

Electronic Supplementary Information to:

**Grafting P3HT Brushes on GO Sheets: Distinctive Properties of the GO/P3HT
Composites due to Different Grafting Approaches**

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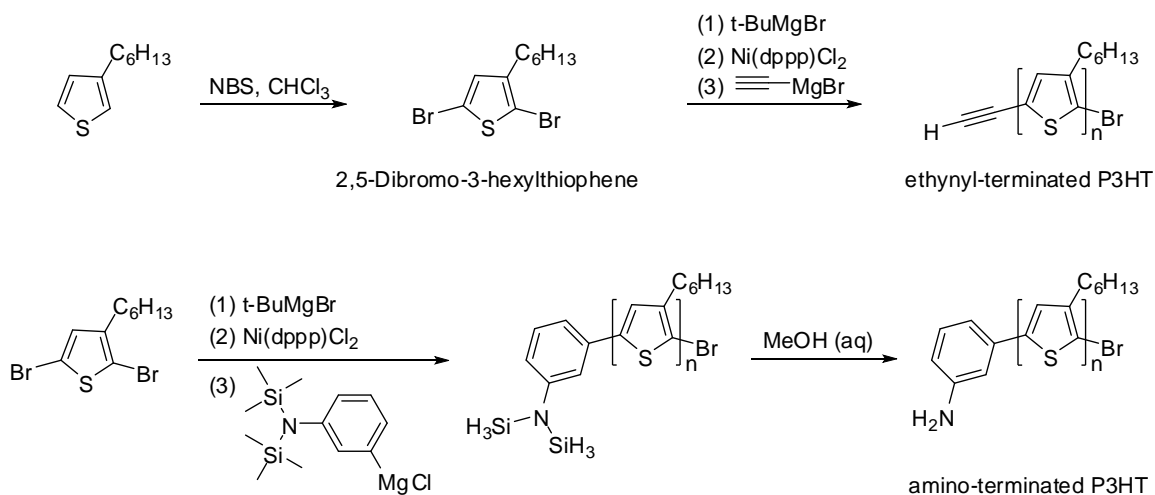
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S1: Synthesis of GO

GO was synthesized from graphite powder by following a modified Hummers' method.¹⁻² In brief, to a concentrated H₂SO₄ solution (25 mL), K₂S₂O₈ (5 g) and P₂O₅ (5 g) were dissolved at 80 °C. Graphite powder (6 g) was added into the acidic solution, and the resultant mixture was stirred at 80 °C for 4.5 h. After cooled down to room temperature, the solution was diluted with deionized (DI) water (1 L), and kept standing overnight. After that, the supernatant was decanted, and the pretreated graphite was obtained by vacuum filtration with a 0.2 μm PTFE membrane and washing with DI water (0.5 L). The precipitate was transferred to a Petri dish and dried in air for 1 d. To a concentrated H₂SO₄ solution (230 mL) below 5 °C was added the pretreated graphite powders and KMnO₄ (30 g). Care must be taken to keep the temperature of the solution below 5 °C. After that, the mixture solution was stirred at 35 °C for 2 h, cooled in an ice bath, and diluted with DI water (460 mL). The solution was further stirred for another 2 h, during which DI water (1.4 L) was added, followed by addition of a H₂O₂ solution (30%, 25 mL). After the reaction mixture was kept standing overnight, the graphite oxide was obtained by centrifugation and subjected to cycles of suspension in 10% HCl solution and separation by centrifugation. A total of 2.5 L of 10% HCl solution was used. In order to remove the free acid and remaining ions, the graphite oxide was subjected to cycles of washing with DI water and separation with centrifugation until the pH value of the supernatant reached 6. Finally, paper-like graphite oxide was obtained after the graphite oxide gel was dried at 50 °C overnight in a vacuum oven.

S2: Synthesis of amino- and ethynyl-terminated P3HT

Scheme S1. Schematic illustration of synthesis of amino- and ethynyl-terminated P3HT.



2,5-Dibromo-3-hexylthiophene. Into a 250 ml round bottom flask, 3-hexylthiophene (5 g, 30 mmol) and THF (100 mL) were added. After the reaction flask was cooled in a bath of water and ice, N-bromosuccinimide (14.39 g, 80.19 mmol) was added slowly. The reaction mixture was stirred at room temperature overnight under the protection of Ar. After that, saturated Na₂CO₃ aqueous solution (6 mL) was added into the reaction mixture. The aqueous phase was extracted twice with hexane, and the hexane solution was mixed with the organic

phase. The combined organic phase was washed with DI water (10 mL×2), brine (10 mL), and finally dried with NaSO₄. The solvent was removed with rotary evaporator. Finally, the product was purified by silica column chromatography using hexane as eluent. In Figure S1 is displayed the ¹H NMR spectrum of 2,5-dibromo-3-hexylthiophene.

