Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Nanoscale J-aggregates of Poly(3-hexylthiophene): Key to electronic interface interactions with graphene oxide as revealed by KPFM

Elisa Palacios-Lidón,*[a] Emin Istif, [b,c] Ana M. Benito, [b] Wolfgang K. Maser,*[b] and Jaime Colchero*[a]

[a]Departamento Física, Edificio CIOyN (Campus Espinardo), Universidad de Murcia, E-30100 Murcia, Spain

[b]Instituto de Carboquímica (ICB-CSIC), E-500018, Spain

[c]present address: Univ. Bordeaux, CNRS, Bordeaux-INP, LCPO, UMR5629, F-33600 Pessac, France

S1. MATERIALS AND METHODS

S1.1 Sample preparation

Preparation of P3HT$_{NPs.}$

First, P3HT with a regioregularity of 92%, a molecular weight of 8100, and a polydispersity index of 1.19 was synthesized, as previously reported.[1] The synthesized P3HT was dissolved in tetrahydrofuran (THF) in a concentration of 1 mg/mL and left to dissolve under magnetic stirring overnight at room temperature. The polymer nanoparticles were synthesized via a re-precipitation technique, involving as a general principle the rapid injection of P3HT dissolved in THF to excess volume of water. In detail, a 2 mL solution of P3HT in THF (1mg/mL was) was rapidly injected into deionized water (10 mL). The resulting solution was sonicated with a tip sonicator for 3 min. Subsequently, remaining THF was evaporated via a vacuum evaporator at 35 °C. Then the final solution was filtered, affording a stable aqueous dispersion of P3HT$_{NPs}$ in a final concentration of 0.2 mg/mL.

Preparation of *in-situ* P3HT$_{NPs}$ – GO

P3HT$_{NPs}$–GO sample was prepared via an *in-situ* re-precipitation approach, involving water dispersions of GO. This enables the formation of P3HT$_{NPs}$ in the presence of GO sheets, as described in our previous work.[1] In brief, an aqueous dispersion of 0.125 mL of GO (4 mg/mL) was diluted to 10 mL by adding deionized water. Then, 2 mL of P3HT solution in THF (1mg/mL) was injected rapidly into the aqueous dispersion of GO under vigorous stirring. The following steps are analogous to those described in the preparation of P3HT$_{NPs}$. The final solution was filtered resulting in stable aqueous dispersion of the in-situ prepared P3HT$_{NPs}$–GO ensembles. As shown in our previous work,[1] the *in-situ* approach creates a unique situation whereby GO critically changes the nanocrystalline stacking of the P3HT chains in the forming nanoparticles towards more planar J-type aggregates (see also section S2.2), which concomitantly establish stable charge-transfer interface interactions with the GO sheets. Processed into films, the resulting P3HT$_{NPs}$–GO (*in-situ*) charge transfer complexes show enhanced photophysical properties.

Preparation of *ex-situ* P3HT$_{NPs}$–GO

An aqueous dispersion of 0.125 mL of GO (4 mg/mL) was added to the aqueous solution of 10 mL of P3HT$_{NPs}$ (0.2 mg/mL) and mixed under magnetic stirring for 30 min. This resulted in a stable aqueous dispersion of *ex-situ* P3HT$_{NPs}$–GOs ensembles, containing the same P3HT$_{NP}$ to GO weight ratio of 1:0.25 as the in-situ prepared sample. As shown in our previous work,[1] in the *ex-situ* samples, achieved through the simple mixing procedure of the already formed materials, the original H-type aggregate structure of the P3HT$_{NPs}$ remains unaffected (see also section S2.2) and does not lead to any specific interface interactions and to an enhancement of the photophysical properties in the P3HT$_{NPs}$–GO (*ex-situ*) systems.

