Fluorescence properties of hydrophilic semiconductor nanoparticles with tridentate polyethyleneoxide ligands

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Supporting Information

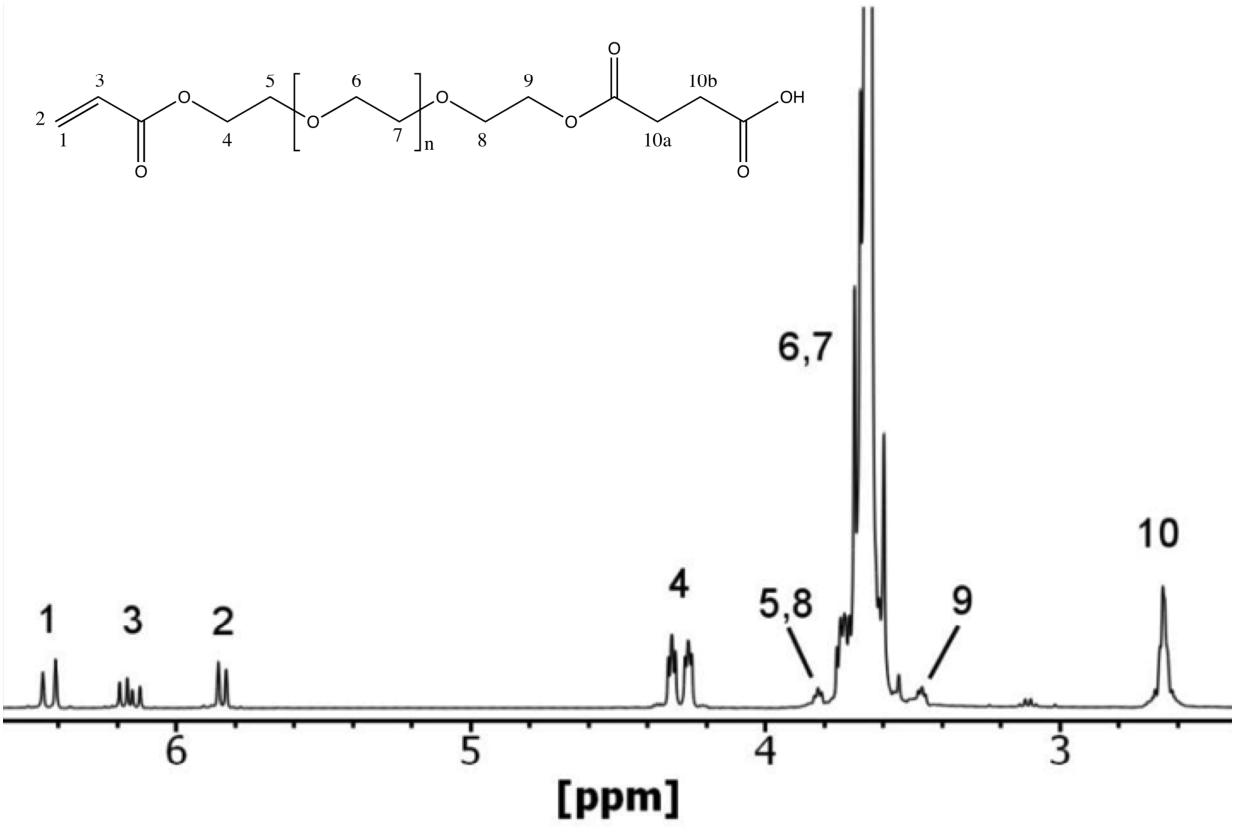

Figure S1. [1]H NMR spectrum of polyethylene oxide monoacrylate modified with succinic acid. The acrylate peaks at 5.8 – 6.4 ppm are preserved. The multiplet at 2.6 ppm originates from the succinate moiety.

