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

Hybrid lead halide $DMAPbX_3$ ($X=Cl^-$ and Br^-) perovskites with multiple functional properties

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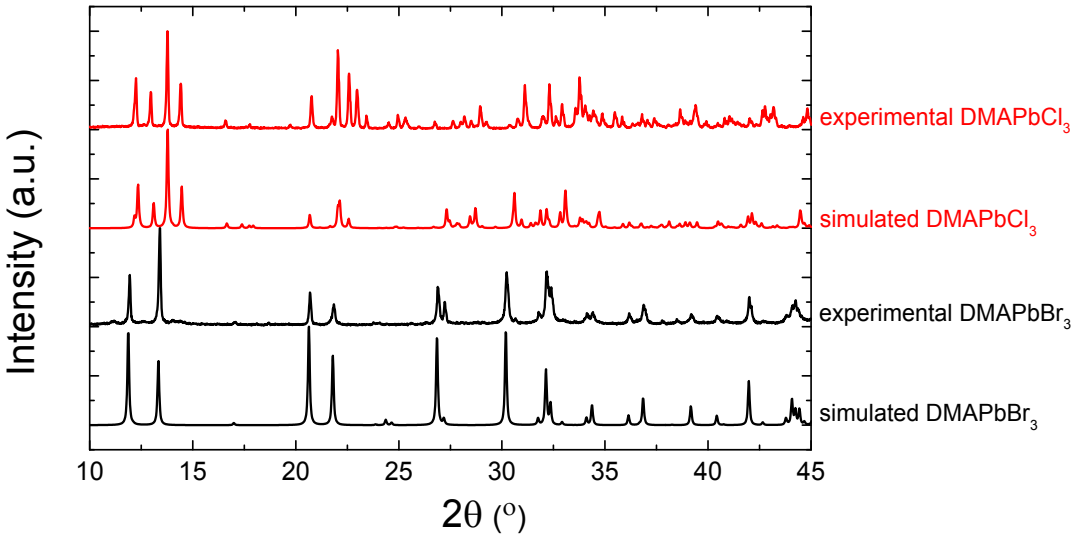

Fig. S1.- Room temperature experimental PXRD patterns for the obtained $DMAPbX_3$ ($X= Cl^-, Br^-$) compounds together with the simulated patterns based on their single crystal structures at room temperature.

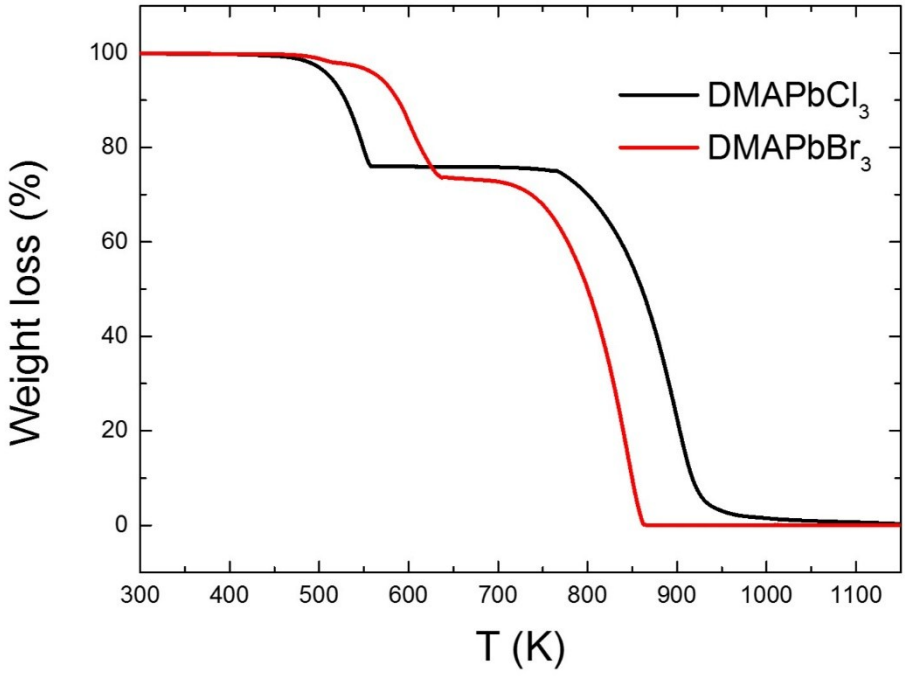

Fig. S2.- TGA decomposition curve for the $DMAPbX_3$ (X= Cl^-, Br^-) compounds.

