Electronic Supplementary Information

Room Temperature Formation of Organic-Inorganic Lead Halide Perovskites: Design of Nanostructured and Highly Reactive Intermediates

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Table S1. The basic chemical properties of different ligands.

Ligand	van der Waals Volume ($cm^3. mol^{-1}$)[a]	Boiling point (℃)	PbI_2 solubility (mg/ml)[b]	$PbI_2.(L)_x$ conversion time (s)[c]	PbI_2/L coordination ratio[d]	Interlayer spacing of $PbI_2.(L)_x$ (Å)
-	-	-	-	-	-	6.918 [e]
TBP	146.05	197	148	300	1:1	15.152
Py	79.89	115	<5	100	1:2	8.598
DMF	77.52	153	475	50	1:1	9.196
DMSO	71.43	189	595	140	1:2	8.437
EDA	68.82	116	<5	50	1:2	-

a) http://www.molinspiration.com/cgi-bin/properties. b) The solubility test was conducted at room temperature (25 ℃). c) The progress of chemical reactions was monitored by UV-vis spectra. d) The data were estimated by TGA. e) The interlayer spacing of PbI_2.

Thermogravimetric analysis (TGA)

The content of L in the $PbI_2.(L)_x$ complexes were estimated by TGA. The TGA results of $PbI_2.(L)_x$ intermediates were shown in **Figure S1**. The $PbI_2.(Py)_2$ and PbI_2.DMF complexes exhibited a one-step decomposition process with weight-loss of 25.41% and 13.34% at 135.49℃ and 113.11℃, respectively. $PbI_2.(DMSO)_2$ intermediate exhibited a two-step decomposition process with weight-loss of 12.40% at each step and was completely decomposed at 142.59℃. Both $PbI_2.(EDA)_2$ and PbI_2.TBP intermediate also shown a two-step decomposition process and completely decomposed at 328.72℃ and 263.71℃ with weight-loss of 19.72% and 23.0%, respectively. The value of *x* is calculated as follows:

$$x = \frac{M_W(PbI_2) \times W_{loss}\%}{M_w(L)(1 - W_{loss}\%)} \qquad (1)$$

where $M_w(PbI_2)$ =461 g/mol, $M_w(L)$ is the molecular weight of ligand, $W_{loss}\%$ is refer to the weight proportion of ligand in the $PbI_2.(L)_x$ intermediates. Then, we can get the content of L in the $PbI_2.(L)_x$ intermediates as we summarized in **Table S1**.

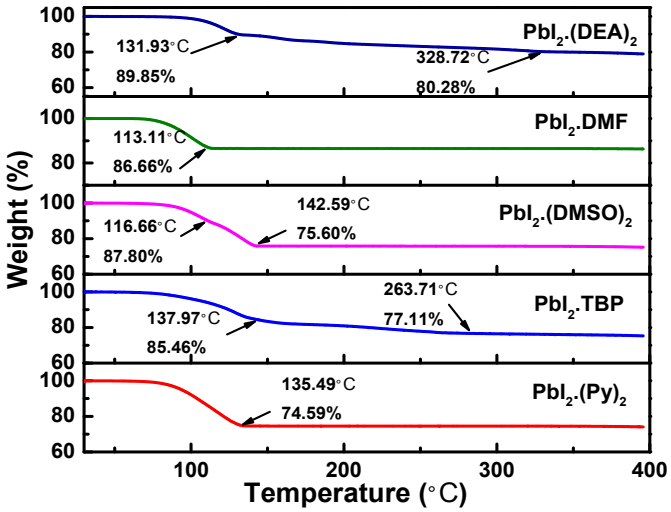

Figure S1. Thermogravimetric analysis (TGA) of $PbI_2.(L)_x$ intermediates.

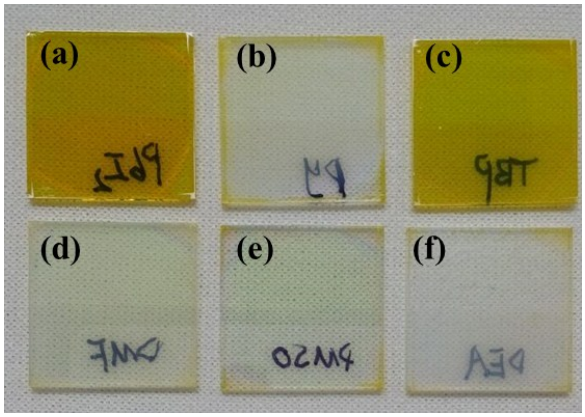

Figure S2. The photographs of $PbI_2.(L)_x$ intermediates in which (a) is PbI_2, (b) is $PbI_2.(Py)_2$, (c) is $PbI_2.TBP$, (d) is $PbI_2.(DMSO)_2$, (e) is $PbI_2.DMF$, and and (f) is $PbI_2.(EDA)_2$ film.

