

# The Enhanced Fluorescence Properties & Colloid Stability of Aqueous CdSe/ZnS QDs Modified with N-alkylated Poly(ethyleneimine)

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## The procedure to synthesize CdSe/ZnS QDs

### Materials

All reagents were used as received without further experimental purification. Cadmium oxide (CdO, 99.99%), sulfur (S, 99.98%, powder), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), selenium (Se, 99.99%, powder), and zinc oxide (ZnO, 99.99% powder) were purchased from Aldrich. n-hexane (analytical grade) and methanol (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China.

### Stock Solution for Cd Precursor and Se Precursor

Solution for Cd Precursor: a mixture (4 g in total) of CdO (0.0154 g, 0.12mmol), OA (0.36mmol), and ODE was loaded in a 25 mL three-neck flask, then it was heated to 240 °C under nitrogen to obtain a colorless clear solution. Stock solution Se: It was made by degassing Se (0.188 g, 2.4 mmol), OA (1.94g, 7.2mmol) and 18ml of ODE in a 50 ml three-neck flask, the mixture was heated to 100 °C for 20 min and subsequently heating the mixture under nitrogen at 220 °C for 3 h. During this time, the color of the mixture changed from transparent to orange and red, and finally turned into yellow.

### Stock Solution for Shell Growth

The zinc precursor solution (0.1 M) was prepared by dissolving ZnO (0.1628 g, 2 mmol) in the mixture of OA (5.64 g, 16 mmol) and ODE (13.70 mL) at 310 °C. The cadmium precursor solution (0.1 M) was prepared by dissolving CdO (0.256 g, 2mmol) in the mixture of OA (5.64 g, 16mmol) and ODE (13.7 mL) at 240 °C. The sulfur precursor solution (0.1 M) was prepared by dissolving sulfur (0.064 g, 2 mmol) in ODE (20 mL) at 150 °C. All precursor solutions were made under a nitrogen flow.

### **Synthesis of CdSe QDs**

Solution for Cd Precursor in 25 ml flask was heated to 280 °C under nitrogen gas flow. Next, 2ml (0.24 mmol) Se stock solution was injected into the above flask. The color of solution turned into light orange right after injection, then changed to orange, light red, red, and dark red as the increase of reaction time. Aliquots were taken at different time intervals, Ultraviolet-visible absorption and photoluminescence (PL) spectra were recorded for each aliquot. PL spanning most of the visible spectra from 470nm to 650nm were obtained. The temperature of the Se precursor for the injection is important for synthesizing high quality CdSe QDs. The temperature range from 20 to 280 °C of Se precursor could be used to synthesize CdSe QDs. But the higher the temperature, the better the quality of CdSe QDs is, and preferably about 280 °C. The resulting CdSe QDs could be dissolved in chloroform, hexanes, and toluene, respectively.

### **Synthesis of CdSe/ZnS core-shell QDs**

Nearly monodisperse CdSe QDs ranging from 1.8 nm to 5.5 nm in diameter were synthesized and purified, respectively. By choosing different sizes of CdSe as core, core-shell QDs with emitting color cover from green to red have been synthesized. A typical synthesis was performed as follows: 3 mL of ODE and 1 g of OA were loaded into a 25 mL reaction vessel. The CdSe QDs in hexane (2.8 nm in diameter,  $2.7 \times 10^{-7}$  mol) were added, and the system was kept at 100 °C under N<sub>2</sub> flow for 30 min to remove the hexane and other undesired materials of low vapor pressure. Subsequently, the solution was heated up to 160 °C under N<sub>2</sub> flow where the shell growth was performed. The amounts of the injection solutions injected for each step were as follows: 0.52 mL of the Cd and S solutions for the first layer and the temperature was slowly raised to ~180°C in ~5 min. 0.77 mL of each injection solution for the second layer and the temperature was slowly raised to ~200°C in ~5 min, 1.1 mL of each injection solution for the third layer and the temperature was slowly raised to ~220°C in ~5 min, 1.45mL of each injection solution for the fourth layer the temperature was slowly raised to ~240°C in ~5 min, and 2.0 mL of each injection solution for the fifth layer and keep the temperature at 240°C for 30 min. This slow temperature jump not only enhances the reaction yield, but also improves the crystallinity. We found that a period of 10 min between each addition was sufficient for the reaction to be completed, because the UV-vis and PL spectra showed no further changes after this time period.

