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A Novel Strategy to Design and Construct AlE-active Mechanofluorochromic Materials *via* Regulation of Molecular

Structure

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Abstract: In this work, we first designed and synthesized tetraphenylene-fused aryl-imidazole derivatives TM-1~4 via regulation of molecular structure, which were consisted of 1Himidazo[4,5-f][1,10]phenanthroline, 1H-phenanthro[9,10-d]imidazole, 4,5-diphenyl-1H-imidazole, 3,3'-(1H-imidazole-4,5-diyl)dipyridine moieties and AIE-active tetraphenylethene units, respectively. The results illustrated that TM-1~4 exhibited obvious AIE characteristics. Meanwhile, TM-2 and TM-3 show excellent solid emission properties (Φ_{TM-2} =13.73% and Φ_{TM-3} =36.21%), whereas TM-1 and TM-4 exhibit the opposite properties ($\Phi_{\text{TM-1}}\text{=}1.48\%$ and $\Phi_{\text{TM-4}}\text{=}4.83\%$). The multiple rotors (pyridine and benzene ring) causes twisted conformations of the molecule that prevents π - π stacking and enhances solid emission(**ΦTM-2**<**ΦTM-3**, ΦΤΜ-1<ΦΤΜ-4). Significantly, TM-2 and TM-3 also exhibited reversible mechanochromic behavior (Emission red shifts: Δλ_{TM-2}=43 nm and $\Delta\lambda_{TM-3}=41$ nm) with color changes between blue and green emissions. The powder X-ray diffraction (PXRD) suggested the disordered state of ground sample could be readily returned to an ordered crystalline. Therefore, the mechanochromisms of TM-2 and TM-3 are ascribable to the phase transformation between crystal and amorphous structure. The single crystal X-ray analysis of TM-2 reveals a twisted conformation for TPE moiety and the absence of π - π intermolecular stacking. These excellent optical properties of TM-2 and TM-3 make them potentially applications mechanochromic materials and imaging agents.

Introduction

In recent several years, organic fluorophores have sparked tremendous interest on account of their promising use in mechanofluorochromic materials,^[1] semiconductor,^[2] bioimaging and sensor,^[3] etc. Among them, mechanofluorochromic, as a functional materials with solid-state emission, is altered on applying mechanical stimuli such as grinding, crushing and pressing^[4] So far, a large number of mechanofluorochromic materials have been reported and applied in anti-counterfeiting, data storage, mechanosensors and light sources, such as borate complexes,^[5] tetraphenylethylene (**TPE**) derivatives,^[6] and so on.^[7] However, there are still lack of a clear design guideline for mechanofluorochromic materials owing to the complicated nature of mechanoresponsive process. Therefore, the search for new organic fluorophores with mechanical discoloration is still a challenge.

Unfortunately, most conventional organic fluorophores subjected to notorious aggregation-caused quenching (ACQ) effect due to extensive π - π stacking interaction in the

aggregated state, which seriously limits the effective applications of the mechanofluorochromic materials. Interestingly, Tang *et al.*^[8] and Park *et al.*^[9] first discovered two unusual phenomena Aggregation Induced/Enhanced Emission (AIE/AIEE), respectively. Therefore, the AIE/AIEE characteristics are contributed to the acquisition of new emissive solid-state fluorophores, and provides a new strategy for designing mechanofluorochromic materials.

The fluorescence emission properties of organic fluorophores, mainly depending on molecular planarity, πconjugate structure, substituted heteroatoms, and so on. Such as the position and number of the nitrogen atoms in the aromatic frameworks exert influence on fluorescence emission properties, the multiple rotors causes twisted conformations of the molecule, prevents π - π stacking and enhances solid emission. TPE, as one representative of AIE fluorophore has been widely utilized for the construction of AIE-active mechanofluorochromic materials owing to its nonplanar π -conjugated structure, and it is a beneficial core for solid-state materials.^[6,10] The structural modulation of TPE moiety by the introduction of novel chemical bonds or substitution of heterocyclic rings would lead to the acquisition of emissive solid-state materials. In this work we first designed and synthesized tetraphenylene-fused aryl-imidazole derivatives TM-1~4 via regulation of molecular structure, which were consisted of 1H-imidazo[4,5-f][1,10]phenanthroline, 1H-phenanthro[9,10-4,5-diphenyl-1H-imidazole d]imidazole, and 3.3'-(1Himidazole-4,5-diyl)dipyridine moieties and AIE-active (Scheme tetraphenylethene units, respectively 1). As we expected, The TM-1~4 still exhibited obvious AIE characteristics. Meanwhile, TM-2 and TM-3 showed



