

# **Total chemical synthesis of a polymer/graphene Nanocomposite**

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## **Supplementary Information**

## Experimental Section

Benzene (Carlo Erba), n-hexane, chloroform, thiophene, and ammonium hydroxide were used as received. Anhydrous iron chloride was vacuum dried at 120 °C. The handling of iron chloride was conducted in an inert atmosphere (argon).

In a typical procedure, 400 mg of iron chloride was added to 20.0 mL of organic solvent (n-hexane, benzene or chloroform) and then submitted to a sonication bath for 5 minutes (137 kHz, 154 W). Separately, 600 µL of thiophene was added to a 50.0 mL round-bottom flask with 20.0 mL of deionised water (previously purged with argon). While the thiophene/water system was magnetically stirred (the rotation speeds used were 250, 1250 and 2000 rpm), the black FeCl<sub>3</sub>/organic solvent dispersion were gently poured with the help of a glass rod. For the PT-chloroform, an inverted procedure was used due to the difference in density with water (i.e, the water/thiophene system was added to the FeCl<sub>3</sub>/organic solvent dispersion). The scheme of film production is illustrated in the Figure 1a. The reaction time was fixed at 3 hours. After this time the stirring was interrupted and the system was kept stationary. During the re-establishment of both the aqueous and organic phase, a red film is homogeneously self-assembled at the liquid-liquid interface, as can be seen in the picture presented in Figure 1b. After 3 h of reaction, the aqueous phase presented a strong orange-brown color, due the solubilization of the iron chloride. In order to eliminate the size products and wash the film, the aqueous phase was removed using a pipette, and approximately 5 mL of fresh water was added. All the system was maintained under magnetic stirring during 5 minutes, and then kept stationary again. This procedure was repeated 5 times. In the same way, the organic phase was removed and changed by toluene, and the procedure repeated 5 times. In the following, the aqueous phase was removed and changed by 5 mL of an aqueous solution of NH<sub>4</sub>OH (10% v/v), to remove the remaining iron species incorporated into the film. This procedure was also repeated 5 times, and then the system was washed again with deionised water. Finally, all the system present in the round bottom flask (water/film/toluene) was transferred to a beaker where the substrates were already inserted. Once the system was stopped, the film was removed pulling the substrate in direction of the interface, as represented in Figure 1c.

Three samples have been prepared, starting from 3 different organic solvents: n-hexane, benzene and chloroform. The samples were named PT-solvent, meaning that PT is synthesized in this particular solvent (e.g., PT-benzene).

The absorption spectra were acquired in a Shimadzu UV-2450 spectrophotometer, directly from the films deposited over quartz substrates.

Raman spectra were acquired in a Renishaw spectrophotometer using a backscattering configuration equipped with a He-Ne laser (632.8 nm). The samples were deposited over silicon substrates. A laser power less than 0.1 mW was used to avoid excessive sample heating.

The FTIR spectra in attenuated total reflectance (ATR) were acquired in a Bruker Vertex-70, using ZnSe as the substrates in which the films were deposited. The ratios described in the text (Raman, IR) were taken from the integrated area of the bands.

The transmission electron microscopy (TEM) images were obtained in a JEOL JEM 120 kV microscopy. The films have been destroyed from the liquid-liquid interface, transformed into a powder and a dispersion of the material was dropped over a carbon-covered copper grid. SAED and EDS measurements were obtained in a FEG-TEM (JEOL JEM-2100F) at 200 kV. The SAED measurements

were obtained with a camera length of 25 cm and were calibrated against a standard evaporated Al (TED PELLA Inc., Al diffraction standard, n° 619). EDS spectrum and mapping images were acquired using STEM mode.

Cyclic voltammetry was performed using a 0.1 mol.L<sup>-1</sup> LiClO<sub>4</sub> in CH<sub>3</sub>CN solution, a Pt wire as the counter-electrode, the PT films deposited over ITO as the working electrode and as Ag wire as the quasi-reference electrode; these electrodes were calibrated against a ferrocene/ferrocenium redox pair in the same conditions. All of the potentials were then referenced to Ag/Ag<sup>+</sup>. CH<sub>3</sub>CN was double-dried in a 3 Å molecular sieve and the measurements were performed under an argon blanket.

