Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Realization of "warm" white light via halide substitution in polar two-dimensional hybrid perovskites $(2meptH_2)PbCl_xBr_{4-x}$

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Table S1. Crystallographic Data and Structure Refinement of $(2meptH_2)PbCl_4$.

Formula	$C_6H_{18}N_2PbCl_4$
Formula weight (g/mol)	467.22
Temperature (K)	100
Crystal system	monoclinic
Space group	*Cc*
a (Å)	23.9782(13)
b (Å)	7.6090(4)
c (Å)	7.8269(5)
α (deg)	90
β (deg)	97.496(5)
γ (deg)	90
V (Å3)	1415.82(14)
Z	4
D_{calcd} (g/cm^3)	2.192
F (000)	872.0
completeness (%)	99.5%
GOF (F^2)	0.690
R_1 (on F_o^2, I >2s(I))	0.0200
wR_2 (on F_o^2, I >2s(I))	0.0409
[a] $R_1 = \Sigma\|\|F_0\|-\|F_c\|\|/\Sigma\|F_0\|$, $\omega R_2 = [\Sigma[\omega(F_0^2-F_c^2)^2]/\Sigma[\omega(F_0^2)^2]]^{1/2}$	

Table S2. The selected bond lengths [Å] and angles [deg] of $(2meptH_2)PbCl_4$.

Pb(1)–Cl(1)	2.8379(59)
Pb(1)–Cl(2)	2.8575(64)
Pb(1)–Cl(2)#2	2.8646(52)
Pb(1)–Cl(3)	2.8692(60)
Pb(1)–Cl(4)	2.8596(66)
Pb(1)–Cl(4)#1	2.8477(57)
Pb(1)–Cl(2)–Pb(1)#3	145.132(162)
Pb(1)#4–Cl(4)–Pb(1)	145.920(173)

Symmetry transformations used to generate equivalent atoms: #1 x, -y, z-1/2 #2 x, -y+1, z+1/2 #3 x, -y+1, z-1/2 #4 x, -y, z+1/2

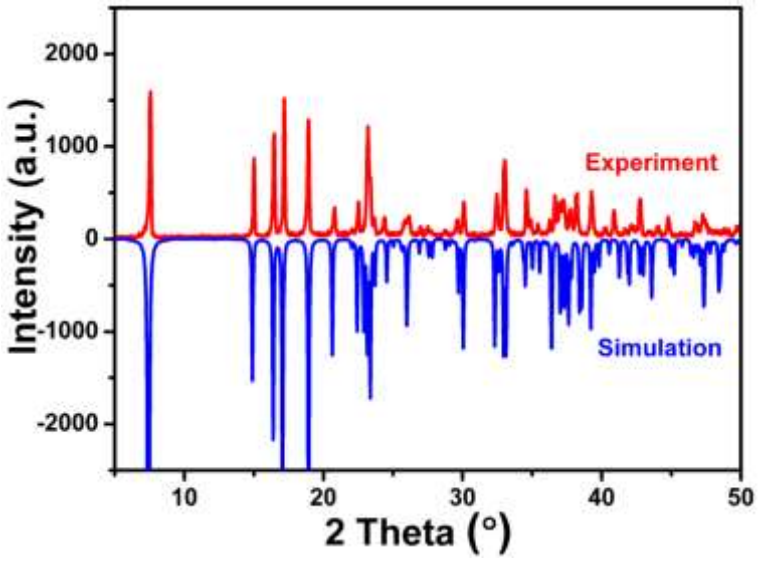

Figure S1. Simulated (blue) and experiment (red) powder X-ray diffraction patterns of (2meptH$_2$)PbCl$_4$**.**

