Two-Dimensional Metal Halide Perovskites containing Triazine based Macrocycles

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I. Introduction

Metal halide perovskites (MHPs) are an emerging type of semiconducting crystal with the structure ABX_3 made up of an A site positively charged cation such as methylammonium (MA), B site metal cation such as lead, and anion X which is a halide such as bromide (Fig. 1).[1] MHPs exhibit important properties such as the ability to produce light when stimulated by electricity known as a light emitting diode (LED).[2]

Previous research has shown incorporation of large organic molecules into the MHP crystal can increase the longevity of the LED by making them more resistant to degradation caused by moisture and air.[3] This work will investigate the incorporation of triazine based macrocycles to improve the light emission by forming 2D layers on 3D bulk crystal resulting in narrowing the emission and/or increasing the emission intensity.

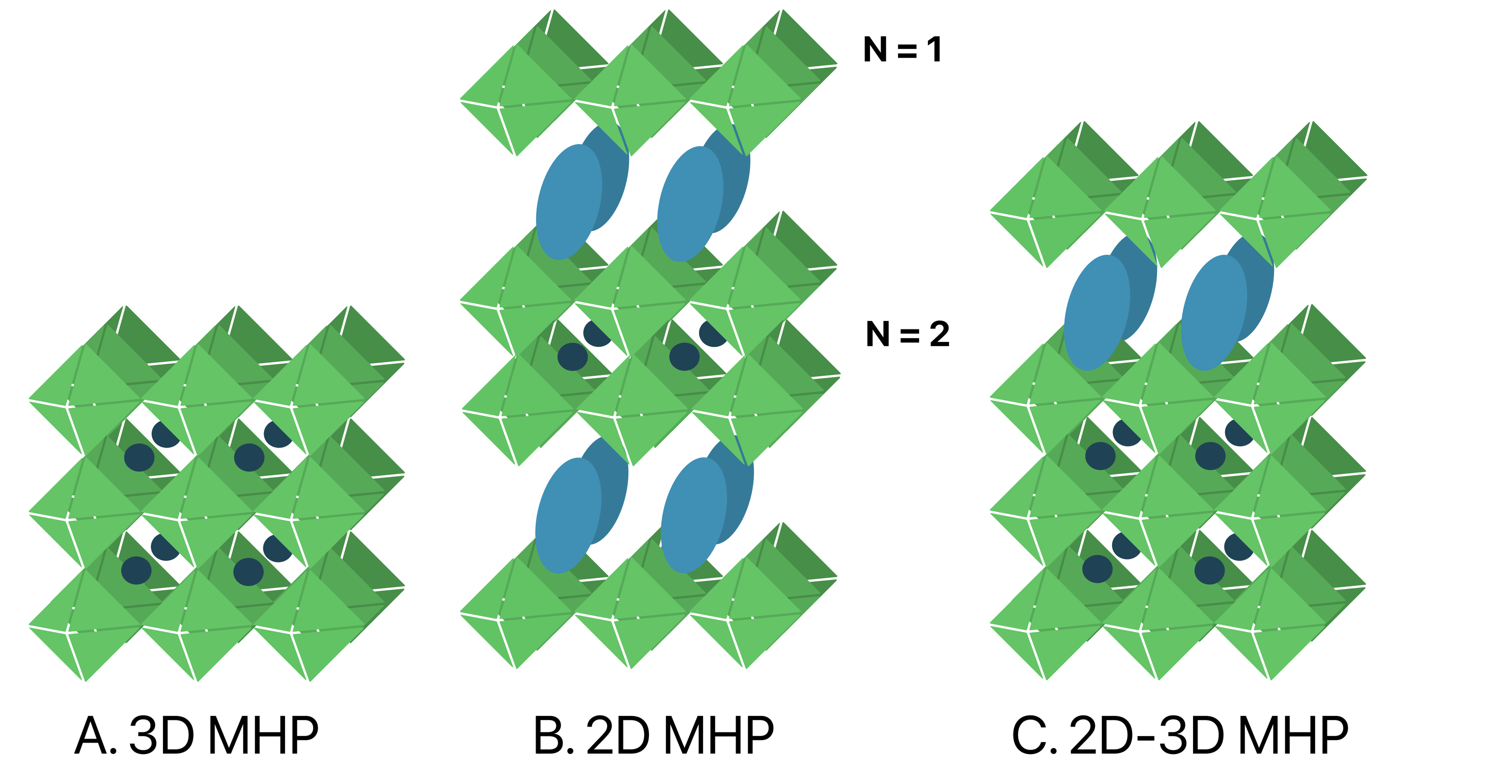
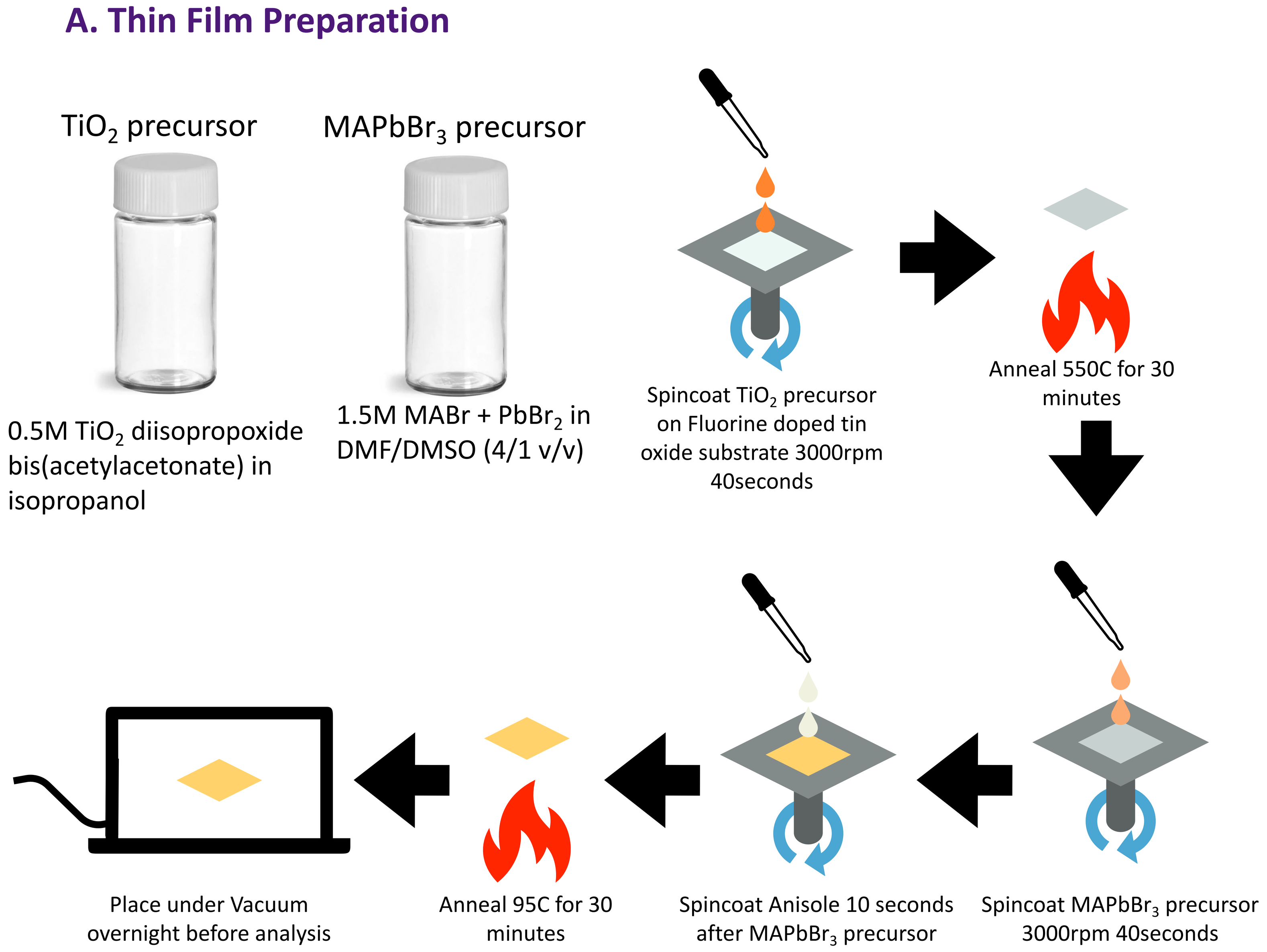


