***Electronic Supplementary Information (ESI)***

# A graphene oxide-based AIE biosensor with high selectivity toward bovine serum albumin

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## Experimental Section

### Materials and instrumentations

Bovine serum albumin (BSA) and all proteins were purchased from Beijing Xin Jing Ke Biotechnology Co. Ltd. (Beijing, China). $CaCl_2$, $CuCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, $ZnCl_2$, $MnSO_4{\cdot}H_2O$, $Pb(NO_3)_2$, $KNO_3$, LiCl, $CdSO_4{\cdot}8H_2O$, $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $Na_2SO_4$, $NaHSO_4{\cdot}H_2O$, $Na_2SO_3$, $NaHSO_3$, $CH_3COONa$, $K_2CO_3$, $K_3PO_4{\cdot}3H_2O$, $Na_2S_2O_3{\cdot}5H_2O$, KSCN, $NaNO_3$, $KClO_4$, $KHCO_3$, $Na_2S$, NaCl, $K_2S_2O_8$, ammonium chloride ($NH_4Cl$), tetrabutylammonium iodide (TBAI), and sodium dodecylbenzenesulfonate (SDBS) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. TPE-$SO_3Na$ was prepared as reported previously.[1] All reagents were of analytical reagent grade and used without further purification. Solutions of all protein samples were prepared by directly dissolving the proteins in deionized (DI) $H_2O$ (3 mg/mL) and stored in a refrigerator. 0.1 mmol of TPE-$SO_3Na$ was dissolved in DI $H_2O$ (10 mL) to afford the corresponding solutions ($1\times10^{-3}$ mol/L), the stock solutions could be diluted to the desired concentration with DI $H_2O$ when needed. GO (2

mg) was dissolved in DI $H_2O$ (10 mL), and sonicated for 40 min to afford 0.2 mg/mL aqueous solution, and then diluted to the desired concentration when needed.

Transmission electron microscope (TEM) was performed on a JEM-2010 at an accelerating voltage of 200 kV. TEM samples were prepared by drying a droplet of the suspension on a carbon grid. Atomic force microscope (AFM) images were obtained from Agilent 5500 using the tapping mode. Photoluminescence (PL) spectra were taken on a Hitachi F-4500 Fluorescence Spectrophotometer. The slits for excitation and emission were set at 5 nm/5 nm.

**Synthesis of Graphite Oxide (GO):** GO was synthesized from natural graphite by the modified Hummers method.[2] $H_2SO_4$ (70 mL) was added into the 250 mL flask filled with graphite (1 g) at room temperature, followed by adding solid $KMnO_4$ (7 g) slowly below 20 $^oC$ (ice bath). Then, the temperature was increased to 35 $^oC$, the mixture was stirred for 2 hrs. Excess water was added into the mixture at 0 $^oC$ (ice bath), and then $H_2O_2$ (30 wt%) was added until there was no gas producing. The mixture was filtered and washed with 1 M HCl aqueous solution and DI water for several times. Exfoliation was carried out by sonicating under ambient condition for 40 minutes.

**Preparation of solutions of metal ions and anions:** 0.1 mmol of each inorganic salt ($CaCl_2$, $CuCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, $ZnCl_2$, $MnSO_4{\cdot}H_2O$, $Pb(NO_3)_2$, $KNO_3$, LiCl, $CdSO_4{\cdot}8H_2O$, $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $Na_2SO_4$, $NaHSO_4{\cdot}H_2O$, $Na_2SO_3$, $NaHSO_3$, $CH_3COONa$, $K_2CO_3$, $K_3PO_4{\cdot}3H_2O$, $Na_2S_2O_3{\cdot}5H_2O$, KSCN, $NaNO_3$, $KClO_4$, $KHCO_3$, $Na_2S$, NaCl, $K_2S_2O_8$) was dissolved in DI water (10 mL) to afford $1\times10^{-2}$ mol/L aqueous solution. The stock solutions could be diluted to the desired concentrations with water when needed.

