Supporting Information

Aqueous Nanoparticle Polymer Solar Cells: Effects of Surfactant Concentration and Processing on Device Performance

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1. SDS migration to film-air interface

Dispersions have been processed on a glass/PEDOT:PSS substrate with different concentrations of SDS. The SDS concentration in the dispersion was varied by removing it from the dispersion using centrifugal dialysis tubes and further removal could be achieved by washing the spin coated layer in a water-ethanol mixture. AFM height images showed clear morphology changes, after several dialysis steps and subsequent washing, ultimately revealing the fine NP morphology (Figure S1). Before removal of the SDS, large structures are visible covering the NP surface. Moreover, a phase shift can be observed between active layers covered with SDS and active layers processed after dialysis and washing indicating compositional changes on the surface. This is in line with a shift in contact angle from approximately 26° without SDS removal, to 62° after centrifugal dialysis, and 106° after washing the active layer. The latter is similar to a chloroform:*o*-DCB processed BHJ. This experiment was performed on PEDOT:PSS covered substrates to overcome the wettability problem of high SDS containing dispersions on PEIE, although these regular configuration solar cells were not working. When a low SDS containing dispersion was spin coated on PEIE the washing step appeared to be necessary to obtain a good layer morphology. When the active layer was directly annealed at 140 °C without performing the washing step, large aggregate structures appeared on the surface due to the agglomeration of the residual SDS molecules. This was also observed by Scalarone *et al.*[1] By performing a washing step in between the drying and annealing of the active layer the SDS could be efficiently removed from the surface as these aggregates are not visible in Figure S2b. This active layer has a rout mean square roughness of 6.3 nm.

