Supporting Information

Dimethylamine Metal Halides for High-Sensitivity Fluorescence Lifetime Thermometry

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Table S1. Crystal data and structure refinement for DMA_4InBr_7 and DMA_3SbBr_6.

Empirical formula	DMA_4InBr_7	DMA_3SbBr_6
Formula weight	858.56	739.46
Temperature	293(2) K	150.0 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	trigonal
Space group	$P2_12_12$	R-3
Unit cell dimensions	a = 10.6364(5) Å, b = 13.3478(7) Å, c = 8.9277(5) Å,	a = b = 28.9960(9) Å, c = 8.2726(11) Å,
Volume	1267.49(11) $Å^3$	6023.5(8) $Å^3$
Z	2	11.999999
Density (calculated)	2.250 g/cm^3	2.4460 g/cm^3
Absorption coefficient	11.964 mm^{-1}	13.299 mm^{-1}
F (000)	804	4081.0448
θ range for data collection	2.979 to 26.365°	2.43 to 26.39°
Index ranges	-12<=h<=13 -16<=k<=16 -10<=l<=11	-36<=h<=36 -36<=k<=36 -10<=l<=10
Reflections collected	7667	39232
Independent reflections	2561 [R_{int} = 0.0299]	2749 [R_{int} = 0.0684]
Completeness to θ = 25.242°	99.8%	99.96%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2561 / 0 / 97	2749 / 0 / 103
Goodness-of-fit	1.055	1.0509
Final R indices [I > 2σ(I)]	R_{obs} = 0.0200 wR_{obs} = 0.0370	R_{obs} = 0.0254 wR_{obs} = 0.0589
R indices [all data]	R_{all} = 0.0231 wR_{all} = 0.0375	R_{all} = 0.0373 wR_{all} = 0.0635
Largest diff. peak and hole	0.320 and -0.382 $e \cdot Å^{-3}$	0.6551 and -0.7697 $e \cdot Å^{-3}$

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR=\{\Sigma[w(|F_o|^2-|F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(F_o^2)+(0.0104P)^2]$ where $P=(F_o^2+2F_c^2)/3$

Table S2. Bond lengths [Å] for DMA_4InBr_7 at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
In(1)-Br(2)[1]	2.6898(4)
In(1)-Br(2)	2.6898(4)
In(1)-Br(1)[1]	2.6558(6)
In(1)-Br(1)	2.6558(6)
In(1)-Br(3)	2.6719(6)
In(1)-Br(3)[1]	2.6719(6)
N(1)-C(4)	1.471(7)
N(1)-C(3)	1.466(8)
N(2)-C(1)	1.462(7)
N(2)-C(2)	1.469(7)

Symmetry transformations used to generate equivalent atoms:
[1] -*x*+1, -*y*+1, *z*

Table S3. Bond angles [°] for DMA_4InBr_7 at 293(2) K with estimated standard deviations in parentheses.

Label	Angles
Br(2)-In(1)-Br(2)[1]	177.68(3)
Br(1)-In(1)-Br(2)[1]	89.543(17)
Br(1)[1]-In(1)-Br(2)	89.542(17)
Br(1)[1]-In(1)-Br(2)[1]	88.896(17)
Br(1)-In(1)-Br(2)	88.895(17)
Br(1)[1]-In(1)-Br(1)	95.16(3)
Br(1)-In(1)-Br(3)[1]	88.676(15)
Br(1)[1]-In(1)-Br(3)[1]	176.15(2)
Br(1)[1]-In(1)-Br(3)	88.676(15)
Br(1)-In(1)-Br(3)	176.15(2)
Br(3)-In(1)-Br(2)[1]	90.913(18)
Br(3)[1]-In(1)-Br(2)	90.912(18)
Br(3)[1]-In(1)-Br(2)[1]	90.760(17)
Br(3)-In(1)-Br(2)	90.761(17)
Br(3)-In(1)-Br(3)[1]	87.49(3)
C(3)-N(1)-C(4)	113.9(4)
C(1)-N(2)-C(2)	114.5(5)

Symmetry transformations used to generate equivalent atoms:
[1] $-x+1, -y+1, z$

Table S4. Bond lengths [Å] for DMA_3SbBr_6 at 150.0 K with estimated standard deviations in parentheses.

