Supporting Information

Solvent Dependent Iodide Oxidation in Metal-Halide Perovskite Precursor Solutions

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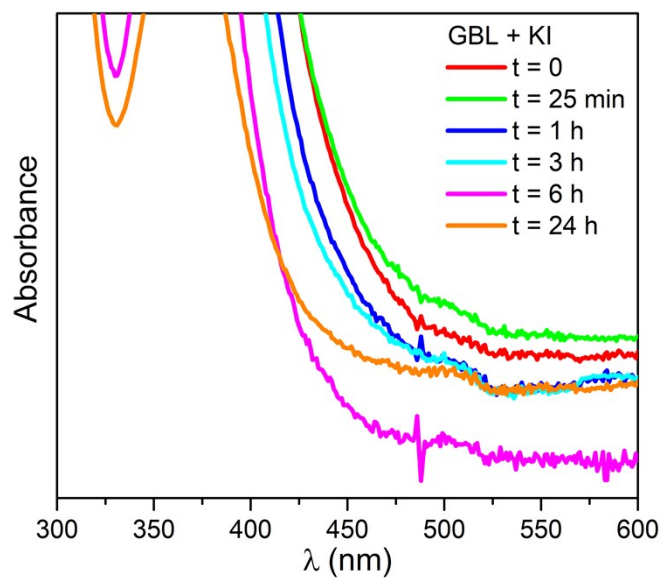**Section S1. Kinetics behavior of KI solutions in GBL**

Figure S1. Absorption spectra of KI 10^{-1} M in GBL recorded at different time, with a magnification on the 300-600 nm region. The shoulder around 500 nm suggest the presence of polyiodides such as I_5^- and I_7^-.
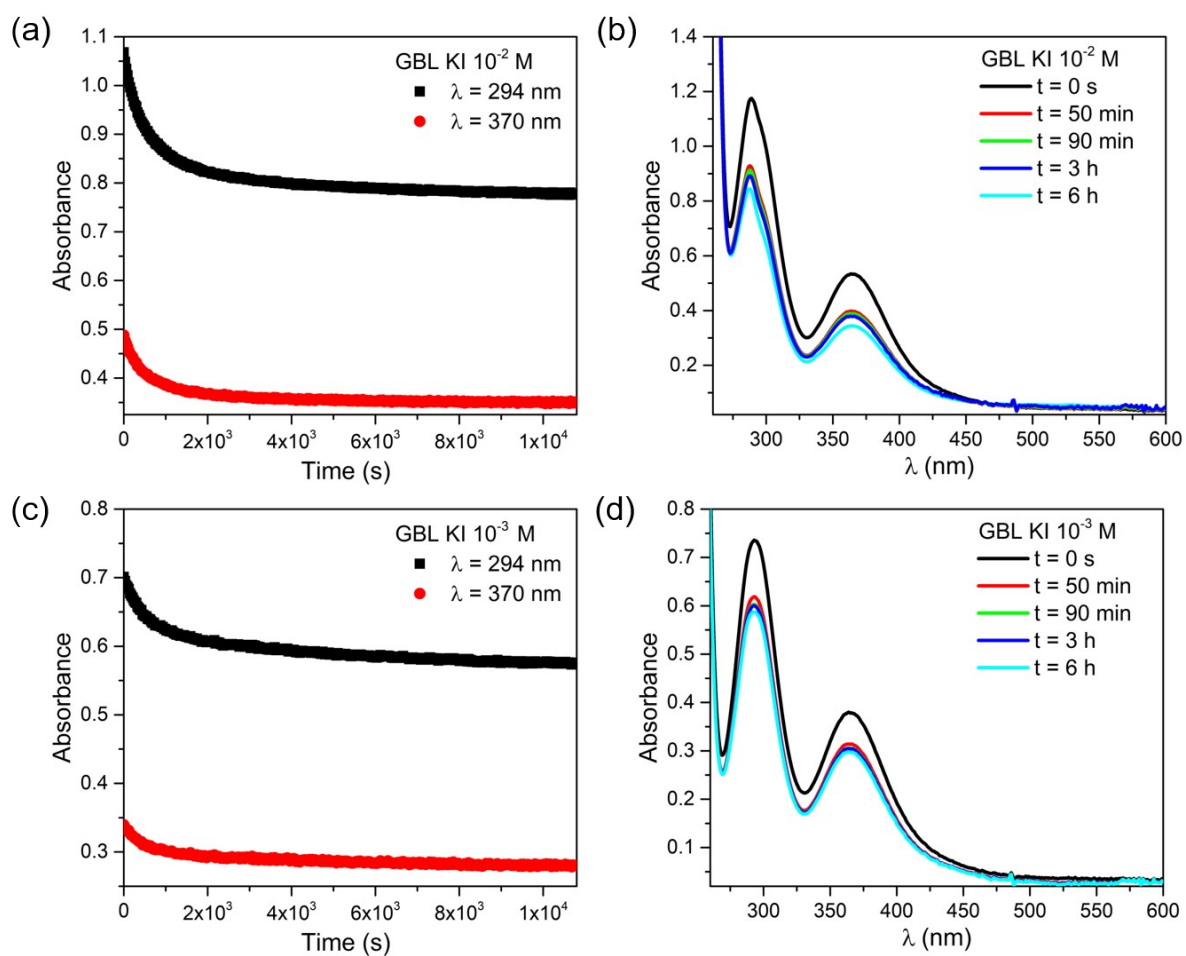
Figure S2. Absorbance intensity - time profile and absorption spectra of KI GBL solutions a, b) 10^{-2} M and c, d) 10^{-3} M.

