Electronic Supplementary Material (ESI) for Nanoscale

Electronic Supplementary Information

The role of size and coating in Au nanoparticles incorporated into bi-component polymeric thin-film transistor

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1. Gold Nanoparticles Synthesis

All materials have been purchased from Aldrich and used without further purification: auric acid ($HAuCl_4 \cdot 3H_2O$), sodium borohydride ($NaBH_4$), tetraoctylammonium bromide ($C_{32}H_{68}BrN$ - TOAB), octadecylamine ($CH_3(CH_2)_{17}NH_2$ - ODA), thiophenol (PhSH – MPT), biphenyl-4-thiol (Ph_2SH – BPT), 1,1′,4′,1″-terphenyl-4-thiol (Ph_3SH – TPT).

The nanoparticles were synthetized with a modified procedure derived from Leff & Co.[1], and with some difference used in previous work performed in our lab[2].

49 mg of Au $HAuCl_4$ was solubilized in 20 ml of MilliQ water. A solution of 200 mg of TOAB in 40 ml of toluene was prepared and added to the water solution. After 45 minutes of vigorous stirring the organic phase turned orange and water becomes transparent. Water phase was then discarded. 1 gr of ODA was dissolved in 40 ml of toluene, and afterwards added to the previous solution while it was vigorous stirred. A fresh solution of 35 mg of sodium borohydride in 4 ml of MilliQ water was added to the gold solution, which quickly turned dark brown. After 10 h the water phase was discarded. This stock solution was then divided in aliquots of 10 ml. For obtaining AuNPs-3.0 nm coated with the three different thiols we used a Ligand Exchange Reaction[3]. To obtain the three different coatings are added to the aliquots: 10 μl of a solution of MPT prepared with 60 μl of MPT diluted in 10 ml of toluene; 1.2 mg of BPT; 0.85 mg of TPT. Every solution was let stirring 18 hours. Obtained crude was purified with multiple precipitations by centrifugation adding ethanol and subsequently removing the surfactant.

AuNPs – 1.3 nm were prepared by digestive using molecular ratio already present in previous work[4] . We followed a procedure that we briefly describe: aliquots of 20 ml of AuNPs – ODA of stock solution were dried under vacuum and then dispersed in 5 ml of toluene with 30-second sonication. 100 μl of MPT were added to one aliquote, 110 mg of BPT to another, 75 mg of TPT to the last one. Solutions turned transparent after 1 hour and were stirred vigorously for 48 hour (TPT solution did not became transparent, because TPT solubility in toluene or chlorobenzene in not enough). The crude was purified with multiple precipitations by centrifugation adding ethanol and subsequently removing the surfactant.

2. AuNPs UV-Vis characterization

Absorption spectra of prepared solution were recorded with a JASCO V-650 UV-Vis Spectrophotometer and quartz cuvettes (HELLMA ANALYTICS). Peaks around λ=510 nm are obtained for 3.0 nm AuNPs related to the surface plasmon resonance. A blue shift is present after LER with thiols. For 1.3 nm AuNPs no peaks are present, and the solution appears transparent.

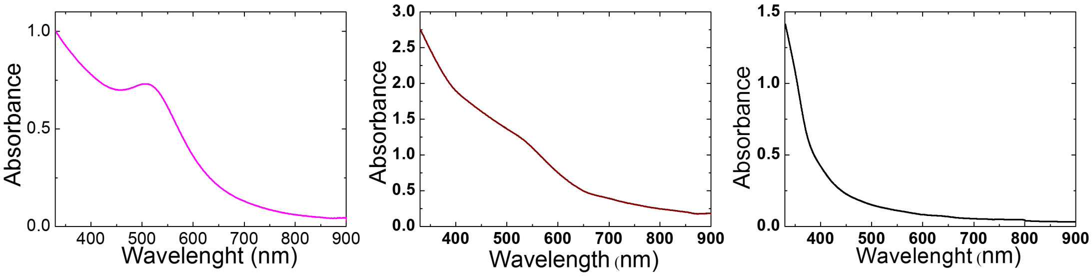

Figure S1. Absorption spectra normalized of (a) 3.0 nm AuNPs/ODA without purification, (b) 3.0 nm AuNPs/BPT after purification, (c) 1.3 nm AuNPs/BPT after purification.