Label	Distances
Sb(2)-Br(4)	2.8322(5)
Sb(2)-Br(4)[1]	2.8322(5)
Sb(2)-Br(3)[1]	2.7953(5)
Sb(2)-Br(3)	2.7953(5)
Sb(2)-Br(2)	2.7679(5)
Sb(2)-Br(2)[1]	2.7679(5)
Sb(1)-Br(1)[2]	2.8004(5)
Sb(1)-Br(1)[3]	2.8004(5)
Sb(1)-Br(1)	2.8004(5)
Sb(1)-Br(1)[4]	2.8004(5)
Sb(1)-Br(1)[5]	2.8004(5)
Sb(1)-Br(1)[6]	2.8004(5)
N(2)-C(4)	1.484(6)
N(2)-C(3)	1.467(6)
N(1)-C(1)	1.447(7)
N(1)-C(2)	1.477(8)

Symmetry transformations used to generate equivalent atoms:
[1] -*x*+1, -*y*+1, -*z*+1; [2] *y*+1/3, -*x*+*y*+2/3, -*z*+2/3; [3] -*y*+1, *x*-*y*, *z*; [4] *x*-*y*+1/3, *x*+2/3, -*z*+2/3; [5] -*x*+*y*+1, -*x*+1, *z*; [6] -*x*+1/3, -*y*+2/3, -*z*+2/3

Table S5. Bond angles [°] for DMA_3SbBr_6 at 150.0 K with estimated standard deviations in parentheses.

Label	Angles
$Br(4)^1$-Sb(2)-Br(4)	180.0
$Br(3)^1$-Sb(2)-Br(4)	90.191(14)
Br(3)-Sb(2)-Br(4)	89.809(14)
Br(3)-Sb(2)-$Br(4)^1$	90.191(14)
$Br(3)^1$-Sb(2)-$Br(4)^1$	89.809(14)
$Br(3)^1$-Sb(2)-Br(3)	180.0
Br(2)-Sb(2)-$Br(4)^1$	91.539(15)
Br(2)-Sb(2)-Br(4)	88.461(15)
$Br(2)^1$-Sb(2)-$Br(4)^1$	88.461(15)
$Br(2)^1$-Sb(2)-Br(4)	91.539(15)
$Br(2)^1$-Sb(2)-$Br(3)^1$	92.283(15)
Br(2)-Sb(2)-$Br(3)^1$	87.717(15)
Br(2)-Sb(2)-Br(3)	92.283(15)
$Br(2)^1$-Sb(2)-Br(3)	87.717(15)
$Br(2)^1$-Sb(2)-Br(2)	180.0
$Br(1)^2$-Sb(1)-$Br(1)^6$	92.384(14)
$Br(1)^6$-Sb(1)-$Br(1)^5$	87.616(14)
$Br(1)^2$-Sb(1)-$Br(1)^3$	180.0
$Br(1)^4$-Sb(1)-$Br(1)^6$	92.384(16)
$Br(1)^2$-Sb(1)-Br(1)	87.616(14)
$Br(1)^5$-Sb(1)-$Br(1)^3$	92.384(14)
$Br(1)^4$-Sb(1)-Br(1)	87.616(16)
$Br(1)^4$-Sb(1)-$Br(1)^3$	87.616(14)
$Br(1)^4$-Sb(1)-$Br(1)^5$	180.0
$Br(1)^6$-Sb(1)-Br(1)	180.0
$Br(1)^4$-Sb(1)-$Br(1)^2$	92.384(14)
$Br(1)^2$-Sb(1)-$Br(1)^5$	87.616(16)
$Br(1)^3$-Sb(1)-Br(1)	92.384(14)
$Br(1)^6$-Sb(1)-$Br(1)^3$	87.616(16)
$Br(1)^5$-Sb(1)-Br(1)	92.384(16)
C(3)-N(2)-C(4)	114.1(4)
C(2)-N(1)-C(1)	113.6(4)

