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AIEgen based polymorphs with solvent regulated crystal-to-crystal switch properties†

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Organic polymorphic materials have attracted considerable interest in recent years owing to their unique photophysical properties and application potential in fluorescent sensors and information storage. However, the preparation of organic polymorphs with crystal-to-crystal switch properties remains challenging, which hampers understanding the relationship between molecular stacking and emission properties. Herein, an AIEgen with tunable polymorphism-dependent emission and solvent regulated crystal-to-crystal switch properties is reported. Two polymorphs, an orange crystal (OC) and a red crystal (RC), of the AIEgen with different emission were obtained by slow evaporation in cultivation solvents (dichloromethane (DCM)/*n*-hexane) with different compositions. The polymorphs can be reversibly switched when exposed to different solvent vapors. Further investigation of the single crystal structures suggests that the molecular stacking mode of the crystal plays an important role in the emission properties. The real-time *in situ* monitoring of the polymorphs with fluorescence spectra and micrographs when exposed to solvent vapor reveals that the capture/release of DCM molecules induces molecular re-arrangements, and thus causes the switch. Such a conclusion is further supported by thermal recovery experiments. Our study on the crystal-to-crystal switch properties of AIEgen based polymorphs has provided insight into the relationship between molecular stacking and emission properties.

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1. Introduction

Organic luminescent materials are highly attractive materials due to their excellent photophysical properties and practical application potential in fluorescent (FL) sensors,¹ information anti-counterfeiting and microlasers.² The traditional organic fluorophores easily form strong intermolecular π - π stacking interactions, and thus are quenched in the aggregation state.³ However, Tang and co-workers discovered compounds with aggregation-induced emission (AIE) properties caused by the restriction of intramolecular motion.⁴ The discovery overcomes the aggregation-caused quenching problem of the traditional materials,⁵ and has promoted the development of organic luminescent solid-state materials.⁶ However, the relationship

between the molecular stacking and the emission properties of solid-state materials still lacks sufficient study.

Crystalline materials show ordered molecular stacking with specific molecular conformations and intermolecular interactions.⁷ The polymorphs of a crystal in different solid-state forms can exhibit completely different emission properties.⁸ Therefore, they have been used as ideal models to study the relationships between molecular stacking and emission properties.⁹ Tang *et al.* prepared two polymorphs of chalcone derivatives with obvious stacking-dependent emission properties.¹⁰ Yang *et al.* reported polymorphs with tunable emission colors upon external stimuli including grinding, heating, and solvent vapor.¹¹ However, these polymorphs collapse easily under the external stimuli and thus fail the crystal-to-crystal switch test, which makes the study of the structure-property relationships challenging.

Herein, we designed and synthesized a compound, DCzFO, with intramolecular charge transfer (ICT) and AIE properties. Two polymorphs of DCzFO, an orange crystal (OC) and a red crystal (RC), with completely different emission were obtained by slow evaporation in solvents with different compositions and their single crystal structures were characterized to explore the relationship between their molecular stacking and emission properties. The results suggest that RC is compactly stacked due to the more planar molecular conformations and stronger intermolecular interactions, and thus exhibits 74 nm

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red-shifted emission as compared with that of **OC**. The real-time *in situ* monitoring of the polymorph exposed to solvent vapor with micrographs and FL spectra suggests that **OC** and **RC** can be reversibly switched when exposed to different solvent vapors. Further investigation suggests that the molecular re-arrangement during the crystal-to-crystal switch is caused by the capture/release of dichloromethane (DCM) molecules. Our work would help to understand the relationship between the molecular stacking and the emission properties of polymorphs.

