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## ***Electronic Supplementary Material***

### **Microstructuration of Poly(3-hexylthiophene) Leads to Bifunctional Superhydrophobic and Photoreactive Surfaces**

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### **Preparation of the polymer layers**

All chemicals used were of analytical grade, from which 3-hexylthiophene ( $\geq 99\%$ ) was purchased from Sigma, while tetrahydrofuran, anhydrous iron(III) chloride, chloroform, and absolute ethanol from VWR International. The water content of chloroform was kept below 50 ppm (monitored by coulometric Karl–Fischer titration) by storing it over 3A zeolites. For reference photocatalytic measurements, the photocatalyst P25 TiO<sub>2</sub> nanoparticles were immobilized by using transparent polyacrylate [poly(ethyl-acrylate co methyl-methacrylate)] copolymer binder material (obtained from Evonik Industries, Germany).

For the synthesis of poly(3-hexylthiophene) (P3HT), chemical polymerization was employed using FeCl<sub>3</sub> as oxidant in chloroform. Chloroform-based solutions of 3-hexylthiophene monomer and FeCl<sub>3</sub> were prepared and mixed at final reagent concentrations of 0.1 and 0.25 mol dm<sup>-3</sup>, respectively. The continuously stirred reaction mixture was kept in a closed vessel on ice bath for 6 h. The formed polymer was filtered on a filter paper (12–15  $\mu\text{m}$  pore size) and washed repeatedly with absolute ethanol to remove the traces of the oxidant. The final product was dried in air under an infrared lamp. Details of the polymerization were described earlier<sup>1</sup>.

Microstructured P3HT films with different surface roughness were prepared by a simple filtration method. Powdered P3HT (190 mg) was dispersed in 10 cm<sup>3</sup> 40/60 v/v% DMF/toluene mixture using an Elmasonic P-type ultrasonic laboratory device (80 kHz frequency, 90% ultrasonication power, T = 25 °C) for different ultrasonication time intervals. The resulted polymer dispersions were filtered through a filter paper (Munktell filter discs; grade: 390; 84 g m<sup>-2</sup>) with a diameter of 7 cm. The specific surface mass of the P3HT films was  $5.0 \pm 0.25$  mg cm<sup>-2</sup> on the surface of the filter paper.

During the photocatalytic benchmarking measurements, P25 TiO<sub>2</sub> (Aeroxide P25 TiO<sub>2</sub>, Evonik Degussa GmbH) was used as a conventional reference photocatalyst. In this case, the films were prepared by spray-coating on the surface of the filter paper and the immobilization of TiO<sub>2</sub> photocatalyst particles was facilitated using transparent polyacrylate binder. The specific surface amount of the TiO<sub>2</sub>/polymer hybrid layer was also 5 mg cm<sup>-2</sup> on the filter paper and the TiO<sub>2</sub>/polymer mass ratio was 60/40 w/w% in the layer. The detailed film forming process was published in our previous articles<sup>2–4</sup>.

### Characterization methods

Static light scattering (SLS) measurements were carried out at fixed scattering angle ( $90^\circ$ ) with different polymer concentrations (0.1–1.0 mg/mL) to determine the weight-average molecular weight ( $M_w$ ) of P3HT polymer. The measurements were carried out with Zetasizer NanoZs (Malvern Instrument) light scattering device. Before measurements the solutions were filtered through 0.22  $\mu\text{m}$  Millipore membrane filters. To obtain the absolute scattering light intensity, toluene was used as a standard. The  $M_w$  can be determined by the angle ( $\theta$ ) and concentration ( $c$ ) dependence of  $Kc/\Delta R\theta$  according to Debye plot formulation<sup>5</sup>. The contact angle of the prepared polymer layers was determined using a drop shape analysis system (EasyDrop, Krüss GmbH, Hamburg, Germany), equipped with a Peltier temperature chamber and a syringe steel needle of 0.5 mm diameter under atmospheric pressure. In the Peltier temperature chamber, the evaporation is negligible and constant temperature ( $25.0 \pm 0.5^\circ\text{C}$ ) is ensured. Distilled water was used as test liquid. According to the sessile drop technique, a drop of water was placed on the plate with the use of a syringe. Using a CCD camera of the goniometer, the drop contour of the registered photo was mathematically described by the Young–Laplace equation using DSA100 software, and the contact angle was determined as the slope of the contour line at the three-phase contact point.

