SUPPLEMENTARY INFORMATION

Facile room temperature synthesis of large graphene sheets from simple molecules

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1. EXPERIMENTAL

Benzene chromasolv plus for HPLC ≥ 99.9% (Sigma Aldrich), n-hexane 99% UV/HPLC spectroscopic (Vetec), toluene 99.5% (Reatec), aqueous solution of NH_4OH 28% (Biotec), sodium dithionite 87% (Dynamic), anhydrous sodium carbonate 99.5% (Vetec), oxalic acid dihydrate 99.6% (Neon) were used as received. Water was milli-Q deionized, and $FeCl_3$ anhydrous 98% (Acros organics) was dried under vacuum at 120 ^{o}C for 3 h, immediately before use.

The chemical synthesis of graphene was carried out in a 50 mL round-flask in which a water/oil liquid/liquid (L/L) interface was created, adding 10 mL of milli-Q deionized water and 10 mL of organic solvent. Four different samples were prepared, based on four aqueous/oil L/L interfaces: neat benzene, a benzene solution in n-hexane (1 μL of benzene in 10 mL of n-hexane), neat n-hexane and a pyridine solution in n-hexane (1 μL of pyridine in 10 mL of n-hexane), resulting in the samples GR-BZ, GR-BZ/HX, GR-HX and GR-PY, respectively. The system was maintained under magnetic stirring (1000 rpm) and a total of 2.0 g of solid anhydrous $FeCl_3$ (previously dried under vacuum at 120 ^{o}C for 3 h) was slowly added to the system in 20 portions of 100 mg, at each 2 min. The system was kept under magnetic stirring at room temperature for 3 h, and after this period the stirring was interrupted and all the product was found as a grey thin film self-assembled at the L/L interface. The film was systematically cleaned to remove soluble side-products of the reaction, according to the following protocol: the aqueous phase was completely removed using a Pasteur pipette, and replaced by ultrapure water keeping the film supported at the L/L interface. This procedure was repeated 10 times. In the following, the organic phase containing benzene was completely removed with the aid of a micropipette, and replaced with toluene to maintain the interface. This procedure was repeated 5 times.

A chemical treatment has been done to remove the excess of iron oxide remaining in the film: the aqueous phase was again completely removed and replaced by aqueous solution of NH_4OH (20% v.v^{-1}). This procedure was repeated 5 times and then the NH_4OH solution was completely removed and replaced by ultrapure water. Then, the DCO method (sodium dithionite-sodium carbonate-oxalic acid) was used, which consists in replacing the aqueous phase of the interfacial system, after cleaning with ultrapure water and NH_4OH solution, by a solution containing oxalic acid and sodium carbonate (0.85 g of each component in 100 mL of ultrapure water). The system (aqueous phase/film/toluene) was heated in a water bath at 80 °C under magnetic stirring, and then, 0.25 g of sodium dithionite was added to the system in small portions over a period of 5 minutes. After cooling, the aqueous phase was again replaced by ultrapure water with the aid of a Pasteur pipette. This procedure was repeated 10 times.

In order to deposit the film at the interface over a substrate, it was removed from the L/L interface using a micropipette, and transferred to a beaker containing the substrate (glass, Si, Si/SiO_2, quartz) fixed to a stem immersed in ultrapure water. The film goes spontaneously to the water/air interface, and the stem was carefully lifted, leading to film deposition over the substrates. A schematic representation of the synthetic procedure and the film deposition, as well as a digital picture of the GR-BZ film deposited over a glass substrate, is presented in Figure S1.

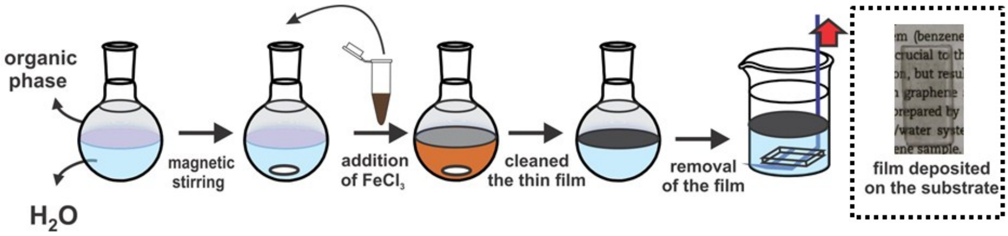

Figure S1 – Schematic of the preparation and film deposition of graphene. At the right a digital picture (1×2 cm) of the GR-BZ film deposited over a quartz substrate (the picture was tooken over a text in order to demonstrate the transparency and homogeneity of the film).

2. CHARACTERIZATION OF THE SAMPLES

The Raman spectra were obtained in a Renishaw spectrophotometer, coupled to an optical microscope, with spatial resolution of 1 μm^2 (objective lens of 50×). The spectral range analyzed was 200 to 3500 cm^{-1} with the thin films deposited under Si/SiO_2 substrate. A He-Ne laser (632.8 nm, 1.96 eV) with a power of 1.2 mW was used.

