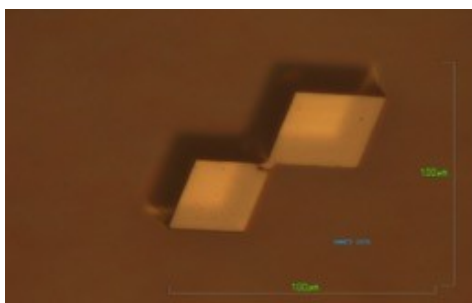


Supplementary Information

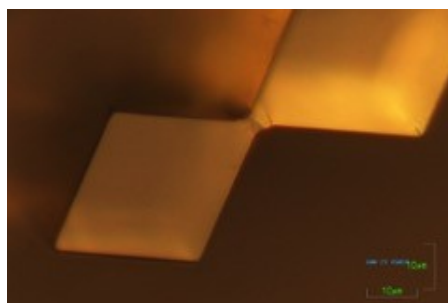
Optoelectronic Properties of Octahedral Molybdenum Cluster-Based Materials at Single Crystal Level

Elena Segura-Sanchis, Ana Moreno, Fernando Ramiro-Manzano, Roberto Fenollosa,
Marta Feliz and Pedro Atienzar

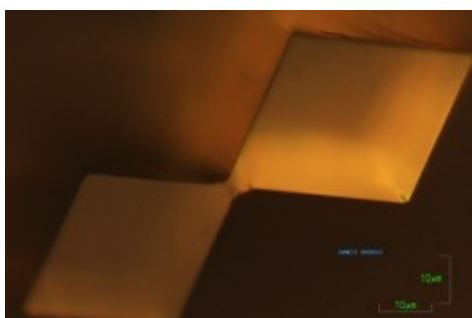
Instituto de Tecnología Química, Universitat Politècnica de València - Consejo Superior de
Investigaciones Científicas (UPV-CSIC), Avd. de los Naranjos s/n, 46022 Valencia.



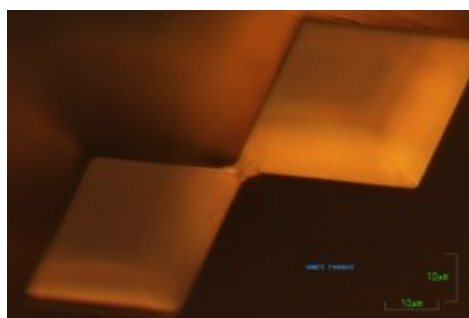
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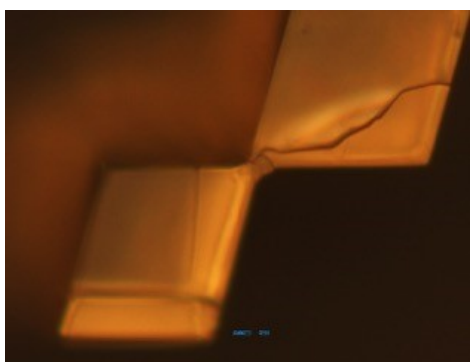
45 minutes



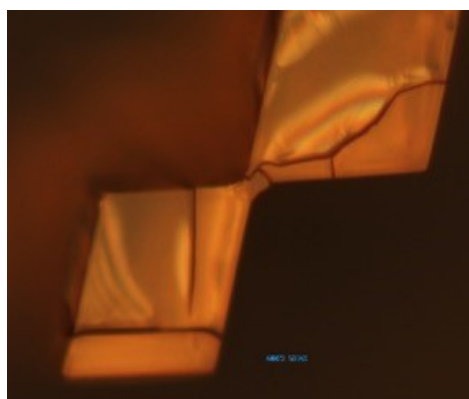
3 hours



24 hours



49 hours



5 days

Figure S1. Time monitoring of the crystalline surface of **MoCl** single crystals under ambient conditions.

