Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Luminescent lanthanide graphene for detection of bacterial spores and cysteine

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Experimental

Materials

Graphite oxides, Ethylenediamine tetraacetic acid (EDTA), $Tb(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, 1,2-Bis(2-aminoethoxy)ethane, $Hg(NO_3)_2$ and dipicolinic acid were purchased from Sigma-Aldrich. All other regents were of analytical reagent grade. Aqueous solutions were prepared with double-distilled water (ddH_2O) from a Millipore system (>18 MΩ cm).

Synthesis of amino-Functionalized Graphene (GA).

Graphene-NH_2 was prepared by vigorously stirring a solution of 20 mg of the graphene oxides, 5mL of 1,2-Bis(2-aminoethoxy)ethane, and 100 mg of KOH in 50 mL of H_2O at 70 ^oC for 24 h. Then 10 mL of 0.5 M $NaBH_4$ solution was added, and the reaction was kept on at 70 ^0C for 2 h. After that, the GP was collected and purified by centrifugation and adequately washed with water several times to remove the impurities and the excess of 1,2-Bis(2-aminoethoxy)ethane by physical absorption.

Synthesis of EDTA Dianhydride (EDTAD).

Ethylenediamine tetraacetic acid (EDTA, 20 g) was placed in a 250 mL three-neck flask equipped with a condenser, a magnetic stirrer and a heating mantle. Acetic anhydride (37.8 mL) and pyridine (25.5 mL) were added to the flask, and the mixture was stirred for 24 h at 63 ^oC. The resulting anhydride was collected by filtration, washed thoroughly with acetic anhydride and dry diethyl ether. The cream-colored powder was then freezedried.

Synthesis of EDTA-Functionalized Graphene (GE).

Graphene-NH_2 (10 mg) was redispersed by sonication in bicarbonate buffer (5 mL,

0.1M) at pH 9.6. EDTA dianhydride (80 mg) was added. After stirring for 2 h, the prepared nanoparticles were separated by centrifuging and then washed four times with bicarbonate buffer and two times with deionized water.

Synthesis of GE-Eu or GE-Tb Complex.

10 mg GE was firstly dispersed in 5 mL H_2O. Then, the solution was added dropwise with Eu $(NO_3)_3$ or Tb $(NO_3)_3$ (5 mL, 0.01M) by sonication and stirred for 3 h. Finally, the products were collected by centrifuging and washed with deionized water several times to remove residual Eu $(NO_3)_3$ or Tb $(NO_3)_3$. The final complexes were dissolved in distilled water, and diluted to a total volume of 5 mL to give a~ 2 mg/mL solution.

Detection of Dipicolinic Acid (DPA).

An aliquot (2 μL) of a stock solution of GE-Tb was added to 500 μL of a 10 mM Tris buffered at pH 7.0. The solution was then excited at 270 nm, and the emission spectrum was recorded. An aqueous solution of DPA was then added incrementally increasing the DPA concentration. After each addition, the sample was excited at 270 nm. Samples were excited at 270 nm, and emission spectra were collected using a Hitachi F4600 Fluorescence Spectrophotometer.

Detection of Cysteine

To measure the quenching effect, solutions of GE-Tb-DPA (4 μgml^{-1} GE-Tb, 6 μM DPA) in 500 μL of Tris−HCl (10 mM, pH7.0) buffer were titrated with 32 μM or 240 μM Hg^{2+} with increasing amounts of cysteine. Samples were excited at 270 nm, and fluorescence emission intensity at 545 was collected.

To determination of cystein, solutions of GE-Tb-DPA/Hg (4 μgml^{-1} GE-Tb, 6 μM

DPA, 32 μM Hg^{2+}) were prepared in 500 μL of buffer and placed in quartz cell. The solutions of amino acids were prepared in distilled water and were added in portions. Samples were excited at 270 nm, and emission spectra were collected.

Characterization: Samples for AFM images were prepared by depositing a dispersed GE-Eu-DPA/H_2O solution (10 μgmL^{-1}) onto a freshly cleaved mica surface and washed with ddH_2O. Tapping mode was used to acquire the images under ambient conditions. FTIR characterization was carried out on a BRUKE Vertex 70 FTIR spectrometer. UV-vis absorbance measurements experiments were carried out on a UV-3600 UV-Vis-NIR Spectrophotometer. Thermogravimetric analysis (TGA) was recorded on a PE TGA-7 thermal analyzer at 10 $^{o}C \cdot min^{-1}$ in an N_2 atmosphere.