**Preparation of solutions of SDBS, $NH_4Cl$, and TBAI:** 0.1 mmol of each of them was dissolved in DI water (10 mL) to afford $1\times10^{-2}$ mol/L aqueous solution. The stock solutions could be diluted to the desired concentrations with water when needed.

**Preparation of the complex of GO and TPE-$SO_3Na$ (GO-TPE-$SO_3Na$):** The solution of GO (0.2 mg/mL) was diluted to the concentration of 0.02 mg/mL (100 mL), TPE-$SO_3Na$ ($1\times10^{-3}$ mol/L, 1 mL) was added to afford the complex of GO and TPE-$SO_3Na$.

**Fluorescence intensity changes of GO-TPE-$SO_3Na$ towards different proteins:** The solution of GO-TPE-$SO_3Na$ was placed in a quartz cell and the fluorescence spectrum was recorded for comparison. After the solution of biomacromolecule was added, the mixture was allowed to stand for 12 min at room temperature before the fluorescence spectrum was recorded.

**Fluorescence intensity changes of TPE-$SO_3Na$ towards different proteins:** The solution of TPE-$SO_3Na$ was placed in a quartz cell and the fluorescence spectrum was recorded for comparison. After the solution of biomacromolecule was added, the mixture was allowed to stand for 12 min at room temperature before the fluorescence spectrum was recorded.

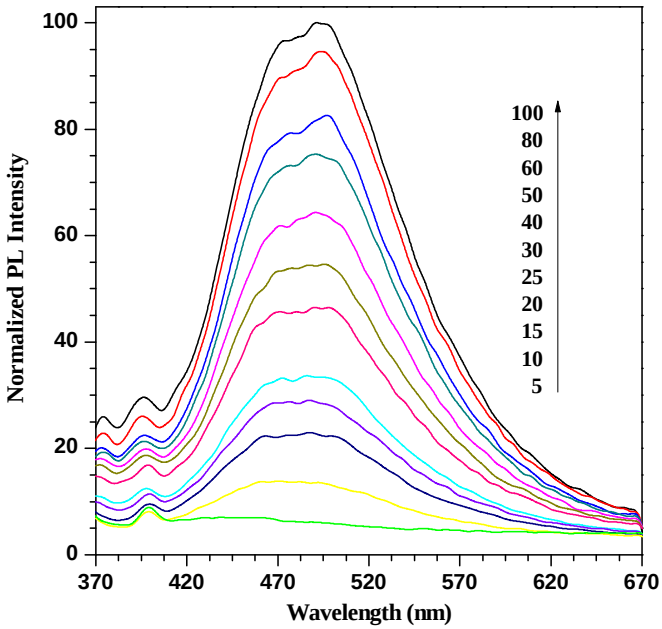


Figure S1. Fluorescence spectra of GO-TPE-$SO_3Na$ complexed with different concentrations of BSA ranging from 5 to 100 $\mu$g/mL (1 $\mu$g/mL=0.0149 $\mu$M). Excitation wavelength (nm): 350.

