Supporting Information

Accurate determination of the index of refraction of polymer blend films by spectroscopic ellipsometry

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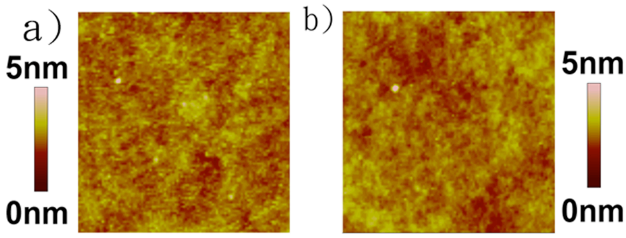

Figure S1 AFM images (2 μm × 2 μm) of P3HT:PCBM films on a) Si and b) glass substrates.

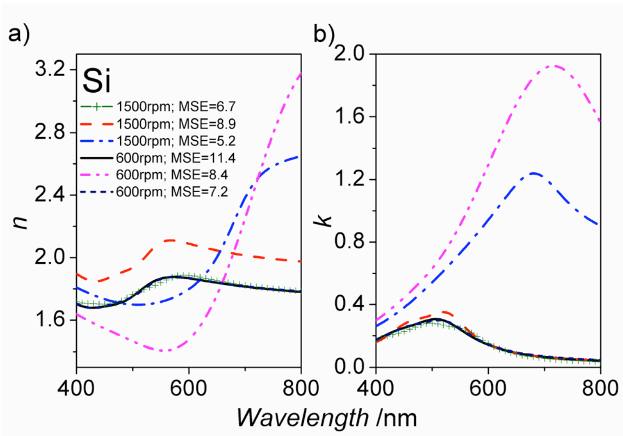

Figure S2. The obtained a) refractive index and b) extinction coefficient values of P3HT:PCBM films from individual fitting of ellipsometry spectra on Si substrate using an oscillator model.

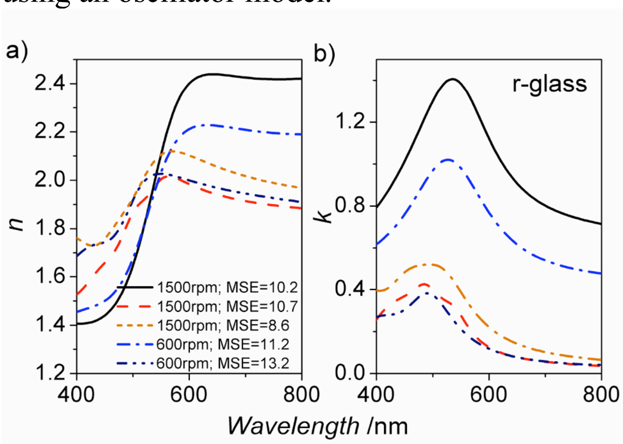

Figure S3. The obtained a) refractive index and b) extinction coefficient values of P3HT:PCBM films from individual fitting of ellipsometry spectra on r-glass substrate using an oscillator model.

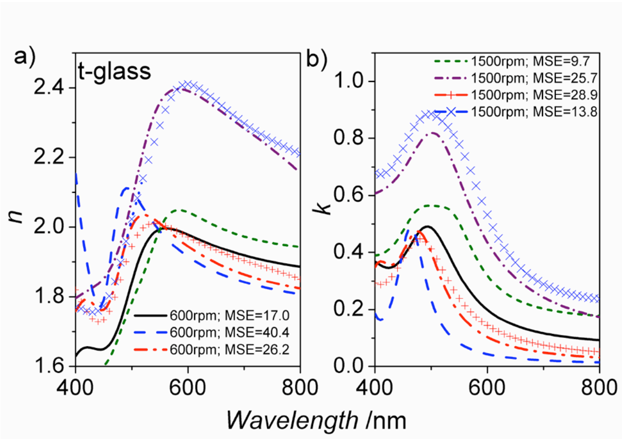

Figure S4. The obtained a) refractive index and b) extinction coefficient values of P3HT:PCBM films from individual fitting of ellipsometry spectra on t-glass substrate using an oscillator model.

