Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Bulk assembly of 0D organic tin(II) chloride hybrid with high anti-water stability

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EXPERIMENTAL SECTION

Materials and preparation: Tin(II) chloride ($SnCl_2$, 99 %), tetrabutylammonium chloride (TBAC, ≥98%), hydrochloric acid (HCl, 38%), and hypophosphoric acid (H_3PO_2, 50 wt.% in water) were purchased from Aladdin reagent and used as received. The single crystals of (TBAC)$CuCl_2$ were prepared via solution temperature-lowering method. Typically, 3 mmol $SnCl_2$ and 3 mmol TBAC were fully dissolved in 10 mL HCl and 1.5 mL H_3PO_2 mixed solution at 130 ℃, and continuously stirred for 2 hours. The above mixed solution was left in the atmosphere for above 24 hours, and bulk crystals of (TBAC)$SnCl_3$ can be obtained.

2.2 Characterization. The parameter of crystal structure was characterized by D8 QUEST single crystal X-ray diffraction (SCXRD) at 220 K. Empyrean Alpha was used to collected powder XRD (PXRD) data. FluoroMax-4 spectrometer was used to measure PL and PLE spectra at RT. The Edinburgh PLS980 was used to collect the PLQY data. The temperature-dependent decay lifetime and PL data were also obtained by FLS980 instrument. The powder absorption spectrum was implemented by UV-3600 spectrometer. HORIBA JY spectrometer was used measure the Raman spectrum excited by 532 nm laser. Quantera II was used to record the X-ray photoelectron spectroscopy (XPS) data. The thermal stability was performed by PE TGA 4000 instrument.

Table S1. Crystal data and structure refinement for (TBAC)$SnCl_3$ single crystal.

Empirical formula	$C_{16}H_{36}Cl_3NSn$
Formula weight	467.50
Temperature/K	220.01(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.7485(5)
b/Å	13.2735(5)
c/Å	18.4175(10)
α/°	90
β/°	104.528(5)
γ/°	90
Volume/Å^3	2307.0(2)
Z	4
ρ_{calc}g/cm^3	1.346
μ/mm^{-1}	1.451
F(000)	960.0
Crystal size/mm^3	0.17 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.826 to 61.996
Index ranges	-12 ≤ h ≤ 10, -18 ≤ k ≤ 16, -25 ≤ l ≤ 25
Reflections collected	19216
Independent reflections	6208 [R_{int} = 0.0174, R_{sigma} = 0.0209]
Data/restraints/parameters	6208/97/232
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0742, wR_2 = 0.2097
Final R indexes [all data]	R_1 = 0.1087, wR_2 = 0.2304
Largest diff. peak/hole / e Å^{-3}	1.86/-1.07

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (TBAC)$SnCl_3$ single crystal. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Sn1	10402.8(5)	7197.8(3)	8520.1(3)	91.9(2)
Cl2	11385.6(19)	8671.8(14)	9255.4(10)	99.2(5)
Cl3	8076(2)	7301.9(17)	8753.7(12)	107.8(6)
Cl4	9732(4)	8106(3)	7347.6(12)	202.7(19)
N9	4939(5)	6833(4)	6451(2)	69.6(11)
C10	5653(7)	7840(4)	6511(3)	78.3(15)
C11	6095(7)	8217(5)	5834(3)	79.7(15)
C14	5827(6)	6031(4)	6218(4)	79.9(15)
C8	3548(6)	6855(7)	5858(4)	95(2)
C18	4713(7)	6645(6)	7212(3)	97(2)
C15	7280(7)	5868(6)	6707(5)	100(2)
C12	6635(9)	9293(5)	5958(5)	107(2)
C13	7189(11)	9691(6)	5325(5)	124(3)
C16	8057(10)	5103(7)	6316(7)	147(4)
C20	3140(40)	5900(40)	7963(19)	175(10)
C7	2460(9)	7477(10)	5861(5)	148(4)
C19	3880(10)	5749(7)	7328(5)	128(3)
C6	1176(14)	7000(14)	5276(10)	147(6)
C17	9480(12)	4864(10)	6751(8)	171(5)
C21	4230(70)	5790(80)	8716(12)	174(13)
C5	-45(14)	7731(15)	5267(10)	155(7)
C6A	1060(20)	7650(20)	5259(17)	152(7)
C5A	420(30)	6620(20)	5374(16)	180(10)
C20A	3925(12)	5775(11)	8202(6)	160(6)
C21A	3069(15)	4911(11)	8337(7)	178(7)

