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Polymorphism-dependent and piezochromic luminescence based on molecular packing of a conjugated molecule

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Different luminescent single crystals of 2-(anthracen-9-yl)-4,5-diphenyl-1*H*-imidazole (**ADPI**) were obtained through construction of different stacking modes with the aid of intermolecular interactions. Both the fluorescence and stacking mode of the crystals can be reversibly tuned by mechanical and thermal forces to make **ADPI** a piezochromic molecule, which represents a unique example of reversibly controlled solid emission. The regulation of π-π stacking between the anthracene planes by mechanical and thermal forces, is suggested as the main driving force for the piezochromic character of **ADPI**.

Introduction

The emergence of optoelectronic technology has initiated great demand for the development of highly efficient fluorescent materials, especially for solid-emissive organic molecules. Conventional organic chromophores developed thus far usually have planar π-conjugated structures and donot emit in solid state due to well-known concentration-induced fluorescence quenching. However, many strategies have been found to be effective in keeping the fluorescence in solid state, such as introducing bulky steric groups,[1] the design of molecules with aggregate-induced emission, [2] and the construction of intermolecular non-covalent interactions to promote non-parallel packing. Among all of these strategies, the construction of intermolecular non-covalent interactions, such as hydrogen bonds, π-π stacking and Van Der Waals force, is especially popular. First, this method is effective at providing solid-emissive materials with high fluorescent quantum yield; second, the intermolecular non-covalent interactions could be easily manipulated by external stimuli to provide environment-sensitive materials, which are of great interest for fundamental research and practical applications, such as sensors, fluorescent switches and optical devices; [3] and third, the change of stacking mode in solid state is a physical change, which is more easily reversible than the chemical reactions and normally does not produce any by-products during the switching process.

It is well known that the luminescence of a molecular system in condensed phase is dependent on the packing modes of the molecules, and significant variation has been found according to the molecular aggregation state of the stacking mode (polymorphism). Mechanical force, as the most reliable and fundamental power source, is also recognised to be able to

change the mode of molecular packing and then induce luminescence changes, known as piezochromism. Although piezochromic materials have been used in various applications in sensors, memory chips, and security inks,[4-7] and a large number of piezochromic materials based on switching of stacking modes have been developed, the fundamental mechanism is barely known. The most investigated piezochromic molecules are based on phenylenevinylene and tetraphenylethylene derivatives,[4, 5] but no one has given a clear explanation of the mechanism. Until now, it has been a significant challenge to design such materials due to our limited knowledge about the packing changes during the piezochromic process. Understanding and controlling molecular arrangements in the solid state is essential for design and fabrication of piezochromic fluorescent materials.

The best way to understand molecular arrangements in solid state is X-ray single crystal analysis. The acquisition of crystalline structure in different phases (polymorphs) provides the best opportunity to investigate the relationship of molecular packing with optical properties. [6] For example, Wang et al synthesised a simple molecule (ANP) based on anthracene and found tuneable emission colours in crystals obtained under different conditions. [7] More importantly, the solid emission of ANP could be switched by mechanical and thermal force. Later, Tian et al successfully correlated the piezochromism of an anthracene-based molecule (BP2VA) with its packing modes, determined by X-ray single crystal diffraction. [8] Even though the fluorescence recovery of the ground BP2VA is not complete, and the XRD results of the powder in different states do not match the single crystal results completely, it still provides a deep understanding of the relationship between the

molecular packing and piezochromic fluorescence for the first time. However, such successful examples are very rare, and until now, it has remained a significant challenge to deeply understand the relationship between molecular stacking and stimulus-responsive fluorescence.[5,9]

Herein, we report a unique example of polymorphism-dependent and piezochromic fluorescence, based on 2-(anthracen-9-yl)-4,5-diphenyl-1*H*-imidazole (**ADPI**, Fig. 1). Single crystals with three polymorphs were obtained by slow evaporation method, which exhibit different emissions. The relationship between the molecular packing and the emissions of the crystals is investigated based on single crystal analysis. And these emissions are comparable to those during piezochromic process, providing valuable reference to disclose the molecular packing changes during piezochromism.

Results and discussion

The design of the **ADPI** dye is based on the following considerations: 1) potential intermolecular interactions (π-π stacking and various hydrogen bonds) may form in the concentrated solution and condensed solid because anthracene is a highly planar structure, and the imidazole unit is a popular intermediate to construct intermolecular hydrogen bonds; 2) terminal phenyl rings can provide valuable steric hindrance to promote non-parallel packing to make **ADPI** emit visible fluorescence in solid state; 3) the donor-acceptor character of the **ADPI** molecule may facilitate intramolecular charge transfer (ICT) to enlarge the Stoke shift and red-shift the fluorescence.