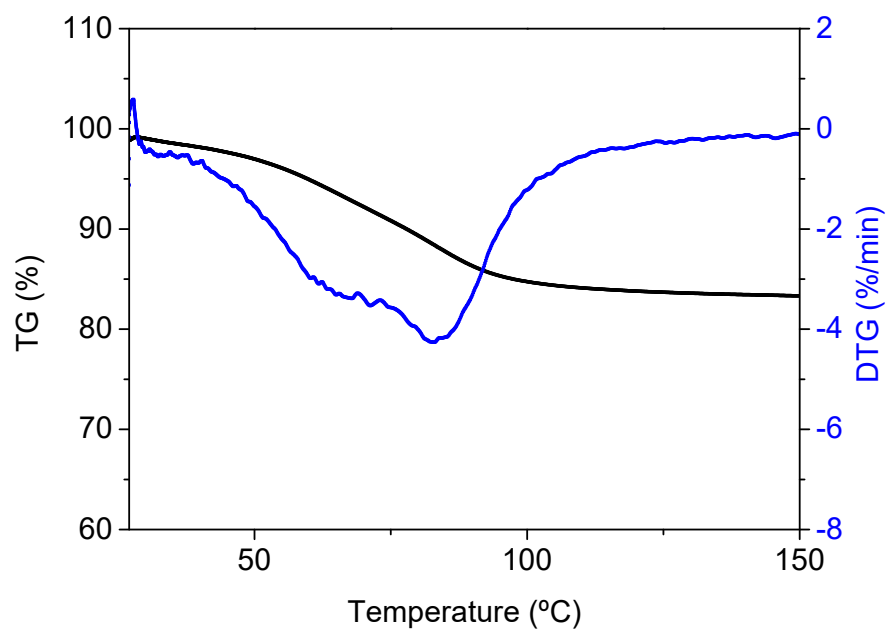


Figure S2. TG/DTG measurement of **MoCl** single crystals under air.

