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# Fluorenone Organic Crystals: Two-Color Luminescence Switching and Reversible Phase Transformations between $\pi-\pi$ Stacking-Directed Packing and Hydrogen Bond-Directed Packing

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**Supporting Information** 

**ABSTRACT:** Organic solid-state luminescence switching (SLS) materials with the ability to reversibly switch the luminescence by altering the mode of molecular packing without changing the chemical structures of their component molecules have attracted considerable interest in recent years. In this work, we design and synthesize a new class of 2,7-diphenylfluorenone derivatives (compounds 1–6) that exhibit



prominent aggregation-induced emission (AIE) properties with high solid-state fluorescence quantum yields (29–65%). Among them, 2,7-bis(4-methoxyphenyl)-9H-fluoren-9-one (2) and 2,7-bis(4-ethylphenyl)-9H-fluoren-9-one (6) display reversible stimuli-responsive solid-state luminescence switching. Compound 2 transforms between red and yellow crystals (the emission wavelength switches between 601 and 551 nm) under the stimuli of temperature, pressure, or solvent vapor. Similarly, compound 6 exhibits SLS behavior, with luminescence switching between orange (571 nm) and yellow (557 nm). Eight X-ray single-crystal structures, characterization of the photophysical properties, powder X-ray diffraction, and differential scanning calorimetry provide insight into the structure-property relationships of the solid-state fluorescence behavior. The results indicate that the variable solid-state luminescence of the fluorenone derivatives is attributed to the formation of different excimers in different solid phases. Additionally, the stimuli-responsive reversible phase transformations of compounds 2 and 6 involve a structural transition between  $\pi-\pi$  stacking-directed packing and hydrogen bond-directed packing. The results also demonstrate the feasibility of our design strategy for new solid-state luminescence switching materials: introduction of both  $\pi-\pi$  stacking and hydrogen bonding into an AIE structure to obtain a metastable solid/crystalline state luminescence system.

# INTRODUCTION

Organic solid-state luminescence switching (SLS) materials that exhibit a reversible stimuli-responsive change of luminescence color in the solid state without changing the chemical structure of their component molecules have attracted special attention in recent years.<sup>1-4</sup> Their tuning and switching to the solid-state luminescence are achieved through altering the mode of their molecular stacking upon physical perturbation, such as heating, grinding, and exposure to chemical vapor. This physical approach to switching the luminescence properties of organic solids is considered to be more promising and easier than controlling molecular structures by chemical reactions, which is frequently hampered by insufficient conversion, irreversible reactions, or the need for strictly maintained operating conditions.<sup>1</sup>

Since a stretching-induced fluorescence-switching polymer was prepared using cyano stilbene derivative-doped low-density polyethylene by Löwe and Weder in 2002,<sup>5</sup> the exploration and synthesis of new SLS materials has become an active field of research. In the past several years, a number of SLS systems based on metal complexes,<sup>6</sup> organic small molecules,<sup>7–21</sup>

dendrimers,<sup>22,23</sup> and polymers<sup>24-28</sup> have been studied. However, current studies of the SLS materials are primarily limited to several classes of compounds, such as anthrace-ne,<sup>9-11,22b,23</sup> pyrene,<sup>7,8,22a,24</sup> cyanostilbene,<sup>5,12,13,14b</sup> and difluoroboron avobenzone<sup>16</sup> derivatives. The design and synthesis of new organic systems that display reversible switching between two luminescent states in the solid state still remain important. One of the primary difficulties in exploring new SLS materials is that a theory to guide the design and preparation of SLS compounds has not yet been developed.<sup>1,7b</sup> The molecular-level understanding of the relationship between the organic molecular packing characteristics and the resulting optical properties is also insufficient. The luminescent properties of a given molecular system usually vary significantly depending on its molecular aggregation state, and it is very difficult to forecast whether a designed molecular model will possess an SLS nature and even more difficult to judge its

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spectroscopic characteristics in its aggregated state, because even a tiny alteration of the chemical structure can greatly influence the SLS behavior of an organic compound. Meanwhile, the fluorescent efficiency of organic luminescent compounds generally becomes very weak in the solid state because of the aggregation-caused quenching (ACQ) effect.

