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Supporting Information

Europium Functionalized Black Phosphorus Quantum Dots as a CRET Platform for Synergistic Enhancing Chemiluminescence

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Materials and regents. Ultrapure water was used in all experiments and prepared using a Millipore water purification system (18.2 MΩ·cm). $EuCl_2$, 2,2,6,6-Tetramethyl-4-piperidine (TEMP), Nitrotetrazolium Blue chloride (NBT) and 5,5-Dimethyl-1-pyrrolineN-oxide (DMPO) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). N-Methylpyrrolidone (NMP), thiourea and ascorbic acid (AA) were obtained from Chengdu chemical regent Co. Ltd. Diethylamine, tertiary butylamine, butylamine, tripropylamine, dipropylamine, formamide, diisopropylamine, trimethylamine, N-propylamine, and all of metal salts were obtained from Chengdu Kelong Chemical Reagent Company, Ltd. All the other reagents were obtained from Chengdu United Institute of Chemical & Reagentat and at least of analytical grade.

Methods. The fluorescence spectra of materials were characterized on a fluorescence spectrophotometer (F-7000, Hitachi Co, Tokyo, Japan). The UV-Vis absorbance spectra of QDs solution were measured by a U-2910 UV-Vis spectrometer. Raman spectrum was obtained from a Lab Ram HR800 Raman spectroscopy (Horiba Jobin Yvon Inc. France, laser excitation wavelength is 633 nm). Transmission electron microscopy (TEM) images and high-resolution TEM images were characterized by JEM-2010 microscope (JEOL Co., Japan) operating at an accelerating voltage of 200 kV. The elemental composition of the materials were studied by EDS of Scanning electron microscope (SEM, S3400, Hitachi). A Philips X'Pert Pro X-ray diffractometer (ESCA Lab 250Xi, Thermo Scientific, USA) were employed to investigate the chemical composition and functional groups of materilas. The Fourier Transform Infrared (FTIR) spectrum was used to characterized the surface functional group of obtained products by a Thermo Nicolet IS10 FT-IR Spectrometer with the range of 400-4000cm^{-1}.

Preparation of bulk BP. Bulk BP crystals were obtained by a short way transport reaction according to the previous report.[1] In detail, 20mg Sn, 10mg SnI_4 and 500mg red phosphorus were sealed in a silica glass ampoule of 10 cm length, an inner diameter of 1.0cm and a wall thickness of 0.25cm. Then, The tube was heated at 923K for 5h, and then the temperature was reduced to 773K at the rate of 0.33K/min, followed with cooling down to room temperature naturally, the bulk BP was collected after washing with hot toluene and acetone for several times and dried under vacuum for further use.

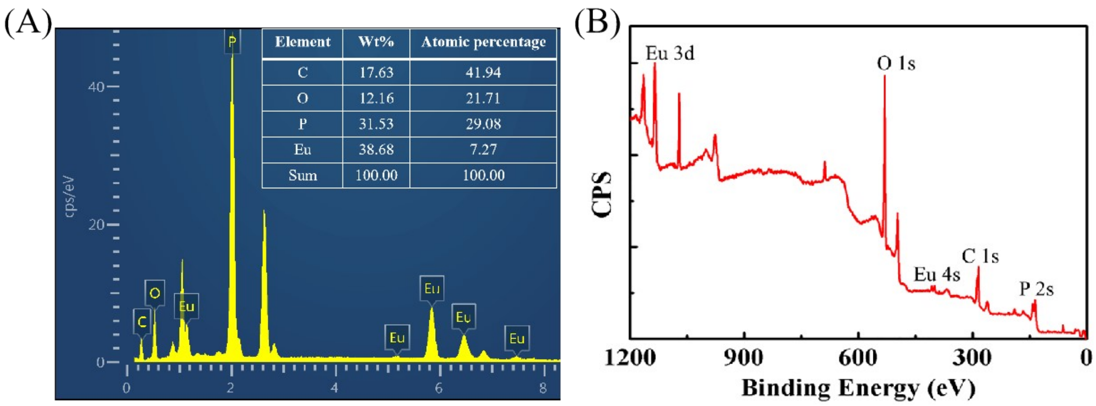
Preparation of Eu-BPQDs. At present, ultrasonic stripping of bulk BP is the most commonly used technique for preparing BPQDs. However, the processing time of this method is long, usually takes several hours or even more than ten hours, and some structural defects are introduced in the synthesis process. In recent years, researchers reported that BPQDs solution can be prepared by solvothermal method, grinding method, blending method and electrochemical stripping method. However, there are still some disadvantages such as time-consuming, expensive and complex operation. Therefore, to find a fast, efficient and convenient synthesis method is still an urgent need. In this work, we synthesized Eu-BPQDs and BPQDs by microwave irradiation method. Compared with other synthesis methods, microwave-assisted method has the advantages of high speed, high efficiency and environmental protection.

