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Vidon Guillaume, Dally Pia, Al-Katrib Mirella, Ory Daniel, Kim Minjin, et al.. The Impact of X-Ray Radiation on Chemical and Optical Properties of Triple Cation Lead Halide Perovskite. 2023 NextPV workshop, Nov 2023, Tokyo, Japan. hal-04306573

HAL Id: hal-04306573

<https://hal.science/hal-04306573>

Submitted on 25 Nov 2023

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The Impact of X-Ray Radiation on Chemical and Optical Properties of Triple-Cation Lead Halide Perovskite

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■ NextPV Tokyo, 2023

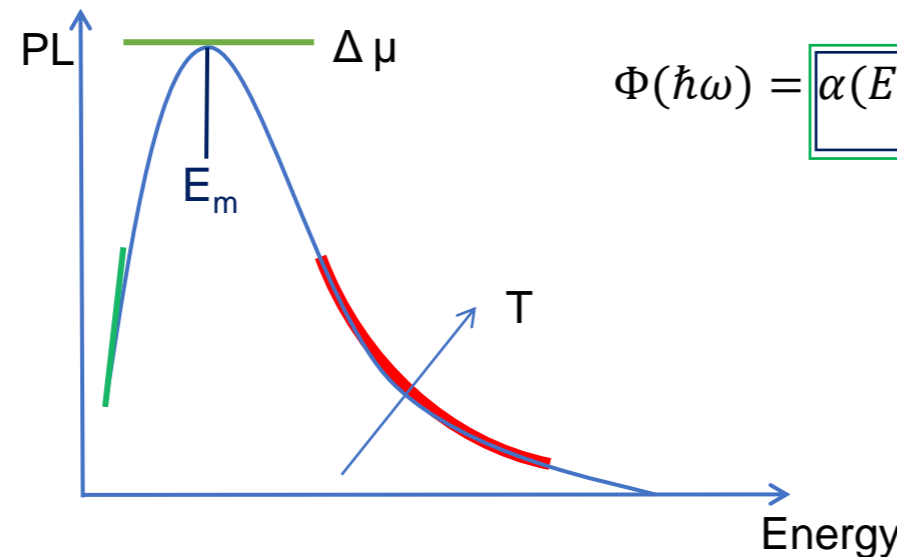
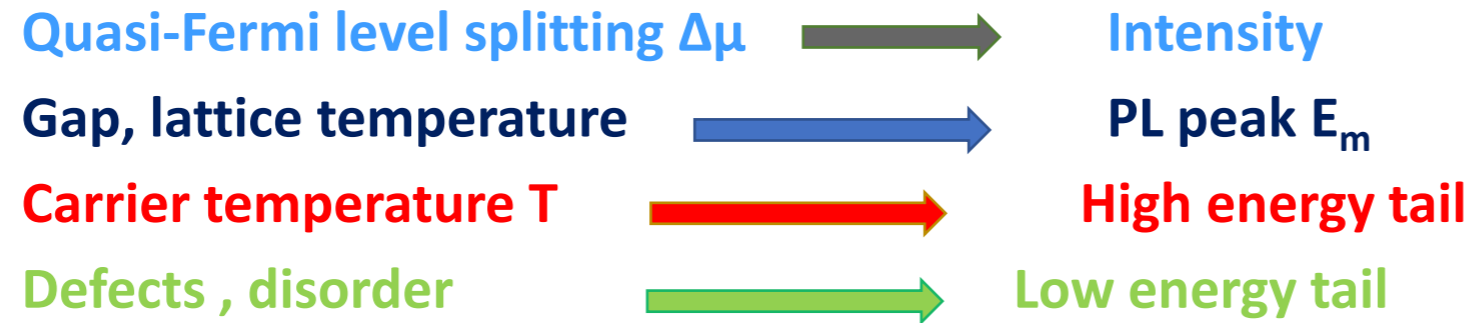


- Halide perovskites are hard to catch!

- Development of techniques for study

- Mostly PL based in IPVF
 - Imaging: Hyperspectral, FLIM
 - Streak camera , 4D
 - PLE
 - Frequency domain: MPL

Use of quantitative light emission from solar cells



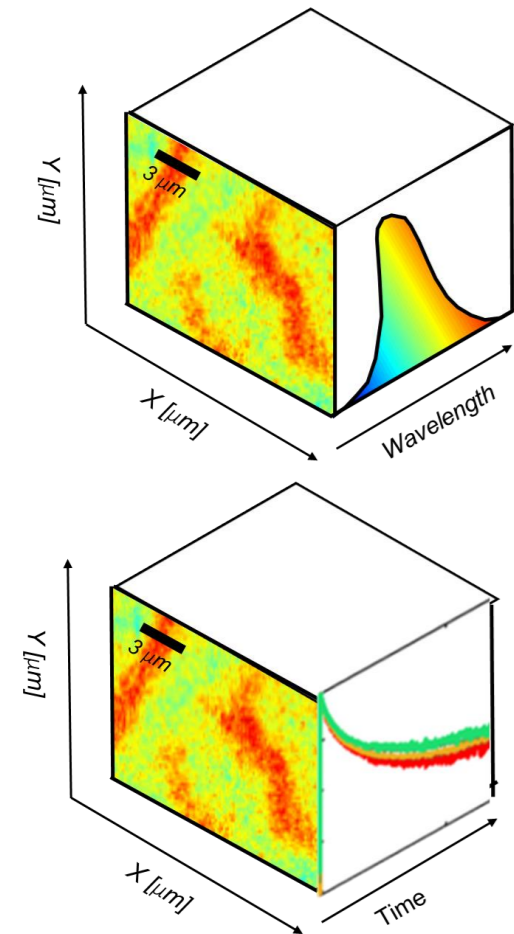
Generalized Planck law:

$$\Phi(\hbar\omega) = \alpha(E) \frac{\Omega}{4\pi^3 \hbar^3 c_0^2} E^2 \frac{1}{\exp\left(\frac{E - \Delta\mu}{kT}\right) - 1}$$

$$\Delta\mu \approx qV$$

(free energy/particle)

T & $\Delta\mu$ are the thermodynamic variables for the energy conversion process



Luminescence mapping

- Contactless & Local properties
- Non-destructive
- Yields relevant materials and device parameters (« Optical Voltmeter »)

Imaging systems

- Hyperspectral imager
- Time-resolved fluorescence imaging



ARTICLE

<https://doi.org/10.1038/s41467-019-09527-w> OPEN

Quantitative optical assessment of photonic and electronic properties in halide perovskite

Adrien Bercegol^{1,2}, Daniel Ory^{1,2}, Daniel Suchet^{2,3}, Stefania Cacovich², Olivier Fournier^{1,2}, Jean Rousset^{1,2} & Laurent Lombez^{2,3}

