Supplementary Information for:

Crystal Structure, Semiconducting and Photoluminescence (PL) Properties in Hybrid Tin Perovskites-Like Materials: $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ and $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$

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Figure S4. PL and PL excitation spectra of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ (1) crystals (λ_{exc} =350nm, blue solid line; λ_{exc} =450nm, green solid line; λ_{em} =435 nm, blue dashed line; λ_{em} =525nm, green dashed line)

Figure S5. PL (λ_{exc} =350nm, blue line; λ_{exc} =450nm, green line) spectra of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ (1) cast film from Ethanol

Figure S6. Normalized PL and PL excitation spectra of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ (2) crystalline powders. λ_{ex} =350nm, blue line λ_{ex} =450nm, green line; λ_{em} =475nm, blue dashed line; λ_{em} =560nm, green dashed line.

Figure S7. Images $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ **(2)** crystals taken with optical and fluorescence microscopy. From the left to the right: cross polarized optical image; fluorescence image, UV light excitation. Scale bar is 30μm.

Figure S8. Normalized photoluminescence (PL) spectrum of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ (2) cast films from water solution; λ_{ex} = 350nm.

Table S1. Crystal data for $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ **(1)** and $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ **(2)**

Compound name	$(C_4H_{14}N_2Cl_2)SnCl_6$ **(1)**	$(C_4H_{14}N_2Cl_2)SnBr_{5.65}Cl_{0.35}$ **(2)**
Empirical formula	$C_4H_{14}N_2Cl_8Sn$	$C_4H_{14}N_2Cl_2\ Br_{5.65}Cl_{0.35}Sn$
Color	Colorless	Colorless
Formula weight ($g.mol^{-1}$)	492.46	743.66
Temperature (K)	293	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$
a (Å)	10.1028(7)	10.3622(3)
b (Å)	7.1224(5)	7.4473 (2)
c (Å)	11.7984 (7)	12.3099 (3)
α, β, γ (°)	90, 108.009(7), 90	90, 109.176(3), 90
V ($Å^3$)	807.37(10)	897.25
Z	2	2
ρ_{calc}, ($g.cm^{-3}$)	2.026	2.753
Absorption correction	Gaussian	Gaussian
Radiation (Å)	CuKα (1.54184)	CuKα (1.54184)
μ (mm^{-1})	24.58	29.12
Crystal Shape	Prism	Prism
Crystal size	0.30 × 0.17 × 0.11	0.26 × 0.16 × 0.10
F (000)	476	679
θ range [°]	3.9 to 76.2	3.7 to 76.0
Collected reflections	6361	13853
R_{int}	0.054	0.102
Data/restrains/parameters	1747/7/110	1881/41/136
R_1, wR_2 [$I > 2\sigma(I)$]	0.0435, 0.1311	0.044, 0.1183
R_1, wR_2 [all data]	0.0442, 0.1335	0.045, 0.1197
Goodness-of-fit on F^2	1.163	1.061
Largest diff. peak/hole/e. $Å^{-3}$	0.67/−1.46	1.18/−0.75

Table S2. Selected bond lengths (Å) and angles (°) for $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ (1).

Sn1— Cl1	2.4322 (15)	C1—C2	1.463 (19)
Sn1— Cl2	2.4289 (11)	C1—N1	1.488 (12)
Sn1— Cl3	2.4068 (12)	C2—Cl5	1.765 (11)
Sn1— Cl4	2.4298 (15)	C3—N2	1.455 (9)
Cl3—Sn1—Cl3^{i}	92.11 (7)	C3—C4	1.502 (14)
Cl3—Sn1—Cl2^{i}	88.77 (5)	C4—Cl6B	1.706 (18)
Cl3^{i}—Sn1—Cl2^{i}	178.78 (4)	C4—Cl6A	1.800 (18)
Cl3—Sn1—Cl2	178.78 (4)	C2—C1—N1	111.9 (13)
Cl3^{i}—Sn1—Cl2	88.77 (5)	C1—C2—Cl5	109.4 (10)
Cl2^{i}—Sn1—Cl2	90.33 (6)	N2—C3—C4	111.2 (7)
Cl3—Sn1—Cl4	90.88 (4)	C3—C4—Cl6B	115.0 (10)
Cl3^{i}—Sn1—Cl4	90.88 (4)	C3—C4—Cl6A	98.1 (17)
Cl2^{i}—Sn1—Cl4	89.95 (4)		
Cl2—Sn1—Cl4	89.95 (4)		
Cl3—Sn1—Cl1	89.61 (4)		
Cl3^{i}—Sn1—Cl1	89.61 (4)		
Cl2^{i}—Sn1—Cl1	89.55 (4)		
Cl2—Sn1—Cl1	89.55 (4)		
Cl4—Sn1—Cl1	179.29 (5)		

