Supporting Information

Ultrafast Preparation of Amine-Free 0D Metal Halides with Near-Unity Emission for X-Ray Scintillators

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Experimental Section

Calculation of light yield. Normalized to the same X-ray attenuation according to the following equation:

$$PC_{Normalized} = \frac{PC_{Measured}}{AE} \#(S1)$$

where $PC_{Measured}$ is the photon counting result obtained by integrating the RL spectra, AE is the X-ray attenuation efficiency of the scintillator at a certain thickness. The scintillation light yield of $Al(DMSO)_6[SbCl_6]$ could be calculated from the following formula:

$$LY_{Al(DMSO)_6[SbCl_6]} = LY_{BGO} \times \frac{PC_{Nomalized}(Al(DMSO)_6[SbCl_6])}{PC_{Nomalized}(BGO)} \#(S2)$$

where LY_{BGO} is the light yield of BGO (10,000 photons·MeV^{-1}), $PC_{Normalized}(Al(DMSO)_6[SbCl_6])$ and $PC_{Normalized}(BGO)$ are the photon counts of $Al(DMSO)_6[SbCl_6]$ and BGO normalized.

Density Functional Theory (DFT) calculations. All simulations were carried out using the Vienna Ab initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) described exchange-correlation interactions. Projector augmented wave (PAW) potentials treated electron-ion interactions. Calculations employed a 400 eV plane-wave cutoff energy and a 3×3×1 Monkhorst-Pack k-point grid for Brillouin zone sampling. Self-consistent field convergence thresholds were set at 10^{-4} eV for energy and 0.02 eV·$Å^{-1}$ for forces. Dispersion corrections were incorporated via the DFT-D3 method.

Supplementary Tables

Table S1. Comparison of synthetic strategies for materials preparation.

Comparison Dimension	$Al(DMSO)_6[SbCl_6]$	$C_{38}H_{36}P_2Sb_2Cl_8$	$(TMS)_2SbCl_5$	$PMA_4NaInCl_8$
Reaction Time	Seconds (Instantaneous)	~50 hours	Several hours	>20 hours
Temperature	Room Temperature	25 °C (RT)	80 °C heating + cooling	100 °C heating + slow cooling (3 °C /h)
Atmosphere	Ambient Air	Ambient (implied)	Not specified	Sealed autoclave
Organic Ligand	No (Amine-Free, DMSO only)	Yes (MPCl)	Yes (TMSCl)	Yes (PMA)
Purification	Low (Centrifugation & Washing)	Slow crystallization & collection	Filtration & slow cooling	Filtration, slow cooling, washing, drying
Synthetic Steps	Simple (One-pot)	Multi-step (Dissolve, mix, stir, diffuse)	Multi-step (Heat, filter, cool)	Complex (Multi-solvent, autoclave, controlled cooling)
Scalability	Excellent (Gram-Scale Demonstrated)	Challenging (Diffusion method)	Limited (Vial scale)	Limited (Autoclave size)
Reference	This work	[30]	[31]	[32]

Table S2. The fluorescence properties of metal composition after modification

Compound	PL Peak (nm)	PLQY (%)	Lifetime (μs)
$Al(DMSO)_6[SbCl_6]$	515	97.65	1.89
$Al(DMSO)_6[InCl_6]$	510	50.00	1.84
$Al(DMSO)_6[BiCl_6]$	520	5.95	1.41
$Ga(DMSO)_6[BiCl_6]$	455	1.07	1.88

Table S3. ICP-OES quantitative analysis of Al and Sb in samples

m_0 (g)	V_0 (mL)	Analyte	C_0 (mg·L⁻¹)	f	C_1 (mg·L⁻¹)	C_x (mg·kg⁻¹)	C_x (%)
0.0131	25	Sb	74.42170185	1	1860.543	142,026.15	14.20
		Al	16.18599172	1	404.650	30,889.30	3.09

