Supporting Information

Excitation-Dependent Multicolor Luminescence with Tunable Afterglow from Te⁴⁺-doped (CytH)₂SnCl₆ for Dynamic Anticounterfeiting

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Experimental section

Materials

Cytosine (Cyt, 98%, Aladdin), tellurium tetrachloride (98%, Energy Chemical), tin tetrachloride (99%, Aladdin), hydrochloric acid (37%, Guanghua Scientific), ethyl acetate (AR, Guanghua Scientific). All chemicals were used as supplied from commercial sources without further purification.

Synthesis of (CytH)₂SnCl₆ single crystals

First, cytosine (0.20 mmol), tin tetrachloride (0.10 mmol) and 1.0 mL hydrochloric acid were mixed in a 15 mL glass vessel and the solution was heated to clear and transparent at a temperature of 120 °C (the setting temperature of heating station) for 30 minutes. After cooling to room temperature, the obtained crystals were washed with ethyl acetate for three times. It was dried under vacuum at 60 °C for 24 hours to obtain (CytH)₂SnCl₆ single crystals.

Synthesis of (CytH)₂SnCl₆:x%Te powders

 $(CytH)_2SnCl_6:x\%Te$ powders were synthesized by loading 0.2 mmol cytosine, $x\% \times 0.10$ mmol of TeCl₄ and $(1-x\%) \times 0.10$ mmol of tin tetrachloride into a 15.0 mL glass vessel containing 1.0 mL HCl. The solution was heated at 120 °C (the setting temperature of heating station) for 30 minutes, followed by the vigorous stirring during the cooling process. The obtained powders were washed with ethyl acetate for three times and then dried in oven at 60 °C for 24 hours.

Characterization

Single crystal X-ray diffraction (SC-XRD)

SC-XRD tests were conducted on Rigaku XtaLab Pro MM007HF DWX diffractometer at 298 K using Cu K α radiation ($\lambda = 1.54184$ Å). The structures were solved by intrinsic phasing method using SHELXT¹ program implanted in Olex2². Refinement with full matrix least squares techniques on F2 was performed by using SHELXL³. Non-hydrogen atoms were anisotropic ally refined and all hydrogen atoms were generated based on riding mode.

Powder XRD

PXRD patterns were recorded on MiniFlex 600 (Rigaku) to examine the crystalline phase.

UV-vis absorption

UV-vis spectra were measured on Lambda 950 UV-vis Spectrometer (PerkinElmer).

Photoluminescence (PL) and excitation (PLE) spectra

Both of PL and PLE spectra were collected on PTI QM-TM (Photon Technology International). Absolute PL quantum vield (OY)

Absolute PL QY was recorded on a HAMAMATSU C11347 spectrometer with integrating sphere with the excitation wavelength of 380 nm for all samples.

Inductively coupled plasma atomic emission spectrometry (ICP-AES)

ICP-AES was applied to detect the molar concentrations of Cd and Sb by using ICPE-9000, Shimadzu.

Delayed PL and PL lifetime

Delayed PL and PL lifetime tests were collected on Edinburgh Instruments (FL 1000). The PL decay curves are fitted with exponential function as given in the following expression:

$$I(t) = \sum_{n}^{i=1} A_i e^{-\frac{t}{\tau_i}}$$

where I(t) is the PL intensity at time t, A_i represents the relative weights of the decay components, τ_i denotes the decay time for the exponential components. The average lifetime is calculated based on the expression below:

$$\tau_{ave} = \sum_{n}^{i=1} A_i \tau_i^2 / \sum_{n=1}^{i=1} A_i \tau_i$$

Computational methodology

Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP)^{4, 5} to investigate the structural and electronic properties of (CytH)₂SnCl₆ and Tedoped (CytH)₂SnCl₆. The crystal structure of (CytH)₂SnCl₆ was determined via X-ray diffraction (XRD) analysis. To model the structure of (CytH)₂SnCl₆:25%Te, Te atoms were substituted randomly for Sn atoms in the crystal lattice according to the specified doping ratio. Structural optimization was performed until the residual forces converged below 0.02 eV·Å⁻¹. The Kohn-Sham equations were solved within a plane-wave basis set with a kinetic energy cutoff of 700 eV. Exchange-correlation effects were treated using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)⁶, and dispersion interactions were incorporated using the DFT-D3 functional with van der Waals corrections.⁷ Brillouin zone sampling for structural optimizations employed a $4 \times 4 \times 3$ Monkhorst-Pack k-point grid. Electronic properties, including the projected density of states (PDOS), were analyzed using the optimized structures. The PDOS was extracted from DOSCAR files generated by VASP, with Brillouin zone sampling performed on a denser $8 \times 8 \times 6$ Monkhorst-Pack k-point grid to ensure computational accuracy. These calculations provided insights into the electronic band structure and electronic properties of both pristine and Te-doped (CytH)₂SnCl₆.

