

Supporting Information

Fluorescent and pH-responsive Diblock Copolymer-coated Core-Shell CdSe/ZnS Particles for Color-Displaying, Ratiometric pH Sensor

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Experimental

Characterization

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX 500. The molecular weights (M_n) and polydispersity indices (PDI) of the synthesized polymers were obtained by size exclusion chromatography (SEC) using a Waters 1515 pump and a Waters 2414 differential refractometer with THF as the eluent at a flow rate of 1 mL/min. SEC was calibrated using PS standards. To characterize the P2VP and PyMMP-*b*-P2VP grafted on the surface of the QDs, the CdSe/ZnS core was first dissolved by adding an excess of DMAP to the polymer-coated QDs in DCM.¹ After stirring at RT until the solution became colorless, the solvent was evaporated. The polymers were then redispersed in THF and characterized by SEC.

The size and dispersion behavior of the CdSe/ZnS QDs were analyzed using TEM (Tecnai G220 S-twin or JEOL JEL-3011 HR) images. A carbon-coated TEM grid was dipped into a dilute solution of QDs for several seconds, dried under air, and examined by TEM. UV-Vis absorption spectra of the QDs were measured using a Varian Cary 500 spectrophotometer. The PL spectra were obtained using a Horiba Jobin Yvon NanoLog spectrophotometer with 365 nm as the excitation wavelength and a 10 mm quartz cuvette. The samples for both UV-Vis and PL measurements were prepared by dissolving (PyMMP-*b*-P2VP)-QDs in a mixture of buffer solution and DMF (10:1 v/v). For the CdSe/ZnS concentration measurements, the extinction values determined experimentally by Yu et al. were used.² The hydrodynamic size of the (PyMMP-*b*-P2VP)-QDs at a given pH was determined via DLS measurements using a Malvern Zetasizer Nano ZS. The (PyMMP-*b*-P2VP)-QDs samples were prepared by first dissolving the QDs in a mixture of buffer solution and DMF (10:1 v/v) and then filtering through a 0.45- μ m syringe membrane filter to remove any dust or aggregated particles.

Synthesis

Synthesis of oleic acid coated CdSe/ZnS quantum dots (1). Red (630 nm) emitting CdSe/ZnS quantum dots were synthesized via a one-pot synthesis method reported previously.³ Briefly, 1 mmol of cadmium oxide, 2 mmol of zinc acetate and 5 mL of oleic acid were heated to 150 °C under a nitrogen atmosphere, and 25 ml of 1-octadecene was added to the mixture. The solution was then heated to 300 °C, and 0.2 mmol of selenium in 0.2 mL of trioctylphosphine was rapidly injected into the reaction flask. After several minutes, 0.3 mL of 1-dodecanthiol was injected into the flask, and the reaction proceeded for 20 min. Then, 2 mmol of sulfur in 1 mL of trioctylphosphine was added to form ZnS shells at the elevated temperature over a period of 10 min. The CdSe/ZnS QDs were purified by centrifugation at 3,600 rpm for 20 min.

Synthesis of trithiocarbonate RAFT chain transfer agent (2). 2-[[[(Butylsulfanyl)-carbonothioyl] sulfanyl]propanoic acid was synthesized according to modified literature procedure.⁴ NaOH aq solution (50 %, 16 g) was added to butanethiol (18.00 g, 200 mmol) and water (30 mL) mixture, followed by addition of acetone (10 mL) to give a colorless solution. The solution was stirred at RT for 0.5 h. Carbon disulfide (14 mL, 17.6 g, 231 mmol) was added to obtain a clear orange solution. The reaction mixture was stirred for 0.5 h and then cooled in an ice bath. 2-Bromopropionic acid (31.37 g, 205 mmol) was added dropwise, followed by 16 g of 50 % aq NaOH solution as a rate to keep the temperature of bath not exceed 30 °C. After the exotherm reaction had terminated, water (30 mL) was added and then the reaction was stirred at RT for 24 hrs. The reaction mixture was diluted with 50 mL of water. Then, 10 M HCl was added at a rate to keep the temperature under ice bath. The yellow oil was obtained, and kept at ice temperature until solidifying the oil. The solid was separated by filtration and washed with cold water then dried. Finally, the products were recrystallized from hexane with gentle stirring to give bright yellow solid crystals (34.8g, 71.2%). ¹H NMR (CDCl₃, 500 MHz) δ 9.9 (br s, 1H), 4.81 (q, *J* = 7.4 Hz, 1H), 3.33 (t, *J* = 7.4 Hz, 2H), 1.66-1.72 (m, 2H), 1.62 (d, *J* = 7.3 Hz, 3H), 1.42-1.46 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

