Supporting Information

Chemiluminescence of black phosphorus quantum dots induced by hypochlorite and peroxide

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Materials and regents. SnI_4 was synthesized by refluxing Sn and I_2 in a mixed solution of glacial acetic acid and acetic anhydride. H_2O_2 and NaClO was purchased from Chengdu chemical regent Co. Ltd. 2,2,6,6-Tetramethyl-4-piperidine (TEMP), Nitrotetrazolium Blue chloride (NBT), 5,5-Dimethyl-1-pyrrolineN-oxide (DMPO) and 1,3-Diphenylisobenzofuran (DPBF) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). All of the experimental solutions were prepared using ultrapure water (18.2 MΩ/cm) which was obtained from a Mili-Q ultrapure system and treated with nitrogen for removing oxygen prior to usage. All the other reagents were obtained from Chengdu United Institute of Chemical & Reagent and at least of analytical grade.

Methods. Batch CL experiments were performed with the Ultra Weak Luminescence Analyzer (BPCL-2-TGC, Institute of Biophysics, Chinese Academy of Sciences, Beijing, PRC). Transmission electron microscopy (TEM) images and high-resolution TEM images were

characterized by JEM-2010 microscope (JEOL Co., Japan) operating at anaccelerating voltage of 200 kV. a Philips X'Pert Pro X-ray diffractometer were employed to collect X-ray diffraction (XRD) patterns with Cu Kα radiation (λ=1.5406 Å) over the range of 5° to 90°. Raman spectrum was measured on a Lab Ram HR800 Raman spectroscopy (Horiba Jobin Yvon Inc. France, laser excitation wavelength is 785 nm). The Binding Energy of BP QDs was investigated by the X-ray photoelectron spectrum (XPS) recorded by an ESCA Lab 250Xi (Thermo Scientific, USA). The Fourier Transform Infrared (FTIR) spectrum was performed by Thermo Nicolet IS10 FT-IR Spectrometer with the range of 400-4000 cm^{-1}. All Fluorescence spectra and CL spectra were operated on a fluorescence spectrophotometer (F-7000, Hitachi Co, Tokyo, Japan). The UV-Vis absorbance of BP QDs solution was measured by a U-2910 UV-Vis spectrometer. Zeta sizer Nano ZS (Malvern Co., UK) was used to characterized the surface charge of the products.

Preparation of bulk BP. Bulk BP crystals were obtained by a short way transport reaction according to the reported literature.[1] In detail, 20 mg Sn, 10 mg SnI_4 and 500 mg red phosphorus were sealed in a silica glass ampoule with 8-10 cm length, an inner diameter of 1.0 cm and a wall thickness of 0.25 cm. Then, the tube was heated at 923K for 5h. After that the temperature was reduced to 773 K at the rate of 0.33 K/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.

Preparation of BP QDs. BP QDs are synthesized via a previous method using BP powder and saturated NaOH N-methyl-2-pyrrolidone (NMP) solution. Typically, the per-grounded 10 mg BP powder and 100 mg NaOH were added into 100 ml NMP solvent to get a BP NMP solution. Then the as-obtained solution was heated to reflux for 6 hr at 140℃ under nitrogen atmosphere, and noteworthy, the solution was bubbled with nitrogen for about 30 min to avoid the oxidation before heating. After naturally cooling to room temperature, the upper suspension was collected by centrifugation. After separating BP QDs and NMP solvent by rotary evaporation and centrifugation at high speed (15000 rpm for 20 min), in order to remove NMP that is not attached to BP QDs, the precipitate was redispersed in water and centrifugation at high speed (15000 rpm for 20 min) for several times. Finally, the acquired products were dried and kept in vacuum for further use. And when being used, the resulted product was dissolved into ultrapure water to form a solution

containing BP QDs for later experiments. (Note: all reagents were bubbled with nitrogen for about 30 min to remove oxygen.)

Chemiluminescent measurement. CL kinetic curves were carried out by the static injection CL analysis with a 2 mL CL quartz vial adjacent to the photomultiplier tube (PMT).