Origin of charge/energy transport in perovskites

ARTICLE

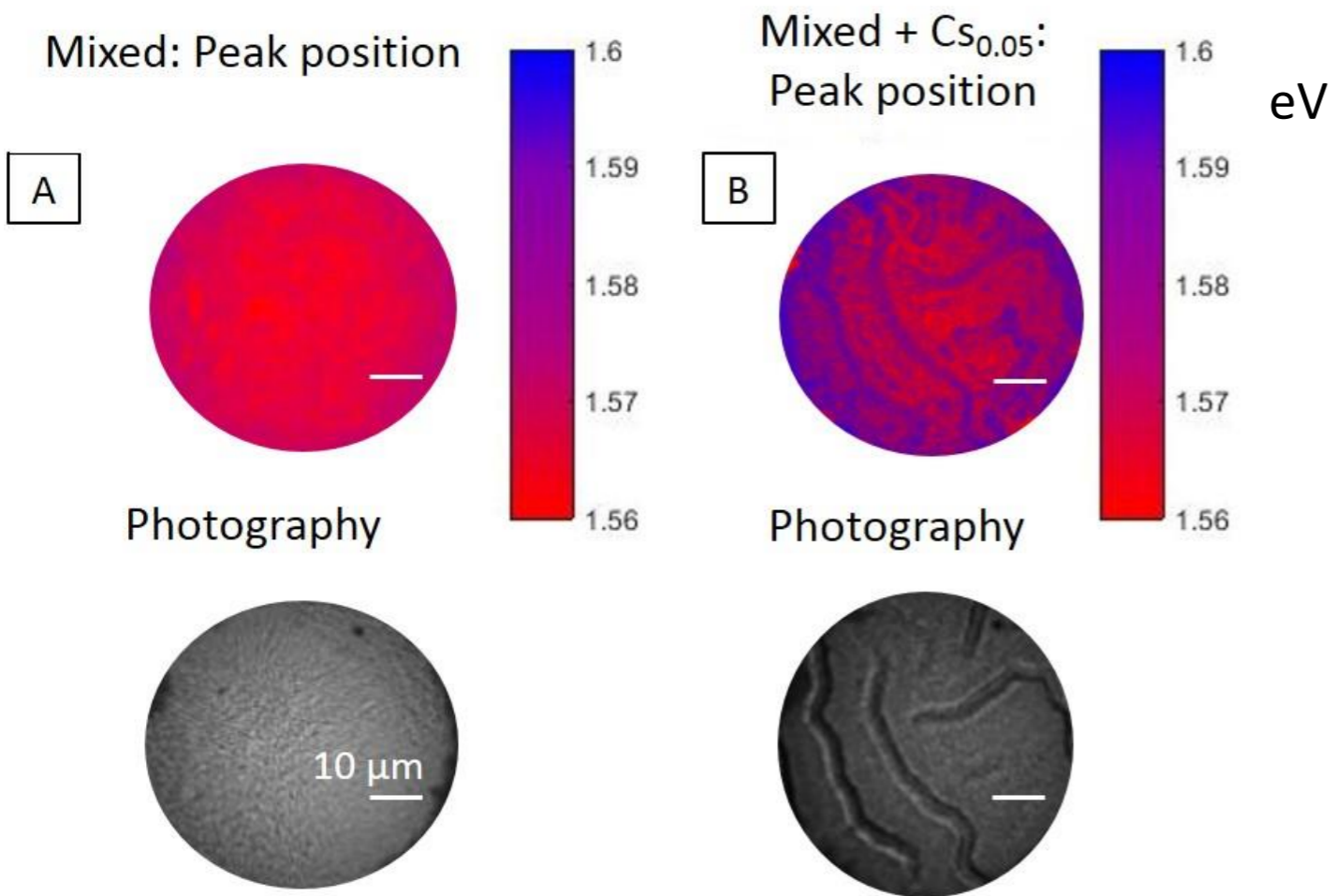
<https://doi.org/10.1038/s41467-022-30426-0> OPEN

Imaging and quantifying non-radiative losses at 23% efficient inverted perovskite solar cells interfaces

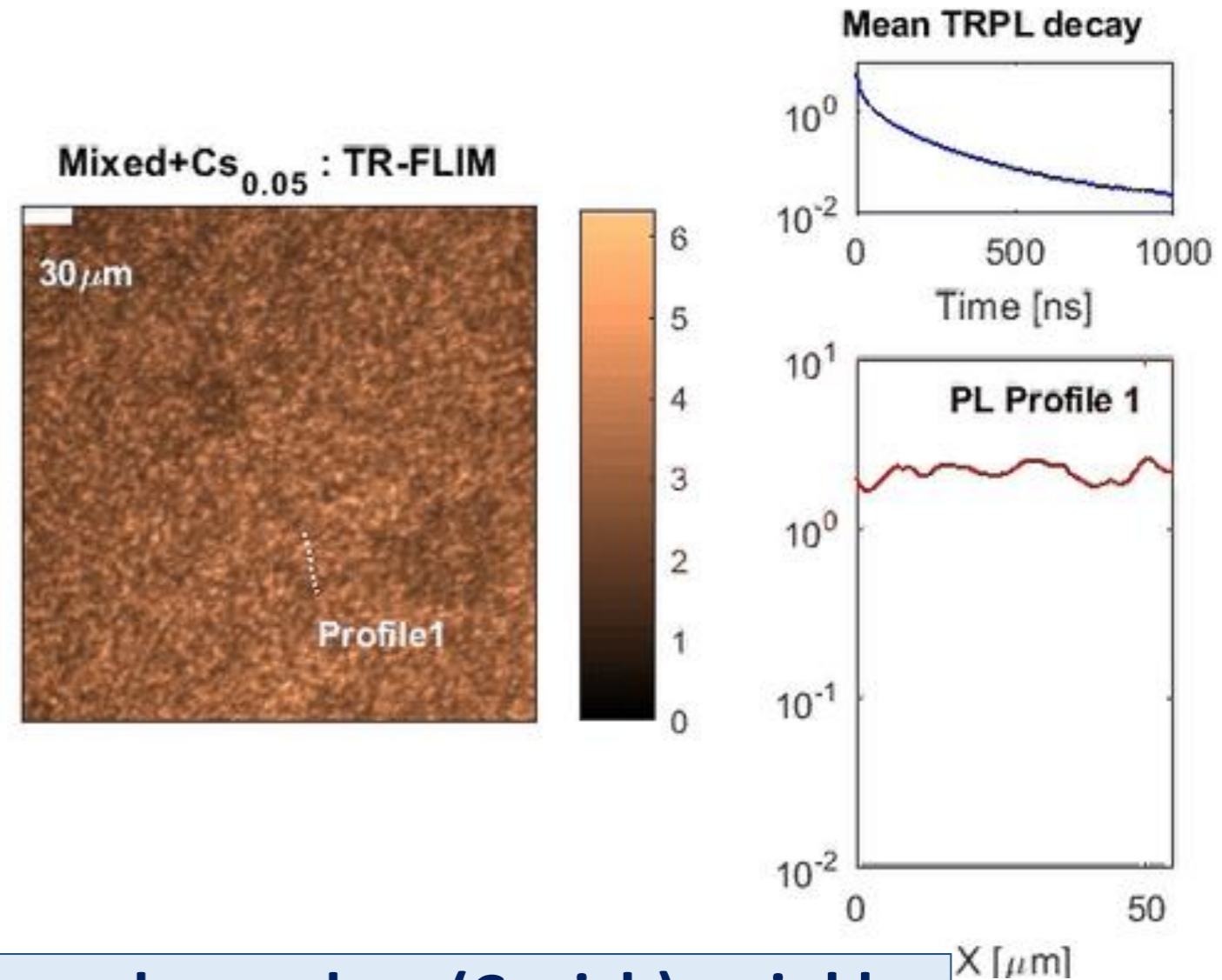
Stefania Cacovich¹, Guillaume Vidon², Matteo Degani³, Marie Legrand^{2,4}, Laxman Gouda³, Jean-Baptiste Puel^{2,4}, Yana Vaynzof⁵, Jean-François Guillemoles¹, Daniel Ory^{2,4} & Giulia Grancini³

Discriminate bulk and surface recombinations

HI : Composition gradients



TR-FLIM : Line profile decays



➤ τ enhanced on (Cs rich) wrinkles

¹A. Bercegol et al., *J. Phys. Chem. C* 122 (2018)

Absorption: required for photoluminescence interpretation

Classical techniques

- Not always relevant to our experimental conditions
- Rarely provides imaging



Generalized Planck's law

$$I_{PL}(z, E_{emit}) = A(E_{emit}) * \frac{2\pi}{\hbar^3 c_0^2} * \frac{E^2}{\exp\left(\frac{E - \Delta\mu(z)}{k_B T}\right) - 1}$$