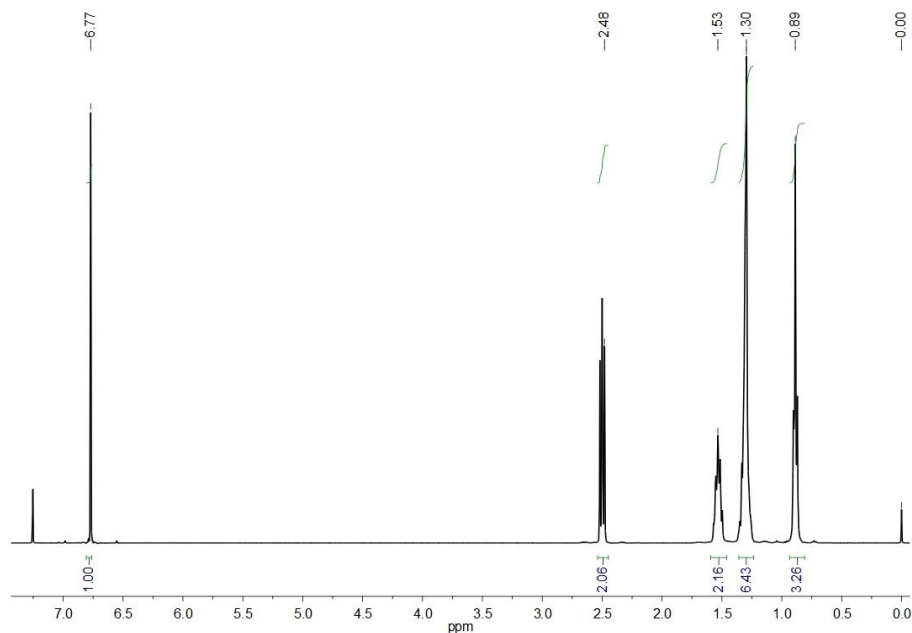


Figure S1. ¹H NMR spectrum of 2,5-dibromo-3-hexylthiophene.

Ethynyl-terminated P3HT. In a typical polymerization, 2,5-dibromo-3-hexylthiophene (1.92 g, 5.9 mmol), anhydrous THF (11 mL) were added in a dry Schlenk flask under the protection of Ar. After the reaction flask was cooled into a bath of water and ice, *tert*-butylmagnesium chloride (3.30 mL, 5.9 mmol, 2 M in diethyl ether) was added dropwise via a syringe. And then, the mixture was stirred at room temperature for 2 h. After the reaction mixture was diluted with anhydrous THF (50 mL), Ni(dppp)Cl₂ was added.

The reaction mixture was stirred for 6 h at room temperature. Then the reaction flask was cooled into a bath of water and ice, and ethynylmagnesium bromide (3.6 mL, 0.5 M in tetrahydrofuran, 30 mol% of the monomer) was added via a syringe to the reaction mixture. The mixture was stirred for an additional 10 min and then poured into methanol to precipitate the polymer. The precipitate was obtained by centrifugation and dried in a vacuum oven. Finally, the polymer was obtained by Soxhlet extraction with chloroform. The solution was concentrated and poured into methanol again to precipitate polymer. Gel permeation chromatography (GPC) characterization showed that the ethynyl-terminated P3HT has a number averaged molecular weight 3070 and polydispersity index (PDI) 1.3. In Figure S2 is displayed the ¹H NMR spectrum of the ethynyl-terminated P3HT. FT-IR spectrum (Figure S3) also confirms the existence of the ethynyl groups on the ends of P3HT chains: the peak at 3310 cm⁻¹ corresponds to the stretching vibration of ≡C-H bond, and the peak at 2095 cm⁻¹ corresponds to the stretching vibration of C≡C bond.

