

## Electronic Supplementary Information

### Soluble graphene composite with aggregation-induced emission

#### feature: the non-covalent functionalization and application in explosive detection

Peiying Li,<sup>a</sup> Zhan Qu,<sup>b</sup> Xin Chen,<sup>a</sup> Xiankuan Huo,<sup>b</sup> Xiucheng Zheng,<sup>a</sup> Dingzhong Wang,<sup>b</sup> Weiping Yang,<sup>b</sup> Lingbo Ji,<sup>b</sup> Pu Liu,<sup>\*,a</sup> and Xiujuan Xu<sup>\*,b</sup>

<sup>a</sup> College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001;

<sup>b</sup> Key Laboratory of Tobacco Flavor Basic Research of CNTC, Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001.

\*Corresponding author E-mail address: [liupu@zzu.edu.cn](mailto:liupu@zzu.edu.cn), [xxjwin@163.com](mailto:xxjwin@163.com).

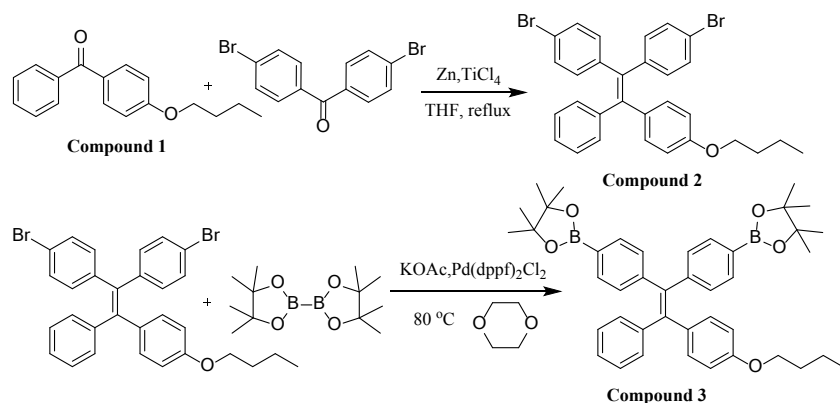


Fig. S1 The synthetic route of Compound 3.

#### Synthesis of Compound 2

Compound 2 was prepared following the experimental procedures described in the literature<sup>[1]</sup>. Into the Schlenk tube, anhydrous THF (100 mL) and zinc powder (11.34 g, 0.17 mol) were added. TiCl<sub>4</sub> (9.11 mL, 86.76 mmol) was added dropwise into the reaction system under N<sub>2</sub> below -10 °C, the mixture was refluxed for 2 h. Then 4,4'-dibromobenzophenone (7.37 mL, 21.69 mmol) and Compound 1<sup>[2]</sup> (5.51 g, 21.69 mmol) were dissolved in anhydrous THF (30 mL), transferred into the tube and refluxed overnight. When the reaction was finished, the mixture was cooled down to room temperature, K<sub>2</sub>CO<sub>3</sub> (aq) was added under stirring. The dispersed insoluble material was removed by filtration, the filtrate was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed applying rotary evaporation procedure. The crude product was purified by column chromatography on silica gel with CHCl<sub>3</sub>/petroleum ether (1:20, v/v) as eluent to give the final product (3.45 g, 27.2%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.21~7.28 (m, 4H, Ar-H), 7.11~7.15 (m, 3H, Ar-H), 7.01~7.03 (m, 2H, Ar-H), 6.67~6.92 (m, 6H, Ar-H), 6.65 (d, *J*=2.0 Hz, 2H, Ar-H), 3.92 (t, *J*=13.2 Hz, 2H, -OCH<sub>2</sub>-), 1.72~1.79 (m, 2H, -CH<sub>2</sub>-), 1.45~1.54 (m, 2H, -CH<sub>2</sub>-), 0.99 (t, *J*=14.8 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C

NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 158.07, 143.32, 142.50, 141.97, 137.34, 135.12, 132.98, 132.42, 131.25, 131.05, 130.94, 127.86, 126.82, 120.47, 113.79, 67.56, 31.35, 19.26, 13.89.