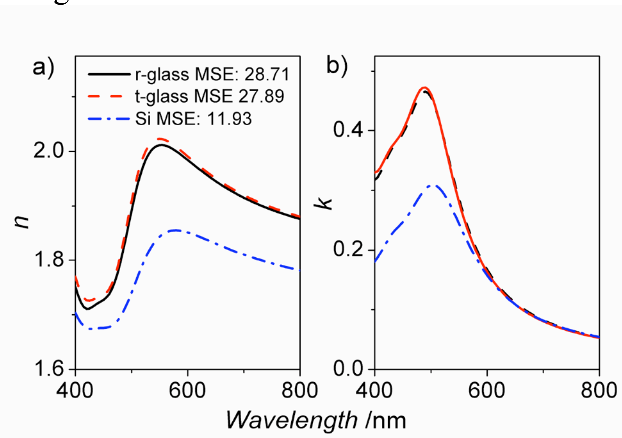

Figure S5. The obtained a) refractive index and b) extinction coefficient values of P3HT:PCBM films from fitting all available data on different substrates.

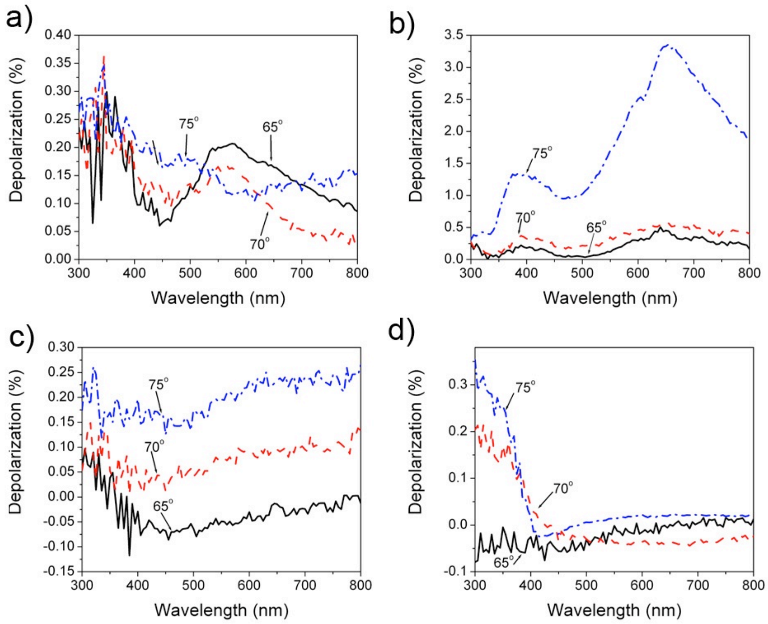

Figure S6 Depolarization spectra for P3HT:PCBM films on a) glass b) Si. Depolarization spectra of individual substrates c) glass and d) Si are also given.

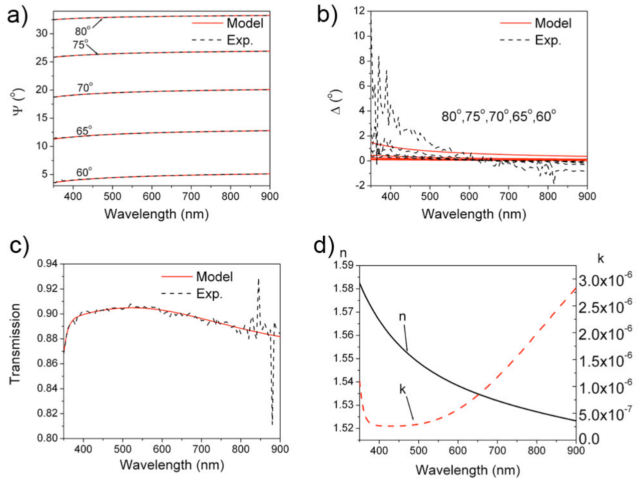

Figure S7 a), b) Spectroscopic ellipsometry and c) transmission data (comparison of model and experiment) and d) obtained *n* and *k* values for glass substrate.