Synthesis of the thiol-terminated RAFT chain transfer agent (3). The thiol-terminated RAFT agent was synthesized via a conventional DCC coupling reaction. Briefly, 16.7 mmol of CTA, 33.4 mmol of mercaptohexanol and 8.4 mmol of DMAP were mixed in 200 ml of DCM. After 15 min, 16.7 mmol of DCC in 20 mL of DCM was added to the mixture, and the color of the solution changed from red to dark yellow. After 36 h, the mixture was filtered, and the solvent was evaporated. The crude products were purified through column chromatography (hexane/ethyl acetate). Finally, a dark yellow oily product was obtained. ¹H NMR (CDCl₃, 500 MHz) δ 4.85 (q, *J* = 7.3 Hz, 1H), 4.15 (t, *J* = 2.9 Hz, 2H), 3.36 (t, *J* =

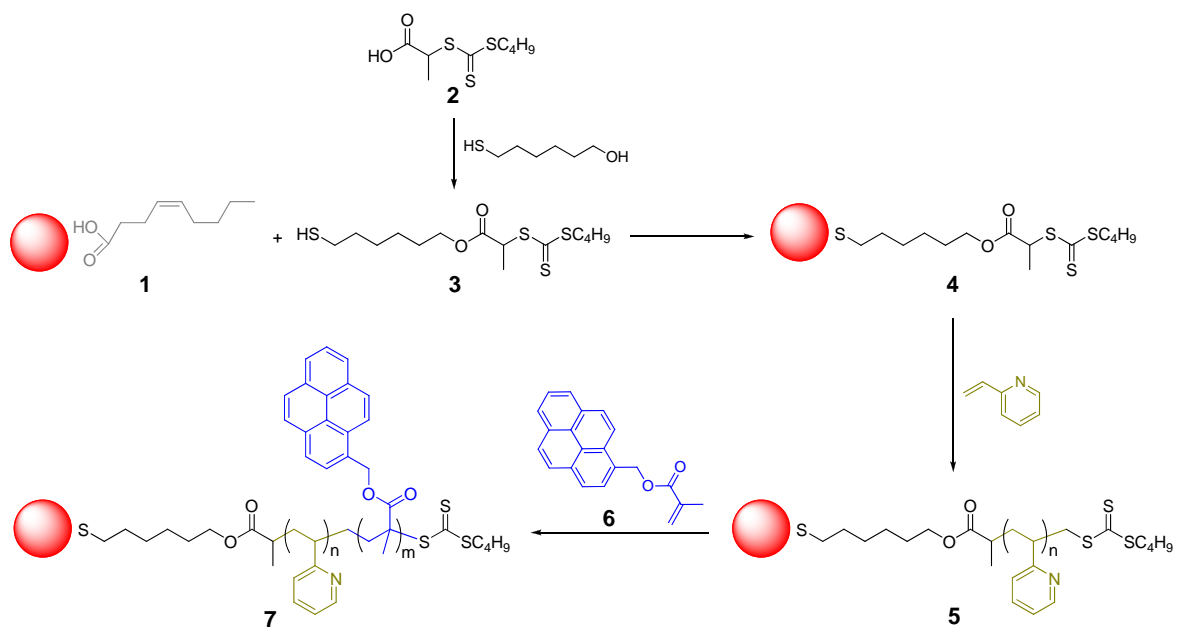
7.3 Hz, 2H), 2.49 (t, $J = 2.4$ Hz, 2H), 1.51-1.74 (m, 7H), 1.62 (d, $J = 7.3$ Hz, 3H), 1.32-1.48 (m, 6H), 0.93 (t, $J = 7.5$ Hz, 3H).

