Supporting information

Tunable Electrochemical Doping and Charge Transport in Non-OMIEC:OMIEC Blends by Microstructure Design

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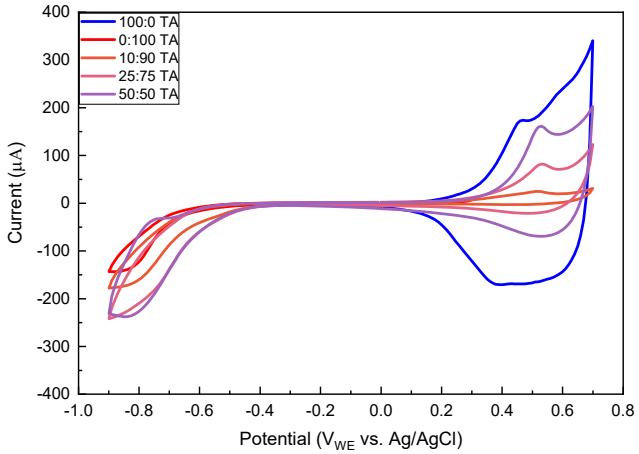

Figure S1: Cyclic voltammetry (CV) of the P3MEEET:$PC_{60}BM$ w:w% thermally annealed (TA) blends. The CV was performed in KCl 0.1M in a 3-electrode setup: FTO-coated glass substrates with the active film on top served as a working electrode (WE), Pt wire served as a counter electrode (CE), and Ag/AgCl pellet as reference electrode (RE). The voltage was applied vs. the RE at a range of +0.7 V<V_{WE}<-0.9 V at a scan rate of 0.1V/s. The voltamogram corresponds to the 10th scan.

