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Multistimuli-Responsive Luminescence of Naphthalazine Based on Aggregation-Induced Emission

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Stimuli-responsive luminescent materials, which are dependent on changes in physical molecular packing modes, have attracted more and more interest over the past ten years. In this study, 2,2-dihydroxy-1,1-naphthalazine was synthesized and shown to exhibit different fluorescence emission in solution and solid states with characteristic aggregation-induced emission (AIE) properties. A remarkable change in the fluorescence of 2,2-dihydroxy-1,1-naphthalazine occurred upon mechanical grinding, heating, or exposure to solvents. According to the characterization by solid-state fluorescence spectroscopy, X-ray crystallography, differential scanning calorimetry, and X-ray powder diffraction, the fluorescence change could be attributed to transitions between two structurally different polymorphs. These significant properties could also give 2,2-dihydroxy-1,1-naphthalazine more potential applications as a multifunctional material.

Introduction

Stimuli-responsive luminescent materials have attracted more and more interest in the field of luminescent organic solids.[1] Of particular interest are organic molecules that can show a change in fluorescence color induced by external stimuli to the solid state.[2] These organic molecules have potential applications in luminescent switches,[3] mechanosensors,[4] security paper, optoelectronic devices, and data storage.[5] A variety of multistimuli-responsive organic molecules, metal complexes, and multicomponent solids and polymers have been developed recently that can respond to temperature, metal ions, mechanical stress, pH, and solvents.[6] Moreover, there are several design strategies that have provided a better understanding of structure–luminescence relationships.

In recent years, a variety of stimuli-responsive luminescent materials based on aggregation-induced emission (AIE) has received attention in particular because of their excellent piezochromism, thermochromism, and solvatochromism.[7] In addition, stimuli-responsive organic molecules based on have also attracted great attention owing to their fundamental importance and potential application.[7b,c,8] Since the fluorescence color and intensity of these molecules are generally sensitive to the molecular configuration and arrangements in their crystalline state,[7d,e,9] interconversion between crystal polymorphs due to external stimuli such as heat or pressure can be applied to design stimuli-responsive luminescent materials. Besides the previously mentioned design strategies, the construction of well-organized multicomponent materials by assembly of two or more units has recently led to the development of other stimuli-responsive luminescent materials.[10]

Pigment Yellow 101 (2,2-dihydroxy-1,1-naphthalazine) is a commercially available yellow pigment exhibiting fluorescence in the crystalline form. It was first synthesized in 1899 and has been produced industrially for decades. This pigment is widely used for the mass coloration of viscose, for printing inks, and for artists' colors.[11] Although a lot of studies about 2,2-dihydroxy-1,1-naphthalazine have been made in solid- and solution-state fluorescence,[12] 2,2-dihydroxy-1,1-naphthalazine has not been investigated as a stimuli-responsive luminescent material. Herein, we synthesized 2,2-dihydroxy-1,1-naphthalazine and found it exhibits different fluorescence emission in solution and solid states, with characteristic AIE properties. A remarkable change in fluorescence of the dye occurred upon grinding, heating, or exposure to solvents. Powder X-ray diffraction (PXRD) and differential scanning calorimetry (DSC) studies indicated the fluorescence change could be a result of the transition between two structurally different polymorphs. We also report the mechanism of multistimuli-response in the solid state based on crystal structure analysis.

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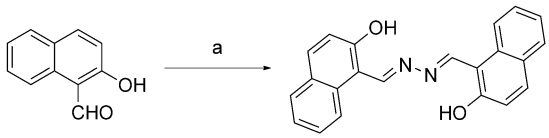
Results and Discussion

AIE properties of the dye molecule in tetrahydrofuran/water

We synthesized 2,2-dihydroxy-1,1-naphthalazine as shown in Scheme 1. We then studied AIE features of the compound in



Scheme 1. Synthesis of 2,2-dihydroxy-1,1-naphthalazine. *Reagents and conditions*: a) 2-hydroxy-1-naphthaldehyde, EtOH, hydrazine hydrate, 60 °C, 2 h, 55 %.

mixtures of tetrahydrofuran (THF) with different water fractions. The dye in pure THF and THF/water mixtures with water fractions lower than 60 % exhibited extremely weak fluorescence signals, while the fluorescence at 535 nm increased dramatically in THF/water mixtures with water fractions from 70 to 80 % (Figure 1 a). We further verified this by observing a 13-fold increase in quantum yield from THF solution ($\Phi_f = 2.5\,\%$) to THF/water with a water fraction of 80 % ($\Phi_f = 32.6\,\%$).