Having sufficiently high fluorescence efficiency is a fundamental issue for luminescent materials in practical applications. In 2001, Tang and co-workers first discovered the anti-ACQ phenomenon of aggregation-induced emission (AIE): a nonemissive compound in organic solution that exhibits an obviously enhanced fluorescence in its aggregated state.<sup>29</sup> In recent studies, several AIE compounds have been found to exhibit stimuli-responsive fluorescence switching behavior.<sup>6c,13,14,23</sup> Therefore, the design and preparation of new solid-state luminescence switching materials based on AIE systems may be an efficient strategy. It is well-known that for an SLS material, the existence of a metastable solid/crystalline state is a prerequisite.<sup>1,8,9</sup> Therefore, modifying and controlling the molecular arrangement in the solid state is very important for the development of SLS materials. As Araki and Wang mentioned,<sup>8,9a</sup>  $\pi - \pi$  stacking and hydrogen bonding are two important factors that determine the mode of molecular packing in the solid/crystalline state. Because of the competition between  $\pi - \pi$  stacking and hydrogen bonding, the introduction of the two factors to the same molecular system may result in a metastable solid/crystalline structure, e.g., a  $\pi - \pi$  stacking-directed structure or a hydrogen bonddirected structure. Therefore, we speculate that the introduction of the two factors ( $\pi$ - $\pi$  stacking and hydrogen bonding) into an AIE system may be an effective design strategy for new SLS materials.

Fluorenone, which has a planar aromatic configuration and an exposed oxygen atom, can satisfy our proposed design strategy of SLS molecules because planar aromatics are prone to  $\pi-\pi$  stacking and exposed oxygen atoms are potential hydrogen-bonding sites. In this study, we present a new class of stimuli-responsive luminescence switching materials in which fluorenone is used as the primary building block. Their molecular structures are shown in Scheme 1; all of the six target

Scheme 1. Molecular Structures of Compounds 1-6  $R_1 = R_2 = R_3 = H$  $R_1 = OCH_3$   $R_2 = R_3 = H$  $R_2 = OCH_3$   $R_1 = R_3 = H$  $R_3 = OCH_3$   $R_1 = R_2 = H$  $R_1 = OCH_2CH_3$   $R_2 = R_3 = H$  $R_1 = CH_2CH_3$   $R_2 = R_3 = H$ 

compounds 1-6 exhibit typical AIE properties and possess high solid-state fluorescence quantum yields (29–65%). Among them, compounds 2 (2,7-bis(4-methoxyphenyl)-9*H*fluoren-9-one) and 6 (2,7-bis(4-ethylphenyl)-9*H*-fluoren-9one) exhibit SLS behavior, and their crystals undergo clear luminescence switching accompanied by corresponding reversible phase transformations under external stimuli. Furthermore, eight single crystals of all six AIE compounds (compounds 2 and 6 have two different crystal phases, namely 2R, 2Y and 6O, 6Y) have been obtained, and their X-ray crystal structures have been determined. These results provide structural evidence that reveals the structure—property relationships of their solid-state fluorescence behavior and also yields further insight into the mechanism of luminescence switching.

### EXPERIMENTAL SECTION

Synthesis and Characterization. The six title compounds 1-6 were synthesized via a one-step Suzuki coupling reaction with 2,7-dibromo-9H-fluoren-9-one and the corresponding phenylboronic acid. Details of the synthesis, purification, and single-crystal preparation processes, along with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy data, mass spectrometry results, elemental analysis characterization, and X-ray single crystal structures, are given in the Supporting Information.

**Spectroscopic Characterization.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance spectrometer (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C) in CDCl<sub>3</sub>. Element analyses (C, H) were performed using a German Vario EL III elemental analyzer. Mass analyses were performed using an Agilent 5973N MSD Spectrometer. UV–visible absorption spectra for the solutions were recorded with a Shimadzu UV-2550 spectrometer. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301PC fluorescence spectrometer. The fluorescence quantum yield ( $\Phi$ ) in solution was determined using rhodamine B in ethanol as a reference according to a previously reported method.<sup>30</sup> Quantum yields of the solid-state powder were determined with a PTI C-701 calibrated integrating sphere system.<sup>31</sup> Steady-state fluorescence spectra and decay curves were obtained using an Edinburgh FLS920 fluorescence spectrometer equipped with a 450-W Xe lamp and a time-correlated single photon counting (TCSPC) card. Reconvolution fits of the decay profiles were performed with F900 analysis software to obtain the lifetime values.

**Powder X-ray Diffraction and Thermal Analysis.** For phase identification, powder X-ray diffraction (XRD) patterns were recorded at room temperature with a Bruker AXS X-ray powder diffractometer using Cu K $\alpha$  radiation. The data were recorded in the 2 $\theta$  mode with a step size of 0.02626°. Differential scanning calorimetry (DSC) measurements were performed to enable a better understanding of the phase transitions, and the curves were obtained with a NETZSCH thermal analyzer (DSC 204 F1) at heating and cooling rates of 10 K/ min under an N<sub>2</sub> atmosphere.