Symmetry transformations used to generate equivalent atoms:
[1] -*x*+1, -*y*+1, -*z*+1; [2] *y*+1/3, -*x*+*y*+2/3, -*z*+2/3; [3] -*y*+1, *x*-*y*, *z*; [4] *x*-*y*+1/3, *x*+2/3, -*z*+2/3; [5] -*x*+*y*+1, -*x*+1, *z*; [6] -*x*+1/3, -*y*+2/3, -*z*+2/3

Table S6. Decomposition temperature of In-based 0D OIMHs.

Compounds	Decomposition temperature (℃)	References
(*R/S*-MBA)$_3$InCl$_6$	200	[1]
(PPA)$_6$InBr$_9$	200	[2]
BA$_6$InCl$_9$	210	[3]
(TUH)$_6$[In$_{0.9573}$Sb$_{0.0427}$Br$_6$]Br$_3$	215	[4]
PBA$_3$[InCl$_6$]·H$_2$O	230	[5]
[(C$_2$H$_5$)$_4$N]InCl$_4$	243	[6]
Sb^{3+}:PA$_6$InCl$_9$	265	[7]
DMA$_4$InBr$_7$	266	This work
[(C$_2$H$_5$)$_4$N]InCl$_2$Br$_2$	283	[6]
[(C$_2$H$_5$)$_4$N]InBr$_4$	315	[6]

Table S7. Decomposition temperature of Sb-based 0D OIMHs.

Compounds	Decomposition temperature (℃)	References
[DPA]$_3$SbCl$_6$	170	[8]
(NII)$_2$SbCl$_5$	200	[9]
[DPA]$_3$SbCl$_6$	200	[10]
(C$_{25}$H$_{22}$P)SbCl$_4$	285	[11]
DMA$_3$SbBr$_6$	290	This work
(C$_{25}$H$_{22}$P)$_2$SbCl$_5$	293	[11]
(PPN)$_2$SbCl$_5$	300	[12]

Table S8. ICP results of DMA$_4$InBr$_7$:*x*%Sb (*x* = 0, 0.5, 1).

Compound	In (mg/L)	Sb (mg/L)	Molar Doping ratio
DMA$_4$InBr$_7$	74.76	0.0394	0.05%
DMA$_4$InBr$_7$:0.5%Sb	80.39	0.9293	1.1%
DMA$_4$InBr$_7$:1%Sb	70.73	2.014	2.6%

Table S9. PLQY, absorption efficiency and external quantum efficiency of DMA_4InBr_7:*x*%Sb (*x* = 0, 0.5, 1).

concentration	0%	0.5%	1%
PLQY	50.4%	62.6%	55.1%
Abs	11.5%	32.8%	40.7%
EQE	5.8%	20.5%	22.4%

Table S10. The E_b and PLQY of In- and Sb-based zero-dimensional OIMHs.

Compound	E_b (meV)	PLQY	References
$[Ph_3EtP]_2SbCl_5$	52.93	64.47%	[13]
Sb:PA_6InCl_9	55.5	61%	[7]
$[MP]_2In_{0.73}Sb_{0.27}Cl_7 \cdot 6H_2O$	59.28	93.34%	[14]
BA_6InCl_9	64	25%	[3]
$(C_4H_{12}N)_2InCl_5$ DMF: Sb^{3+}	68.7	99.3%	[15]
BA_6InCl_9: Sb	73	95%	[3]
DMA_4InBr_7	89	50.4%	This work
5%Sb^{3+}-doped $(Gua)_3InCl_6$	94.4	95.72%	[16]
DMA_4InBr_7:1%Sb	106	55.1%	This work
$(C_{25}H_{22}P)_2SbCl_5$	131	98.6%	[11]
$Cs_2InCl_5 \cdot H_2O$: 5%Sb	136.95	95%	[17]
DMA_4InBr_7:0.5%Sb	189	62.6%	This work
$DMA_4In_{1-x}Sb_xCl_7$ (x = 1.90%)	659.46	97.85%	[17]

Table S11. Some typical organic-inorganic metal halides for fluorescence lifetime thermometry and their relative sensitivities (S_r).

