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Dyes and Pigments



Highly efficient solid-state emission of diphenylfumaronitriles with fullcolor AIE, and application in explosive sensing, data storage and WLEDs

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ABSTRACT ARTICLE INFO Keywords: Luminescent materials with aggregation-induced emission (AIE) have attracted extensive attentions for their Fumaronitrile strong emission in aggregated states. Although all kinds of AIE luminogens have been recently developed, it is AIF difficult to realize full-color AIE which is popular for the various applications in optoelectronic fields. Herein, a Emission class of diphenylfumaronitrile core-based dyes emitting in a wide region from near ultraviolet (382 nm) to near-Data storage infrared (682 nm) have been synthesized and well characterized. It is found that the emission wavelength of the WLED dyes severely depends on the peripheral substituent, including electron-withdrawing trifluoromethyl (1), methyl Explosive (2), electron-pushing methoxyl (3), and bulky aromatic amine (7-9), and that the substituting location imposes great effect on the emission intensity of multiple-substituted dyes (4-6). Compound 4 with two methyl substituting at 3,4-position gives a ultrahigh quantum yield of 93% for unique packing structure. 1–3 and 7 can be used in explosive detecting and data storage for their emission sensitive to picric acid and external stimuli, respectively. When 4 and 8 applied in white-light-emitting diodes (WLEDs), a pure white emission can be ob-

tained with 90 of CRI and (0.32, 0.32) of CIE.

1. Introduction

Organic materials with efficient luminescence in the aggregate states are very important for the practical advanced applications of biomedicine [1,2] and optoelectronic devices, such as organic laser [3], luminescent displays and illumination [4-9]. One of the main challenges in this field is the fact that the emission of conventional luminophores is often weakened or even totally quenched in the solid or aggregate states, as a result of the notorious photophysical effect of aggregation-caused quenching (ACQ) [10]. The reason causing ACQ is that most luminophores with a panel-like structure exhibit undesirable intermolecular interactions (like π - π stacking) in the aggregate states, or form excimers or exciplexes in excited states, resulting in non-radiation decay of excitons. To reduce ACQ, several strategies, such as introducing bulky substituent, adopting spiro and branched molecular structure, have been proposed [11-15]. Tang, Park, and their respective co-workers observed the aggregation-induced emission (AIE) phenomenon which overcomes fluorescence quenching in the aggregated state [16,17]. For AIE luminophores, no elaborate work needs to be done to interrupt the aggregation process. Instead, the aggregate formation can be taken advantage of, to generate efficient solid emission. To date, a large number of AIE-active dyes based on silole or arylethene structure have been developed [18-25]. Despite successful examples of solidstate emissive materials based on the AIE effect, it is still challenging to design AIE-active fluorophores with tunable solid-state emission that covers the whole visible (especially near IR) region.

Donor-acceptor-donor (D-A-D) type compounds based on fumaronitrile core (A unit) have recently attracted significant attention for their AIE or aggregation induced emission enhancement (AIEE) activity [26–30]. For example, The DPF derivatives containing aromatic amine could display strong red AIE, and be employed as nanoprobe for targeted cellular and computed tomography (CT) imaging with good photostability and low cytotoxicity [27,29]. *N*-Phenylcarbazole-based fumaronitrile dye could switch its emission color between green and orange and be used to fabricate two-color emission in organic lightemitting diodes (OLEDs) [26]. Tetraphenylethene and hexaphenylbenzene was employed as the donor unit to construct D-A-D diphenylfumaronitrile (DPF) derivatives exhibiting strong emission in aggregate state and pronounced and sensitive response on the stimuli of mechanic force and amines [28,30].

Motivated by the good performance of DPF dyes in optoelectronic fields, we chose DPF as core to design and synthesize AIE-active fluorophores (1-9) with highly efficient and tunable solid-state emission from two aspects (Fig. 1): (i) introducing the different peripheral substituted groups with push-pull electronic effect (1-3 and 7-9); (ii) changing the substituted location of groups at benzene ring of DPF

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PIGMENTS

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Fig. 1. Structure of DPF derivatives.