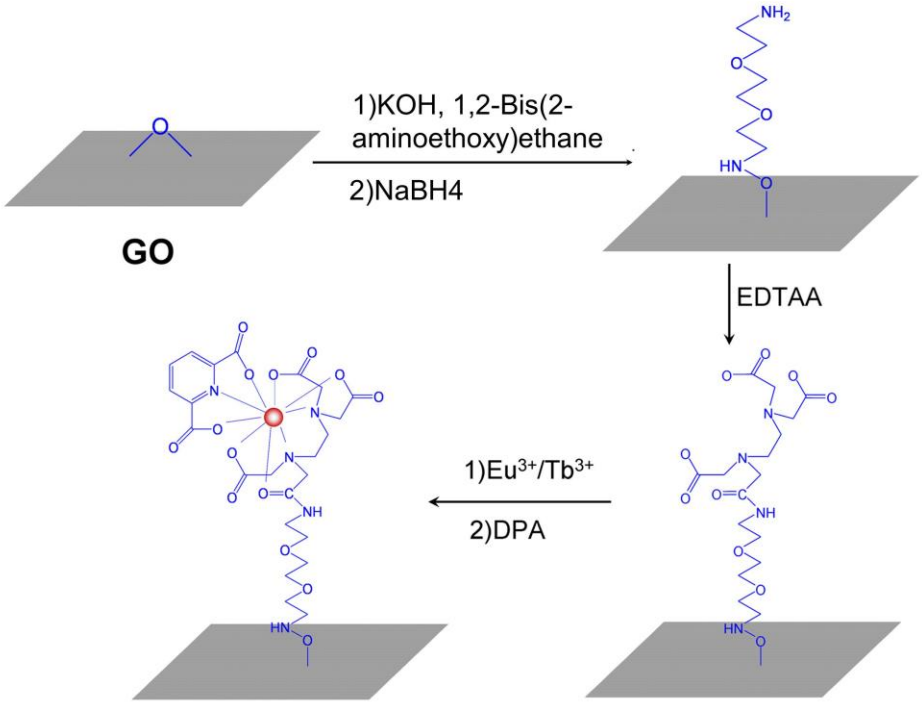

Figure S1. Synthetic steps for luminescent Eu(Ⅲ)/Tb(Ⅲ)-complex covalently modified graphene.

