

## Supporting Information

### **Engineer the Energy Gap of Black Phosphorene Quantum Dots by Surface Modification for Efficient Chemiluminescence**

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**Chemicals and Reagents.** All chemicals reagents were used at least of analytical grade and without further purification treatment. N-methylpyrrolidone (NMP), ethylenediamine (EN), Sn and I<sub>2</sub> were obtained from Kelong Reagent Company (Chengdu, China). Sodium azide (NaN<sub>3</sub>), Dimethyl-1-pyrrolineN-oxide (DMPO) and 2,2,6,6-Tetramethyl-4-piperidine (TEMP) were bought from Sigma-Aldrich Chemical Company (St. Louis, MO, USA). Thiourea, Nitro blue tetrazolium chloride (NBT), ascorbic acid (AA) and methanol were purchased from Huatao Chemical Reagent Company (Chengdu, China). Other reagents obtained from equipment office in Sichuan University. All solution was prepared using deionized water (18.2 MΩ/cm), which was treated with a Mili-Q ultrapure system.

**Preparation of bulk BP.** The bulk BP crystal were prepared through reported method of a short way transport reaction. Typically, put Sn (20 mg), SnI<sub>4</sub> (10 mg) and red phosphorus (500 mg) in a quartz tube and sealed quartz tube in a vacuum condition. The parameters of the silica glass ampoule: length of 8-10 cm, an inner diameter of 1.0 cm and a wall thickness of 0.25 cm. Then, the tube was heated by a set-up warming step: 923K for 5h, the temperature was reduced to 773 K at the rate of 0.33 K/min, cooling down to room temperature for 8h. Finally, the Bulk BP was purified by washing with hot toluene and acetone for several times. Dried under vacuum and collected it.

**Preparation of NH<sub>2</sub>-functionalized black phosphorene quantum dots (N-BPQDs).** N-BP QDs were fabricated using an ultrasound exfoliation technique combined with solvothermal treatment. In a typical process, 20 mg of the bulk BP crystals and 2 mL NMP were first ground together for 30 min. Then the obtained mixture, 50mL NMP, and 50mg NaOH were added into a bottle and bubbled with nitrogen for another 30 min to avoid the oxidation. After the bottle was sealed

carefully, the BP solution was sonicated in an ice-bath for 10 h at the power of 500 W. The result mixture was centrifuged at 8000 rpm for 10 min to remove any non-exfoliated bulk BP and simultaneously collect the upper suspension with BP QDs. In order to separated BP QDs and NMP solvent, the supernatant was further treated by high speed centrifugation (15000 rpm for 20 min) and rotary evaporation. The precipitates were redispersed in 50mL ethylenediamine and transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (100 mL), the solution was heated at 80 °C for 2 h. The resulting mixture was cooled down to ambient temperature naturally. The N-BPQDs was included in light yellow ethylenediamine transparent liquid. To obtain N-BPQDs aqueous solution, ethylenediamine was removed via rotary evaporation method at 40 °C. Finally, the acquired products were dried and kept in vacuum for further use. And when being used, the resulted product was dissolved into deionized water to form a solution containing N-BP QDs for later experiments.

**Instruments.** The UV-vis absorption patterns were obtained by U-2910 spectrometer (Hitachi Co., Tokyo, Japan). Fluorescence spectra were detected on an F-7000 fluorescence spectrophotometer (Hitachi, Japan). The nanoparticle size and morphology were characterized by a transmission electron microscope (TEM, HRTEM, JEOL, Japan). The chemical structure of product was analyzed with a Raman spectrometer (Lab RAM HR, Ram HR800, laser excitation wavelength 785 nm) and an IS10 FT-IR Spectrometer (Thermo Inc., America). X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface composition of the samples with an X-ray photoelectron spectrometer (Thermo Scientific, USA) using monochromatic Al K $\alpha$  radiation (1361 eV). Electron paramagnetic resonance (EPR) spectra were measured on a Bruker E-500 instrument (microwave power 12.72 mW, microwave frequency 9.77 GHz, modulation frequency 100 kHz, and sweep width 3480 G). Fluorescence lifetime was measured on a Fluorolog-3spectrofluorometer (Horiba JobinYvon) with a Delta Diode (406 nm, DD-405L) as the excitation source and a picosecond photon detection module (PPD-850) as the detector.