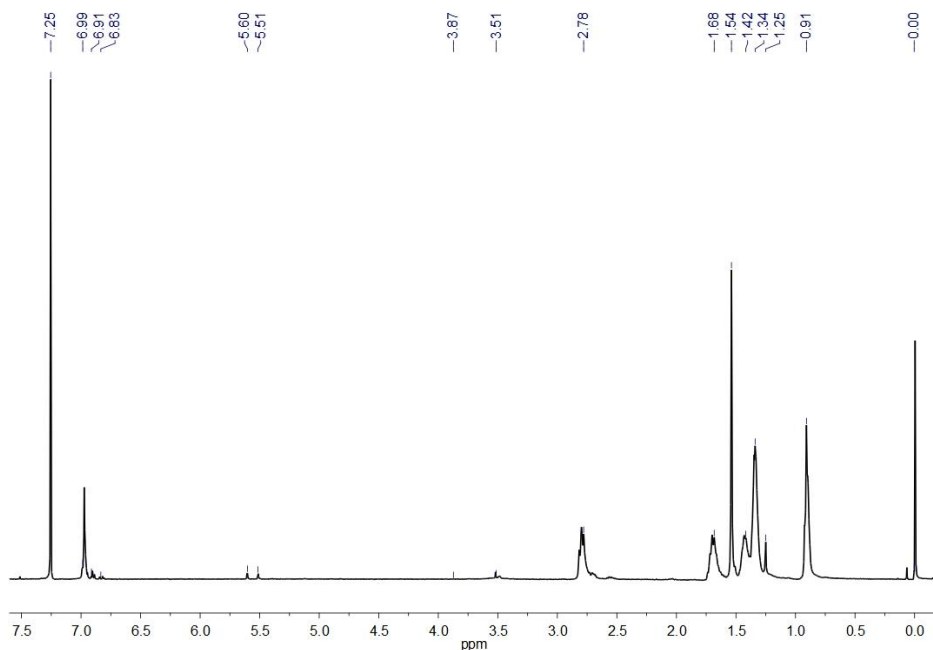


Figure S2. ^1H NMR spectrum of the ethynyl-terminated P3HT.

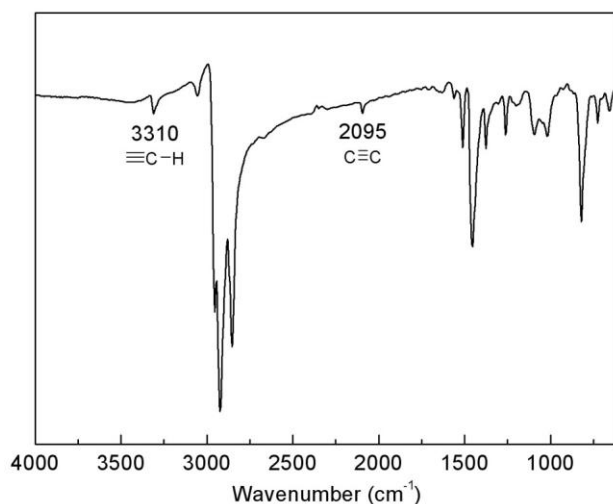


Figure S3. FT-IR spectrum of ethynyl-terminated P3HT.

Amino-terminated P3HT. In a typical polymerization, 2,5-dibromo-3-hexylthiophene (1.92 g, 5.9 mmol), anhydrous THF (11 mL) were added in a dry Schlenk flask under the protection of Ar. After the reaction flask was cooled into a bath of water and ice, *tert*-butylmagnesium chloride (3.30 mL, 5.9 mmol, 2 M in diethyl ether) was added dropwise via a syringe. And then, the mixture was stirred at room temperature for 2 h. After the reaction mixture was diluted with anhydrous THF (50 mL), Ni(dppp)Cl₂ was added.

The reaction mixture was stirred for 6 h at room temperature. Then the reaction flask was cooled into a bath of water and ice, and 3-(bis[trimethylsilyl]amino)phenylmagnesium chloride (6 mL, 1.0 M in tetrahydrofuran, equal to the amount of the monomer) was added via a syringe to the reaction mixture. The mixture was stirred for an additional 10 min and

then poured into methanol to precipitate the polymer. Alcoholysis reaction of the bis(trimethylsilyl)amino groups occurred after the reaction mixture was poured into methanol. The precipitate was obtained by centrifugation and drying in a vacuum oven. Finally, the polymer was obtained by Soxhlet extraction with chloroform. The solution was concentrated and poured into methanol again to precipitate polymer. GPC characterization showed that the amino-terminated P3HT has a number averaged molecular weight 3200 and PDI 1.6. In Figure S4 is displayed the ^1H NMR spectrum of the amino-terminated P3HT. FT-IR spectrum (Figure S5) further confirms the existence of amino groups on the ends of P3HT chains: the peaks at 3466 and 3381 cm^{-1} corresponds to stretching vibration of the N-H bonds.

