Poly(maleic anhydride *alt*-1-tetradecene) derivatives control zeta potential and hydrodynamic size of encapsulated quantum dots

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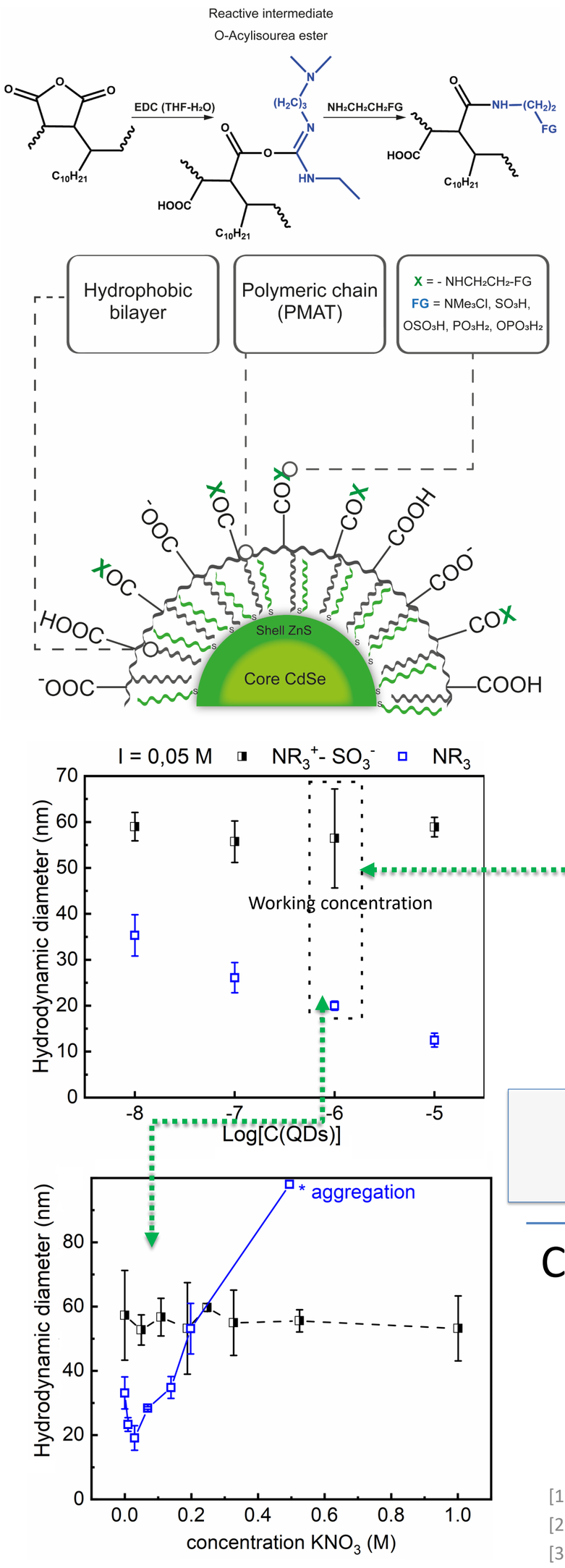
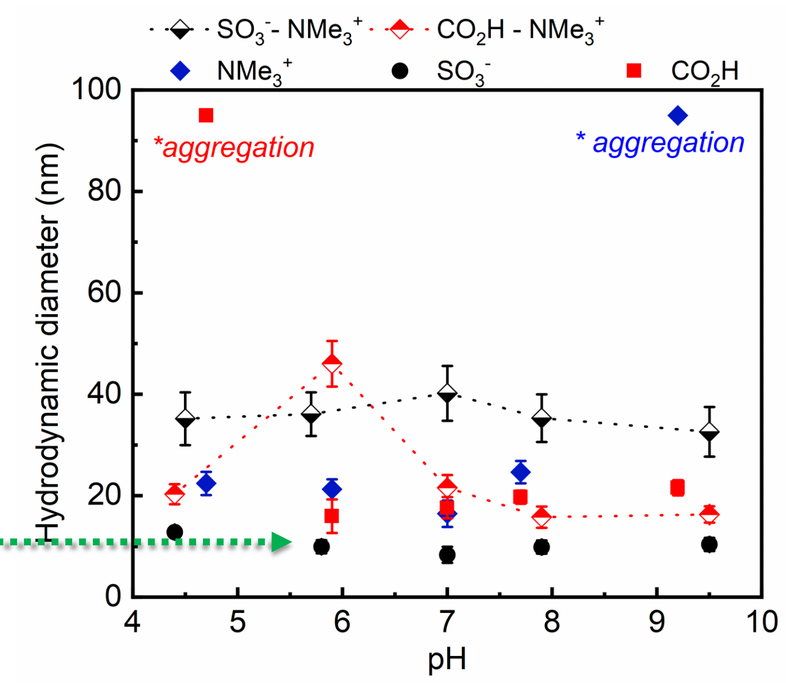
The aim of this work was