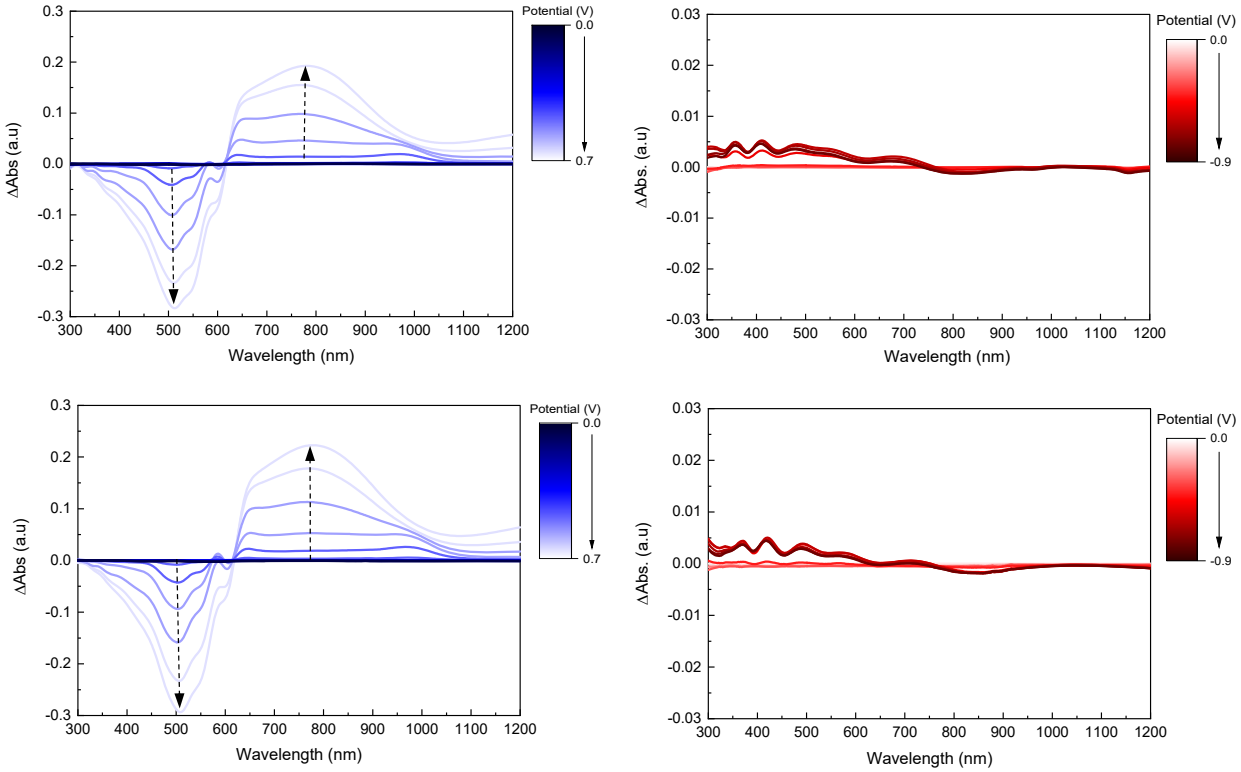

Figure S2: Spectroelectrochemical absorption changes of AC (top) and TA (bottom) films of pristine materials. Blue- P3MEEET; red- $PC_{60}BM$. The changes in absorption are calculated with respect to the spectrum recorded at V=0V, where both materials are undoped.

The polymer (blue curves) shows a gradual change in the absorption peak at ~780 nm, correlated to the formation of a positive polaron, rising on the expanse of the $\pi - \pi^*$ absorption band of the neutral polymer at 500nm-550nm.[1] For the fullerene film (red curves) no significant changes in absorption are seen, confirming that pristine $PC_{60}BM$ doesn't undergo electrochemical doping.