(4–6). All of these DPF derivatives display AIE with high quantum yields in the solid state. The maximum improved times of fluorescent quantum yield (Φ_f) in solid than solution reach 4650 for compound **6**. A systematic fine-tuning of the band gap can be realized with emissive peaks cover a very wide range from near ultraviolet (382 nm, for **1**) to near-infrared (682 nm, for **9**) regions. To the best of our knowledge, such wide-range AIE from the same fluorophore is rarely reported. Interestingly, the substituted location of methoxy has big influence on the emissive intensity. Compound **4** shows ultrahigh luminescence efficiency with 93% of quantum yield for unique packing structure. These dyes with strong AIE display huge potential in the application of explosive sensing, data storage and white LEDs (WLEDs).

2. Experimental section

2.1. General information

Electronic spray ion (ESI) mass spectra were recorded on an Agilent G6520B spectrometer. MALDI-TOF mass spectra were recorded on Bruker microflex LRF spectrometer. NMR spectra were measured in CDCl₃ on a Bruker Ascend 400 FT-NMR spectrometer; ¹H and ¹³C chemical shifts were quoted relative to the internal standard tetramethysilane. UV–vis spectra were obtained on a Shimadzu UV-2600 spectrophotometer. The emission spectra were probed on Shimadzu RF-5301PC fluorescence spectrophotometer. Differential scanning calorimetry was done on a Mettler DSC822e instrument under flowing N₂ gas at a heating rate of 10 °C min⁻¹. The fluorescence lifetime and absolute Φ_F values of solution and solid were measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6 inch integrating sphere.

All of the reagents and solvents used, were obtained from commercial suppliers and were used without further purification unless otherwise noted. Thin layer chromatography was performed on G254 silica gel plates of Qingdao Haiyang Chemical. Column chromatography was conducted on Yantai Huanghai brand silica gel (200–300 mesh).

2.2. Synthesis

2.2.1. General procedure for the synthesis of 1-6

Phenylacetonitrile derivatives (1 mmol) and iodine (0.25 g, 1 mmol) were dissolved in 5 mL of dry diethyl ether. Sodium methoxide solution newly prepared from sodium (0.05 g, 2.1 mmol) and 5 mL of methanol was added slowly (over a period of 30 min) into the reaction solution at dry ice temperature under a nitrogen atmosphere. The reaction solution was allowed to warm by replacing the dry ice bath with an ice-water

bath before the temperature rose to above 0 °C. The reaction solution was stirred for another 3–4 h at room temperature, and then the reaction was quenched with 3–6% hydrochloric acid at less than 10 °C, and filtered to isolate the solid which was rinsed with cold methanol-water solution to wash away ionic substances. The reaction mixture was extracted with ethyl acetate, washed by saturated brine and then dried over anhydrous MgSO₄. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography or recrystallization to give the pure product.

2.2.1.1. 2,3-Bis(4-(trifluoromethyl)phenyl)fumaronitrile (1). White powder; Yield 74%; mp 228.3 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.98 (d, *J* = 8.34 Hz, 4H), 7.84 (d, *J* = 8.4 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 134.70, 133.99, 133.66, 129.27, 126.50, 125.86, 115.68; HRMS (ESI) *m*/*z* [M+H]⁺ calcd 367.0670, found 367.0673.

2.2.1.2. 2,3-Di-p-tolylfumaronitrile (2). White powder; Yield 80%; mp 203.5 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.74 (d, J = 8.3 Hz, 4H), 7.33 (d, J = 8.1 Hz, 4H), 2.44 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 142.33, 129.94, 129.40, 128.64, 124.60, 117.03, 21.58; HRMS (ESI) m/z [M +Na]⁺ calcd 281.1055, found 281.1055.

2.2.1.3. 2,3-Bis(4-methoxyphenyl)fumaronitrile (3). Green powder; Yield 73%; mp 201.5 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.79 (d, J = 8.9 Hz, 4H), 7.01 (d, J = 8.9 Hz, 4H), 3.89 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.89, 130.46, 124.65, 122.73, 117.33, 114.60, 55.57; HRMS (ESI) m/z [M+Na]⁺ calcd 313.0953, found 313.0957.