Table S3. Bond lengths and bond angles for (TBAC)$SnCl_3$ single crystal.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/˚
Sn1	Cl2	2.4349(19)	Cl3	Sn1	Cl2	96.37(7)
Sn1	Cl3	2.416(2)	Cl4	Sn1	Cl2	94.39(9)
Sn1	Cl4	2.416(3)	Cl4	Sn1	Cl3	94.29(11)
N9	C10	1.498(8)	C10	N9	C14	111.3(4)
N9	C14	1.500(7)	C10	N9	C8	110.6(5)
N9	C8	1.513(7)	C14	N9	C8	106.5(5)
N9	C18	1.495(7)	C18	N9	C10	104.8(5)
C10	C11	1.504(9)	C18	N9	C14	112.4(5)
C11	C12	1.520(9)	C18	N9	C8	111.4(5)
C14	C15	1.492(9)	N9	C10	C11	117.3(5)
C8	C7	1.346(12)	C10	C11	C12	110.4(5)
C18	C19	1.485(8)	C15	C14	N9	117.3(5)
C15	C16	1.549(12)	C7	C8	N9	125.0(7)
C12	C13	1.498(11)	C19	C18	N9	118.9(6)
C16	C17	1.452(14)	C14	C15	C16	108.4(7)
C20	C19	1.534(19)	C13	C12	C11	113.1(6)
C20	C21	1.53(2)	C17	C16	C15	113.5(10)
C7	C6	1.565(9)	C21	C20	C19	109.1(19)
C7	C6A	1.544(10)	C8	C7	C6	104.1(10)
C19	C20A	1.601(11)	C8	C7	C6A	130.1(18)
C6	C5	1.532(10)	C18	C19	C20	112.4(17)
C6A	C5A	1.531(10)	C18	C19	C20A	104.4(8)
C20A	C21A	1.476(15)	C5	C6	C7	103.7(11)
			C5A	C6A	C7	95.0(15)
			C21A	C20A	C19	106.2(10)

Table S4. Comparison of the Photophysical Properties for Selected Low Dimensional Metal Halides.

Components	Excitation peak (nm)	Emission peaks (nm)	Stokes shift (nm)	FWHM (nm)	Dimensionality	Ref.
$(C_{13}H_{19}N_4)_2PbBr_4$	349	460	111	66	0D	1
Cs_4SnBr_6	340	540	200	—	0D	2
$(C_4N_2H_{14}Br)_4SnBr_6$	355	570	215	105	0D	3
$(C_8H_{14}N_2)_2SnBr_6$	425	507	82	157	0D	4
Rb_2CuBr_3	300	385	85	54	1D	5
K_2CuCl_3	291	392	101	54	1D	6
$C_5H_{16}N_2Pb_2Br_6$	285	565	280	198	1D	7
(N-MEDA)[$PbBr_4$]	388	558	170	165	2D	8
$(OCTAm)_2SnBr_4$	350	600	250	136	2D	9
$(C_6H_{13}NH_3)_2SnBr_4$	~335	618	283	136	2D	10
(TBAC)$SnCl_3$	263	523	260	56	0D	This work