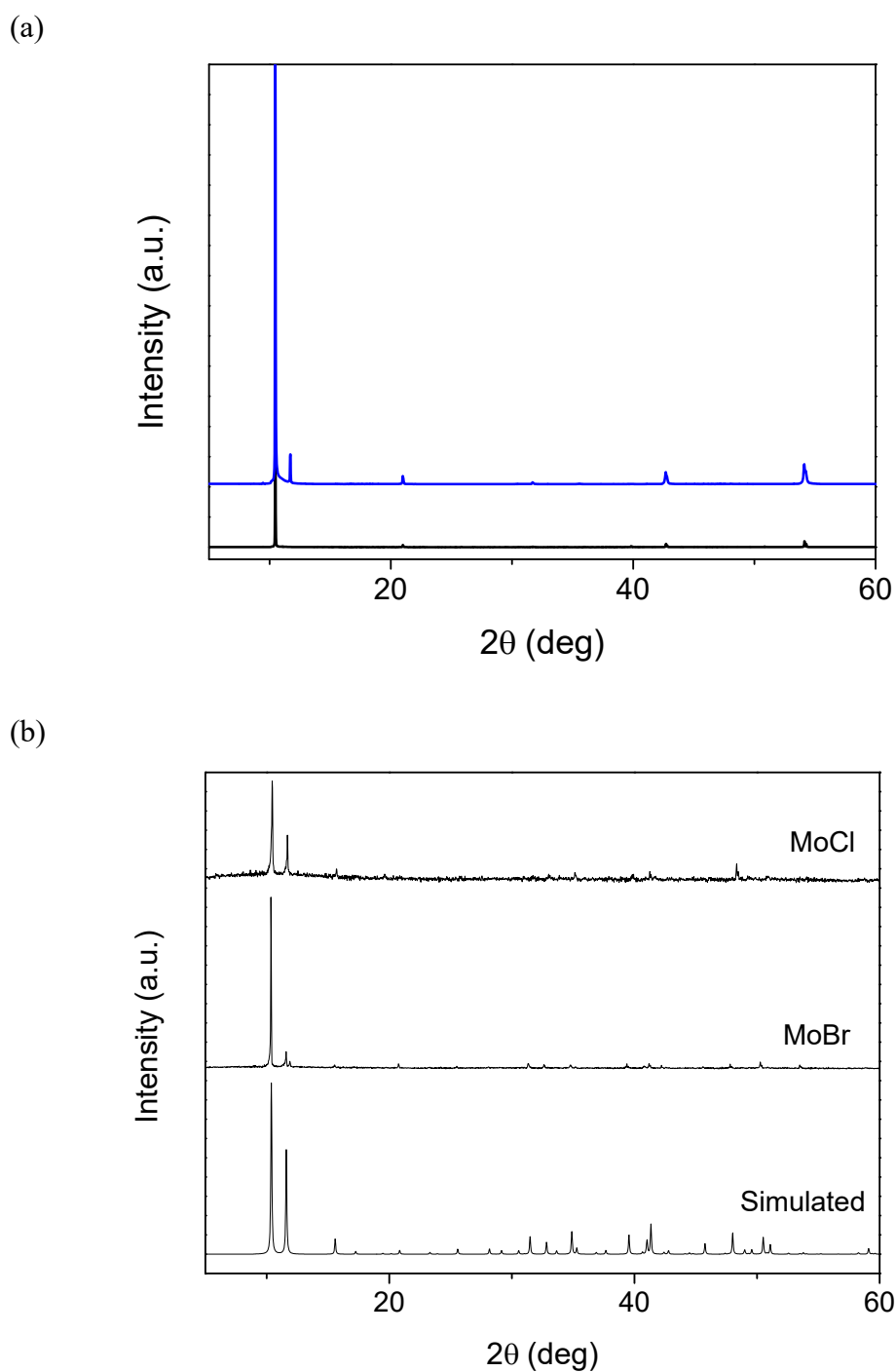


Figure S3. (a) Powder X-ray diffraction patterns of freshly prepared (black line) and aged (blue line) **MoCl** single crystals. (b) Powder X-ray diffractograms (from top to bottom) of aged **MoCl** and **MoBr** polycrystalline samples and the simulated pattern obtained from **MoBr** single crystal X-ray diffraction (ref. 15 of the manuscript).

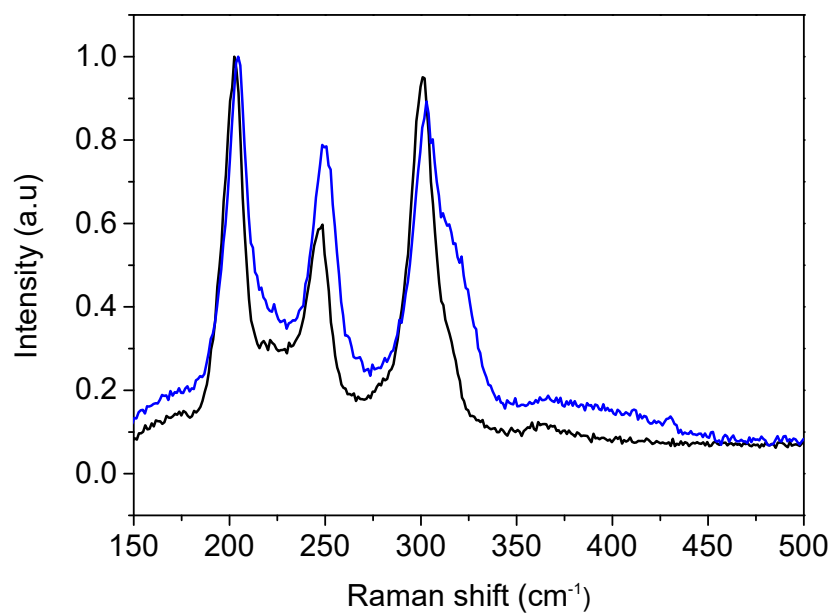
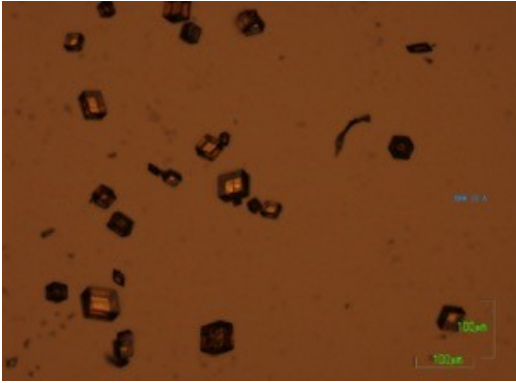
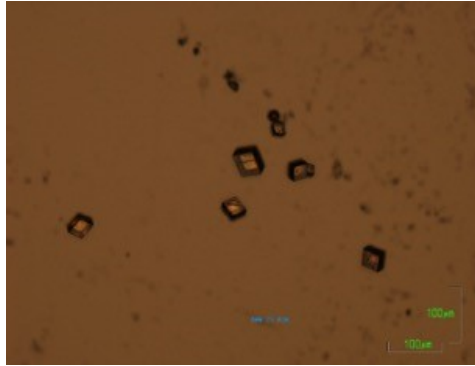


