Supporting Information

Regulating Properties of Quantum Dots: Effect of Methyl Side Groups of Mercapto Acids

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Synthesis of MBA

17.2 g (0.2mol) of γ-butyrolactone, 15.2 g (0.2mol) of thiourea and 40 g (0.24mol) of hydrobromic acid (48% in water) was refluxed with mechanical stirring for 12 hours. The reaction product was adjusted to strongly alkaline with a solution of 25 g of sodium hydroxide in 90 mL of water. The intermediate isothiourea derivative was then hydrolyzed by refluxing for 2 hours before it was cooled to room temperature and acidified with sulphuric acid (pH=2) and extracted with ether (3×100mL). The solvent was evaporated, and then the residue was further distilled to give 15.0 g (62%) of product.

Synthesis of MVA

A mixture of 2.0 g (11mmol) of 5-bromopentanoic acid, 1.1 g (14mmol) of thiourea and 11ml of water was refluxed with mechanical stirring for 3 hours before 7.5ml of 3M NaOH was added. After another 1 hour of refluxing, the mixture was cooled to room temperature. The sulphric acid (or hydrochloric acid) was added to adjust the pH to 2. The mixture was extracted by ether (6*30ml) and dried by $MgSO_4$ overnight. After removing solvent, crude MVA was obtained. Crude MVA could be further purified by silica gel column chromatogram with ethyl acetate. Yield 1.3g (89%).

Synthesis of 3MBA

3MBA was synthesized from crotonic acid and thioacetic acid via 3-acetylmercaptobutyric acid by adding 26mL of thioacetic acid to 20 g of crotonic acid. The reaction mixture was stirred for 24 h at 25^{o}C and subsequently for 6 h at 50^{o}C. For alkaline hydrolysis, the obtained 3-acetyl mercaptobutyric acid was treated with mixture of 105mL concentrated ammonia and 105mL of deionized water for 30min. The solution was acidified to pH=3 with sulfuric acid (98%) and extracted with 2×150 mL of diethyl ether. The organic phase was collected and the aqueous phase was further treated with diethyl ether to obtain the remaining 3MBA. By distillation, 16.12g of 3MBA was finally obtained. Yield: 57.5%.

Synthesis of MMBA

6mL of thioacetic acid and 5.01 g of tiglic acid was mixed and stirred for 24 h at 25 ^{o}C before heated at 50 ^{o}C for 45 h. Then the solution was treated with mixture of concentrated ammonia and water for 30min. Afterwards, the solution was acidified to pH=3 with concentrated sulphuric acid. The product was extracted by ether (5×150mL). Solvent evaporated under reduced pressure, yellow crude product was further purified by silica gel column chromatogram in ether. Yield: 1.3g (89%).

Synthesis of MDMPA

The mixture containing 100mL of HBr (40 wt%) and 5.04 g of 2,2-dimethyl-3-hydroxypropionic acid was refluxed for 96 h before it was cooled to room temperature. Then 100mL of ether was added into the mixture and the pH of the mixture was adjusted to 1~2 by NaOH. The mixture was extracted by chloroform (5×100mL) to obtain crude intermediate 3-bromo-2,2-dimethylpropanoic acid. 1.13g of crude intermediate 3-bromo-2,2-dimethylpropanoic acid was mixed with 90mL of anhydrous tetrahydrofuran, 866 uL of triethylamine and 0.80g of potassium thioacetate and stirred overnight. After the removal of tetrahydrofuran, the mixture was treated with 1M HCl (2×100mL). Purified by silica gel column chromatogram in hexane and ethyl acetate (4:1), crude intermediate 3-(acetylthio)-2,2-dimethylpropanoic acid was obtained. 0.36g of crude intermediate 3-(acetylthio)-2,2-dimethylpropanoic acid was mixed with 7.5mL of concentrated ammonia and 7.5mL of deionized water and stirred for 15min at room temperature. Then the solution was acidified with concentrated HCl and extracted by ether (2×50mL). MDMPA could be obtained by removing solvent. Yield: 0.3g (5%).

Measurement of QY

Samples for absorption and fluorescence measurement were carried out immediately after they were prepared by the hydrothermal method. The solution of QDs was diluted to avoid fluorescent self-quenching before measurement. Samples were excited at 450 nm with fluorescein (pure, J&K, QY=79%) in 0.1M NaOH as the fluorescent standard reference. The fluorescein was cross-calibrated at 480nm using Rhodamine 6G (pure, J&K, QY=95%) in absolute ethanol to ensure that the experimental quantum yields matched their literature counterparts within ±5%.

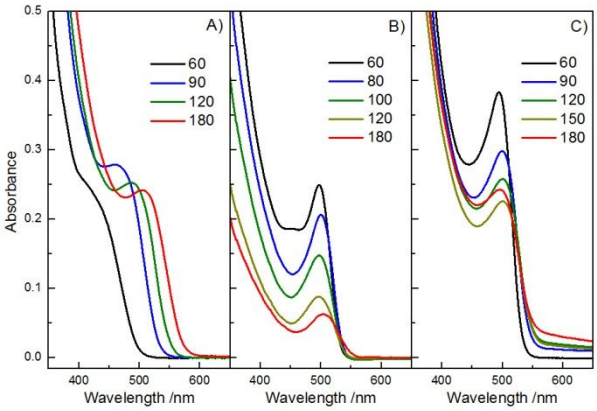

Fig. S7 Temporal evolution of the absorption spectra of QDs capped with MVA (A), MMBA (B) and MDMPA (C).