

## Supplementary Material

Title: Optical Characterization of Non-Covalent Interaction between Non-Conjugated Polymers  
and Chemically Converted Graphene

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### Experimental section

Chemically converted graphene (CCG) prepared from graphite by the oxidation-exfoliation-reduction route as we previously reported was used in this study.<sup>(1)</sup> The poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA) with different molecular weights, 1-pyrenebutyric acid (PB) and 5, 10, 15, 20 - tetrakis(1-methyl-4-pyridinio)porphyrin (TmPyP) were all obtained from Sigma Aldrich. The PB-CCG, TmPyP-CCG, PB-CCG-PEO/PVA and TmPyP-CCG-PEO/PVA solutions were prepared by mixing a certain amount of CCG dispersion with PB/TmPyP solutions, followed by the addition of certain amount of aqueous polymer solutions.

The florescent spectra were obtained by Varian Cary Eclipse Fluorescence Spectrophotometer, and the UV-Vis spectra were collected by using a Varian Cary 300 UV-Vis spectrometer. To prepare the samples for UV-Vis measurement, 0.4 ml of CCG dispersion (0.1 mg/ml) was added to 20 ml of TmPyP solution (1  $\mu$ M), followed by the addition of given amounts of PEO or PVA solution (0.5 mg/ml).

Atomic force microscopy (AFM) (Multimode IV, Bruker) was used to characterize the PEO@CCG and PVA@CCG composite (mass ratios of CCG to polymer are 2:1 and 5:1, respectively, with the concentration of CCG being 0.005 mg/ml) which were drop-casted on freshly cleaved mica surface.

Attenuated total reflection (ATR) FT-IR spectra were obtained on a single reflection ATR plate on Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific). The differential scanning calorimetry (DSC) tests were performed on a Perkin-Elmer Pyris 1 DSC system. The samples were scanned over a range of 0 – 120 °C at a scan rate of 10 °C/min. The PEO@CCG samples for ATR-FTIR and DSC were prepared by vacuum filtration of PEO@CCG dispersion through a membrane filter (Millipore, 0.2 µm) to get a paper-like film. The Thermogravimetric (TGA) (Perkin-Elmer SII TG/DTA 6300, Pyris thermogravimetric analyzer) analysis was conducted from 50 °C to 500 °C with a heating rate of 5 °C/min.

