Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Elucidation of the Role of Guanidinium Incorporation in Single-Crystalline $MAPbI_3$ Perovskite on Ion Migration and Activation Energy

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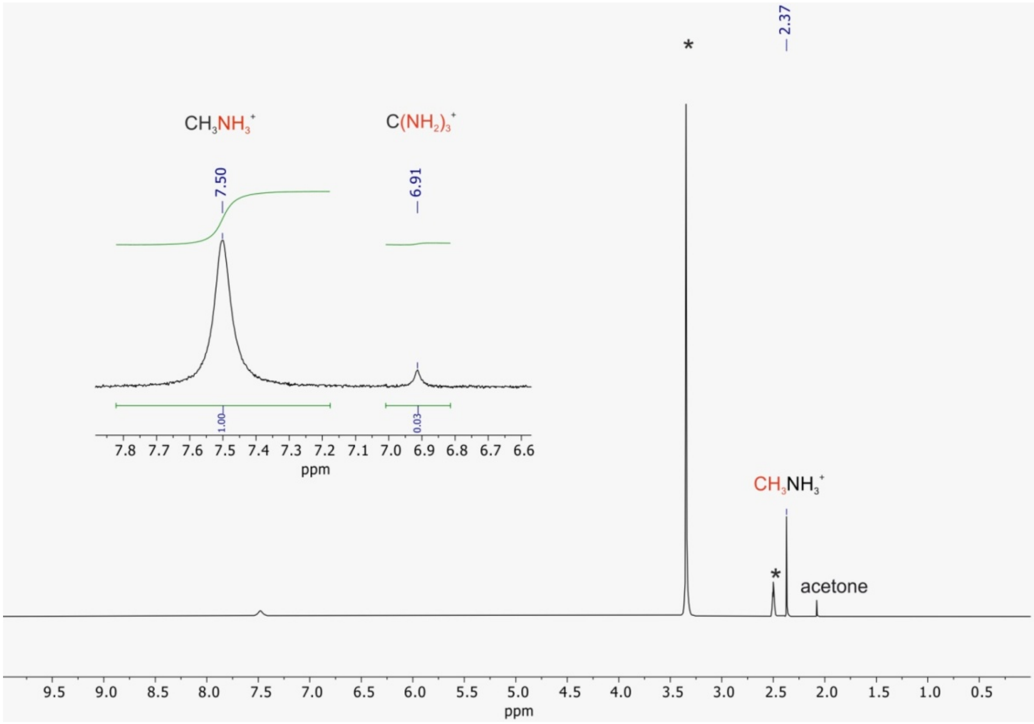

Fig. S1 ^{1}H NMR spectra of $MAPbI_3$ and $GUA_{0.015}MA_{0.985}PbI_3$ single crystals. The GUA/MA ratio was calculated using the integrated values for the resonances belonging to amine group of GUA (6.91 ppm) and MA (7.50 ppm). The peaks marked as * correspond to DMSO-d_6 and water.

The GUA/MA ratio was calculated using the integrated values for NH_3^+ and $(NH_2)_3^+$ of the resonances belonging to MA and GUA, respectively:

