Electronic Supporting Information for

X-ray excitable luminescent polymer dots doped with iridium(III) complex

Yasuko Osakada,*[a,b] Guillem Pratx,[c] Lindsey Hanson,[a] Paige Elana Solomon,[a] Lei Xing*[c] and Bianxiao Cui*[a]

[a]Department of Chemistry, Stanford University, Stanford, CA 94305, USA

[b]PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

[c]Department of Radiation Oncology, School of Medicine, Stanford University, Stanford, CA 94305, USA

* Corresponding; yosakada@stanford.edu (YO), bcui@stanford.edu (BC) and lei@stanford.edu (LX).

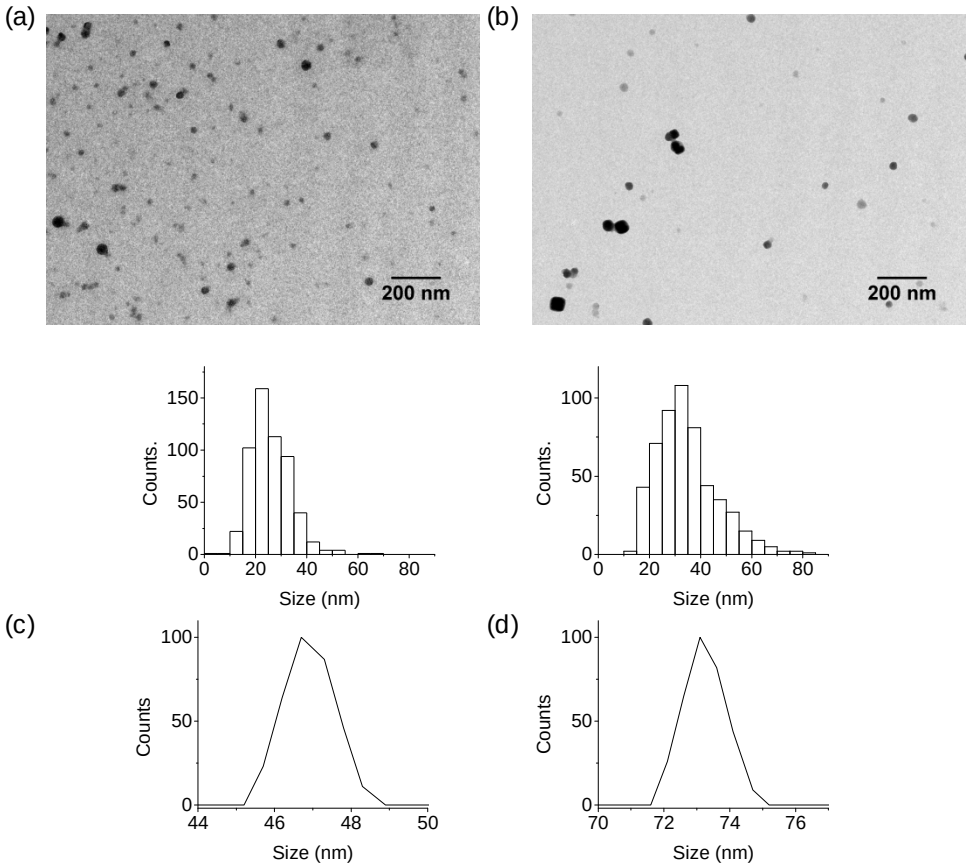

Fig. S1 (a,b) TEM characterization of the polymer dots (P-dots). TEM images and size distributions of non-doped PVK P-dots (a) and iridium (Ir, III) complex-doped P-dots (500 μg/ml in THF for the synthesis), respectively. Sample was mounted on copper grids and stained with OsO_4 to increase the contrast. (c,d) Hydrodynamic diameter of non-doped (c) and doped (d) P-dots.