2.2.1.4. 2,3-Bis(3,4-dimethoxy-5-methylphenyl)fumaronitrile (**4**). Yellow powder; Yield 45%; mp 201.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.49 (m, 2H), 7.38 (d, J = 2.2 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 3.97 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 151.81, 149.15, 124.78, 122.74, 122.71, 117.44, 111.17, 111.07, 56.18, 56.13; MALDI MASS m/z [M + H + Na]²⁺ calcd 374.1243, found 374.1260.

2.2.1.5. 2,3-Bis(3,5-dimethoxyphenyl)fumaronitrile (5). Yellow powder; Yield 63%; mp 227.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.94 (d, J = 2.2 Hz, 4H), 6.61 (t, J = 2.2 Hz, 2H), 3.86 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 161.17, 133.48, 125.66, 116.54, 106.64, 104.14, 55.70; MALDI MASS m/z [M+H]⁺ calcd 351.1345, found 351.1310.

2.2.1.6. 2,3-Bis(3,4,5-trimethoxyphenyl)fumaronitrile (6). Yellow powder; Yield 80%; mp 201.1 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.07 (s, 4H), 3.94 (d, *J* = 2.6 Hz, 18H); ¹³C NMR (CDCl₃, 100 MHz) δ 153.44, 141.07, 127.03, 124.10, 117.09, 106.23, 61.11, 56.44; MALDI MASS *m*/*z* [M+H]⁺ calcd 411.1556, found 411.1557.

2.2.2. General procedure for the synthesis of 7-9

Compound **10** (0.12 g, 0.3 mmol) and aromatic amine (0.8 mmol) were mixed with 5 mL of dry toluene in a round flask containing a stir bar. Then, Pd(OAc)₂ (14.4 mg, 0.64 mmol), P(*t*-Bu)₃ (0.2 mL, 0.8 mmol) and K₂CO₃ (0.32 g, 2.4 mmol) were also added and stirred under nitrogen at 110 °C for about 12 h. Reaction mixture was cooled to room temperature, extracted with ethyl acetate, and washed by saturated brine and then dried over anhydrous MgSO₄. After the solvent was removed under reduced pressure, the crude product was and purified by column chromatography using ethyl acetate and petroleum ether as the eluent, affording a pure dark-red solid.

2.2.2.1. 2,3-Bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)fumaronitrile

(7). Aurantius powder; Yield 52%; mp 317.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.14 (m, 4H), 7.55 (m, 8H), 7.02 (m, 8H), 6.40 (m, 4H), 1.70 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 145.12, 140.39, 131.44, 131.38, 131.14, 130.99, 126.55, 125.39, 124.62, 121.57, 116.71, 114.93, 36.23, 30.88; HRMS (ESI) *m*/*z* [M+H]⁺ calcd 645.3018, found 645.3020.



Scheme 1. Synthesis routes of DPF derivatives.

2.2.2.2. 2,3-Bis(4-(di-p-tolylamino)phenyl)fumaronitrile (8). Red powder; Yield 46%; mp 223 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.9 Hz, 4H), 7.12 (dd, J = 28.2, 8.3 Hz, 16H), 7.00 (d, J = 8.9 Hz, 4H), 2.37 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 150.72, 143.77, 134.56, 130.28, 129.75, 126.04, 123.79, 120.45, 119.24, 117.91, 20.94; MALDI MASS *m*/*z* [M+H]⁺ calcd 621.3018, found 621.3034.

2.2.2.3. 2,3-Bis(4-(bis(4-methoxyphenyl)amino)phenyl)fumaronitrile

(9). Deep red powder; Yield 46%; ¹H NMR (CDCl₃, 400 MHz) δ 7.62 (d, J = 8.9 Hz, 4H), 7.12 (d, J = 9.0 Hz, 8H), 6.88 (d, J = 8.9 Hz, 12H), 3.81 (d, J = 3.3 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 157.05, 151.10, 139.21, 129.78, 127.75, 123.14, 120.12, 118.01, 117.76, 115.03, 55.52; HRMS (ESI) m/z [M+H]⁺ calcd 685.2815, found 685.2819.