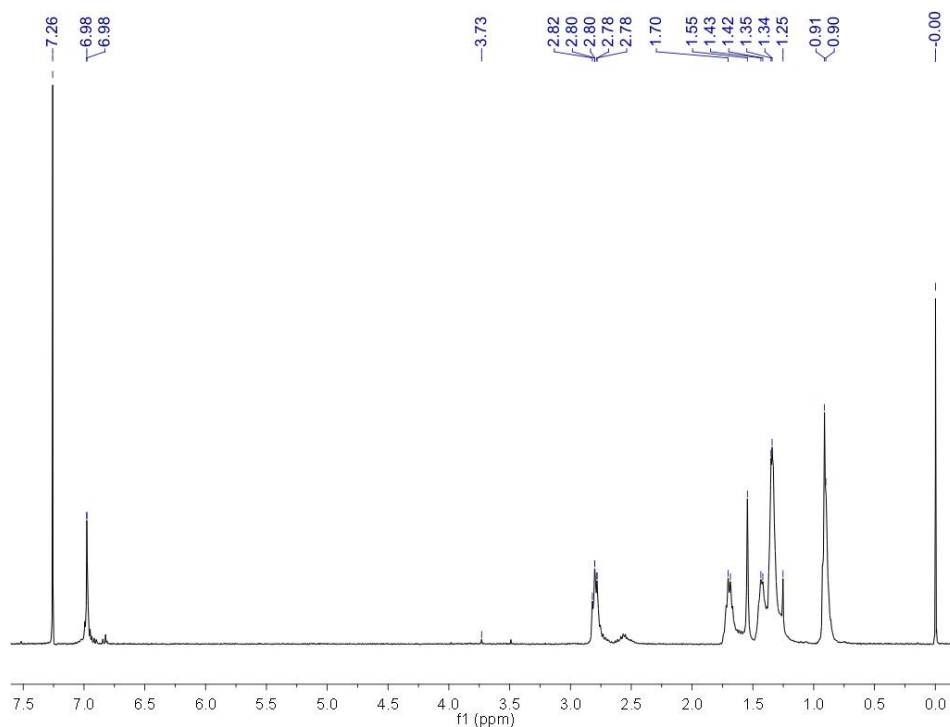


Figure S4. ^1H NMR spectrum of the amino-terminated P3HT.

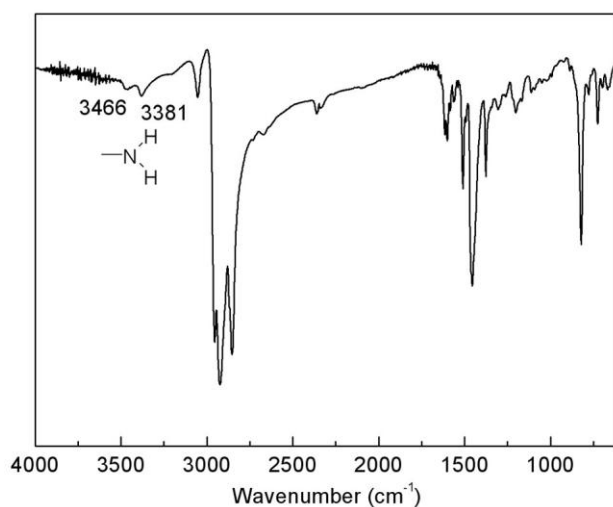


Figure S5. FT-IR spectrum of the amino-terminated P3HT.

S3: Characterization methods.