**Single-Crystal X-ray Diffraction.** Eight single crystals were obtained through slow diffusion of their respective organic solutions for several days at room temperature. (For details, see the Supporting Information). Because all the title crystals are stable under ambient conditions, the data collection was performed without any inert gas protection at room temperature on a Bruker SMART APEX-II CCD area detector using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data reduction and integration and global unit cell refinements were performed using the INTEGRATE program of the APEX2 software package. Semiempirical absorption corrections were applied using the SCALE program for the area detector. The structures were solved by direct methods and refined using the full-matrix least-squares methods on  $F^2$  using SHELX.<sup>32</sup>

#### RESULTS AND DISCUSSION

**AIE and Photophysical Properties.** Contrary to fluorene derivatives, which generally exhibit excellent luminescent properties and have been widely studied as optoelectronic materials, fluorenone compounds, which contain keto groups, are almost nonemissive in solution. It is usually thought that this class of molecules possesses a higher charge-transfer  $\pi - \pi^*$  state than the  $n - \pi^*$  state.<sup>33</sup> In this case, the radiative transition is forbidden according to Kasha's rule, and the single-molecular emission is very weak. As shown in Figure 1a and 1b, our synthesized fluorenone compounds 1-6 are no exception, and



**Figure 1.** (a) Photos of the THF solutions  $(20 \ \mu\text{M})$  and as-prepared solid powders of compounds 1–6 under natural light and (b) 365-nm UV light. (c) UV-visible absorption spectra of the THF solutions  $(20 \ \mu\text{M})$  of compounds 1–6. (d) PL spectra of the THF solutions  $(20 \ \mu\text{M})$  of compounds 1–6. (e) PL spectra of the THF/water solutions  $(20 \ \mu\text{M})$ , 80% water) of compounds 1–6. (f) normalized PL spectra of the as-prepared solid powders of compounds 1–6. (g) UV-visible absorption spectra and (h) normalized PL spectra of the concentrated THF solutions  $(60 \ \mu\text{M})$  of compounds 1–6.

they exhibit almost no fluorescence (fluorescence quantum yield  $\Phi \sim 1\%$ ; see Table 1) in dilute tetrahydrofuran (THF) solution. However, their respective as-prepared powders exhibit strong fluorescence under 365-nm UV light with  $\Phi$  ranging from 29% to 65% ( $\Phi$  in the solid state is obtained in a calibrated integrating sphere; see Figure 1a and 1b). Thus, these compounds exhibit typical AIE behavior.

A solvent-poor-solvent photoluminescence (PL) test, which is commonly used for studying the AIE phenomenon,<sup>29,34,35</sup> was performed to explore the luminescent behavior of the prepared fluorenone derivatives. Because water is a poor solvent of compounds 1-6, the molecules will aggregate in THF/water mixtures with high water contents. Thus, the luminescence from such systems is primarily attributed to molecule aggregation, not the single molecule in solution. Figure 1d and 1e shows the PL spectra of compounds 1–6 in THF (20  $\mu$ M) and THF/water (80 vol% water, 20  $\mu$ M). The six title compounds all exhibit drastic changes in the fluorescent intensity from the nonfluorescent THF solutions to the strongly fluorescent THF/water mixtures, with the fluorescence quantum yield increasing by several 10-fold (Table 1). This finding confirms that all six of the fluorenone compounds are highly AIE-active.

Meanwhile, obvious spectral changes in the position of emission peaks of the six compounds in THF (20  $\mu$ M) and THF/water (20  $\mu$ M) were observed. The PL maxima ( $\lambda_{em}$ ) of compounds **1–6** in the THF/water mixtures were red-shifted 150 nm relative to those in the pure THF solutions (20  $\mu$ M);

Table 1. Spectroscopic Data for Compounds 1-6

	solution in THF <sup>a</sup>				solution in THF/water $^{a}$ (80% water)			crystalline powder		
	$\lambda_{abs} (nm)$	$\lambda_{\rm em}~({\rm nm})$	$\Phi^b$	$\tau^{c}(ns)$	$\lambda_{ m abs} ( m nm)$	$\lambda_{\rm em}  ({\rm nm})$	Φ	$\lambda_{\rm em} \ ({\rm nm})$	$\Phi^d$	$\tau$ (ns)
1	288, 323, 337	360, 375	0.011	-	286, 341, 471	534	0.48	534	0.61	18.0
$2R^{e}$	290, 340	368, 385	0.012	1.0	294, 334, 476	548	0.43	601	0.32	4.47
2Y								551	0.57	14.5
3	286, 324, 336	363, 378	0.013	_	285, 334, 479	560	0.31	573	0.29	4.22
4	279, 322, 335	364, 378	0.015	_	283, 327, 470	528	0.52	529	0.65	15.4
5	291, 341	373, 388	0.012	_	288, 338, 480	552	0.40	561	0.40	9.12
60 <sup>f</sup>	292, 325, 339	362, 379	0.015	1.0	270, 340, 458	545	0.41	571	0.39	7.17
6Y								557	0.52	14.8

<sup>*a*</sup>With  $c = 2.0 \times 10^{-5}$  mol/L. <sup>*b*</sup>Fluorescence quantum yield was determined using rhodamine B in ethanol as a standard. <sup>*c*</sup>Fluorescence lifetime. <sup>*d*</sup>Fluorescence quantum yield in the solid state was obtained using a calibrated integrating sphere. <sup>30</sup> <sup>*c*</sup>The red crystal and yellow crystal of compound 2 are named **2R** and **2Y**, respectively. <sup>*f*</sup>The orange crystal and yellow crystal of compound 6 are named **6O** and **6Y**, respectively.



