Isostructural Solvates of Naturally Occurring Allocryptopine Exhibit Both Mechanochromic and Hydrochromic Luminescent Properties

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ABSTRACT: We discovered four new solvates for naturally sourced allocryptopine. The new found crystalline forms are isostructural and have similar crystal structures and packing patterns. However, they exhibit obviously different fluorescence appearance. In addition, the acetone solvate SA, N,N-dimethylformamide solvate SD, and tetrahydrofuran solvate ST also present both luminescent mechanochromic and hydrochromic properties.

INTRODUCTION

Solid-state organic compounds exhibiting switchable and variable fluorescence have colossal potential uses in fluorescent switches,1,2 small molecule sensing,3−6 detection of stress,7 and optical devices8 and are attracting more and more attention. Luminescent chromism is the phenomenon that a material presents a major and reversible change in photoluminescence color in response to external stimulation. The external stimulation includes several factors, such as heat, pressure, mechanical force, solvent, water, etc. Among these, the mechanochromism (color changes upon mechanical stimulus) attracted particular attention and more than 500 reports on the materials with mechanochromism have been published so far.10 Up to date, several strategies, such as organic synthesis,11−16 polymorphism,17−21 solvate,22−24 and co-crystal,25−29 have been applied to obtain the luminescent mechanochromic materials. Recently, our group successfully discovered a new naturally occurring and metal-free organic material with both mechanochromism and solvatochromism properties by solid form screening.30,31

Except for the mechanochromism, solvatochromism (color changes upon exposure to different solvents) is another interesting and worthwhile phenomenon. Hydrochromism is a subclass of solvatochromism, referring to the reversible color change of a solid in response to external water molecules. Hydrochromic materials have many applications, such as monitoring the water content of organic solvents,32 detecting humidity,33,34 use as rewritable paper,35 and mapping human sweat pores.36 Over the past decade, the research on luminescent mechanochromism or hydrochromism alone has rapidly grown and several studies have been reported, however, reports on materials that exhibit both luminescent mechanochromism and hydrochromism are still rare.

Allocryptopine (ALP, Scheme 1) is one of the protopinetype alkaloids and has been isolated from several plants (Papaveraceae, Fumariaceae, Ranunculaceae, and Rutaceae). It plays an important role in plant defense mechanisms against biotic stress and has a number of biological effects in mammals.37 Two crystalline forms (α and β) of ALP have been reported.38,39 Its fluorescence properties in aqueous and organic solutions were also studied by Kubala, etc.40 However, the luminescent chromic property of ALP solid state has not been fully studied yet.

In this work, we performed a comprehensive solid-state screening on ALP. Four different solvates were uncovered (acetone solvate SA, tetrahydrofuran (THF) solvate ST, N,N-dimethylformamide (DMF) solvate SD, and hydrate HG), and the single crystal structures, physicochemical properties were...
fully characterized. Interestingly, these crystals exhibit similar crystal structures and packing patterns. In addition, both mechano- and solvatochromism were observed among various crystalline forms.

**RESULTS AND DISCUSSION**

To discover suitable luminescent chromic crystals, comprehensive crystallization screening experiments were conducted with a variety of solvents and crystallization methods. Four different crystalline forms of ALP were obtained. Acetone solvate SA, THF solvate ST, and N,N-dimethylformamide solvate SD could all be prepared by slow evaporation or slurrying in ALP acetone, tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) solutions, respectively. Hydrate HG could be obtained by vacuum-drying the acetone solvate SA, THF solvate ST, and DMF solvate SD and then keeping them under high relative humidity (RH) condition (>90%). The obtained crystallized samples were fully characterized by X-ray powder diffraction (XRPD) analysis (Figure 1). The results show that all solvates and hydrates exhibit similar XRPD patterns, indicating they are isostructural solvates. In addition, the experimental XRPD data of these solvates were in accordance with their single-crystal stimulated ones from their corresponding single-crystal structures. Fourier-transform infrared (FTIR) spectroscopy was also used to distinguish these four isomorphic crystals. As shown in Figure S1, THF solvate ST and hydrate HG present very similar FTIR spectra and crystalline forms SA and SD exhibit distinct IR curves. Different from ST and HG, acetone solvate SA and DMF solvate SD show obvious signals for carbonyl C=O stretching vibration corresponding (1712 cm\(^{-1}\) for SA and 1681 cm\(^{-1}\) for SD) to the carbonyl group in their contained solvent acetone and DMF molecules.