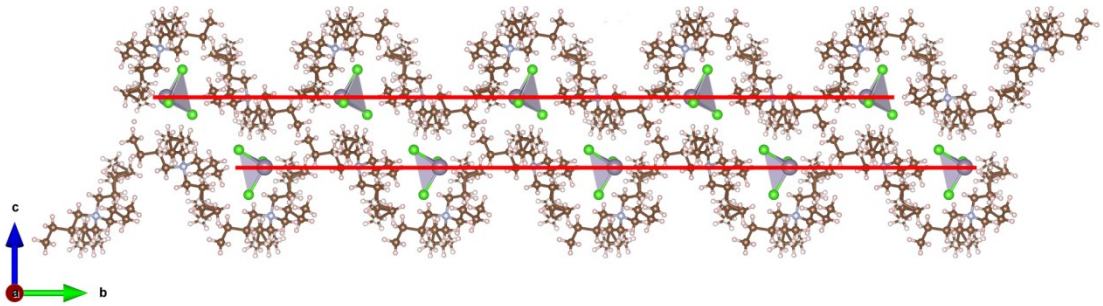

Figure S1. The crystal structure of (TBAC)$SnCl_3$ viewed long the a-axis direction, it can be clearly see that the $[SnCl_3]^-$ clusters are arranged in a straight line along the *b*-axis.

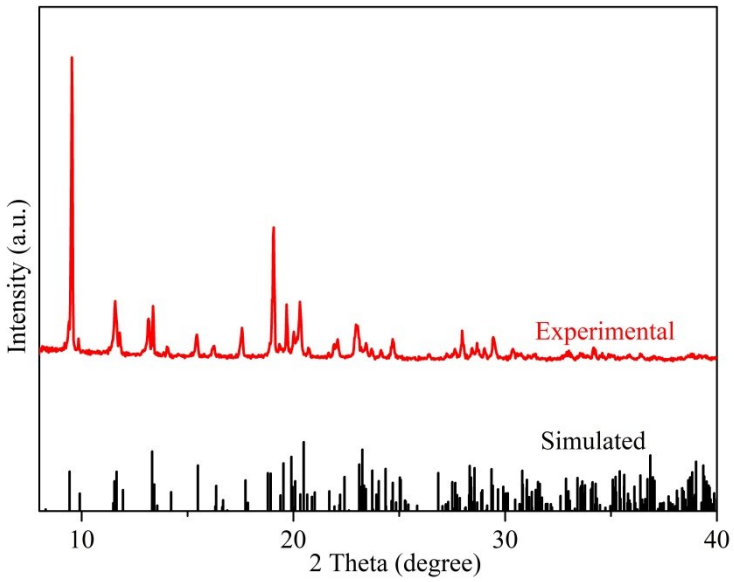

Figure S2. Experimental and simulated PXRD patterns of (TBAC)$SnCl_3$.