Figure 1. A) Bulk 3D MHP crystal representation with lead-bromide as the green octahedra with interior A-site as the dark green circle. B) Example of 2D perovskite with the blue oval representing the macrocycle with extended layers of octahedra N = 1 and N = 2. C) 2D-3D mixture with the 2D layer forming on top of the 3D crystal.

II. Experimental

A. Thin Film Preparation



II. Experimental

A. Macrocycle Preparation

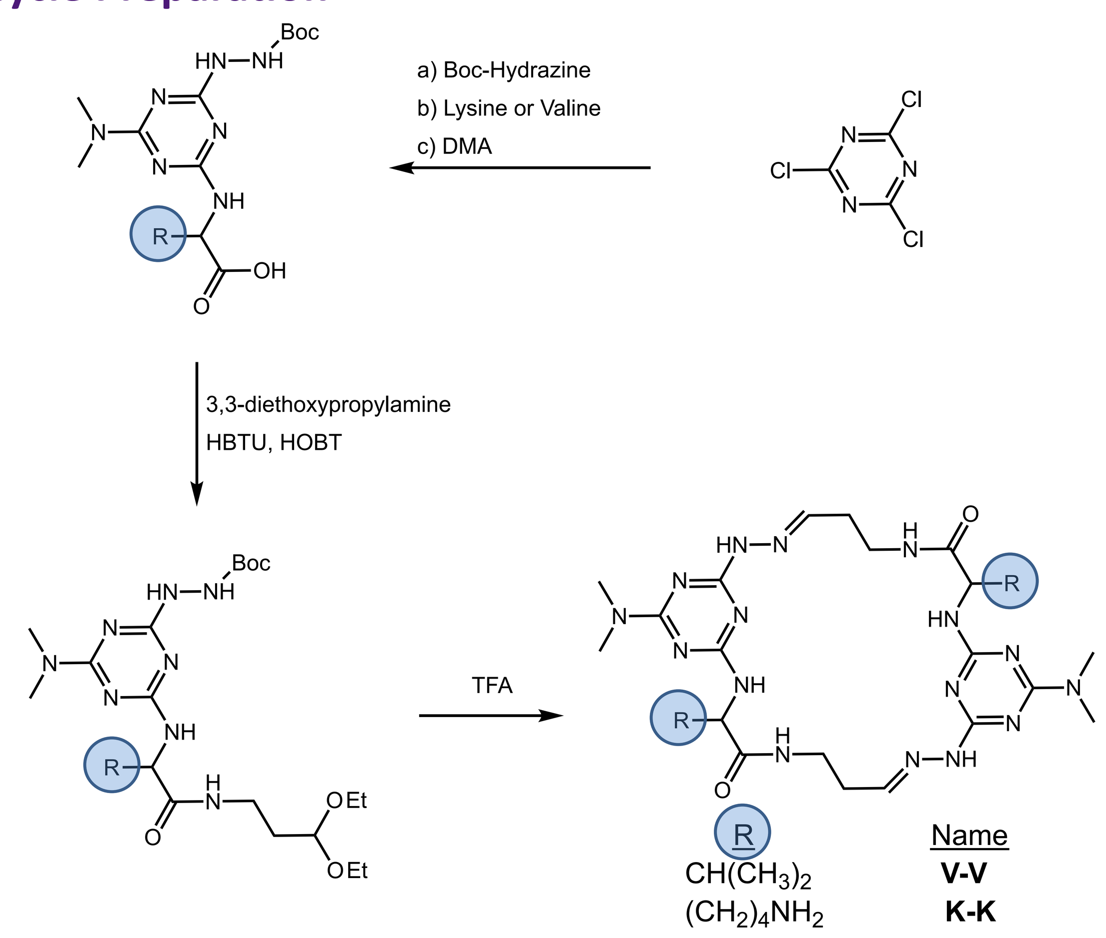


