# Non-specific adsorption of charged quantum dots on supported zwitterionic lipid bilayers: Real-time monitoring by *in-situ* quartz crystal microbalance with dissipation

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## Supporting Information

### Experimental

**Materials.** 1,2-Dioleoyl-*sn*-glycero-3-phosphocholine (DOPC, purity 99%) and dioleoyltrimethylammonium propane (DOTAP, purity 99% were purchased from Avanti Polar Lipids (Alabaster, AL). 3-mercaptopropionic acid (MPA, 99%) was purchased from Aldrich. 2-aminoethanethiol hydrochloride (AET, 98%) was purchased from Acros. Selenium powder (99%) was provided by Aldrich. Cadium choloride (99%) was provided by Aldrich. Other reagents used including chloroform (99.8%, Laboratory-Scan Ltd.), tris(hydroxymethyl)aminomethane (Tris, 99.9+%, Aldrich), sodium chloride (99.8%, Riedel-deHaen), cacium chloride-2-hydrate (99%, Riedel-deHaen), and sodium borohydride (merch, 96%) were of the highest purity available. All the chemicals were used without further purification.

The buffer solutions used throughout the experiment were Tris buffer containing 10 mM Tris and 100 mM NaCl. The pH was adjusted to 8.0 with a 2.0 M HCl solution. Milli-Q water (Barnstead, compact ultrapure water system) with a resistivity of 18.3 MΩ·cm was used. The percentages mentioned throughout the paper are in molar fraction unless otherwise stated.

**Preparation of Vesicles.** Vesicles were prepared by extrusion. Briefly, phospholipid mixtures were obtained by mixing the appropriate volumes of phospholipid solutions in chloroform and allowed to dry in a stream of nitrogen, followed by desiccation under vacuum for 8 h to remove the residual organic solvent. The resulting phospholipid film was resuspended in Tris buffer overnight. The solution was then extruded 15 times through polycarbonate membranes (100 nm pore size) to produce uniform vesicles. The final concentration of the vesicles was 1 mg/mL. The vesicles were stored under 4 ℃, and used within two weeks.

**Preparation and characterization of QDs.** CdSe QDs were prepared by aqueous synthesis method reported by Rogach et al. Briefly, for preparation of MPA or AET-capped QDs , 2 mmol $CdCl_2$ was dissolved in 100 ml water with 1 ml MPA or AET; the pH of the solution was adjusted to 10.0 or 6.0 with 1 M NaOH. Then the fresh 1 mmol NaHSe solution was quickly injected into the $N_2$ saturated $Cd^{2+}$ solution under fast stirring. The solution was refluxed at 100 ℃ for 2 h. The CdSe nanocrystals were precipitated out by ethanol, and collected by centrifugation. It was stored under 4 ℃, and diluted with tris buffer before use.

TEM mages were recorded by a JEOL-2010 electron microscope operated at 200 kV. UV-Vis spectra were measured on a MILTON ROY Spectronic 3000 Array instrument. Zeta potential was measured by Zeta Potential Analyzer (Brookhaven Instruments Corporation).

The sizes of these QDs determined from TEM and UV-Vis adsorption were of about 2-3 nm as shown in Figure S1, which is very consistent with reports of other researchers.[27-28]