2. Results and discussion

2.1. Design and synthesis of DCzFO

Scheme 1 shows the synthesis route to **DCzFO**. The compound was prepared by a one-step reaction between 2,7-dibromo-9-fluorenone and 9H-carbazole. It is designed as a donor-acceptor molecule, where a fluorenone unit functions as the electron-acceptor. The carbazole group with strong electron-donating capability serves as the electron donor.¹² ICT occurs from the carbazole groups to the fluorenone moiety. The good molecule planarities of the fluorenone and carbazole units are conducive to the assembly of well-ordered structures. The chemical structure of the compound is confirmed by ¹H NMR, ¹³C NMR, ESI-TOF and X-ray single-crystal structural analysis. The detailed synthesis procedure and characterization can be found in the ESI† (Fig. S1–S3).

2.2. ICT and AIE properties of DCzFO

The photophysical properties of **DCzFO** were investigated in different polarity solvents. As shown in Fig. 1a, **DCzFO** exhibits two absorption bands centered at 340 nm and 460 nm, which are respectively due to the π - π^* transition and the ICT from the electron-donating carbazole units to the electron-accepting fluorenone unit.¹³ Altering the solvent polarity shows no significant effect on the absorption spectra of **DCzFO** (Fig. 1a) but affects its FL emission remarkably (Fig. 1b). With the increase of the solvent polarity, the FL emission peak of **DCzFO** gradually red-shifts from 543 nm to 602 nm.¹⁰ The electronic structure of **DCzFO** was then determined by density functional theory calculations to better understand its ICT feature (Fig. 1c). As expected, the highest occupied molecular orbital is located over the whole molecule and the lowest unoccupied molecular orbital is mainly found on the fluorenone unit, indicating the ICT feature of **DCzFO**.^{8a,13}

The AIE properties of **DCzFO** were then investigated. DMSO is a good solvent of the compound and water is a poor solvent. It is not emissive in the good solvent. Therefore, the emission behaviors of **DCzFO** aggregates were investigated in DMSO/H₂O solutions with different water fractions (f_w). The FL emission

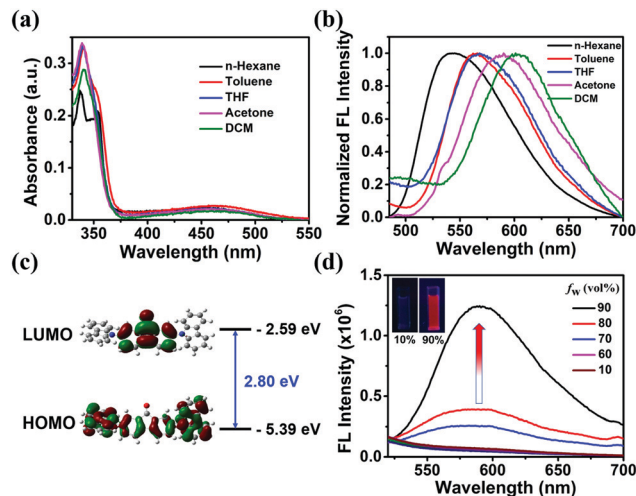
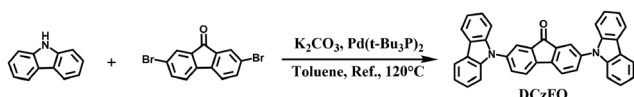


Fig. 1 (a) UV-vis and (b) normalized fluorescence (FL) spectra (λ_{ex} = 365 nm) of **DCzFO** (10 μ M) in different solvents. (c) Optimized geometry and calculated HOMO and LUMO levels for **DCzFO**. (d) FL spectra (λ_{ex} = 365 nm) of **DCzFO** (10 μ M) in DMSO/H₂O mixtures with different water fractions (f_w). Inset: FL images of **DCzFO** (10 μ M) in DMSO/H₂O mixtures with f_w = 0% and 90% under irradiation with 365 nm UV light.