[KI]	y_0	A_1	τ_1 (s)	R^2
10^{-2} M	0.8073 ± 0.0006	0.236 ± 0.002	690 ± 10	0.99
10^{-3} M	0.6008 ± 0.0004	0.095 ± 0.001	699 ± 13	0.99

Table S1. Fitting parameters for the $y = A_1 * \exp(-x/\tau_1) + y_0$ monoexponential fit for kinetics of KI 10^{-2} and 10^{-3} M in GBL.

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Section S2. Determination of molar absorption coefficient of I_3^- in GBL

To estimate the molar absorption coefficients (ε) of I_3^- in GBL, we prepared a 0.104 M KI solution in GBL and waited 3 hours to measure its absorption spectrum, Figure S3a, according to our results on kinetic measurements of diluted KI solutions in GBL (see main text). Then, we dropped small amounts of this solution, *i.e.* 100, 200 and 300 μL, in 2 mL of water, where the ε is well-known (see main text), and we registered the corresponding absorption spectra, Figure S3b.
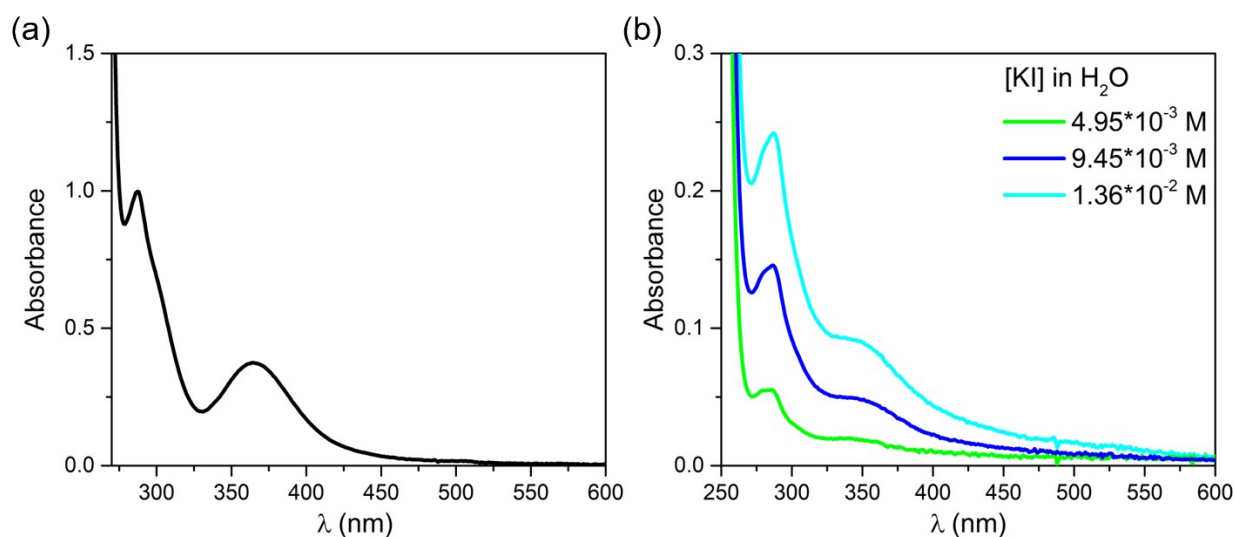

Figure S3. Absorption spectra of a) 0.104 M KI solution in GBL after 3 hours from its preparation and b) its dilutions in water.

