

## Supplementary Information

for the manuscript

### Interplay of electrostatics and lipid packing determines binding of charged polymer coated nanoparticles to model membranes

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#### 1. Isotherm of DMPC lipid:

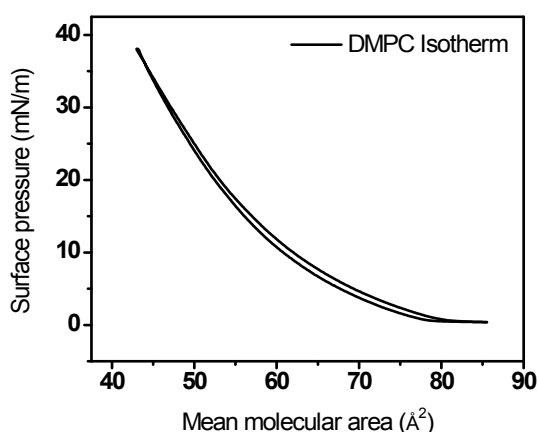


Fig. S1: Surface pressure ( $\pi$ ) – mean molecular area ( $A$ ) isotherm of DMPC lipid at air-water interface at 27C

1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) lipid was dissolved in chloroform at a typical concentration of 0.5mg/ml and 50  $\mu$ l of this solution was spread over at the air-water interface of Langmuir-Blodgett (LB) trough (Biolin Scientific, medium size, 75 mm x 324 mm) using Hamilton microlitre syringe. Trough water temperature was maintained at 27C. After spreading the solution, trough was left for 15 minutes allowing the chloroform to evaporate and lipids to form a homogeneous Langmuir monolayer. Compression-decompression isotherms were recorded at constant barrier compression rate of 5 mm/min. Surface pressure was measured by platinum plate Wilhelmy balance. Fig. S1 shows a typical isotherm.

#### 2. Quantum Dot (QD) synthesis and characterization:

## 2.1 QD synthesis :

Hydrophobic CdSe/ZnS core-shell type quantum dot (QD) has been synthesized according to previously reported method.<sup>1</sup> In brief, 25 mg CdO, 284 mg stearic acid and 5 mL octadecene was mixed in a 25 mL three necked flask and degassed for 15 minutes under N<sub>2</sub> atmosphere. Next, it was heated to 200°C to produce an optically clear solution. Then the mixture was cooled down to room temperature followed by addition of 1.3 g octadecylamine and 0.6 g trioctylphosphine oxide. Next, the mixture was heated again under N<sub>2</sub> atmosphere and Se solution (selenium solution was prepared by dissolving 20 mg Se in 2 mL trioctylphosphine at 80°C) was injected rapidly to the mixture at 280°C. The CdSe growth was quenched rapidly after 5 minutes by adding cold octadecene. The CdSe particles were purified first with acetone and then with chloroform/ethanol by precipitation and redispersion method. Finally precipitated particles were dissolved in 10 mL octadecene for ZnS shelling.

For ZnS shelling Zn precursor (prepared by dissolving 126 mg zinc stearate in 2 mL octadecene) and sulfur precursor (prepared by dissolving 6.4 mg sulfur powder in 2 mL octadecene at 80 °C) were alternately injected to the purified CdSe nanoparticles in 10 mL octadecene mixed with 2.7 g octadecylamine at 190 °C under N<sub>2</sub> atmosphere. The solution obtained was purified first with acetone and then with toluene-ethanol by precipitation and redispersion method. The final precipitate was dissolved in cyclohexane for polymer coating.

Hydrophobic QD was transformed into hydrophilic QD via previously reported polyacrylate coating method.<sup>2</sup> For preparation of cationic QD, 10 mL Igepal reverse micelle solution was prepared and mixed with hydrophobic CdSe/ZnS, 100 µL of N-(3-aminopropyl) methacrylamide solution (18 mg dissolved in 100 µL water), 100 µL poly (ethylene glycol) methacrylate solution (36 µL dissolved in 100 µL water), 100 µL (bis[2-(methacryloyloxy)ethyl] phosphate) solution (6 µL dissolved in 100 µL water) and 100 µL tetramethylethylenediamine. The optically clear solution was taken in a three necked flask followed by purging with N<sub>2</sub> gas. Next, 100 µL aqueous solution of 3 mg ammonium persulfate was added and the reaction was allowed to continue for an hour under N<sub>2</sub> atmosphere. Finally the reaction was quenched by adding minimum amount of ethanol. The precipitated particles were washed several times with ethanol and chloroform and finally dissolved in water. For preparation of anionic QD, N-(3-aminopropyl) methacrylamide solution was replaced with 100 µL 3-sulfopropyl methacrylate solution (24 mg dissolved in 100 µL water) and all other procedures remain same. The polymer coated nanoparticles were purified by a precipitation redispersion method using Na<sub>2</sub>HPO<sub>4</sub> salt followed by dialysis using a 14000 MWCO cellulose membrane. The final aqueous solution was used for membrane interaction study.

