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Electronic Supporting Information

Influence of Solvent Additive on Chemical and Electronic Environment of

Wide Bandgap Perovskite Thin Films

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Table S1 and S4



Figure S1: Images of MAPbBr₃ based (a) perovskite precursor solutions and (b) thin films made from those solutions.



Figure S2: Top-view SEM images of (a) 0 wt.%, (b) 1 wt.%, (c) 2 wt.% and (d) 5 wt.% DIO additive $MAPbI_{3-x}Cl_x$ based perovskite films. Scale bars, 10µm and 200 nm (inset).



Figure S3: Top-view SEM images of (a) 0 wt.%, and (b) 1 wt.% DIO additive MAPbI₃ based perovskite films. Scale bars, $1\mu m$ and 100 nm (inset).



Figure S4: FESEM cross-section images of (a) 0 wt.%, (b) 1 wt.%, (c) 2 wt.% and (d) 5 wt.% DIO additive MAPbBr₃ based thin films prepared on glass substrates.



Figure S5: Atomic force microscopy (AFM) images of MAPbBr₃ with (a) 0%, (b) 1%, (c) 2% and (d) 5% DIO additive based perovskite thin films.



Figure S6: Atomic force microscopy (AFM) images of MAPbI_{3-x}Cl_x with (a) 0%, (b) 1%, (c) 2% and (d) 5% DIO additive based perovskite thin films.



Figure S7: HRXPS core level photoemission lines for (a) C 1s, (b) I 3d (c) Br 3d and (d) Pb 4f of MAPbBr₃ based perovskite thin films with different concentration of DIO.



Figure S8: HRXPS core level photoemission lines for (a) I 3d, and (b) Pb 4f of MAPbI₃ based with (red solid line) and without (black solid line) DIO additive perovskite thin films.



Figure S9: (a) Wide XPS spectra of MAPbI_{3-x}Cl_x based with and without DIO additive thin films and corresponding HRXPS photoemission lines of (b) C 1s, (c) I 3d, and (d) Pb 4f. HRXPS core level photoemission line for Cl 2p for (e) with (1 wt.%) and (f) without DIO additive MAPbI_{3-x}Cl_x based perovskite thin films.



Figure S10: (a) XRD pattern of MAPbBr₃ based perovskite thin films with different concentration of DIO into the perovskite precursor solution. First order diffraction peak of (b) MAPbI_{3-x}Cl_x, and (c) MAPbI₃ with (1 wt.%) and without DIO additive. The inset represents the XRD pattern in the range of 5^{0} to 60^{0} .

Figure **S10a** shows that the X-ray diffraction peak intensity of 1 wt.% DIO additive MAPbBr₃ film increases by about three times than w/o DIO additive MAPbBr₃ film. However, 2 wt.% and 5 wt.% DIO additive films have lower diffraction intensity with respect to w/o DIO additive perovskite film, which is consistent with the top view SEM images of respective films. The same trend of enhanced crystallization is also observed in the MAPbI₃. $_xCl_x$ (Figure **S10b**) with (1 wt.%) and w/o DIO films. However, in case of MAPbI₃ (figure **S8c**), there is slight reduction in the diffraction peak intensity of the DIO additive MAPbI₃ film.

Figure **S11b**, and **S11c** represent the absorption spectrum of MAPbI_{3-x}Cl_x, and MAPbI₃ with (1 wt.%) and w/o DIO additive films, respectively. We do not observe any significant change in the absorption edge of with and w/o DIO additive films in both cases. Since there is very less amount of Cl⁻ (table **S1**) is present in with and w/o DIO additive MAPbI_{3-x}Cl_x based perovskite thin films. So, it is not expected to see any significant change in the absorption edge for DIO additive film. Further, since there is already I⁻ present in the MAPbI₃ films, hence the addition of extra I⁻ via DIO (1 wt.%) doesn't result in any significant shift in the absorption edge.



