

Electronic Supplementary Information: "Wrap-and-Wrest" mechanism of fluorescence quenching of CdSe/ZnS quantum dots by surfactant molecules identified

Ewelina Kalwarczyk,^a Natalia Ziebach,^a Tomasz Kalwarczyk,^a Robert Hołyst,^a and Marcin Fiałkowski^{*a}

^a Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

E-mail: fialkowski@ichf.edu.pl

1 Characterization of quantum dots

In order to determine the hydrodynamic radius of quantum dots we performed dynamic light scattering (DLS) measurements. The best fit to the experimental data (shown in Fig. S1) was obtained using double-exponential function. This indicates the presence of two types of objects in the sample, moving with different diffusion coefficient and as a result - having different hydrodynamic radius. The smaller hydrodynamic radius (8.6 nm) was ascribed to single QDs, whereas the bigger ones (83.8 nm) corresponded to the aggregates of QDs. Considering the fact that the intensity of the DLS signal scales with the sixth power of the particle size it occurs that QDs solution contain mainly free quantum dots with minor number of aggregates.

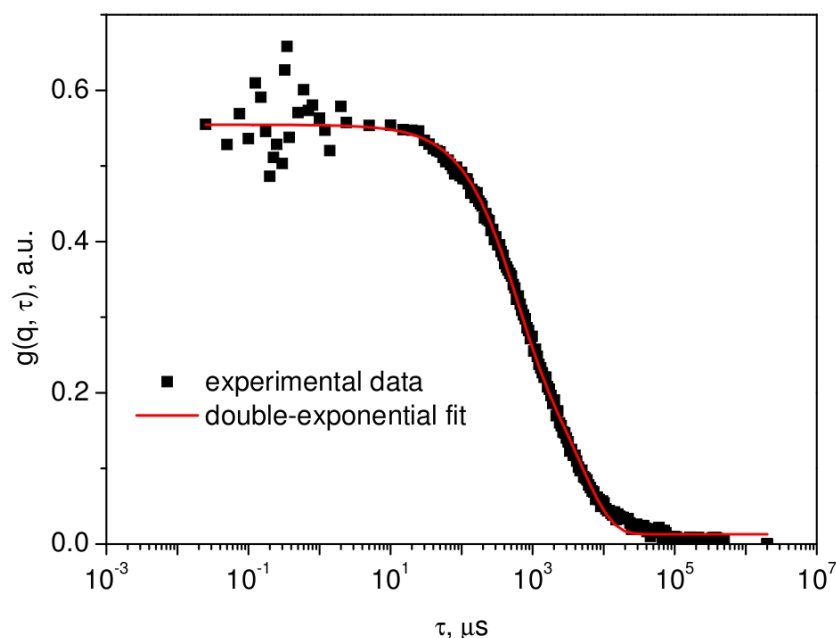


Figure S1: The DLS data obtained for QDs dissolved in water together with double-exponential fitting curve. The data was collected at 45°.

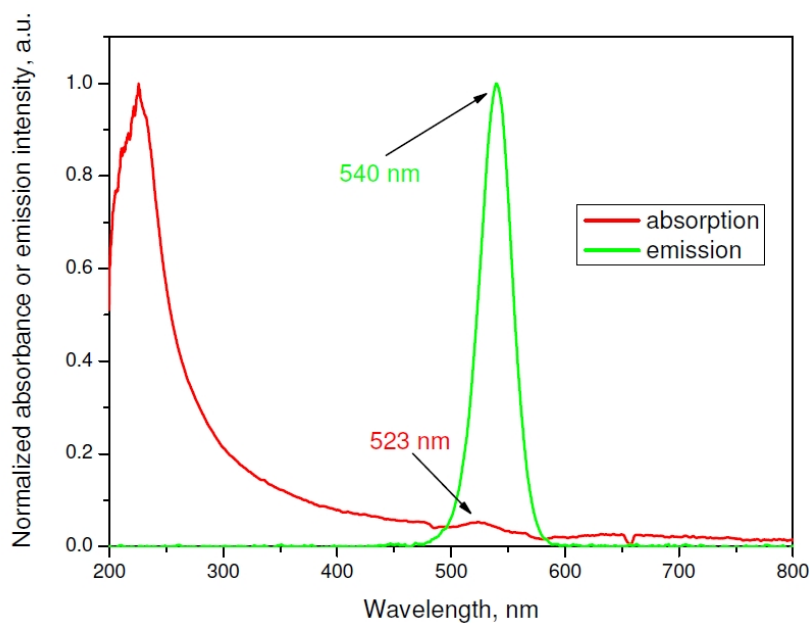


Figure S2: Normalized absorption (red) and emission (green) spectra of QDs used in the experiments. QDs exhibit absorption in UV-vis spectral range, with relatively small maximum at 523 nm. The maximum of emission of QDs falls at 540 nm (FWFM = 30 nm).

