

Electronic Supporting Information

Dual-Fluorescent Composites of Graphene Oxide and Poly(3-hexylthiophene) Enable the Ratiometric Detection of Amines

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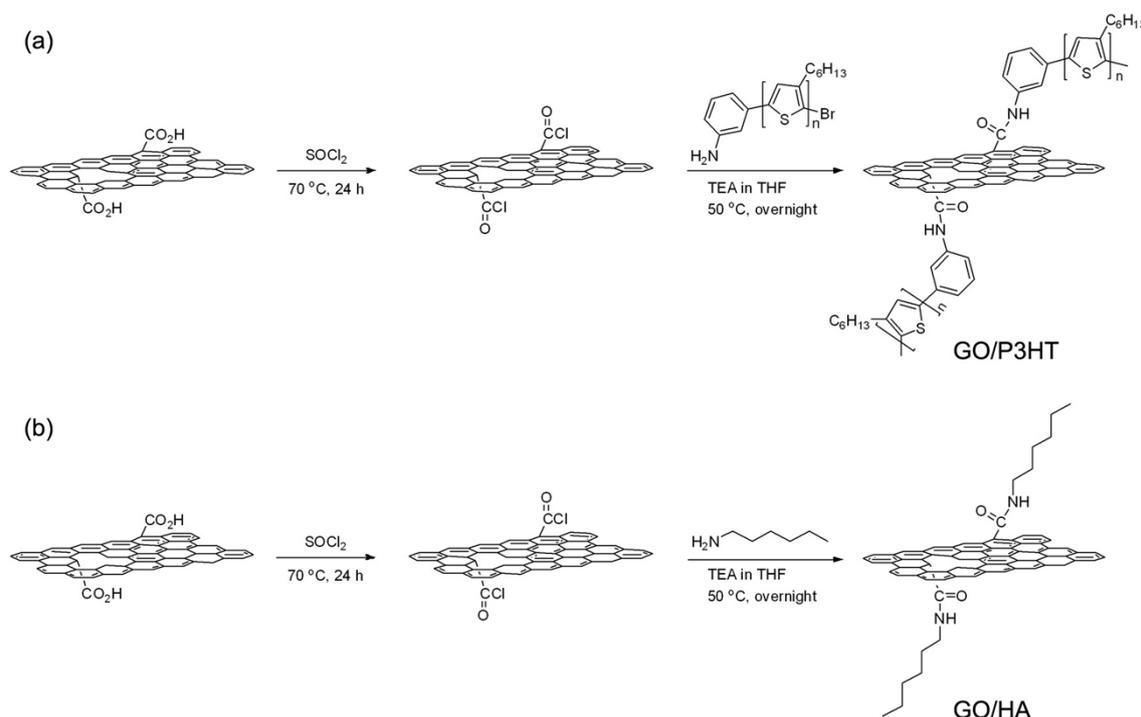
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S1: Synthesis and characterization of the GO/P3HT and GO/HA composites

UV-visible spectra were recorded on a Cary 5000 UV-Vis-NIR spectrometer. PL spectra were recorded with a Hitachi F-4600 spectrophotometer. Thermogravimetric analysis (TGA) was carried out with a Q50 TGA at a scanning rate of 5 °C·min⁻¹ under the protection of N₂. 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/P3HT and GO/HA composite suspensions in chloroform on 400 mesh copper grids with supporting carbon films. Confocal microscopy images were acquired with a Nikon C1si laser scanning confocal microscopy with 408 nm diode laser excitation, and the samples were prepared by Langmuir–Blodgett method. 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. Theoretical calculation of the molecular orbital energy levels of GO/HA and GO/polythiophene composites was performed on Gaussian 09 software at the B3LYP/6-31G(d) level.

Scheme S1. Schematic illustration of synthesis of (a) GO/P3HT and (b) GO/HA composites.