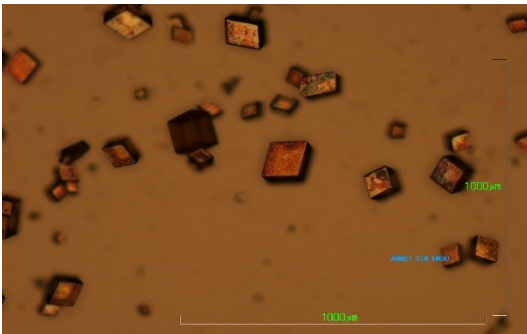
Figure S4. Raman spectra of freshly prepared (black line) and aged (blue line) **MoCl** single crystals ($\lambda_{\text{exc}} = 785 \text{ nm}$).



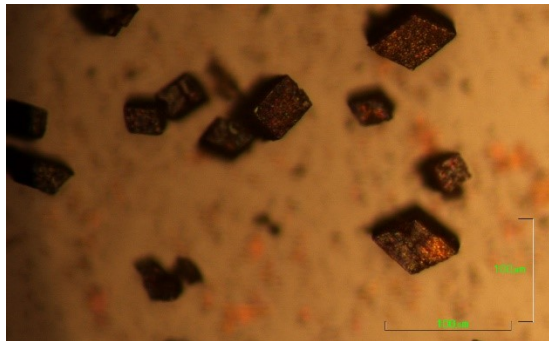
Dry crystals



Crystals with acetonitrile

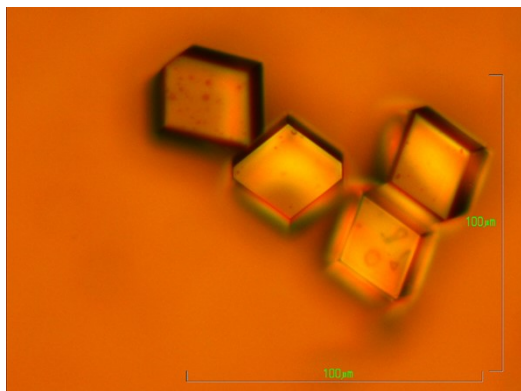


Dry crystals

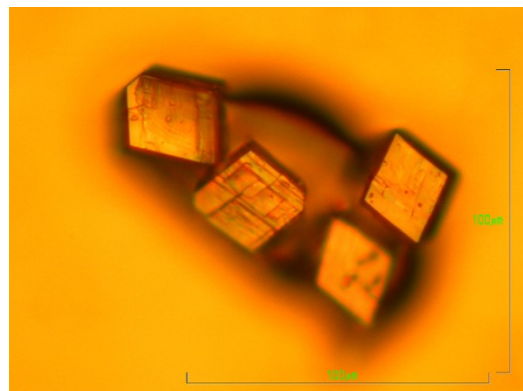


Crystals with dichloromethane

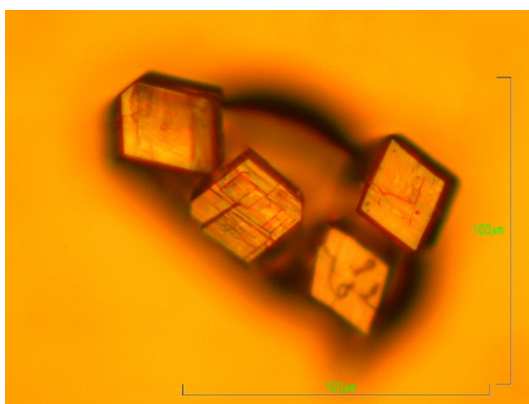
Figure S5. Evolution of **MoCl** crystals before and after contact with CH_3CN and CH_2Cl_2 .



