Supporting Information

3-Mercaptobutyric Acid as an Effective Capping Agent for Highly Luminescent CdTe Quantum Dots: New Insight into Selection of Mercapto Acids

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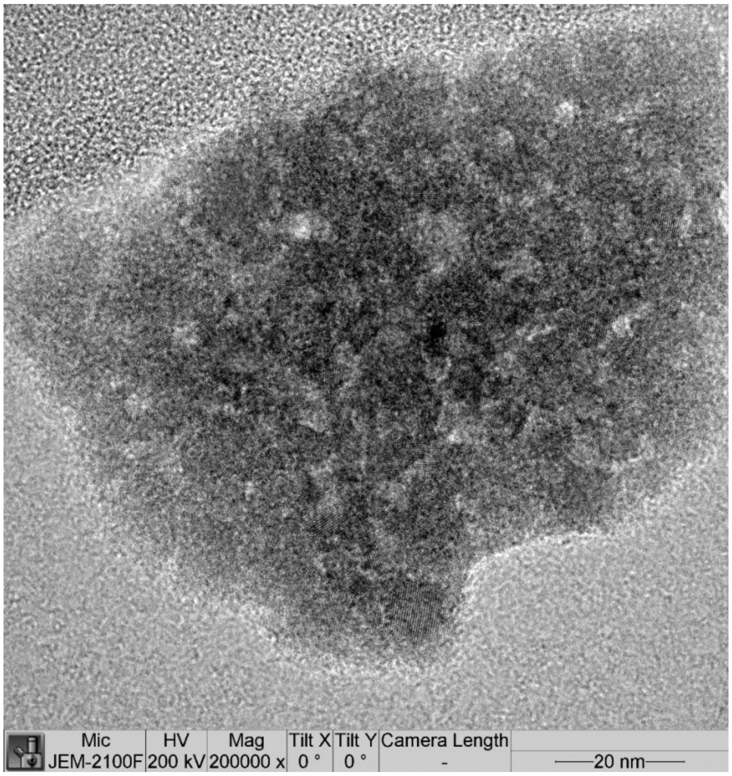


Figure S1. High-resolution TEM image of precursor solution of TGA-modified CdTe QDs.