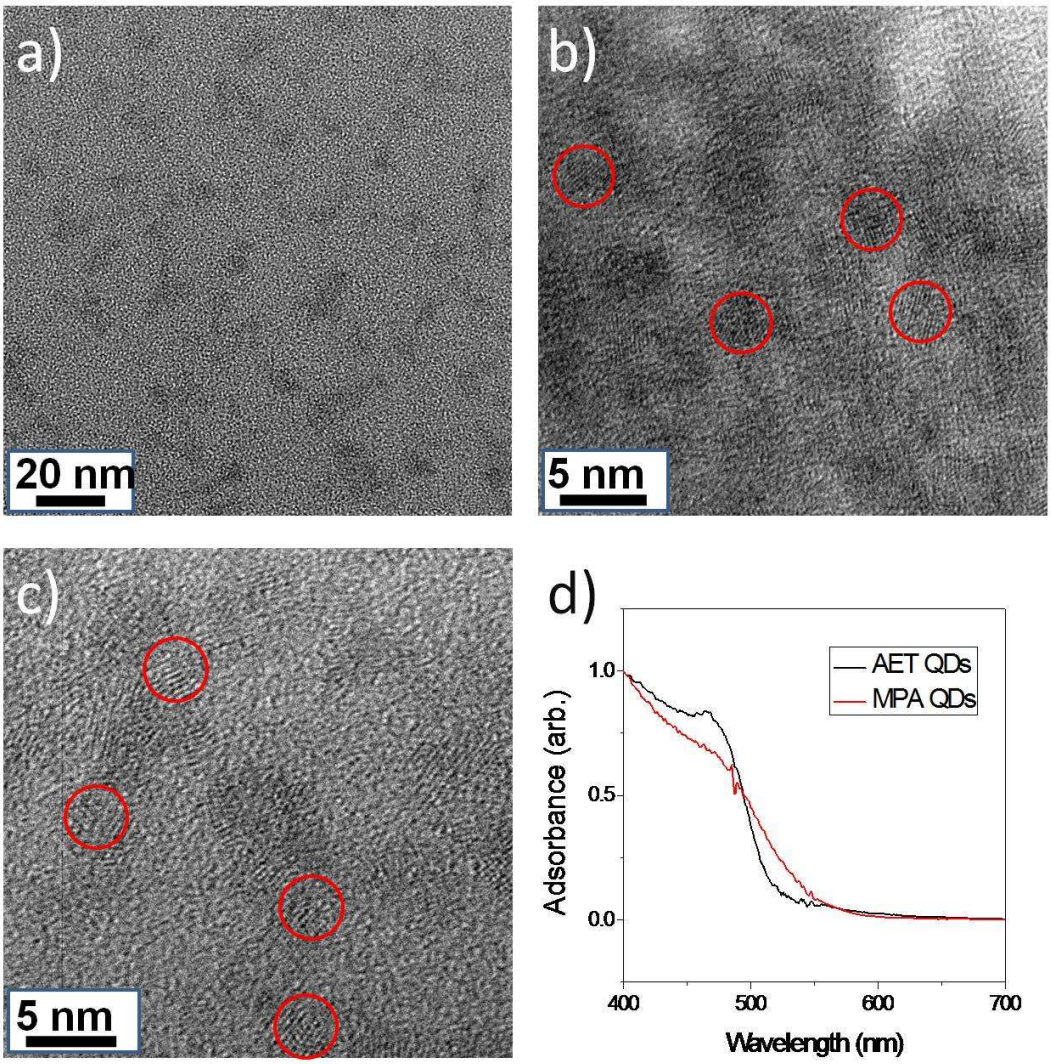
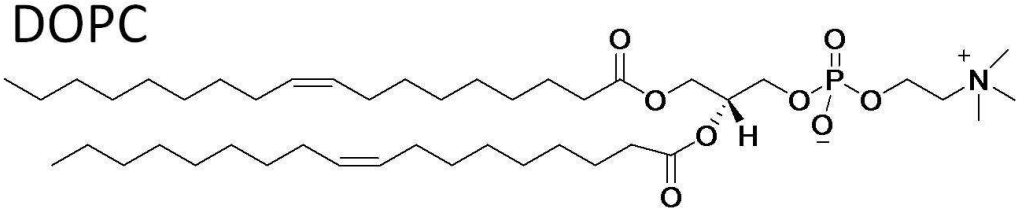



**Figure S1.** (a) Typically TEM image of as-synthesized MPA-capped CdSe QDs (scale bar: 20 nm); (b) and (c) are the HR-TEM images of MPA-capped QDs and AET-capped QDs, respectively; (d) UV-Vis spectra of MPA-capped and AET-capped CdSe QDs.