In addition, when illuminated with UV light, solutions of the dye in 80 % water exhibited strong fluorescence compared to that for 10 % water (inset in Figure 1 b). We then investigated THF/water solutions of 2,2-dihydroxy-1,1-naphthalazine by UV/Vis spectroscopy (Figure S1 in the Supporting Information). This fluorescence could be ascribed to a mechanism involving free rotation around N–N and C–C single bonds in good solvents and restricted rotation in poor solvents due to the formation of molecular aggregates.

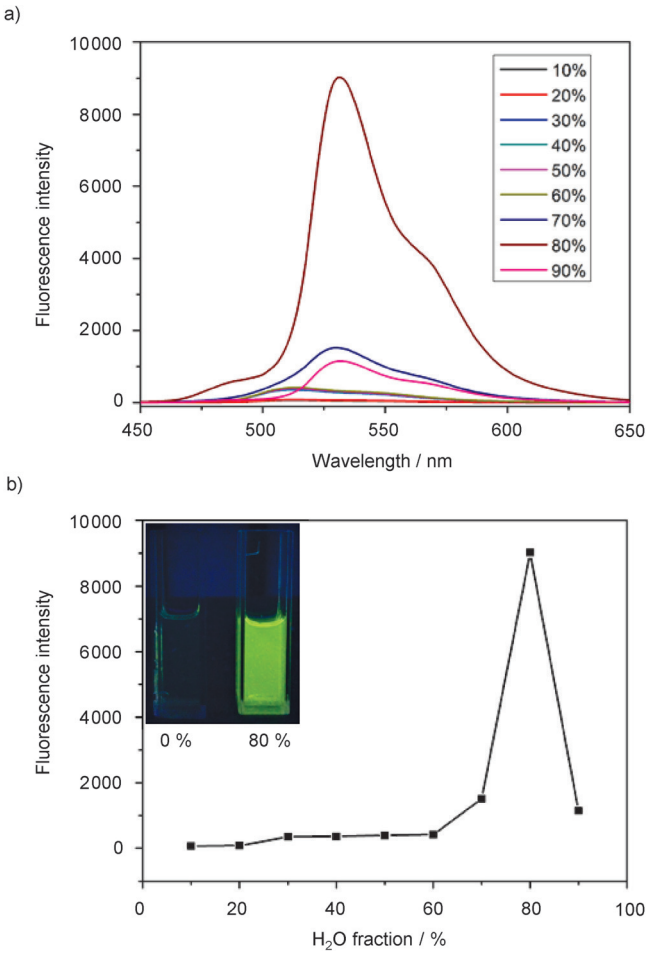


Figure 1. a) Fluorescence spectra of 2,2-dihydroxy-1,1-naphthalazine (10 μM, $\lambda_{ex} = 400$ nm) in THF/water with different water percentages. b) Plot of maximum fluorescence intensity vs. % water. Inset: image of 2,2-dihydroxy-1,1-naphthalazine in THF/water mixtures with 0 % (left) and 80 % water (right) under UV illumination at 365 nm.