^1H NMR spectra were obtained on a Bruker Avance 400 spectrometer (400 MHz) using tetramethylsilane (TMS, 0 ppm) or the residual proton resonance of the solvent CHCl_3 (7.26 ppm) as the internal standard. Solid state ^{13}C CP/MAS NMR spectra were obtained on a Bruker AV-300 spectrometer (spinning speed of 9.5 kHz, recycle delay 5s, scanning times of 1500~1700) using tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million (ppm). Molecular weight and PDI of the polymers were measured with a GPC 515-2410 system in THF using polystyrene standard. FT-IR spectra were recorded on an Excalibur 3100 spectrometer with a resolution of 0.2 cm^{-1} using KBr pellets. Raman spectra were recorded on a Renishaw inVia-Reflex confocal Raman microscope with an excitation wavelength of 532 nm. UV-visible spectra were recorded on a Cary 5000 UV-Vis-NIR spectrometer. P3HT solution, GO and GO/P3HT suspensions in THF were used for UV-visible measurement. Photoluminescence (PL) spectra were recorded with a Hitachi F-4600 spectrophotometer. Time-resolved PL was recorded on a streak camera setup. The excitation pulse was generated using a Ti:Sapphire laser (Coherent Chameleon Ultra) with a 130 fs pulse duration operated at 80 MHz and frequency doubling in a BBO crystal. The PL was collected at 90 degrees from the excitation light and directed into a monochromator (Acton SP2300, Princeton Instrument) that was coupled with a streak camera (OPTOSCOPE SC-102, Optronis, Germany). The instrument response function was ca. 20 ps. Thermogravimetric analysis (TGA) was carried out with a Q50 TGA at a scanning rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under the protection of N_2 . A PHI Quantera Scanning X-ray Microprobe with a monochromated Al K α radiation of 1486.7 eV was used for elemental analyses of GO and the other GO composites. Atomic force microscope (AFM) images were recorded on an Agilent Technologies 5500 atomic force microscope by means of tapping mode with a silicon cantilever having a spring constant of $20\text{-}30\text{ N}\cdot\text{m}^{-1}$ and a resonating frequency of 320-350 kHz. GO specimens for AFM observation were prepared by coating an aqueous GO suspension onto a newly cleaved mica substrate. GO/P3HT specimens for AFM observation were prepared by using the following steps: (1) the GO/P3HT composite suspension in hot THF was added into a cold anisole to increase the crystallinity of the P3HT grafted on GO sheets; (2) after being kept standing overnight, the GO/P3HT composite suspension in anisole was coated on the surfaces of newly cleaved mica slides to obtain separate GO/P3HT sheets for AFM observation. Transmission electron microscope (TEM) observation was performed on a JEOL JEM-2100 TEM operated at 200 kV. TEM samples were prepared by dropping the GO aqueous suspension, P3HT solution in THF, and the GO/P3HT composite suspensions in anisole on 400 mesh copper grids with supporting carbon films.

S4: NMR data for the covalent bonding of P3HT and GO sheets

In Figure S6 are displayed the solid state ^{13}C CP/MAS NMR spectra of P3HT, GO, GO(C)/P3HT and GO(A)/P3HT composites. P3HT yields a spectrum containing two groups of resonances: the resonances between 10 and 35 ppm are ascribed to the carbons of hexyl groups; and the resonances between 120 and 140 ppm are due to the carbons of thiophene rings. GO yields a spectrum containing three groups of feature resonances: the resonances between 50 and 85 ppm represent the carbons in the epoxide and hydroxyl groups; the resonances between 120 and 145 ppm belong to the unoxidized sp^2 carbons of the graphene network; and the resonances between 150 and 175 ppm arise from the carbonyl groups.³ As expected, GO(C)/P3HT and GO(A)/P3HT composites contain the feature resonances of both P3HT and GO. Furthermore, GO(C)/P3HT composite gives a shoulder resonance at ca. 138 ppm, which can be attributed to the carbons (CR) in the triazole groups.⁴⁻⁵ On the other hand, the resonances corresponding to the unoxidized sp^2 carbons of the graphene network and the carbons of amide groups in the spectrum of GO(C)/P3HT composite are slightly shifted to higher fields as compared to those in the spectrum of GO. This result is in agreement with a previous report.³ Therefore, the NMR data further support that P3HT chains have been covalently bonded to GO sheets for both GO(C)/P3HT and GO(A)/P3HT composites.

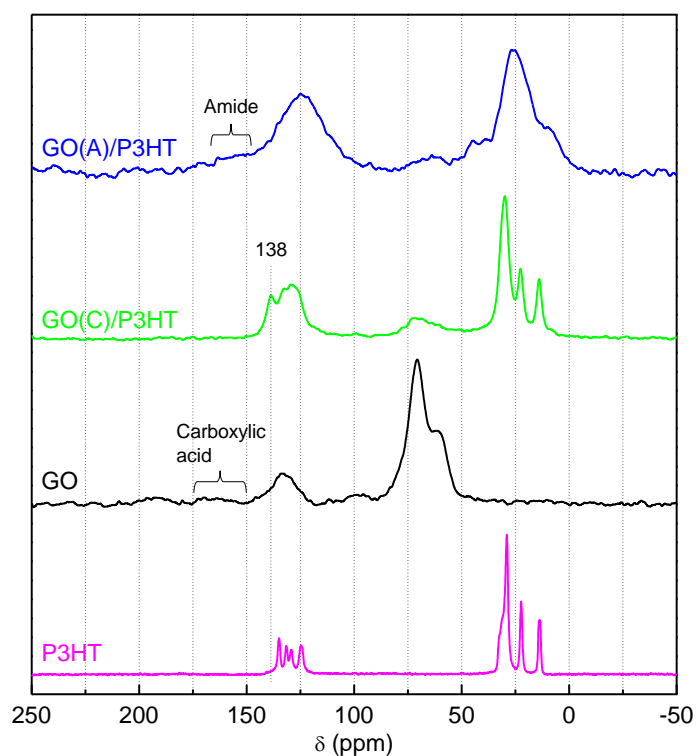


Figure S6. Solid state ^{13}C CP/MAS NMR spectra of P3HT, GO, GO(C)/P3HT and GO(A)/P3HT composites.