Scheme 1. The molecular structure of TM-1~4

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excellent solid emission properties, whereas **TM-1** and **TM-4** exhibited the opposite properties. Significantly, **TM-2** and **TM-3** also exhibited reversible mechanochromic behavior with color changes from blue to green. The powder X-ray diffraction (PXRD) suggested that the disordered state of ground sample can be readily returned to an ordered crystalline. The single crystal X-ray analysis of **TM-2** further confirmed a twisted conformation for moiety and the absence of π - π intermolecular stacking. In particular, the fluorophores could be applied in living cells.

Results and Discussion

The synthetic routes towards the fluorophores TM-1, TM-2, TM-3 and TM-4 are shown in Scheme 2. The TM-1, TM-2, TM-3 and TM-4 were synthesized by a classical "one-pot" reaction of the compound 1 with ammonium acetate and 1,2-diaryl ethylenedione in good yields. The TM-1, TM-2, TM-3 and TM-4 were characterized with ¹H NMR and ¹³C NMR spectroscopy, HRMS (Figures S1-S13). TM-2 were further characterized by X-ray single crystal structural analysis.



Scheme 2. Synthetic routes of TM-1~4

Firstly, the UV-vis absorption spectra of TM-1, TM-2, TM-3 and TM-4 in water/THF mixtures solvents (water fraction, fw=0-95%) were investigated, respectively. The TM-1, TM-2, and TM-3 exhibit two major absorption wavelength range of about 270 nm-315 nm and 315 nm-400 nm, in solvent mixtures with f_w≥80%, the absorption peaks decreases and slight sways (Figures S14a-c in the Supporting Information). The absorption peaks of TM-4 at 330 nm, when fw reaches 80%, and the absorption peak red shifts (Figures S14d in the Supporting Information). The absorption bands can be assigned to the π - π * transition and the charge transfer (CT) transition. Subsequently, their emission spectra were tested in water/THF mixtures (water fraction, $f_w=0.95\%$) for investigating the AIE properties. The TM-1, TM-2, TM-3 and TM-4 were nearly non-emissive in pure THF solution, but they became strong emissive in higher water contents (>70%), which reveals that they still retain AIE active because of the twisted conformation for TPE moiety (Figures 1a-h). The molecular structures of TM-1 and TM-4 contain nitrogen heterocycles (phenanthroline and pyridine ring). We further investigated the effect of acids on their fluorescence emission. As shown in Figure S15, with the addition of acid (HCI: 0 to 10 μ M) it leads to a gradual decrease of emission intensity. The results showed that the acid can quench the fluorescence of the **TM-1** and **TM-4**.



Figure 1. Fluorescence emission spectra of 5 μ M TM-1(a), TM-2(c), TM-3(e) and TM-4(g) in water/THF mixtures solvents with different f_w (0-95%). Plots of the fluorescence emission intensity with different f_w (0-95%) (TM-1 (b), TM-2 (d), TM-3 (f) and TM-4 (h). λ_{ex} =350 nm, d_{ex}=5.0 nm, d_{em}=10 nm.