Figure 2. (a) Photos of both the red crystal 2R and yellow crystal 2Y of compound 2 under natural light (NL) and 365-nm UV light (UV). (b) Photos of the crystalline phase transformation of 2Y from yellow to red to yellow; i: heating at 115 °C for approximately 1 min, and ii: heating to melt and then cooling quickly. (c) UV-visible absorption spectra of 2R and 2Y crystalline powders. (d) Normalized PL spectra of 2R and 2Y crystalline powders, quenched 2R (after melting 2R and then quenching), and heated 2Y (heating 2Y at 115 °C for 1 min) crystalline powders.

this effect was accompanied by the disappearance of the vibronic structure in the spectra (Figure 1e). Furthermore, drops of the dilute solutions of these compounds ( $<30 \ \mu$ M) on a thin-layer chromatography plate did not luminesce, even after solvent evaporation, because the spot can be regarded as a dilute solid-state solution. These phenomena are similar to those reported in Tao's study.<sup>34</sup> However, the spectral change is different from the spectral characteristics of the majority of

previously reported AIE dyes, whose enhanced luminescence is caused by restricted intramolecular rotation of peripheral aromatic rings or the effects of intramolecular planarization in their aggregated states.<sup>29,35</sup> In those AIE systems, the luminescence, whether from their organic solutions or aggregated states, originates from the single molecule, and their peak positions of PL maxima are not significantly different in the two different states. Here, the shapes of the greatly red-

shifted, unstructured luminescence spectra of the six fluorenone compounds in THF/water and the compounds' long fluorescence lifetime in the solid state (see Table 1) are typical features of excimer emission. In fact, the excimers of the six title compounds not only exist in aggregated states but also form quite easily in concentrated organic solutions. Figure 1g shows the absorption spectra of the THF solutions of compounds 1-6 with concentration of 60  $\mu$ M. In comparison with Figure 1c, the emergence of a new, wide absorption band that peaks at approximately 450 nm in Figure 1g indicates the formation of the excimers. These kinds of excimers formed from such prearranged ground-state aggregates or dimers are generally termed "static excimers".<sup>36</sup> In their corresponding normalized PL spectra in  $60-\mu$ M THF solutions (Figure 1h), two primary emission bands peaked at approximately 380 and 540 nm are observed. On the basis of the above results, we can deduce that the peak at approximately 380 nm with a vibronic structure originates from single-molecule emission and that the peak at approximately 540 nm originates from excimer emission. Notably, the six title compounds display similar absorption (Figure 1c) and emission (Figure 1d) properties in dilute THF solutions (20  $\mu$ M), suggesting that their ground- and excitedstate electronic structures are similar. However, their absorption (Figure S1b in the Supporting Information) and emission (Figure 1f) spectra in the solid state, especially the emission peaks ranging from 534 nm (green) to 601 nm (red), are significantly different, which may imply that there are differences in their respective excimers.

Luminescence Switching Properties of Compound 2. The SLS properties of the six title fluorenone derivatives were investigated. Two of them (compounds 2 and 6) exhibit intriguing solid-state two-color luminescence switching by thermal, mechanical, or organic solvent vapor stimuli.

As shown in Figure 2a, the two crystals of compound 2, which were obtained from THF and dichloromethane, exhibit entirely different color and luminescent properties. Upon crystallization from THF, compound 2 packed to form red rhombic crystals (2R) that exhibit red emission at 601 nm, which is the same as that of the as-prepared crystalline powder precipitated directly from the reaction solution. In contrast, upon crystallization from dry dichloromethane, yellow rectangle crystals (2Y) were obtained, and they exhibit yellow emission at 551 nm. Interestingly, when heating the yellow crystal 2Y to 115 °C using a microscopic melting-point apparatus with a heating rate of  $\sim 2$  K/min under ambient condition (or directly heating the yellow crystal 2Y at 115 °C for approximately 1 min), we observed the color change of crystal 2Y from yellow to red, with an emission peak at 601 nm (Figure 2b, 2c, and 2d). Thus, thermal treatment changed not only its emission spectrum but also its absorption spectrum. This result implies that external stimuli cause the static excimer to change from one form in the yellow crystal to another in the red crystal. Upon heating the red crystal to its melted state at approximately 220 °C and then quickly cooling (quenching) it, a yellow solid sample (crystalline powder), which exhibited almost the same color and luminescence (552 nm) as the original yellow crystal 2Y (551 nm), was formed (Figure 2b, 2c, and 2d).