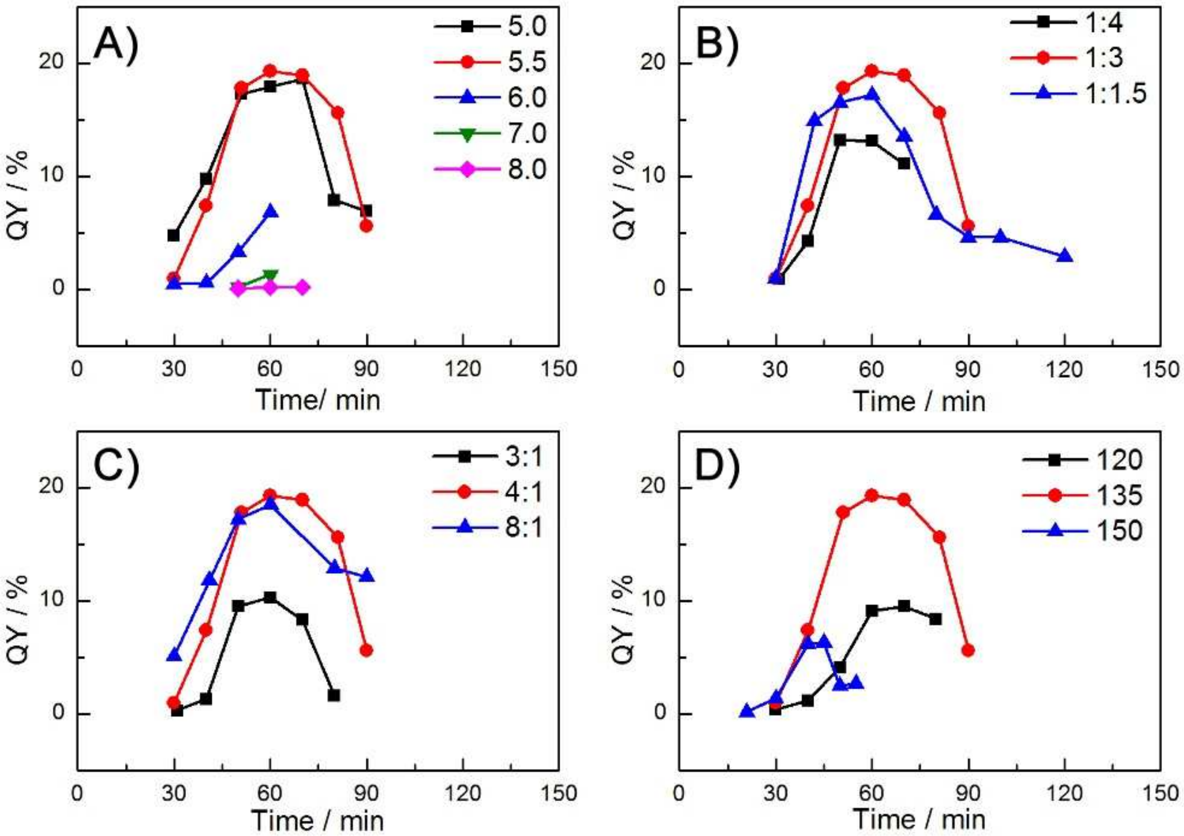


Figure S2. The QY of as-synthesized TGA-modified QDs as a function of reaction time at different experiment condition: (a) different pH, Cd:TGA:TeO_3^{2-}=1:3:0.25 and reaction temperature=135 °C, (b) different Cd/TGA ratio, pH=5.5, Cd:TeO_3^{2-}=1:0.25 and reaction temperature=135 °C (c) different Cd/Te ratio, pH=5.5, Cd:TGA=1:3 and reaction temperature=135°C, and (d) different reaction temperature, Cd:TGA:TeO_3^{2-}=1:3:0.25 and pH=5.5