The X-ray diffractograms were obtained using a low-angle accessory, the incident angle of 0.1 ° in a Shimadzu XRD-6000 equipment, with CuKα radiation (λ = 1.5418 Å), 40 kV voltage and 40 mA. For the accomplishment of the measurements three layers of thin film were deposited in glass slides in order to minimize the contribution of the substrate.

X-ray photoelectron spectra (XPS) were acquired using a Thermo Scientific ESCALAB 250Xi spectrometer equipped with hemispherical type electron energy analyzer. A flood source was used to generate a diffuse beam of low energy electrons and Ar^+ ions were used during all measurements in order to avoid surface loading. A monochromatic excitation energy Al Kα (hv = 1486.6 eV) was used with X-rays spot size of 650 µm. The electron energy analyzer was operated at a constant throughput of 100 eV and 25 eV for high resolution and survey spectra, respectively. To acquire and process XPS spectra, Thermo Scientific Avantage XPS software (version 5.87) was used. A linear combination of Gaussian and Lorentzian functions was selected for the spectra adjustment, while the Shirley function was used for background correction. For all spectra, the binding energy calibration was performed using the Au ($4f_{5/2}$) line at 84.0 eV.

Scanning electronic microscopy (SEM) images were obtained on a Tescan SEM-FEG (field emission gun) equipment, employing secondary electron detectors, backscattered electrons and X-ray dispersive energy (EDS) using a voltage of 10 kV. The samples were deposited directly on the Si substrate to perform the analysis.

The atomic force microscopy (AFM) images were carried out in the phase mode using a SPM 9700 (Shimadzu) microscope. Preparation of the sample to obtain the AFM images was as follows: after all the washing process, part of the film was removed from the interface using a Pasteur pipette and transferred to another volumetric round flask. To this flask were added 10 drops of isopropanol and placed on bath ultrasound for 30 seconds for dispersion. This procedure was performed in order to obtain isolated graphene sheets. In the following, the isopropanol dispersion was dropped over a Si/SiO_2 substrate where the measurements were performed.

Thermogravimetric analysis was performed in a TA Instruments SDT Q600, with heating rate equal to 5 ^{o}C min^{-1} and under air atmosphere.

Transmission electron microscopy (TEM) images were obtained in a JEOL 120 kV instrument in mode bright field and dark field. The samples were prepared either by depositing the film directly from the L/L interface to the copper grids coated with a carbon thin film, or by destroying the film, followed by their dispersion in isopropanol. A drop of this dispersion was deposited over copper grids coated with a carbon thin film and dried at room temperature in a desiccator. Electron diffraction patterns were obtained at the same TEM equipment calibrated against a polycrystalline gold sample.

The GC-MS analyzes were performed on a Shimadzu QP2010 Plus spectrometer, operating in the electron impact ionization mode (70 eV) coupled to a Shimadzu GC-2010 gas chromatograph. The samples were eluted on a DB-5 capillary column (30 m × 0.25 mm di; 0.25 µm film thickness; Agilent Technologies; Santa Clara, CA), under a flow of 1 mL min^{-1} . The initial column temperature was 70 °C, held for 2 minutes. After that time, the temperature increased from 15 °C min^{-1} to reach 190 °C, remaining at that value for 1 minute. Then it was increased to 260 °C with increments of 10 °C min^{-1} and finally to 285 °C with increments of 5 °C min^{-1} remaining at that temperature for 10 minutes.

For the ESI-MS analysis, 500 µL of each sample were diluted in 500 µL of acetonitrile and the MS analyzes were performed in the microOTOF-Q III mass spectrometer (Bruker Daltonik, GmbH). The electrospray source was operated in the negative mode. High purity nitrogen (> 98%) was used as desolvation, nebulizer, and collision gas. For desolvation, the temperature was kept at 200 °C and the flow of nitrogen at 5 L min^{-1}. Nebulizer pressure was kept at 0.4 bar and the capillary voltage set at -5000 V. The Q-TOF conditions were as follows: End plate offset: -500 V; Funnel 1: 200 Vpp; Funnel 2: 200 Vpp; Hexapole RF: 200 Vpp; Collision RF: 150 Vpp; Transfer Time: 80 µs; Pre Pulse Storage: 5 µs; Ion Energy Quadrupole: -8 eV; Rolling Average: 2 x 1 Hz. The mass spectra were acquired and processed using a Bruker Compass DataAnalysis Software (Bruker Daltonik, GmbH).

3. RESULTS

Raman Data

The intensity ratio between the D and the G bands (I_D/I_G ratio) can be related to the amount of defects in the graphene sample, as well as to estimate the mean distance between two defects (L_D) or the size of the graphene cluster (L_A). All these data (average between all the spectra collected from each sample) for the samples prepared here is presented in Table S1, showing that the values are almost comparable between all samples.