The stability of ALP crystalline forms was assessed by detailed thermal analyses (Figure S2). Apparent one-step water mass loss could be seen in the thermogravimetric analysis (TGA) thermogram, and the weight loss results were determined as 7.6, 9.3, 9.2, and 4.3% for acetone solvate SA, THF solvate ST, DMF solvate SD, and hydrate HG, respectively. The water content of HG was redetermined by the Karl Fischer (KF, 4.5%) method. Accordingly, the three solvates could be assigned as hemi-acetone (calculated 7.3%), hemi-DMF (calculated 9.0%), and hemi-THF (calculated 8.8%) solvates, with monohydrate (calculated 4.6%). In addition, the solvent stoichiometry of acetone solvate SA, THF solvate ST, and DMF solvate SD was further confirmed by single-crystal X-ray diffraction (SCXRD). The differential scanning calorimetry (DSC) curves revealed a wide endothermic peak for the solvent release for each crystal. The DSC endotherm signals also echoed the weight loss steps in the TGA diagrams.

Fluorescent color differences among ALP crystals were characterized by solid-state fluorescent spectra (SFS) analysis (Figure 2). The different colors and maximum emission wavelengths were exhibited in ALP solvates’ SFS diagrams. Under UV excitation (\(\lambda_{\text{ex}} = 365\) nm), THF solvate ST had a violet color and exhibited a photoluminescence peak at 444 nm. Acetone solvate SA and DMF solvate SD presented similar maximum emission wavelengths (452.8 nm for SA and 451.4 nm for SD). However, they showed obviously different emission appearances: SA had a wathet blue tint, and SD exhibited a royal blue color. Among the four crystalline forms, the hydrate HG had the longest emission wavelength (491 nm) and it presented a green appearance. The solid-state UV−vis absorption characteristics of these materials are plotted in Figure 3. The four solvates show differences in \(\lambda_{\text{max}}\) (310 nm...
for hydrate HG, 312 nm for acetone solvate SA, 217 and 317 nm for DMF solvate SD, and 304 nm for THF solvate ST). Interestingly, different from the other three crystals, SD presents one more peak at 217 nm, corresponding to the absorption of the included solvent DMF.

To obtain insight into the emission mechanism of ALP, we prepared and analyzed single crystals of acetone solvate SA, THF solvate ST, and DMF solvate SD. The crystallographic data of these crystalline forms are summarized in Table 1. These solvates have similar unit cell parameters. They crystallize in both $P2_1/n$ space group monoclinic system. The difference is in the angles (109.686(2) for SA, 110.100(5) for SD, and 111.1380(10) for ST, respectively). The crystal structure analysis shows that the three crystals present similar packing patterns (Figure 4), confirming that they are isostructural. In addition, in all three solvates, there is no hydrogen bond among ALP molecules (Figure S3). The main intermolecular interactions are $\pi-\pi$ interactions. The $\pi-\pi$ interactions in acetone solvate SA, THF solvate ST, and DMF solvate SD are shown in Figure 4. Between the two neighboring ALP molecules, the centroid-to-plane and centroid-to-centroid distances are 5.103 and 3.474 Å in SA, 5.100 and 3.513 Å in SD, and 5.202 and 3.491 Å in ST, respectively. The three crystalline forms present similar centroid-to-plane distances. SA and SD also exhibit nearly identical centroid-to-centroid distances. Hence, SA and SD have similar maximum emission wavelengths. In comparison, ST has the longest centroid-to-centroid distance, indicating that ALP molecules in ST pack less compactly and have weaker $\pi-\pi$ interactions. It was well known that crystal phases with stronger $\pi-\pi$ interactions show maximum emission at a longer wavelength region, whereas those with relatively weaker $\pi-\pi$ interactions exhibit maximum emission at a shorter wavelength region. As a result, ST exhibits the shortest maximum emission wavelength.

The electronic structures of acetone solvate SA, THF solvate ST, and DMF solvate SD are theoretically calculated by density functional theory (DFT). The single-crystal structure data was used for calculation without any structural optimization. The

