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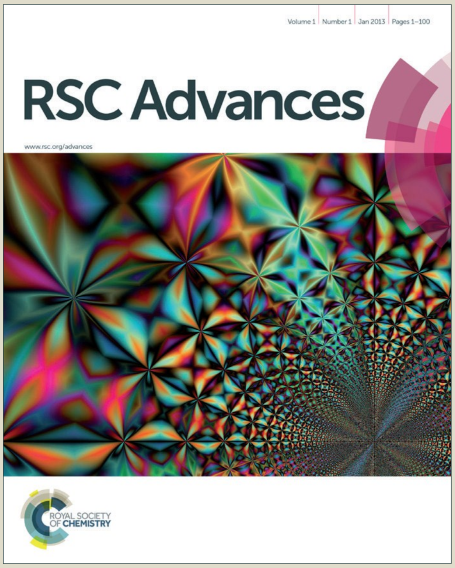
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ARTICLE

# Covalent Functionalization of Graphene with Polythiophene through Suzuki Coupling Reaction

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In our tentative previous work, graphene was covalent functionalized by hexylbenzene and poly(9,9-dihexylfluorene) (PF) through Suzuki coupling reaction. In this paper, thiophene and polythiophene (PTH) were grafted to brominated graphene (Br-Gra) in the same polymeric method. The obtained conjugated system modified graphene was characterized by various techniques, including Fourier transform-infrared (FT-IR), Ultraviolet-vis (UV-vis), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), Fluorescence emission spectra, $^1$H-NMR spectra, and Raman spectroscopy. All the results revealed that thiophene and PTH were successfully grafted to the graphene. What's more, colour changing of their solution ( Br-Gra doesn't dissolve in THF, while both thiophene grafted graphene (Gra-3TH) and PTH grafted graphene (Gra-PT) dissolve in THF, and exhibit black and green color in THF respectively), which caused by electron-energy transfer between graphene and conjugated polymer was also observed. These polymeric conjugated system modified graphene materials may open an interesting field for the application of graphene in photoelectric devices.

## 1. INTRODUCTION

With their advanced and excellent properties, carbon nanomaterials, including fullerene, carbon nanotubes, and graphene, have generated a great deal of interest in academia and industry. Among them, graphene, a honeycomb lattice of carbon atoms which spatial structure is a two-dimensional thin film,[1-4] has become one of the most exciting topics of research in recent years due to its unique physicochemical properties. It has a large theoretical specific surface area (close to 2600 $m^2g^{-1}$),[5] ultrahigh electron mobility (200000 $cm^2v^{-1}s^{-1}$),[6] high Young's modulus (⍰1.0 TPa),[7] superior thermal conductivity (~5300 W/m·K)[8,9] good electrical conductivity,[10] and its optical transmittance is so strong that the optical absorbance of graphene has since been measured at just 2.3 %.[11] Due to the perfect and diverse performances of graphene, it makes the graphene and the graphene-based hybrid materials have many potential applications in various research areas, such as electronics,[12] energy storage and conversion (supercapacitors,[13] lithium ion batteries,[14,15] fuel cells,[16,17] solar cells,[18,19] bioscience/biotechnologies,[20,21] and photovoltaic devices,[22,23] and so on. Graphene shows superlative properties attractive for a wide range of potential applications. In order to meet specific requirements demanded for particular applications, the surface functionalization of graphene materials is essential. Various covalent and non-covalent functionalization methods have been developed for preparing graphene materials with appropriate structures and properties. Graphene and graphene oxide (GO) can be covalently bonded to the surfaces by amide bonding,[24,25] diazonium salt, atom transfer radical polymerization or

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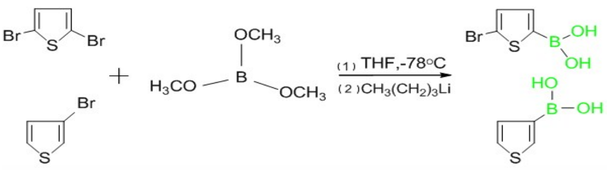
click chemistry.[26-28] For example, porphyrin, polymer, per-fluorophenylazide, and even nanoparticles can be covalently bonded to graphene.[29] Among these polymers, PTH shows unique photophysical properties. Those materials of PTH grafted graphene are pursued as active materials in polymer light emitting diodes, lasers, and nanohybrid optoelectronic/photovoltaic devices.[30-33] As shown in the aforementioned examples, the covalent functionalization of polymers on graphene-based sheets holds versatile possibility due to the rich surface chemistry of GO or reduction of graphene oxide. Nevertheless, the reason for non-covalent functionalizations to be another popular method enthused by many reseachers to functionalize graphene nanosheets since this method is relied on Van der Waals force or p-pinteraction of aromatic molecules on the surface of the graphene nanosheets , which can avoid generating defects and disrupting the conjugation and changing the chemical structure on the graphene surface. For this reason, a lot of novel strategies for noncovalently functionalizing the surface of graphene or GO were reported recently. As an application example, the graphene nanosheets were noncovalently modified with 1-pyrenebutyric acid N-hydroxysuccinimide ester to provide binding sites for ferritin molecules to create a novel nanostructured materials using for biosensors via one facile biomimetic synthesis reported by the group of Wei.[34] The similar researches that graphene and graphene oxide nanosheets were noncovalently modified also reported by teams of Jinhui Wang and Haixia Wang respectively[35,36] According to the previous reports, it has been found that both the covalent and noncovalent modification techniques are very effective in the preparation of graphene-based materials.