2 Characterization of surfactants' solutions

Table S1: Hydrodynamic radius (in nm) of $C_{12}E_n$ surfactant micelles measured in aqueous solutions of molar concentration from 0.001 M - 0.2M.

c_{surf}	0.2 M	0.1 M	0.05 M	0.01 M	0.001 M
$C_{12}E_8$	3.0	3.7	3.5	3.5	4.3
$C_{12}E_9$	3.9	5.1	3.9	3.9	3.7
$C_{12}E_{10}$	3.0	3.5	3.7	4.1	4.0

Table S2: pH values of the surfactant solution for five molar concentration. The pH was measured using a pH meter equipped with a glass electrode suitable for viscous solutions.

c_{surf}	0.2 M	0.1 M	0.05 M	0.01 M	0.001 M
$C_{12}E_8$	2.42	2.51	2.73	3.20	4.24
$C_{12}E_9$	2.47	2.49	2.89	3.21	3.88
$C_{12}E_{10}$	2.40	2.50	3.60	3.88	4.26

3 Quantum dots in surfactants' solutions

3.1 Estimation of the number of surfactant molecules needed to form bilayer at the surface of QD

We estimated the number of surfactant molecules needed to create bilayer at the surface of QD. To do so, we assume that the number of surfactant molecules, N , needed to create a spherical surface of a radius R depends on the radius of the hydrophilic head of surfactant, r_{head} , according to relation:

$$N = 4 \frac{R^2}{r_{\text{head}}^2} \quad (1)$$

By replacing N and R with respectively, the aggregation number of C_{12}E_8 ($N_{\text{agg}} = 120$) and the hydrodynamic radius of C_{12}E_8 micelle ($R_{\text{h,mic}} = 3.7$ in $\text{pH} = 1$) we get the radius of C_{12}E_8 head, $r_{\text{head}} = 0.68$ nm. Then, assuming that the first and the second layer of C_{12}E_8 molecules at the surface of QD is formed in a distance $R_1 = 8.6$ nm and $R_2 = 16$ nm from the center of QD respectively, we get that the bilayer consists of 2853 molecules. This number of C_{12}E_8 molecules corresponds to 24 micelles which is of the same order of magnitude as the experimentally determined number (40) of C_{12}E_8 micelles needed to quench the fluorescence of QD in $\text{pH} \approx 1$.

3.2 DLS of quenched QDs

As in the case of solution of QDs in water, the DLS data obtained for quenched QDs in the presence of $C_{12}E_8$ in $pH \approx 1$ were fitted with double-exponential function. The fitting procedure gave two distinct diffusion coefficients and as a result to two different hydrodynamic radii. The bigger value of $R_h = (54.0 \pm 3.0)$ nm was ascribed to partially broken aggregates of QDs (the same that were present in case of QDs in water). The smaller value of $R_h = (17.7 \pm 0.6)$ nm was ascribed to single QD surrounded with bilayer of $C_{12}E_8$.

