

Multimodal Correlative Microscopy to Study the Chemical and Energetic Landscape of Alloyed Halide Perovskites

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Metal halide perovskites have shown exceptional performance in optoelectronic devices, including tandem photovoltaics[1, 2] and LEDs[3]. However, their impressive performance is surprising given that they exhibit several forms of heterogeneity, namely spatially varying deep charge carrier trap densities[4], structural heterogeneity in the form of multiple phase inclusions and impurities[5, 6], as well as considerable chemical heterogeneity[7, 8]. All these variations are considered to be negative in conventional semiconductors and so halide perovskites high performance in spite of these has meant they have been referred to as ‘defect tolerant’. The micro-nanoscale variations of these properties in halide perovskites means that microscopic imaging of these materials is essential to obtain a full understanding of their properties rather than an obtaining an ensemble average at the macroscale.

Here, I will discuss how we resolve this paradoxical defect tolerant behaviour by providing an overall visualisation of the landscape – both chemical and energetic – that charge carriers experience in halide perovskites[9]. We have developed a multimodal, correlative microscopy suite consisting of a calibrated, wide-field, hyperspectral optical microscope, a transient absorption microscope (TAM) and a hard X-ray synchrotron nanoprobe microscope. The hyperspectral microscope allows us to extract quantitative values of device relevant parameters such as the quasi-Fermi level splitting (the maximum voltage produced by the solar cell), the Urbach energy (a measure of disorder in the material) and the local photoluminescence quantum efficiency (PLQE). We find in alloyed halide perovskites that microscopically, the Urbach energy correlates well with the PLQE as one might expect lower disorder to lead to higher emission yields (Fig. 1).

When we correlate the hyperspectral with the nanoprobe synchrotron measurements capable of measuring nano X-ray fluorescence and diffraction to probe chemical composition and crystal structure respectively with ~50 nm resolution[10], we find that the regions with the highest PLQE and lowest disorder correlate strongly with areas of higher bromide content (Fig. 2). We find that the optoelectronic properties show only a very weak dependence on local strain of up to 1%, strain magnitudes that would be detrimental to III-V semiconductors[11]. Paradoxically, these regions also exhibit a red-shifted photoluminescence peak whereas bromide tends to blue-shift the bandgap. To understand this, we employed the TAM setup, capable of probing the excited carrier populations microscopically with temporal and energetic resolution. We find that in regions with high emission yield and high Br, the carrier population starts at high energies as we would expect but rapidly funnels to nanoscale lower energy sites whereas in the regions with low Br and low emission yield, this funnelling does not occur.

These nanoscale energetic gradients funnel carriers away from trap states and onto low disorder, high emission yield sites (Fig. 2d). Taken together, these measurements reveal the complicated and competitive landscape for charge carriers in these materials, where nanoscale energetic funnels endow these materials with enhanced defect tolerance.

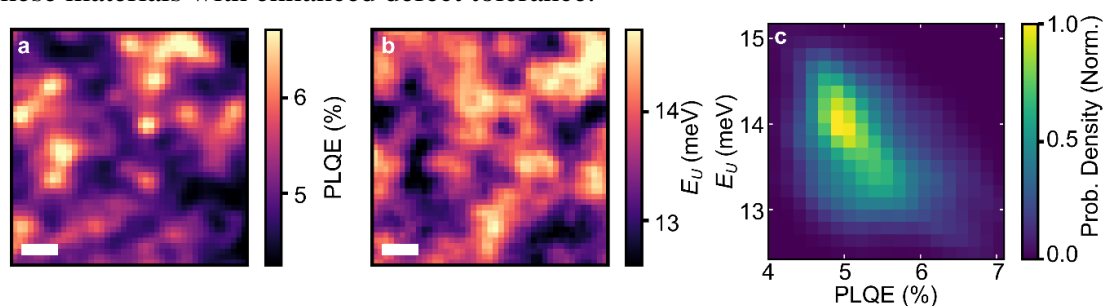


Figure 1: Correlation of PLQE and Urbach energy in alloyed metal halide perovskite film. (a) PLQE and (b) Urbach energy maps of a perovskite film measured in the hyperspectral microscope. (c) 2D kernel density estimate plot showing statistically significant correlation between the two properties spatially. Scale bars are 1 μm .

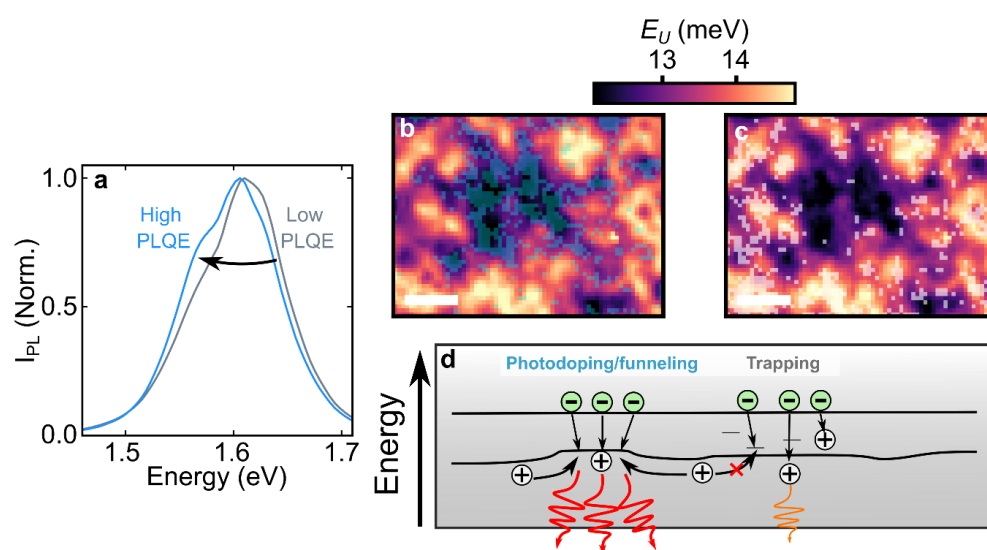


Figure 2. Optoelectronic and chemical correlations. (a) PL spectra extracted from the highest (blue) and lowest (grey) PLQE regions showing red shifted emission from most emissive regions. (b) Urbach energy map of perovskite film overlaid with the highest Br and (c) lowest Br regions respectively. (d) Schematic showing carriers funnelling into low energy regions in High Br regions while carriers are trapped in low Br regions. Scale bars are 2 μm .

References:

- [1] A Al-Ashouri et al., *Science* **370**(6522) (2020), p. 1300.
- [2] J Xu et al., *Science* **367**(6482) (2020), p. 1097.
- [3] YH Kim et al., *Nature Photonics* (2021).
- [4] TAS Doherty et al., *Nature* **580**(7803) (2020), p. 360.
- [5] AS Doherty Tiarnan et al., *Science* **374**(6575) (2021), p. 1598.

- [6] S Macpherson et al., arXiv e-prints (2021), p. arXiv:2107.09549.
- [7] JP Correa-Baena et al., *Science* **363**(6427) (2019), p. 627.
- [8] S Feldmann et al., *Nature Photonics* **14**(2) (2020), p. 123.
- [9] K Frohna et al., *Nature Nanotechnology* **17**(2) (2022), p. 190.
- [10] PD Quinn et al., *Journal of Synchrotron Radiation* **28**(3) (2021), p. 1006.
- [11] YA Bioud et al., *Nature Communications* **10**(1) (2019), p. 4322.