Electronic Supplementary Information *for*

A Simple and Efficient Phosphorescent Probe for Iodide-Specific Detection Based on Crystallization-Induced Phosphorescence of Organic Ionic Crystals†

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1. Experimental Details.

Materials and Reagents. Triple-distilled water was utilized throughout the whole experimental process. Tetraphenylphosphonium chloride (TPP Cl), tetraphenylphosphonium bromide (TPP Br), tetraphenylphosphonium iodide (TPP I), methyltriphenylphosphonium chloride (MTPP Cl), methyltriphenylphosphonium bromide (MTPP Br), tetraphenylphosphonium iodide (MTPP I), and silver fluoride (AgF) were purchased from Sigma-Aldrich Company (Shanghai, China). All sodium salts and human serum were bought from J&K Scientific Company (Shanghai, China). Human serum samples were acquired from Jinhua Central Hospital. HEPES solution (10 mM, pH 7.4) was used as the buffer solution. All reagents were of analytical grade and all phenylphosphonium halides were recrystallized for further use.

Characterization of Solid-State Photoluminescence of All Samples. Steady PL spectra of all samples were performed on an Edinburgh Instruments model FLS980 fluorescence spectrophotometer equipped with a xenon arc lamp using a front face sample holder. Time-resolved measurement for fluorescence was conducted with EPL-series lasers, and long-lived measurement for phosphorescence was carried out with a μF2 microsecond flashlamp. Time-delayed PL spectra were recorded using a μF2 microsecond flashlamp and a time-gated module.

Synthesis of Tetraphenylphosphonium Fluoride (TPP F). Tetraphenylphosphonium chloride (1.13g, 3.0 mmol) and silver fluoride (0.38 g, 3.0 mmol) were added into a fixed amount of water (50 mL), and the resulting mixture was fully stirred for 1 h. White AgCl precipitate was generated during the stirring, and then removed by filtration. The filtrate was condensed to produce massive white precipitates, and the resulting precipitates (TPP F) were dried and further recrystallized in ethanol. M.P. 96−98 °C. ^{1}H NMR (600 MHz, CD_3CN) δ (ppm) 7.68(m, 8H), 7.75(m, 8H), 7.92(m, 4H). ^{13}C NMR (150 MHz, CD_3CN) δ (ppm) 136.4 (J = 0.02), 135.7 (J = 0.06), 131.40 (J = 0.09). ^{19}F NMR (565 MHz, CD_3CN) δ (ppm) -153.9. ^{31}P NMR (243 MHz, CD_3CN) δ (ppm) 21.7.

Quantitative Detection of Iodide ion Based on Tetraphenylphosphonium Chloride (TPP Cl). A TPP Cl solution with a fixed concentration (0.1 M) in HEPES buffer (pH 7.4) was first prepared, and then different amounts of iodide ions in the range of 0.0 – 700.0 μM were separately added into the preceding TPP Cl solution. The PL spectra of the resulting mixture were recorded at the excitation of 380 nm using a xenon arc lamp. Selectivity test of the assay to iodide ion was conducted as follows. A certain amount of each chosen anion (500.0 μM) such as NO_3^-, PO_4^{3-}, CO_3^{2-}, $CH_3CO_2^-$, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, S^{2-}, ClO_3^-, IO_3^-, F^-, Cl^-, Br^- and I^- was separately added into a TPP Cl solution (0.1 M) in HEPES buffer, and then the resulting solution was monitored using fluorescence spectrometer at 430 nm emission. To evaluate the possible interference from other anions to iodide detection, an equivalent amount of each anion was first mixed the iodide ion, and then the resulting mixture was added into a TPP Cl solution (0.1 M). The PL intensities of the mixtures were recorded at 430 nm emission. For the time-gated detection of iodide ion, the protocol is same to the normal detection of iodide ion with the replacement of a xenon arc lamp with a μF2 microsecond flashlamp, and a delay time of 10.0 μs was used to acquire the PL spectra. A fixed amount of human serum (9.0 μL) in 3.0 mL of TPP Cl buffer solution was used as a complex matrix with a significant autofluorescence. All the detections were repeated at least three times.