The sliding contact angle was also measured by the tilting plate method as follows: a waterdrop of 25  $\mu\text{L}$  was placed on the polymer surface with a micropipette and waited for 10 s to achieve equilibrium position. The placed water drop starts to roll-off after tilting the polymer surface at a particular tilt angle. Five runs were taken to finalize the sliding angle value for each sample<sup>6</sup>. For determining surface free energy values of the superhydrophobic polymer layers, the Zisman method was employed at  $25.0 \pm 0.5^\circ\text{C}$ <sup>7</sup>. In this case, ethanol/water mixture (0/100 5/95 15/85 30/70 40/60 100/0 v/v%) with systematically increasing surface tension values (21.82, 32.98, 42.08, 55.73, and 72.01  $\text{mN m}^{-1}$ , respectively) were employed as test liquids.

The surface roughness of the polymer layers was investigated by profilometry. A mechanical profilometer (Form Talysurf Series 2 from Taylor Hobson Ltd., Leicester, Great Britain) was used with resolutions of 0.25  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 3 nm in x, y, and z directions, respectively. The surface structure and the morphology of the prepared P3HT layers were examined by field

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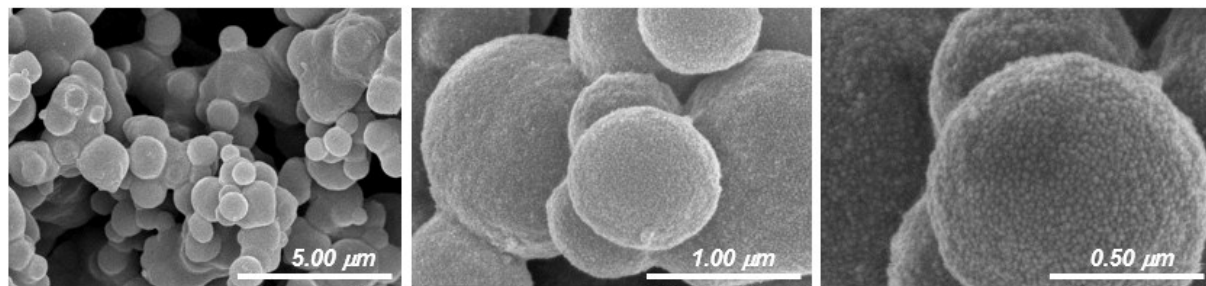
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emission scanning electron microscopy (SEM–Hitachi S-4700 microscope), applying a secondary electron detector and 5 kV acceleration voltage. For the optical characterization of the P3HT and the TiO<sub>2</sub> thin films, diffuse reflectance UV–vis spectra were recorded with a CHEM 2000 UV–vis (Ocean Optics Inc.) spectrophotometer equipped with an integrating sphere.