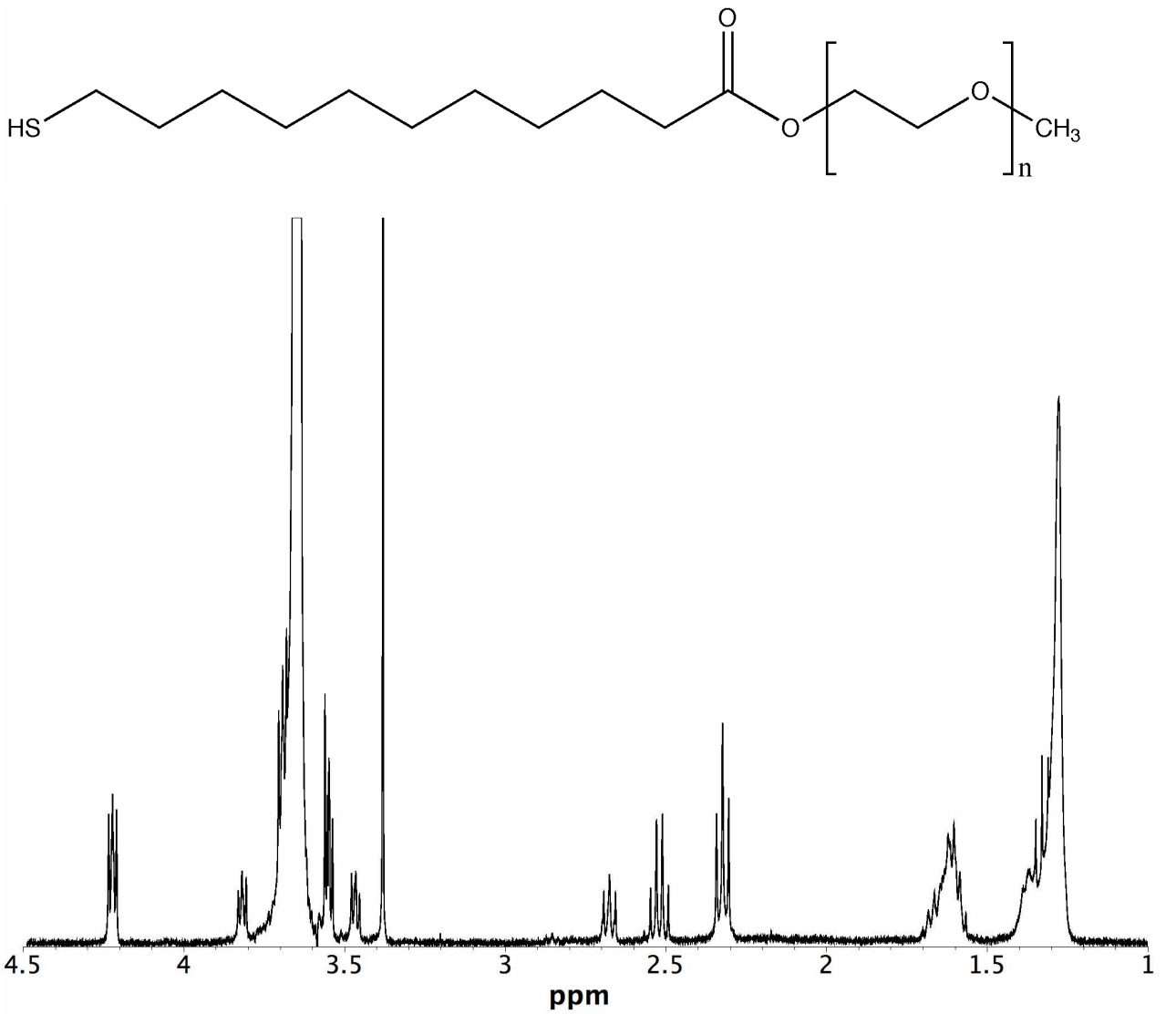

Figure S2. 1H NMR spectrum and structure of $PEO(SH)_1$

NMR data of $PEO(SH)_1$:

