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# Favorable Morphology and Compositional Distribution Enables Efficient and Stable Quasi-2D Dion-Jacobson Perovskite Solar Cells

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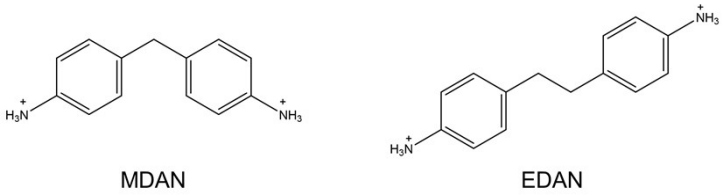


**Scheme S1.** The molecular structures of MDAN and EDAN.

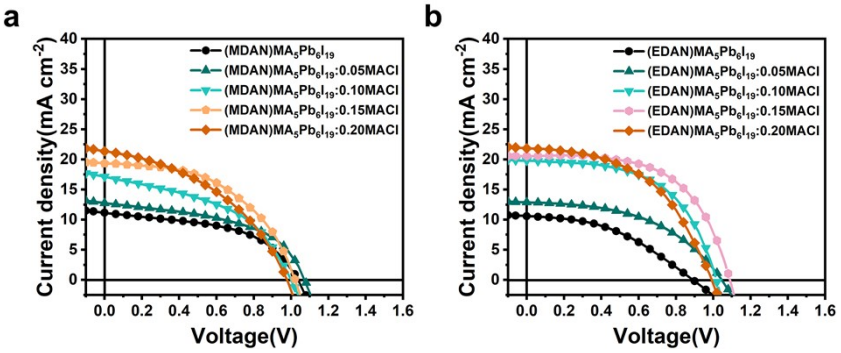


**Figure S1.** (a,b) The *J-V* curves of devices based on (MDAN/EDAN)$MA_5Pb_6I_{19}$ with different MACl additive

content, respectively.

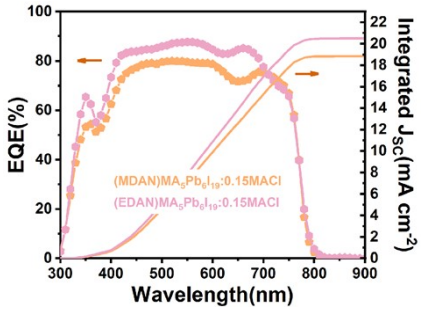


**Figure S2.** External quantum efficiency (EQE) spectra and their integrated current density curves of (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl devices.

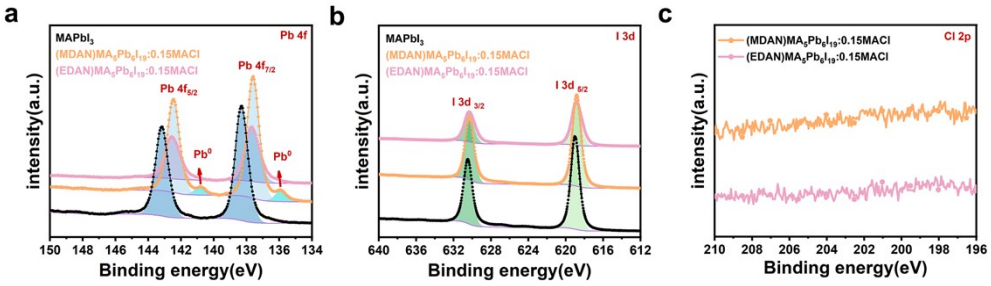


**Figure S3.** The (a) Pb 4f and (b) I 3d peaks in XPS spectra of $MAPbI_3$ and (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl films. (c) Cl 2p core level XPS spectra of (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl films.