The position, profile and full width at half maximum (FWHM) values of the 2D band can also be used to identify the number of stacked sheets in graphene samples. The 2D bands of monolayer graphene has just one spectral component, while in the bilayer graphene, the 2D band is lorentzian deconvoluted in 4 components. The analysis of the 2D band of the spectra indicates the presence of mono-, bi- and multi-layer graphene, but majority bilayer. Some illustrative examples of the representative profile found in the samples are presented in Figure S2.

Table S1 – Some information collected from the Raman spectra of the samples. The data presented here consists of an average of almost 30 spectra collected at different point of each sample, and it refers only to spectra presenting the graphene-like spectral profile (in which representative features are presented at the left side of the Figure 1).

sample	G band (cm^{-1})	D band (cm^{-1})	I_D/I_G	2D band (cm^{-1})	FWHM 2D (cm^{-1})	L_A (nm)	L_D (nm)
GR-BZ	1581	1334	1.2±0.5	2660	51.0±8.9	36,7	9,2
GR-BZ/HX	1583	1334	1.0±0.5	2662	51.0±8.7	44,0	11,0
GR-HX	1583	1332	1.1±0.3	2663	52.8±7.9	40,0	10,0
GR/Py	1582	1332	1.5±0.3	2659	58.9±5.4	29,3	7,3

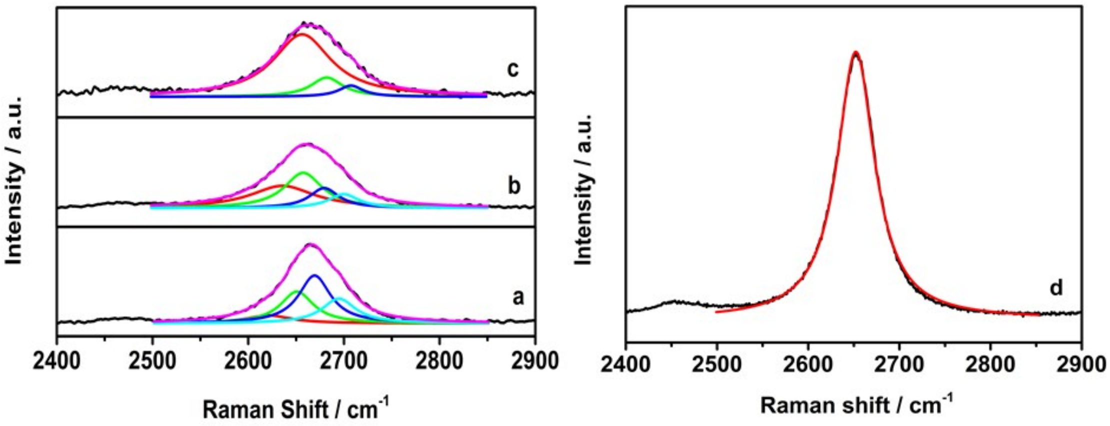

Figure S2 – Deconvolution of the 2D band of different spectra collected of the samples: GR-BZ (a), GR-BZ/HX (b,d) and GR-HX (c). (a) and (b) present deconvolution profile of bi-layer graphene; (c) of multi-layer graphene and (d) of single-layer graphene.

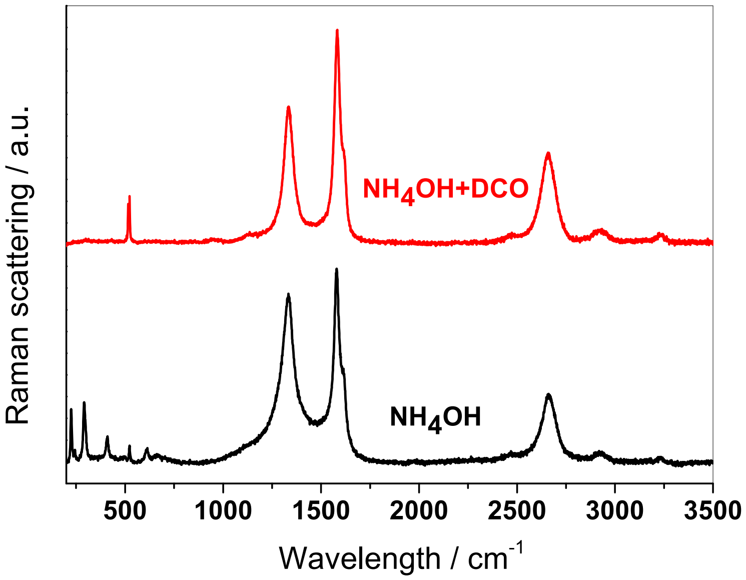

Figure S3 – Raman spectra of the GR-BZ sample after treatment with NH_4OH solution (black) and after the DCO treatment (red) to reduce the amount of iron oxide remaining in the film. In the black curve, bands at 225,243,292, 408 and 610 nm corresponds to iron oxide vibration modes (α-Fe_2O_3 and Fe_3O_4). In the red curve, the band at 520 nm corresponds to Si used to calibrate the system.