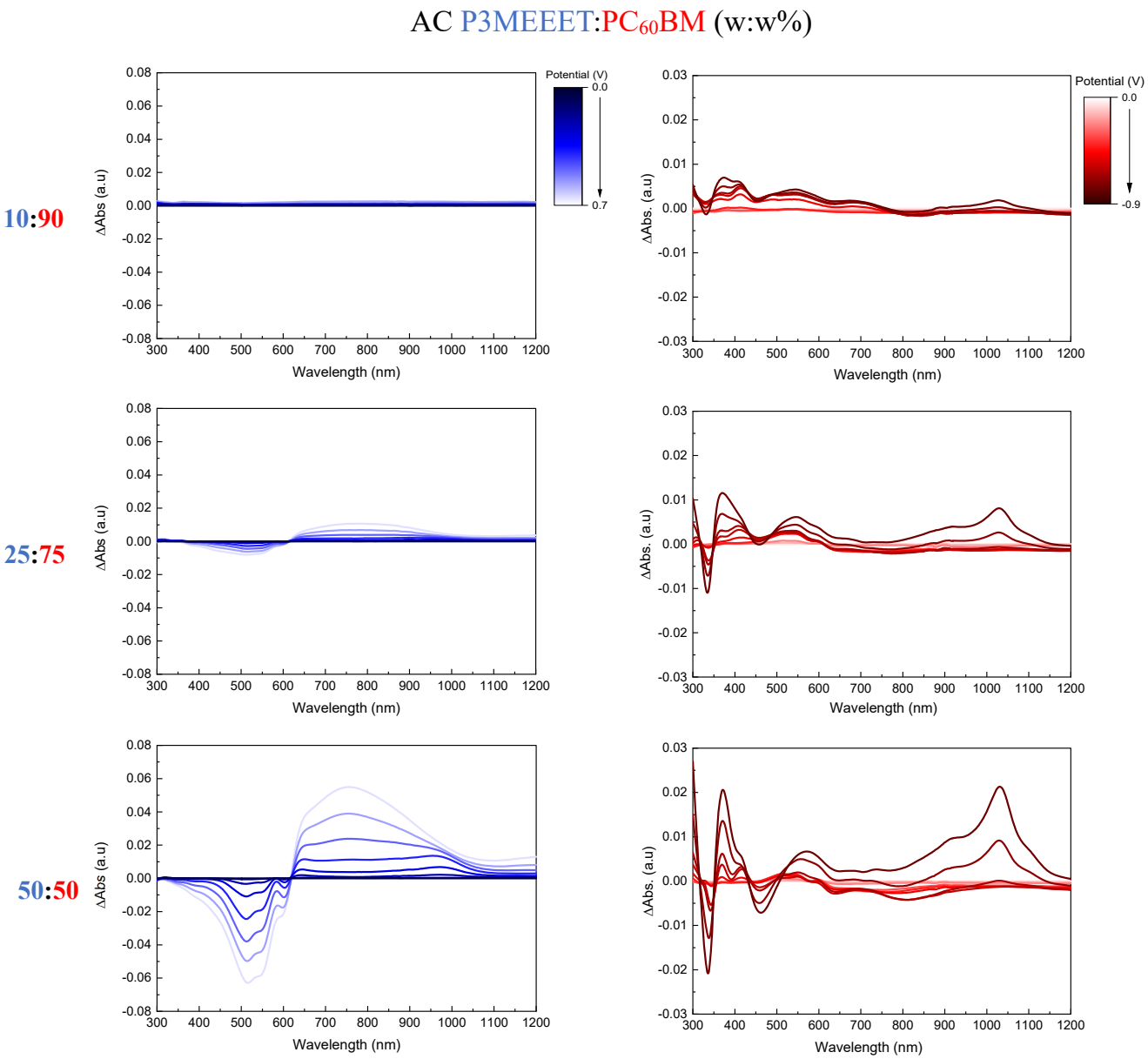

Figure S3: Spectroelectrochemical absorption changes of AC P3MEEET:$PC_{60}BM$ blends, measured at -0.9 to 0.7V (vs. Ag/AgCl) with voltage steps of 0.1V. Blue curves represent absorption changes due to doping of the polymer in the positive bias, while the red curves represent the doping of the fullerene in the negative bias.

