



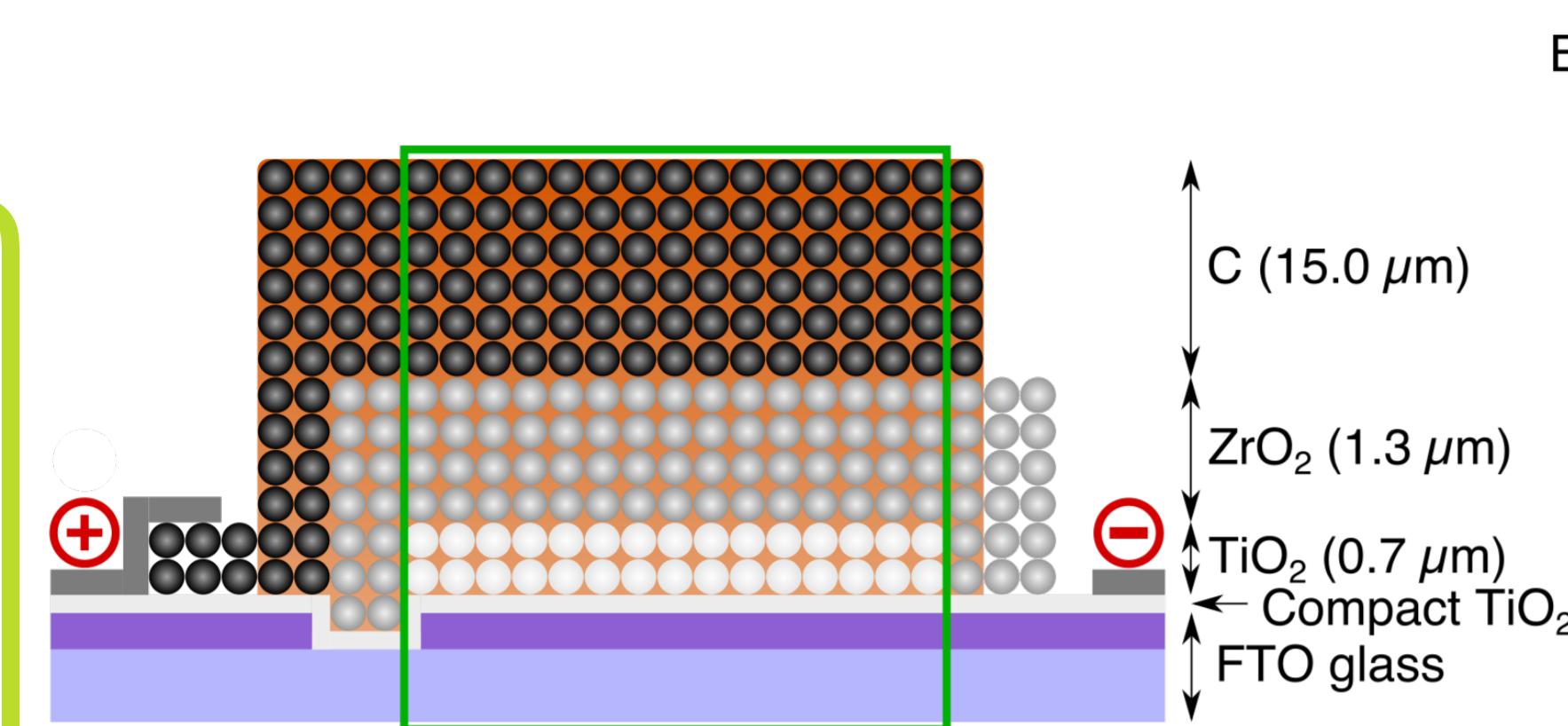
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# Investigating the Superoxide Formation and Stability in Mesoporous Carbon Perovskite Solar Cells with an Aminovaleric Acid Additive