Symmetry codes: (i) x, −y+1/2, z.

Table S3. Selected bond lengths (Å) and angles (°) for $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ (2).

Sn1—Cl3^{i}	2.463 (17)	Br3—Sn1—Br2^{i}	88.47 (8)
Sn1—Cl3	2.463 (17)	Br2—Sn1—Br2^{i}	90.78 (16)
Sn1—Br3^{i}	2.5678 (6)	Cl3^{i}—Sn1—Br1	90.1 (7)
Sn1—Br3	2.5678 (6)	Cl3—Sn1—Br1	90.1 (7)
Sn1—Br2	2.588 (2)	Br3^{i}—Sn1—Br1	89.94 (2)
Sn1—Br2^{i}	2.588 (2)	Br3—Sn1—Br1	89.94 (2)
Sn1—Br1	2.5989 (8)	Br2—Sn1—Br1	89.23 (5)
Sn1—Br4	2.6039 (8)	Br2^{i}—Sn1—Br1	89.23 (5)
Cl3^{i}—Sn1—Cl3	81.4 (16)	Cl3^{i}—Sn1—Br4	88.9 (7)
Cl3^{i}—Sn1—Br3^{i}	174.6 (8)	Cl3—Sn1—Br4	88.9 (7)
Cl3—Sn1—Br3^{i}	93.2 (8)	Br3^{i}—Sn1—Br4	90.99 (2)
Cl3^{i}—Sn1—Br3	93.2 (8)	Br3—Sn1—Br4	90.99 (2)
Cl3—Sn1—Br3	174.6 (8)	Br2—Sn1—Br4	89.83 (5)
Br3^{i}—Sn1—Br3	92.26 (3)	Br2^{i}—Sn1—Br4	89.83 (5)
Cl3^{i}—Sn1—Br2	86.1 (7)	Br1—Sn1—Br4	178.66 (3)
Br3^{i}—Sn1—Br2	88.47 (8)	C1—N1	1.468 (15)
Br3—Sn1—Br2	178.89 (6)	C1—C2A	1.470 (17)
Cl3—Sn1—Br2^{i}	86.1 (7)	C1—C2B	1.54 (2)
Br3^{i}—Sn1—Br2^{i}	178.89 (6)	C2A—Cl1A	1.769 (19)
C3—C4	1.454 (17)	C2B—Cl1B	1.77 (3)
C4—Cl2B	1.779 (14)	C3—N2	1.446 (11)
C4—Cl2A	1.87 (5)	N1—C1—C2A	117.3 (12)
		N1—C1—C2B	129 (10)
		C1—C2A—Cl1A	109.7 (12)
		C1—C2B—Cl1B	94 (2)
		N2—C3—C4	113.3 (9)
		C3—C4—Cl2B	115.2 (11)
		C3—C4—Cl2A	99 (2)

Symmetry codes: (i) x, $-y+1/2$, z.

Table S4. Hydrogen-bonding geometry (Å, °) for $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ (1).