Test Strips for Iodide ion Detection Based on Solid-Substrate Room-Temperature Phosphorescence. Fifty strips made from filter papers were first immersed in a concentrated TPP Cl solution (0.2 M) for 1 min, and then dried at room temperature to acquire test strips. A series of varying amounts of iodide ions in the range of 0.0 – 38.1 μg were separately dropped on the test strips, and the PL spectra of the resulting test strips were recorded at 370 nm excitation light and photographed under a UV lamp after they were dried. The selectivity test was run according to the preceding procedure by adding different anions including NO_3^-, PO_4^{3-}, CO_3^{2-}, $CH_3CO_2^-$, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, S^{2-}, ClO_3^-, IO_3^-, F^-, Cl^-, Br^- and I^-. The concentration for each of them is 38.1 μg.

Viability Test and Confocal Microscopy Imaging of Iodide Ion in Live Cells. A standard MTT assay was used to evaluate viability of human HepG2 cells treated with TPP Cl. In a typical procedure, HepG2 cells were seeded in 96-well plates at a density of 3×10^4 cells per well, and then were incubated with different amounts of TPP Cl (0.0 – 200.0 μM) at 37 ^{o}C for 24 h. A certain amount of MTT solution (0.1 mL, 0.5 mg mL-1 in DMEM) was added to each well after the culture medium was removed, and the incubation was continued at 37 ^{o}C for 3 h. The control group for HepG2 cells was washed with PBS buffer twice. A fixed amount of DMSO (150.0 μL) was then introduced into each well and 10 min of incubation was conducted. The absorbance of each well at 490 nm was recorded with a multifunctional microplate reader (Molecular Devices SpectraMax M5, America). Cell viability was expressed by the ratio of the absorbance of the sample group to that of the control group. Phosphorescence imaging experiment was performed on a Leica TCS SP8 model confocal laser scanning microscope (Germany) with an excitation at 405 nm and a variable bandpass emission filter (410 – 650 nm). HepG2 cells grown on a glass-bottom culture dish using a standard culture solution were equally divided into three groups. The first group acts as the blank. The second group was incubated with a 100.0 μM TPP Cl solution at for 30 min, and then washed three times with PBS buffer. The third group was first treated with a TPP Cl solution for 30 min, and then incubated with a KI solution (100.0 μM) after these cells were washed with PBS buffer. All three groups of HepG2 cells were imaged using the confocal laser scanning microscope at the emission range of 410 – 600 nm.

Double Encryption Application. A number “88” was first written on a filter paper with a 5% starch solution, and then a number “66” was covered on the above number with a concentrated TPP Cl solution (0.2 M). After the filter paper was dried, an iodine solution was painted on the filter homogenously, and a $Na_2S_2O_3$ solution (0.1 M) was then added on purple number “88”. The purple “88” gradually disappeared as drying the

paper accompanying the appearance of blue-emissive “66” under the excitation of UV light.

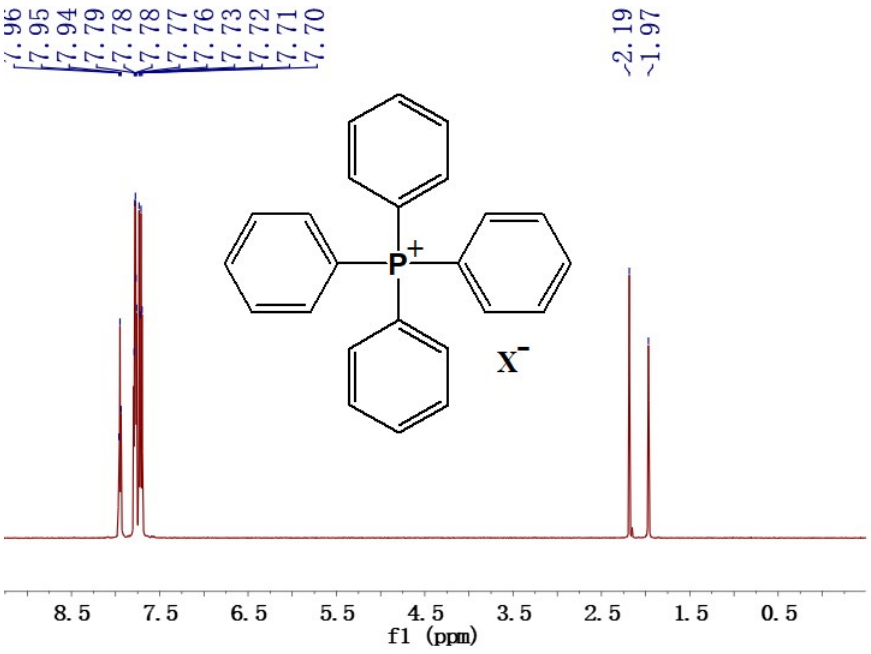

Figure S1. ^{1}H NMR spectrum of TPP halides in CD_3CN.

