

Supporting Information

Calculation of Surface Proportion of 4CPTES and PTES from Infrared Spectrum

The first step in the calculation of the proportion of 4CPTES and PTES on a mixed monolayer surface is to identify integrated intensities from the infrared spectrum which are unique to each modifier (that is, there are no contributions from the other molecule). Figure S1 shows how the two peaks identified in the article can be analyzed to find such integrated intensities. It is assumed that the ratio of A and B in the 4CPTES only sample is characteristic of those modes in 4CPTES and is therefore a constant across the sample set. The contribution (B') of 4CPTES to the peak Γ in mixed samples is then calculated as:

$$\frac{B}{A} = \frac{B'}{A'} \rightarrow A' \frac{B}{A} = B' \quad (\text{S1})$$

B' can then be subtracted from Γ to get the contribution (C') of PTES to Γ :

$$C' = \Gamma - \frac{B}{A} A' \quad (\text{S2})$$

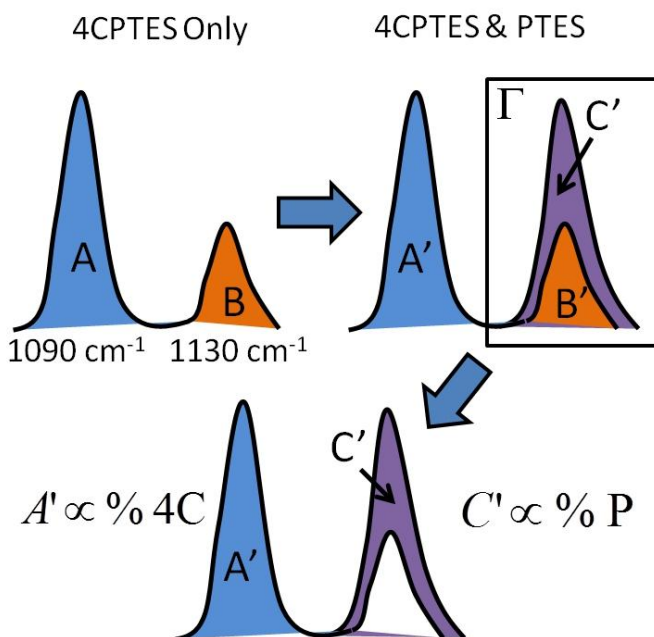


Figure S1: Diagram demonstrating calculation of integrated intensity contributed by PTES to the peak at 1130 cm^{-1} (boxed, labeled Γ). The peak at 1090 cm^{-1} is contributed only by 4CPTES and is not present in PTES only samples, while the peak at 1130 cm^{-1} has contributions from both molecules. Using the 4CPTES-only treated sample, the ratio of the two peaks A and B is taken as constant. Using this constant, the contribution (B') from 4CPTES to the peak Γ in mixed 4CPTES/PTES samples is calculated from the integrated intensity of the peak A' which is contributed by 4CPTES only. B' is subtracted from Γ to find the contribution C' from PTES only.

In this way the integrated intensities unique to each modifier (A': 4CPTES, C': PTES) can be obtained.

Now that characteristic integrated intensities have been obtained for both 4CPTES and PTES they need to be normalized to account for any differences in oscillator strength, bonding orientation, etc. that might contribute to the intrinsic absorptivity of the mode. To begin the process, it is noted that the integrated intensities of the modes A' and C' are proportional to the number of 4CPTES (n_{4C}) and PTES (n_P) molecules on the surface, respectively, through proportionality constants α and γ :

$$A' = \alpha n_{4C} \quad C' = \gamma n_P \quad (\text{S3})$$

It is then assumed for the purposes of this calculation that for the 4CPTES and PTES only samples the number of molecules on the surface is the same (n_{tot}):

$$A = \alpha n_{tot} \quad \& \quad C = \gamma n_{tot} \quad (\text{S4})$$

By dividing A' by A and C' by C, a quantity independent of oscillator strength, etc. can be obtained:

$$\frac{A'}{A} = \frac{n_{4C}}{n_{tot}} \quad \& \quad \frac{C'}{C} = \frac{n_P}{n_{tot}} \quad (\text{S5})$$