2.3. Theory calculation

Molecular Simulations were performed on Gaussian 09 program. Geometry at ground state was fully optimized by the density functional theory (DFT) method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G* basis set.

2.4. Single-crystal X-ray diffraction (SXRD) analysis

The single crystals of **6** and **7** were mounted on a glass fiber for the X-ray diffraction analysis. Data sets were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer equipped with graphite monochromatic Cu-*K* α radiation ($\lambda = 1.54184$ Å). The single crystals were kept at 100 K for **6** and 296 K for **7** during data collection. The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package. All non-hydrogen atoms were refined anisotropically displacement parameters, and all hydrogen atoms in the ideal positions attached to their parent atoms.

2.5. Preparation of aggregates

Stock THF solutions of the molecules with a concentration of 0.1 mM were prepared. An aliquot (1 mL) of this stock solution was transferred to a 10 mL volumetric flask. After adding an appropriate amount of THF, water was added quickly under vigorous stirring to furnish 10 μ M THF/water mixtures with water fractions of 0–90 vol %. Emission spectra of the resultant mixtures were measured immediately.

2.6. LED devices

The light-emitting diodes (LEDs) used for the white electroluminescence were supplied by Shenzhen Chundaxin Optoelectronic Corp. A certain proportion of sieved samples are mixed into curable adhesive (7550-1A/B). They are stirred evenly and clockwise, and put into vacuum to remove bubbles for 10 min, and then deposited on the LED chip. The forward current of the LED is 350 mA. Electroluminescence (EL) measurements of the LEDs were carried out at room temperature using an Everfine HAAS-2000. In order to collect light, the LED is placed in an integrating sphere with a diameter of 30 cm, and a spectral radiometer (wavelength accuracy < 0.3 nm) and a programmable test power LED 300 E are coupled to a high-precision array.

3. Results and discussion

3.1. Molecular design and synthesis

To tune the emission properties of solid state of DPF, a series of DPF derivatives were designed through changing substituted group (compound 1-3 and 7-9) and substituted location (compound 4-6) of benzene rings (Fig. 1). Substituted groups including electron-withdrawing trifluoromethyl (1), electron-pushing methoxyl (3), and bulky aromatic amine (7-9) are adopted to adjust the intramolecular charge transfer (ICT) effect, and consequently luminescent color of DPF derivatives. Changing substituted location is expected to regulate the emissive intensity of DPF in solid state by controlling intermolecular packing mode.

Compound 1-6 were synthesized by a simple one-step reaction from corresponding arylacetonitrile in good yield (Scheme 1). Such a dimerization reaction also gave a intermediate (compound 10) which could react with different aromatic amine through C-N bond coupling catalyzed by $Pd(OAc)_2$ to yield compound 7–9. All of the compounds were purified by recrystallization or silica gel column chromatography. Their structure was confirmed by ¹HNMR, ¹³CNMR, HRMS (ESI) and MALDI MASS. The method of solvent evaporation was adopted to culture single crystals of these dyes. Only the crystals of 6 and 7 have good quality for the characterization of single-crystal x-ray diffraction (SC-XRD). Their ellipsoid plot of molecules in the crystals is shown in Fig. S1 with fine data summarized in Table S1. Two benzene rings in both 6 and 7 are parallel and twisted with fumaronitrile core. The dihedral angle between benzene and core is 49.4° for 6, and 40.4° for 7 (Fig. S2). The large dihedral angle of 6 would weaken ICT and cause the blueshifted emission in crystal, relative to solution.