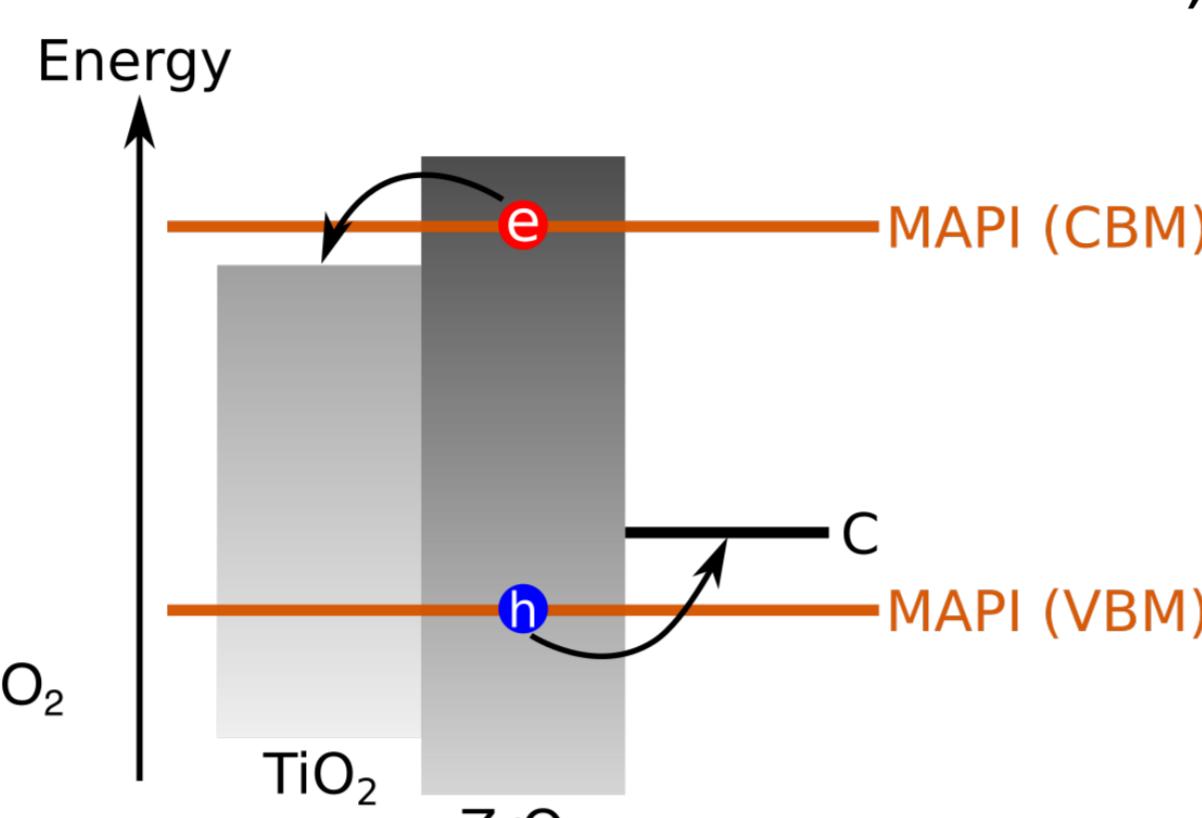
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Perovskite solar cells have attracted a great deal of attention thanks to their high efficiency, ease of manufacturing, and potential low cost. However, the stability of these devices to moisture and oxygen is considered their main drawback and needs to be addressed. Mesoporous carbon perovskite solar cells (m-CPSC), consisting of three mesoporous layers ( $\text{TiO}_2/\text{ZrO}_2/\text{C}$ ) infiltrated with  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPI) perovskite, have presented excellent lifetimes of more than 10 000 h when the additive  $\text{NH}_2(\text{CH}_2)_4\text{CO}_2\text{HI}$  (5-aminovaleric acid iodide; 5-AVAI) is used to modify the perovskite structure (AVA-MAPI) [1]. Yet, the role of 5-AVAI in enhancing the stability has yet to be determined. Here, we show how 5-AVAI hinder superoxide formation.