The GO/P3HT and GO/HA composites were synthesized using a variation of a previously reported method (Scheme 1).^[1] A typical procedure is as follows: GO (10 mg) was dispersed in anhydrous DMF (1.5 mL) with the aid of sonication for 3 h. To the GO suspension in DMF, SOCl₂ (20 mL) was added, and the solution was refluxed at 70 °C for ca. 24 h. The resulting GO material was obtained by centrifugation, and further cleaned by 5 cycles of washing with anhydrous THF and centrifugation. To the material dispersed in anhydrous THF (10 mL) was added an amino-terminated P3HT (200 mg) solution in anhydrous THF (60 mL). Afterward, the reaction mixture was cooled to 0 °C and anhydrous

triethylamine (2 mL) was added dropwise into the reaction flask. The reaction was allowed to proceed at 50 °C for 24 h. Finally, the product was obtained by centrifugation at 17000 rpm for ca. 2 h, followed by 5 cycles of washing with anhydrous THF and centrifugation. In order to obtain a maximum grafting density, an excess of P3HT was used. The GO/HA composite was prepared in a similar manner using 1-hexylamine in lieu of the amino-terminated P3HT. Note: In the synthesis of the GO/P3HT composite, two amino-terminated P3HT samples were used: one with a number average molecular weight (M_n) of approximately 6500 Da and the other with a M_n of approximately 3100 Da. The products synthesized with excess of the amino-terminated P3HT were labeled as GO/P3HT-6500-Ex and GO/P3HT-6500-Co. The grafting density was controlled by using a decreased quantity of amino-terminated P3HT, and the corresponding product was labeled as GO/P3HT-6500-Co.

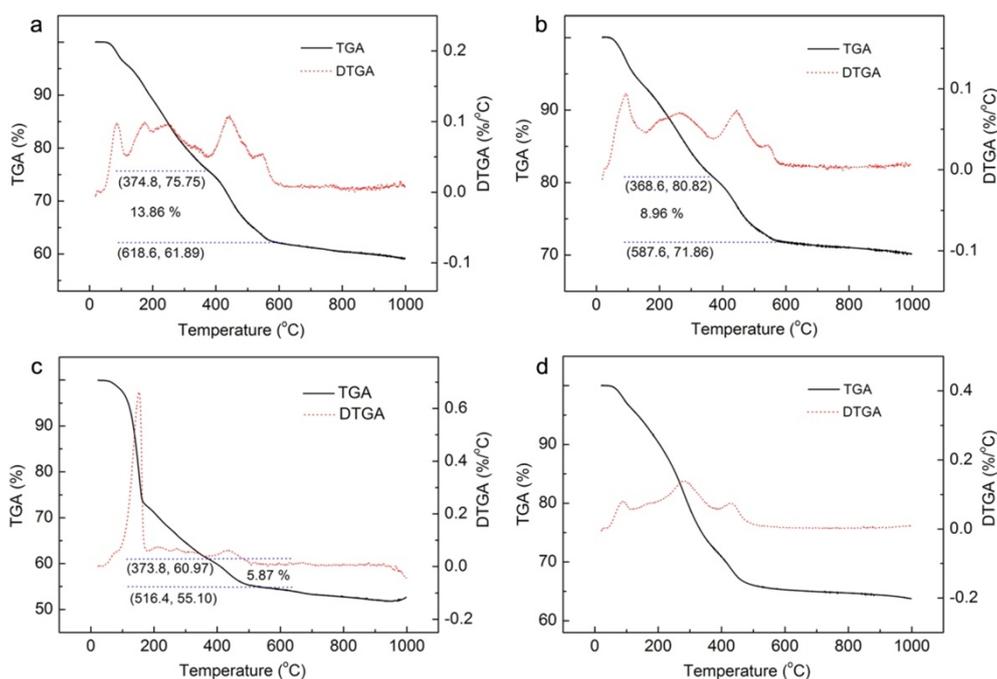


Figure S1. TGA curves of (a) GO/P3HT-6500-Ex (grafting density 13.9%), (b) GO/P3HT-6500-Co (grafting density 9.0%), (c) GO/P3HT-3100-Ex (grafting density 5.9%), and (d) GO/HA composite.

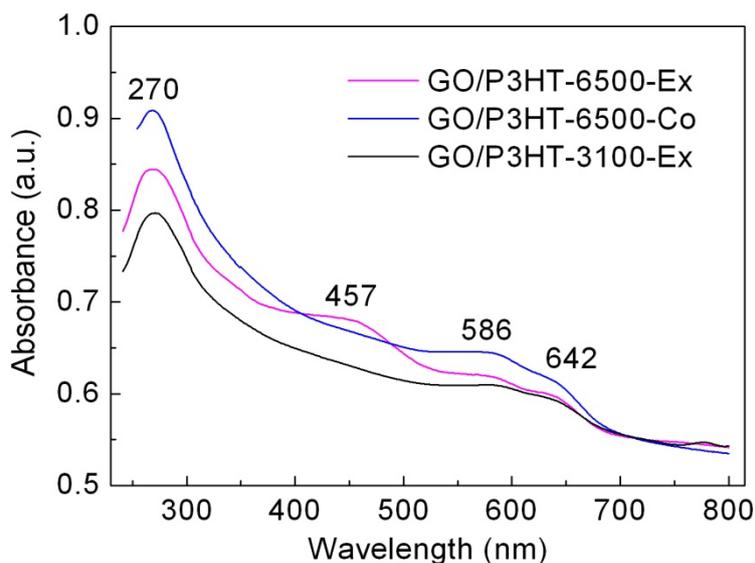


Figure S2. UV-visible spectra of GO/P3HT composites.

