Electronic Supplementary Information

On the role of the capping agent and nanocrystal size in photoinduced hydrogen evolution using CdTe/CdS quantum dots sensitizers

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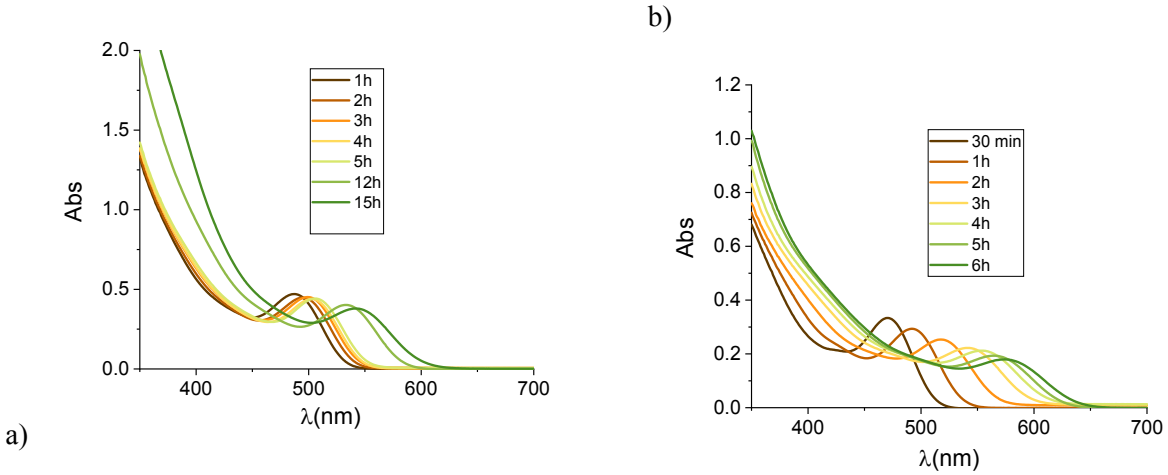


Figure S1. Absorption spectra of a) **MAA** and b) **MSA** QDs at different time during the synthesis ([QDs] = 3.2-11 μM for **MAA** QDs, [QDs] = 1.3-19 μM for **MSA** QDs, aqueous solutions, pH 10.5).

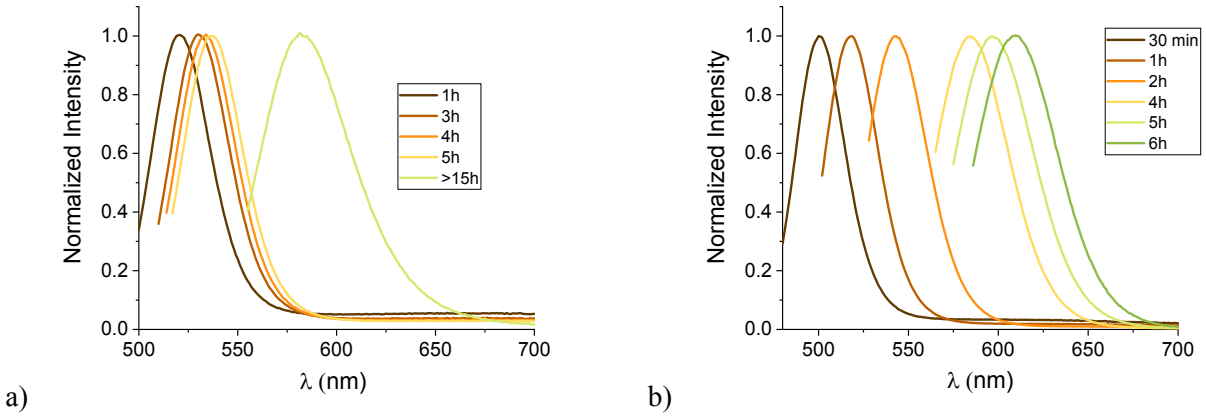


Figure S2. Emission spectra of a) **MAA** and b) **MSA** QDs at different time during the synthesis ([QDs] = 3.2-11 μM for **MAA** QDs, [QDs] = 1.3-19 μM for **MSA** QDs, aqueous solutions, pH 10.5, excitation is performed at the absorption maximum of the excitonic band, see Figure S1).