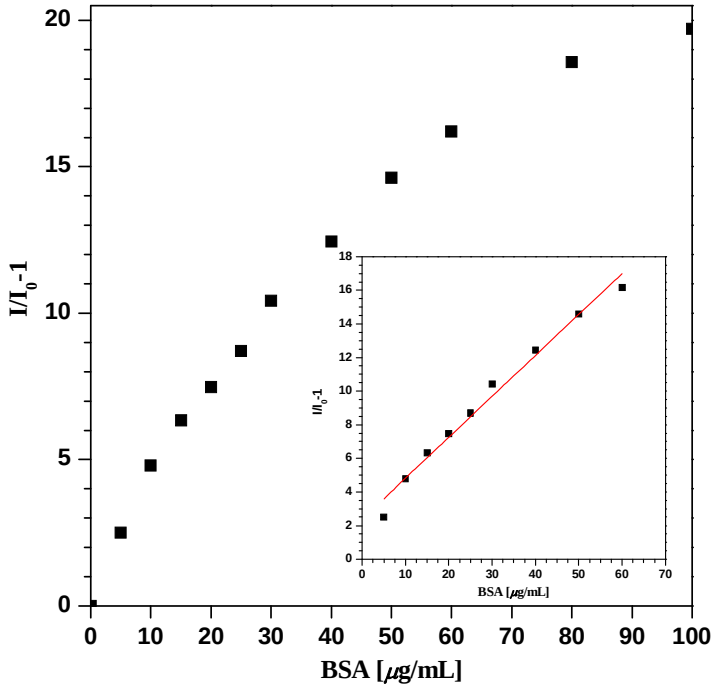


Figure S2. Calibration plot of fluorescence intensity changes ($I/I_0$-1) of GO-TPE-$SO_3$Na towards BSA versus the concentration of BSA ($\mu$g/mL), the inset shows the calibration plot at low concentrations of BSA (up to 60 $\mu$g/mL). Excitation wavelength (nm): 350.

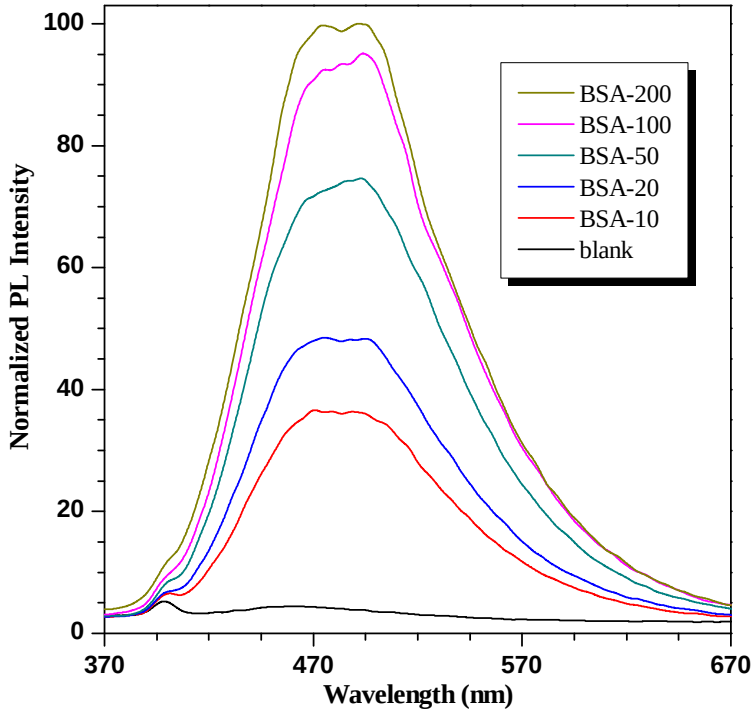


Figure S3. Fluorescence spectra of TPE-$SO_3$Na upon the addition of BSA at different concentrations ($\mu$g/mL). Excitation wavelength (nm): 350.