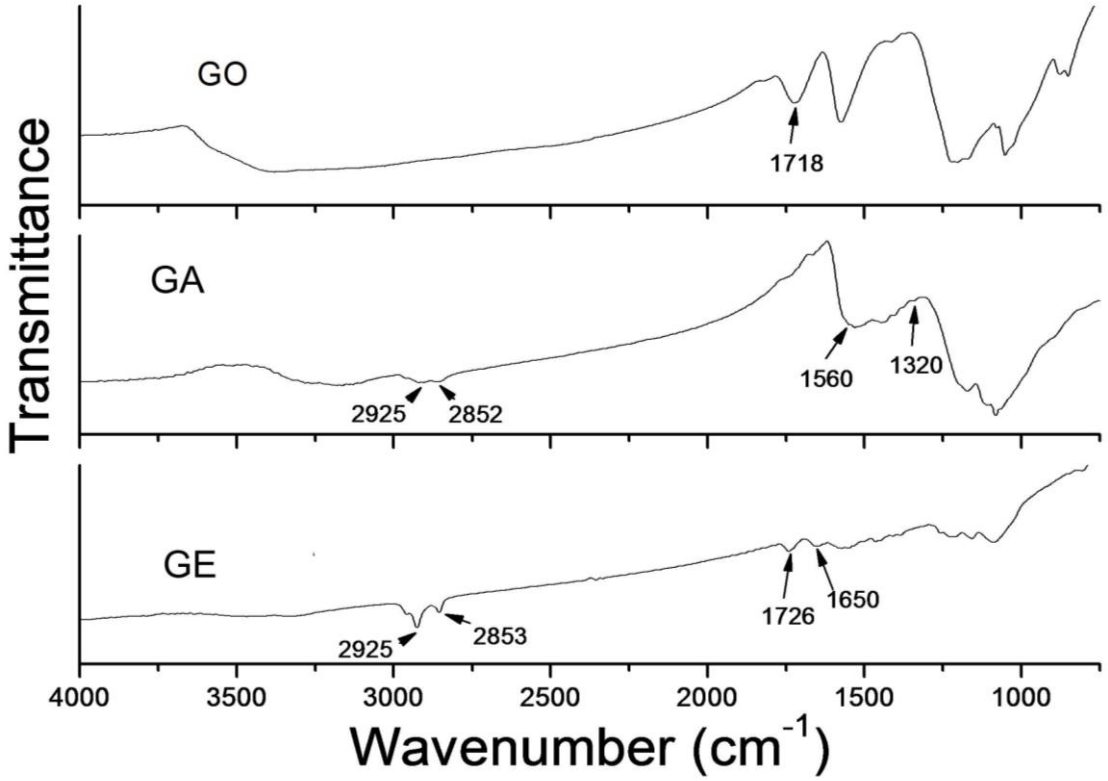

Figure S2. FT-IR spectra of GO, GA (Graphene-NH_2) and GE (Graphene-EDTA).