3. AuNPs TEM size characterization

The Transmission Electron Microscopy (TEM) experiments have been carried out on a Jeol 2100 microscope with a LaB6 filament as electron source, operating at 200kV. The TEM micrographs have been acquired on an Orius camera. The microscope is equipped with an EDX JED 2300T detector and BF and DF detectors for operation under the scanning TEM (STEM) mode. The microscope resolution is 0.1 nm in the TEM mode and 1 nm in STEM.

Prior to analysis, the specimens have been diluted in Toluene solution for AuNPs specimen and a chlorobenzene solution for the blend P3HT/AuNPs with samples with a concentration of 1 mg/ml for the former and a concentration of 1 mg/ml of P3HT with 0.1 mg/ml AuNPs. For the TEM experiments, 1 to 3 drops of solution have been deposited on a holey carbon film deposited on a 300 mesh copper grid. Afterwards, the samples have been left to dry in air at the room temperature, for at least 30 minutes.

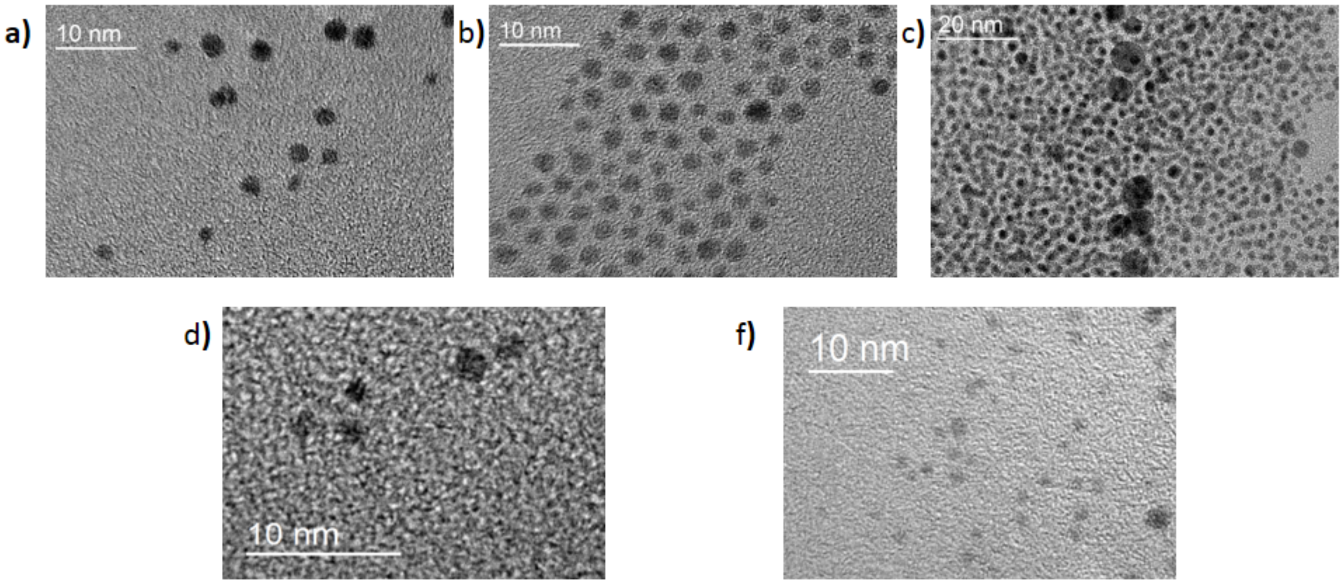

Figure S2. TEM images of the synthesized coated AuNPs drop-cast on carbon-coated, gold-plated copper microscope grids. (a) 3.0 nm AuNPs/MPT, (b) 3.0 nm AuNPs/BPT, (c) 3.0 nm AuNPs/TPT, (d) 1.3 nm AuNPs/MPT, (e) 1.3 nm AuNPs/BPT.