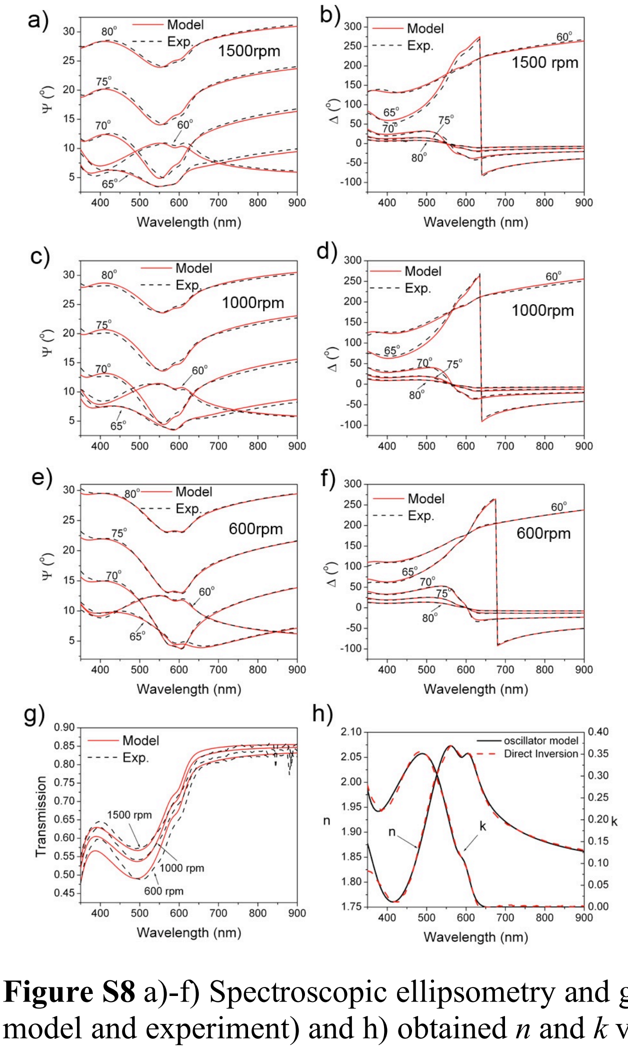

Figure S8 a)-f) Spectroscopic ellipsometry and g) transmission data (comparison of model and experiment) and h) obtained *n* and *k* values of P3HT:PCBM films for RAE data with GOM Model (with EMA layer for surface roughness). MSE=6.84. Direct inversion *n* and *k* values are also shown for comparison.

Table 1 GOM model parameters of P3HT:PCBM films, corresponding to the fit shown in Fig. S8.

Oscillator type	MSE	6.84
	$\varepsilon_{1\infty}$	2.59±0.02
T-L Oscillator 1	Amp (eV^2)	27±1
	C (eV)	0.75 ±0.01
	En (eV)	2.242 ± 0.008
	Eg (eV)	1.89±0.01
Gaussian Oscillator 2	F_2 (eV^2)	0.16±0.01
	Γ_2 (eV)	0.100±0.009
	ω_2 (eV)	2.074±0.003
Gaussian Oscillator 3	F_3 (eV^2)	1.80±0.06
	Γ_3 (eV)	0.82±0.05
	ω_3 (eV)	4.12±0.05