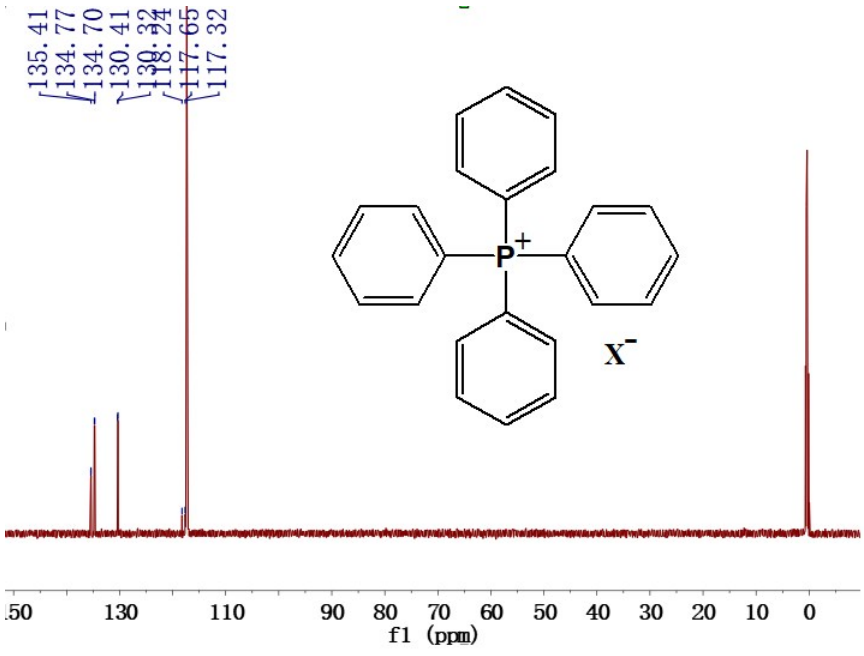

Figure S2. ^{13}C NMR spectrum of TPP halides in CD_3CN.