$x = [(NH_2^+)_{GUA}/6] = 0.03/6 = 0.005$

$y = [(NH_3^+)_{MA}/3] = 1/3 = 0.333$

$$\%GUA = \frac{x}{x+y} * 100\% = \frac{0.005}{0.005+0.333} \cong 1.5\%$$

$$\%MA = \frac{y}{x+y} * 100\% = \frac{0.333}{0.005+0.333} \cong 98.5\%$$

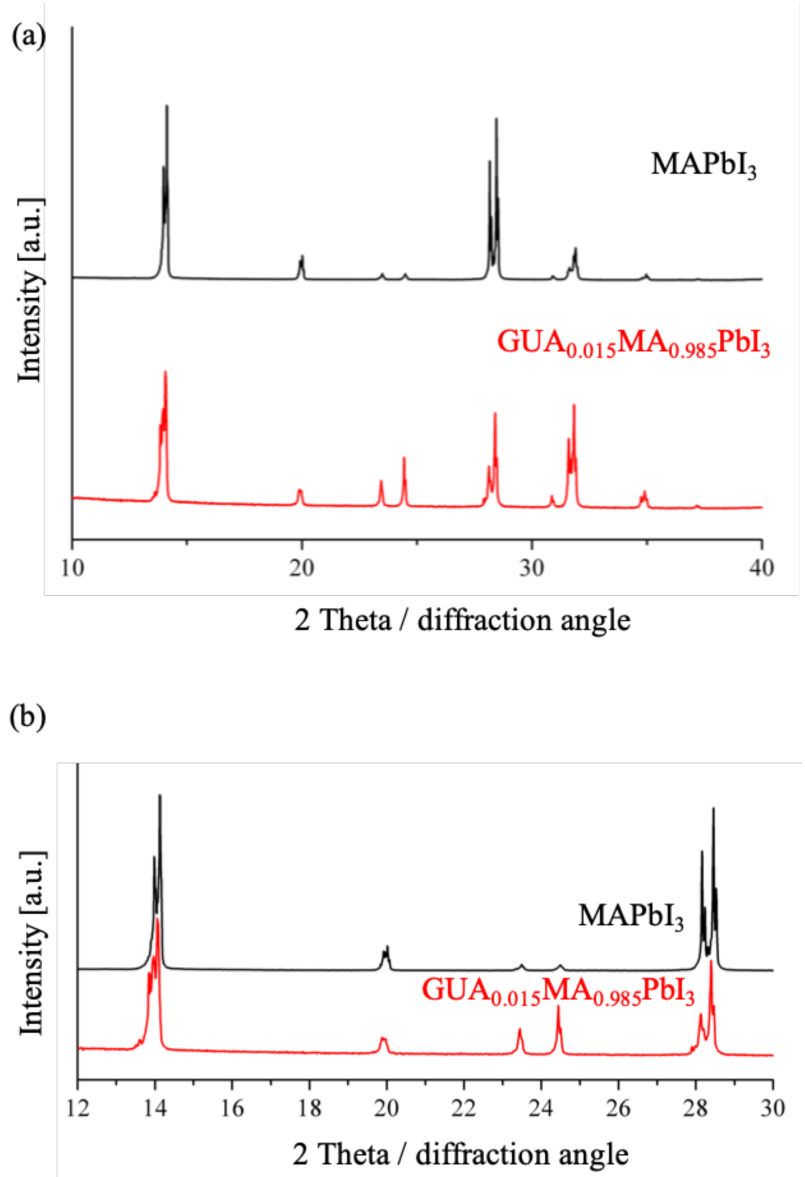

Fig. S2 pXRD patterns of $MAPbI_3$ and $GUA_{0.015}MA_{0.985}PbI_3$ single crystals ground to powder in the range of (a) 10-40 2θ and (b) 12-30 2θ, indicating a small shift of the peaks to lower angles upon introduction of GUA cations.

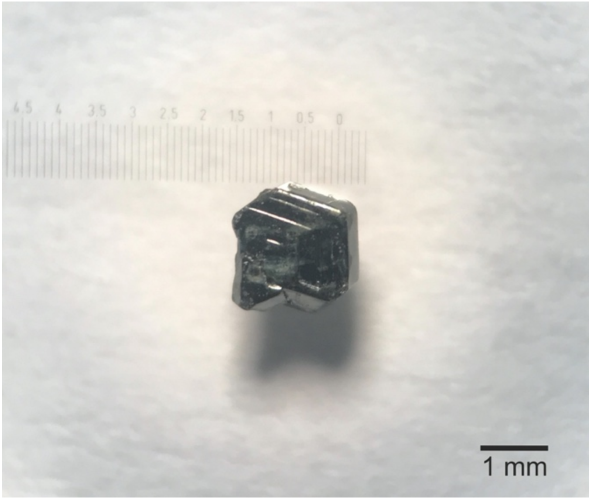

Fig. S3 Image of $GUA_{0.015}MA_{0.985}PbI_3$ single crystal.