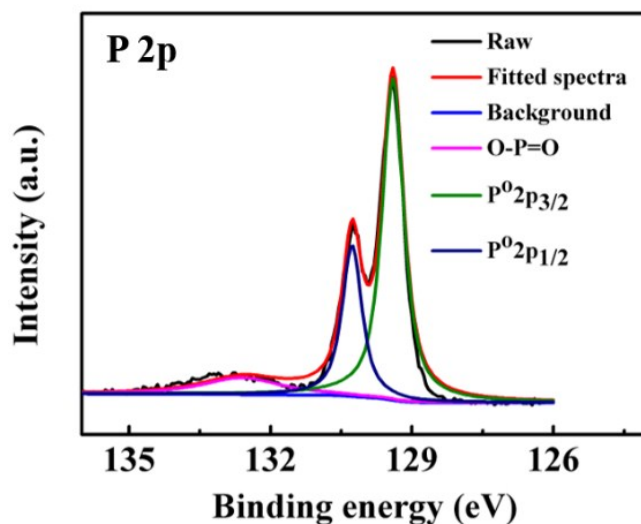
**Chemiluminescence analysis.** All CL measurements were performed on a BPCL luminescence analyzer (BPCL-2-TGC, Beijing, China) with static injection method. Photomultiplier tube (PMT Hamamatsu, Japan) was used to record CL signal, and data was collected and converted to the computer for subsequent acquisition. CL spectrum was collected by the BPCL luminescence analyzer with optical filters (400–640 nm), which were placed between the quartz vial and the detector.

In details, 800  $\mu$ L of N-BP QDs or control solutions (including EN and unmodified BP QDs) was placed in a CL quartz vial near the PMT, and the CL emission reaction was rapidly initiated when 200  $\mu$ L of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution was automatically injected. The CL curve was detected by the voltage of the PMT (0.8 kV) with an interval of 0.1 s for data acquisition.

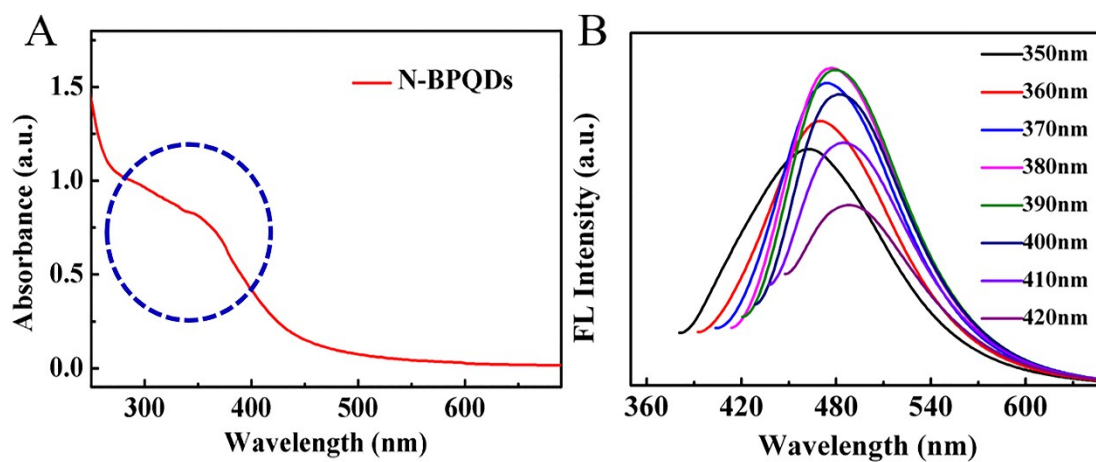
**CL spectrum of N-BP QD/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems:** The CL spectrum of N-BP QD/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems were obtained by the BPCL luminescence analyzer with optical filters (400–640 nm), which were placed between the quartz vial and the detector.