Fig. 1 Chemical structure and HOMO, LUMO levels of **ADPI**

ADPI was synthesized in a straightforward manner by a simple one-step reaction, starting from 9-anthracene carboxaldehyde and benzil.[10] The ^{1}H NMR spectrum of the purified sample is identical to reported data (See supporting information). The lowest energy spatial conformation of **ADPI** was theoretically calculated based on quantum computations using the quantum chemistry software package GAMESS platform.[11] Geometry optimisations are determined with Becke's three-parameter density functional (B3LYP) method using the 6-311G (d, p) basis set.[12] The HOMO of the compound showed dispersed electron cloud distributions on the entire molecule, whereas the electron cloud of the LUMO showed concentrated distribution on the anthracene core, indicating that the electrons followed the flow direction from the phenyl group to the anthracene core in the excited state. Therefore, photoinduced ICT may occur in the **ADPI** molecule, which may lead to enlarged Stokes shift and decreased emission intensity with increasing solvent polarity.[13]
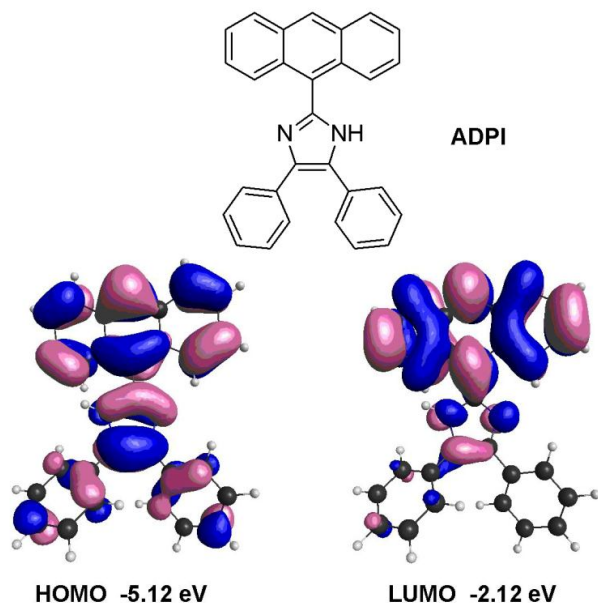

Fig. 2 Absorption (A) and fluorescent spectra (B) of **ADPI** in different solvents (1.0×10^{-5} mol/L) and in solid state. λ$_{ex}$= 365 nm

The photophysical properties of **ADPI** in solutions are investigated in different organic solvents. The compound shows typical absorption features of anthracene chromophore between 300 and 400 nm, which are characteristic of π-π* transitions. Slight bathochromic solvent-dependent properties were found

for **ADPI**, showing ICT characteristics (Fig. 2A), in accordance to DFT calculations. The small spectral shift with solvent polarity suggests poor ICT efficiency. Most likely, the anthracene and imidazole are located at different planes. The slight red-shift of the fluorescent emission of **ADPI** with polarity of solvents also supports the weak ICT process. Only the fluorescence in methanol is unique, and it shifts to the blue region. The emission of **ADPI** was located at 474 nm in the diluted solution of methanol (1.0×10^{-5} mol/L, $Q_F = 46\%$), consistent with a previous report. [10] This finding indicates that **ADPI** molecules may have comparatively strong interactions with methanol, such as hydrogen bonds between imidazole and the methanol. [14] Alternately, the emission wavelengths of **ADPI** in both methanol and chloroform were slightly red-shifted (3~5 nm), with the concentration in the range of 10^{-5} to 10^{-3} mol/L, indicating that the aggregation of **ADPI** is not severe in such a concentration range (Fig. S5).
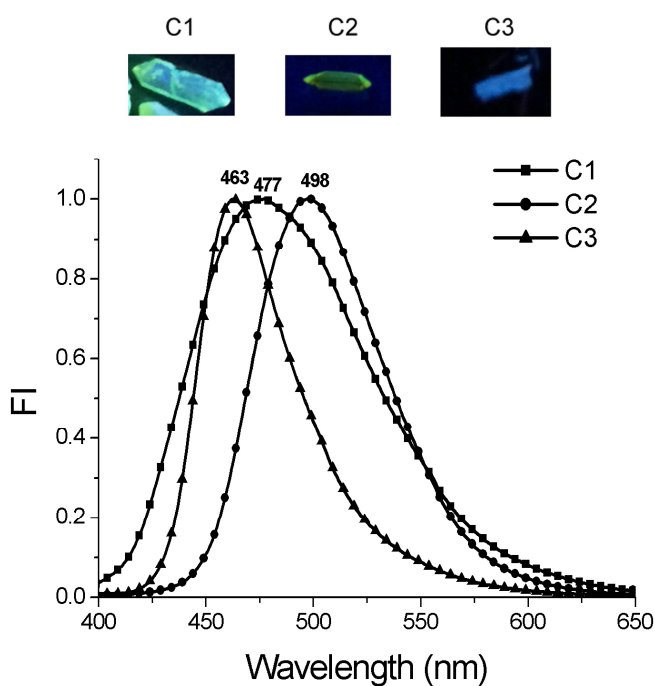