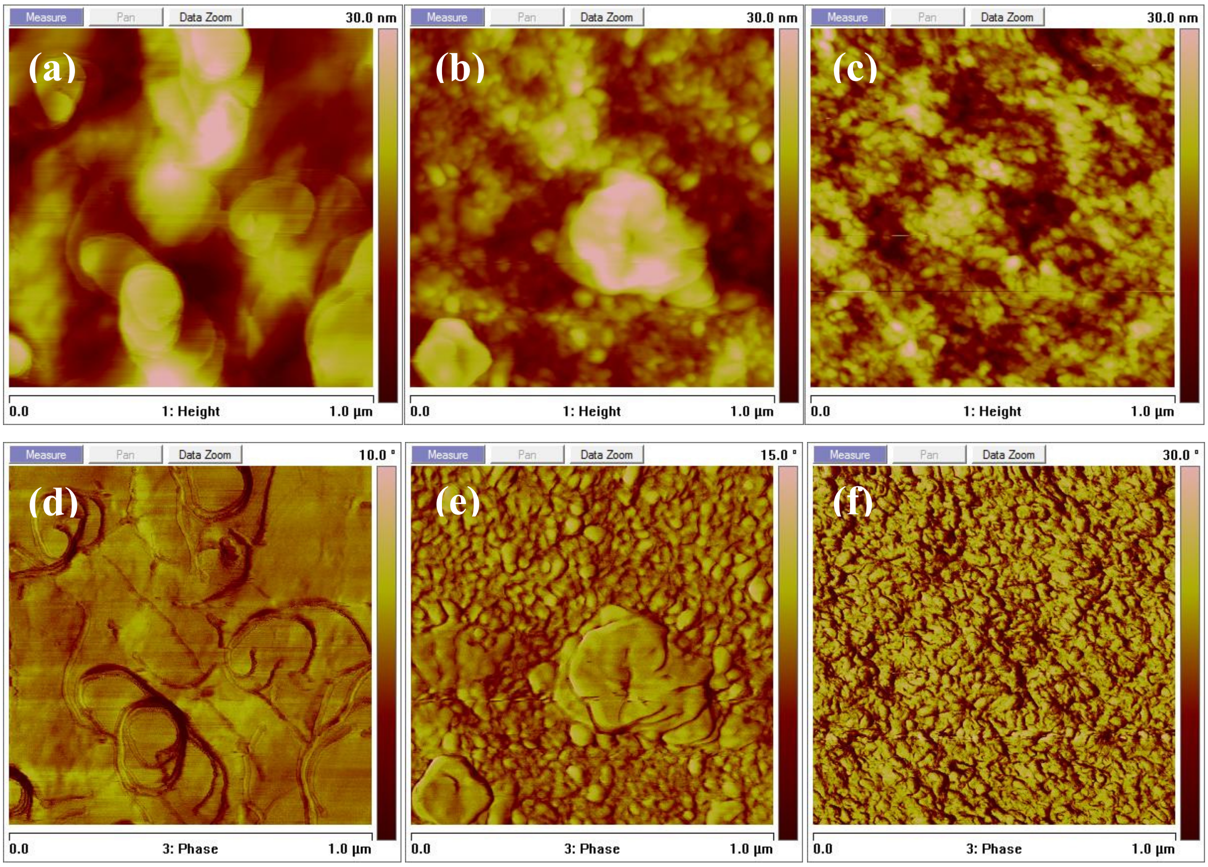

Figure S1. AFM height (a-c) and phase (d-f) images of PDPP5T:[60]PCBM NP dispersions spin coated on a PEDOT:PSS coated glass substrate and subsequently dried for 5 min. at 110°C without dialysis (a, d), after 10 centrifugal dialysis steps (b, e), and after 10 centrifugal dialysis steps and subsequent washing of the active layer in a 50:50 water/ethanol mixture (c, f).

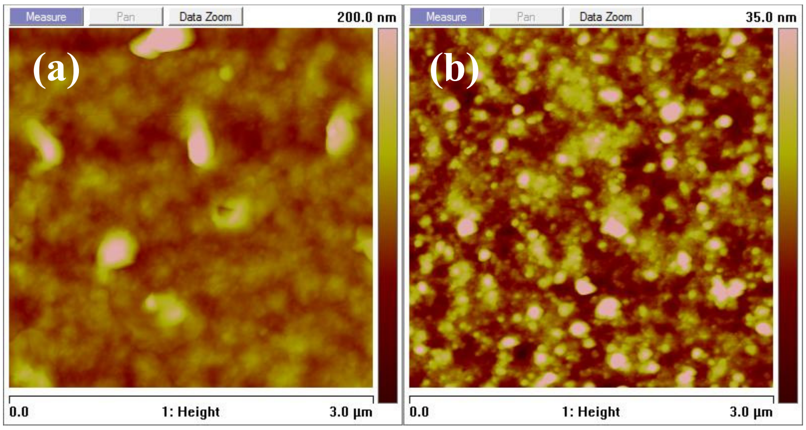

Figure S2. AFM height images of PDPP5T:[60]PCBM layers spin coated on PEIE. The layers are dried at 110°C, thermally annealed at 140°C, and measured without (a) and with (b) washing of the active layer in a water/ethanol mixture.

2. Performance of solar cells processed on ZnO versus PEIE

Devices were fabricated with ZnO and PEIE as electron transporting layer (ETL). Devices on PEIE were more reproducible and therefore further optimization has been done for these devices only. The highest achieved PCEs obtained from NPs synthesized with a starting SDS concentration of 41.2 mM, are similar for both device configurations. The device on ZnO was processed from a 20 v/v% EtOH containing dispersion while the dispersion used for the PEIE device has been aged for one day.

Table S1. Device parameters for optimized cells with ZnO and PEIE as ETL.[a]

d (nm)	ETL	$J_{\mathrm{SC,\,EQE}}$ (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
46	ZnO	7.30	0.54	0.44	1.71
66	PEIE	7.21	0.51	0.53	1.98

[a] NPs have been synthesized utilizing a starting SDS concentration of 41.2 mM.

3. Effect of annealing on BHJ

Annealing at 140 °C for 10 min. is necessary to merge the NPs together and improve the charge transport of NP solar cells. The same procedure lowers the performance of the chloroform:*o*-DCB processed BHJs, where $P_{\max}$ decreases from 5.1 mW/cm^2 to about 4.2 mW/cm^2 after annealing. This is mainly caused by a decrease in current density and FF as is shown in Figure S3.