To gain more insight into the SLS properties of compound 2, we studied the phase characteristics of the related samples using powder XRD analysis. As shown in Figure 3a, the powder pattern of the heated 2Y (after thermal treatment at 115 °C for 1 min) is different from that of the yellow crystal 2Y but is



Figure 3. (a) Powder XRD profiles of crystals 2R and 2Y, quenched 2R, and heated 2Y. (b) DSC profiles of the red crystal 2R and yellow crystal 2Y.

almost identical to that of the red crystal 2R with decreased peak intensities. Likewise, the powder XRD of quenched 2R(which was obtained by melting 2R and then quenching) exhibited weak but clear reflection peaks that were in good agreement with the peaks observed in 2Y, which suggested the same molecular arrangement in quenched 2R as in the crystal 2Y. Differential scanning calorimetry (DSC) measurements were also performed for 2R and 2Y (Figure 3b) to understand the phase transformation. The two different crystals have almost the same melting points ( $217.4 \degree C$  for 2R and  $218.0 \degree C$ for 2Y), whereas the yellow crystal 2Y displays an exothermic peak at approximately  $109 \degree C$ , which indicates that yellow crystal 2Y could undergo a phase transformation to the thermodynamically more-stable red crystal. This result is identical to that of the heating experiment with 2Y.

Apart from thermally induced reversible phase transformation, mechanical and organic solvent vapor stimuli can also produce similar results. For example, grinding the **2Y** yellow crystalline powder yielded a red powder that exhibited luminescence the same as that of **2R**, and exposure of the red crystalline powder **2R** to dichloromethane fumes yielded a yellow powder (Figure S4 in the Supporting Information). All of the original crystals and treated crystals were very stable over the course of the experiments at room temperature in air, which suggests that these compounds have potential for application as an optical recording material.

To explore the reversible phase transformation and luminescence mechanism in depth, significant efforts were exerted to obtain single crystals of the title compounds. Eight single crystals, including two each from compounds 2 (2R and 2Y) and 6 (6O and 6Y), were obtained. Their X-ray single-crystal structures were determined, and selected crystallo-graphic data are given in Table 2.

Table 2. Selected Crystallographic Data for Compounds 1-6

	1	2R	2V	3	4	5	60	6V
	-	21	21	5	-	5	00	01
formula	$C_{25}H_{16}O$	$C_{27}H_{20}O_3$	$C_{27}H_{20}O_3$	$C_{27}H_{20}O_3$	$C_{27}H_{20}O_3$	$C_{29}H_{24}O_3$	$C_{29}H_{24}O$	$C_{29}H_{24}O$
fw [g·mol <sup>−1</sup> ]	332.38	392.43	392.43	392.43	392.43	420.48	388.48	388.48
crystal color	pale yellow	red	yellow	reddish-orange	yellow	reddish-orange	orange	yellow
crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$Cmc2_1$	$P2_1/c$	$Cmc2_1$	Pbcn	C222 <sub>1</sub>	Pnma	$P2_1/n$	$P2_1/c$
a [Å]	34.844(3)	11.0929(11)	41.590(3)	21.194(2)	10.0490(8)	11.5953(17)	13.7657(12)	20.7401(18)
b [Å]	6.8460(5)	8.7240(6)	6.9057(4)	11.4105(11)	14.9454(14)	7.1473(18)	9.4828(8)	5.8060(4)
c [Å]	7.2121(6)	21.0781(18)	7.0345(5)	8.0612(6)	13.6607(11)	26.346(3)	16.2158(15)	18.9202(15)
$\beta$ [deg]	90.00	104.607(2)	90.00	90.00	90.00	90.00	94.677(1)	111.537(2)
V [Å <sup>3</sup> ]	1720.4(2)	1973.9(3)	2020.3(2)	1949.4(3)	2051.7(3)	2183.4(7)	2109.7(3)	2119.2(3)
Ζ	4	4	4	4	4	4	4	4
$ ho_{ m calcd} \ [g/ m cm^3]$	1.283	1.321	1.290	1.337	1.270	1.279	1.223	1.218
$\mu \; [\mathrm{mm}^{-1}]$	0.077	0.085	0.083	0.086	0.082	0.082	0.072	0.072
T [K]	298(2)	298(2)	298(2)	298(2)	298(2)	293(2)	298(2)	298(2)
$\substack{\theta_{\min}-\theta_{\max}\\[\deg]}$	3.03-25.01	2.38-25.02	2.94-25.01	3.24-25.01	2.73-25.02	2.91-25.02	2.61-25.01	2.88-25.02
$\begin{bmatrix} R/wR\\ [I > 2\sigma_{(1)}] \end{bmatrix}$	0.0346/0.0781	0.0450/0.0969	0.0489/0.0959	0.0436/0.0850	0.0335/0.0759	0.1405/0.3184	0.0588/0.1549	0.0894/0.2094