Figure S11: (a) Tauc plot in order to derive the optical band gap of MAPbBr₃ based perovskite thin films with different concentration of DIO into the perovskite precursor solution. Absorption spectra of with and without DIO additive (b) MAPbI_{3-x}Cl_x, (c) and (c) MAPbI₃ based perovskite thin films



Figure S12: (a) Schematic of thin film nucleation and growth rate of perovskite film with different concentration of DIO in the perovskite precursor solution. Schematic diagram of Ostwald ripening occurs with (b) 0 wt.%, (c) 1 wt.%, (d) 2 wt.% and (e) 5 wt.% DIO additive perovskite films.

Thin film growth and evolution (Ostwald ripening):

Ostwald ripening is a phenomenon in solid solutions that describes the inhomogeneous changes in the structure over the time i.e. small crystal dissolves and grows into larger crystals. The concentration of dissolved components near the small particle boundary is always higher than that near the bigger particle boundary. Hence, there is always a concentration gradient of the dissolved component between the surface/boundary of large crystal and small crystal. This is known as Fick's law, which describe the mass transfer of the dissolved components from the smaller particle to larger particle.¹ This can be understood by the relation between the particle radius and chemical potential on the surface of the particle.

$$\mu = \mu_0 + \frac{2\gamma V}{r} \tag{1}$$

Where, μ is the chemical potential on the surface of the particle, μ 0 is the chemical potential for a flat surface, r is the radius of particle, V is the molar volume and γ is the surface energy. Thus, smaller particle have high chemical potential at the surface than the larger particles.

The dissolution and growth of perovskite crystals can also be understood by equation (1). The small grain having a large chemical potential continuously undergoes the dissolution process. However, large grain having small chemical potential undergoes growth process. The large grain continuously grows until the inverse flux of the dissolved components from the small grain stops. And later on during thermal annealing, smaller domains (due to presence of DIO, whose boiling point is higher than the host solvent DMF) fuses to form compact film with large domains (figure 2) and less nucleation sites. Whereas, without DIO film have more nucleation sites with fast crystal growth, providing relatively smaller domains as seen in morphological studies (figure 2). However, rate of crystallization is further retarded due to

increased concentration of DIO (2 wt.% and 5 wt.%) in the perovskite precursor solution. This results in even lesser nucleation sites with bigger domains.



Figure S13: Dark J-V characteristic of (a) $MAPbI_{3-x}Cl_x$ and (b) $MAPbBr_3$ based perovskite solar cells with different concentration of DIO.



Figure S14: J-V-L characteristics of (a) with and (c) without DIO additive MAPbBr₃ PeLEDs. EQE and luminescence efficiency (cd/A) for (b) with and (d) without DIO additive MAPbBr₃ based PeLEDs, respectively. Inset of (a) and (c) represents the picture of glowing LED fabricated from with and without DIO additive perovskite films, respectively.

Electroluminescence Studies

Figure **S14a** and **S14c** represents the J-V-L characteristics of with and without DIO additive MAPbBr₃ based PeLEDs, respectively. Figure **S14b** and **S14d** represents the external quantum efficiency (EQE %) and luminescence efficiency (cd/A) for with and without DIO additive MAPbBr₃ based PeLEDs, respectively. The current density for without DIO additive MAPbBr₃ based PeLEDs, respectively. The current density for without DIO additive MAPbBr₃ based PeLEDs is almost one order higher than that of with DIO based PeLEDs. We expect that the lower current density is due to improved morphology by addition of 1 wt.% DIO. We observe that 1 wt.% DIO additive MAPbBr₃ based PeLEDs has the highest

luminescence of 350 cd m⁻² and 0.67 cd A⁻¹ at 5V. However, without DIO additive PeLEDs has the highest luminescence of 142 cd m⁻² and 0.037 cd A⁻¹ at 5V.



Figure 15: Current-voltage characteristics of (a) $MAPbI_{3-x}CI_x$ and (c) $MAPbBr_3$ based with (1 wt.%) and w/o DIO additive solar cells under 1 sun illumination without using BCP as an interlayer between $PC_{61}BM$ and Ag. External quantum efficiency of (b) $MAPbI_{3-x}CI_x$ and (d) $MAPbBr_3$ based with (1 wt.%) and w/o DIO additive solar cells.