For the UV-Vis spectroelectrochemical measurements, a ITO substrate coated with the PT film was used inside a quartz cuvette containing the same electrolyte employed for the cyclic voltammetry measurements (0.1 mol.L<sup>-1</sup> LiClO<sub>4</sub> in CH<sub>3</sub>CN). The energy levels were calculated considering that Ag/Ag<sup>+</sup> is found to be 4.7 V higher related to vacuum.<sup>[43]</sup>

The thicknesses of the films were evaluated using a Dektak 3 profilometer. For determining the charge carrier mobility, hole-only devices were built by spin-coating a layer of PEDOT:PSS over patterned ITO and heating at 110°C under an N<sub>2</sub> atmosphere overnight to remove water. The PT films were then deposited over the PEDOT/ITO and, subsequently, an Al layer (100 nm) was thermally evaporated over the films.

The photovoltaic devices were built using the architecture FTO/PEDOT:PSS/PT-film/C<sub>60</sub>/Al. The PEDOT:PSS layer was spin coated (6000 RPM, 30 s) over FTO substrates (sheet resistivity of 5-10 Ω.□<sup>-1</sup>) and annealed at 110 °C under vacuum overnight prior to device assembly. The thickness of PEDOT:PSS was 50 nm. The FTO films with PEDOT were then coated with the PT-films as described above for interfacial film deposition. The process was repeated, composing two PT layers over the FTO/PEDOT:PSS. The devices were then dried at 100 °C to evaporate the solvent. Finally, 30 nm of C<sub>60</sub> and 100-200 nm of Al were evaporated through a mask over the PT films, creating patterned area of cells to light exposure. The *I*<sub>x</sub>*V* curves and the IPCE were obtained using a 6487 Keithley picoamperemete under AM1.5 illumination (Oriel 77700 monochromator, Phillips Lamp 250 W).

## Vibrational analysis of Figure 2

Vibrational spectroscopy was used to gain insight on the chemical structures of the films. Raman (514.5 nm) and infrared (IR) spectra are presented in Figure 2, confirming the occurrence of unsubstituted polythiophene (Fig. 2a-c). The  $sp^2$  structure of the pure graphene sample is evidenced by the Raman spectrum in Figure 2d, featuring three main bands located around 1350, 1588 and 2700  $cm^{-1}$ , assigned to the D, G and G' bands, a fingerprint of graphene and  $sp^2$  carbon materials.<sup>30</sup> Due to the strong resonant effect of PT in Raman spectrum, we could not observe the graphene modes in the spectrum of PT-benzene (Fig. 2a), although its observation within the polymer is more straightforward using electron microscopy techniques as will be presented. Comparing the polythiophene spectrum of samples prepared with benzene, chloroform and hexane, we observe that the solvent has influence over the quality of the PT. It becomes evident that the samples prepared with hexane (Fig. 2c) are different from those prepared with benzene and chloroform, whose spectra (Raman and IR) are comparable (Fig. 2a-2b). Three main features confirms this: **(1)** the ratio of the symmetric ( $\sim 1439\text{ cm}^{-1}$ ) to the antisymmetric ( $1490\text{ cm}^{-1}$ ) (IR spectrum) stretching mode of  $C_{\alpha}=C_{\beta}$  ( $I_{\text{sym},1439}/I_{\text{asym},1490}$ ) is much higher for PT-hexane, indicating much lower conjugation lengths;<sup>31,32</sup> **(2)** the ratio of  $701\text{ cm}^{-1}$  band (out-of-plane ring symmetric bending) in Raman spectrum over side bands ( $650, 681, 759\text{ cm}^{-1}$ ) is much lower in PT-hexane indicating more distorted PT chains;<sup>31</sup> **(3)** the ratio of  $700/782\text{ cm}^{-1}$  band in IR spectrum (out-of-plane C-H bending in the 2-monosubstituted and 2,5-disubstituted, respectively) is higher in PT-hexane, indicating lower degree of polymerization. This result indicates that the polythiophene produced in the samples PT-chloroform and PT-benzene are structurally comparable. The reason why the PT-hexane is structurally inferior to the other samples is related to the poor interaction of alkanes with  $FeCl_3$ , while chloroform and benzene are known to have strong interaction with Lewis acids.<sup>17,19,33</sup>

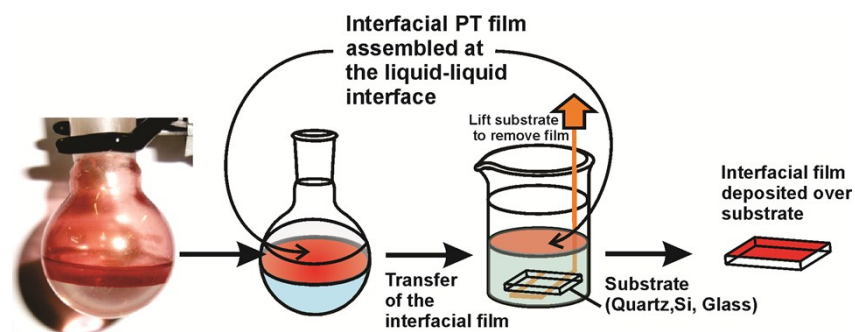


Figure S1. Film removal. Scheme of interfacial film removal and deposition over substrates