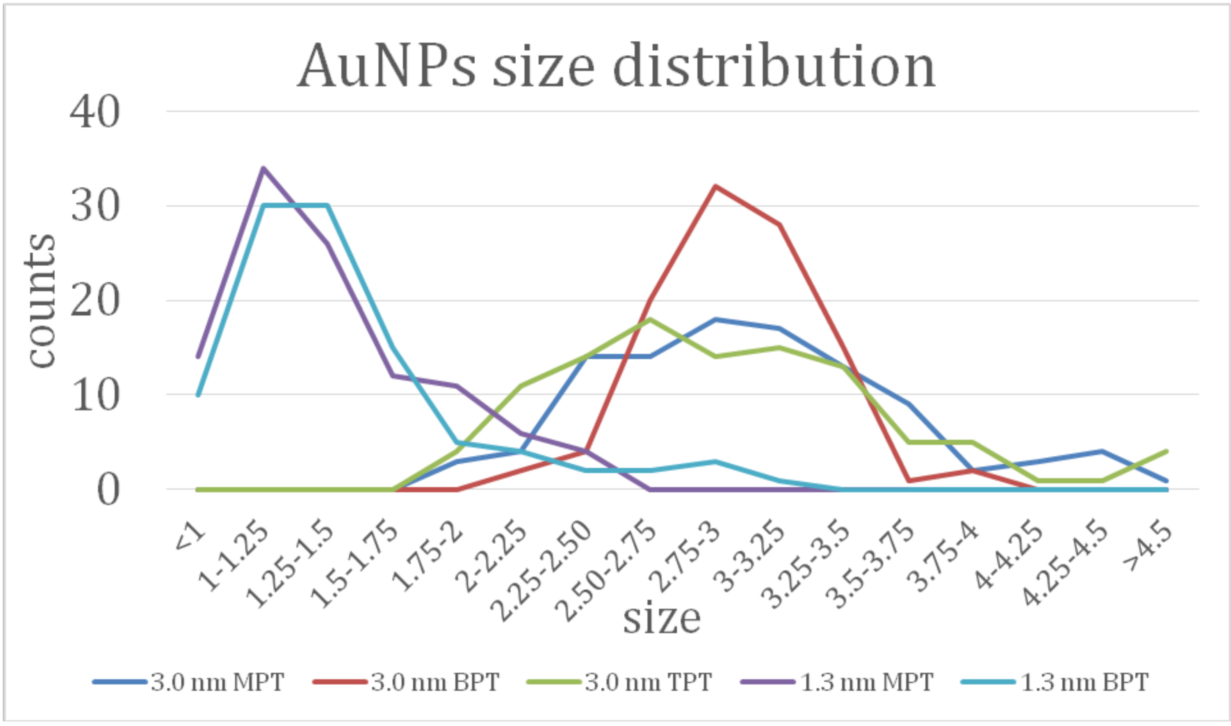

Figure S3. Size diagram distribution foqr the different NPs studied, as determined on TEM images. The mean diameter and the standard deviation of the population of particles are expressed in table S1. The values represent a statistic measure of more than 100 particles for each sample.

Table S1 Average sizes

	Avg. Size (nm)
3nm NPs/MPT	3.0 ±0.6
3nm NPs/BPT	3.0 ±0.3
3nm NPs/TPT	3.0 ±0.9
1.3nm NPs/MPT	1.3 ±0.4
1.3nm NPs/BPT	1.3 ±0.4