If A'/A and C'/C are added, the following is obtained:

$$\frac{A'}{A} + \frac{C'}{C} = \frac{n_{4C} + n_P}{n_{tot}} \quad (\text{S6})$$

$n_{4C} + n_P$ is the total number of molecules on the sample surface and ideally $n_{4C} + n_P = n_{tot}$. However, experimentally this is not the case and there is variation in the total number of molecules on each sample. This is true of the 4CPTES and PTES samples, but the assumption that they have the same number of molecules allows a convenient and robust mathematical formulation for calculating the fraction of each molecule on the surface. To calculate the fraction of each molecule on the surface, simply divide the normalized intensity due to 4CPTES or PTES by the total normalized intensity:

$$\frac{A'/A}{A'/A + C'/C} = \frac{n_{4C}}{n_{4C} + n_P} \quad (\text{S7})$$

$$\frac{C'/C}{A'/A + C'/C} = \frac{n_P}{n_{4C} + n_P} \quad (\text{S8})$$

For each experimental variable (A, A', B, and Γ) needed for the calculation, the average value from all experiments was used. The uncertainty in each variable was taken to be the largest deviation from the average across all the experiments. The uncertainty in C', C and each of the fractions $n_{4C}/n_{4C} + n_P$ and $n_P/n_{4C} + n_P$ was determined from standard propagation of uncertainty.

Water Contact Angle Measurements

Sample	CA (deg.)	Δ CA (deg.)
PTES	50.8	2.4
2:1 P:4C	47.9	2.1
1:2 P:4C	45.6	1.7
4CPTES	42.4	3.3
Control	31.1	1.0

Table S1: Water contact angle (CA) measurements of each of the four surface treatments and the deposition control sample (see experimental section for explanation of this control). The listed contact angle measurements are an average from all experiments. The uncertainty (Δ CA) in the measurements is the mean square average of the uncertainties from each experiment. The uncertainty in each experiment was taken as the standard deviation of multiple measurements of the sample.

Atomic Force Microscopy Measurements

Surface Treatment	RMS Roughness (nm)
Control	1.6 \pm 0.2
PTES	1.2 \pm 0.1
2:1 P:4C	2.0 \pm 0.1
1:2 P:4C	1.7 \pm 0.2
4CPTES	2.0 \pm 0.8

Table S2: RMS roughness determined from topographic scans of treated ZnO surface. Reported values are an average calculated from all scans taken and the uncertainties reported are the standard deviation of the roughnesses.