For H_2O_2-ClO^- and BP QDs-H_2O_2-ClO^- CL systems, 800 uL H_2O_2 solution or BP QDs-H_2O_2 mixture solution was placed in the quartz vial, then 200 uL ClO^- were quickly injected, followed by the collection of CL signal. For ClO^--BP QDs CL and H_2O_2-BP QDs systems, an 800 uL solution of BP QDs was placed in the quartz vial. When 200 uL of ClO^- or H_2O_2 solution automatically injected, the reaction was rapidly initiated and CL signal was and the CL signal was detected by the PMT and exported to the computer for data acquisition.

Condition: the concentrations of ClO^-, H_2O_2, and BP QDs were 5 mM, 1 mM, and 0.2 mg/mL for all the four CL systems; Voltage of the PMT was set at 0.8 kV; the time interval was set as 0.1 s.

CL measurement for TATP detection. TATP was synthesized by mixing readily available H_2O_2 and acetone (following supplied the detail of synthesis and characterization of TATP). TATP powder was dissolved in acetone to obtain a series of TATP solution with different concentrations (0.1-100 mg/mL). Caution: because of its sensitivity to impact, friction, and temperature changes, TATP has to be handled in small amounts and safely stored in the fridge.

The CL detection of TATP consisted of two parts. Firstly, 200 μL acidic hydrolysis of TATP solution and 800 μL BP QDs solution were premixed in a 2 mL quartz cuvette, and then 200 μL of 5 mM ClO^- were quickly injected, followed by the collection of CL signals with the luminescence analyzer.

Acidic hydrolysis of TATP. 2 mL of 4 M HCl was added into 1 mL TATP solution and the mixture was allowed to stand for 30 min, 2 mL of 4 M NaOH was droped into the above solution in order to neutralize the sample.

The synthesis of TATP. The TATP were prepared via Keinan et al.[2] reported method, 1.36 mL of H_2O_2 (30%) and 1.9 mL of acetone were mixed in a small beaker under ice-bath, followed 0.48 mL of concentrated sulfuric acid was added drop wise with constant stirring and keeping the temperature below 4 ℃ during the entire process. Then the mixture was kept at room temperature and stirred for 24 h. The resulting white precipitate was collected by filtration, thoroughly washed with 25 mL of

the solvent mixture comprised of 30% acetone and 70% water, and vacuum-dried to afford TATP before stored in a refrigerator for further use.

Figure 1s. (A) FTIR and (B) ^{1}H NMR spectra of TATP (The inset is photograph of the TATP). The characteristic band around 1175 cm^{-1} is attributed to the C-O in FTIR spectrum. An intense peak at 1.46 ppm was observed in figure 1s B, this chemical shift is very close to 1.41 ppm estimated theoretically using ChemBiodraw Ultra 11 (CambridgeSoft Corp., Cambridge, MA), all the results indicated the successful synthesis of TATP.

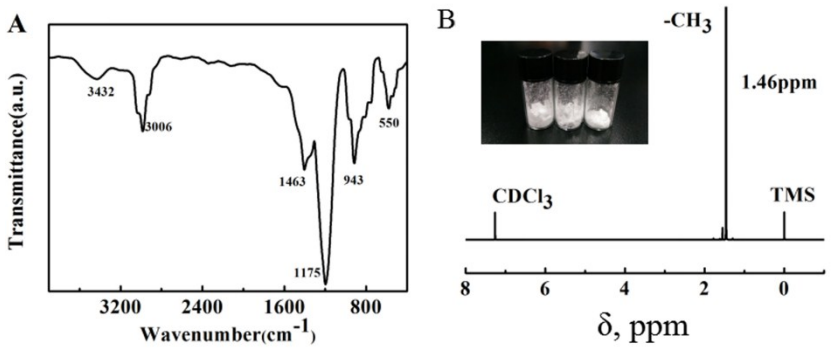


Figure 2s. High resolution XPS spectrum (A) P2p peaks from the bulk BP, (B) P^{0}2p peaks, (C) P^{V}2p peaks (D) C1s peaks from BP QDs and (E) C1s peaks from the isolated NMP. From figure 2s A-B, two intense peaks at 129.3 eV and 130.2 eV in the P2p spectrum are assigned to 2p3/2 and 2p1/2 orbitals of zero-valent phosphorous (P^{0}), which is a symbol of BP. In figure 2s C, the binding energy at 131.4,132.2, 133.8 and 132.8 eV are identified as C-P and O-P=O band, the existence of 132.8 eV implied that BP QDs were partially oxidized in the process of synthesis. In figure 2s-D, four peaks at 284.0 eV, 284.6 eV, 286.1 eV, and 287.9 eV can be assigned to C-P, C-C, C-N, C=O band, respectively, compared with C1s HR XPS isolated NMP (figure 2s-E), the formation of new band C-P (at 284eV) and characteristic band from NMP clearly demonstrated the functionalization of BP QDs with NMP.