Firstly, the photophysical properties and fluorescence quantum yields (ϕ_F) of TM-1, TM-2, TM-3 and TM-4 in the solid state were measured. The absorption peaks of TM-1, TM-2, TM-3 and TM-4 showed at 403, 411, 406 and 386 nm, respectively (Fig. S16 in the Supporting Information and Table 1). The corresponding fluorescence emission peaks are 583, 454, 448 and 449 nm (Figure 2a) with ϕ of 1.48%, 13.73%, 36.21% and 4.83%, respectively. It is noteworthy that TM-2 and TM-3 showed bright blue fluorescence emission, while TM-1 and TM-4 exhibted very weak fluorescence emission in solid state under UV lamp (365 nm) (Figure 2c). The fluorescence emission color and intensity showed good agreement with ϕ and emission bands. In solid states, the free rotation of the phenyl groups in TPE moiety were suppressed for TM-1 and TM-4, and thus decreased the corresponding nonradioactive decay. However, the fluorescence emission intensity of TM-1 and TM-4 was still weak (ϕ_{TM-1} =1.48%, ϕ_{TM-4} =4.83%). The phenomenons are probably attributed to the presence of phenanthroline and pyridine rings in the molecular scaffolds, which could produce other non-radiative decay process via increasing the intersystem crossing (ISC) efficiency (S1 \rightarrow T1), and leading to a decrease in the fluorescence quantum yield.^[6c,11] Meanwhile, TM-2 and TM-3

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show excellent solid emission properties (Φ_{TM-2} =13.73% and Φ_{TM-3} =36.21%). Obviously, the results further indicated that π -expanded nitrogen heterocyclic (phenanthroline and pyridine rings) of such kinds of organic fluorophores quench the solid fluorescence emission. Meanwhile, the multiple rotors (**TM-3** and **TM-4**) causes twisted conformations of the molecule that prevents π - π stacking and enhances solid emission(Φ_{TM-2} < Φ_{TM-3} , Φ_{TM-1}
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Figure 2. (a) Normalized fluorescent spectra of **TM-1**, **TM-2**, **TM-3** and **TM-4** in solid state. $\lambda_{ex,TM-1}$ =400 nm, $\lambda_{ex,TM-2-4}$ =350 nm, d_{ex} =3.0 nm, d_{em} =3 nm. (b) Excerpts of lifetime-decays spectra of **TM-1**, **TM-2**, **TM-3** and **TM-4** in solid state. (c) The picture of colors from the powders of **TM-1**, **TM-2**, **TM-3** and **TM-4** under ambient light (top) and 365 nm UV light (bottom).

Table 1 Photophysical properties of TM-1, TM-2, TM-3 and TM-4 in solid state.

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	λ_{abs} (nm)	λ_{em} (nm)	Φ	т/ns
TM-1	403	583	1.48%	4.14
TM-2	411	454	13.73%	1.30
TM-3	406	448	36.21%	1.56
TM-4	386	449	4.83 %	1.29

In view of the good solid-state fluorescence emission properties of TM-2 and TM-3, we have further studied their mechanochromic properties. After grinding, the bright blue emitting of TM-2 and TM-3 can to bright green emitting and the emission peaks are remarkable red-shifted to a range from 454 to 497 nm($\Delta\lambda$ = 43 nm) and 448 to 489 nm ($\Delta\lambda$ = 41 nm) (Figure 3a and 3c), respectively. The emission peak position and fluorescence color after soaking (EtOH) treatment are close to those before grinding. It is worthy noting that their mechanochromic effect are reversible. To explore insight into the the mechanisms of emission color changes, powder X-ray diffraction (PXRD) measurements were used to investigate the structures of molecular aggregation before and after grinding. Many diffraction sharp curves of the untreated sample, indicating that the TM-2 and TM-3 are ordered arrangement forms of crystals. However, after grinding, The diffraction peaks weakened or vanished, which indicated an amorphous structure. Furthermore, when soaked with EtOH, the sharp diffraction peaks, similar to those of the as-prepared sample, could be reappeared (Figure 3b, 3d). The results suggesting the amorphous state of ground sample can be readily recovered to crystalline. Therefore, the mechanochromism of TM-2 and TM-3 should be attributed to the phase interconversion between crystal and amorphous. The red-shift in emission spectra is ascribable to the change from the twisted crystalline to the planar amorphous state reflecting enhanced conjugation.^[12] The PXRD study reveals that the destruction of solid state molecular packing from the crystal state and amorphous state is a key factor of mechanochromism.