3.2. Regulation on emission wavelength

The optical properties of the synthesized diaryfumaronitrile derivatives were investigated in solids and DCM solution at room temperature. As expected, DPF derivatives 1-3 and 7-9 display distinctly different luminescent color in solids under 365 nm UV light, and a redshifted emission with the increasing electron-pushing ability of the terminal groups (Fig. 2). Their maximum emission peaks cover a very wide range from near ultraviolet to near-infrared region. For example,



Fig. 2. Photographs (a) under nature light (upper) and UV light (bottom), and emission spectra (b) of dye **1–3** and **7–9** in solid.

compounds 1 and 9 in solid exhibits 382 nm and 682 nm of emission, respectively. The compounds present a fast decay with the average lifetime (τ_{av}) ranging from 2.4 ns to 35.7 ns. It indicates that their emission is originated from the prompt fluorescence of single excited state. The representative time-resolved transient emissive decay of 1–3 and 7–9 in solids are plotted in Fig. S3a. Six compounds show relatively high Φ_f in solid, especially for compounds emitting visible light with Φ_f up to 76.8%. All of them are poorly emissive in DCM solution with Φ_f less than 2%, consequently exhibiting an obvious AIE activity. The improved times of Φ_f in solid than solution ranges from 16 to 710. Their photophysical data are summarized in Table 1.

Absorption and emission spectra of these dyes in DCM are shown in Fig. S4. Compared with compounds 1–3, 7–9 show a significant red shift in absorption and emission band. It should be attributed to the strong electron-rich properties of the bulky aromatic amines, which makes 7–9 form D- π -A- π -D structure and cause strong ICT effect

between fumaronitrile (as acceptor) and aromatic amine (as donor). It can be confirmed by simulated calculation using density functional theory (DFT) with B3LYP/6-31G (d) as basis sets. Theory calculations give their frontier orbital distribution and excited energy levels (Fig. S5). The HOMO and LUMO of **1–3** delocalize on whole molecules. However, the HOMO of **7–9** mainly distributes in the aromatic amine section, while their LUMO concentrates on fumaronitrile core. As a result, the electron transfer from HOMO to LUMO is of an ICT character, which results in the large red-shift of absorption and emission band of **7–9**, relative to **1–3**. The time-dependent DFT (TD-DFT) calculated results of the first 3 singlet excited states of compound **1–3** and **7–9** are given in Tables S2–S7. The calculated vertical absorption transition energy (S1) has much better agreement with the experimental ones with a deviation less than 0.31 eV (Table S8).

3.3. Regulation on emission intensity

Diphenylfumaronitrile derivatives **4–6** have same terminal groups (methoxyl) as compound **3**, but different substituted location and quantity. Fig. 3a shows the photograph of **4–6** in solids under UV light, as well as photoluminescence spectra. All of them present yellow-green light with emission band located at 545 nm, 560 nm and 535 nm, respectively. It indicates that the quantity and locality of the substitutes have little influences on the luminescent wavelength. However, **4–6** exhibit distinctly different emission intensity with Φ_f changing from 93% of compound **4–**6% of compound **5** (Table 1). High luminescent efficiency of **4** and **6** in solid is originated from their high k_r of 0.066, while **5** gives a very high k_{nr} of 0.357. Their lifetime in solid is in the range of 7.01–14.2 ns with the emissive decay plot shown in Fig. S3b.

Different solid-state emissive efficiency of 4-6 should be caused by their different packing structure. Single crystal structure of 6 shows that the methoxy group at 4-position of benzene ring is perpendicular to the ring (Fig. S2). The conformation can effectively inhibit molecules from forming π - π stacking. Besides, every molecule can be fixed by surrounding other six molecules through hydrogen bonding of C-H...N (2.736 Å) and C-H-O (2.504 Å and 2.347 Å), and weak interaction of C–H ... π (3.465 Å), as shown in Fig. 3b and c. Consequently, the inhibition of molecular motion results in large k_r of **6**. Unfortunately, the crystal quality of 4 and 5 is not enough good for SC-XRD analysis. However, from the optimized structure of 4-6 (Fig. S6), it is found that they have different conformation. In the case of 5, two methoxyl groups are coplanar with benzene ring, which easily makes the molecules of 5 form two kinds of π - π stacking in aggregated state: head to head, or head to tail (Fig. S7). The detrimental π - π stacking results in large k_{nr} and low Φ_f of **5**. For compound **4**, one of two methoxy groups is also perpendicular to benzene ring, like the conformation of 6 in single crystal structure, which can avoid forming π - π stacking of molecules. Additionally, two benzene rings in 4 are twisted with a 78° of dihedral,

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Experimental data of photophysical properties of dye 1-9 in DCM solution and solid state.