#### Synthesis of Compound 3

Compound 2 (3.50 g, 6.23 mmol), bis(pinacolato)diboron (3.95 g, 15.56 mmol), KOAc (3.66 g, 37.36 mmol), Pd(dppf)<sub>2</sub>Cl<sub>2</sub> (0.14 g, 3 mol%) and anhydrous 1,4-dioxane (45 mL) were added into the Schlenk tube under Ar atmosphere. At the temperature of 80 °C, the mixture was stirred overnight. After cooling down to the room temperature, the mixture was extracted with ethyl acetate for three times and concentrated. The crude product was purified by column chromatography on silica gel with ethyl acetate/n-hexane (1:15, v/v) as eluent to get Compound 3 as white solid (1.35 g, 31.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.51~7.57 (m, 4H, Ar-H), 7.08~7.11 (m, 3H, Ar-H), 7.02~7.04 (m, 6H, Ar-H), 6.92 (dd, 2H, Ar-H, *J*<sub>1</sub>= 2.0 Hz, *J*<sub>2</sub>= 7.4 Hz), 6.62 (dd, 2H, Ar-H, *J*<sub>1</sub>= 2.0 Hz, *J*<sub>2</sub>= 8.2 Hz), 3.9 (t, 2H, -OCH<sub>2</sub>-, *J*= 6.4 Hz), 1.71~1.78 (m, 2H, -CH<sub>2</sub>-), 1.44~1.53 (m, 2H, -CH<sub>2</sub>-), 1.34 (s, 24H, -CH<sub>3</sub>), 0.965 (t, 3H, -CH<sub>3</sub>, *J*= 7.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 146.89, 134.13, 134.01, 132.51, 131.39, 130.77, 127.65, 113.62, 83.65, 67.44, 31.37, 24.89, 19.26, 13.88.

#### Synthesis of Compound 5

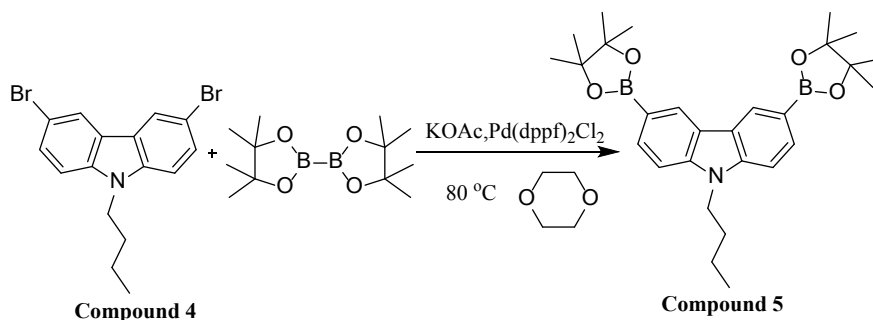


Fig. S2 The synthetic route of Compound 5.

Compound 4<sup>[3]</sup> (3.88 g, 10.20 mmol), bis(pinacolato)diboron (6.47 g, 25.50 mmol), KOAc (6.01 g, 61.20 mmol), Pd(dppf)<sub>2</sub>Cl<sub>2</sub> (0.22 g, 3 mol%) and anhydrous 1,4-dioxane (70 mL) were added into the Schlenk tube under Ar atmosphere. At the temperature of 80 °C, the mixture was stirred overnight. After cooling down to the room temperature, the mixture was extracted with ethyl acetate for three times and concentrated. The crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:14, v/v) as eluent to get the final product (2.01 g, 41.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.16 (s, 2H, Ar-H), 7.57 (dd, *J*=8.8 Hz, 2H, Ar-H), 7.31 (d, *J*=8.8 Hz, 2H, Ar-H), 4.27 (t, *J*=14.4 Hz, 2H, -NCH<sub>2</sub>-), 1.79~1.87 (m, 2H, -CH<sub>2</sub>-), 1.32~1.42 (m, 2H, -CH<sub>2</sub>-), 0.95 (t, *J*=14.8 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 139.2, 128.9, 123.4, 123.2, 111.9, 110.3, 43.0, 30.9, 20.5, 13.8.

#### Synthesis of Compound 7

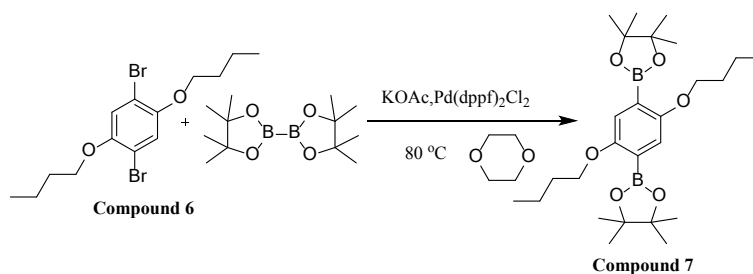


Fig. S3 The synthetic route of Compound 7.

Compound 6<sup>[4]</sup> (0.25 g, 0.65 mmol), bis(pinacolato)diboron (0.42 g, 1.64 mmol), KOAc (0.38 g, 3.95 mmol), Pd(dppf)<sub>2</sub>Cl<sub>2</sub> (20.45 mg, 4.3 mol%) and anhydrous 1,4-dioxane (40 mL) were added into the Schlenk tube under Ar atmosphere. At the temperature of 80 °C, the mixture was stirred overnight. After cooling down to room temperature, the mixture was extracted with ethyl acetate for three times and concentrated. The crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:50, v/v) as eluent. The final product was 0.19 g and the yield was 62.2%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.01 (s, 2H, Ar-H), 3.96 (t, *J*=12.4 Hz, 4H, -OCH<sub>2</sub>-), 1.76 (m, 4H, -CH<sub>2</sub>-), 1.55 (m, 4H, -CH<sub>2</sub>-), 1.35 (s, 24H, -CH<sub>3</sub>), 0.97 (t, *J*=14.8 Hz, 6H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 157.70, 119.93, 83.49, 69.45, 31.69, 25.02, 19.18, 13.92.