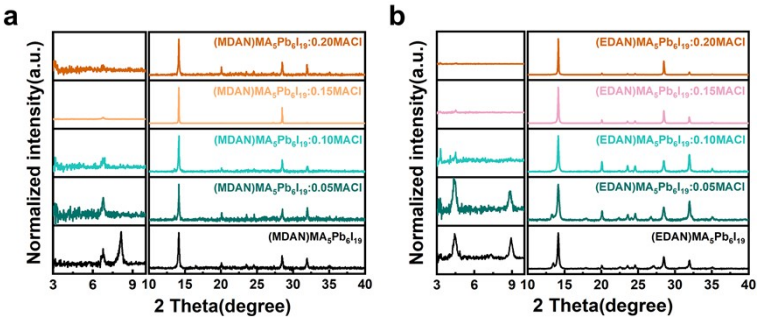


**Figure S4.** (a,b) The XRD spectra of (MDAN/EDAN)$MA_5Pb_6I_{19}$ films with different MACl additive content.

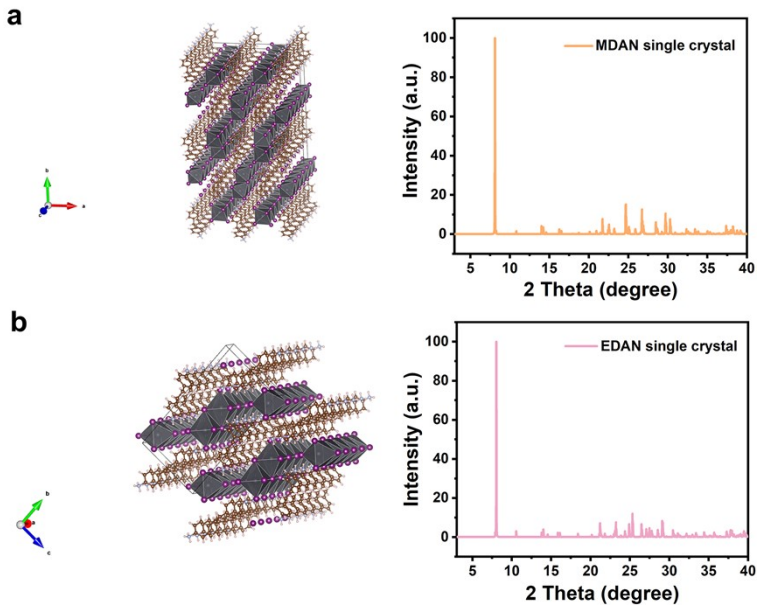


**Figure S5.** (a,b) The single crystals of (MDAN/EDAN)$PbI_3$ (n = 1) and corresponding simulated XRD patterns.

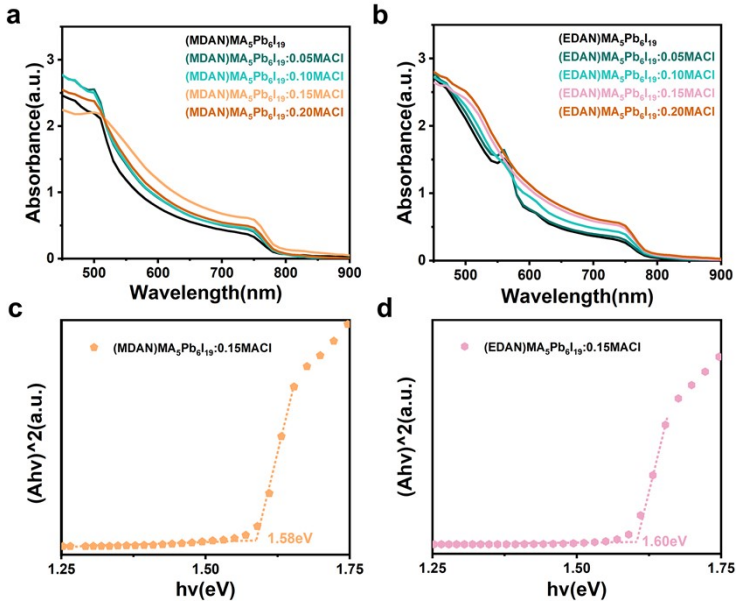


**Figure S6.** (a,b) The UV-vis absorption spectra of (MDAN/EDAN)$MA_5Pb_6I_{19}$ films with different MACl additive content, respectively. (c,d) The Tauc plots of (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl, respectively.