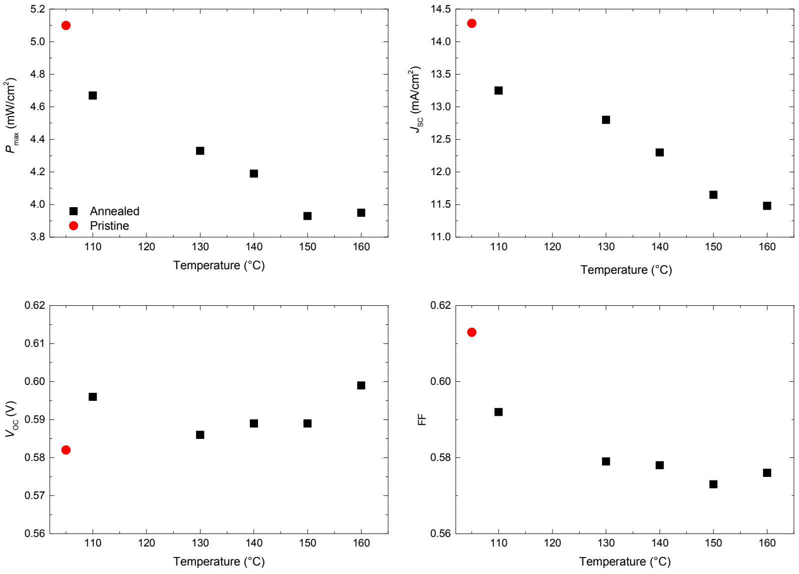

Figure S3. Effect of annealing on the solar cell parameters of a PDPP5T:[60]PCBM BHJ.

4. Modelling of absorption spectra: *n* and *k* values

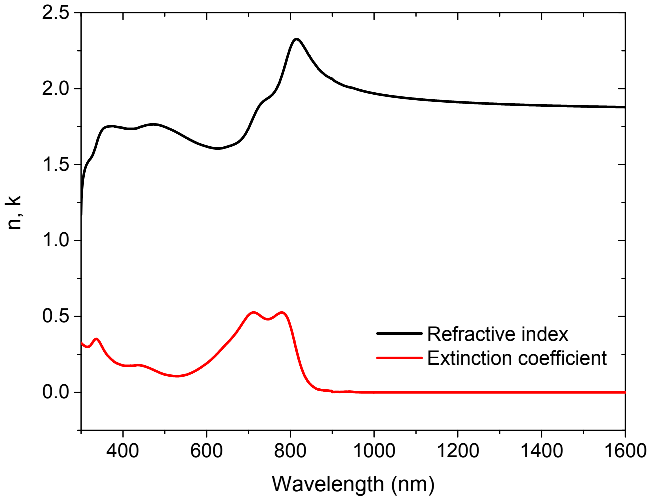

Figure S4. Refractive index (black line) and extinction coefficient (red line) of the active layer containing PDPP5T and [60]PCBM in a 1:2 ratio processed from chloroform with 4.8 vol.% *o*-DCB.

5. Effect of layer thickness on device performance: device statistics

NPs were spin coated into an inverted device structure without aging of the dispersion.

Table S2. Device statistics of solar cells made with different thickness.[a,b]

d (nm)	# cells[c]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
47	4	4.88±0.12 (4.99)	0.53±0.002 (0.53)	0.55±0.003 (0.54)	1.41±0.03 (1.44)
51	4	5.38±0.06 (5.43)	0.55±0.002 (0.55)	0.53±0.002 (0.53)	1.57±0.01 (1.58)
60	3	6.48±0.18 (6.44)	0.53±0.03 (0.55)	0.49±0.02 (0.51)	1.71±0.11 (1.80)
68	4	7.03±0.18 (7.20)	0.55±0.001 (0.56)	0.44±0.005 (0.45)	1.73±0.04 (1.79)
93	3	6.60±0.13 (6.74)	0.50±0.10 (0.55)	0.38±0.08 (043)	1.28±0.50 (1.59)

[a] Average ± standard deviation (highest value). [b] NPs have been synthesized utilizing a starting SDS concentration of 20.3 mM. [c] Number of working cells out of four tested.