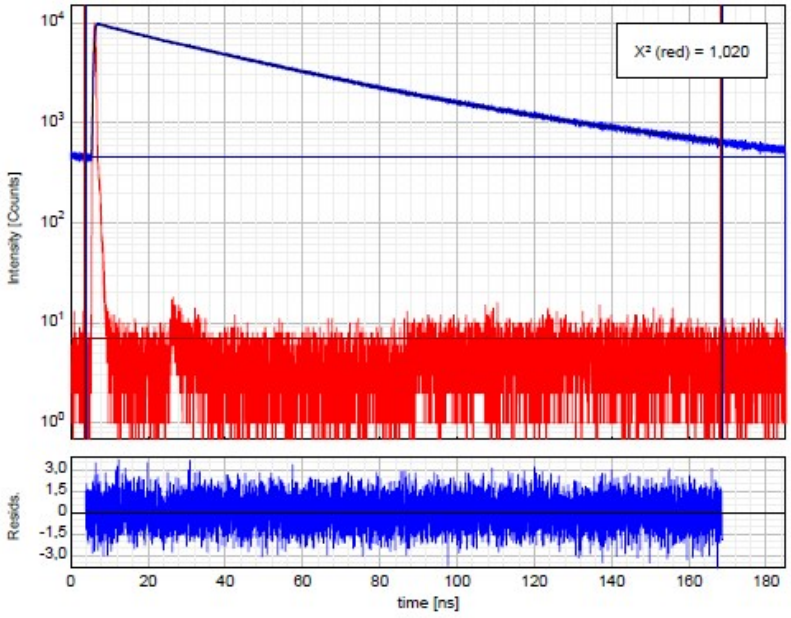


Figure S3. Fluorescence decay of **MPA** QDs with d = 3.3 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 50 ns (84%), τ_2 = 19 ns (11%), τ_3 = 1.4 ns (5%), average lifetime is equal to $<\tau>$ = 44 ns.

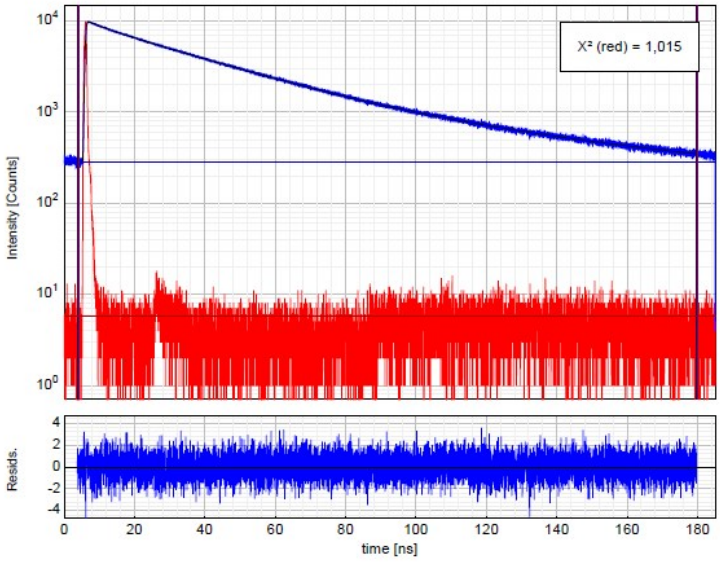


Figure S4. Fluorescence decay of **MPA** QDs with d = 2.8 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 44 ns (61%), τ_2 = 22 ns (32%), τ_3 = 1.7 ns (7%), average lifetime is equal to $<\tau>$ = 34 ns.

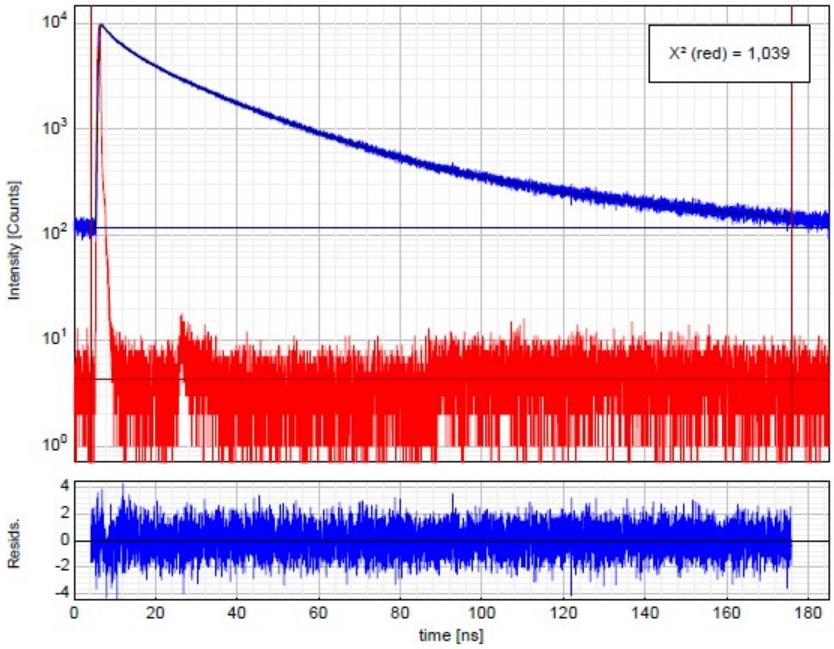


Figure S5. Fluorescence decay of **MAA** QDs with d = 3.2 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 34 ns (35%), τ_2 = 2.5 ns (26%), τ_3 = 12 ns (39 %), the average lifetime is $\langle\tau\rangle$ = 17 ns.