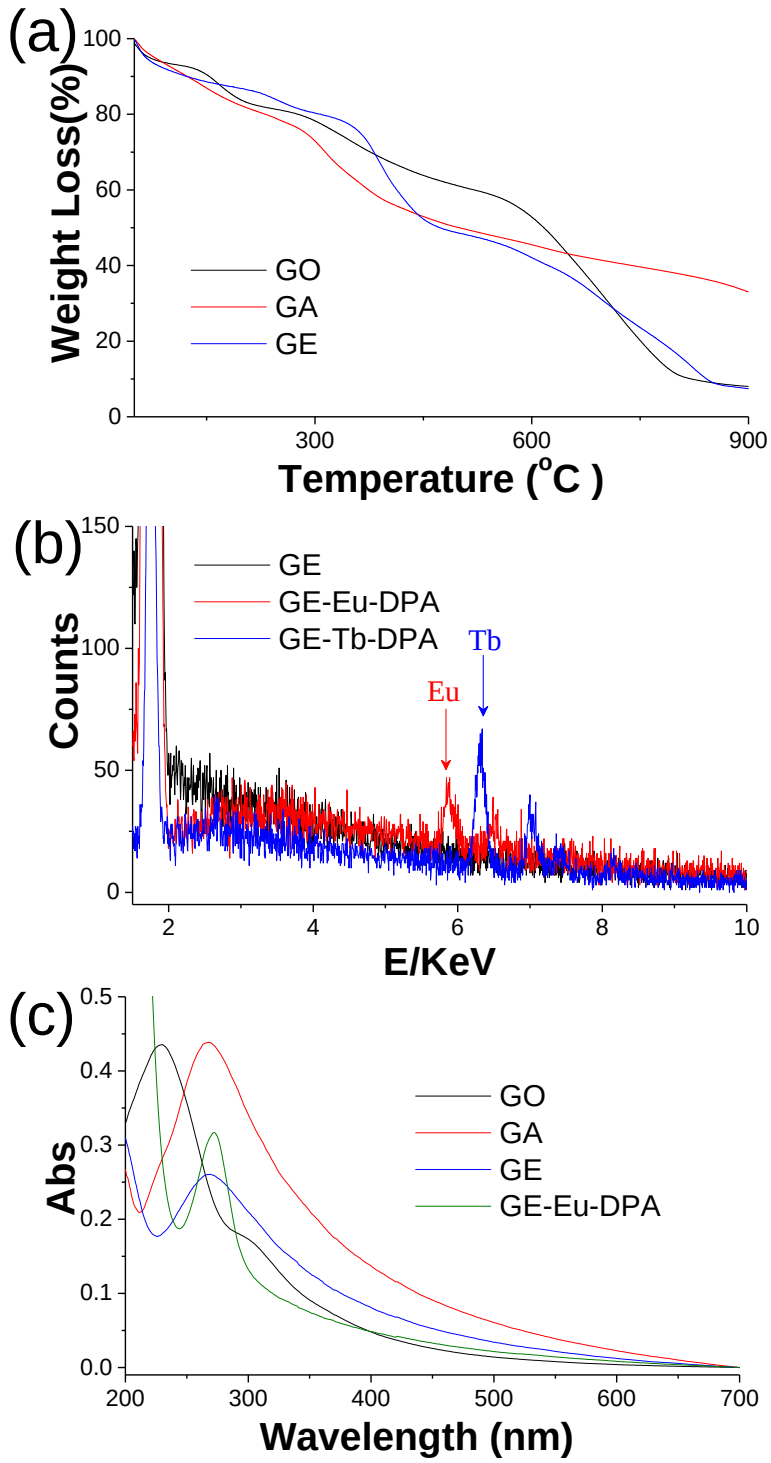

Figure S3. (a) Thermogravimetric analysis for GO (black), GA (red) and GE(blue) in N_2 atmosphere with a ramp of 10 °C/min. (b) EDX spectra of GE (black), GE-Eu-DPA (red) and GE-Tb-DPA (blue). (c) UV/Vis spectra for GO (black), GA(red), GE(blue) and GE-Eu-DPA (green) in ddH_2O.

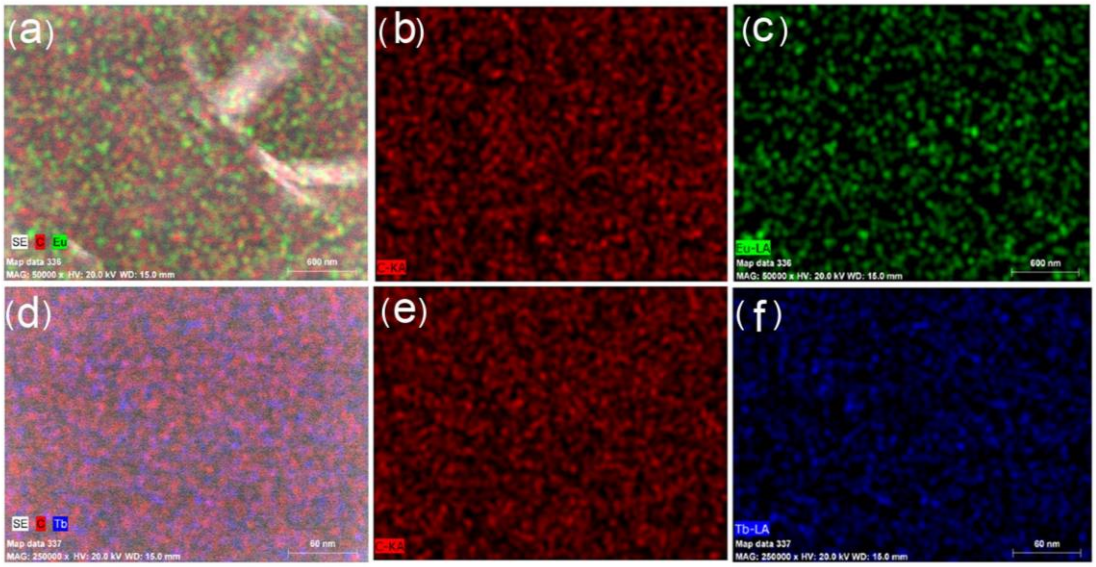

Figure S4. Elemental mapping images of GE-Eu-DPA or GE-Tb-DPA sheets. (a) the overlay of all the elemental mappings of GE-Eu-DPA, (b) Carbon and (c) Eu; (d) the overlay of all the elemental mappings of GE-Tb-DPA, (e) Carbon and (f) Tb. The images indicate the homogeneous dispersion of Eu and Tb on graphene sheets.