Piezofluorochromic and solvatochromic behavior of the dye

Next, we studied solid emission properties of 2,2-dihydroxy-1,1-naphthalazine. While the as-prepared solid powder of 2,2-dihydroxy-1,1-naphthalazine (1-Form) exhibited strong yellow luminescence ($\Phi_f = 31.5\,\%$,) under UV irradiation, after we ground it gently using a spatula or mortar and pestle, it was converted to a green luminescent powder (2-Form, $\Phi_f = 20.2\,\%$). This change occurred only at the pressed area (Figure 2 b). Interestingly, this luminescence change from yellow to green could also be induced upon the addition of some solvents (e.g. THF, 1,4-dioxane) (Figure 2 d). The normalized emission spectra of these two forms of 2,2-dihydroxy-1,1-naphthalazine are shown in Figure 2 a. We observed a hypsochromic shift of 13 nm in the emission spectra from the 1-Form powder ($\lambda_{max} = 543$ nm) to 2-Form powder ($\lambda_{max} = 530$ nm). In addition, upon volatilization of the THF, we obtained dye crystals (3-Form), which also displayed a remarkable change from yellow to green luminescence under UV upon grinding using a mortar & pestle (Figure 2 c). In the emission spectra, we observed a hypsochromic shift of 36 nm from the 3-Form powder ($\lambda_{max} = 566$ nm) to the 2-Form powder ($\lambda_{max} = 530$ nm). In Figure S2 in the Supporting Information, we assign the International Commission on Illumination (CIE 1931) colors for the samples according to the fluorescence color change before and after grinding. 2,2-Dihydroxy-1,1-naphthalazine at various states and conditions was also investigated by UV/Vis spectrophotometry (Figure S3 in the Supporting Information).

Interestingly, while the maximum emission of the 3-Form was a single peak at 566 nm, a second emission peak was detected at 530 nm after it was ground. This remarkable fluorescence change of the 3-Form powder due to characteristic piezochromic effects is more prominent compared to 1-Form.

Thermochromic behavior of the dye

Aside from affecting the fluorescence of 2,2-dihydroxy-1,1-naphthalazine by grinding and changing the solvent, tunable solid-state emission could also be realized through heat stimulus which could affect the mode of molecular packing. We found the transformation from yellow to green luminescence could be realized when the 3-Form was heated to 285 °C to

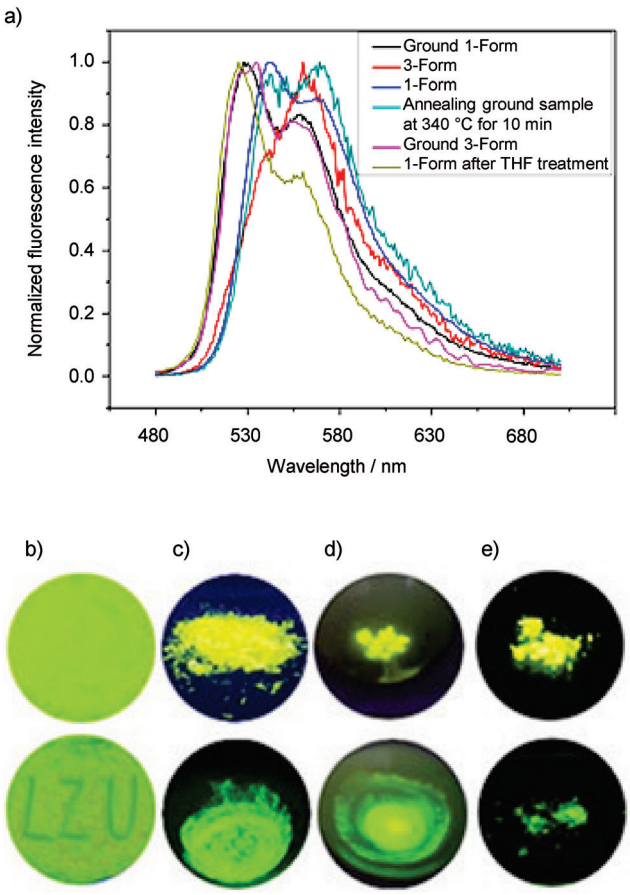


Figure 2. a) The normalized fluorescence spectra of 2,2-dihydroxy-1,1-naphthalazine in various states (Forms 1-3) and conditions; $\lambda_{ex} = 360$ nm. b) Photograph of the 1-Form cast on a filter paper before (top) and after (bottom) writing "LZU" with a metal spatula under UV light ($\lambda_{ex} = 365$ nm). c) Photograph of the unprocessed 3-Form (top) and ground sample (bottom). d) Photograph of the 1-Form before (top) and after THF treatment (bottom). e) Photograph of the 3-Form before (top) and after annealing at 285 °C (bottom) under UV irradiation ($\lambda_{ex} = 365$ nm).