Absorptivity

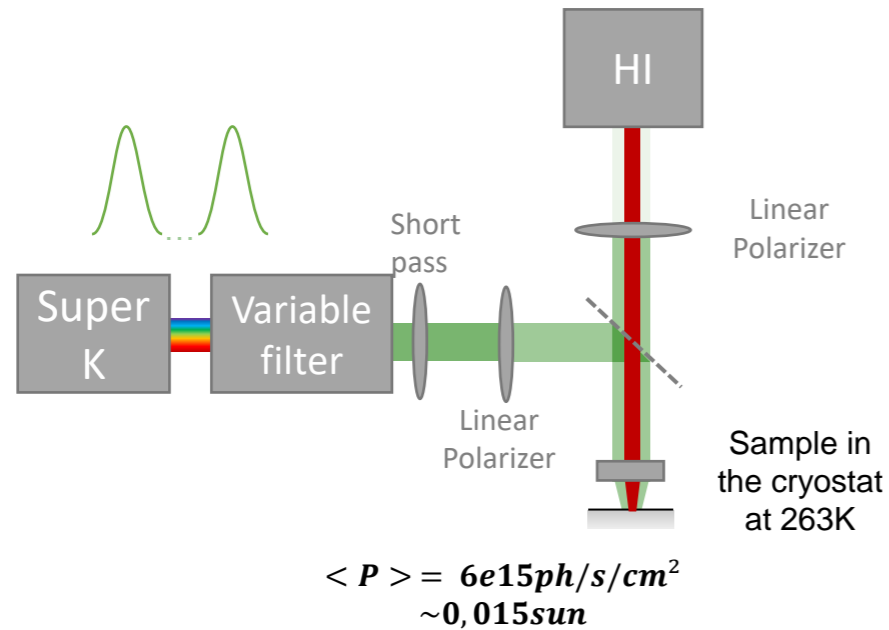
Grey body radiation

$$\Delta\mu(z) = f(A(E_{excit}))$$

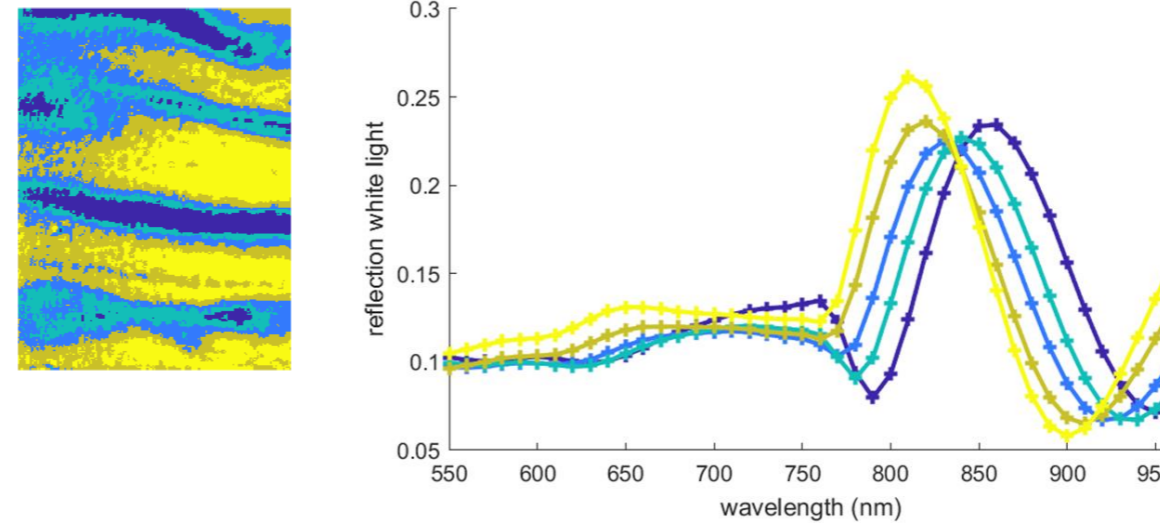
Photoluminescence
Excitation (PLE)

Challenges

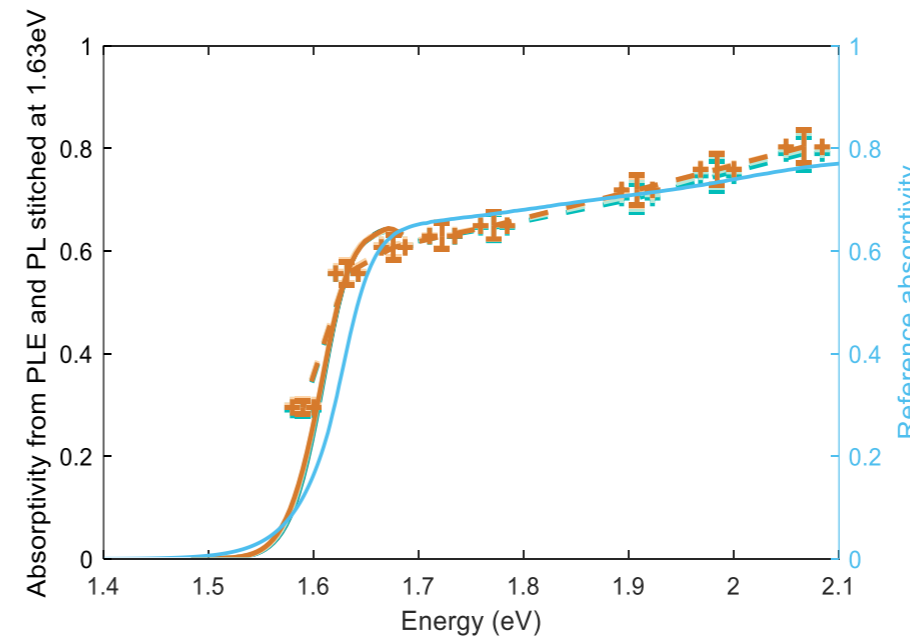
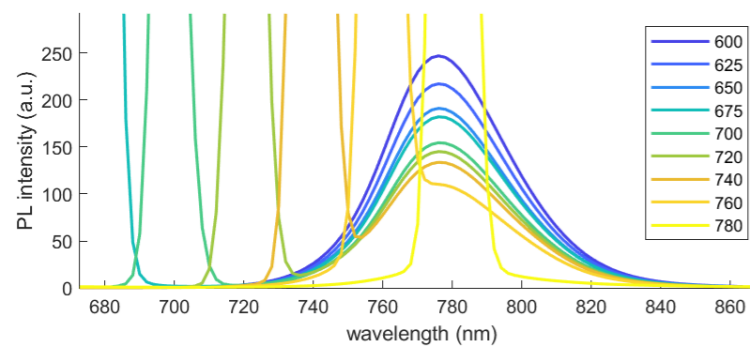
- Small absorption values both critical and hard to measure
- Disentangle influences of layers and texturing