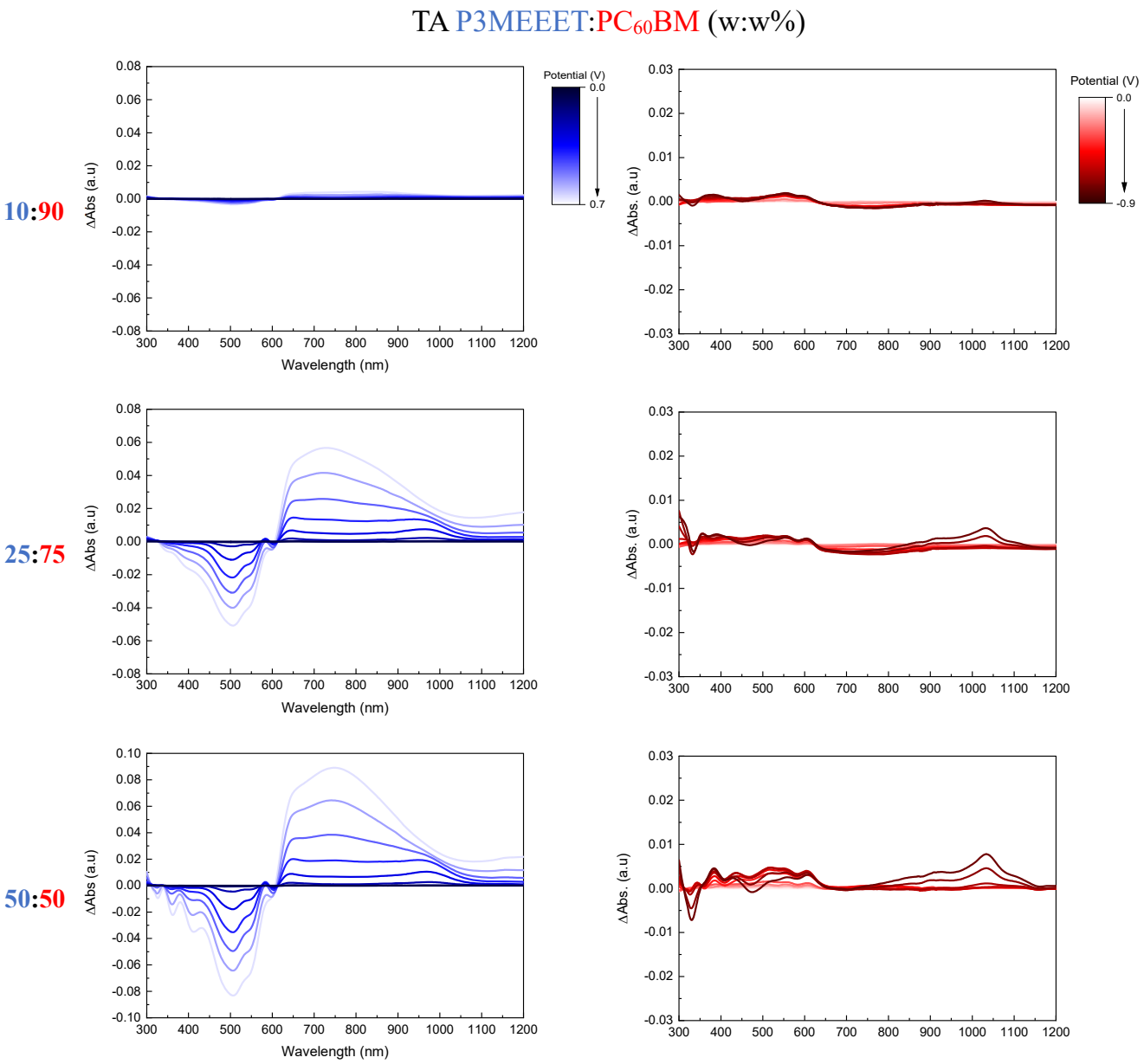

Figure S4: Spectroelectrochemical absorption changes of TA P3MEEET:$PC_{60}BM$ blends, measured at -0.9 to 0.7V (vs. Ag/AgCl) with voltage steps of 0.1V. Blue curves represent absorption changes due to doping of the polymer in the positive bias, while the red curves represent the doping of the fullerene in the negative bias.

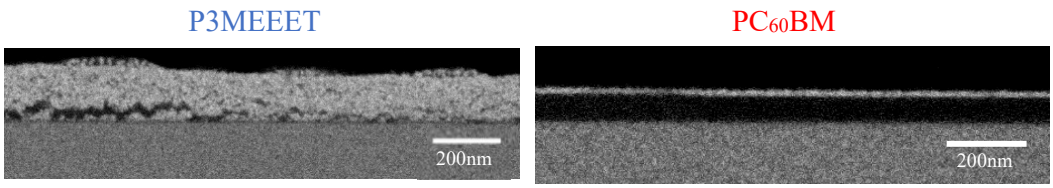

Figure S5: Cross-section BSE HRSEM micrographs of spin-coated pristine P3MEEET and pristine $PC_{60}BM$ films after the VPI staining process.

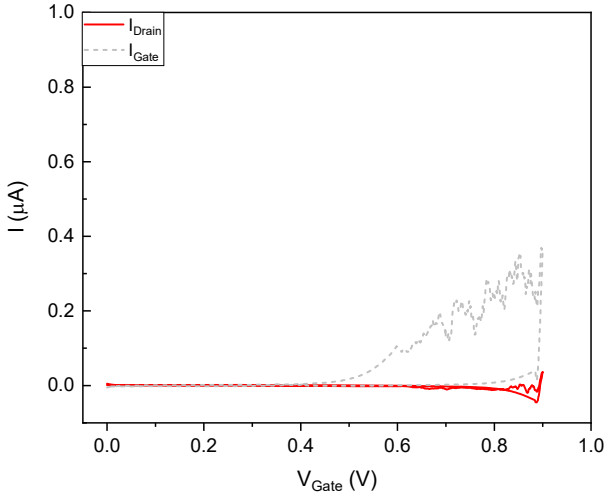

Figure S6: Transfer characteristics of pristine $PC_{60}BM$ AC films in 0.1M KCl. V_D=0.3V; device dimensios W=6000µm, L=30µm.