Fig. 3 Fluorescent images and photoluminescent spectra of the single crystals cultivated from different solvents

Single crystal analysis is a helpful tool to investigate the relationship between the molecular packing and luminescence properties. To gain a clear understanding of the structure-properties relationship of **ADPI** molecule, we made many efforts to grow single crystals from different solvents, as the fluorescence of single crystals may explain their emissions under different aggregate states. Finally, three types of **ADPI** crystals, named **C1**, **C2** and **C3**, with three different emissions were successfully obtained from solvents of ethyl acetate/petroleum ether (1: 4), ethyl acetate/petroleum ether (3:1) and methanol, respectively. As shown in Fig. 3, **C1** exhibits a broad emission band (half width 96 nm) centred at

477 nm, while **C2** and **C3** emit at 498 nm (half width 71 nm) and 463 nm (half width 52 nm), respectively. Their different emissions indicate that the molecular packing modes should be different.

Although an anthracene ring is usually highly planar to produce strong π-π stacked structure, very weak π-π interactions of anthracene rings were found in **C1**. As shown in Fig. 4, the anthracene planes between adjacent **ADPI** molecules in **C1** are not parallel arranged; instead, molecules adopt a stacking mode of Λ-shaped aggregate, and the dihedral angles are measured to be 26.06 and 25.61º. However, partial overlap (approximately 10%) of the anthracene planes was found, and the distance of neighbouring anthracene planes was approximately 3.9~4.3 Å, manifesting weak π-π interactions. This packing mode is further stabilised by triangle shaped intermolecular H-bonds between neighbouring imidazoles. The H-bonds described here are considered as strong intermolecular interactions because of the short distance between nitrogen and proton on the imidazole (N1…H3A 2.094 Å, N4…H5A 2.132 Å). Other contacts C-H…C between phenyl rings were also found, but the interactions are much weaker than the H-bonds between imidazoles. Another important feature is that the anthracene and imidazole rings are not in the same plane (dihedral angle from 68.82º to 71.29º for different **ADPI** molecules), which is consistent with the weak ICT character. The existence of these intermolecular H-bonds, and the steric hindrance of phenyl rings should be responsible for the poor planar π-π stacking of anthracene planes.