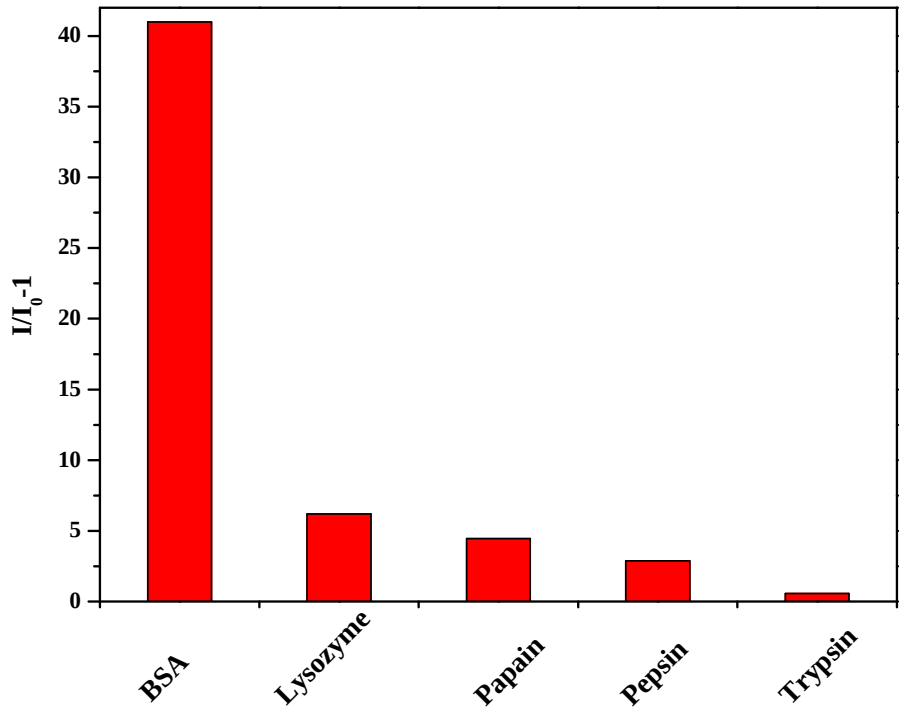


Figure S4. Fluorescence intensity changes ($I/I_0$-1) of GO-TPE-$SO_3Na$ towards different proteins, including BSA, lysozyme, papain, pepsin and trypsin, at the same concentration of 200 $\mu$g/mL. Excitation wavelength (nm): 350.

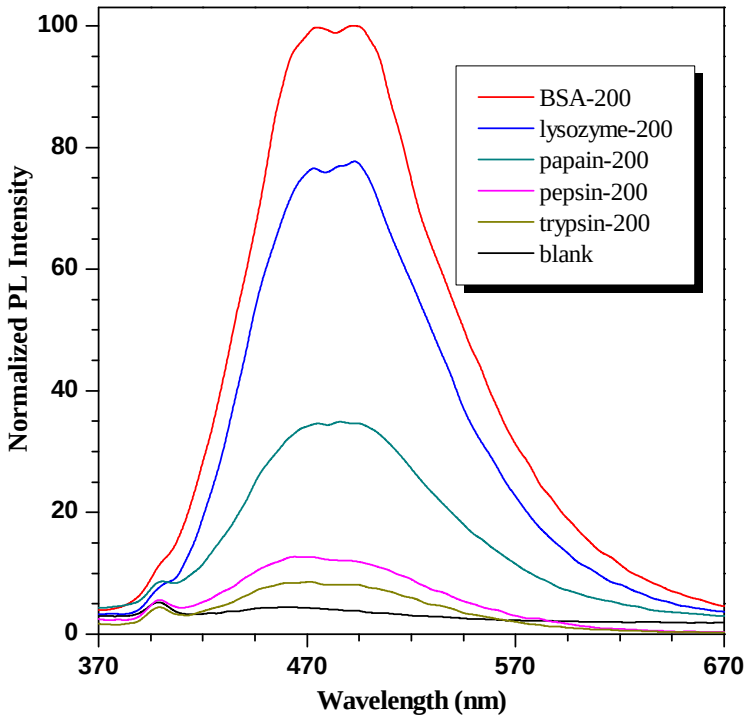


Figure S5. Fluorescence spectra of TPE-$SO_3Na$ upon the addition of different proteins at the same concentration of 200 $\mu$g/mL. Excitation wavelength (nm): 350.

