Supporting Information

Dynamic Microscopy Study of Ultrafast Charge Transfer in Hybrid P3HT:hyper-branched CdSe Nanoparticle Blend for Photovoltaics

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S1. Experimental Setup

Ultrafast Confocal Microscope

The experimental setup of the ultrafast confocal microscope is shown in Figure S1. It is driven by 10- μ J, 150-fs pulses at 1kHz repetition rate and 800 nm wavelength produced by an amplified Ti:Sapphire laser (Quantronix model Integra-C). The fraction of the pulse energy reflected by a first beam splitter (BS1 in the figure S1) is frequency doubled passing through a second-harmonic crystal to generate the pump pulses at 400 nm. The transmitted part is focused in a sapphire plate to produce a white light continuum spanning the 450-800 nm wavelength range, used as a probe beam. Pump and probe pulses, synchronized by a computer-controlled delay line with ~5-fs accuracy, are collinearly recombined by a dichroic beam splitter (BS2 in the figure) and focused on the sample by a high numerical aperture air microscope objective (100×, NA=0.75).



Figure S1: Experimental setup of the ultrafast confocal microscope. BS1 and BS3 are 50% beam splitters, while BS2 is a dichroic beam splitter. SHG: second harmonic generation crystal; OBJ: microscope objective; PZT: piezo-translator; PMT: photomultiplier; IF: interference filter.

The sample is raster scanned by a piezotranslator with nm accuracy on a $100 \times 100 \ \mu\text{m}^2$ scan area, thus allowing the acquisition of three-dimensional linear transmission $T(x,y,\lambda)$ images as a function of sample position (x,y) and probe wavelength λ . By modulating the pump beam with a mechanical chopper and demodulating the collected probe light at the same frequency, we also simultaneously register four-dimensional differential transmission $\Delta T/T(x,y,\lambda,\tau)$ images, which also depend on the pump-probe delay τ . The minimum detectable signal is $\Delta T/T \sim 10^{-4}$. Our instrumental temporal and spatial resolutions are 150 fs and 300-400 nm, depending on probe wavelength. ¹

SKFM Experimental Setup

All SKFM images were recorded simultaneously in air with a commercial AFM system (Xe-100 Park Systems) with Enhanced EFM technique in single pass mode. Enhanced SKFM allowed us to acquire Surface potential and topography maps simultaneously in a single step. Images were recorded with scan rate of 0.1-0.2Hz employing silicon tip with NSC-36 Ti-Pt coating (Park-System), apex radius < 15 nm, $k \approx 2 \text{ N m}^{-1}$ and resonant frequency ~ 155 KHz. To induce charge dissociation at the donor-acceptor interface the samples were illuminated with a white tungsten halogen lamp. The image analysis and quantitative estimation of the surface voltage was carried out using both the XEI (Park System) software and Gwyddion (ver. 2.19) software.

S2. Sample preparation

Film Deposition

The nanocrystals/polymer solution (1:1 w/w ratio) has been spin-coated at 3000 rpm onto ITO-glass substrate covered with a 100 nm thick gold film.

Nanocrystals solution

CdSe Hyperbranched nanoparticles have been synthesized according to a published literature procedure.² In order to remove the surfactants bound to the surface of nanocrystals, a pyridine treatment has been performed. First, the nanocrystals have been dissolved in anhydrous pyridine and stirred under reflux for 24h, then they have been precipitated with hexane and dispersed in a solvent mixture (chloroform:pyridine=9:1).

Polymer Solution

The polymer used is regioregular poly(3-hexylthiophene) (P3HT) purchased from Rieke Metals. We used a regioregular P3HT 1,2-dichlorobenzene solution at a concentration of 12 mg/mL.

S3. AFM image on both gold and Glass

Atomic force microscopy image were performed with commercial AFM system (Xe-100 Park system) operating in non contact mode equipped with large area scanners (100 μ m x 100 μ m) which had a z-range of 12 μ m. The scanner was calibrated in the x-y directions by using a 1 μ m platinum coated calibration grating. The images were acquired in air at room temperature by using NANOSENSORSTM SSS-NCHR cantilevers with silicon tip with a radius of curvature < 5 nm and a nominal force constant of 42 Nm-1. In order to better resolve small phase features and borders, phase images have been used in this study. The scanner frequency ranged between 0.1 and 0.2 Hz.



Figure S2 (a,c) Topography and (b,d) Phase image of P3HT:CdSe hyperbranched 100nm thick film on a glass substrate $(5x5\mu m^2)$ and gold substrate $(3x3\mu m^2)$, respectively.

S4. Pump probe spectra of Pristine P3HT

Standard pump-probe spectra on the pristine P3HT film, as measured on ~150 μ m spot, are presented and used as references for interpretation of the confocal signal. Figure S3 shows the spectral evolution of the pump-probe signal at ultrafast time scale, ranging from 200 fs to 20 ps time delay. In the pristine cristalline-P3HT film (Figure S3 Panel I)^{3,4} it is possible to distinguish a ground state photobleach (PB) contributions, which produce a positive signal, where the pronounced vibronic feature at 600 nm is due to high crystallization order. At around 620 nm a photobleaching (PB) signal overlaps with Stimulated Emission (SE). The Δ T/T signal turns negative above 630 nm due to overlap with photoinduced absorption (PA). The PA band extending in the near IR spectral region and peaking at 700 nm is assigned to interchain charge-pairs, also named polaron pairs, that are instantaneously photogenerated in the pure crystalline P3HT phase.⁴



Figure S3: (a) Pump-probe spectra averaged on 150 μ m diameter spot. Different colors represent the temporal spectral evolution up to 20 ps. Pump beam is at λ =400 nm wavelength at 100 nJ/cm² pump energy.

SUPPORTING REFERENCES

(1) Polli, D.; Grancini, G.; Clark, J.; Celebrano, M.; Virgili, T.; Cerullo, G.; Lanzani, G. *Adv. Mater.* **2010**, *22*, 3048–3051.

(2) Kanaras, A. G.; Sönnichsen, C.; Liu, H.; Alivisatos A. P. Nano Lett. 2005, 5 (11), 2164–2167.

(3) Korovyanko, O. J.; Österbacka, R.; Jiang, X. M.; Vardeny, Z. V.; Janssen, R. A. J.; *Phys. Rev. B*, **2001**, *64*, 235122-235127.

(4) Guo, J.; Ohkita, H.; Benten, H.; Ito, S. J. Am. Chem. Soc. 2009, 131, 16869–16880.