In this paper, based on the concept of covalent functionalized the surface of graphene, two thiophene monomer, 3-thiopheneboronic acid and 5-bromo-2-thienylboronic acid were synthesized and covalently attached to the graphene by Suzuki coupling reaction.[37-39]We hope that the synthesized systems, graphene covalently functionalized with thiophene and PTH would become a ideal active layer of electron donor-acceptor applied to the high-efficient energy conversion devices. The PTH is used as one of the most commonly candidate for photodetector and photovoltaic applications due to its high mobility, the good solubility, and the film giving properties as well as the rather low bandgap.[40] As an example, the PTH was used as a excellent polymeric donors to modify fullerene acceptors applied to a efficient solar cells reported by Thompson et al.[41] The important practical significance of this work is to design a strong electronic interaction and good bandgap matching between the chemically bonded PTH and graphene to enhance charge transport. Moreover, attachment of thiophene and PTH was significantly improved the solubility of the graphene-based material in organic solvents, and electron-energy transfer leading to colour changing was observed. We hope that these kinds of carbon nanohybrid structures( including fullerene, carbon nanotubes, and graphene ) with $\pi$ -conjugated polymer to be utilized in a variety of practical optoelectronic devices.

## 2. EXPERIMENTAL SECTION

***2.1 Materials.*** Graphite powder, liquid bromine, hydrazine hydrate, trimethyl borate, n-butyl lithium and tetrakis(triphenyl-phosphine)palladium ($Pd(PPh_3)_4$), 3-bromothiophene, 2,5-dibromothiophene were purchased from Sinopharm Chemical Reagent Co. Ltd. All other chemicals were of analytic grade, and redistilled water was used throughout the experiment.

***2.2 Preparation of aryl boronic acid.*** The preparation of 3-thiopheneboronic acid and 5-bromo-2-thienylboronic acid started from 3-bromothiophene and 2,5-dibromothiophene, respectively (Scheme 1). In a typical procedure,[42,43]under nitrogen atmosphere, 2,5-dibromothiophene (0.93 ml , 8 mmol) was treated with n-butyl lithium (3.84 mL, 9.6 mmol) in THF (40 ml) at -78 $^{o}$C in a flask. After an hour, anhydrous trimethyl borate (1.09 mL, 9.6 mmol) was dropwise added into the mixture. Then the mixture was heated to room temperature for 0.5 h and kept stirring overnight. Finally, it was poured into ether, washed with $H_2O$, and dried with anhydrous magnesium sulfate. After removing the solvent, a solid was obtained. 3-thiopheneboronic acid was synthesized in the same way. The 3-thiopheneboronic acid has been respectively synthesized by Leermann and Molander et al[44,45] and the 5-bromo-2-thienylboronic acid has been also synthesized by Tietz et al.[46] Fig. 1 (a), $^1$H-NMR of 3-thiopheneboronic acid (400 MHz, DMSO-$d_6$ ): d(ppm) 7.42 (d, H), 7.47 (m, H), 7.97 (d, H), 8.02 (s, 2H). Fig. 1 (b), $^1$HNMR of 5-bromo-2-thienylboronic acid (400 MHz, DMSO-$d_6$ ): d(ppm) 7.23-7.24 (d, H), 7.48-7.49 (d, H), 8.39 (s, 2H).



Scheme 1. Preparation of 3-thiopheneboronic acid and 5-bromo-2-thienylboronic acid.