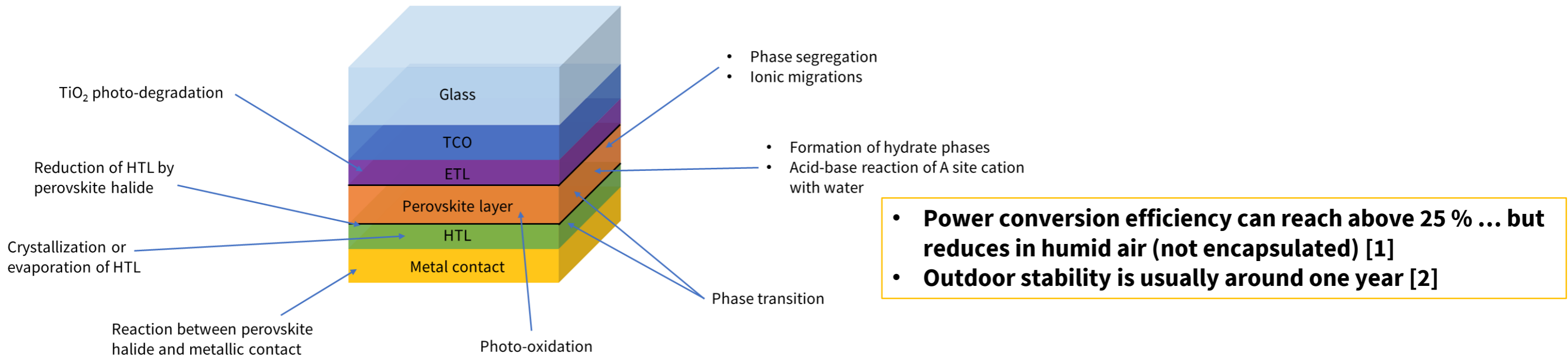
PLE spectra & Reflectivity maps



PL spectra for different excitation wavelengths



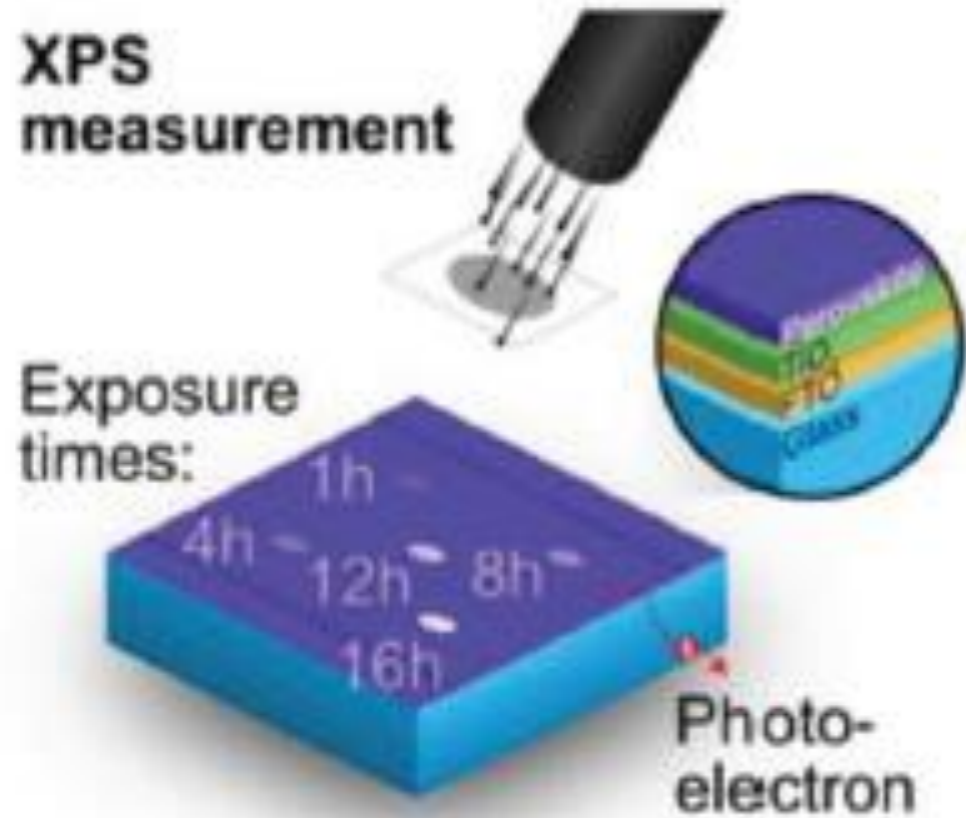
Absorption and thickness maps



Triggering factors:



[1] M. Jeong et al., “Stable perovskite solar cells with efficiency exceeding 24.8% and 0.3-V voltage loss,” *Science* (1979), vol. 369, no. 6511, pp. 1615–1620, 2020.
[2] M. U. Ali, H. Mo, Y. Li, et W. Chen, « Outdoor stability testing of perovskite solar cells : necessary step toward real-life applications », *APL Energy*, vol. 1, n° 2, sept. 2023.



- Ions, e-, photons, ... most spectroscopies lead to changes in the materials
- Exposing HaP's to X-rays to investigate surfaces leads to damage in optoelectronic properties
- Study as a function of fluence of optoelectronic properties of perovskites, spatially resolved

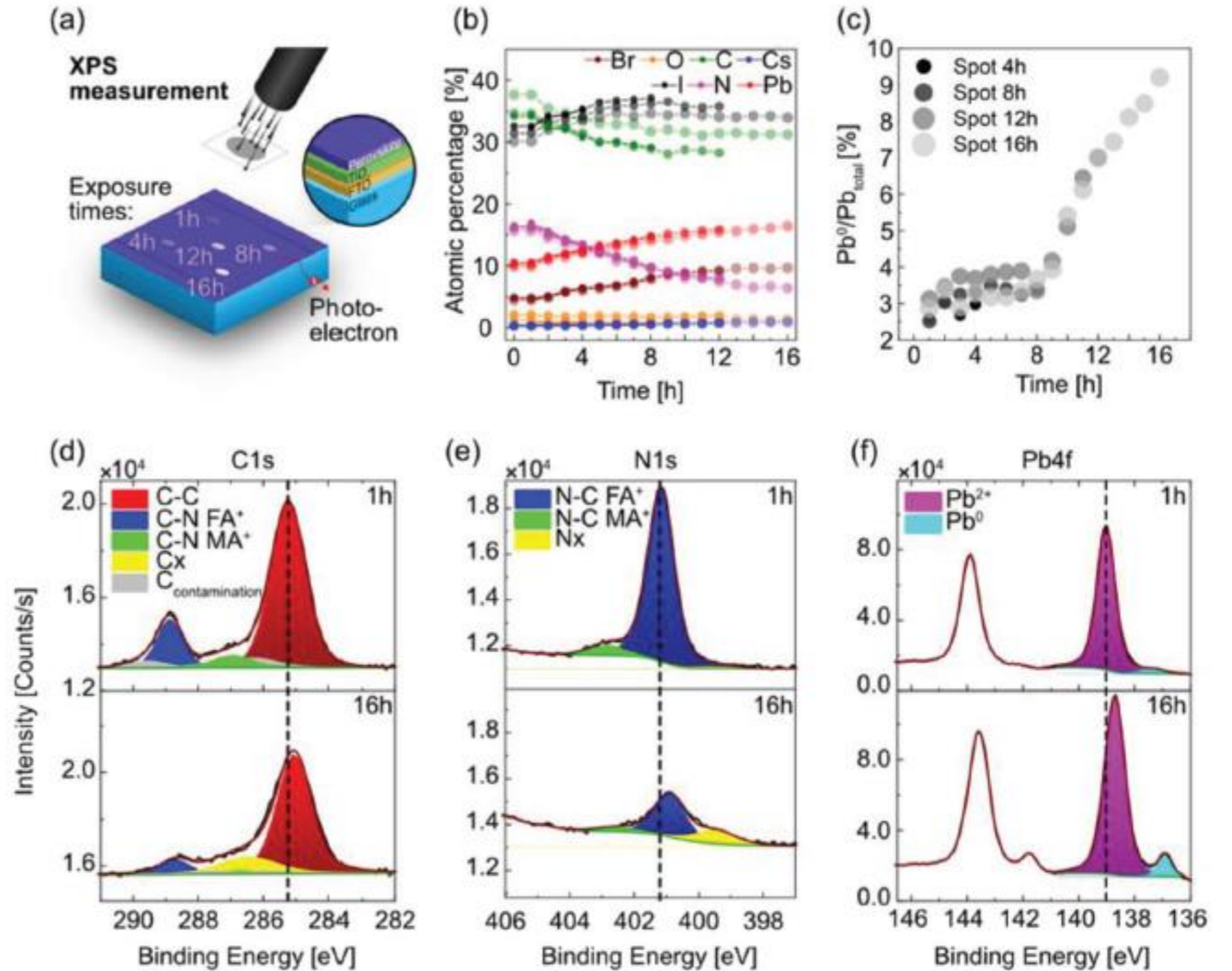
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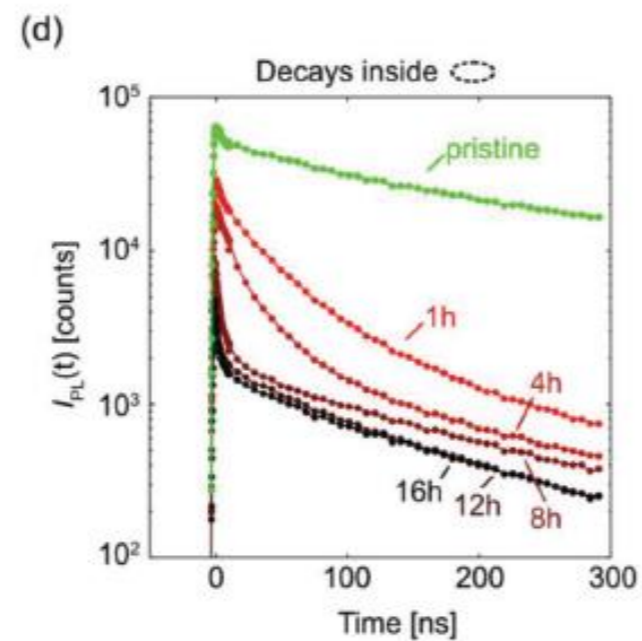
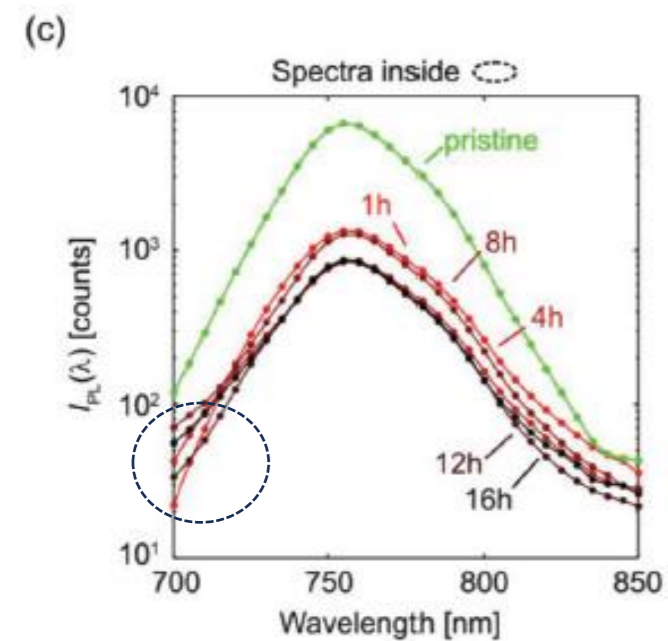
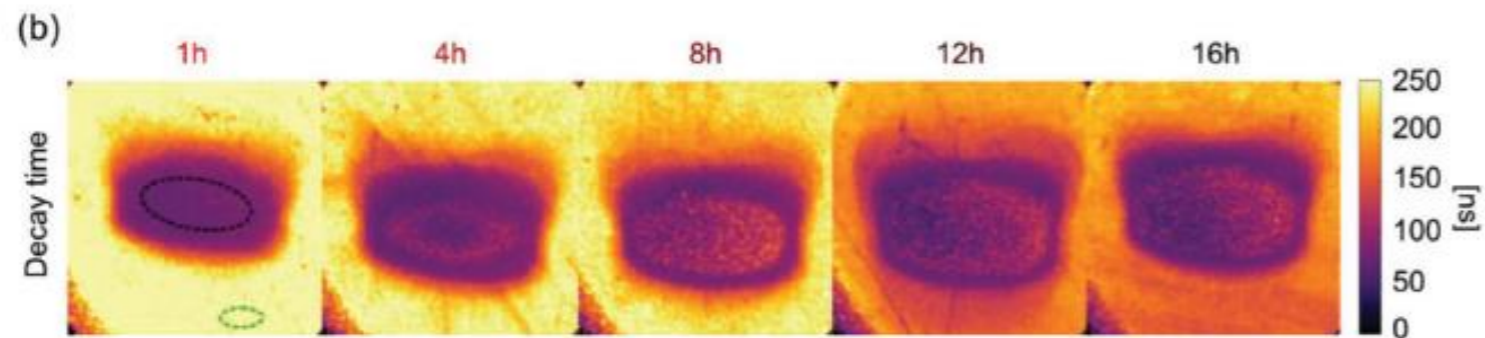
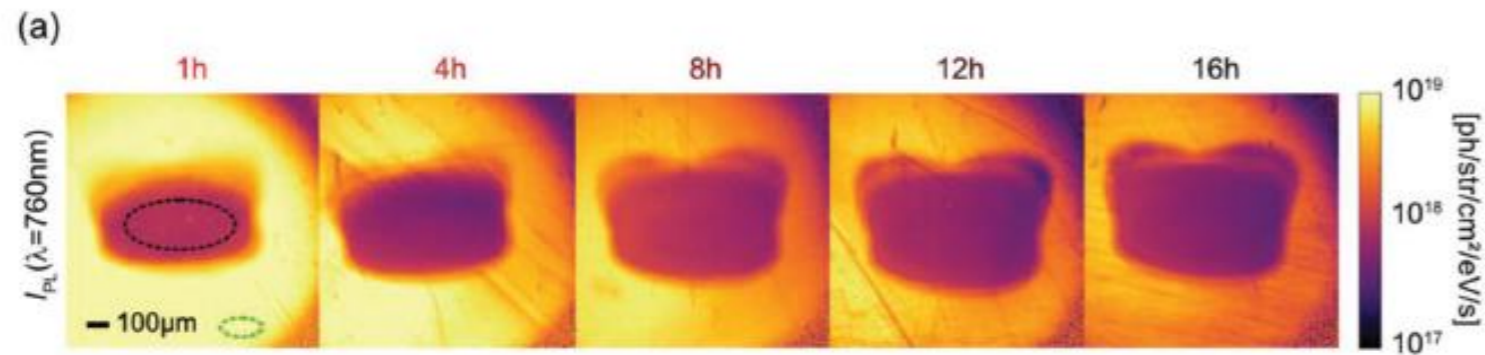
Chemical damage