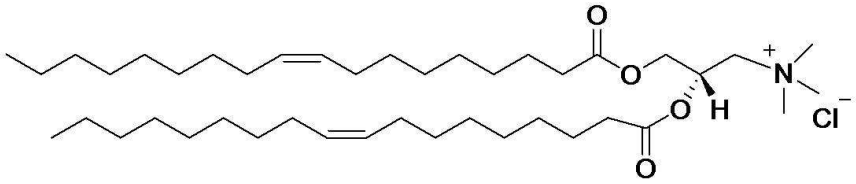
**Dissipative Quartz Crystal Microbalance.** Dissipative QCM measurements were performed with a QCM-Z500 system (KSV Instruments, Finland) equipped with a temperature control unit QCM-501. The technique is based on the resonant oscillation of a piezoelectric quartz crystal disk at a frequency ($f$) and energy dissipation ($D$), which, respectively, characterize the mass and the viscoelastic property of the molecules adsorbed on the crystal surface. In vacuum or air, if the layer is rigid, evenly distributed, and much thinner than the crystal, $\Delta f$ is related to $\Delta m$ by the Sauerbrey equation, $\Delta f = -n\Delta m/C_f$, where $n$ = 1, 3, 5, ..., is the overtone number and $C_f$ = 17.7 ng·cm$^2$·Hz$^{-1}$ at $f$ =5 MHz is the mass-sensitivity constant. The dissipation factor is defined by $\Delta D = E_d/2\pi E_s$, where $E_d$ and $E_s$ are, respectively, the energies dissipated and stored during one cycle of oscillation. If not stated otherwise, dissipations and changes in normalized frequency of the third overtone ($n$ = 3, i.e., 15 MHz) will be presented. For a given experiment, the silica crystal was initially exposed to Tris buffer and rinsed several times until the baseline was stable. Then, the buffer was replaced by a vesicle solution and the subsequent deposition of vesicles was monitored in time. After the formation of bilayer, different amount of QDs solution was introduced into the QCM chamber. All of the dissipative QCM measurements were carried out at 25 (±0.1□℃).

**Formation of supported lipid bilayers on QCM crystal** In order to address the interaction of nanoparticles with lipid bilayer, a zwitterionic lipid DOPC and cationic lipid DOTAP was chosen as model system. Their structures were shown in Figure S2 a and b. The formation of DOPC on silica substrate through vesicle fusion is well established and investigated by QCM-D. The well defined "U"-shaped features in QCM-D could be used to monitor the formation and quality of supported lipid bilayer, as shown in Figure S2 c. Typically, the equilibrium $\Delta f$ was found to be around 75-80 Hz in the formation of a good lipid bilayer on the QCM crystal. The formation dynamics of bilayer was only slightly changed under different ionic strength or mixed with charged lipid such as DOTAP.

a) DOPC



b) DOTAP



c)

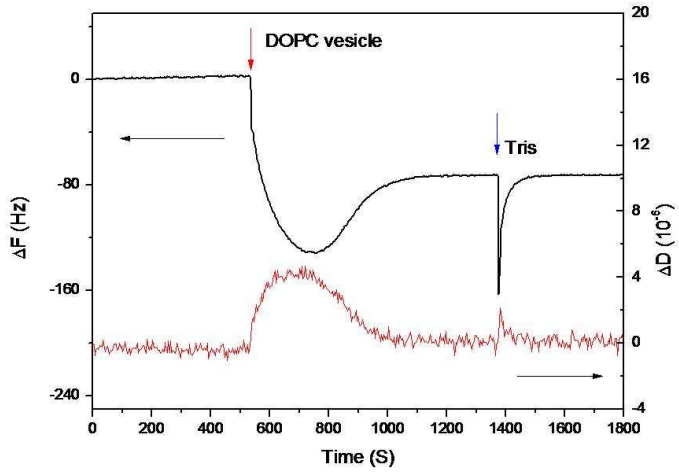



**Figure S2.** (a) and (b) are the chemical structures of DOPC and DOTAP, respectively. (c) is the typical QCM-D curve monitored the formation process of supported lipid bilayer through the vesicle fusion.