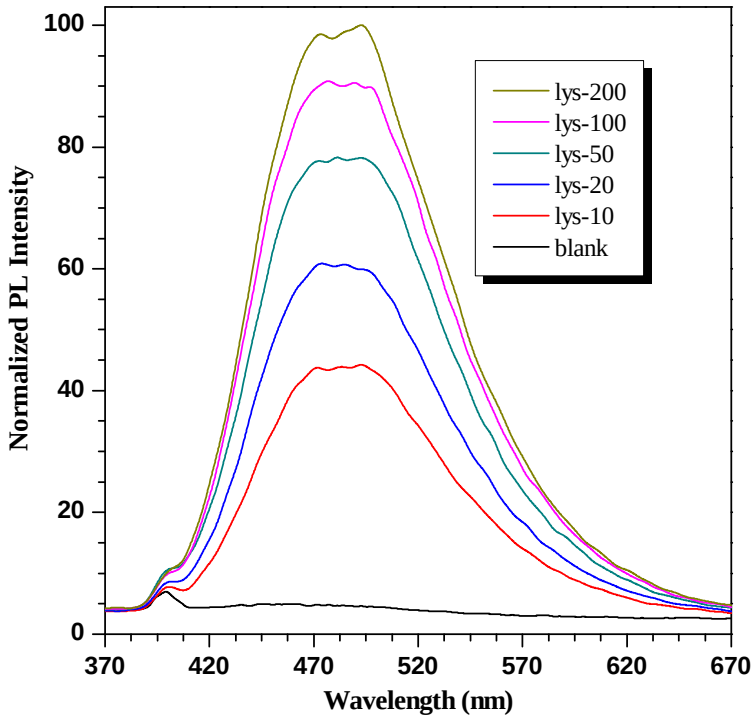


Figure S6. Fluorescence spectra of TPE-$SO_3Na$ upon the addition of lysozyme at different concentrations ($\mu$g/mL). Excitation wavelength (nm): 350.

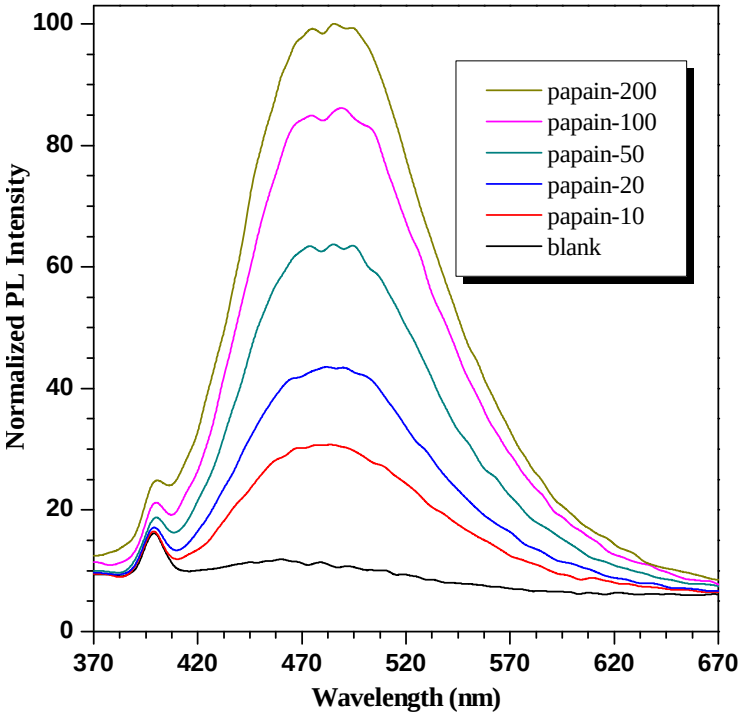


Figure S7 Fluorescence spectra of TPE-$SO_3Na$ upon the addition of papain at different concentrations ($\mu$g/mL). Excitation wavelength (nm): 350.