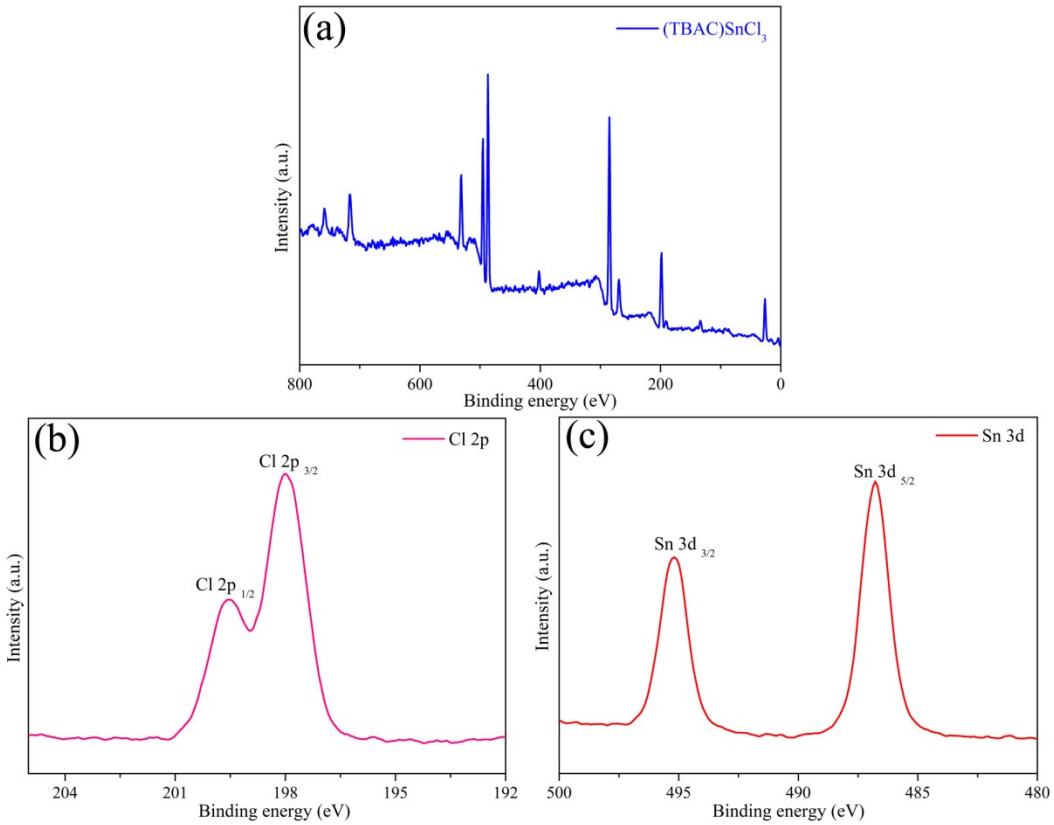

Figure S3. X-ray photoelectron spectroscopic (XPS) analysis of (TBAC)$SnCl_3$ powders and the high-resolution spectra of (b) Cl 2p and (c) Sn 3d.

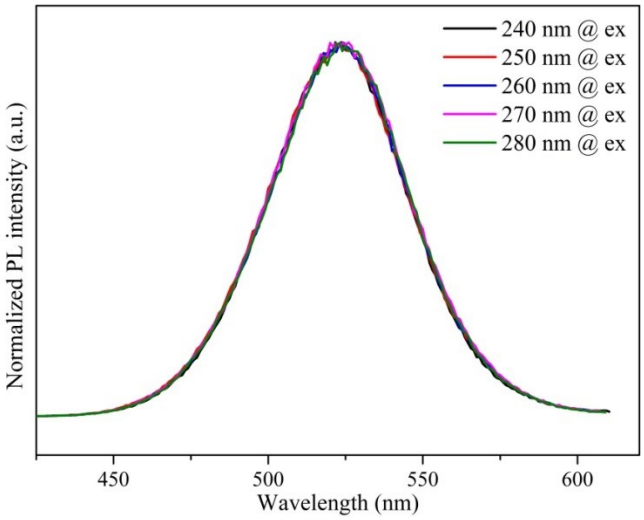

Figure S4. Excitation-wavelength dependent PL spectra of (TBAC)$SnCl_3$ SCs at room temperature.

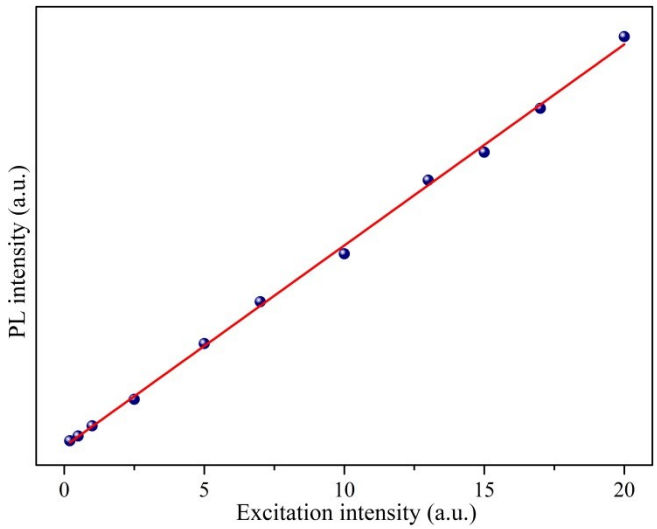

Figure S5. The PL intensity versus excitation power for (TBAC)$SnCl_3$ SCs at room temperature.