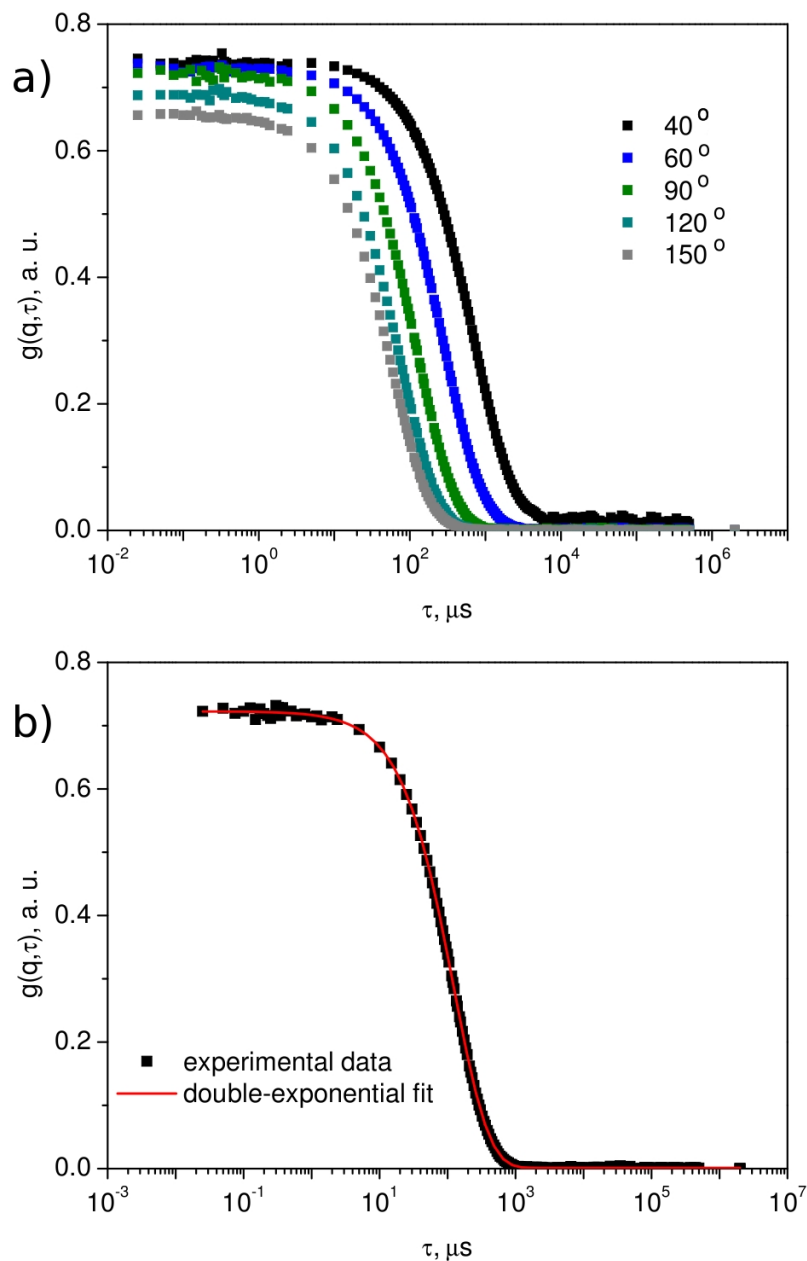


Figure S3: a) DLS experimental data collected for quenched sample of QDs and 9.25×10^{-4} M $C_{12}E_8$ in $pH \approx 1$. Experimental points of different colors correspond to measurements made at different angles. b) Double-exponential fitting curve for the quenched sample of QD in $pH \approx 1$. The data were collected at 90° .

3.3 Fluorescence lifetimes of QDs in the presence of $C_{12}E_{10}$

We applied fluorescence lifetime imaging microscopy (FLIM) technique in order to determine the changes of fluorescence lifetimes of quantum dots under the influence of surfactant ($C_{12}E_{10}$) and/or pH conditions. The resulting fluorescence decay profiles are shown in Figure S4. The fluorescence decay curves were fitted with double-exponential function. The resulting fluorescence lifetimes are collected in Table S3.