The thermal stability of the GO/P3HT and GO/HA composites was estimated using thermogravimetric analysis (TGA). The grafting density of the GO/P3HT composites was calculated from the mass loss that corresponded to P3HT component in the TGA curves. The grafting density for the three GO/P3HT composites was calculated to be 13.9% for GO/P3HT-6500-Ex, 9.0% GO/P3HT-6500-Co, and 5.9% for GO/P3HT-3100-Ex (Figure S1). The UV-visible spectra of the suspensions of GO/P3HT composites in chloroform are shown in Figure S2. The GO/P3HT-6500-EX composite, which has the highest grafting density among the three composites synthesized, showed clear splitting of the new absorption bands, reflective of a stacked, polymeric structure.^[2]

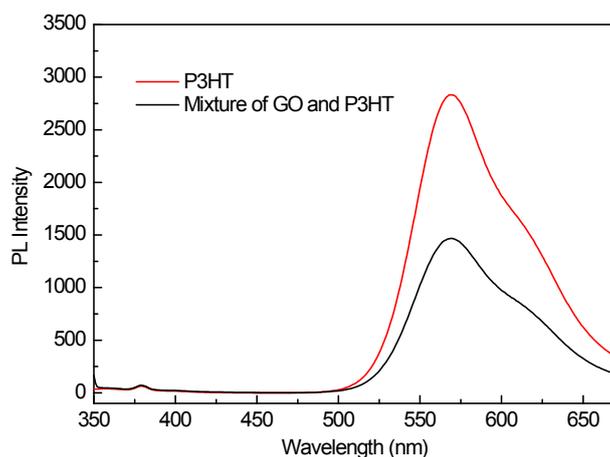


Figure S3. PL spectra of a P3HT solution and a suspension of GO/P3HT mixture with P3HT accounting for ca. 13.9% ($\lambda_{\text{ex}} = 340$ nm).