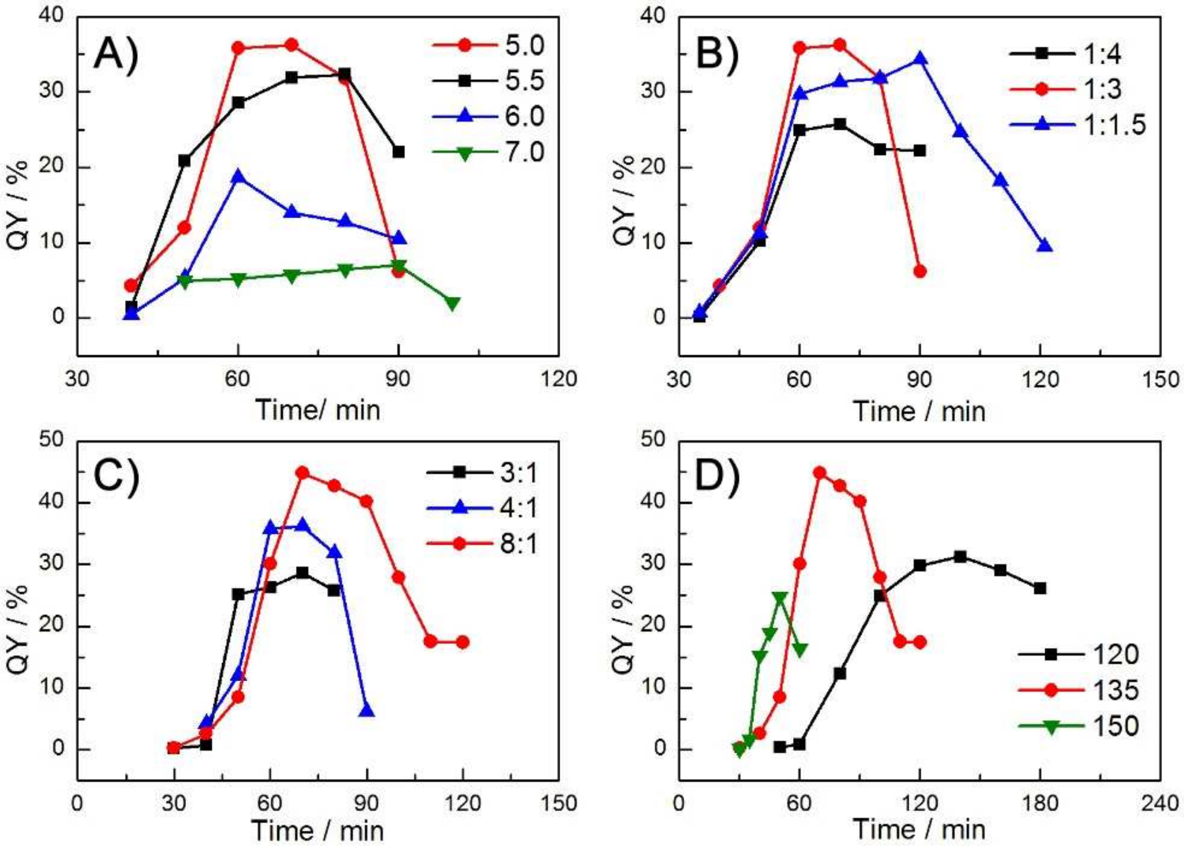


Figure S3. The QY of as-synthesized TLA-modified QDs as a function of reaction time at different experiment condition: (a) different pH, Cd:TLA:TeO_3^{2-}=1:3:0.25 and reaction temperature=135 ^{o}C, (b) different Cd/TLA ratio, pH=5.5, Cd:TeO_3^{2-}=1:0.25 and reaction temperature=135 ^{o}C (c) different Cd/Te ratio, pH=5.5, Cd:TLA=1:3 and reaction temperature=135 ^{o}C, and (d) different reaction temperature, Cd:TLA:TeO_3^{2-}=1:3:0.25 and pH=5.5