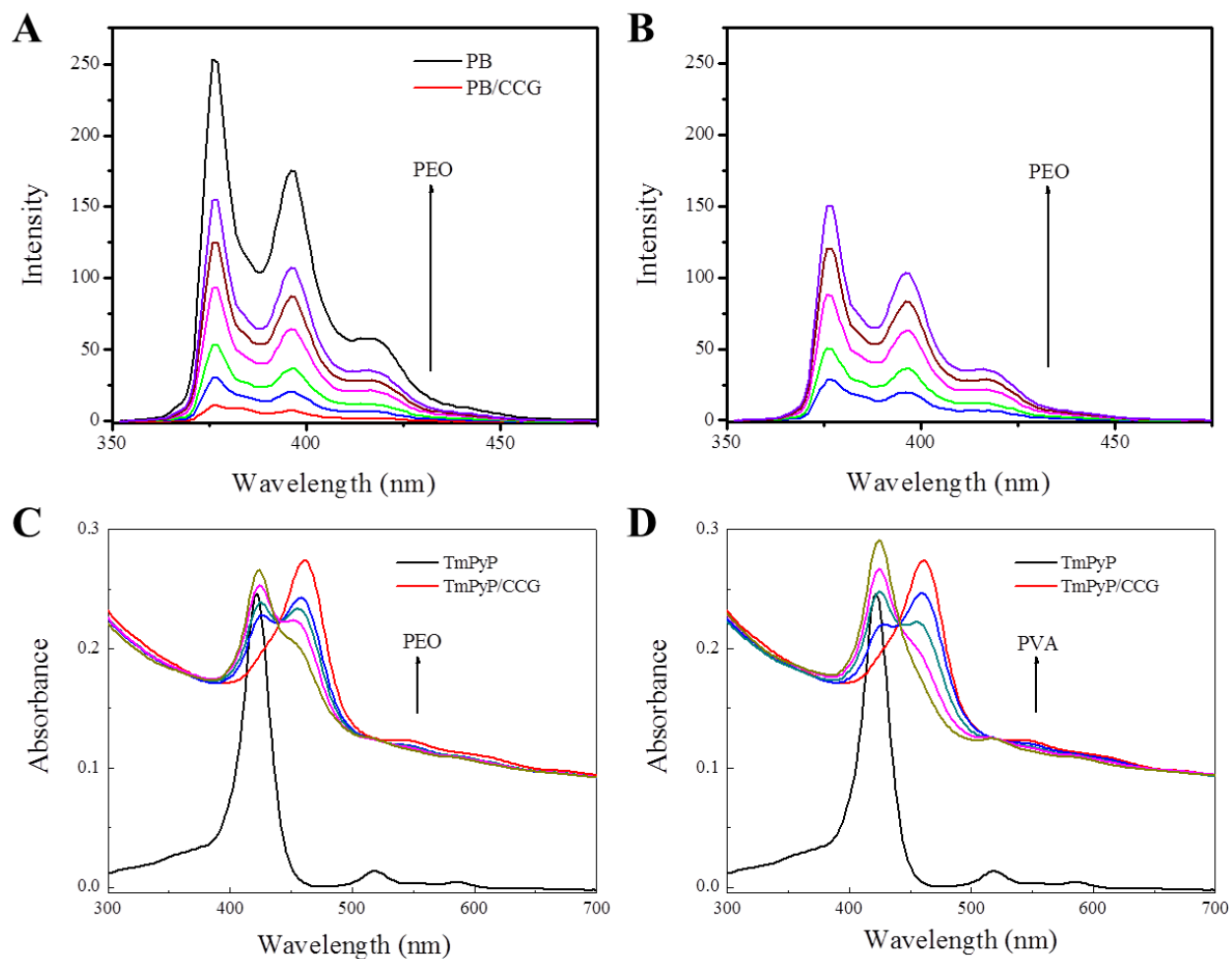


Figure S1 Fluorescence spectra of PB/CCG with different amounts of PEO (A) before and (B) after filtration. Similar peak values were obtained from fluorescence spectra before and after filtration, with the fluorescence intensity increasing with increased addition of PEO to the solution. This demonstrates that increased amount of PB molecules are dissociated from the surface of CCG into the bulk solution; Adsorption spectra of TmPyP/CCG with different amounts of (C) PEO and (D) PVA. The increased addition of these non-conjugated polymers gradually recovers the spectrum to the adsorption peak position of TmPyP, as also observed from the fluorescence spectra.

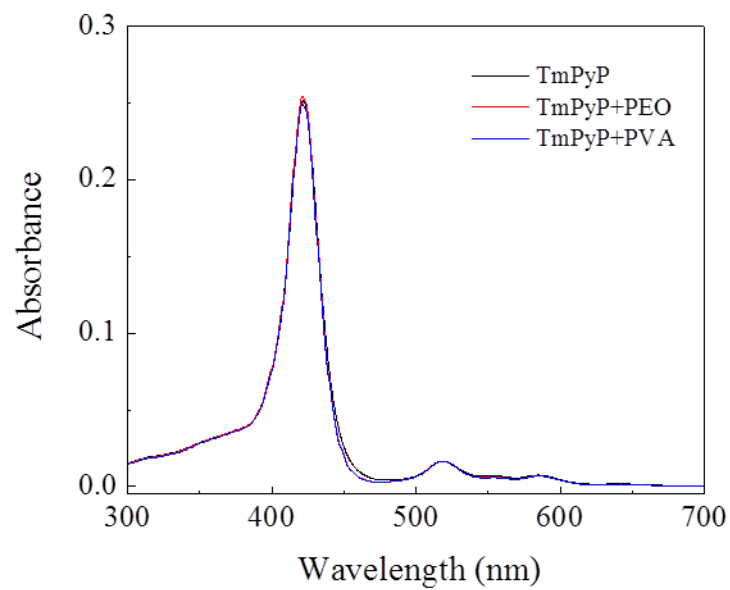


Figure S2 Adsorption spectra of TmPyP, TmPyP/PEO, and TmPyP/PVA solutions. There is no peak shift with the addition of polymers, indicating that there is no strong interaction between TmPyP and PEO/PVA.