Figure 3. fluorescence emission spectra of TM-2 (a) and TM-3 (c), as synthesized, grinded and soaked solids, Inset) photographs TM-2 (a) and TM-3 (c), as synthesized, grinded and soaked solids under 365 nm UV light. Powder X-ray diffractograms changes of TM-2 (b) and TM-3 (d), as synthesized, grinded and soaked solids.

The slow evaporation of EtOH/ acetonitrile solvent mixtures was used to grow single crystals for TM-2 (CCDC: 2082247) at room temperature, and then analyzed by single crystal X-ray diffraction. CCDC-2082247 (TM-2) contains 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/structures. TM-2 single crystal is belonged to monoclinic crystal system and $P2_1/c$ space group. The unit cell parameters are as follows: a=19.7046(18) Å, b=10.2384(7) Å, c=17.9682(16) Å, α =90°, β =114.755(11)° and γ =90° (Table 2). As shown in Figure 4, the crystal structure of TM-2 shows twisted conformation of TPE moiety, and adopt a head-to-tail slipped stacking arrangement. The molecular stacking structure provided large amounts of cavities, making it susceptible to destruction of the lattice by external forces, and leaded to excellent mechanochromic properties.^{6e} Whereas, no π - π stackings between aromatic rings are formed. The twisted conformation promotes intramolecular rotations in solution leading to weak



Figure 4. Crystal structure and packing arrangements of TM-2.

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fluorescence. In the packing diagram of **TM-2**, the intermolecular C-H… π (2.690 Å and 2.644 Å) weak interactions lead to a loose packing motif (Figure 4). So it exhibts a high fluorescence quantum yield in solid state. Therefore, The order of $\phi_{\text{TM-2}} < \phi_{\text{TM-3}}$ and $\phi_{\text{TM-1}} < \phi_{\text{TM-4}}$ are attributed to twisted conformations of benzene and pyridine ring, hindering π - π stacking in solid state. To sum up, the π - π stacking patterns play an important role for improving solid emission.

Table 2 Crystal data and structure refinement for TM-2

Identification code	TM-2
Empirical formula	C ₄₁ H ₂₈ N ₂
Formula weight	548.65
Temperature/K	99.98(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	19.7046(18)
b/Å	10.2384(7)
c/Å	17.9682(16)
α/°	90
β/°	114.755(11)
γ/°	90
Volume/Å3	3291.9(5)
Z	4
pcalcg/cm3	1.107
μ/mm-1	0.492
F(000)	1152.0
Crystal size/mm3	0.12 × 0.11 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2O range for data collection/°	9.854 to 146.99
Index ranges	-19 ≤ h ≤ 23, -7 ≤ k ≤ 12, -22 ≤ l ≤ 21

Reflections collected	12879
Independent reflections	6435 [Rint = 0.0714, Rsigma = 0.1068]
Data/restraints/parametrs	6435/0/392
Goodness-of-fit on F2	0.974
Final R indexes [I>=2σ (I)]	R1 = 0.0666, wR2 = 0.1551
Final R indexes [all data]	R1 = 0.1131, wR2 = 0.1802
Largest diff. peak/hole / e Å-3	0.45/-0.34

To illuminate the electronic and geometry structure of such kinds of fluorophore, the theoretical calculations were performed according to the density functional theory (DFT) with the Gaussian 16 programs.^[13] The optimised geometries structures for TM-1, TM-2, TM-3 and TM-4 show twisted conformation, and effectively block π - π stacking. The lowest unoccupied molecular orbitals (LUMOs) energy level in TM-1, TM-2, TM-3 and TM-4 are mostly located on the TPE unit and imidazole, whereas the highest occupied molecular orbitals (HOMOs) energy levels of TM-1, TM-2, TM-3 and TM-4 are locate in the entire molecules. The theoretical band gap for TM-1, TM-2, TM-3 and TM-4 are 3.62 eV, 3.54 eV, 3.58 eV and 3.64 eV respectively (Figure 5). Such density changes of the electron clouds indicated that the four molecules had an ordinary intramolecular charge transfer process. The optimised geometries structure of TM-3 and TM-4 confirmed that the dihedral angles between imidazole ring and phenyl or pyridine rings were 38.68° and 44.21°, the change of fluorescence quantum yield of solid-state emission was attributed to twisted conformations of the molecule.