Figure 2. Macrocycle Synthetic scheme. Two macrocycles were prepared and used different amino acids to form different R groups, one amine terminated (K-K) , one isopropyl terminated (V-V).

III. Results

A. Perovskite Thin Films (- Macrocycle)

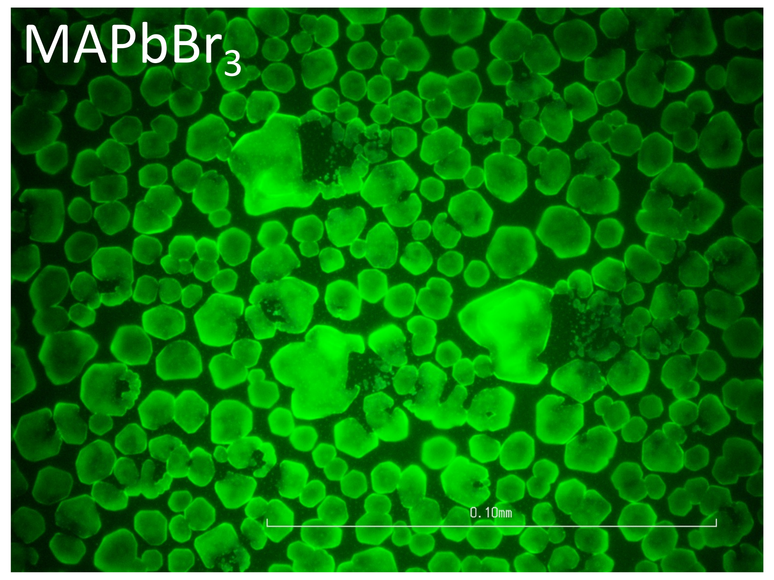


Figure 3. Photoluminescent (PL) image of $MAPbBr_3$ thin film.

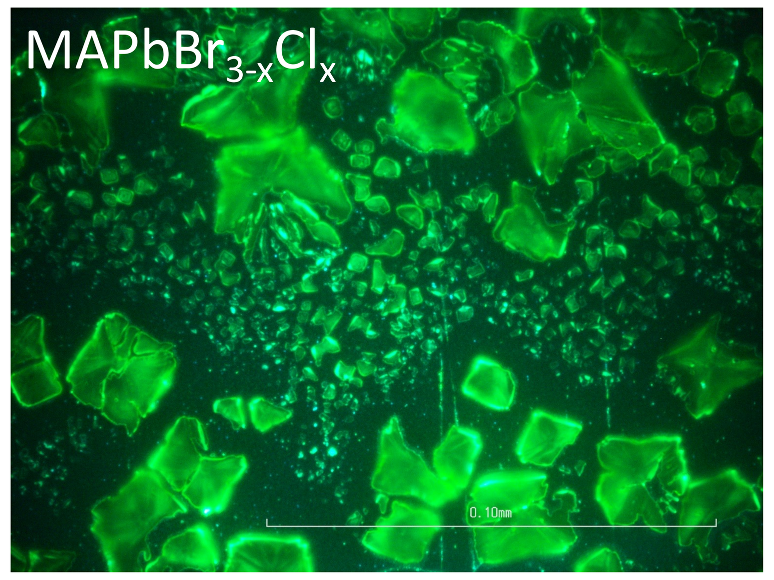


Figure 4. PL image of $MAPbBr_{3-x}Cl_x$ thin film. MACl is excess in precursor solution.