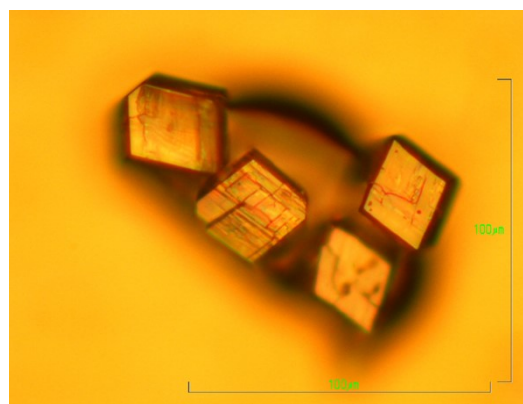
Dry sample



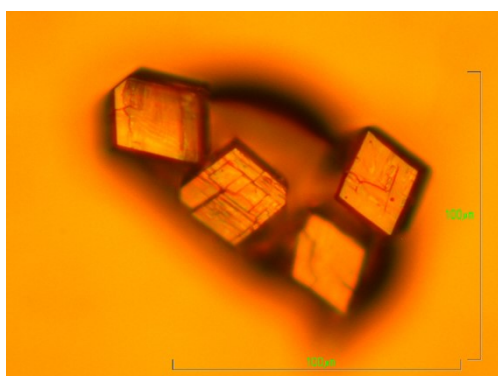
Wet sample. Time 0



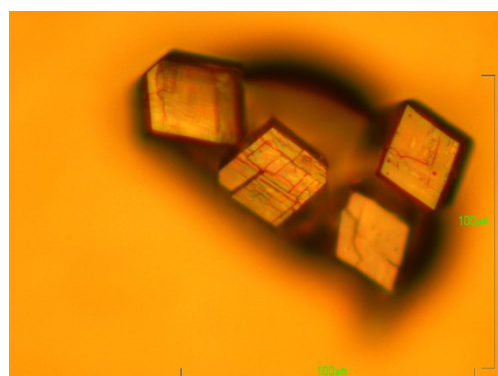
Wet sample, 1 hour



Wet sample, 3 hours



Wet sample, 24 hours



Wet sample, 28 days

Figure S6. Dry MoCl_5 crystals and their evolution after contact with BMIMBF_4 .