S2: Theoretical calculations

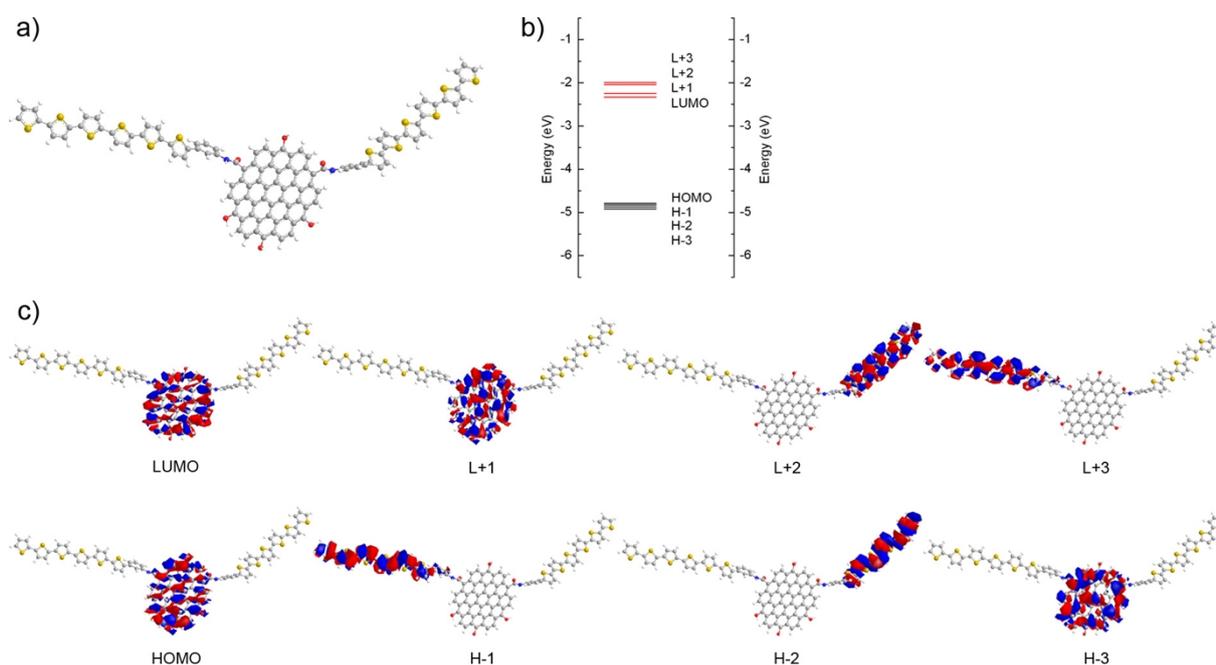


Figure S4. Calculated band structures of GO linked to a conjugated polymer: (a) ball-and-stick model of GO/sextithiophene, (b) molecular orbital energy levels of GO/sextithiophene, (c) molecular orbitals of GO/sextithiophene.

S3: TEM images of the GO/HA composite

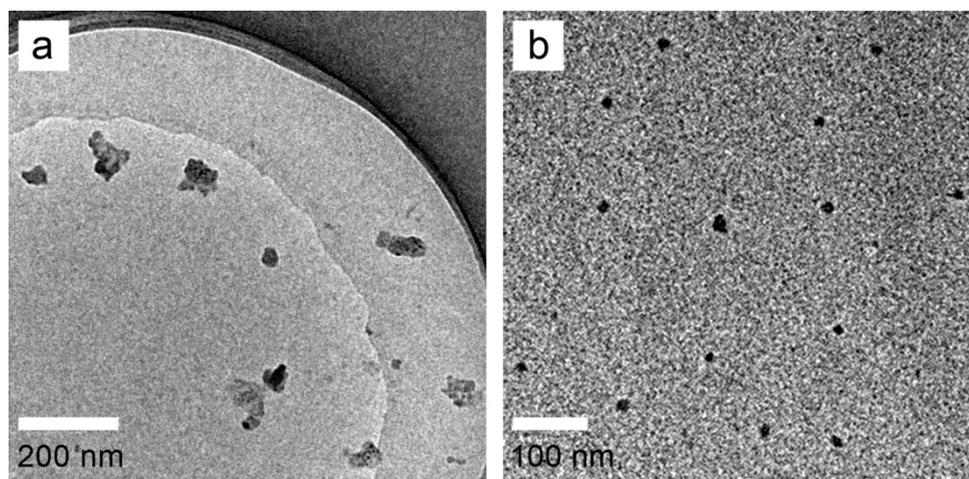


Figure S5. TEM images of the GO/HA composite: (a) large-sized sheets, and (b) small-sized particles.