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C2—H2*E*···Cl2^{i}	0.97	2.93	3.489 (12)	118
C4—H4*B*···Cl3^{ii}	0.97	2.90	3.748 (10)	147
C4—H4*C*···Cl4^{iii}	0.97	2.93	3.734 (12)	141
C4—H4*B*···Cl3^{ii}	0.97	2.90	3.748 (10)	147
C4—H4*D*···Cl4^{iv}	0.97	2.98	3.822 (12)	146
N1—H1*C*···Cl2^{v}	0.89	2.64	3.474 (6)	156
N1—H1*D*···Cl1^{vi}	0.89	2.69	3.5774 (7)	174
N1—H1*E*···Cl1	0.89	2.66	3.367 (6)	137
N1—H1*E*···Cl3^{vii}	0.89	2.92	3.649 (6)	140
N2—H2*A*···Cl2^{vii}	0.89	2.71	3.349 (5)	130
N2—H2*A*···Cl3	0.89	2.89	3.681 (6)	149
N2—H2*B*···Cl2^{iii}	0.89	2.76	3.349 (5)	125
N2—H2*B*···Cl2^{viii}	0.89	2.90	3.449 (6)	122
N2—H2*B*···Cl4^{iii}	0.89	2.80	3.5778 (7)	147
N2—H2*C*···Cl2^{ix}	0.89	2.59	3.449 (6)	164

Symmetry codes: **(i)** $-x+1, y+1/2, -z$; **(ii)** $-x+2, y+1/2, -z+1$; **(iii)** $x, y+1, z$; **(iv)** $-x+2, -y+1, -z+1$; **(v)** $-x+1, -y, -z$; **(vi)** $-x+1, -y+1, -z$; **(vii)** $x, -y+1/2, z$; **(viii)** $-x+1, -y+1, -z+1$; **(ix)** $-x+1, y+1/2, -z+1$.

Table S5. Hydrogen-bonding geometry (Å, °) for $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ (2)

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N1—H1*E*···Br2^{i}	0.89	2.72	3.587 (7)	165
N1—H1*E*···Cl3^{i}	0.89	2.90	3.77 (3)	164
N1—H1*F*···Br1^{ii}	0.89	2.89	3.7443 (8)	162
N1—H1*G*···Br1^{iii}	0.89	2.82	3.478 (8)	132
N1—H1*G*···Br3^{iv}	0.89	3.10	3.861 (6)	145
C2*A*—H2*B*···Br2^{i}	0.97	3.13	3.97 (2)	146
C4—H4*B*···Br3^{v}	0.97	2.85	3.706 (13)	147
C4—H4*C*···Br4^{vi}	0.97	3.00	3.829 (15)	144
C4—H4*B*···Br3^{v}	0.97	2.85	3.706 (13)	147
C4—H4*D*···Br4^{vii}	0.97	3.13	3.941 (15)	142
N2—H2*E*···Br2^{viii}	0.89	2.83	3.467 (6)	130
N2—H2*E*···Br3	0.89	3.08	3.866 (7)	149
N2—H2*E*···Cl3^{viii}	0.89	2.96	3.59 (3)	129
N2—H2*F*···Br2^{vi}	0.89	2.88	3.467 (6)	125
N2—H2*F*···Br2^{ii}	0.89	3.03	3.593 (8)	123
N2—H2*F*···Br4^{vi}	0.89	2.97	3.7449 (8)	146
N2—H2*F*···Cl3^{vi}	0.89	2.96	3.59 (3)	129
N2—H2*F*···Cl3^{ii}	0.89	2.90	3.42 (3)	120
N2—H2*G*···Br2^{ix}	0.89	2.73	3.593 (8)	165
N2—H2*G*···Cl3^{ix}	0.89	2.56	3.42 (3)	163

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; **(ii)** −*x*+1, −*y*+1, −*z*+1; **(iii)** *x*, *y*, *z*+1; **(iv)** *x*, −*y*+1/2, *z*+1; **(v)** −*x*+2, *y*+1/2, −*z*+1; **(vi)** *x*, *y*+1, *z*; **(vii)** −*x*+2, −*y*+1, −*z*+1; **(viii)** *x*, −*y*+1/2, *z*; **(ix)** −*x*+1, *y*+1/2, −*z*+1.

