Electronic Supplementary Material (ESI) for Dalton Transactions.

# Supporting Information

## Identification and Characterization of the Intermediate Phase in Hybrid Organic–Inorganic $MAPbI_3$ Perovskite

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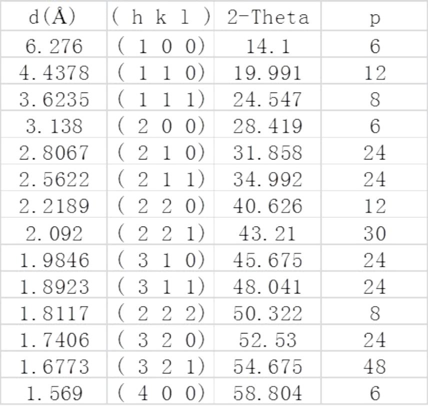
## 1. Calculated XRD data

The calculated XRD data of the interplanar distance (d), miller indices (hkl), peak position (2θ) and the multiplicity (p) for $CH_3NH_3PbI_3$ using the MDI Jade 6.5 software. The crystal structure parameters for the cubic phase of $CH_3NH_3PbI_3$ are ρ=4.1643g/cm$^3$, V=247.2Å$^3$, $Pm\bar{3}m$, Z = 1; Cell constant [1]: a=6.276 Å and α=90°. The calculated XRD data for cubic phase of $CH_3NH_3PbI_3$ is shown below:

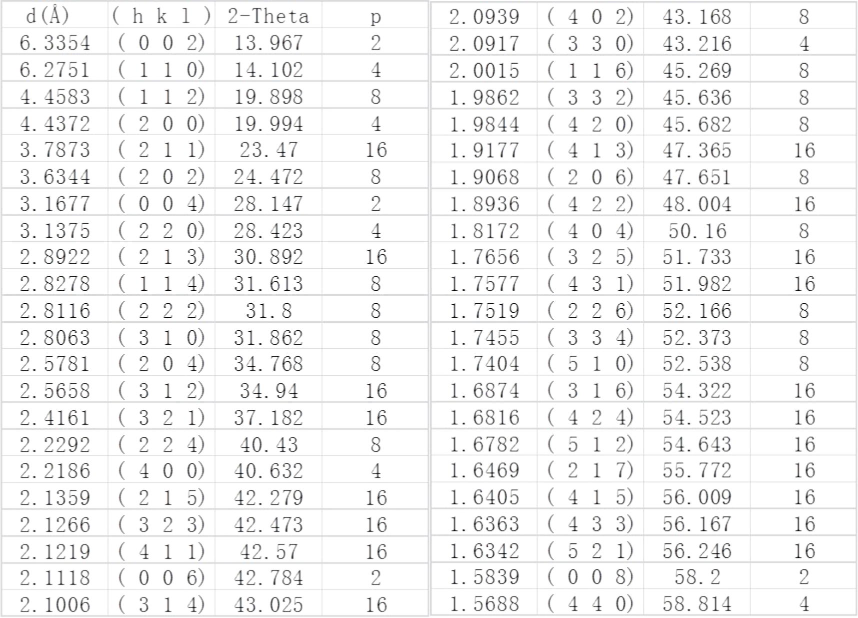
**Table S1.** Calculated XRD data for cubic phase of $CH_3NH_3PbI_3$



| d(Å) | ( h k l ) | 2-Theta | p |
|---|---|---|---|
| 6.276 | ( 1 0 0) | 14.1 | 6 |
| 4.4378 | ( 1 1 0) | 19.991 | 12 |
| 3.6235 | ( 1 1 1) | 24.547 | 8 |
| 3.138 | ( 2 0 0) | 28.419 | 6 |
| 2.8067 | ( 2 1 0) | 31.858 | 24 |
| 2.5622 | ( 2 1 1) | 34.992 | 24 |
| 2.2189 | ( 2 2 0) | 40.626 | 12 |
| 2.092 | ( 2 2 1) | 43.21 | 30 |
| 1.9846 | ( 3 1 0) | 45.675 | 24 |
| 1.8923 | ( 3 1 1) | 48.041 | 24 |
| 1.8117 | ( 2 2 2) | 50.322 | 8 |
| 1.7406 | ( 3 2 0) | 52.53 | 24 |
| 1.6773 | ( 3 2 1) | 54.675 | 48 |
| 1.569 | ( 4 0 0) | 58.804 | 6 |

The calculated XRD data for tetragonal phase of $CH_3NH_3PbI_3$ is shown in **Table S2**. The crystal structure parameters for the tetragonal phase of $CH_3NH_3PbI_3$ are ρ=4.1264g/cm$^3$, V=997.9Å$^3$, I4/mcm, Z=4; Cell constant [1]: a=8.8743Å, b=8.8743Å, c=12.6708, and α=β=γ=90°.

**Table S2.** Calculated XRD data for tetragonal phase of $CH_3NH_3PbI_3$



| d(Å) | ( h k l ) | 2-Theta | p |
|---|---|---|---|
| 6.3354 | ( 0 0 2) | 13.967 | 2 |
| 6.2751 | ( 1 1 0) | 14.102 | 4 |
| 4.4583 | ( 1 1 2) | 19.898 | 8 |
| 4.4372 | ( 2 0 0) | 19.994 | 4 |
| 3.7873 | ( 2 1 1) | 23.47 | 16 |
| 3.6344 | ( 2 0 2) | 24.472 | 8 |
| 3.1677 | ( 0 0 4) | 28.147 | 2 |
| 3.1375 | ( 2 2 0) | 28.423 | 4 |
| 2.8922 | ( 2 1 3) | 30.892 | 16 |
| 2.8278 | ( 1 1 4) | 31.613 | 8 |
| 2.8116 | ( 2 2 2) | 31.8 | 8 |
| 2.8063 | ( 3 1 0) | 31.862 | 8 |
| 2.5781 | ( 2 0 4) | 34.768 | 8 |
| 2.5658 | ( 3 1 2) | 34.94 | 16 |
| 2.4161 | ( 3 2 1) | 37.182 | 16 |
| 2.2292 | ( 2 2 4) | 40.43 | 8 |
| 2.2186 | ( 4 0 0) | 40.632 | 4 |
| 2.1359 | ( 2 1 5) | 42.279 | 16 |
| 2.1266 | ( 3 2 3) | 42.473 | 16 |
| 2.1219 | ( 4 1 1) | 42.57 | 16 |
| 2.1118 | ( 0 0 6) | 42.784 | 2 |
| 2.1006 | ( 3 1 4) | 43.025 | 16 |
| 2.0939 | ( 4 0 2) | 43.168 | 8 |
| 2.0917 | ( 3 3 0) | 43.216 | 4 |
| 2.0015 | ( 1 1 6) | 45.269 | 8 |
| 1.9862 | ( 3 3 2) | 45.636 | 8 |
| 1.9844 | ( 4 2 0) | 45.682 | 8 |
| 1.9177 | ( 4 1 3) | 47.365 | 16 |
| 1.9068 | ( 2 0 6) | 47.651 | 8 |
| 1.8936 | ( 4 2 2) | 48.004 | 16 |
| 1.8172 | ( 4 0 4) | 50.16 | 8 |
| 1.7656 | ( 3 2 5) | 51.733 | 16 |
| 1.7577 | ( 4 3 1) | 51.982 | 16 |
| 1.7519 | ( 2 2 6) | 52.166 | 8 |
| 1.7455 | ( 3 3 4) | 52.373 | 8 |
| 1.7404 | ( 5 1 0) | 52.538 | 8 |
| 1.6874 | ( 3 1 6) | 54.322 | 16 |
| 1.6816 | ( 4 2 4) | 54.523 | 16 |
| 1.6782 | ( 5 1 2) | 54.643 | 16 |
| 1.6469 | ( 2 1 7) | 55.772 | 16 |
| 1.6405 | ( 4 1 5) | 56.009 | 16 |
| 1.6363 | ( 4 3 3) | 56.167 | 16 |
| 1.6342 | ( 5 2 1) | 56.246 | 16 |
| 1.5839 | ( 0 0 8) | 58.2 | 2 |
| 1.5688 | ( 4 4 0) | 58.814 | 4 |