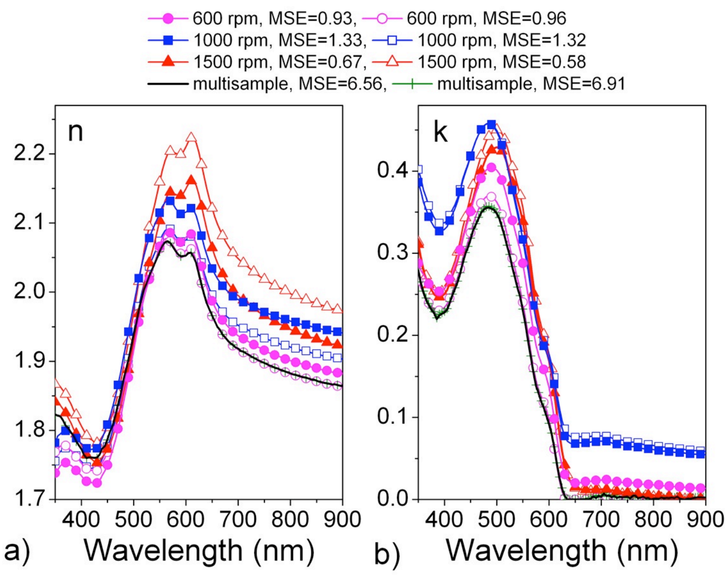

Figure S9 Fitting results for a) n and b) *k* obtained by direct inversion of data for individual samples and for multisample fit (RAE data with EMA). The solid line and closed symbols indicate data fitting both ellipsometry and transmission data, open symbols and dashed line with "+"symbols indicate fitting ellipsometry data only. It can be observed that for single sample fitting there are significant differences in obtained values with and without transmission data, while for multisample fit similar values are obtained. Therefore, multisample analysis is advisable to be performed if circumstances permit (films with different thickness can be prepared and the optical functions do not exhibit significant thickness dependence). While obtaining a good fit is more difficult for multisample analysis, it is more likely that the obtained solution represents a good description of the optical properties of the material.

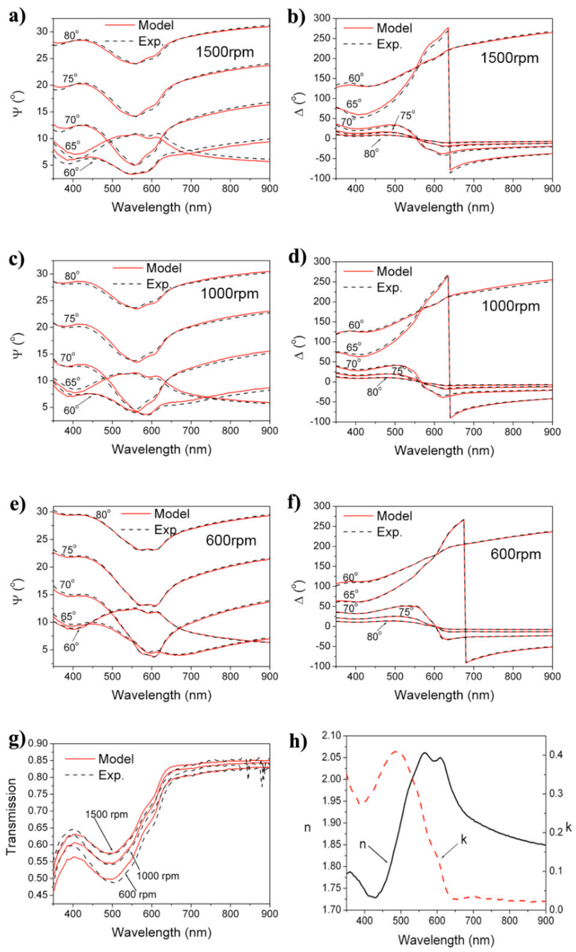

Figure S10 a)-f) Spectroscopic ellipsometry and g) transmission data (comparison of model and experiment) and h) obtained *n* and *k* values for RAE data of P3HT:PCBM using a model that does not include a EMA to describe the surface roughness. MSE=6.91.