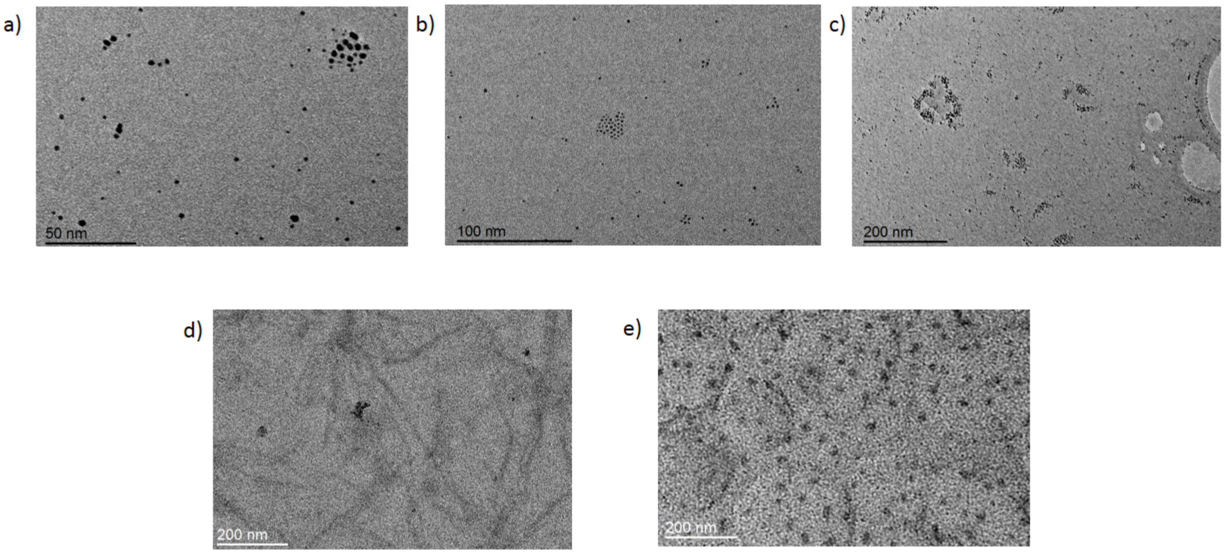

Figure S4. TEM images a blend of P3HT/AuNPs drop-cast on carbon-coated, gold-plated copper microscope grids. (a) 3.0 nm AuNPs/MPT, (b) 3.0 nm AuNPs/BPT, (c) 3nm AuNPs/TPT, (d) 1.3 nm AuNPs/MPT, (e) 1.3 nm AuNPs/BPT.

4. Blends and devices preparation

Every solution was dried under reduced pressure, the obtained solid was weighted and then chlorobenzene was added in proportion to obtain 50% weight/weight ratio (Au/solvent) solution. Under nitrogen atmosphere solution of P3HT and AuNPs/P3HT were prepared: each solution had a ratio P3HT/solvent w/w of 100%, for 3.0 nm-AuNPs 5%, 10%, 20% (n, 2n, 4n) and for 1.3 nm-AuNPs 0.25%, 0.5%, 1% (n, 2n, 4n) to obtain solution with approximately the same number of AuNPs.

Solution were stirred at 50° for 30 minutes to ensure complete miscibility of the components. OTFTs were prepared spin coating cold solutions on n^{++}-Si/SiO_2 substrates pre-patterned interdigitated gold source and drain electrode (IPMS Fraunhofer) for 60 sec at 1500 rpm (100 µl drop) and then annealed for 2h at 75 °C.

5. Parameter extraction

The charge carrier mobility was calculated from the drain-source current I_d versus gate voltage V_g in the saturation regime measured in nitrogen atmosphere using equation (S1)

$$\mu_{SAT,p} = \frac{2\cdot\left(\frac{\partial\sqrt{I_{D,Sat}}}{\partial V_{gs}}\right)^2}{C_{insulator}\frac{W}{L}} \tag{S1}$$

Table S2 Average mobility values extracted from the saturation regime

Semi conductive Active layers	Mobility of n blends ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	Mobility of 2n blends ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	Mobility of 4n blends ($cm^2 \cdot V^{-1} \cdot s^{-1}$)
P3HT	$(9.4\pm0.6)\times10^{-3}$	/	/
P3HT/AuNPs – 3.0 nm MPT	$(4.7\pm1.5)\times10^{-3}$	$(3.3\pm0.8)\times10^{-3}$	$(3.7\pm1.4)\times10^{-3}$
P3HT/AuNPs – 3.0 nm BPT	$(4.1\pm0.6)\times10^{-3}$	$(3.0\pm0.6)\times10^{-3}$	$(2.9\pm1.2)\times10^{-3}$
P3HT/AuNPs – 3.0 nm TPT	$(8.6\pm1.9)\times10^{-3}$	$(7.4\pm2.0)\times10^{-3}$	$(6.5\pm1.9)\times10^{-3}$
P3HT/AuNPs – 1.3 nm MPT	$(1.30\pm0.14)\times10^{-2}$	$(1.60\pm0.15)\times10^{-2}$	$(1.8\pm0.3)\times10^{-2}$
P3HT/AuNPs – 1.3 nm BPT	$(1.9\pm0.2)\times10^{-2}$	$(1.8\pm0.2)\times10^{-2}$	$(7.7\pm1.8)\times10^{-3}$