The calculated XRD data for $PbI_2$·DMF complex is shown in **Table S3**. The corresponding crystal structure parameters [2] are ρ=3.696g/cm$^3$, V=959.86Å$^3$, monoclinic $P2_1/n$, Z = 4, Cell constant: a=4.5380 Å, b=18.2704Å, c=11.5897 Å and β=92.69°:

**Table S3.** Calculated XRD data for $PbI_2$· DMF complex

| d(Å) | ( h k l) | 2-Theta | p |
|---|---|---|---|
| 7.1714 | ( 0 2 1) | 12.332 | 4 |
| 5.7885 | ( 0 0 2) | 15.294 | 2 |
| 5.5181 | ( 0 1 2) | 16.048 | 4 |
| 5.3898 | ( 0 3 1) | 16.433 | 4 |
| 4.8895 | ( 0 2 2) | 18.128 | 4 |
| 4.5676 | ( 0 4 0) | 19.418 | 2 |
| 4.3996 | ( 1 1 0) | 20.167 | 4 |
| 4.2899 | (-1 0 1) | 20.688 | 2 |
| 4.2489 | ( 0 4 1) | 20.89 | 4 |
| 4.1957 | ( 0 3 2) | 21.158 | 4 |
| 4.1763 | (-1 1 1) | 21.257 | 4 |
| 4.1553 | ( 1 0 1) | 21.366 | 2 |
| 4.0606 | ( 1 2 0) | 21.87 | 4 |
| 4.0518 | ( 1 1 1) | 21.918 | 4 |
| 3.883 | (-1 2 1) | 22.883 | 4 |
| 3.7824 | ( 1 2 1) | 23.501 | 4 |
| 3.7757 | ( 0 1 3) | 23.543 | 4 |
| 3.6363 | ( 1 3 0) | 24.459 | 4 |
| 3.5857 | ( 0 4 2) | 24.81 | 4 |
| 3.5822 | (-1 1 2) | 24.835 | 4 |
| 3.5548 | ( 0 2 3) | 25.029 | 4 |
| 3.5071 | (-1 3 1) | 25.375 | 4 |
| 3.4846 | ( 0 5 1) | 25.542 | 4 |
| 3.4324 | ( 1 3 1) | 25.937 | 4 |
| 3.4283 | ( 1 1 2) | 25.969 | 4 |
| 3.3919 | (-1 2 2) | 26.252 | 4 |
| 3.2604 | ( 1 2 2) | 27.331 | 4 |
| 3.2597 | ( 0 3 3) | 27.337 | 4 |
| 3.2175 | ( 1 4 0) | 27.703 | 4 |
| 3.1327 | (-1 3 2) | 28.468 | 4 |
| 3.127 | (-1 4 1) | 28.521 | 4 |
| 3.0899 | ( 0 5 2) | 28.871 | 4 |
| 3.0737 | ( 1 4 1) | 29.027 | 4 |
| 3.0451 | ( 0 6 0) | 29.305 | 2 |
| 3.0282 | ( 1 3 2) | 29.472 | 4 |
| 3.0089 | (-1 0 3) | 29.665 | 2 |
| 2.9689 | (-1 1 3) | 30.074 | 4 |
| 2.9478 | ( 0 4 3) | 30.296 | 4 |
| 2.9449 | ( 0 6 1) | 30.326 | 4 |
| 2.8942 | ( 0 0 4) | 30.87 | 2 |
| 2.8726 | ( 1 0 3) | 31.108 | 2 |
| 2.8586 | ( 0 1 4) | 31.264 | 4 |
| 2.8579 | (-1 2 3) | 31.272 | 4 |
| 2.8529 | (-1 4 2) | 31.329 | 4 |
| 2.8449 | ( 1 5 0) | 31.419 | 4 |
| 2.8378 | ( 1 1 3) | 31.5 | 4 |
| 2.7817 | (-1 5 1) | 32.151 | 4 |
| 2.7733 | ( 1 4 2) | 32.252 | 4 |
| 2.7591 | ( 0 2 4) | 32.423 | 4 |
| 2.744 | ( 1 5 1) | 32.606 | 4 |
| 2.7403 | ( 1 2 3) | 32.651 | 4 |
| 2.6976 | (-1 3 3) | 33.182 | 4 |
| 2.6949 | ( 0 6 2) | 33.216 | 4 |
| 2.6533 | ( 0 5 3) | 33.753 | 4 |
| 2.6141 | ( 0 3 4) | 34.275 | 4 |
| 2.5981 | ( 1 3 3) | 34.492 | 4 |
| 2.5835 | (-1 5 2) | 34.694 | 4 |
| 2.5462 | ( 0 7 1) | 35.219 | 4 |
| 2.5277 | ( 1 6 0) | 35.485 | 4 |
| 2.5239 | ( 1 5 2) | 35.539 | 4 |
| 2.5127 | (-1 4 3) | 35.703 | 4 |
| 2.4831 | (-1 6 1) | 36.144 | 4 |
| 2.4702 | (-1 1 4) | 36.339 | 4 |
| 2.4562 | ( 1 6 1) | 36.554 | 4 |
| 2.4448 | ( 0 4 4) | 36.731 | 4 |
| 2.4317 | ( 1 4 3) | 36.935 | 4 |
| 2.4051 | (-1 2 4) | 37.358 | 4 |
| 2.3905 | ( 0 6 3) | 37.596 | 4 |
| 2.3794 | ( 0 7 2) | 37.778 | 4 |
| 2.3689 | ( 1 1 4) | 37.951 | 4 |
| 2.339 | (-1 6 2) | 38.455 | 4 |
| 2.3228 | (-1 5 3) | 38.734 | 4 |
| 2.3114 | ( 1 2 4) | 38.933 | 4 |
| 2.3072 | (-1 3 4) | 39.006 | 4 |
| 2.297 | ( 0 1 5) | 39.186 | 4 |
| 2.2946 | ( 1 6 2) | 39.23 | 4 |
| 2.2838 | ( 0 8 0) | 39.422 | 2 |
| 2.2688 | ( 0 5 4) | 39.694 | 4 |
| 2.2665 | ( 2 0 0) | 39.736 | 2 |
| 2.2619 | ( 1 7 0) | 39.82 | 4 |
| 2.2583 | ( 1 5 3) | 39.886 | 4 |
| 2.2493 | ( 2 1 0) | 40.054 | 4 |
| 2.2444 | ( 0 2 5) | 40.144 | 4 |
| 2.2406 | ( 0 8 1) | 40.215 | 4 |
| 2.2298 | (-1 7 1) | 40.419 | 4 |
| 2.2275 | (-2 1 1) | 40.462 | 4 |
| 2.2241 | ( 1 3 4) | 40.527 | 4 |
| 2.2102 | ( 1 7 1) | 40.792 | 4 |
| 2.1998 | ( 2 2 0) | 40.994 | 4 |