Crystal **C2**, which exhibits green fluorescence, performs a completely different packing mode with **C1**. The most striking aspect is that no π-π stacking between neighbouring anthracene planes was observed. As shown in Fig. 4, the anthracene planes are nearly vertically arrayed (the dihedral angle is measured to be 74.95º). This packing mode is also stabilised by intermolecular H-bonds, such as H4A…C16 2.837 Å; H11A…H14A 2.391 Å. Interestingly, imidazole rings only interact with the solvent molecules ethyl acetate (Fig. S7). Herein, solvent molecules act as stopper to inhibit the H-bond formation between imidazole rings, thus preventing the interaction of neighbouring anthracene planes. Additionally, the dihedral angle between anthracene and imidazole rings is measured to be 87.85º, indicating a very low ICT efficiency. Therefore, the green emission of crystal **C2** could be ascribed to the monomer of the **ADPI** molecule. It needs to be noted that there may be many packing styles to induce non-aggregated arrangement to produce monomer emission, if the intermolecular π-π interactions are interrupted. This is also proven by another experimental fact that crystal (**C4**) from the mixture of ethyl acetate and cyclohexane also emits green fluorescence (centred at 492 nm). Similar to **C2**, there was observed no π-π stacking in **C4** (Fig. S8). Another similarity between **C2** and **C4** is that the imidazole rings only interact with solvent ethyl acetate, and no other hydrogen bonds are found.
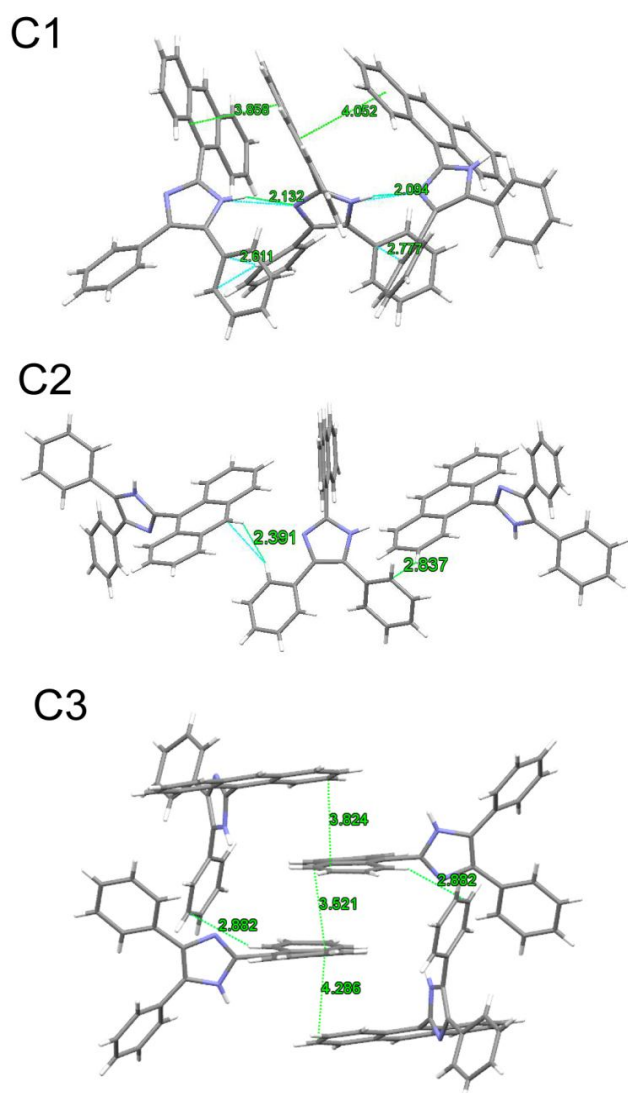
C1

C2

C3

Fig. 4 Stacking modes of **ADPI** molecules in three single crystals

Fig. 5 (A) Fluorescent spectra of **C1** upon grinding and heating; (B) XRD patterns of **C1** upon grinding and heating