then undergo a slow annealing process. This color change is shown in Figure 2e. Furthermore, the 2-Form could be restored to its initial state (1-Form) upon heating until it melts and then cooling quickly. Normalized emission spectra also verify that the annealing of the 2-Form affords the 1-Form (Figure 2a). Thus, the transformation between the 1-Form and 2-Form is reversible.

To further understand the switching between the three states of 2,2-dihydroxy-1,1-naphthalazine upon thermal treatment, the three forms were then analyzed by differential scanning calorimetry (DSC) (Figure 3). The 3-Form showed a big endothermic peak at 285 °C before the melting point at 320 °C, while for the 1-Form and 2-Form one peak appeared at the melting point of 320 °C. This result implied that the endothermic peak of the 3-Form that emerged at 285 °C was supposed to be a phase transition point, and annealing at this temperature might induce molecular reorganization in the polymorph 2-Form as well.

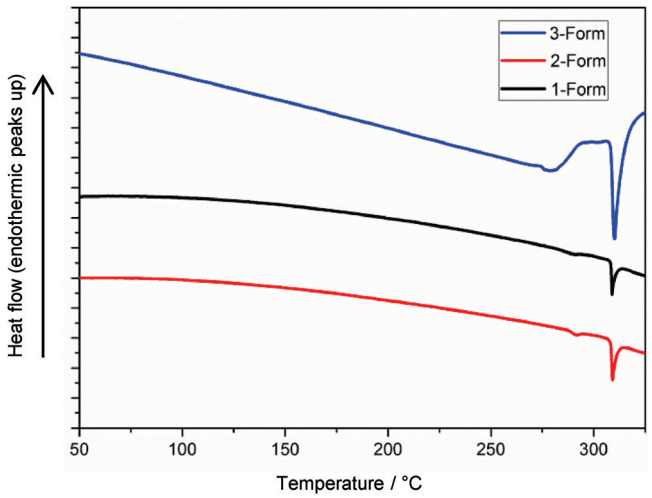


Figure 3. Differential scanning calorimetry curves of the 1-Form, 2-Form, and 3-Form of 2,2-dihydroxy-1,1-naphthalazine.

Powder X-ray diffraction analysis of the dye

To obtain insights into the relationship between 2,2-dihydroxy-1,1-naphthalazine structure and its tunable fluorescence properties, we performed powder X-ray diffraction (PXRD) experiments. The 1-Form and 3-Form clearly exhibited sharp and intense reflections in the their PXRD profiles, which are indicative of microcrystalline structures. However, their PXRD profiles exhibited different diffraction peaks (Figure 4). More importantly, the 2-Form also existed as a crystalline rather than an amorphous powder, which did not display reflection peaks similar to that of the 1-Form and 3-Form. At the same time, the THF-treated 1-Form powder had the same reflection peaks as the ground 3-Form powder. The ground 1-Form powder displayed different reflection peaks compared to the ground 3-Form powder because surplus reflection peaks of the 1-Form still existed. Thus, 2,2-dihydroxy-1,1-naphthalazine has two different polymorphs, namely the 3-Form and the 2-Form. The 1-Form is a combination of the other two. Moreover, fluorescence spectroscopy provided evidence for only two forms ($\lambda_{max} = 530$ nm and $\lambda_{max} = 566$ nm). The tunable fluorescence properties were connected to different molecular arrangements in two polymorphs.

