Development of Ultrabright Semiconducting Polymer Dots for Ratiometric pH Sensing

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Supporting Information

Selection and Optimization of Pdot-Dye Pair. We wanted to create a ratiometric, pH sensitive Pdot based on FRET that could be excited at a single wavelength with two different color emissions. The first step was to select a suitable donor-acceptor pair. We chose fluorescein as the FRET acceptor because its absorption profile and emission intensity are highly dependent on pH. In particular, we thought changes in the absorption profile of fluorescein at different pH values would allow us to modulate the FRET efficiency between the donor (Pdot matrix) and the acceptor (fluorescein molecules).

To optimize the FRET efficiency between the Pdot matrix and fluorescein, it was important to select a suitable donor polymer based on its spectroscopic properties. Here, we examined several semiconducting polymers, including poly(2,5-di(3',7'-dimethyloctyl)phenylene-1,4-ethynylene (PPE), poly(9,9-dioctylfluorenyl-2,7-diyl)

(PFO), and poly[{9,9-dioctyl-2,7-divinylene-fluorenylene}-alt-co-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene}] (PFPV). We found there was insufficient energy transfer from PFO Pdots to fluorescein, rendering the pH response of PFO-fluorescein unsatisfactory. We also found with PFPV Pdots that there was extensive undesirable overlap in the emission spectra of PFPV and fluorescein (Figure S1). In contrast, PPE Pdots exhibited excellent energy transfer to fluorescein because of the substantial spectral overlap between the emission spectrum of PPE and the absorption spectrum of fluorescein (Figure 1A).

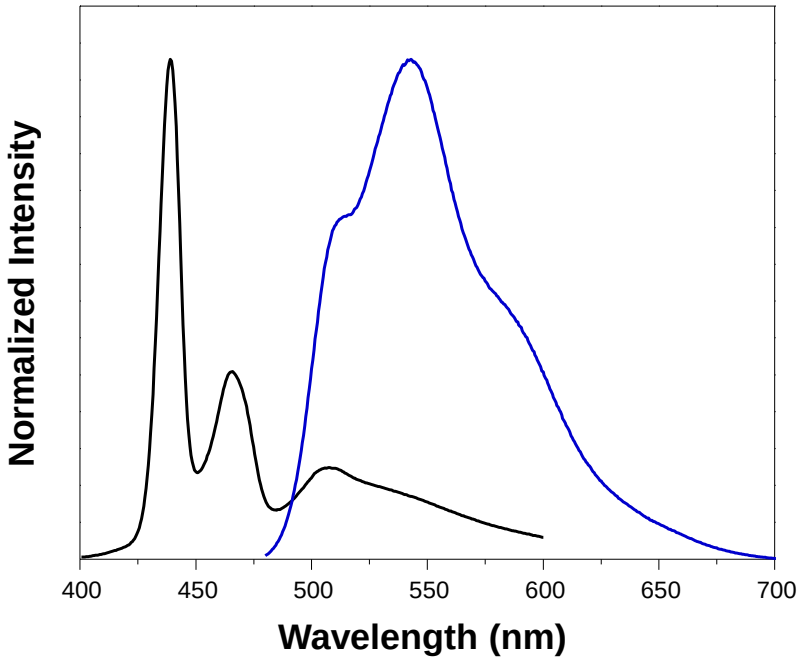

Figure S1. Emission spectra of PFO Pdot-fluorescein complex (black line) and pure PFPV Pdots (blue line) in pure water. The excitation wavelength for PFO-fluorescein and PFPV was 380 nm and 450 nm, respectively.

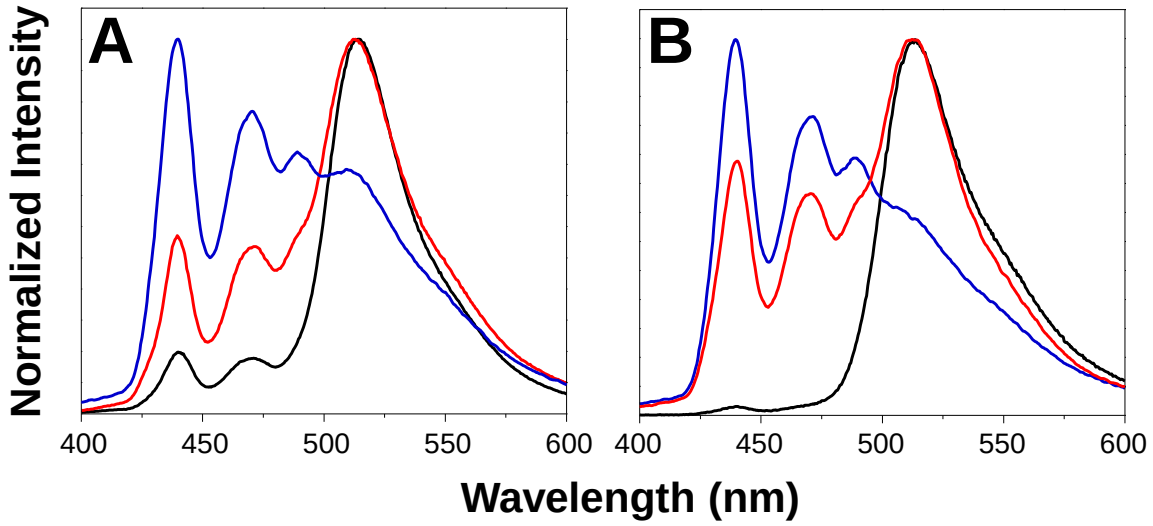

Figure S2. Examination of the optimal blending percentage. (A) Three different blending percentages of PS-SH in the PPE polymer were investigated for routes A and C. The PS-SH was conjugated to fluorescein after Pdot formation. The blue, red, and black lines show the ratio of 15%, 30%, and 45% of PS-SH in PPE polymers at pH=7, respectively. (B) Three different blending percentages of PS-NH_2-fluorescein in the PPE polymer were studied for route B. The blue, red, and black lines show the percentages of 50%, 60%, and 70% of PS-NH_2-fluorescein in PPE polymers at pH=7, respectively.