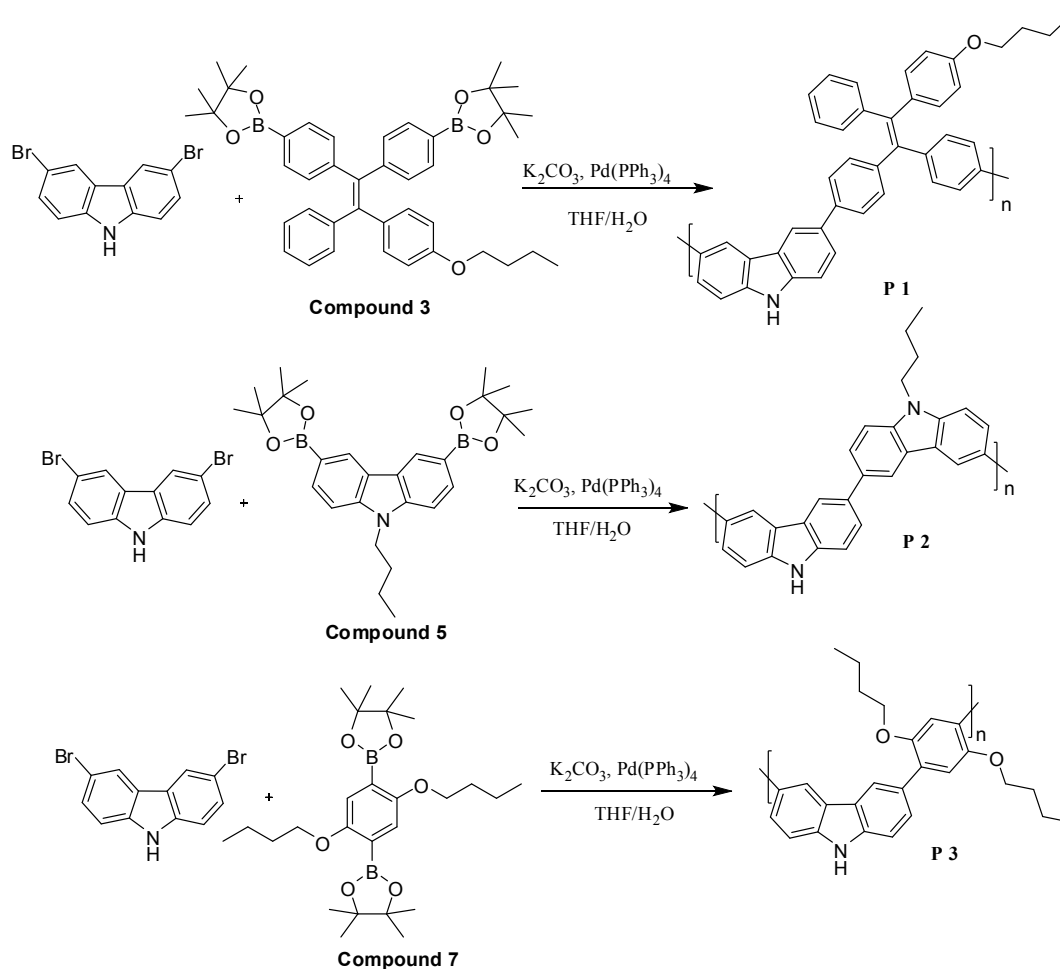


Fig. S4 The synthetic route of polymers.

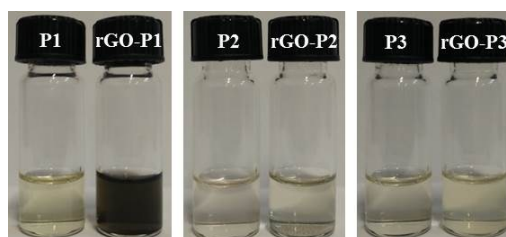


Fig. S5 Photographs of P1, P2, P3 and their functionalized composite rGO-P1, rGO-P2, rGO-P3. Concentrations: 1.5 mg/mL.