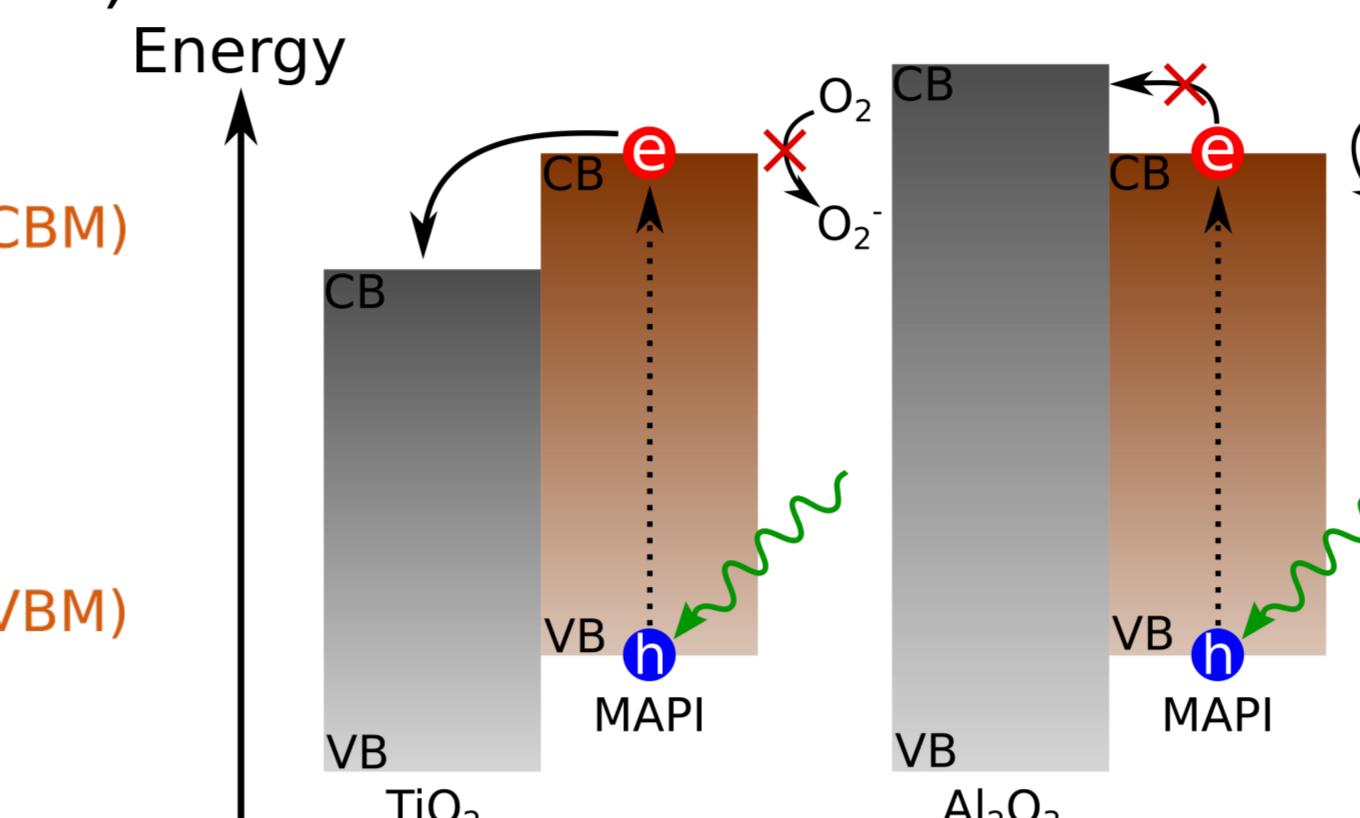
## a)