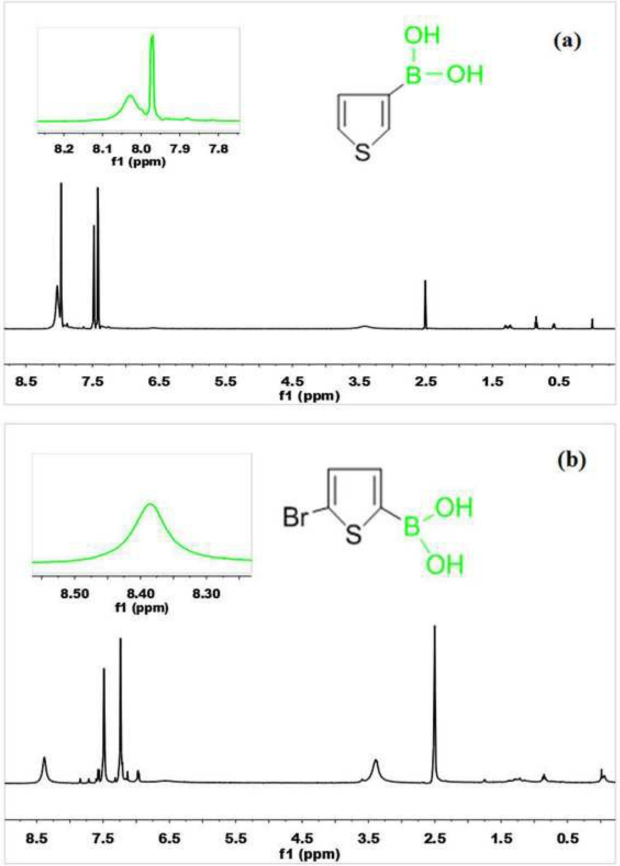
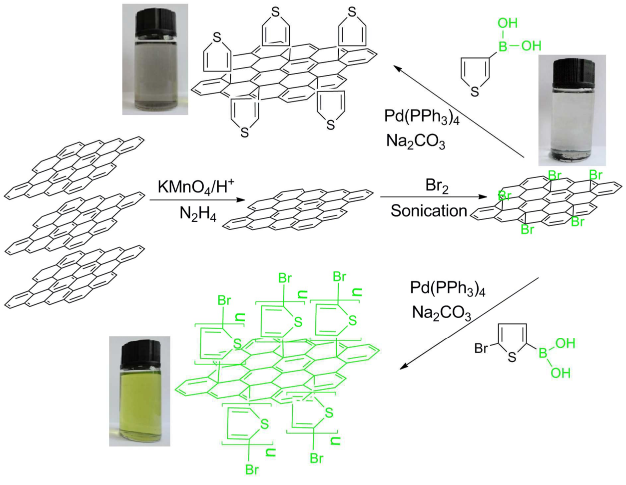


Fig. 1 1H-NMR (400 MHz, DMSO-$d_6$)of 3-thiopheneboronic acid (a) and 5-bromo-2-thienylboronic acid (b).

***2.3 Thiophene and PTH grafted graphene through Suzuki coupling reaction.*** Br-Gra was synthesized by directly ultrasonic assisted bromination with the reduction of graphite oxide,[47] which was reduced by hydrazine hydrate from graphite oxide prepared via a modified Hummers method according to the literature.[48,49] The structure and synthetic route of the Br-Gra was shown in Scheme 2.[37] As reported in our previous work, technique of XPS was used to determine the chemical composition of the surface of the Br-Gra and its result exhibited that the characteristic peak of C −Br bond in the Br-Gra, the values of Br3p(1/2), Br3p(3/2), Br3d is at 190.5eV, 183.5eV, 70.5eV respectively.[37] This result is conforming to the law of thermal exfoliation/reduction of graphite in the bromine gaseous atmosphere[50]and refluxing the reduced graphene oxide with bromine/hydrobromic acid.[51] This also confirmed that the preparation method of Br-Gra in our experiment is correct.

Thiophene and PTH grafted graphene (Scheme 2) was synthesized via Suzuki coupling reaction.[52-54] The PTH grafted graphene was prepared as follows, 5-bromo-2-thienylboronic acid (0.687 g, 1.5 mmol), 5 mL of degassed toluene, 0.02 g of $Pd(PPh_3)_4$, tetrabutylammonium bromide (0.1 g), 2 mL of 2M aqueous sodium carbonate solution and Br-Gra dispersion (0.092 g per 5 mL water) were added to a two-neck flask under nitrogen atmosphere. Then the mixture was stirred vigorously at 80-90 °C for 72 h. Finally the mixture was poured into a mixture of 100 mL HCl; methanol (1 : 100), and washed with methanol and water. Further purification was conducted by washing with refluxed acetone in Soxhlet extractor for 2 days, and dried under vacuum at room temperature, and then black and block solid was obtained. And Gra-3TH was synthesized in the same way as well as PTH.



Scheme 2. The procedure for synthesis of Gra-3TH and Gra-PT.