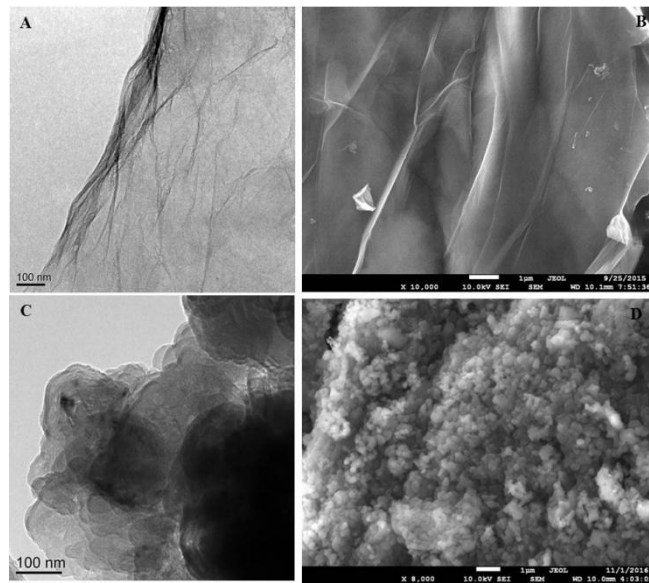


Fig. S6 TEM images of GO (A) and P1 (C), SEM images of GO (B) and P1 (D).

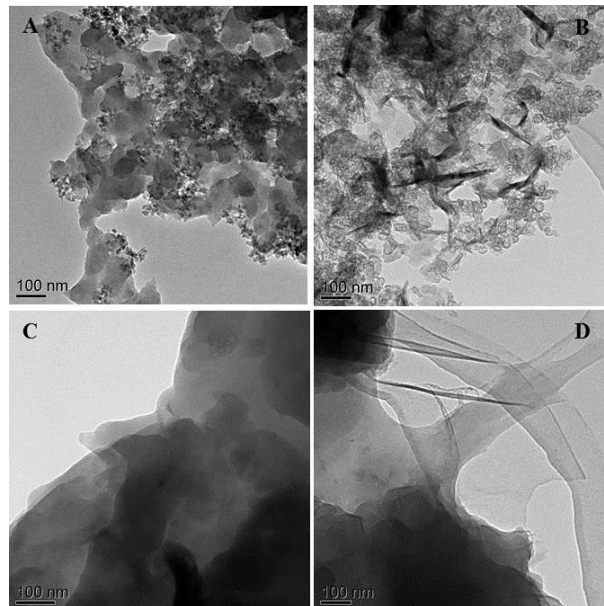


Fig. S7 TEM images of P2 (A), rGO-P2 (B), P3 (C) and rGO-P3 (D).

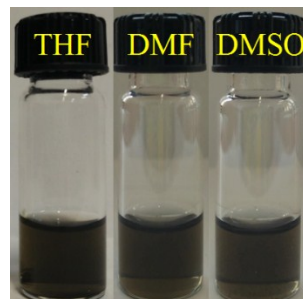


Fig. S8 Photographs of rGO-P1 solutions in different organic solvents, from left to right: THF, DMF and DMSO. Concentrations: 1.5 mg/mL.

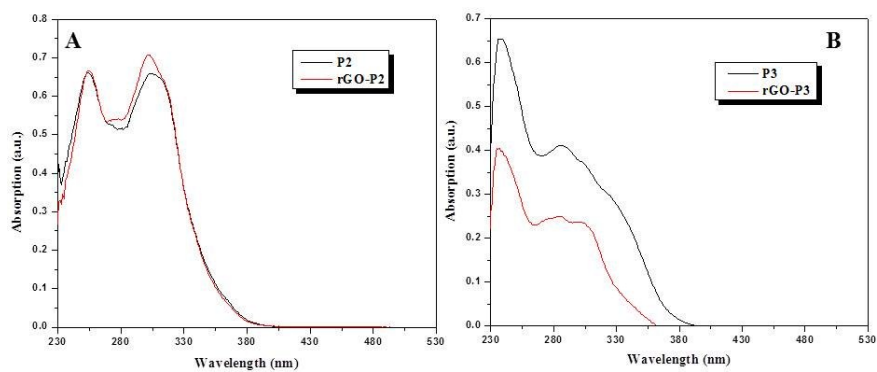


Fig. S9 (A) UV-vis absorption spectra of rGO-P2 and P2; (B) UV-vis absorption spectra of rGO-P3 and P3.