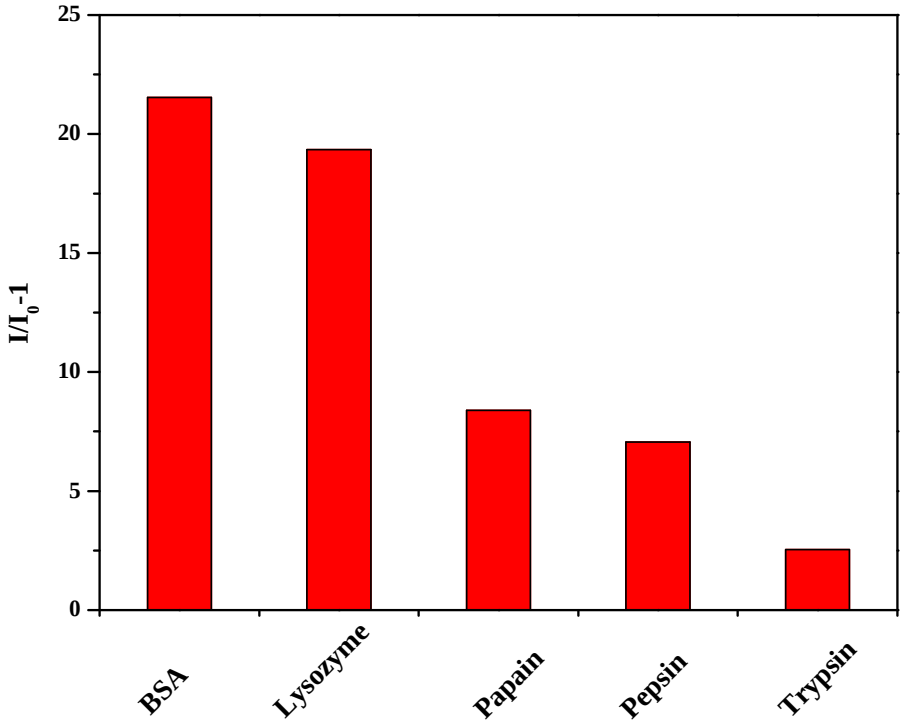


Figure S8. Fluorescence intensity changes ($I/I_0$-1) of TPE-$SO_3Na$ towards different proteins at the same concentration of 200 $\mu$g/mL. Excitation wavelength (nm): 350.

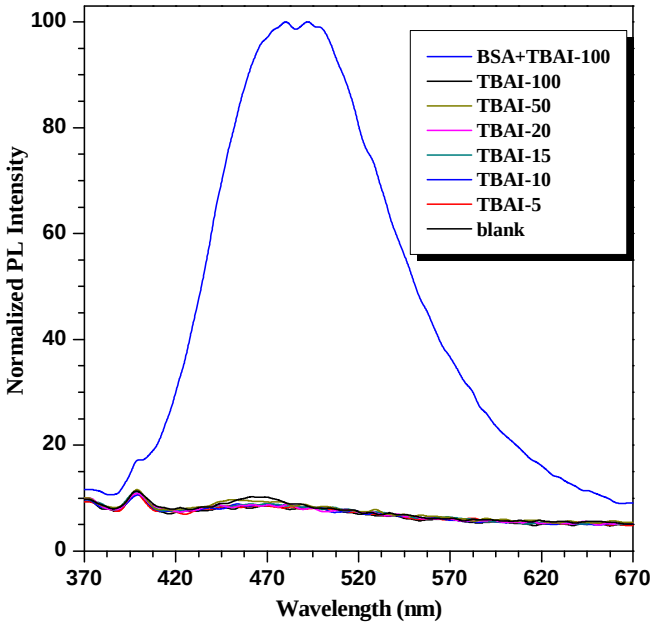


Figure S9. Fluorescence spectra of GO-TPE-$SO_3Na$ complexed with TBAI at different concentrations ($\mu$M), with and without BSA (1.5 $\mu$M)