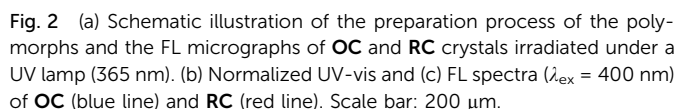
intensity changed slightly as f_w varied in the range 10–60% and increased dramatically as f_w increased to 70%. **DCzFO** exhibits 26-fold stronger FL emission intensity in the DMSO/H₂O mixture with an f_w of 90% than in pure DMSO, showing typical AIE characteristics (Fig. 1d). The AIE properties of **DCzFO** can result in strong solid-state FL emission.¹⁴

2.3. Solid-state emission and crystal structure of DCzFO

The as-prepared **DCzFO** shows a yellow emission peak at 575 nm (Fig. S4, ESI†). The rigid planar structure of the fluorenone and carbazole units endows **DCzFO** with outstanding crystallization capacity. A rod-like orange crystal (**OC**) of **DCzFO** was obtained by slow evaporation under ambient conditions in a DCM/*n*-hexane mixture with $v:v = 1:3$. Increasing the volume ratio of DCM in the DCM/*n*-hexane mixture to $v:v = 1:1$ results in a needle-like red crystal (**RC**). The main peaks of the ¹H NMR spectra of **OC** are similar to those of **RC**, indicating the polymorphism property of **DCzFO** (Fig. S5, ESI†). However, the polymorphs exhibit different morphologies and FL colors (Fig. 2a, insets). As shown in Table 1 and Fig. 2c, **OC** exhibits orange FL emission peaking at 581 nm with a quantum yield of ~19.3%. **RC** displays red FL emission peaking at 655 nm ($\Phi_F = 4.3\%$). The FL color was determined by the Commission Internationale de l'Éclairage 1931 coordinates (Fig. S6a, ESI†). Compared with that of **OC**, the absorption band of **RC** is broader and red-shifted. In addition, the nonradiative rate of **RC** is 6-fold higher than that of **OC**. Therefore, it is speculated that more energy from the excitation of **RC** is lost during the nonradiative process, resulting in the weaker FL intensity and lower quantum yield.¹⁰ Such vastly different solid-state emission properties of **OC** and **RC** may be ascribed to their different stacking modes.^{11,14c} To confirm the hypothesis, the stacking modes of **OC** and **RC** were investigated by powder X-ray diffraction (PXRD).



Scheme 1 Synthetic route to and the structure of **DCzFO**.



Crystal	λ_{FL} (nm)	τ_{FL} (ns)	Φ_{F} (%)	k_{r} (10^7 s^{-1})	k_{nr} (10^7 s^{-1})
OC	581	8.6	19.3	2.2	9.1
RC	655	1.7	4.3	2.5	55.0

To further understand the solid-state emission behaviors, the crystal structures of the two polymorphs were determined by X-ray single-crystal structure analysis. The results are summarized in Table S3 (ESI[†]). **OC** is a crystal system of monoclinic space group $P2_1/c$ with unit cell parameters of $a = 19.8760(19)$ Å, $b = 7.9623(9)$ Å and $c = 17.0139(19)$ Å. Its unit cell contains four **DCzFO** molecules (Fig. S8a, ESI[†]). The twisted conformation of each molecule with the large dihedral angle between the fluorenone moiety and carbazole rings results in a nearly vertical position relative to the carbazole units on the two end sides (Fig. 3a and c). Therefore, the **DCzFO** molecules are conjugated in a head-to-tail staggered molecular stacking mode along the a -axis direction in **OC** (Fig. S9, ESI[†]). Weak π - π interactions (4.036–4.111 Å) and low overlap degrees of the fluorenone conjugate planes are also observed in **OC**, which is attributed to the twisted molecular conformation of **DCzFO** and large steric hindrance (Fig. S9c, ESI[†]). Each molecule connects to its adjacent molecules by next-nearest-neighbor intermolecular H-bonds (C–H...O) with a length of 2.528 Å, nonclassical intermolecular H-bonds (C–H...N) with a length of 3.443 Å and weak C–H... π interactions with lengths of 2.929 Å and 3.571 Å. No obvious π - π interaction is observed (Fig. S9b, ESI[†]). The C–H...O hydrogen bond (2.528 Å) between the O atom of the