Dye	Solution			Solid					
	λ_{ab} nm	$\lambda_{em} \ nm$	$arPhi_{ m f}$ %	$\lambda_{em} \ nm$	$arPhi_{f}^{\mathrm{a}}$ %	$\tau_{a\nu}$ ns	k_{r} , $b ns^{-1}$	$k_{\rm nr}$, cns ⁻¹	
1	314	389	0.33	382	15 (45)	2.4	0.062	0.355	
2	348	401	0.13	431	77 (591)	17.7	0.043	0.013	
3	380	431	0.15	504	67 (445)	35.7	0.019	0.009	
4	407	516	1.75	545	93 (53)	14.2	0.066	0.005	
5	346	585	0.29	560	6 (21)	2.63	0.023	0.357	
6	390	540	0.01	535	47 (4650)	7.01	0.066	0.076	
7	456	588	1.07	600	17 (16)	10.2	0.016	0.082	
8	503	671	2.04	660	45 (22)	4.5	0.100	0.122	
9	510	677	0.01	682	7 (710)	7.6	0.009	0.122	

^a Value in the bracket is improved times of Φ_f in solid than solution.

^b Radiative rate constant $k_r = \Phi_f / \tau_{av}$.

^c Non-radiative rate constant $k_{nr} = (1-\Phi_f)/\tau_{av}$.



Fig. 3. (a) Emission spectra of dye 4-6 in solid. Inset: Photographs of dye 4-6 under UV light. (b, c) Stacking structure of dye 6 in crystal.

not like the parallel conformation in **5** and **6**. The twisted conformation of **4** makes molecules form unique head-to-tail packing structure which is different from that of **5** (Fig. S7). The unique head-to-tail packing of **4** not only prevents molecular π - π stacking, but also induces two adjacent molecules form weak interaction, such as CH ... π , which fixes molecules and suppresses their movement, consequently producing very high Φ_{f} . The twisted structure of two benzene rings reasonably exists in crystal of a PDF derivative [31]. A weak interaction of CH ... π (2.91 Å) is found in its packing structure (Fig. S7).

3.4. Nanoparticles and sensing for explosive

The AIE properties of these derivatives were assessed by another typical experiment, in which a good solvent (THF) and a poor solvent (water) are added successively to generate their nanoparticles. The nanoparticles would be strongly emissive for the restriction of intramolecular motions [32]. As expected, the aggregates of 1-3 and 7-9 in THF/water are more strongly emissive, compared with their solution (Fig. 4a-f). The compounds are fairly weakly emissive in the dilute THF and in the mixture solvents of THF-water with low water fraction. However, the intensity of emission peak increases with the content of water, reaching maximum at the water fraction of 90% (for 2, 3, 8 and 9), 80% (for 1), and 50% (for 7), respectively. The emissive intensity in nanoparticles is improved ca. 80-1000 times than that in THF. As shown in Fig. 4, the formed aggregates of these compounds emit similar light as their crystal, covering a wide range from near ultraviolet to near-infrared region. Interestingly, different water fraction causes 7 different luminescent colors, which should be attributed to the different packing mode of molecules of 7, because dihydroacridine-based derivatives are polymorphic forms in aggregated states [33-35].

