# Work Function Modulated Water-Soluble Anode Interlayer with Copper-Ion Doping for Precise Signal Detection in Organic Photodiodes

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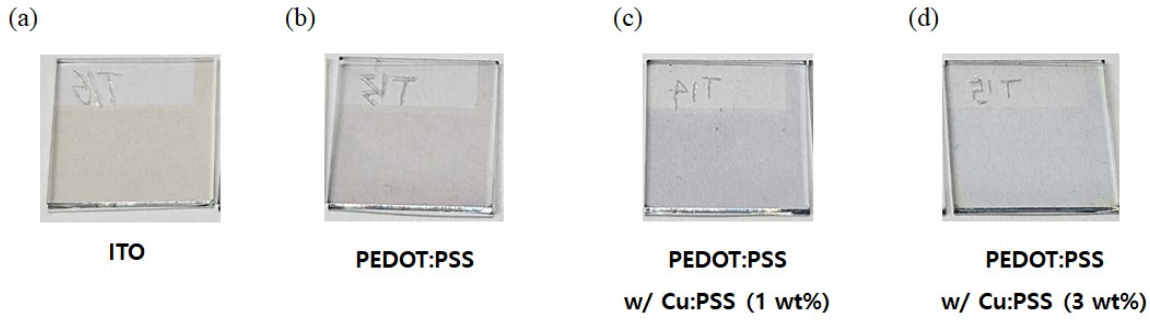


**Figure S1.** Photographs of the (a) pristine ITO substrate, with (b) PEDOT:PSS, (c) PEDOT:PSS with Cu:PSS (1 wt%), and (d) PEDOT:PSS with Cu:PSS (3 wt%) thin film.

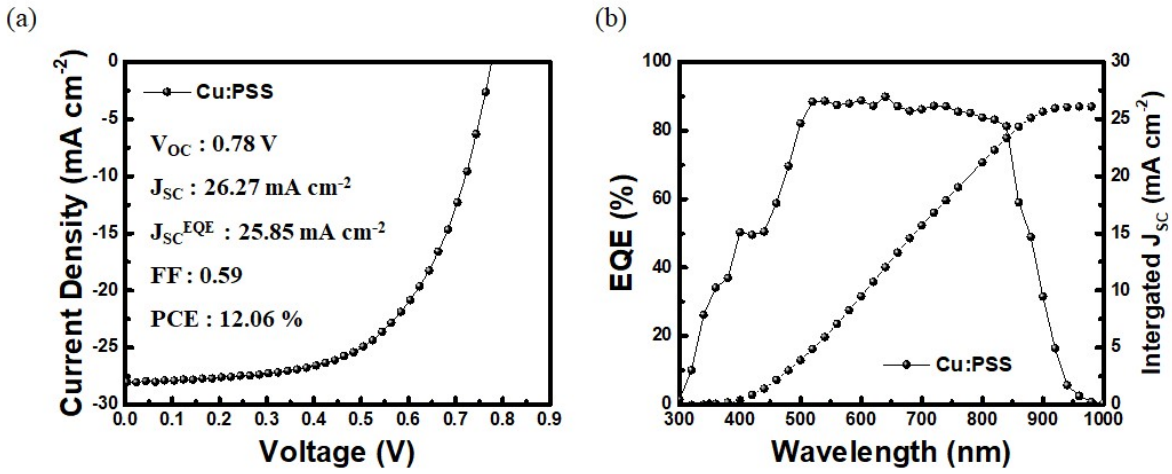


**Figure S2.** (a) J-V characteristics under AM 1.5G irradiation at 100 mW cm$^{-2}$. (b) EQE spectra for the devices based on Cu:PSS (100 wt%).

