | 8.9 | 37 | 0.18 | 0.46 | 0.20 |
| II | 546 | 3.9 | 1332 | 1.06 | 1.56 | 0.56 |
| III | 547 | 3.0 | 39419 | 8.47 | 9.68 | 3.47 |

^{a)}Device configuration: ITO/NPB (50 or 60 nm)/X (20 nm)/TPBi (30 or 40 nm)/LiF (1 nm)/Al (100 nm); for device I: X = TPETPAN, NPB: 60 nm, TPBi: 40 nm; for device II: X = HTPETPAN, NPB: 50 nm, TPBi: 30 nm; for device III: X = TPATPAN, NPB: 50 nm, TPBi: 30 nm. Abbreviations: λ_{\max} = EL maximum, V_{on} = turn-on voltage, L_{\max} = maximum luminance, PE_{\max} = maximum power efficiency, CE_{\max} = maximum current efficiency and EQE = maximum external quantum efficiency.

performs poorly, showing turn-on voltage (V_{on}), maximum luminance (L_{max}), power efficiency (PE_{max}), current efficiency (CE_{max}) and external quantum efficiency (EQE) of 8.9 V, 37 cd m⁻², 0.18 lm W⁻¹, 0.46 cd A⁻¹ and 0.20%, respectively. Such poor performance may be ascribed to the weak emission of the vacuum deposited film as well as inefficient charge transport. The EL device of HTPETPAN is turned on at a lower voltage (3.9 V), emitting more intensely ($L_{max} = 1332$ cd m⁻²) and efficiently ($PE_{max} = 1.06$ lm W⁻¹, $CE_{max} = 1.56$ cd A⁻¹ and $EQE = 0.56\%$). Even higher EL performance was observed in TPATPAN. It turns on at a low bias of 3.0 V with high L_{max} (39 419 cd m⁻²) and efficiencies ($PE_{max} = 8.47$ lm W⁻¹, $CE_{max} = 9.68$ cd A⁻¹ and $EQE = 3.47\%$). Considering the molecular difference, such data suggest the way to balance EL performance of TPAN-based luminogens through modulation of the electron-donating (D) or accepting (A) ability of the substituents.

In summary, a new design strategy towards efficient mechanochromic luminogens with high contrast is developed. Synergy interplay between the highly twisted conformation and effective intermolecular interaction endows the resulting compounds with AIE characteristics, high solid-state efficiency, and high contrast mechanochromism with large emission color/wavelength changes (from blue to yellow and up to 78 nm) and remarkable efficiency variations (up to 24%). The mechanism for such phenomenon is stemmed from the planarization of the twisted conformations and destruction of the multiple van der Waals forces and C–H···π, C–H···H–C and C–H···N intermolecular interactions in the crystal state upon mechanical stimulation. The transformation between the crystalline and amorphous state is reversible aided by thermal or solvent fuming process. We are now exploring the applicability of such new strategy and it works well to produce efficient mechanochromic luminogens with high contrast, particularly those with D–A structures, thus paving the way for their versatile applications in rewritable optical media, information storage and imaging, OLEDs, and other optoelectronic devices.

Experimental Section

General Information: Compound **3** was prepared according to our previous procedures.^[14] All other starting materials were purchased from Aldrich. ¹H and ¹³C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer. HRMS spectra were measured on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. The $\Phi_{F,S}$ values in THF solutions were estimated using quinine sulfate ($\Phi_F = 54.6\%$ in 0.05 M H₂SO₄) as standard, while the solid-state efficiencies were determined using an integrating sphere. Single-crystal X-ray diffraction intensity data were collected on a Bruker–Nonics Smart Apex CCD diffractometer with graphite-monochromated Mo K_α radiation. Processing was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10).

Synthesis of TPETPAN. Into a two-necked round-bottom flask (100 mL) were added of TPAN-Br (540 mg, 1.5 mmol), TPE-B(OH)₂ (**3**) (677 mg, 1.8 mmol) and Pd(dppf)Cl₂ (21.4 mg, 0.03 mmol). The flask was evacuated under vacuum and then flushed with dry nitrogen three times. THF (20 mL) and sodium carbonate solution (2 M, 3 mL) were injected into the flask and the mixture was refluxed for 2 days. After slowly cooled to room temperature, the solution was poured into water and extracted with dichloromethane. The collected organic layer was washed with water and brine twice, and then dried over anhydrous

Na₂SO₄. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography using chloroform/hexane (gradually increased from volume ratio of 1:7 to 1:5) as eluent. A white solid was obtained in 88% yield. ¹H NMR (400 MHz, CDCl₃, δ): 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.41, 7.33, 7.31, 7.30, 7.28, 7.27, 7.26, 7.25, 7.23, 7.21, 7.19, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.07, 7.06, 7.05, 7.04, 7.02; ¹³C NMR (100 MHz, CDCl₃, δ): 157.51, 143.64, 143.29, 141.28, 140.46, 140.37, 139.16, 137.58, 133.57, 131.85, 131.37, 131.30, 130.75, 130.04, 129.94, 129.87, 129.00, 128.43, 127.77, 127.69, 126.68, 126.50, 126.01, 120.08, 111.27; HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₄₇H₃₃N 611.261; found 611.255.

CCDC 911167, 911168 and 911169 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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