^{1}H-NMR: δ [ppm] (400 MHz, $CDCl_3$): 4.22 (t, 2H, -C**H**$_2$-O-CO-), 3.64 (m, 180 H, -(C_2**H**$_4$O)$_n$-), 3.38 (s, 3H, -OC**H**$_3$), 2.52 (q, 2H, -C**H**$_2$SH), 2.32 (t, 2H, -O-CO-C**H**$_2$-), 1.73-1.50 (m, 4H, -C**H**$_2$-CH_2-SH, -C**H**$_2$-CH_2-CO-O-), 1.45-1.10 (m, 13H, -CH_2-C**H**$_2$-CH_2- and -S**H**).

The triplet at 2.68 ppm can be assigned to the disulphide, which is formed by oxidation under open-air conditions.

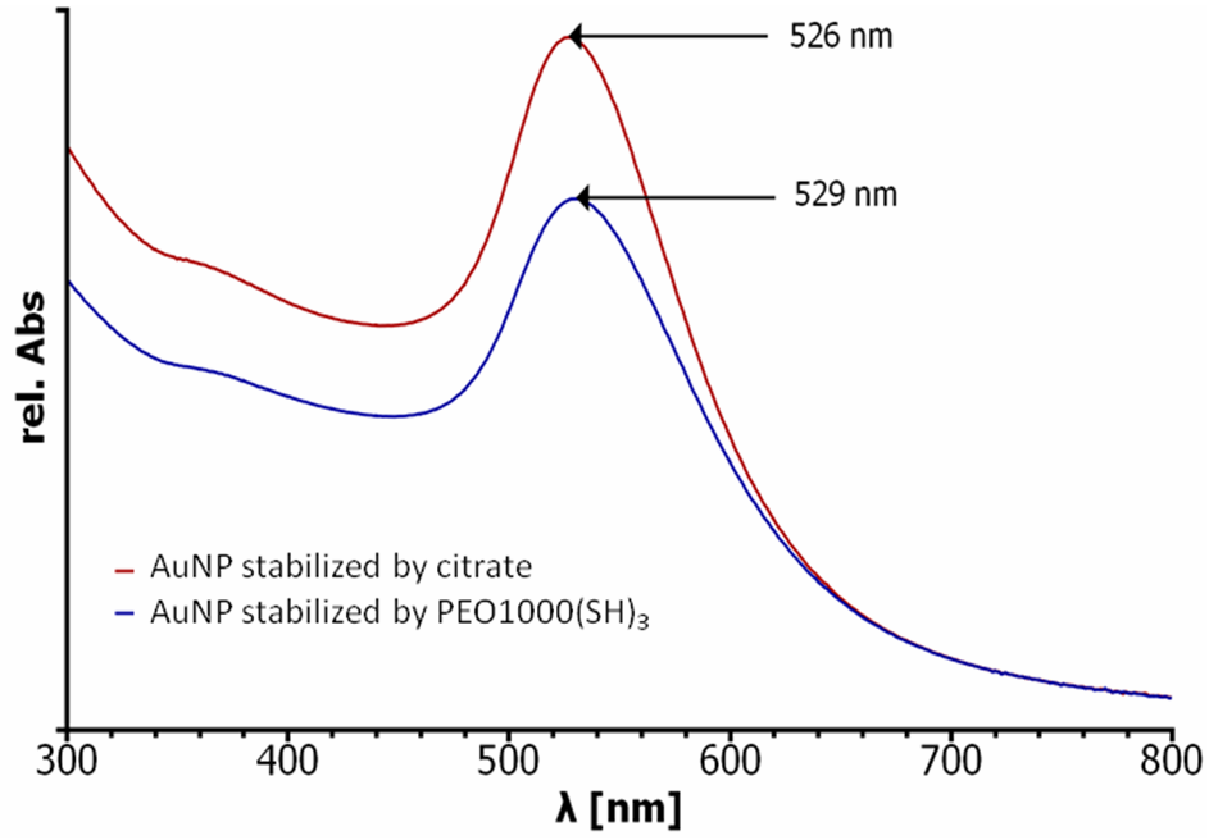

Figure S3: Gold nanoparticles (AuNP) stabilized by citrate and after ligand exchange with PEO1000$(SH)_3$. Ligand exchange of gold nanoparticles was achieved by adding aqueous ligand solution to a solution of citrate stabilized gold nanoparticles. The exchanged citrate molecules were removed by three steps of centrifugation and redispersion of the particles in water.

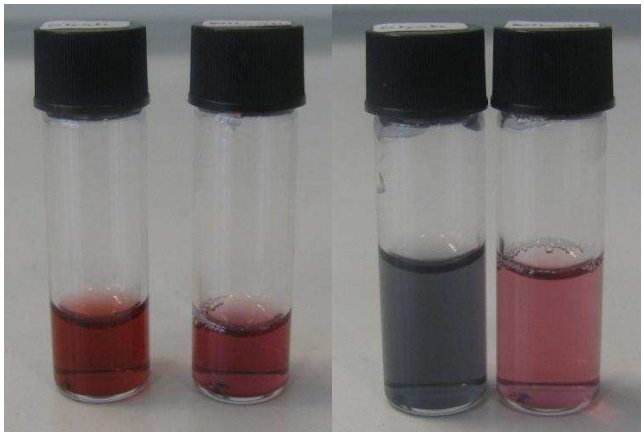

Figure S4: Left picture: AuNPs stabilized by citrate (left) and PEO1000$(SH)_3$ (right). Right picture: The same samples after addition of 1 mL NaCl solution (1 M). The blue color of the citrate stabilized particles indicates agglomeration, while the PEO-capped particles remain unchanged.

