

## Copper (II)-doped semiconducting polymer dots for nitroxyl imaging in live cells

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### Supporting Information

**Materials and Characterizations.** Poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(1,4-benzo-{2,1'-3}-thiadazole)] (PFBT, MW 73000 Da, polydispersity, 3.0) and polystyrene graft ethylene oxide functionalized with carboxyl groups (PS-PEG-COOH, MW 21700 Da of PS moiety; 1200 Da of PEG-COOH; polydispersity, 1.25) were purchased from Polymer Source Inc. (Quebec, Canada). Angeli's salt was purchased from Cayman Chemical (Michigan, USA). All other chemicals and solvents, including tetrahydrofuran and CuCl<sub>2</sub>, were purchased from Sigma-Aldrich unless indicated elsewhere. The carboxyl-functionalized PFBT (PC<sub>30</sub>, MW, 9500 Da; polydispersity, 1.2; carboxyl percentage, 30%) was prepared according to our previous report.<sup>1</sup>

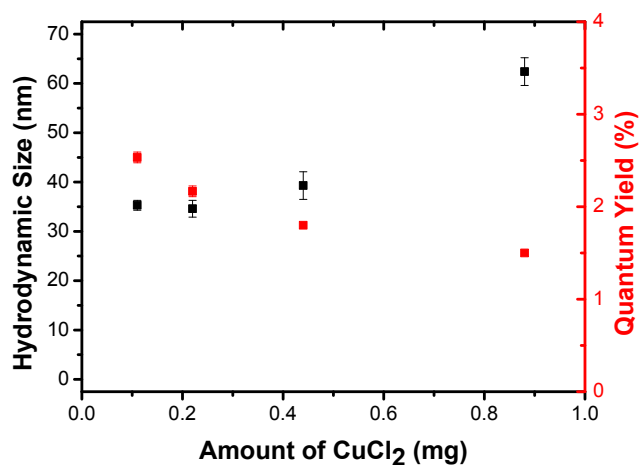
A transmission electron microscope (FEI Tecnai F20, 200 kV) was used to study the size and morphology of the Pdots. The hydrodynamic size and zeta potential of Pdots were investigated with a dynamic light scattering instrument (Malvern Zetasizer Nano ZS). UV-Vis spectra of the Pdots were measured with a DU 720 scanning spectrophotometer (Beckman Coulter, Inc., CA USA). A Fluorolog-3 fluorimeter (HORIBA Jobin Yvon, NJ USA) was used to measure the fluorescence spectra of Pdots, and the quantum yields were obtained with a Hamamatsu photonic multichannel analyzer C10027 equipped with CCD integrating sphere.

**Preparation of Pdot-PFBT/PC<sub>30</sub>-Cu<sup>2+</sup>.** Pdot-PFBT/PC<sub>30</sub>-Cu<sup>2+</sup> were prepared using a nanoprecipitation method. Briefly, a 5-mL tetrahydrofuran (THF) solution containing 0.25 mg of PFBT-C<sub>30</sub>, and 0.22 mg of CuCl<sub>2</sub> was stirred for 1 hour. Then, the 5 mL PC<sub>30</sub>-Cu<sup>2+</sup> mixture was mixed with 0.25 mL of 1 mg/mL PFBT (73K) and 0.1 mL of 20 µg/mL of PS-PEG-COOH with shaking and then quickly injected into 10 mL of water under vigorous sonication. The extra THF was removed by evaporating with protection of nitrogen gas. The final Pdot-PFBT/PC<sub>30</sub>-Cu<sup>2+</sup> solution was filtrated through a 0.45 µm cellulose membrane filter. Then, the Pdot-PFBT/PC<sub>30</sub>-Cu<sup>2+</sup> was concentrated with centrifugal filtration (MW 100KDa) and passed through gel filtration using Sephacryl HR-300 gel media to purify it.

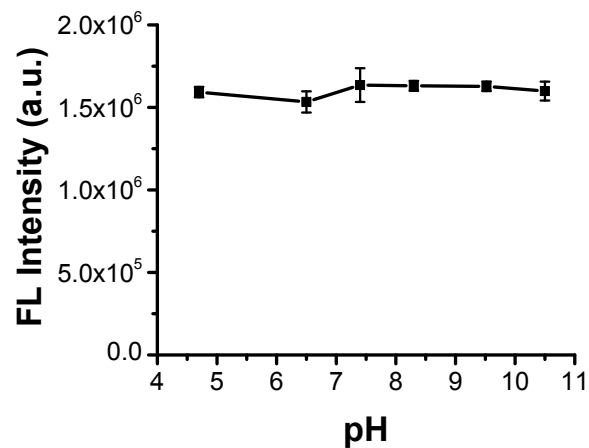
**Table S1.** Summary of photophysical properties of Pdot-PFBT/PC<sub>30</sub> and Pdot-PFBT/PC<sub>30</sub>-Cu<sup>2+</sup>.

	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	QY <sup>a</sup> (%)
Pdot-PFBT/PC <sub>30</sub>	450	540	15.5
Pdot-PFBT/PC <sub>30</sub> -Cu <sup>2+</sup>	450	540	3.8

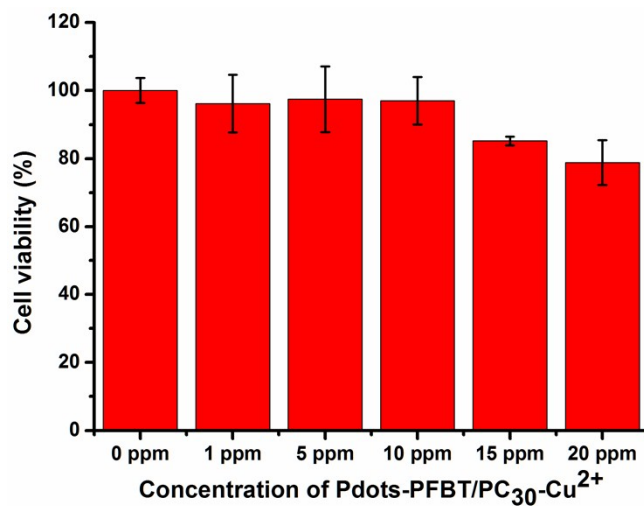
<sup>a</sup>Quantum yield was measured at a 450-nm excitation.



**Fig. S1** The effect of amount of CuCl<sub>2</sub> on the size and quantum yield of Pdots. Based on the results, 0.22 mg was chosen as the optimal amount of CuCl<sub>2</sub> as it did not increase the size of Pdots but quenched the Pdots efficiently.



**Fig. S2** pH effect on the fluorescence intensity of Pdots-PFBT/PC<sub>30</sub>-Cu<sup>2+</sup> (1ppm).  $\lambda_{\text{ex}} = 450 \text{ nm}$ ,  $\lambda_{\text{em}} = 537 \text{ nm}$ .



**Fig. S3** Cell viability of MCF-7 after incubation with different concentrations of Pdots-PFBT/PC<sub>30</sub>-Cu<sup>2+</sup> for 24 hours.

#### References:

1. X. Zhang, J. Yu, C. Wu, Y. Jin, Y. Rong, F. Ye and D. T. Chiu, *ACS Nano*, 2012, **6**, 5429-5439.