Compound	Work range (K)	S_r (K^{-1})	References
TPP_2SbBr_5	256-324	0.045	[18]
$(C_{10}H_{22}N)_6SbBr_9 \cdot H_2O$	290-340	0.045	[19]
$ODASn_2I_6$	275-350	0.014	[20]
$(C_4N_2H_{14}I)_4SnI_6$	313-383	0.055	[21]
$[C(NH_2)_3]_2SnBr_4$	173-243	0.060	[21]
$(MePPh_3)_2ZnCl_4$: 0.30 Bi^{3+}	57-100	0.090	[22]
DMA_4InBr_7:1%Sb	300-356	0.070	This work

Table S12. The fluorescence lifetime of DMA_4InBr_7:1%Sb during heating-cooling cycles.

lifetime	310 K	320 K	330 K	340 K
τ_1 (μs)	1.39	1.04	0.67	0.39
τ_2 (μs)	1.37	1.05	0.60	0.34
τ_3 (μs)	1.48	0.95	0.61	0.41
τ_4 (μs)	1.43	1.03	0.65	0.40
τ_{ave} (μs)	1.42	1.02	0.63	0.39

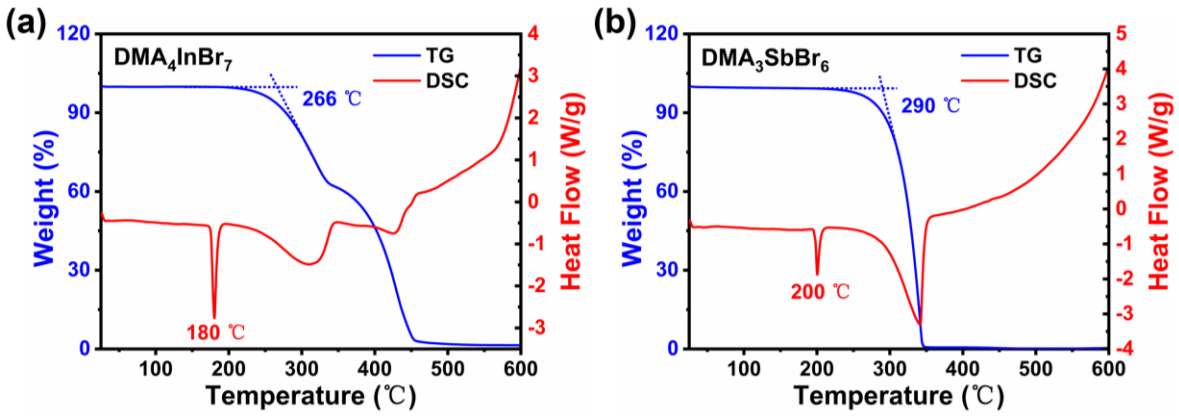

Figure S1. The thermogravimetric analysis and differential scanning calorimetry data for powder samples of DMA_4InBr_7 and DMA_3SbBr_6.