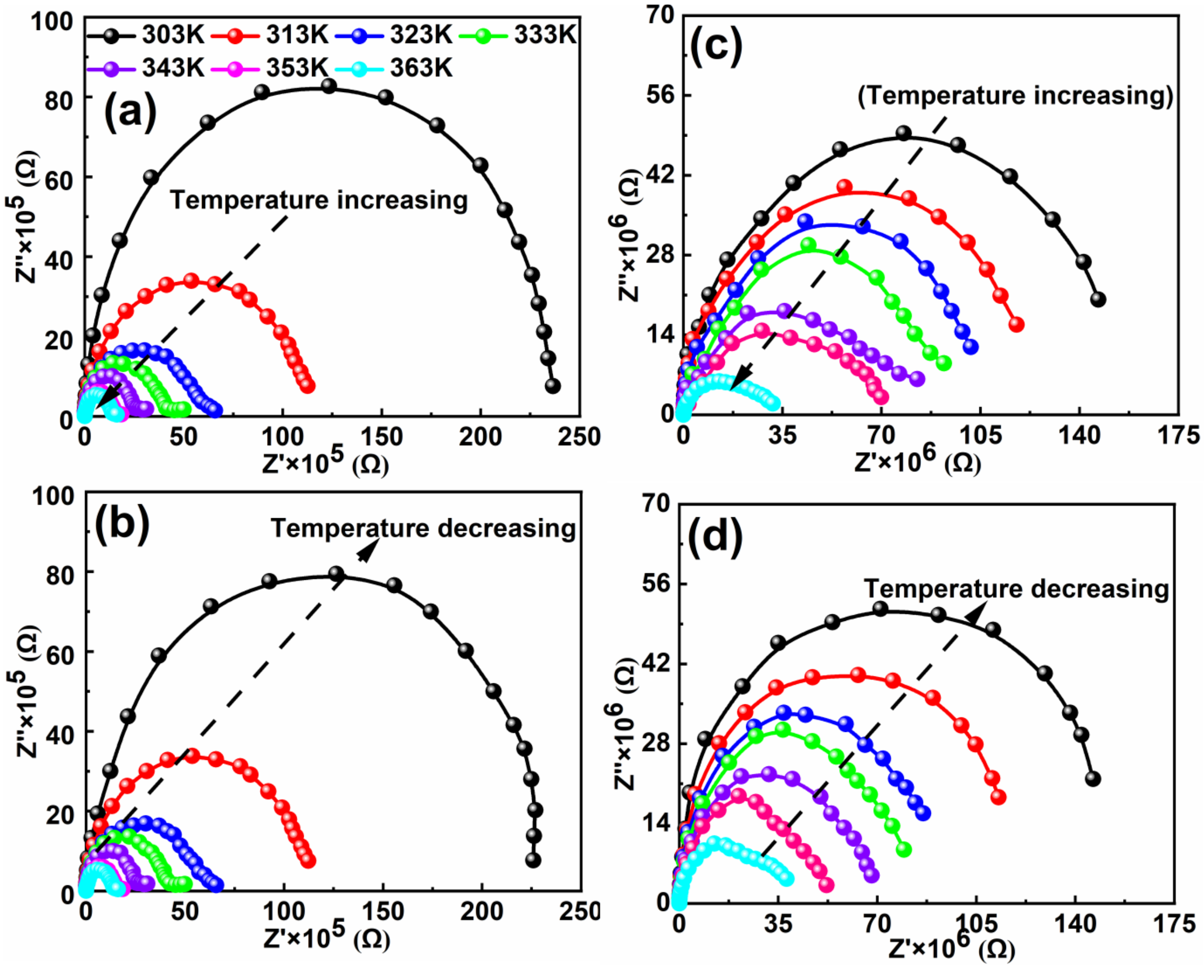

Fig. S4 Nyquist plots of the (a-b) $MAPbI_3$ and (c-d) $GUA_{0.015}MA_{0.985}PbI_3$ single crystals at 0 V DC bias in the frequencies ranged from 1 MHz to 1 Hz as a function of temperature (313-363 K).

