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Naphthaldehyde-based Schiff base dyes: aggregation-induced emission and high-contrast reversible mechanochromic luminescence†

 Lingyi Shen,^{‡a} Chang-Jin Yu,^{‡a} Hai-Fang Xie,^a Na Xu,^a Hong Xu,^a Ya-Li Huang,^a Carl Redshaw,^{id *b} Xing Feng,^{id *c} and Qi-Long Zhang^{*a}

Mechanochromic luminescent materials have attracted intense attention because of their excellent reversible optical behaviour, but the mechanism of the stimuli responsive behaviour remains ambiguous. Herein, a novel naphthaldehyde-based Schiff base, namely N^2,N^6 -bis(2-(2-hydroxynaphthalen-1-yl)phenyl)pyridine-2,6-dicarboxamide (**HNP**) exhibiting both aggregation enhanced emission (AIEE) and excited state intramolecular proton transfer (ESIPT) characteristics has been synthesized. The mechanism of the reversible mechanochromism was investigated *via* experimental and theoretical procedures. Crystalline **HNP** exhibits a reversible mechanochromism from yellow to orange emission under external stimulus and back to yellow emission by fuming under a dichloromethane atmosphere. Single crystal X-ray diffraction analysis indicated that the compound **HNP** adopts two types of molecular conformations with different intramolecular torsion angles. Meanwhile, DFT and TD-DFT calculations demonstrated that the torsion angle change directly affects the electronic distribution, resulting in a discriminable energy gap. Clearly, the different molecular conformations play a crucial role in triggering the reversible mechanochromism upon grinding. Additionally, **HNP** is an excellent fluorescent probe for detecting Cu(II) ions in solution. Thus, this example not only provides clear evidence to clarify the mechanism of reversible mechanochromism, but also offers a new on-off chemosensor for Cu(II) ion detection.

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1. Introduction

Mechanochromic luminescent (MCL) materials are a classical type of multifunctional material that can change emission colour reversibly under external stimulus, and these materials exhibit high efficiency toward diverse applications in sensors,¹ information anti-counterfeiting,² memory chips and optoelectronic devices.³ Organic materials with mechanochromic luminescence properties show unique advantages⁴ such as low cost,

precise molecular structures with tunable optical properties. Moreover, molecular components with a twisted conformation have been utilized for constructing MCL materials, such as tetraphenylethylene,⁵ cyanostyrene,⁶ carbazole,⁷ *etc.*

Aggregation-induced emission (AIE), is an abnormal fluorescence phenomenon, where a type of molecule is weakly fluorescent in solution but exhibits high fluorescence in the aggregated state.⁸ Organic luminescent materials with the AIE characteristic have shown great potential in organic light-emitting diodes,⁹ photodynamic therapy,¹⁰ fluorescent probes,¹¹ *etc.* Excited-state intramolecular proton transfer (ESIPT) is a classical fluorescence process, where the proton can transfer from a hydrogen bond donor (*e.g.* -OH and -NH₂) to a hydrogen bond receptor (*e.g.* = N- and C=O)¹² *via* a tautomeric transformation under irradiation, resulting in a large red-shifted emission. Specifically, the combination of the AIE and ESIPT features can be used to overcome environmental sensitivity to avoid self-absorption.¹³

Schiff base compounds have wide versatility and exhibit good solubility in common solvents, in addition to being easily functionalized when needed for various applications. Previously, our group reported that the tetraphenylethylene functionalized

^a Research Center for Molecular Medical Engineering, School of Basic Medical Science, Guizhou Medical University, Guiyang 550004, China.

E-mail: gzuqlzhang@126.com

^b Department of Chemistry, University of Hull, Cottingham Road, Hull, Yorkshire HU6 7RX, UK. E-mail: c.redshaw@hull.ac.uk

^c Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, School of Material and Energy, Guangdong University of Technology, Guangzhou 510006, P. R. China. E-mail: hyxhm@sina.com

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‡ L. Shen and C.-J. Yu contributed equally to this work.