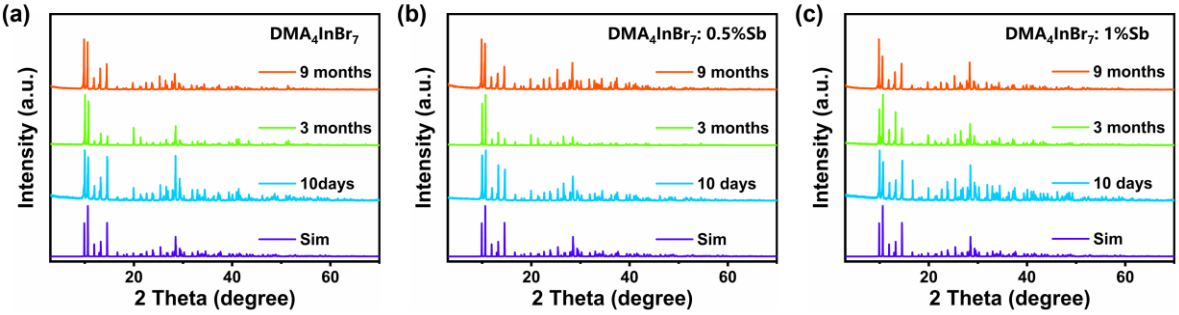

Figure S2. The PXRD of DMA_4InBr_7:*x*%Sb (*x* = 0, 0.5, 1) after 10 days, 3 months and 9 months.

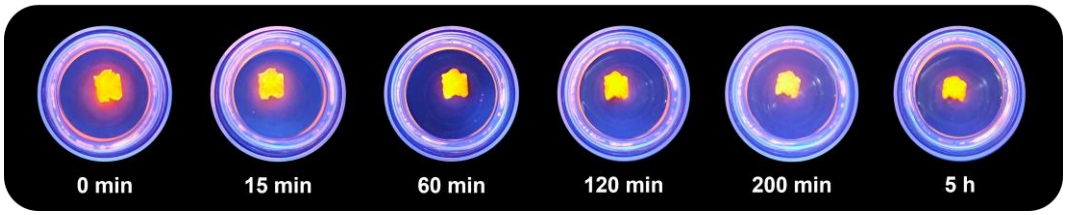

Figure S3. Photographs of DMA_4InBr_7:1%Sb after immersion in ethanol for 5 hours under UV irradiation.

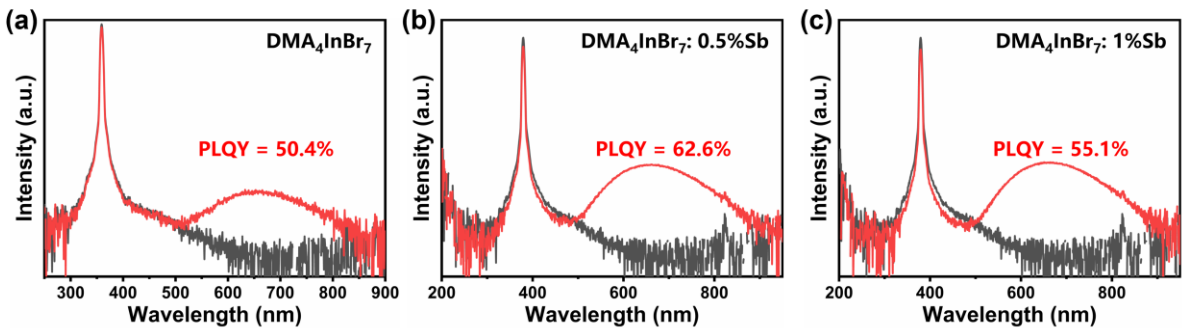

Figure S4. Photoluminescence quantum yield of DMA_4InBr_7:*x*%Sb (*x* = 0, 0.5, 1).

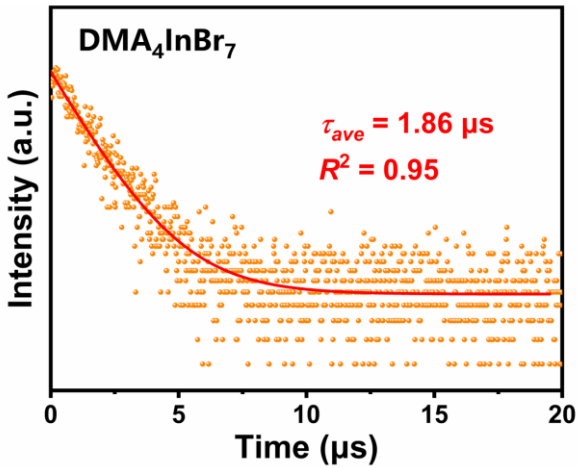

Figure S5. Luminescence decay curve of DMA_4InBr_7.