Table S4. Crystal data and structure refinement

Parameter	Value
Empirical formula	$C_{12}H_{36}AlCl_6O_6S_6Sb$
Formula weight	830.20
Temperature (K)	100.00(10)
Crystal system	trigonal
Space group	*R-3* (No.148)
a (Å)	13.4727(4)

b (Å)	13.4727(4)
c (Å)	15.2171(4)
α (°)	90
β (°)	90
γ (°)	120
Volume (Å^3)	2392.06(16)
Z	3
ρ_{calc} (g·cm^{-3})	1.729
μ (mm^{-1})	15.665
F(000)	1254.0
Crystal size (mm^3)	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection (°)	13.142 to 133.012
Index ranges	-16 ≤ h ≤ 15, -10 ≤ k ≤ 14, -18 ≤ l ≤ 13
Reflections collected	2129
Independent reflections	914 [Rint°= 0.1518, Rsigma°= 0.0923]
Data/restraints/parameters	914/21/55
Goodness-of-fit on F2	1.287
Final R indexes [I>=2σ (I)]	R1°= 0.1119, wR2°= 0.2727
Final R indexes [all data]	R1°= 0.1164, wR2°= 0.2770
Largest diff. peak/hole (e Å^{-3})	0.03/-0.01

Table S5. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U_{eq}
Sb01	10000	10000	50000	33.1(10)
S002	6006.3(15)	4840.9(16)	2306.2(12)	38.2(10)
Cl03	8535.3(16)	8243.8(16)	4023.5(11)	42.9(10)
Al04	6667	3333	3333	35.9(15)
O005	6968(5)	4602(4)	2612(3)	39.7(15)
C006	6603(9)	6327(8)	2477(6)	52(2)
C007	6052(8)	4794(8)	1156(7)	51(2)

Table S6. Selected bond lengths (Å)

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Sb01	Cl031	2.6517(17)	S002	C007	1.754(11)
Sb01	Cl03	2.6517(17)	Al04	O0056	1.896(5)
Sb01	Cl032	2.6517(17)	Al04	O005	1.896(5)
Sb01	Cl033	2.6517(17)	Al04	O0057	1.896(5)
Sb01	Cl034	2.6517(17)	Al04	O0058	1.896(5)
Sb01	Cl035	2.6517(17)	Al04	O0059	1.896(5)
S002	O005	1.554(5)	Al04	O00510	1.896(5)
S002	C006	1.765(9)			

Table S7 Selected Bond angles (°)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl03^1	Sb01	Cl03^2	91.66(6)	C007	S002	C006	100.6(5)

Cl03[1]	Sb01	Cl03	180	O005[6]	Al04	O005[7]	89.9(2)
Cl03[3]	Sb01	Cl03	88.34(6)	O005[6]	Al04	O005[8]	90.1(2)
Cl03[4]	Sb01	Cl03[3]	180	O005	Al04	O005[8]	180
Cl03[5]	Sb01	Cl03	91.66(6)	O005[9]	Al04	O005[7]	180
Cl03[4]	Sb01	Cl03	91.66(6)	O005	Al04	O005[7]	89.9(2)
Cl03[2]	Sb01	Cl03[3]	91.66(6)	O005[9]	Al04	O005[8]	89.9(2)
Cl03[1]	Sb01	Cl03[5]	88.34(6)	O005[10]	Al04	O005[6]	180.0(3)
Cl03[2]	Sb01	Cl03[4]	88.34(6)	O005[10]	Al04	O005	90.1(2)
Cl03[2]	Sb01	Cl03	88.34(6)	O005[9]	Al04	O005[6]	90.1(2)
Cl03[5]	Sb01	Cl03[4]	91.66(6)	O005[10]	Al04	O005[8]	89.9(2)
Cl03[2]	Sb01	Cl03[5]	180.00(6)	O005[10]	Al04	O005[7]	90.1(2)
Cl03[1]	Sb01	Cl03[3]	91.66(6)	O005[7]	Al04	O005[8]	90.1(2)
Cl03[5]	Sb01	Cl03[3]	88.34(6)	O005	Al04	O005[6]	89.9(2)
Cl03[1]	Sb01	Cl03[4]	88.34(6)	O005	Al04	O005[9]	90.1(2)
O005	S002	C006	103.7(4)	O005[10]	Al04	O005[9]	89.9(2)
O005	S002	C007	104.1(4)	S002	O005	Al04	122.4(3)

Supplementary Figures

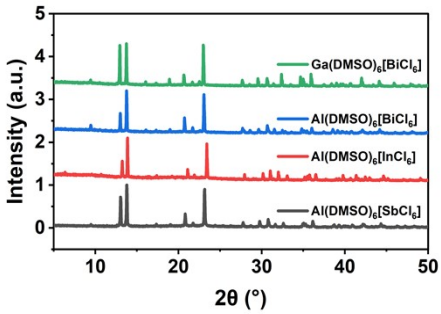

Figure S1. XRD spectrum after changing the metal composition.