Synthesis of CdSe/ZnS particles coated with RAFT agent (4). First, 20 mg of CdSe/ZnS QDs dissolved in THF were mixed with 0.1 g of thiol-terminated RAFT agent. The mixture was then stirred at 40 °C for 12 h under a nitrogen atmosphere. The solution was precipitated with hexane, and centrifugation at 4,000 rpm for 20 min was used to remove the excess thiol-terminated RAFT agent. Finally, the precipitated QDs were dissolved in 3 mL of benzene.

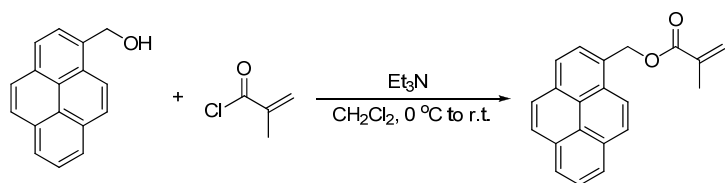
Preparation of (1-pyrene)methyl-2-methyl-2-propenonate (PyMMP)⁵ (6). 1-Pyrenemethanol (2 g, 8.62 mmol) was added to triethylamine (1.8 mL, $d = 0.726$ g/mL, 12.93 mmol) in CH_2Cl_2 (80 mL) at 0 °C. Methacryloyl chloride was prepared as a yellow oil from the reaction of 2-methylacrylic acid and thionyl chloride,⁶ and this reagent (897 mg, 8.62 mmol) was then added dropwise to the above solution over a period of 10 min. This reaction mixture was stirred at room temperature for 6 h and then diluted with excess EtOAc. The separated organic layer was washed with aqueous 0.1% aq HCl, water, and brine before it was dried over MgSO_4 and concentrated in vacuo. The solid residue was purified by column chromatography (hexane:ethyl acetate = 10:1) to yield the product (2.15 g, 83%) as a pale yellow solid. ^1H NMR (CDCl_3 , 500 MHz) δ 8.32 (d, $J = 9.2$ Hz, 1H), 8.22 (t, $J = 6.7$ Hz, 2H), 8.16-8.19 (m, 2H), 8.01-8.11 (m, 4H), 6.15 (s, 1H), 5.92 (s, 2H), 5.57 (s, 1H), and 1.97 (s, 3H).

Polymerization of P2VP from the surface of CdSe/ZnS-CTA (5). To a solution of RAFT-coated QDs in benzene, 0.2 g of 2VP monomer and 1 mg of AIBN were added. The mixture was degassed and heated to 60 °C for 12 h. Then, P2VP coated CdSe/ZnS was precipitated with hexane, isolated by centrifugation, and dried in ambient air conditions.

Polymerization of PyMMP from the surface of P2VP coated CdSe/ZnS (7). To a solution of P2VP-CdSe/ZnS in benzene, 10 mg of PyMMP monomer and 1 mg of AIBN were added. The mixture was degassed and heated to 60 °C for 12 h. Then, (PyMMP-b-P2VP)-CdSe/ZnS QDs were precipitated with hexane and isolated by centrifugation. The centrifugation was repeated several times to remove unreacted PyMMP monomers, which was confirmed by TLC.