***2.4 Characterization.*** FT-IR and UV-vis spectroscopy absorption were recorded on a Perkin-Elmer 983 and S-3100 spectrophotometer, respectively. The thermal stability was determined by TGA (STA409PC, Netzsch, Germany). The XPS was carried out on a Perkin-Elmer PHI5400 ESCA. The $^1$H-NMR spectra were measured on a Varian MecryPlus 400NB at room temperature with TMS as internal standard. Fluorescence emission spectra were obtained using an AB-series 2 luminescence spectrometer. Raman spectroscopic measurements were conducted at room temperature by a Raman spectrometer in the back-scattering configuration. The 514.5 nm Ar$^+$ laser was operated at 50 mW.

## 3. RESULTS AND DISCUSSION

3.1 Characteristics of thiophene and PTH grafted graphene. Thiophene and PTH grafted graphene composites were fabricated through Suzuki coupling reaction, which was catalyzed by Pd(PPh$_3$)$_4$. The mechanism of palladium-catalyzed cross-coupling reactions in the synthesis of multi-aryl compounds could be illustrated as the joining of an aryl unit containing a leaving group such as iodo, bromo, chloro to an aryl unit with an organometallic or boronic acid moiety.[55] Centrifugation was used to remove the non-reacted Br-Gra, and various techniques were carried out to ensure that the graft reaction was successfully completed.

***3.2 FT-IR Spectra Analysis.*** Fig. 2A-F show the FT-IR spectra for GO, Graphene, Br-Gra, PTH, Gra-3TH and Gra-PT. The GO shows characteristic peaks at 3410, 1730, 1050, and 1620 cm$^{-1}$ due to the hydroxyl (O–H) group, carboxylic acid (C-O) group, C–O group, and C–C skeletal vibration of GO, respectively. Compare with the spectrum of the GO, the intensity of O-H bond stretching vibration (at 3410 cm$^{-1)}$ in the graphene was weakened obviously, which indicates that the GO was reduced by hydrazine hydrate completely. The spectrum of the PTH show the characteristic peak at 1097 cm$^{-1}$, attributed to the stretching vibration of C-S bond in the thiophene monomer reported by the team of Ramasamy when they covalently functionalized the graphene oxide with a 3-thiophene acetic acid monomer by an esterification reaction.[56] In addition, the same peaks were also found in the spectrums of the Gra-3TH and Gra-PT. The presence of C-S stretching vibration peaks confirms the success of thiophene monomer grafting with graphene. Compared with the spectrum of graphene, the characteristic peaks of C-Br bond in Br-Gra is at around 500-700 cm$^{-1}$ showed as some sharp peaks,[37,50]but in the two grafted graphene materials they were almost disappeared. This further indicates that thiophene and PTH were successfully attached to the surfaces of graphene. Besides, the characteristic peak of C-B bond stretching vibration (around 1018 cm-1 )[57] in the PTH was still present while disappeared in the spectrums of Gra-3TH and Gra-PT. Thus, all these observations suggest that grafted graphene materials were successful fabricated.

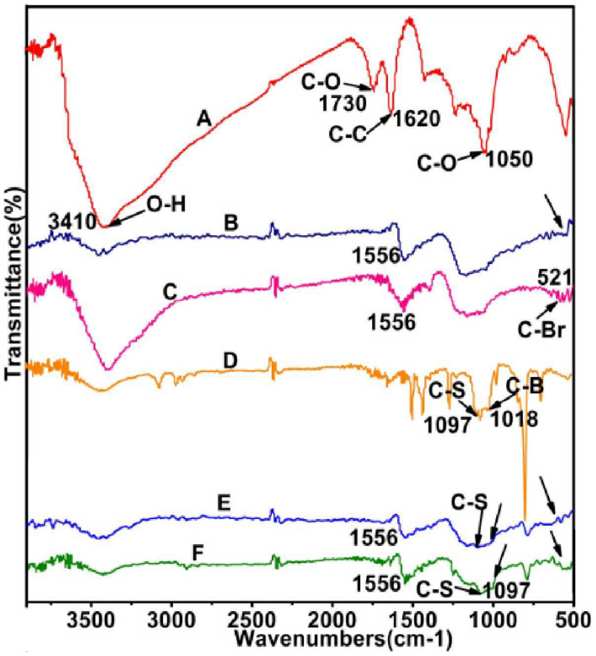


Fig. 2 FT-IR spectra of (A)GO, (B)Graphene (C)Br-Gra, (D) PTH, (E) Gra-3TH and (F) Gra-PT.

