

Copper (II) and iron (II) ion sensing with semiconducting polymer dots

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Supporting Information

Materials. The following inorganic salts were purchased from Sigma-Aldrich and used as received: copper(II) sulfate, potassium chloride, sodium chloride, nickel(II) sulfate, iron(II) sulfate, magnesium(II) sulfate, cobalt(II) sulfate, calcium sulfate, zinc sulfate, and lead sulfate. PSMA and THF (anhydrous, $\geq 99.9\%$, inhibitor-free) were also purchased from Sigma-Aldrich. All other chemical reagents were purchased from Polymer Source Inc. and used as received without further purification. High purity water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used throughout the experiment.

Preparation, Characterization, and Application of Functionalized Pdots for Cu^{2+} and Fe^{2+} Measurements. Typically, $40 \mu\text{g}$ of PFBT and $8 \mu\text{g}$ of PSMA were dissolved into 5 mL of THF. This mixture was then quickly injected into 10 mL of water under vigorous sonication. The THF was then removed by purging with nitrogen on a 96

°C hotplate for one hour. The resulting Pdot solution was filtered through a 0.2 μm cellulose acetate membrane filter to remove any aggregates formed during preparation.

The particle size was determined by DLS and TEM to be ~ 21 nm in diameter. TEM images of the synthesized Pdots were acquired using a FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. For TEM, a drop of Pdot aqueous solution was placed onto a carbon-coated grid and allowed to evaporate at room temperature. The absorption spectra of Pdots were measured using UV-visible spectroscopy (DU 720, Beckman Coulter, Inc., CA USA). For the fluorescence measurements, 0.2 $\mu\text{g/mL}$ of Pdots was prepared in 10 mM of HEPES buffer (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; pH 7.4) and various concentrations of copper or iron ions were introduced into the Pdot solutions. The fluorescence spectra were collected using a Fluorolog-3 fluorometer (HORIBA Jobin Yvon, NJ USA).

For the determination of Cu^{2+} and Fe^{2+} in simulated biological backgrounds, the PS-COOH *co* PFBT Pdots (0.2 $\mu\text{g/mL}$) and PFBT *co* PFTBT Pdots (0.2 $\mu\text{g/mL}$) were added into the diluted (1:20 v/v with high purity water) EMDM (D5921, Sigma) solutions, which contained various inorganic salts, amino acids, vitamins, and other supplementary components.¹ After that, solutions containing 10 μM and 15 μM of Cu^{2+} and Fe^{2+} were prepared by adding the CuSO_4 and FeSO_4 into EMDM solutions for the subsequent fluorescence measurements. The concentration of Cu^{2+} and Fe^{2+} were then determined by adding EDTA into solutions as described in the main text.

