Supporting Information

Stable Inverted Small Molecular Organic Solar Cells Using a P-doped Optical Spacer

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Estimation of doping concentration of p-MeO-TPD layer

A p-type doped MeO-TPD layer was deposited by co-evaporation of MeO-TPD and F6-TCNNQ in vacuum. The doping concentration of the p-MeO-TPD layer was calculated by the ratio of the XPS intensities of the F1s peaks of F6-TCNNQ to the O1s peaks of MeO-TPD.[1] **Figures S1(a)** and **(b)** represent the XPS intensities of O1s peaks and F1s peaks, respectively. In our experiment, the p-MeO-TPD layer shows a molar ratio of 0.1393, which is converted to 7.66 wt%.

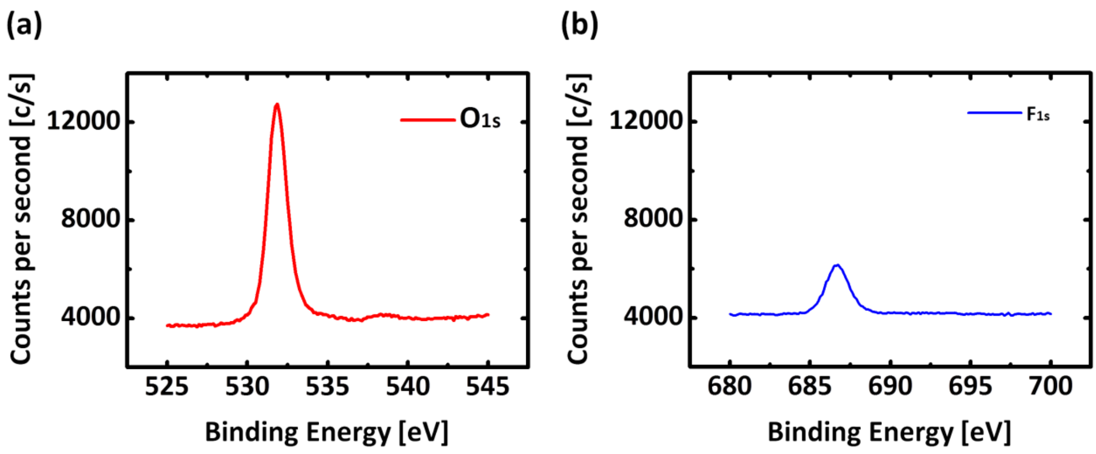

Figure S1. XPS data of p-type doped MeO-TPD by F6-TCNNQ (a) XPS intensity data of **(a)** O1s peak and **(b)** F1s peak.

N-type doping and PEIE layer inserted devices

Figure S2 (a) shows the *J-V* characteristics of the inverted devices using n-type doping and a PEIE layer. The solar cell parameters of these devices are summarized in **Table S1**. Acridine orange base (AOB) was used as an air stable n-type dopant for the C_{60} layer in this study. [2] AOB can donate electrons to the C_{60} matrix by light excitation and this process is irreversible.[3] The device using n-type doping for efficient charge injection showed a relatively low current density compared to the device with a PEIE layer. This is partly due to the exciton quenching in the n-doped C_{60} layer because organic materials usually have low electrical permittivity (ε = 3 ~ 4). As a result, J_{sc} was increased from 9.66 mA/cm^2 to 10.46 mA/cm^2 upon replacing the n-doped C_{60} layer with a PEIE layer. Therefore, the PCE of the inverted device was increased from 3.13% to 3.59 %.

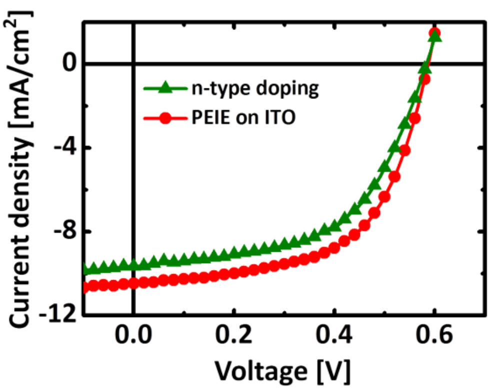

Figure S2. Performance of inverted devices with n-type doping and PEIE *J-V* characteristics of inverted devices using n-type doping and PEIE layer.

Thickness effect of p-MeO-TPD on the internal quantum efficiency (IQE) of the devices

If there happens to be no electrical loss with an increased thickness of optical spacer because of its high conductivity, the thicker spacer would not affect the *FF* and IQE of the devices. To investigate the thickness effect on the device's performance, we fabricated inverted devices using p-MeO-TPD as an optical spacer with varying thickness from 15 to 65 nm. **Figures S3(a)** and **(b)** show an minimum IQE, which is equal to the external quantum efficiency (EQE) divided by absorption of the inverted SMOSC with MoO_3 and MeO-TPD layers.

At a wavelength of 300 ~ 600 nm, IQE rapidly decreased with an increase in thickness of the optical spacers in both cases, especially when they is thicker than 25 nm. **Figures S3(c)** and **(d)** represent the simulated absorption ratio of C_{70}, BHJ and optical spacer layers according to the thickness of the optical spacer. Indeed, the optical spacers are quite absorptive at the spectral region, and therefore, C_{70} and optical spacers are competing in absorbing incident light. As the absorbed light by optical spacers cannot contribute to photocurrents, a decreased IQE can be attributed to the non-negligible absorption by the thick optical spacers. On the other hand, at a wavelength of 600 ~ 850 nm, optical spacers do not interfere with the active layers' absorption. Thus, the IQE was only related to charge extraction ability of the optical spacers in the spectral region. The IQE of the MoO_3 device was decreased with an increased spacer thickness due to its low conductivity, while the IQE of the MeO-TPD device remained almost unchanged (**Fig. S3(b)**).