**Figure 1s.** High resolution XPS spectrum P2p peaks from the BPQDs. Two peaks located at 129.4 eV and 130.2 eV in the

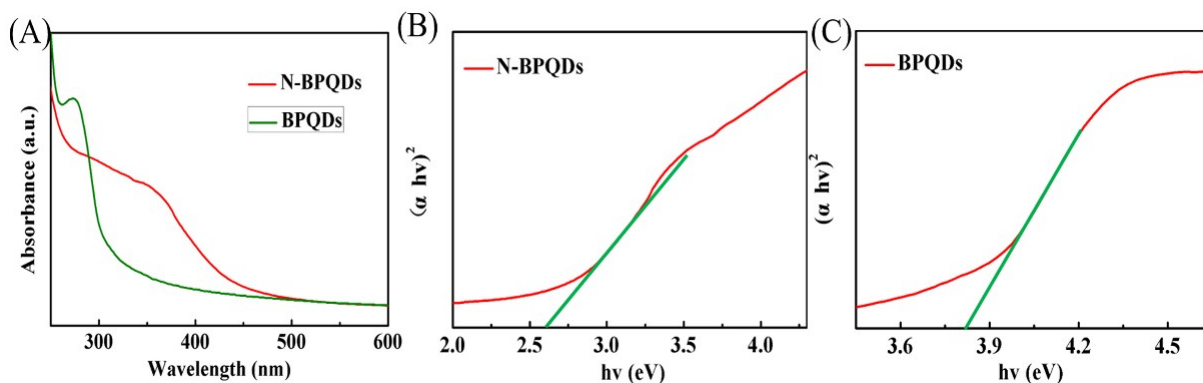
P2p spectrum originating from 2p<sub>3/2</sub> and 2p<sub>1/2</sub> orbitals of zero-valent phosphorous (P<sup>0</sup>). It is a symbol of BP crystal. The binding energy at 132.6 eV ascribed to O-P=O band, which implied that BP QDs were partially oxidized in the process of synthesis.



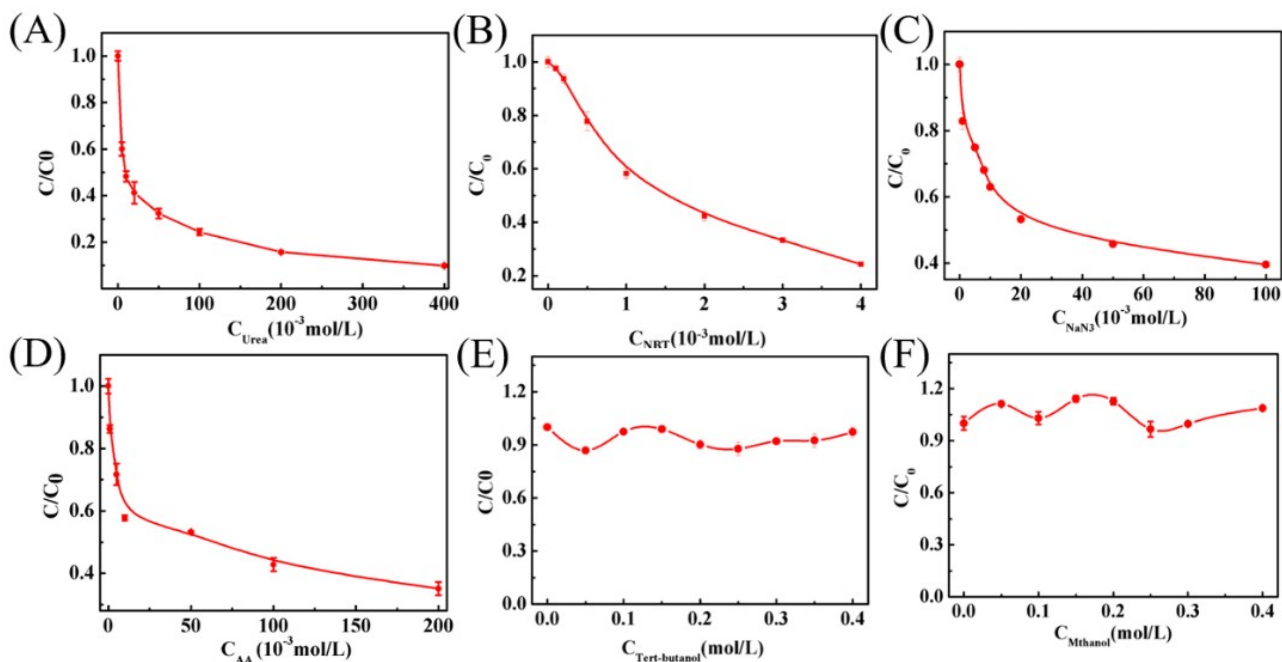
**Figure 2s.** (A) UV-vis spectrum and (B) fluorescence spectra of N-BPQDs under different excitation wavelength. (legend: the concentration of N-BPQDs solution is 5 mg/mL)