Scheme S1. Synthesis of (PyMMP-*b*-P2VP)-CdSe/ZnS QDs



Scheme S2. Synthesis of (1-Pyrene)methyl 2-methyl-2-propenonate (PyMMP) (6)

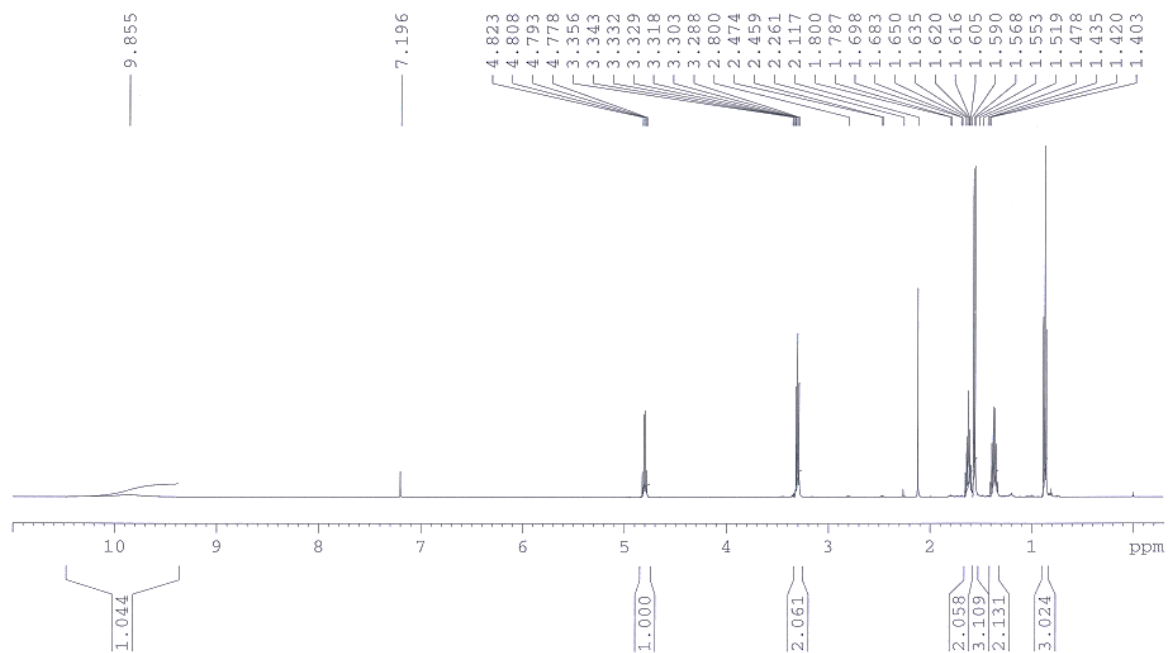


Figure S1. $^1\text{H-NMR}$ of trithiocarbonate RAFT chain transfer agent (**2**)

