Methanol-induced luminescence vapochromism based on a Sb^{3+} -doped organic indium halide hybrid

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ABSTRACT Ion doping has been demonstrated as a practical approach to achieving highly efficient luminescence in both inorganic phosphors and organic-inorganic hybrids. The as-formed doping species show great potential in optoelectronic applications due to their high photoluminescence quantum yield (PLQY) and excellent stability. Herein, we report highly emissive Sb^{3+} -doped indium halides $(\text{C}_6\text{H}_{18}\text{N}_2)\text{InCl}_5\cdot\text{H}_2\text{O}:\text{Sb}$ ($\text{C}_6\text{H}_{18}\text{N}_2^{2+} = N,N,N',N'$ -tetramethylethane-1,2-diammonium) prepared by solution evaporation methods with an emission that peaked at 565 nm and a PLQY of 74.6%. Photophysical characterizations and density functional theory computational studies verify the broadband emission originating from a self-trapped exciton. Interestingly, a drastic red shift of the emission peak from 565 to 663 nm with yellow luminescence turning to red is observed once the $(\text{C}_6\text{H}_{18}\text{N}_2)\text{InCl}_5\cdot\text{H}_2\text{O}:\text{Sb}$ hybrid is exposed to methanol vapor. Moreover, when the methanol-exposed hybrid is put in air, the emission reverts to 565 nm in several minutes. Single-crystal X-ray diffraction studies show a subsequent structure distortion upon the coordination of methanol to the $\text{Sb}(\text{III})$ center, which is responsible for the drastic red shift of the emission. Encouragingly, we found that $(\text{C}_6\text{H}_{18}\text{N}_2)\text{InCl}_5\cdot\text{H}_2\text{O}:\text{Sb}$ exhibits a specific response to methanol vapor after screening a series of volatile organic compounds with different polarities. Besides, a negligible change of the emission intensity is observed after several cycles of uptaking and releasing methanol. The high fatigue resistance and specific solvent response of the Sb^{3+} -doped indium halide make it a very promising methanol detector.

Keywords: organic metal halide hybrid, Sb^{3+} doped, self-trapped exciton emission, luminescence vapochromism

INTRODUCTION

Low-dimensional, lead-free metal halide hybrids are receiving more and more attention due to their low toxicity and high stability, along with excellent optical properties [1–4]. Particularly, as isolated metal halide anionic species surrounded by organic cations to form periodical host-guest structures, zero-dimensional (0D) organic metal halide hybrids (OMHHs) provide an excellent platform to exhibit intrinsic properties of metal halide species with little or without interactions between adja-

cent species [5–13]. The reported 0D hybrids exhibit diverse topologies from octahedron to pyramidal [14], seesaw structure [15], and linear and triangular trimer clusters [16–18] with tunable emissions covering the entire visible spectrum from blue to green, yellow, orange, red, and even the near-infrared region [7,17,19–24]. The optoelectronic applications based on 0D hybrids are extended from light-emitting diodes (LEDs) [25–28] to scintillators [29–31], thermography, and sensors [32,33].

Ionic doping with rare-earth ions (such as Eu^{3+} and Tb^{3+}), Bi^{3+} , Cu^+ , and Mn^{2+} has been an efficient approach to enhance the photophysical properties without modifying the crystal structures in many perovskite nanocrystals [34–38]. This strategy is also reliable for low-dimensional metal halides, especially for the 0D metal halides [20,39]. Among the active ion doping procedures, Sb^{3+} doping has been the most explored and effective approach to tune photoluminescence (PL) and enhance emission intensity [22,40–45]. For instance, the PL intensity of $\text{Rb}_2\text{InCl}_5(\text{H}_2\text{O})$ was relatively weak with a PL quantum yield (PLQY) of ~1.5%, but a dramatic enhancement was observed with the PLQY boosting to 90% upon Sb^{3+} doping [43]. Moreover, PL tuning was realized by regulating the Sb^{3+} doping concentration to 0D $(\text{C}_9\text{NH}_{20})_9[\text{Pb}_3\text{Cl}_{11}](\text{ZnCl}_4)_2$ with the emission red-shifted from green to yellow and finally to orange [44]. In addition, white emission and even near-infrared emission were achieved by Sb^{3+} doping [22,42]. Due to the highly efficient emission, related optoelectronic devices have been demonstrated as down-conversion LEDs [41]. Nevertheless, the investigation regarding the application of Sb^{3+} doping hybrids as vapor-sensitive sensing materials is still in its infancy to the best of our knowledge [40].