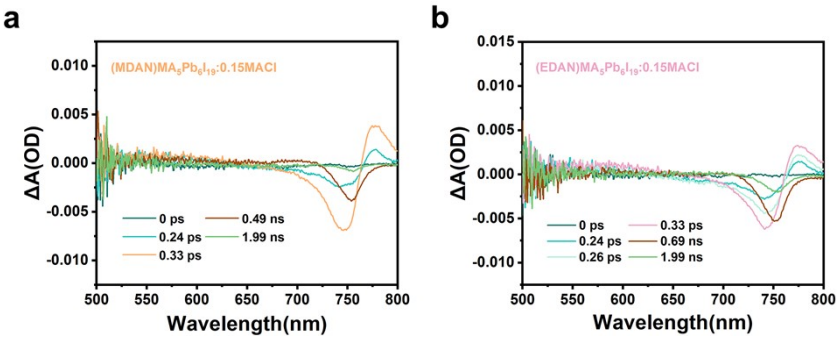


**Figure S7.** (a,b) The TA spectra of (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl films under front excitations at different times.

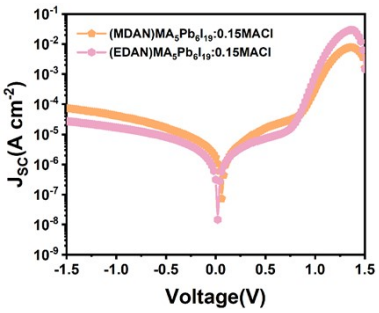


**Figure S8.** The *J–V* curves of the (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl devices under dark.

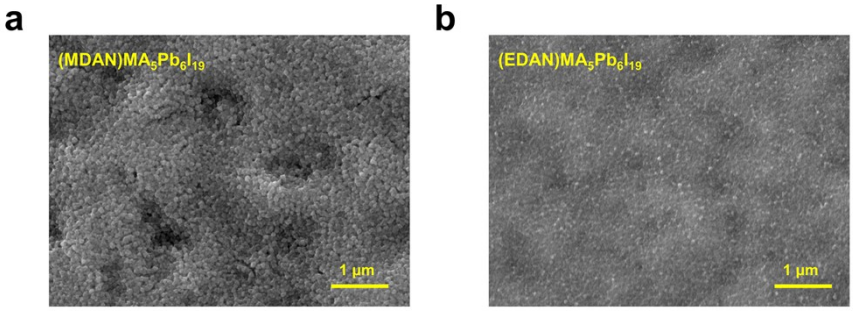


**Figure S9.** (a,b) The SEM image of (MDAN/EDAN)$MA_5Pb_6I_{19}$ films without MACl additive.

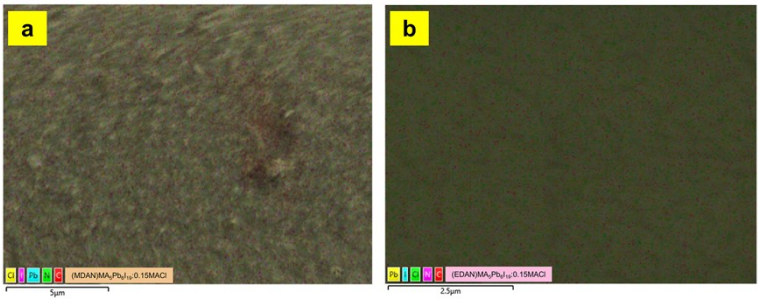


**Figure S10.** The EDS distribution images of the (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl films.

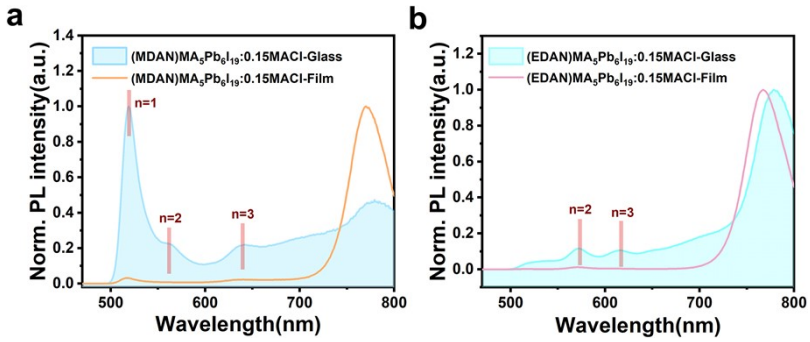


**Figure S11.** The PL spectrum of (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl films excited from glass and film sides.