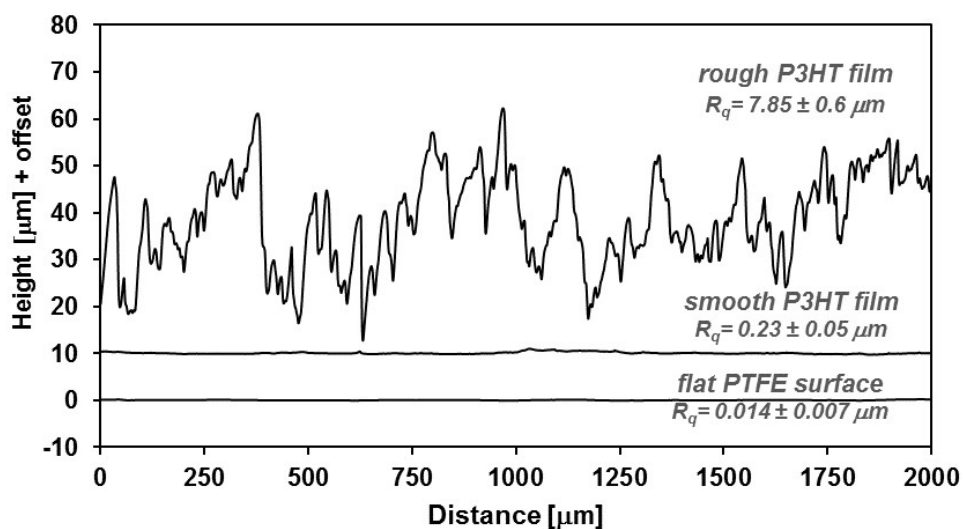
The photocatalytic activities of the prepared layers were verified through ethanol degradation tests at the solid/gas interface. To quantify the degradation of ethanol as organic test molecule, gas chromatographic measurements were carried out (Shimadzu GC-14B). Samples were taken after 5, 10, 15, 30, 45, 60, 90, 120, 150, and 180 min of illumination. During the photocatalytic measurements, 5 µl ethanol was injected to the reaction chamber containing 38.5 cm<sup>2</sup> sized P3HT layers, fixed at 5 cm (LED light source) and 26 cm (Solar simulator) distance from the samples. The  $c/c_0$  values were calculated from peak areas determined as the function of illumination time, where  $c$  is the concentration of ethanol at time ( $t$ ) and  $c_0$  is the initial concentration ( $c_0 = 0.36 \text{ mmol dm}^{-3}$ ). The measured values were specified on the surface of the polymer films. Beside the decreasing ethanol concentration, the formed acetaldehyde as main intermediate product and CO<sub>2</sub> were also measured. The power density of the light incident on the polymer surface was measured with a power meter (Thorlabs GmbH, Germany).

### **Analysis of the morphology and surface roughness**

The dependence of the water contact angle on the surface roughness has been described by Wenzel's and Cassie–Baxter's models<sup>8,9</sup>. These idealized models can be applied under the assumption that water droplets are sufficiently larger than the surface roughness. Generally, hydrophilic surfaces (of contact angle less than 90°) become more hydrophilic, while hydrophobic surfaces (of contact angle more than 90°) become more hydrophobic upon roughening. This is another way of formulating Wenzel's law<sup>8</sup>, which elaborates on the increased surface area of a rough sample compared to a chemically identical smooth one. Later it has been pointed out that not the interfacial area, but the contact line is what determines the contact angle<sup>9</sup>. Yet, Wenzel's equation has become classical and it is still widely used.



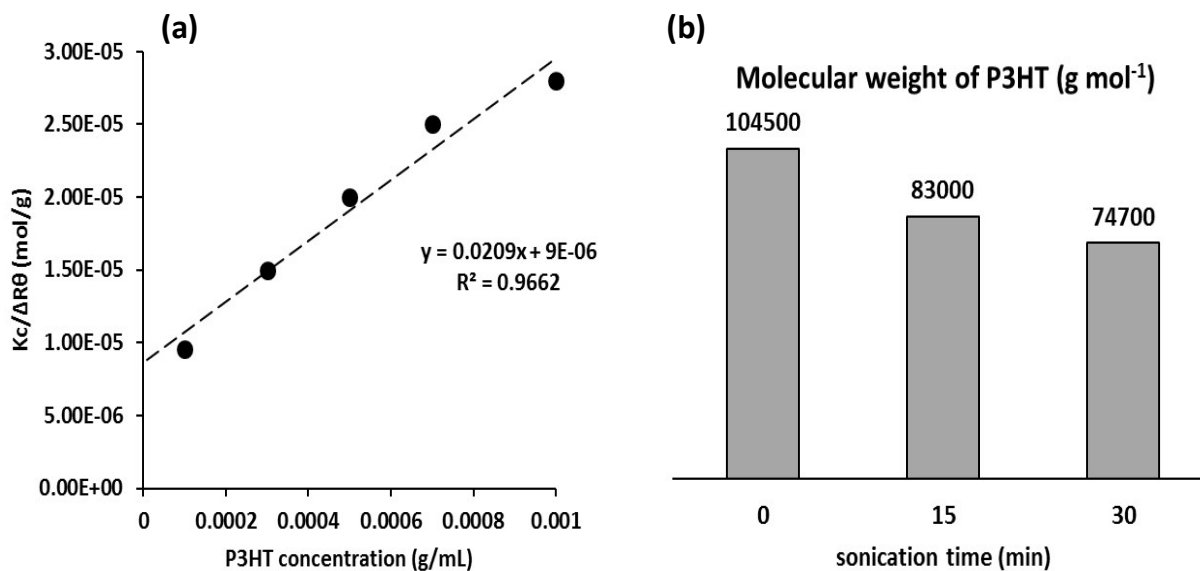
**Fig. S1.** SEM images of the rough P3HT surface after 10 min sonication time at different magnifications.