SEM images

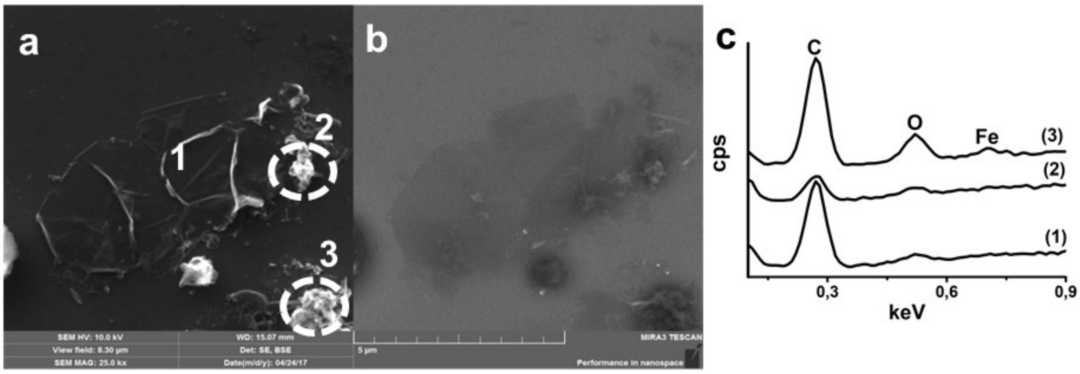

Figure S4 - SEM images of the sample GR-BZ collected using secondary electrons (a) and backscattering electrons (b); (c) EDS spectra collected in the points marked in (a).

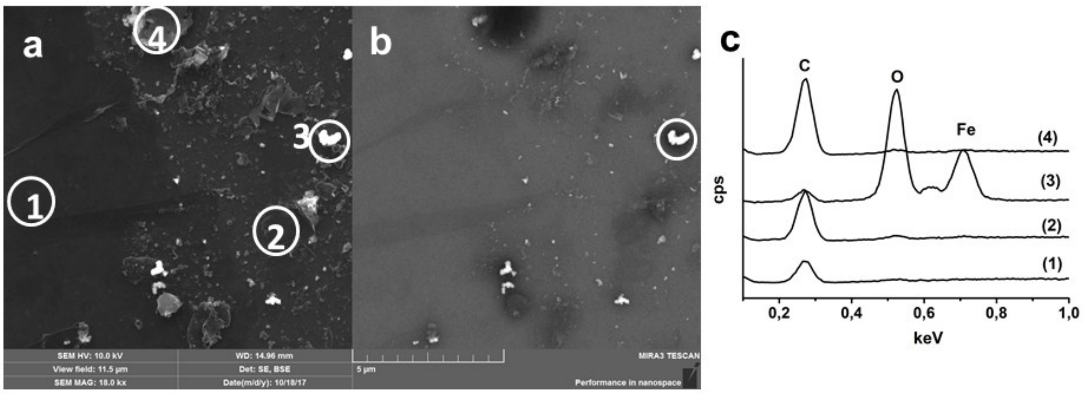

Figure S5 - SEM images of the sample GR-HX collected using secondary electrons (a) and backscattering electrons (b); (c) EDS spectra collected in the points marked in (a).

TEM and SAED data

The selected area electron diffraction (SAED) pattern of the area presented in the TEM image of Figure S6a is shown in Figure S6b. The electron diffraction pattern shows the typical six spot set organized in a hexagonal structure. The interplanar distance due to the (0,-1,1,0) reflection is 0.213 nm, as expected for graphene. The presence of some interference in the ED pattern is noticeable, due to the side-products of the reaction discussed in the manuscript, and observable in the TEM image presented in the Figure S6a.

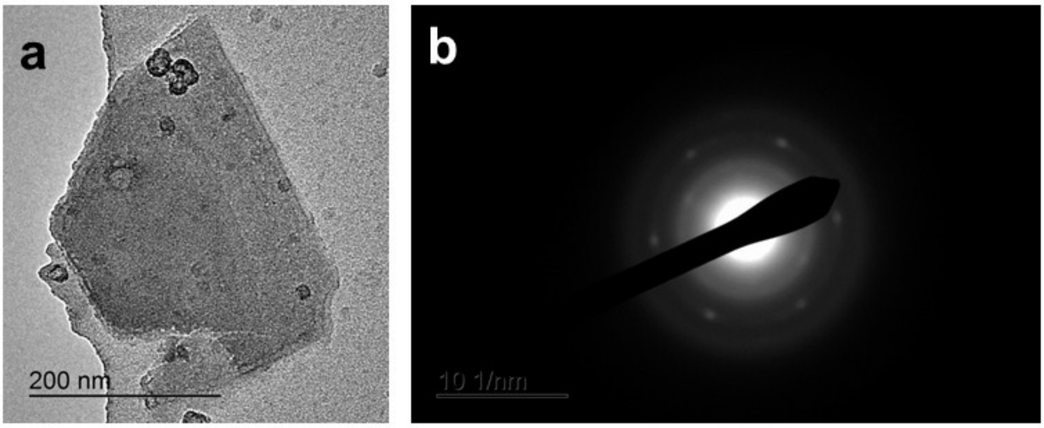

Figure S6 – (a) TEM image and (b) electron diffraction pattern collected from the selected area shown in (a).