Herein, we report a highly emissive Sb -doped OMHH, $(\text{C}_6\text{H}_{18}\text{N}_2)\text{InCl}_5\cdot\text{H}_2\text{O}:\text{Sb}$ (**H1**, $\text{C}_6\text{H}_{18}\text{N}_2^{2+} = N,N,N',N'$ -tetramethylethane-1,2-diammonium), which exhibits a broad yellow emission with a peak of 565 nm, a PLQY of 74.6% and a lifetime of 3.07 μs . Excitation-dependent PL, power density-dependent PL, and transient absorption (TA) demonstrate a self-trapped exciton (STE) feature of the broadband emission. Density functional theory (DFT) study in the ground and excited states of the center shows that a large structural distortion occurs after photoexcitation, further confirming the nature of STE emission. Interestingly, **H1** undergoes a drastic red shift of the emission from 565 to 663 nm with the conversion of yellow to red luminescence upon exposure to methanol vapor. To figure out

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the mechanism of reversible luminescence vapochromism, single crystals of $(\text{C}_6\text{H}_{18}\text{N}_2)\text{InCl}_5(\text{MeOH})\cdot\text{H}_2\text{O}\cdot\text{Sb}$ (**H2**) were successfully obtained, which exhibit dual emission bands that peaked at 490 and 663 nm with a PLQY of 1.6%. The high-energy band originates from organic cations, and the low-energy band is ascribed to triplet state decay of the $\text{InCl}_5(\text{MeOH})$ centers. The same emission behavior between methanol-exposed **H1** and **H2** indicates that the uptake and release of methanol in the InCl_5 centers are responsible for the reversible luminescence vapochromism. Encouragingly, the hybrid **H1** shows a specific response to methanol vapor after screening a series of volatile organic compounds (VOCs) with different polarities such as methanol, ethanol, acetone, dichloromethane (DCM), dimethylformamide (DMF), and dimethylsulfoxide (DMSO). **H1** demonstrates excellent fatigue resistance based on monitoring the change in PL intensity, which shows a negligible variation after several cycles of methanol uptake and release.

EXPERIMENTAL SECTION

Reagents

Antimony acetate ($\text{Sb}(\text{OAc})_3$, 97%) was purchased from Macklin Reagent Co., Ltd. Indium oxide (In_2O_3 , 99.99%) and N,N,N',N' -tetramethylethylenediamine ($\text{C}_6\text{H}_{16}\text{N}_2$, 99.9%) were purchased from Adamas Reagent Co., Ltd. Hydrochloric acid (HCl, 36%–38% in water by weight), methanol, ethanol, acetonitrile (MeCN), acetone, DCM, chloroform, *n*-hexane, DMF, and DMSO were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All reagents and solvents were used without further purification.

Synthesis

For the synthesis of **H1**, 0.19 mmol $\text{Sb}(\text{OAc})_3$, 0.86 mmol In_2O_3 , and 2.87 mmol $\text{C}_6\text{H}_{16}\text{N}_2$ were put into a 50-mL round-bottom flask equipped with a reflux condenser. Then, 2 mL HCl and 6 mL methanol were added. The precursor was dissolved completely and the solution became transparent after heating at 120°C for 2 h. After cooling to room temperature, the crude product was exposed in the beaker and evaporated naturally for three days, giving colorless crystals. The crystals were washed with methanol and diethyl ether for two times for further use. The synthesis of **H2** was similar to that of **H1** except the cooling process. The colorless crystals of **H2** were obtained by slowly cooling down the precursor solution. The cooling rate was controlled at around 1°C min^{−1} by manually adjusting the heating controller by 5°C every five minutes until to room temperature. This process was completed within 2 h, during which **H2** was generated on the bottle wall. It should be noted that the **H2** should be took out within 2 h and wrapped with dust-free tissue for further use as it would gradually re-dissolve in the mother liquor. Besides, the obtained **H2** should not be purified with other solvents, as it would transform into **H1** once the methanol was dissociated from **H2**.