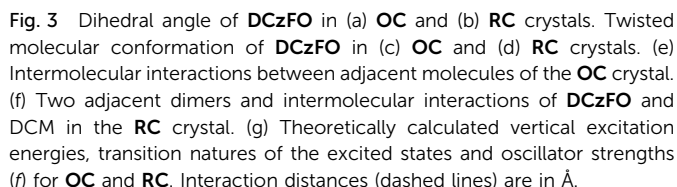


Fig. 3 Dihedral angle of **DCzFO** in (a) **OC** and (b) **RC** crystals. Twisted molecular conformation of **DCzFO** in (c) **OC** and (d) **RC** crystals. (e) Intermolecular interactions between adjacent molecules of the **OC** crystal. (f) Two adjacent dimers and intermolecular interactions of **DCzFO** and DCM in the **RC** crystal. (g) Theoretically calculated vertical excitation energies, transition natures of the excited states and oscillator strengths (f) for **OC** and **RC**. Interaction distances (dashed lines) are in Å.

RC is formed in a different molecular stacking mode from the head-to-tail staggered molecular stacking mode for **OC**. It is also a monoclinic crystal system, but belongs to the space group *C2/c* with unit cell parameters of $a = 35.988(2)$ Å, $b = 10.9785(6)$ Å, and $c = 13.4888(10)$ Å. There are eight **DCzFO** molecules in the unit cell, which are parallel to each other in a slightly staggered orientation. Therefore, the molecular conformation of **DCzFO** in **RC** is more planar than that in **OC** (Fig. 3b and d). It is worth noting that four DCM molecules are detected in the crystal lattice of **RC** (Fig. S8b, ESI[†]), suggesting that it plays a key role in the molecular stacking of **RC**. Strong intermolecular interactions including C–H $\cdots$ O (2.290 Å) hydrogen bonds and C–H $\cdots$ Cl (2.822 Å) halogen bonds are found between **DCzFO** and DCM molecules, which restrict the molecular conformation of **DCzFO**. The two carbazoles on both ends are almost horizontal. The planar molecular conformation increases the molecular overlap and electronic transition, which causes larger electronic excited-state delocalization as compared with that of **OC**. The crystal density of **RC** is measured to be 1.385 mg mm^{−3}, higher than that of **OC** (Table S3, ESI[†]).

The molecules in **RC** completely overlap with each other along the long molecular axis, and thus form a tightly stacked structure *via* strong π - π interactions (3.446 Å). Along the crystallographic *c*-axis, a typical step-like stacking structure is observed (Fig. 3f). The DCM molecule serves as a linker to connect two adjacent molecules tightly *via* C-H...Cl (2.822 Å) and C-H...O (2.290 Å) hydrogen bonds, which results in “dimers”. The “dimers” are antiparallel to each other with a small slip angle of 24.54° along the *b*-axis. The distance between the adjacent “dimers” is only ~3.566 Å (Fig. S10b, ESI†). Such a short distance is indicative of strong π - π stacking. Therefore, the “dimers” are packed to form an infinite 3-dimensional staggered space network (Fig. S10c, ESI†). The orderly stacked structure of the single crystal in the preferred orientation immensely increases the degree of conjugation.¹⁰

To further discover the emission properties of **OC** and **RC**, theoretical calculations were performed through the hybrid quantum mechanics and molecular mechanics (QM/MM) approach (Fig. S11, ESI†). The calculations indicate that the molecular conformation has a significant influence on the excited state properties of **DCzFO**, as shown in Fig. 3g. The **OC** conformer has a higher S_1 energy level (3.08 eV) than **RC** (2.89 eV), resulting in a red-shift in the FL spectra. In addition, the change of the molecular conformation affects the oscillator strength (f) of the S_1 - S_0 transition. With the dihedral angle of the two carbazole groups decreasing, the f value reduces from 0.1125 to 0.0628, suggesting a lower Φ_F value and stronger emission for the **RC** crystal.¹⁵