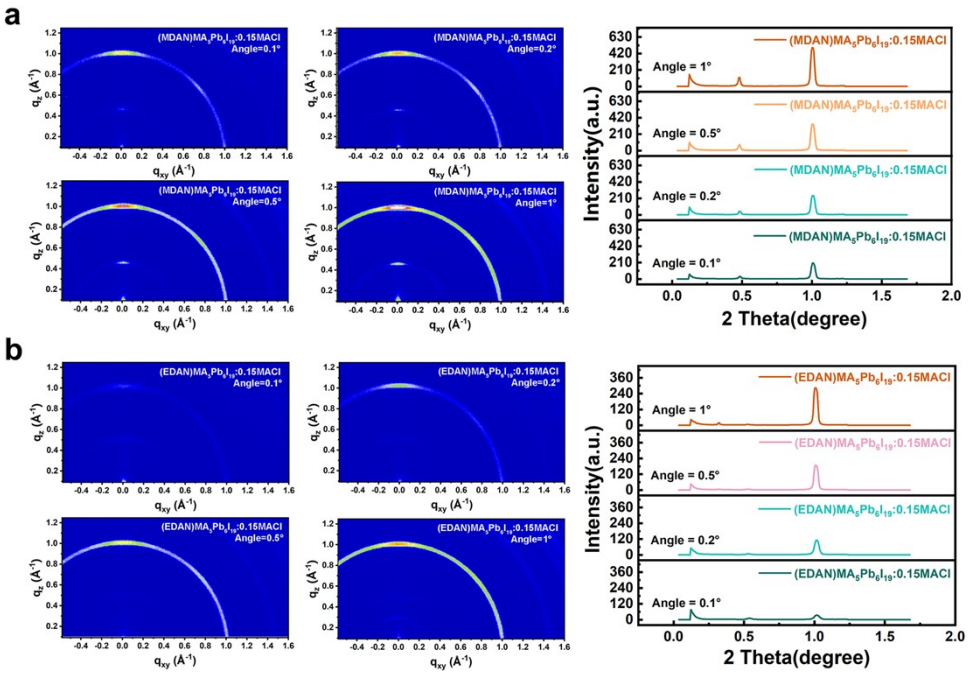


**Figure S12.** (a,b) The GIWAXS patterns of (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl films with different incident illumination angles and corresponding 2D GIWAXS profiles patterns along out of the plane direction.

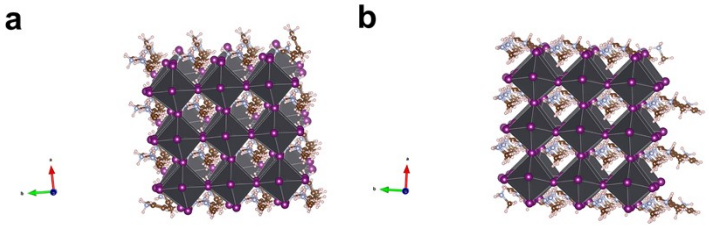


**Figure S13.** The simulated crystal structure of (a) (MDAN)$MA_5Pb_6I_{19}$ and (b) (EDAN)$MA_5Pb_6I_{19}$ along the c-axis.

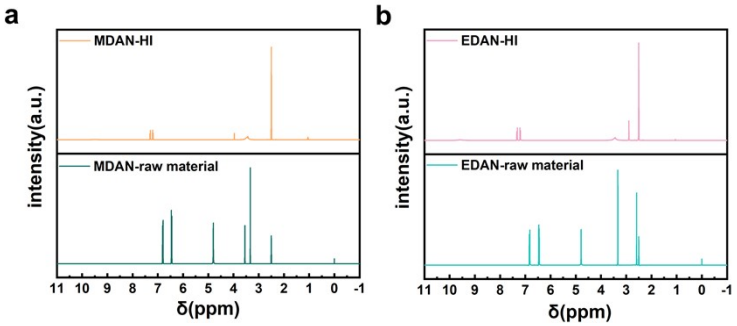


**Figure S14.** The $^{1}$H NMR spectra of (a) MDAN and $MDANI_2$ and (b) EDAN and $EDANI_2$ in $d_6$-DMSO.

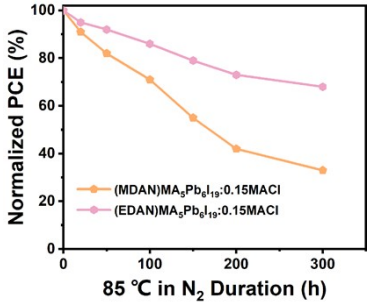


**Figure S15.** The thermal stability measurement of $(MDAN)MA_5Pb_6I_{19}$:0.15MACl and $(EDAN)MA_5Pb_6I_{19}$:0.15MACl devices stored in nitrogen at 85 ℃.

