Amphiphilic $p$-sulfonatocalix[4]arene-coated CdSe/ZnS quantum dots for the optical detection of the neurotransmitter acetylcholine

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1. Preparation of CdSe/ZnS quantum dots (QDs)

a) CdSe QDs: The mixture of CdO (13 mg, 0.1 mmol) and stearic acid (250 mg) was loaded into a 25 mL three-necked flask and heated to 200 °C under Ar flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. Then, TOPO (3 g) and hexadecylamine (1 g) were added, and the mixture was heated to 300 °C. At this temperature, the Se solution (80 mg Se in 1 mL trioctylphosphine, TOP) was quickly injected by means of a syringe. The reaction mixture was stirred for a few minutes at 260 °C, yielding a deep red solution of CdSe nanocrystals. The mixture was allowed to cool down to 60 °C and 20 mL of chloroform was added. Then CdSe nanocrystals were precipitated by addition of methanol. The precipitate was dissolved in 10 mL of chloroform, and an insoluble material was removed by centrifugation. The CdSe nanocrystals were recovered by addition of methanol, and the product was separated by centrifugation and air-dried at room temperature.

b) Overcoating of CdSe QDs with ZnS: The mixture of one batch CdSe nanocrystals and 5 g of TOPO was heated to 210 °C under Ar flow. A Zn-S stock solution (1.2 mL) was slowly added to the CdSe nanocrystal solution by a syringe, and the mixture solution was stirred at 110 °C for 5 h. (The Zn-S stock solution was prepared by mixing 3.5 mL (3.5 mmol) of ZnEt$_2$ hexane solution (1M) and 0.52 mL (2.5 mmol) of (TMS)$_2$S in 6.0 mL TOP.) The solution was allowed to cool down to 60 °C and 20 mL of chloroform was added. Then CdSe/ZnS nanocrystals were precipitated by addition of methanol. The product was separated by centrifugation and air-dried at room temperature.


The tetrasodium salts of $p$-sulfonatocalix[4]arene (1.0 g, 1.3 mmol) was mixed with NaOH (1.0 g, 25 mmol) in 5 mL water and 20 mL dimethyl sulfoxide. Then, 4 mL (29 mmol) of 1-bromohexane was added, and the mixture was heated at 50 °C for 24 h. After cooling, the solution was diluted with methanol to precipitate. The precipitate was dissolved in 5 mL of water and an insoluble material was removed by filtration. The product was precipitated from the filtrate by addition of ethanol. This operation was...
repeated three times in order to remove NaBr. $^1$H NMR data for 3 (Me$_2$SO-$d_6$): $\delta$ 1.00 (CH$_3$(CH$_2$)$_5$, s, 12H), 1.46 (CH$_3$(CH$_2$)$_3$CH$_2$CH$_2$O-, s, 24H), 2.03 (CH$_3$(CH$_2$)$_3$CH$_2$CH$_2$O-, s, 8H), 3.34 (ArCH$_2$Ar, d, $J$ 12.6 Hz, 4H), 3.96 (CH$_3$(CH$_2$)$_3$CH$_2$CH$_2$O-, t, 8H), 4.44 (ArCH$_2$Ar, d, $J$ 12.6 Hz, 4H), 7.21 (ArH, s, 8H).


1 mg of TOPO capped CdSe/ZnS QD was dispersed in 1 mL of tetrahydrofuran, and then 20 mg of 3 was added. After the mixture dispersion was sonicated for 30 second using a bath-type sonicator, 3 mL of dimethylformamide was added. The sedimented precipitate was separated using a centrifuge and dispersed in 20 mL water. The aqueous QD dispersion was sonicated for 5 min and filtered using 0.2 $\mu$m disposal filter.