S5: TGA and differential TGA curves of GO, amino-terminated P3HT, ethynyl-terminated P3HT, GO(C)/P3HT and GO(A)/P3HT composites

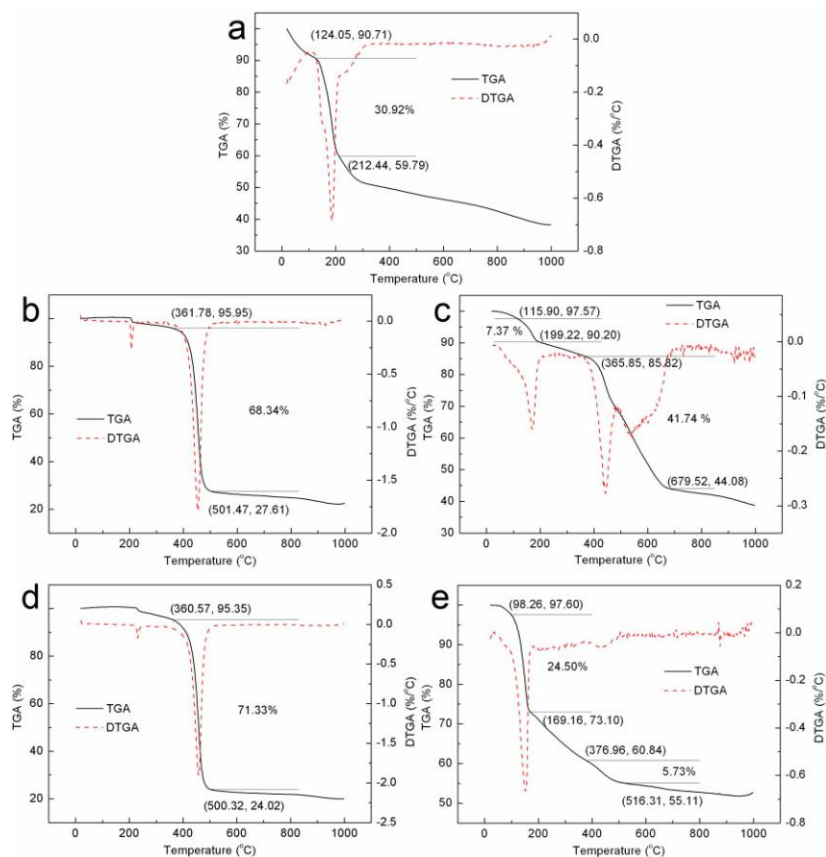


Figure S7. TGA and differential TGA curves of (a) GO, (b) ethynyl-terminated P3HT, (c) GO(C)/P3HT composite, (d) amino-terminated P3HT, and (e) GO(A)/P3HT composite.

S6: Survey XPS of GO/APTMS composite

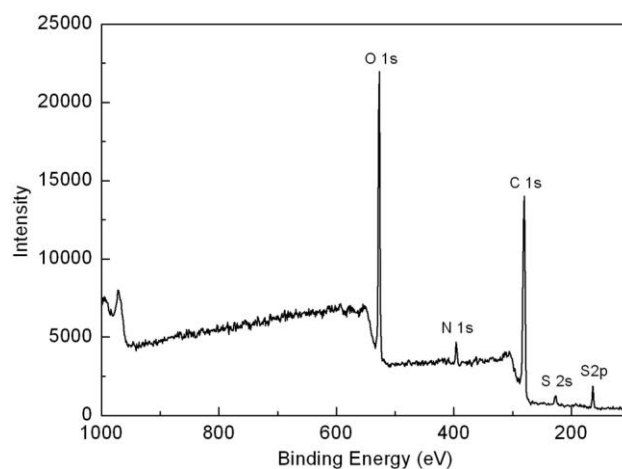


Figure S8. Survey XPS of GO/APTMS composite.