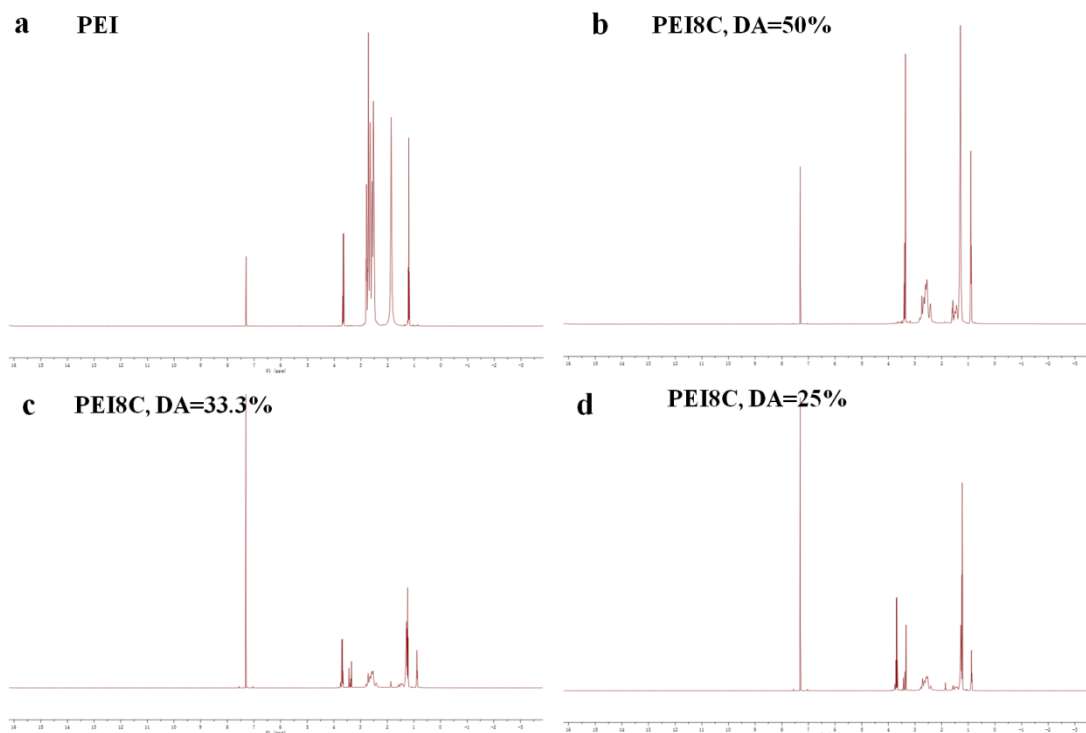
### **The procedure for Synthesizing ODA-Ag QDs**

Ag NCs were made by adding AgNO<sub>3</sub> (0.5 g) to solvent octadecylamine (ODA, 10 mL) at 180 °C. The mixture was magnetically stirred for 10 min in air. After reaction, particles were collected at the bottom of the beaker.

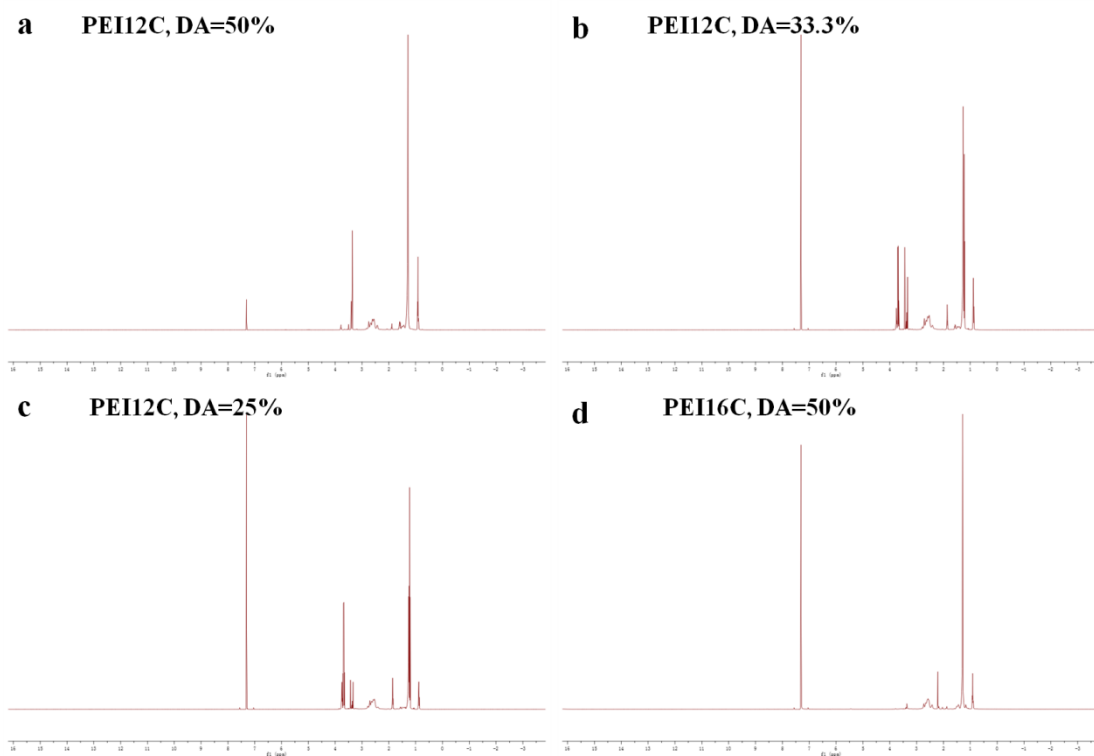
### **The procedure for synthesizing OA-Fe<sub>3</sub>O<sub>4</sub> QDs**