The calculated XRD data for $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ is shown in **Table S4**. The corresponding crystal structure parameters [2] are ρ=3.035g/cm$^3$, V=1239.59Å$^3$, monoclinic P2$_1$/n, Z = 2, Cell constant: a=10.3937 Å, b=11.3055Å, c=10.5519 Å and β=91.298°:

**Table S4.** Calculated XRD data for $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$

| d(Å) | ( h k l ) | 2-Theta | p |
|---|---|---|---|
| 7.7129 | ( 0 1 1) | 11.463 | 4 |
| 7.6505 | ( 1 1 0) | 11.557 | 4 |
| 7.4881 | (-1 0 1) | 11.809 | 2 |
| 7.3204 | ( 1 0 1) | 12.08 | 2 |
| 6.2429 | (-1 1 1) | 14.175 | 4 |
| 6.1447 | ( 1 1 1) | 14.403 | 4 |
| 5.6528 | ( 0 2 0) | 15.664 | 2 |
| 5.2746 | ( 0 0 2) | 16.795 | 2 |
| 5.1955 | ( 2 0 0) | 17.052 | 2 |
| 4.9825 | ( 0 2 1) | 17.787 | 4 |
| 4.9656 | ( 1 2 0) | 17.848 | 4 |
| 4.78 | ( 0 1 2) | 18.547 | 4 |
| 4.7209 | ( 2 1 0) | 18.781 | 4 |
| 4.5116 | (-1 2 1) | 19.661 | 4 |
| 4.4741 | ( 1 2 1) | 19.827 | 4 |
| 4.3768 | (-1 1 2) | 20.273 | 4 |
| 4.3425 | (-2 1 1) | 20.434 | 4 |
| 4.3091 | ( 1 1 2) | 20.595 | 4 |
| 4.2764 | ( 2 1 1) | 20.754 | 4 |
| 3.8565 | ( 0 2 2) | 23.043 | 4 |
| 3.8252 | ( 2 2 0) | 23.234 | 4 |
| 3.7441 | (-2 0 2) | 23.745 | 2 |
| 3.6602 | ( 2 0 2) | 24.297 | 2 |
| 3.6352 | (-1 2 2) | 24.467 | 4 |
| 3.6155 | (-2 2 1) | 24.602 | 4 |
| 3.5961 | ( 1 2 2) | 24.737 | 4 |
| 3.577 | ( 2 2 1) | 24.871 | 4 |
| 3.5542 | (-2 1 2) | 25.033 | 4 |
| 3.5489 | ( 0 3 1) | 25.072 | 4 |
| 3.5427 | ( 1 3 0) | 25.116 | 4 |
| 3.4823 | ( 2 1 2) | 25.559 | 4 |
| 3.3662 | (-1 3 1) | 26.456 | 4 |
| 3.3577 | ( 0 1 3) | 26.524 | 4 |
| 3.354 | (-1 0 3) | 26.554 | 2 |
| 3.3506 | ( 1 3 1) | 26.582 | 4 |
| 3.3132 | (-3 0 1) | 26.888 | 2 |
| 3.3117 | ( 3 1 0) | 26.899 | 4 |
| 3.3082 | ( 1 0 3) | 26.929 | 2 |
| 3.269 | ( 3 0 1) | 27.258 | 2 |
| 3.2155 | (-1 1 3) | 27.72 | 4 |
| 3.1794 | (-3 1 1) | 28.041 | 4 |
| 3.175 | ( 1 1 3) | 28.081 | 4 |
| 3.1403 | ( 3 1 1) | 28.398 | 4 |
| 3.1215 | (-2 2 2) | 28.573 | 4 |
| 3.0724 | ( 2 2 2) | 29.039 | 4 |
| 3.0663 | ( 0 3 2) | 29.098 | 4 |
| 3.0505 | ( 2 3 0) | 29.252 | 4 |
| 2.9858 | ( 0 2 3) | 29.9 | 4 |
| 2.9533 | ( 3 2 0) | 30.237 | 4 |
| 2.9515 | (-1 3 2) | 30.256 | 4 |
| 2.9409 | (-2 3 1) | 30.368 | 4 |
| 2.9305 | ( 1 3 2) | 30.479 | 4 |
| 2.9201 | ( 2 3 1) | 30.589 | 4 |
| 2.8845 | (-1 2 3) | 30.977 | 4 |
| 2.8584 | (-3 2 1) | 31.267 | 4 |
| 2.8552 | ( 1 2 3) | 31.303 | 4 |
| 2.8483 | (-2 1 3) | 31.38 | 4 |
| 2.8325 | (-3 1 2) | 31.56 | 4 |
| 2.8298 | ( 3 2 1) | 31.59 | 4 |
| 2.8264 | ( 0 4 0) | 31.63 | 2 |
| 2.7927 | ( 2 1 3) | 32.022 | 4 |
| 2.7778 | ( 3 1 2) | 32.198 | 4 |
| 2.7301 | ( 0 4 1) | 32.777 | 4 |
| 2.7273 | ( 1 4 0) | 32.811 | 4 |
| 2.6561 | (-2 3 2) | 33.717 | 4 |
| 2.6443 | (-1 4 1) | 33.872 | 4 |
| 2.6373 | ( 0 0 4) | 33.964 | 2 |
| 2.6367 | ( 1 4 1) | 33.972 | 4 |
| 2.6256 | ( 2 3 2) | 34.12 | 4 |
| 2.6106 | (-2 2 3) | 34.323 | 4 |
| 2.5984 | (-3 2 2) | 34.488 | 4 |
| 2.5978 | ( 4 0 0) | 34.497 | 2 |
| 2.571 | ( 0 3 3) | 34.868 | 4 |
| 2.5683 | ( 0 1 4) | 34.905 | 4 |
| 2.5675 | ( 2 2 3) | 34.916 | 4 |
| 2.5559 | ( 3 2 2) | 35.08 | 4 |
| 2.5502 | ( 3 3 0) | 35.162 | 4 |
| 2.5318 | ( 4 1 0) | 35.425 | 4 |
| 2.5062 | (-1 1 4) | 35.799 | 4 |
| 2.5054 | (-1 3 3) | 35.811 | 4 |
| 2.496 | (-3 0 3) | 35.95 | 2 |
| 2.4913 | ( 0 4 2) | 36.021 | 4 |
| 2.4883 | (-3 3 1) | 36.066 | 4 |
| 2.4861 | ( 1 3 3) | 36.098 | 4 |
| 2.4828 | ( 2 4 0) | 36.149 | 4 |
| 2.4806 | ( 1 1 4) | 36.181 | 4 |
| 2.4743 | (-4 1 1) | 36.277 | 4 |
| 2.4694 | ( 3 3 1) | 36.352 | 4 |
| 2.4496 | ( 4 1 1) | 36.655 | 4 |
| 2.4401 | ( 3 0 3) | 36.803 | 2 |
| 2.4374 | (-3 1 3) | 36.846 | 4 |
| 2.4285 | (-1 4 2) | 36.985 | 4 |
| 2.4226 | (-2 4 1) | 37.079 | 4 |
| 2.4167 | ( 1 4 2) | 37.172 | 4 |
| 2.4109 | ( 2 4 1) | 37.265 | 4 |
| 2.39 | ( 0 2 4) | 37.604 | 4 |
| 2.3852 | ( 3 1 3) | 37.682 | 4 |