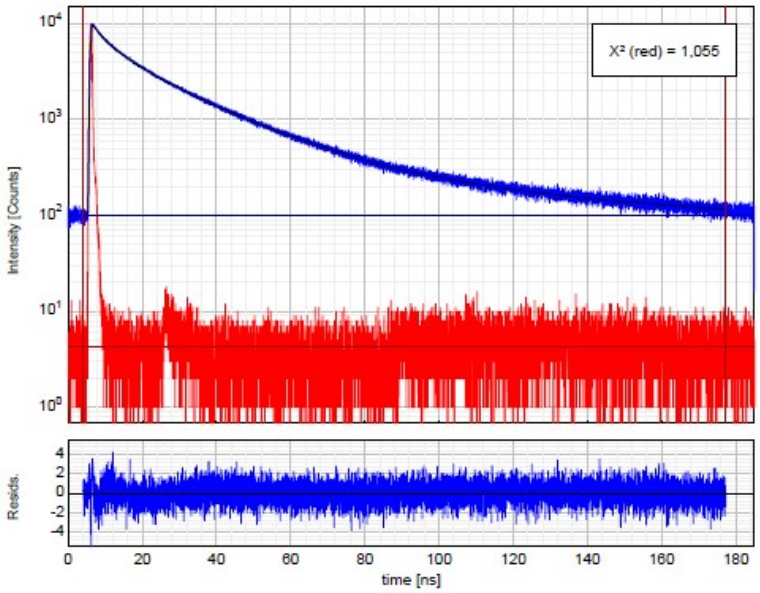


Figure S6. Fluorescence decay of **MAA** QDs with d = 2.6 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 31 ns (28%), τ_2 = 11 ns (44%), τ_3 = 2 ns (28%), the average lifetime is $\langle\tau\rangle$ = 14 ns.

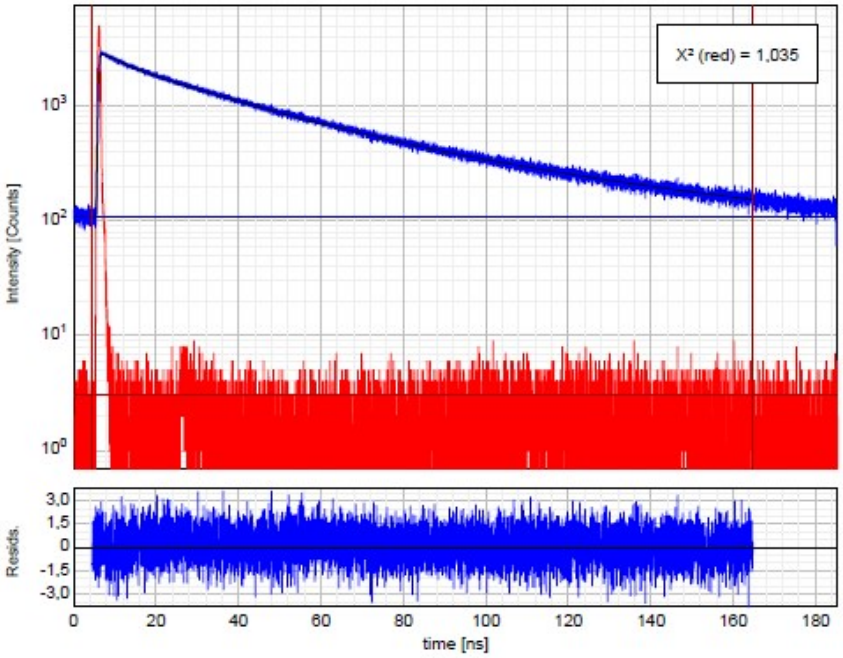


Figure S7. Fluorescence decay of **MSA** QDs with d = 3.4 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 56 ns (44%), τ_2 = 5 ns (14%), τ_3 = 25 ns (42%), the average lifetime is $<\tau>$ = 36 ns.

