Utilising Multi-Modal Spectroscopy to Probe Detrimental Charge-Carrier Recombination via Retaining Trap States in $CsPbBr_3$

Joshua R. S. Lilly[1], Vincent J.-Y. Lim[1], Yuliia Kominko[2,3], Gebhard J. Matt[2,3], Vitalii Bartosh[2,3]

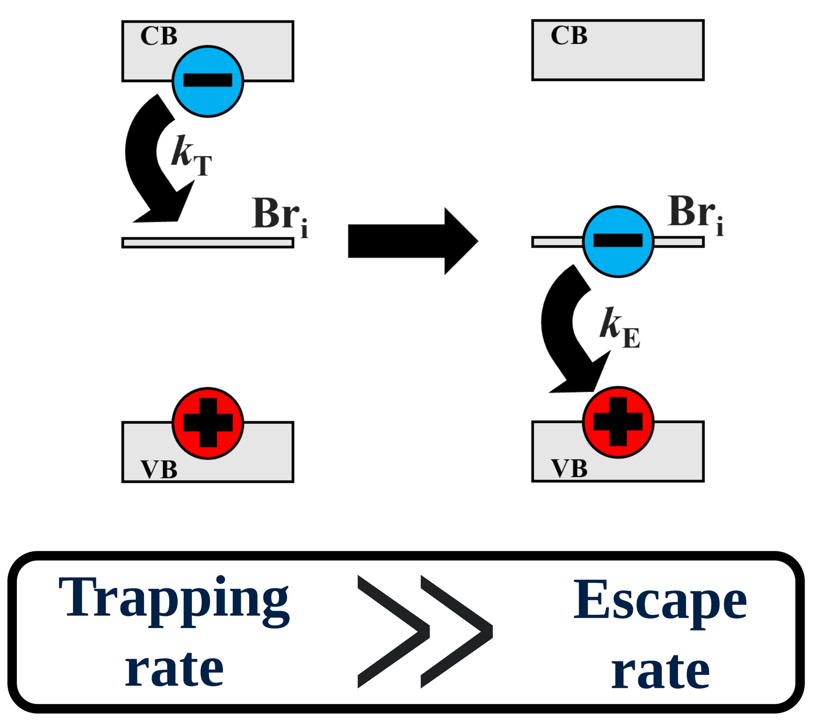
Qimu Yuan[1], Maksym V. Kovalenko[2,3], Michael B. Johnston[1], Laura M. Herz[1,4,*]

UNIVERSITY OF OXFORD

Introduction

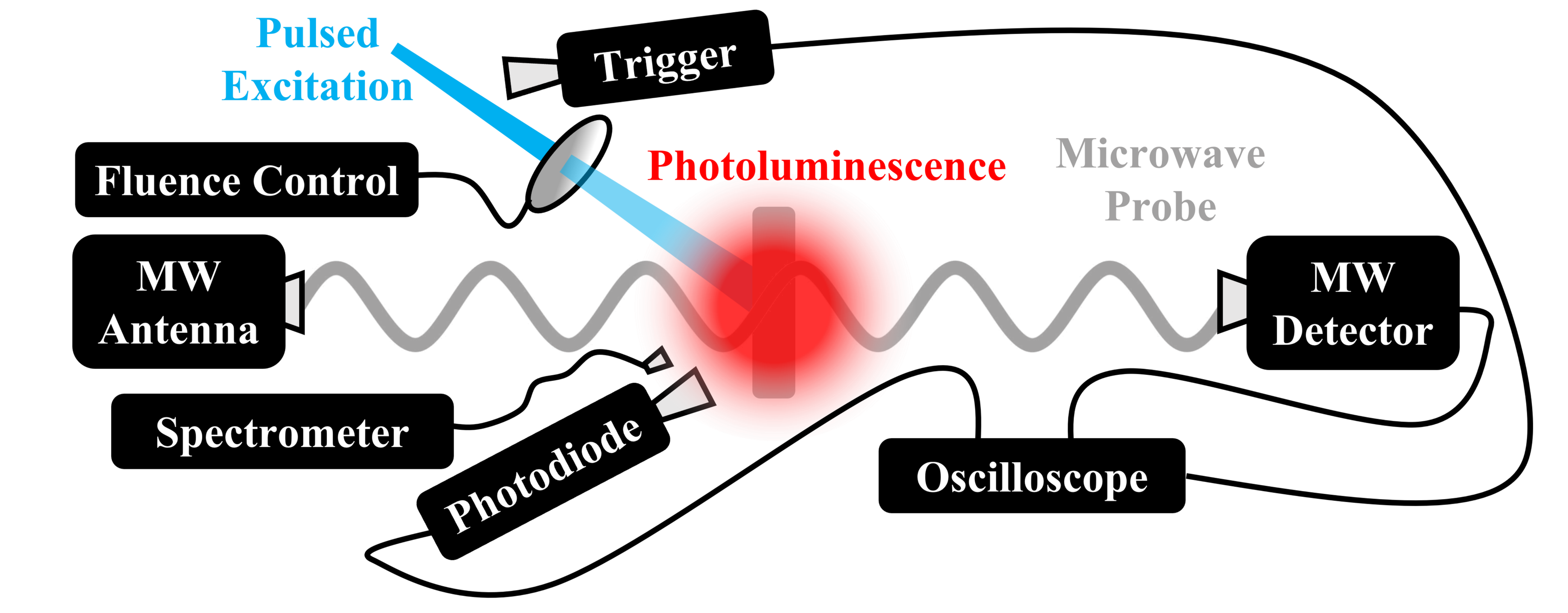
- **$CsPbBr_3$** is an inorganic semiconductor that has been utilised as an active material in a range of **functional devices**, including **solar cells** [1].
- However, the **performance of these devices** can often be **limited by detrimental charge-carrier recombination** via trap states.
- In this study, we investigate charge-carrier recombination via **retaining traps** through application of a dynamic model to concurrently acquired time-resolved photoluminescence (**TRPL**) and time-resolved microwave photoconductivity (**TRMC**) transients.