***3.3 The Raman spectroscopy.*** In conjunction with FT-IR spectroscopy, Raman scattering as a non-destructive tool, which is sensitive to the electronic structure, remains indispensable to study carbon nanomaterials. The significant structural changes occurring during the chemical processing from graphene to Br-Gra, and then to the covalent functionalizated graphenes, are also reflected in their Raman spectra (Fig. 3). In previous reported, the presence of defects is indicated by the appearance of a D band at approximately 1350 cm$^{-1}$, which is attributed to the sp$^3$-hybridized carbon atoms in the network, whereas pristine $sp^2$ lattice carbon atoms in the network appear as a G band at approximately 1560 $cm^{-1}$.[50] Similarly, in our work, the graphene, Br-Gra, Gra-3TH and Gra-PT exhibit the corresponding G-bands at 1588 $cm^{-1}$, 1594 $cm^{-1}$, 1580 $cm^{-1}$, and 1580 $cm^{-1}$ along with the D-band at 1285 $cm^{-1}$,1297 $cm^{-1}$,1340 $cm^{-1}$ and 1341 $cm^{-1}$, respectively. The $I_D/I_G$ (the integrated intensity of the D band divided by the integrated intensity of the G band) indicates the extent of disorder present in the graphene sheets. In our case, the $I_D/I_G$ values of Graphene, Br-Gra, Gra-3TH and Gra-PT were found to be 1.00, 1.15, 1.14, and 1.2, respectively, indicating that the extent of disorder in the samples are gradually increasing. It is interesting to note that the intensity of the D band is higher than the G band for functionalized compounds due to the defects and partially disordered crystal structure of the graphene sheets, suggesting that the sheets have high defect content. This phenomenon is also noticed in most of the previous works.[56,58,59] This indirectly illustrates that the covalent functionalization was achieved by the C-C bond between the graphene and thiophene ring.

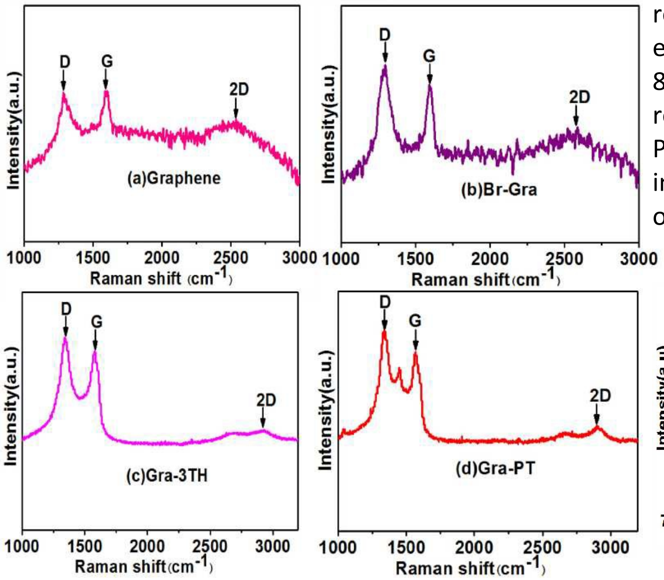


Fig. 3 Raman spectra of the (a) Graphene, (b) Br-Gra, (c) Gra-3TH and (d) Gra-PT.

***3.4 XPS Spectra Analysis.*** Fig. 4 (a) and (b) show the XPS results for Gra-PT and Gra-3TH, respectively. Both the XPS spectrum of Gra-3TH and Gra-PT show the presence of carbon (C 1s), oxygen (O 1s), and sulfur (S 2p). The C ls (284.8 eVs) peak of grafted graphene materials matches with the $sp^2$ hybridized graphitic carbon[60] while the peak of O 1s (532.3 eV) is attributable to C-O bonds in GO that has not been completely reduced.[37,50] Obviously, the presence of S 2p (164.1 eV), corresponding to C-S bond in ring of thiophene, confirms the successful graft of thiophene and PTH to graphene. In a similar reported, $CH_2OH$-terminated regioregular poly(3-hexylthiophene) was chemically grafted onto carboxylic groups of GO via esterification reaction and the same result of XPS spectra analysis was proved.[31,56,61] The high-resolution XPS spectra of S 2p are shown in Fig. 4 (c) and Fig. 4 (d) for Gra-PT and Gra-3TH respectively, from 120 eV to 180 eV, in which both exhibit the obvious peaks for the presence of sulfur (S 2p). In comparison, the intensity of the S 2p in Gra-PT is more stronger than that of Gra-3TH and this is due to the sulfur content in Gra-PT (12.57 at%) is 4.47 times of the Gra-3TH (2.81 at%). Moreover, it can work out that about 33.07 % and 7.39 % of thiophene monomers were grafted to the graphene for Gra-PT and Gra-3TH, respectively. The high-resolution XPS spectra of C1s, O1s for Gra-PT and Gra-3TH are shown in Fig. 4 (e), (g) and in Fig. 4 (f), (h) respectively. The percentage contents of the major elements, C1s and O1s, were 71.97 at%, 15.47 at% and 86.21 at%, 10.97at% for Gra-3TH and Gra-PT respectively. Therefore, the ratios of Gra-3TH and Gra-PT were calculated as 7.85 and 4.65 respectively, which indicate the extent of deoxygenation of the graphite oxide during the process reduced by hydrazine hydrate.