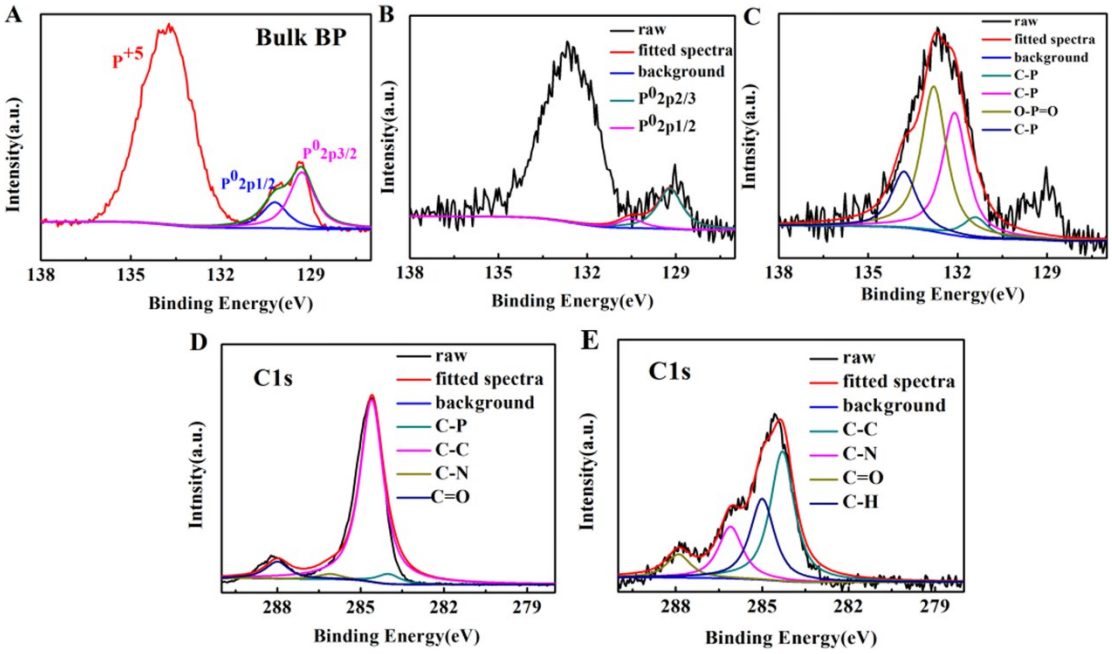


Figure 3s. FT-IR spectra of BP QDs, isolate NMP and bulk BP. Compared with FT-IR spectra of isolate NMP and bulk BP, functional groups of NMP are found in that of BP QDs and a new P-O-C bond (at 1576 cm^{-1}) was formed, which indicates the oxidation from BP QDs and the interaction between NMP and BP QDs.

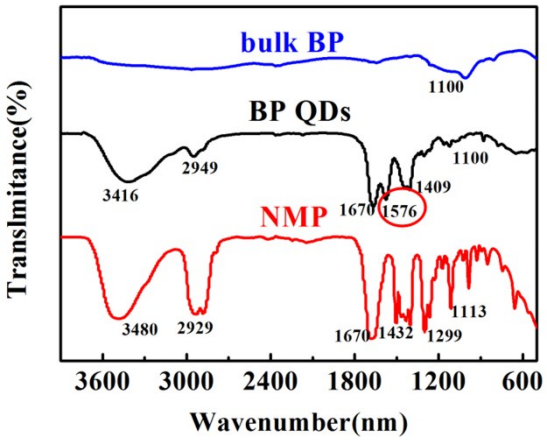


Figure 4s. (A) UV–vis spectrum and (B) fluorescence spectra of BP QDs. (legend: the concentration of BP QDs solution is 0.2 mg/mL and the dispersant is ultrapure water which bubbled with nitrogen for about 30 min to remove oxygen)