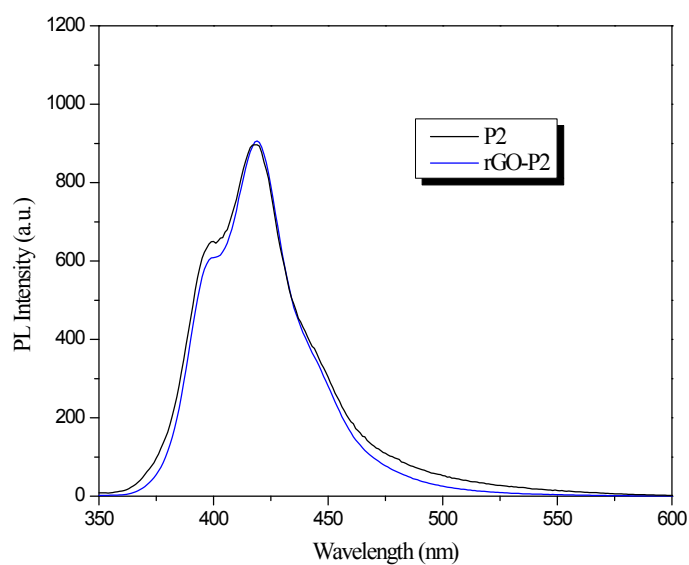


Fig. S10 Fluorescent spectra of P2 and rGO-P2 in THF.

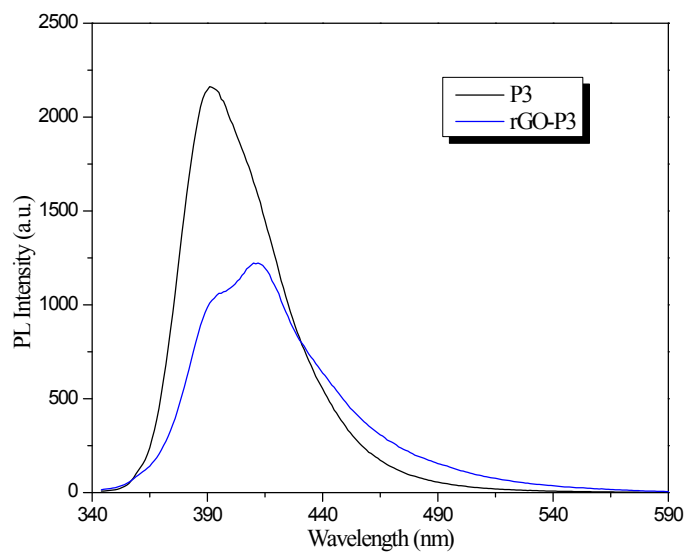


Fig. S11 Fluorescent spectra of P3 and rGO-P3 in THF.

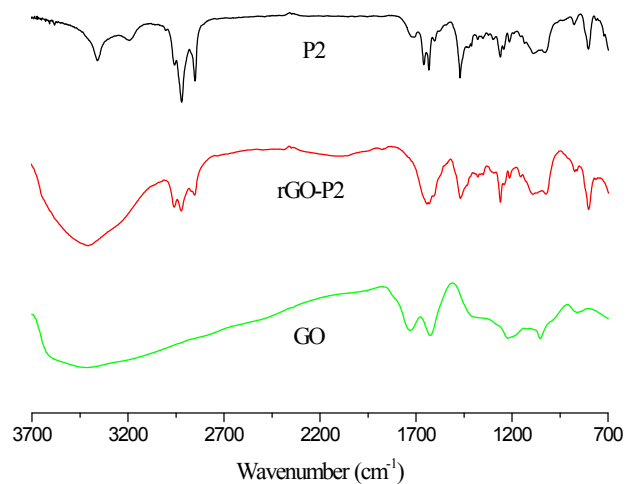


Fig. S12 IR spectra of GO, rGO-P2 and P2.

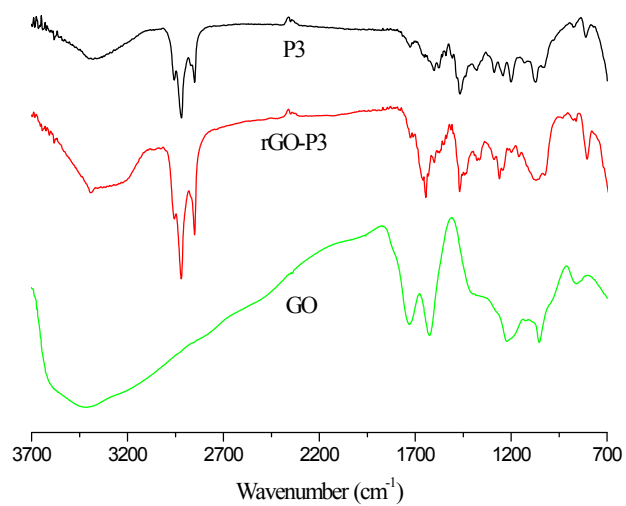


Fig. S13 IR spectra of GO, rGO-P3 and P3.