Typically, 2mL NMP reagent and 10mg BP were ground in mortar for 1 hour to obtain uniform black phosphorus powder. Transfer the mixture to a 150 ml round bottom flask, added 100 mL NMP reagent and 100 mg sodium hydroxide, and the resulting mixture was heated using a commercial microwave system. Specific experimental parameters: Heating time is 1 hour, heating temperature is 140 °C, microwave frequency is 375W. After the solution was naturally cooled, the obtained solution was centrifuged for 10 minutes at the speed of 8000rpm. The supernatant was taken as the stable dispersion of BPQDs in NMP. In order to further separate solvent and quantum dots, the solution was rotationally evaporated under vacuum heating. After removing most of the solvent, ethanol was added into the solution for high speed centrifugation. The above steps are repeated to wash away small molecules of organic solvent adhered to the surface, and finally the obtained solid is subjected to vacuum drying overnight. In order to obtain europium modified BPQDs, the obtained solid was redissolved in ethanol, the excess of anhydrous europium chloride was added, and then the mixture was stirred for twelve hours. The Eu-BPQDs was obtained by high speed centrifugation and dried in vacuum and stored in vacuum condition for later use. The synthesis of unmodified BPQDs is identical to the above steps except that there is no subsequent europium modification.

The physical mixture of europium ion and unmodified BP QD sample was obtained by ultrasonic treatment of the mixture of $EuCl_2$ and unmodified BPQDs for 2 min.

Chemiluminescence Measurements. All CL signals were obtained by static injection CL detection with a Ultra Weak Luminescence Analyzer (BPCL-2-TGE, Beijing, China). Typically, 800 μL of Eu-BPQD solutions or control solutions (including $EuCl_2$, unmodified BPQDs and the physical mixture of $EuCl_2$ and unmodified BPQDs) were placed in a CL quartz vial near the PMT, and the CL emission reaction was rapidly initiated when 200 μL of ethylenediamine solution was automatically injected. The CL emission of the mixture of Eu-BPQD and common organic amine are also studied, including diethylamine, tertiary butylamine, butylamine, tripropylamine, dipropylamine, formamide, diisopropylamine, trimethylamine and N-propylamine. The reaction conditions were as follows: the concentrations of organic amine, unmodified BPQDs, and Eu-BPQD were 10 mM, 10 μg/mL, and 10 μg/mL, respectively. The CL emission was detected by the voltage of the PMT (0.8 kV) with an interval of 0.1 s for data acquisition, and data was collected and converted to the computer for subsequent acquisition.

CL spectrum of Eu-BPQD/$K_2S_2O_8$ systems: The CL spectrum of Eu-BPQD/ ethylenediamine (EN) systems were obtained by the BPCL luminescence analyzer with optical filters (400−640 nm), which were placed between the quartz vial and the detector.



Element	Wt%	Atomic percentage
C	17.63	41.94
O	12.16	21.71
P	31.53	29.08
Eu	38.68	7.27
Sum	100.00	100.00

Figure 1s. (A) The energy-dispersive X-ray spectroscopy (EDS) spectrum and (B) the XPS survey scan spectrum from the Eu-BPQDs.