Figure S16: Thermal stability for photovoltaic parameters of with and without DIO additive MAPbBr₃ based perovskite solar cell without encapsulation under continuous exposure to 1Sun irradiation.



Figure S17: Thermal stability for photovoltaic parameters of with and without DIO additive $MAPbI_{3-x}Cl_x$ based perovskite solar cell without encapsulation under continuous exposure to 1Sun irradiation.

Thermal Stability: We observed that DIO additive devices have better stability than without DIO additive devices. The improved stability due to DIO additive is in under study by doing Raman spectroscopy as a function of time from fresh and aged cells, which will be published elsewhere. The focus of this manuscript is on influence of DIO on the perovskite film formation and then connects the crystallization kinetics to the devices performance and stability is out of interest of this paper. We observed that after 360 minutes of continuous illumination of 1 Sun irradiation, without DIO additive MAPbBr₃ device degraded by 80% of its original value. However, with DIO additive MAPbBr₃ device degraded by 40% only. The stability is further more in DIO additive MAPbI_{3-x}Cl_x solar cells and the degradation is even less than 20% after 360 minutes.

Perovskite Films	C (Atomic %)	N (Atomic %)	O (Atomic %)	Br (Atomic %)	Cl (Atomic %)	ا (Atomic %)	Pb (Atomic %)
MAPbBr3	46.48	10.64	23.31	15.77	-	-	3.79
1% DIO	49.59	17.27	7.81	19.55	-	0.46	5.31
2% DIO	53.05	12.78	9.66	18.74	-	0.77	4.99
5% DIO	38.67	10.79	34.84	11.90	-	0.85	2.95
MAPbI _{3-x} Cl _x	-	-	-	-	1.62	76.43	21.95
1% DIO	-	-	-	-	0.43	77.55	22.05

Table S1: Elements present in with and w/o DIO additive perovskite thin films obtained

 through EDS measurement.

Table S2: Surface chemical composition of with and w/o DIO additive based perovskite thinfilms characterized through XPS measurement.

Perovskite Films	C (Atomic %)	N (Atomic %)	O (Atomic %)	Br (Atomic %)	Cl (Atomic %)	ا (Atomic %)	Pb (Atomic %)
MAPbBr3	44.59	7.96	6.09	28.11	-	-	13.25
1% DIO	44.58	10.15	4.56	27.87	-	0.49	12.35
2% DIO	28.04	15.69	2.00	38.42	-	1.55	14.30
5% DIO	48.75	10.53	8.11	21.45	-	2.95	8.22
MAPbI _{3-x} Cl _x	41.27	8.67	5.38	-	-	34.08	10.59
1% DIO	38.09	9.17	4.84	-	-	36.58	11.32

Table S3: First, second and third order diffraction peak position of DIO additive (with different weight percentage) MAPbBr₃ based perovskite thin films.

DIO %	1 st order 2θ (Degree)	2 nd order 2θ (Degree)	3 rd order 2θ (Degree)
0	15.11	30.29	46.05
1	15.09	30.27	46.02
2	15.06	30.24	45.97
5	15.03	30.15	45.83

Table S4: The photovoltaic parameters achieved for with and without DIO additive perovskite thin film based solar cells without BCP as an interlayer between $PC_{61}BM$ and Ag over an area of 4.5 mm².

Devices	V _{cc} (V)	J _{sc} (mA/ cm²)	J _{sc} EQE (mA/ cm ²)	FF (%)	PCE (%)	cd/A	EL _{EQE} (%)
MAPbBr ₃	1.16	3.50	3.20	49	2.00	0.037	0.013
With DIO	1.42	7.91	5.86	53	6.0	0.67	0.24
MAPbl _{3-x} Clx	0.908	16.84	16.17	51.05	8.00	-	-
With DIO	0.922	21.2	19.47	56.6	11.1	-	-

References:

¹ R. J. Stoke, D. F. Evans, *Fundamentals of Interfacial Engineering* (Wiley-VCH, 1996), chap.3.