X-ray crystallographic analysis

PXRD experiments revealed two existing polymorphs of 2,2-dihydroxy-1,1-naphthalazine, but did not explain the molecule stacking structure in detail. We therefore carried out X-ray crystallographic analysis. The resolved structures and crystal data are shown in Figure 5 and Figure S5 in the Supporting Information. Firstly, we observed intramolecular hydrogen bonds, which provides a structural basis for high-efficiency AIE properties. Secondly, the molecular packing of 2,2-dihydroxy-1,1-naphthalazine consists certainly of planar molecular sheets driven by the π–π intermolecular interactions which can be used to tune solid-state molecular arrangements. We have

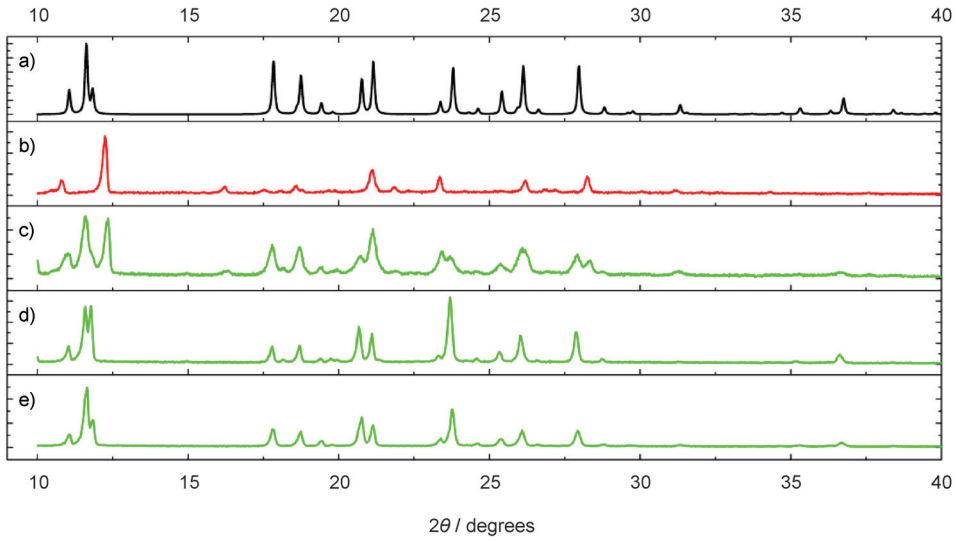


Figure 4. a) Simulated XRD patterns calculated from the crystallographic data of the 3-Form. b) Measured XRD pattern of as-prepared 1-Form solid powder; c) Measured XRD pattern of the 1-Form powder after grinding; d) Measured XRD pattern of the 1-Form powder after treatment with THF; e) Measured XRD pattern of the 3-Form powder after grinding.

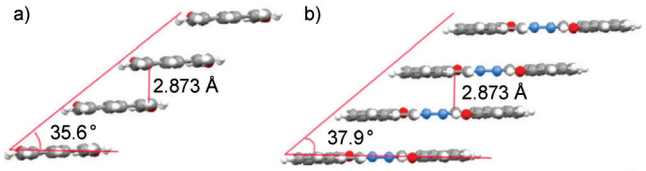


Figure 5. Crystal structure of the 3-Form. a) Side view and illustration of pitch angle and interlayer distance. b) Front view and illustration of roll angle and interlayer distance.

seen that the molecular sheets in the 3-Form crystal were arranged in slip stacks along the short molecular axis with a pitch angle of 35.6°, whereas that along the long molecular axis is 37.9°, as shown in Figure 5. The interlayer distance between the adjacent molecular sheets in the 3-Form crystal is 2.873 Å.

Mechanism of multistimuli response in the solid states

The packing of 2,2-dihydroxy-1,1-naphthalazine consists of planar molecular sheets driven by π–π intermolecular interactions. This kind of molecule tends to form J-type aggregation, H-type aggregation, or a dimer. For 2,2-dihydroxy-1,1-naphthalazine, different slip-stack features form two possible polymorphs. H-type and J-type aggregations correspond to $\theta > 54.7°$ and $\theta < 54.7°$, respectively. Because X-ray crystallographic analysis indicated that the molecular sheets in the 3-Form crystal are arranged in slip stacks along the short molecular axis with a pitch angle of 35.6°, the 3-Form has J-type aggregation, and the other polymorph has H-type aggregation. Tunable fluorescence properties can be affected by the different slip-stack features of the two polymorphs. Moreover, the three crystals showed a decrease in the fluorescence quantum yield (3-Form: 35%, 1-Form: 32%, 2-Form: 20%), which also suggests that π–π stacking interaction is enhanced from 3-Form to 1-Form to 2-Form. Therefore, the different stacking modes in the two polymorphs reasonably result in different molecular aggregation states and thus lead to different fluorescence colors.