Preparation of discontinuous thin films

1 mL stock solutions of *in-situ* P3HT$_{NPs}$–GO, ex-situ P3HT$_{NPs}$–GO and P3HT$_{NPs}$ were diluted to 5 mL with deionized water in order to avoid the agglomeration of the individual nanostructures in thin film. The bare GO dispersion was

also diluted to a final concentration 0.01 mg/mL. The diluted samples were spray coated on ultra-flat ITO substrate (previously cleaned with isopropanol several times), which were placed on a heating plate (65 °C). The coated surface area was 0.5 cm × 0.5 cm. The spray gun passed a maximum of 5 times over the substrate, thus enabling the formation of discontinuous films consisting of samples in the form of isolated individual objects.

S.1.2 Experimental Techniques

SFM and KPFM measurements

Morphology and surface potential (SP) were studied at ambient conditions using a home-made Scanning Force Microscopy (SFM). For all experiments, Platinum coated silicon tips (Olympus, k = 3 N/m and f = 75 kHz) have been used. Image acquisition and processing was performed with freely available WSxM software.[2] Images were acquired using the oscillation amplitude as signal for topography feedback (so called Amplitude Modulation AM-SFM) at very low reduction of the oscillation frequency ($a_{set}/a_{free} \approx 0.9\text{-}0.95$), which implies non-contact attractive operation regime.[3] With these operation parameters, measurements are performed in a non-perturbative low interaction mode, needed to acquire quantitative low noise SP measurements.[4] KPFM images were acquired in frequency modulation mode (FM-KPFM) with an AC voltage U_{ac}=500mV at ν_{el} =7 kHz. In this mode the electrostatic properties are measured using the *force gradient* of the electrostatic interaction induced by the tip-sample voltage $U_{el}(t)=U_{ac}\cos(\nu_{el}\, t)$; the corresponding frequency shift (more precisely: the phase variation of the in-phase component of the cantilever oscillation) is analyzed with an external Lock-In amplifier. More details of KPFM set-up and SFM operation in our experiments are described elsewhere.[4]

Surface Potential measurement

In our set-up, we define the SP as the inverse of the (experimental) voltage needed to minimize electrostatic tip-sample interaction when the sample is grounded and the tip voltage U_{tip} is controlled by the feedback of the KPFM controller: $SP=(U_{sample}-U_{tip})=-U_{tip}$, since the sample is grounded (U_{sample}=0). More technically: the SP is the (dc) voltage $-U_{tip}$ that gives $U_{1v\_LockIn}=0$, with U_{1v_lockIn} the first harmonic of the in phase output of the lock-in amplifier that measures the electrostatic tip-sample interaction induced by an (ac) voltage $U_{el}(t)$ applied between tip and sample. In our set-up the *SP* then corresponds to the work function difference $\Delta\Phi/e = (\Phi_{tip} - \Phi_{sample})/e$ = SP, where Φ_{tip} and Φ_{sample} are the work functions of tip and sample, respectively, and *e* is the magnitude of the electron charge (positive number).[5] In a SP image, a positive SP region of the sample therefore corresponds to a material with a higher Fermi/HOMO level as compared to the tip, and thus a lower work function and a lower electronegativity. If the tip is stable during data acquisition then the Pt tip can be considered a stable reference electrode and changes in the measured SP can be directly correlated with local changes of the surface potential/electronegativity of the sample. In the experiments described in the present work, for convenience and easier interpretation, the ITO substrate has been chosen as reference for all SP values, which implies subtraction of a constant offset for all experimentally measured SP ($SP_{offset} = SP_{Pt} - SP_{ITO}$). For all data shown, a positive SP value therefore corresponds to a material with a lower work function and a lower electronegativity than the ITO substrate; and vice versa, a negative SP value to a material with a higher work function and a higher electronegativity.

Reproducibility of our experiments was checked on different sets of samples with different tips. Although the relative amount of electro-optical response during the large variety of experiments may vary slightly between similar samples, the observed behavior of each specific region is the same independently of the sample and the specific tip.