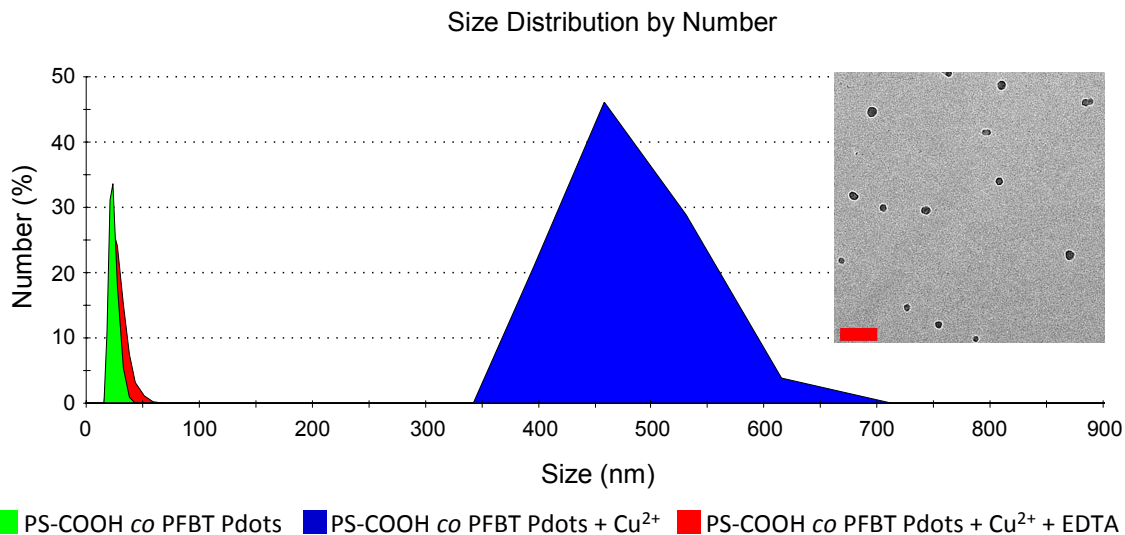


Figure S1. Dynamic light scattering measurements of Pdots before and after addition of Cu²⁺, as well as after addition of EDTA. Hydrodynamic diameter of PS-COOH *co* PFBT Pdots measured by DLS in water (■) and in 30 μM Cu²⁺ solution (■), as well as after the addition of 30 μM EDTA to the Cu²⁺ containing solution (■). The right inset shows the TEM image of the Pdots after the addition of EDTA to the Cu²⁺ containing solution. The scale bar is 100 nm.

To further investigate if large aggregates (micron-size) of Pdots were formed after the addition of copper ions, which can result in a noticeable scattering feature in the UV/VIS spectrum, we performed UV/Vis measurements on the Pdot solution before and after the addition of Cu²⁺. As shown in Figure S2, no obvious scattering feature, such as baseline elevation, could be observed after the addition of Cu²⁺, consistent with the DLS and TEM data that indicated the presence of only small aggregates. The easy re-dispersion of the Pdot aggregates after introducing EDTA also suggests that the Pdots did not form large agglomerates that would be difficult to re-disperse. This hypothesis is also supported by DLS and TEM measurements as shown in Figure S1, in which the size of Pdots returned back to ~ 20 nm after the addition of EDTA.

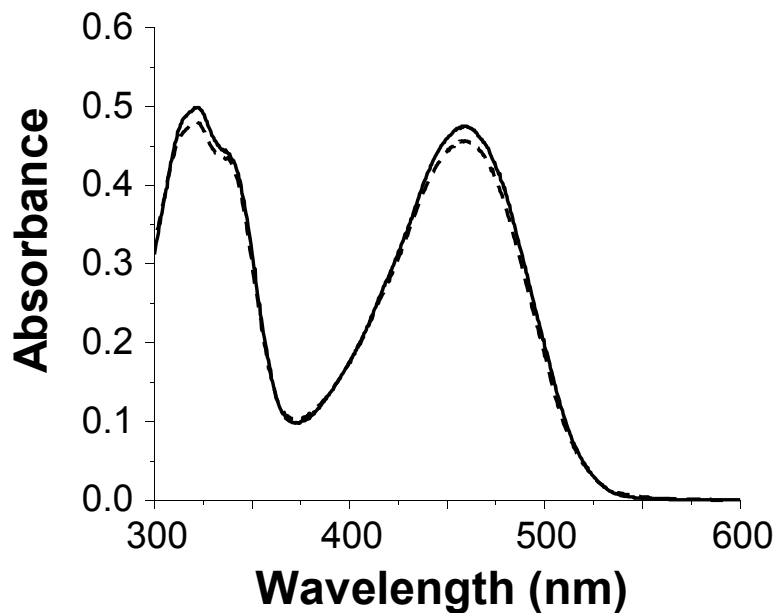


Figure S2. The absorption spectra of PS-COOH *co* PFBT Pdots before (solid line) and after (dashed line) the addition of Cu²⁺. Note the slight decrease in the absorption intensity after Cu²⁺ addition, which we attribute to dilution of the solution when we added the Cu²⁺ solution.

To study the effect of Pdot concentration on the fluorescence response to copper ions, we prepared two different concentrations, with one higher (i.e. 5.0 ppm) and the other one lower (i.e. 0.1 ppm) than the concentration we used in the main text (i.e. 0.2 ppm). The results showed that the aggregation-induced self-quenching behavior was concentration independent. In all cases, the fluorescence quenched by copper ions could be reversed by adding EDTA.