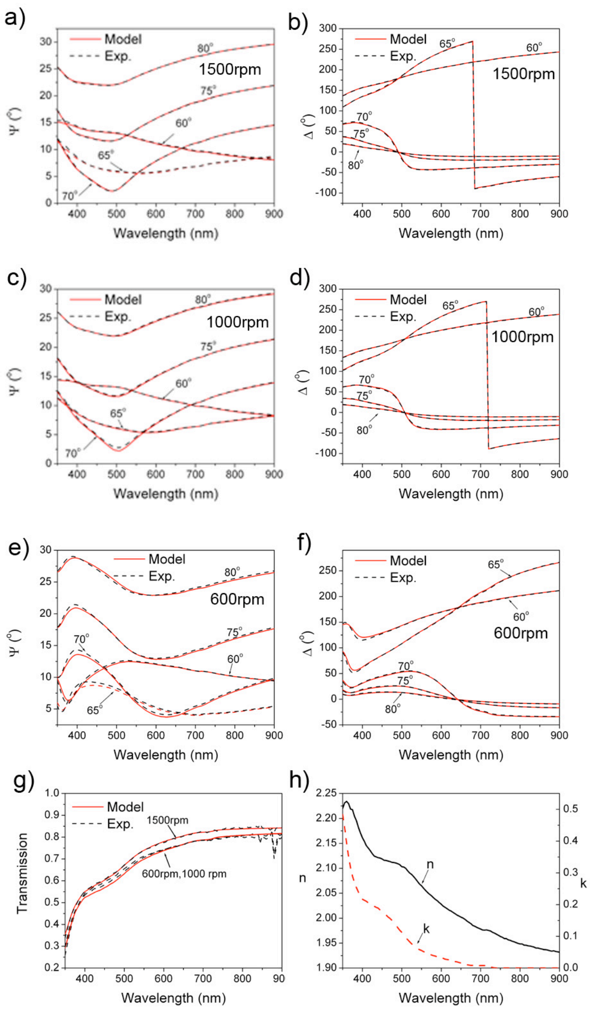

Figure S11 a)-f) Spectroscopic ellipsometry and g) transmission data (comparison of model and experiment) and h) obtained *n* and *k* values for RAE data for PCBM. MSE=4.53.

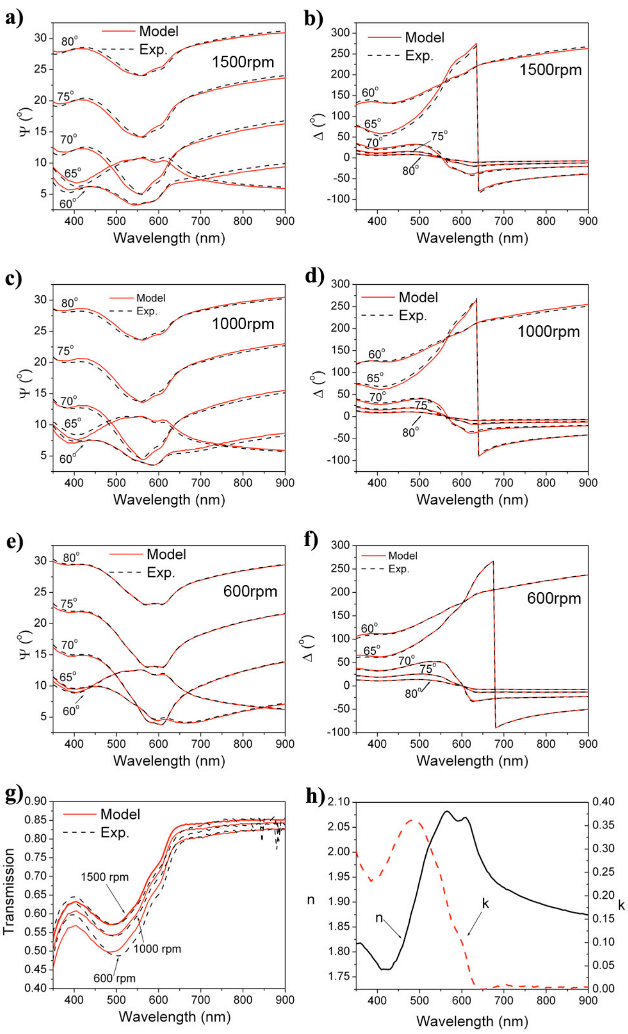

Figure S12. a)-f) Spectroscopic ellipsometry and g) transmission data (comparison of model and experiment) and h) obtained *n* and *k* values for RAE data of P3HT:PCBM using a model that includes a EMA (PCBM only, 50%) to describe the surface roughness. MSE=6.49.