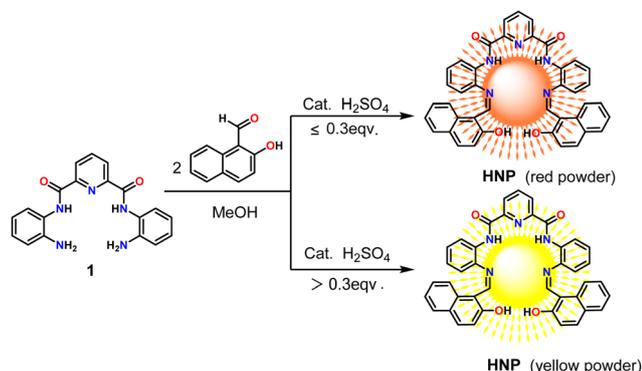
salicylaldehyde Schiff-base with the aggregation-induced enhanced emission (AIEE) property is an excellent fluorescent probe for Cu(II) ion detection¹⁴ and we note that a naphthyl-based Schiff base zinc complex has been used for cellular uptake studies.¹⁵ Moreover, the coordination mode of a salicylaldehyde Schiff-base fluorescent probe toward Cu(II) was evaluated by single crystal X-ray diffraction.¹⁶ In recent years, many Schiff base MCL compounds have been reported¹⁷ and proved to be excellent fluorescence carriers with high-contrast reversible mechanochromic luminescence properties.¹⁸ Generally, photoluminescence spectra, scan/transmission electron microscopy, and powder X-ray-diffraction are the typical techniques employed for understanding the mechanochromic mechanism. However, understanding the intrinsic mechanism of MCL behaviour remains an enormous challenge.

In this work, a Schiff base compound **HNP** was synthesized *via* a facile one-step synthetic method, which exhibits typical AIEE plus ESIPT characteristics. Due to the presence of the flexible Schiff base skeleton, the AIEE-active molecule **HNP** adopts a twisted molecular conformation *via* several strong intra/inter-molecular interactions, which leads to different emissions in the crystalline state. More interestingly, this crystal displays high-contrast reversible mechanochromic luminescence properties *via* orange and yellow emission, and this result is ascribed to the different molecular conformations in the crystal packing. The relationship between the molecular packing and the emission properties is discussed to understand in greater depth the reversible mechanochromic mechanism, *via* single crystal X-ray diffraction, SEM, and photoluminescence spectroscopy, as well as theoretical calculations. Moreover, Schiff base **HNP** can act as a 'turn-off' fluorescence sensor for potential applications in Cu²⁺ detection.

2. Results and discussion

2.1 Synthesis

The synthetic route to Schiff base *N*²,*N*⁶-bis(2-(2-hydroxynaphthalen-1-yl)phenyl)pyridine-2,6-dicarboxamide (**HNP**) is presented in Scheme 1. The intermediate *N,N'*-(2-aminophenyl)-2,6-dicarboxylimide pyridine (**1**) was synthesized according to a previous report.¹⁴ Treatment of **1** with 2-hydroxy-1-naphthaldehyde dissolved



Scheme 1 Synthesis of compound **HNP**.

in methanol afforded the target red compound **HNP** in 78% yield. Interestingly, a yellow powder was obtained when more than 0.3 equivalents of H₂SO₄ catalyst was added to the reaction, which shows the same characterization data for the ¹H/¹³C NMR spectroscopy (Fig. S1 and S2, ESI[†]) and high-resolution mass spectrometry (HRMS) (Fig. S3, ESI[†]) as compound **HNP**.

2.2 Photophysical properties

The UV-vis absorption spectra and photoluminescence (PL) spectra of compound **HNP** were measured in seven solutions (CH₃OH, EtOH, CHCl₃, THF, DCM, DMSO and DMF) and are shown in Fig. S4 (ESI[†]). The absorption band at λ = 319 nm represents the electronic transition of the Schiff base unit,¹⁹ and the absorption peak at λ = 396 nm is tentatively assigned to the electron–electron transition from the Schiff base to the amide–pyridine ring, which is greatly affected by the polarity of the solvent.²⁰ Meanwhile, the wide absorption wavelength range from 419 nm to 475 nm is due to the formation of intramolecular hydrogen bonds.²¹ In addition, the compound **HNP** exhibits weak fluorescence in all solvents, but the fluorescence intensity is stronger in weak polarity solvents (such as CHCl₃, THF and DCM) than in strong polarity solvents (CH₃OH, EtOH, DMF and DMSO). Moreover, the compound exhibits a red-shifted emission in the protic solvents methanol and ethanol as compared to DMSO, and this may be ascribed to the presence of the —OH group which can stabilize the enol conformation and lead to the adoption of a twisted intramolecular charge transfer (TICT) process.²²