Based on these results, the relationship between the emission properties of **DCzFO** and its stacking mode can be concluded as follows (Fig. S12, ESI†). **DCzFO** can exhibit emission in a wide range from $\lambda_{em} = 575$ nm (original powder) to $\lambda_{em} = 655$ nm (**RC**). Each emission state corresponds to a distinct molecular stacking mode. The original **DCzFO** powder is in the monomeric state with negligible intermolecular interactions and thus exhibits no molecular stacking. Therefore, the emission properties of **DCzFO** in the solid state are influenced by the molecular stacking mode, which can be regulated by the molecular conformation and intermolecular interactions.¹⁶ The more planar molecular conformation and stronger intermolecular interactions result in the more compact stacking structure of **RC** with dramatically red-shifted emission and weaker FL intensity.

2.4. Solvent vapor regulated crystal-to-crystal switch

The emission properties of solid-state materials can be altered with external stimuli, such as solvent vapor, heating, and grinding.¹⁷ When **OC** is exposed to DCM vapor, the emission peak of the sample (**OC-fumed**) red-shifts to 654 nm, accompanied by an obvious FL color change from orange to red. **OC-fumed** exhibits a similar FL spectrum to that of **RC** ($\lambda_{em} = 655$ nm), and, *vice versa*, the **RC** sample fumed with *n*-hexane vapor (**RC-fumed**, $\lambda_{em} = 579$ nm) exhibits a similar FL emission peak to that of **OC** ($\lambda_{em} = 581$ nm) (Fig. 4a and b). The transitions can be repeated for at least three cycles without variation in intensity (Fig. 4c). In addition, both **OC-fumed** and **RC-fumed** exhibit strong diffraction peaks, showing that the fumed samples maintain the integrity of the corresponding crystal structure (Fig. 4d). The diffraction

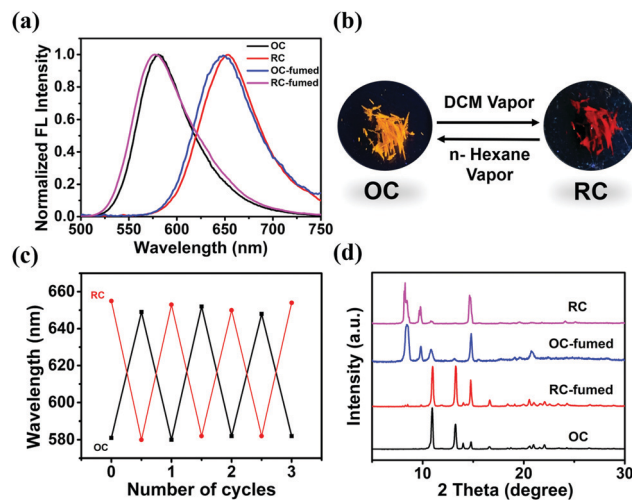


Fig. 4 (a) Normalized FL spectra ($\lambda_{ex} = 400$ nm) of the original **OC** and **RC** and the corresponding fumed samples, **OC-fumed** and **RC-fumed**, under excitation at 365 nm. (b) FL images of the crystals before and after vapor fuming. (c) Cyclic FL emission of the crystal-to-crystal switch. (d) Powder diffraction pattern of the original and fumed crystals.

pattern of **OC-fumed** is in good agreement with that of **RC**, and the diffraction pattern of **RC-fumed** matches that of **OC** well, indicating that the solvent vapor can directly induce a crystal-to-crystal switch between **OC** and **RC**.

To better understand the crystal-to-crystal switch, the process was monitored *in situ* under a microscope upon the FL emission change during the vapor fuming. An **OC** sample fixed on a quartz plate was put in a Petri dish containing DCM vapor (Fig. 5a). The color and the FL emission spectra of the sample were recorded every 5 min. It is found that the color of the crystal began to change from both end sides when fumed for 5 min. The main body of the crystal gradually exhibits a red FL color as the fuming time is prolonged from 5 min to 50 min. The entire crystal shows similar red emission to **RC** in 60 min (Fig. 5a). The spectra recorded during the fuming clearly reveal an intermediate state during the crystal-to-crystal switch in the DCM vapor, accompanied by changes of the emission wavelength and intensity (Fig. 5b). The emission switch of **RC** to **OC** is observed upon exposure to *n*-hexane vapor in 3 h (Fig. 5c). The detailed results of the variations in the FL spectra and FL intensity with the fuming time can be found in Fig. S13 (ESI†). These real-time observations further indicate that the solvent vapor can induce a crystal-to-crystal switch between **OC** and **RC**.