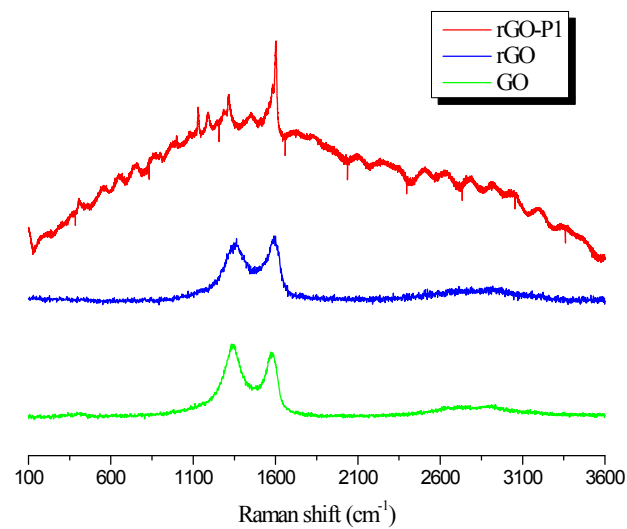


Fig. S14 Raman spectra of rGO-P1, GO and rGO.

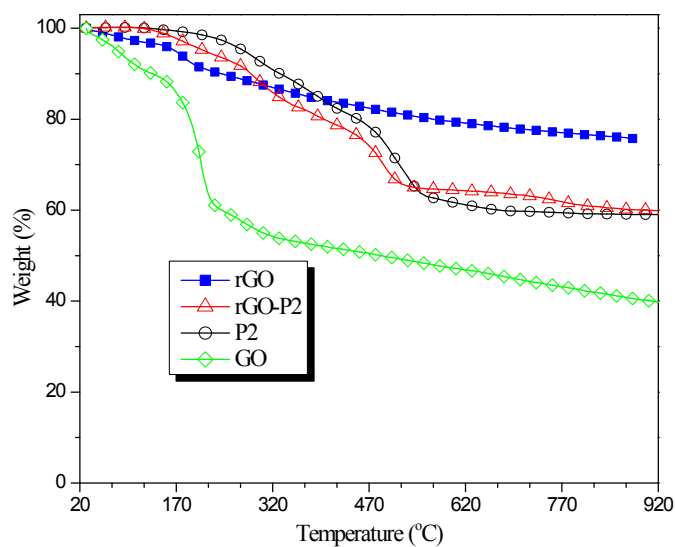


Fig. S15 TGA curves of P2, GO, rGO and rGO-P2.

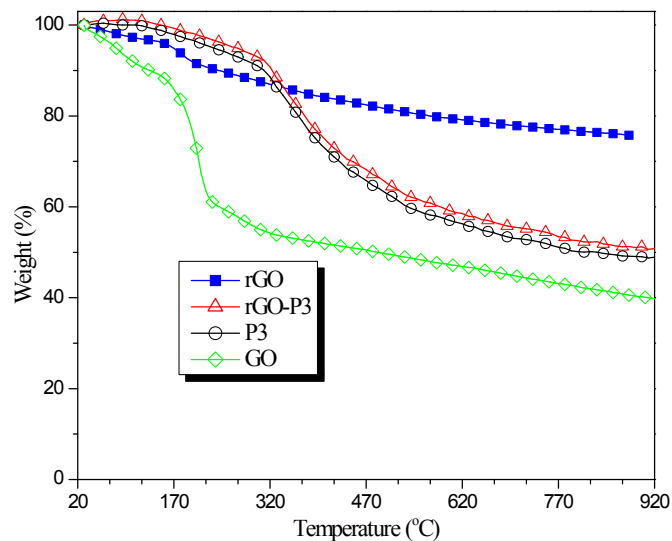


Fig. S16 TGA curves of P3, GO, rGO and rGO-P3.

Table S1 Summarization about the reported TPE-based polymers for the detection of PA.

Probing platform	Detectable concentration of PA ( $\mu\text{M}$ )	Concentration range of PA (mM)	Quenching constant ( $K_{sv}, \text{M}^{-1}$ )	references
TPE-BOZ	0.01	0~0.5	$1.134 \times 10^7$ (0-0.4 $\mu\text{M}$ )	[27a]
Poly(aryleneonylene)	4.36	0~0.37	$2.33 \times 10^5$ (870-1610 $\mu\text{M}$ )	[27b]
polytriazoles	0.436	0~0.218	$1.1 \times 10^5$ (43.6-130.9 $\mu\text{M}$ )	[27c]
TPE-containing conjugated polymers	0.74	0~0.17	-	[27d]