2.3 Aggregation-induced emission properties

To understand the effect of water on the emission process, the UV-vis spectra and photoluminescence (PL) spectra characteristics were studied in a mixture of THF/H₂O with different water fractions (*f_w*). As shown in Fig. S5, (ESI[†]) the peak at 419–475 nm gradually decreases, which may be attributed to the blocking of the ESIPT by the intermolecular H-bonding between the **HNP** and H₂O.²³ On the other hand, as shown in Fig. 1, a dual emission in THF was observed under excitation (λ_{ex} = 350 nm), the short-wavelength emission originating from enol emission and the latter from keto emission.²² Moreover, the shorter-wavelength emission decreased gradually with the increase of water content, and eventually disappeared when the water fraction (*f_w*) increased to more than 80%. This is attributed to molecular aggregation, resulting in strengthened intramolecular H-bonding, which is a key factor for an efficient ESIPT process.¹² Furthermore, **HNP** emits weak orange emission with a maximum emission peak at 588 nm, as the water fraction (*f_w*) increased from 0% and 70%, and the emission intensity gradually decreased with the increase of water content. This is consistent with the UV-vis spectra, which show that the fluorescence intensity is reduced. As the water fraction (*f_w*) increased from 70% to 95%, the emission intensity was enhanced *ca.* 3.5-fold, indicating that **HNP** exhibits a clear aggregation-induced enhanced emission (AIEE). To further investigate the aggregation-induced emission (AIE) properties of **HNP**, the emission spectra were recorded with a different



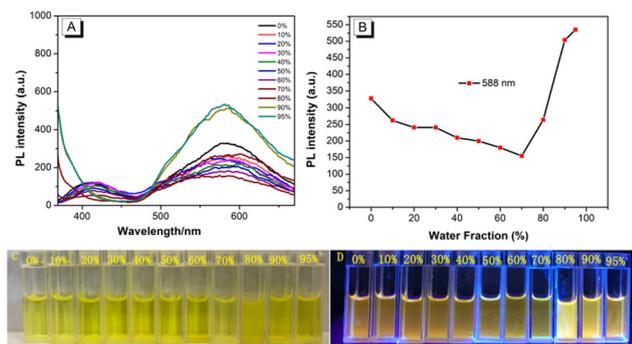


Fig. 1 (A) Fluorescence spectra of the fluorescent probe ($2.00 \times 10^{-5} \text{ mol L}^{-1}$) at different water contents ($\lambda_{\text{ex}} = 350 \text{ nm}$) in THF. (B) The effect of water volume fraction on the fluorescence probe at 588 nm. (C) Photographs of the fluorescent probes in THF solution containing different water components under natural light. (D) Photographs of the fluorescent probes in THF solution containing different water components under 365 nm UV light.

excitation ($\lambda_{\text{ex}} = 440 \text{ nm}$) and higher concentration ($5.00 \times 10^{-5} \text{ mol L}^{-1}$) in THF solution using different THF/water mixtures. The results revealed almost the same trend, where the overall fluorescence intensity was enhanced (Fig. S6, ESI[†]). Moreover, the stability of the probe **HNP** at various pH values was examined in the THF/water ($V_{\text{THF}}/V_{\text{water}} = 1/9$, Tris-HCl buffer) system (Fig. S7, ESI[†]). With the changing pH, the absorbance of **HNP** gradually decreases as the pH value increases from 1.00 to 3.00, while the absorbance exhibits a slight change over the pH range from 5.00 to 12.00. On the other hand, the fluorescence intensity remains unchanged in the pH range from 1.00 to 12.00. This result indicated that the Schiff-based compound **HNP** was stable at various pH values from 2.00 to 12.00.

2.4 Mechanochromism properties

As we know, most AIE luminogens exhibit excellent reversible mechanochromism properties under external stimulation. Considering the flexibility of the molecular structure of **HNP**, the reversible mechanochromism behaviour was studied. The yellow compound **HNP** displays a bright orange emission with a maximum emission peak at $\lambda_{\text{em}} = 540 \text{ nm}$, ($\Phi_f = 5.44\%$). Once the yellow compound **HNP** was ground, the powder emitted a large, red-shifted emission with $\lambda_{\text{maxem}} = 662 \text{ nm}$ ($\Phi_f = 1.55\%$), and the fluorescence lifetime (τ) changed from 5.35 ns (**HNP-y**) to 1.81 ns. Moreover, the red emission powder could recover the yellow emission under a CH_2Cl_2 atmosphere, indicating that **HNP** displays reversible mechanical stimuli-responsive properties. Furthermore, the samples of **HNP** before and after grinding were evaluated by powder X-ray diffraction. As shown in Fig. 2, the crystal sample **HNP-y** exhibits sharp intensity peaks, indicative of a good microcrystalline structure, while powdered **HNP-r** displays weak and broad diffraction peaks, and the peaks at $2\theta = 12^\circ$ and 16° almost disappeared after grinding, indicating that the molecular arrangement displays a large change with a red-shifted emission. Moreover, the diffraction peak of **HNP-r** can return back to a sharp peak *via* CH_2Cl_2