Size histogram (area of the graphene sheets)

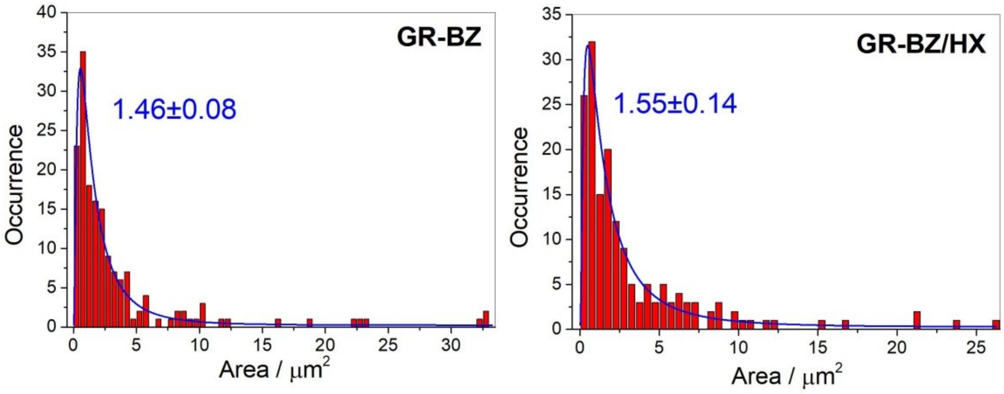

Figure S7 – Size histograms of the area of graphene sheets present in the samples GR-BZ (a) and GR-BZ/HX (b). Histograms were obtained by counting 165 graphene sheets on SEM and AFM images of each sample. The lognormal Gaussian fitting (blue line in the Figure) shows the average area of the graphene sheets as 1.46±0.08 and 1.55±0.14 μm² for the samples GR-BZ and GR-BZ/HX, respectively. For both samples, approximately 43% of sheets have area higher than 2 μm², and 31% higher than 3 μm².

X-ray diffraction data

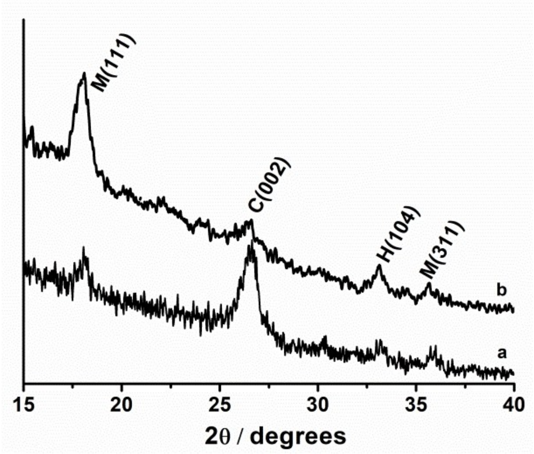

Figure S8 – X-ray diffractometry profile of the samples GR-BZ (a) and GR-BZ/HX (b). The symbol M corresponds to peak due to the magnetite (Fe_3O_4), H to the hematite (α-Fe_2O_3) and C to Carbon.

XPS data

Table S2 – C1s XPS data

		GR-BZ	**GR-BZ/HX**	**GR-HX**
Peak (eV)	**attribution**	**% atomic**	**% atomic**	**% atomic**
284.5	C=C (sp^2)	72.2	76.1	67.5
285.5	C-C/C-H (sp^3)	13.3	14.0	15.4
286.6	C-O (sp^3)	7.6	5.1	11.4
288.6	C=O (sp^2)	6.9	4.8	5.7
sp^2/sp^3 ratio		79.1/20.9	80.9/19.1	73.2/26.8

Thermogravimetric analysis

The fraction of each component in the sample was estimated by thermogravimetric analysis (TGA). In order to collect enough amount of product to get a trustable TGA, it was necessary to repeat approximately 20 synthetic procedures. In this experiment, after the 3 hours of each reaction the film obtained at the L/L interface was completely removed with the aid of a micropipette and dried at 70 ^{o}C. After accumulating all necessary material mass, the measurement was performed under air. No further treatment for the iron content removal has been carried out in the samples, which means that the TGA analysis was performed over the raw sample, as it was obtained. The TGA data obtained for the GR-BZ sample is presented in Figure S9.