**Figure 4.** X-ray crystallographic packing of red crystal **2R** (a–c) and yellow crystal **2Y** (d–f). (a) Side view of red crystal **2R** packing. (b) Top view and illustration of the  $\pi$ - $\pi$  stacking in **2R**. (c) Side view and illustration of the hydrogen bonding in **2R**. (d) Side view of red crystal **2Y** packing. (e) Side view of **2Y** yellow crystal packing: the gray molecules are parallel to each other, and the orange molecules are also parallel to each other. However, the gray and the orange molecules are not parallel, and the dihedral angle between the two fluorenone units is 24.2°. (f) Top view of **2Y** yellow crystal packing and illustration of the hydrogen bonding and C–H… $\pi$  interactions.

The different molecular packings of red crystal **2R** and yellow crystal **2Y** are shown in Figure 4. For red crystal **2R**, the obvious characteristic molecular pairs can be observed in the packing diagram.  $\pi - \pi$  stacking interactions with a contact distance of 3.47 Å join every two up-down adjacent molecules (Figure 4a and 4b). Intermolecular  $\pi - \pi$  interactions play a major role in the molecular packing, and we can conclude that the crystal of **2R** is a  $\pi - \pi$  stacking-directed structure. Weak C–

H…O hydrogen bonds also exist in the **2R** crystal (Figure 4c), and they hold the molecule pairs together to result in the formation of a 3D structure. However, for yellow crystal **2Y**, the gray molecules at the top are not parallel to the orange molecules at the bottom, and there are no  $\pi-\pi$  interactions in the crystal (Figure 4d and 4e). The molecules are linked by hydrogen bonds with bond lengths of 2.50 Å and arranged into 2D sheets (Figure 4f), which are further stacked into 3D

structures based on weak C-H··· $\pi$  interactions (Figure S5 in the Supporting Information). Therefore, we can regard the hydrogen bonds as the guiding force in the crystal packing of 2Y. In addition, the emission maxima of compound 2 in its THF/water (80% water) solution (20  $\mu$ M) and concentrated THF solution (60  $\mu$ M) (Figure 1e and 1h) are located at 547 and 550 nm, respectively, which are similar to the maxima of vellow crystal 2Y (551 nm). This similarity indicates that the structures of their aggregated states in concentrated THF and THF/water solutions are the same as the hydrogen bonddirected structure of yellow crystal 2Y, and this type of structure is kinetically controlled. Thus, we can understand the phase transformation from yellow crystal 2Y to red crystal 2R as being a structural transition from the kinetically stable hydrogen bond-directed packing to the thermodynamically stable  $\pi - \pi$  stacking-directed packing.

Notably, the crystal packing of compound 1 (Figure S8 in the Supporting Information) is very similar to that of yellow crystal **2Y**. However, there is no phase transformation or luminescence switching observed in the crystal of 1, which is different from **2Y**. In the crystal structure of red crystal **2R**, the hydrogen atom of the methoxy group forms a weak hydrogen bond with the closest oxygen atom of the carbonyl group (C=O) (Figure 4c), which aids in the stabilization of the crystal structure. However, there is no formation of such a hydrogen bond in crystal 1. This is the reason why compound 1 does not form such a packing.

Regarding the different luminescence mechanisms of 2R and 2Y, at the single molecule level, the most obvious difference between 2R and 2Y lies in the torsional configuration, i.e., the dihedral angles between the fluorenone core and the 2,7-linked phenyl rings are different (Figure S6 in the Supporting Information). For 2Y, the dihedral angles between the fluorenone and the 2,7-linked phenyl rings are both 32.2°. For 2R, the two dihedral angles are not identical: one is 17.3°, and the other is 32.2°. Theoretical calculations based on the single molecule suggest that both the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of 2R and 2Y are very similar (Figure S13 in the Supporting Information), which indicates that the small differences in their molecular structure does not cause significant changes in their absorption and emission spectra. This result further illustrates that their luminescence does not come from the single molecule species but rather the excimers.

In the 2R crystal structure,  $\pi - \pi$  stacked molecular pairs (dimers) form the excimers (Figure 4b). The two molecules overlap with the electronegative five-membered ring (which involves the carbonyl group of the five-membered ring) that faces the electropositive benzene ring (Figure 4b), which facilitates the two molecules forming an excimer in the ground state, i.e., static excimer. When the excimers are excited, they do not undergo any energy-consuming configurational rearrangement. Consequently, the red crystal 2R has a shorter fluorescence lifetime ( $\tau = 4.47$  ns, Figure 5) and a higher fluorescence quantum yield ( $\Phi = 0.32$ ) at the emission maximum of 601 nm than a typical  $\pi - \pi$  aggregate. For the yellow crystal 2Y, its single-crystal structure reveals that the excimers are formed by two adjacent and parallel 2Y molecules through hydrogen bonds (Figure 4f). As shown in Figure S13 in the Supporting Information, upon one molecule being excited, the electrons of the LUMO are confined mostly in the fluorenone core, and greater electron density is present on the



