Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Raman spectroscopy insights into the α – and δ- phases of Formamidinium Lead Iodide ($FAPbI_3$)

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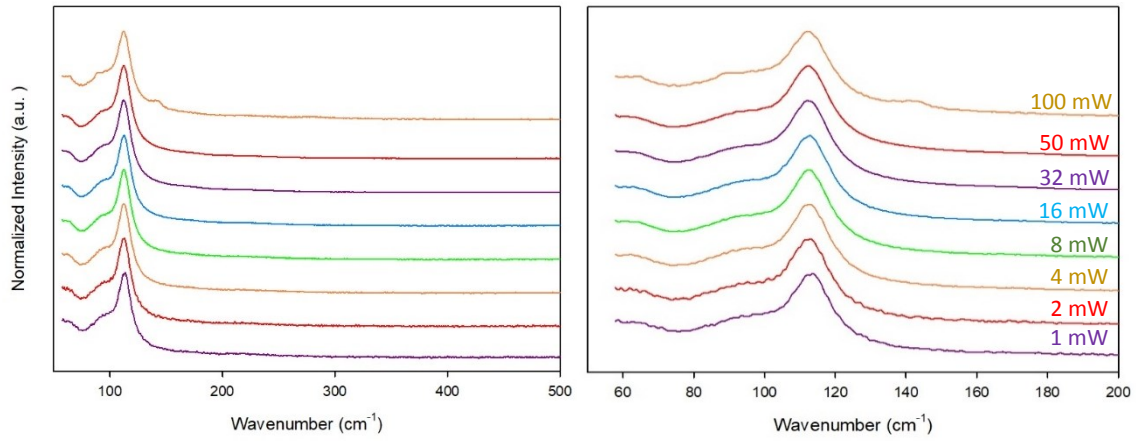
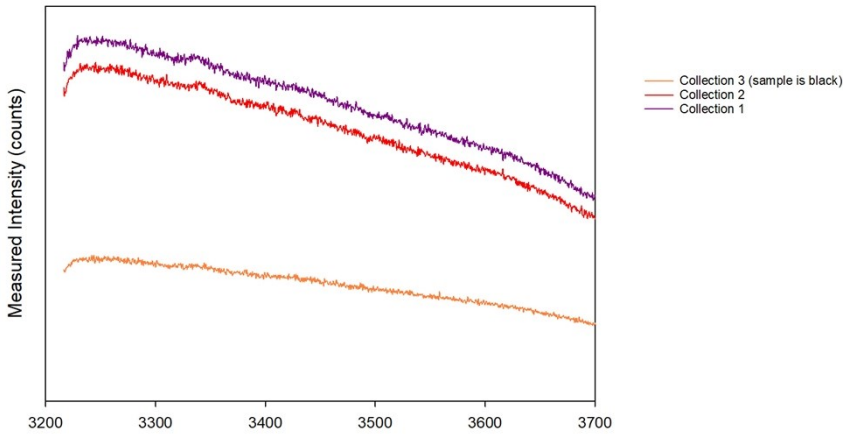
In the main body of this piece, we stated a 2mW laser power was used in exploring the transformation. Before determining this to be a suitable laser power, our initial collection looked at a range (**SI Figure 1**) with the δ-$FAPbI_3$ sample. With the use of 100 mW, the sample was observed to be black under the lense, showing this power rating had degraded the sample which is further evident from the additional peaks we attribute to be PbO. Although it would seem there is no change in the recorded spectra from 1 mW to 50 mW, we need to mindful that data is collected over multiple accumulations.



SI Figure 1: Initial collection of the yellow-phase Raman spectra with varying laser powers. Laser power values refer to the output from the laser source.

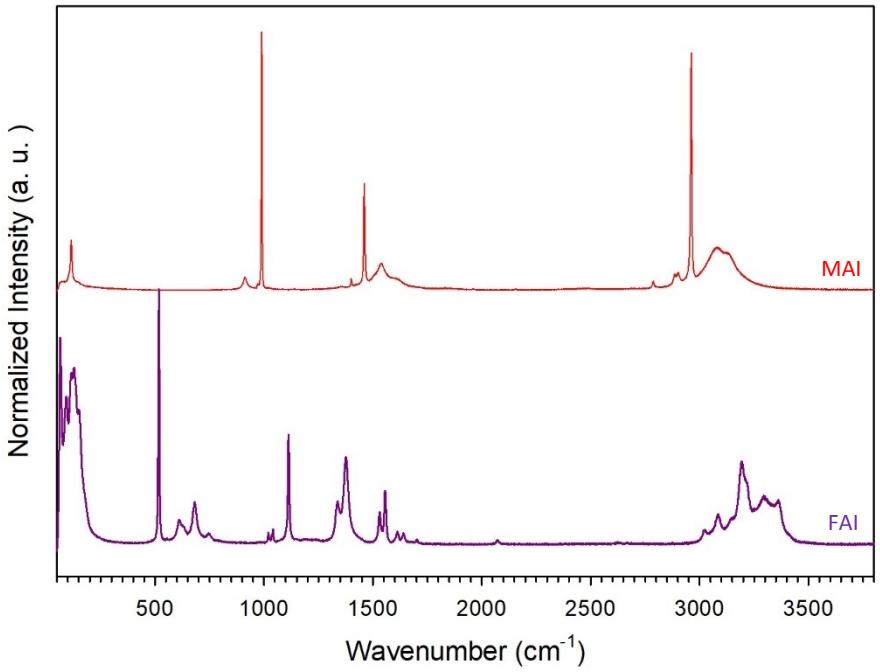
Thus, for example, our observations for the 40 mW 3200 – 3700 cm^{-1} region showed the sample to remain yellow with a water band in the first accumulation, with this observation remaining true in the second accumulation although with loss of intensity in the water band, before transforming to black on the third accumulation (**SI Figure 2**).



SI Figure 2: Initial data collection in the region of 3200 up to 3700 cm^{-1} at 40 mW after the consecutive accumulation collections.

Therefore although after the first accumulation, it may see the power rating is suitable, we need to be conscious the sample isn't going to change or degrade when we collect multiple accumulations, which lead to our reasoning of using a low power rating: to ensure thorough data collection which accurately represents the sample, without causing undetectable changes (before initial measurement is completed) or degradation.

We have recorded the Raman spectra of FAI and MAI as reference. To those unfamiliar to Raman spectroscopy, we would like to reiterate the lack of organic modes shown in the $FAPbI_3$ phase is due to the symmetry make up of this compositions, and while the FAI spectra (**SI Figure 3**) shows multiple modes, we need to be mindful these are different compositions and the unit cell for each will have a different arrangement.



SI Figure 3: Raman spectra of precursor FAI, in addition to MAI for reference.