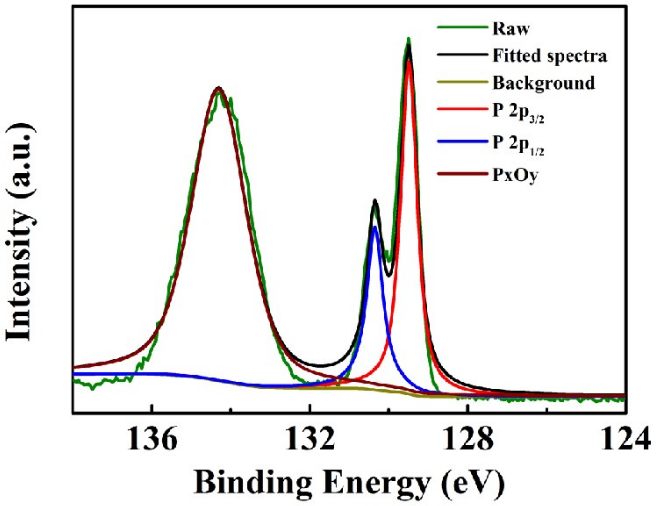


Figure 2s. The fitting analysis of the P 2p peaks of XPS spectra from BPQDs. The binding energies located at 129.5 and 130.4 eV correspond to the 2p3/2 and 2p1/2 orbitals of zerovalent phosphorus (P^0), respectively, which also proved the formation of BP crystalline BP. A obvious peaks emerged at 134.3 eV revealing the presence of P^{5+}, indicating unavoidable oxidizing of BP during the sample preparation. They were all observed in the P 2p XPS spectrum of the Eu-BPQDs.

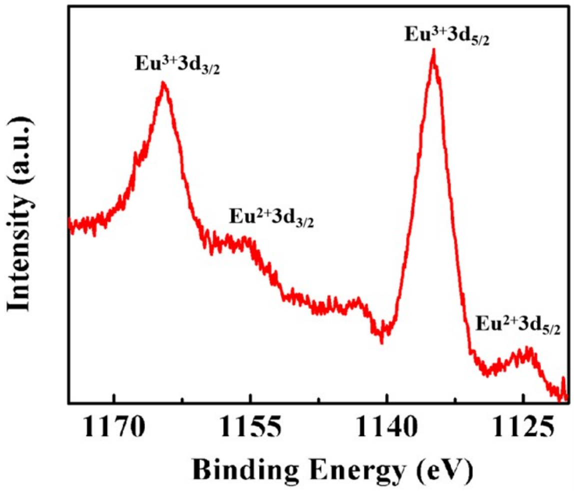


Figure 3s. The fitting analysis of the Eu 3d peaks of XPS spectra from Eu-BPQDs. Two intense peaks at 1165.5 eV, 1155.2 eV, 1135.4 eV and 1124.1 eV in the Eu 3d spectrum are assigned to the spin-orbit splitting of the 3d state into $3d_{5/2}$ and $3d_{3/2}$ of both Eu(III) and Eu(II), which demonstrated that the oxidation state of Eu within Eu-BPQDs is a mixture of Eu(II)/Eu(III) oxidation states.

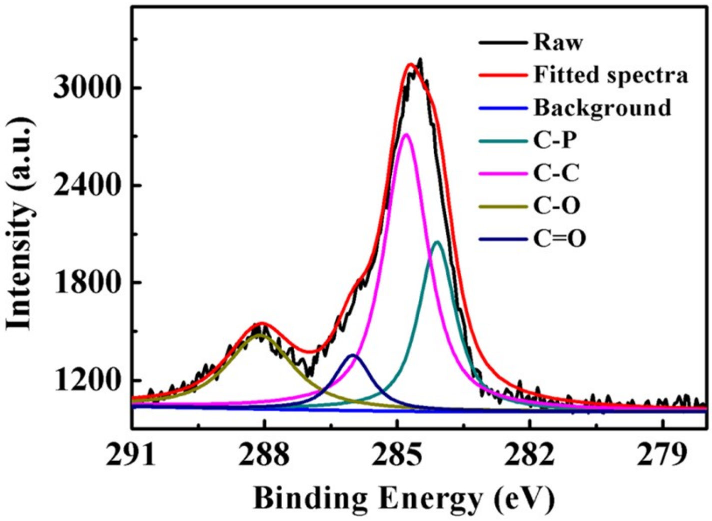


Figure 4s. The fitting analysis of the C1s peaks of XPS spectra from Eu-BPQDs. Four obvious peaks emerged at 284.0 eV, 284.8 eV, 286.4 eV and 288.8 eV assigning to C-P, C-C, C-O and C=O bonding. The result suggested that complex shell composed with functional groups possibly were formed on the surface of Eu-BPQDs, and which could improved the stability of Eu-BPQDs and further used in aqueous solution.