## b)



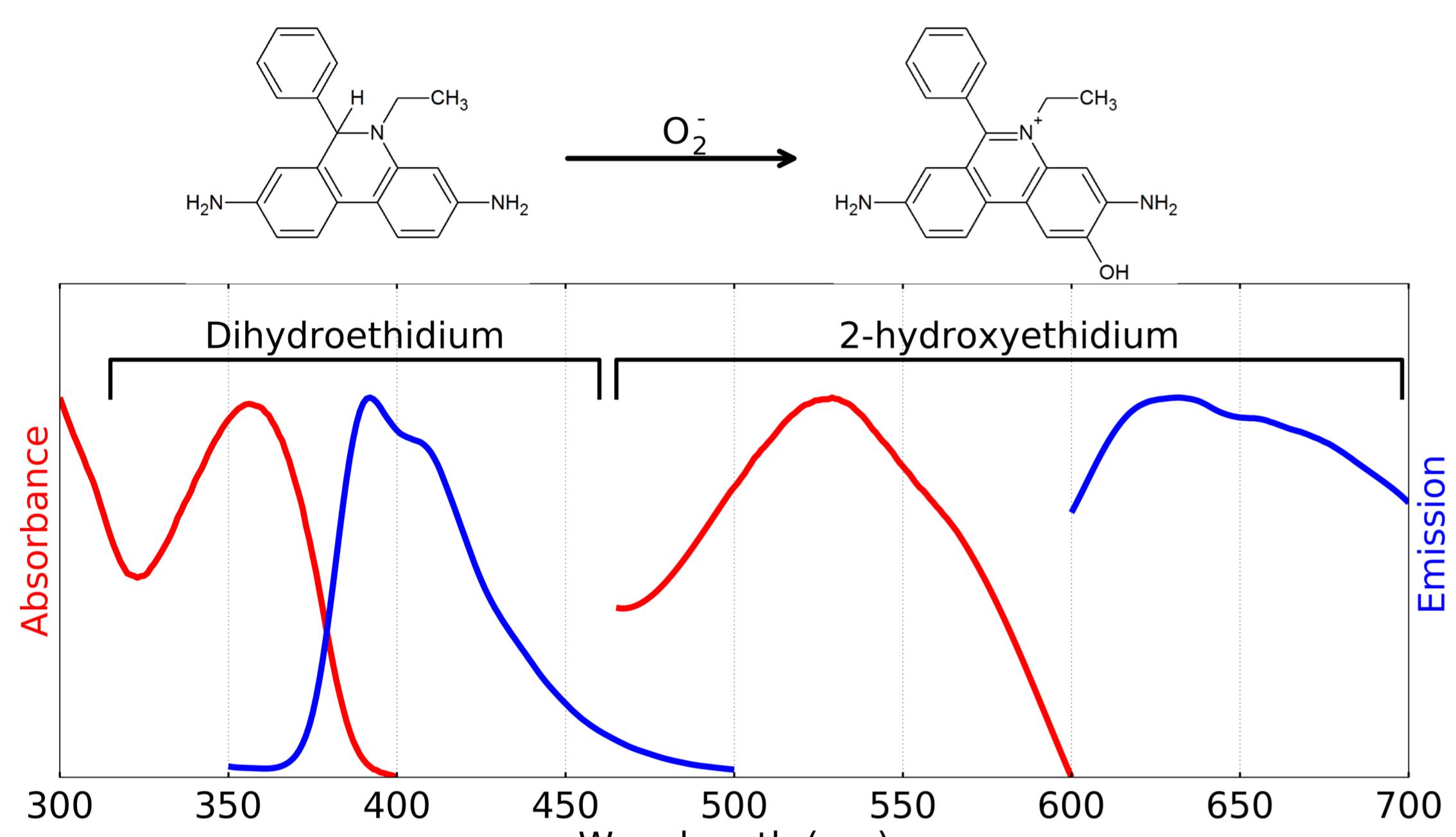
## c)



