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Aggregation-induced ratiometric emission and mechanochromic luminescence in pyrene-benzohydrazonate conjugate

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Luminogenic materials with aggregation-induced emission (AIE) have recently aroused great attention due to the potential application in many fields. However, the aggregation induced ratiometric luminescence in addition to emission turn-on has been scarcely studied. Here, a structure tunable pyrene benzohydrazonate-based molecule platform exhibits drastic aggregation-induced color change ($\Delta\lambda_{\text{em,max}}$ ~ 130 nm) and high solid-state quantum yield (Q.Y_{max} \sim 54.5%). The exciting switch behaviour is triggered by intermolecular hydrogen-bonding through the carbohydrozone bridge giving rise to fixation of the molecular conformations. In addition, by virture of multiple excimer state of pyrenyl unit, a broad range of carbohydrozonebased materials with high contrast mechanochromic luminescence have been developed. These systems represent stimuli-responsive optoelectronic switching devices leading toward multistate dynamic molecular systems in both solution and solid.

The development of efficient organic luminogenic materials in the solid and aggregate states are crucial for the potential application in the field of advanced OLED and biosensor.¹ Traditional investigations on luminescence have been generally performed in the diluted state, where the emitting molecule can be approximately treated as isolated one without being perturbed by intermolecular interaction.² The studies of dilution solution could provide the fundamental information on luminescence processes at molecular level. The conclusion for concentrated solution can not be simply duplicated from the diluted solution, which frequently exhibit the different emitting behaviour. The emission of a luminophore is typically weakened when molecules are aggregated due to energy transfer and the formation of excimers and exciplexes, namely aggregation-caused quenching (ACQ). Recently, a reversal phenomenon called aggregation-induced emission (AIE) has been put forward. In this case, the isolated fluorogens show the

negligible emission due to the nonradiative decay through

intramolecular motion. The intramolecular rotation can be blocked when aggregation state of these molecules forms, giving rise to strong emission. A well-known AIE fluorogen is tetraphenylethene (TPE), in which the restriction of intramolecular motion (RIM) of its multiple phenyl rotors against its ethylene stator has been proposed to account for its strong fluorescence in the aggregation state.^{3,4} It was also recognized that formation of hydrogen bonds between luminogens can rigidify their molecular structures,⁵⁻¹⁰ which helps reduce the nonradiative decay of their excitons and maximize the probability of radiative transitions. To our best knowledge, most of the AIE systems have been identified on the basis of intensity turn-on at a specific wavelength, however, AIE sensors with fluorescence colour change are desirable, as they endow a dimension with the discriminative power and allow visualization by naked-eye.¹¹



Fig. 1. (a) The chemical structure of model complex **ph-ph** and pyrene-containing benzohydrazonate derivatives **1-3**. (b) Proposed 1-D hydrogen bonding chain of the carbohydrozone unit. (c) Mercury representation of hydrogen bonding structure along the crystallographic *a* axis in model complex **ph-ph** from X-ray diffraction data.

In the previous studies, we and other groups have developed carbohydrozone derivatives for metal coordination and sensing platform in which the proton attached on the imine N atom is released upon metal coordination or acid-base neutralization giving rise to more π -conjugation system.¹²⁻¹⁵ To further test the active hydrogen hypothesis, the model complex **ph-ph** was synthesized,

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⁺Electronic supplementary information (ESI) available: Synthesis details, additional spectroscopic data CV plot and etc. CCDC 1826737 contains the crystallographic data.



Fig. 2 (A) PL spectra of **2** in DMF/H₂O mixtures with different volume fractions of H₂O. (B) Cyclic voltammograms of **2** in DMF and aqueous DMF (20%) containing 0.05 mol L⁻¹ of tetrabutylammonium hexafluorophosphate (TBAPF₆) (C) PL spectra of **3** in DMF/H₂O mixtures with different volume fractions of H₂O. Inset: Emission color change from blue to yellow in aqueous DMF with $f_w = 0 - 90\%$ under 365 nm UV light. (D) Plots of normalized PL intensity of **3** versus *fw* at different emission wavelengths. $\lambda_{ex} = 365$ nm, *C* = 10 µM.

and its crystal structure was determined.(For details, see Table S1, ESI) X-ray diffraction analysis revealed that the trans-NH proton in ph-ph would be accessible for intermolecular hydrogen bonding (Fig. S2, ESI). Fig. 1c shows that, indeed, this type of complex adopts the anticipated trans conformation and consequently forms hydrogen-bonded chains in the crystalline state. The hydrogen bonding parameters is as following: d(N···O)=2.854(3) Å; d(H···O)=1.875Å; <NH···O=169.2°. The C-N and N-N bond distances of being 1.350(2) Å and 1.389(2) Å, respectively, fall within the intermediate one between the normal single and double bond within carbohydrozone block, which is indicative of the conjugate structure along the carbohydrozone bridge. The feasible modulation of self-assembled hydrogen bonding structure from benzohydrazonate inspired us to creat a molecule with simple structure but controllable assembly property to show a novel mode of AIE luminescence.¹⁶⁻²¹ Here, our effective strategy is to introduce a multiple excimer state of pyrene into benzohydrazonate platform. The multistable emitting states can be manipulated in the manner of aggregation-induced ratiometric luminescence and high-contrast mechanochromism, which distinguished from traditional turn-on mode in the AIE systems.²