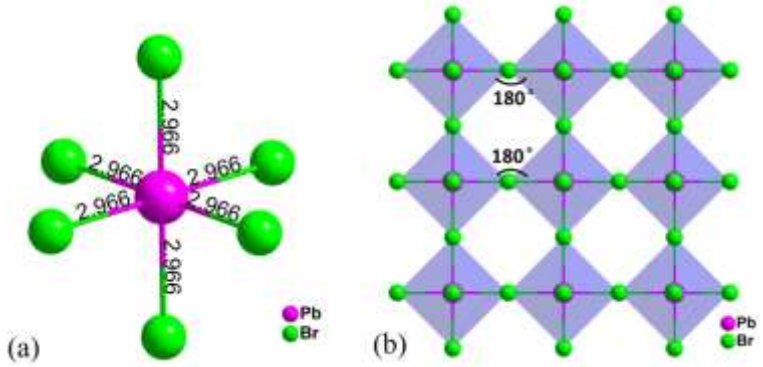

Figure S2. (a) The PbBr$_6$ octahedron of MAPbBr$_3$. (b) The inorganic layer of the corner-sharing PbBr$_6$ octahedron of MAPbBr$_3$.

Table S3. Crystallographic data and structure refinement of $(2meptH_2)PbCl_xBr_{4-x}$.

Formula	$C_6H_{18}N_2PbCl_{1.4}Br_{2.6}$	$C_6H_{18}N_2PbCl_{0.6}Br_{3.4}$	$C_6H_{18}N_2PbCl_{0.2}Br_{3.8}$
Formula weight (g/mol)	582.79	617.35	636.16
Temperature (K)	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*Cc*	*Cc*	*Cc*
a (Å)	24.280(2)	24.3453(17)	24.3895(10)
b (Å)	7.8130(5)	7.8535(3)	7.8879(3)
c (Å)	8.0236(6)	8.1277(5)	8.2067(3)
α (deg)	90	90	90
β (deg)	98.476(3)	98.776(6)	98.966(2)
γ (deg)	90	90	90
V (Å3)	1505.45(19)	1535.79(16)	1559.53(10)
Z	4	4	4
D_{calcd} (g/cm^3)	2.571	2.670	2.709
F (000)	1059.2	1112.8	1145.6
completeness (%)	99.2%	99.7%	99.7%
GOF (F^2)	1.074	1.054	1.073
R_1 (on F_o^2, I >2s(I))	0.0730	0.0579	0.0408
wR_2 (on F_o^2, I >2s(I))	0.2326	0.1658	0.1245

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$, $\omega R_2 = [\Sigma[\omega(F_0^2-F_c^2)^2]/\Sigma[\omega(F_0^2)^2]]^{1/2}$

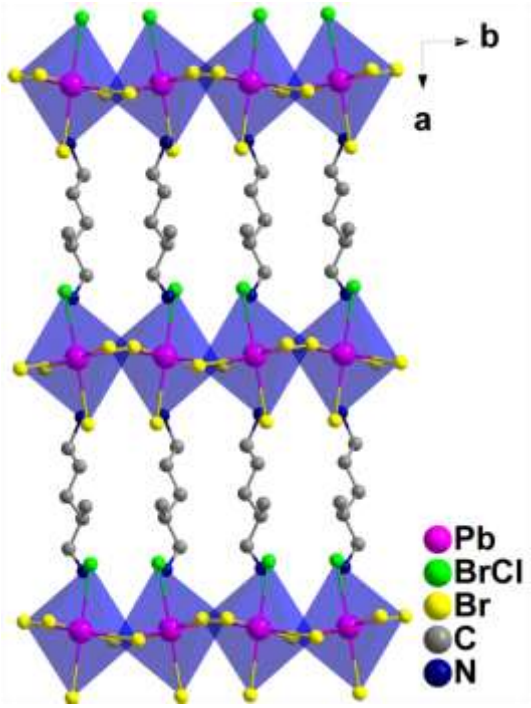

Figure S3. Packing structure of $(2meptH_2)PbCl_{0.6}Br_{3.4}$, the hydrogen atoms are omitted for clarity.

Table S4. Distortion (Δ*d)* of individual "PbX_6" octahedron and the average Pb-X-Pb angles of $(2meptH_2)PbCl_xBr_{4-x}$.