Prompted by the AIE characteristic of these compounds, we utilized them to detect explosive. Picric acid (PA) was used as a model explosive, due to its commercial availability. From the emission spectra of nanoaggregates of compound 1-3 and 7-9 in the mixture solvents of THF-water (Fig. S8), it is found that there is a spectral overlap between the absorption band of PA and the emissive bands of compound 1-3. Consequently, the nanoaggregates of compound 1-3 are selected as probes and expected to recognize PA through fluorescence quenching resulting from the energy transfer from nanoaggregates to PA. As shown in Fig. 5, the emissions of the nanoaggregates are really weakened when PA was gradually added but without changing its emission peak positions, indicating that no other emissive species are formed. The emission quenching can be clearly discerned at a PA concentration as low as 1 ppm. At a PA concentration of 0.18 mM for compound 1, 0.22 mM for compound 2, and 0.26 mM for compound 3, virtually no light can be detected by the spectrofluorometer. The Stern-Volmer plot of relative emission intensity (I_0/I -1) values versus PA concentrations in nanoaggregates in the aqueous mixtures give curve bending upward instead of linear (Fig. 5 right), indicating that the fluorescence quenching becomes more efficient with increasing quencher concentration. The plots in low content of PA are linear and give quenching constants of 56082 M^{-1} for **1**, 30353 M^{-1} for **2** and 17760 M^{-1} for **3**. Compound **1** shows higher sensitivity to PA than compound 2 and 3, due to the large overlap between the absorption band of PA and the emissive band of compound 1 (Fig. S8).

3.5. Multi-stimuli-responsive emission

Materials with multi-stimuli-responsive emission have recently captured significant attention due to the potential application in information processing [14,15,23–25,36–38]. Compound 7 displays a morphology-dependent emission, as shown in Fig. 4d. It is possible to regulate the morphology, and eventually emission by external stimuli, like heat, mechanical pressure and solvent. To study the effect of heat on the emission of 7, the pristine orange solid (named as 7-O) of 7 was first analyzed by DSC. Fig. S9 shows that two endothermic peak at $62 \degree C$



Fig. 4. Emission spectra of dye 1 (a), 2 (b), 3 (c), 7 (d), 8 (e) and 9 (f) in H_2O/THF mixture (5 × 10⁻⁵ mol/L) at different content of water.

and 173 °C in the DSC plot of **7-O**. The former is corresponding to T_g , while the latter should be caused by phase transition of **7**. Consequently, **7-O** was first treated by heating at 200 °C for 5 min, and found to be turned into a yellow-light-emitting solid (**7-Y**) with 20.2% of Φ_f , as shown in Fig. 6a. Then, both of **7-O** and **7-Y** can be transferred into a red sold (**7-R**, $\Phi_f = 9.7\%$) through grinding with a glass rod. Interestingly, **7-R** can be changed back into **7-O** by fuming in acetone, and into

7-Y by heating at 200 °C. As a result, fluorescence switching of **7** between three kinds of solid-states has been realized by external stimuli. Their emission spectra are shown in Fig. 6b.

Based on the above multi-stimuli-responsive emission of compound 7, an erasable data storage process was designed by employing mechanical force and solvent as external stimuli, as shown in Fig. 6c. A glass rod is used to handwrite on the 7-Y powders supported by a piece



Fig. 5. Sensing for explosive PA by **1** (a), **2** (b) and **3** (c) in H₂O/THF mixture ($5 \times 10^{-5} \text{ mol/L}$). Emission spectra change (left) and Stern-Volmer plots of (I_0/I -1) values (right) versus PA concentration. I = peak intensity and $I_0 = \text{peak}$ intensity at [PA] = 0 mM.

of filter paper. Two letters 'FJ' are written and recognized for their different fluorescent color from background. Then the red-light-emitted letters can be erased by grinding the background with the glass pod, because the **7**-**Y** turned into **7**-**R**. In the next writing, the letters 'FJ' with yellow luminescence are written with a Chinese brush, employing CH_2Cl_2 as ink. Last, the yellow letters can be erased by fuming in CH_2Cl_2 vapor, due to **7**-**R** returned into initial **7**-**Y**. As a result, a reusable and reversible writing/erasing process is developed.

3.6. White LEDs

Solid-state illumination from WLEDs will become mainstream light sources in recent 10 years for the significant advantages, such as lower energy consumption, safer application, and higher efficiency, compared with traditional ones [9,39–42]. However, most of reported white-light materials and WLEDs exhibit color rendering index (CRI) values less than 85 for the mismatching emission at blue, green and red regions,



Fig. 6. (a) Photos of **7-O**, **7-Y** and **7-R**, and mutual conversion upon external stimuli of heating (H), grinding (G), and fuming (F). (b) Emission spectra of **7-O**, **7-Y**, **7-R**, fumed **7-R**, and heated **7-R**. (c) Photos of rewritable data recording processes.