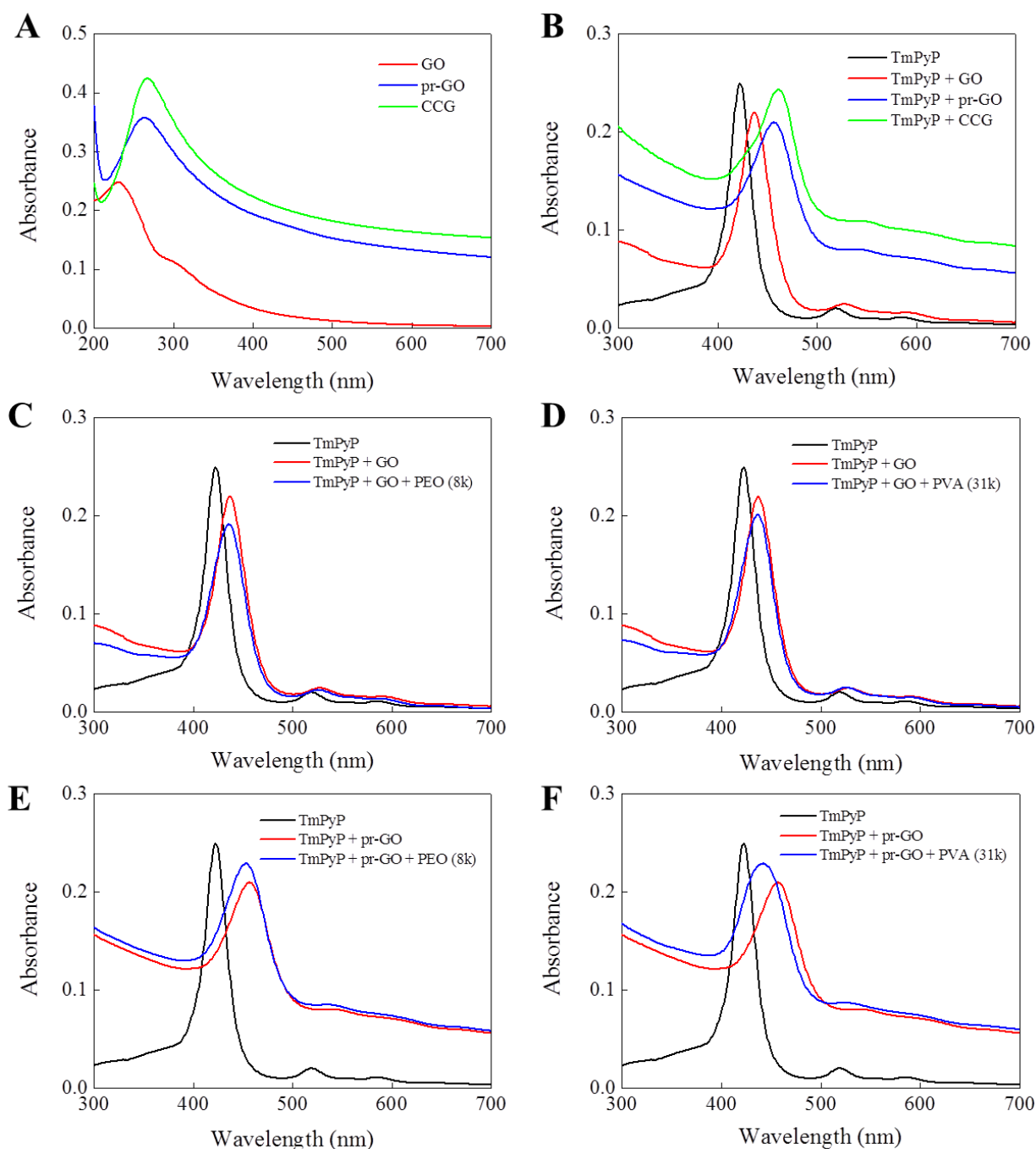


Figure S3 (A) Absorption spectra of GO, CCG and partially reduced GO (pr-GO). The pr-GO solution is obtained by thermal reduction of GO solution for 20 minutes. (B) Absorption spectra of TmPyP, TmPyP/GO, TmPyP/pr-GO and TmPyP/CCG. Adsorption spectra of TmPyP, TmPyP/GO and TmPyP/GO mixed with (C) PEO and (D) PVA; and adsorption spectra of TmPyP, TmPyP/pr-GO and TmPyP/pr-GO mixed with (E) PEO and (F) PVA.