6. Induced leakage by rough active layers

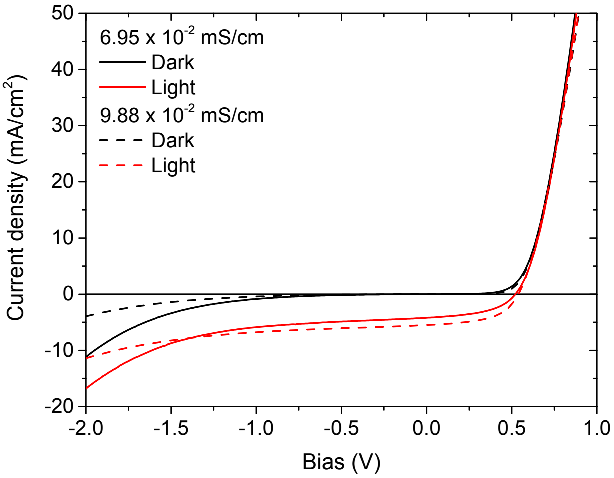

Figure S5. *J–V* characteristics of solar cells in dark (black lines) and light (red lines) processed from two different dispersions having a conductivity of 6.95 × 10^{-2} mS/cm (solid lines) and 9.88 × 10^{-2} mS/cm (dashed lines).

7. Optimizing the dispersion conductivity: device statistics

Table S3 shows that many shorted devices have been fabricated when the SDS concentration was too high and the conductivity was above 1 mS/cm. This was caused by the de-wetting of the dispersion on the PEIE coated ITO substrate. By optimizing the conductivity, the amount of shorted devices could be reduced, however, not prevented. Table S4 shows that when the SDS concentration is too low the performance of the solar cell is not optimal due to a high leakage current.

Table S3. Device statistics of NP solar cells from dispersions with different conductivity.[a,b]

κ (mS/cm)	Aggregation	# cells[c]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
6.95×10^{-2}	Yes	3/4	4.09±0.12 (4.20)	0.50±0.03 (0.52)	0.43±0.05 (0.48)	0.88±0.16 (1.05)
7.19×10^{-2}	Slightly	4/4	5.63±0.15 (5.72)	0.50±0.01 (0.51)	0.48±0.01 (0.49)	1.33±0.09 (1.42)
9.88×10^{-2}	No	2/4	5.62±0.18 (5.75)	0.53±0.003 (0.55)	0.51±0.01 (0.51)	1.56±0.08 (1.61)
1.28×10^{-1}	No	0/20	Shorted			
1.47×10^{-1}	No	0/16	Shorted			
2.06×10^{-1}	No	0[d]				

[a] Average ± standard deviation (highest value). [b] NPs have been synthesized utilizing a starting SDS concentration of 20.3 mM. [c] Number of working cells / number of cells tested. [d] The dispersion was not wetting at all on the substrate and no layer could be formed.

Table S4. Device statistics on the solar cells prepared from the dispersion having a conductivity of 6.95×10^{-2} mS/cm.

Thickness (nm)	# cells[a]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
34	4	Shorted			
39	4	Shorted			
41	3	4.09±0.12 (4.20)	0.50±0.03 (0.52)	0.43±0.05 (0.48)	0.88±0.16 (1.05)
47	1	4.10	0.33	0.33	0.45
51	4	4.76±0.15 (4.92)	0.42±0.03 (0.44)	0.36±0.02 (0.38)	0.71±0.09 (0.81)

[a] Number of working cells out of four tested.

Table S5. Device statistics on the solar cells prepared from the dispersion having a conductivity of 9.88×10^{-2} mS/cm.

Thickness (nm)	# cells[a]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
32	4	Shorted			
37	2	4.84±0.49 (5.18)	0.54±0.00 (0.54)	0.53±0.02 (0.51)	1.39±0.09 (1.45)
39	2	5.62±0.18 (5.75)	0.53±0.003 (0.55)	0.51±0.01 (0.51)	1.56±0.08 (1.61)
47	1	5.32	0.52	0.46	1.27

[a] Number of working cells out of four tested.

8. Determining the optimal conductivity for small NPs

An optimal conductivity of 9.88×10^{-2} mS/cm was found for NPs synthesized from a starting SDS concentration of 20.3 mM. When increasing the SDS concentration to 41.2 mM, NPs of about 34 nm could be synthesized instead of 42 nm. Due to the decrease in size and the concomitant increase in surface area more SDS is required to obtain a stable dispersion. Therefore also the conductivity level at which aggregation and wetting are balanced will be at a higher value. To optimize the processing of solar cells made from these small NPs, device performance was measured with respect to the conductivity of the dispersion. An optimal conductivity of $\sim 1.9 \times 10^{-1}$ mS/cm was found (Table S4).