## 2. Calculated grain size

The average grain size was calculated by the Halder-Wagner method as provided by the Rigaku PDXL software. In the Halder-Wagner method, the integral breadth components described by the Lorentzian and Gaussian functions, are due to the size and strain effects. The grain size and strain were calculated using the equation:

$$\left(\frac{\beta\cdot\cos\theta}{\sin\theta}\right)^2=\frac{K\lambda}{D}\cdot\frac{\beta}{\tan\theta\cdot\sin\theta}+16\varepsilon^2$$

Here, the integral breadth β, is due to both small crystallite sizes and microstrains, K is the Scherrer constant depending on the crystallite configuration, D is the crystallite size, λ is the wavelength of Cu $K_\alpha$ radiation and ε is weighted average strain. By plotting $(\beta/\tan\theta)^2$ against β/(tanθ·sinθ), the y-intercept gives the mean value of the strain and the slope gives the crystallite size. The plots of annealed samples shown in figure S1 and S2 were drawn based on the perovskite peaks only and the peaks of intermediate phase were omitted. The data of average grain size is summarized in table S5.

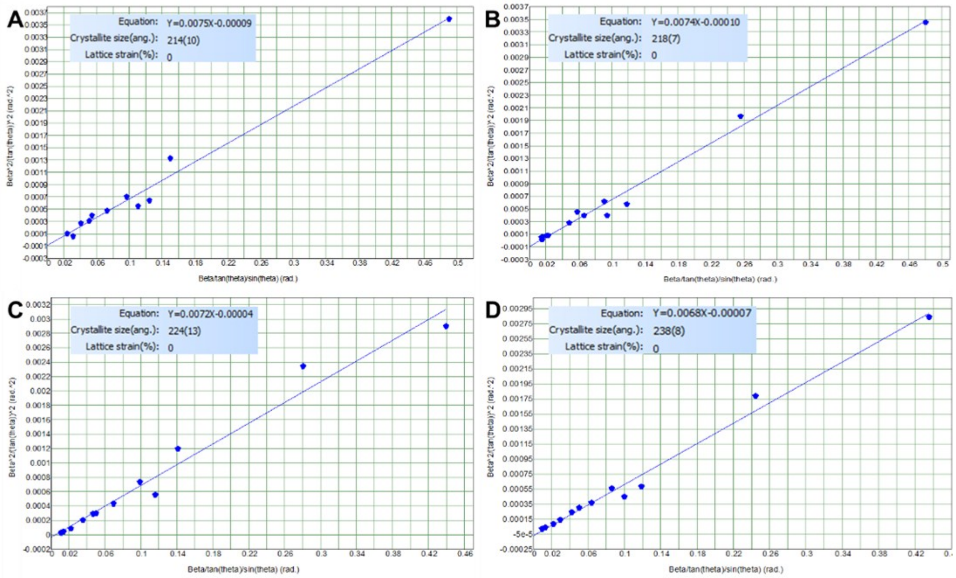


**Figure S1.** The grain size calculated by Halder-Wagner method of samples annealed at 70°C for A) 15min, B) 30min, C) 45min and D) 60 min.

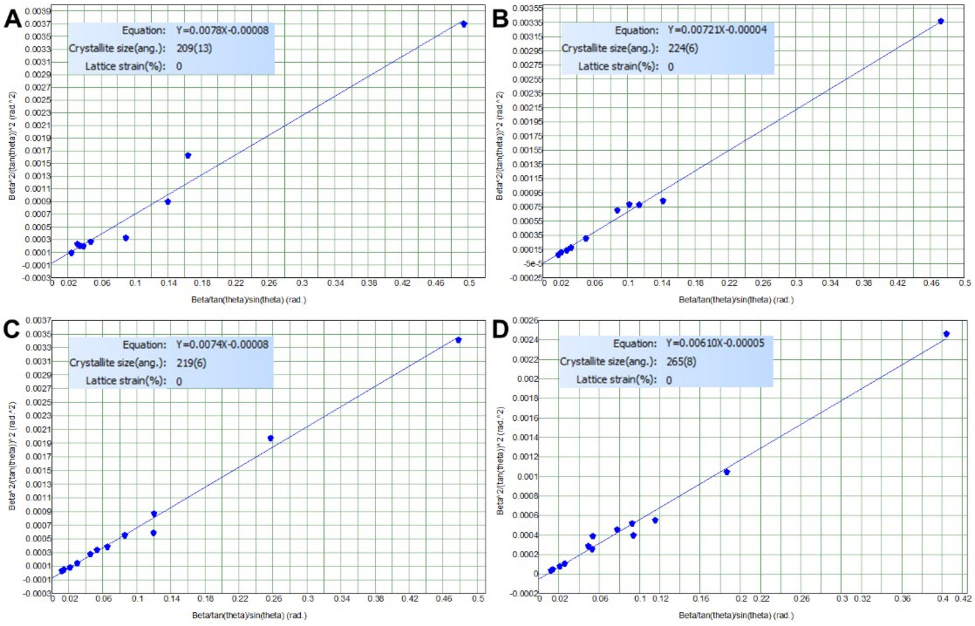


**Figure S2.** The grain size calculated by Halder-Wagner method of samples annealed at A) 40°C, B) 50°C, C) 60°C, D) 80°C for 60 min.