The thermogravimetric analysis showed 3 events of mass loss: i) the first event between 20 - 133 °C is attributed to water loss (6%); ii) the second one between 230 - 430 °C corresponding to the oxidation of amorphous carbon (18.5%) and iii) the third one between 430 - 610 °C related to the graphene oxidation (25.9%). The residue attributed to the iron species was 49.6%. So, considering only the carbon-based portion of the sample, we can estimate that it is 58% of graphene and 42% of amorphous carbon.

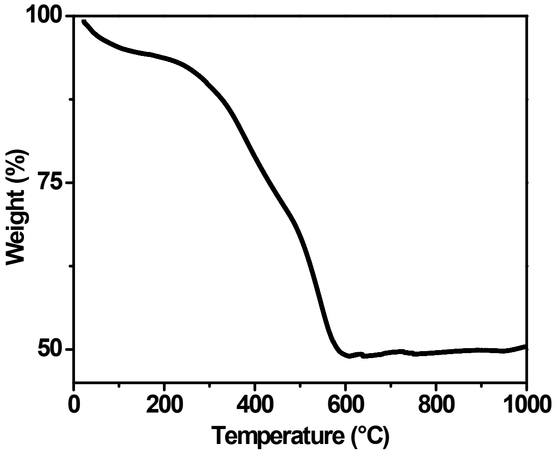

Figure S9 – TGA of the sample GR-BZ, under air atmosphere.

Experiments without water

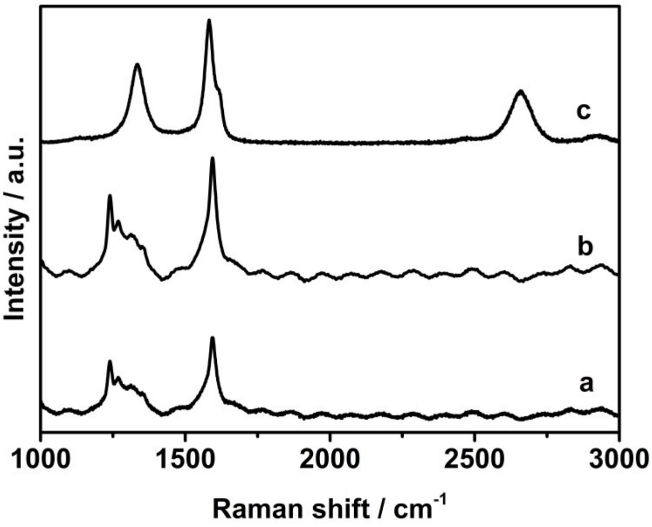

Figure S10 – (a) Raman spectra of the product of the reaction carried out employing the same experimental condition as employed to synthesize the sample GR-BZ, but without water; (b) Raman spectra of the product of the reaction carried out employing the same experimental condition as employed to synthesize the sample GR-BZ, but using a benzene/ethylene glycol to originate the L/L interface, and without water; (c) Raman spectra of the sample GR-BZ. The bands at 1238, 1270, 1309, 1351 and 1593 observed in (a) and (b) are fingerprints of the polymer of benzene, Poly-paraphenilene (PPP).

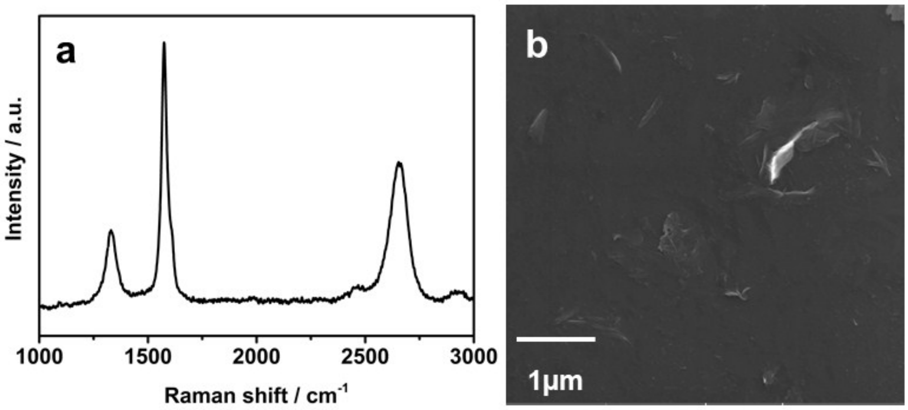

Figure S11 – Raman spectrum (a) and SEM image (b) of the product obtained from the reaction carried out in a benzene/triethylamine L/L system.

GC-MS and ESI-MS

The organic phase remaining after the reaction was analyzed further by gas chromatography coupled to mass spectrometry (GC-MS) and electrospray ionization quadrupole time-of-flight mass spectrometry (ESI-MS). It is noticeable that even for the HPLC grade solvents, there are some impurities, identified as aliphatic hydrocarbons and phthalates.