Characterizations

Single-crystal X-ray diffraction (SCXRD) data of all compounds were recorded using Bruker D8 ADVANCE with a graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. The structure was solved by the direct method using a SHELXL-97 program. Powder XRD (PXRD) patterns were recorded using Rigaku MiniFlex 600 with a Cu-K α ($\lambda = 1.54184$ Å) radiation in

the range of 5°–50° at a scan rate of 5° min^{−1}. PL properties, including emission and excitation spectra in solid state at room temperature, were measured on an FLS920 Edinburgh fluorescence spectrometer. In addition, PL quantum efficiency measurements were performed using the same light source with an additional integrating sphere. Time-resolved emission data were recorded at room temperature using the FLS920 spectrofluorometer. The dynamics of emission decay were monitored using the time-correlated single-photon counting capability of FLS920 (1024 channels, 50- μs window) with data collection for 10,000 counts. Excitation was provided by an Edinburgh EPL-375 picosecond pulsed diode laser. Ultraviolet-visible (UV-Vis) absorption spectra were obtained using a PerkinElmer LAMBDA 950 UV-Vis spectrophotometer using BaSO_4 powder as a reflectance reference. The absorption spectra were obtained using powders from single crystals. Elemental analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out through a HORIBA Jobin Yvon ULTIMA2 instrument. Femtosecond pump-probe TA measurements were performed on a HELIOS (Ultrafast systems) spectrometer using a regeneratively amplified femtosecond CaF_2 crystal laser system (Spitfire Pro-F1KXP, Spectra-Physics; frequency, 1 kHz; max pulse energy, ~4 mJ; pulse width, 120 fs).

Computational methods

To explore the geometrical structure variation between the ground state (G0) and the lowest-energy triplet state (T1), structural optimization was implemented in a Gaussian 16 program package for SbCl_5^{2-} . The geometrical structures of SbCl_5^{2-} in the G0 and T1 states as isolated molecules were optimized by restricted and unrestricted DFT methods, respectively, with the gradient-corrected correlation functional PBE1PBE. During the optimization process, the convergent values of maximum force, root-mean-square (RMS) force, maximum displacement, and RMS displacement were set by default. In the calculations, the Stuttgart-Dresden basis set and the effective core potentials were used to describe the Sb atom, whereas the Cl atom was described by the all-electron basis set of 6-311 + G*. The optimized structures were proved to be the minimal point in the potential energy surface by the number of imaginary frequencies (Nima = 0).

RESULTS AND DISCUSSION

Structural characterizations

The single crystals of **H1** were synthesized by slowly evaporating a hot mixed solution of methanol and HCl containing $\text{Sb}(\text{OAc})_3$, In_2O_3 , and $\text{C}_6\text{H}_{16}\text{N}_2$ in a 1:4.5:15 molar ratio. The crystal structure was determined by SCXRD. As shown in Fig. 1a, b, **H1** crystallized in the *P*-1 space group with the In(III) center bonded to five Cl atoms to form a square pyramidal geometry. Each anionic complex of $[\text{InCl}_5]^{2-}$ is spatially isolated by one $\text{C}_6\text{H}_{18}\text{N}_2^{2+}$ and one water molecule to show a typical 0D structure. It should be mentioned that the organic part is disordered in structure. Details of the SCXRD data are listed in Tables S1 and S2. The PXRD patterns match well with the simulated patterns from SCXRD, confirming the high phase purity of **H1** (Fig. 1c). To further obtain the actual contents of In and Sb, ICP-OES was conducted. The results shown in Table S3 reveal that both In and Sb were found in the hybrid, and the actual ratio is close to the feed ratio.