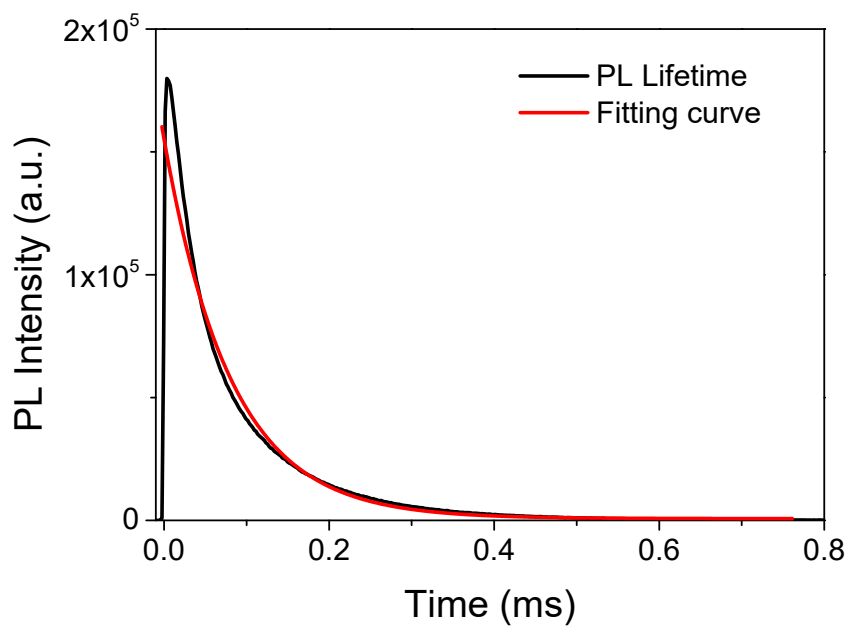
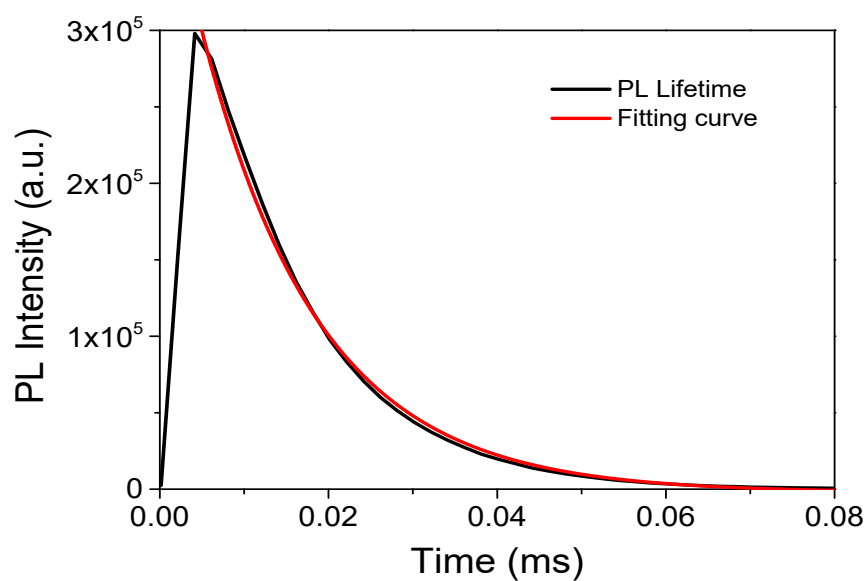


Figure S7. Luminescence decays lifetime of **MoBr** (top) and **MoCl** (bottom) single crystals (black lines). The red line corresponds to the fitting of a single-exponential decay model.

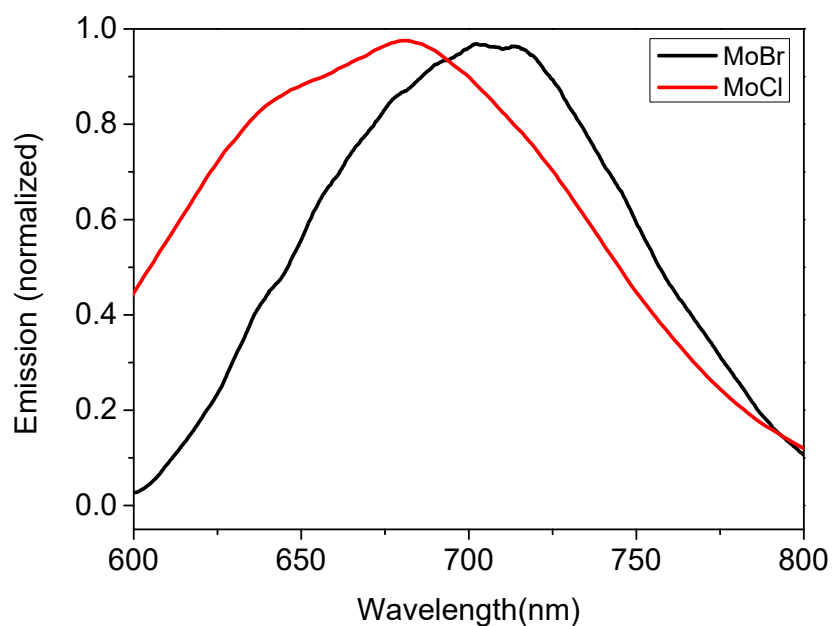


Figure S8. PL spectra of selected **MoCl** (red) and **MoBr** (black) single crystals selected among >20 single crystal specimens.

