Supporting Information

Two-photon excited quantum dots with compact surface coatings of polymer ligands used as an upconversion luminescent probe for dopamine detection in biological fluids

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/

Part S1. Preparation of multidentate polymers

Typically, 1 g of poly(acrylic acid) (PAA, ~14 mmol of -COOH, M_w ~ 2000) was dissolved in 25 mL of dimethyl sulfoxide (DMSO), stirred at 40 °C for 24 h. 0.37 g of mercaptoethylamine (MEA, 4.8 mmol) was dissolved in 10 mL of DMSO, which was mixed with the above solution. Then, 1 mg of *N*-hydroxysuccinimide (NHS, 9 mmol) dissolved in 5 mL DMSO was added, and the resultant mixture was protected from light and bubbled with N_2 flow for 30 min at 40 °C. Subsequently, 0.74 g of *N*,*N*'-diisopropyl-carbodiimide (DIC, 5.8 mmol) was added dropwise over a course of 40 min under vigorous stirring and nitrogen flow. The reaction was allowed to proceed for 4 days at 50 °C in the dark. Afterward, 15 mL of piperidine was added, and the reaction solution was further stirred for 3 h to de-protect the primary amines. 0.5 g of *β*-mercaptoethanol (BME, 6.5 mmol) was added to quench the reaction. The solution was stirred for an additional 2 h at 50 °C. Then the reaction system was cooled to room temperature, centrifuged and filtered, followed by the addition of 40 wt% of NaOH solution to precipitate the polymers with *ca.* 22.5 % of carboxylic acid functional groups modified with the portion of MEA. The precipitates were washed three times with the hot DMSO (50 °C) and then with acetone at room temperature. After filtration, the resulting products (poly(acrylic acid)-*graft*-mercaptoethylamine, PAA-g-MEA) were dried in vacuum at room temperature (with yield of 82.5 % based on MEA), and stored in a vacuum desiccator.

Part S2. Surface modifiaction of PAA-g-MEA coated CdTe QDs

PAA-*g*-MEA coated CdTe QDs were modified by coupling PEG-NH_2 on the surface of QDs directly. In a typical experiment, 1.0 mg mL^{-1} of CdTe QDs dispersed in water were treated with 10 mg mL^{-1} of 6-arm poly(ethylene glycol)-amine (PEG-NH_2) for 10 min under the action of ultrasonic. And then, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) hydrochloride was added (10 mM). The resulting mixture was sonicated for an additional 1 h, followed by the addition of EDC (40 mM) and N-hydroxy-succinimide (NHS, 20 mM), with stirring for 24 h. The reaction was terminated by adding mercaptoethanol. Finally, the reaction solution was purified by centrifugation (12 000 rpm) for 1 h, and the supernatant was collected as products, which were diluted with PBS to obtain surface modified CdTe QDs for further uses in following experiments.

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Part S3. Characterization of the prepared CdTe QDs

The as-prepared CdTe QDs (Sample **No.3**) were characterized by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). As shown in Fig. 2a, these QDs were quasi-spherical particles, with a uniform size and average diameter of ~4.6 nm. The high-resolution TEM (inset of Fig. 2a) and XRD patterns (Fig. S2) indicated that the lattice parameters of QDs fitted well to the zinc blende structure of bulk CdTe crystal. Moreover, the average hydrodynamic diameter of the QDs sample was ~7.8 nm, measured by DLS (Fig. 2b). Based upon the difference of the diameters detected from DLS and TEM, the surface coating thickness of multidentate polymers (PAA-*g*-MEA) was calculated to be ~1.6 nm. In general, such compact surface coating was responsible for the high colloidal/photo-stability and bright (high PLQYs) of the as-prepared QDs.