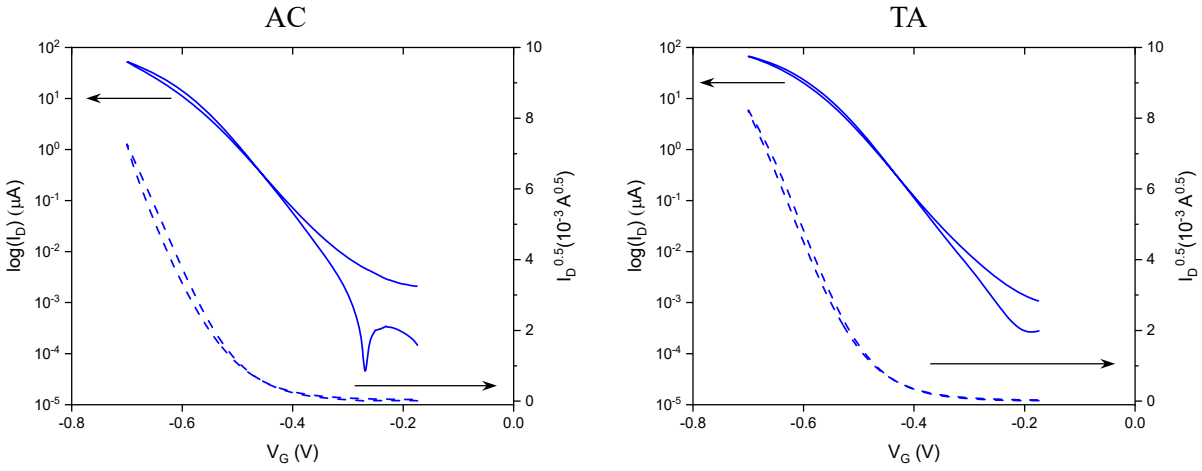

Figure S7: Transfer characteristics of P3MEEET films. Left – AC; Right – TA.