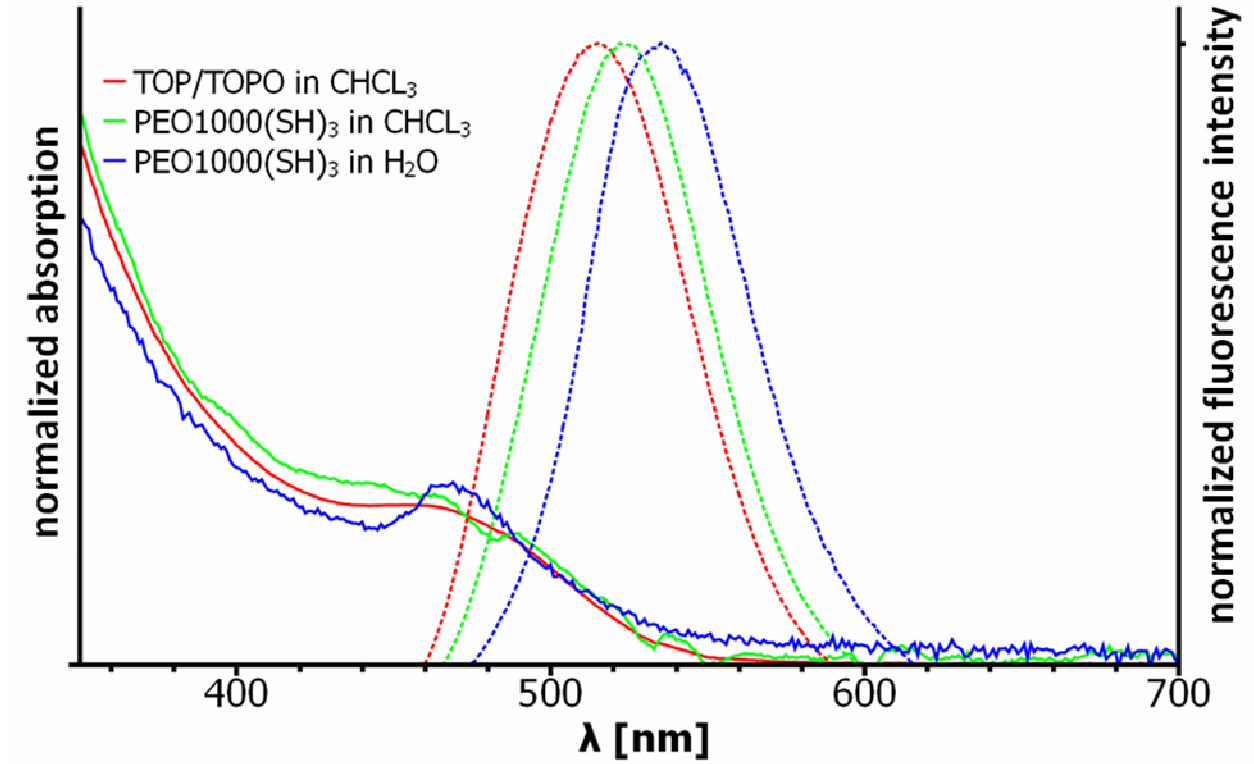

Figure S5: Emission and absorptions spectra of InP/ZnS-NP before and after modification with PEO1000(SH)$_3$-ligands. Ligand exchange of InP/ZnS nanoparticles was achieved analogously to the method for CdSe/CdS/ZnS nanoparticles. Quantum yields of the shown particles were determined to be 30 % for hydrophobic particles, 45 % for particles after ligand exchange in chloroform and 27 % after transfer into water. The relatively large shift of the emission maximum compared to CdSe/CdS/ZnS particles was attributed to the thinner ZnS shell and a therefore larger solvatochroistic effect.

Discussion on the Systematical Error for the Calculation of Particle Concentrations

The particle concentration was calculated by the empirical formula by Peng and coworkers (Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003,** *15*, 2854-2860). It was developed for CdSe core particles, and the application on core/shell/shell particles as employed in this work is expected to have a significant systematical error. In short, the particle size is first determined by a polynomial formula from the wavelength at the first absorption maximum.

$$D = 1.6122 \times 10^{-9}\,\lambda^4 - 2.6575 \times 10^{-6}\,\lambda^3 + 1.6242 \times 10^{-3}\,\lambda^2 - 0.4277\,\lambda + 41.57$$

Then the extinction coefficient is calculated from the particle diameter as

$$\varepsilon = 5857\,(D)^{2.65}$$