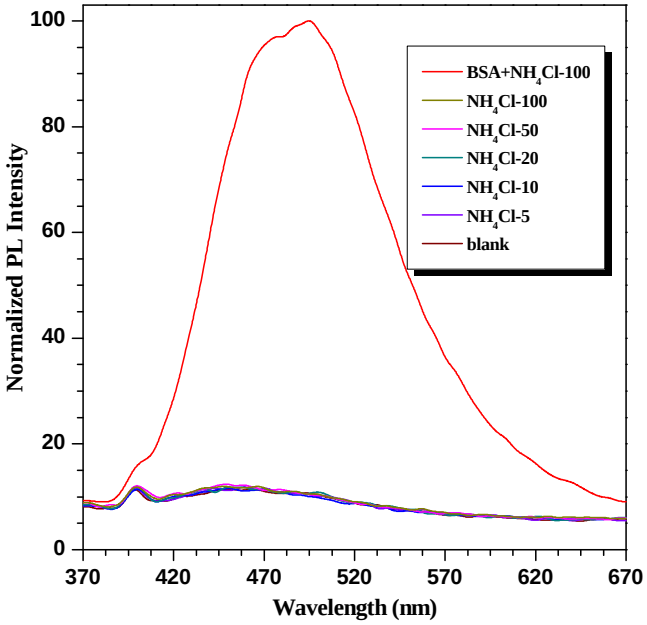


Figure S10. Fluorescence spectra of GO-TPE-$SO_3Na$ complexed with $NH_4Cl$ at different concentrations ($\mu$M), with and without BSA (1.5 $\mu$M)

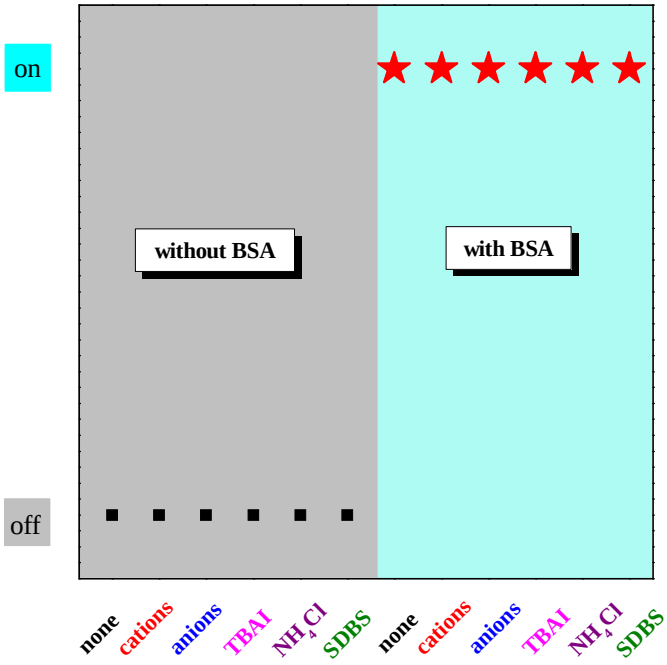


Figure S11. The "turn-on" and "off" fluorescence phenomena of GO-TPE-$SO_3Na$ complexed with different interferent, including cations, anions, TBAI, $NH_4Cl$, and SDBS, at the concentration of 15 $\mu$M, with and without BSA (1.5$\mu$M). The cations used here were $Ca^{2+}$, $Cu^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Pb^{2+}$, $K^{+}$, $Li^{+}$, $Cd^{2+}$, $Ni^{2+}$, and $Co^{2+}$, while anions were $SO_4^{2-}$, $HSO_4^{-}$, $SO_3^{2-}$, $HSO_3^{-}$, $CH_3COO^{-}$, $CO_3^{2-}$, $PO_4^{3-}$, $S_2O_3^{2-}$, $SCN^{-}$, $NO_3^{-}$, $ClO_4^{-}$ , $HCO_3^{-}$, $S^{2-}$, $Cl^{-}$, and $S_2O_8^{2-}$.

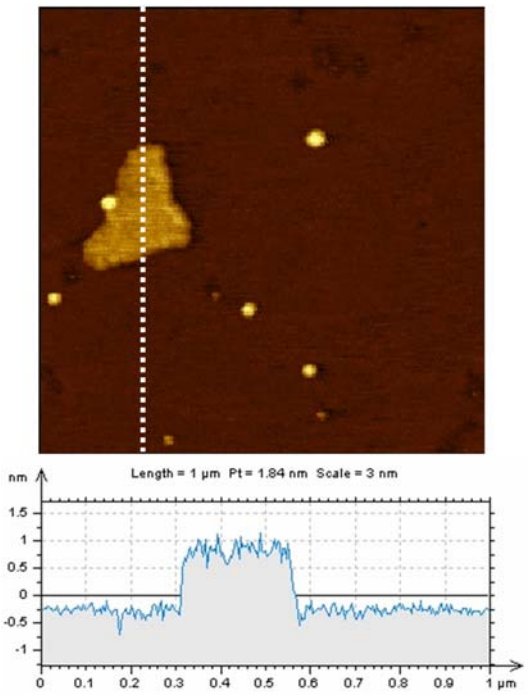


Figure S12. AFM image of GO-TPE-$SO_3Na$, scan size: 1 $\mu$m×1 $\mu$m.