Iodine evaporation

Loss of organic Cations

Ultimately Pb⁰ formation

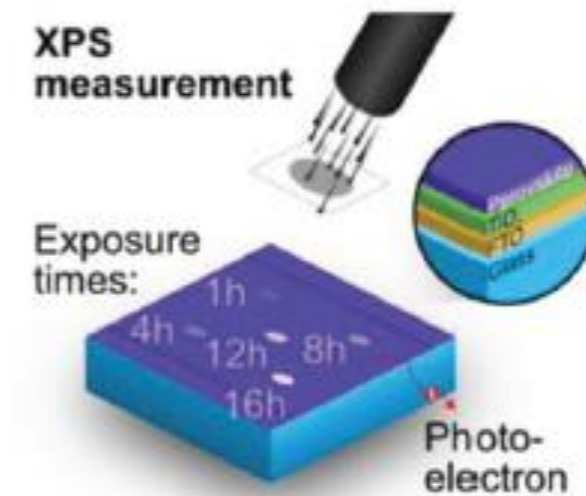




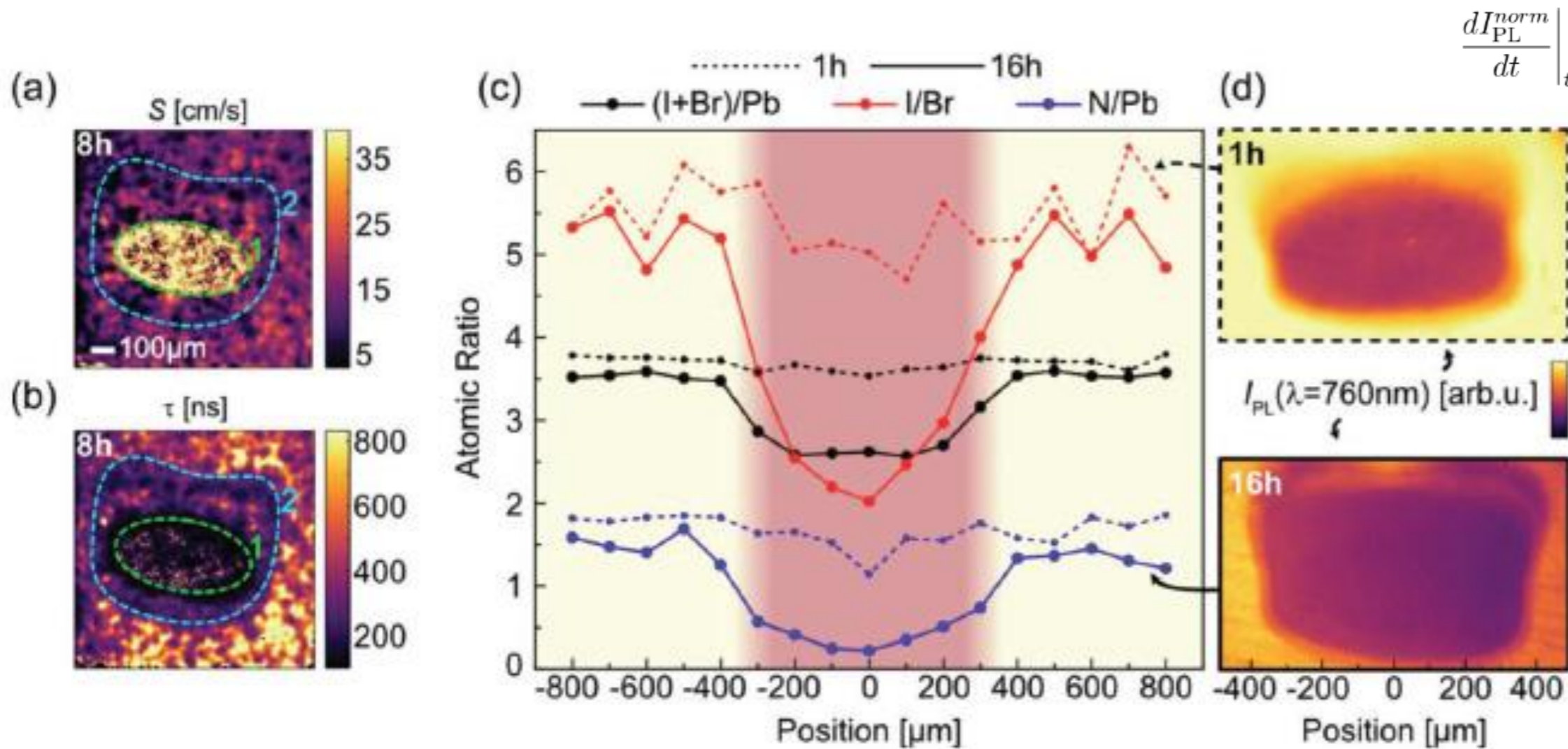
Perovskite degradation seen by PL & TRPL

Correlation between CW intensity and (long) decay time

Signature of new phase?