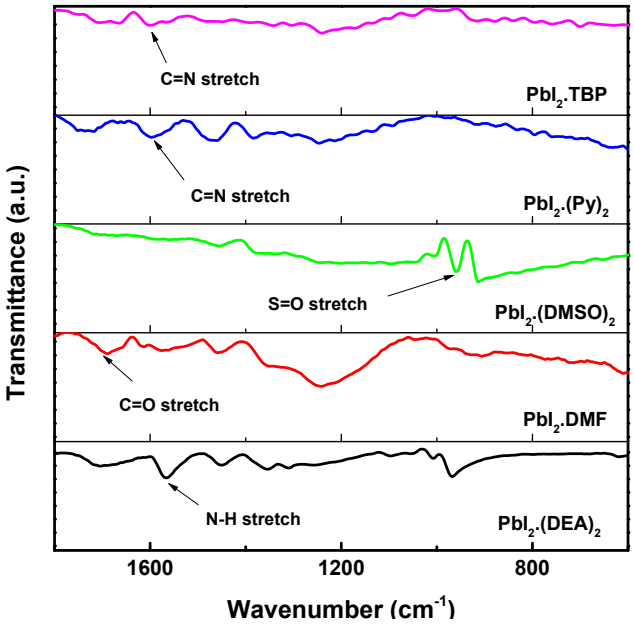

Figure S3. Fourier transform infrared spectrometer (FTIR) of $PbI_2.(L)_x$ complexes.

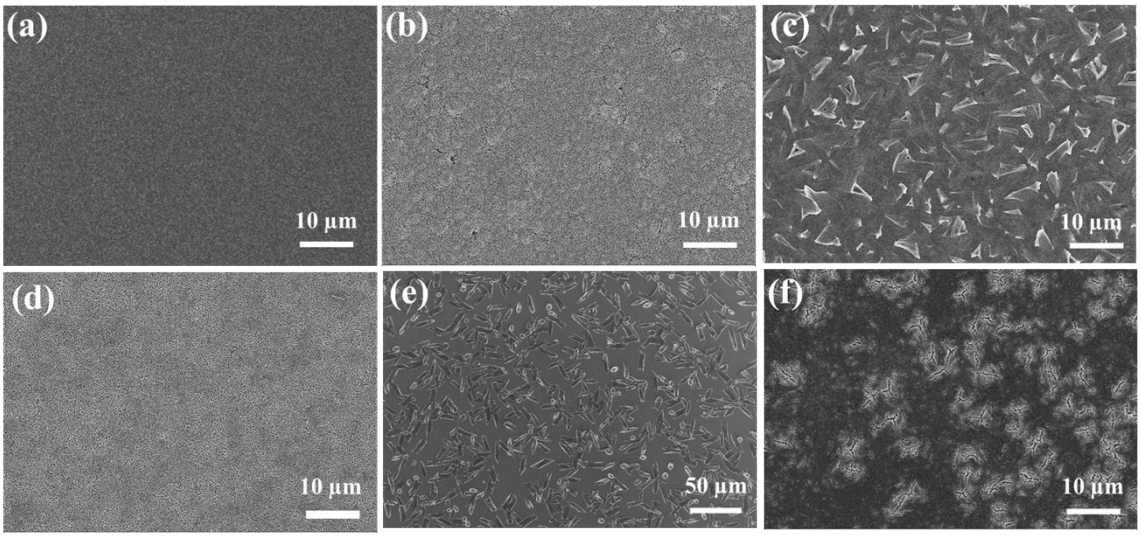

Figure S4. Top-view SEM images of $PbI_2.(L)_x$ intermediates with low magnification in which (a) is untreated PbI_2, (b) is $PbI_2.(Py)_2$, (c) is PbI_2.TBP, (d) is $PbI_2.(DMSO)_2$, (e) is PbI_2.DMF and (f) is $PbI_2.(EDA)_2$ film.