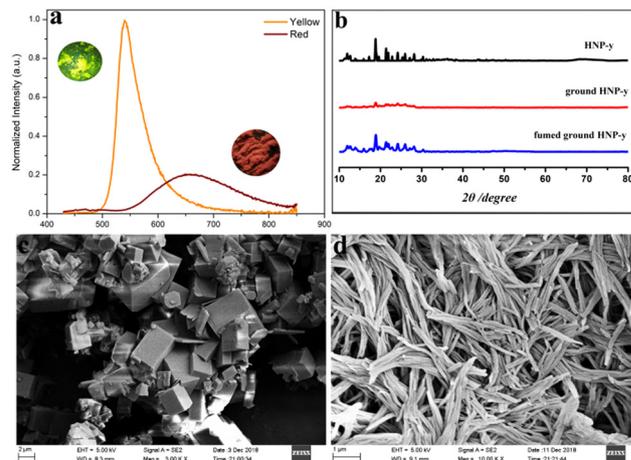


Fig. 2 (a) Fluorescence spectra of powdered **HNP-y** (orange line) and powdered **HNP-r** (red line). (b) PXRD patterns of crystals of **HNP-y** and **HNP-r** and when ground and after fuming with CH_2Cl_2 . SEM image of **HNP** powder under different fluorescent emissions (c) yellow and (d) red.

fuming, and the emission colour changes from red to orange, and this process agrees with their optical behaviour. Additionally, the morphology of the samples **HNP-y** and **HNP-r** was also investigated by scanning electron microscopy (SEM). As shown in Fig. 2c, crystalline **HNP-y** exhibits a block 3D aggregate structure, while powdered **HNP-r** shows a 2D fibrous-like structure along the same direction (Fig. 2d), indicating that **HNP** show different morphology before and after grinding, which was further characterized by the UV-Vis absorption spectra and is illustrated in Fig. S8 (ESI[†]). After fuming with CH_2Cl_2 , the UV-vis absorption of the samples is almost overlapped with the crystalline **HNP-y**.

2.5 Single crystal structure analysis

Single crystal X-ray diffraction is an efficient tool to visualize the molecular conformation and for understanding the relationship between the molecular packing and the optical behaviour. Thus, we attempted to cultivate crystals of **HNP** by slow solvent evaporation at room temperature. Firstly, pure **HNP** (20 mg) was dissolved in a chloroform/ethanol mixture to obtain block red crystals (**HNP-r**); yield 12 mg. Then, the mother liquor was collected to afford yellow needle crystals (**HNP-y**) (yield 6 mg). Both molecular structures of the crystals **HNP-y** and **HNP-r** were confirmed by single crystal X-ray diffraction analysis, and the key crystal data are summarized in Table S1 (ESI[†]). The **HNP-y** crystal belongs to the triclinic crystal system with the space group $P\bar{1}$, and the asymmetric unit cell of **HNP-y** contains two molecules. Meanwhile, the crystal **HNP-r** crystallises in the higher symmetrical monoclinic system with the $C2/c$ space group, and each asymmetric unit contains four molecules. The ORTEP diagrams of **HNP-y** and **HNP-r** are shown in Fig. S9 (ESI[†]).

As shown in Fig. 3, the two terminal naphthyl rings in the crystal **HNP-y** adopt an intersecting type conformation, whereas the situation observed in **HNP-r** is almost coplanar.