Part S4. Comparison of QDs-based PL probe for DA detection

Freeman et al. reported that fluorophore-labeled DA linked to phenyl boronic acid-functionalized CdSe-ZnS QDs was utilized to develop competitive assays for the determination of DA [19]. Therein, DA was analyzed with a limit of detection (LOD) of 1 μM. Since any vicinal diol binds to the boronic acid ligand, the analytical value of this method was limited due to the lack of selectivity. Shamsipur et al. reported thioglycolic acid-capped CdTe QDs- laccase hybrid for sensitive detection of DA [20]. Laccase enzyme catalyzed the oxidation of DA, inducing the PL quenching of QDs. This sensor gave a linear calibration over a DA concentration range of 0.3~100 μM (LOD = 0.16 μM). Liu et al. developed 3-aminophenyl boronic acid-functionalized $CuInS_2$ QDs as a near-infrared PL probe for DA determination [21]. The phenylboronic acid of functionalized QDs would form boronate esters with phenyl compounds with vicinal diols, resulting in a quenched PL signal. This analysis for the detection of DA exhibited a linear range of 0.5~40 μM, with a LOD of 0.2 μM. Zhao et al. prepared (3-aminopropyl)triethoxysilane-capped luminescent ZnO QDs for the detection of DA, based upon an electron transfer from QDs to oxidized DA-quinone, indicating a linear proportion in DA concentration range of 0.05~10 μM (LOD = 12 nM) [22]. Ai et al. developed a nanosensor for DA based on PL quenching of silica-coated QDs [23]. DA-quinone (formed by the oxidation of DA) was captured on the silica surface and quenched the PL of QDs by an electron transfer process. PL intensity of QDs was a linear in the DA concentration range from 0.5 μM to 0.1 mM, with a LOD of 0.241 μM. Mu et al. designed adenosine-capped CdSe/ZnS QDs for the DA determination, arising from DA molecules binding onto the surface of QDs that triggered an electron transfer [24]. This probe showed 29.3 nM of LOD in the linear detection range of DA concentration (100 nM~20 μM).

References

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Supporting Information

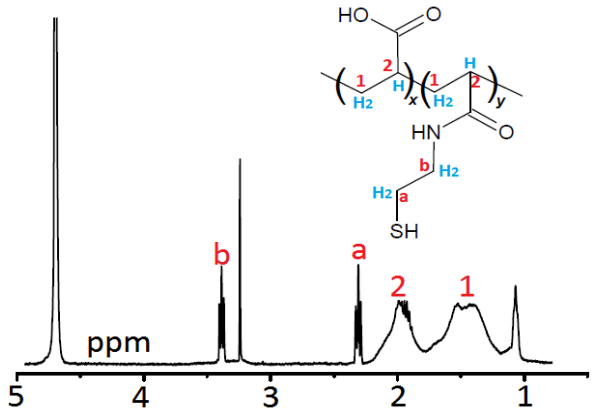

Fig. S1. ^{1}H-NMR spectra of the as-prepared PAA-*g*-MEA polymers.

The nominal 15% of grafting percentage PAA-*g*-MEA polymers were characterized by ^{1}H-NMR (Fig. S1). The actual -SH groups per single PAA chain determined by ^{1}H-NMR spectrum to be ~3.6 of -SH groups based on the peak area ratio between -CH_2 groups from PAA backbone (at 1.35 ppm) and -CH_2 groups connected to –SH groups from the MEA portion (at 2.32 ppm).

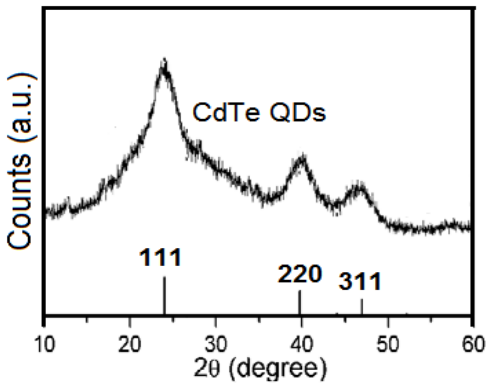

Fig. S2. XRD patterns of the as-prepared CdTe QDs (Sample **No.3**) with PL emitted at 551 nm.

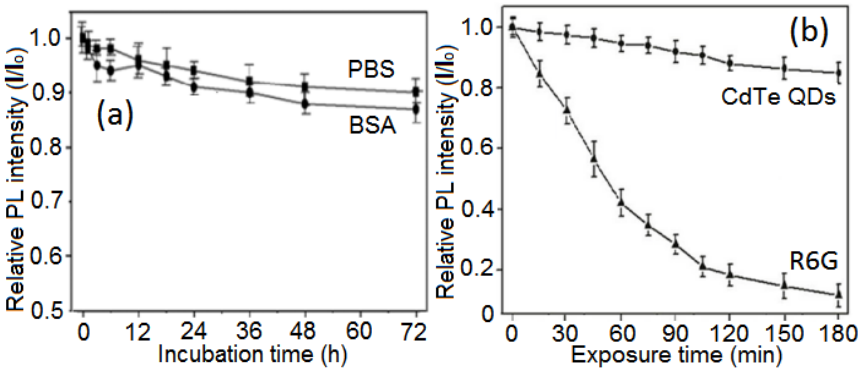

Fig. S3. (a) Colloidal stabilities of CdTe QDs (Sample **No.3**, 0.1 mg mL^{-1}) incubated with 10 mM of PBS (at pH 7.4) and 10 mM of BSA for 0~72 h at 37 °C. (b) Photostability measurements of the QDs (1.0 mg mL^{-1}) and R6G molecules (1 μM) under continuous excitation for 0~180 min with a laser.