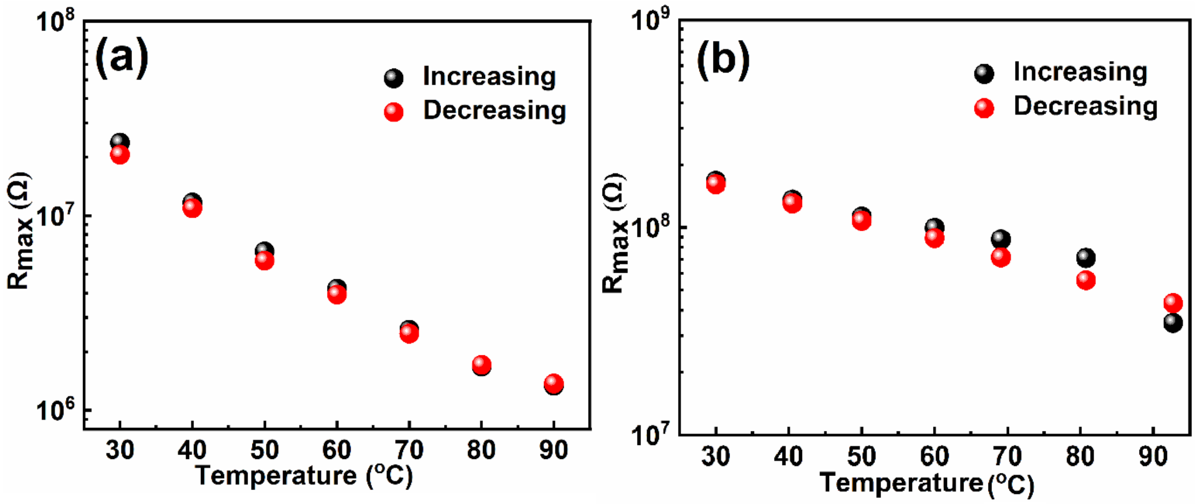

Fig. S5. The real part of Nyquist spectra of the (a-b) $MAPbI_3$ and (c-d) $GUA_{0.015}MA_{0.985}PbI_3$ single crystals as a function of temperature (313-363 K).

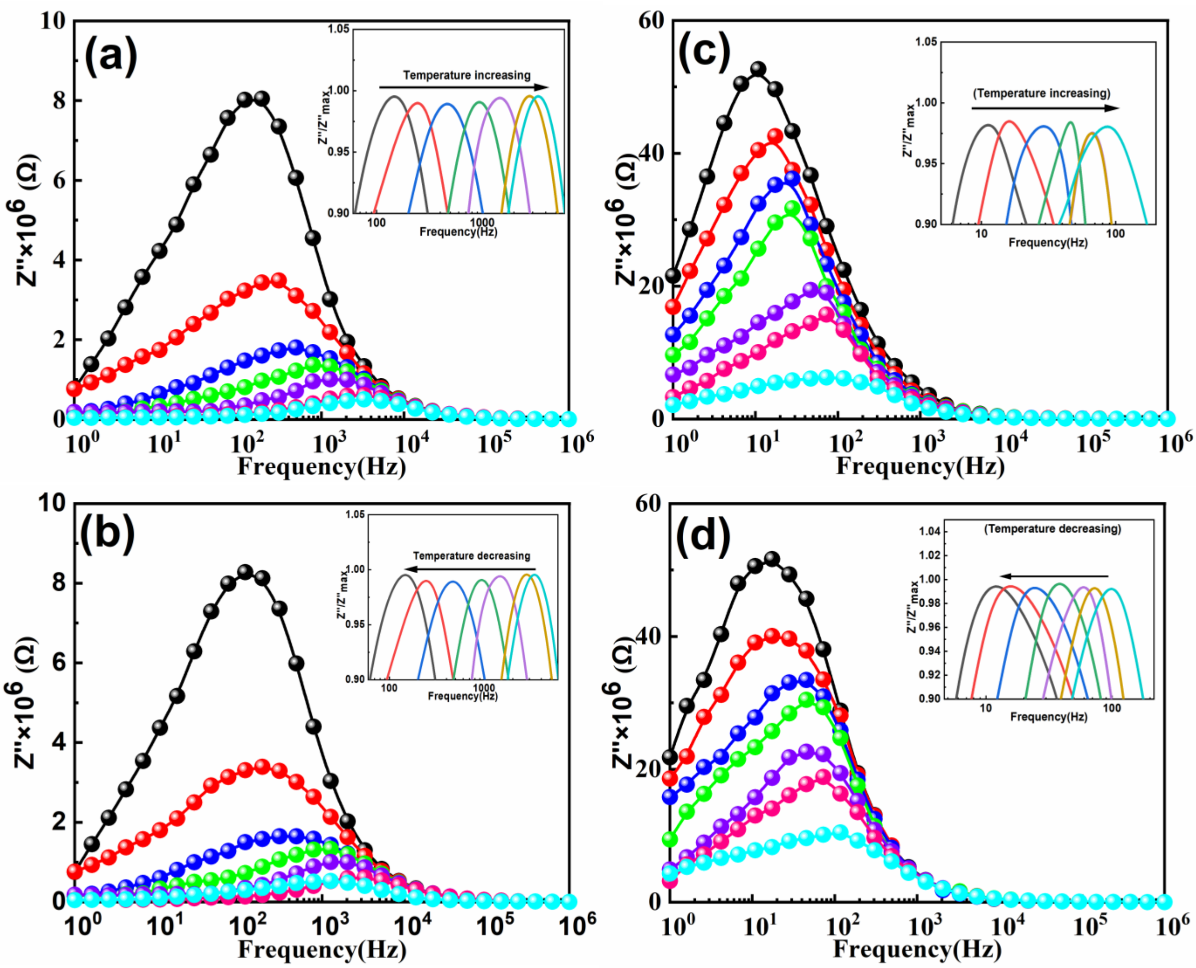

Fig. S6 The complex impedance part of (a-b) $MAPbI_3$ and (c-d) $GUA_{0.015}MA_{0.985}PbI_3$ single crystals as a function of frequency and temperature during increasing and decreasing temperature cycles.