As demonstrated above, **DCzFO** molecules are loosely stacked in the **OC** crystal. In contrast, **RC** is more compactly stacked, and DCM molecules are found in its crystal lattices. Therefore, the release/inclusion of DCM molecules may play a key role in the switch between **OC** and **RC**. When **OC** is exposed to DCM vapor, the DCM molecules can enter its loose lattices and interact with **DCzFO** molecules. The robust intermolecular interactions between **DCzFO** and DCM inhibit the structure conformation, leading to the crystal-to-crystal switch from **OC** to **RC**. The hypothesis is confirmed by ^1H NMR analyses of the samples before and after vapor treatment (Fig. S14, ESI†).

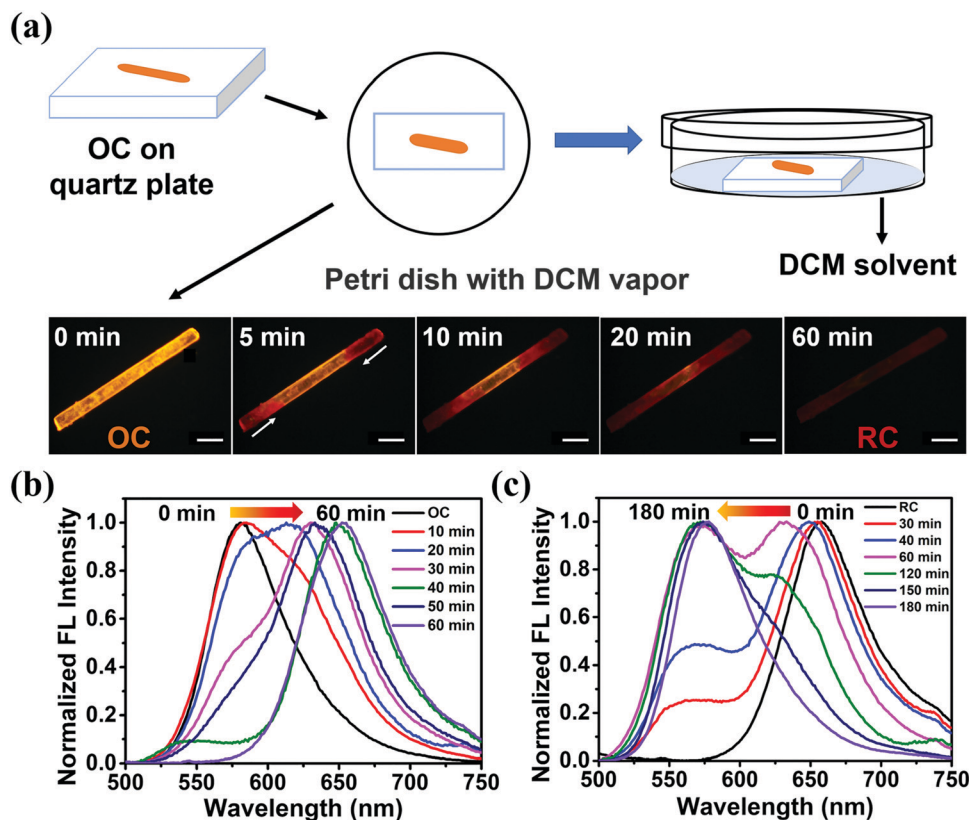


Fig. 5 (a) Schematic vapor fuming process of **OC** in a Petri dish with DCM vapor and micrographs showing the crystal-to-crystal switching process upon vapor fuming under UV irradiation (365 nm). (b) Normalized FL spectra ($\lambda_{\text{ex}} = 400$ nm) of **OC** at 10 minute intervals from 0 to 60 min. (c) Normalized FL spectra ($\lambda_{\text{ex}} = 400$ nm) of **RC** at 10 minute fuming time intervals from 0 to 180 min. Scale bar: 200 μm .