Table S6. Performance of NP solar cells made from dispersions with different conductivity.[a]

κ (mS/cm)	Aggregation	#cells[b]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
1.01×10^{-1}	Yes	1	4.72	0.47	0.47	1.04
1.31×10^{-1}	Yes	3	4.72± 0.05 (4.69)	0.38±0.01 (0.39)	0.41±0.01 (0.42)	0.74±0.03 (0.77)
1.69×10^{-1}	Yes	1	5.83	0.50	0.42	1.24
1.86×10^{-1}	No	2	5.71± 0.02 (5.72)	0.51± 0.01 (0.52)	0.41±0.02 (0.43)	1.21±0.08 (1.27)
2.27×10^{-1}	No	1	5.40	0.41	0.38	0.84
2.98×10^{-1}	No	1	5.42	0.46	0.39	0.98

[a] Average ± standard deviation (highest value). [b] Number of working cells out of four tested.

9. Absorbance of a PDPP5T:[70]PCBM dispersion

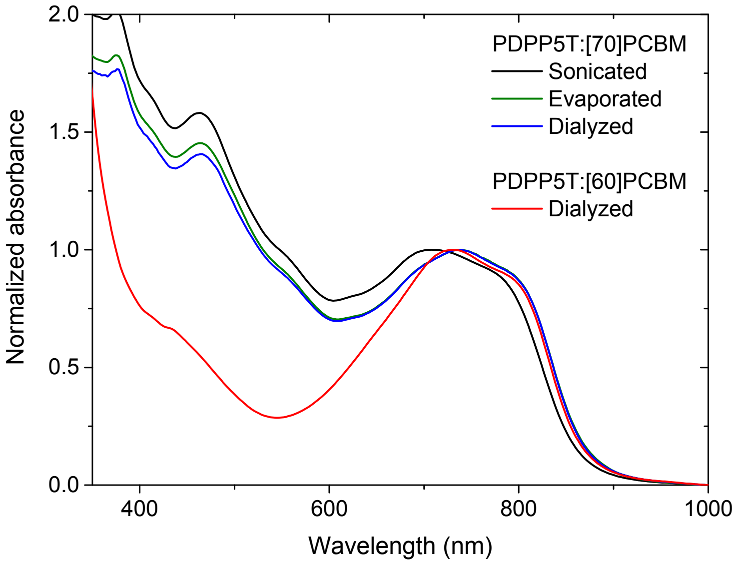

Figure S6. Absorbance (normalized) spectra of a PDPP5T:[70]PCBM dispersion after sonication (black line), chloroform evaporation (green line), and after dialysis (blue line) compared to the dialyzed PDPP5T:[60]PCBM dispersion after dialysis (red line).

10. [70]PCBM as acceptor material: device statistics

Table S7. Devices statistics for PDPP5T:[70]PCBM NP solar cells.[a]

d (nm)	#cells[b]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
67	4	10.70±0.26 (11.00)	0.53±001 (0.54)	0.42±0.02 (0.43)	2.35±0.21 (2.58)
50	3	9.34± 0.13 (9.49)	0.54±0.003 (0.54)	0.47±0.003 (0.48)	2.38±0.05 (2.44)
36	4	6.70±0.18 (6.87)	0.51±0.004 (0.51)	0.50±0.003 (0.50)	1.69±0.06 (1.74)

[a]Average ± standard deviation (highest value). [b]Number of working cells out of four tested.

11. Aging of dispersion: device statistics

Table S8. Device statistics for solar cells processed from an aged 43 nm NP dispersion.

Day	*d* (nm)	#cells[a]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
0	75	3	6.72±0.16 (6.90)	0.51±0.01 (0.52)	0.45 ±0.01 (0.46)	1.54±0.09 (1.65)
1	85	3	9.20±0.60 (9.49)	0.48±0.04 (0.51)	0.43±0.02 (0.44)	1.93±0.37 (2.12)
2	81	4	8.32±0.31 (8.52)	0.53±0.01 (0.52)	0.47±0.004 (0.47)	2.04±0.06 (2.09)
5	86	3	8.31±0.21 (8.53)	0.51±0.002 (0.51)	0.44 ±0.001 (0.45)	1.89±0.04 (1.93)
9	80	4	8.00±0.17 (8.09)	0.50±0.01 (0.51)	0.46±0.01 (0.47)	1.85±0.09 (1.93)

[a] Number of working cells out of four tested.