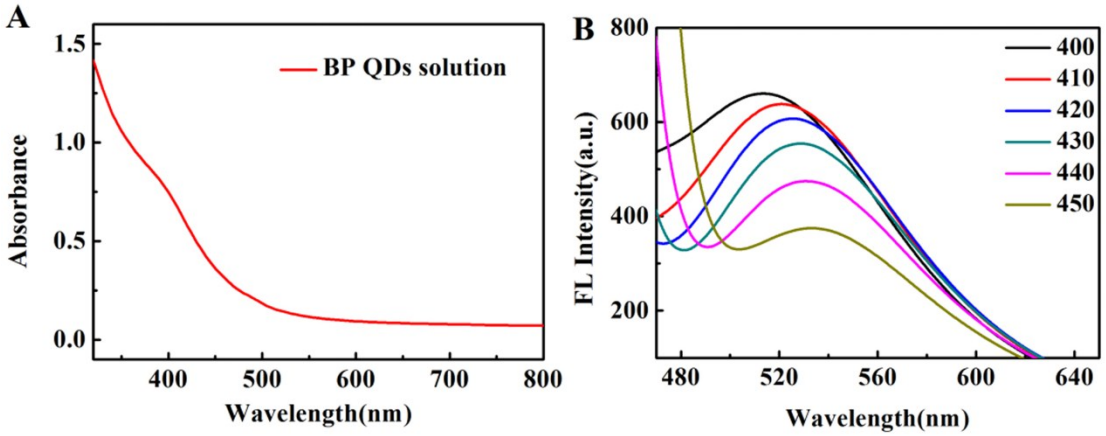


Figure 5s. Effects of different trap agents for reactive oxygen species (ROS) on the CL intensity of BP QDs-H_2O_2-ClO^- system. (Legend: the CL signals were monitored according to the same procedure in static injection CL analysis, except radical scavengers with different concentrations was mixed with BP QDs-H_2O_2-ClO^- mixture solutions. The CL inhibition was calculated as C/C_0 showed the effects of radical scavengers on the CL of BP QDs-H_2O_2-ClO^- system, where C_0 and C were the CL intensities without and with radical scavengers, respectively. Condition: ClO^- 5 mM, H_2O_2 1 mM, BP QDs 0.2 mg/mL, NaN_3 0.5 mM AA 0.5 mM, thiourea 1 mM and NBT 1 mM.)

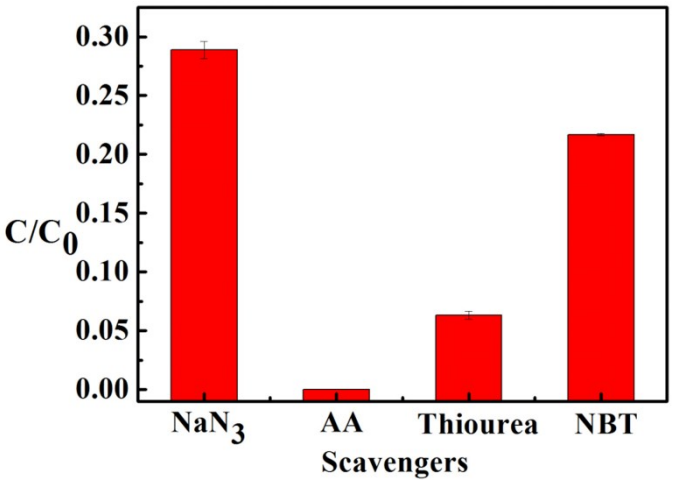


Figure 6s. Time-dependent absorption spectra of the DPBF in BP QDs-H_2O_2-ClO^- system. (legend: 800uL of ethanol solution with DPBF (20 ug/mL) and different concentration BP QDs solution (200 uL) were stirred in the dark for 100 min, then H_2O_2 (0.1mmol/L, 200uL) and ClO^-(1mmol/L, 200 uL) were added into above mixture, the obtained samples were tested by a UV/vis spectrometer.)