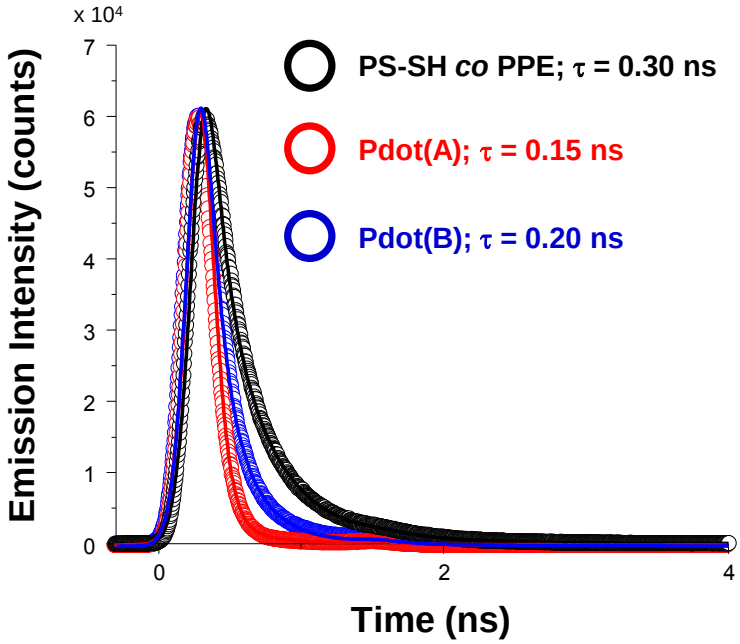

Figure S3. Time resolved fluorescence decay of Pdots before (i.e. bare PS-SH *co* PPE Pdots; black circles) and after conjugation to fluorescein (i.e. Pdot(A); red circles, and Pdot(B); blue circles) in pure water.

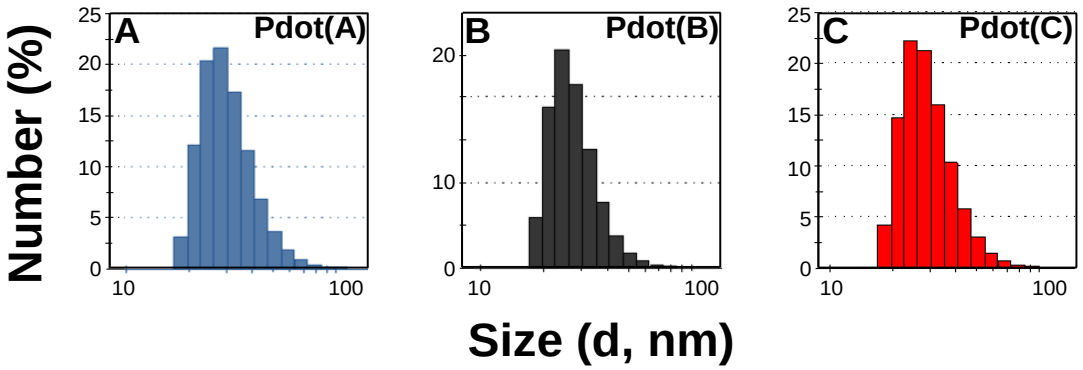

Figure S4. Dynamic light scattering measurements of three different types of PPE-fluorescein Pdots. Hydrodynamic diameters of (A) Pdot(A), (B) Pdot(B), and (C) Pdot(C).

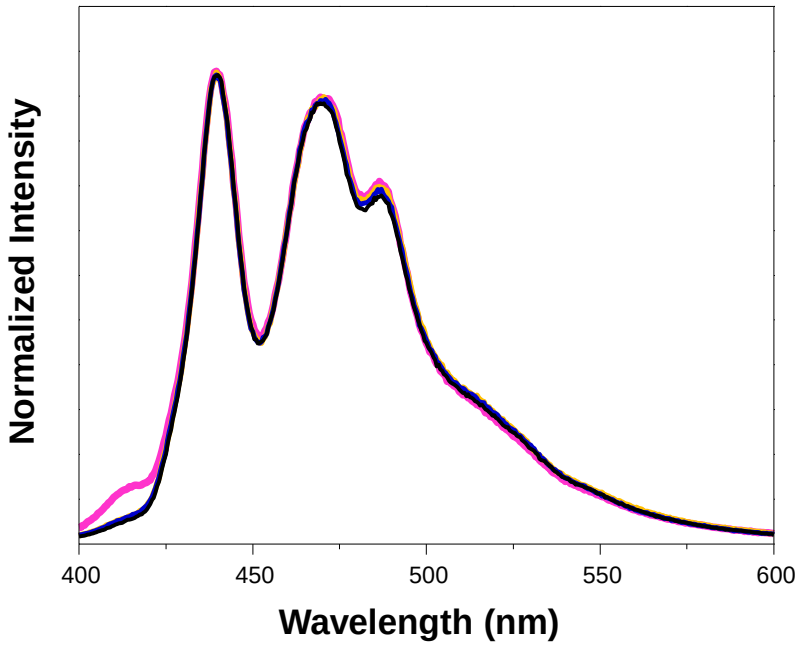

Figure S5. Fluorescence spectra of bare PPE Pdots at pH ranging from 5 to 8. Pink line: pH=5, gold line: pH=6, black line: pH=7, blue line: pH=8.