Compound	Br_4	$Cl_{0.2}Br_{3.8}$	$Cl_{0.6}Br_{3.4}$	$Cl_{1.4}Br_{2.6}$	Cl_4
Δ*d* ($\times 10^6$)	4.3447	3.1229	15.4788	45.0656	13.5364
Pb-X-Pb [deg]	145.39	145.44	146.0	146.4	145.53

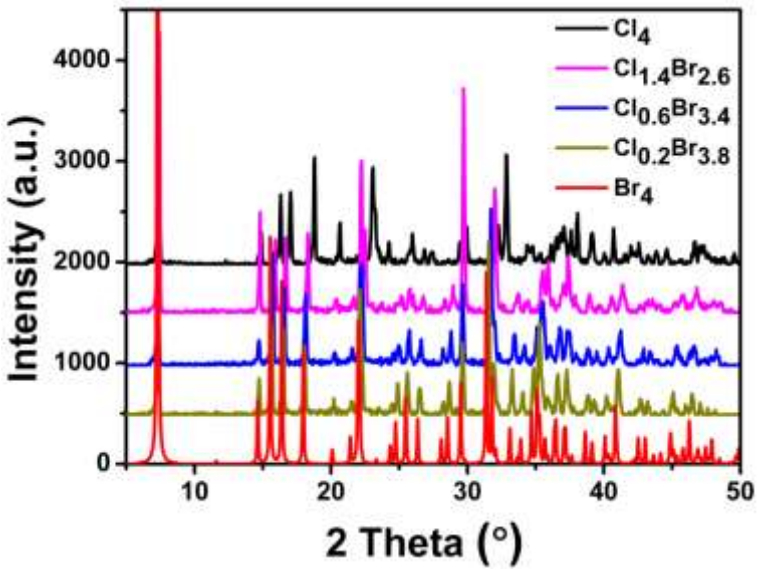

Figure S4. PXRD patterns of $(2meptH_2)PbCl_xBr_{4-x}$.

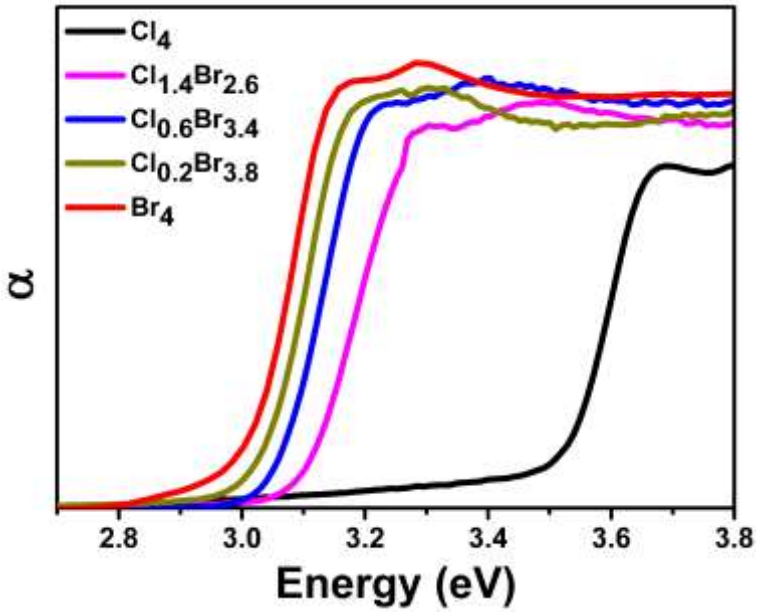

Figure S5. Optical absorption spectra of $(2meptH_2)PbCl_xBr_{4-x}$.

Table S5. The detailed PL data of $(2meptH_2)PbCl_xBr_{4-x}$.