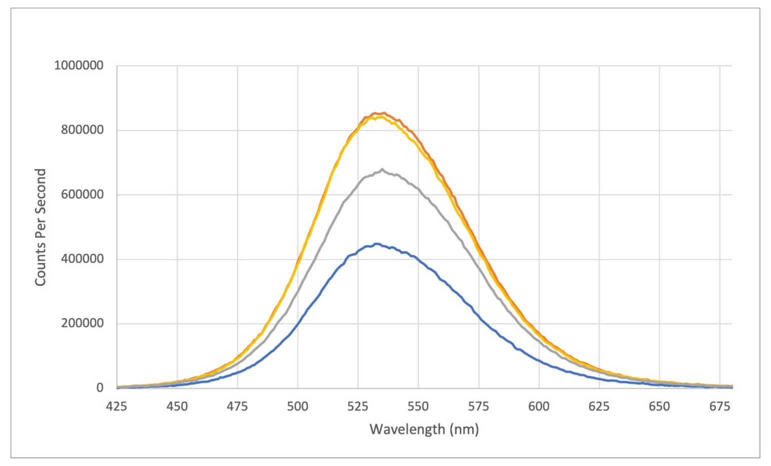


Figure 5. PL spectra of $MAPbBr_3$ thin film from multiple locations on substrate. Average lambda max of 537 ($\pm$0.9) nm Average FWHM 33.6 ($\pm$4.0) nm

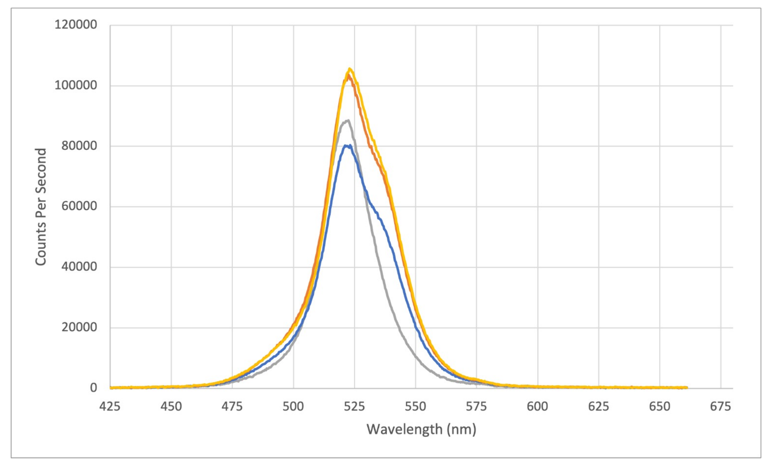


Figure 6. PL spectra of $MAPbBr_{3-x}Cl_x$ thin film from multiple locations on substrate showing 2 modes of light emission. Primary lambda max of 524 ($\pm$1.6) nm Average FWHM 30.1 ($\pm$3.9) nm

Acknowledgments

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III. Results

B. Perovskite Thin Films (+ Macrocycle)

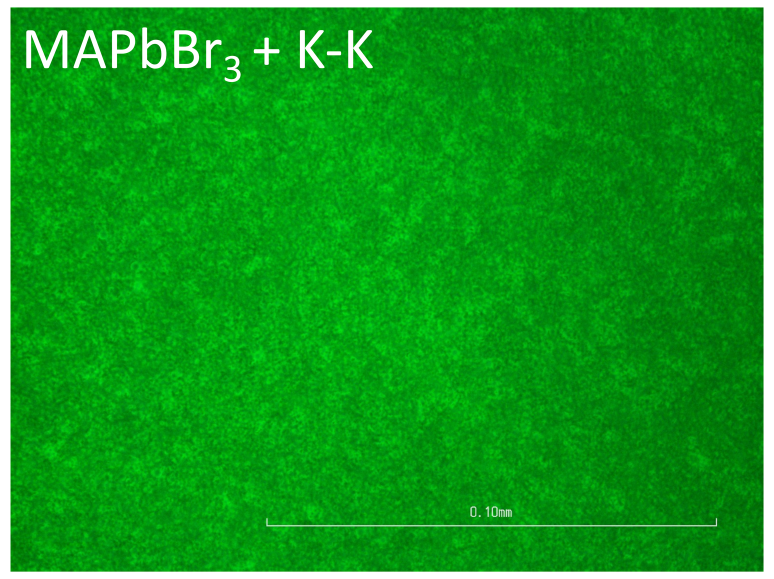

Figure 7. PL image of $MAPbBr_3$ + K-K thin film.