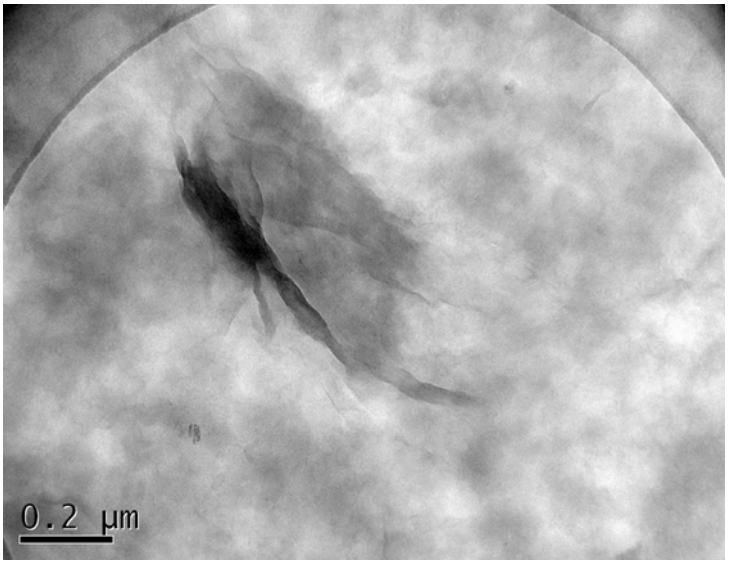


Figure S13. TEM image of GO-TPE-$SO_3Na$.

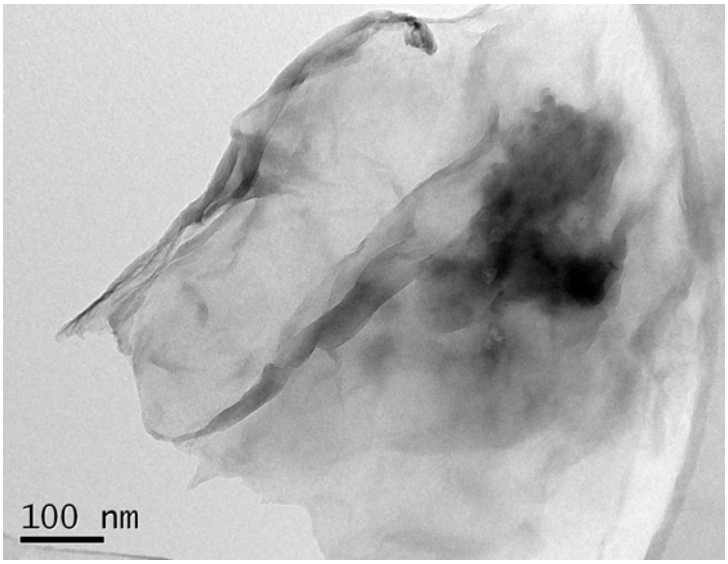


Figure S14. TEM image of GO-TPE-$SO_3Na$ complexed with BSA.

## References

(1). H. Tong, Y. Hong, Y. Q. Dong, M. H. 1ussler, Z. Li, J. W. Y. Lam, Y. Dong, H. H.-Y. Sung, I. D. Williams, and B. Z. Tang, *J. Phys. Chem. B.,* 2007, **111**, 11817-11823.

(2). W. S. Hummers Jr., and R. E. Offeman, *J. Am. Chem. Soc.,* 1958, **80**, 1339.