Sample	(CytH) ₂ SnCl ₆
Empirical formula	$(C_4H_6N_3O)_2SnCl_6$
Formula weight	555.63
Temperature/K	298.15
Radiation/Å	Cu K α (λ = 1.54184)
Crystal system	triclinic
Space group	p1
a/Å	6.9087(2)
$b/{ m \AA}$	7.0884(2)
c/Å	9.2696(4)
$lpha/^{\circ}$	101.806(3)
$eta /^{\circ}$	98.339(3)
γ/°	90.488(2)
V/Å ³	439.30(3)
Ζ	1
$ ho_{calc}$ (g/cm ³)	2.100
completeness to θ_{\max}	96.0%
GOF	1.087
$R_{ m int}$	0.0294
final <i>R</i> indexes $[I > 2\sigma(I)]^a$	$R_1 = 0.0220, wR_2 = 0.0584$
R indexes (all data) ^a	$R_1 = 0.0220, wR_2 = 0.0584$
largest diff. peak and hole,	1 07/ 0 60
e Å- ³	1.077-0.07

Table S1. Crystal data of $(CytH)_2SnCl_6$.

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR_2 = \{ [\Sigma w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2] \}^{1/2}; w = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP], \text{ where } P = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP] \}$

= $[\max(F_o^2, 0) + 2Fc^2]/3$ for all data.



Figure S1. (a) Intermolecular hydrogen-bonding interaction between CytH⁺ and [SnCl₆]²⁻. (b) Intermolecular hydrogen-bonding interaction among CytH⁺. (c) Structure of [SnCl₆]²⁻ polyhedron.

Samples	Te atomic ratio
(CytH) ₂ SnCl ₆ :0.5%Te	0.39%
(CytH) ₂ SnCl ₆ :2.5%Te	2.20%
(CytH) ₂ SnCl ₆ :5.0%Te	4.48%
(CytH) ₂ SnCl ₆ :10.0%Te	11.2%

Table S2. Te^{4+} contents of $(CytH)_2SnCl_6$ detected through ICP-AES.



Figure S2. (a) Absolute PL QY test of (CytH)₂SnCl₆. (b) PL QY values of (CytH)₂SnCl₆:x%Te with different doping levels of Te⁴⁺.



Figure S3. CIE chromaticity diagram of (CytH)₂SnCl₆:x%Te under different excitation wavelength, (a) 330 nm, (b) 350 nm and (c) 390 nm.

Table S3 . Fitting param	eters of PL decay curves	s for (CvtH) ₂ S	SnCl ₆ :x%Te at 515 nm
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Sample	A_1	$\tau_1 (ms)$	A ₂	$\tau_2 (ms)$	A ₃	$\tau_{3}\left(ms\right)$	$\tau_{avg}(ms)$
(CytH) ₂ SnCl ₆	0.482	1.85	0.378	21.5	0.140	171.1	126.4
(CytH) ₂ SnCl ₆ :0.5%Te	0.586	2.83	0.310	38.7	0.104	201.3	135.1
(CytH) ₂ SnCl ₆ :2.5%Te	0.675	1.54	0.277	8.8	0.048	154.4	107.1
(CytH) ₂ SnCl ₆ :5.0%Te	0.710	0.26	0.252	10.1	0.038	130.2	86.9
(CytH) ₂ SnCl ₆ :10.0%Te	0.770	0.16	0.206	7.7	0.024	115.6	73.7

Table S4. Fitting parameters of PL decay curves for (CytH) ₂ SnCl ₆ :x%Te at 590 nm.							
Sample	A ₁	$\tau_{1}\left(\mu s\right)$	A ₂	$\tau_2 (\mu s)$	A ₃	$\tau_{3}\left(\mu s\right)$	$ au_{ m avg}$ (µs)
$(CytH)_2SnCl_6:0.5\%Te$	0.938	2.2	0.061	12.2	0.001	202.2	9.4
$(CytH)_2SnCl_6:2.5\%Te$	0.928	2.2	0.071	11.8	0.001	230.0	10.0
$(CytH)_2SnCl_6:5.0\%Te$	0.910	2.4	0.089	11.1	0.001	418.8	16.1
(CytH) ₂ SnCl ₆ :10.0%T e	0.930	2.5	0.069	12.3	0.001	408.8	18.0



Figure S4. Temperature-dependent XRD of (CytH)₂SnCl₆:10%Te.



Figure S5. Open air stability test. (a) XRD and (b) PL spectrum of of (CytH)₂SnCl₆:10%Te placed in open air for different days. Temperature: ~10-25 °C, humidity: ~70%.



Figure S6. Water stability test of (CytH)₂SnCl₆:10%Te.

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