| Table 1. Crystallographic Data for Solvates of ALP |
|-----------------------------------------------|
| **SD** | **SA** | **ST** |
| **empirical formula** | $C_{45}H_{46}N_3O_{11}$ | $C_{45}H_{46}N_2O_{11}$ | $C_{46}H_{46}N_2O_{11}$ |
| **crystal system** | monoclinic | monoclinic | monoclinic |
| **space group** | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| a (Å) | 10.6658(19) | 10.5721(11) | 10.8577(2) |
| b (Å) | 14.335(3) | 14.2791(15) | 14.2462(3) |
| c (Å) | 13.962(3) | 13.9602(16) | 13.9180(3) |
| α (deg) | 90 | 90 | 90 |
| β (deg) | 110.100(5) | 109.686(2) | 111.1380(10) |
| γ (deg) | 90 | 90 | 90 |
| V (Å³) | 2004.7(7) | 1984.3(4) | 2007.99(7) |
| D (g·cm⁻³) | 1.333 | 1.324 | 1.328 |
| Z | 2 | 2 | 2 |
| T (K) | 296.15 | 173 | 173 |
| wR | 0.1414 | 0.1362 | 0.1325 |
| R wR | 0.0940 | 0.0457 | 0.0264 |
| GoF | 0.935 | 1.022 | 1.077 |
| CCDC number | 1818855 | 1818853 | 1818854 |

Figure 4. Packing patterns (left) and $\pi-\pi$ interactions (right) for ALP solvates.
roles between ALP and its neighboring solvent molecules were demonstrated by importing all molecules in the unit cell. Figure 5 illustrates the representative molecular orbital amplitude plots of the three crystalline forms and gives all electronic structures for comparison. The highest occupied molecular orbitals (HOMOs) of solvate SD are fully located within the solvent DMF molecules, and the HOMOs of solvates SA and ST are fully located within the ALP molecules. The lowest unoccupied molecular orbitals (LUMOs) of SD and ST are both distributed on the solvents DMF and THF molecules, respectively. In comparison, the LUMOs of crystal SA are also mainly located within its included solvent acetone molecules. The difference is that, for SA, there are few LUMOs located within the ALP molecules. The theoretical band gaps for SD, SA, and ST are 0.22, 0.48, and 0.52 eV, respectively. The lowest band gap in SD suggests the longest emission wavelength, and the highest band gap in ST suggests the shortest emission wavelength.

Interestingly, it could be found that the emission behavior of the four solvates has something to do with the polarities of their included solvents. The polarity trend of the four included solvents is water > DMF > acetone > THF, and the trend of the emission wavelength is hydrate HG > DMF solvate SD > acetone solvate SA > THF solvate ST. Obviously, the emission colors were bathochromically shifted with the solvent polarity increasing. The bathochromic shift implied the existence of the intramolecular charge-transfer state. Such conclusion is consistent with the calculation results.

Mechanochromism and Hydrochromism. To study the luminescent mechanochromic properties of the four crystalline forms, all solvates were ground by a ball mill and the results are presented in Figure 6. The results show that, after grinding, the acetone solvate SA, DMF solvate SD, and THF solvate ST exhibit prominent mechanochromism. For example, the emission color of violet ST gradually turned cyan as the milling time went on. The mechanochromic processes were also verified by the solid-state fluorescent spectra (Figure S4). Upon grinding, the maximum emission wavelength $\lambda_{\text{em, max}}$ of ST is bathochromically shifted to about 471.2 nm and the corresponding $\Delta\lambda_{\text{em, max}}$ is 27.2 nm. Interestingly, after grinding, the other two solvates SA and SD also changed to cyan AmS. All three luminescent mechanochromic processes are reversible. The obtained blue green AmS could be converted back to SA, SD, and ST by slurrying in acetone, DMF and THF, respectively. In comparison, the hydrate HG only shows little changes of its photoluminescence color upon grinding. Its
emission color was changed from green to pale green. In addition, this process is irreversible and the obtained pale green AmH could not be transformed to HG by slurrying.

To gain insights into the mechanism for the mechanochromism, X-ray powder diffraction (XRPD) analysis of the four crystalline forms was conducted before and after milling. The results indicated that the mechanochromism is based on crystalline-to-amorphous phase transitions. The XRPD pattern of powdered samples of the four crystals showed intense diffraction peaks (Figure S5). In contrast, the XRPD analyses of the ground powders revealed featureless patterns, indicating the presence of an amorphous phase. The crystallinity of the amorphous state could be largely improved by the reverting back processes discussed above, accompanied with the emergence of similar sharp diffraction peaks and different emission colors, lending evidence to the presumption that the changing of the included solvents raised the different emission properties.