The **OC** sample fumed with DCM vapor exhibits ^1H NMR peaks of the DCM solvent, implying that DCM molecules enter **OC** lattices to form a co-crystal. The different DCM peak intensity of **OC-fumed** and **RC** is ascribed to the capacity of trapping DCM of the single crystal incubation and the fuming process. In contrast, the DCM peaks of the **RC-fumed** sample are very weak or even disappear. Therefore, the crystal-to-crystal switch from **RC** to **OC** is ascribed to the removal of the DCM molecules in **RC**.

In addition to solvent vapor, heating can induce the switch from **RC** to **OC**. The heated **RC** sample (**RC-h**) exhibits a similar FL emission spectrum to that of **OC**, accompanied by increased FL intensity (Fig. S15, ESI †). ^1H NMR analyses also suggest the absence of DCM in **RC-h** (Fig. S16, ESI †). The removal of DCM enhances the movement of molecules, which induces the re-arrangement of molecules back to the stacking structure of **OC**. Based on these observations, it can be concluded that removing the solvent molecules from the crystalline lattice causes molecular re-arrangement, and eventually leads to the crystal-to-crystal switch from **RC** to **OC** upon solvent vapor fuming and heating (Fig. S17, ESI †).

2.5. Distinct mechanochromic luminescence properties of **OC** and **RC**

The emission properties of a crystal can be tuned by adjusting its stacking modes through external force stimuli. The emission

peak of **OC** red-shifts from 581 nm to 597 nm with reduced FL intensity as it is ground with a pestle (**OC-G**). In contrast, the ground sample of **RC** (**RC-G**) exhibits blue-shifted emission from 655 nm to 630 nm with stronger FL intensity (Fig. 6). The detailed photophysical properties of the ground samples can be found in Table S2 and Fig. S18 (ESI †). Similar to the bulk crystals, the ground samples also exhibit reversible emission switch behaviors when exposed to solvent vapor (Fig. S19, ESI †). These results suggest that the modulation of molecular stacking involves changes of molecular conformations and intermolecular interactions.

The distinctive mechanochromic luminescence (ML) properties of **OC** and **RC** are due to their different molecular conformations and intermolecular interactions. **OC** is loosely stacked with twisted conformations *via* only weak C–N $\cdots\pi$ interactions. The weak intermolecular interactions and loose crystalline lattice are easily destroyed when subjected to external forces, which explains its red-shifted ML.¹⁸ **RC** is more tightly stacked *via* multiple intermolecular interactions. However, the intermolecular interactions between DCM and **DCzFO** can be destroyed by external force, which breaks the “dimers” and strong molecule conjugation, and thus causes blue-shifted ML emission.^{8a} In addition, the destruction of the close crystalline lattices also removes DCM to some extent, which explains the reversible emission behaviors of the **OC-G** and **RC-G** samples.