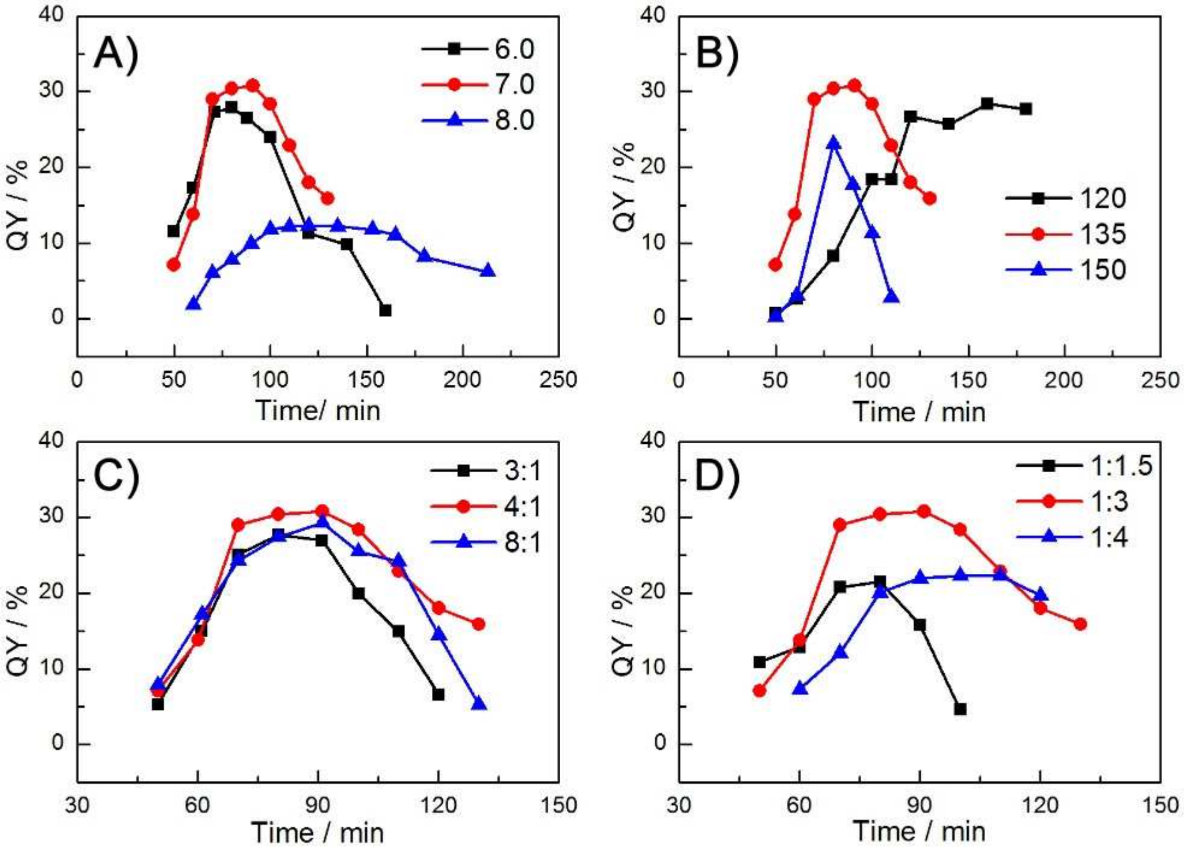


Figure S4. The QY of as-synthesized MPA-modified QDs as a function of reaction time at different experiment condition: (a) different pH, Cd:MPA:TeO_3^{2-}=1:3:0.25 and reaction temperature= 135 °C, (b) different reaction temperature, pH=7.0 and Cd:MPA:TeO_3^{2-}=1:3:0.25 (c) different Cd/Te ratio, pH=7, Cd:MPA=1:3 and reaction temperature= 135 °C, and (d) different Cd/MPA ratio, Cd: TeO_3^{2-}=1: 0.25, pH=7.0 and reaction temperature= 135 °C.