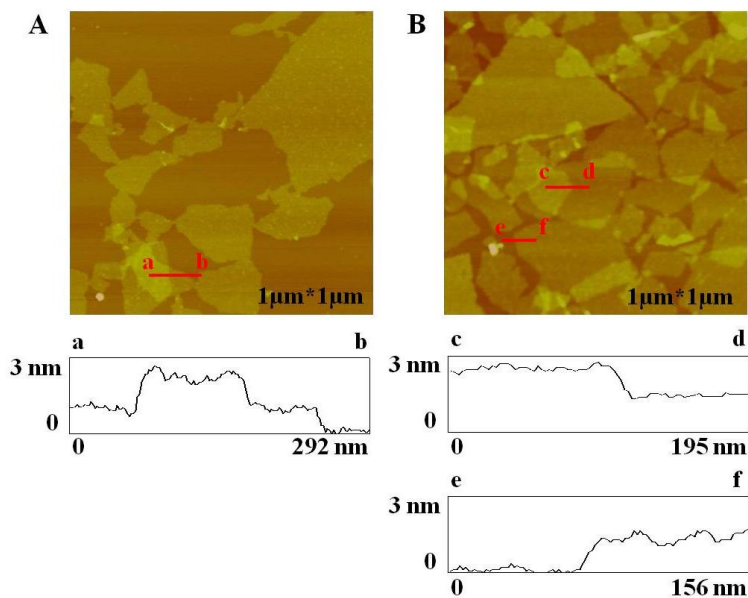


Figure S4 AFM images and height profile of (A) PEO@CCG (Mw of PEO: 8k) composite and (B) PVA@CCG (Mw of PVA: 31k) composite with mass ratio of 5:1 (CCG to polymer) prepared by drop casting on mica surface.

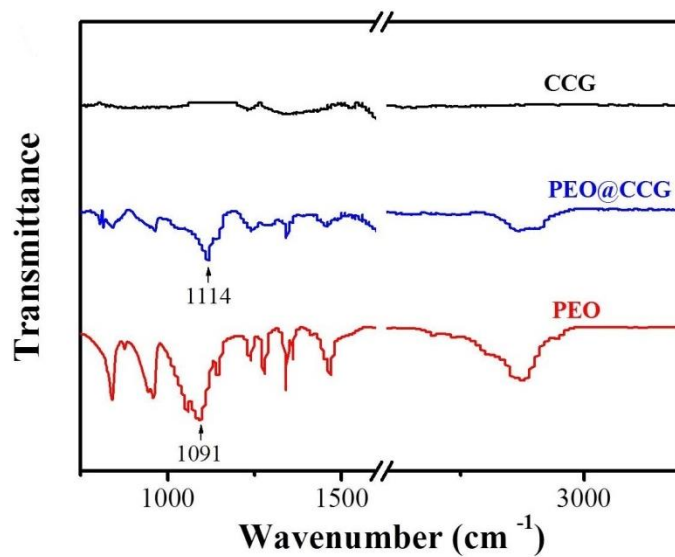


Fig. S5 ATR-FT-IR spectra of vacuum-filtrated films composed of CCG, PEO@CCG and PEO, respectively.

Fourier transform infrared spectroscopy (FTIR) test was conducted to study the interaction between PEO and CCG. As shown in Figure S5, the spectrum of PEO@CCG shows clearly the characteristic peaks of PEO. Particularly, the vibration at 1091 cm<sup>-1</sup> of PEO, which is the typical peak for the formation of hydrogen bonding in PEO with CNT found, is red-shifted by 23 cm<sup>-1</sup> in that of PEO@CCG composite, indicating the presence of hydrogen bonding formed between CCG and PEO.<sup>(2)</sup>