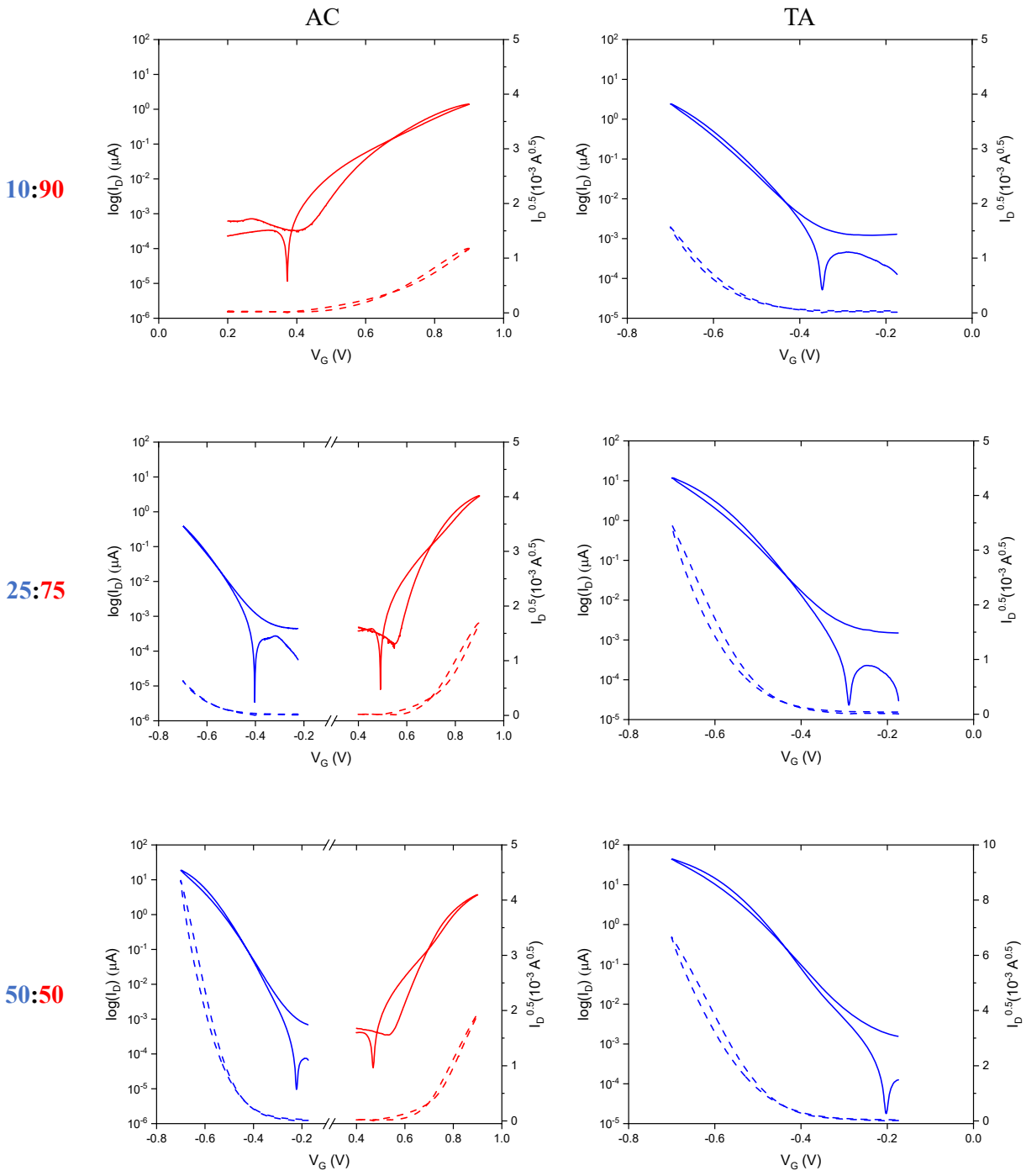

Figure S8: OECT transfer characteristics of AC and TA P3MEEET:$PC_{60}BM$. Blue represents p-type operation, red represents n-type operation. If only p-type or n-type curve is shown, no performance was recorded for the other polarity.

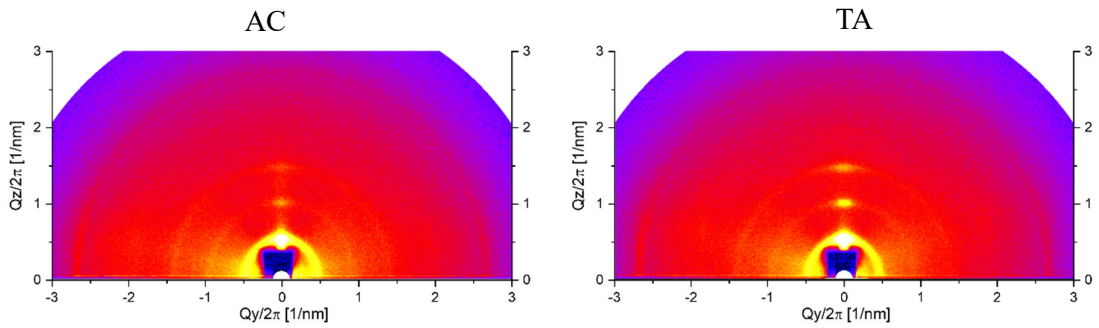

Figure S9: Grazing incidence wide-angle x-ray scattering (GIWAXS) of P3MEEET AC (left) and TA (right) films.