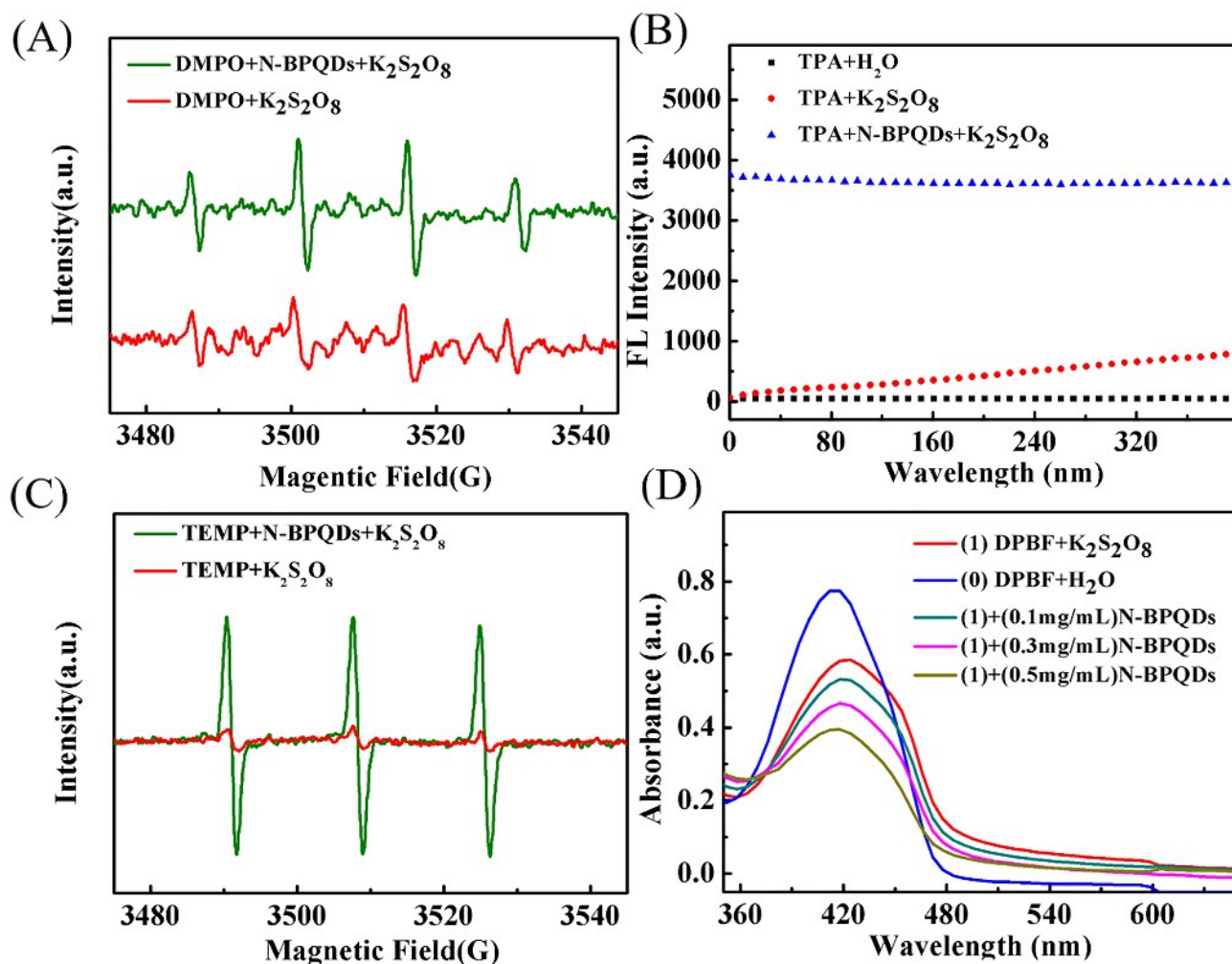
**Figure 3s.** The UV–vis spectra of N-BPQDs and BPQDs (A). Band gap value of BPQDs (B) and N-BPQDs (C).