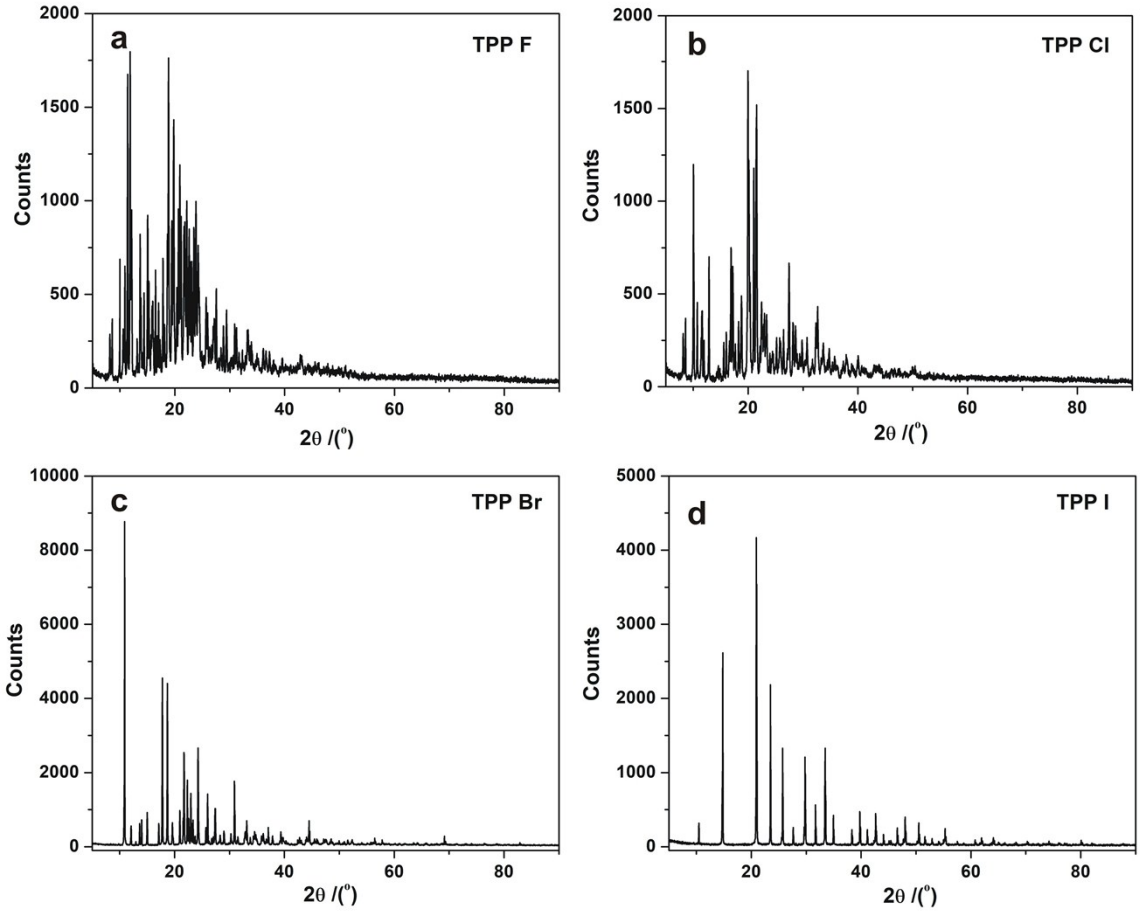

Figure S3. X-ray powder diffraction spectra of tetraphenylphosphonium fluoride (a), tetraphenylphosphonium chloride (b), tetraphenylphosphonium bromide (c) and tetraphenylphosphonium iodide (d).

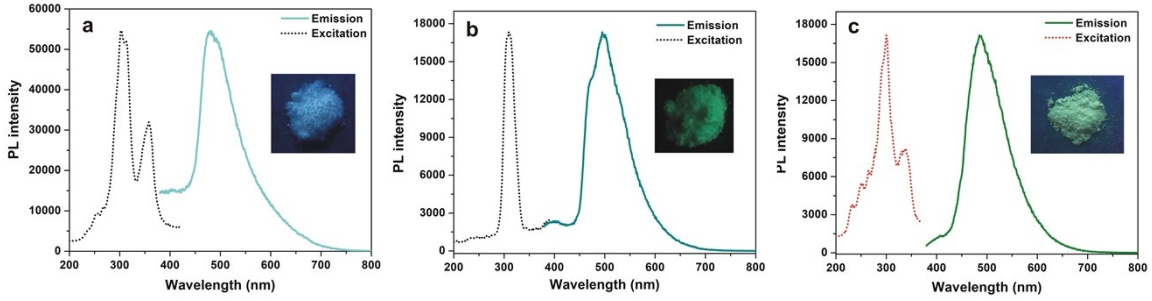

Figure S4. PL spectra of tetraphenylphosphonium fluoride (a), tetraphenylphosphonium chloride (b) and tetraphenylphosphonium bromide (c) crystals. Insets: corresponding luminescence images under the UV light.

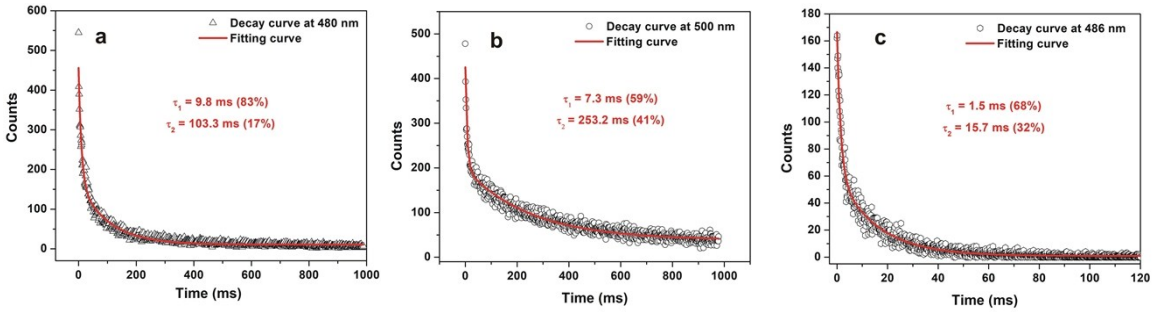

Figure S5. Time-resolved PL decay curves of tetraphenylphosphonium fluoride (a), tetraphenylphosphonium chloride (b) and tetraphenylphosphonium bromide (c) crystals.

