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

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Supporting Information

Materials and Characterizations. Poly[(9,9-diocetylfluoren-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 CuCl₂, were purchased from Sigma-Aldrich unless indicated elsewhere. The carboxyl-functionalized PFBT (PC₃₀, MW, 9500 Da; polydispersity, 1.2; carboxyl percentage, 30%) was prepared according to our previous report.¹

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/PC₃₀-Cu²⁺. Pdot-PFBT/PC₃₀-Cu²⁺ were prepared using a nanoprecipitation method. Briefly, a 5-mL tetrahydrofuran (THF) solution containing 0.25 mg of PFBT-C₃₀, and 0.22 mg of CuCl₂ was stirred for 1 hour. Then, the 5 mL PC₃₀-Cu²⁺ 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/PC₃₀-Cu²⁺ solution was filtrated through a 0.45 µm cellulose membrane filter. Then, the Pdot-PFBT/PC₃₀-Cu²⁺ 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$_{30}$ and Pdot-PFBT/PC$_{30}$-Cu$^{2+}$.

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<thead>
<tr>
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<th>$\lambda_{\text{ex}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>QY$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pdot-PFBT/PC$_{30}$</td>
<td>450</td>
<td>540</td>
<td>15.5</td>
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<tr>
<td>Pdot-PFBT/PC$_{30}$-Cu$^{2+}$</td>
<td>450</td>
<td>540</td>
<td>3.8</td>
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$^a$Quantum yield was measured at a 450-nm excitation.

**Fig. S1** The effect of amount of CuCl$_2$ on the size and quantum yield of Pdots. Based on the results, 0.22 mg was chosen as the optimal amount of CuCl$_2$ as it did not increase the size of Pdots but quenched the Pdots efficiently.
**Fig. S2** pH effect on the fluorescence intensity of Pdot-PFBT/PC$_{30}$-Cu$^{2+}$ (1ppm). $\lambda_{\text{ex}} = 450$ nm, $\lambda_{\text{em}} = 537$ nm.

**Fig. S3** Cell viability of MCF-7 after incubation with different concentrations of Pdot-PFBT/PC$_{30}$-Cu$^{2+}$ for 24 hours.

**References:**