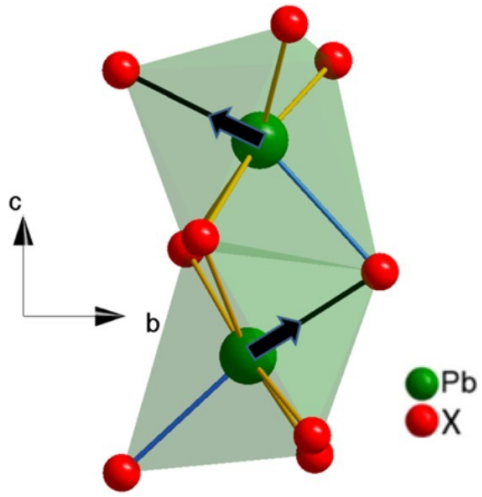

Fig. S3.- Structural detail of $[Pb_2X_9]$ dimers present on the LT-phase of $DMAPbX_3$ (X= Cl^-, Br^-), where the arrows represent the Pb-off-center shift towards one of the corners of the $[PbX_6]$ octahedra.

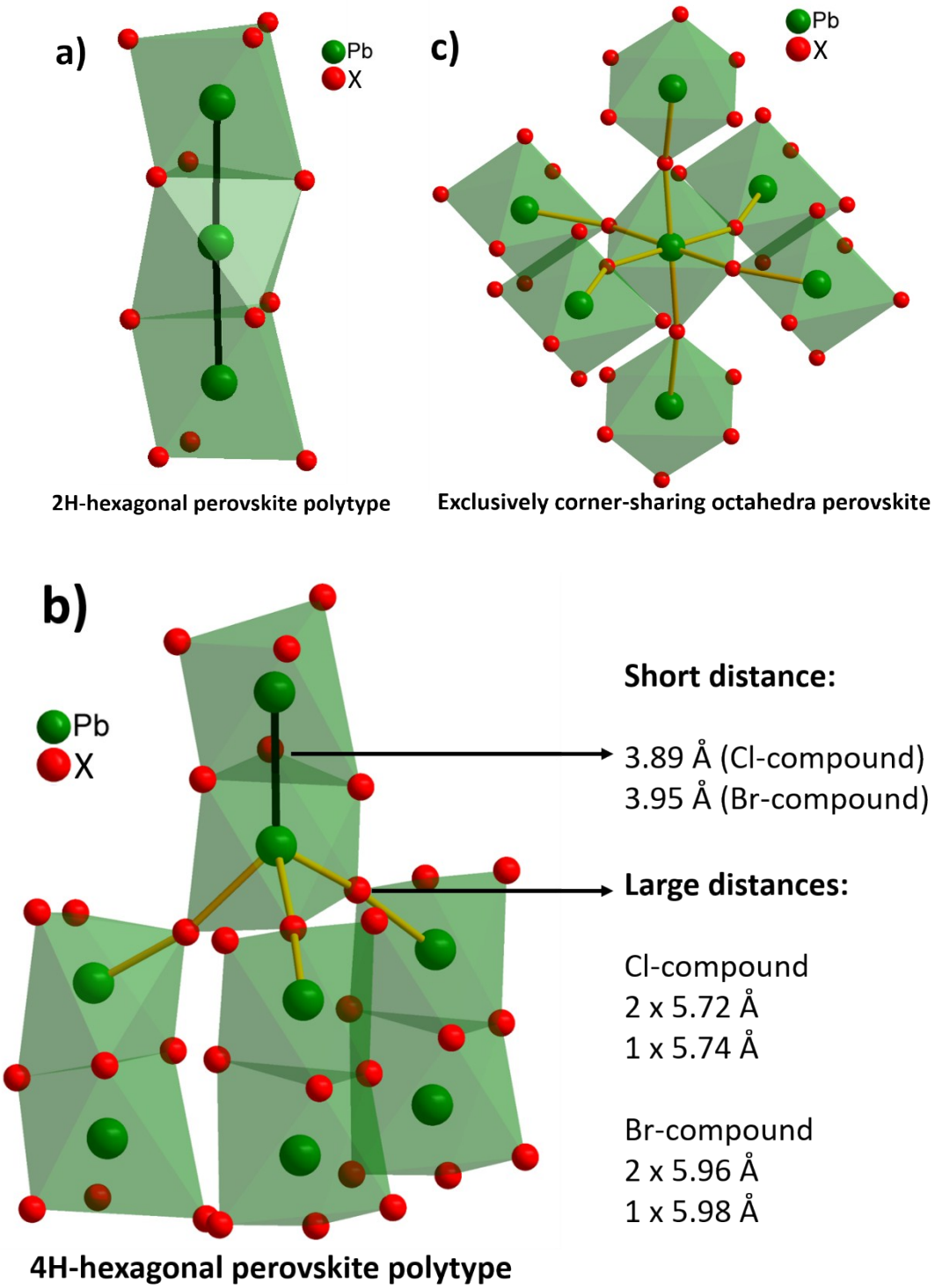

Fig. S4.- a) Structural detail of 2H-hexagonal perovskite polytype, where we remark that each octahedra is linked to two nearest neighbours by face-sharing. The two Pb^{2+}- Pb^{2+} distances are shown by a solid line. b) Structural detail of $DMAPbX_3$ (X= Cl^-, Br^-) compounds, where we remark that each octahedra is linked to four nearest neighbours (one by face-sharing and three by corner-sharing). The four Pb^{2+}- Pb^{2+} distances are shown by a solid line. c) Structural detail of perovskite, where we remark that each octahedra is linked to six nearest neighbours by corner-sharing. The six Pb^{2+}- Pb^{2+} distances are shown by a solid line.