Table 2

Electroluminescent data of WLEDs based on dye 4 and 6 with small amount of 8.

which does not satisfy the demand of solid-state lighting applications [43-47]. The yellow emission of compound 4 and 6 with high quantum yields encourage us to apply them in white LEDs driven by blue chip. The compounds were first mixed with A/B glue, and then deposited on a commercially available blue LED consisting of a packaged complete Epileds InGaN chip exhibiting an emission at about 460 nm under a 350 mA of current (Fig. S10). The loading amount of compound 4 or 6 in glue was controlled in the range of 0.3–5%. The electroluminescent data are summarized in Table S9. Compared with compound 6, 4 give higher luminous efficiency (up to 56 lm/W) at low loading amount, due to higher Φ_f of **4** than **6**. However, the CRI of WLEDs based on **4** is low and below 60 for the absence of blue or red emission. 6-based WLEDs show relatively high CRI up to 82, but unsatisfactory CIE in the range from (0.23, 0.25) to (0.23, 0.31). The correlated colour temperature (CCT) of these WLEDs can be adjusted from 5760 K to 26540 K. Their electroluminescence spectra are shown in Figs. S11 and S12.

To improve the CRI and regulate the CIE of WLEDs, A very small amount of compound 8 with red emission was added into the glue to fabricate the four WLED devices. Such small amount of **8** can improve CRI of WLEDs (Device 1–3) containing **4** from 60 to 90, which is close to true nature white light, accompanied by (0.30, 0.30) of CIE and 8049 K of CCT (Table 2). **8** also make **6**-based WLED (Device 4) realize 89 of CRI, 6358 K of CCT, and (0.32, 0.32) of CIE which is very close to the CIE of pure white light (0.33, 0.33). Electroluminescence spectra of the WLEDs based on **4**, **6** and **8** under a 350 mA of current are displayed in Fig. 7. All of electroluminescent spectra cover whole visible region from 380 nm to 750 nm, consequently producing a white emission with CIE of ca. (0.30 ± 0.02, 0.31 ± 0.02). Photos of the WLED (Device 4) based on compound **6** and **8** with and without a forward current are shown in Fig. 7d (inset).

4. Conclusions

In conclusion, we designed and synthesized successfully a series of AIE-active fluorophores (1-9) base on diphenylfumaronitrile. Their photoluminescence spectra can be tuned from near ultraviolet to nearinfrared regions, due to the different push-pull electronic effect of peripheral substituted groups. Single crystal structure and calculation results indicate the substituted location of peripheral groups can affect the packing mode of 4-7, consequently adjust their luminescent efficiency. The nanoparticles of dyes with trifluoromethyl (1), methyl (2) and methoxyl (3), formed in aqueous solution, could effectively sensing explosive PA for the fluorescence quenching resulted from energy transfer. Compound 7 with dihydroacridine shows morphology-dependent and multi-stimuli-responsive emission, which can be used in data storage technology. Compound 4 with two methyl substituting at 3,4-position displays a highly efficient solid-state emission ($\Phi_f = 93\%$) and can be employed to fabricated WLED with high CRI of 90 and pure white-light CIE of (0.30, 0.30). These results are highly valuable for the further design of smart AIE materials with highly-efficient and tunable solid-state emissions.

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Device	Dye	Loading Amount (%)	CIE	CCT (K)	CRI	Luminous flux (lm)	Luminous efficiency (lm/W)
1	4:8	0.33:0.0016	(0.29, 0.33)	7652	83	38	35
2		0.33:0.0020	(0.29, 0.31)	8106	87	40	36
3		0.3:0.0020	(0.30, 0.30)	8049	90	32	29
4	6:8	2.5:0.004	(0.32, 0.32)	6358	89	45	40



Fig. 7. Electroluminescent spectra of WLEDs device 1-4 (a-d). Inset: photos of device 4 without and with forward current.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107829.

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