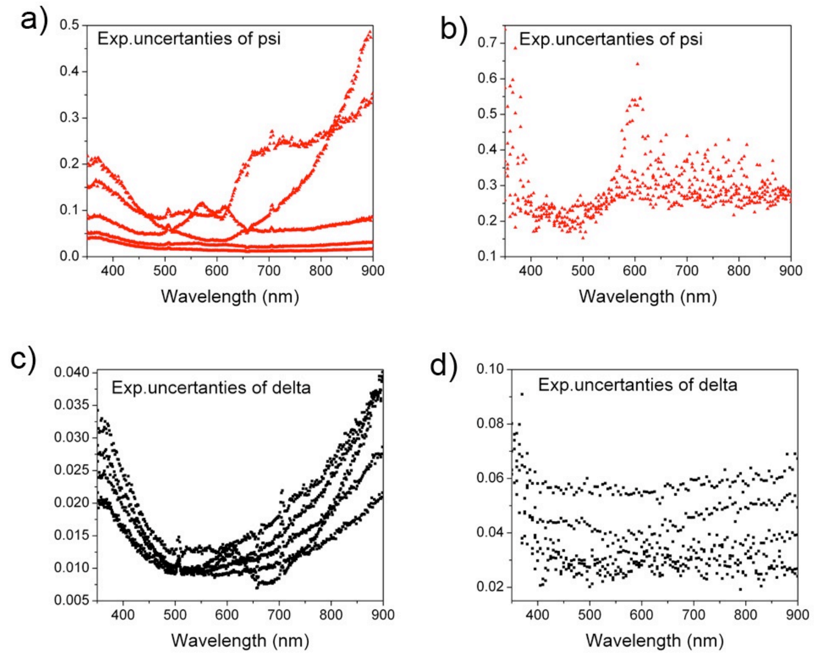

Figure S13 Experimental uncertainties for a),c) RCE b), d) RAE.

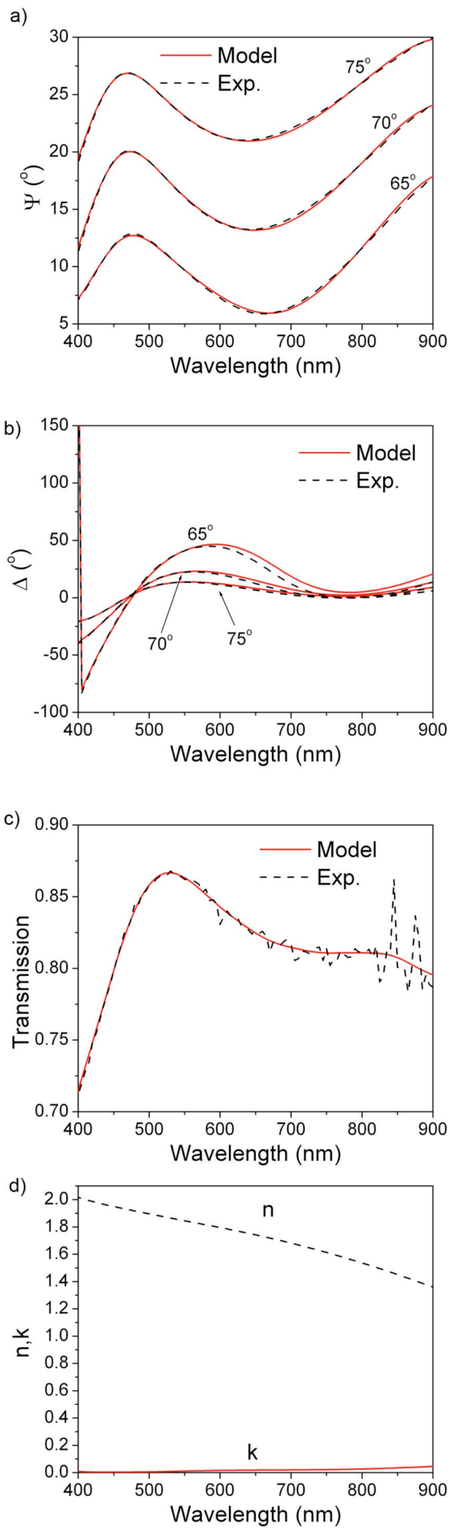

Figure S14 a), b) Spectroscopic ellipsometry and c) transmission data (comparison of model and experiment) and d) obtained *n* and *k* values for RAE data for ITO. Obtained MSE value was 6.95. The data are in good agreement with previous report,[44] even though in our case graded layer was not needed to obtain a good fit. It should be noted that the optical functions of ITO will be dependent on the deposition conditions and hence substrates from different providers may exhibit differences in *n* and *k.* For consistent device modeling, it is recommended that the ITO substrates used are characterized first, rather than taking the data from the literature.