## 2.2 QD size determination :

For measuring diameter of CdSe/ZnS core-shell transmission electron microscope (TEM) images were taken using Technai G2 T20 microscope at an accelerating voltage of 200kV. Aqueous solution of QDs were deposited on carbon coated copper mesh grid and dried properly before imaging. Figure S2 shows the typical images of both the cationic and anionic QDs. Insets show corresponding histograms along with the Gaussian fit.

For determining hydrodynamic diameter of QDs dynamic light scattering (DLS) technique was employed using BI-200SM instrument (Brookhaven Instrument Corporation). Fig. S3 shows distribution of QD size.

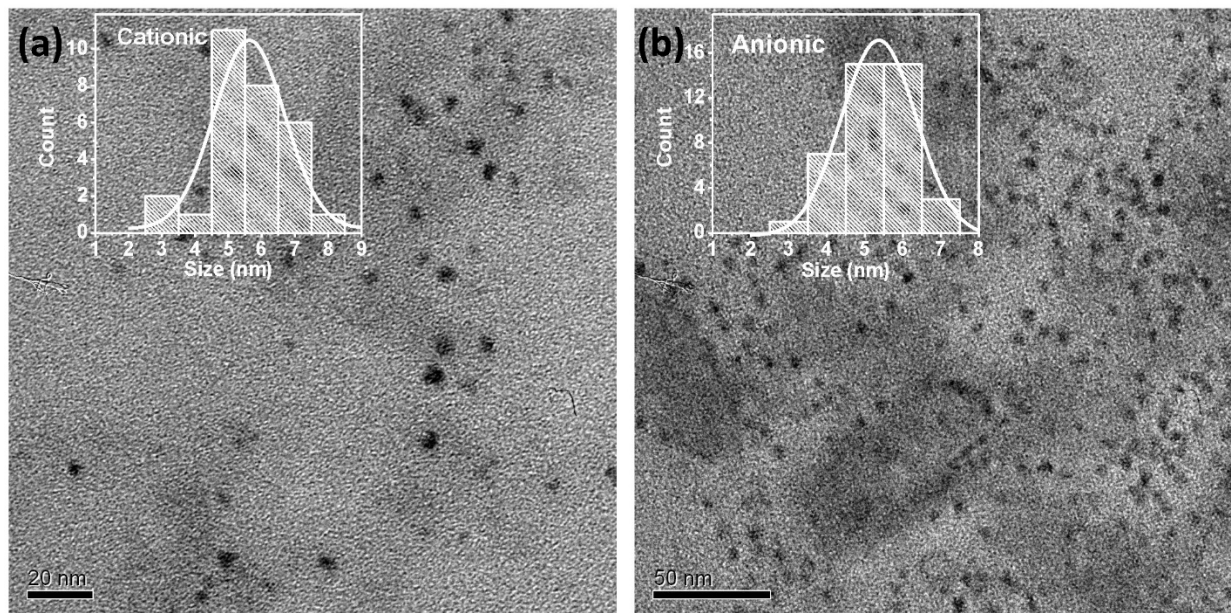


Fig S2: Transmission electron microscope (TEM) image of (a) anionic and (b) cationic QDs. Insets show their size distributions.