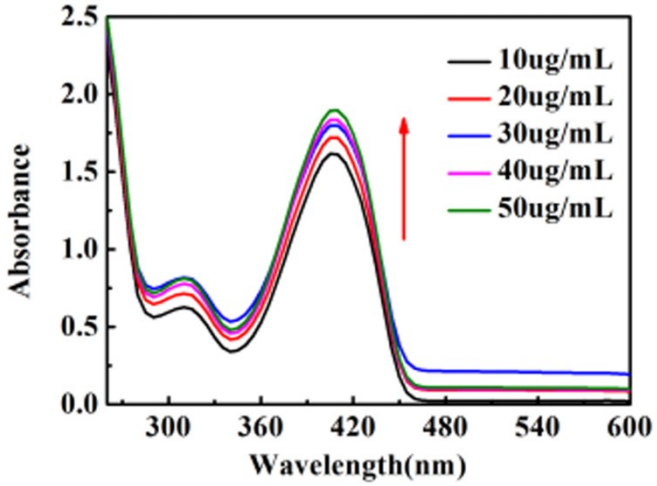


Figure 7s. The XPS spectra (A-B), and zeta potentials (C-D) of BP QDs before and after CL reaction.

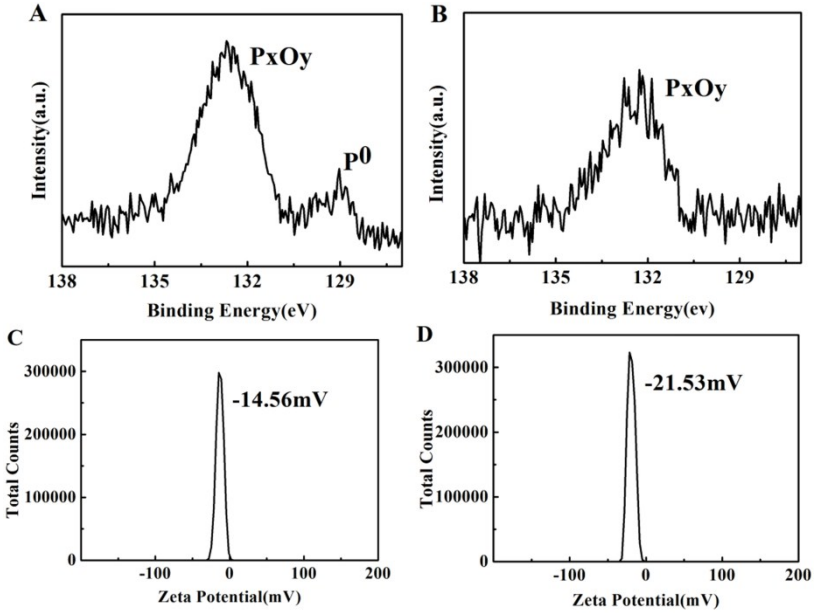


Fig 8s. Schematic illustration of CL mechanism in the BP QDs-H_2O_2-ClO^- system.