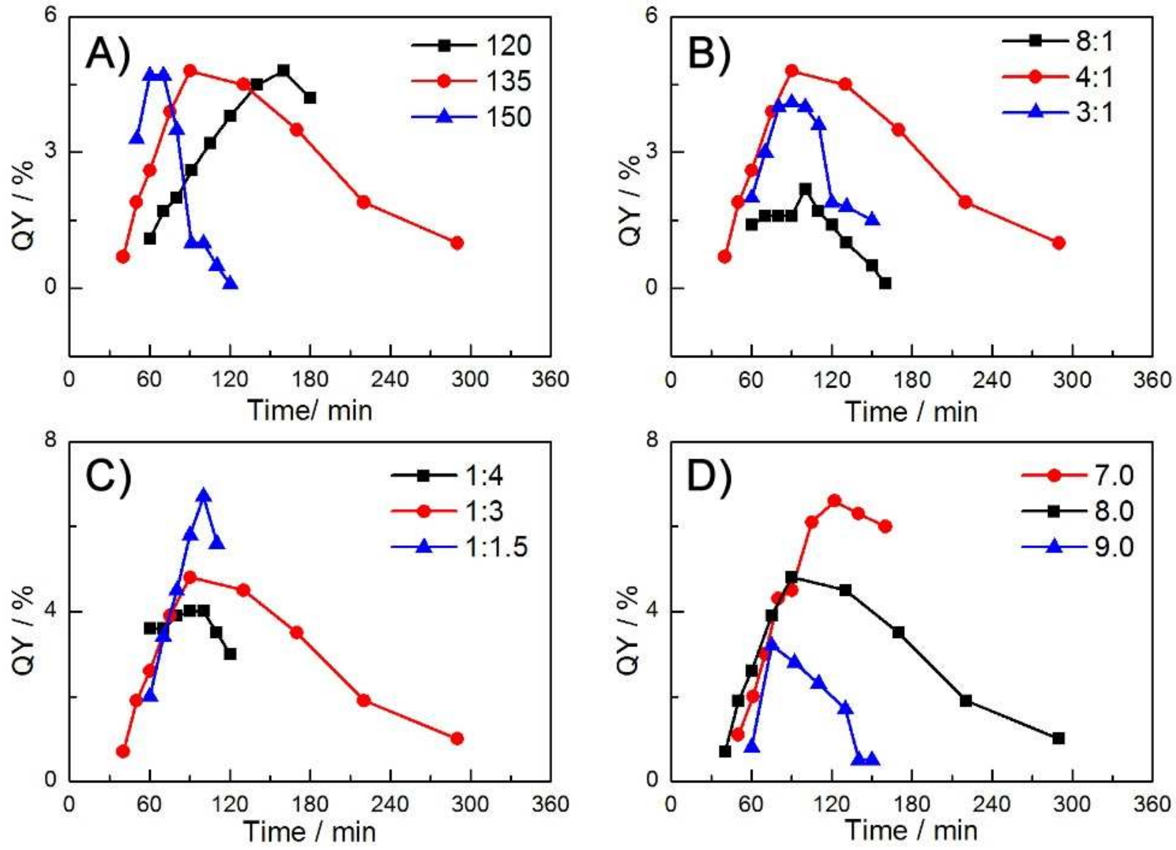


Figure S5. The QY of as-synthesized MBA-modified QDs as a function of reaction time at different experiment condition: (a) different reaction temperature, pH=7.0 and Cd:MBA:TeO_3^{2-}=1:3:0.25 (b) different Cd/Te ratio, pH=7.0, Cd:MBA=1:3 and reaction temperature=135 °C (c) different Cd/3MBA ratio, pH=7.0, Cd:TeO_3^{2-}=1:0.25 and reaction temperature=135 °C and (d) different pH, Cd:MBA:TeO_3^{2-}=1:3:0.25 and reaction temperature=135 °C.