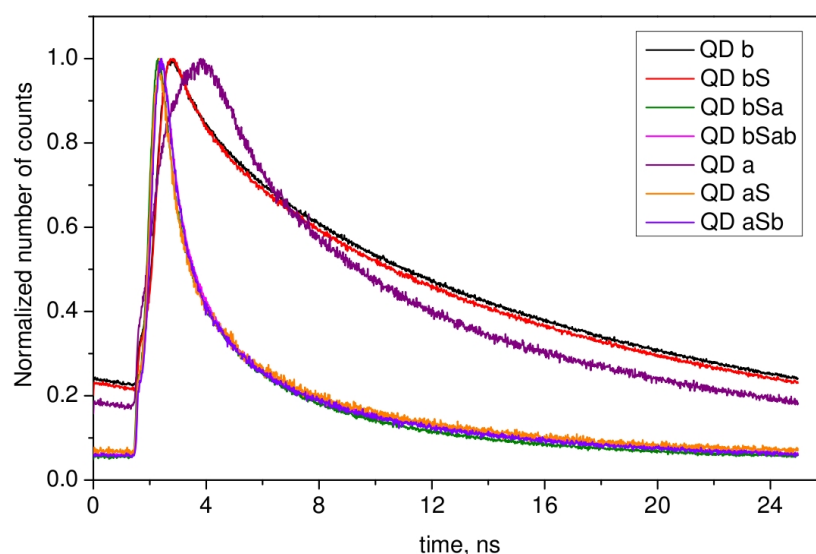


Figure S4: The changes of fluorescence lifetimes of QDs in the presence of $C_{12}E_{10}$ at different pH conditions. The signs in legend denotes, respectively: QD - quantum dots; S - surfactant – $C_{12}E_{10}$; a - acidic conditions, $pH \approx 1.5$; b - basic conditions, $pH \approx 13$. The order of appearance of the signs corresponds to the order of changes made in the sample. For example, “QD bSa” denotes the solution of quantum dots that was firstly basified to $pH \approx 13$, then surfactant was added and finally the sample was acidified to $pH \approx 1.5$.

Table S3: Fluorescence lifetimes (in ns) of quantum dots in the presence of $C_{12}E_{10}$ and acidic ($pH \approx 1.5$) or basic ($pH \approx 13$) conditions. The descriptions of samples are the same as in the Figure S4.

sample	t_1	t_2
QD b	1.8	14.3
QD bS	1.6	13.7
QD bSa	1.3	6.2
QD bSab	1.3	7.3
QD a	2.7	13.7
QD aS	1.2	6.8
QD aSb	1.2	7.1

3.4 Changes of absorption spectra of QDs in the solution of $C_{12}E_8$

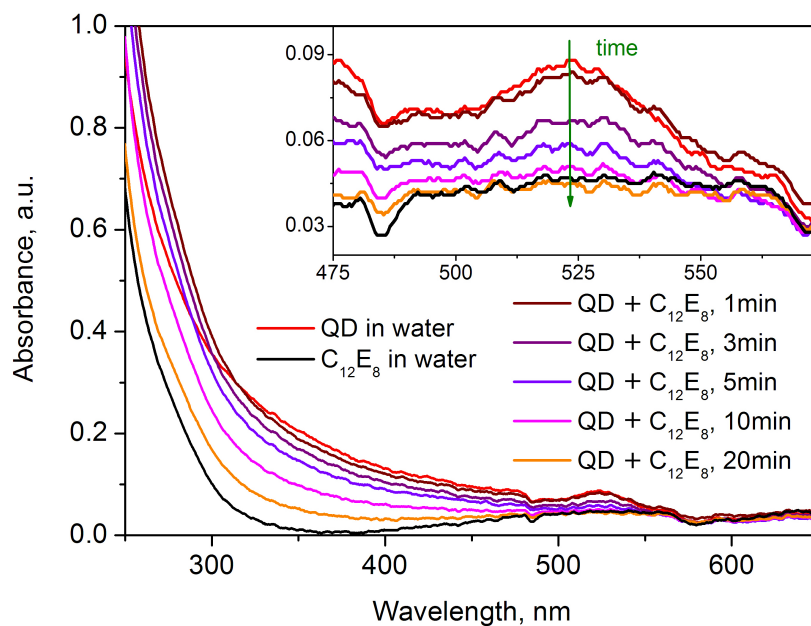


Figure S5: The absorption spectra of QD and 0.2 M $C_{12}E_8$ in water as well as the time evolution of absorption spectra of QDs after mixing with $C_{12}E_8$. As indicated in the legend, the subsequent spectra were recorded after 1, 3, 5, 10 and 20 minutes after mixing of QDs with surfactant. In the insert – the enlargement of the spectra around the spectral range corresponding to the maximum of absorption of QDs in visible range.