Determination of Surface Photovoltage

To study the photo-induced electro-optical, the SFM is implemented in an inverted optical microscope (Nikon Eclipse TE2000-E). The sample is illuminated from the bottom through the main objective (40x (NA = 0.6, W.D. = 3.6-2.8 mm) Nikon objective (Plan Fluor type)) of the inverted microscope using a collimated monochromatic LED (λ=535 nm). More details of the experimental set-up are described elsewhere.[6]

To study the photo-induced processes a "two pass" methodology is employed where each scan line of an image is recorded twice, one with the illumination on, and a second time with the illumination off; the illumination protocol of this method therefore involves cyclic periods of illumination and darkness with the duration of a line scan (about 1s each). From the data acquired during the "two pass" technique, two (almost) simultaneous images are reconstructed, one in darkness (SP^{off} image) and the other one under illumination (SP^{on} image). The working principle, data processing and capabilities of this method are explained in detail elsewere.[7]

When two successive images are acquired, one totally in darkness (SP^{dark} image), and another one with the illumination always on (SP^{ilum} image), the corresponding time delay between illumination and darkness is (at least) the time corresponding to the acquisition of a whole image. Typically images have 256 or 512 lines and the acquisition time can vary between, several minutes up to and hour.

When electro-optical processes are fast (in our context: much faster than about 1s, the typical time of a scan line), then it is equivalent to either apply the "two-pass" technique or to acquire two KPFM images, one always in darkness and another one always with illumination. However, if sufficiently slow processes occur, then these two set of images are not equivalent. From the point of view of electrooptics, we may interpret that the "two pass" methods gives a pair of "on" and "off" SP^{off}/SP^{on} images which are effectively separated only by the time of a *line* scan (about 1s even though the total acquisition of data takes much longer), while a pair of SP^{dark}/SP^{ilum} are separated by (at least) the time of an image acquisition and thus a much larger (time difference can several orders of magnitude).

To discriminate between "fast" and "slow" processes, and to exclude possible artifacts due to (photo-) degradation, in our experiments we acquire several images, as shown in **Fig. S1**. First, an image SP^{dark} in (total) darkness is acquired, then using the "two pass" technique two additional images SP^{off}/SP^{on} are obtained, then a whole image SP^{ilum} with the illumination on is acquired and finally a second image SP^{dark} in (total) darkness is measured. If no degradation occurs –which has been the case in all our experiments- the first SP$^{\mathrm{dark}}$ image taken in darkness coincides with the second SP$^{\mathrm{dark}}$ image taken at the end of the acquisition protocol.

A variety of behaviors can in principle be observed if the electro-optical processes are comparable or slower than the SFM acquisition time (**Fig. S1**). If electro-optical processes are (much) slower when the illumination is turned on as compared to when the illumination is turned off, then in our illumination protocol we expect that during the time of a line scan the SP has not sufficient time to reach the full value of the surface potential SP$^{\mathrm{ilum}}$, then SP$^{\mathrm{dark}}$ ≈ SP$^{\mathrm{on}}$≈ SP$^{\mathrm{off}}$ and we expect a small value for SP$^{\mathrm{on}}$ - SP$^{\mathrm{off}}$ (blue line in **Fig. S1**). This behavior is not observed in our experiments. On the contrary, if electro-optical processes are (much) faster when the illumination is turned on (green line in **Fig. S1**) as compared to when the illumination is turned off, then in SP$^{\mathrm{ilum}}$ ≈ SP$^{\mathrm{on}}$ and we expect a large value for SP$^{\mathrm{on}}$ - SP$^{\mathrm{off}}$. Finally, if electrooptical processes are sufficiently fast (faster than a line scan, red line in **Fig. S1**) when the illumination is turned on as well as when the illumination is turned off, then SP$^{\mathrm{dark}}$ ≈ SP$^{\mathrm{off}}$ and SP$^{\mathrm{ilum}}$ ≈ SP$^{\mathrm{on}}$. With this in mind, we define the following surface photo-voltages in order to differentiate between fast and slow processes: the (total) SPV is SPV= SP$^{\mathrm{on}}$ -SP$^{\mathrm{dark}}$, the slow is SPV$^{\mathrm{slow}}$= SP$^{\mathrm{off}}$-SP$^{\mathrm{dark}}$ and the fast is SPV$^{\mathrm{fast}}$= SP$^{\mathrm{off}}$-SP$^{\mathrm{dark}}$; with this definition SPV = SPV$^{\mathrm{slow}}$ + SPV$^{\mathrm{fast}}$.