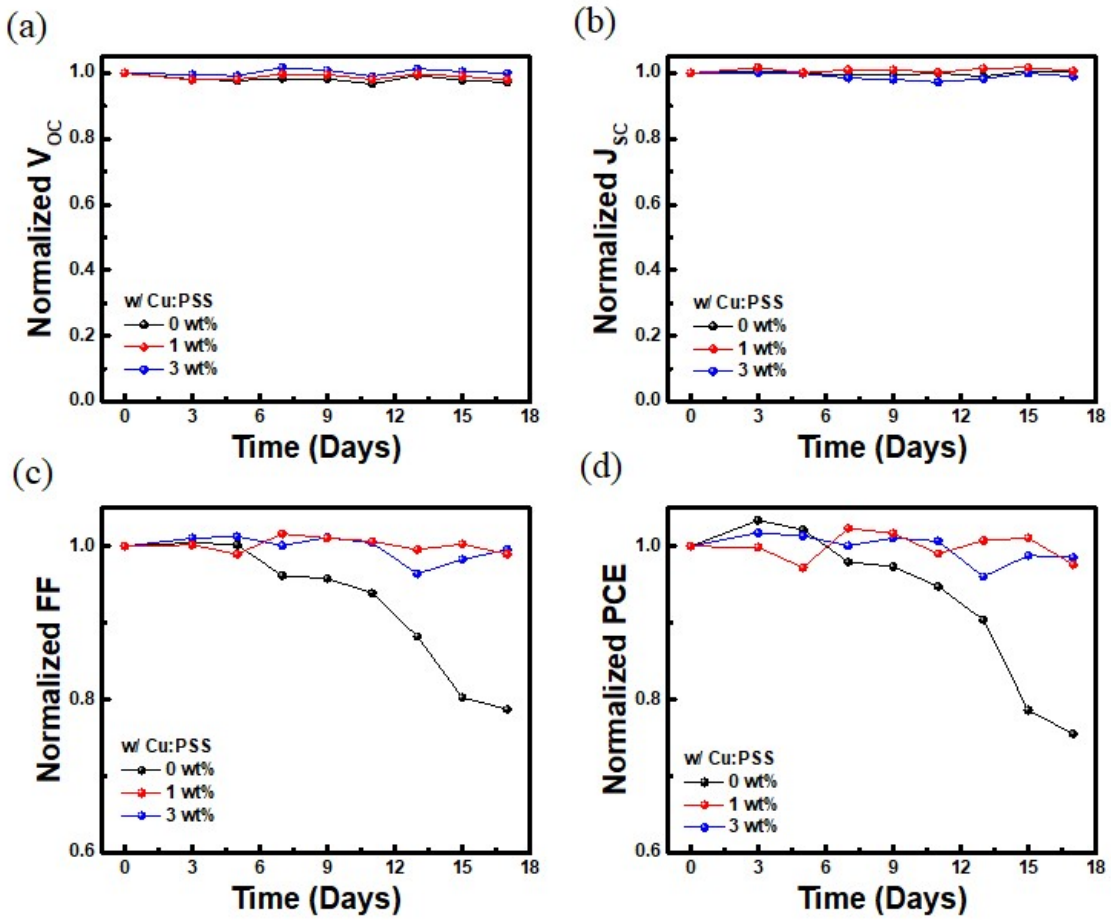


**Figure S3**. Time-dependent photovoltaic parameters (a) $V_{OC}$, (b) $J_{SC}$, (c) FF, and (d) PCE for the devices with different HTLs.