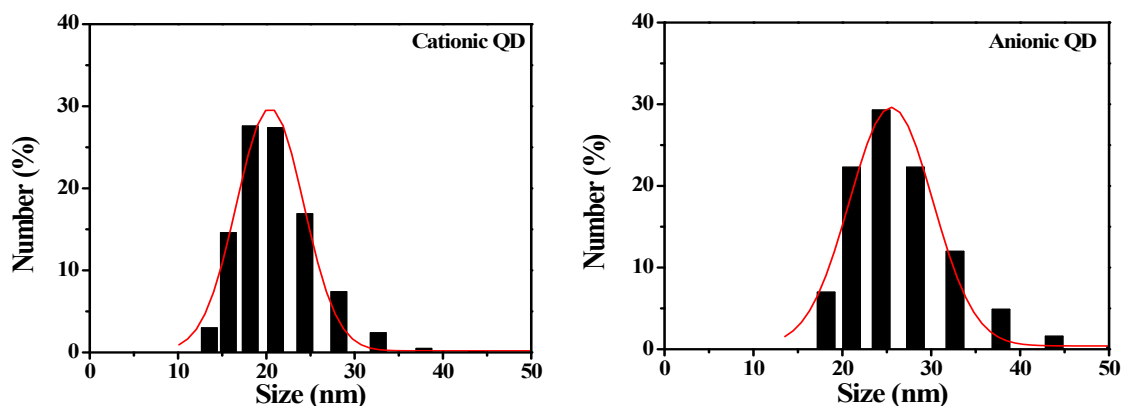


Fig S3: Hydrodynamic size of cationic and anionic QDs

### 2.3 Spectra of QDs :

Figure S4 shows the UV-visible absorption spectra of QD solutions in water using quartz cell of 1cm path length. Figure S5 shows the photoluminescence spectra of the QD solutions in water.

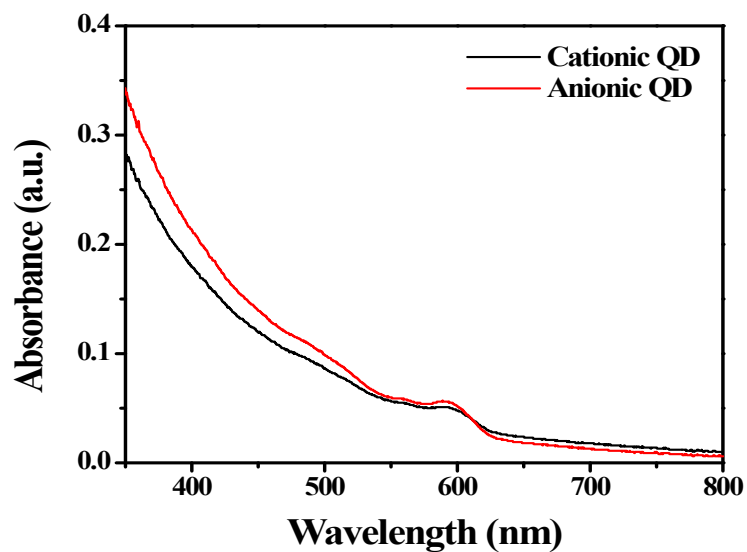


Fig S4: UV-visible absorption spectra of cationic and anionic QDs

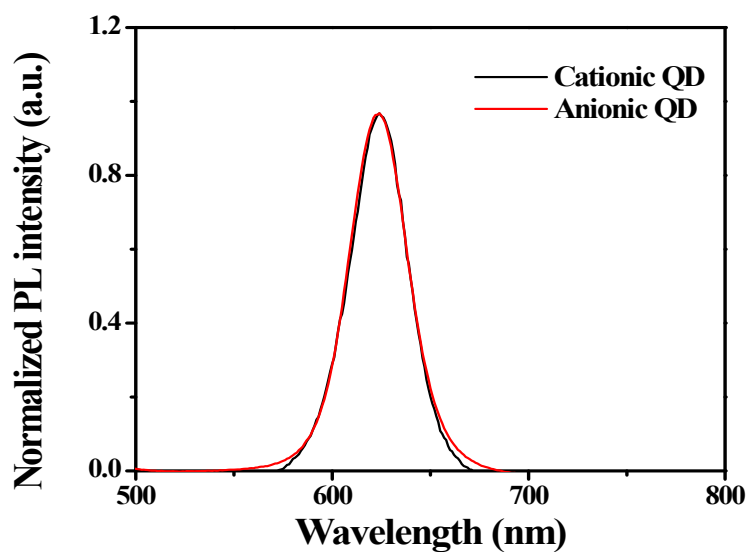


Fig S5: Photoluminescence spectra of cationic and anionic QDs

### 3. XR data of S37 bilayer

X-ray reflectivity (XR) data and fits of DMPC bilayer deposited at 37mN/m (S37pb) and then incubated in cationic QD solution (S37pa) are shown in Fig. S6. Corresponding electron density profiles (EDP) extracted from fits are shown in inset. Details of sample preparation, data collection and analysis have been described in main manuscript. Table S1 shows the parameters extracted from XR data fitting.