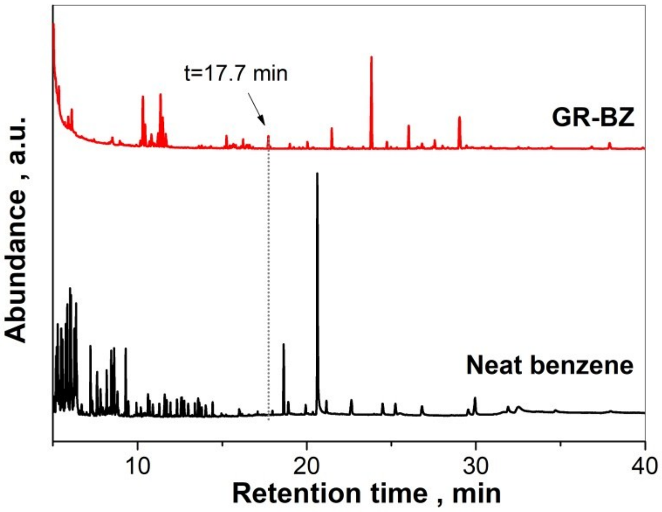

Figure S12 – GC profiles for GR-BZ and neat benzene

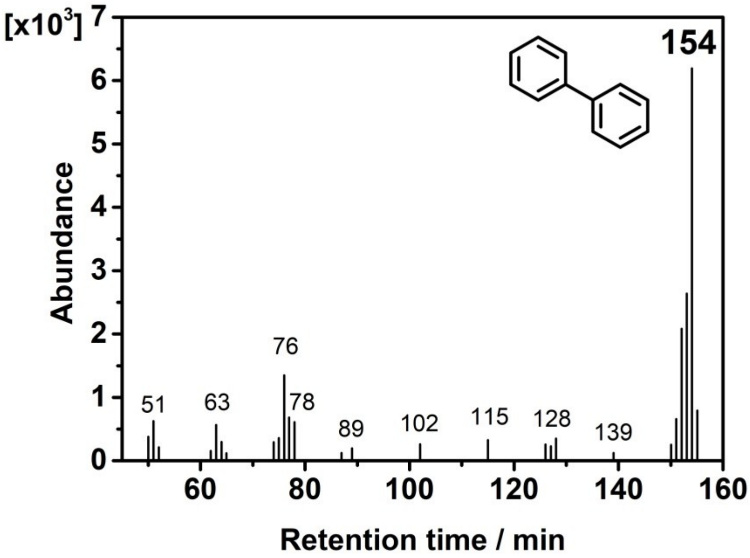

Figure S13 – GC-MS for GR-BZ at retention time of 17.7 min

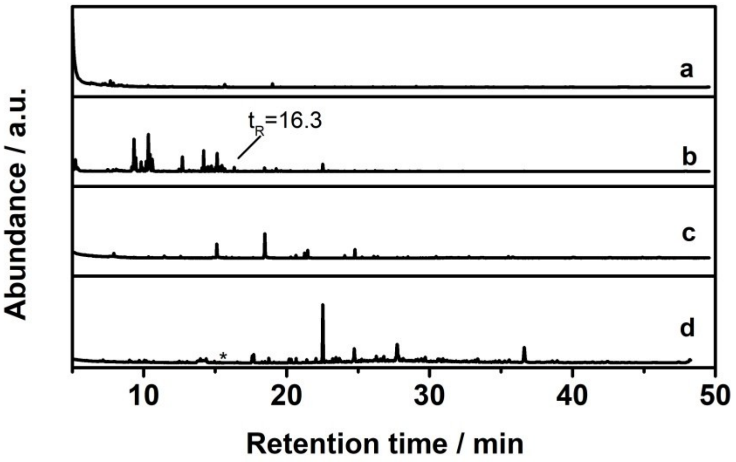

Figure S14 – GC profiles for (a) neat n-hexane (b) organic phase from the synthesis of GR-HX (c) n-hexane distilled from the organic phase of the synthesis of GR-HX, without the signal of biphenyl; (d) reuse of distilled n-hexane from c, that was employed in another synthesis of GR-HX, again evidencing the signal of biphenyl.

