**Supplementary Information** 

## Anodic Electrogenerated Chemiluminescence of Quantum Dots: Sizes and Stabilizers Matter

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## Part 1 Experimental details

**Synthesis of the water-soluble QDs.** CdTe QDs were prepared using the reaction between  $Cd^{2+}$  and  $H_2Te$  gas in the presence of 3-mercaptopropionic acid (MPA) or 2-mercaptoethylamine (MEA) as stabilizers according to the approach described in the reference.<sup>1</sup> Briefly, 62.5 mL of 0.498 g CdClO<sub>4</sub>·6H<sub>2</sub>O (0.0012 mol) was mixed with MPA ( $3.1 \times 10^{-3}$  mol) and the pH of the mixture was adjusted to 11 by dropwise addition of 1 M NaOH. The clear solution was bubbled with highly pure N<sub>2</sub> for 30 min. Then, H<sub>2</sub>Te gas (generated by the reaction of 0.05 g ( $1.14 \times 10^{-3}$  mol) of Al<sub>2</sub>Te<sub>3</sub> lumps with 4 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub> under N<sub>2</sub> atmosphere) is passed through the solution together with a slow nitrogen flow for 20 min, and the solution was refluxed at 110 °C in an oil bath under N<sub>2</sub> gas for different periods of time. The MEA-capped CdTe QDs was also synthesized using the general procedure, except using MEA as stabilizer and adjusting the pH of the mixture to 5.0. The obtained QDs solution was stored in a refrigerator at 4 °C. The concentration of the nanoparticles was estimated with the UV-Vis spectrum according to the empirical equations proposed by Peng and co-workers.<sup>2</sup>

Synthesis of the radical trapper 5-*tert*-butoxycarbonyl-5-methyl-1-pyrroline-n-oxide (BMPO). The radical scavenger, BMPO, was synthesized as Scheme S1:<sup>3</sup>

(1) Synthesis of tert-Butoxyl 2-bromopropionate. 8.2 g tert-butanol (0.11 mol) and 8.5 g pyridine (0.11 mol) were dissolved in 50 mL choloroform, and then 21.6 g 2-bromopropionyl bromide (0.1 mol) in 10 mL choloroform was dropped slowly into the above mixture with stirring at 0 °C. The mixture reacted at room temperature for 2 h. Then the reaction mixture was washed with 80 mL H<sub>2</sub>O, 80 mL 10% H<sub>2</sub>SO<sub>4</sub> and 50 mL saturated sodium bicarbonate solution twice until it became colorless. The colorless reaction mixture was dried with magnesium sulfate and the solvent was removed in a rotary evaporator to obtain pure *tert*-butoxyl 2-bromopropionate.

(2) Synthesis of butoxyl 2-nitropropionate. 18.7 g tert-butoxyl 2-bromopropionate (0.1 mol) was added with stirring to a mixture of 150 mL anhydrous dimethylformamide, sodium nitrite (13.4 g, 0.19 mol) and phloroglucinol (17.3 g, 0.11 mol). The mixture reacted at 25 °C for 3.5 h. Then the reaction mixture was poured into 300 mL ice-cold water with 50 mL ether, followed by extracted with ether ( $3 \times 50$  mL), washed with saturated sodium bicarbonate solution three times, and dried with magnesium sulfate. At last, removal of the solvent resulted in the residual yellow liquid, which was distilled to give butoxyl 2-nitropropionate.

(3) Synthesis of 2-butoxycarbonyl-2-nitro pentanal. 11.8 g butoxyl 2-nitropropionate (0.067 mol) was added to a sodium ethoxide solution, and 6.5 mL acrolein was subsequently added. The mixture was refluxed at 40  $\sim$  50 °C for 4 h, acidified with 0.2 mL acetic acid, and extracted with 80 mL dry ether. The ether extract was then passed through a silica gel column and eluted with a 3:1 mixture of hexane: ethyl acetate. The solvent was removed to yield 2-butoxycarbonyl-2-nitro pentanal.

(4) Synthesis of dioxolan derivative. The 2-butoxycarbonyl-2-nitro pentanal was refluxed in 90 mL benzene containing ethylene glycol (8.3 g, 0.13 mol) and *p*-toluene sulfonic acid (50 mg). The obtained 1:3 dioxolan derivative was distilled to yield pure product.

(5) Synthesis of BMPO. The dioxolan derivative was reduced with zinc dust (8.0 g) in 70 mL of 50% aqueous ethanol containing2.0 g of ammonium chloride at  $0 \sim 5$  °C. After stirring for 3.5 h, the mixture was filtered, and the filtrate was concentrated and extracted with  $4 \times 25$  mL chloroform. The chloroform extract was then dried and the solvent was evaporated. The residual oil was treated with 100 mL 0.3 M HCL at room temperature until complete hydrolysis and liberation of the aldehyde. Then 10 mL concentrated ammonia solution was added to this acid solution and extracted with  $4 \times 25$  mL chloroform after saturating with sodium borate. The chloroform extract was dried and removal of the solvent yielded a white solid. The white solid was recrystallized with methanol to yield pure BMPO solid.

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Part S2: Characterization of the obtained quantum dots (QDs)

**Figure S1.** Absorption and PL spectra ( $\lambda_{ex} = 380 \text{ nm}$ ) of as prepared CdTe nanocrystals. The stabilizers used were MEA (A), and MPA (B, C). The average size of CdTe nanoparticles is 1.84 nm, 1.83 nm and 3.13 nm, respectively.

Part S3: Mechanism for ECL behaviors of CdTe QDs



**Figure S2.** (A) ECL curves of 1.4  $\mu$ M MPA-capped CdTe QDs with continuous cyclic potential scan from 0 V to +1.8 V. The average size of CdTe QDs is 3.13 nm. (B) ECL curve of 1.4  $\mu$ M MPA-capped CdTe QDs at the first scan and the tenth scan. Scanning rate: 50 mV·s<sup>-1</sup>. (C) CV curves of 1.4  $\mu$ M MPA-capped CdTe QDs with continuous cyclic potential scan from 0 V to +1.8 V. Scanning rate: 50 mV·s<sup>-1</sup>.



**Figure S3.** CV and ECL curves of 1.4  $\mu$ M MPA-capped CdTe nanoparticles in 0.01 M air-saturated PBS (pH 7.4). The average size of CdTe QDs is 3.13 nm. Scanning rate: 50 mV·s<sup>-1</sup>.



**Figure S4.** PL (line a) and ECL (line b: +1.2 V; line c: +1.7 V) spectrum of the MPA-capped CdTe QDs. The average particle size is 3.13 nm.



**Figure S5.** Dependence of ECL intensity on MEA concentration in pH 7.4 PBS containing 1.4  $\mu$ M MPA-capped CdTe QDs collected at air-free and air-saturated.

## REFERENCES

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