To evaluate the colloidal stability of CdTe QDs, an aqueous suspension of the QDs (1.0 mg mL^{-1}) was incubated in 10 mM of PBS (at pH 7.0) and 10 mM of BSA at 37 °C. The corresponding PL intensities were recorded at different time intervals (0~72 h). In addition, to testify the photostability of CdTe QDs, aqueous suspension of QDs

was excited by 405 nm laser (50 mW), and the corresponding PL intensities were measured at different time points (0~180 min). In this study, R6G molecules were selected as a reference. Briefly, R6G aqueous solution (1 μM) was continuously excited by a 405 nm laser (50 mW), and the corresponding PL intensities were recorded at different excitation times (0~180 min). As exhibited in Fig. S3a, up to 87% of PL intensity was preserved after incubation for 72 h with PBS and BSA, which denoted that the PL of QDs is highly stable in aqueous solutions and biological mediums. Moreover, the photostability of QDs was investigated by continuously exciting the QDs with a laser. As illustrated in Fig. S3b, the QDs were estimated by continuous excitation with a 405 nm laser (0.05 W), and little photobleaching (< 10%) was observed after excitation for 180 min. As a reference, dramatic (no less than 90%) photobleaching of R6G was found after continuous excitation with a 405 nm laser (0.05 W) for 180 min. These results mentioned above suggested that the as-prepared CdTe QDs have high colloidal/photo-stability, showing the potential capacity for chem./bio-sensing and bio-imaging applications.

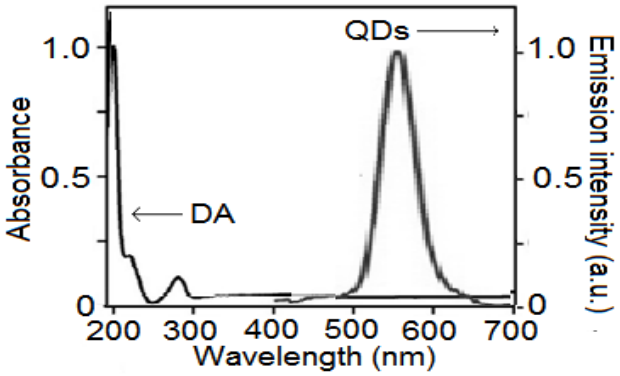

Fig. S4. Normalized UV-vis absorption spectrum of DA and normalized UCL emission spectrum of QDs.

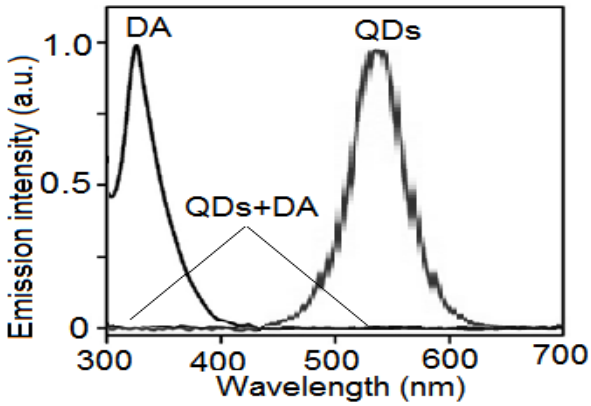

Fig. S5. Normalized PL emission spectrum of DA (10 μM), UCL emission spectrum of QDs (1.0 mg mL^{-1}) and UCL emission spectrum of the mixture of QDs and DA in 10 mM of PBS (at pH 7.4).

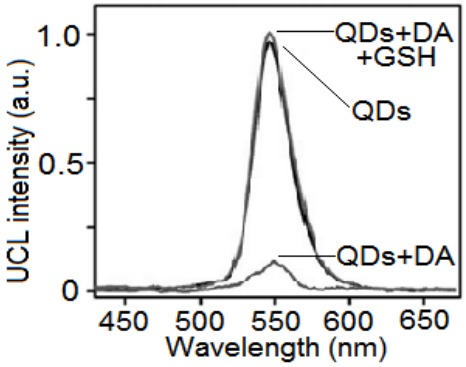

Fig. S6. UCL emission spectra of QDs (1.0 mg mL^{-1}), the complex of QDs and DA (10 μM), and the complex after the addition of GSH (12.5 μM) in 10 mM of PBS (at pH 7.4).