Compounds **1-3** were prepared in the similar manner to that of ph-ph through using pyrene-1-carbaldehyde instead of benzaldehyde. (for details, see ESI). They have the poor solubility in most of organic solvents and water but is completely soluble in polar solvents, such as DMF and DMSO. The strongest absorption was located at *ca*. 370 nm (λ_{max}) in solution with shoulder peaks at 380 nm and 400 nm (Fig. S3, ESI) Upon increasing amount of water in DMF solution, the absorption didn't significantly change until the water fraction (fw) reaches *ca* 90% for **1** and 80% for **2** and **3**, at which they began to aggregate. All the compounds display a distinct and well-known fluorescent spectra of pyrene moieties centered at *ca*. 410 nm in DMF solution, which can be attributed to the monomeric emission of pyrenyl group. The monomeric emission exhibits small red shift under the low water fraction (fw). When the water fraction went higher, it is interesting to observe the original



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Fig. 3 (A) Plots of relative PL intensity (I/I₀) and (B) change of emission maximum ($\Delta\lambda$) versus solvent fraction (fs) of **3**. Concentration = 10⁻⁵ M, λ_{ex} = 365 nm, I₀ = intensity at f_s = 0%.

peak collapsed in the emission spectra and a new peak obtained its intensity at *ca*. 550 nm for compound **2** (Fig. 2A). The ratiometric fluorochromism could be readily detected by the naked-eye from blue to yellow (inset in Fig 2A). The CV as well as DPV measurements of all the compounds were also carried out in dry DMF and wet DMF (fw. 20%) solutions, respectively (Fig. S5-S7, ESI).²³ The electrochemical behavior of **2** as representative was plotted by cyclic voltammetry (CV) under a N₂ atmosphere (Fig. 2B). The quasireversible potentials (E = $(E_p^{\text{ox}} + E_p^{\text{red}})/2$) are -500 mV *versus* Ag⁺/Ag for complex **2**, which are attributed to the oneelectron reduction of a carbohydrozone group. However, the redox process was switched off in a wet DMF solution with fw of 20%, which reflect the difference in conductivity in the presence of bulk water.

Likewise, the transition from fluid phase to aggregation state occurs at the water fraction of *ca.* 80% for compound **3**.(Fig. 2C). Upon further increasing water fraction, the new emission with larger stokes shift develops and finally obtain its 5-*fold* enhancement in emission intensity compared to the molecularly dispersed state (Fig. 2D), demonstrating that the longer-wavelength emission is an AIE phenomenon. The ratiometric AIE is uncommon in that the large emission maximum shift (above 100 nm) was due to the formation of hydrogen-bonding aggregate state.

The PL analysis of all molecules indicated that their photophysical properties behave in the similar manner, and the longerwavelength emission showed unusual AIE effect. The shorterwavelength emission at *ca.* 440 nm increased as the humidity in DMF aqueous media rose and then decreased upon forming aggregate. The similar phenomenon has been recently observed in some simple molecules with nonconjugation structure, which is ascribed to intramolecular through-space conjugation between the "isolated" phenyl rings.²⁴ In this case, the shift of emission maximum should be associated with the solvent polarity. To further check this point, the PL spectra of **3** as representative in the presence of other nonsolvent with relatively weak polarity, such as CH₃OH, CH₂Cl₂ and CH₃CN, were measured and compared (Fig. S8, ESI). Fig. 3A and 3B showed the relationship between the relative Published on 20 June 2018. Downloaded on 6/21/2018 3:43:32 AM

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emission intensity (I/I₀) and change of emission maximum ($\Delta\lambda$) and the nonsolvent fraction. Upon increasing the water fraction (fw) in DMF/water mixture from 0 to 98 %, the FL intensity increased 8.9 times accompanying with an $\Delta\lambda$ value to 130 nm. Under the same *fs* (solvent fraction) change, neither *I*/*I*₀ nor $\Delta\lambda$ showed the noticeable change.

To confirm the formation of luminogen aggregated in DMF/water mixtures, dynamic light scattering (DLS) measurement of **2** was conducted. According to the DLS results as shown in Fig. 4, the average diameters of the particles are about 955 nm with 90% water content in DMF/H₂O mixture. It was suggested that the aggregation driven growth is one of the reasons for the ratiometric AIE. We thus used the scanning electron microscope (SEM) to examine the morphological structure of the white precipitates. As can be seen from Figure 4(b), the precipitates are one-dimensional microsticks with diameters down to a few hundred nanometers and lengths up to several micrometers.



Fig. 4. (a) Dynamic light scattering (DLS) results showing the particle size diameter at f_w = 90% and (b) SEM image showing size of aggregates.