**Table S5.** Calculated grain sizes for samples annealed at 70 $^{o}$C and 40-80 $^{o}$C

| **Temperature ($^{o}$C)** | **70** | **70** | **70** | **70** | **40** | **50** | **60** | **80** |
|---|---|---|---|---|---|---|---|---|
| **Time (min)** | **15** | **30** | **45** | **60** | **60** | **60** | **60** | **60** |
| **Grain size (Å)** | **214(10)** | **218(7)** | **224(13)** | **238(8)** | **209(13)** | **224(6)** | **219(6)** | **265(8)** |

***Values in the parentheses are the standard deviation.**

## 3. The crystal structure of intermediate phase

The lattice parameters of the crystal structure of the intermediate phase in the sample heated at 70°C for 10min are estimated by using the pattern indexing function in the MDI Jade software. The peaks belonging to the tetragonal perovskite were omitted in the calculation of the intermediate phase peaks. The estimated crystal parameters were found to be: Cell Type = Monoclinic, P2$_1$/c, Cell constant: a= 11.2080 Å, b=12.4523 Å, c=13.7248 Å, α=90.0°, β=119.7222°, γ=90.0°, V=1663.51 Å$^3$, ρ=4.0365 g/cm$^3$, assuming the Chemical Formula =$PbI_2 \cdot 3CH_3NH_3I \cdot C_3H_7NO$ and Z=4.0, ρ= 3.0152 g/cm$^3$ with a formula of PbI2·MAI·2MA·DMF.

The 2θ error window is the maximum error limit and was set to be 0.3°, the 2θ Range was from 10.0° to 60.0°, the average Δ2θ value was 0.0472°, the average Δd value was 0.00776 nm. The estimated deviation for 2θ and d are summarized in table S6:

**Table S6.** Pattern indexing calculations for $PbI_2$-MAI-DMF intermediate phase

| ( h k l ) | 2T(cal) | 2T(obs) | Delta | d(cal) | d(obs) | Del-d |
|---|---|---|---|---|---|---|
| ( 0 1 1) | 10.265 | 10.265 | 0 | 0.86105 | 0.86104 | 0 |
| (-1 1 1) | 11.005 | 11.005 | 0 | 0.80332 | 0.80332 | 0 |
| ( 1 1 0) | 11.53 | 11.4 | 0.13 | 0.76687 | 0.77556 | -0.00869 |
| (-1 0 2) | 13.006 | 13.006 | 0 | 0.68015 | 0.68015 | 0 |
| ( 0 0 2) | 14.853 | 14.9 | -0.047 | 0.59596 | 0.59407 | 0.00189 |
| ( 1 1 1) | 15.987 | 15.987 | 0 | 0.55393 | 0.55393 | 0 |
| (-2 0 2) | 16.852 | 16.815 | 0.037 | 0.52568 | 0.52681 | -0.00114 |
| (-2 1 1) | 17.412 | 17.372 | 0.04 | 0.50889 | 0.51006 | -0.00117 |
| (-2 1 2) | 18.304 | 18.309 | -0.005 | 0.48429 | 0.48415 | 0.00014 |
| (-1 2 2) | 19.311 | 19.081 | 0.23 | 0.45925 | 0.46474 | -0.00549 |
| (-1 1 3) | 20.76 | 20.717 | 0.043 | 0.42752 | 0.42839 | -0.00087 |
| ( 0 3 1) | 22.665 | 22.568 | 0.097 | 0.39199 | 0.39366 | -0.00167 |
| (-1 2 3) | 24.201 | 24.154 | 0.046 | 0.36746 | 0.36815 | -0.00069 |
| (-3 1 2) | 24.898 | 24.642 | 0.255 | 0.35733 | 0.36097 | -0.00364 |
| ( 1 2 2) | 25.422 | 25.384 | 0.038 | 0.35007 | 0.35059 | -0.00052 |
| (-2 0 4) | 26.182 | 26.263 | -0.081 | 0.34008 | 0.33905 | 0.00103 |
| ( 2 2 1) | 27.045 | 27.1 | -0.055 | 0.32942 | 0.32877 | 0.00066 |
| (-3 2 2) | 27.859 | 27.719 | 0.139 | 0.31998 | 0.32156 | -0.00158 |
| ( 0 4 0) | 28.651 | 28.698 | -0.047 | 0.31131 | 0.31081 | 0.0005 |
| ( 1 4 0) | 30.114 | 30.101 | 0.013 | 0.29651 | 0.29664 | -0.00013 |
| ( 0 4 2) | 32.42 | 32.405 | 0.015 | 0.27593 | 0.27606 | -0.00013 |
| ( 3 1 1) | 32.771 | 32.789 | -0.018 | 0.27305 | 0.2729 | 0.00015 |
| (-2 1 5) | 33.4 | 33.411 | -0.012 | 0.26806 | 0.26796 | 0.00009 |
| ( 3 2 1) | 35.127 | 35.159 | -0.032 | 0.25526 | 0.25504 | 0.00023 |
| ( 2 3 2) | 36.192 | 36.033 | 0.159 | 0.24799 | 0.24905 | -0.00106 |
| ( 2 4 1) | 36.983 | 36.969 | 0.014 | 0.24286 | 0.24295 | -0.00009 |
| (-3 4 3) | 38.654 | 38.669 | -0.015 | 0.23274 | 0.23265 | 0.00009 |
| (-2 5 2) | 40.028 | 40.049 | -0.021 | 0.22507 | 0.22495 | 0.00012 |
| ( 4 1 1) | 42.011 | 42.003 | 0.007 | 0.21489 | 0.21492 | -0.00004 |
| (-3 2 6) | 42.394 | 42.395 | -0.001 | 0.21303 | 0.21303 | 0.00001 |
| (-3 5 2) | 43.665 | 43.7 | -0.035 | 0.20712 | 0.20697 | 0.00016 |
| (-1 5 4) | 45.326 | 45.304 | 0.022 | 0.19991 | 0.2 | -0.00009 |
| ( 1 6 1) | 46.094 | 46.153 | -0.059 | 0.19676 | 0.19652 | 0.00024 |
| (-1 6 3) | 48.147 | 48.1 | 0.047 | 0.18884 | 0.18901 | -0.00017 |
| ( 3 5 1) | 48.916 | 48.92 | -0.005 | 0.18605 | 0.18603 | 0.00002 |
| ( 1 0 6) | 51.25 | 51.246 | 0.004 | 0.17811 | 0.17812 | -0.00001 |
| ( 1 6 3) | 52.673 | 52.689 | -0.016 | 0.17363 | 0.17358 | 0.00005 |
| (-2 7 1) | 54.067 | 54.123 | -0.055 | 0.16947 | 0.16931 | 0.00016 |
| ( 4 4 2) | 55.764 | 55.82 | -0.056 | 0.16471 | 0.16456 | 0.00015 |
| (-1 6 5) | 56.368 | 56.4 | -0.032 | 0.16309 | 0.163 | 0.00009 |
| (-1 1 8) | 58.239 | 58.288 | -0.05 | 0.15829 | 0.15817 | 0.00012 |
| ( 1 7 3) | 59.544 | 59.541 | 0.002 | 0.15513 | 0.15513 | -0.00001 |