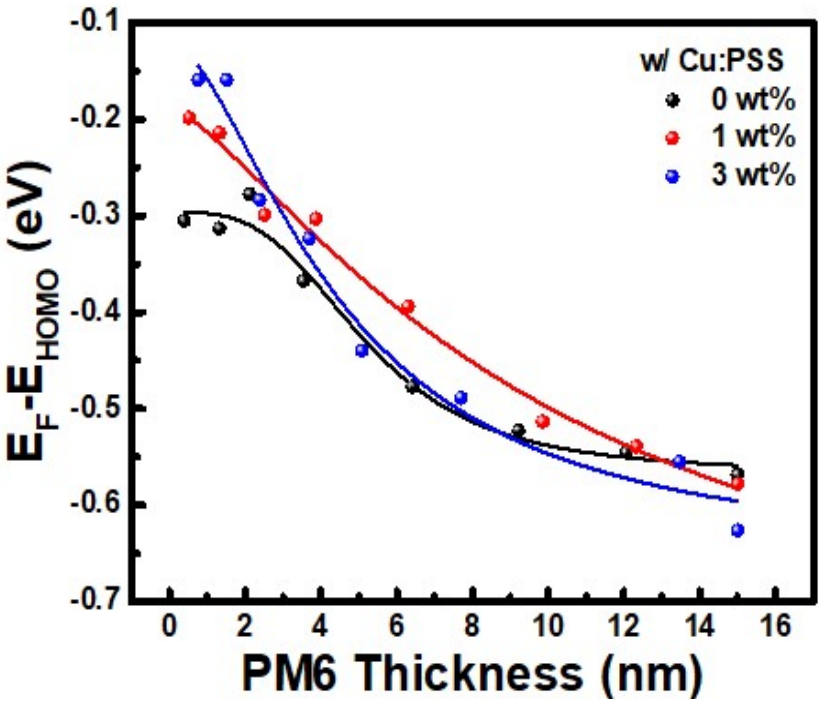


**Figure S4**. Electronic structure of the different HTLs based on observed changes in Ψ, IP, and EA.

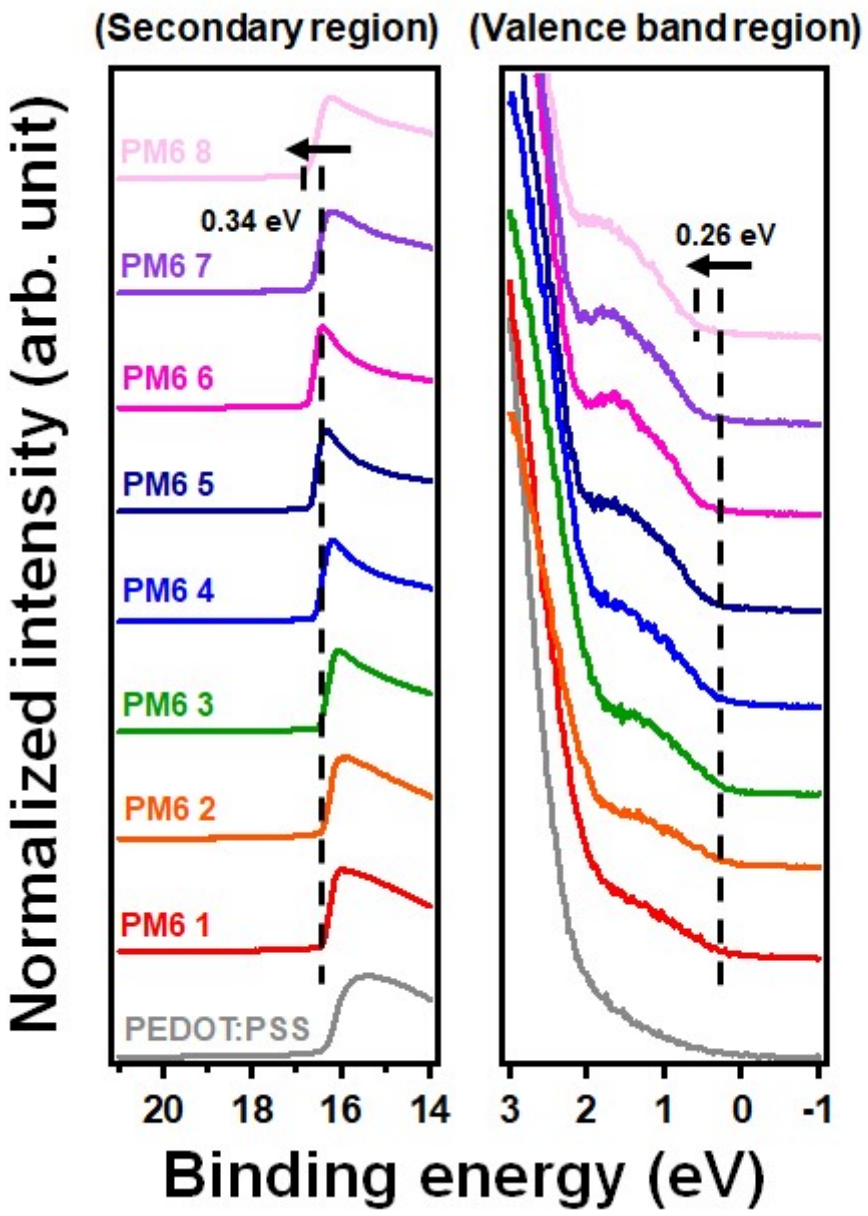


**Figure S5.** UPS spectra of PEDOT:PSS films with different thicknesses deposited on PM6 films.

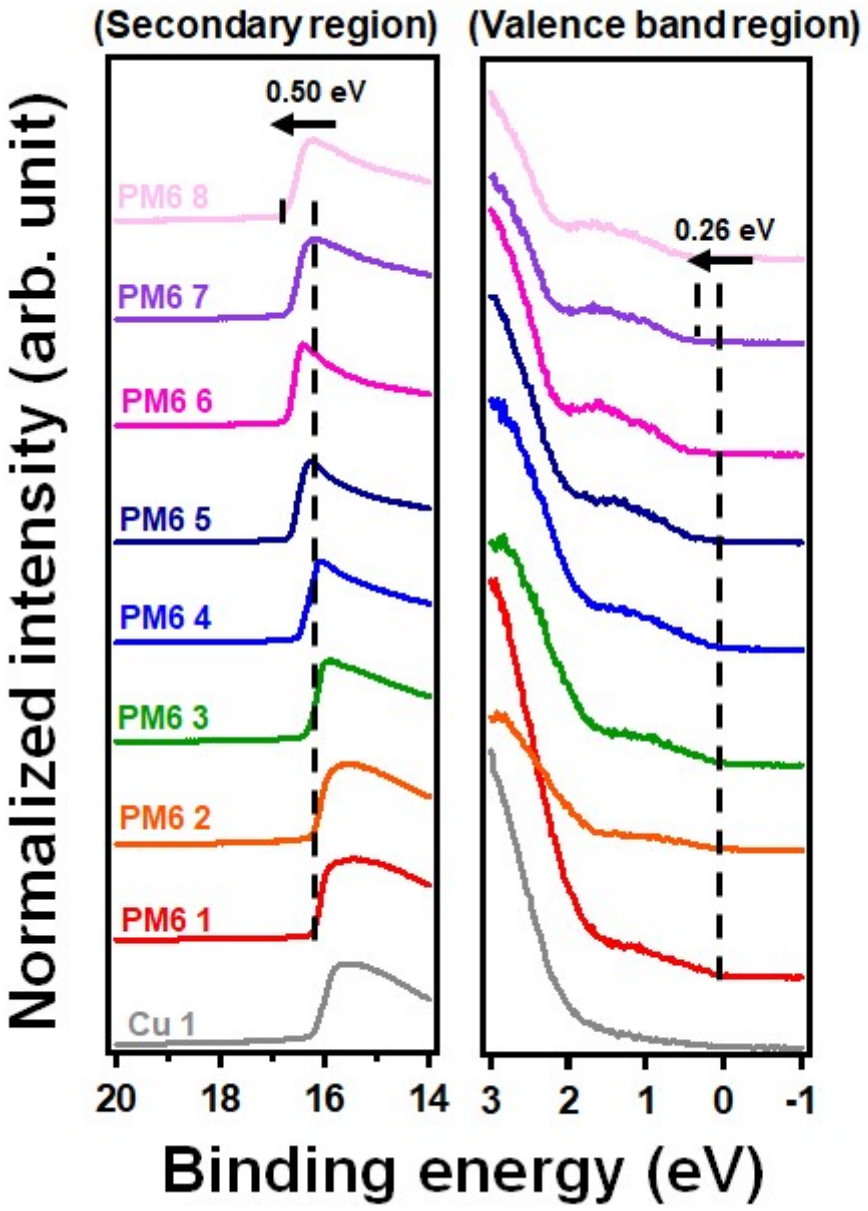


**Figure S6.** UPS spectra of PEDOT:PSS with Cu:PSS (1 wt%) films with different thicknesses deposited on PM6 films.