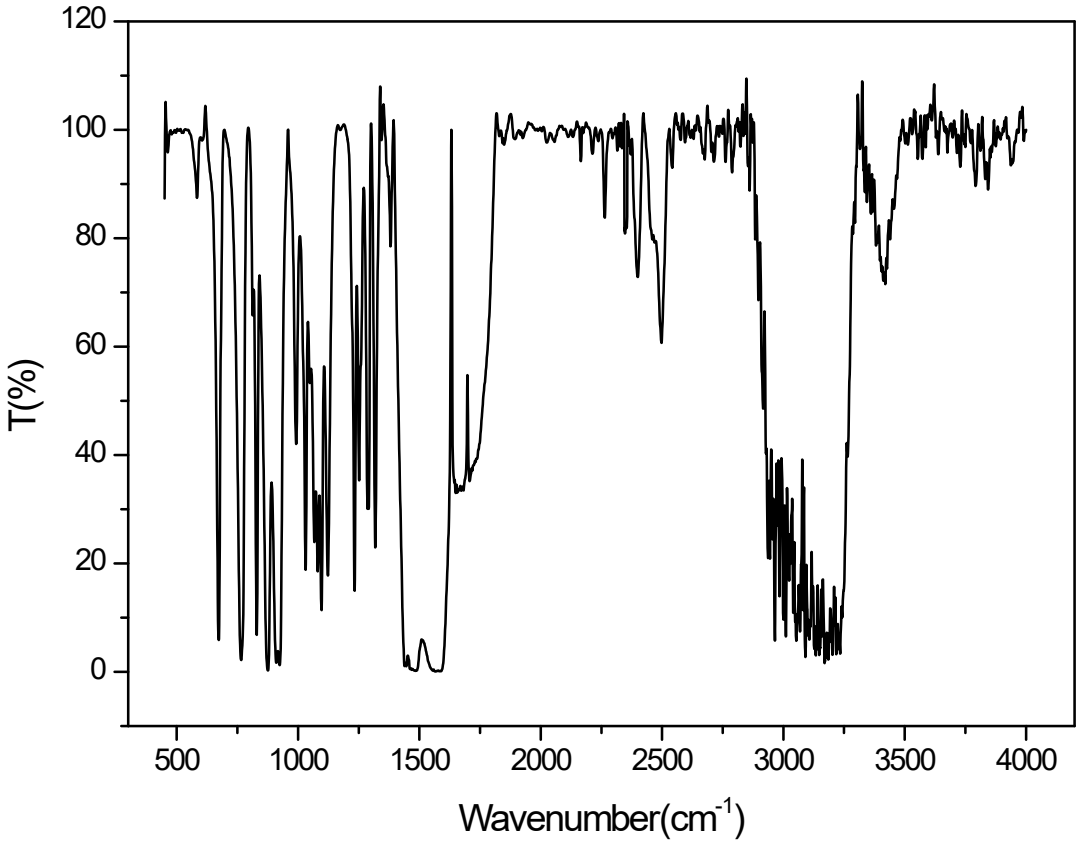


Figure S1. IR spectrum of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ (1)