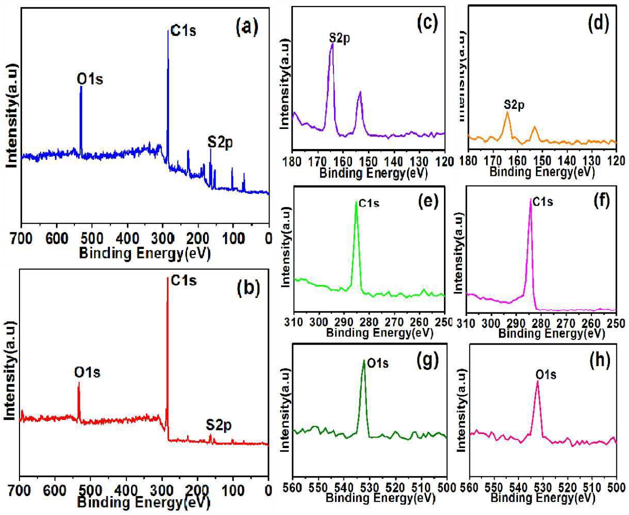


Fig. 4 XPS survey spectra of (a) Gra-PT and (b) Gra-3TH. The high-resolution XPS spectra of S2p, C1s, O1s for

Gra-PT and Gra-3TH are shown in Figure 4 (c), (e), (g) and in Figure 4 (d), (f), (h) respectively.

***3.5 Thermal stability of the grafted graphene materials.*** The thermal properties, an important factor for photovoltaic application, were measured by TGA. Fig. 5 depicts the TGA curves of Br-Gra, Gra-PT and Gra-3TH. The Br-Gra exhibited good thermal stability ( in Fig. 5A), losing just about 7 % of their weight on heating from approximately 160 to 500 °C. The TGA profile of Br-Gra very closely resembles that of the double-walled carbon nanotubes functionalized with Br$_2$, which shows a decomposition step between 100 and 425 °C reported by Colomer and Bulusheva et al.[62,63] The thermal properties of grafted graphene materials are shown in Fig. 5B and C respectively. The Gra-3TH exhibits only a few weight loss at 27-160 °C, but most weight loss between 160 and 500 °C, about 10 %, corresponding to a sulfur content of ~ 2.81 at %, probably due to the loss of thiophene monomer. This value is larger than the total sulfur concentration derived from the XPS data. The observed discrepancy is possibly due to surface-sensitivity of XPS and neglect of the oxygen-containing species, which also contribute to the sample loss. However, the total weight loss of the Gra-PT sample between 245 and 500 °C is ~25 wt %, corresponding to a sulfur content of ~ 12. 57 at %. This value is less than the total sulfur concentration derived from the XPS data and this is also ascribed to the surface-sensitivity of XPS. The total weight loss of the Gra-PT is mostly closed to poly(3,4-propylenedioxythiophene) covalently functionalized with graphene oxide nanosheets , which total mass loss is estimated to be around 25 wt % reported by Kumar et al.[58] On the other hand, as expected, the degree of functionalization from the gradual mass loss of the Gra-3TH and Gra-PT suggests that around 10 wt % of thiophene monomer and 25 wt % of the PTH have been functionalized respectively. Obviously, the weight loss of Gra-PT is more larger than of Gra-3TH, this phenomenon is also observed by group of Xu and Song respectively,[64,65] Who covalently functionalized 7-bromo-9,9-dioctylfluorene-2-carbaldehyde with multi-walled carbon nanotubes (MWCNTs) and they found that mono-fluorene-functionalized MWCNTs, which displayed only 15 % weight loss at 600 °C The but polyfluorenes-functionalized MWCNTs started to decompose at about 150 °C and lost about 50 % of their weight at 600 °C. This regulation is also consistant with our previous work, which shows that the weight loss of hexylbenzene grafted graphene (Gra-BH) is less than PF grafted graphene (Gra-PF).[37]

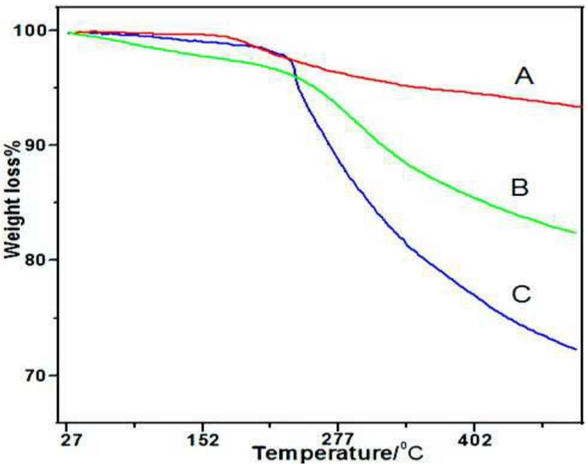


Fig. 5 TGA curves of (A) Br-Gra, (B)Gra-3TH and (C) Gra-PT .