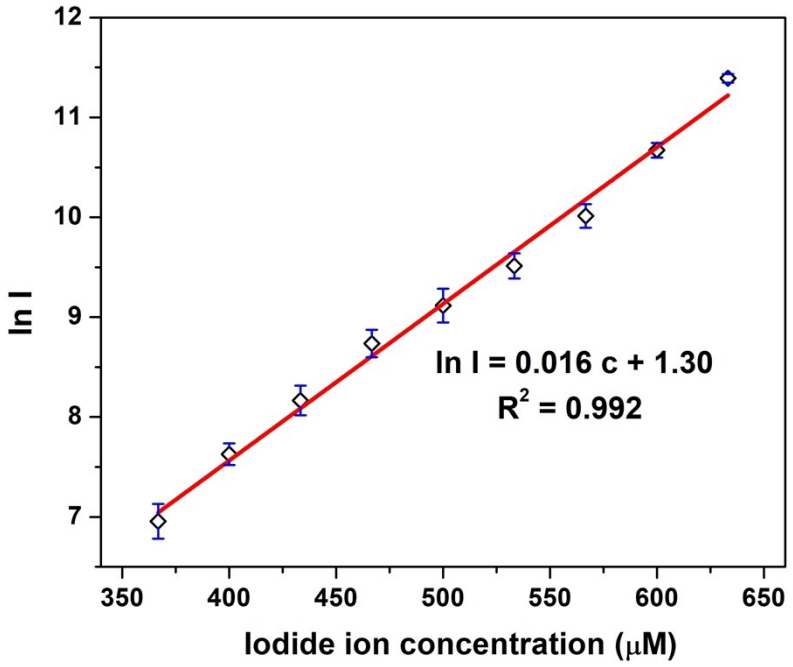

Figure S6. Calibration curve between ln I and iodide ion concentration in the range of 366.7 – 633.3 μM.

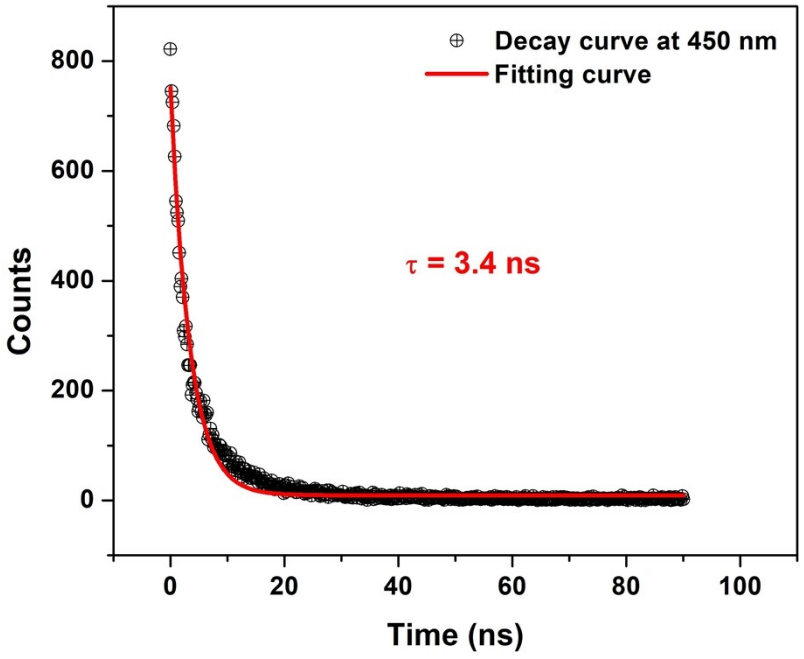

Figure S7. Time-resolved PL decay curve of human serum.