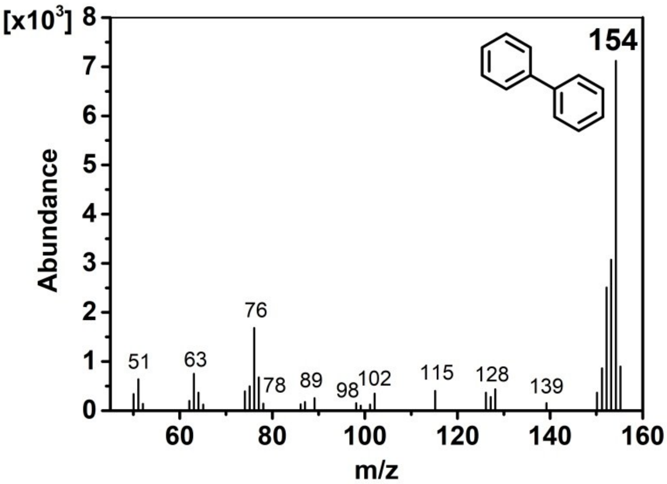

Figure S15 – GC-MS for GR-HX at retention time of 16.3 min

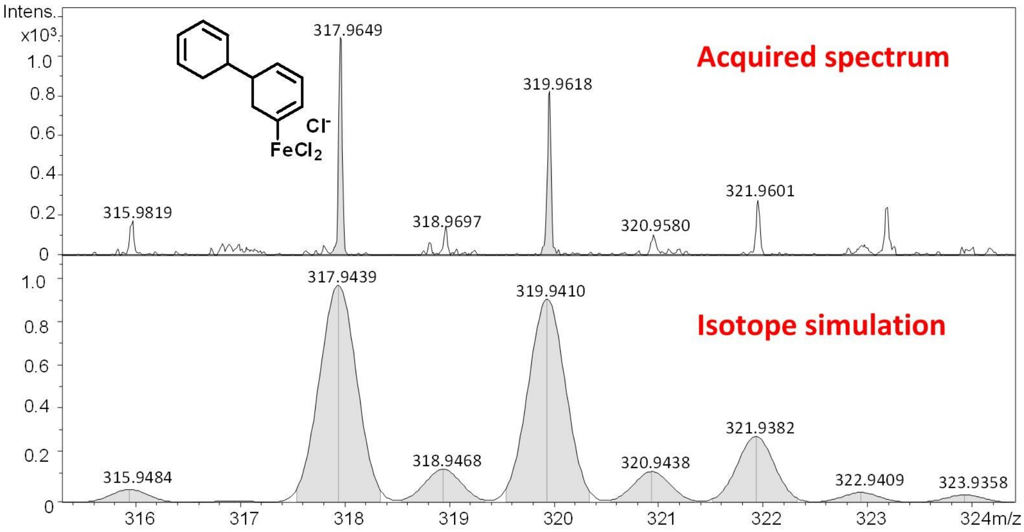

Figure S16 – ESI-MS (-) acquired and predicted for the GR-HX sample for the signal of m/z 318

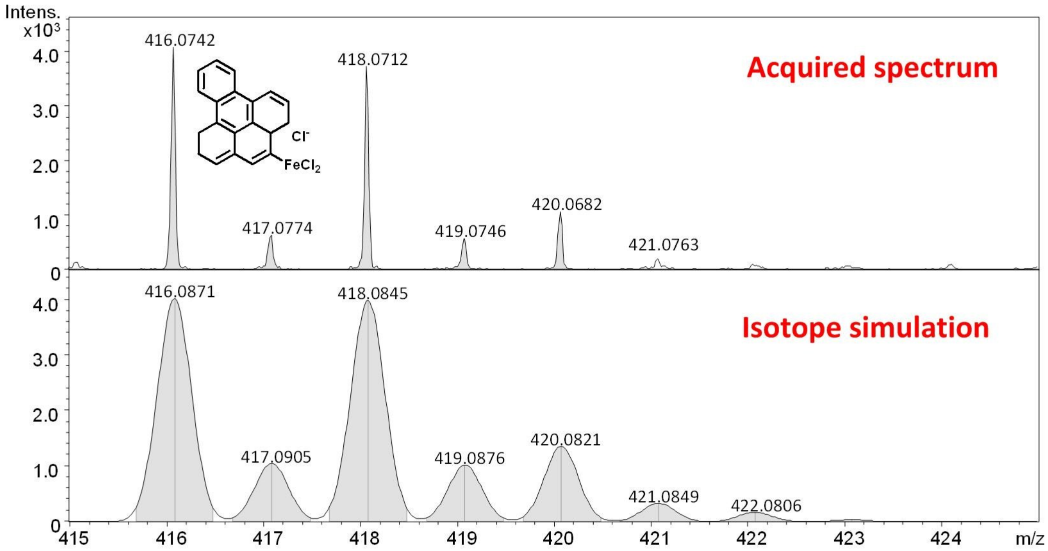

Figure S17 – ESI-MS (-) acquired and predicted for the GR-HX sample for the signal of m/z 416

Survey XPS spectra of the GR-PY sample

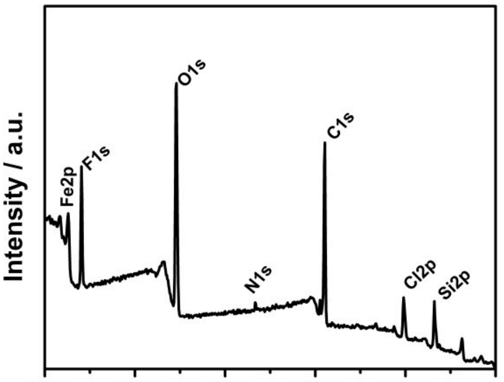

Fig S18 – Survey XPS spectra of the sample GR-PY.