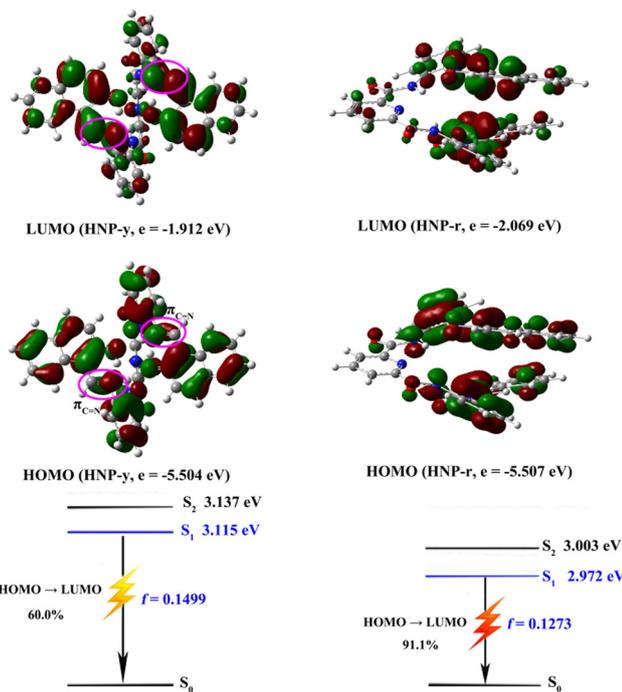


Fig. 5 The frontier orbitals and theoretically calculated vertical excitation energies, transition natures of the excited states and oscillator strengths for **HNP-y** and **HNP-r**.

the f value reduces from 0.1499 to 0.1273, suggesting that a decreased twist of the dihedral angle results in a red-shifted emission with weaker emission. Therefore, it would be a useful strategy to change the ability of the electron donor or electron acceptor to regulate the charge transfer efficiency in order to achieve a high fluorescence yield in this type of luminescence material.

2.7 Fluorogenic Cu^{2+} sensing

In order to evaluate the sensing properties of **HNP**, its sensing properties in THF with several metal cations (solutions of Hg^{2+} , Cr^{3+} and Mg^{2+} and Zn^{2+} were prepared from their chloride salts; solutions of Cu^{2+} , Cd^{2+} , Pb^{2+} , Ca^{2+} , Co^{2+} , Ba^{2+} , Ag^{+} , Ni^{2+} , Li^{+} , K^{+} , Na^{+} , Al^{3+} , Zn^{2+} and Fe^{3+} were prepared from their nitrate salts) were investigated by UV-vis absorption and fluorescence measurements (Fig. 6). The absorption spectra of **HNP** showed that the absorption peak at 396 nm remained unchanged upon addition of several kinds of metal ions except in the case of Cu^{2+} and Co^{2+} . Upon addition of Cu^{2+} , the absorbance located at 396 nm was red shifted to 443 nm. Except for Co^{2+} , other metal ions had little effect on the absorption. The fluorescence emission at 588 nm upon excitation by 440 nm was quenched upon addition of Cu^{2+} , while other metal cations had little effect on the fluorescence intensity of the probe. Moreover, competition experiments were conducted, and as shown in Fig. S11 (ESI[†]), other metal ions did not interfere with the recognition of **HNP** toward Cu^{2+} , with the exception of Co^{2+} which had a slight effect on the probe detection of Cu^{2+} , indicating that the probe had strong anti-interference

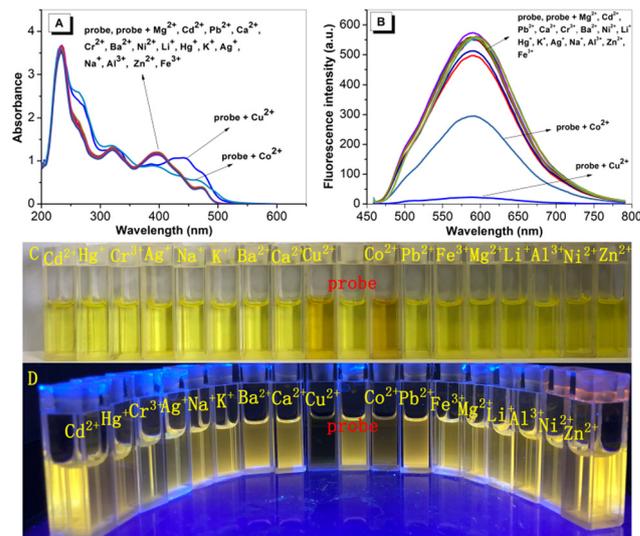


Fig. 6 (A) UV-vis absorption spectra and (B) fluorescence spectra of fluorescent probes ($5.00 \times 10^{-5} \text{ mol L}^{-1}$) interacting with different metal ions ($1.00 \times 10^{-4} \text{ mol L}^{-1}$) in THF solution ($\lambda_{\text{ex}} = 440 \text{ nm}$); (C) photographs of the probes interacting with metal ions under natural light; (D) photographs of the probes interacting with metal ions under 365 nm UV illumination.