S7: C 1s XPS of GO, GO(C)/P3HT and GO(A)/P3HT composites

The composition of GO(C)/P3HT and GO(A)/P3HT composites was also characterized using C 1s XPS. In Figure S9 is displayed the C 1s XPS of GO, GO(C)/P3HT and GO(A)/P3HT composites. GO yields a C 1s XPS (Figure S9a) that contains two dominant peaks at 284.7 and 286.7 eV corresponding to the C-C and C-O species, as well as two weak peaks at 287.5 and 288.8 eV corresponding to the C=O and O-C=O species. The peaks at 286.7, 287.5, and 288.8 eV confirm that GO contains oxygen-containing groups such as hydroxyl, epoxide, carbonyl, and carboxylic acid groups. In contrast, the peaks for C-O species in the C 1s XPS of GO(C)/P3HT composite is reduced (Figure S9b), indicating that the relative content of C-O species have been reduced in the composite. In addition to that, two new peaks corresponding to C-S and C-N species, which are attributed to the carbons in the thiophene rings and the triazole rings, appears at 285.5 and 285.7 eV in the C1s XPS of GO(C)/P3HT.⁶⁻⁸ This result indicates that P3HT chains have been covalently linked to GO sheets. The similar phenomenon has been observed in the C1s XPS of GO(A)/P3HT composite (Figure S9c). It also contains two weak peaks corresponding to C-S and C-N species, which results from the thiophene rings and the carbons connected to the amide bonds. Furthermore, the peak at 288.8 eV in the C 1s XPS of GO(A)/P3HT composite is ascribed to N-C=O species, indicating covalent bonding of P3HT chains and the GO sheets. Therefore, we can conclude that the decreased intensity of the peaks corresponding to oxygen-containing groups in the GO(C)/P3HT and GO(A)/P3HT composites are due to the partial reduction of GO, which might be caused thermally,⁹⁻¹⁰ and covalent incorporation of P3HT, which carries no oxygen.

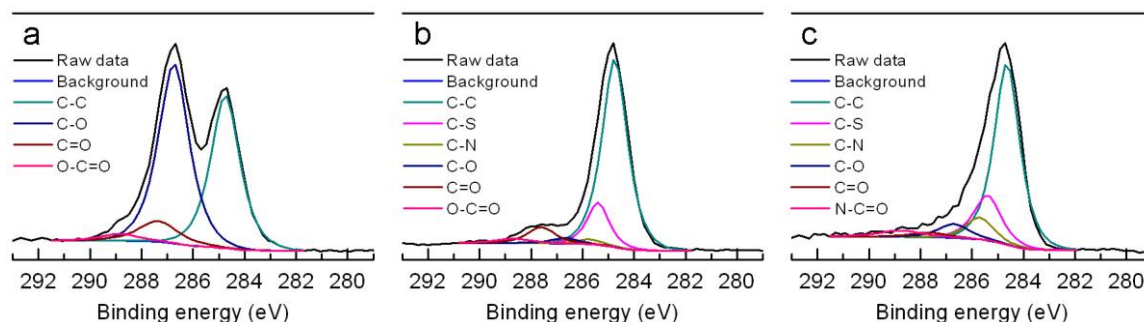


Figure S9. C 1s XPS of (a) GO, (b) GO(C)/P3HT composite, and (c) GO(A)/P3HT composite.

S8: Optical images of chemically reduced samples of GO, GO(C)/P3HT and GO(A)/P3HT composites dispersed in THF

Chemical reduction of GO, GO(C)/P3HT composite, and GO(A)/P3HT composite was performed in the corresponding dispersions in THF using hydrazine hydrate (50-60% aqueous solution) in a concentration ratio of sample:hydrazine = 1 mg:1 mmol. (Note: the trace of water in the hydrazine hydrate does not affect the solubility of P3HT in THF.) The reduction was accomplished by keeping the three bottles on a 60 °C hot plate. After GO was reduced, the reduced GO (RGO) turned black and got precipitated (Figure S10a). In contrast, the chemically reduced samples of GO(C)/P3HT and GO(A)/P3HT composites were still stably dispersed in THF (Figure S10b and S10c).

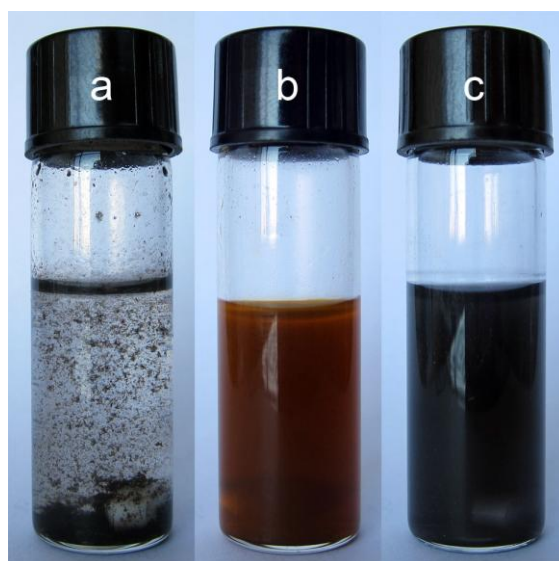


Figure S10. Optical images of chemically reduced samples of (a) GO, (b) GO(C)/P3HT composite, and (c) GO(A)/P3HT composite dispersed in THF.