The blue emissive crystal **C3** has quite different crystalline data with those of **C1** and **C2**. The planar overlap of anthracene planes was the main feature in **C3**, with an overlapping degree of approximately 30% and a distance of 3.5~4.3 Å. Another character is the parallel packing of anthracene planes, resulting in the formation of *H*-aggregate of the molecules and blue-shift of the fluorescence. Comparing the π-π stacking found in **C1** and **C3**, the interactions in **C3** are much stronger, due to shorter distance and greater overlapping degree. A "boat"-shape anthracene ring was found in **C3** (Fig. S9), while the anthracene rings exhibit comparatively planar structures in **C1** and **C2**. The above results indicate that the planarity of anthracene in the **ADPI** molecule is an important factor for its fluorescence. Planar anthracene usually leads to red-shifted fluorescence,[7] and the "boat"-shape anthracene in **C3** may be another factor to induce shorter emission wavelength compared to **C1** and **C2**. The anthracene ring is almost vertical to imidazole (dihedral angle 89.55º, 71.38º), manifesting poor ICT efficiency.
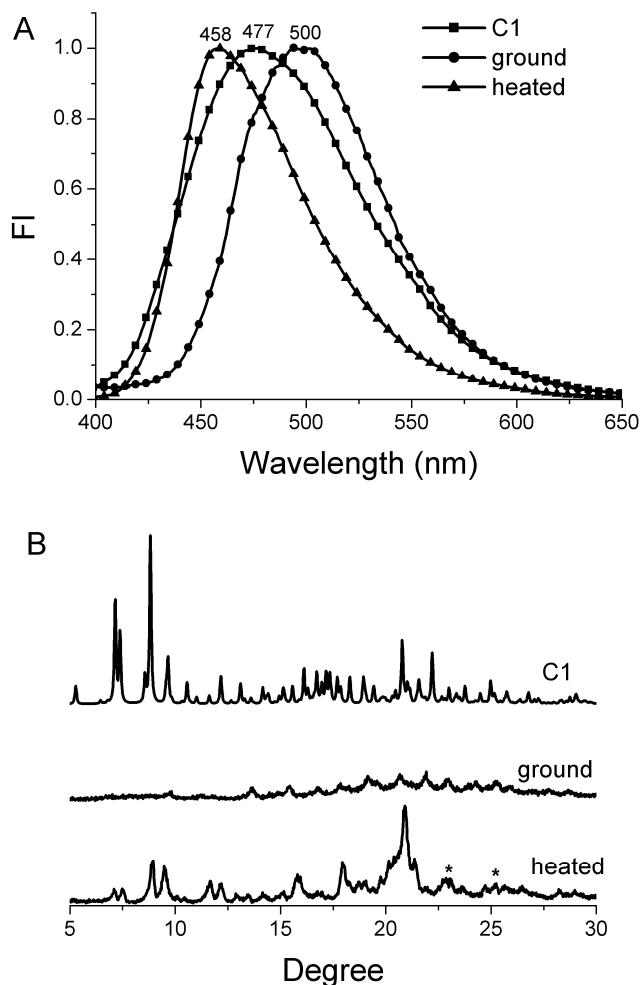
The different packing makes **ADPI** emit quite different emissions, and the packing modes might be tuned by external stimuli, which is of great interest for various applications. To our interest, mechanically grinding the crystal **C1** turns its emission to pure green and the emission was centred at 500 nm (Fig. 5A). The green fluorescence of the ground sample is almost identical to the monomer emission without π-π stacking, as found in **C2**. However, the ground sample is in an amorphous state according to the XRD analysis, which means that the long range intermolecular π-π stacking is destroyed by the mechanical force (Fig. 5B). Therefore, the piezochromic fluorescence modulation of **ADPI** can not be attributed to crystal-to-crystal phase transition, which is difficult to be carried out due to the instability of crystal upon external stimuli. Although successful example has been reported,[15] in most cases the crystals would break or collapse into powder under heat or mechanical pressure. For **ADPI** crystals, they turned non-transparent under heating (Fig. S10). Therefore, it is not possible to use X-ray single crystal diffraction technique to characterize samples after external forces. After heating the ground sample, the emission blue-shifts to 458 nm, which is

quite similar to the emission of crystal **C3**. XRD patterns of the heated sample gives a series of diffractions, manifesting new microcrystalline-like structure was produced.[16] Especially there appear new peaks around 23º and 25º, suggesting that more intense π-π interactions are present. These diffractions are in accordance to the d spacings 3.87 and 4.05 Å, which are also found in the structure of **C3**. Therefore, the blue fluorescence of the heated sample could be the result of more intense intermolecular π-π stacking.
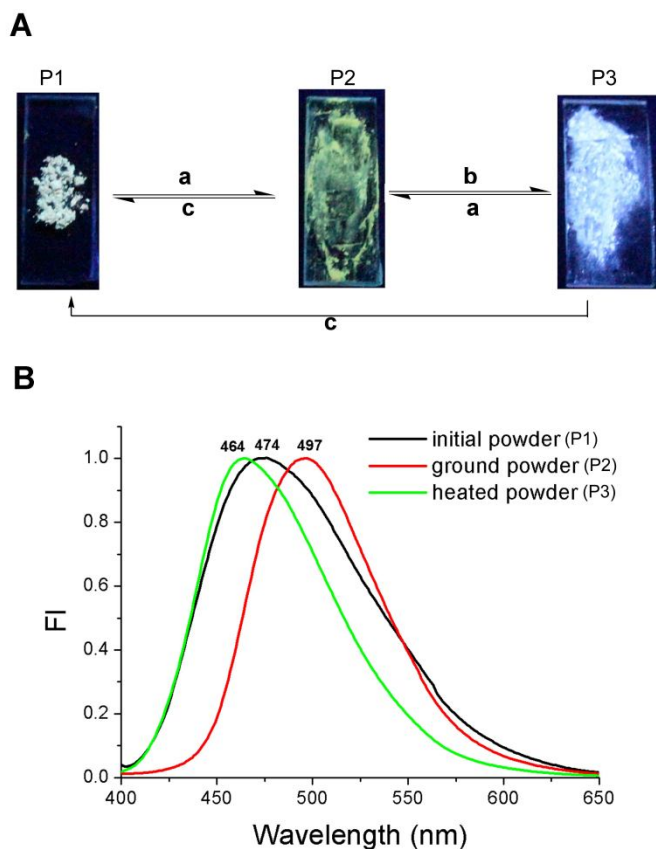