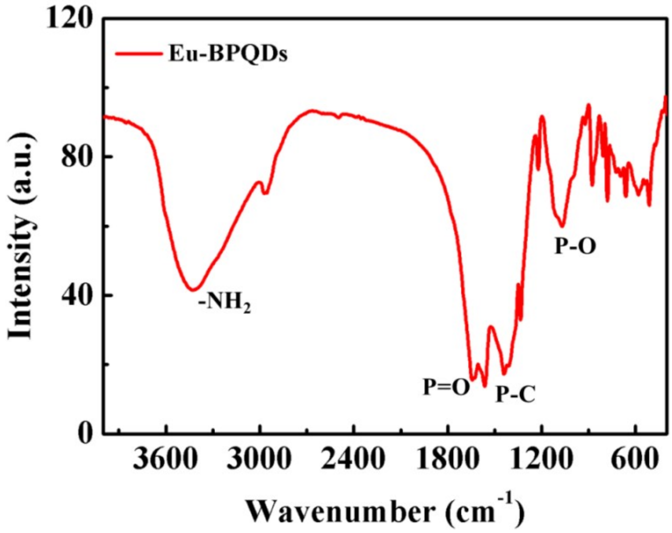


Figure 5s. Fourier transform infrared spectra of Eu-BPQDs. The broad absorption bands centered at ~3386 cm^{-1}, ~1620 cm^{-1}, ~1570 cm^{-1} and ~1200 cm^{-1} can be ascribed to the -NH$_2$, P=O, P-C and P-O stretching modes. The FTIR results further demonstrate that some functional groups were formed on the surface of Eu-BPQDs, which is are beneficial for the stability of Eu-BPQDs and further used in aqueous solution.

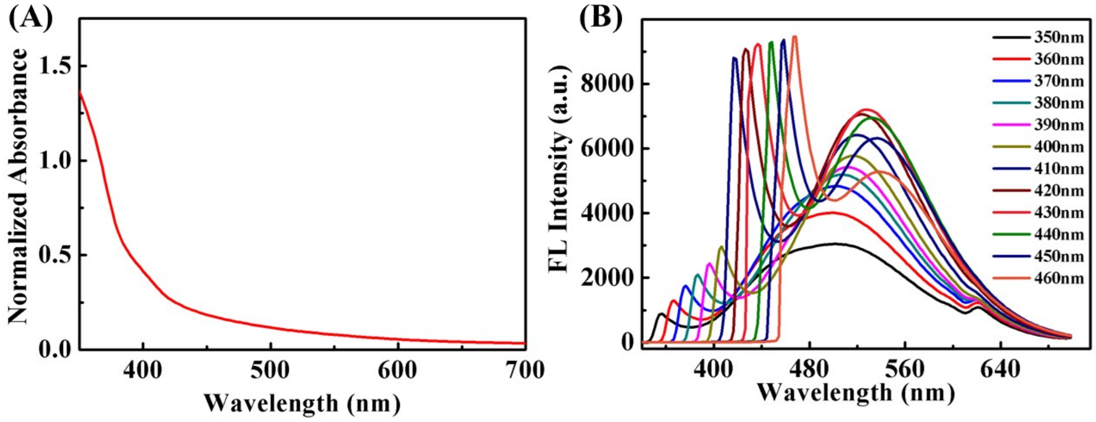


Figure 6s. (A) UV–vis spectrum and (B) Fluorescence spectra of Eu-BPQDs under different excitation wavelength (Legend: the concentration of Eu-BPQDs solution is 5 mg/mL).