6. Output characteristics of all blends (20 µm devices)

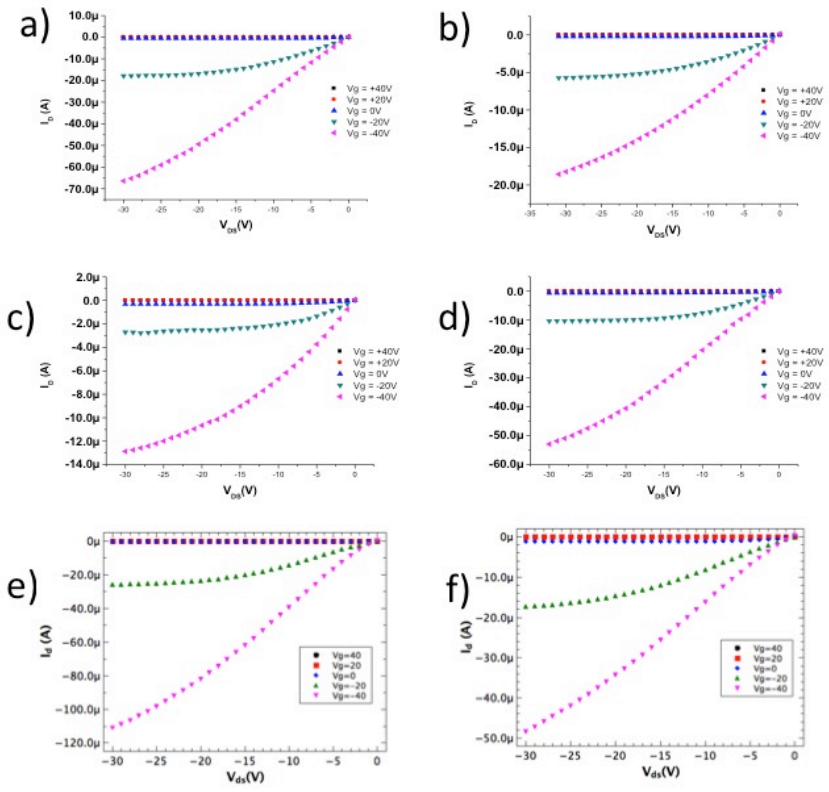

Figure S5. Transfer characteristics for (a) P3HT based OFET. (b) P3HT/AuNPs-3.0 nm MPT. (c) P3HT/AuNPs-3.0 nm BPT. (d) P3HT/AuNPs-3.0 nm TPT. (e) P3HT/AuNPs-1.3 nm MPT. (f) P3HT/AuNPs-1.3 nm BPT.

In Fig. S5 we report representative transfer characteristics for all the different system studied. Drain Voltage 0 to -30 and each for each curve the gate voltage is setted at: (40, 20, 0, -20, -40) Volt.

7. Analysis of the threshold voltage (V_{th})

Threshold voltage values have been extracted from the transfer characteristic of devices in saturation regime. In Fig. S6 we report the values obtained for P3HT, 10% 1.3 nm AuNPs – BPT and 10% 3.0 nm AuNPs – BPT. The blends show general more positive values for AuNPs blends with respect to P3HT pristine device and all systems show a shift to more negative values with increasing channel length.