Fig. 6 (A) Fluorescent images of **ADPI** powder under external stimuli (a: grinding; b: heating; c: vacuum evaporation of **ADPI** solution); (B) photoluminescent spectra of the initial, ground, heated powder (Fluorescent images were taken under 365 nm UV light)

The piezochromic property is also found in **ADPI** powder. The solid powder was obtained by vacuum evaporation of the eluents (ethyl acetate:petroleum ether = 1:4, the same solvent with **C1**) from the column (marked as **P1**, Fig. 6). As shown in Fig. 6B, **ADPI** emits blue fluorescence centred at 474 nm in solid powder (Q_F = 3.3%). Interestingly, after being ground, **ADPI** powder shows a clear red-shifted (23 nm) green emission (λ_{max}= 497 nm, Q_F = 2.9%) under 365 nm light irradiation (marked as **P2**). This transition can also be realized under applied pressure (Fig. S11B). After being heated above 120 ºC, the fluorescence of the ground powder slowly returned back to its initial blue emission, and finally, the emission of the heated sample reaches 464 nm (Q_F = 1.6%, **P3**). The interconversion of the three states with their distinct emission colours is completely reversible. Grinding or pressing **P1** produces **P2**,

and annealing of **P2** produces **P3**. By dissolving the samples of **P2** or **P3** in ethyl acetate and then removing the solvents by vacuum evaporation, **P2** and **P3** could be completely converted to **P1**. These three states are invariable after been laid aside for one week (Fig. S12), and no by-product was produced during this process according to TLC analysis. Therefore, the emission changes of these three states should be caused by molecular packing.

To gain more insight into the origin of the piezochromic properties of **ADPI** in powder state, Powder X-ray Diffraction (PXRD) measurements and Differential Scanning Calorimeter (DSC) were taken for the three powders during piezochromism. The fluorescence of **ADPI** should be mainly dependent on the π-π stackings of anthracene rings. The PXRD pattern of the initial powder **P1** exhibits comparatively sharp reflections, indicating an ordered microcrystalline-like structure. Most of the diffractions in **P1** are comparable with those of **C1** only with weaker diffraction intensity, especially in the range of 15-25º, indicating that the initial powder adopts similar molecular arrangement as that of the **C1** polymorph (Fig. S13). The initial aggregation state was clearly changed by grinding, showing amorphous features. Similar with ground sample of **C1**, it also show green emission centred at 497 nm. It's intelligible that **P2** emits monomer emission, due to the absence of intermolecular π-π stacking. Upon heating, the diffraction patterns of **P3** are almost identical with the sample obtained by heating **C1**. DSC curves show that the ground sample has an endothermic transition peak at 69º, responding to cold-crystallisation transition, which is ambiguous for the unground sample (Fig. S14). These results indicate that the reversible piezochromic fluorescence should be mainly induced by the changes of π-π stacking between neighbouring anthracene planes.

To further demonstrate the important role of anthracene and imidazole rings in the piezochromism, a series of structurally similar derivatives are synthesised, in which phenyl ring or naphthalene were used instead of anthracene ring (compound **TPI** and **NDPI**). As expected, these compounds exhibit no piezochromic property due to the deficiency of potential π-π interactions (Fig. S15). The hydrogen bonds formed between imidazole rings also play an important role, which promotes the formation of different aggregation states. If the proton on imidazole was substituted by a methyl group (compound **AMDPI**), it also loses the piezochromic property. The above results indicate that the incorporation of π-π stacking between the anthracene plane, and the intermolecular H-bond between imidazoles is the main driving force for the piezochromic character of **ADPI**.

Conclusions

In conclusion, we found a unique example (**ADPI**) of polymorphism-dependent fluorescence, and investigate the structure-properties relationship in detail based on single crystal analysis. And the emissions of **ADPI** could be reversibly tuned by mechanical and thermal forces, showing typical piezochromic property. Based on PXRD studies, their different

fluorescence emissions during the piezochromic process are ascribed to the different π-π stackings between adjacent anthracene planes and their conformations of the molecules. The hydrogen bonds formed between imidazole rings also play an important role in its packing. Especially, the emissions during piezochromism are comparable to those crystals, providing valuable reference to disclose the molecular packing changes during piezochromism. Future work will focus on the development of piezochromic molecules with significant fluorescence differences.

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Notes and references

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