Luminescence characteristics and mechanism

Photophysical properties were investigated using UV-Vis absorption spectra and steady-state PL. As shown in Fig. 2a, **H1** exhibits an intense absorption band at approximately 220 nm and moderate-intensity bands at 290 to 400 nm, which are tailing to 550 nm. The absorption profile of **H1** is in accordance with that of the previously reported $\text{Rb}_2\text{InCl}_5(\text{H}_2\text{O})$ and $\text{InCl}_6(\text{C}_4\text{H}_{10}\text{SN})_4\cdot\text{Cl}:\text{Sb}^{3+}$ [40,43]. Besides, it almost overlapped with the excitation spectrum in the low-energy region. Hybrid **H1** exhibits bright yellow emission upon UV light irradiation, with an emission peak at 565 nm and a PLQY of 74.6%. The decay lifetime is determined as 3.07 μs with the feature of triplet state decay, similar to that of the previously reported Sb-based or In-based 0D OIMHs (Fig. S1) [40]. Furthermore, a large Stokes shift of 238 nm and full width at half maximum of 141 nm were observed. Long-lived luminescence and broad emission band along with a large Stokes shift indicate the nature of STE emission.

To further validate the emission behavior of STEs, the dependence of luminescence on the excitation wavelength and excitation power density was investigated. As shown in Fig. S2, the emission peak remains unchanged with the excitation wavelength varying from 280 to 360 nm, implying that only one excited state is responsible for the emission. Moreover, the emission intensity shows a linear dependence with the excitation power density, thus ruling out defect-induced emission (Fig. 2b). Furthermore, a femtosecond TA spectrum of **H1** was obtained as direct evidence of STEs.

As shown in Fig. 2c, a broad positive photoinduced absorption is observed across the probe region (480–670 nm), providing direct evidence that STEs are responsible for the yellow emission. It should be mentioned that the absorption peak at 600 nm results from frequency doubling of excitation wavelength at 300 nm. The DFT study on the SbCl_5 center was performed in both the ground and excited states. As depicted in Fig. S3, the structure in the excited state shows an obvious distortion com-

Figure 1 (a) Crystal packing pattern of **H1**. (b) A perspective view of **H1**, showing an organic cation, In(III) coordination anion, and solvate H_2O . (c) Measured and simulated PXRD patterns of **H1**.

Figure 2 (a) Absorption, excitation, and emission spectra of **H1**. (b) Change in PL intensity of **H1** under different excitation power densities. (c) Pseudocolor TA plot of **H1** upon excitation at 300 nm. (d) Proposed luminescent mechanism of **H1**.

pared with that in the ground state, which is easily identified from the bond lengths and bond angles listed in Table S4.

Methanol detection and analysis

Interestingly, the yellow emission of **H1** turned into weak red emission upon its exposure to methanol vapor for several minutes (Fig. 3a). As shown in Fig. S4, the red-emissive powder exhibits distinct diffraction patterns in comparison with **H1**, suggesting the formation of a new phase after absorbing methanol. More interestingly, the red emission could return back to yellow once methanol vapor was removed. The recovered yellow powder shows the same diffraction patterns as **H1** (Fig. S5), indicating the same phase as that of **H1**. The changes of the emission bands during the transformation were also monitored, as shown in Fig. 3b. The hybrid **H1** shows a strong emission peak at 565 nm with a PLQY of 74.6%, which progressively reduced upon exposure of **H1** to methanol vapor. Meanwhile, a new weak emission emerged at 663 nm with a PLQY of 1.6%. Upon methanol vapor removal, the emission at 565 nm reemerged in several minutes with a PLQY of 74.0%. Therefore, a solvent-induced structural transformation is most likely responsible for the reversible luminescence vapochromism.