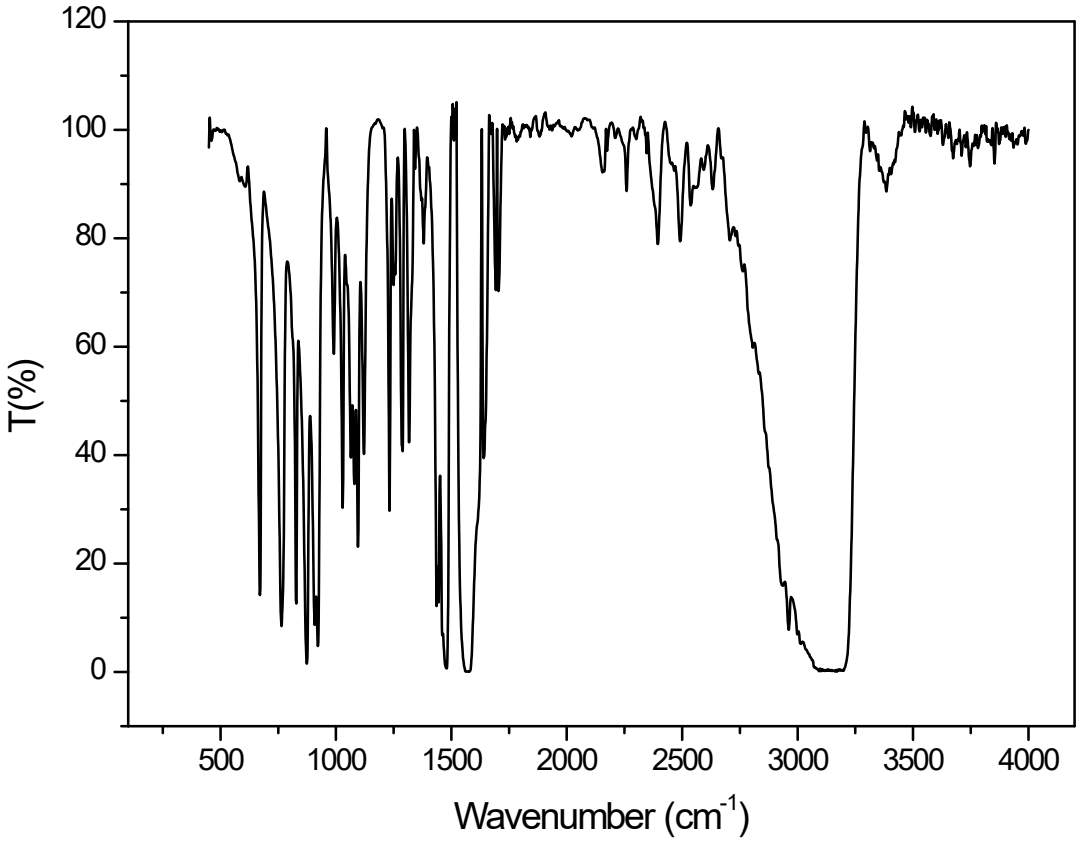


Figure S2. IR spectrum of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ (2).

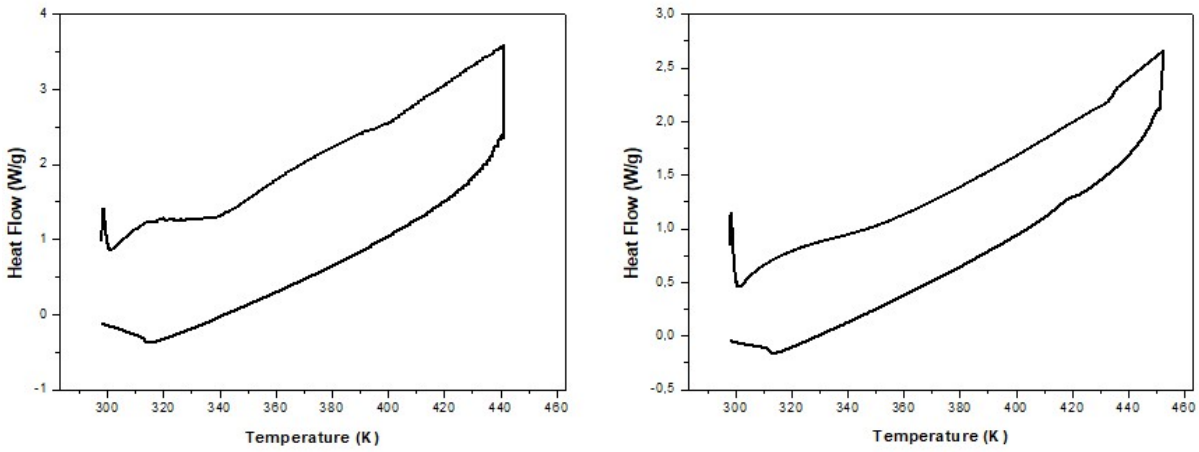


Figure S3. DSC heating and cooling curves for compounds $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ (1) **(a)** and $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ (2) **(b)**.