Compound	CIE	CRI	CCT	PLQE
Br_4	(0.24, 0.23)	91	61872	3.37%
$Cl_{0.2}Br_{3.8}$	(0.22, 0.23)	86	54928	3.17%
$Cl_{0.6}Br_{3.4}$	(0.25, 0.28)	87	15137	2.54%
$Cl_{1.4}Br_{2.6}$	(0.29, 0.33)	86	8162	1.67%
Cl_4	(0.39, 0.43)	84	3958	1.05%

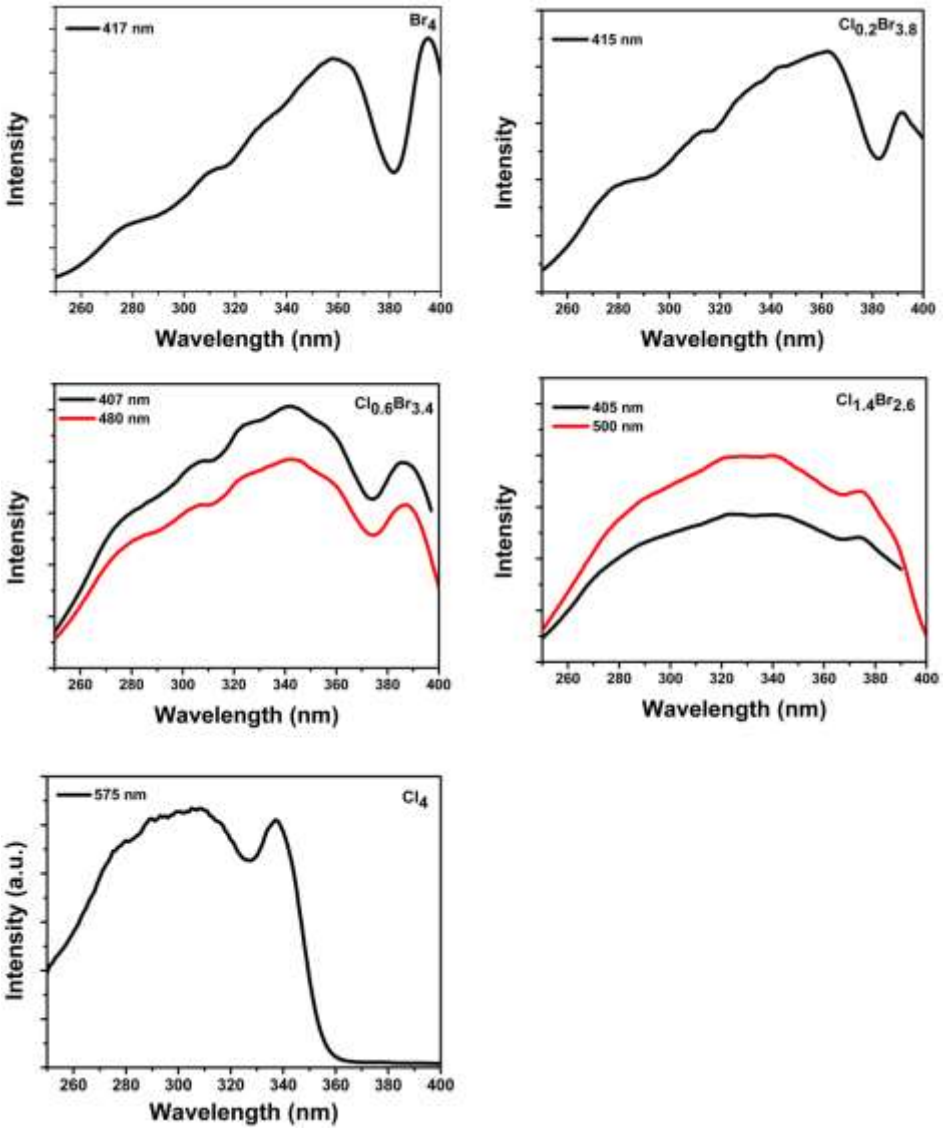

Figure S6. Excitation spectra of $(2meptH_2)PbCl_xBr_{4-x}$.