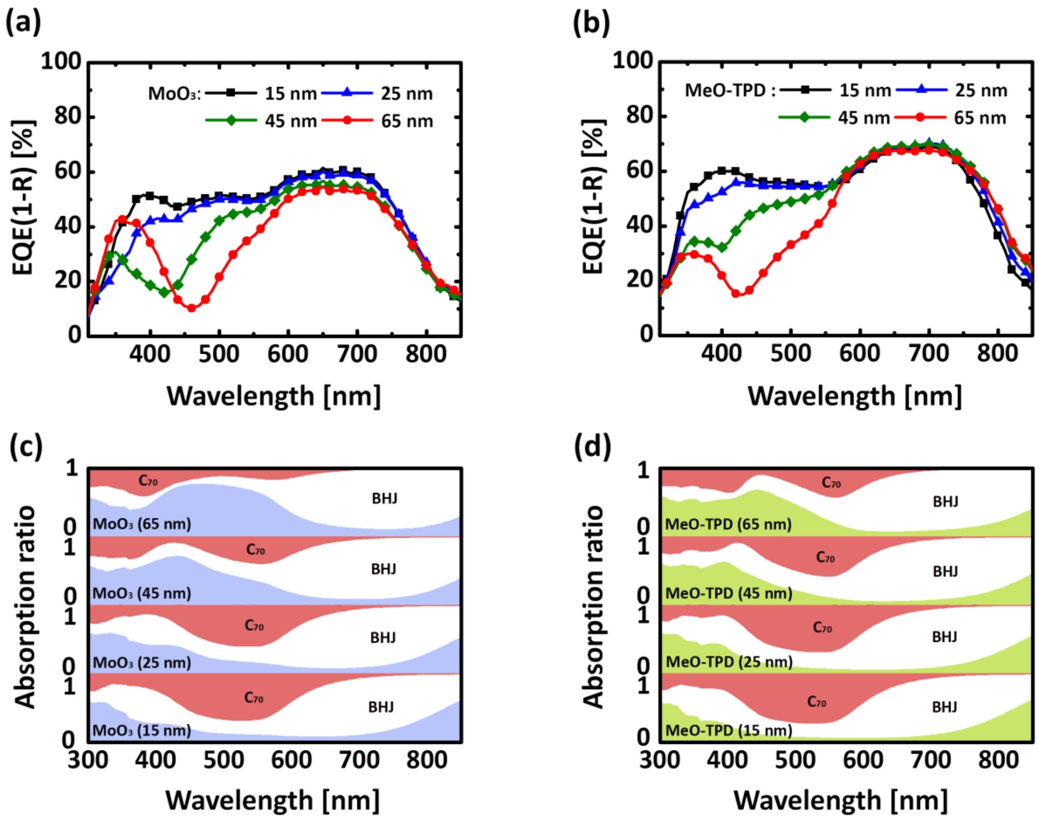

Figure S3. External quantum efficiency divided by total absorption (EQE/(1-R)) and simulated absorption ratio of inverted devices according to the thickness of MoO_3 and MeO-TPD layers. The EQE/(1-R) of inverted devices with varying thicknesses of **(a)** MoO_3 and **(b)** MeO-TPD layers. **(c)(d)** Simulated absorption ratio of the C_{70}, BHJ, and optical spacer layers with various thicknesses (c: MoO_3 layer, d: MeO-TPD).

Lateral conductivity measurement

The conductivity of MoO_3 and p-MeO-TPD layers was measured by constructing a lateral conductivity measurement setup, which has typically been used for estimating the conductivity of doped organic materials.[4] To measure the conductivity of each material, an Ag electrode (100 nm) was firstly deposited using our patterned mask, followed by desired materials of 50 nm in the middle part of substrates. Then, thermally deposited lateral channels were formed. Lastly, currents at a high voltage condition (10 V) were measured using KEITHLEY 2400.

Figure S4(a) shows the current through the lateral channel and the sample configuration is shown in the inset. The channel's width, length, and thickness were 1.1 cm, 0.2 cm, and 50 nm, respectively. The conductivity of thermally deposited MoO_3 and p-MeO-TPD layers were 1.851×10^{-6} S/cm and 7.803×10^{-4} S/cm, respectively. The high conductivity of p-doped MeO-TPD can effectively transfer charge carriers from active layers to anode.

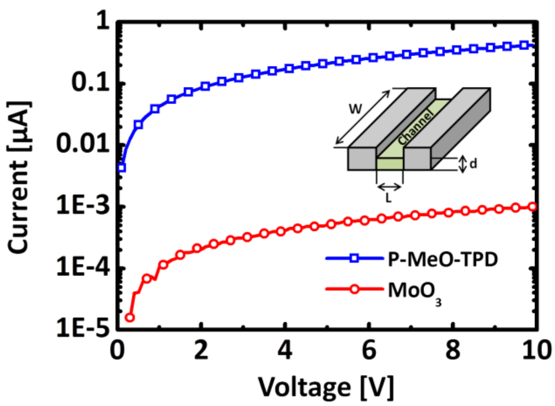

Figure S4. Currents flow through channel *I-V* characteristics of samples for lateral conductivity measurement of MoO_3 and p-MeO-TPD.

Table S1. The devices' characteristics of inverted devices using n-type doping and PEIE layer

Devices	V_{oc} [V]	J_{sc} [mA/cm²]	*FF*	*PCE* [%]
ZnPc:C_{60} with n-type C_{60}	**0.58**	**9.66**	**0.56**	**3.13**
ZnPc:C_{60} with PEIE	**0.59**	**10.46**	**0.58**	**3.59**

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