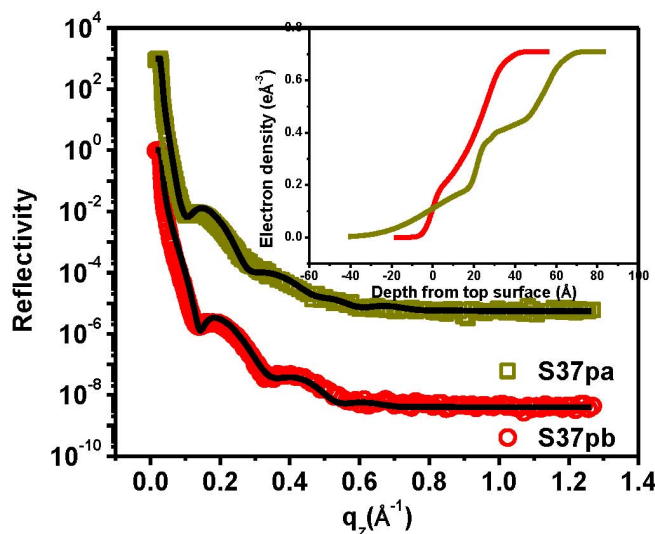


Fig S6: X-ray reflectivity data of bilayers S37pb and S37pa. Symbols correspond to data and solid lines represent best fit to the respective data. Reflectivity profiles are shifted vertically for clarity. Corresponding electron density profiles (EDP) extracted from fits are shown in inset.

Table S1: Parameters obtained from fits of XR data for S37 bilayer

Layer	S37pb			S37pa		
	Thickness (Å)	e density (eÅ <sup>-3</sup> )	Roughness (Å)	Thickness (Å)	e density (eÅ <sup>-3</sup> )	Roughness (Å)
QD	-	-	-	21.61	0.22	18.13
Head	4.00	0.22	3.46	7.60	0.38	2.39
Tail	7.10	0.2	1.67	9.40	0.41	1.33
Tail	10.79	0.31	4.51	10.95	0.45	5.4
Head	7.20	0.53	4.96	7.20	0.53	3.08
SiO <sub>x</sub>	8.36	0.66	3.34	8.36	0.66	3.34

#### 4. ITC measurements:

Isothermal titration calorimetry (ITC) data was recorded using GE Microcal ITC 200. For ITC experiments DMPC vesicle solution was prepared by extrusion method using Avanti Mini Extruder and 100 nm filter papers. From DLS experiments vesicle size was found  $\sim 125$  nm. In ITC experiments, in each injection  $2 \mu\text{l}$  of QD solution of concentration  $5 \mu\text{g}/\text{ml}$  was used for titration to the vesicle solution. The temperature was maintained at  $37^\circ\text{C}$ .

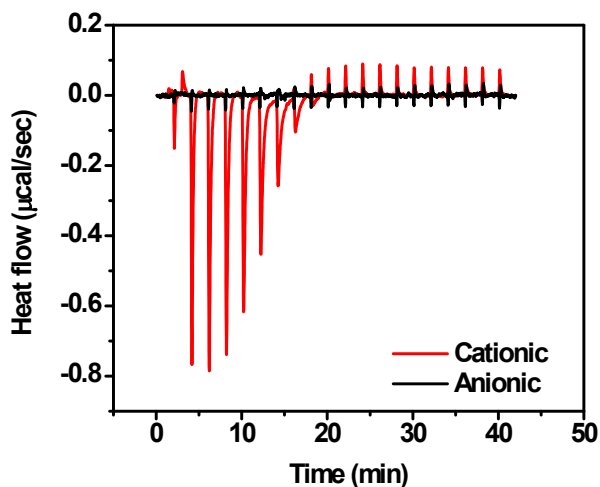


Fig S7: Isothermal titration calorimetry data showing heat transfer rate when cationic (red) and anionic (black) QDs were injected to DMPC vesicle solution.

We have performed ITC measurements which provide amount of heat exchange during the binding of QDs with bilayer of DMPC vesicles. Figure S2 shows heat flow for each injection with time. The measurements were carried out at  $37^\circ\text{C}$  with same QD solution of concentration  $5 \mu\text{g}/\text{ml}$ . For the cationic QDs initially interaction was exothermic (heat released) but with increase of QD concentration it turned to endothermic (heat absorbed). Initially at lower concentration of QDs, heat was released from the reaction corresponding to binding induced distortion in vesicle bilayer. With increase of QD concentration, the reaction attains equilibrium when further injection of QDs does not influence vesicles and relatively small amount of heat is absorbed. On the other hand, for anionic QDs no such heat change was observed. This is also in support of our other observations that anionic QDs are not able to induce any change in lipid bilayer.

#### References:

1. J. J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson and X. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 12567.
2. A. Saha, SK Basiruddin, R. Sarkar, N. Pradhan and N. R. Jana, *J. Phys. Chem. C*, 2009, **113**, 18492–18498.