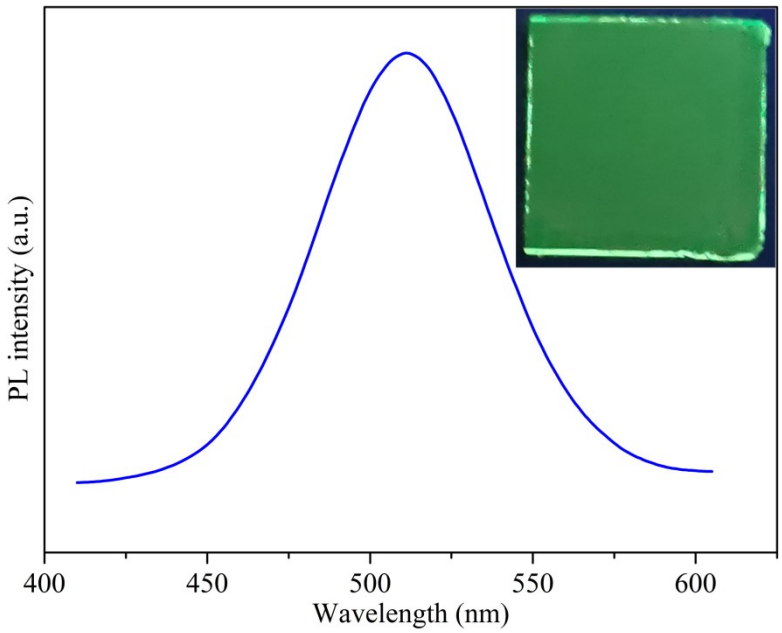

Figure S6. The PL spectrum of (TBAC)$SnCl_3$ film at room temperature, and the inset shows the optical photographs of (TBAC)$SnCl_3$ film under 254 nm UV light.

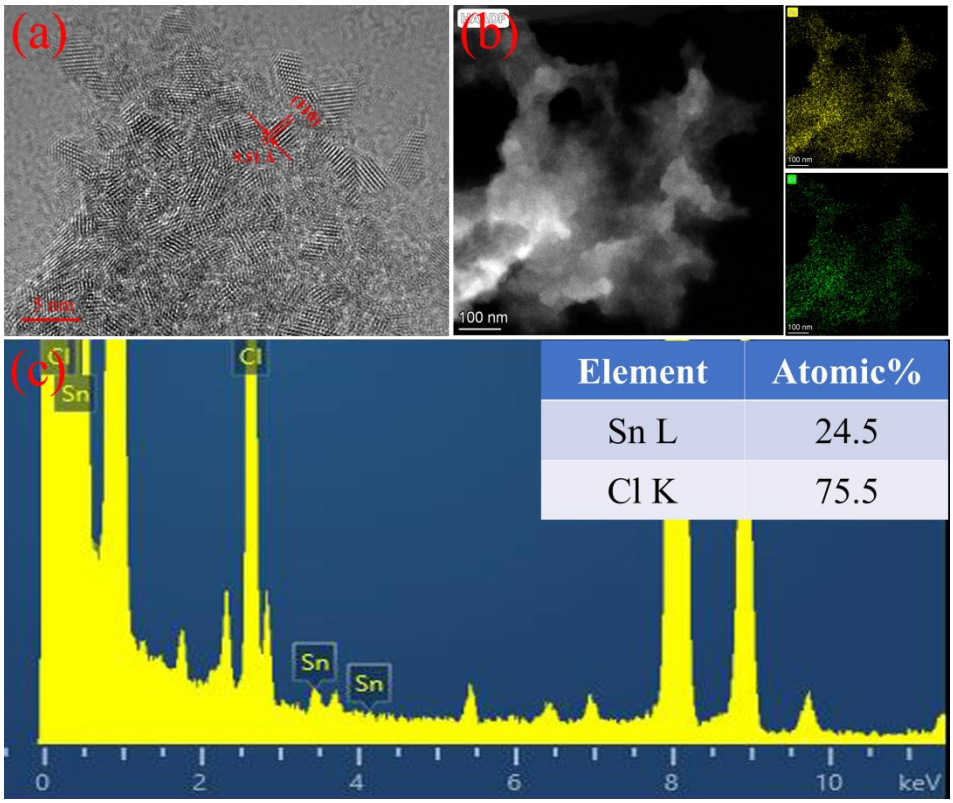

Figure S7. (a) The HRTEM, (b) The high-angle annular dark-field (HAADF) image and (c) The EDS analysis of the (TBAC)$SnCl_3$.