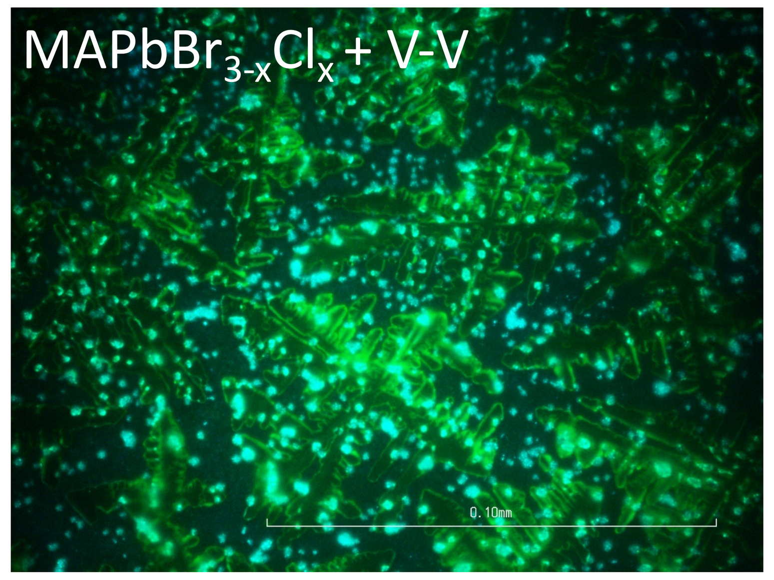

Figure 8. PL image of $MAPbBr_{3-x}Cl_x$ + V-V thin film.

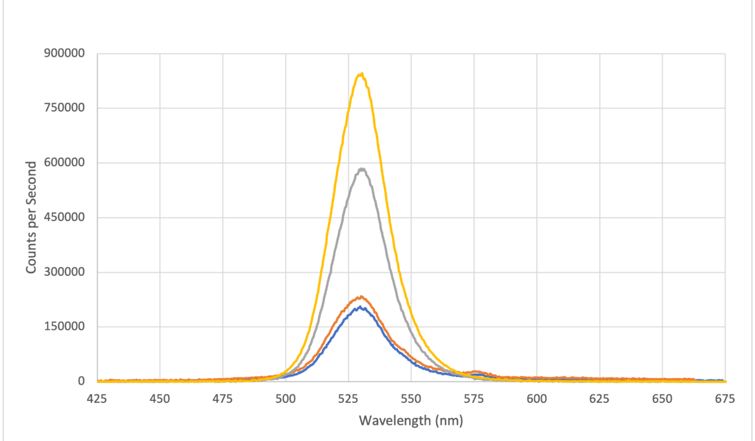

Figure 9. PL spectra of $MAPbBr_3$ + K-K thin film from multiple locations on substrate. Average lambda max of 536 ($\pm$0.45) nm Average FWHM 23.6 ($\pm$0.8) nm