Table S9. Device statistics on the solar cells fabricated after one day aging

d (nm)	# cells[a]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	P_{max} (mW/cm^2)
59	2	4.99±0.59 (5.40)	0.50±0.02 (0.52)	0.49±0.04 (0.52)	1.25±0.30 (1.46)
64	2	6.95±0.06 (6.99)	0.51±0.002 (0.51)	0.48±0.002 (0.48)	1.67±0.00 (1.67)
81	3	7.76±0.13 (7.84)	0.53±0.005 (0.53)	0.47±0.005 (0.48)	1.94±0.04 (1.97)
85	3	9.20±0.60 (9.49)	0.48±0.04 (0.51)	0.43±0.02 (0.44)	1.93±0.37 (2.12)

[a] Number of working cells out of four tested.

12. Best NP device versus an optimized BHJ

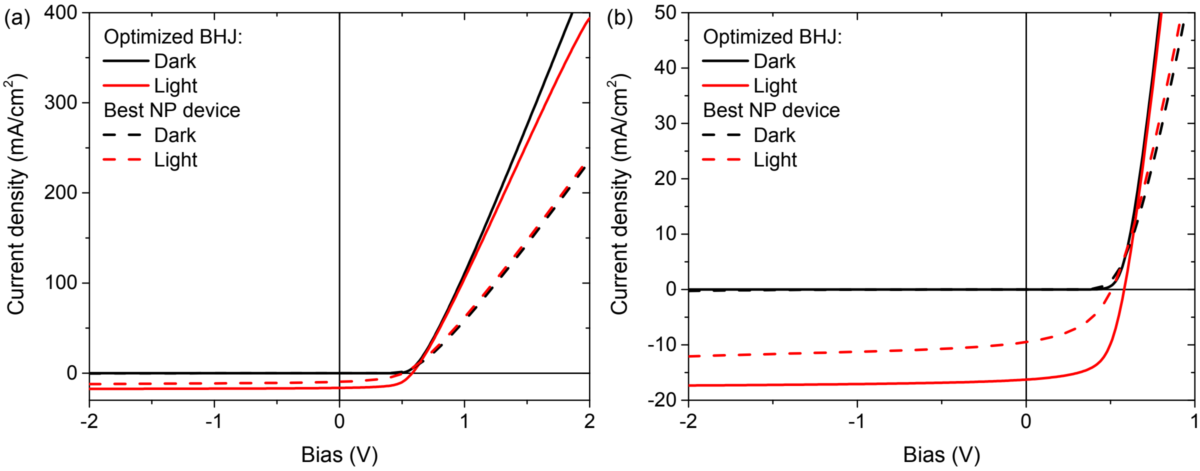

Figure S7. *J*–*V* characteristics of the best performing NP device (dashed line) compared to the optimized BHJ device (solid line) made from PDPP5T:[60]PCBM processed from a mixture of chloroform with 4.8 vol.% *o*-DCB. Panel (b) shows the same data as panel (a) on a different scale.