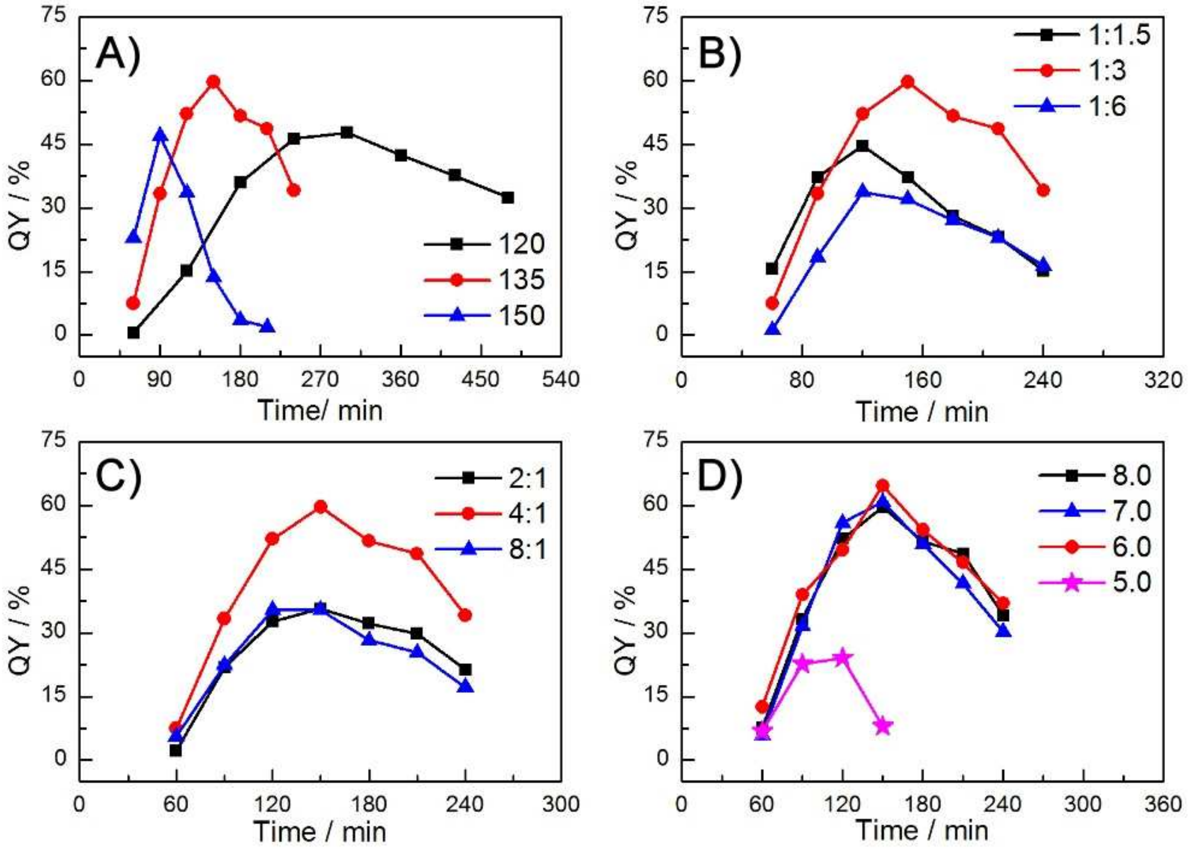


Figure S6. The QY of as-synthesized 3MBA-modified QDs as a function of reaction time at different experiment condition: (a) different reaction temperature, pH=7.0 and Cd:3MBA:TeO_3^{2-}=1:3:0.25, (b) different Cd/3MBA ratio, pH=7.0, reaction temperature=135 ^{o}C and Cd: TeO_3^{2-}=1: 0.25 (c) different Cd/Te ratio, pH=7.0, reaction temperature=135 ^{o}C andCd: 3MBA=1:3 and (d) different pH, Cd:3MBA:TeO_3^{2-}=1:3:0.25 and reaction temperature=135 ^{o}C.

S7: The Measurement of QY of CdTe QDs

The fluorescent measurement was carried out immediately after samples of QDs were prepared. Briefly, 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%. The QY was calculated using the following equation:

$$Q_s = Q_r \times \frac{I_s \times A_r \times n_s^2}{I_r \times A_s \times n_r^2}$$

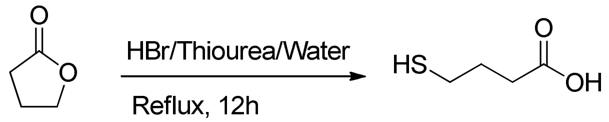
Where Q = quantum yield; I = integrated area of emission spectrum; A = absorbance at the excitation wavelength; n is the refractive index of the solvent; and the subscripts s and r refer to the CdTe NCs and the reference, respectively.

Reference

(1)http://www.jobinyvon.co.uk/SiteResources/Data/MediaArchive/files/Fluorescence/applications/quantumyieldstrad.pdf

(2) Talapin, D. V.; Rogach, A. L.; Shevchenko, E. V.; Kornowski, A.; Haase, M.; Weller, H. *J. Am. Chem. Soc.* **2002**, *124*, 5782.

