Singlet Fission and Triplet Transfer to a Metal Halide Perovskite Absorber

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This talk outlines an investigation of triplet transfer from tetracene (Tc) to a metal halide perovskite (HaP) absorber. To date, transfer of singlet fission (SF)-generated triplet excitons into HaPs has remained elusive.[1-3] The present study involves a device structure based on that leading to triplet transfer to Si, with a double interface Tc/zinc phthalocyanine (ZnPc)/Si.[4] The charge transfer to the perovskite absorber is expected to follow a similar mechanism, provided that an adequate device electronic structure can be realized. Accordingly, the relative positions of the Tc, ZnPc and HaP energy levels would be such that the triplet excitons dissociate at the ZnPc-HaP interface, the electron is transferred directly to the HaP conduction band minimum (CBM), temporarily leaving the hole in the ZnPc HOMO and forming a charge-separated (CS) state ($ZnPc^+$–HaP^-) with energy between the triplet energy and the HaP energy gap. The ZnPc-HaP interface electronic structure is designed to allow the subsequent barrier-less transfer of the hole to the HaP.

We demonstrate here an energetically and functionally coupled SF–HaP system using Tc as the triplet source and methylammonium mixed tin–lead iodide perovskite $MA(Sn_xPb_{1-x})I_3$ as acceptor. Tc singlet excitons formed upon absorption of photons with energy $h\nu \geq 2.4$ eV can undergo fission and generate two triplet excitons with energy 1.25 eV each from one singlet exciton with energy 2.4 eV. The composition of the HaP absorber is therefore optimized with x = 0.5 – 0.75 to yield an energy gap of ~1.20 eV. The ultrathin (1-2 nm) ZnPc layer introduced between Tc and the HaP forms a stepwise molecular level alignment and stabilizes the charge-separated (CS) state ($ZnPc^+$–HaP^-) matched to the HaP energy gap.

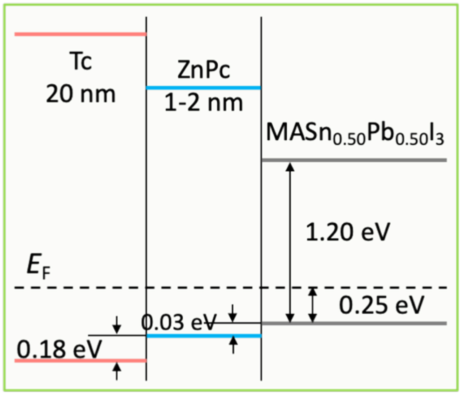

Figure 1: Energy diagram of the Tc/ZnPc/ $MA(Sn_{0.5}Pb_{0.5})I_3$ double interface determined via UPS/IPES, showing relative positions of the Tc and ZnPc HOMO and LUMO vs. perovskite VBM and CBM.

UPS and IPES are used to determine the full electronic structure of the double interface Tc/ZnPc/$MA(Sn_xPb_{1-x})I_3$ (Fig. 1). The ZnPc HOMO, slightly shallower than the Tc HOMO, forms a barrier-less interface for the hole transfer to the HaP. Furthermore, the energy of the charge separated state, i.e. energy difference between the HaP CBM and the ZnPc HOMO at the interface (~1.23 eV), lies between the Tc triplet energy (1.25 eV) and the HaP energy gap (1.20 eV), favorable for triplet transfer.

The full device built to test for triplet transfer is shown in Fig. 2A, with PEDOT:PSS as the hole transport/contact layer and C_{60}/BCP as the electron transport/contact layer. The top electrode is a Ag grid (Fig. 2B) allowing top illumination, assisted by a thin ITO layer to reduce resistance. Several $MA(Sn_{0.55}Pb_{0.45})I_3$ devices are built: (i) without Tc/ZnPc (control), (ii) with Tc only, (iii) with Tc/ZnPc. Larger gap HaP (x = 0.25) devices are also built without and with Tc/ZnPc.

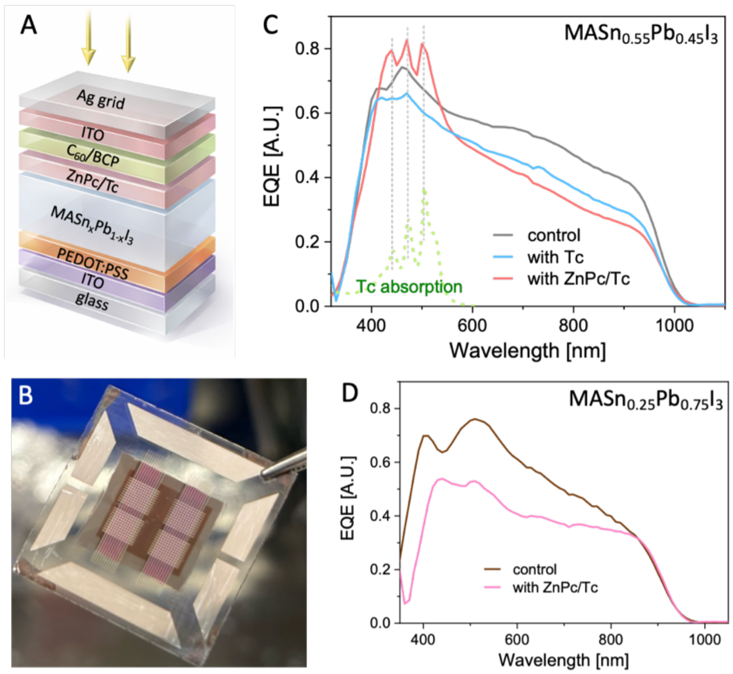

Figure 2: (A) Device: glass/ITO/PEDOT:PSS/$MASn_xPb_{1-x}I_3$/(ZnPc/Tc)/C_{60}/BCP/ITO/Ag grid electrodes; (B) Top view of the Ag grids; (C) External quantum efficiency (EQE) spectra of the $MASn_{0.55}Pb_{0.45}I_3$ control device (black), Tc/$MASn_{0.55}Pb_{0.45}I_3$ (blue), and Tc/ZnPc/$MASn_{0.55}Pb_{0.45}I_3$ (red). (D) EQE spectra of $MASn_{0.25}Pb_{0.75}I_3$ based devices before and after Tc/ZnPc deposition.

The results of external quantum efficiency (EQE) measurements of these devices are shown in Fig. 2C and 2D. The EQE from the Tc/ZnPc/$MA(Sn_{0.55}Pb_{0.45})I_3$ device exhibits a clear SF-assisted Tc-correlated signature under illumination, with three peaks in the 450-500 nm region that precisely match the Tc absorption spectrum. The device built without the ZnPc intermediate layer show very weak features in that wavelength range, emphasizing the crucial role of the intermediate layer. Finally, devices built with $MA(Sn_{0.25}Pb_{0.75})I_3$ show not evidence of triplet transfer (Fig. 2D), consistent with the fact that the gap of the absorber (1.35 eV) is too large for transfer of the 1.25 eV triplets.

Taken together, the spectroscopy and device data underscore the potential of singlet fission to boost perovskite solar-cell efficiency. Further details will be provided during the talk.

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2. Guo, D. et al., Charge Transfer Dynamics in a Singlet Fission Organic Molecule and Organometal Perovskite Bilayer Structure. *J. Mater. Chem. A* **2020**, *8* (11), 5572–5579.
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4. Nagaya N. et al., Exciton Fission Enhanced Silicon Solar Cell, *Joule* **2025,** *9*, 101965