



Synthesis of reduced graphene oxide-poly(phenyleneethynylene) hybrids. A supramolecular and photophysical analyses



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ABSTRACT

Functionalization of graphene oxide (GO) by esterification or amidation reactions with a series of conjugated phenyleneethynylene (PPEs) copolymers bearing different electron-donating and/or withdrawing groups was achieved by microwave irradiation in just 90 min. Copolymers as well as GO-PPE hybrids were characterized by Raman, UV–Vis, static and dynamic fluorescence spectroscopy, transmission electron microscopy, X-rays diffraction and scanning tunneling microscopy. Effective interaction of the copolymers with GO is evidenced by a strong quenching of the PPE's fluorescence quantum yield (ϕ), and by an increase of the non-radiative decay constant (K_{nr}); features that suggest energy transfer from PPEs copolymers to GO. HRTEM shows that the molecules of copolymers self-assemble in blocks resembling bricks or board-like shapes that can be classified as smectic LCs materials as a general term to identify their mesomorphism. Functionalization is mainly carried out at the edges of the GO sheets, so the GO-sheets are not totally covered, even by increasing the PPE-vs-GO ratio because of the trend of the PPEs in to self-assemble in an “edge-on” conformation, meaning that the conjugated backbones are parallel to the GO surface, rather than in “face-on”, where the backbones are flat-lying on the GO surface.

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1. Introduction

Functionalization of GO with conjugated polymers (GO-CPs) is an attractive research line in electronic and optoelectronic area, in particular for photovoltaic applications from the point of view of i) the development of electrodes, i.e. dispersed GO-PCs layers can be deposited on glass slides by techniques such as Langmuir-Blodgett, dipping, etc. The deposited layers can further be submitted to a GO reduction process increasing and/or modulating the hole or electron mobility of the deposited layers, ii) or as buffer layers or iii) even as active layers in organic heterojunction photovoltaic devices. The key parameters for efficient organic photovoltaic devices are fast charge separation and efficient transport to the electrodes, so it is of crucial importance to assure that materials present a good interpenetrating donor-acceptor phase without segregation.

Generally, the active layer in organic bulk heterojunction solar cells is composed of an electron donor conjugated polymer and electron acceptor material, e.g. fullerene, carbon nanotube or graphene. There are many reports where graphene or graphene oxide were used as electron acceptor for solar cells applications [1–3].

Generally, two strategies are used to obtain graphene and graphene oxide interaction with conjugated polymers. The first one consists of π - π interactions between conjugated parts of graphene with the polymer backbone [4]. The second one is based on the direct covalent connection [5] of the functional conjugated polymers on the GO by means of esterification, amidation, click chemistry, nitrene chemistry, radical addition, etc. The esterification reaction seems to be a practical via for attaching a conjugated polymer to graphene oxide, but the polymer must bear hydroxyl groups in the side chains. In this respect, the Sonogashira polycondensation reaction supports a large variety of functional groups including the hydroxyls in monomers without being disturbed, but carboxylic acids of GO require activation with a proper catalyst. In what concerns to the functionalization, Salavagione [6] suggests that it is important to use an excess of esterified macromolecule owing to the lack of data about the quantity of carboxylic groups on

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GO's surface. A typical example is the esterification of hydroxyl terminated poly(3-hexyl thiophene) with GO (4:1 w/w) [7]. However, the main drawback of the GO functionalization is still the long reaction times due to the difficulty to exfoliate the GO sheets for esterification reactions.

Microwave irradiation (MI) as a suitable and rapid heating method was used for preparing exfoliated graphite [8,9] and recently, it was applied for performing graphene oxide exfoliation and reduction [10] including the heating of its suspensions in aqueous or organic media [11]. It has been demonstrated that MI promotes not only the GO exfoliation by interpenetrating the wave between GO sheets, but also the carboxylic acid groups are activated. In this work a series of phenyleneethynylene (PPEs) copolymers were synthesized bearing hydroxyl terminated chains in order to esterify the GO, a particular copolymer bearing hydrazide in the main chain (**EV**) was also evaluated in order to carry out reactions with the epoxy groups that usually are found in the GO plane. The GO chemical functionalization by MI was carried out in 90 min, instead of the typical 6 days applied by thermal chemical solution via. Functionalized GO-PPE's hybrids were characterized by Raman spectroscopy, where the D (1350 cm^{-1}), G (1585 cm^{-1}), and the ethynylene ($\sim 2200\text{ cm}^{-1}$) vibration bands were clearly identified. Energy transfer process from the PPE's to the GO was also determined, since the fluorescence of the PPE's with quantum yield e.g. of 63% for **EV** is drastically shouted down to 5.0%, for its GO-EV hybrid.