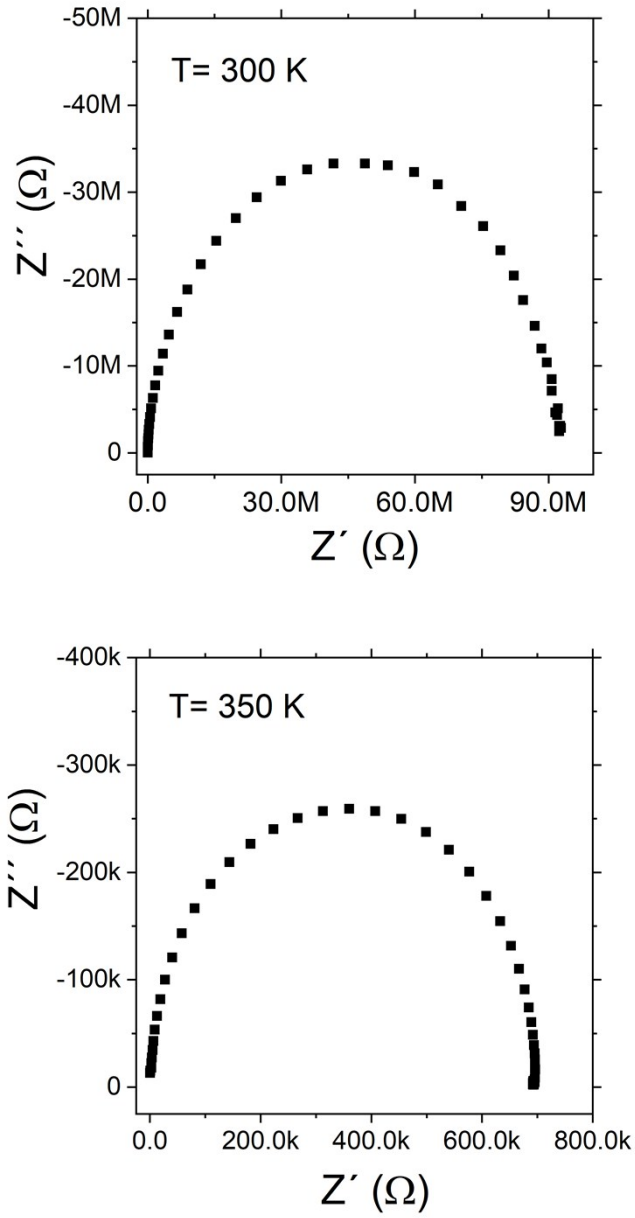

Fig. S5.- Impedance complex plane plots for the $DMAPbCl_3$ sample at T=300 K (top) and T=350 K (bottom)

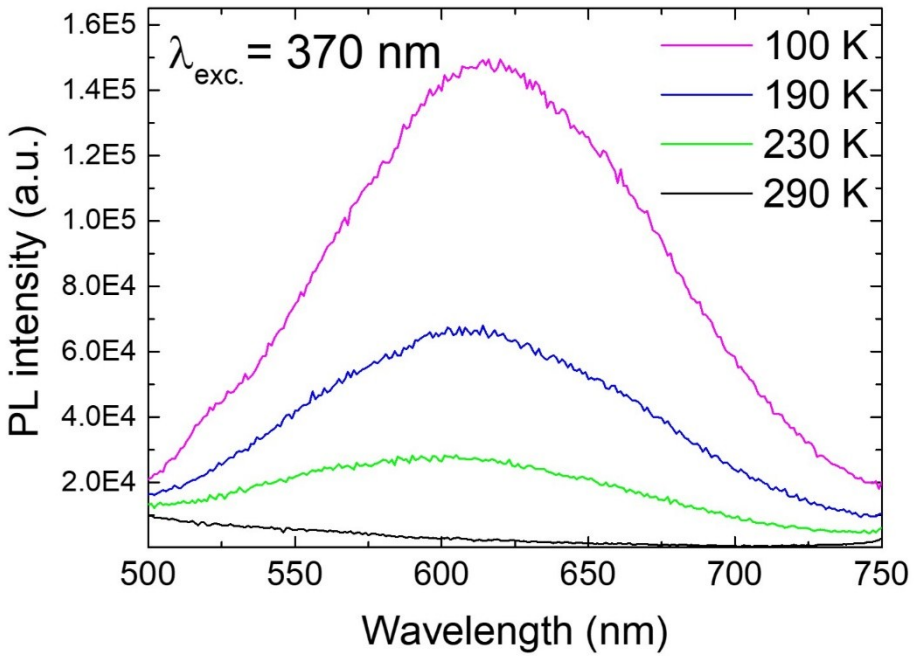

Fig. S6. Photoluminescence (PL) spectra for $DMAPbBr_3$ with excitation wavelength of 370 nm at different temperatures.

Table S1. Data collection, cell and refinement parameters from the single crystal X-ray diffraction studies carried out at T=320 K and T=100 K for the $DMAPbX_3$ compounds.