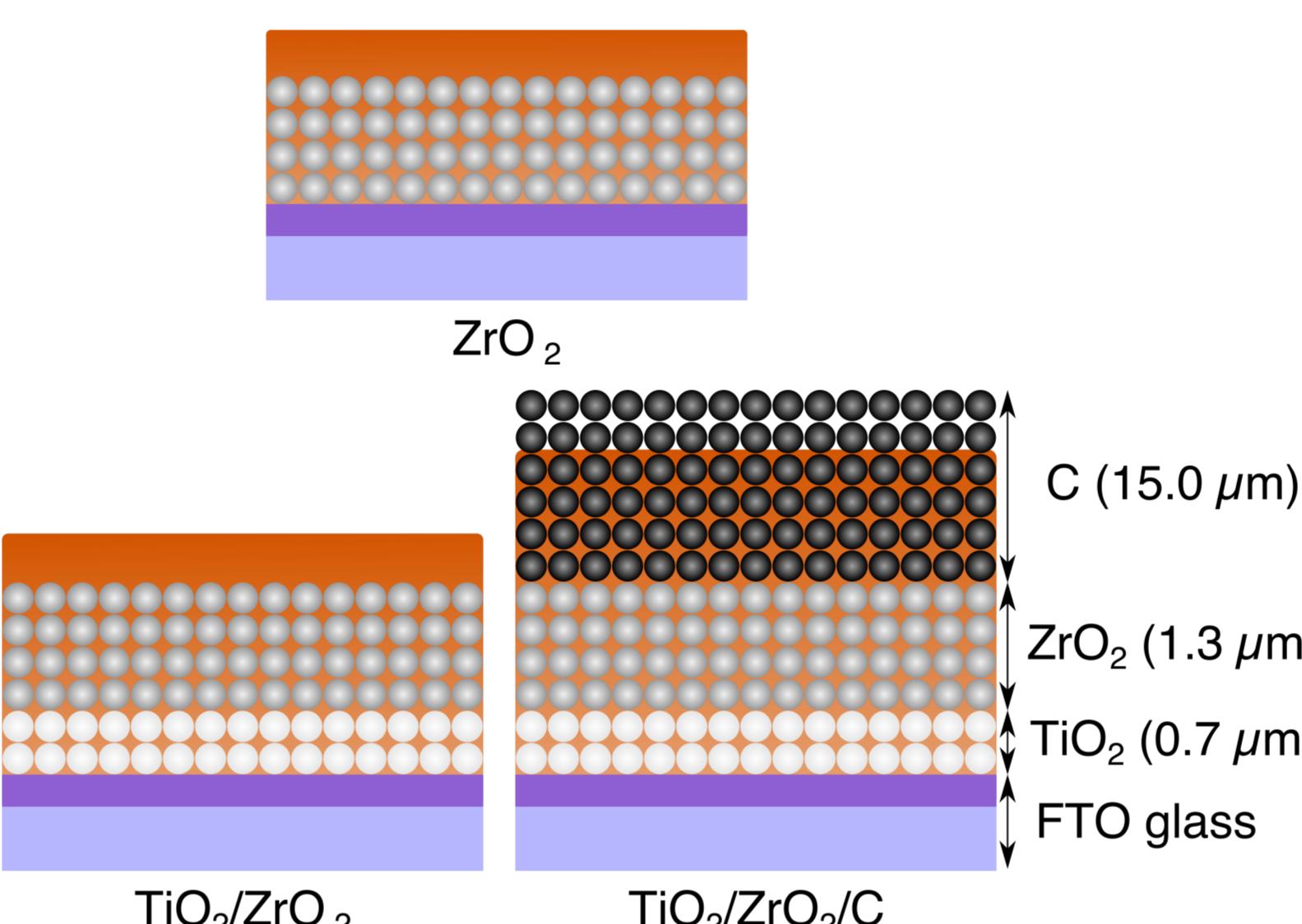
**Figure 1:** a) Schematic and b) band diagram of an m-CPSC (the photoactive area infiltrated with perovskite is highlighted in green) and c) superoxide formation process. If the conduction band minimum (CBM) of the electron transport layer (ETL) has a lower energy than the CBM of the perovskite, the electron can be injected in the ETL (left). In the opposite case, the photoelectron can react with molecular oxygen present in the air to form superoxide (right) vacancies,

- ▶ Superoxide is formed when an excited electron in the conduction band of MAPI gets trapped in an iodide vacancy-induced trap states [2].
- ▶ Iodide vacancies are energetically favourable sites for the reduction of oxygen into superoxide [2].
- ▶ Superoxide can then react with MAPI to degrade into lead iodide.