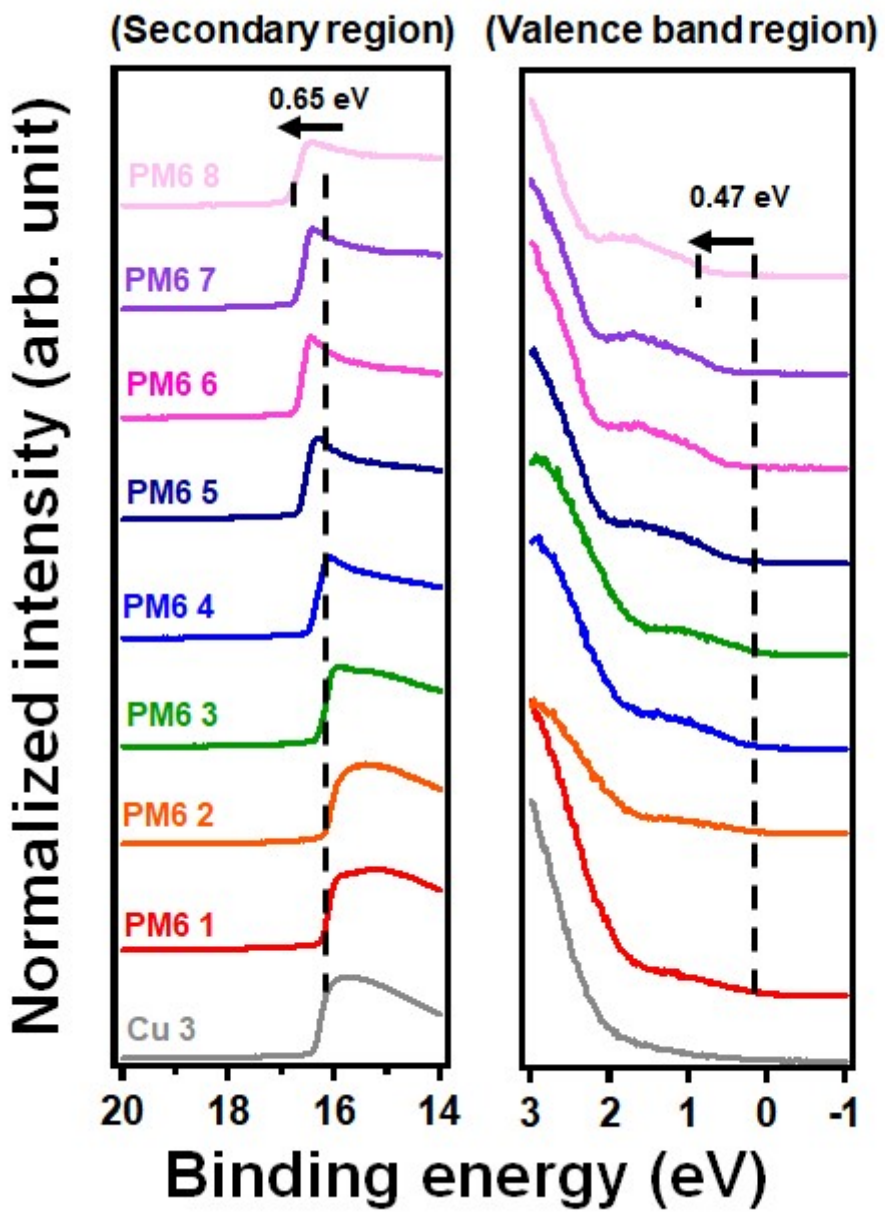


**Figure S7.** UPS spectra of PEDOT:PSS with Cu:PSS (3 wt%) films with different thicknesses deposited on PM6 films.

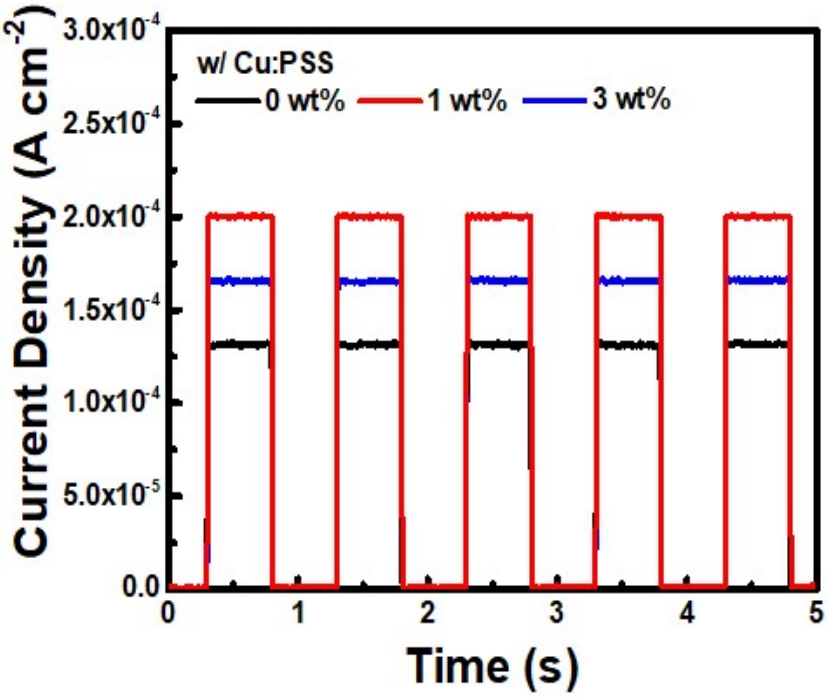


**Figure S8.** LED light source on and off response measurements with multiple cycles for 5 seconds. (LED: 454 nm).

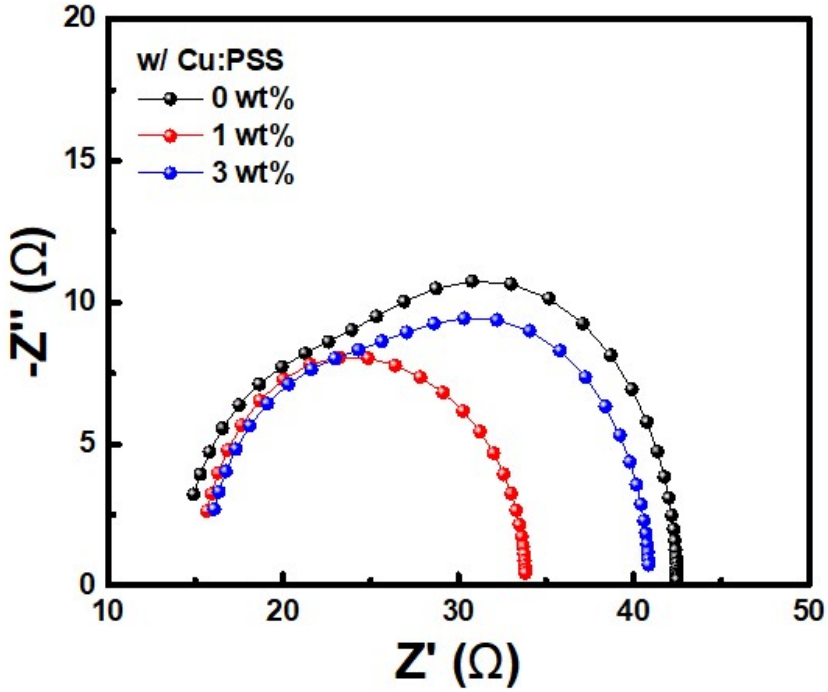