Considering these values, from the typical absorption peaks of I_3^- in water, *i.e.* 288 and 353 nm, we estimated its concentration. Then, with a simple dilution calculation ($C_iV_i = C_fV_f$, where C and V stand for concentration and volume, respectively, and the subscripts i and f mean "initial" and "final", respectively) we calculated the concentration of I_3^- that is supposed to be present in the mother GBL solution, Table S2. Being the I_3^- dissociation in water larger than in organic solvents,[1] we reasonably expect the I_3^- concentration to be higher in GBL and, therefore, the reported values should be considered as an upper limit with respect to the real

case. From the average of these concentrations, 5.96 x 10^{-5} M, and taking the absorbance values from the 0.104 M KI solution spectrum of Figure S3a, we finally estimated the ε of I_3^- in GBL, Figure S4.

Sample	$A_{288\ nm}$	$[I_3^-]$ diluted solution (M)	$[I_3^-]$ mother solution (M)	$A_{353\ nm}$	$[I_3^-]$ diluted solution (M)	$[I_3^-]$ mother solution (M)
100 μL	0.053	2.65 x 10^{-6}	5.57 x 10^{-5}	0.018	1.36 x 10^{-6}	2.86 x 10^{-5}
200 μL	0.144	7.20 x 10^{-6}	7.92 x 10^{-5}	0.047	3.56 x 10^{-6}	3.92 x 10^{-5}
300 μL	0.241	1.21 x 10^{-5}	9.28 x 10^{-5}	0.088	6.67 x 10^{-6}	5.11 x 10^{-5}

Table S2. Absorbance and concentrations of KI solutions in GBL diluted in water and corresponding calculated concentrations in the mother solutions.
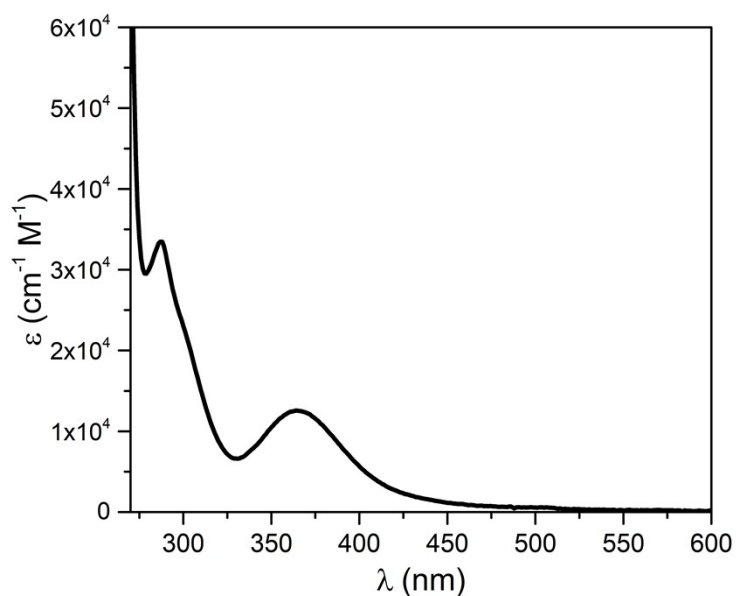

Figure S4. Estimated molar absorption coefficients (ε) of I_3^- in GBL.
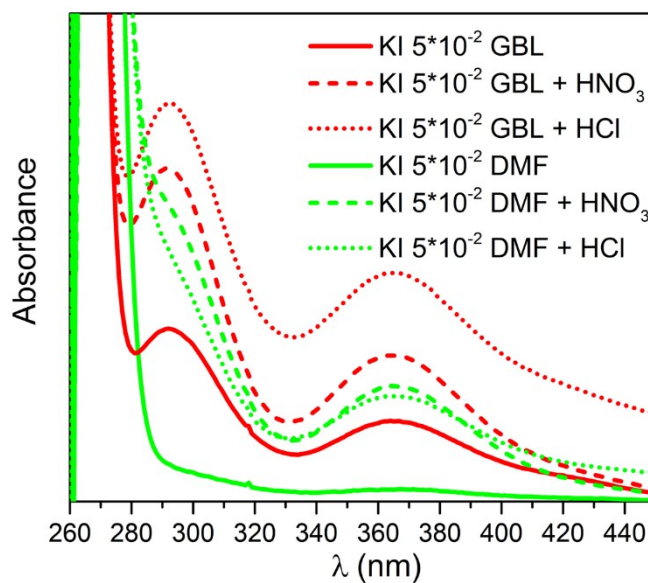
Section S3. Factors influencing the oxidation of I⁻

Figure S5. Absorption spectra of KI 5 x 10^{-2} M in DMF and GBL with and without addition of 1% *v/v* of 5 x 10^{-2} M aqueous solutions of acids (HCl, HNO₃).