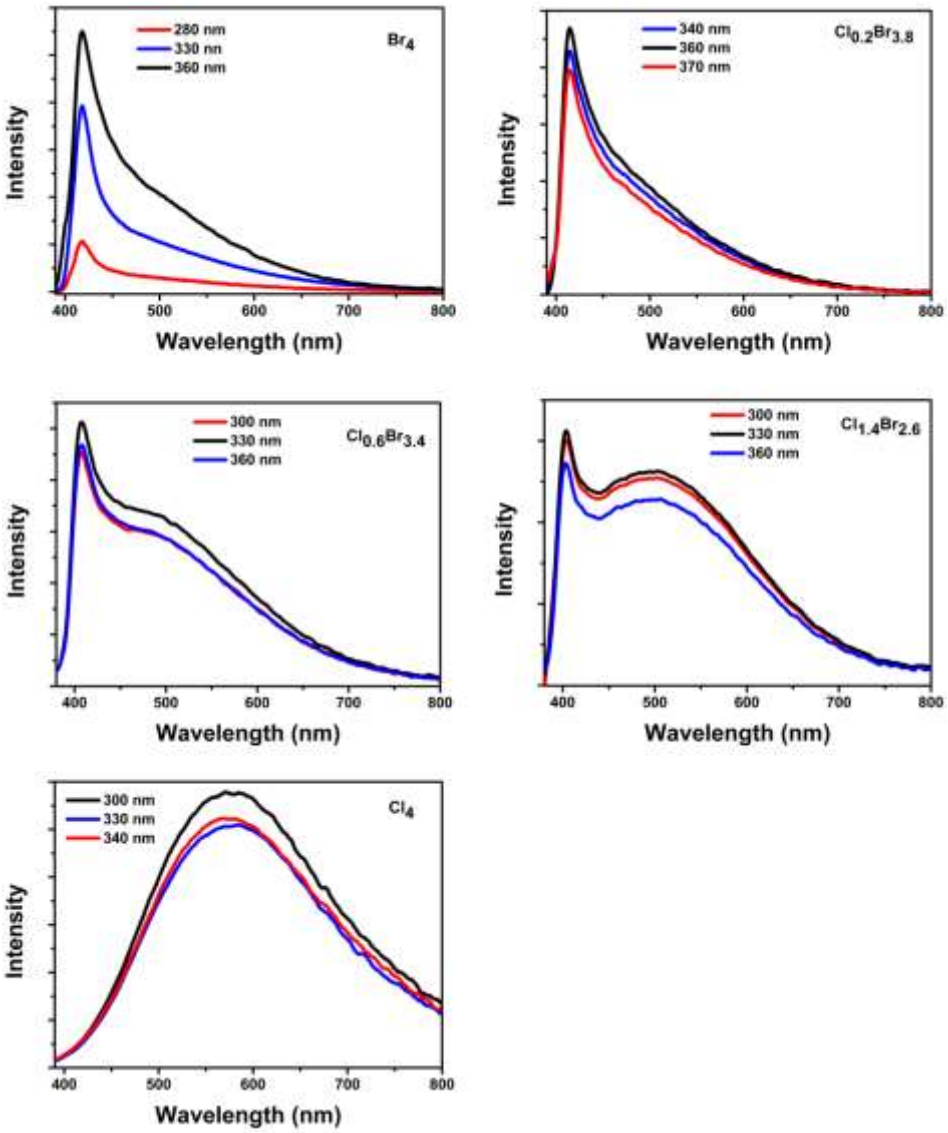

Figure S7. Emission spectra of $(2meptH_2)PbCl_xBr_{4-x}$ measured at different excitation wavelength.