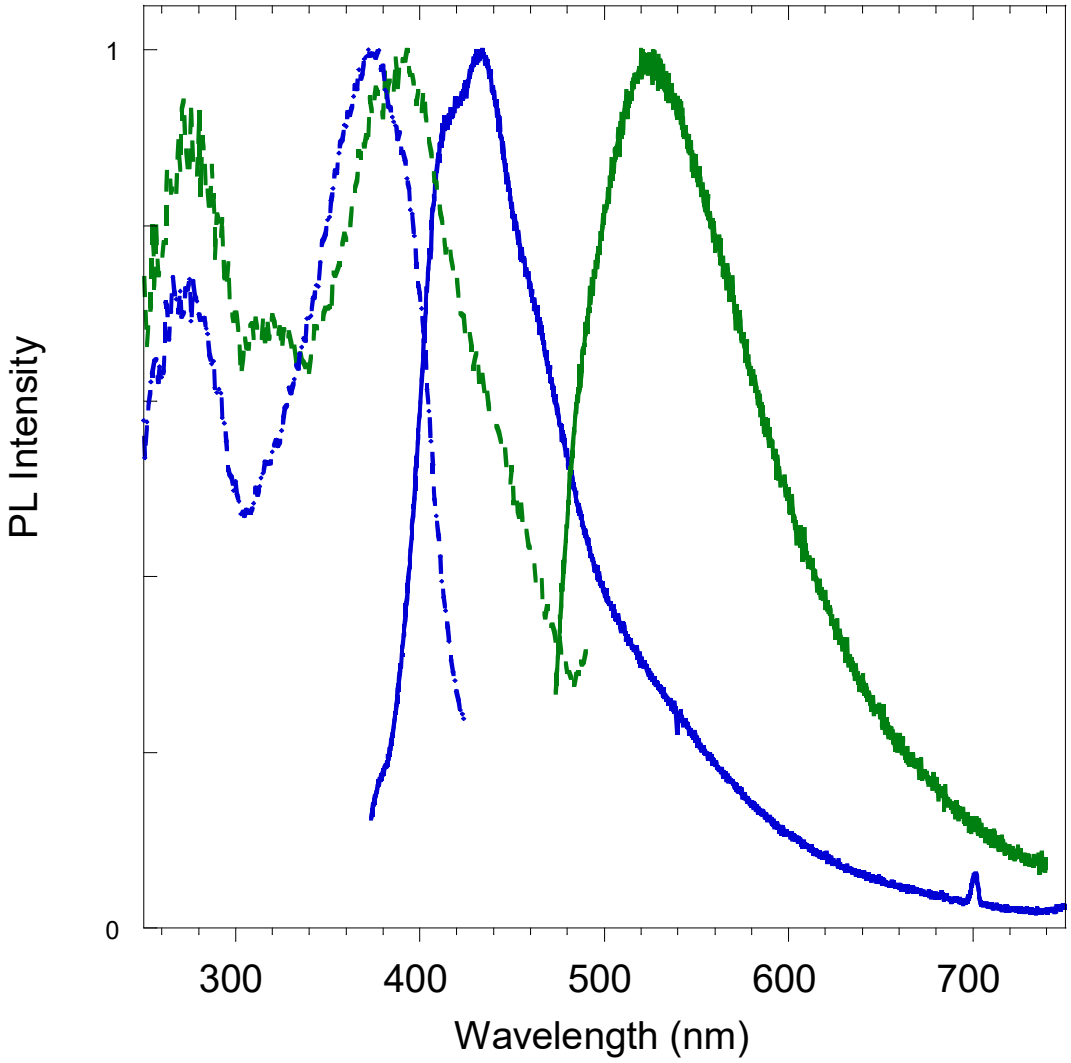


Figure S4. PL and PL excitation spectra of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnCl_6$ (1) crystals (λ_{exc} =350nm, blue solid line; λ_{exc} =450nm, green solid line; λ_{em} =435 nm, blue dashed line; λ_{em} =525nm, green dashed line)

