## **Supplementary Information**

## Charge Transfer Process in ZnO/MAPbl<sub>3</sub> Heterojunctions of Perovskite Solar Cells (PSCs) Sensing by Surface-Enhanced Raman Scattering

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Fig.S1 The cross-sectional images of perovskite films on bare ZnO a) and

ZnO/MPY b) substrates.



Fig. S2 Transient photoluminescence spectra of MPY molecules on glass

and ZnO substrate.



Fig. S3 Statistical result of the bands intensity at 1061, 1118, 1319, and

1426 cm<sup>-1</sup> with 10000 points as statistical objects.



Fig. S4 UPS spectra of the cut-off region a) and valence band edge region b) for MAPbI<sub>3</sub> films with different precursor ratios of 1.7, 1.0, 0.65, and 0.65 after annealing at 150 °C for 45 min, respectively.

The work function of  $MAPbI_3$  films is determined by the difference

between the photon energy (21.2 eV) and the binding energy of the secondary cut-off edge (Figure S3a). According to Figure S3, the MAPbI<sub>3</sub> films with precursor ratios of 1.7, 1.0, 0.65, and 0.65-annealed are estimated to be 16.12 eV, 16.94 eV,16.68 eV and 16.60 eV, respectively. As shown in Figure S3b, the valance band spectra of MAPbI<sub>3</sub> films with precursor ratios of 1.7, 1.0, 0.65, and 0.65-annealed are estimated to be 0.55 eV, 1.25 eV, 0.85 eV and 0.95 eV from Fermi level. The bandgap of all MAPbI<sub>3</sub> perovskite films was set to 1.55 eV because the changed precursor ratio did not change the bandgap. The location for conduction band and valance band of MAPbI<sub>3</sub> films with precursor ratios of 1.7, 1.0, 0.65, and 0.65-annealed are listed in Table S1.

**Table S1.** The location for conduction band and valance band of  $MAPbI_3$  films with precursor ratios of 1.7, 1.0, 0.65, and 0.65-annealed

| Energy/eV                 | MAPbl <sub>3</sub> -1.7 | MAPbl <sub>3</sub> -1.0 | MAPbl₃-0.65 | MAPbl₃-0.65<br>annealing |
|---------------------------|-------------------------|-------------------------|-------------|--------------------------|
| secondary cut-off<br>edge | 16.12                   | 16.94                   | 16.68       | 16.60                    |
| work function             | 5.08                    | 4.26                    | 4.52        | 4.60                     |
| valence band edge         | 0.55                    | 1.25                    | 0.85        | 0.95                     |
| conduction band           | 4.08                    | 3.96                    | 3.82        | 4.00                     |
| valance band              | 5.63                    | 5.51                    | 5.37        | 5.55                     |



Fig. S5 XRD pattern of four kinds of MAPbI<sub>3</sub>



Fig.S6 Ultraviolet-visible absorption spectra of four kinds of  $MAPbI_3$  (with

inset showing the Tauc analyses)



Fig. S7 Statistical result of the band intensity of MPY molecules at 1319

 $cm^{-1}$  (b<sub>2</sub>) in the ZnO/MAPbI<sub>3</sub> heterojunction with 10000 points as

statistical objects.

|                                       | τ <sub>1</sub> |         | τ <sub>2</sub> |         |               |
|---------------------------------------|----------------|---------|----------------|---------|---------------|
|                                       | lifetime       | content | lifetime       | content | <b>τ</b> (ns) |
|                                       | (ns)           | (%)     | (ns)           | (%)     |               |
| MAPbl <sub>3</sub> -1.7               | 6.6            | 22.0    | 94.1           | 78.0    | 74.9          |
| MAPbl <sub>3</sub> -1.0               | 6.5            | 23.5    | 41.4           | 76.5    | 33.2          |
| MAPbl <sub>3</sub> -0.65              | 33.3           | 13.5    | 415.1          | 86.5    | 363.7         |
| MAPbI <sub>3</sub> -0.65<br>annealing | 35.2           | 16.8    | 271.8          | 83.2    | 232.1         |

**Table S2.** Transient photoluminescence species of MAPbI<sub>3</sub> with different precursor ratio on MPY-modified ZnO



Fig. S8 The absorbance of  $\mathsf{MAPbI}_3$  at different compositions.

Supplementary information for the charge transfer degree pCT:

The  $\rho$ CT(k) of an individual molecular band in the Raman spectrum (use an index k to identify) can be determined using the following equation:

$$\rho_{\text{CT}}(\text{K}) = \frac{I^{\text{K}}(\text{CT})I^{\text{K}}(\text{SPR})}{I^{\text{K}}(\text{CT})I^{0}(\text{SPR})}$$

where I<sup>k</sup>(CT) is the intensity of a band in which the charge-transfer contributes to the SERS intensity. It is necessary to select two reference bands in the spectrum region where there is no charge-transfer contribution to the intensity. One of the two bands is I<sup>0</sup>(SPR), where the intensity of the totally symmetric band is only the SPR contribution to the intensity. If the k-band is totally symmetric, the contribution from SPR dominates the intensity, and  $I^{k}(SPR) = I^{0}(SPR)$ . If it is nontotally symmetric, the main contribution to the intensity arises from the charge transfer. At this moment, I<sup>k</sup>(SPR) is usually quite small, and it can be assumed to be zero in many cases. The charge-transfer contribution to totally symmetric modes are usually small and do not affect these total intensities very much. Thus, we could select the intensity of the 1022 cm<sup>-1</sup> ( $1a_1$ ) band as  $I^{0}(SPR)$ . The band at 1241 cm<sup>-1</sup> (3b<sub>2</sub>) was selected for the investigation of the charge-transfer mechanism.