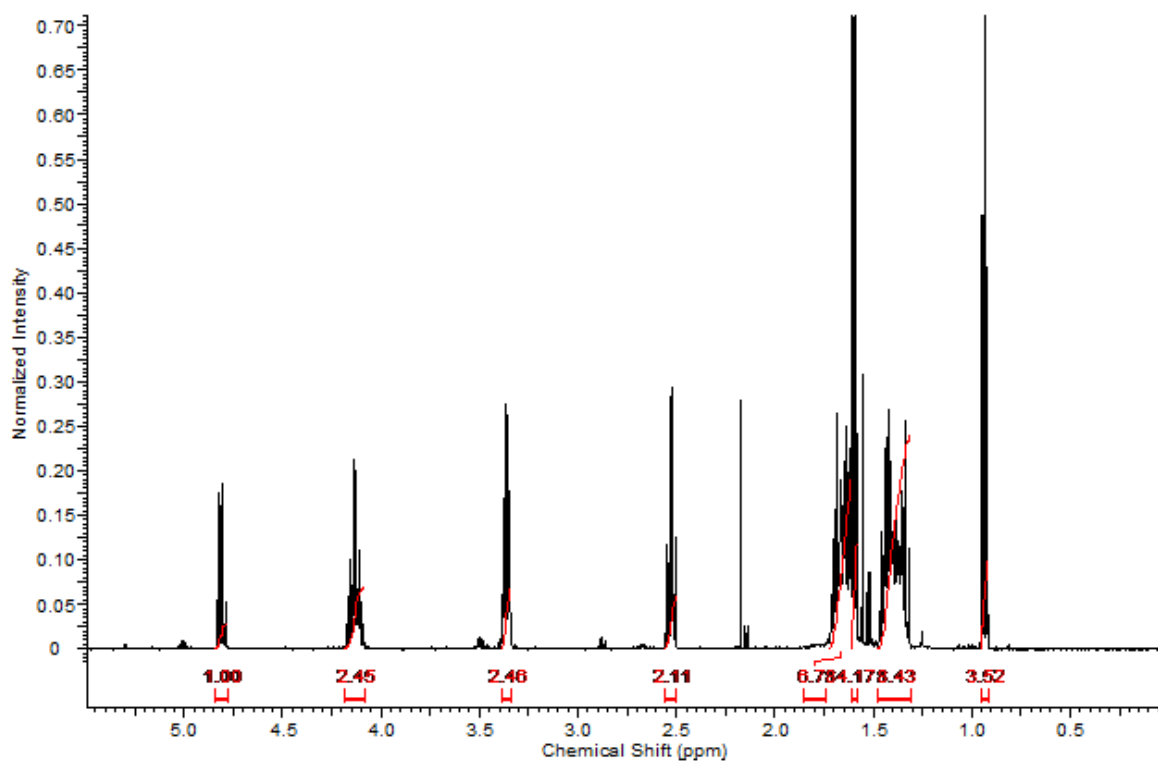


Figure S2. $^1\text{H-NMR}$ of thiol terminated RAFT chain transfer agent (**3**).

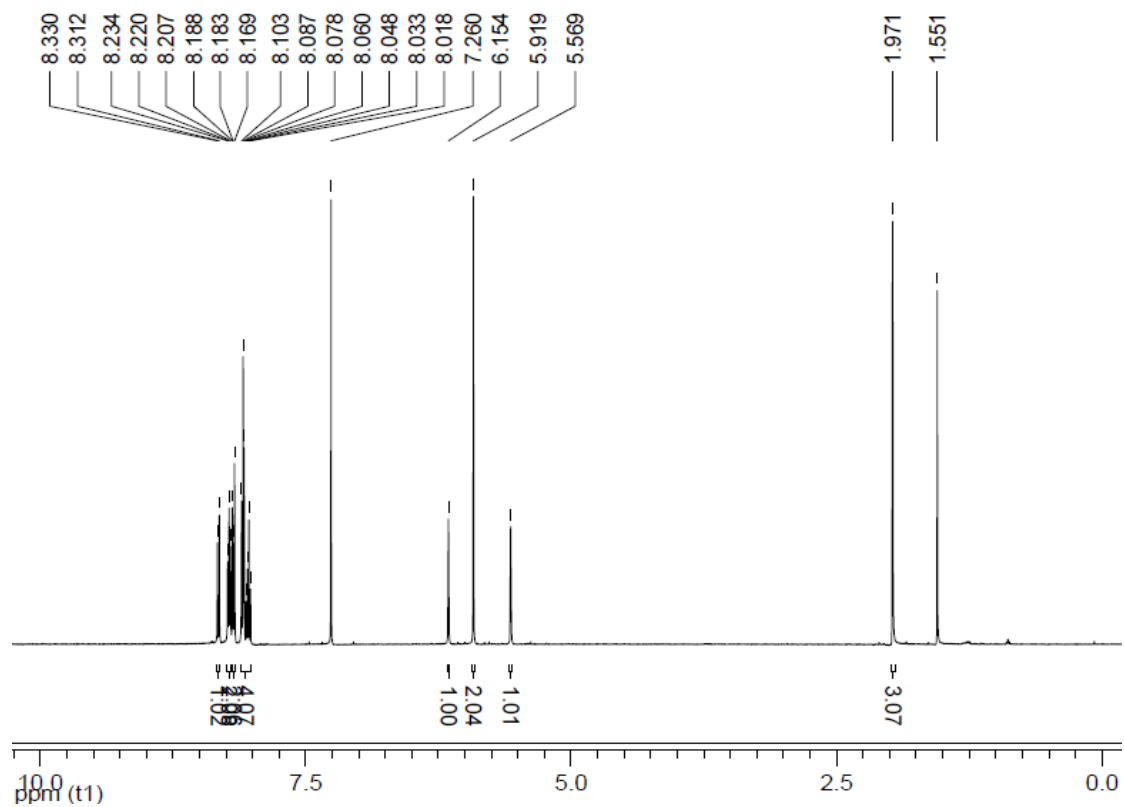


Figure S3. $^1\text{H-NMR}$ of *(1-Pyrene)methyl 2-methyl-2-propenonate* (PyMMP) (**6**)