Poly(phenyltriazolylcarboxylate)s (PPTC)	2.18	0-0.65	$5.14 \times 10^4$ (0-87.3 $\mu\text{M}$ )	[27e]
Poly(aroyltriazole)s (PATAs)	4.36	0-0.17	$2.1 \times 10^4$ (0-43.6 $\mu\text{M}$ )	[27f]
Poly(tetraphenylethylene-co-cyclotriphosphazene) TPE-CP	0.436	0-0.17	-	[27g]
Donor-only polymer film	0.0087	0-0.3	$2.8 \times 10^4$ (0-80 $\mu\text{M}$ )	[27h]
TPE polymers with different bridge groups	4.36	0-0.29	-	[27i]
Poly(acrylate) with TPE pendant	10.9	0-0.65	$9.72 \times 10^4$ (0-175 $\mu\text{M}$ )	[27j]
Hyperbranchedpolytriazoles	-	0-0.45	56484 (0-90 $\mu\text{M}$ )	[28a]
TPE-based conjugated hyperbranched polymer	7.29	0-0.196	$3.99 \times 10^4$ (0-74.2 $\mu\text{M}$ )	[28b]
Hyperbranchedconjugated poly(tetraphenylethylene)	4.36	0-0.52	$4.38 \times 10^4$ (0-170 $\mu\text{M}$ )	[28c]
Hyperbranched polymer constructed from carbazole and TPE	1.44	0-0.13	-	[28e]

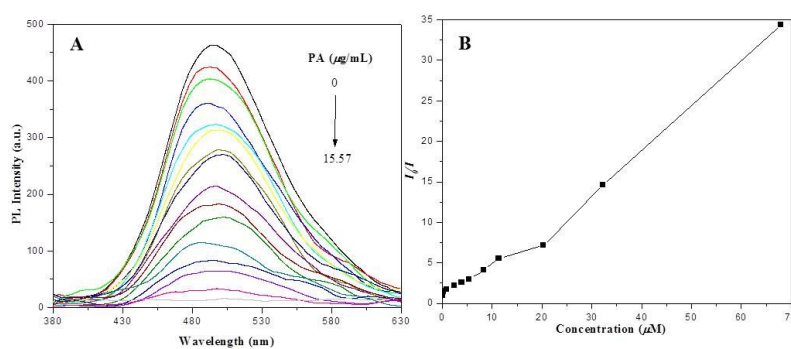


Fig. S17 (A) PL spectra of P1 with different PA concentrations in THF/H<sub>2</sub>O mixture with 99% water fraction. P1 concentration: 10  $\mu\text{M}$ ; excitation wavelength: 356 nm. (B) Stern-Volmer plots of ( $I_0/I$ ) value versus the concentration of PA in THF/H<sub>2</sub>O mixture with 99% water fraction.  $I_0$ =intensity at [PA]=0  $\mu\text{M}$ .



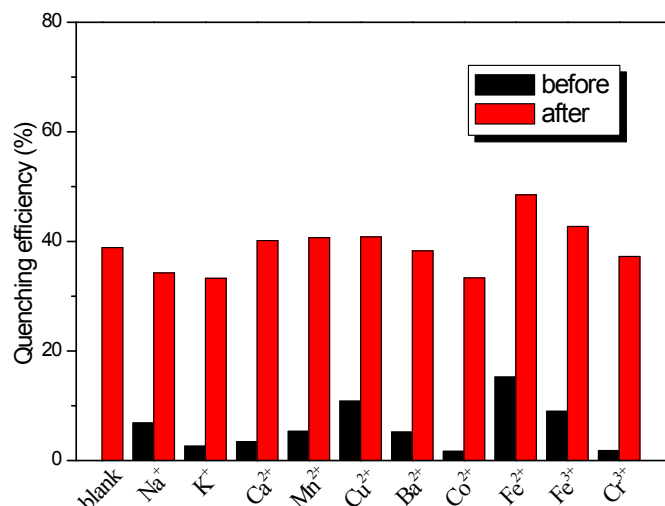


Fig. S18 Quenching efficiency of rGO-P1 with different metal ions (68  $\mu\text{M}$ ) and before and after the addition of PA (0.57  $\mu\text{M}$ , 0.13 ppm).

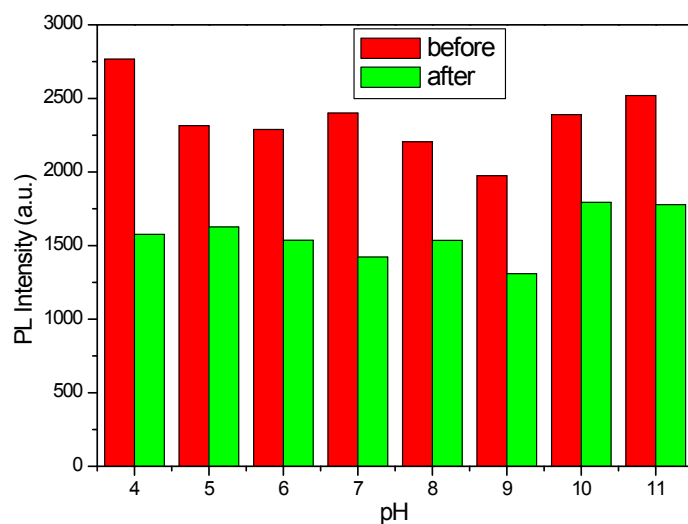


Fig. S19 PL intensity changes of rGO-P1 before and after the addition of PA (0.57  $\mu\text{M}$ , 0.13 ppm), under different pH conditions.