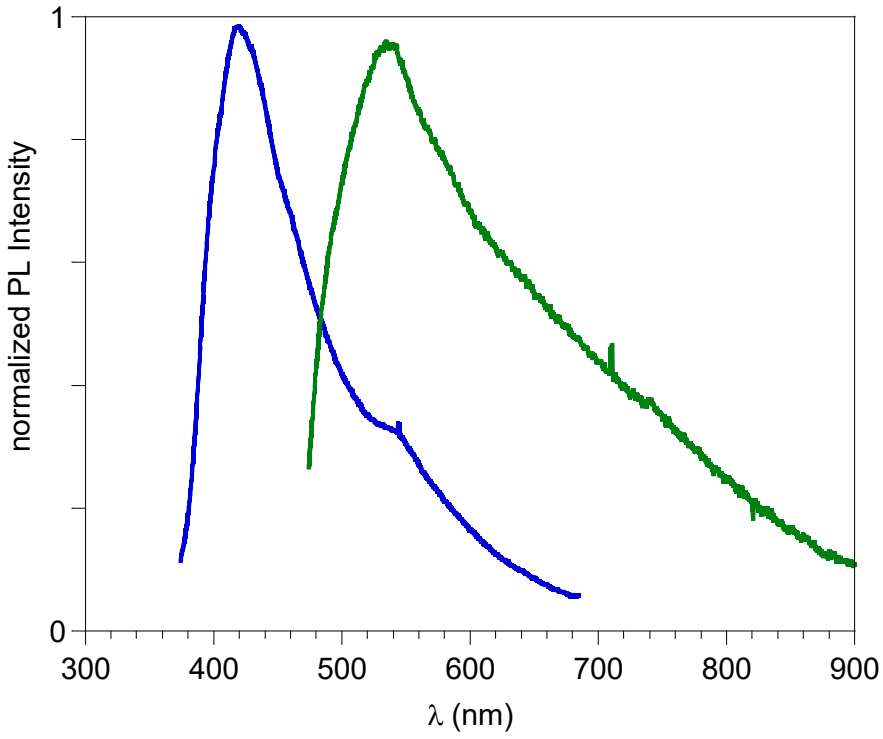
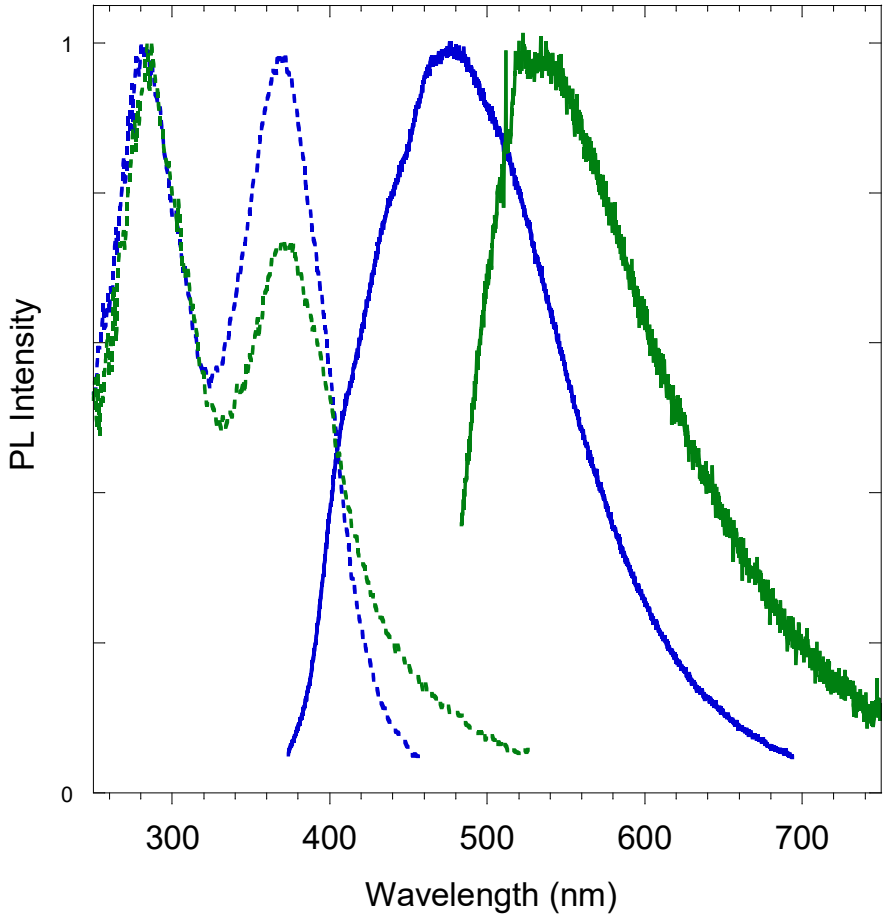