S4: Confocal fluorescence images of the GO/P3HT composite

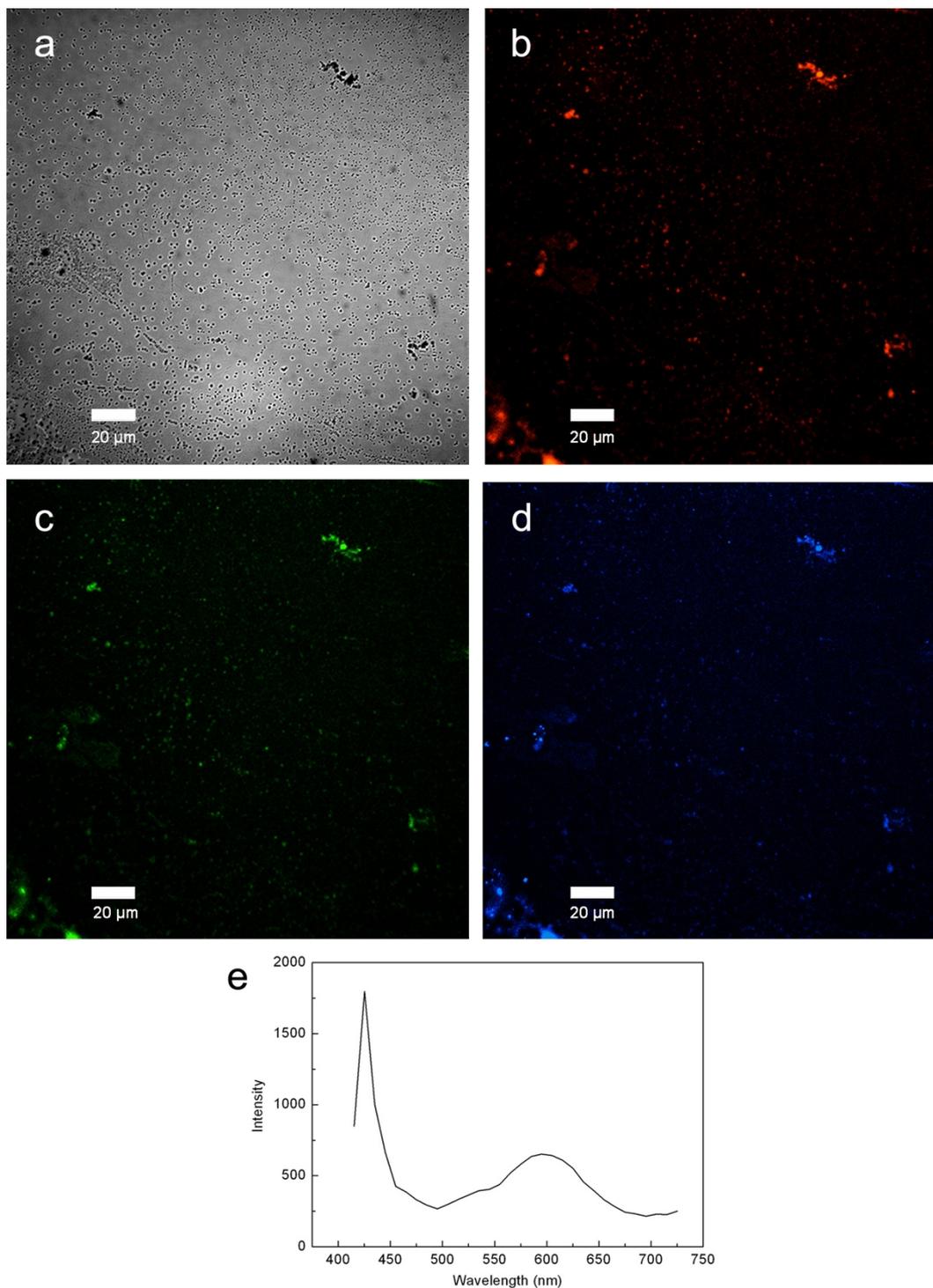


Figure S6. Confocal fluorescence images of a GO/P3HT composite film (grafting density 13.9%), as detected with different band pass filters: (a) bright field, (b) 567.5-642.5 nm, (c) 500-530 nm, and (d) 432.5-467.5 nm. (e) The spectrum obtained from the GO/P3HT film, indicating that the GO/P3HT film shows the similar PL properties as the suspension.

S5: Fluorescent responses of P3HT and the GO/HA composite to aniline and nitrobenzene

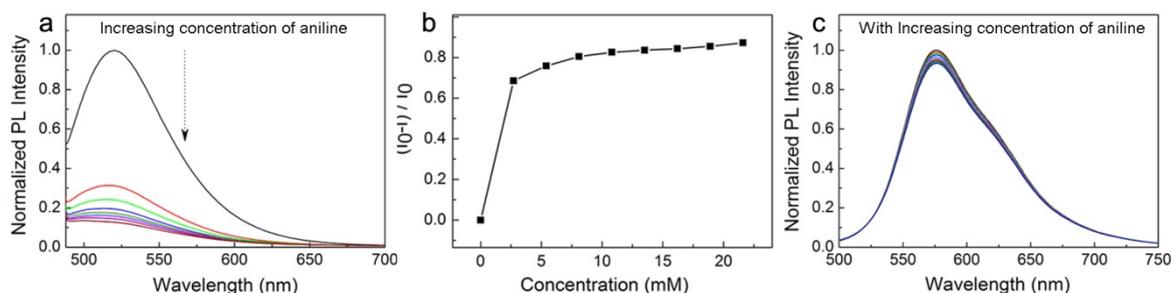


Figure S7. (a) PL emission spectra of the GO/HA composite (0.04 mg mL⁻¹ in chloroform, $\lambda_{\text{ex}} = 460$ nm) in the presence of various concentrations of aniline (from 2.7 to 21.6 mM), (b) emission intensity ratio $(I_0 - I) / I_0$ of GO/HA plotted as function of the concentration of aniline, and (c) PL emission spectra of P3HT (5.5 × 10⁻⁴ mg mL⁻¹ in chloroform, $\lambda_{\text{ex}} = 450$ nm) in the presence of various concentration of aniline (from 2.7 to 21.6 mM).