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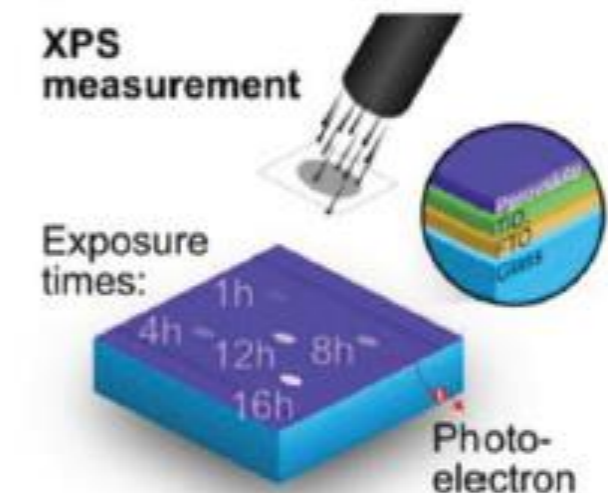


$$\left. \frac{dI_{\text{PL}}^{\text{norm}}}{dt} \right|_{t=0} = -2 \left[\frac{1}{\tau} + 2\alpha S + \alpha^2 D \right] - \frac{4}{3} k_2 \alpha n_\gamma$$

G. Vidon, S. Cacovich, M. Legrand, A. Yaiche, D. Ory, D. Suchet, J.-B. Puel, J.-F. Guillemoles, *Phys. Rev. Appl.* **2021**, *16*, 044058

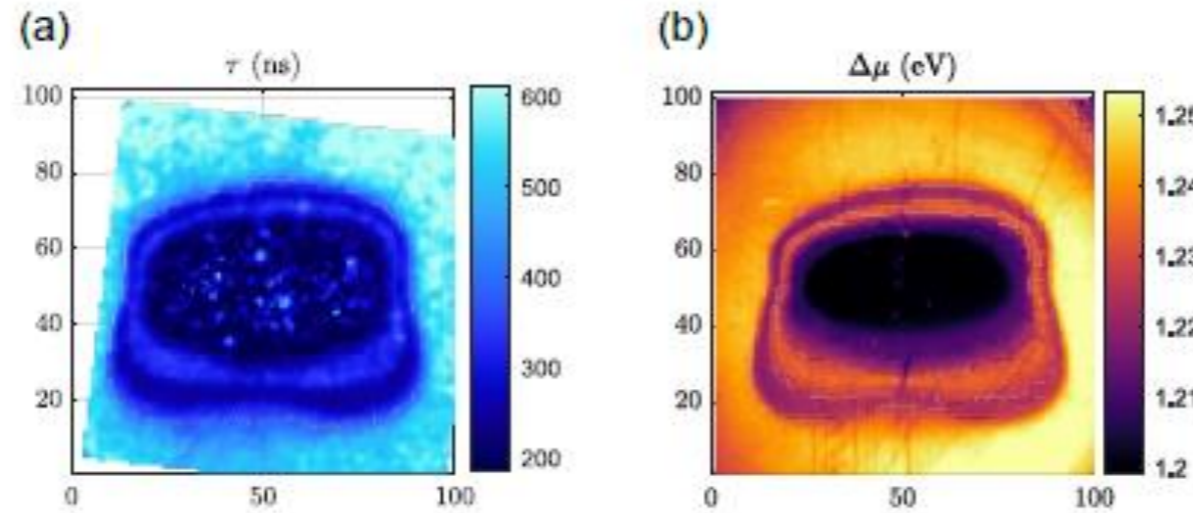
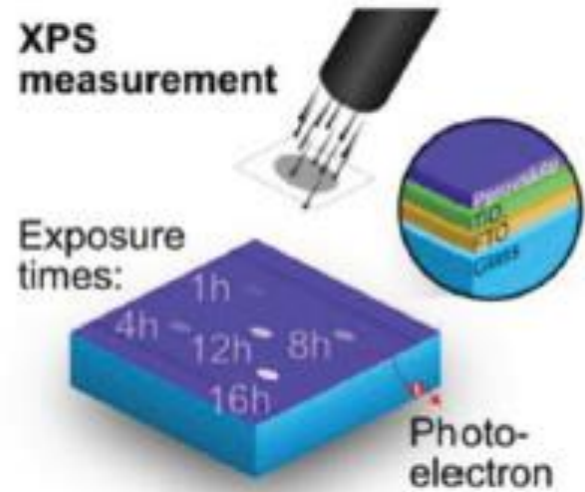
Fitting of decays enable separation of surface and bulk (short time scaling laws)

Correlation of CW PL intensity of the main peak with spatially resolved XPS ($\sim 50 \mu\text{m}$ spot)

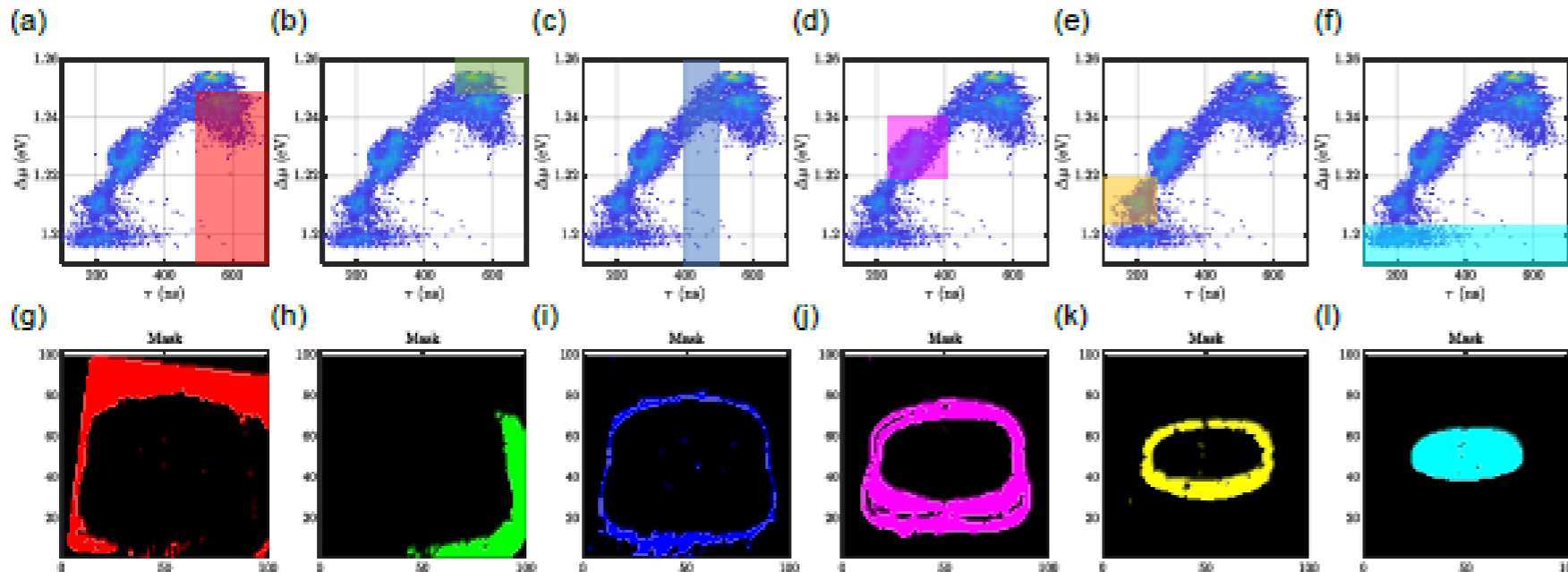
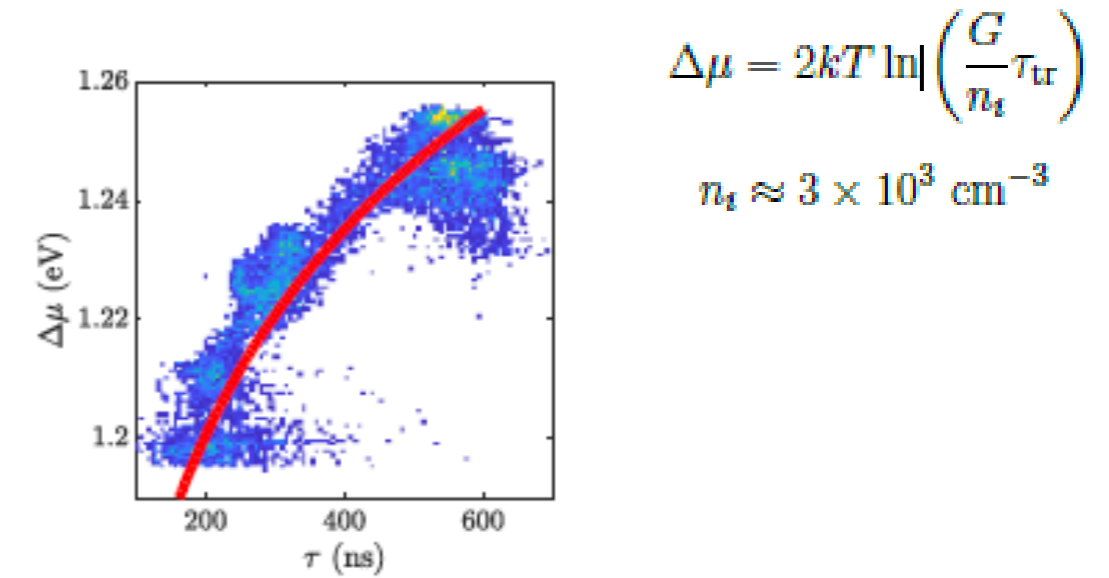
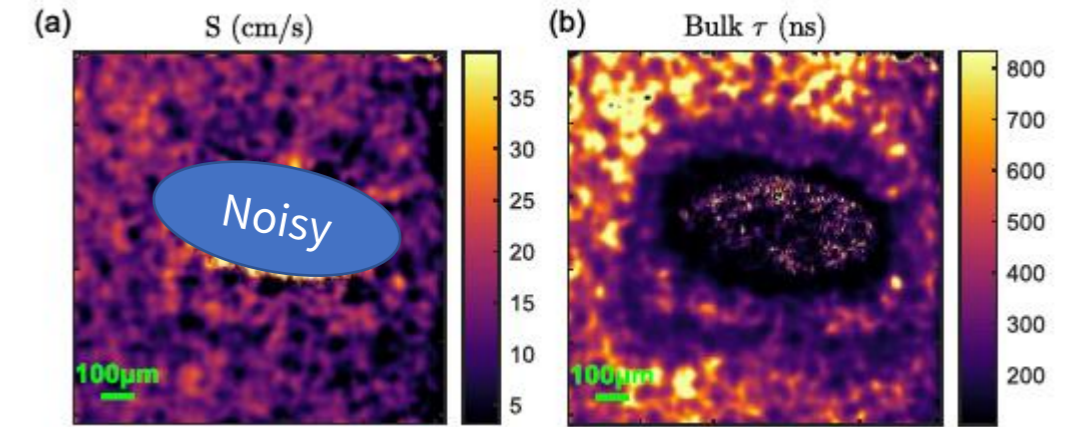