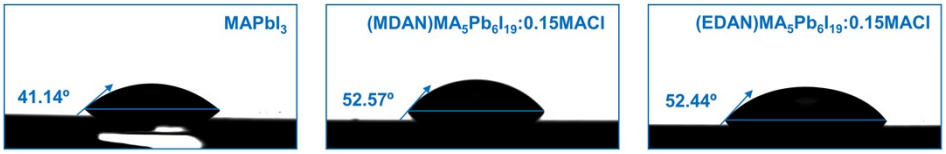


**Figure S16.** The photo image of water on $MAPbI_3$, $(MDAN/EDAN)MA_5Pb_6I_{19}$:0.15MACl films.

**Table S1.** The solar cell device parameters based on (MDAN)$MA_5Pb_6I_{19}$ with different MACl content. The average values are calculated from 20 devices.

| Nominal Composition | $V_{OCave}$ (V) | $J_{SCave}$ (mA cm$^{-2}$) | $FF_{ave}$ (%) | $PCE_{ave}$ (%) | $PCE_{max}$ (%) |
|---|---|---|---|---|---|
| (MDAN)$MA_5Pb_6I_{19}$ | 1.03 | 10.67 | 48.3 | 5.33 | 5.76 |
| (MDAN)$MA_5Pb_6I_{19}$:0.05MACl | 1.08 | 12.06 | 49.4 | 6.43 | 6.69 |
| (MDAN)$MA_5Pb_6I_{19}$:0.10MACl | 1.01 | 17.47 | 44.3 | 7.65 | 7.80 |
| (MDAN)$MA_5Pb_6I_{19}$:0.15MACl | 0.98 | 19.76 | 48.8 | 9.31 | 9.65 |
| (MDAN)$MA_5Pb_6I_{19}$:0.20MACl | 0.94 | 19.58 | 41.8 | 7.71 | 8.60 |

**Table S2.** The solar cell device parameters based on (EDAN)$MA_5Pb_6I_{19}$ with different MACl content. The average values are calculated from 20 devices.

| Nominal Composition | $V_{OCave}$ (V) | $J_{SCave}$ (mA cm$^{-2}$) | $FF_{ave}$ (%) | $PCE_{ave}$ (%) | $PCE_{max}$ (%) |
|---|---|---|---|---|---|
| (EDAN)$MA_5Pb_6I_{19}$ | 0.90 | 9.60 | 42.24 | 3.61 | 3.84 |
| (EDAN)$MA_5Pb_6I_{19}$:0.05MACl | 1.01 | 12.17 | 47.13 | 5.81 | 6.45 |
| (EDAN)$MA_5Pb_6I_{19}$:0.10MACl | 1.05 | 16.09 | 53.94 | 9.20 | 11.0 |
| (EDAN)$MA_5Pb_6I_{19}$:0.15MACl | 1.05 | 21.45 | 50.64 | 11.6 | 13.2 |
| (EDAN)$MA_5Pb_6I_{19}$:0.20MACl | 0.95 | 21.87 | 46.07 | 10.2 | 10.8 |

**Table S3.** The single crystal data and refinement of (MDAN)$PbI_3$(n = 1).

| | | |
|---|---|---|
| **Bond precision:** | c-c = 0.0429 Å | Wavelength = 1.34139 |
| **Cell:** | a = 25.2869(12) Å<br>b = 42.894(2) Å<br>c= 4.5074(2) Å<br>alpha = 90 º<br>beta = 90 º<br>gamma = 90 º | |
| **Temperature:** | 193 k | |
| | **Calculated** | **Reported** |
| **Volume** | 4889.0(4) Å$^3$ | 4889.0(4) Å$^3$ |
| **Space group** | F d d 2 | F d d 2 |
| **Hall group** | F 2 -2d | F 2 -2d |
| **Moiety formula** | 2($PbI_3$), $C_{13}H_{16}N_2$ | $Pb_2I_6$, $C_{13}H_{16}N_2$ |
| **Sum formula** | $C_{13}H_{16}I_6N_2Pb_2$ | $C_{13}H_{16}I_6N_2Pb_2$ |
| **Mr** | 1376.08 | 1376.06 |
| **Dx, g cm$^{-3}$** | 3.739 | 3.739 |
| **Z** | 8 | 8 |