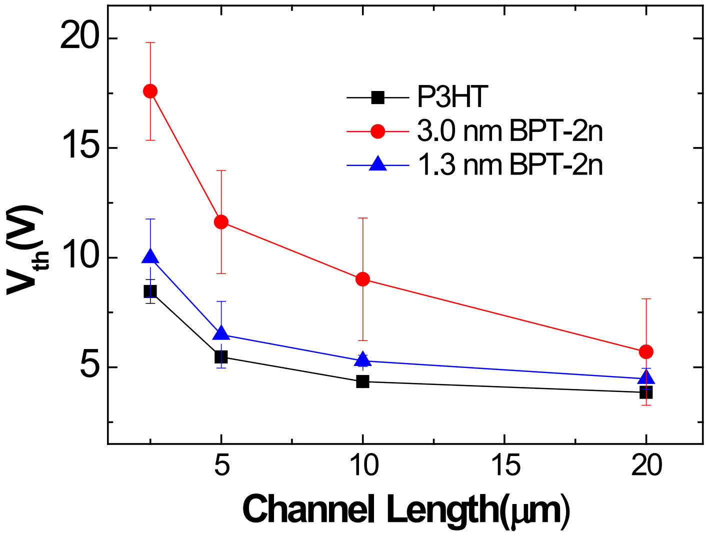

Figure S6. Plot of V_{th} values for P3HT, 1.3 nm BPT/AuNPs blend, 1.3 nm BPT/AuNPs blend.

8. UV-Vis film characterization

On glass substrate, 200 µl of solution of P3HT, P3HT/AuNPs-3.0 nm (MPT; BPT;TPT; coated – n,2n,4n amount of NPs in P3HT blend), P3HT/AuNPs-1.3 nm (MPT;BPT;TPT; coated – 0 n,2n,4n amount of NPs in P3HT blend) are spin-coated at 1000 rpm for 60 seconds, and then annealed for 120' at 75°. Spectra have been recorded with a JASCO V-650 UV-Vis Spectrophotometer with a sample holder for glass substrates.

Here a reported the values obtained for $A_{0\text{-}0}/A_{0\text{-}1}$ peak absorbance ratio and the exciton bandwidth values associated to them. We used the equation S2[5]

$$\frac{A_{0-0}}{A_{0-1}} = \left(\frac{1 - 0.24W/E_p}{1 + 0.0073W/E_p} \right)^2 \qquad \text{(S2)}$$

Table S3 peak ratio of all the thin films studied are reported with the associated exciton bandwidth

	0-0/0-1 ratio	W (meV) (free exciton bandwidth)
P3HT	0.955 ±0.005	0.013±0.001
1.3 nm MPT	0.934 ±0.002	0.020±0.001

1.3 nm BPT	0.934 ±0.004	0.020±0.001
3.0 nm MPT	0.925 ±0.004	0.022±0.001
3.0 nm BPT	0.921 ±0.002	0.023±0.001
3.0 nm TPT	0.929 ±0.001	0.021±0.001

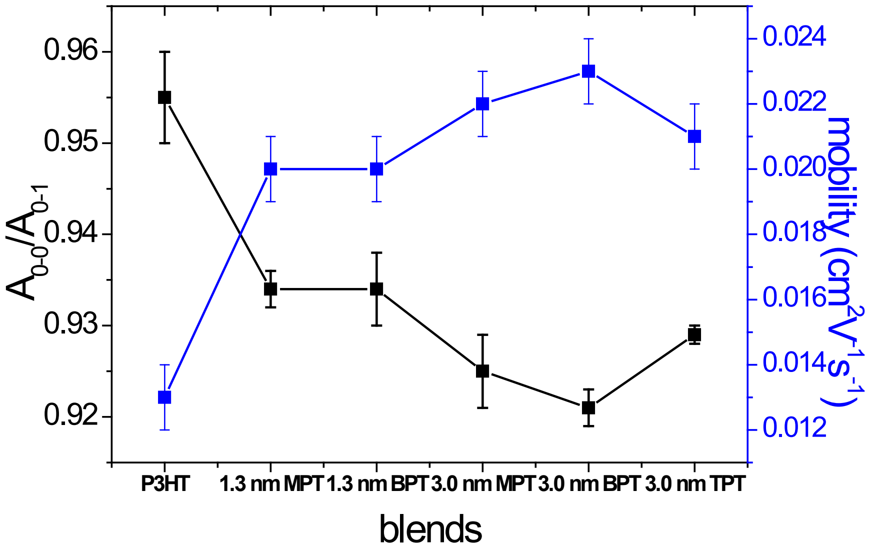

Figure S7. Plot of the values of Absorbance ratio (red) compared with the values obtained for the exciton bandwidth (blue) for all the blends studied