Correlation lifetime and quasi Fermi level splitting

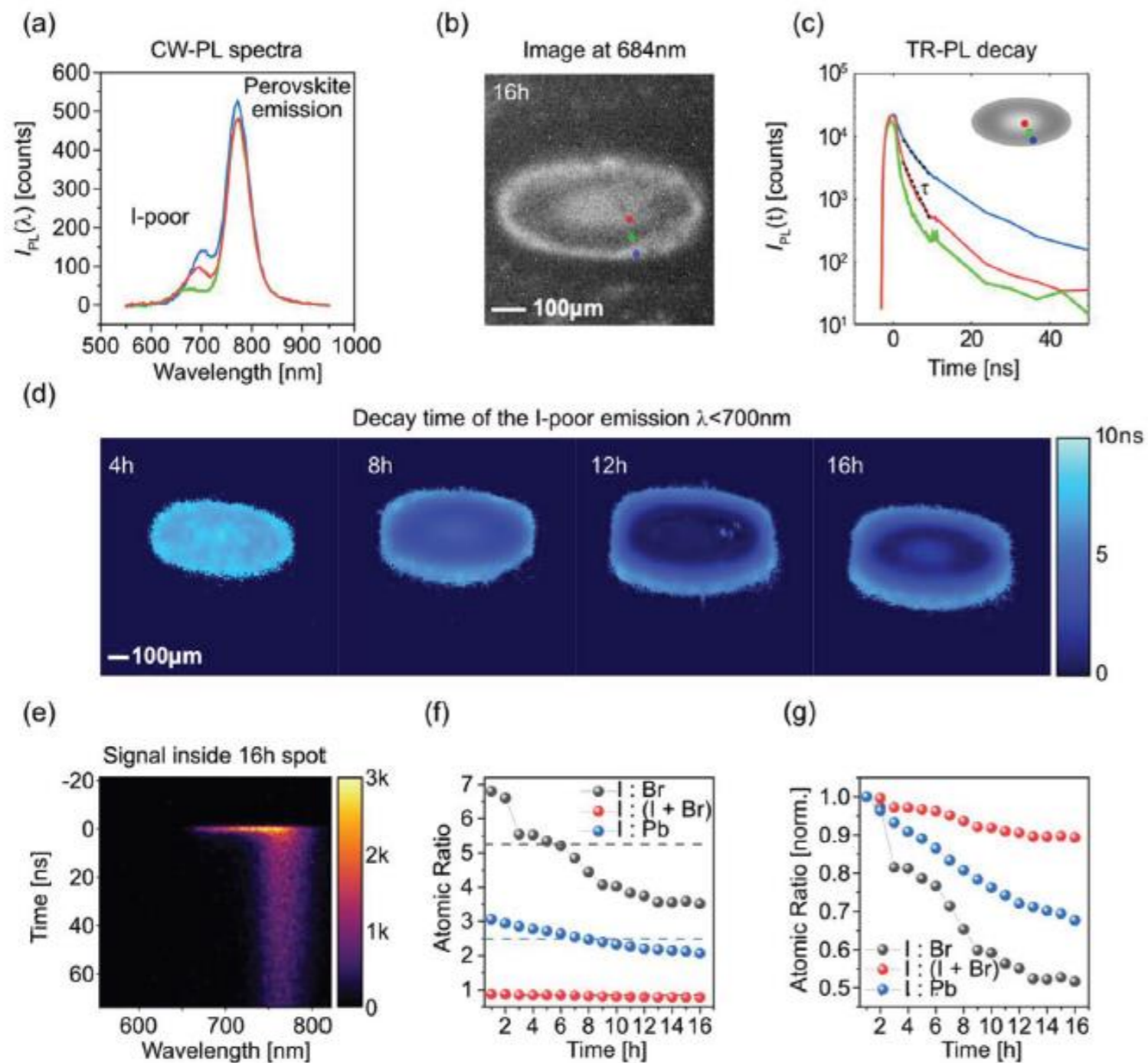
X-Ray damage => CW and TRPL image correlations



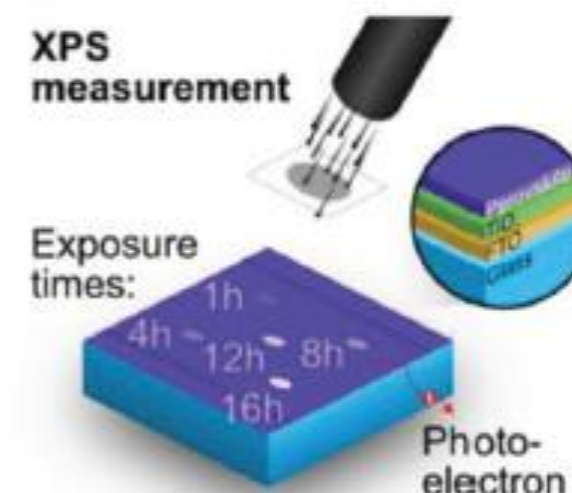
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Bulk recombinations increases
Local correlation (no free parameter)



Large fluence leads to I-poor compound with PL signal (larger gap)