## Introduction



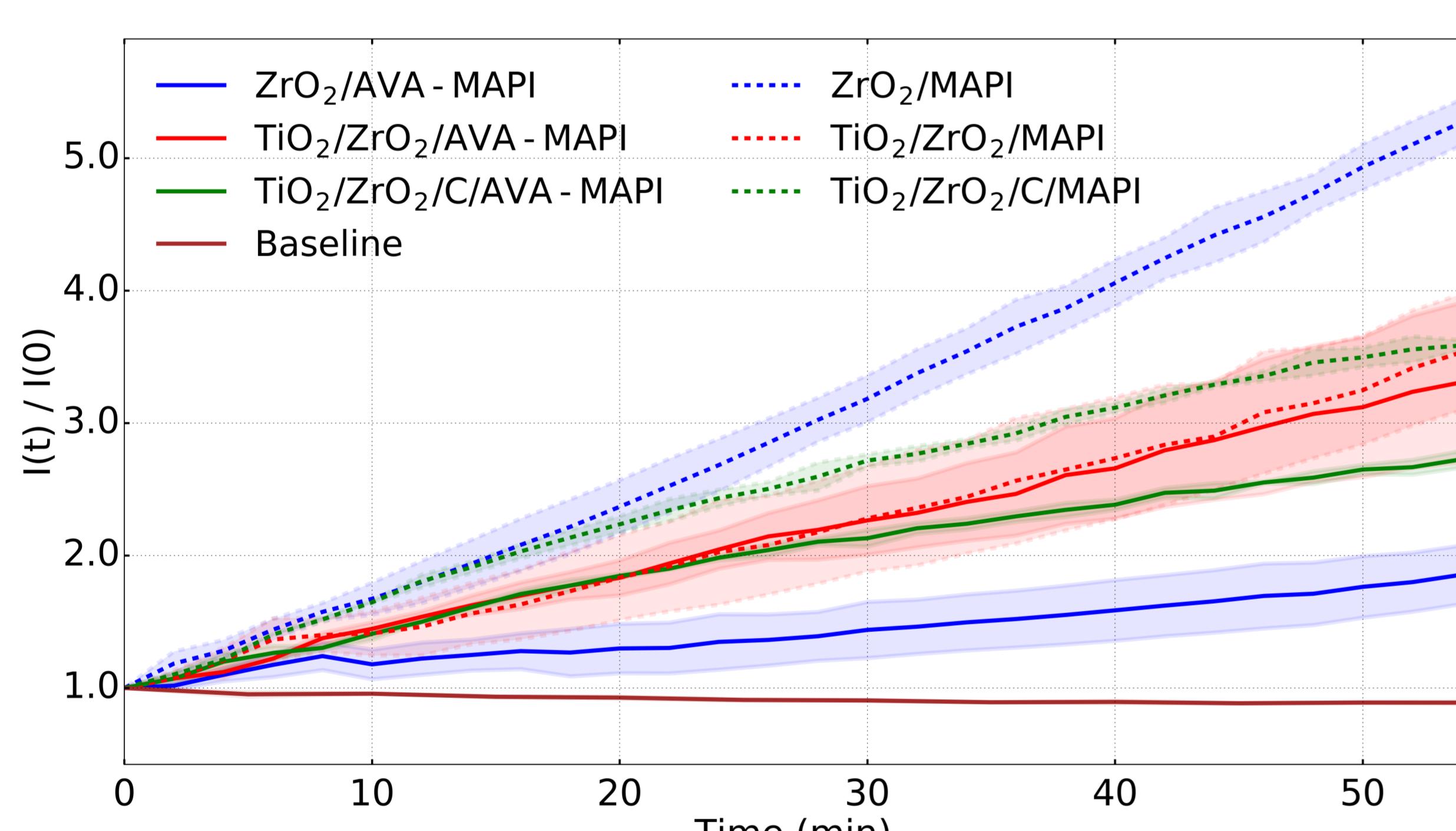
**Figure 2:** Absorbance and fluorescence of dihydroethidium and 2-hydroxyethidium