**Figure S9.** Impedance spectroscopy under AM 1.5 G illumination at 100 mW $cm^{-2}$ with sample bias of $V_{OC}$ of the device with different HTLs.

**Table S1.** Energy levels of different thickness of PM6 deposited on ITO/PEDOT:PSS derived

from UPS data.

| | Work function | $E_F$-$E_{HOMO}$ | IP |
|---|---|---|---|
| w/ Cu:PSS (0 wt%) | 4.842 | | |
| PM6 1 (0.39nm) | 4.759 | 0.305 | 5.064 |
| PM6 2 (1.32nm) | 4.764 | 0.313 | 5.077 |
| PM6 3 (2.11nm) | 4.706 | 0.278 | 4.984 |
| PM6 4 (3.54nm) | 4.607 | 0.367 | 4.974 |
| PM6 5 (6.41nm) | 4.493 | 0.477 | 4.97 |
| PM6 6 (9.22nm) | 4.429 | 0.523 | 4.952 |
| PM6 7 (12.06nm) | 4.483 | 0.545 | 5.028 |
| PM6 8 | 4.410 | 0.568 | 4.978 |

**Table S2.** Energy levels of different thickness of PM6 deposited on ITO/PEDOT:PSS with

Cu:PSS (1 wt%) derived from UPS data.