Empirical formula	**$C_4H_{16}Cl_6N_2Pb_2$**	**Cl_3Pb + Disordered cation**	**$C_4H_{16}Br_6N_2Pb_2$**
Formula weight	719.29	313.55	986.03
Temperature	100(2) K	320(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Hexagonal	Orthorhombic
Space group	$P2_12_12_1$	$P6_3/mmc$	$P2_12_12_1$
Unit cell dimensions	a = 8.5000(2) Å b = 13.4458(4) Å c = 14.1302(5) Å	a = b = 8.3732(3) Å c = 13.9808(9) Å	a = 8.7631(4) Å b = 13.9568(6) Å c = 14.7110(7) Å
Volume	1614.93(8) $Å^3$	848.88(9) $Å^3$	1799.23(14) $Å^3$
Z	4	4	4
Density (calculated)	2.958 Mg/m^3	2.453 Mg/m^3	3.640 Mg/m^3
Absorption coefficient	21.787 mm^{-1}	20.702 mm^{-1}	31.990 mm^{-1}
F(000)	1280	532	1712
Crystal size	0.30 x 0.17x 0.03 mm^3	0.30 x 0.17 x 0.03 mm^3	0.19 x 0.18 x 0.12 mm^3
Theta range for data collection	2.09 to 33.31°.	2.81 to 23.85°.	2.01 to 25.41°.
Index ranges	-13<=h<=13, -20<=k<=20, -21<=l<=21	-4<=h<=0, 0<=k<=9, 0<=l<=15	-10<=h<=10, -16<=k<=16, -17<=l<=17
Reflections collected	167744	21132	201429
Completeness (theta max.)	99.1 % (33.31º)	100.0 % (23.85º)	100.0 % (25.41º)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14329 / 0 / 134	806 / 0 / 13	23098 / 18 / 142
Goodness-of-fit on F^2	1.028	1.097	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0426 wR2 = 0.1097	R1 = 0.0517 wR2 = 0.1458	R1 = 0.0979 wR2 = 0.2229
R indices (all data)	R1 = 0.0511 wR2 = 0.1142	R1 = 0.0653 wR2 = 0.1580	R1 = 0.1360 wR2 = 0.2577
Largest diff. peak and hole	2.795 and -4.597 $e.Å^{-3}$	0.467 and -0.670 $e.Å^{-3}$	4.214 and -2.844 $e.Å^{-3}$

Table S2- Pb-Cl bond lengths (Å) for $DMAPbCl_3$ at T= 100 K and 320 K.

T=100 K				**T=320 K**	
Pb(1)-Cl(1)	2.928(3)	**Pb(2)-Cl(2)^{ii}**	3.136(3)	**Pb(1)-Cl(2)**	2.849(5)
Pb(1)-Cl(2)	2.685(3)	**Pb(2)-Cl(3)**	2.800(3)	**Pb(1)-Cl(3)**	2.8756(9)
Pb(1)-Cl(3)	2.840(3)	**Pb(2)-Cl(4)**	2.960(3)		
Pb(1)-Cl(4)	2.825(3)	**Pb(2)-Cl(5)**	2.696(3)		
Pb(1)-Cl(5)	3.161(3)	**Pb(2)-Cl(6)**	2.807(4)		
Pb(1)-Cl(1)^{i}	2.887(3)	**Pb(2)-Cl(6)^{iii}**	2.903(4)		

i) 1/2+x,1/2-y,1-z; ii) 1/2-x,1-y,-1/2+z; iii) 1/2+x,1/2-y,-z

Table S3- Pb-Br bond lengths (Å) for $DMAPbBr_3$ at T= 100 K and 295 K.

T=100 K				**T=295 K**	
Pb(1)-Br(1)	3.007(7)	**Pb(2)-Br(2)^{ii}**	3.212(6)	**Pb(1)-Br(1)**	2.998*
Pb(1)-Br(2)	2.841(6)	**Pb(2)-Br(3)**	2.958(7)	**Pb(1)-Br(2)**	2.997*
Pb(1)-Br(3)	2.959(7)	**Pb(2)-Br(4)**	3.059(7)		
Pb(1)-Br(4)	2.999(7)	**Pb(2)-Br(5)**	2.851(6)		
Pb(1)-Br(5)	3.255(6)	**Pb(2)-Br(6)^{iii}**	3.003(8)		
Pb(1)-Br(1)^{i}	3.042(8)	**Pb(2)-Br(6)**	2.974(8)		

i) 1/2+x,1/2-y,1-z; ii) 1/2-x,1-y,-1/2+z; iii) 1/2+x,1/2-y,-z

*Data from GIYQUA (CSD) Ref. [44].