Luminescent hydrochromic properties of the discovered crystalline forms were investigated by treatment with water under various conditions. The results show that acetone solvate SA, THF solvate ST, and DMF solvate SD all exhibit obviously luminescent hydrochromic properties. For example, exposure of blue powder SD to water vapor causes obvious color changes. After 10 min, part of SD on the periphery was quickly converted to white and nearly all of the SD powder could be transformed to white by fuming with water vapor for 3 h (Figure 7). This white powder could be finally transited to green after 3 days by keeping in the water vapor. To understand the mechanism for this hydrochromism, the transition process was also checked by XRPD and FTIR (Figures S6 and S7). The results show that, during this conversion, the XRPD of SD remained unchanged. For FTIR, the peak of O–H stretching vibration at 3150–3700 cm⁻¹ gradually turned stronger as the steaming time went on, indicating the growing of water content. Meanwhile, the peak at 1712 cm⁻¹ corresponding to the carbonyl group on DMF molecule remained. Similar XRPD patterns and microchanged FTIR spectra before and after hydration clearly reveal that the emission color changes induced by water treatment result from alterations of the water contents. The other two solvates SA and ST could be converted to green hydrate HG (Figure S8) as well. These conversions are reversible, and the obtained green HG could be reconverted back to SA, SD, and ST by slurrying in acetone, DMF, and THF, respectively.

CONCLUSIONS

In conclusion, three new solvates and one hydrate of natural sourced alkaloid allocryptopine were discovered by comprehensive crystallization screening experiments with a variety of solvents and crystallization methods. The four crystalline forms show similar XRPD patterns, indicating that they are isostructural related. The crystal structures of the three solvates are disclosed by SCXRD, and the data analysis show that they have similar unit cell parameters and packing patterns. The luminescent properties of these four isostructural crystals were investigated under UV irradiation. These isomorphous crystalline forms exhibit significantly different fluorescent colors: acetone solvate SA is wathet blue, DMF solvate SD is royal blue, THF solvate ST is violet, and hydrate HG presents a green color. Finally, the luminescent chromism for these solids was studied and the three solvates exhibit both mechanochromism and hydrochromism properties.

EXPERIMENTAL SECTION

Materials. The raw material of allocryptopine used in the present study was obtained from Micolta Bioresource Company, with 98% purity. The used solvents were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd.

Preparation of SA. SA was prepared by slurrying the raw material of allocryptopine (ALP) in acetone at room temperature. SA also could be obtained by slow evaporation from ALP acetone solution.

Preparation of SD. SD was prepared by slurrying the raw material of allocryptopine (ALP) in N,N-dimethylformamide (DMF) at room temperature. SD also could be obtained by slow evaporation from ALP DMF solution.

Preparation of ST. ST was prepared by slurrying the raw material of allocryptopine (ALP) in tetrahydrofuran (THF) at room temperature. ST also could be obtained by slow evaporation from ALP THF solution.

Preparation of HG. Hydrate HG could be obtained by vacuum-drying the solvates SA, ST, and SD and then keeping them under high relative humidity condition.

Thermal Analysis. Differential scanning calorimetry (DSC) was performed on a PerkinElmer DSC 8500 module, and thermogravimetric analysis (TGA) was carried out using a Netzsch TG 209F3 equipment. Samples were placed in open alumina pans for the TG experiments and in airtight aluminum sample pans for DSC experiments. For both DSC and TGA experiments, the sample size is 3–5 mg, the heating rate is 10 K/min, and the N₂ flow is 10 mL/min.

Single-Crystal X-ray Diffraction (SCXRD). A Bruker Smart Apex II diffractometer was used to collect single-crystal X-ray diffraction data using graphite monochromator Mo Kα radiation (λ = 0.71073 Å). The SANT program was used to integrate and scale the intensity data. The structures were solved by direct methods and refined by full matrix least-squares on F². All nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropically. Hydrogen atoms on nitrogen and oxygen atoms were located from difference electron density maps. Hydrogen atoms on carbon atoms were fixed by calculation.

X-ray Powder Diffraction (XRPD). A Bruker D8-ADVANCE X-ray diffractometer was used to recorded the XRPD patterns using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA power. XRPD patterns were collected under
ambient conditions over the 2θ range 3–40° at a scan rate of 15° min⁻¹.

Polarizing Microscopy (PLM). A XPV-400E polarizing microscope was used to record the PLM pictures using a JVC TK-C9201 EC digital video recorder. A XPH-300 hot stage was used to heat the samples.

Solid-State Fluorescent Spectra (SFS). A Hitachi F-7000 fluorescence spectrophotometer was used to collect the SFS data using a 650-0161 solid sample holder. The SFS experiments were performed with a scan speed of 240 nm min⁻¹. The emission and excitation slits were 5 nm.

Water Content Determination. The water contents of the three hydrates and their corresponding amorphous states were determined by a Mettler Toledo C20 Coulometric KF Titritator.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01267.

X-ray crystallographic data (CCDC number), PXRD, TGA, DSC, SFS, and hydrochromism (CIF)(CIF)(CIF)

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Notes

The authors declare no competing financial interest.

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