properties. The results of UV-Vis absorption spectra and fluorescence spectra show that the probe has high specificity toward copper ions. Moreover, fluorescence titration experiments of Cu^{2+} were carried out in THF. As shown in Fig. S12 (ESI[†]), the absorbance of the probe at 396 nm gradually decreased with the increase of Cu^{2+} concentration; meanwhile, a new absorbance at 443 nm gradually increased. Moreover, the fluorescence intensity of the probe decreased gradually at 588 nm, and the fluorescence quenching rate reached 95.35% when two equivalents of Cu^{2+} were added. Additionally, the combination ratio between them was further determined by the equal mole continuous transformation method (Job's plot). As shown in Fig. S13 (ESI[†]), through the fluorescence spectrum, it can be seen that probe/probe + Cu^{2+} has an inflection point at 0.33, indicating that the mixing ratio between probe and Cu^{2+} is 1:2.

Furthermore, the detection limit of probe **HNP** for Cu^{2+} was calculated to be $1.8 \times 10^{-7} \text{ mol L}^{-1}$ from the fluorescence titration experiments following the IUPAC method (Fig. S14, ESI[†]).²⁵ On the basis of the 2:1 stoichiometry, the association constant between **HNP** and Cu^{2+} was estimated to be $5.70 \times 10^3 \text{ mol L}^{-1}$ by using the Benesi-Hildebrand equation (Fig. S15, ESI[†]).²⁶

The crystal structure is important for us to understand the coordination mode and molecular packing. Fortunately, single crystals of complex **HNP-Cu** were obtained by slow evaporation from solutions in ethanol at room temperature. The crystal data are summarized in Table S1 (ESI[†]). The complex **HNP-Cu** crystallizes in the orthorhombic system and each unit cell contains two complex molecules. Moreover, as shown in Fig. S16a (ESI[†]), one **HNP** molecule coordinates with two Cu^{2+} ions, which is consistent with the titration experiments. Each Cu atom is four-coordinate with four atoms (oxygen and



nitrogen atoms), which results in removal of the hydrogen ions of the hydroxyl groups and thus the process of ESIPT was intercepted, so that it shows fluorescence quenching. The two planes of the terminal aromatic rings of **HNP** are parallel; therefore, a 1D chain was formed by countless helices in the same direction *via* intermolecular $\pi \cdots \pi$ interactions ($d \approx 3.30 \text{ \AA}$) and intramolecular hydrogen bond interactions (Fig. S16b, ESI[†]). **HNP** is a highly selective and sensitive chemosensor for Cu^{2+} ions.

3. Conclusions

In summary, we report here a naphthaldehyde based Schiff base material with both excited state intramolecular proton transfer and AIEgen fluorescence emission which can undergo a polymorphic switch on changing the solvent. Crystals of both **HNP-y** and **HNP-r**, with different emission colours were obtained by slow evaporation in chloroform/ethanol mixtures. Single crystal X-ray diffraction data and DFT calculations show that the **HNP-r** molecule is formed in a more compact stacking mode due to the smaller dihedral angle of the terminal aromatic ring planes and stronger intermolecular interactions, resulting in a red-shifted emission and weaker fluorescence emission. The multiple stimuli-responsive behaviour of **HNP** results in mechanochromic luminescence and its ability to act as a sensitive chemosensor for the Cu^{2+} ion. Our work provides a strategy for further understanding the relationship between the molecular structure and the emission mechanism at the molecular level and for the design of multi-stimuli responsive materials and can contribute to the understanding and the future design of new mechanochromic luminescent materials. It will stimulate a new approach for the realization of mechanochromic luminescent materials and provide a new understanding of the nature of mechanochromic behaviour.

Author contributions

Lingyi Shen carried out the experiments, wrote the paper and analyzed the X-ray structure. Chang-Jin Yu, carried out the experiments and wrote the paper. Hai-Fang Xie and Na Xu carried out the experiments. Hong Xu analyzed the experimental data. Ya-Li Huang provided experimental guidance. Xing Feng provided experimental guidance and design. Carl Redshaw analyzed the experimental data and revised the paper. Qi-Long Zhang provided research ideas, designed the experiments and modified the paper.

Conflicts of interest

There are no conflicts to declare.

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