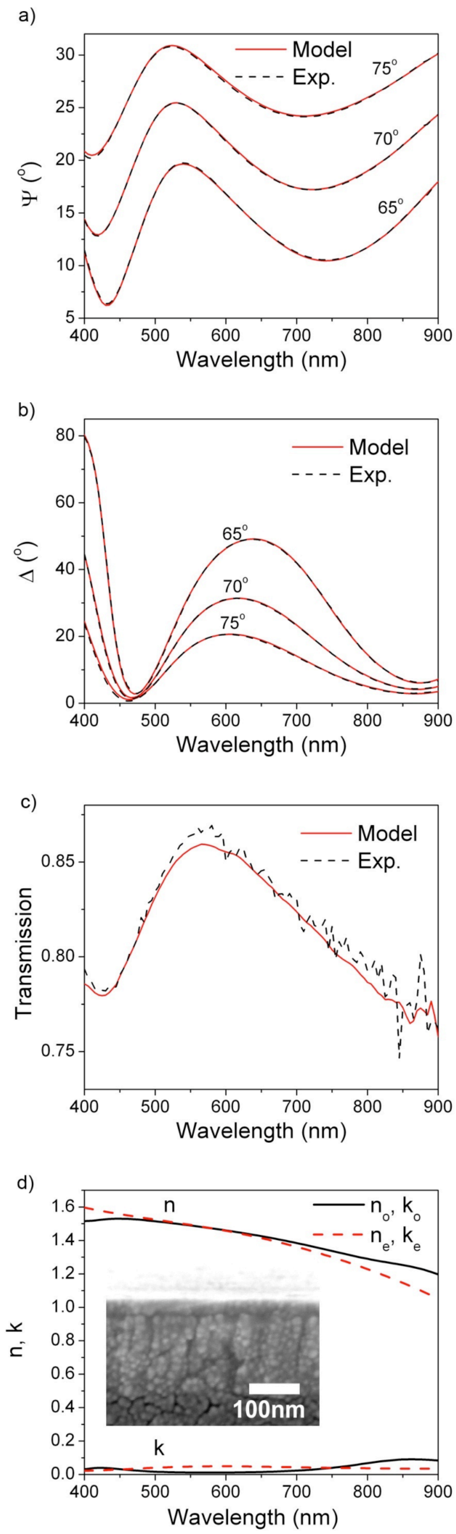

Figure S15 a), b) Spectroscopic ellipsometry and c) transmission data (comparison of model and experiment) and d) obtained *n* and *k* values for RAE data for PEDOT:PSS. The inset shows the SEM cross-section image of PEDOT:PSS on ITO/glass. Obtained MSE value is 1.69, and the obtained thickness values were 41.6 nm for the ellipsometry sample and 37.8 nm for the transmission sample (samples are spincoated under same conditions on two different substrates since rough back surface glass is needed for ellipsometry). This is in good agreement with thickness estimate from SEM for PEDOT:PSS on ITO/glass spincoated under identical conditions, which is ~37 nm. The obtained values of *n* and *k* are different compared to those reported in the literature,[45] but it should be noted that the literature data have been derived for much thicker PEDOT films which were polymerized after coating the monomer solution, rather than spin-coating the commercial PEDOT:PSS for solar cell applications. Such significant difference in the sample preparation could result in a significant difference of sample properties. The conductivity of samples reported in Ref.[45] is 480 S/cm, while the resistivity of PEDOT:PSS Baytron PVP AI 4083 is 500-5000 Ω/cm. Due to large difference in the electronic properties, significant differences in the optical properties, especially at longer wavelengths, would be expected. It should also be noted that in this case we performed the fitting for a device structure, i.e. PEDOT:PSS/ITO/glass. It is expected that improved estimate of the optical functions of PEDOT:PSS could be obtained by a rigorous multisample analysis as that performed for P3HT:PCBM, but this is beyond the scope of this paper.