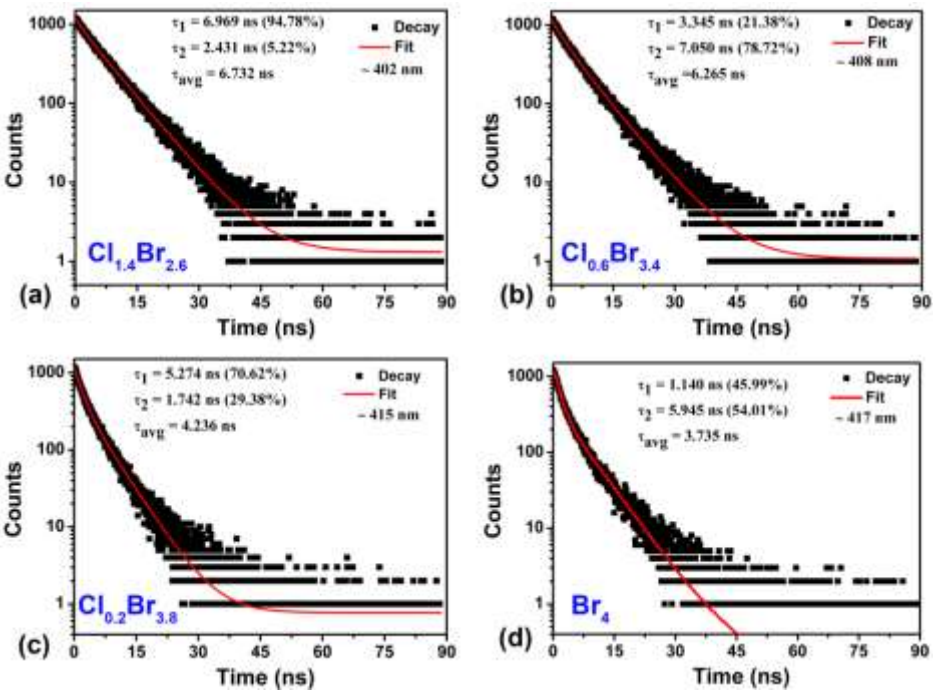

Figure S8. Time-resolved PL decay and fit of the higher-energy narrow peak (τ_h) of $(2meptH_2)PbCl_xBr_{4-x}$.

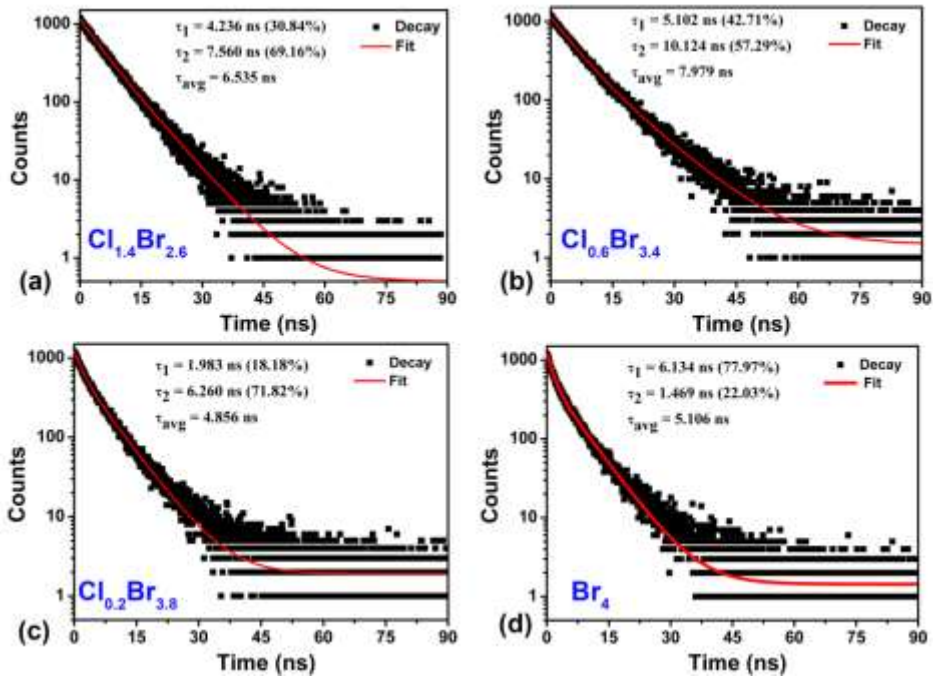

Figure S9. Time-resolved PL decay and fit of the lower-energy peak (τ_l) of $(2meptH_2)PbCl_xBr_{4-x}$.