Solvent	pH (estimated)	pKa [ref. 2]
DMSO	6-7	31,0
DMF	6	38,0
GBL	4-5	24,3
ACN	5-6	24,9

Table S3. pH values estimated from litmus paper measurements and calculated pKa of the employed solvents.
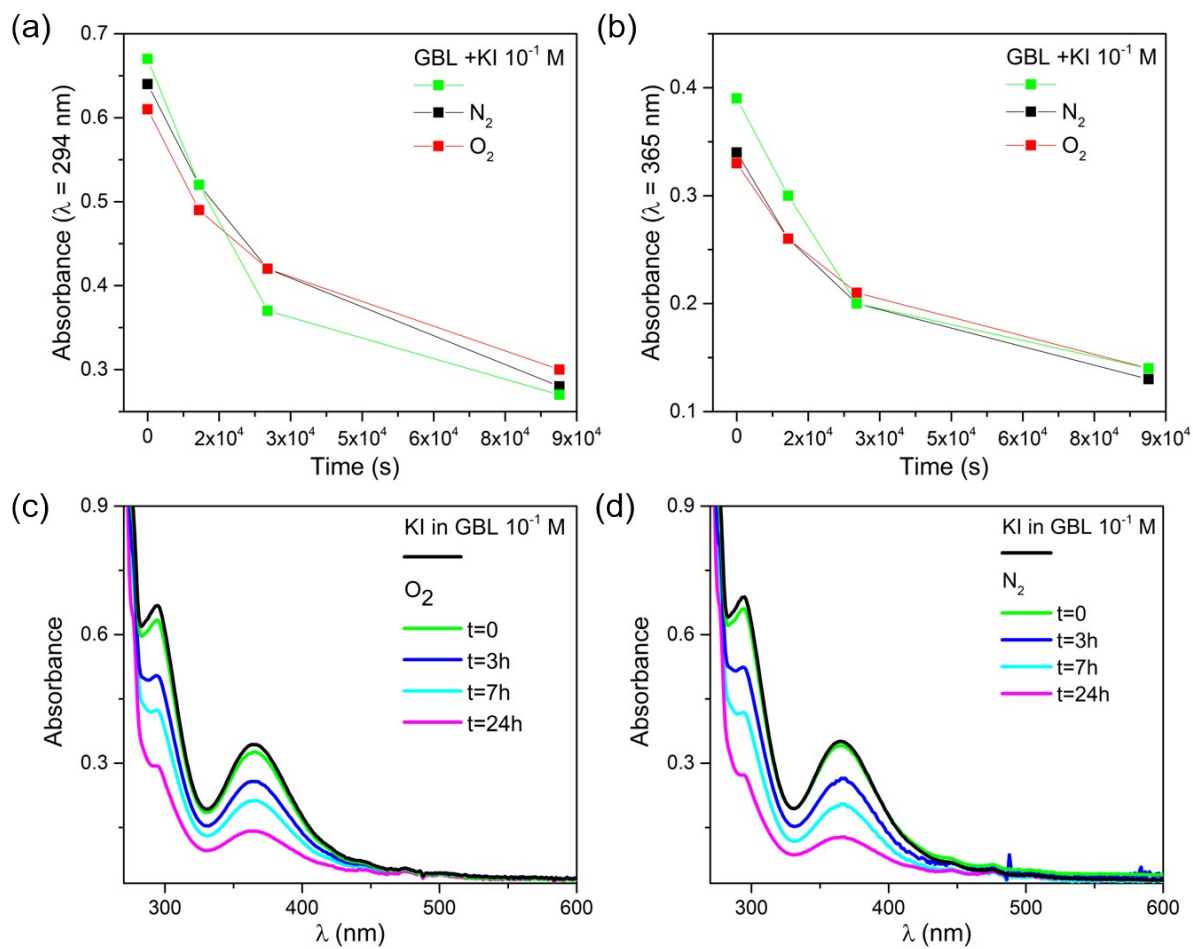
Figure S6. Effect of O_2 and N_2 in the absorption spectra of KI 0.1 M in GBL. Absorption data at different recording time for KI 0.1 M in GBL as is, saturated with N_2 and with O_2 at a) 294 nm and b) 365 nm; absorption spectra of KI 0.1 M in GBL at different time (c for O_2 and d for N_2).
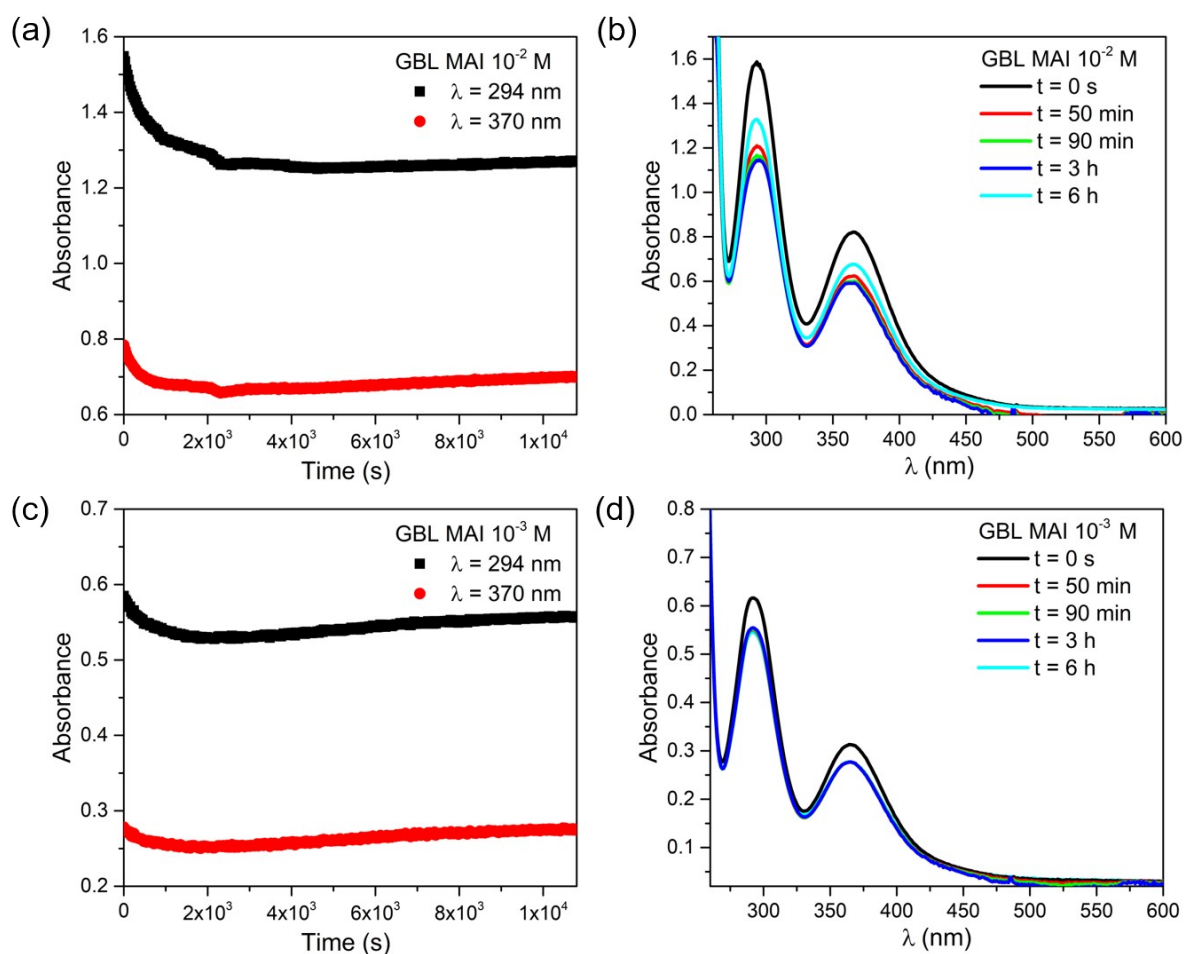
Figure S7. Absorbance intensity - time profile and absorption spectra of MAI GBL solutions

a, b) 10^{-2} M and c, d) 10^{-3} M.

References

(1) Baucke, F. G. K.; Bertram, R.; Cruse, K. The Iodide-Iodine System in Acetonitrile: Evaluation of Standard Thermodynamic Data on the Association $I^-+I_2 \rightarrow I_3^-$ from Potentiometric Measurements at 25 and 50°C. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1971**, *32* (2), 247–256. https://doi.org/10.1016/S0022-0728(71)80190-0.
(2) Marvin version 22.22, ChemAxon (https://www.chemaxon.com)