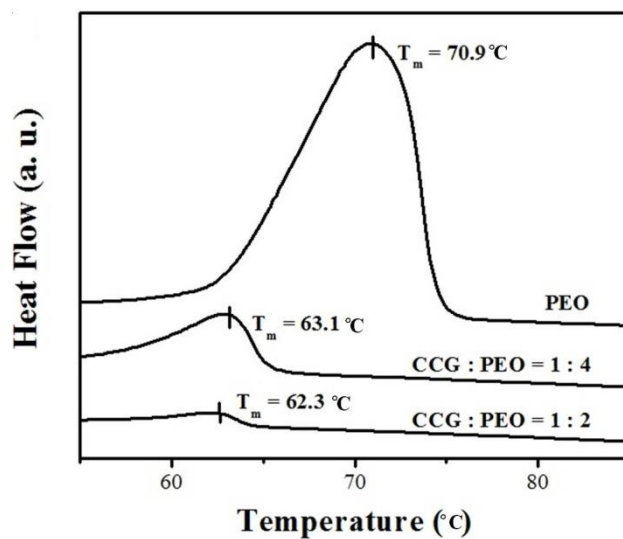


Fig. S6 DSC data of PEO and PEO in PEO@CCG composite with different weight ratios, clearly showing the decrease of the melting point of PEO when mixed with CCG. This suggests that the crystallinity degree of PEO is decreased with the increase of CCG content,<sup>(3)</sup> further indicating the strong interaction between CCG and PEO.

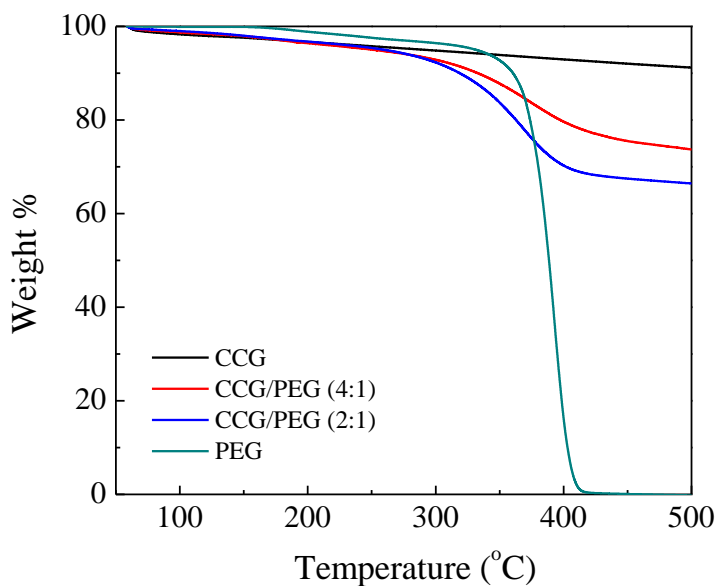


Fig S7 Thermogravimetric analysis (TGA) analysis of CCG, PEG (Mw: 8k) and CCG/PEG(8k) composites



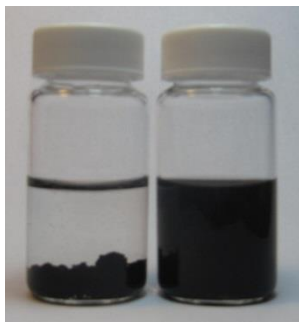


Fig. S8 Photos of CCG dispersions after subject to sonication. (Left) without the addition of polymer; (Right) with 20 wt% of PEO (Mw: 8k). We found that when CCG dispersion prepared by using the procedure reported in Ref. 1 was subject to sonication (BRANSON Digital Sonifier, frequency: 20KHz, amplitude: 20%) for 1 hour, sonication-induced shearing forces led to aggregation of CCG as a result of intensified collision between CCG sheets by sonication (Left). However, with PEO present, such re-aggregation of CCG was prevented (Right).

## References

1. D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace. *Nat. Nanotechnol.* **2008**, *3*, 101-105.
2. Y. Mathey, R. Clement, C. Sourisseau, G. Lucazeau. *Inorg Chem.* **1980**, *19*, 2773-9.
3. H. Z. Geng, R. Rosen, B. Zheng, H. Shimoda, L. Fleming, J. Liu, et al. *Adv Mater.* **2002**, *14*, 1387-90.