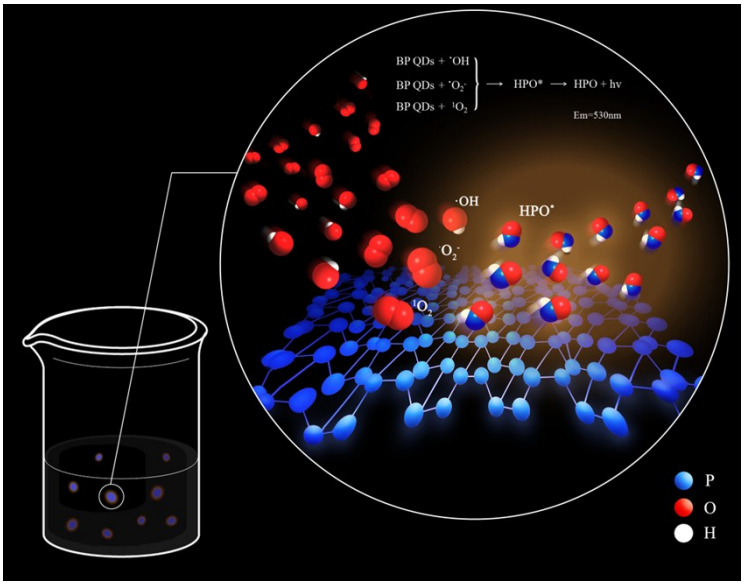


Figure 9s. (A-C) Effects of pH, ClO^- concentration and BP QDs concentration on the CL detection system; (D) Effect of acidic hydrolysis time of TATP on CL intensity. (legend: (A) the concentration of H_2O_2, ClO^- and BP QDs were 10 umol/L, 5 mmol/L and 0.1 mg/L; (B) the concentration of H_2O_2 and ClO^- were 5 umol/L and 5 mmol/L; (C) the concentration of H_2O_2 and BP QDs were 5 umol/L and 0.1 mg/L; (D) the concentration of ClO^-, BP QDs and TATP were 5 mmol/L, 0.2 mg/L and 50 mg/L).

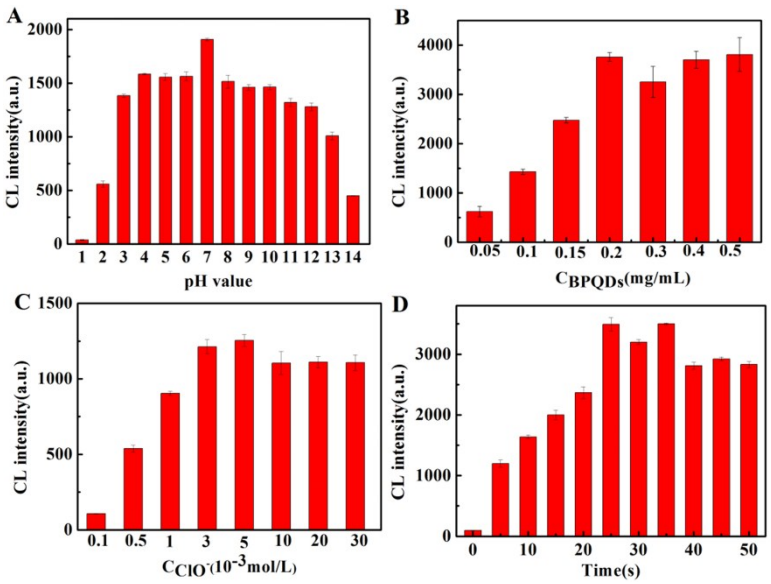
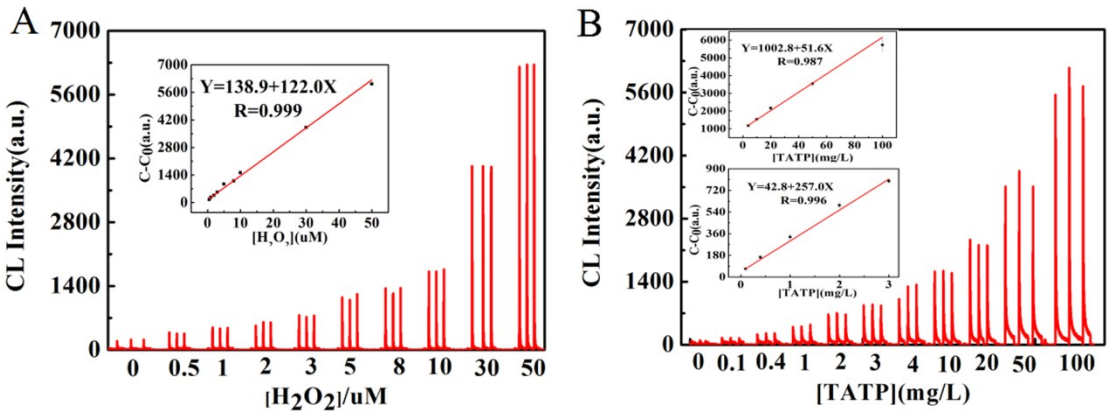


Figure 10s. Linear relationship between CL intensities with different concentration (A) H_2O_2 (B) TATP.



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.
2. R. K. Faina Dubnikova, A. Joseph, Z. Yehuda, B. Roland, I. Harel, A. Aaron, and K. Ehud., *J. Am. Chem. Soc.,* 2005**, 127**, 1146-1159.