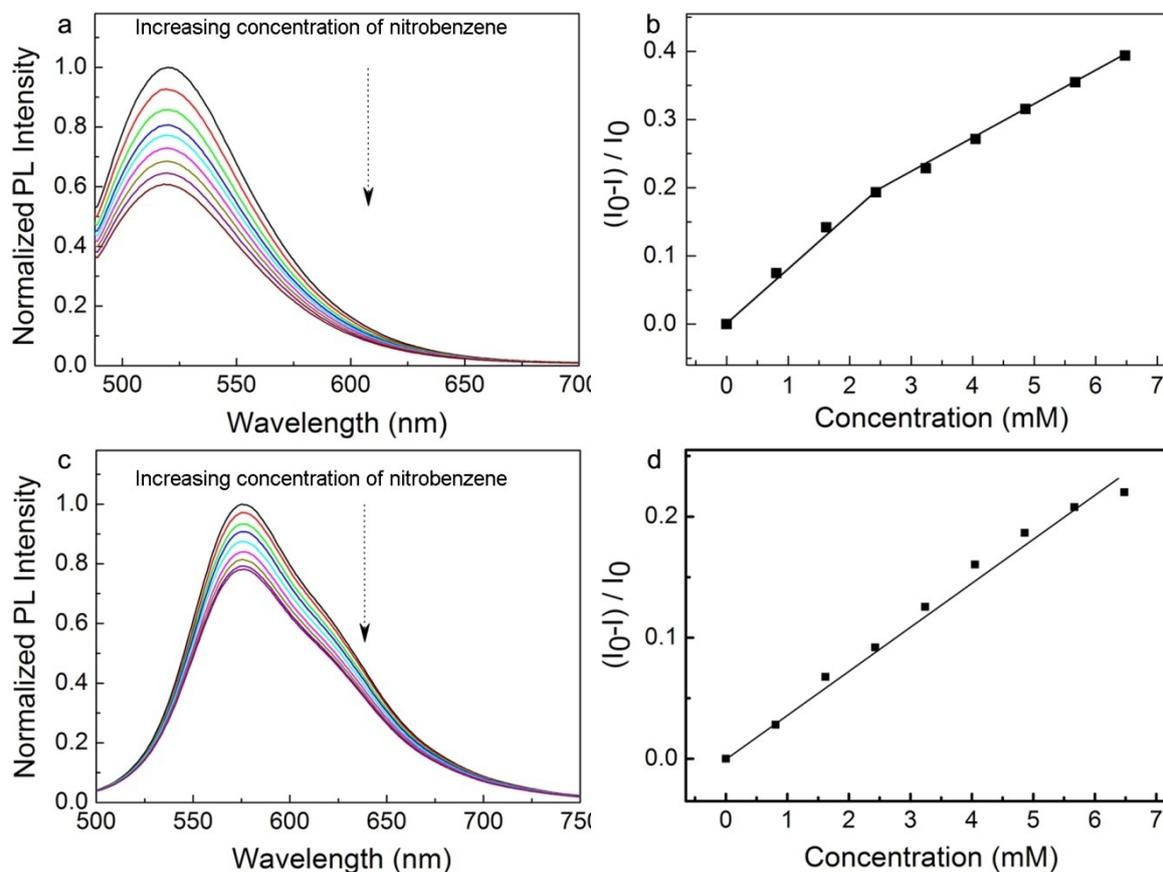


Figure S8. (a) PL emission spectra of GO/HA composite (0.04 mg mL⁻¹ in chloroform, $\lambda_{\text{ex}} = 460$ nm) in the presence of various concentrations of nitrobenzene (from 0.81 to 6.48 mM), (b) emission intensity ratio $(I_0 - I) / I_0$ of GO/HA plotted as function of the concentration of nitrobenzene, (c) PL emission spectra of P3HT (5.5 × 10⁻⁴ mg mL⁻¹ in chloroform, $\lambda_{\text{ex}} = 450$ nm) in the presence of various concentrations of nitrobenzene (from 0.81 to 6.48 mM), and (d) emission intensity ratio $(I_0 - I) / I_0$ of P3HT plotted as function of the concentration of nitrobenzene.

References:

- [1] D. Meng, J. Sun, S. Jiang, Y. Zeng, Y. Li, S. Yan, J. Geng, Y. Huang, *J. Mater. Chem.* **2012**, *22*, 21583-21591.
- [2] T. Yamamoto, D. Komarudin, M. Arai, B. L. Lee, H. Sugauma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda, H. Matsuda, *J. Am. Chem. Soc.* **1998**, *120*, 2047-2058.