Figure S5. PL (λ_{exc}=350nm, blue line; λ_{exc}=450nm, green line) spectra of [Cl-$(CH_2)_2$-$NH_3]_2SnCl_6$ (1) cast film from Ethanol



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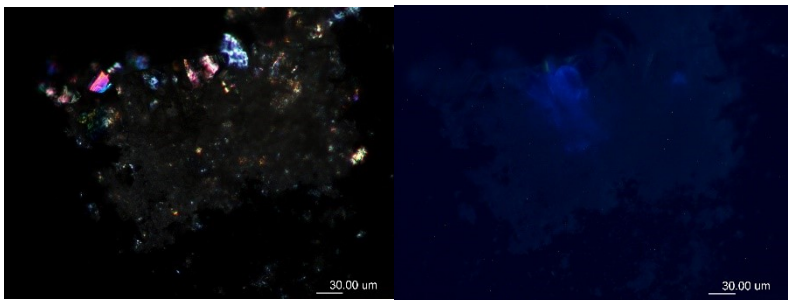

Figure S7. Images $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ **(2)** crystals taken with optical and fluorescence microscopy. From the left to the right: cross polarized optical image; fluorescence image, UV light excitation. Scale bar is 30μm.

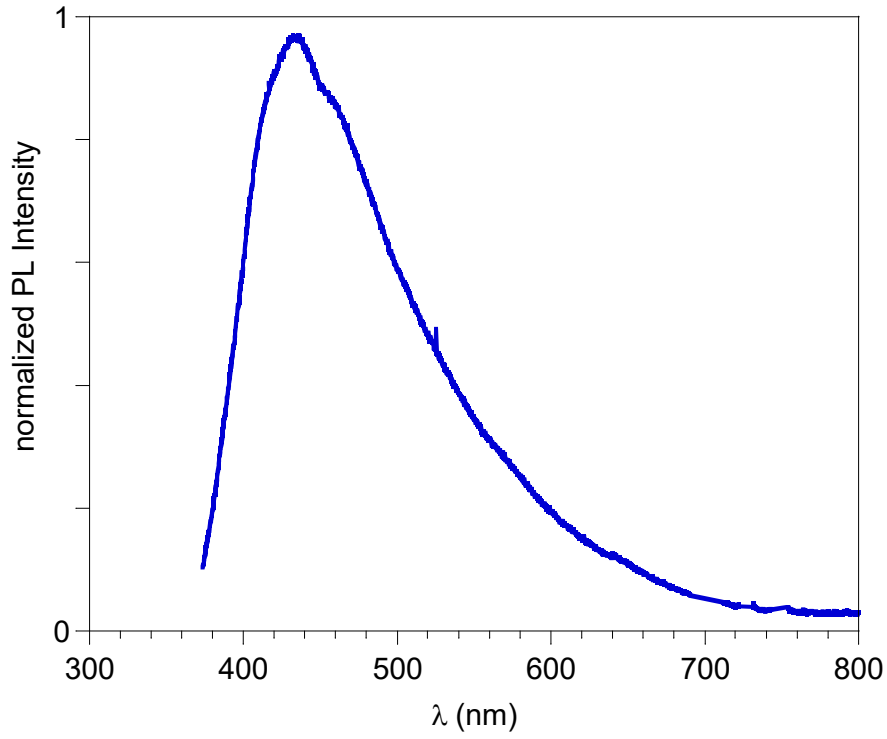

Figure S8. Normalized photoluminescence (PL) spectrum of $[Cl\text{-}(CH_2)_2\text{-}NH_3]_2SnBr_{5.65}Cl_{0.35}$ **(2)** cast films from water solution; λ_{ex} = 350nm.