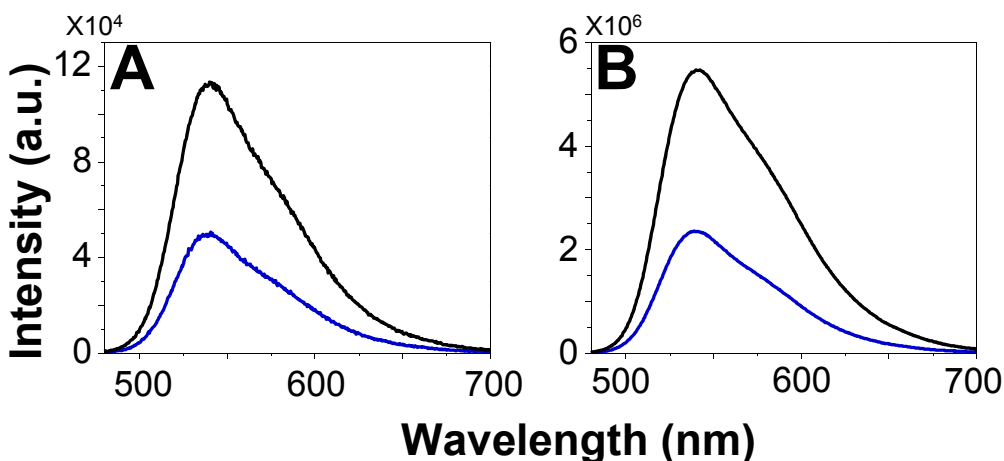


Figure S3. Effect of different concentrations of PS-COOH *co* PFBT Pdots on the emission response to Cu^{2+} . (A) Fluorescence of 0.1 ppm PS-COOH *co* PFBT Pdot solution before (black line) and after (blue line) Cu^{2+} addition. (B) Fluorescence of 5.0 ppm PS-COOH *co* PFBT Pdot solution before (black line) and after (blue line) Cu^{2+} addition.

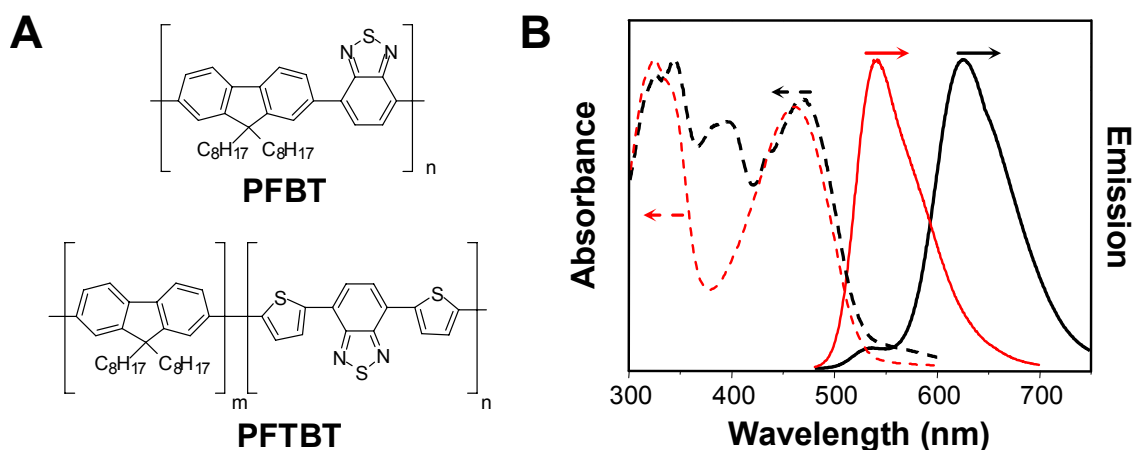


Figure S4. Chemical structures and optical properties of the Pdots. (A) Chemical structures of PFBT and PFTBT. (B) The absorption and emission of PS-COOH *co* PFBT Pdots were shown in a dashed red line and a solid red line, respectively; the dashed black line and the solid black line denote the absorption and emission spectra of PFBT *co* PFTBT Pdots, respectively.

References

- (1) <http://www.sigmaaldrich.com/etc/medialib/docs/Sigma/Formulation/d5921for.Par.0001.File.tmp/d5921for.pdf>