To validate the solvent-induced structural transformation, the crystals were grown by slowly cooling down the preheated mixed solution of methanol and HCl containing $\text{Sb}(\text{OAc})_3$, In_2O_3 , and $\text{C}_6\text{H}_{16}\text{N}_2$ in a 1:4.5:15 ratio. The obtained needlelike colorless crystals were demonstrated to be methanol-bound species with the formula $(\text{C}_6\text{H}_{18}\text{N}_2)\text{InCl}_5(\text{MeOH})\cdot\text{H}_2\text{O}\cdot\text{Sb}$ (**H2**) by X-ray crystallography. As shown in Fig. S6, the structure displays a distorted octahedral configuration with a space group of $P2_1/m$, where the In atom is coordinated with five Cl atoms and a methanol molecule to give a $[\text{In}(\text{Sb})\text{Cl}_5\text{OMe}]^{2-}$ octahedral geometry. The crystallographic data and selected bond parameters of **H2** are listed in Tables S1 and S2, respectively. As revealed by the PXRD measurements, **H2** displays the same diffraction patterns as those of red-emissive powder, indicating that both have similar structures (Fig. S5). Moreover, **H2** exhibits the same emission as that of methanol-exposed **H1**, with dual emission bands peaking at 490 nm (weak) and 663 nm (strong) and the decay life times of the two peaks are 0.42 ns and 1.75 μs , respectively, further demonstrating their structural similarity (Figs S7–S9). It should be mentioned that a high-energy emission band at 490 nm results most probably from the organic

cation $\text{C}_6\text{H}_{18}\text{N}_2^{2+}$ as the precursor $\text{C}_6\text{H}_{18}\text{N}_2\text{Cl}_2$ (Figs S8, S10, S11) shows a similar emission band with a comparable lifetime. To get insight on the drastic red shift of the emission once methanol was bound to **H1**, the distortion degrees of bond lengths (Δd) and angles (σ^2) were evaluated for $[\text{InCl}_5]^{2-}$ and $[\text{InCl}_5\text{OMe}]^{2-}$ using Equations (1–4), where d_n is the length of $\text{In}(\text{Sb})\text{--Cl}$ and $\text{In}(\text{Sb})\text{--O}$ bonds, d is the average bond length, and θ_n is the bond angle of coordination geometry around the $\text{In}(\text{III})$ or $\text{Sb}(\text{III})$ center. As shown in Table S5, both Δd and σ^2 of $[\text{InCl}_5\text{OMe}]^{2-}$ are significantly larger than those of $[\text{InCl}_5]^{2-}$. Since the distortion degree is highly increased after methanol coordination to the $\text{In}(\text{III})$ center, it is reasonable that such a large structural distortion results in a drastic red shift with the emission conversion of **H1** to **H2**.

$$\sigma^2 = \frac{1}{11} \sum_{n=1}^{12} (\theta_n - 90^\circ)^2 \text{ (Six coordination),} \quad (1)$$

$$\sigma^2 = \frac{1}{7} \sum_{n=1}^8 (\theta_n - 90^\circ)^2 \text{ (Five coordination),} \quad (2)$$

$$\Delta d = \frac{1}{6} \sum_{n=1}^6 [(d_n - d) / d]^2 \text{ (Six coordination),} \quad (3)$$

$$\Delta d = \frac{1}{5} \sum_{n=1}^5 [(d_n - d) / d]^2 \text{ (Five coordination).} \quad (4)$$

Specific screening and stability testing

To evaluate whether the luminescence vapochromism is universal to other VOCs, common solvents with different polarities in our laboratory were selected to investigate the PL change after being exposed to the vapor of the corresponding solvents. As shown in Fig. 4a, the emission of **H1** undergoes a rapid red shift in response to methanol vapor, and the entire transformation is completed in less than 30 min. Besides, the emission remains unchanged when kept exposed to methanol vapor for 4 h. In striking contrast, a distinct color change was not observed when **H1** was exposed to the vapor of ethanol, MeCN, acetone, *n*-hexane, DCM, or chloroform vapor. Additionally, the emission was quenched upon exposure of **H1** to the vapor of high-polarity solvents such as DMF, DMSO, and water. Conclusively, **H1** has a specific response to methanol, which is likely due to the small molecular volume of methanol as well as its low dissociation and binding energy. Furthermore, the stability of **H1** after several cycles of release and uptake of methanol was investigated by

Figure 3 (a) Photographs of PL color change of **H1** upon exposure to methanol vapor and air under UV light at 365 nm for two cycles. (b) PL spectrograms of **H1** upon methanol uptake and release for two cycles.