Figure 5. Optimised geometries and spatial distribution of the HOMO, LUMO of TM-1, TM-2, TM-3 and TM-4.

In order to explore the application of the TM-1, TM-2, TM-3 and TM-4 as fluorescent agents in celluler imaging. confocal fluorescent microscopy was used to study the application of the TM-1, TM-2, TM-3 and TM-4 for staining of the live cells. B-16 cells were incubated with 5 μ M TM-1, TM-2, TM-3 and TM-4 for 20 mins at 37 °C, respectively. The cells incubated with the fluorophores displayed significantly fluorescence signs (Figure 6b, e, h, and k). These results demonstrated that TM-1, TM-2, TM-3 and TM-4 were cell membrane permeable and capable of fluorescence imaging in living cells. These fluorophores

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have potential applications in the biomedical fields.



Figure 6. Fluorescence images of B-16 cells incubated with 5 μ M TM-1, TM-2, TM-3 and TM-4 for 20 min at 37 °C, (b, e, h, k) fluorescence imaging of TM-1, TM-2, TM-3 and TM-4; (a, d, g, i) bright-field image; (c, f, i, l) overlay of parts a and b, d and e, g and h, j and k, respectively. Scale bar=20 μ m. λ_{EX} =405 nm, λ_{em} =470±40 nm.

Considering the wide range of applications of mechanofluorochromic materials in chemical engineering and materials science, it is crucial to reveal the structureproperty relationships through chemical modification. In other words, it is crucial to understand the mechanism of fluorescence regulation. As showed in Figure 7, it is clear that the introduction of different nitrogen heterocyclic scaffolds and multiple rotors on the same TPE montys is a facile strategy to change solid-state emission the properties. Introduction of nitrogen heterocyclic scaffolds (phenanthroline and pyridine rings) could produce other non-radiative decay process via increasing the ISC efficiency (S1 \rightarrow T1),^[6c,11] and leading to a decrease in the fluorescence quantum yield $(\Phi_{TM-1}(\text{phenanthroline}) < \Phi_{TM-1})$ $_4$ (pyridine) < ϕ_{TM-2} (phenanthrene) < ϕ_{TM-3} (benzene)). DFT calculations showed that the conformation of nonplanar molecules (multiple rotors: benzene and pyridine rings) improved the fluorescence quantum efficiency because of preventing π - π stacking ($\phi_{TM-2} < \phi_{TM-3}$ and $\phi_{TM-1} < \phi_{TM-4}$). The results showed that the fluorescence properties were closely related to the molecular planarity, π-conjugate structure and substituted heteroatoms. The microchemical structure modification based on TPE core maybe provide a good strategy for the synthesis of mechanofluorochromic materials.



Figure 7. Proposed mechanism of fluorescence regulation.