| | | |
|---|---|---|
| **Mu ($mm^{-1}$)** | 58.693 | 58.693 |
| **F000** | 4720.0 | 4720.0 |
| **F000'** | 4663.87 | |
| **h, k, lmax** | 30, 50, 5 | 30, 50, 5 |
| **Nref** | 2252 [1279] | 2167 |
| **Tmin, Tmax** | 0.001, 0.003 | 0.012, 0.100 |
| **Tmin'** | 0.000 | |

**Table S4.** The single crystal data and refinement of (EDAN)$PbI_3$(n = 1).

| | | |
|---|---|---|
| **Bond precision:** | c-c = 0.0102 Å | Wavelength = 0.71073 |
| **Cell:** | a = 4.5872(2) Å<br>b = 22.3629(10) Å<br>c = 12.7917(6) Å<br>alpha = 90 º<br>beta = 98.823(2) º<br>gamma = 90 º | |
| **Temperature:** | 193 k | |
| | **Calculated** | **Reported** |
| **Volume** | 1296.77(10) $Å^3$ | 1296.77(10) $Å^3$ |
| **Space group** | P 21/n | P 1 21/n 1 |
| **Hall group** | -P 2yn | -P 2yn |
| **Moiety formula** | $PbI_3$, $C_7H_9N$ | $Pb_2I_6$, $C_{14}H_{18}N_2$ |
| **Sum formula** | $C_7H_9NPbI_3$ | $C_{14}H_{18}N_2Pb_2I_6$ |
| **Mr** | 695.05 | 1390.08 |
| **Dx, g cm-3** | 3.560 | 3.560 |
| **Z** | 4 | 2 |
| **Mu (mm-1)** | 20.110 | 20.110 |
| **F000** | 1196.0 | 1196.0 |
| **F000'** | 1178.25 | |
| **h, k, lmax** | 5, 29, 16 | 5, 29, 16 |
| **Nref** | 2981 | 2975 |
| **Tmin, Tmax** | 0.092, 0.134 | 0.027, 0.095 |
| **Tmin'** | 0.059 | |

**Table S5.** The EDS distribution of elements total spectrum of (MDAN)$MA_5Pb_6I_{19}$:0.15MACl films.

| Element | Apparent concentration | Wt % | Wt % *Sigma* |
|---|---|---|---|
| C | 11.2 | 11.6 | 0.05 |
| N | 15.1 | 3.37 | 0.06 |
| Cl | 0.03 | 0.01 | 0.02 |
| I | 90.3 | 53.2 | 0.10 |
| Pb | 53.9 | 31.9 | 0.10 |

| | |
|---|---|
| Total content | 100 |

**Table S6.** The EDS distribution of elements total spectrum of (EDAN)$MA_5Pb_6I_{19}$:0.15MACl films.

| Element | Apparent concentration | Wt % | Wt % *Sigma* |
|---|---|---|---|
| C | 8.47 | 8.54 | 0.06 |
| N | 14.7 | 2.96 | 0.06 |
| Cl | 1.22 | 0.52 | 0.03 |
| I | 105.1 | 57.7 | 0.13 |
| Pb | 54.5 | 30.3 | 0.13 |
| Total content | | 100 | |

**Table S7.** The PL lifetimes of (MDAN/EDAN)$MA_5Pb_6I_{19}$:0.15MACl films.

| | $A_1$ | $\tau_1$/ns | $A_2$ | $\tau_2$/ns |
|---|---|---|---|---|
| (MDAN)$MA_5Pb_6I_{19}$:0.15MACl | 0.95 | 7.4 | 0.05 | 32 |
| (EDAN)$MA_5Pb_6I_{19}$:0.15MACl | 0.85 | 21 | 0.15 | 89 |