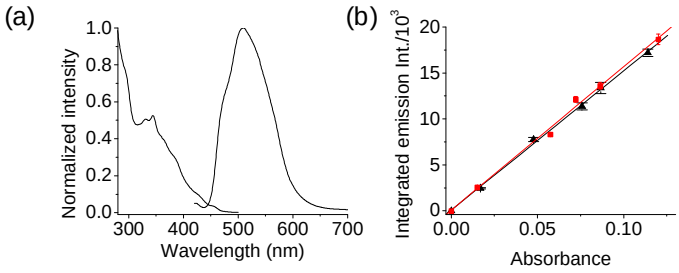

Fig. S2 (a) The excitation spectra (Em; 510 nm) and emission spectra (Ex; 400 nm) of Ir(III) complex-doped P-dots. (b) Effects of oxygen molecule on the dependence of luminescence of Ir(III) complex-doped P-dots in the sample under aerobic condition (same as Fig. 2c and shown in black) and in de-aerated sample (square, shown in red). Integrated emission intensity is plotted as a function of absorption for Ir(III) complex-doped P-dots.

(a) (b)

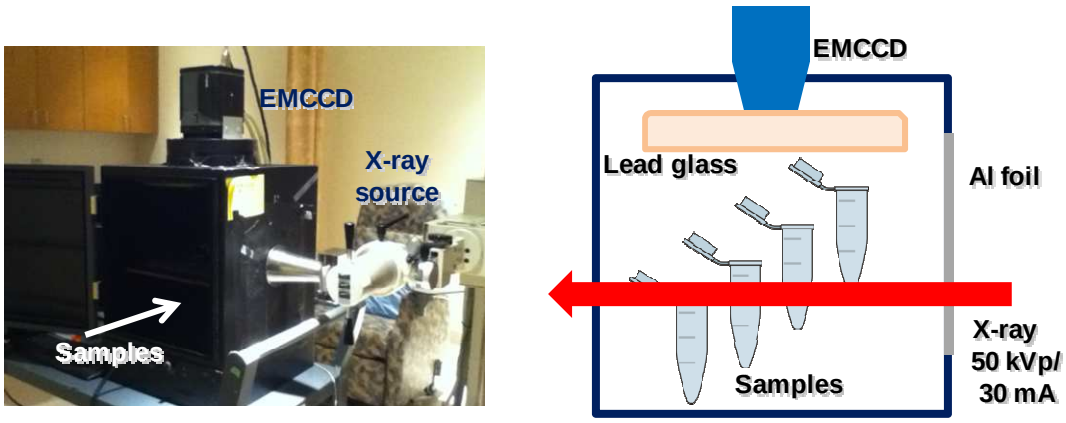

Fig. S3 (a) Photograph and (b) schematic view of the experimental setup used for X-ray luminescence imaging. The samples were irradiated with X-ray from the side and the emission was collected with an EM-CCD camera placed on the top.

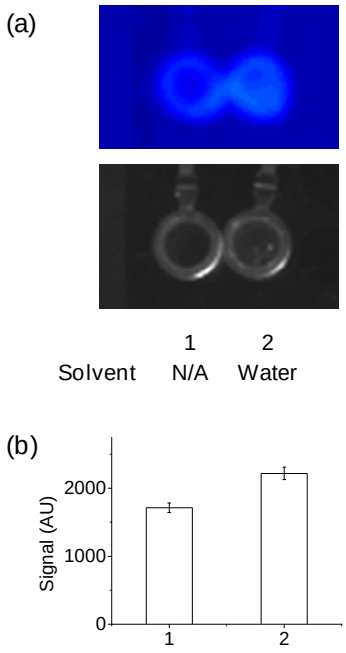

Fig. S4 (a) Representative image of X-ray induced luminescence (top) and bright field image (bottom). From left, blank tube, H_2O. (b) The quantitative luminescence yield of the samples shown in (a).

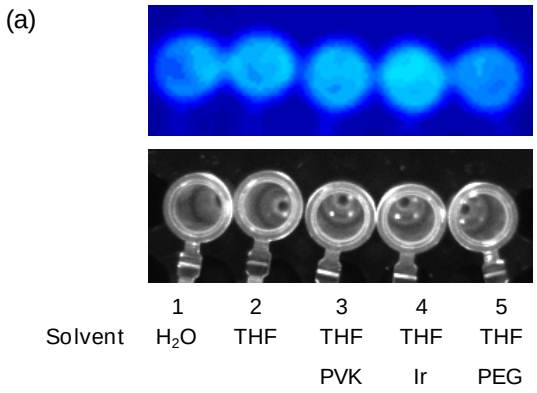

Fig. S5 (a) Representative image of X-ray induced luminescence (top) and bright field image (bottom). From left, H_2O, THF, PVK in THF, Ir(III) in THF and PEG in THF (same amount as P-dots, 500 μg/ml in THF solution for the synthesis). (b) The relative luminescence yield of the samples shown in (a).