Conclusion

In summary, a series of microstructural change tetraphenylene-fused imidazole derivatives (TM-1, TM-2, TM-3 and TM-4) have been first designed and synthesized by a classical "one-pot" reaction. The chemical structures of these fluorophores were fully confirmed by ¹H NMR, ¹³C NMR, and HRMS. The TM-1, TM-2, TM-3 and TM-4 manifest obvious AIE characteristics. It is noteworthy that TM-2 and TM-3 showed wonderful solid-state emission $(\Phi_{TM-2}=13.73\%$ and $\Phi_{TM-3}=36.21\%)$. The results could further indicated that π-expanded nitrogen heterocyclic (phenanthroline and pyridine rings) of such kinds of organic fluorophores quench the solid fluorescence emission (ϕ_{TM} $_1$ =1.48%, Φ_{TM-4} =4.83%). Meanwhile, the multiple rotors (TM-3 and TM-4) causes twisted conformations of the molecule, prevents π - π stacking and enhances solid emission ($\phi_{TM-2} < \phi_{TM-3}$, $\phi_{TM-1} < \phi_{TM-4}$). The optimised geometries structure of TM-3 and TM-4 confirmed that the dihedral angles between imidazole ring and phenyl or pyridine rings were 38.68° and 44.21°, the increasing fluorescence quantum yield ($\phi_{TM-2} < \phi_{TM-3}$, $\phi_{TM-1} < \phi_{TM-4}$) of solid-state emission was attributed to twisted conformations of the molecule. Significantly, TM-2 and TM-3 also exhibited reversible mechanochromic behavior (blue to green). The powder X-ray diffraction (PXRD) suggested the disordered state of ground sample can be readily returned to an ordered crystalline. Therefore, the mechanochromisms of TM-2 and TM-3 are ascribable to the phase transformation between crystal and amorphous structure. The single crystal X-ray analysis of TM-2 reveals a twisted conformation for TPE moiety and the absence of π - π intermolecular stacking. In particular, these fluorophores have been successfully applied in living cells. These excellent optical properties of TM-2 and TM-3 make them potentially applications in mechanofluorochromic materials and imaging agents. Fruther, we really hope TMs will be applied in anti-counterfeiting, data storage. mechanosensors and light sources with high functional performance.

Experimental Section

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Compound 1 was prepared according to the literature.^[14] H NMR (400 MHz, CD_2CI_2) δ 9.88 (s, 1H), 7.61-7.59(m, 2H), 7.20(d, *J*=8.2 Hz, 2H), 7.14-7.12(m, 9H), 7.05-7.01(m, 6H).

TM-1/TM-2: 4-(1,2,2-triphenylvinyl)benzaldehyde (0.15 mmol), ammonium acetate (0.75 mmol) and 1,10-phenanthroline-5,6-diketone or Phenanthrenequinone (0.18mmol) in 5 mL acetic acid were stirred and refluxed for 3.5 h. And then cooled to room temperature, the mixtures were poured into 20 mL water. The precipitate was filtered and washed with water, EtOH, respectively, dried to give **TM-1** and **TM-2**.

TM-1: Yield: 58.9%, ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.69 (s, 1H), 9.03 (d, *J*=2.9 Hz, 2H), 8.91 (d, *J*=8.1 Hz, 2H), 8.02 (d, *J*=8.2 Hz, 2H), 7.84 (dd, *J*=7.8, 4.3 Hz, 2H), 7.24-7.12 (m, 11H), 7.05 (d, *J*=7.1 Hz, 4H), 7.00 (d, *J*=6.3 Hz, 2H). ¹³C NMR (100 MHz, DMSO-d₆) δ 150.37, 147.59, 143.03, 142.95, 142.73, 141.39, 139.93, 131.31, 130.72, 130.68, 130.59, 129.96, 127.93, 127.83, 126.76, 126.66, 125.73, 123.43. HRMS: calcd for $C_{39}H_{27}N_4^+$ [M+H]⁺: calcd for 551.2230, found m/z 551.2227.

TM-2: Yield: 78.4%, ¹H NMR (400 MHz, DMSO-*d*₆) δ13.37 (s, 1H), 8.85 (dd, *J*=14.0, 8.4 Hz, 2H), 8.54 (dd, *J*=17.2, 7.8 Hz, 2H), 8.06 (d, *J*=8.2 Hz, 2H), 7.79-7.68 (m, 2H), 7.66-7.59 (m, 2H), 7.23-7.10 (m, 11H), 7.05 (d, *J*=6.6 Hz, 4H), 7.00 (d, *J*=6.3 Hz, 2H).¹³C NMR (100 MHz, DMSO-d₆) δ 148.80, 144.09, 143.09, 143.02, 142.81, 141.22, 140.03, 137.03, 131.22, 130.74, 130.68, 130.61, 128.38, 127.90, 127.82, 127.65, 127.50, 127.11, 127.03, 126.92, 126.72, 126.61, 125.59, 125.31, 125.11, 124.05, 123.69, 122.35, 121.93, 121.84. HRMS: calcd for C₄₁H₂₈N₂Na⁺ [M+Na]⁺: calcd for 571.2145. found m/z 571.2114.