Conclusions

We have synthesized 2,2-dihydroxy-1,1-naphthalazine and demonstrated its aggregation-induced emission (AIE) properties. Its fluorescence colors can be switched by grinding, heating, or exposure to solvents (THF/1,4-dioxane). Based on powder X-ray diffraction (PXRD) and differential scanning calorimetry (DSC) experiments, the fluorescence change could be a result of a transition between two structurally different polymorphs. We have also reported the mechanism of multistimuli response in the solid states based on crystal structure analysis. These significant properties could lead to more potential applications for 2,2-dihydroxy-1,1-naphthalazine as a multifunctional material.

Experimental Section

Materials and instruments: 2-hydroxy-1-naphthaldehyde was purchased from Gracia Chengdu Chemical Technology Co., Ltd. (Chengdu, China). All other reagents and solvents were purchased from Tianjin Guangfu Chemical Technology Co., Ltd. (Tianjin, China) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL-ECS-400 MHz spectrometer (Tokyo, Japan). Single-crystal XRD measurements were carried out on a Bruker APEX-II CCD diffractometer (Billerica, USA) operating at 50 KV and 30 mA using Mo K_α radiation ($\lambda = 0.71073$ Å). PXRD patterns were determined with a Rigaku-Dmax 2400 diffractometer (Tokyo, Japan) using Cu K_α radiation over the 2θ range of 10–70°. Steady-state luminescence spectra were measured on an Edinburgh Instruments FSL920 fluorescence spectrometer (Livingston, UK). Quantum yields of the solid-state samples were determined by an absolute method using an integrating sphere 31 (150 mm diameter, $BaSO_4$ coating) on an Edinburgh Instrument FLS920. TGA and DSC experiments were performed on TGA/DSC 1 Mettler-Toledo thermal analyzer (Greifensee, Switzerland) up to 400 °C at a heating rate of 10 °C min^{-1} under an N_2 atmosphere.

2,2-Dihydroxy-1,1-naphthalazine: 2-hydroxy-1-naphthaldehyde (1.72 g, 10 mmol) was dissolved in absolute EtOH (50 mL), followed by addition of 80% hydrazine hydrate (0.31 mL, 5 mmol), and the mixture was heated to 60 °C for 2 h. Precipitates were filtrated and washed with absolute EtOH thrice then dried. Pure 2,2-dihydroxy-1,1-naphthalazine was obtained as a yellow solid powder (1.8 g, 55%); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 12.84$ (s, 2H), 9.96 (s, 2H),

8.61 (d, $J=8.5$ Hz, 2H), 8.00 (d, $J=9.0$ Hz, 2H), 7.88 (d, $J=8.2$ Hz, 2H), 7.58 (t, $J=6.4$ Hz, 2H), 7.41 (t, $J=7.4$ Hz, 2H), 7.25 ppm (d, $J=9.0$ Hz, 2H); ^{13}C NMR (400 MHz, [D$_6$]DMSO): $\delta=100.1$, 109.1, 119.5, 122.3, 124.2, 128.5, 129.2, 132.6, 135.2, 160.4, 161.2 ppm; HRMS-ESI m/z $[M+NH_4]^+$ calcd for $C_{22}H_{20}N_3O_2$: 358.1550, found: 358.1549.

CCDC 1033236 contains the supplementary crystallographic data for the structural X-ray diffraction analysis for 2,2-dihydroxy-1,1-naphthalazine. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk.

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Keywords: aggregation-induced emission · fluorescence · luminescent materials · multistimuli-responsive materials · polymorphs

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