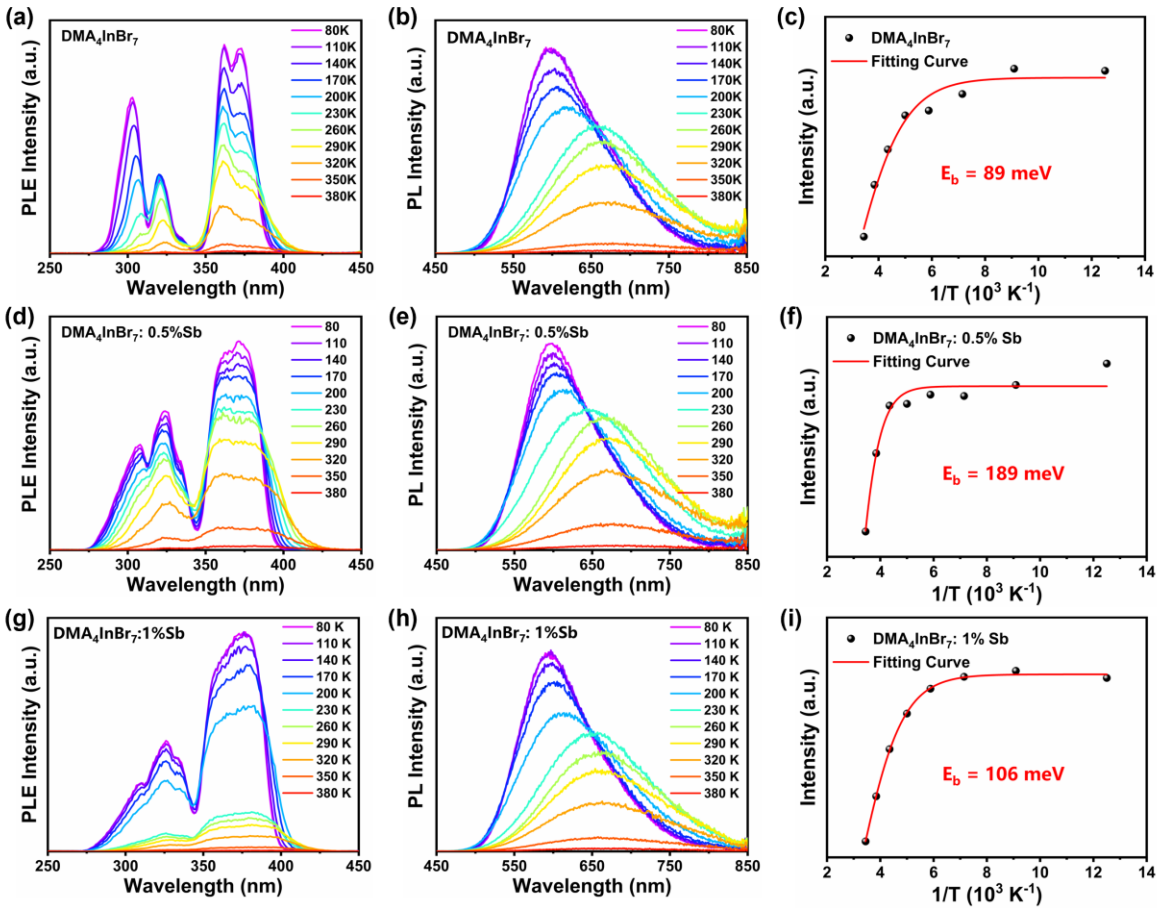

Figure S6. a) Temperature-dependent PLE spectra; b) PL spectra and c) E_b fitting curve of DMA_4InBr_7; d) Temperature-dependent PLE spectra; e) PL spectra and f) E_b fitting curve of DMA_4InBr_7:0.5%Sb; g) Temperature-dependent PLE spectra; h) PL spectra and i) E_b fitting curve of DMA_4InBr_7:1%Sb.