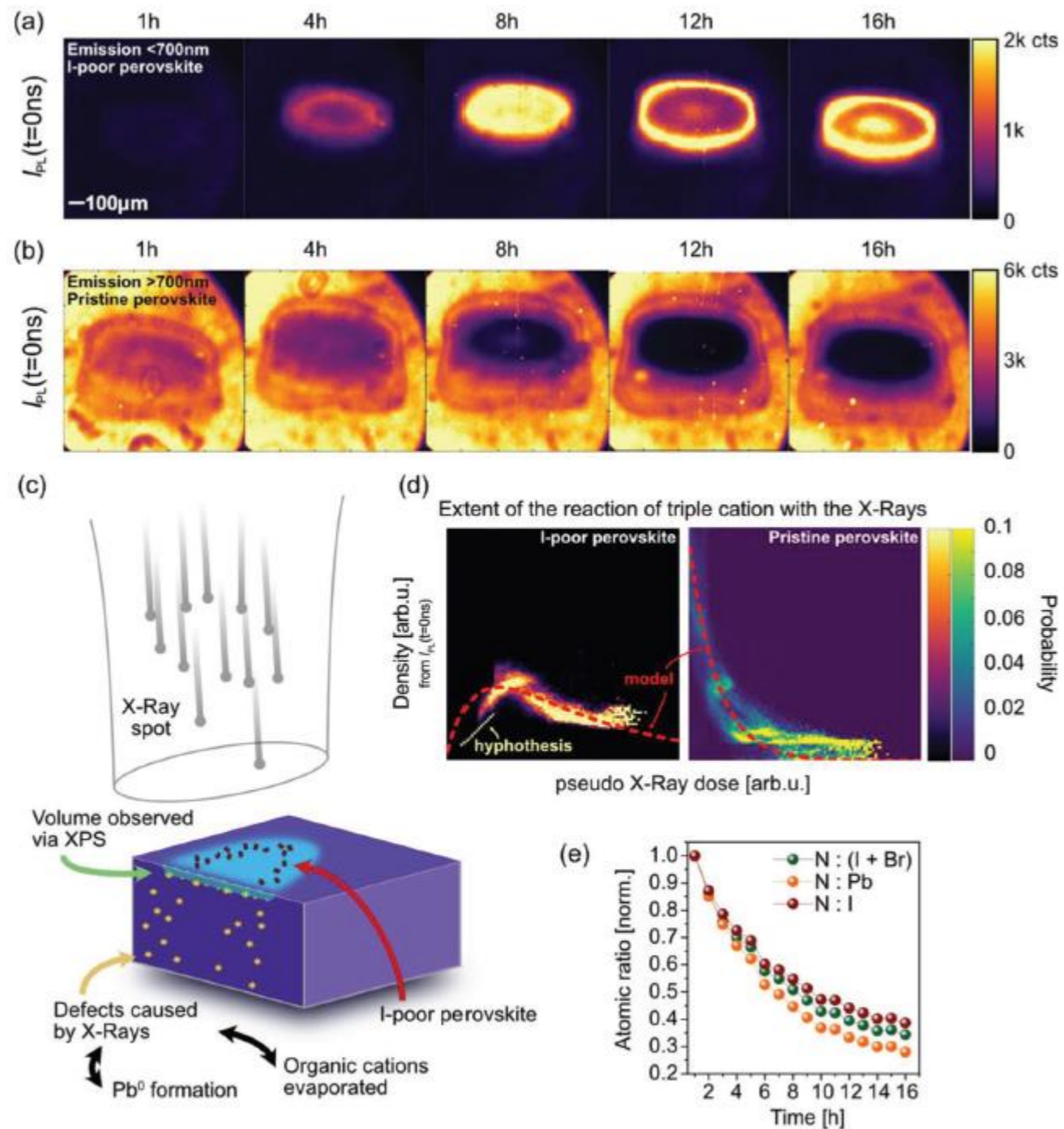


Figure 5. a) Maps of intensity of $I_{PL}(t = 0 \text{ ns})$ from the TR-FLIM experiment for $\lambda < 700 \text{ nm}$ b) Similar but for the emission $\lambda > 700 \text{ nm}$. c) Scheme of the degradation processes. d) Plot of the extent of the reaction between X-ray and the formation of the I-poor perovskite as obtained via analysis of the spatial information contained in the $I_{PL}(t = 0 \text{ ns})$ photoluminescence images. Red dotted lines are the model given in Supporting Information for the parameters $f_{1/2} = 0.5$; $\sigma_1 = 1/12$; $\sigma_2 = 1/50$. e) Atomic ratios obtained from XPS surface composition, normalized.

Correspondance between long exposure and higher X-ray flux

Creation of intermediate species ($\text{PbI}_x?$) with lower I and organic moities

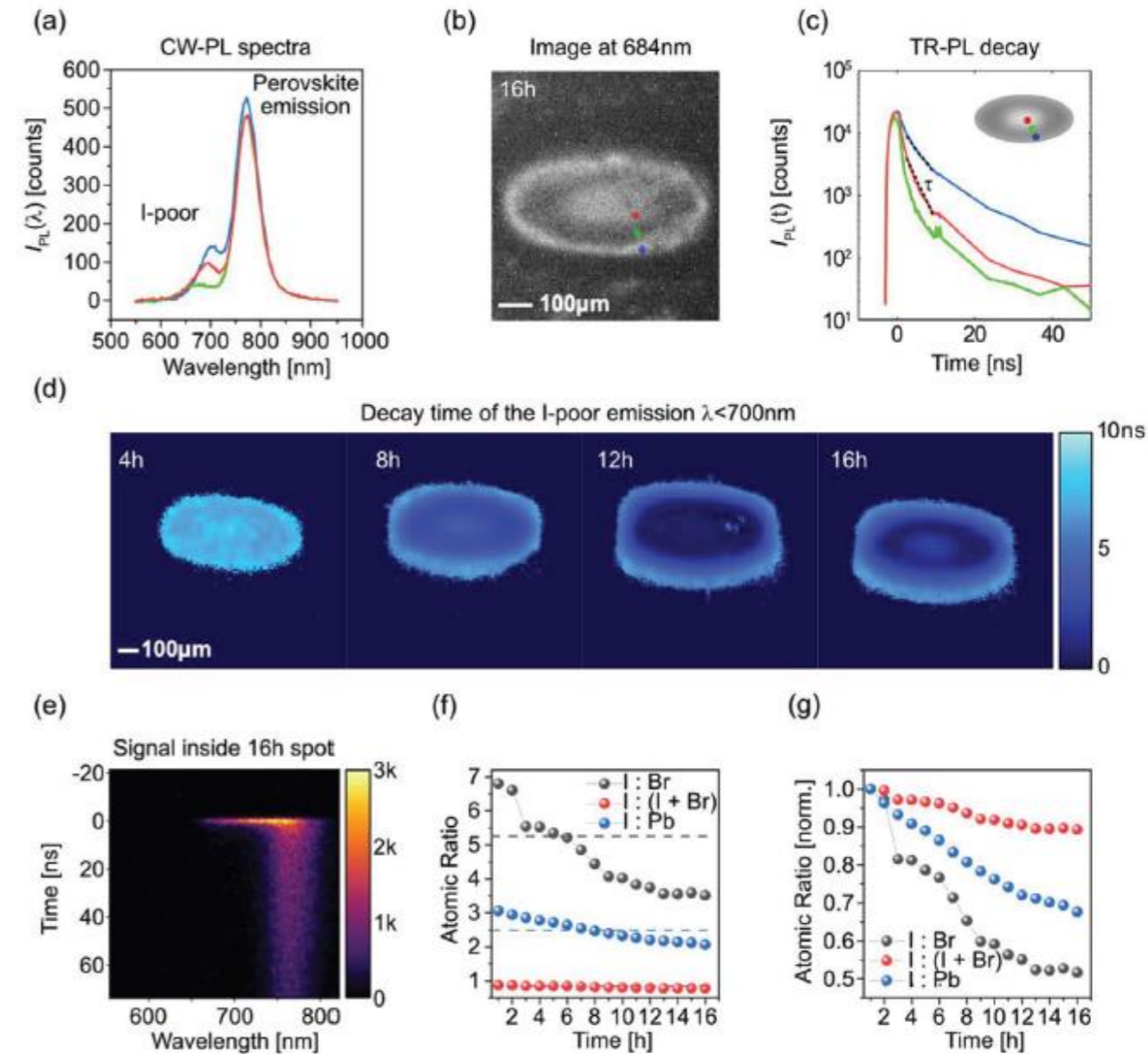
(Species 1) + (X-ray) \rightarrow (Species 2) + (other species)

(Species 2) + (X-ray) \rightarrow (other species)

$$\frac{dN_1}{dt} = -\phi_X(t)\sigma_1 N_1$$

$$\frac{dN_2}{dt} = f_{12}\phi_X(t)\sigma_1 N_1 - \phi_X(t)\sigma_2 N_2$$

- Exposing HaP's to X-rays to investigate surfaces leads to damage in optoelectronic properties
- Reported by synchrotron sources ($< 10^{17}$ ph cm^{-2} s^{-1}) and XPS (10^{13} ph cm^{-2} s^{-1})
- Damage correlated with surface Pb increase, halogen depletion and ultimately Pb° formation
 - Appearance of secondary PL peaks => kinetics



G. Vidon et al, *Adv. Funct. Mater.* **2023**, 33, 2304730

Maryline Ralairisoa et al. , *Small Methods* 2023