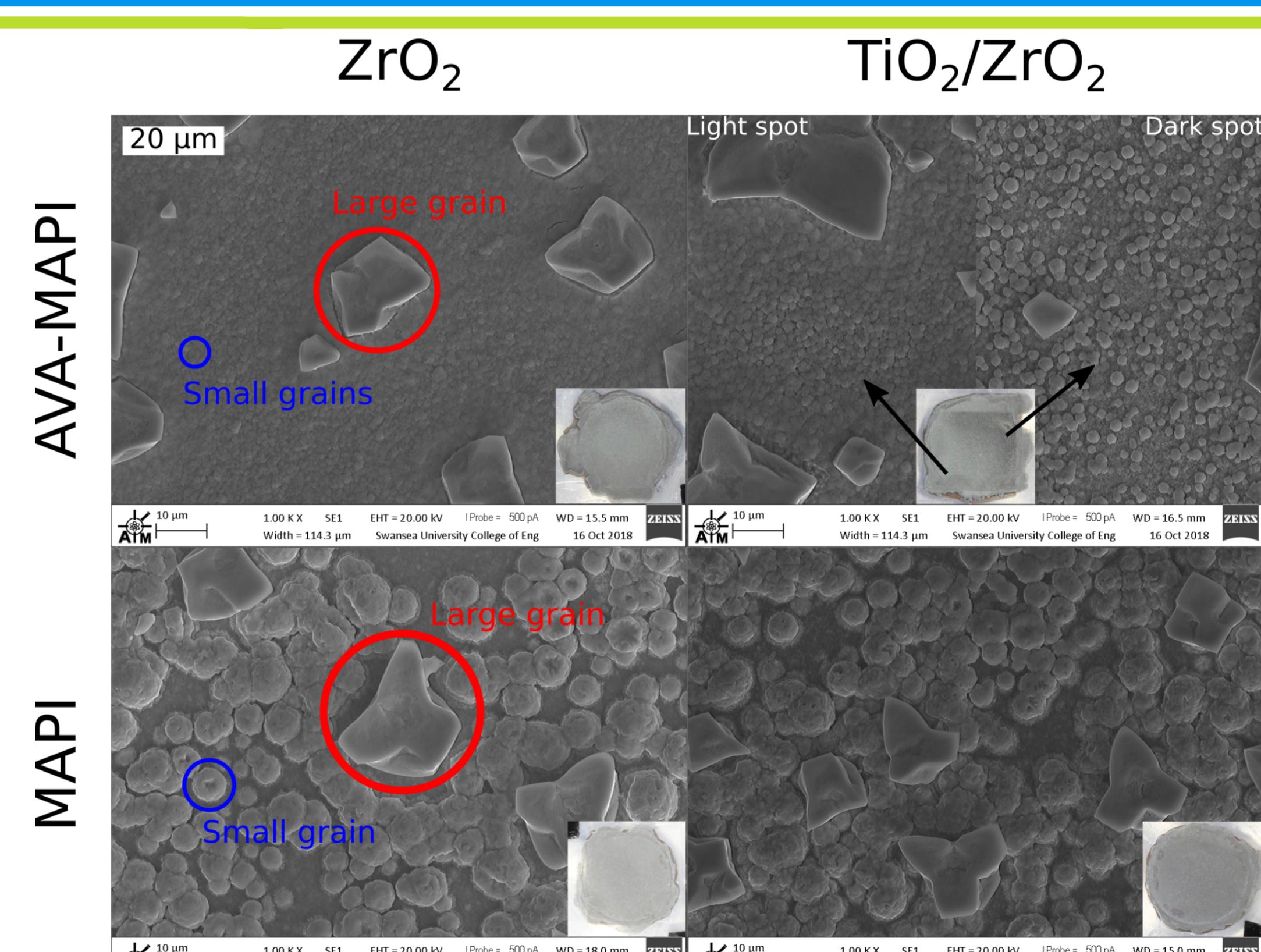
**Figure 3:** Schematic of the film architectures studied.  $\text{ZrO}_2$  and  $\text{TiO}_2/\text{ZrO}_2$  samples have a perovskite capping layer whereas full stacks did not (owing to the thickness of the carbon layer).