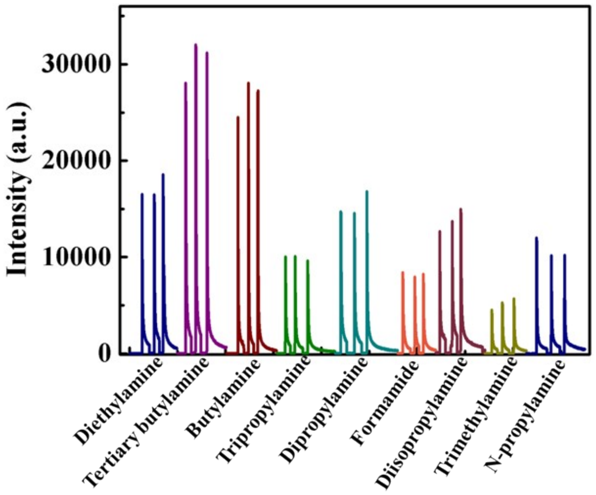


Figure 7s. The chemiluminescence curve were obtained from Eu-BPQDs and some common organic amine (including: diethylamine, tertiary butylamine, butylamine, tripropylamine, dipropylamine, formamide, diisopropylamine, trimethylamine and N-propylamine).

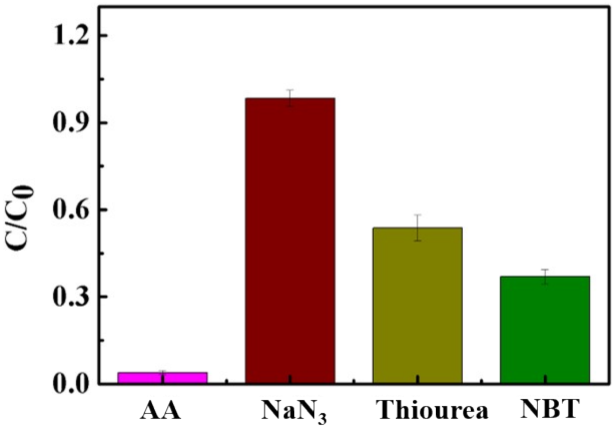


Figure 8S. Effects of different active oxygen radical scavengers on the CL intensity of Eu-BPQDs/ethylenediamine solution.

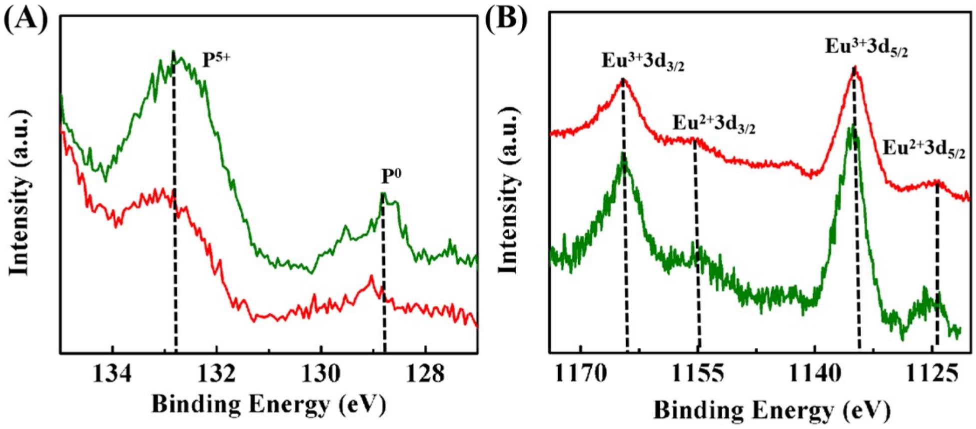


Figure 9S. (A) The P 2p XPS spectra and (C) Eu 3d XPS spectra of Eu-BPQDs: (red curve) before reaction with ethylenediamine and (green curve) after reaction with ethylenediamine.

References

1. M. Köpf, N. Eckstein, D. Pfister, C. Grotz, I. Krüger, M. Greiwe, T. Hansen, H. Kohlmann, T. Nilges, J. Cryst. Growth., 2014, 405, 6-10.