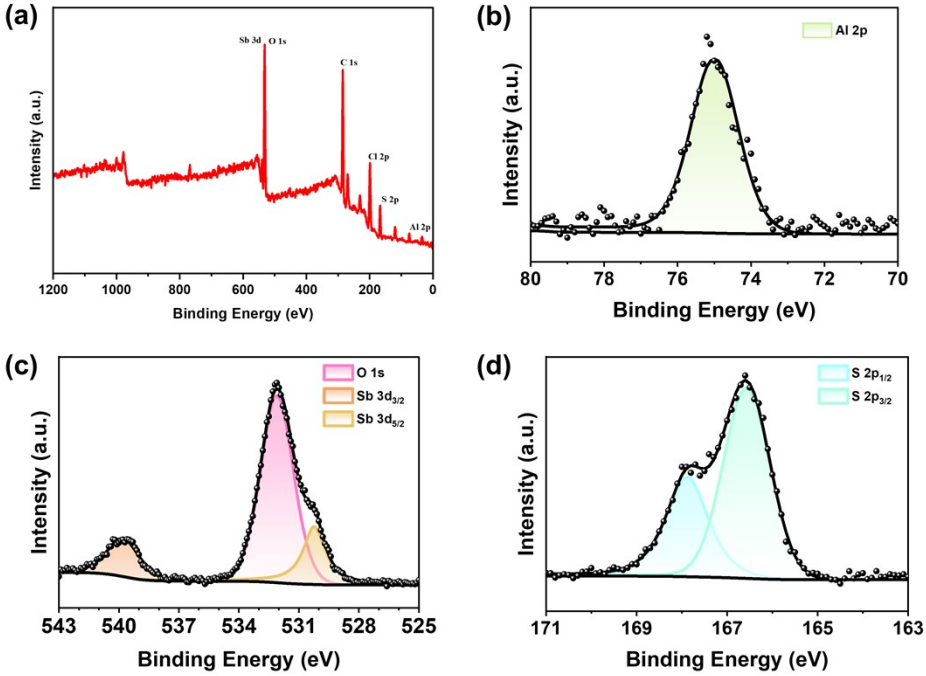

Figure S2. XPS spectra of $Al(DMSO)_6[SbCl_6]$: (a) Full survey scan, (b) Al 2p, (c) O 1s and Sb 3d, (d) S 2p.

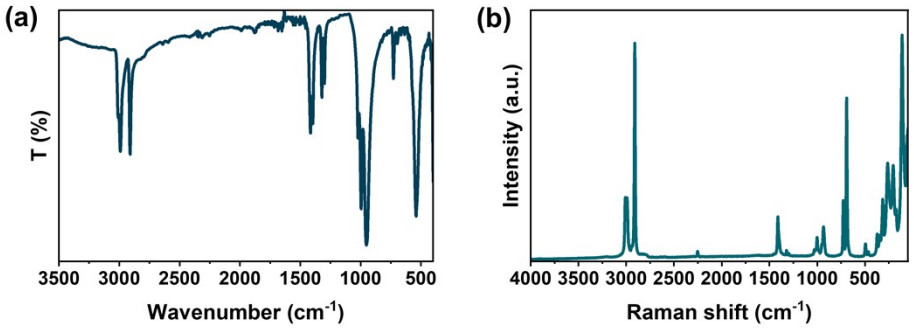

Figure S3. (a) FTIR and (b) Raman spectra of $Al(DMSO)_6[SbCl_6]$

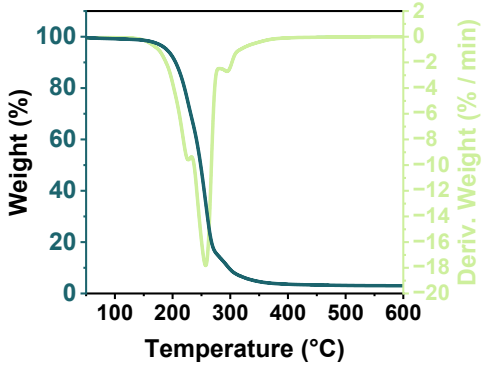

Figure S4. TGA curves of $Al(DMSO)_6[SbCl_6]$ under nitrogen.