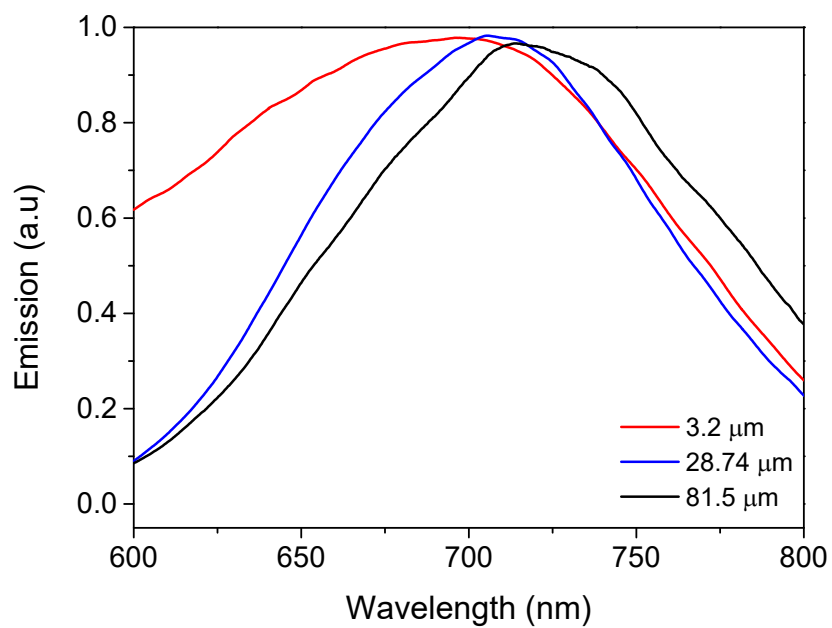


Figure S9. Emission wavelengths depending on **MoBr** single crystal size.

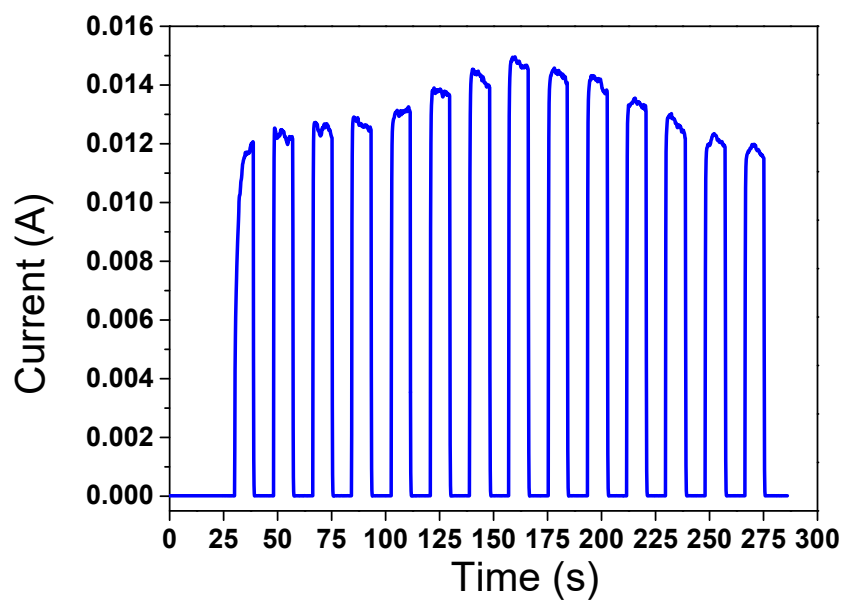


Figure S10. Current-time (I-t) curves under 405 nm LED light with 0.1 Hz light on/off cycles of a single crystal of MAPbBr₃ under $\lambda_{\text{exc}} = 405$ nm.