## Correlation of the electronic structure of an interconnection unit with the device performance of tandem organic solar cells

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Figure S1 shows the evolution of the UPS spectra near the onset (left side) and the valence band region (right side) as a function of the thickness for different doping concentrations. All binding energies are referenced to the Fermi level ( $E_F$ ) of ITO. The vacuum level ( $E_{VAC}$ ) shift, depletion width ( $W_D$ ) of the *p*-HTL and the positions of the HOMO levels are analyzed with increasing layer thickness and the results are indicated using the vertical lines in the figures. The vacuum level and the HOMO level positions are determined by interpolating the shoulder of each signal and the background of the spectra.<sup>1, 2</sup> The vacuum level shift between BCP and Ag is in the range of 0.34 eV~0.4 eV, and the  $E_F$ -HOMO level of BCP is around 2.78 eV for all the doping concentrations. When the undoped layer is used, there is no vacuum level shift at the Ag/TAPC interface (Figure S1a). Interestingly, the onset and the HOMO level positions move toward lower binding energies when the *p*-HTL is introduced, which become larger as the doping concentration increases (Figure S1b-d). Moreover, the saturation thickness of the *p*-HTL becomes narrower with increasing doping concentration. With a doping concentration of 5 mol.%, the UPS data was not obtained due to the low carrier density in the doped layer.





**Figure S1**. UPS measurements of BCP(3 nm)/Ag(0.3 nm)/p-TAPC with different doping concentrations of (a) 0 mol.%, (b) 11 mol.%, (c) 18 mol.% and (d) 25 mol.%. The vertical lines represent the changes in the vacuum level and the HOMO level.The thickness of each layer is indicated in the brackets with a nm scale.



**Figure S2.** (a) The *J*-*F* characteristics of  $Mp^{++}p^{+}p^{++}M$  devices with different doping concentrations of *p*-TAPC in the full scale and (b) linear *J*-*F* characteristics with different

doping concentrations in the ohmic region. The open symbols represent measured values and the solid lines indicate linear fits.

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