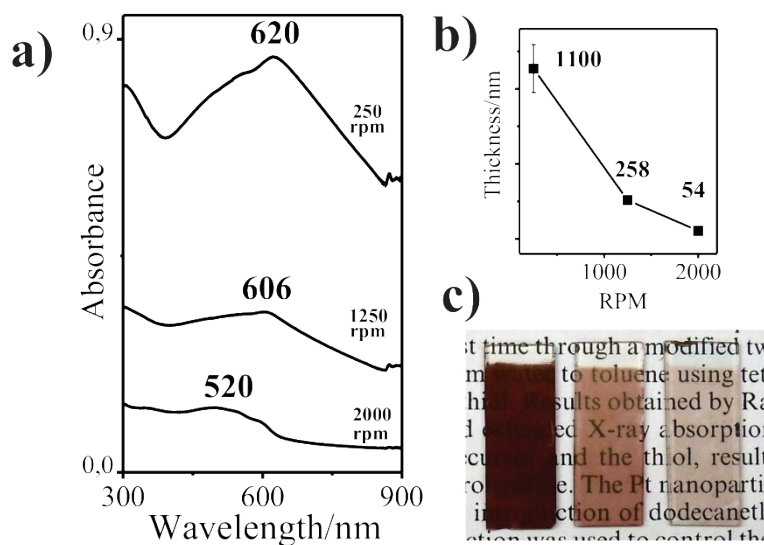


Figure S2. Effect of magnetic stirring speed of the synthesis of PT. (a) UV-Vis spectrum showing the effect of the speed on the UV-Vis spectrum; (b) effect on the thickness of the film; (c) photographs of the films (from left to right, films synthesized with 250, 1250 and 2000 RPM)

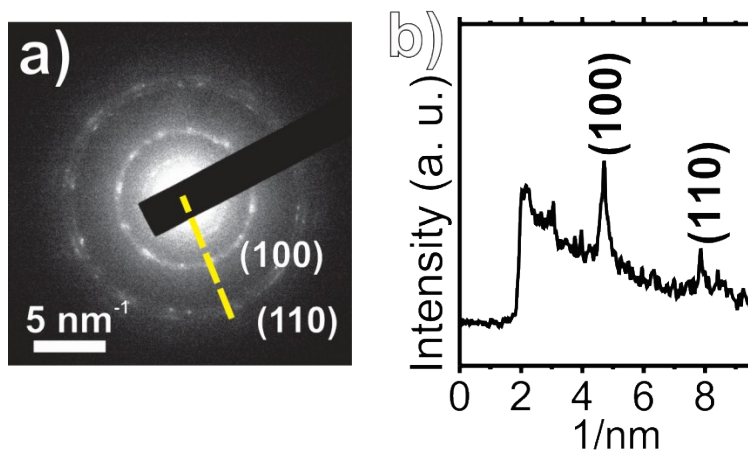


Figure S3. SAED of Figure 3c (a) and the corresponding intensity profile (b) along the dashed arrow presented in (a).