S8: Synthesis of MBA

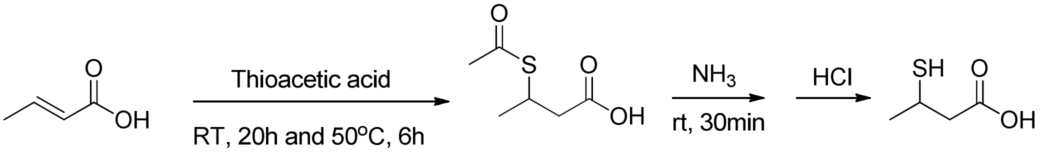


MBA was synthesized according to literature. 17.2 g (0.2mol) of γ-butyrolactone, 15.2 g (0.2mol) of thiourea and 40 g (0.24mol) of hydrobromic acid (48% in water) was refluxed with mechanical stirring for 12 hours. The reaction product was adjusted to strongly alkaline with a solution of 25 g of sodium 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 γ-mercaptobutyric acid. ^{1}HNMR ($CDCl_3$, ppm) 1.36 (t, 1H), 1.94 (m, 2H), 2.51 (m, 4H), 10.23 (b, 1H). ^{13}CNMR ($CDCl_3$, ppm) 23.84, 28.64, 32.37, 179.54.

Reference

Schotte, L. *Arkiv foer Kemi* **1955**, *8*, 457.

S9: Synthesis of 3MBA

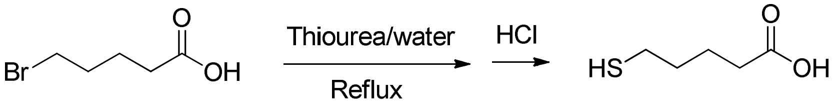


3MBA was synthesized from crotonic acid and thioacetic acid via 3-acetylmercaptobutyric acid by adding 6mL of thioacetic acid to 20 g of crotonic acid. The reaction mixture was stirred for 24 h at 25 °C and subsequently for 6 h at 50 °C. For alkaline hydrolysis, the obtained 3-acetyl mercaptobutyric 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%. Anal. Calcd. for $C_4H_8O_2S$: C, 39.98; H, 6.71; S, 26.63; Found: C, 39.89; H, 6.77; S, 26.44. 1HNMR ($CDCl_3$, ppm) 1.42(d, 3H), 1.88(d, 1H), 2.67(m, 2H), 3.37(m, 1H), 10.48(b, 1H); 13CNMR ($CDCl_3$) 24.77, 30.84, 45.55, 177.56

Reference

Luetke-Eversloh, T.; Bergander, K.; Luftmann, H.; Steinbuechel, A. *Biomacromolecules* **2001**, *2*, 1061.

S10: Synthesis of MVA



2.0g (11mmol) of 5-bromovaleric acid, 1.1g (14mmol) of thiourea and 11mL of water were added into a flask. This mixture was refluxed with mechanical stirring for 3 hours. 7.5mL of 3.0 M sodium hydroxide was added in product. Then the mixture was refluxed for 1 hour. The solution was acidified with sulphuric acid (pH=2) and extracted with ether (6×30mL). The organic phase was dried by $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The yellow crude product was purified by silica gel column chromatogram with ether. Yield: 1.3g (89%) of product. Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.75; H, 7.51; S, 23.89; Found: C, 45.06; H, 7.48; ^{1}HNMR (400MHz, $CDCl_3$, ppm) 1.37(t, 1H), 1.71(m, 4H), 2.39 (t, 2H), 2.54(t, 2H), 9.62(b, 9.62); ^{13}CNMR (400MHz, $CDCl_3$, ppm) 23.32, 24.18, 33.21, 33.44, 179.77.