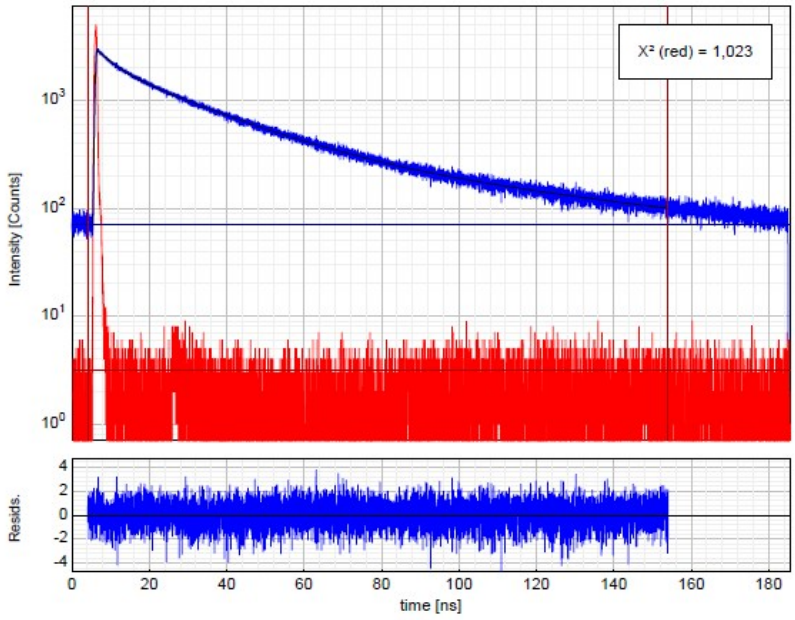


Figure S8. Fluorescence decay of **MSA** QDs with d = 2.8 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 63 ns (17%), τ_2 = 4 ns (28%), τ_3 = 22 ns (55%), the average lifetime is $<\tau>$ = 24 ns.

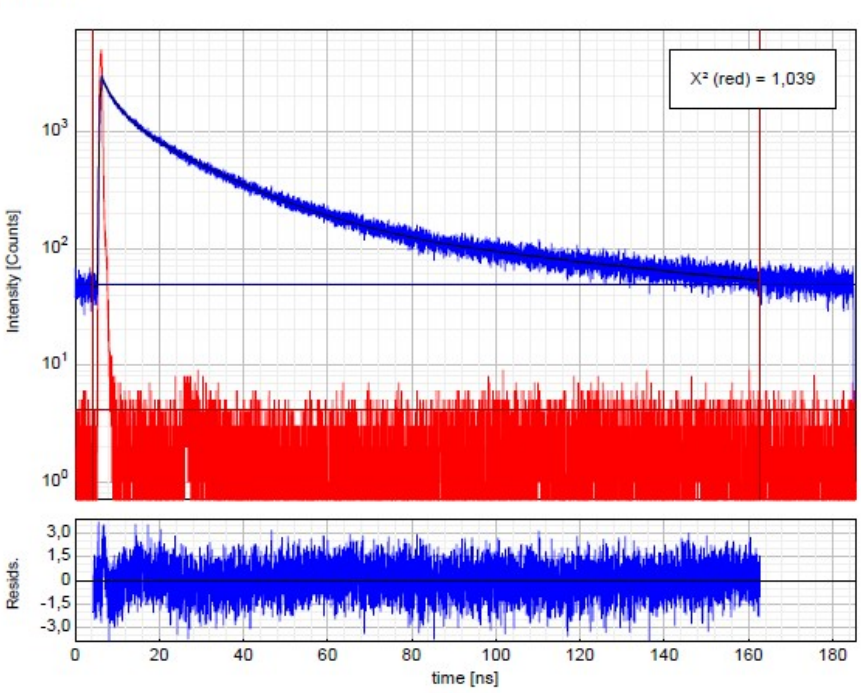


Figure S9. Fluorescence decay of **MPA** QDs with d = 1.7 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 3 ns (48%), τ_2 = 18 ns (45%), τ_3 = 80 ns (7%), the average lifetime is $\langle\tau\rangle$ = 15 ns.