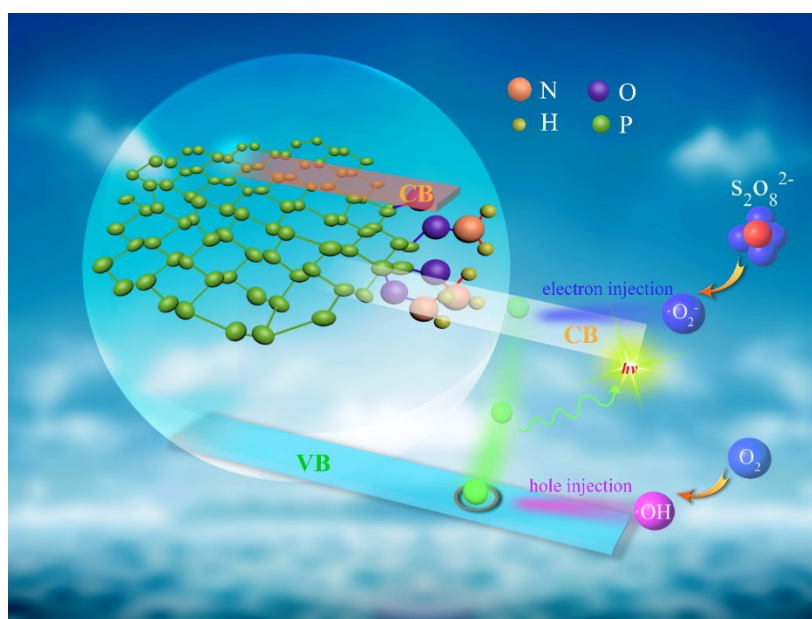
**Figure 4s.** Effects of different trap agents for reactive oxygen species (ROS) on the CL intensity of N-BPQDs/ $K_2S_2O_8$  system. (Legend: the CL intensity was recorded according to the same procedure in static injection CL analysis, except radical scavengers with different concentrations was mixed with N-BPQDs/ $K_2S_2O_8$  mixture solutions. The CL inhibition was calculated as  $C/C_0$  showed the effects of radical scavengers on the CL of N-BPQDs/ $K_2S_2O_8$  system, where  $C_0$  and  $C$  were the CL intensities without and with radical scavengers, respectively.)



**Figure 5s.** Fig. 3 (A and C) ESR spectra and fluorescence kinetic study on  $\cdot\text{OH}$  generation in the N-BP QDs/ $\text{K}_2\text{S}_2\text{O}_8$  CL system. (B) ESR spectra of  $^1\text{O}_2$  generated in the N-BPQDs/ $\text{K}_2\text{S}_2\text{O}_8$  CL system. (D) UV absorption spectra of DPBF in the N-BPQDs/ $\text{K}_2\text{S}_2\text{O}_8$  CL system,  $\text{K}_2\text{S}_2\text{O}_8$  solution and the mixture of different concentration of N-BPQDs with  $\text{K}_2\text{S}_2\text{O}_8$  solution. Conditions: DMPO 0.01 mol/L, TEMP 0.01 mol/L, TPA 5 mmol/L, DPBF 0.2 mg/mL,  $\text{K}_2\text{S}_2\text{O}_8$  10mmol/L.



**Figure 6s.** Schematic illustration of the CL mechanism in the N-BPQD/ $K_2S_2O_8$  system



**Figure 7s.** Effects of (A) pH on the CL system. (B) The FL spectra of N-BPQDs in pH 2 and pH 7 condition. (C) The effects of (C)  $K_2S_2O_8$  concentration and (D) N-BPQDs concentration on the CL system.