Figure 4 (a) Luminescent images (UV light irradiation at 365 nm) of **H1** exposed to the vapor of different VOCs for 0, 30, 60, 120, and 240 min. (b) Change in PL intensity of **H1** upon uptake and release of methanol in five cycles.

monitoring the change of PL intensity, as shown in Fig. 4b. The PLQY of **H1** shows a negligible change after five cycles, indicating high stability during the transformation process. The specific recognition and high stability enable the hybrid **H1** as an effective detector for methanol which is useful in methanol detection applications such as fake wine authentication and methanol leakage detection.

CONCLUSIONS

In summary, we have successfully prepared a highly emissive Sb³⁺-doped organic-inorganic hybrid **H1** featuring STE emission with an emission peak of 565 nm and an emissive lifetime of 3.07 μs. The STE behavior induced by structural reorganization was further validated by excitation-wavelength- and excitation-power-density-dependent PL along with TA and DFT computational studies. Interestingly, the as-formed hybrid shows reversible luminescence vapochromism in response to methanol vapor. Further characterizations demonstrate that the reversible transformation stems from severe structural distortion around the Sb(III) coordination center due to the binding and dissociation of methanol molecules in the crystal lattice. Encouragingly, **H1** exhibits a specific response to methanol after screening a series of VOCs with different polarities. Besides, the hybrid shows high stability with a negligible change of the emission intensity after several cycles of methanol uptake and release. The high fatigue resistance and specific response to methanol make it a potentially effective methanol detector. Our work enriches the family of ionic doping luminescent materials and provides a versatile approach for the design of specific recognition sensors for VOCs.

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Conflict of interest The authors declare that they have no conflict of interest.

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基于铟(III)掺杂的氯化铟杂化材料通过甲醇诱导实现的蒸汽变色

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摘要 离子掺杂已被证明是在无机荧光粉和有机-无机杂化材料中实现高效发光的一种有效方法。掺杂体系大多具有较高的光致发光量子产率(PLQY)和优异的稳定性,因此在光电器件领域有着潜在的应用前景。本文采用同价离子掺杂的策略,通过溶液蒸发方法制备了高效发光的 Sb^{3+} 掺杂的铟基卤化物($\text{C}_6\text{H}_{18}\text{N}_2$) $\text{InCl}_5 \cdot \text{H}_2\text{O}:\text{Sb}$ ($\text{C}_6\text{H}_{18}\text{N}_2^{2+} = \text{N,N,N',N'}$ -四甲基乙烷-1,2-二铵),其发射峰值为565 nm, PLQY为74.6%。光物理性质表征和密度泛函理论(DFT)计算研究证明了该宽带发射起源于自陷激子。当($\text{C}_6\text{H}_{18}\text{N}_2$) $\text{InCl}_5 \cdot \text{H}_2\text{O}:\text{Sb}$ 杂化材料暴露于甲醇蒸气中时,在365 nm的紫外光激发下,其发射峰从565 nm显著红移到663 nm,发光颜色由黄色变为红色;当将暴露于甲醇的杂化材料置于空气中时,几分钟后其发射将恢复到原来的565 nm的黄光发射。单晶X射线衍射研究表明,甲醇与 $\text{Sb}(\text{III})$ 中心配位后的结构畸变是导致发射红移的原因。在筛选了一系列不同极性的挥发性有机溶剂(VOC)后,我们发现($\text{C}_6\text{H}_{18}\text{N}_2$) $\text{InCl}_5 \cdot \text{H}_2\text{O}:\text{Sb}$ 对甲醇蒸汽表现出特定的响应。此外,当材料吸收和释放甲醇的几个循环后,其发射强度未发生明显变化。高抗疲劳性和专一的溶剂响应使这种 Sb^{3+} 掺杂的铟基卤化物能够成为非常有前景的甲醇检测材料。