## 4. Comparison of DMF complexes

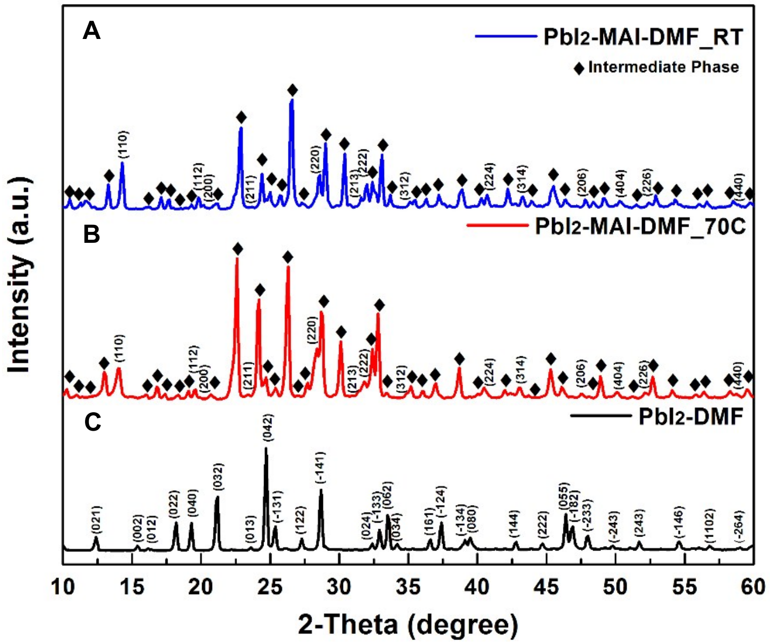


**Figure S3.** The XRD patterns of perovskite films annealed (A) at room temperature for 30 min and (B) 70 °C for 10 min under vacuum (12.7 torr); (C) $PbI_2$-DMF complex, labeled peaks in the sample PbI2-MAI-DMF_RT belonging to the tetragonal perovskite transformed during the XRD measurement.

## 5. Atomic Compositions by XPS

**Table S7.** Elemental Analysis and Relative Peak Area in XPS High-Resolution Spectra

| Composition | Parameter | C1s | N1s | O1s | I3d5 | Pb4f |
|---|---|---|---|---|---|---|
| | RSF | 0.314 | 0.499 | 0.733 | 6.302 | 9 |
| | Corrected RSF | 5.108 | 8.405 | 12.864 | 129.641 | 163.615 |
| Intermediate phase | at.% | 55.89 | 7.63 | 9.69 | 17.38 | 9.41 |
| | Peak Area | 15305.1 | 3438.03 | 6681.47 | 120783.3 | 82546.74 |
| dark phase | at.% | 27.28 | 16.84 | 1.88 | 39.05 | 14.95 |
| | Peak Area | 3078.88 | 3126.44 | 535.16 | 111824.2 | 54045.48 |

## 6. X-ray induced transformation of the intermediate phase to perovskite

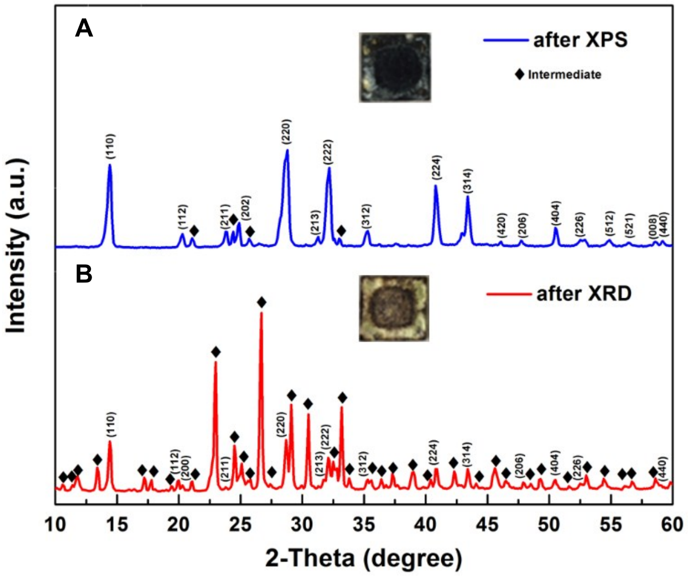


**Figure S4.** XRD patterns of A) sample 70C_10 min after XPS (180 min) and B) after XRD (20 min) measurement, showing that both lead to perovskite formation, but XPS is cleaner because of long time exposure to intense X-ray. The insets show photographs of the resulting samples.

## 7. UV-visible spectra of complexes

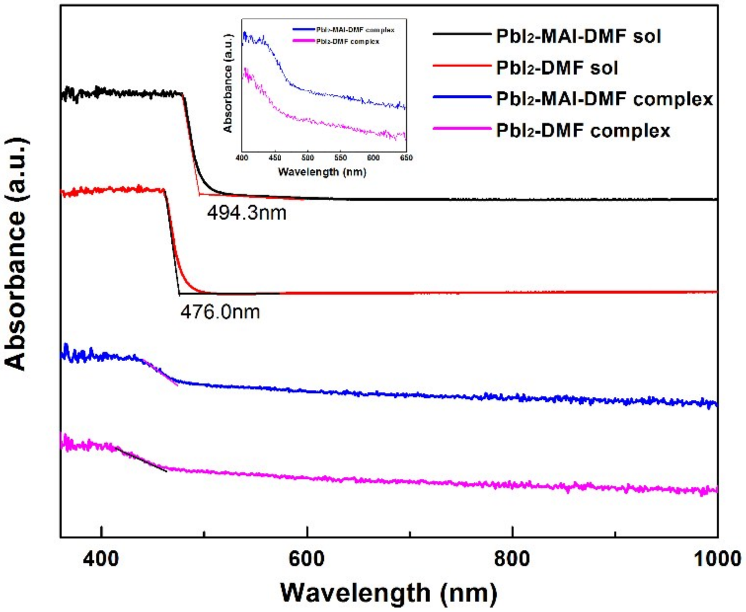


**Figure S5.** UV-visible spectra of 1M $PbI_2$-MAI-DMF solution (black), 1M $PbI_2$-DMF solution (red), $PbI_2$-DMF complex (blue) and the $PbI_2$-MAI-DMF complex (magenta). The inset shows a magnified view of the spectra of $PbI_2$-DMF complex and $PbI_2$-MAI-DMF complex.

## 8. SEM images and EDX spectrum

The SEM images and EDX spectrum of the sample after XPS are shown in Figure S6 and S7. After the XPS measurement, there was no oxygen detected in the dark center region of the sample and only Pb and I were detected in the small marginal yellow area. This could be due to the decomposed product of intermediate phase on the surface. The non-stoichiometric atomic ratio come from the rough surface of the sample, the structural changing, and surface degradation by X-ray irradiation during the XPS measurement.