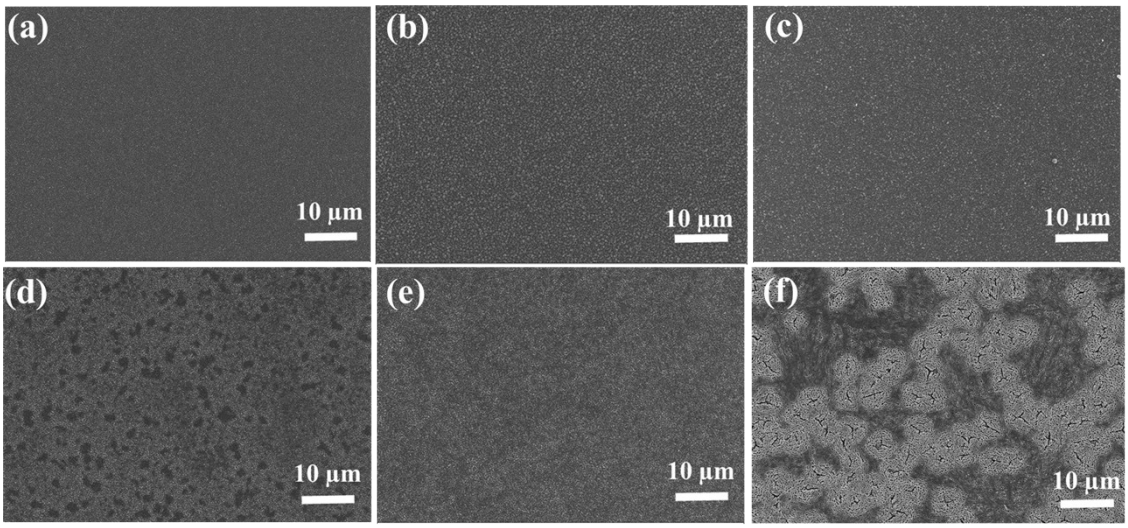

Figure S5. Top-view SEM images of $CH_3NH_3PbI_3$ films with low magnification from (a) PbI_2, (b) $PbI_2.(Py)_2$, (c) PbI_2.TBP, (d) $PbI_2.(DMSO)_2$, and (e) PbI_2.DMF on NiO_x/ITO substrate. (f) Top-view SEM image of $PbI_2.(EDA)_2$ film after dipping into CH_3NH_3I solution with low magnification.

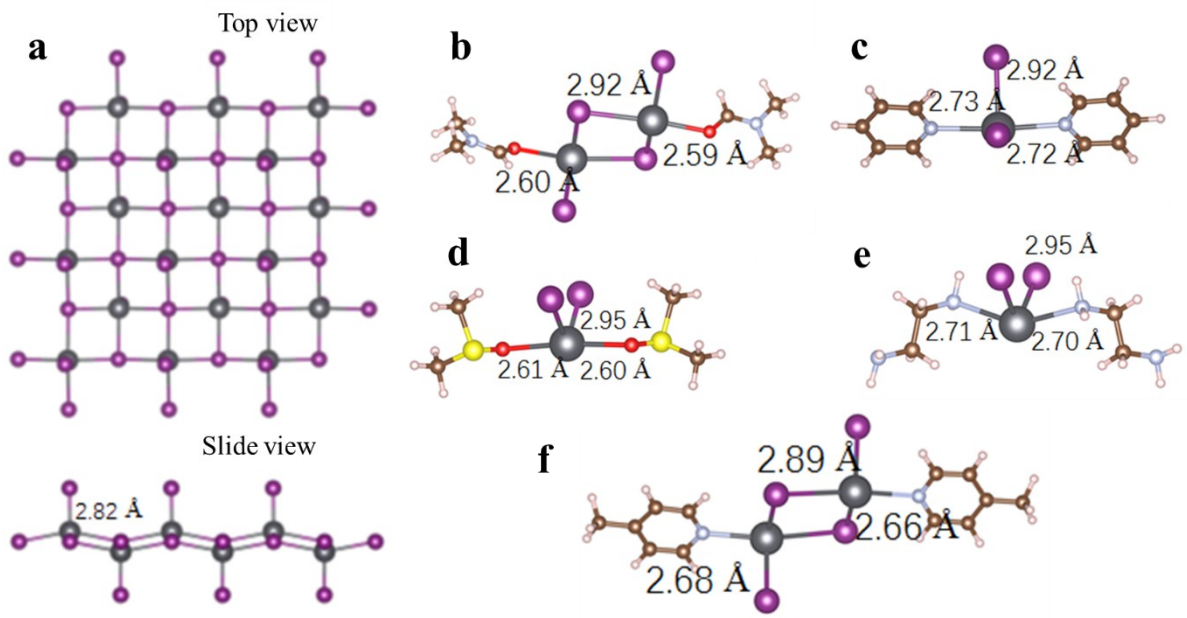

Figure S6. Crystallographic structures of PbI_2 (a), PbI_2.DMF (b), PbI_2.$(Py)_2$ (c), PbI_2.$(DMSO)_2$ (d), PbI_2.$(EDA)_2$ (e), and PbI_2.TBP (f).

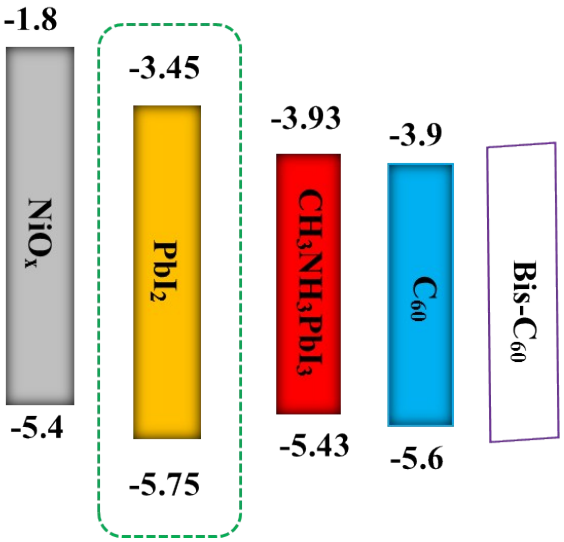

Figure S7. Energy diagram of each material in the PVSC device, with energy levels given in eV.