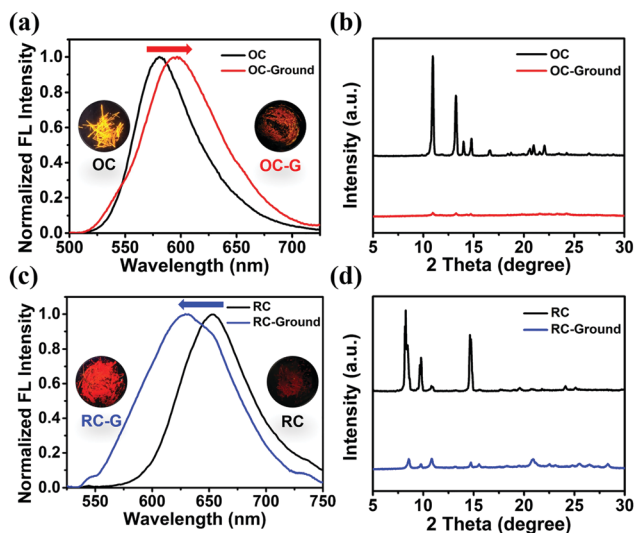


Fig. 6 (a) Normalized FL spectra ($\lambda_{\text{ex}} = 400$ nm) and (b) PXRD patterns of OC before and after being ground. (c) Normalized FL spectra ($\lambda_{\text{ex}} = 400$ nm) and (d) PXRD patterns of RC before and after being ground.

The multiple stimuli-responsive behaviors of the polymorphs are summarized in Fig. 7a. Inspired by its solvent induced crystal-to-crystal switch properties, the application potential of DCzFO is demonstrated in data encryption under UV light irradiation. The compound 3,4,9,10-perylenetetracarboxylic dianhydride (PDA) exhibits similar FL properties (Fig. S20, ESI[†]). As shown in Fig. 7b, a digit pattern “888” with a weak red FL color is achieved with RC and PDA powder under UV light irradiation. The color of the RC in the pattern changes from red to orange accompanied by enhanced luminescence intensity when fumed with *n*-hexane vapor. In contrast, the color of the PDA powder in the pattern shows no obvious change when fumed with *n*-hexane vapor. As a result, orange digits “567” appear under UV light irradiation. The pattern “567” is successfully restored to the original pattern “888” upon fuming with DCM vapor. Therefore, DCzFO has great application potential as a candidate material for data encryption and security.

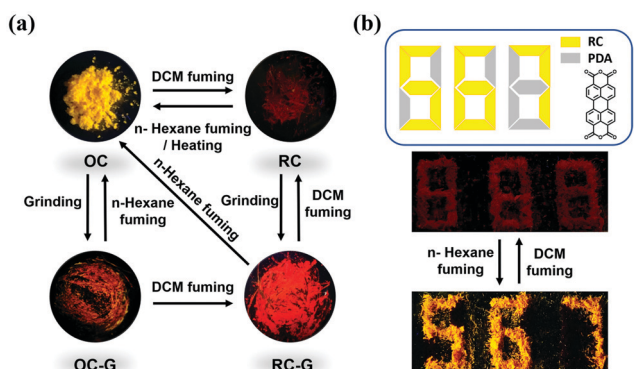


Fig. 7 (a) FL images of the crystal-to-crystal switching processes in response to multiple stimuli. (b) Application of the RC responsive behavior to solvent vapor in FL encryption: a pattern “888” is drawn with RC (yellow) and 3,4,9,10-perylenetetracarboxylic dianhydride (PDA) (gray). The red pattern is reversibly switched to orange pattern “567” upon vapor fuming.

3. Conclusions

In summary, we have reported a polymorphic AIEgen material with a solvent regulated crystal-to-crystal switch feature. Two polymorphs, OC and RC, with different emission properties are obtained by slow evaporation in DCM/*n*-hexane mixtures with different volume ratios. DCM molecules are found in RC. The relationship between molecular stacking and the emission properties is explored. A crystal-to-crystal switch is observed between OC and RC when exposed to *n*-hexane vapor and DCM vapor, respectively. RC is formed in a more compact stacking mode due to the more planar molecular conformation and stronger intermolecular interactions, and thus exhibits remarkably red-shifted emission and weaker FL emission. The real-time monitoring of the *in situ* fuming process with micrographs and the FL emission suggests that the molecular re-arrangements caused by capture/release of DCM molecules are responsible for the crystal-to-crystal switch. Multiple stimuli-responsive behaviors of the polymorphs are demonstrated, especially their distinct ML properties. A solvent vapor regulated simple pattern for data encryption and security is achieved with RC under UV light irradiation. Our work has provided a strategy to further understand the relationship of molecular stacking and emission properties for crystal-to-crystal switching.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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