Retaining Trap States



- In $CsPbBr_3$, significant recombination occurs via **retaining trap states** → attributed to electron capture at **bromide interstitial defects** [2]
- The 'retaining' nature of the electron trap causes a **remanent hole population** to form → **a clear spectroscopic signature**

Multi-Modal Spectroscopy



Spectrally-Resolved Photoluminescence | **Time-Resolved Photoluminescence** | **Time-Resolved Microwave Conductivity**

Process Engineering

Deposition Technique	Enhanced Stoichiometric Control	Enhanced Film Crystallinity
Thermal Co-Evaporation from Dual Source (reference)	✗	✗
Thermal Co-Evaporation from Single Crystal Source	✓	✗
Confined Melt Fabrication from Single Crystal Source	✓	✓

- **Improved stoichiometric control** → inhibit formation of Br_i?
- **Improved film crystallinity** → investigate potential preferential defect formation of Br_i at grain boundaries?

Dynamic Recombination Model

$$\frac{dn(t)}{dt} = -k_{Bi}n(t)p(t) - k_M n(t) - k_T n(t)$$

$$\frac{dn_T(t)}{dt} = k_T n(t) - k_E n_T(t)p(t)$$

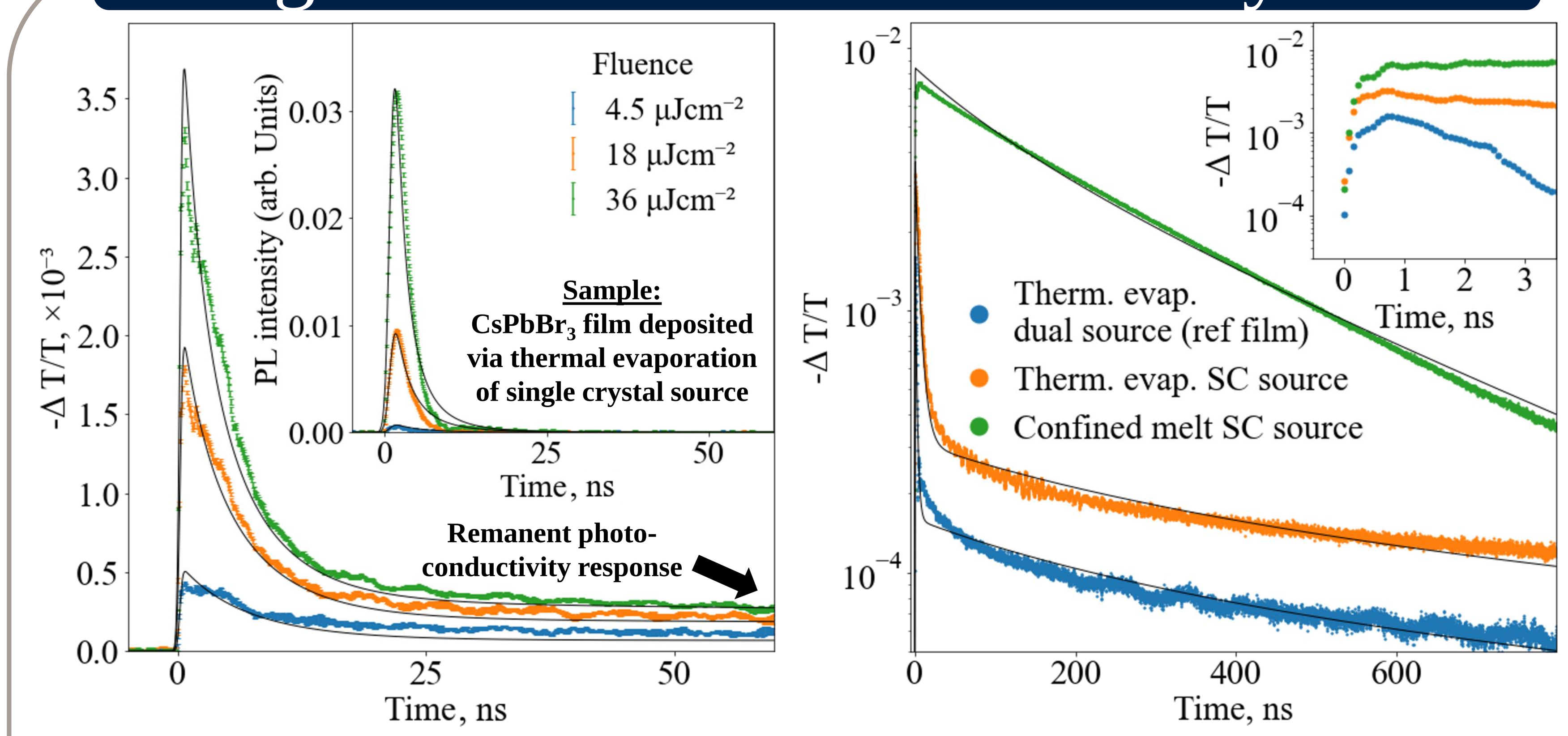
$$p(t) = n(t) + n_T(t)$$

$$-\frac{\Delta T}{T}(t) \propto \frac{n(t)+p(t)}{2}$$

$$I_{PL}(t) \propto k_{Bi}n(t)p(t)$$

k_T is the rate at which electrons are **captured into retaining trap states** → For optimal device performance, **we want to minimise k_T**