FeO(OH) (0.178g, 2.00nmol) was added to the mixture containing paraffin oil (5mL) and OA (1.13g, 4.00m mol) in a three-necked flask. The mixture was heated to 150 °C for 15 min under nitrogen, and then heated to 320 °C for another 30 min after it was heated to 430 °C for 5 min. During this time, the solution turned from turbid

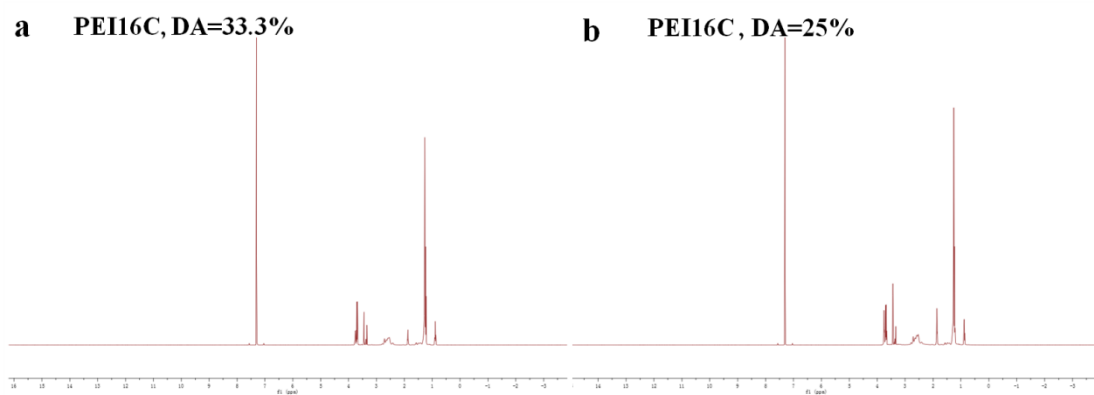
black to clear reddish-brown as the iron source material dissolved. Ultimately, the obtained clear black solution was cooled to room temperature slowly. A mixture of hexane (10 mL) and methanol (100 mL) was added to the mixture to precipitate the NCs. The NCs were separated by centrifugation and then washed for three times with the mixture of hexane and methanol. These NCs can be easily redispersed in chloroform.