S11: Synthesis of CdSe QDs

CdSe QDs were synthesized by the method reported by Chen and coworkers with some modification. First, 0.02 M sodium selenosulphate was prepared by refluxing 0.5 g sodium sulfite and 0.05 g selenium powders in 33 mL water at 80 ^{o}C under nitrogen atmosphere until all of the selenium powder was dissolved. The prepared colorless sodium selenosulphate solution was stored under in sealed flasks for later use. In a typical process to synthesize CdSe QDs, solution containing cadmium acetate and MPA was adjusted to pH 9.3 with 1 M NaOH solution. The solution was then de-aereated by bubbling with nitrogen for 1 h. Under vigorous stirring, desired amounts of the stored oxygen-free 0.02 M sodium selenosulphate solution were injected. The concentration of cadmium in the final solution was 5 mM with the molar ratio of Cd to MPA 1:2.4 and Cd to Se 10:1. After another stirring for 30 min, 15ml of the solution was transferred a 25-mL Teflon-lined stainless steel autoclave and incubated in an oven at 165 ^{o}C for a desired period. Afterward, the autoclave was cooled by hydro-cooling method. Resulting samples were kept at room temperature in the dark.

Reference

Chen, X. F.; Hutchison, J.; Dobson, P.; Wakefield, G. *Journal of Materials Science* **2009**, *44*, 285.

S12: Aqueous synthesis of CdTe QDs using NaHTe

CdTe QDs were synthesized by the method reported by Zhang and coworkers (Ref. 36) with some modification. Briefly, freshly prepared NaHTe solution was injected into a de-aerated solution containing Cd^{2+} and mercapto acid before the final solution was transferred into autoclaves and heated in the oven. Typically, $[Cd^{2+}]$ = 1.25 mM, Cd : Te : mercapto acid= 1 : 0.5 : 2.4 , pH = 9.0, 135 °C. The comparison between the QY of as-synthesized TGA-modified, MPA-modified and 3MBA-modified QDs as a function of reaction time was shown in Figure S12.

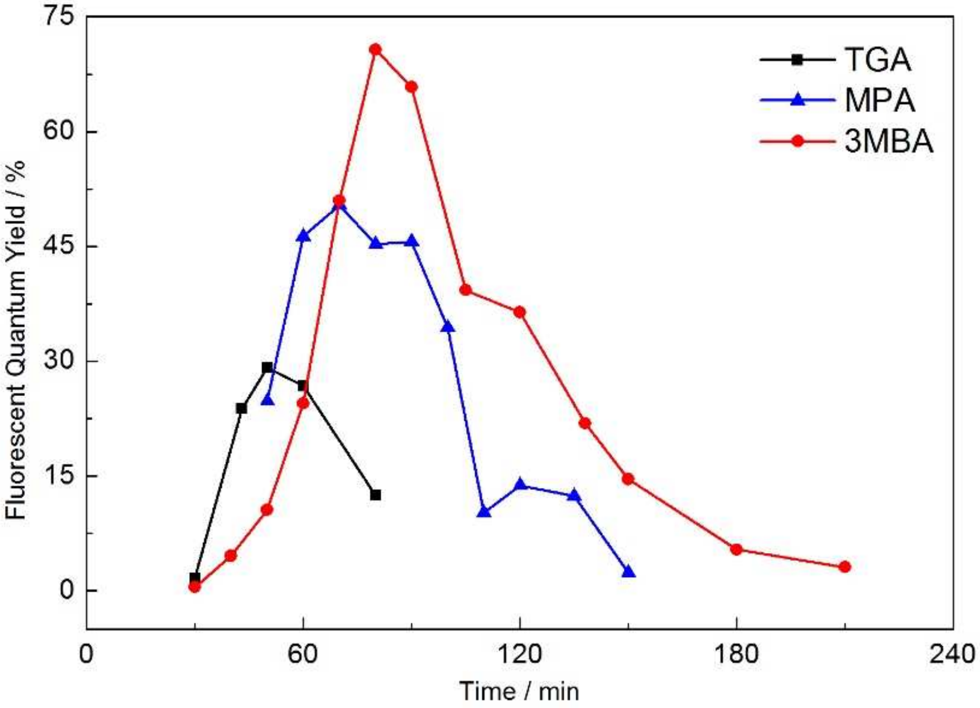


Figure S12. The QY of as-synthesized QDs using different mercapto acids as a function of reaction time with NaHTe as Te source.