

## Supplementary Information

### Eco-friendly processing of solar cells: Electrostatic stabilization of surfactant-free organic nanoparticle dispersions by illumination

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**Table S1:** We investigated the influence of oxygen on the precipitation process, since oxygen might act as an electron acceptor or might cause surface modifications of the nanoparticles by reaction with the polymers. For this experiment, we degassed solvent and non-solvent using the freeze-pump-thaw technique and conducted the nanoprecipitation of P3HT/THF (0.5 g/L) into methanol (1:5 v/v) inside a nitrogen glovebox (chloroform is not to be used in our gloveboxes for technical reasons). Subsequently, we performed the nanoprecipitation under the same conditions in air. Each standard deviation originates from 3 independent experiments. Within this experimental error, we observed no difference in the resulting nanoparticle size in presence or absence of oxygen. We conclude that oxygen, if any, plays only a minor role in the determination of the nanoparticle size.

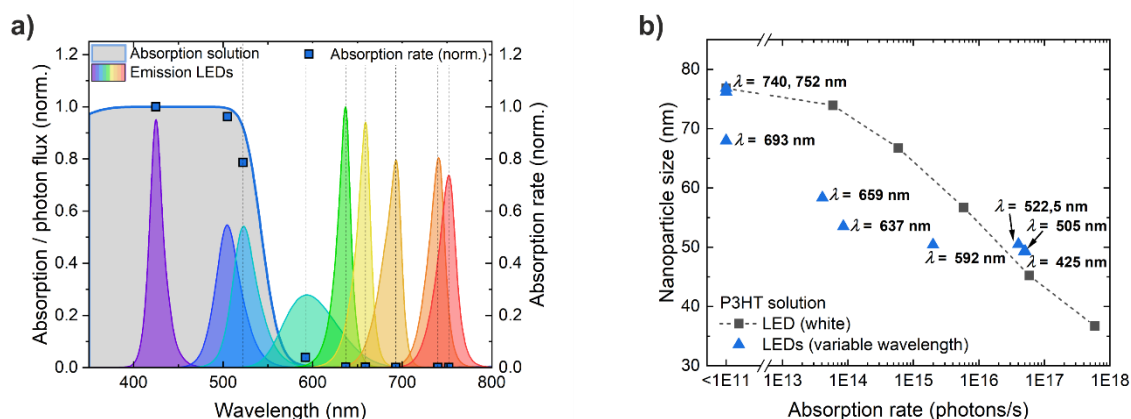
|                           | In the dark    | Under illumination (100 W/m <sup>2</sup> ) |
|---------------------------|----------------|--|
| Under nitrogen (glovebox) | 104.4 ± 1.3 nm | 80 ± 2 nm                                  |
| In air                    | 107.3 ± 1.5 nm | 77.4 ± 1.2 nm                              |

**Table S2:** In order to demonstrate that (in the experiments performed in this work) the concentration step of the dispersions can be omitted but still relevant results can be gained, we carried out the following control experiment: Four P3HT dispersions were prepared by nanoprecipitation of a P3HT/chloroform solution (0.5 g/L) in ethanol (1:4 v/v) under white light illumination (200 W/m<sup>2</sup>). The average nanoparticle size was determined by DLS, a first time right after nanoprecipitation and a second time after evaporation of the chloroform and reduction of the ethanol (*i.e.* a total reduction to 20% of the initial volume). The observed minor decrease in nanoparticle size may be explained by the removal of chloroform, which may induce some swelling of the nanoparticles. An alternative explanation may be the presence of agglomerates in the initial dispersion, which adhere to the beaker walls during the solvent/non-solvent evaporation. Since the sensitivity of DLS increases with the nanoparticle size, smallest amounts of (non-visible) agglomerates would be sufficient to change the measurement data. Omitting the concentration of dispersions is, therefore, viable and facilitates the experimental procedures. The faster process also warrants a better comparability of results as side processes can be neglected.