| | Work function | $E_F$-$E_{HOMO}$ | IP |
|---|---|---|---|
| w/ Cu:PSS (1wt%) | 4.949 | | |
| PM6 1 (0.52nm) | 4.959 | 0.199 | 5.158 |
| PM6 2 (1.32nm) | 4.952 | 0.214 | 5.166 |
| PM6 3 (2.51nm) | 4.833 | 0.299 | 5.132 |
| PM6 4 (3.86nm) | 4.689 | 0.303 | 4.993 |
| PM6 5 (6.30nm) | 4.522 | 0.394 | 4.916 |
| PM6 6 (9.86nm) | 4.467 | 0.513 | 4.980 |
| PM6 7 (12.33nm) | 4.481 | 0.539 | 5.020 |
| PM6 8 | 4.458 | 0.578 | 5.036 |

**Table S3.** Energy levels of different thickness of PM6 deposited on ITO/PEDOT:PSS with

Cu:PSS (3 wt%) derived from UPS data.

| | Work function | $E_F$-$E_{HOMO}$ | IP |
|---|---|---|---|
| w/ Cu:PSS (3wt%) | 4.808 | | |
| PM6 1 (0.76nm) | 4.947 | 0.159 | 5.107 |
| PM6 2 (1.51nm) | 4.992 | 0.159 | 5.152 |
| PM6 3 (2.38nm) | 4.855 | 0.284 | 5.138 |
| PM6 4 (3.69nm) | 4.710 | 0.323 | 5.034 |
| PM6 5 (5.08nm) | 4.512 | 0.439 | 4.952 |
| PM6 6 (7.70nm) | 4.463 | 0.489 | 4.952 |
| PM6 7 (13.47nm) | 4.429 | 0.532 | 4.961 |
| PM6 8 | 4.289 | 0.626 | 4.916 |

**Table S4**. XPS survey peak table of the PEDOT:PSS.

| w/ Cu:PSS (0 wt%) | Start BE | Peak BE | End BE | Height CPS | FWHM eV | Area (P) CPS.eV | Area (N) TPP-2M | Atomic % |
|---|---|---|---|---|---|---|---|---|
| Cu2p | 970 | 934 | 927 | 207.12 | 0 | 3595.78 | 3.54 | 0.08 |
| S2p | 174 | 168.81 | 160 | 22348.76 | 2.17 | 59158.1 | 462.63 | 10.32 |
| C1s | 294 | 284.82 | 280 | 128859.94 | 1.25 | 206902.48 | 2901.3 | 64.75 |
| O1s | 540 | 532.26 | 528 | 77292.25 | 2.37 | 195156.86 | 1113.41 | 24.85 |

**Table S5**. XPS survey peak table of the PEDOT:PSS with Cu:PSS (1 wt%).

| w/ Cu:PSS (1 wt%) | Start BE | Peak BE | End BE | Height CPS | FWHM eV | Area (P) CPS.eV | Area (N) TPP-2M | Atomic % |
|---|---|---|---|---|---|---|---|---|
| Cu2p | 970 | 935.6 | 927 | 4476.25 | 3.46 | 45795.65 | 45.12 | 1.01 |
| S2p | 174 | 168.72 | 160 | 23050.37 | 2.16 | 56584.48 | 442.48 | 9.91 |
| C1s | 294 | 284.82 | 280 | 135217.91 | 1.22 | 204413.78 | 2866.41 | 64.2 |
| O1s | 540 | 532.18 | 528 | 87669.76 | 1.9 | 194720.63 | 1110.85 | 24.88 |

**Table S6**. XPS survey peak table of the PEDOT:PSS with Cu:PSS (3 wt%).

| w/ Cu:PSS (3 wt%) | Start BE | Peak BE | End BE | Height CPS | FWHM eV | Area (P) CPS.eV | Area (N) TPP-2M | Atomic % |
|---|---|---|---|---|---|---|---|---|
| Cu2p | 970 | 935.59 | 927 | 7246.03 | 3.56 | 84422.37 | 83.17 | 1.84 |
| S2p | 174 | 168.63 | 160 | 23673.11 | 2.14 | 55783.9 | 436.19 | 9.66 |
| C1s | 294 | 284.77 | 280 | 136615.03 | 1.23 | 205369.22 | 2879.7 | 63.8 |
| O1s | 540 | 532.14 | 528 | 91184.42 | 1.8 | 195344.18 | 1114.37 | 24.69 |