Table S6. The average lifetimes of $(2meptH_2)PbCl_xBr_{4-x}$.

Compound	τ_h (ns)	τ_l (ns)
Br_4	3.735	5.106
$Cl_{0.2}Br_{3.8}$	4.236	4.856
$Cl_{0.6}Br_{3.4}$	6.265	7.979
$Cl_{1.4}Br_{2.6}$	6.732	6.535
Cl_4	/	3.824

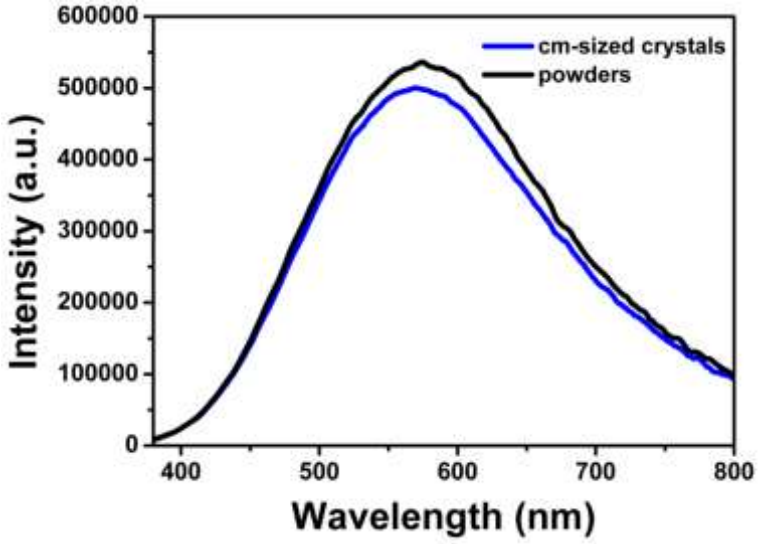

Figure S10. Emission spectra of powders and crystals (black and blue) of $(2meptH_2)PbCl_4$.

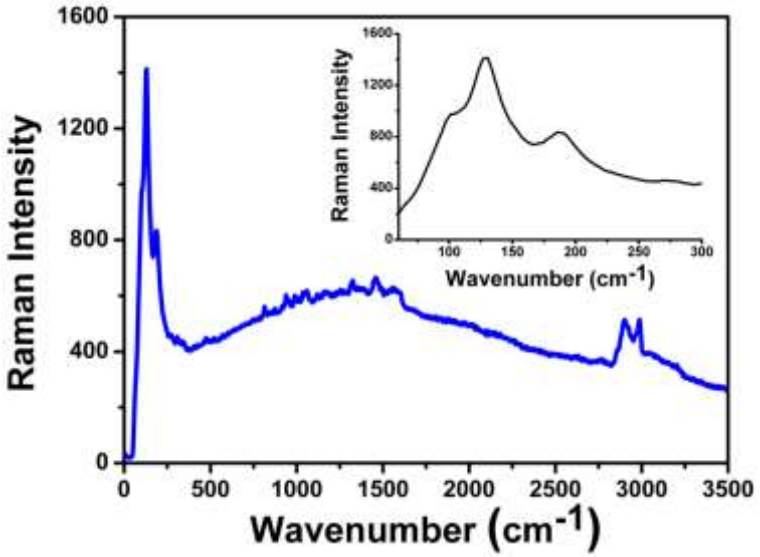

Figure S11. Raman spectrum of $(2meptH_2)PbCl_4$. Inset: Peaks shift from 60 cm^{-1} to 300 cm^{-1}.