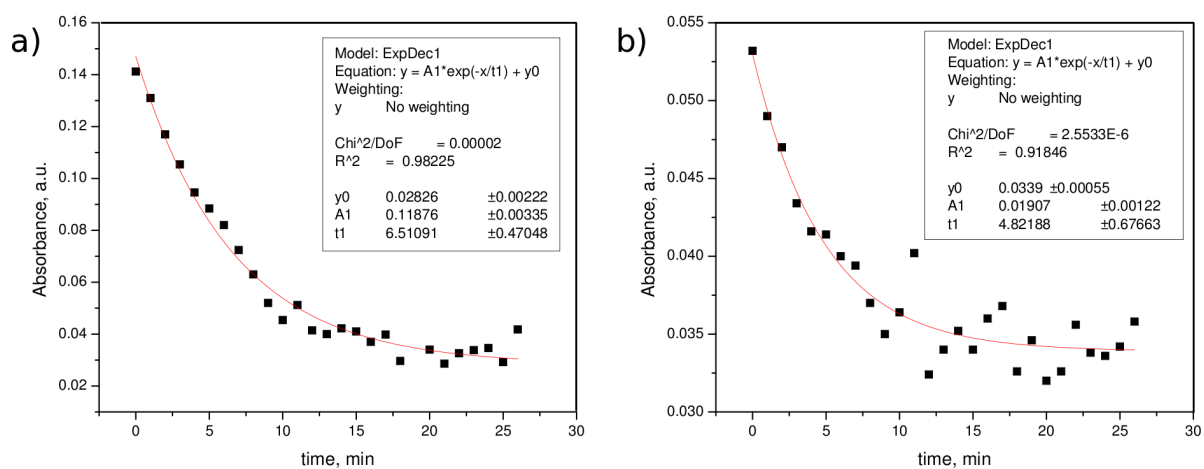


Figure S6: Decay of absorbance of QDs in the presence of 0.2M $C_{12}E_8$. Panels a) and b) correspond to decay of absorbance measured at 350 nm and 523 nm respectively. Observed decay of absorbance was fitted with monoexponential function resulting in characteristic decay time equal to: (6.51 ± 0.47) min and (4.82 ± 0.68) min for absorbance decay measured at 350 nm and 523 nm respectively.

3.5 Estimation of the characteristic collision time between the QD and a micelle

Diffusion coefficient, D of a sphere of radius R can be calculated from the Stokes-Einstein relation,

$$D = \frac{k_B T}{6\pi R \eta}, \quad (2)$$

where T is the absolute temperature, k_B is the Boltzmann constant, and η is the viscosity of the solvent (here: water). The radii of the micelles formed by all $C_{12}E_n$ surfactants vary in the range from 3 to 5 nm (see Table S1). Thus, one can take $R_{\text{mic}} = 4$ nm as a rough estimate of the average radius of the micelle. Relation (2) yields the characteristic diffusion coefficient of a micelle, $D_{\text{mic}} = 5.4 \cdot 10^{-7}$ cm²/s. Diffusion coefficient calculated for the QD of the radius $R_{\text{QD}} = 8.6$ nm is $D_{\text{QD}} = 2.5 \cdot 10^{-7}$ cm²/s. The average number of collisions, F , occurring per unit time between the QD and the micelles can be calculated within the Smoluchowski's coagulation theory (M. Smoluchowski, *Z. Phys. Chem.*, 1917, **92**, 129), and is given by the following formula:

$$F = 4\pi(D_{\text{mic}} + D_{\text{QD}})(R_{\text{mic}} + R_{\text{QD}})c_{\text{mic}}N_A, \quad (3)$$

where c_{mic} and N_A denotes the micelle molar concentration in solution and the Avogadro constant respectively.

As an example, we calculate the value of F for $C_{12}E_8$ for the lowest and the highest surfactant concentrations. This surfactant is characterized by the aggregation number equal to 120. It yields the micelle molar concentrations, $8.33 \cdot 10^{-5}$ and $1.57 \cdot 10^{-3}$ M for, respectively, the surfactant concentration 0.01 and 0.2 M. The corresponding collision frequencies calculated from Eq. (3) are $6.24 \cdot 10^5$ and $1.18 \cdot 10^7$ 1/s for the surfactant concentration 0.01 and 0.2 M, respectively. The characteristic collision time, τ_{coll} is related to the collision frequency by the following relation:

$$\tau_{\text{coll}} = \frac{1}{F}. \quad (4)$$

The collision times calculated from the above relation are $1.6 \cdot 10^{-6}$ and $8.5 \cdot 10^{-8}$ s for the concentration 0.01 and 0.2 M, respectively. Quite similar values of the characteristic collision times are also obtained for the $C_{12}E_9$ and $C_{12}E_{10}$ surfactants.