**Figure 5.** Fluorescence lifetime profiles of (a) the red crystal **2R**, yellow crystal **2Y**, and **2** in THF ( $20 \mu$ M) and (b) the orange crystal **6O**, yellow crystal **6Y**, and **6** in THF ( $20 \mu$ M).

oxygen atom of the carboxyl group. At this time, the oxygen atom with high electronegativity is inclined to bind the electropositive hydrogen atoms of an adjacent ground-state molecule (the forbidden relaxation of the singlet excited state allows sufficient time for the binding to occur). Opportunely, the prearranged ground-state aggregate in such crystal packing is very convenient for excimer formation. Because of the long charge-transfer distance and the high stability of the photo-excited state, the **2Y** crystal exhibits a long fluorescence lifetime ( $\tau = 14.5$  ns, Figure 5) at the yellow fluorescence peak of 551 nm.

Luminescence Switching Properties of Compound 6. We observed the SLS behavior of compound 6 during its preparation and purification. After the reaction, the solution of compound 6 was naturally cooled from the reaction temperature (80 °C), and a yellow floccule precipitated from the reaction system. When filtered and rinsed with dichloromethane, the yellow floccule immediately turned into reddishorange crystals. Subsequently, the orange block single crystal (60) and the yellow lamellar single crystal (6Y) were obtained by slow diffusion of their dichloromethane and THF solutions, respectively, for several days at room temperature. Under 365nm UV light, they exhibited charming orange (571 nm) and yellow (557 nm) emissions (Figure 6a and 6d), respectively. Similar to compound 2, compound 6 can accomplish a reversible phase transformation accompanied by two-color emission switching. As shown in Figure 6b, upon heating at approximately 90 °C for 1 min, the orange crystal quickly changed its color to bright yellow, with an emission peak at 559 nm (Figure 6c and 6d). When the heated crystal was then exposed to dichloromethane vapor for 1 min at room



**Figure 6.** (a) Photos of the orange crystal **60** and yellow crystal **6Y** of compound **6** under natural light (NL) and 365-nm UV light (UV). (b) Photos of the crystalline phase transformation of **60** from orange to yellow to orange; i: heating at 90 °C for approximately 1 min, and ii: exposure to  $CH_2Cl_2$  vapor for approximately 1 min. (c) UV-visible absorption spectra of **60** and **6Y** crystalline powders. (d) Normalized PL spectra of **60** at 90 °C for ~1 min), and heated **60** (produced by heating **60** at 90 °C for ~1 min) crystalline powders.

temperature, it returned to an orange crystal with a 573-nm luminescence (Figure 6d). The reversible phase transformation was also verified by powder XRD analysis and DSC measurements (Figure S12 in the Supporting Information). The XRD reflection peaks of the heated **60** sample, which was obtained by heating **60** at 90 °C for approximately 1 min, matched well with those of the yellow crystal powder **6Y**, and those of the  $CH_2Cl_2$ -fumed **6Y** sample matched well with those of the orange crystal **60**.

Figure 7 shows the crystal packing structures of both the orange crystal **60** and yellow crystal **6Y**. In **60** (Figure 7a), there are molecular pairs bound by  $\pi-\pi$  stacking interactions in which the adjacent molecular planes overlap by about 40% (Figure 7b); the distance between them is approximately 3.61 Å. It is this  $\pi-\pi$  stacking-bound excimer (dimer) that generates the orange emission of the crystal upon excitation. Meanwhile, weak hydrogen bonds and  $C-H\cdots\pi$  interactions also play a role in the stability of the crystal structure (Figure 7c). Surprisingly, there seems to be a "Z-shaped channel" in this crystal structure (Figure 7a). We tried to find some small solvent molecules (e.g.,  $CH_2Cl_2$ ) in the "channel" to check whether solvent molecules that were involved in the crystal packing affected the transformation of the two different crystal phases. However, the result was counterintuitive. In the case of **6Y**, the aromatic

frameworks of the two adjacent molecules barely overlapped (Figure 7d and 7e); thus, the  $\pi$ - $\pi$  stacking interactions in the structure are very weak. Hydrogen bonding, as the leading intermolecular force in this packing, stabilizes the crystal structure. The dimer, which is held together in a side-by-side arrangement by hydrogen bonds (Figure 7f), can be easily found in the packing.