- ▶ Dihydroethidium (emits at ~390 nm) can react with superoxide to form 2-hydroxyethidium (emit at ~660 nm) (Figure 2).
- ▶ Superoxide formation in MAPI was monitored by tracking the fluorescence intensity  $I(t)/I(t=0)$  of 2-hydroxyethidium over time [2].
- ▶ Mesoporous substrates  $\text{ZrO}_2$ ,  $\text{TiO}_2/\text{ZrO}_2$  and  $\text{TiO}_2/\text{ZrO}_2/\text{C}$  were used to understand the role of each layer (Figure 3).

## Methodology



**Figure 4:** Superoxide formation of MAPI and AVA-MAPI drop-casted on  $\text{ZrO}_2$ ,  $\text{TiO}_2/\text{ZrO}_2$  and  $\text{TiO}_2/\text{ZrO}_2/\text{C}$  architectures (each curve is the average of two samples and the area correspond to the samples spread).



**Figure 5:** SEM images of the capping layer of MAPI and AVA-MAPI drop-casted in  $\text{ZrO}_2$  and  $\text{TiO}_2/\text{ZrO}_2$  with inserts showing a photograph of the sample. The  $\text{TiO}_2/\text{ZrO}_2/\text{AV}-\text{MAPI}$  sample presented lighter and darker areas as indicated by the black arrows.

## Results

- ▶ A lower superoxide formation is measured in  $\text{TiO}_2/\text{ZrO}_2/\text{MAPI}$  than in  $\text{ZrO}_2/\text{MAPI}$  and is explained by electron extraction from the perovskite to the  $\text{TiO}_2$  layer, thus preventing their trapping.
- ▶ MAPI generates more superoxide than AVA-MAPI in  $\text{ZrO}_2$  and  $\text{TiO}_2/\text{ZrO}_2/\text{C}$  (Figure 4). This is explained by the much compact layer formed by the perovskite grains in AVA-MAPI samples which prevent oxygen diffusion in the samples (Figure 5). This counterbalance the smaller grains formed in AVA-MAPI sample which are expected to generate more superoxide due to their higher surface/volume ratio and thus higher surface defect concentration.
- ▶ The higher superoxide formation in  $\text{TiO}_2/\text{ZrO}_2/\text{AV}-\text{MAPI}$  than in  $\text{ZrO}_2/\text{AV}-\text{MAPI}$  is explained by the slightly higher porosity of the grains in the  $\text{TiO}_2/\text{ZrO}_2/\text{AV}-\text{MAPI}$  sample, hence allowing easier oxygen diffusion in the film.

## Conclusion

Superoxide formation in m-CPSC is dependent on a combination of competitive factors including oxygen diffusion, sample morphology, grain size, and defect concentration. Although intricate, superoxide formation in AVA-MAPI and MAPI infiltrated in mesoporous layers can summarised as...



## References

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- [2] N. Aristidou *et al.*, Nat. Commun. 2017, 8, 15218
- [3] E. V. Péan *et al.*, Adv. Func. Mat. 2020, 1909839

## Acknowledgments

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