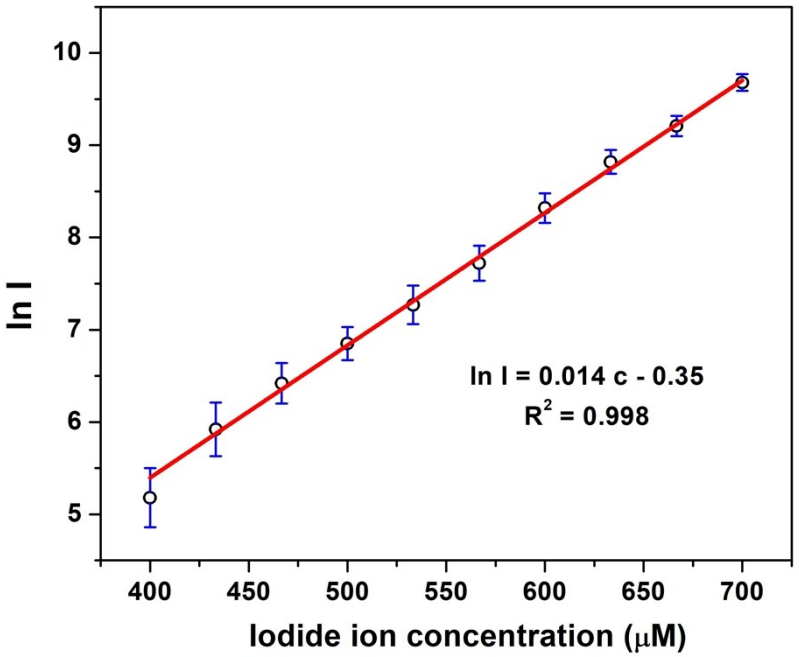

Figure S8. Calibration curve between natural logarithm of PL intensity (ln I) and iodide ion concentration in the range of 400.0 –700.0 μM for time-gated detection of iodide ion.

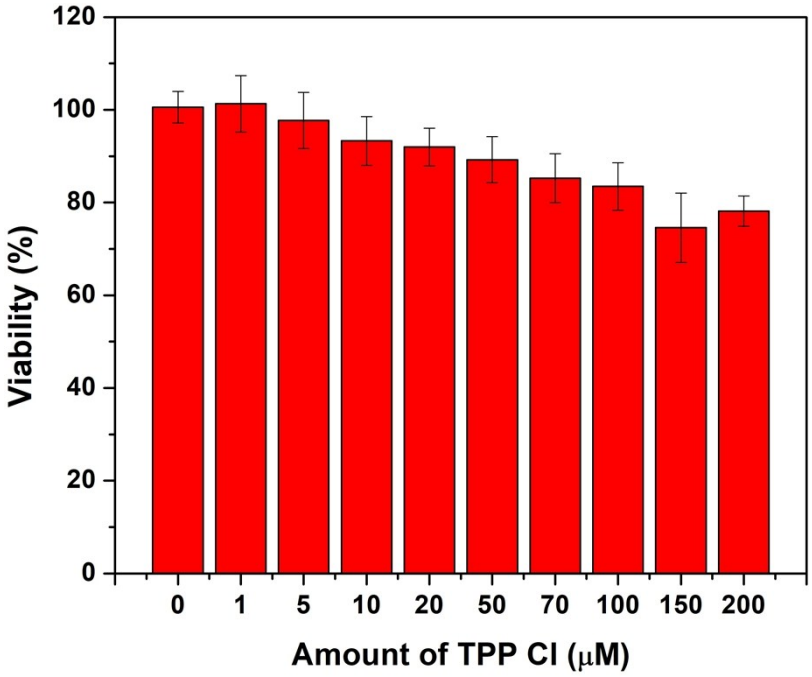

Figure S9. Effect of tetraphenylphosphonium chloride (TPP Cl) on the viability of human HepG2 cells.

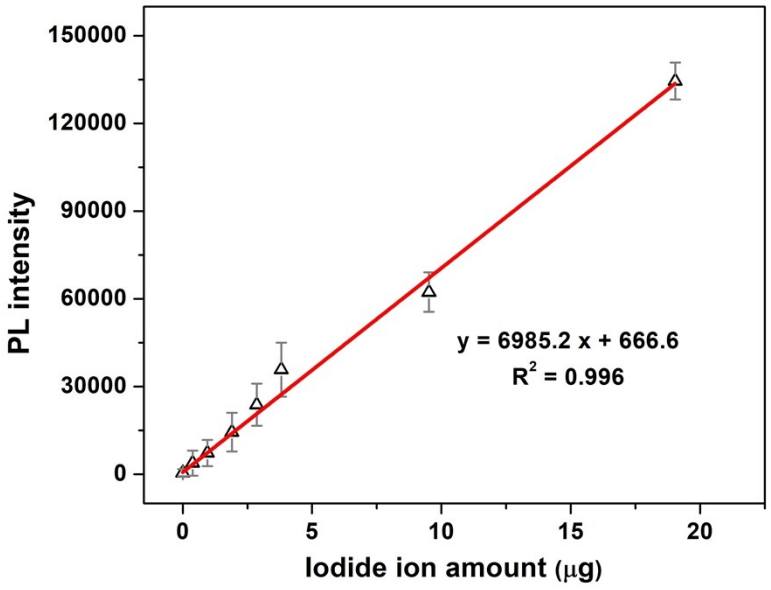

Figure S10. Calibration curve between PL intensity and iodide amount in the range of 0.4 – 19.0 μg based on iodide test strips.