**Fig. S2.** Microscale surface roughness values ( $R_q$ ) of the smooth and rough P3HT films and the profilometry curve of the conventional flat PTFE (Teflon) surface.

### Molecular weight ( $M_w$ ) of the P3HT polymer

The molecular weight of the P3HT conducting polymer was determined by the angle ( $\Theta$ ) and concentration ( $c$ ) dependence of  $Kc/\Delta R\Theta$  according to Debye plot formulation (Fig. S3a). The  $M_w$  of the P3HT polymer was  $104500 \text{ g mol}^{-1}$ , but the initial  $M_w$  decreased to  $74700 \text{ g mol}^{-1}$  after 30 min sonication time (Fig. S3b). This indicates the partial fragmentation or degradation during the sonication process.



**Fig. S3.** Debye plot obtained from static light scattering measurements for the P3HT polymer (a). The effect of sonication time on the molecular weight values of the polymer (b).

Viscosimetry measurements were also carried out, and the Mark–Kuhn–Houwink equation was employed. The following Mark–Kuhn–Houwink equation is applicable to many polymers and is extensively used to determine molecular weight ( $[\eta] = K M^a$ , where  $K$  and  $a$  both are constants). These constants ( $K$  and  $a$ ) both vary with polymers and solvents<sup>10</sup>. In the case of P3HT  $K$  and  $a$  are  $1.253 \cdot 10^{-2} (\text{cm}^3 \text{g}^{-1})$  and 0.77, respectively, in toluene at 25 °C<sup>11</sup>.

Using these constants, the average molecular weight of the synthesized P3HT polymer was 101600 g mol<sup>-1</sup> determined by viscosimetry measurements using an Ostwald Capillary Viscometer. The figure shows the calculated reduced viscosity values ( $\eta_{\text{red}}$ ) as a function of the polymer concentration. The value of intrinsic viscosity  $[\eta]$  can be calculated by extrapolating graph of reduced viscosity to zero concentration.