Finally, the concentration can be estimated from Lambert-Beer's law. It is corrected by relating the measured half-width at half-maximum *w* of the absorption peak to the one used by Peng's group (14 nm).

Table S1: Measured and calculated values for the Peng formula employed in this work

	CdSe core particles	***CdSe/CdS/ZnS core/shell/shell particles***
λ [nm]	549	569
w [nm]	16	20
D [nm]	3.0	3.5
ε [L mol^{-1} cm^{-1}]	109601	160676
Abs [a.u.]	0.05	0.05
c [nmol/L]	521	445

The measured and calculated values for the particles used in this publication are presented in table S1. A red shift of the absorption maximum of approximately 20 nm was found for all samples produced. The increase in diameter of 0.5 nm correlates well with TEM findings. The extinction coefficient of CdSe/CdS/ZnS particles is 47 % larger than that of pure CdSe cores, which results in a systematically lower calculated concentration. Recent work by Mulvaney and coworkers (Jasieniak, J.; Smith, L.; van Embden, J.; Mulvaney, P.; Califano, M., Re-examination of the Size-Dependent Absorption Properties of CdSe Quantum Dots, *J. Phys. Chem. C* **2009**, *113*, 19468-19474) states that the Peng formula overestimates the particle concentration of CdSe for the particle size discussed here by about 60 %.

This method does therefore not allow for an exact calculation, but is sufficient for a rough estimation of the particle concentration.