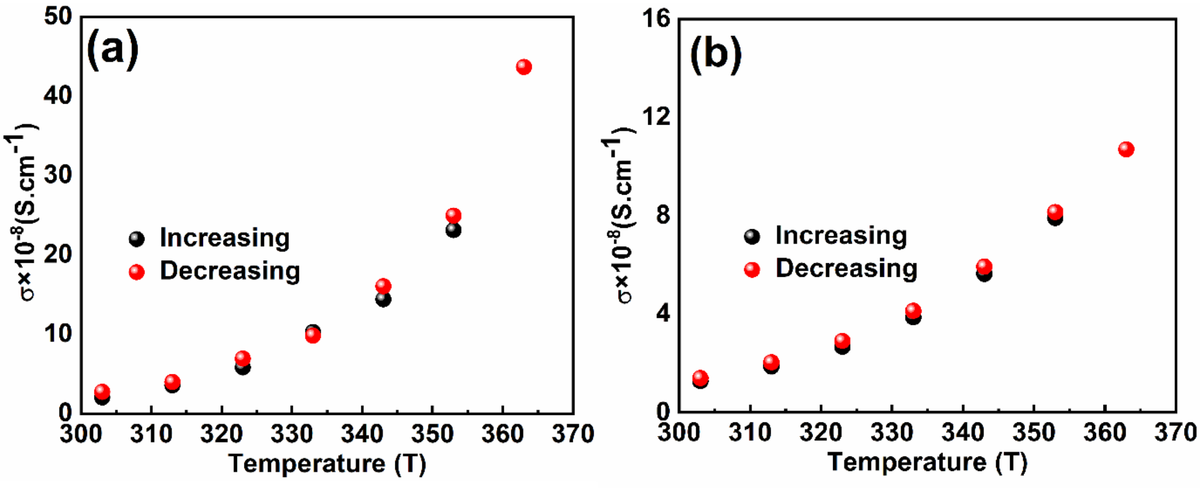

Fig. S7 The temperature-dependent conductivity of (a) $MAPbI_3$ and (b) $GUA_{0.015}MA_{0.985}PbI_3$ single crystals.

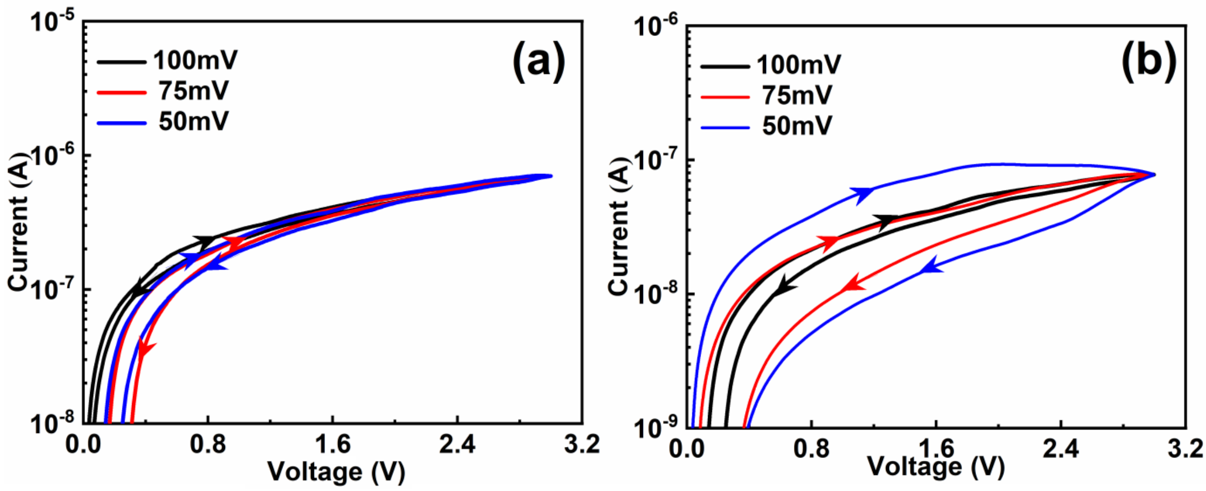

Fig. S8 Dark I-V curves of (a) $MAPbI_3$ and (b) $GUA_{0.015}MA_{0.985}PbI_3$ single crystals measured under forward and reverse biases as a function of scan rate.