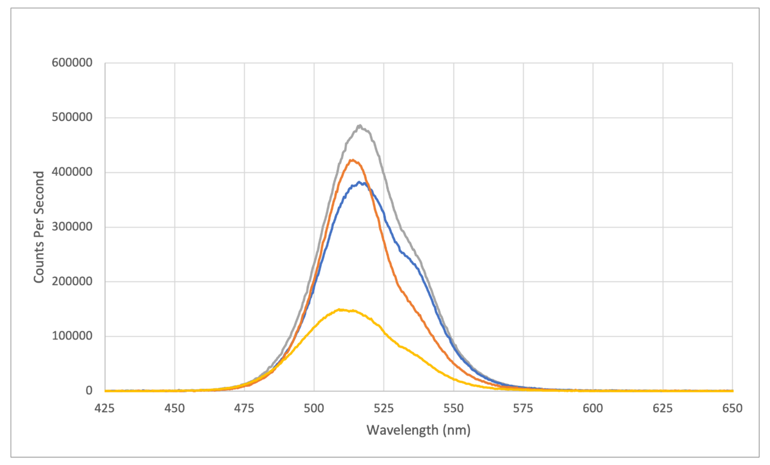

Figure 10. PL spectra of $MAPbBr_{3-x}Cl_x$ + V-V thin film from multiple locations on substrate. Primary lambda max of 511 ($\pm$3.5) nm Average FWHM 34.3 ($\pm$3.4) nm

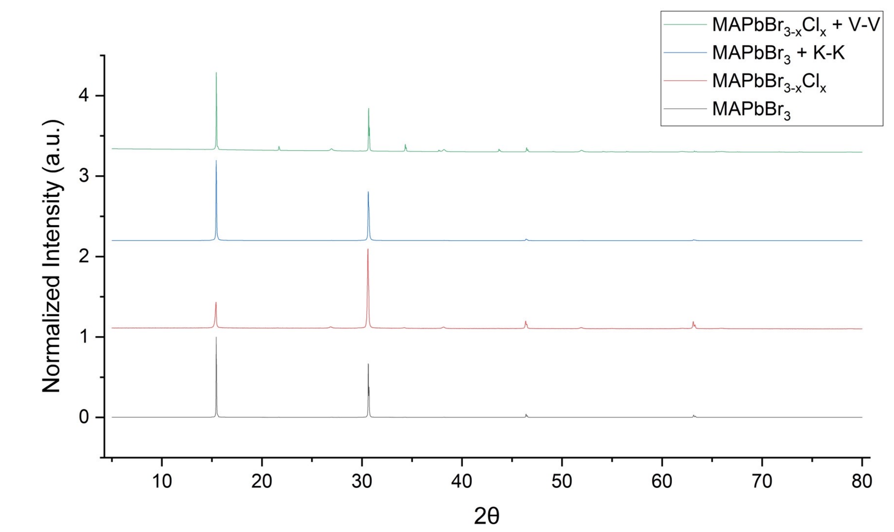

Figure 11. Powder x-ray diffractogram of thin films showing peak locations consistent with Cubic Pm3m phase and line widths consistent with high crystallinity material.

IV. Conclusions

- Addition of V-V to $MAPbBr_{3-x}Cl_x$ increases the separation of the two light emission peaks enhancing halide segregation and reducing the crystal size.
- Addition of K-K to $MAPbBr_3$ showed a decrease in the FWHM of the emission and more thin film like morphology.

V. Future Work

- Step-wise addition of the Macrocycle to form 2D layers on 3D crystal
- Small angle X-ray diffraction to interrogate the possible 2D layers

VI. References

1. Jaffe, A.; Lin, Y.; Beavers, C. M.; Voss, J.; Mao, W. L.; Karunadasa, H. I., High-Pressure Single-Crystal Structures of 3D Lead-Halide Hybrid Perovskites and Pressure Effects on their Electronic and Optical Properties. *ACS Central Science* **2016,** *2* (4), 201-209.
2. Dey, A.; Polavarapu, L. *et al*., State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021,** *15* (7), 10775-10981.
3. Azmi, R.; Ugur, E.; Seitkhan, A.; Aljamaan, F.; Subbiah, A. S.; Liu, J.; Harrison, G. T.; Nugraha, M. I.; Wang, C.-L.; Anthopoulos, T. D.; Schwingenschlogl, U.; De Bastiani, M.; Aydin, E.; De Wolf, S. Damp heat-stable perovskite solar cells with tailored-dimensionality 2D/3D heterojunctions. *Science* **2022**, *376* (6588), 73– 77,