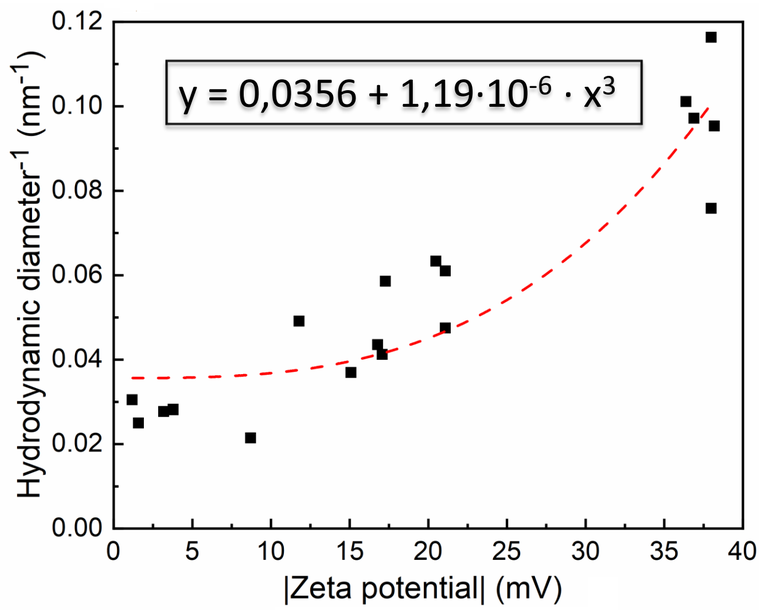
to show the relationship between zeta potential and hydrodynamic diameter of quantum dots encapsulated with derivatives of poly(maleic anhydride alt-1-tetradecane) (PMAT). Dynamic light scattering technique was fundamental in the research.

Methods.

Core-shell QDs CdSe/ZnS ($\lambda_{pl\ max}$ = 567 nm) was synthesized using high-temperature colloidal synthesis in organic solvent. Modification of PMAT was performed using standard carbodiimide linker. Solubilization of QDs was done using encapsulation technique. Zeta potential and hydrodynamic size of encapsulated colloidal QDs were measured using Malvern Zetasizer Nano ZS90 instrument.







Hydrodynamic diameter of QDs with high zeta potential is stable in all pH range and remains less than ~ 20 nm. However, QDs with a zwitterionic shell shows an increase 2 times in diameter if zeta potential value approaches zero.

The observed effect can be explained by taking into account two components: collective and self-diffusion. When an interaction parameter is introduced to Stokes-Einstein equation, we get a cubic dependence of inverse hydrodynamic diameter versus zeta potential. The free term of fitting gives $D_0 = 1.74 \cdot 10^{-11}$ $m^2 \cdot s^{-1}$, which is collective diffusion contribution to overall diffusion coefficient.

$$D_0 = \frac{kT}{3\pi\eta d} \Rightarrow \frac{1}{d} = \frac{3\pi\eta D_0}{kT}(1 + 1.45\varphi) + \frac{9\pi\eta D_0 \varphi (ze_0)^2}{\varepsilon a^4 (kT)^2} \cdot \zeta^3$$

Electrostatic component of diffusion coefficient increase with QDs concentration in case of high zeta potential value. This data correlates with *D vs C(KNO₃)* dependence, where salting-out effect leads to decrease of surface charge and corresponding diameter increase can be seen. However, QDs concentration does not influence hydrodynamic diameter for zero-charged zwitterionic QDs.

Conclusions

Modification of PMAT allows obtaining QDs with well-defined zeta potential in the range from –38 to +20 mV while hydrodynamic diameter remains less than 50 nm.

Two components in diffusion coefficient can be extracted from DLS measurements. Collective diffusion coefficient equals $1.74 \cdot 10^{-11}$ $m^2 \cdot s^{-1}$, while electrostatic component increases with zeta potential. Concentration of QDs and ionic strength do not influence hydrodynamic size of zero-charged QDs.

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