		Lifetime (μs)
Monomer in toluene	Under aerobic condition	0.063
	Under Ar	0.686
P-dots in water	Under aerobic condition	0.172
	Under Ar	0.180

Table S1 Luminescence lifetimes for Ir(III) complex-doped P-dots and Ir(III) monomer. Estimated fitting error was ±20%.

Experiments.

Materials.

Polystyrene graft ethylene oxide functionalized with carboxylic end group (PEG-COOH, Mn total 36,500, Mn of each branch; 4600) was purchased from Polymer Source Inc. (Quebec,Canada). Tris(2-(2,4-difluorophenyl)pyridine)iridium (III) and polyvinylcarbazole (PVK) polymer (Mw; 25,000-50,000) and the other reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals were used as received.

Synthesis of Ir complex doped biocompatible P-dots.

Cyclometalated Ir(III) complex-doped P-dots in aqueous solution were prepared by using a modified precipitation method.[1] In a typical preparation, iridium(III) complex, PVK and PEG-COOH were dissolved in tetrahydrofuran (THF) to make a 2 mg/ml stock solution, respectively. Ir(III) complex and two polymers were diluted in THF to produce a solution mixture with various concentrations of Ir complex (0-600 μg/ml), a PVK concentration of 100 μg/ml and PEG-COOH concentration of 200 μg/ml. The mixture was sonicated to make a homogeneous solution. 300 μl of solution mixture in THF was added to 1 ml of milliQ water in a sonicator bath. The THF was evaporated with a speed vac. and the solution was filtered through a 0.22 micron filter. Water was added to make 1 ml of stock solution of P-dots. For the spectrum measurement of P-dots upon X-ray irradiation, P-dots were concentrated approximately 10-times with spin column (viva spin 500, 50 kDa MWCO).

Characterization of P-dots doped with cyclometalated Ir(III) complex.

Absorption spectra were measured with a JASCO V-630Bio absorption spectrophotometer. Fluorescence spectra were measured with a JASCO FP-8200 spectrofluorometer. Transmission electron microscopy (TEM) was carried out on JEOL TEM1230 transmission electron

microscope. The TEM sample was prepared by dropping the P-dots solution on 200 mesh copper grids (TED PELLA, Redding, CA). The grids were then dried, stained with OsO_4 and imaged. Particle size was manually analyzed with ImageJ software. Luminescence lifetime was measured with a PTI EasyLife instrument using 405 nm LED for excitation of samples. A long pass filter (515 nm, OG515, Edmund Optics, Barrington, NJ, USA) was used to observe luminescence from cyclometalated Ir(III). Curve fitting and analysis were performed using Origin software. The lifetime was determined by a single exponential curve fitting.

X-ray experiments.

X-ray radioluminescence imaging was performed as previously described.[2, 3] In brief, the X-ray source (Therapax SXT 150, Elimpex) voltage and current were set to 50 kV and 30 mA, respectively, and the beam was filtered with 0.4 mm aluminum foil. X-ray luminescence was measured with an electron-multiplying CCD (EM-CCD) camera (ImagEM C9100-13, Hamamatsu) using a *f*/0.95 lens, 256X256 pixels, and exposure time of 10 s, and an EM gain of 100. The relative signal intensity was shown as 1 for H_2O as reference. The image was processed with MATLAB software to obtain the luminescence intensity data using water as reference. For spectrum measurement, a monochromator (Princeton Instruments, Acton SP2150) was used with an exposure time and EM gain of 20 s and 100, respectively.

References.

1. Y. Osakada, L. Hanson and B. Cui, *Chem. Commun.*, 2012, **48**, 3285-3287.
2. G. Pratx, C. M. Carpenter, C. Sun, R. P. Rao and L. Xing, *Opt. Lett.*, 2010, **35**, 3345-3347.
3. C. Sun, G. Pratx, M. Carpenter Colin, H. Liu, Z. Cheng, S. Gambhir Sanjiv and L. Xing, *Adv. Mater.*, 2011, **23**, H195-199.