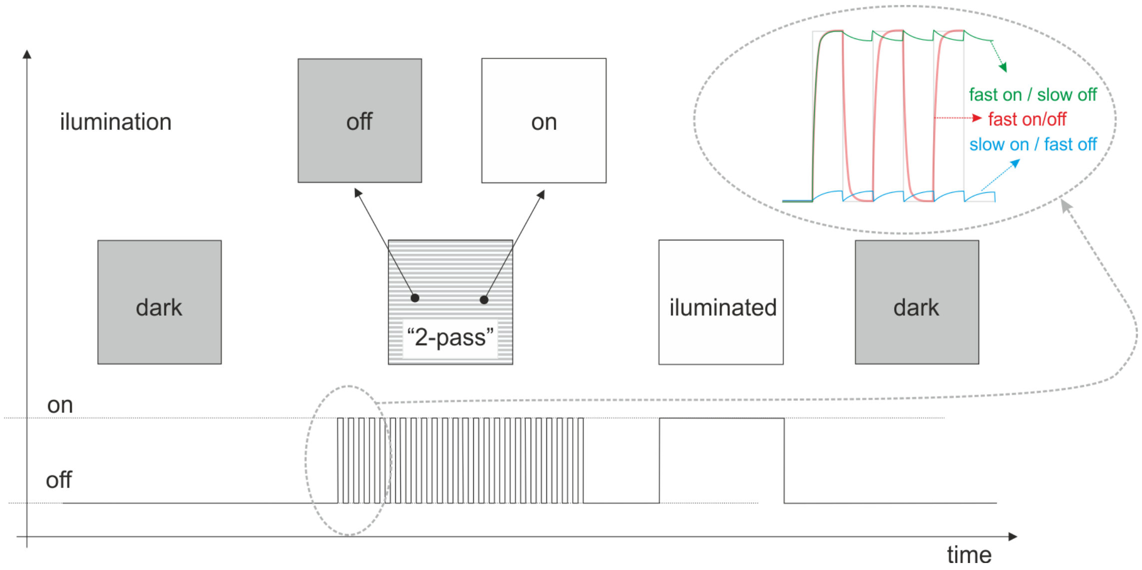

Figure S1. Sketch describing how the sample is illuminated during a typical experiment to determine the nanoscale Surface Photovoltage. For all experiments, (at least) topography and SP are acquired. First, a sample is imaged in darkness, then on the same location a "two-pass" technique is applied where each scan line is acquired twice, one in darkness and another one with the illumination on. From this data, two images are extracted, one corresponding to scan lines with illumination, and another one with scan lines in darkness. Finally, two additional images are acquired one with the illumination on during the whole time of image acquisition and the other in total darkness. The inset in the upper right shows the different response of the surface potential to an optical excitation that in principle may be observed depending on whether the electro-optical processes are sufficiently fast (red), the excitation is slow (blue) or the de-excitation is slow (green); see main text for more detail.