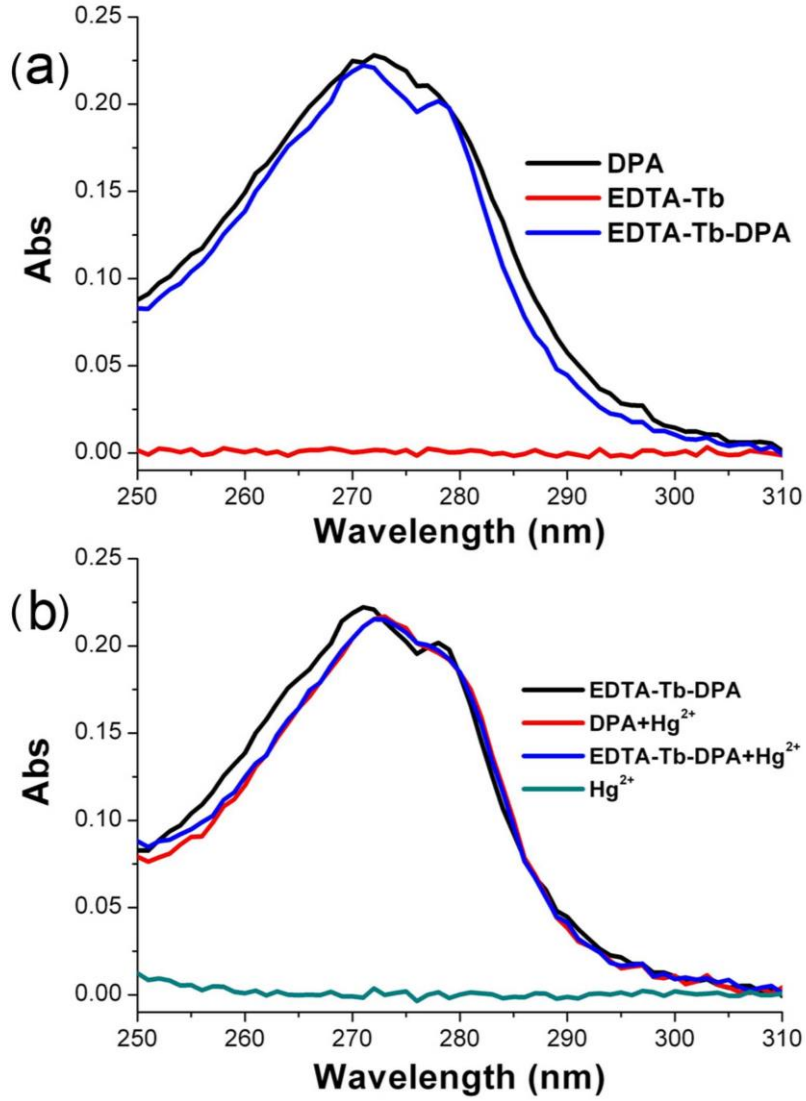

Figure S5. (a) UV/Vis spectra for 2.5 µM DPA (black), 2.5 µM EDTA-Tb (red) and 2.5 µM EDTA-Tb-DPA (blue) in ddH_2O. (b) UV/Vis spectra for 2.5 µM EDTA-Tb-DPA (black), 2.5 µM DPA+ 50 µM Hg^{2+} (red), 2.5 µM EDTA-Tb-DPA+ Hg^{2+} (blue) and 50 µM Hg^{2+} (cyan) in ddH_2O.

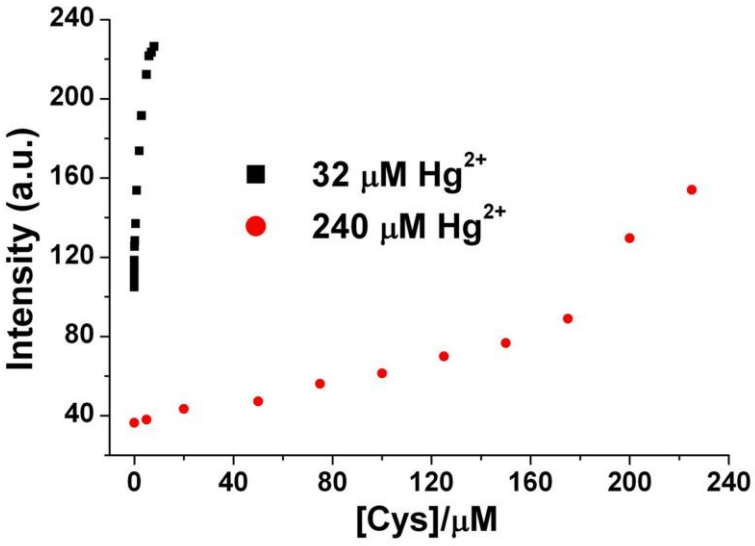

Figure S6. Fluorescence emission intensity (545 nm) of GE-Tb-DPA containing 32 μM or 240 μM Hg^{2+} with increasing amounts of cysteine.