In order to disclose whether the potential structure change occurs in the presence of water, compound **3** was chosen as representative and ¹H NMR spectra was monitored through D₂O titration experiment. From the ¹H NMR titration spectroscopy data in Fig. 5, the resonance at 11.95 ppm continued to become weak upon increasing the water fraction to 20%, suggesting that proton on imine site is active toward the potential proton exchange and/or intermolecular hydrogen bonding. The presence of water also causes significant upfield shifts of the H_a signals and downfield shifts of hydrogen atom on the phenyl ring, indicative of the tiny change of the conjugation in the presence of bulk water.



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It is well known the luminescence from an organic emitter can be modulated in solid through substituent effect.²⁵ Since the molecule of benzohydrazonate terminal can be easily modified with the different substituents, the resulting fluorescent is expected to be chromically tunable. Compounds **1-3** are strongly emissive under UV light in the solid state (Fig. S10, ESI). Upon excitation at 365 nm, compound **1** shows the strongest emission band with the peak maximum at 502 nm and quantum yield of 54.5% (Table S1). Although the monomer emission position is insensitive to the substituent effect, the compounds **2** and **3** show the obvious blueshift relative to **1**. Furthermore, the absolute luminescence quantum yield of **1** (54.5%) is significantly high relative to the values observed for the others (3.79 – 4.81%), indicative of the substituent effect on the solid emitting.

The strong solid-state emission and the possibility of multiple excimer-like emission behavior of pyrenyl unit encouraged us to study the mechanochromic properties.²⁶⁻³¹ The emission spectra of pyrenyl-benzohydrazonate 2-3 pristine and ground solid are studied and shown in Fig. 6 together with the spectra in diluted solution in the manner of multistable emtting state(For 1, see Fig.S11, ESI). The pristine solid compound 2 and 3 shows 54 nm and 42 nm red-shift compared to the spectra of monomer state. Furthermore, upon grinding using a mortar and a pestle, the blueemitting pristine solids were converted to yellowish green emitting solids and the emission peaks exhibit varying degree of red-shift, i.e., 16, 64 and 80 nm for 1, 2 and 3, respectively. Such the remarkable multistable luminochromism may be associated with the different excimer-like states, excimer 1 (E1) and excimer 2 (E2), for pyrenyl-base compounds. Furthermore, the emission of excimer 2 could be converted to excimer 1 after heating treatment at approximately 120 °C for several minutes. Beside the emission response to the force and heat stimuli, all compounds also displayed a response to solvent vapor. After exposure to the dichloromethane vapor, the yellowish-green emission could be recovered to the initial emission of the pristine sample, and the reversible switching between emission of the two different states could be repeated after many cycles.

In order to establish the origin and mechanism of the reversible piezochromic behavior, the UV-vis spectra in the solid state of the pristine and ground state of the selected complexes were obtained. The results show complete consistency of the absorption bands for all of the complexes (Fig. S12, ESI). The significant change in emission spectra upon grinding are, therefore, not attributed to the structure change. Powder XRD was carried out to investigate the

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possible phase transformation. The sharp peaks in the XRD pattern (Fig. S13, ESI) unambiguously indicate that the pristine sample has a well-ordered crystalline structure. The ground sample exhibits identical diffraction signals, which indicates that the grinding cannot form the amorphous phase. Because the crystalline phase is unresponsive to mechanical grinding, the distinct luminescence response to force implies that the solid packing involving π ··· π and N-H···O intermolecular interactions are strong enough for stabilization of crystalline phase under mechanical grinding. Such a red shift frequently arises from the conformational planarization induced by the high pressure.³³



Fig. 6 Multistate emission spectra of compound 2 and 3 in diluted solution, pristine, ground and annealed solids and the photographs taken under 365 nm UV illumination.

Fourier transform infrared spectroscopy (FTIR) measurement was implemented under vacuum to further confirm H-bonding self-assembled structures at molecular level. For the pristine solid, the broad vibrational bands were observed at around 3200 and 3000 cm⁻¹ (Fig. S14, ESI), the former of which can be assigned to the NH stretching vibration, remarkably lower than that of the free N–H group (*ca.* 3400 cm⁻¹), whereas the latter is characteristic of an NH deformation vibration of carbohydrozone units.³⁴ This is in accord with a previous report on strong H-bonded urea units.³⁵ Upon a certain pressure, the vibration cannot show obvious change and the resultant H-bonded arrays are less disordered.

To conclude, a pyrenyl-benzohydrazonate molecular platform was prepared and photophysical properties were investigated, which showed unusual ratiometric aggregation-induced emission and mechanochromic luminescence. We proposed a novel strategy for developing pyrenyl-based AlEgens by introducing intermolecular hydrogen bonding in aqueous media to strengthen the π -conjugation structure. The weak emission in DMF solution is stemmed from the pyreny monomer. The strong emission in the presence of water was dominantly attributed to the formation of the intermolecular H-bonding system, thus preventing the rotation of carbohydrozone groups. The excimer structure showed slight disorder upon mechanical grinding, which could be restored by fuming or heating. As an important application, the spectroscopic properties and luminescence color change in the solid state were reversible upon grinding and fuming or heating. We believe that these studies can arrive in a deeper insight into the atypical AIE mechanism and develop rewritable media, pressure sensors and security inks in the future.

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