On the basis of the packing structures of 6O and 6Y, we can speculate about the process of molecular rearrangement during the phase transformation. Upon heating the orange crystal 60 at approximately 90 °C, the molecule facing the "Z-shaped channel" is provided with enough energy to overcome the C-H... $\pi$  interactions and move toward the empty space along the direction of the yellow arrows (Figure 7a) until a distance at which the molecule combines with another by hydrogen bonding to form a dimer (Figure 7f). Simultaneously, the single-molecule configuration changes from a twisted to a coplanar conformation because of the hydrogen bonding (Figure S7 in the Supporting Information). The dimer bound by  $\pi - \pi$  stacking interactions also struggles to separate to form a new hydrogen-bonded dimer. Thus, the phase transformation from a  $\pi - \pi$  stacking-directed structure (60) to a hydrogen bond-directed structure (6Y) is accomplished.



**Figure 7.** X-ray crystallographic packing of **60** (a, b, c) and **6Y** (d, e, f) crystals. (a) Side view of **60** orange crystal packing. (b) Top view and illustration of  $\pi$ - $\pi$  stacking in **60**. (c) Side view and illustration of the hydrogen bonding and C-H··· $\pi$  interactions in **60**. (d) Side view of **6Y** yellow crystal packing. (e) Top view and illustration of the  $\pi$ - $\pi$  stacking in **6Y**. (f) Side view and illustration of the hydrogen bonding in **60**.



Figure 8. Procedures of writing and erasing the luminescent images of (a) compound 2 and (b) compound 6. Scale bar: 1 cm.

We think that compounds 1, 3, 4, and 5 do not exhibit SLS properties because they form strong and very stable crystal packing structures (see Figures S8–S11 in the Supporting Information), which are immune to external stimuli. To verify our hypothesis, the concentration-dependent absorption spectra of the THF/hexane (v:v = 1:1) solutions of compounds 1–6 were measured, which can monitor the formation of dimer aggregates and acquire the dimerization constants  $K_D$ . As shown in Figures S14 and S15 in the Supporting Information, upon increasing concentration, the new, wide absorption bands between 400 and 500 nm appeared and arose, which indicates the formation of dimer aggregates (static excimers). Though the single-molecule (monomer) absorption at 285 nm also arose, the increase became more and more slow with increasing concentration, which indicates the consumption of monomers.

Then the dimerization constants  $K_D$  values were calculated by fitting of the UV/vis spectral data according to the isodesmic model with nonlinear least-squares regression analysis (see Supporting Information for details).<sup>37</sup> Compounds 1, 3, 4, and 5 exhibit  $K_D$  values higher than those of compounds 2 and 6. The results show that the dimer aggregates of compounds 1, 3, 4, and 5 are stronger than those of compounds 2 and 6, which may testify to the stable crystal packing structures of compounds 1, 3, 4, and 5.

**Demonstration of Writing and Erasing.** As a demonstration of potential applications in optical recording and security ink materials, stimuli-responsive writing and erasing examples for compounds 2 and 6 are shown in Figure 8. The red film (Figure 8a) was prepared by coating an ethanol suspension of 2R red crystalline powder on a silicon wafer.

When exposed to dichloromethane vapors using an "OK" sign stamp for about 2 min, the luminescence of the fumed region of the film changed from red to yellow. Thus, a yellow "OK" sign was stamped on the red "paper". The red "nails" of the "OK" sign were obtained by subsequent pressing of their corresponding positions. Upon heating the whole "paper" at 120 °C for 1 min, the yellow "OK" sign could be erased easily. A similar process can be performed to draw and erase an orange "benzene ring" on yellow "paper" using the yellow crystalline powder of **6O**, as shown in Figure 8b. The results suggest that the materials have potential for application as optical recording materials.

## CONCLUSIONS

In this study, we discovered a new class of AIE solid-state luminescence switching materials in which 2,7-diphenylfluorenone was used as the molecular skeleton. The prepared AIE materials exhibit pronounced stimuli-responsive two-color solid-state luminescence switching properties. On the basis of the photophysical, X-ray single-crystal structural powder XRD and DSC, we explored the mechanism of their solid-state luminescence and found that their different emissions are due to the formation of different excimers. Furthermore, their reversible phase transformations, which involve a transition between a  $\pi - \pi$  stacking-directed structure and a hydrogen bond-directed structure, were discussed in detail. Both their SLS and AIE features make these compounds promising candidates for optical recording, temperature or organic vapor sensing, and light-emitting systems. Furthermore, in this work, we proposed an effective design strategy for the preparation of new SLS materials: introduction of both  $\pi - \pi$  stacking and hydrogen bonding into an AIE structure. This strategy is very likely to produce a metastable solid/crystal, which will lead to a phase transformation accompanied by solid-state luminescence switching under external stimuli.

### ASSOCIATED CONTENT

## **S** Supporting Information

Eight X-ray crystallographic files of compounds 1-6 in CIF format; synthesis, characterization, relevant spectral and crystal structural graphs of compounds 1-6; powder XRD and DSC profiles of compound 2; solid-state luminescence switching properties of compound 2 under mechanical and solvent vapor stimuli; theoretical calculations and results and determination of the dimerization constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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