S9: UV-visible spectra of P3HT and GO(C)/P3HT composites with different grafting densities

In Figure S11 are displayed the UV-visible spectra of P3HT and GO(C)/P3HT composites with different grafting densities (18 and 42 % weight loss of P3HT component from TGA). Different grafting densities of P3HT brushes on GO sheets were obtained by controlling the grafting densities of APTMS on the surfaces of GO sheets during the silylation reaction. As a result, the extent of the red shift of the absorption maximum decreased with decreasing the grafting density. And the background for the GO(C)/P3HT(18%) composite was significantly enhanced due to the higher content of GO in the composite. This result is well in agreement with the proposed crowding induced planarization of the backbones of P3HT. Further study on the effect of grafting conjugated polymers on GO sheets is undergoing in our group.

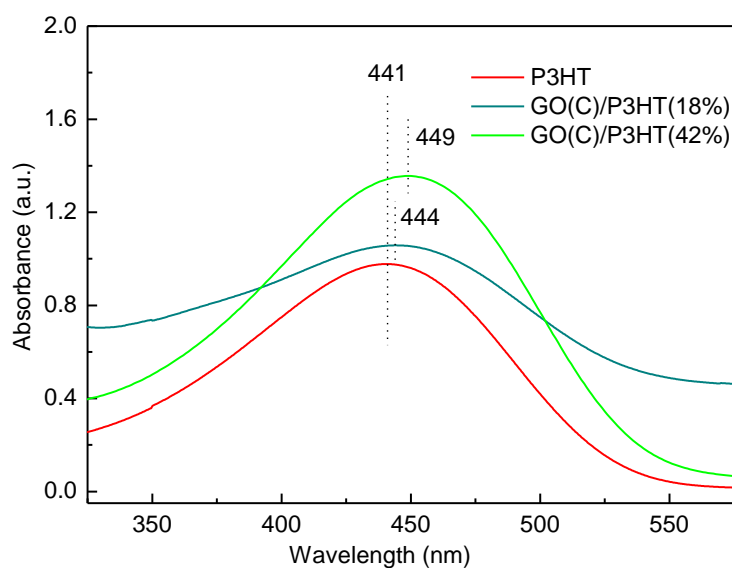


Figure S11. UV-visible spectra of P3HT and GO(C)/P3HT composites with different grafting densities.

S10: PL decay curves of P3HT and GO(C)/P3HT composites

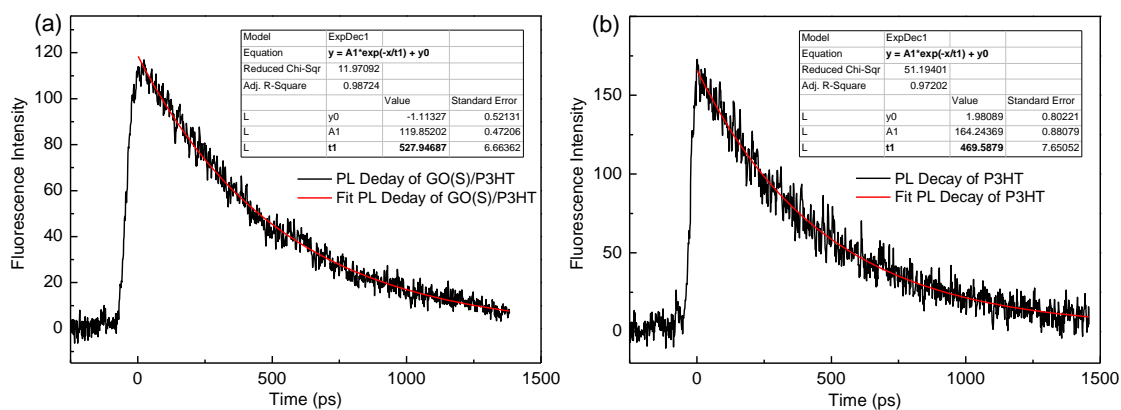


Figure S12. PL decay curves of (a) P3HT and (b) GO(C)/P3HT composites.

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