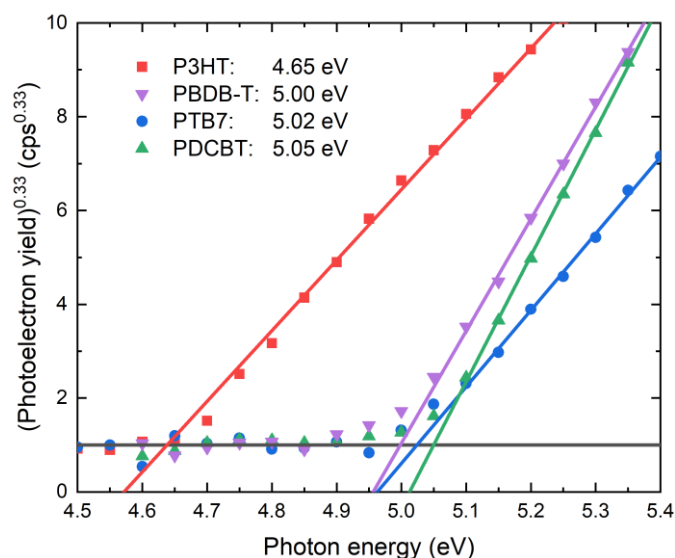
| Sample number | Nanoparticle size before concentration (nm) | Nanoparticle size after concentration (nm) |
|---------------|---|--|
| 1             | 46  | 45   |
| 2             | 41  | 37   |
| 3             | 42  | 40   |
| 4             | 42  | 39   |

**Table S3:** We observed considerable differences in the nanoparticle size of P3HT dispersions synthesized under the same conditions but with analytical grade ethanol from different batches (P3HT/chloroform, 0.5 g/L, precipitated in ethanol, 1:4 v/v). The certificate of analysis did not reveal any differences between the batches. However, we measured a slightly higher conductivity of the second batch. Indeed, an increased concentration of unspecific electrolytes in the second batch may well account for larger nanoparticles.

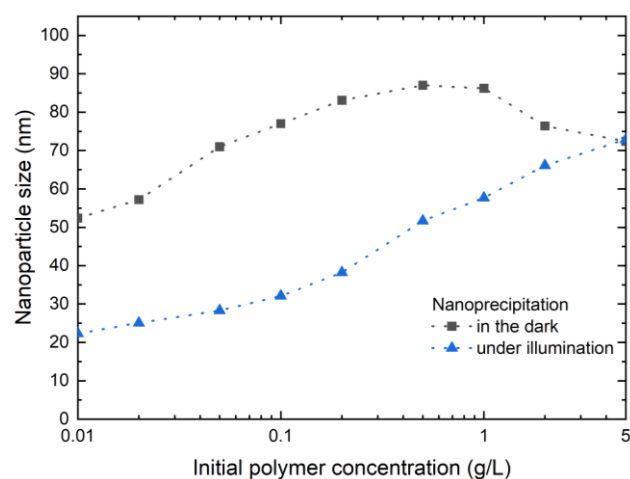
| Ethanol batch | Illumination                        | Nanoparticle size (nm) |
|---------------|-------------------------------------|------------------------|
| 1             | dark (<0.01 W/m <sup>2</sup> )      | 87                     |
| 1             | illuminated (100 W/m <sup>2</sup> ) | 46                     |
| 2             | dark (<0.01 W/m <sup>2</sup> )      | 118                    |
| 2             | illuminated (100 W/m <sup>2</sup> ) | 51                     |



**Figure S1:** When calculating the absorption rate from the spectral overlap of the light source with the absorption of the P3HT solution, we find no correlation between changing the white-light intensity and changing the photoexcitation source. (a) Comparison of the emission spectra of the LEDs with equivalent photon flux as used for sample illumination during nanoprecipitation and the absorption spectra (1-transmittance) of a typical P3HT solution. (b) The nanoparticle sizes after nanoprecipitation under illumination with different irradiances of white light and after nanoprecipitation under illumination from individual LEDs are rather uncorrelated.



**Figure S2:** Measurement of the ionization potential of semiconducting P3HT, PTB7, PDCBT and PBDB-T thin films by photoelectron spectroscopy in air (PESA). P3HT exhibits the lowest ionization potential.



**Figure S3:** The nanoprecipitation of P3HT/chloroform solutions in ethanol (1:4 v/v) yields different nanoparticle sizes, depending on the initial polymer concentration. When nanoprecipitated under illumination, the nanoparticles are smaller, but the difference between nanoprecipitation in the dark and under illumination diminishes towards higher polymer concentrations.