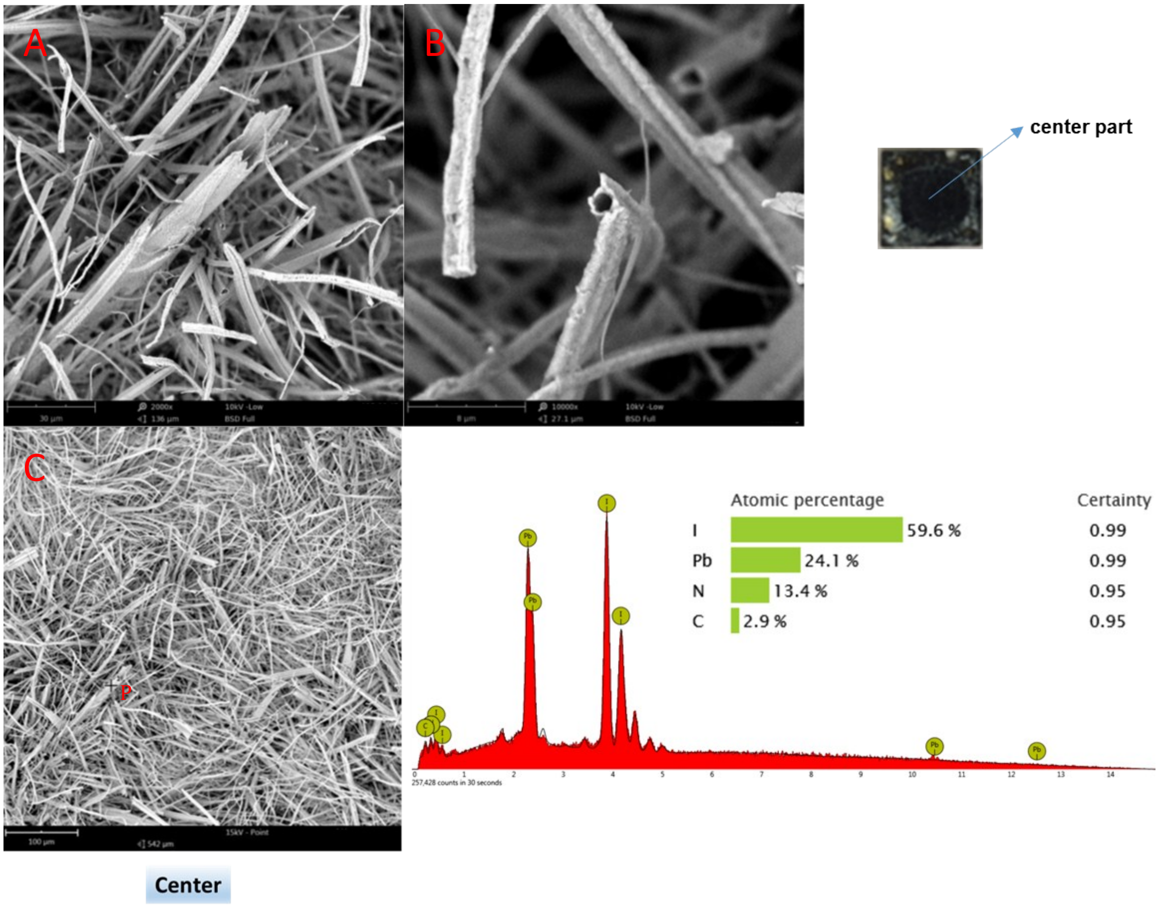


**Figure S6.** The SEM images and EDX spectrum of the sample after XPS acquired at A) 2000x magnification and B) 10000x magnification. C) EDX spectrum acquired at point P of the sample in image C. The scale bar is 100 μm. Both the images and the spectrum were collected at the center of the sample.

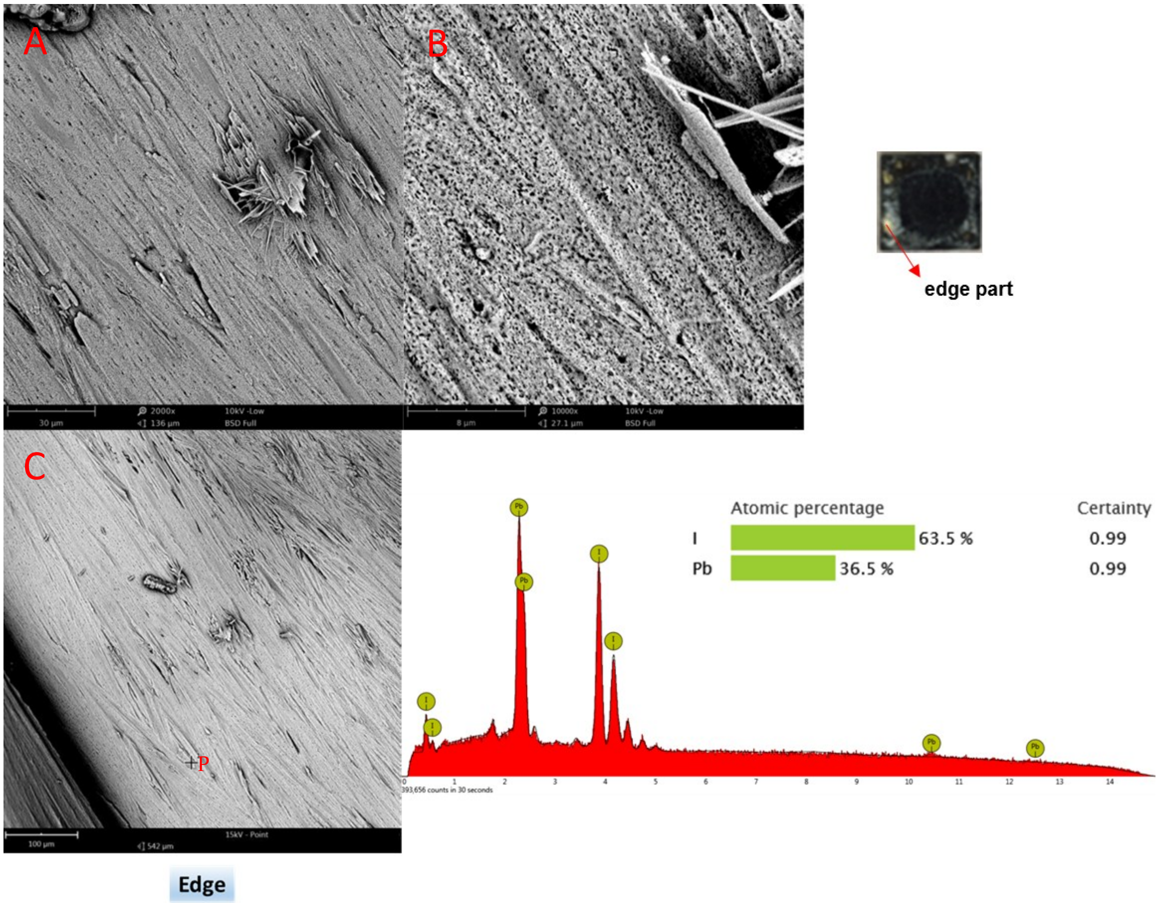


**Figure S7.** The SEM images and EDX spectrum of the sample after XPS acquired at the edge of the same sample from figure S4 at A) 2000x magnification and B) 10000x magnification. C) EDX spectrum acquired at point P in image C. The scale bar is 100 µm.