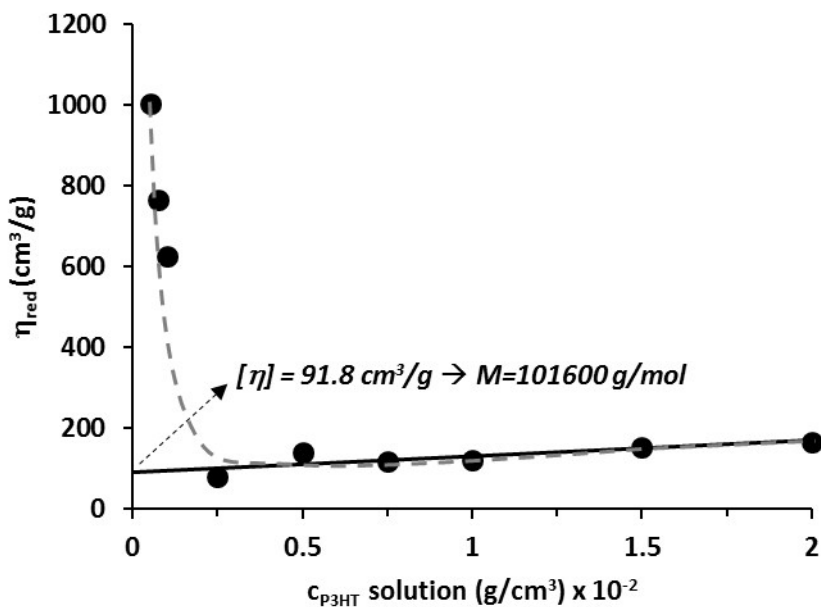
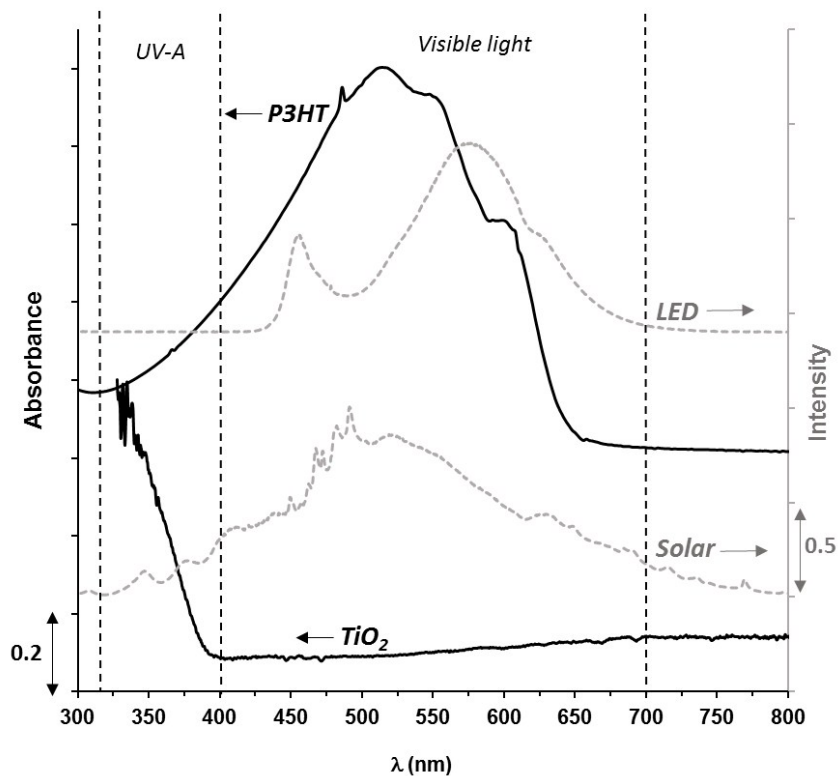


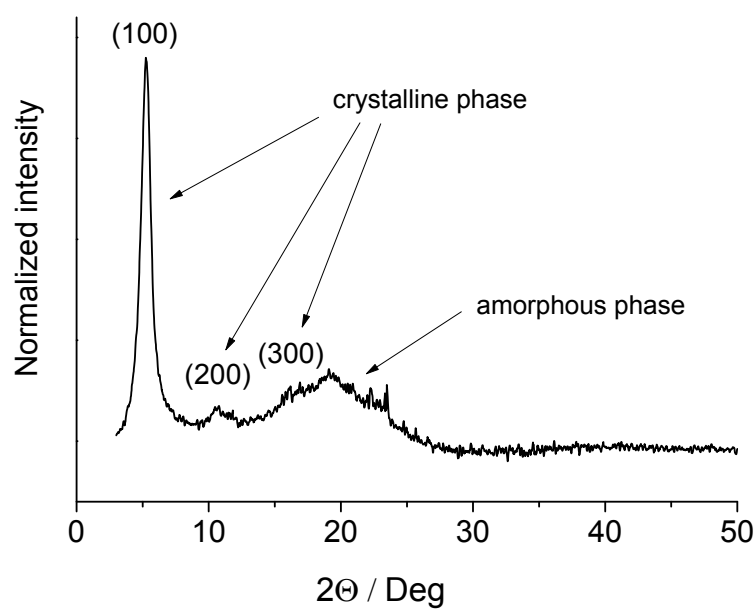
Fig. S4 Determination of the molecular weight of P3HT by viscosimetry.