9. Ambient photoelectron spectroscopy

Ambient photoelectron spectroscopy measurements were performed by sampling in each measurement an area of about 4 mm^2 (beam size) by using a Photoelectron Yield Spectrometer operating in air (PYSA), Model AC-2 from Riken Keike Co., Ltd. The work function of P3HT on Au(111) were measured by extrapolating the energy point (in eV) where the square root of the photoelectron yield begins to rise upon excitation from the ground state. Figure S8 displays the variation of the square root of the photoelectron yield as a function of the incident energy. Samples were prepared by drop-casting 300 µl of every solution (P3HT 100% w/w); AuNPs-3.0 nm MPT, BPT, TPT and AuNPs-1.3 nm MPT, BPT) on warm Au(111) substrate evaporated on mica. The results presented here encompass a statistical average over 4 different measurements per sample.

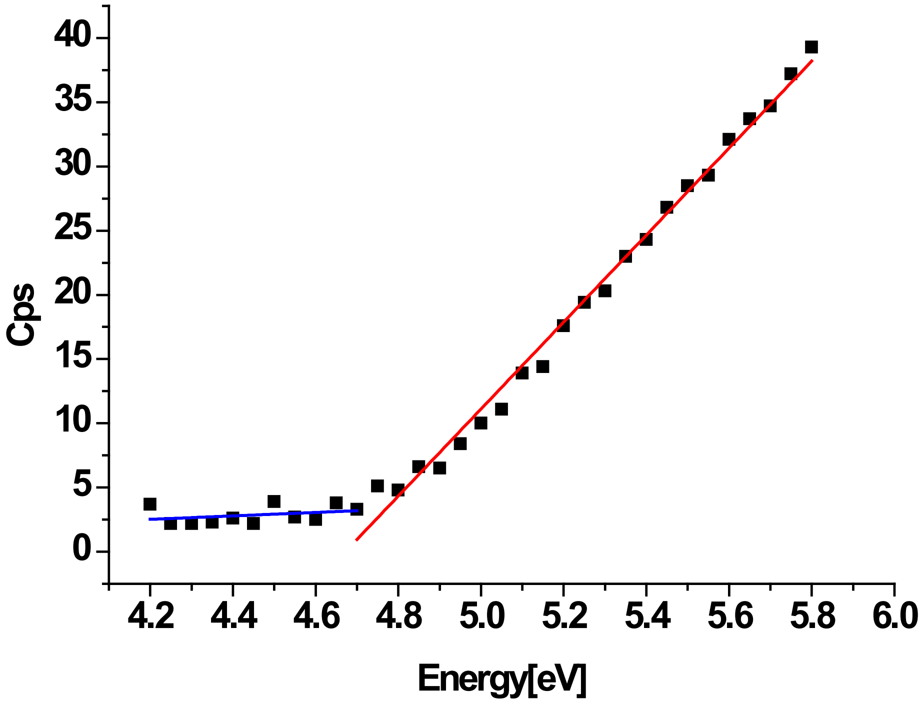

Figure S8. Photoelectron yield spectra for P3HT as example of raw data. Work functions were estimated from the x-axis intercept.

Table S4 Extracted values of ionization potential (I_p). Each value is obtained by averaging measurements recorded on 4 samples. The results are portrayed in Fig. 4

Materials	**I_p (eV)**
P3HT	4.69±0.02
AuNPs-3nm-MPT	4.73±0.02
AuNPs-3nm-BPT	4.78±0.02
AuNPs-3nm-TPT	4.79±0.02
AuNPs-1.3 nm-MPT	4.61±0.03
AuNPs -1.3 nm-BPT	4.60±0.06

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