***3.6 Solubility of the thiophene and PTH grafted graphene.*** As shown in Fig. 6, the PTH exhibits a light yellow color in THF while the Gra-PT presents a bright green color in THF, and they both emit a green light under UV irradiation (365 nm). This color is distinct from the Gra-PF which dissolved in THF exhibits a bright blue light under the same conditions (Fig. 7).[37] The difference should be attributed to different ultraviolet absorption wavelength between the Gra-PT (263 nm and 411 nm) and Gra-PF (302 nm and 359 nm) and the discrepancy of ultraviolet absorption wavelength is determined by the different electron and energy transfer between the two conjugated systems. However, the Gra-3TH shows a black color in THF and no emit light under the UV-irradiation. This result is similar to hexylbenzene grafted to graphene because both the thiophene and hexylbenzene are small molecules. Compared with the Br-Gra, the thiophene and PTH grafted graphene displayed much better dispersibility in common organic solvents, such as THF.[37,65,66] The change of the observed colour indicates that there is a strong interaction between the excited state of thiophene, PTH and graphene in the hybrids. This can be ascribed to electron and energy transfer between the two conjugated systems, which is facilitated by the direct linkage mode of the two moieties by the C-C bonds. The intermolecular donor-acceptor interaction between the two moieties may involve charge transfer from the aryl to the graphene.[24,67]

Fig. 6 Photographs of the (1) PTH, (2) Gra-3TH and (3)Gra-PT . 5 mg of PTH , Gra-3TH and Gra-PT were dispersed in 10 mL of THF assisted by sonication, followed by centrifugation for 15 min at a 3200 rpm, after which 6 mL of each supernatant was taken.

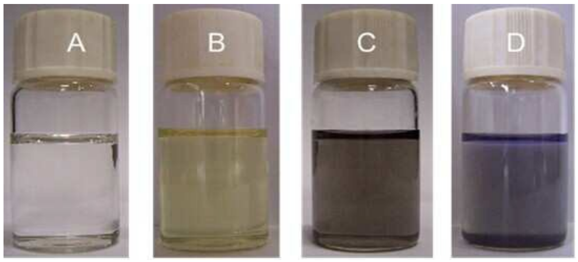


Fig. 7 Photographs of the (A) Br-Gra, (B) PF, (C) Gra-BH and (D) Gra-PF. 5 mg of Br-Gra, PF, Gra-BH and Gra-PF were dispersed in 10 mL of THF assisted by sonication, followed by centrifugation for 15 min at a 3200 rpm, after which 6 mL of each supernatant was taken.

***3.7 UV-vis Absorption Spectra Analysis.*** Many conjugated polymers can be physically absorbed on the surface of fullerenes, nanotubes and graphene. To further confirm that thiophene and PTH are not physically absorbed, but attached to the surface by chemical bonding, optical properties studies were therefore carried out. Fig. 8 shows UV-vis absorption spectra of Br-Gra, PTH, Gra-3TH, Gra-PT, a physically blended sample of Br-Gra and PTH in THF. Br-Gra shows a weak absorption band at 248 nm, while the PTH spectrum exhibits two absorptions at 248 nm, 406 nm, respectively. The Gra-PT also shows two peaks at 263 nm and 411 nm, and the absorption at 263 nm, which should be the corresponding Br-Gra peak at 248 nm with a red-shift of 15 nm. A similar band is also observed for Gra-3TH at 263 nm and Gra-3TH exhibits another new shoulder at 289 nm. The blended sample exhibits a broad absorption at 251 nm and 404 nm, with a blue-shift of 12 nm and 7 nm compared with two absorptions of Gra-PT. This is consistent with the result for PTH grafted multi-walled carbon nanotube and porphyrin modified graphene,[39,67] exhibiting red shift and a new shoulder. The UV-vis result for grafted graphene materials demonstrates covalent bonding between the conjugated system ( thiophene and PTH) and graphene again.