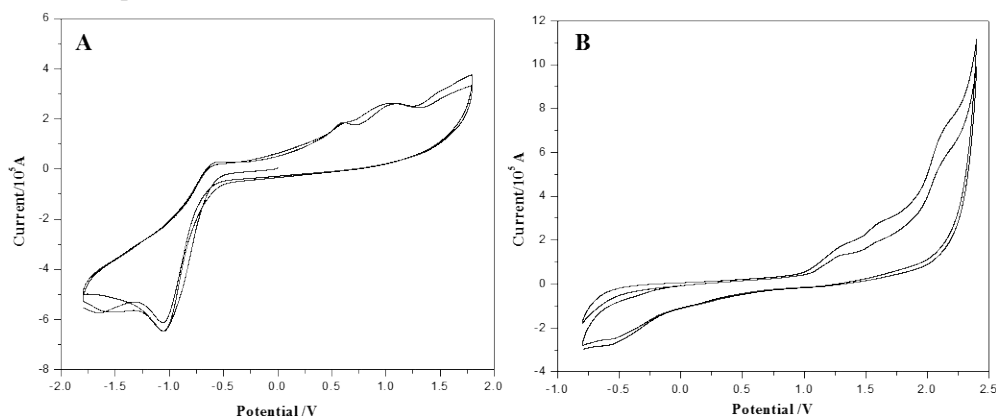


Fig. S20 Cyclic voltammograms of rGO-P1 (A) and P1 (B) in acetonitrile.  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.36)$ ,  $E_{\text{LUMO}} = -(E_{\text{red}} + 4.36)$ ,  $E_{\text{ox}}$  and  $E_{\text{red}}$  for rGO-P1 was 0.59 V and -1.1 V, respectively.  $E_{\text{ox}}$  for P1 was 1.05,  $E_{\text{LUMO}}$  of P1 was calculated by the equation of  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$ ,  $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$ , the  $\lambda_{\text{onset}}$  of P1 was 408 nm.

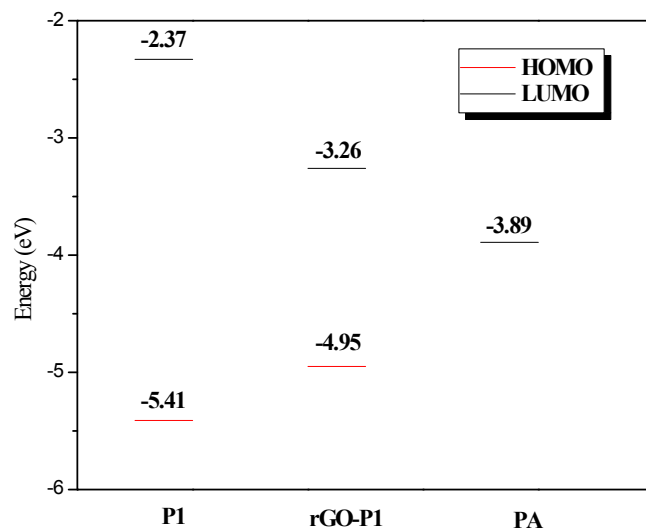


Fig. S21 Graphical representation of HOMO and LUMO energy levels of P1, rGO-P1 and PA.  $E_{\text{LUMO}}$  of PA was reported to be -3.89 eV (Macromolecules, 2011, 44, 5089-5092).

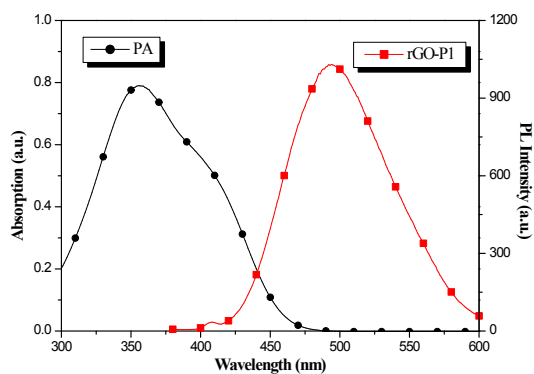


Fig. S22. Spectral overlap of the absorption spectra of PA and the emission spectrum of rGO-P1 in THF/H<sub>2</sub>O (v/v=1/99) mixture.

#### References

1. M. J.Uddin, P. N. P.Rao, E.E. Knaus, *Bioorganic & Medicinal Chemistry Letters*, **2004**, *14*, 1953-1956.
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3. H. Zhu, B. Shi, K. Chen, P. Wei, D. Xia, J. H. Mondal, F. Huang, *Org. Lett.*, **2016**, *18(19)*, 5054-5057.
4. K. Shen, L. Qin, H. G. Zheng, *Dalton Trans.*, **2016**, *45*, 16205-16210.