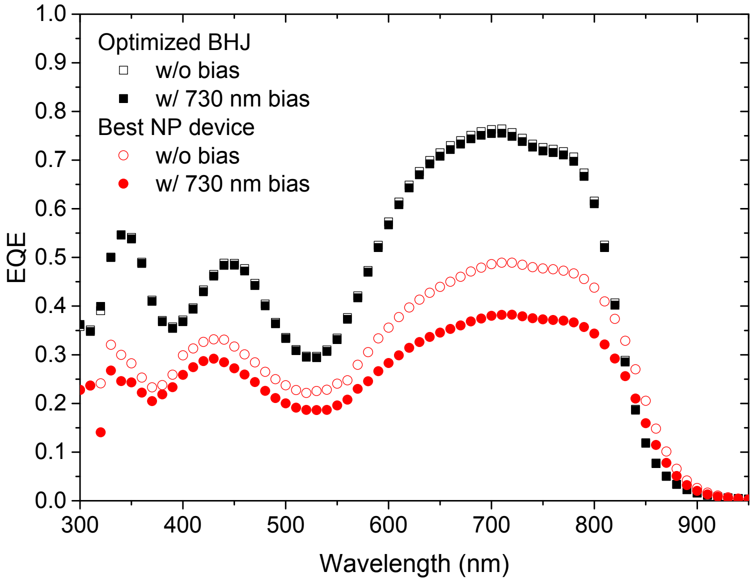

Figure S8. EQE measurements of an optimized BHJ device processed from a mixture of chloroform with 4.8 vol.% *o*-DCB without (open black squares: $J_{\mathrm{SC,\,EQE}}$ = 16.73 mA/cm^2) and with (solid black squares: $J_{\mathrm{SC,\,EQE}}$ = 16.57 mA/cm^2) 730 nm light bias compared to the EQE of the best performing NP device without (open red circles: $J_{\mathrm{SC,\,EQE}}$ = 11.32 mA/cm^2) and with (solid red circles: $J_{\mathrm{SC,\,EQE}}$ = 9.07 mA/cm^2) 730 nm light bias.

Table S10. Performance of best NP device compared to a BHJ made from PDPP5T and [60]PCBM.

Device	*d* (nm)	$J_{\mathrm{SC,\,EQE}}$ (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
NP	85	9.07	0.51	0.44	2.03
BHJ	100	16.6	0.58	0.60	5.77

13. Aging of small NPs

Table S11. One day aging effect on the performance of solar cells processed from 31 nm particles.

Day	*d* (nm)	$J_{\mathrm{SC,\,EQE}}$ (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
0	72	6.69	0.55	0.46	1.70
1	70	7.13	0.56	0.47	1.89
1	66	7.21	0.51	0.53	1.98

14. Effect of ethanol addition and aging on NP size

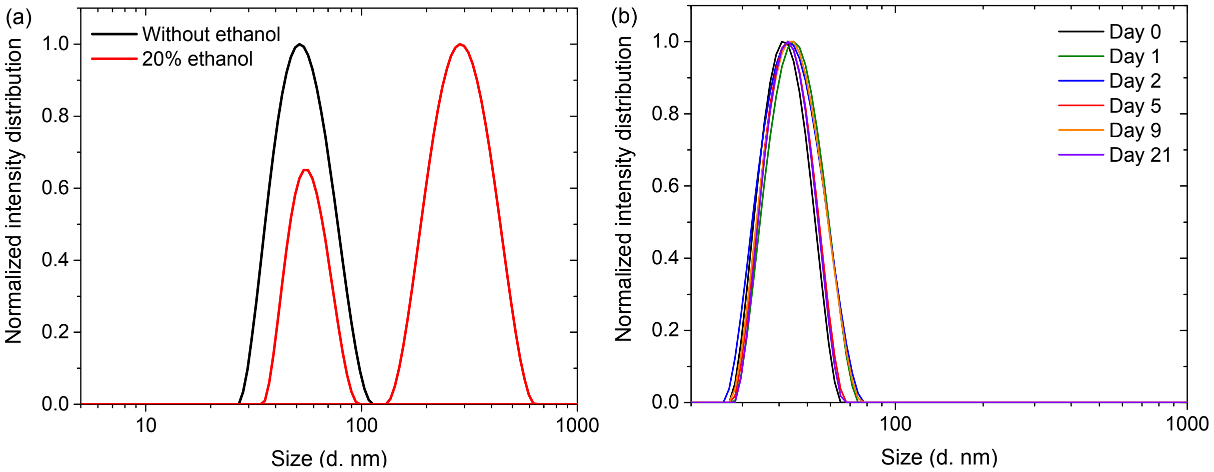

Figure S9. DLS measurements. (a) The effect of adding ethanol on the NP size. (b) The effect of aging on the NP size distribution.

References

(1) Scalarone, D.; Lazzari, M.; Castelvetro, V.; Chiantore, O. Surface Monitoring of Surfactant Phase Separation and Stability in Waterborne Acrylic Coatings. *Chem. Mater.* **2007**, *19*, 6107–6113