TM-3: 4-(1,2,2-triphenylvinyl)benzaldehyde (0.2 mmol), NH₄OAc (1 mmol) and 1,2-diphenylethane-1,2-dione (0.3mmol) in 5 mL acetic acid were stirred and refluxed for 3.5 h. And then cooled to room temperature, the mixtures poured into 20 mL water. The precipitate was filtered and washed with water, EtOH, respectively, dried to give **TM-3**. Yield: 50.5%, ¹H NMR (400 MHz, DMSO-*d*₆) δ12.60 (s, 1H), 7.84 (d, *J*=8.2 Hz, 2H), 7.50 (dd, *J*=18.2, 7.4 Hz, 4H), 7.43 (t, *J*=7.3 Hz, 2H), 7.36 (t, *J*=8.0 Hz, 1H), 7.29 (t, *J*=7.4 Hz, 2H), 7.19-7.11 (m, 10H), 7.07-6.99(m, 8H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 145.15, 143.08, 140.17, 137.17, 135.11, 130.98, 130.70, 130.63, 128.60, 128.36, 128.22, 128.12, 127.86, 127.80, 127.72, 127.01, 126.64, 126.56, 126.48, 124.57. HRMS: calcd for C₄₁H₃₁N₂⁺ [M+H]⁺: calcd for 551.2482. found m/z 551.2474.

TM-4: 4-(1,2,2-triphenylvinyl)benzaldehyde (0.15mmol), NH4OAc (0.76 mmol) and 1,2-di(pyridin-2-yl)ethane-1,2dione (0.23mmol) in 5 mL acetic acid were refluxed for 3.5 h. And then cooled to room temperature, the mixture was added to the dilute solution of NaOH, brought pH to about 7.0, and extracted with CH₂Cl₂; then the organic phase was dried by anhydrous Na₂SO₄, filtered and evaporated in residue was subjected to vacuo. The column chromatography eluting with ethyl acetate/petroleum ether (1:4) to give TM-4. Yield: 22.2%, ¹H NMR (400 MHz, DMSO-d₆) 5 12.92 (s, 1H), 8.66 (s, 1H), 8.51 (s, 1H), 8.17 (d, J=7.7 Hz, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.86-7.75 (m, 2H), 7.31 (s, 2H), 7.19-7.10 (m, 10H), 7.05-6.98 (m, 8H). ¹³C NMR (100 MHz, DMSO-d₆) δ154.07, 148.66, 145.64, 143.45, 143.10, 142.93, 141.01, 140.14, 136.56, 136.01,

130.90, 130.71, 130.68, 130.63, 127.97, 127.87, 127.79, 126.65, 126.56, 125.16, 123.68, 122.41, 122.12. HRMS: calcd for $C_{39}H_{29}N_4^+$ [M+H]⁺: calcd for 553.2387. found m/z 553.2409.

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Conflicts of interest

There are no conflicts to declare.

Keywords: Dyes • Mechanofluorochromic materials• AIE-active • Organic fluorophores • Tetraphenylethylene

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In this work, we first designed and synthesized tetraphenylene-fused aryl-imidazole derivatives **TM-1~4** via regulation of molecular structure. The results illustrated that **TM-1~4** exhibited obvious AIE characteristics. Meanwhile, **TM-2** and **TM-3** show excellent solid emission properties (Φ_{TM-2} =13.73% and Φ_{TM-3} =36.21%), whereas **TM-1** and **TM-4** exhibit the opposite properties (Φ_{TM-1} =1.48% and Φ_{TM-4} =4.83%). The multiple rotors (pyridine and benzene ring) causes twisted conformations of the molecule that prevents π - π stacking and enhances solid emission(Φ_{TM-2} < Φ_{TM-3} , Φ_{TM-1} < Φ_{TM-4}). Significantly, **TM-2** and **TM-3** also exhibited reversible mechanochromic behavior (Emission red shifts: $\Delta\lambda_{TM-2}$ = 43 nm and $\Delta\lambda_{TM-3}$ = 41 nm) with color changes between blue and green emissions.

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