## 9. Recovery by DMF vapor

Degradation of perovskite thin films could be caused by moisture and oxygen in air and from sunlight induced photodegradation. The composite degradation process could be described as [3, 4]:

$$CH_3NH_3PbI_3 \xrightleftharpoons{H_2O} CH_3NH_3I(aq) + PbI_2(s) \qquad (1)$$

$$CH_3NH_3I(aq) \rightleftharpoons CH_3NH_2(aq) + HI(aq) \qquad (2)$$

$$4HI(aq) + O_2 \xrightleftharpoons{h\nu} 2I_2(s) + 2H_2O \qquad (3)$$

$$2HI(aq) \xrightleftharpoons{h\nu} H_2\uparrow + I_2(s) \qquad (4)$$

In the presence of $H_2O$, the perovskite $CH_3NH_3PbI_3$ can decompose into $CH_3NH_3I$ solution and $PbI_2$. Based on the equilibrium reaction (1-4) this deterioration is reversible. It is possible to recover the perovskite thin film from degradation, provided the chemical constituents remain present in the sample, even in separated phases. The DMF vapor can wet the degraded film and make a more uniform film by rearranging the molecular distribution (an intermediate phase).

Recovery of the degraded perovskite thin films coated on the Fluorine doped Tin Oxide (FTO) glass substrates was performed demonstrating the reversibility of the phase degradation process in the following protocol. In a nitrogen-filled glove box, the perovskite solution was deposited on the FTO glass at 3000 rpm for 30 s and then dried on a hot plate first at 70 °C for 5 min followed by 100 °C heating for 10 min. The prepared sample was placed in the dark, but accessible to air with humidity of 50% for a week. This recovery process was designed to remove any absorbed water from the perovskite film using DMF vapor as performed in the following protocol: 1. Placing the sample inside the vacuum oven and then put a petri dish filled with 5 mL pure DMF solvent aside; 2. Providing vacuum to oven chamber at a pressure of 12.7 torr for five minutes; 3. Purging the chamber with air and removing the petri dish containing the DMF and repeat step 2; 4. Repeating the cycling steps 2 and 3 for 2 more times; 5. Setting the DMF treated sample in a tube furnace under argon atmosphere; 6. Heating the sample first at 50 °C for 20 min and then at 100 °C for an additional 10 min. The sample undergoing different stages in line with the recovery protocol is shown in **Figure S8A**.

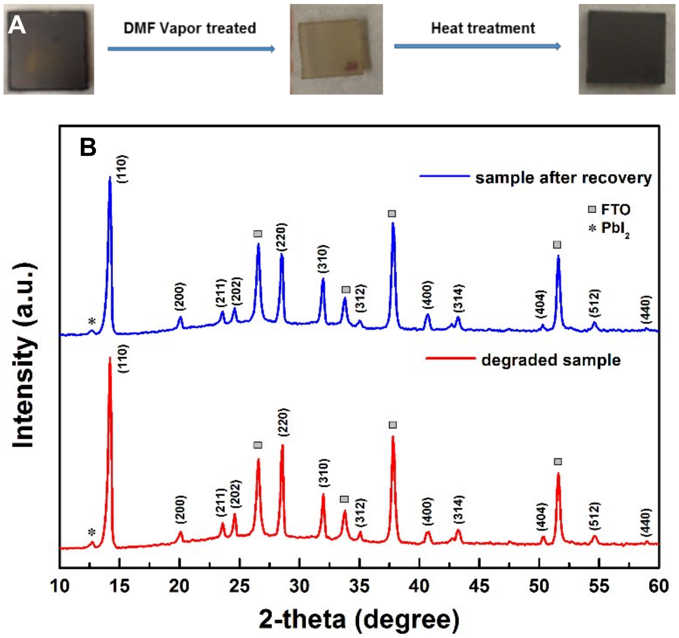


**Figure S8.** Photographs of the sample A) at different stages from before recovery , treated three times with DMF solvent under vacuum (12.7 torr), to after heat treatment at 100 °C under Ar atmosphere; B) XRD patterns of perovskite films coated on FTO glass degraded for 7 days (red) and after recovery (blue) via the procedure described above.

The XRD patterns of the degraded sample before and after the recovery are shown in **Figure S8B**. As a result of the above procedure, the integral area intensity ratio of the diffraction peaks assigned to perovskite vs. $PbI_2$ after the recovery was 90.06 and thus larger than the peak ratio of 75.37 before the recovery. The control experiment of recovery only by heat treatment in the same procedure was shown in **Figure S9** indicating simply heat treatment cannot make a healing effect and may result in an increased amount of $PbI_2$ phase.

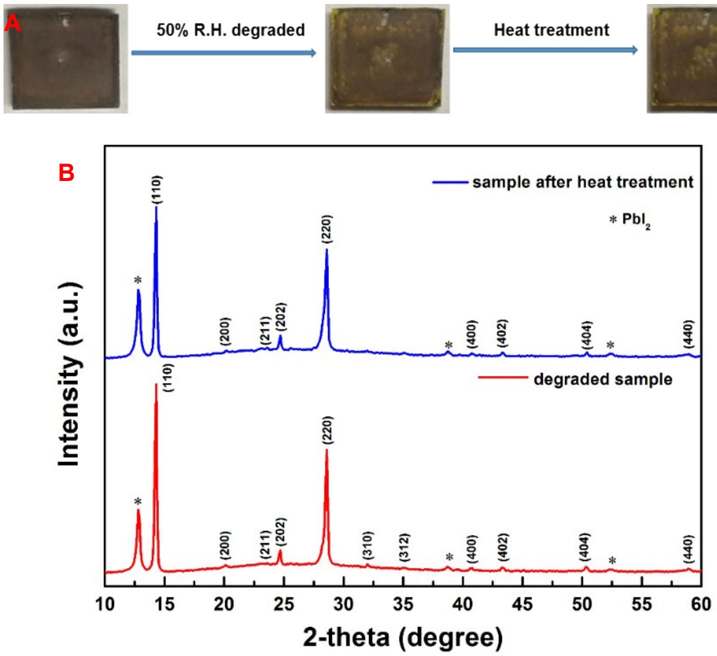


**Figure S9.** A) Photographs of the stages from a fresh perovskite film prepared by spin coating at 3000 rpm for 40s to perovskite exposed to R.H. 50% for 7 days followed by heat treatment. B) The XRD patterns of corresponding perovskite films.

A sample degraded under 50% humidity for 1 week was used as a control and was heat treated without using DMF vapor compared to the one with DMF vapor treatment. It was found that the degraded $PbI_2$ was present in the spin-coated film after 7 days exposure under R.H. 50%. The amount of the $PbI_2$ phase in the film increased after an initial heat treatment at 50 °C for 20 min and then 100 °C for 10 min. The ratio of the integrated area of the diffraction peaks assigned to perovskite versus $PbI_2$ before the heat treatment is 1.92 (Peak height ratio: 8617:2765=3.12), which is larger than the 1.25 ratio after heat treatment (Peak height ratio: 6887:3022= 2.28).

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