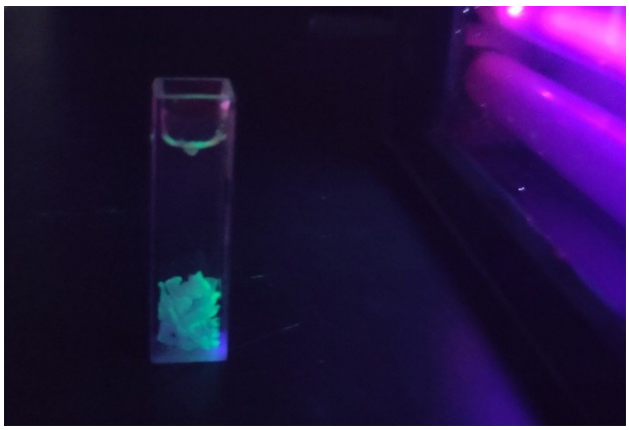

Figure S8. The optical image of (TBAC)$SnCl_3$ SCs under 254 nm UV lamp in the deionized water after 24 hours.

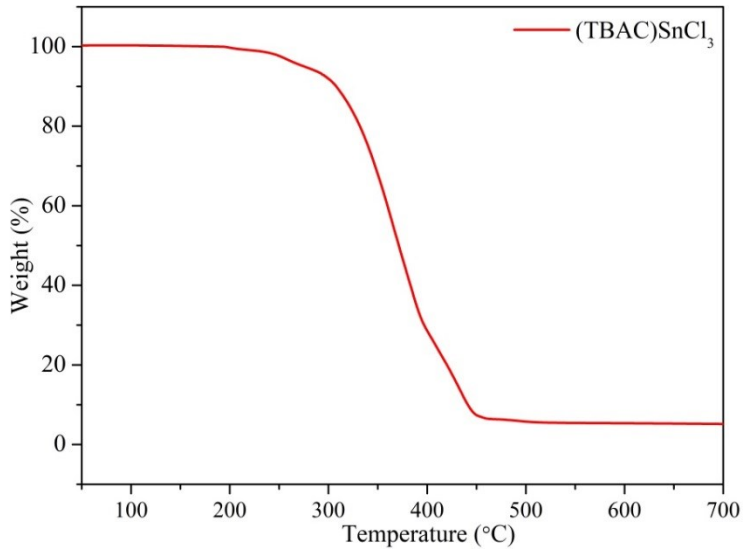

Figure S9. TG curve of (TBAC)$SnCl_3$ powders.

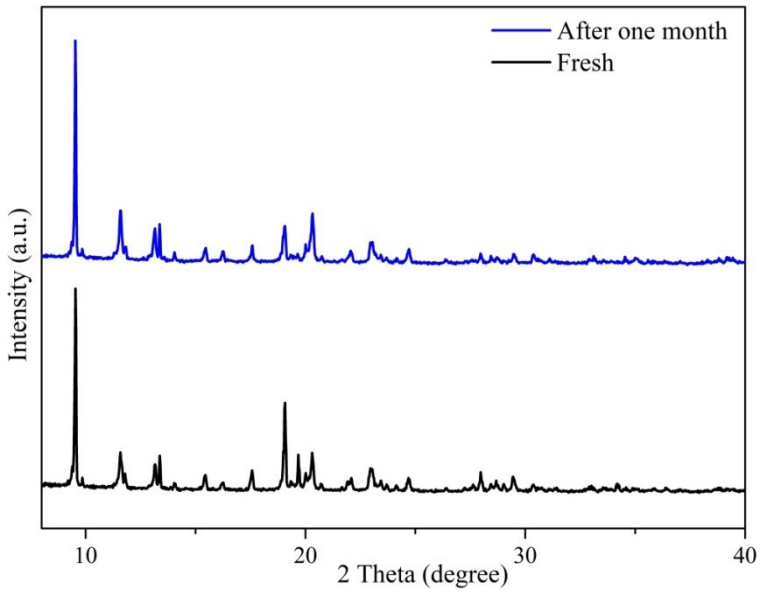

Figure S10. PXRD patterns of (TBAC)$SnCl_3$ before and after exposure to atmospheric environment (～55 % relative humidity) for one month.

References

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