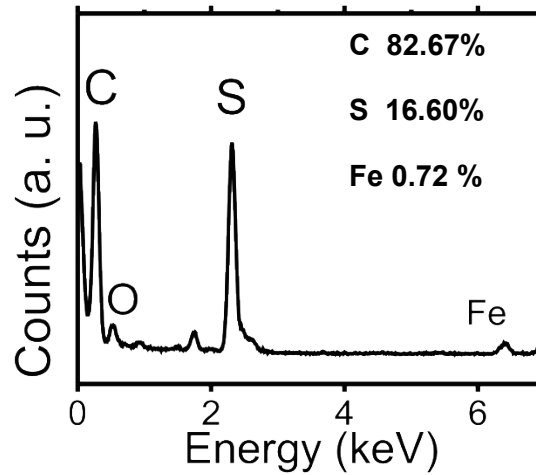
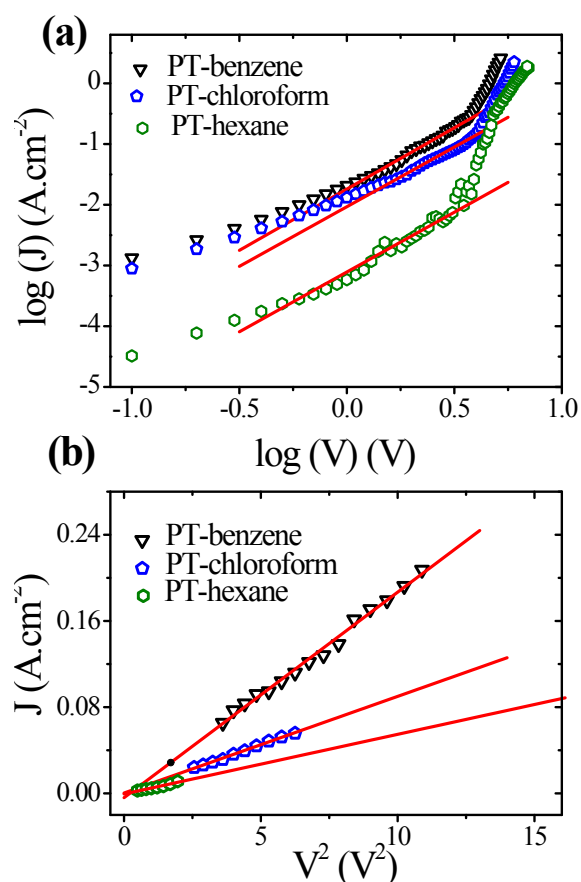


Figure S4. EDS spectrum of Figure 3c

**Mobility of the films:** Mobility of the films was calculated from space-charge limited current (SCLC) measurements (Macedo, A. G. et al. Hole mobility effect in the efficiency of bilayer heterojunction polymer/C[sub 60] photovoltaic cells. Applied Physics Letters 98, 253501 (2011)). The  $\log(J) \times \log(V)$  curves are presented in Figure S5a. The first range in  $\log(V)$  corresponds to ohmic regime, as slope equals to 1. The data range in the curves that fits to slope equal to 2 (SCLC regime) are extracted from the curves (represented as red lines in Fig S5a) and plotted as  $J \times V^2$  in Fig S5b. The SCLC obeys to the Mott-Gurney equation (Equation 1), in which  $\epsilon = \epsilon_r \cdot \epsilon_0$  ( $\epsilon_r$  is the permittivity of the polymer, taken as 3,  $\epsilon_0$  is the permittivity of the vacuum),  $\mu$  is the effective mobility,  $J$  is the current density,  $V$  is the applied voltage and  $L$  is the thickness. Then, mobility was calculated by linear fit of the  $J \times V^2$  curves. Thickness (average values) of the samples were acquired from profilometer and are 289, 224, 260 and 242 nm for PT-Benzene, PT-Chloroform, PT-Hexane, respectively. All films were synthesized using the same magnetic stirring rotation.

$$(1) \quad J = \frac{9}{8} \cdot \epsilon \cdot \mu \cdot \frac{V^2}{L^3}$$



**Figure S5.** (a)  $\log(J)$  vs  $\log(V)$  and (b)  $J$  vs  $V^2$ . The fitted curves in (a) corresponds to slope equal to 2. The data range of (a) is then plotted in (b) to apply the Mott-Gurney equation

**Table S1.** Energy levels (eV) ( $E_{\text{LUMO/HOMO}}$ ) for the PTs (electrochemical onset), energy separation between HOMO and LUMO ( $E_g$ ) and SCLC hole mobility ( $\mu$  in  $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ). The average values ( $\mu_0^{\text{avg}}$ ) and maximum values ( $\mu_0^{\text{max}}$ ) of mobility are presented

	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$E_g$	$\mu_0^{\text{avg}}$	$\mu_0^{\text{max}}$
PT-benzene	-5.47	-4.03	1.44	$1 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$
PT-chloroform	-5.48	-4.07	1.41	$3.2 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$
PT-hexane	-5.35	-3.57	1.78	$3.1 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$

**Table S2.** Photovoltaic Parameters\* of device built with PT-benzene and PT-chloroform

Active layer	$V_{\text{OC}}$ [V]	$J_{\text{SC}}$ [ $\text{mA} \cdot \text{cm}^{-2}$ ]	FF [%]	$\eta$ [%]
PT-benzene	0,44	-0,24	26	0,027
PT-chloroform	0,32	-0,09	23	0,007

\* $V_{\text{oc}}$  - open circuit voltage;  $J_{\text{SC}}$  - short circuit current density; FF - fill factor (in %);  $\eta$  - conversion efficiency (in %)