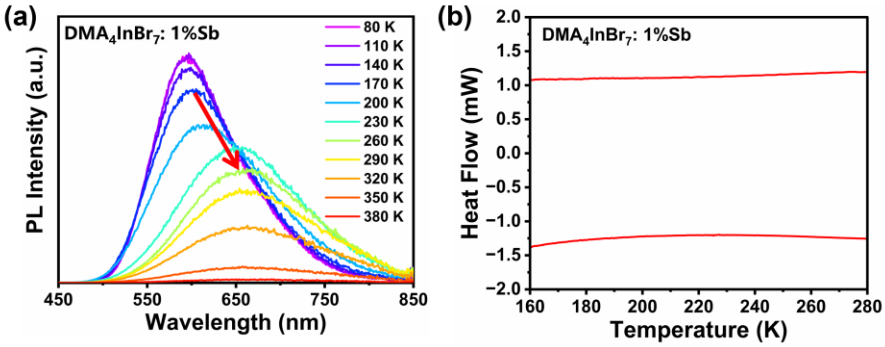

Figure S7. a) Temperature-dependent PL spectra of DMA_4InBr_7:1%Sb; b) DSC curves of DMA_4InBr_7:1%Sb between 160 K and 280 K.

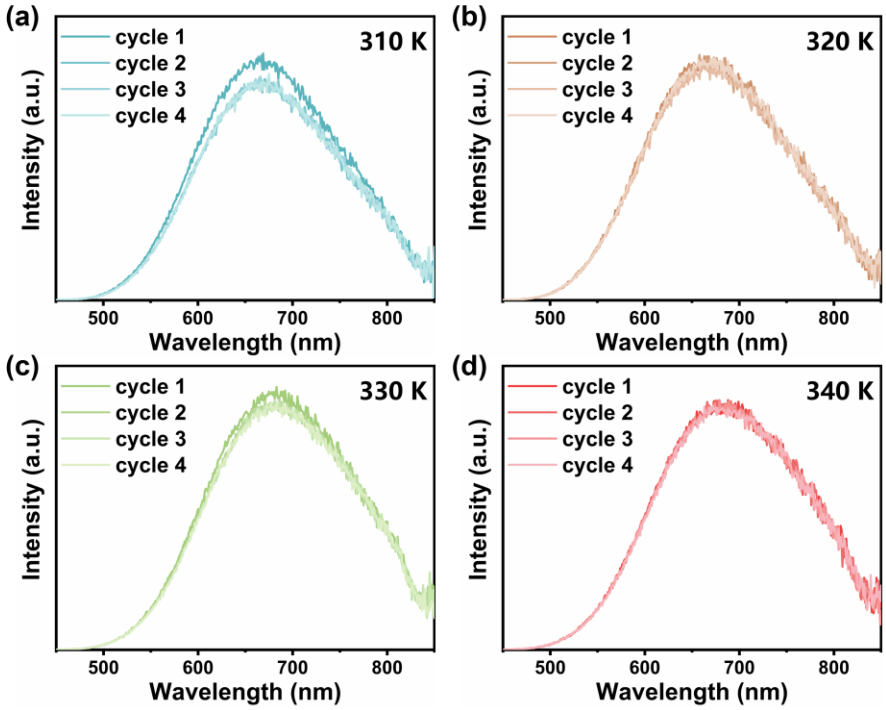

Figure S8. The fluorescence intensity of DMA_4InBr_7:1%Sb throughout repeated cooling and heating cycles in the ranges of 310 K to 320 K and 330 K to 340 K.

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