2. Experimental section

2.1. Equipment and methods

The microwave copolymerizations were carried out in close quartz vials in a Microwave Apparatus Monowave 300 from Anton Parr at 300 Watts of constant irradiation power, during 90 min at $190\text{ }^{\circ}\text{C}$ and 600 rpm. ^1H (300 MHz), ^{13}C NMR (75.4 MHz) spectra were obtained at room temperature with a Jeol Eclipse spectrometer using CDCl_3 as solvent and internal reference. The molecular weights were determined by GPC on an HP 1100 HPLC using PS standards and refractive index as detector. A series of three HP PLGel columns were used: 10^3 , 10^5 and 10^6 \AA and THF as the mobile phase at $40\text{ }^{\circ}\text{C}$ and 1 mL/min. Raman spectra were recorded on a Horiba Xplora equipment, focusing the sample as powders on microscopic slide with a $10\times$ objective. The excitation wavelength was 785 nm and the Nanoled power was 25% of total laser power (25 mW). Spectra were acquired with 10s acquisition time and 5 cycles, spectral resolution of 2 cm^{-1} . For electron microscopy studies, all of the materials were deposited by casting from CHCl_3 (2 mg/mL) solutions on Lacey carbon grids and were examined by SAED and HRTEM techniques in an FEI-TITAN-200-300 kV field emission gun microscope, which has a symmetrical condenser-objective lens type S-TWIN (with an spherical aberration $C_s = 1.25\text{ mm}$). All of the STM images were obtained at ambient conditions using a compact STM AA5000 Scanning Probe Microscope from Angstrom Advanced Inc. Calibration of the scanner tube was performed by means of atomic resolution images obtained from commercial HOPG sample, exfoliated before each measurement by the adhesive tape method. All measurements were performed in the constant-current mode. Details on the experiment bias and current set-point are given below the images. The raw and FFT images were processed from WSxM 5.0 [12] and Gwyddion software with the aim to reduce noise and normally observed drift. The samples were prepared by directly depositing a drop ($\sim 1\text{--}2\text{ }\mu\text{L}$) of diluted solutions ($10^{-4}\text{--}10^{-5}\text{ M}$) of copolymers in phenyloctane. Small and wide angle X-ray scattering patterns were obtained with an Anton Paar SAXSess mc^2 SWAXS instrument using $\text{CuK}\alpha$

radiation at a wavelength of 0.1542 nm. STM characterization was performed by using a tip mechanically cut from Pt/Ir wire (80/20, diameter 0.25 mm, Nanoscience) and another one prepared from tungsten by electrochemical etching in KOH solution using an applied voltage of 4 V. The photophysical characterization was carried out in spectroscopic grade (Aldrich) toluene, THF and CH_2Cl_2 . UV-Vis and fluorescence spectra were recorded on an Agilent 8453 spectrophotometer and a Perkin Elmer LS50B spectrofluorimeter or Horiba Quantamaster 8075-11, respectively. Fluorescence quantum yield (ϕ) was obtained according to literature method [13] with quinine sulphate (0.1 M in H_2SO_4) as standard. Three different solutions with optical density at the excitation wavelength <0.1 were analyzed at $25.0 \pm 0.3\text{ }^{\circ}\text{C}$ by using a circulating water bath and the values were averaged. The excitation wavelength is reported in the tables. Lifetimes were obtained by TCSPC (Time-correlated single photon counting) with a Témpro Horiba equipment with a 370 nm nanoLED. A 0.01% suspension of Ludox AS40 (Aldrich) in ultrapure water was used for the prompt signal. Calibration of the equipment was realized with a POPOP [1,4-Bis(4-methyl-5-fenil-2-oxazolyl)benzene] methanol solution (optical density <0.1 and lifetime of 0.93 ns [14]). Data were fit in the software DAS6 available with the equipment.

2.2. Synthesis

Experimental procedures, chemical and physicochemical characterization of each compound are given in the supplementary information section.

3. Results and discussion

3.1. Copolymers synthesis and characterization

One semi-rigid copolymer hereafter named **EV** and three rigid rod-like copolymers named **EC**, **LC** and **MJ** were synthesized according to the chemical routes given in Scheme 1 and Scheme 1S (supporting information).

In general the pathway involved only two basic reactions: i) amidation of the 4-iodo benzoic acid **1** with hydrazine hydrate **2** under the EDAC/DMAP-mediated protocol in CH_2Cl_2 , to give 4-iodo-N'-(4-iodobenzoyl)benzohydrazide **3** in 53% yield, and the esterification of 2,5-dibromobenzoic acid **1S** with three different bromoalkanes **3S**, **4S**, **5S** by the action of DBU, Scheme 1S (supporting information). Then, ii) the Sonogashira Pd/CuI cross-coupling polymerization between the corresponding diiodo or dibromo terminated monomer **3**, **6**, **6S**, or **8S** with the corresponding ethynylene **4**, **5** or **7** to afford the copolymers **EV** in 57%, **LC** 70%, **MJ** 85% and **EC** in 67% yield. The relatively moderate yields of **EV** and **EC** are due to the fact that DMF was used as a co-solvent for the polymerization, it is well known that co-solvents highly increase the molecular weights giving rise to insoluble aggregates. After polymerization, each copolymer was submitted to a metal decomplexation process by precipitation once in a methanol sodium dithiocarbamate solution, and twice with clean methanol. The shortest oligomers were eliminated by preparative SEC column (Biorad, Bio-Beads SX1) using toluene as eluent.

The proton resonance peaks of PPEs are broader than those of the corresponding monomers; it was observed that the acetylenic protons disappeared and in contrast, the protons near the iodine or bromine could be identified, suggesting that all of the chains are mainly halogen terminated, Fig. 1S (supporting information). The calculated average molecular weight (Mw), number average molecular mass (Mn), and polydispersity index (PI) using PS standards and refraction index as detector are: Mw = 33729, Mn = 25668, PI = 1.31 for **MJ**; Mw = 11006, Mn = 4909, PI = 2.24 for **LC**;

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