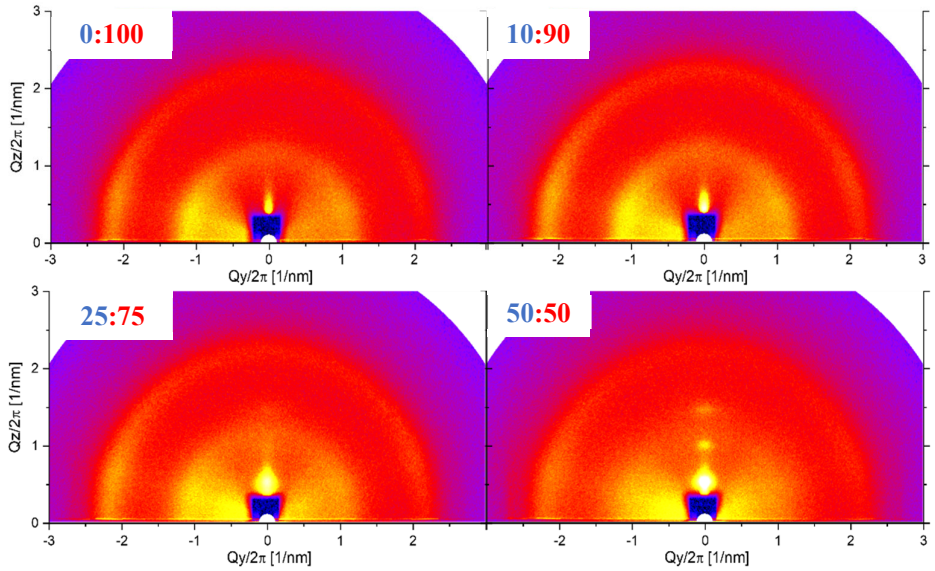

Figure S10: Grazing incidence wide-angle x-ray scattering (GIWAXS) of AC P3MEEET:$PC_{60}BM$ blends in various compositions (10:90 w:w%, 25:75 w:w%, 50:50 w:w%) , compared to pristine an AC $PC_{60}BM$ film (0:100 w:w%).

Table S1: Volumetric capacitance for p-type doping (+0.7V) and n-type doping (-0.9V) as extracted from the effective capacitance at a frequency of 1Hz. For each composition, the calculated value is an average of at least 5 pixels.

Polymer composition (wt%)	**p-type C* ($F \cdot cm^{-3}$)**	**n-type C* ($F \cdot cm^{-3}$)**
0	-	16.9±3.0
10	5.5±1.6	24.6±1.7
25	24.4±8.2	44.4±3.5
50	52.2±4.3	43.2±4.5
100	207.4±8.0	-

The volumetric capacitance of the fullerene was calculated assuming the whole volume of the film contributes to the capacitance. But, as we have seen from the CV and SEC results, $PC_{60}BM$ on its own does not undergo volumetric doping. In addition, Ginger et al. showed that for a thermally annealed film of $PC_{60}BM$ exposed to 0.1M KCl solution, there is almost no mass uptake (ions or water) during doping/de-doping cycles measured by electrochemical quartz crystal microbalance (EQCM).[2] Thus, the C* value for the pristine as-cast fullerene, 17±3 $F \cdot cm^{-3}$, doesn't necessarily reflect the actual capacitive behavior of the film.

To further understand the capacitive ability of the $PC_{60}BM$ film we consider the other extreme, and assume that the only contribution to the capacitance is the formation of an electric double layer (EDL) at the interface of the fullerene film and the electrolyte, suggesting no ion penetration at all, and calculate the double layer capacitance (C_{DL}) by dividing the effective capacitance with the working electrode area, receiving a value of 93±16 $\mu F \cdot cm^{-2}$. This value is one to two orders of magnitude higher compared to typical values of C_{DL} electrolyte gated OFETs, ranging from 1-10 $\mu F \cdot cm^{-2}$,[3] and two orders of magnitude higher compared to the reported capacitance measured for a water-gated organic field effect transistor (WGOFET) based on a $PC_{60}BM$ active layer.[4] Therefore, the accumulation of ions at the film/electrolyte interface is also not a true depiction of the capacitive behavior of the $PC_{60}BM$ working electrode when in contact with an electrolyte. We suggest that pristine as-cast $PC_{60}BM$ acts somehow in between those two descriptions, where it allows some ion penetration thanks to its amorphous nature (Figure S10), but not through the entire bulk of the film.

References

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