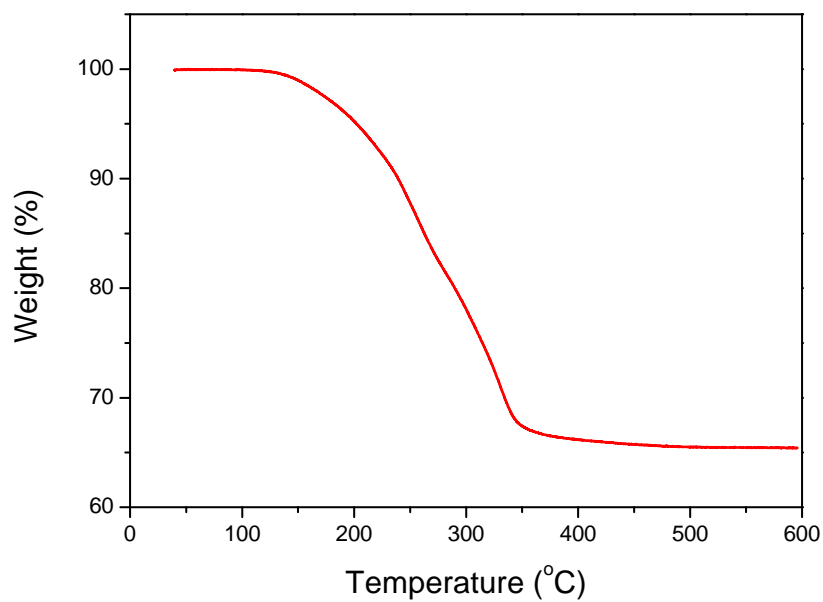


Figure S4. TGA of RAFT coated QDs.

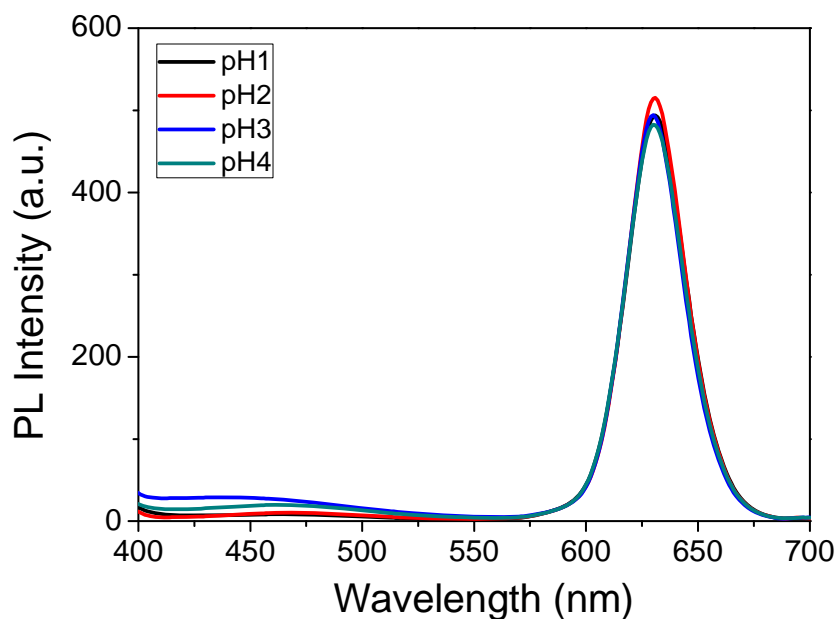


Figure S5. PL spectra of P2VP-QDs as a function of pH.

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