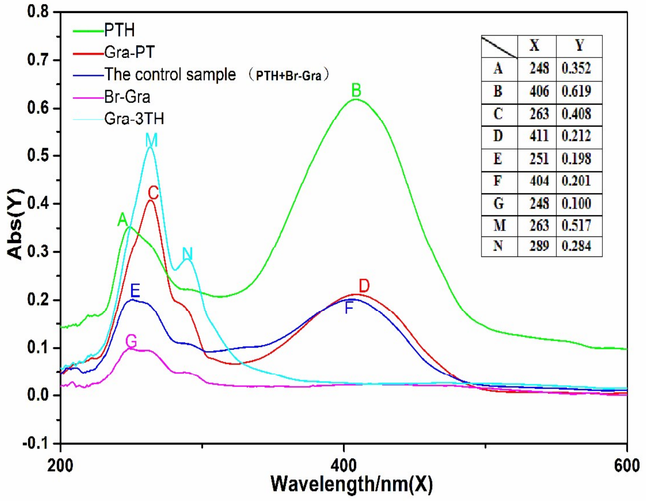


Fig. 8 UV-vis absorption spectra of (1) PTH, (2) Gra-PT, (3) The conttrol sample (PTH+Br-Gra) and (4) Br-Gra, (5) Gra-3TH.

***3.8 Fluorescence Emission Spectra Analysis.*** The fluorescence spectra of PTH, Gra-3TH and Gra-PT are shown in Fig. 9 for comparison. In previous reports, conjugated systems were all grafted to carbon nanotubes and graphene through the formation of amide bond, like poly fluorene-covalent-modified multi-walled carbon nanotubes and porphyrincovalently functionalized graphene.[37,65] In these combined conjugated systems, luminescence quenching was observed. In our work, thiophene and PTH grafted graphene were synthesized through the formation of C-C bond, and different fluorescence properties were obtained. In THF solution, PTH emitted light in the green region with a peak at 521 nm, Gra-3TH emitted light in the invisible region with one peaks at 411 nm while in the case of Gra-PT, the emission of PTH grafted on the surface of graphene was apparently enhanced with a strong emitted peak at 508 nm.

Obviously, the $\gamma$ max of Gra-PT has a blue-shift of 11 nm compared with the emitted light of PTH. Possible pathways for the fluorescence enhancement and blue-shift of the excited Gra-PT could be observed for poly-thiophene copolymers, in that a perfect conjugated system was obtained through the formation of C-C bond.[67,68] In previous work, the porphyrin and fullerene fluorescence spectra results indicate that the pure graphene didn't show fluorescence properties.[67] In these grafted graphene materials, the improvement of the effective intramolecular energy may also be facilitated by a through-bond mechanism, as a result of the direct linkage mode of the two moieties by the C-C bond.[68]

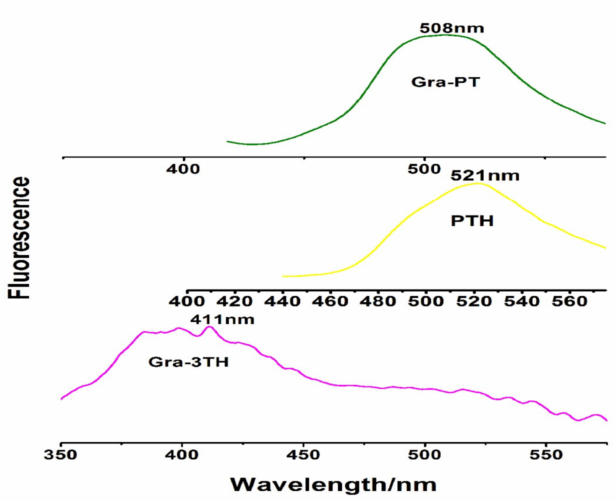


Fig. 9 Fluorescence emission spectra of Gra-PT, PTH and Gra-3TH.

## 4. CONCLUSIONS

In summary, in our work, thiophene and PTH chains have been covalently grafted onto graphene sheets via a Suzuki coupling reaction, which was catalyzed by $Pd(PPh_3)_4$. The resultant of thiophene-grafted and PTH-grafted Graphene sheets possess good solubility in common organic solvents while the remarkable difference of the quantity of grafted thiophene proved by XPS and TGA leads to different color and optical properties for the Gra-3TH and Gra-PT. But on the other hand, this also facilitates the structure/property characterization and device fabrication by solution processing. A variety of spectroscopic measurements indicated that chemical grafting of thiophene and PTH onto graphene induced a strong electronic interaction, leading to an enhanced electron delocalization and a slightly reduced band gap energy for the graphene bound thiophene and PTH, with respect to pure thiophene and PTH. These findings will not only enable nanohybrid structures with $\pi$-conjugated polymer and graphene to be utilized in a variety of practical optoelectronic devices but also further expand the applications of this fascinating allotropic family of carbon.

## ACKNOWLEDGMENT

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