### Optical properties

The optical properties of the P3HT films were measured by UV-vis spectroscopy (Figure S5.). The spectrum of the commercially available P25 TiO<sub>2</sub> was also determined for reference. In the case of P3HT a broad peak was seen between 315–675 nm with a maximum of 515 nm, so that the absorbance peak of the polymer was covered almost the whole UV-A/visible range. It was also shown that P25 TiO<sub>2</sub> film shows a characteristic light absorption edge in the UV-A range ( $\lambda < 390$  nm), which can be assigned to the bandgap of TiO<sub>2</sub>. The determined bandgap ( $E_g$ ) of P25 TiO<sub>2</sub> was 3.2 eV; in good agreement with the previously reported data. The emission spectra of the used solar simulator and LED light source are also presented for reference (grey dashed curve). The emission spectrum of the solar simulator was located between 300–800 nm, while the onset wavelength of the used LED light source was 420 nm and it has two maxima at 416 and 580 nm. The photocatalytic measurements were performed 5 cm distance from the LED lamp, while in the case of solar simulator the distance was 26 cm. The power density of the light sources was also measured from these distances. In case of solar simulator this value was 48.77 mW cm<sup>-2</sup>, while the LED light source was shown much lower value, 0.92 mW cm<sup>-2</sup>.



**Fig. S5.** The normalized absorbance spectra of the photoreactive P3HT polymer and P25 TiO<sub>2</sub> films (black continuous curves) and the normalized emission spectra of used light sources (grey dashed curves).