S2. RESULTS

S2.1 Individual Material Characterization

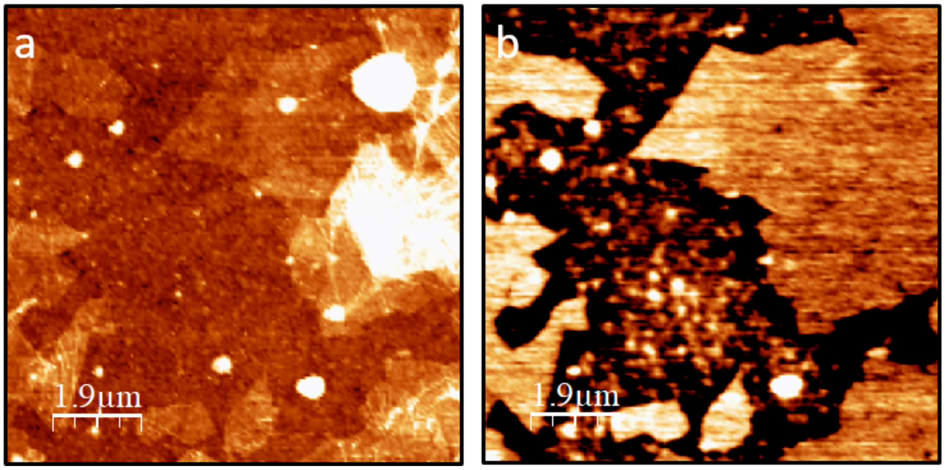

Figure S2. (a) Topography (z=15 nm) and (b) SP^{dark} (color scale 0-70mV) of the GO on ITO. The z scale of the SP^{dark} image is saturated to highlight the SP differences relative to the ITO substrate depending if one ($\Delta SP_{GO}^{1} = 80mV$), two($\Delta SP_{GO}^{2} = 60mV$) or more GO ($\Delta SP_{GO}^{>2} = 20mV$) sheets are stacked.

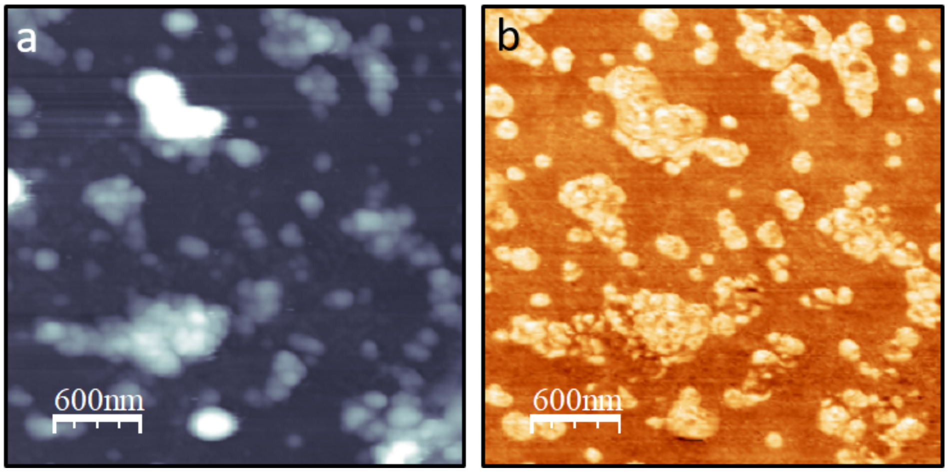

Figure S3. (a) Topography (z=200 nm) and (b) SP^{dark} (color scale 500 mV) low magnification images of the $P3HT_{NPs}$ on ITO.

S2.2 UV-Vis absorption spectra

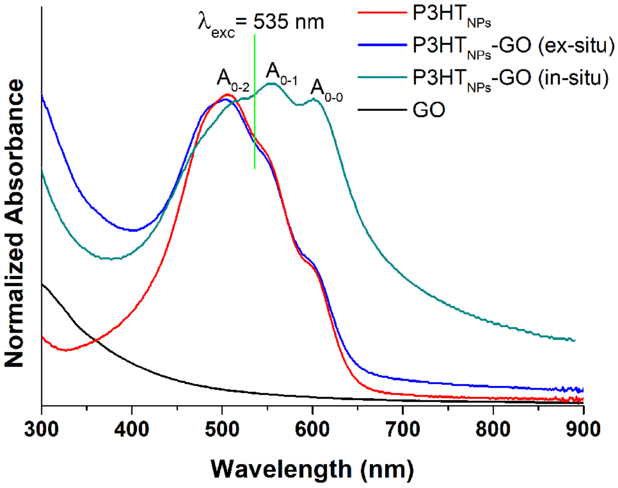

Figure S4. UV-Vis absorption spectra of P3HT$_{NPs}$, P3HT$_{NPs}$–GO (ex-situ), P3HT$_{NPs}$–GO (in-situ) and GO. The P3HT$_{NPs}$ spectra are normalized to the A_{0-2} vibronic transition. A vertical green line at 535 nm indicates the excitation wavelength used for the KPFM measurements under illumination.