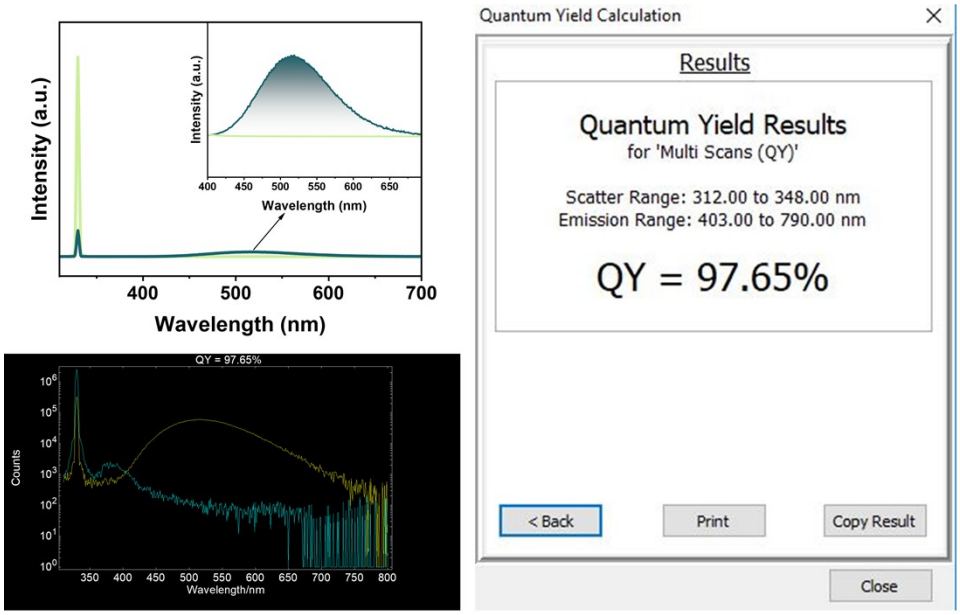

Figure S5. PLQY result of $Al(DMSO)_6[SbCl_6]$.

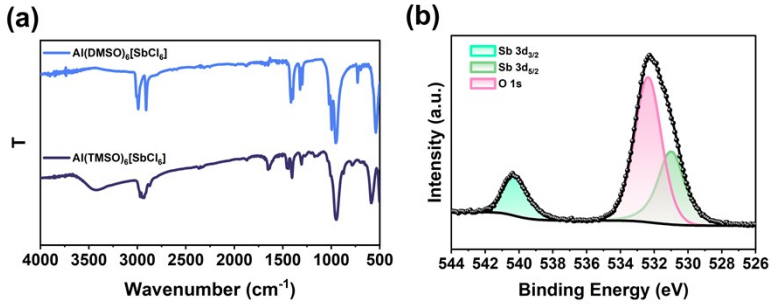

Figure S6. FTIR and XPS spectra (O 1s) of $Al(TMSO)_6[SbCl_6]$.

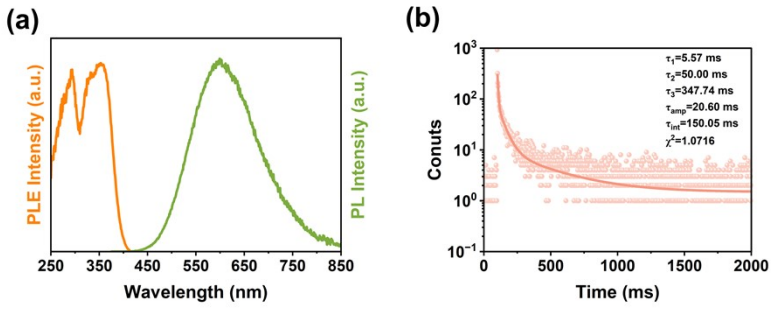

Figure S7. PL, PLE and TRPL spectra of $Al(TMSO)_6[SbCl_6]$

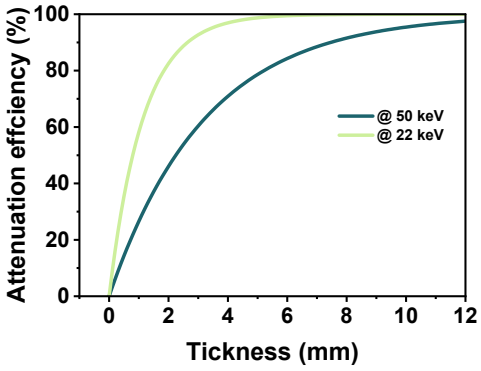

Figure S8. Thickness-dependent X-ray attenuation efficiency at 50 keV and 22 keV of $Al(DMSO)_6[SbCl_6]$