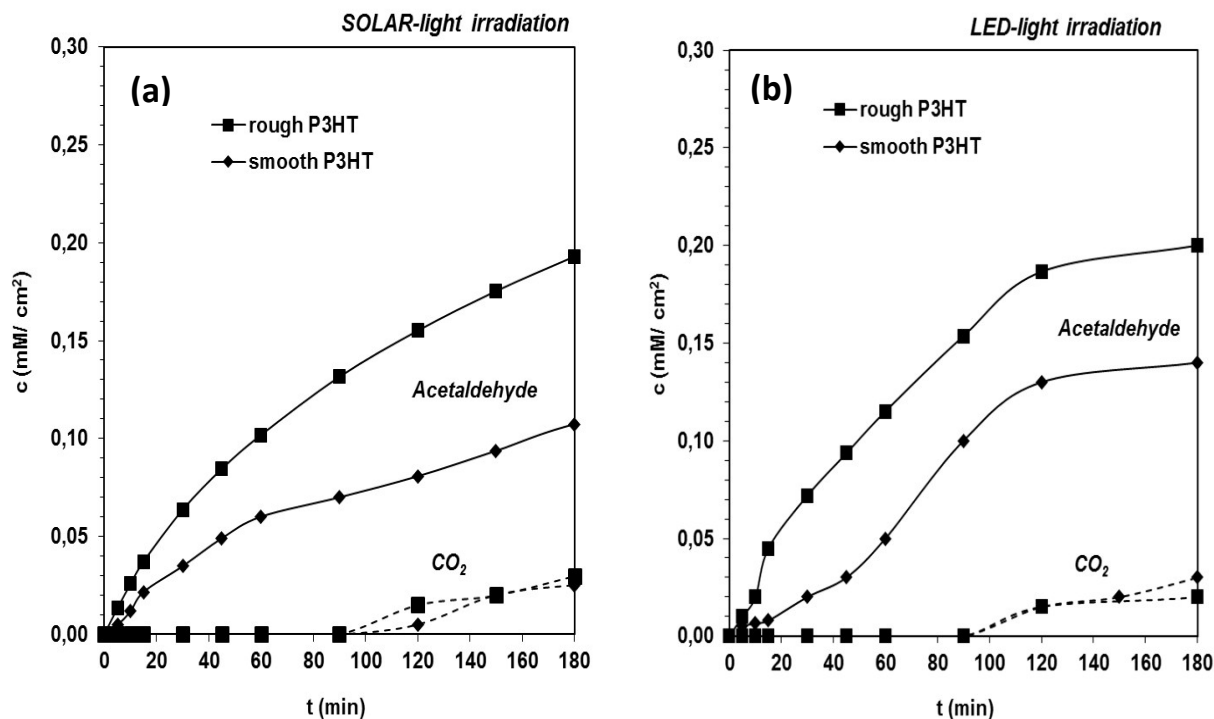


**Fig. S6.** XRD pattern of the as prepared P3HT powder.



### Photodegradation mechanism of ethanol as a model volatile organic compound

To probe the photocatalytic efficiency of the P3HT films, we investigated the photodegradation of a test molecule, ethanol. Beside the decreasing ethanol concentration, the formed acetaldehyde as main oxidized intermediate product and CO<sub>2</sub> as a product were measured under both solar- and visible LED-light irradiation (Figure S7.).

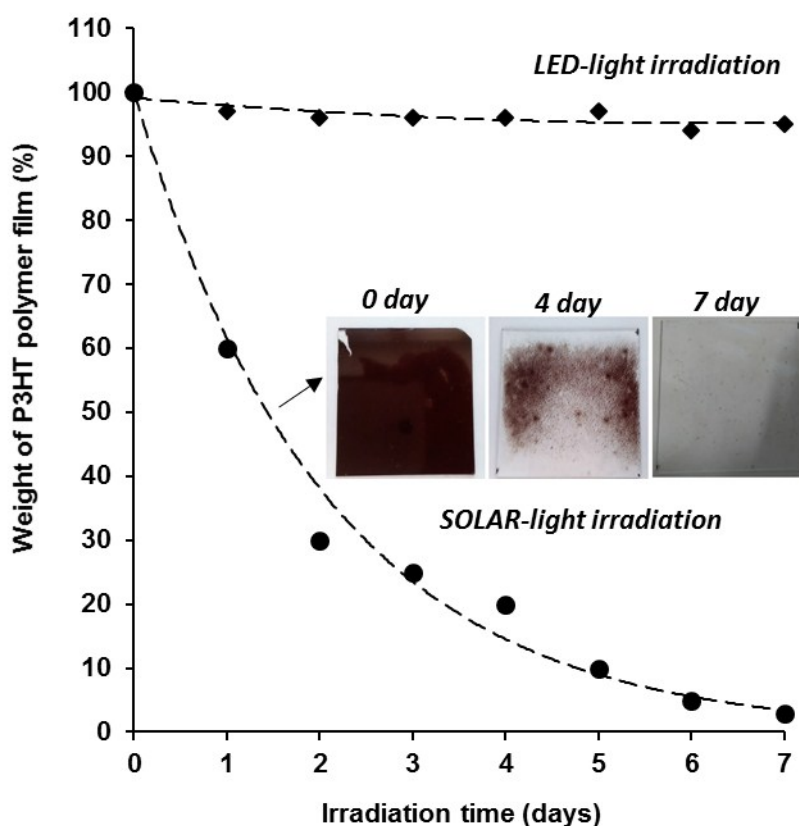


**Fig. S7.** Kinetics curves of acetaldehyde and CO<sub>2</sub> formation on smooth and rough P3HT films as a function of illumination time under simulated solar (a) and LED light (b) irradiation (solar  $\lambda = 280\text{--}900$  nm and LED  $\lambda = 420\text{--}700$  nm).

### Self-photodegradation of the P3HT polymer thin film

The self-photodegradation of the 25 cm<sup>2</sup> P3HT polymer thin film with 1 mg cm<sup>-2</sup> surface polymer content) was measured gravimetrically using an analytical balance (Denver Instrument SI-234) under continuous long-term light irradiation with both simulated sunlight and visible light<sup>12</sup>. According to the results, the photocatalysis induced weight loss of the polymer film was very

pronounced in the case of solar-light irradiation (Figure S8), however, in the case of visible LED light irradiation, the measured weight loss that is the photocatalytic degradation of the polymer was negligible due to the above-mentioned low light intensity ( $\sim 1 \text{ mW cm}^{-2}$ ).



**Fig. S8.** The gravimetrically measured weights of the P3HT thin films ( $1 \text{ mg cm}^{-2}$  surface polymer content) as a function of illumination time using solar- and visible LED light irradiation. The inserted images represent the thin P3HT film during the irradiation process.

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