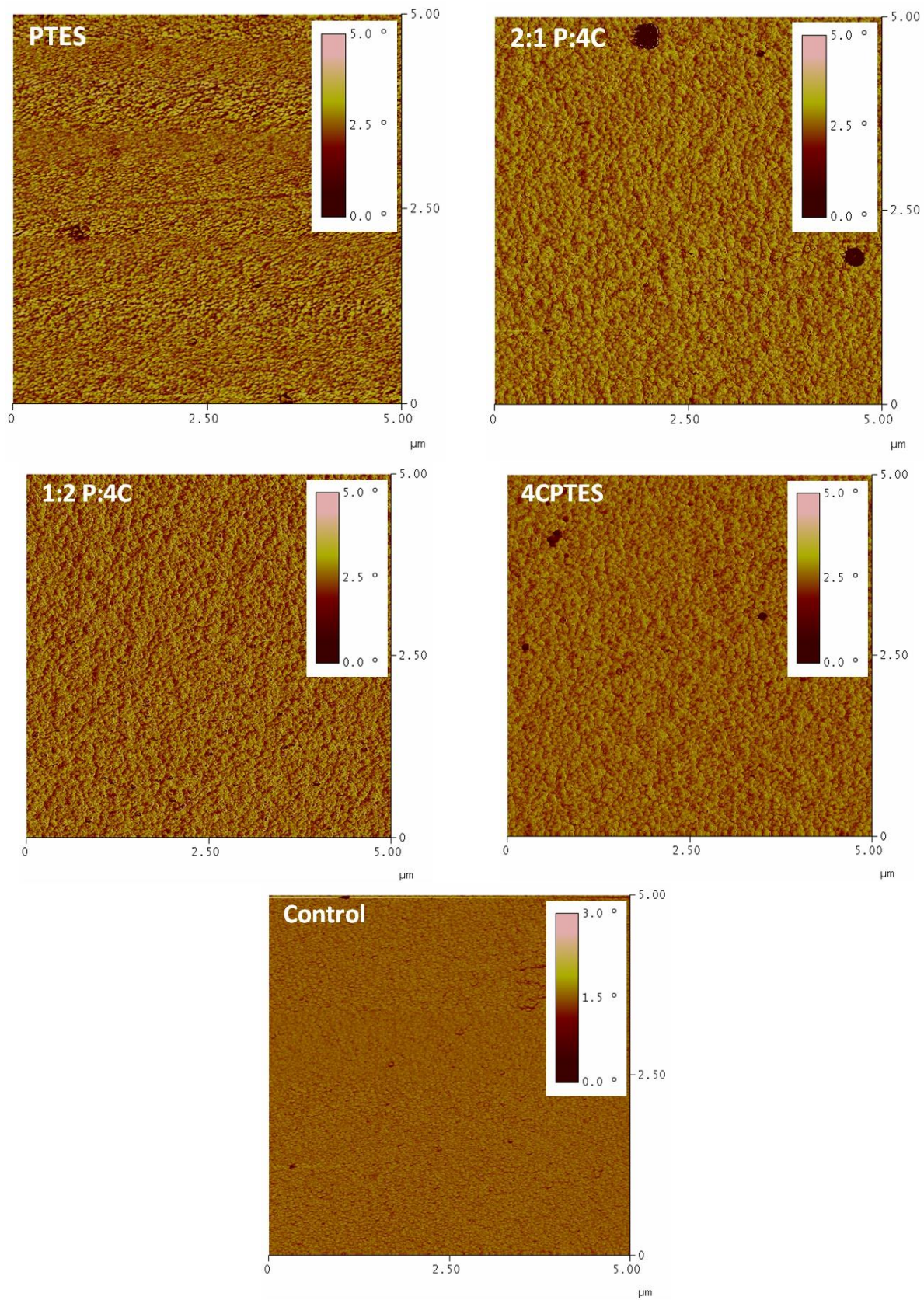


Table S3: AFM phase images of treated ZnO surfaces.

Dark J-V Curves

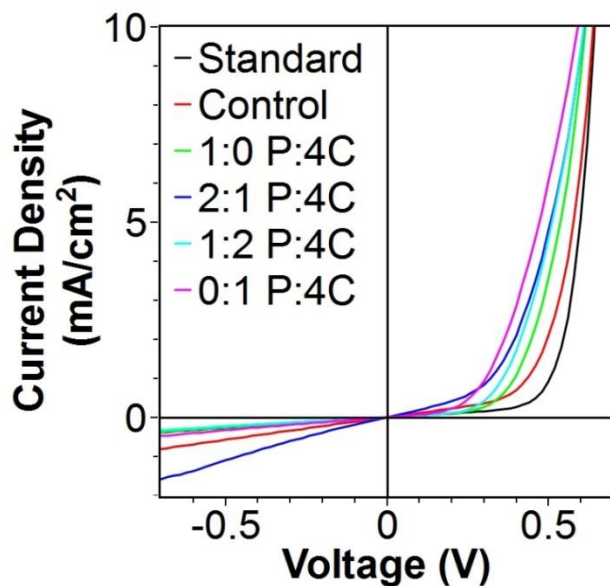


Figure S2: J-V Curves of the treated ZnO P3HT:PCBM devices in the dark.

Sample	R_{sh} ($k\Omega\text{ cm}^2$)
Standard	2.00
Control	0.89
1:0 P:4C	2.10
2:1 P:4C	0.53
1:2 P:4C	2.40
0:1 P:4C	1.62

Table S4: Shunt resistance calculated from the dark J-V curves at $V = 0$.

While there is significant variation in the shunt resistances between treatments, there is no clear trend suggesting that V_{oc} is correlated with shunt resistance in the dark. This is in agreement with Ref. 6 in the main text, who also found no correlation between dark curve shunt resistance and V_{oc} . There is, however, a correlation between the vacuum level shift (contact potential difference) caused by the interface dipole and the diode turn-on voltage as would be expected.

Effect of Light Soaking

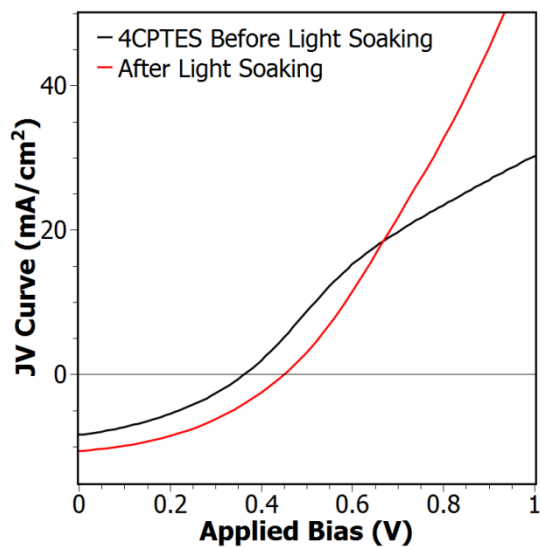


Figure S3: J-V curves of 4CPTES-treated ZnO devices before and after light soaking. A double-diode or s-kink is present before light soaking and is minimized after 20 min. of light soaking. With light soaking, the V_{oc} is correspondingly increased.