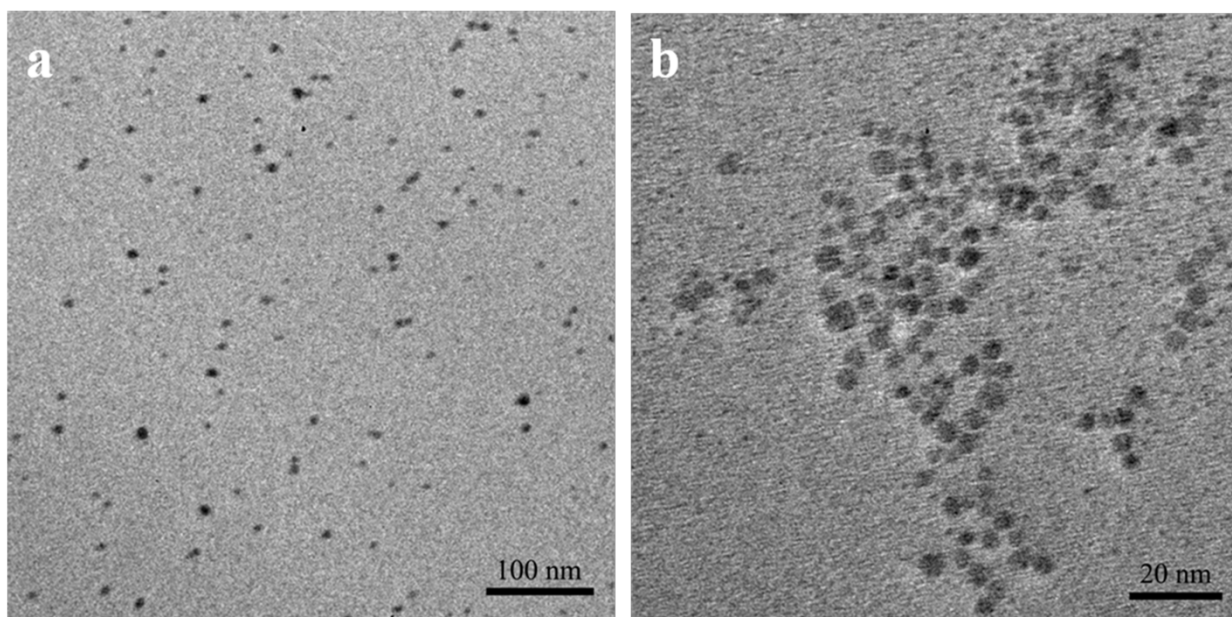
**Fig. S1.** <sup>1</sup>H NMR spectra of (a) PEI and PEI8C with (b) 50%, (c) 33.3%, and (d) 25% DA.



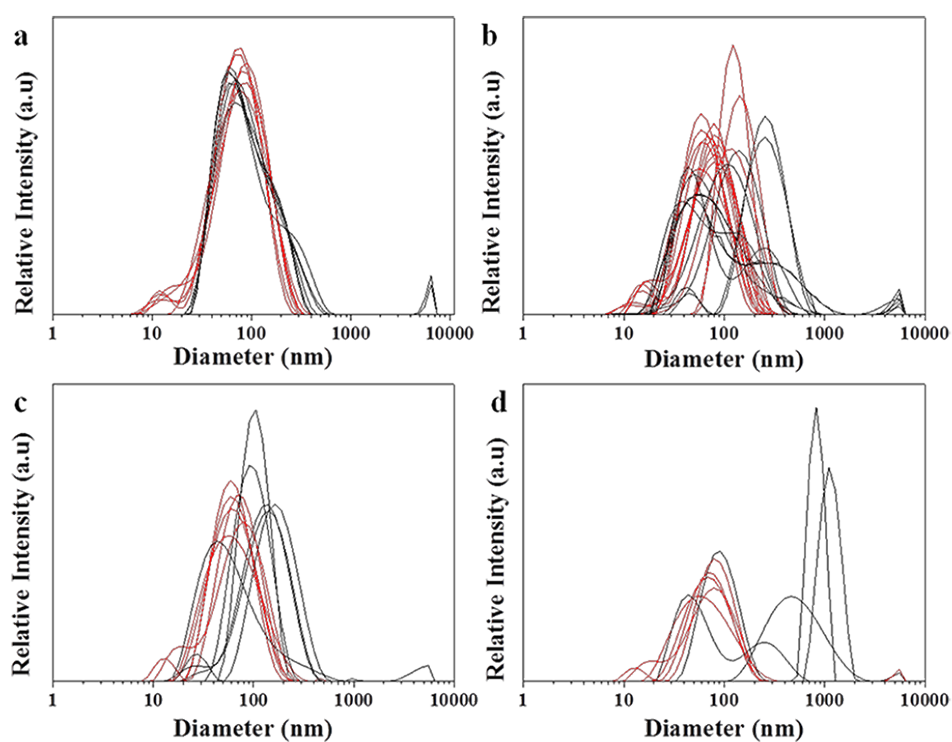
**Fig. S2.** <sup>1</sup>H NMR spectra of PEI12C with (a) 50% (b) 33.3% and (c) 25% DA; (d) PEI16C with the 50% DA



**Fig. S3.** <sup>1</sup>H NMR spectra of PEI16C with (a) 33.3% and (b) 25% DA;



**Fig. S4.** TEM images of (a) PEI12C-Ag and (b) PEI12C-Fe<sub>3</sub>O<sub>4</sub>



**Fig. S5.** (a) Temperature, (b) pH, (c) PBS buffer, and (d) NaCl solution stability tests of red emitting PEI-QDs (black solid line) and PEI12C-QDs (red solid line). The hydrodynamic diameters depicted in Fig. S5 were determined from the intensity distribution