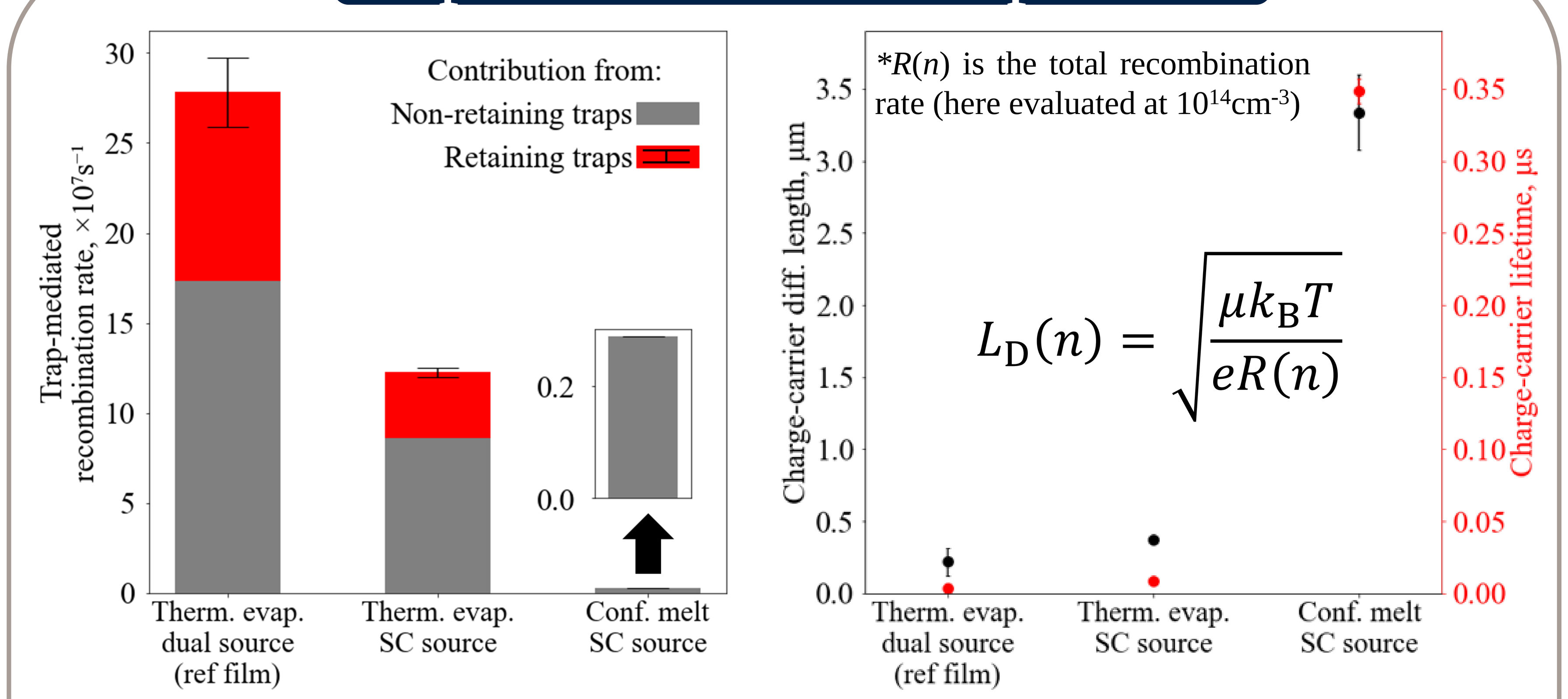
Charge-Carrier Recombination Dynamics



Recombination model → Accurately reproduces the **simultaneously acquired TRPL and TRMC** decay transients

Remanent photoconductivity response → Indicative of substantial recombination via **retaining trap states** → Present for both films fabricated via thermal evaporation

Optoelectronic Properties



Rate of **retaining-trap-mediated recombination** for film fabricated via confined melting of SC source

Below detectable limit!

For the $CsPbBr_3$ film fabricated via **confined melting** of a SC source:

- Charge-carrier lifetime: **>300ns**
- Charge-carrier mob.: **>10cm^{2}V^{-1}s^{-1}**
- Charge-carrier diff. length: **>3μm**

Conclusions

- When **solely** utilising enhanced stoichiometric control methods (**SC source**) → only **minor reduction** in rate of recombination via retaining trap states observed
- However, we have evidenced that in **highly-crystalline films** (fabricated via confined melting of SC source), recombination via halide interstitial defects **can effectively be completely eliminated** → excellent optoelectronic performance
- Consequently, it is suggested that **halide interstitial defects** have a **propensity to form near grain boundaries** → potential link to ion migration dynamics [3]

Related Projects

- The film fabricated via **confined melting of a single crystal source** was used as an active layer in a novel photodetector design → reduced rate of trap-assisted recombination **allowed exceptional device performance to be achieved** [4]
- Utilising the above **multi-modal spectroscopy suite** → **performance-limiting** trap-states associated with Ruddlesden-Popper defects were identified in **$CsPbI_3$** [5]

1. Department of Physics, University of Oxford, UK
2. Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland
3. Empa, Dübendorf, Switzerland
4. Institute of Advanced Study, Technical University of Munich, Germany

* Corresponding Author

UKRI Engineering and Physical Sciences Research Council

OXFORD PV — The Perovskite Company

[1] D. N. Dirin *et al.*, Chem. Mater. 28, 23 (2016)
[2] A. M. Ulatowski *et al.*, Adv. Func. Mater. 33, 51 (2023)
[3] Y. Zhou *et al.*, Adv. Mater. 36, 2305567 (2023)
[4] G. J. Matt, …, **J. R. S. Lilly** *et al.*, Submitted
[5] W. Li,…, **J. R. S. Lilly** *et al.*, Adv. Mater. 37, 2501788 (2025)