The UV-Vis spectra of the P3HT$_{NPs}$ materials (Figure S4) reveal a broad π-π* absorption band between 400 nm to 700 nm. It is characterized at its low-energy side by three vibronic A_{0-n} peaks, whereby n refers to the number of vibrational quanta coupled to the electronic transition. While P3HT$_{NPs}$ and P3HT$_{NPs}$–GO (ex-situ) spectra are identical, especially in what concerns the vibrational peak positions and intensities, the situation has changed significantly for P3HT$_{NPs}$–GO (in-situ) showing an important modification in the relative A_{0-1} and A_{0-0} intensities, accompanied by a slight red-shift in their peak positions.

The A_{0-0}/A_{0-1} intensity ratios provide an easy approach to define the type of stacking of P3HT chains, according to the model developed by Spano [8]. For systems with $A_{0-0}/A_{0-1} < 1$ the P3HT chains are packed in a face-to-face order (H-aggregates) favoring interchain interactions with a rather high excitonic coupling constant. This is the case for P3HT$_{NPs}$ and for P3HT$_{NPs}$–GO (*ex-situ*) samples. For P3HT$_{NPs}$–GO (*in-situ*) systems however, the situation is approaching a value of 1, indicating a transition towards an end-to-end arrangement of the P3HT chains (J-aggregates) favoring interchain interactions with a rather low excitonic coupling constant. This is about 10 times lower compared to the one for P3HT$_{NPs}$ or P3HT$_{NPs}$–GO (*ex-situ*) samples. This situation, unique to the P3HT$_{NPs}$–GO (in-situ) samples, which furthermore show enhanced interface interactions as indicated for example by the red-shift of the A_{0-n} peaks (for more detailed discussion see [1]), eases the charge separation of photo-induced charges along the P3HT chains and its transfer to GO, as confirmed in the KPFM experiments carried out under illumination. The employed excitation wavelength of 535nm, indicated as green line in Figure S2, ensures excitation of the P3HT$_{NPs}$ systems (please note that the absorption of GO at this wavelength is negligible) and, moreover, the involvement of the A_{0-0} and A_{0-1} vibronic states, relevant for the transport properties of the P3HT chains.

REFERENCES

---

1 E. Istif, J. Hernandez-Ferrer, E.P. Urriolabeitia, A. Stergiou, N. Tagmatarchis, G. Fratta, M.J. Large, A.B. Dalton, A.M. Benito, WK. Maser, *Adv. Funct. Mater.,* 2018, 1707548.

2 I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A.M. Baro, *Rev. Sci. Instrum.* 2007, ***78***, 013705.

3 A.S. San Paulo, R. García, *Phys. Rev. B* 2002, **66**, 041406-9.

4 E. Palacios-Lidón, B. Pérez-García, J. Colchero, *Nanotechnology* 2009, ***20***, 085707.

5 Kelvin Probe Force Microscopy: From Single Charge Detection to Device Characterization. S. Sadewasser, Th. Glatzel (Eds.), Springer, Cham, Switzerland, 2018.

6 E. López-Elvira, E. Escasain, A.M. Baro, J. Colchero, E. Palacios-Lidon, *Polymer Degradation and Stability 2011*, **96**, 1279-1285.

7 E. Escasain, E. Lopez-Elvira, A.M. Baro, J. Colchero, E. Palacios-Lidon, *Nanotechnology* 2011, ***22***, 375704.

8 F.C. Spano, C. Silva, Annu. Rev. Phys. Chem. 2014, **65**, 477-500.