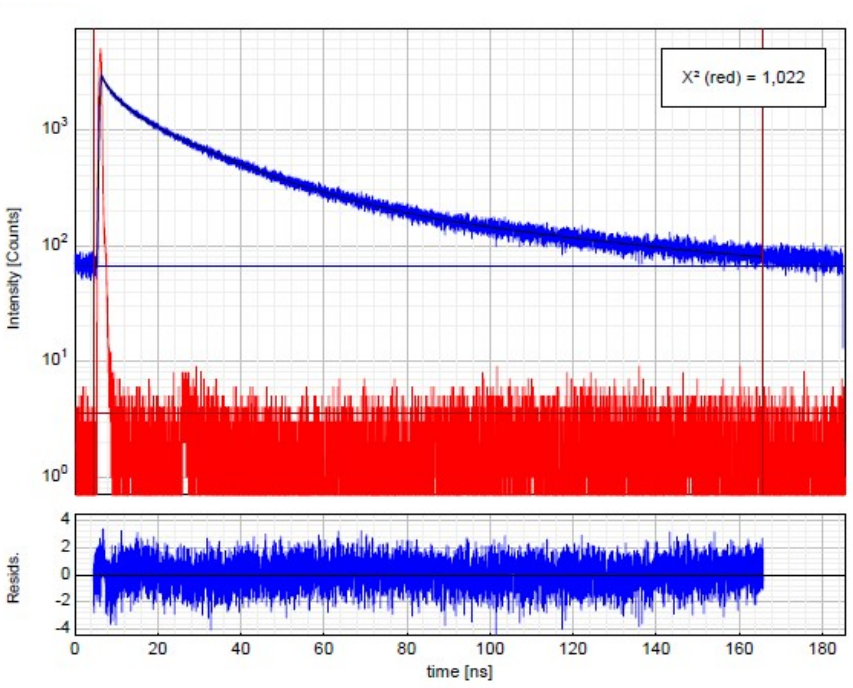


Figure S10. Fluorescence decay of **MPA** QDs with d = 2.4 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting lead to three time-constants: τ_1 = 12 ns (69%), τ_2 = 3 ns (38%), τ_3 = 19 ns (50%), the average lifetime is $\langle\tau\rangle$ = 19 ns.

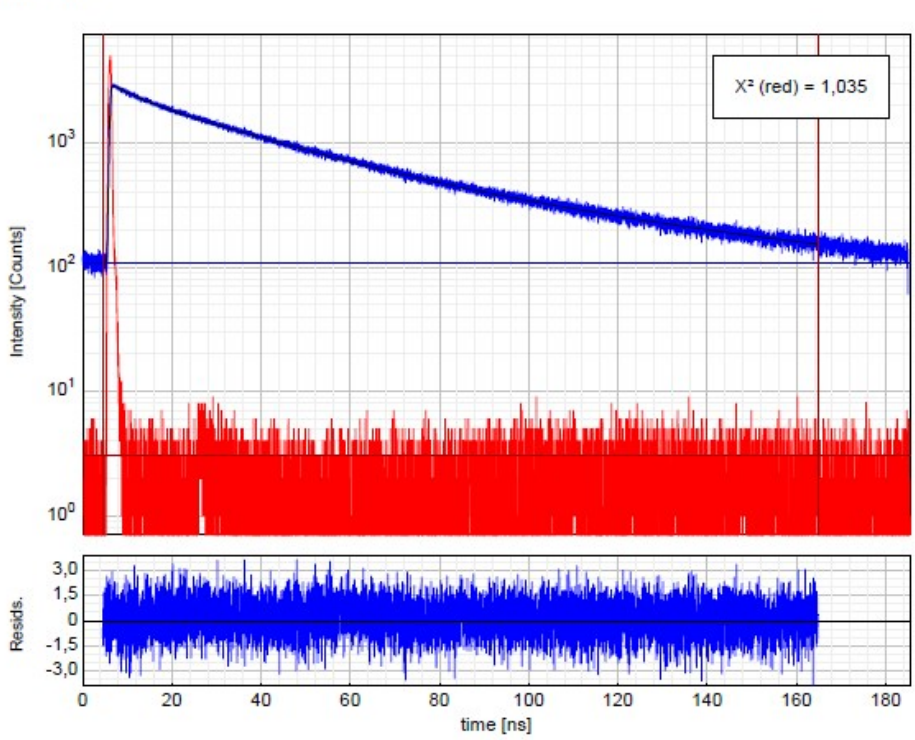


Figure S11. Fluorescence decay of **MPA** QDs with d = 3.1 nm in water measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 56 ns (44%), τ_2 = 5 ns (14%), τ_3 = 25 ns (42%), the average lifetime is $<\tau>$ = 35 ns.

Table S1: EDS Elementary composition of **MPA**, **MSA** and **MAA** QDs samples reported as atomic concentration ratio in order to correlate Cd, Te and S content. Sample **MPA** after photocatalysis experiment is also reported for comparison purpose.

At %	**MPA**	**MSA**	**MAA**	**MPA after photocatalysis**
Te/Cd	12,6	20,3	24,7	32,5
S/Cd	51,7	52,4	59,0	82,0
Te/S	24,9	38,6	42,6	39,6

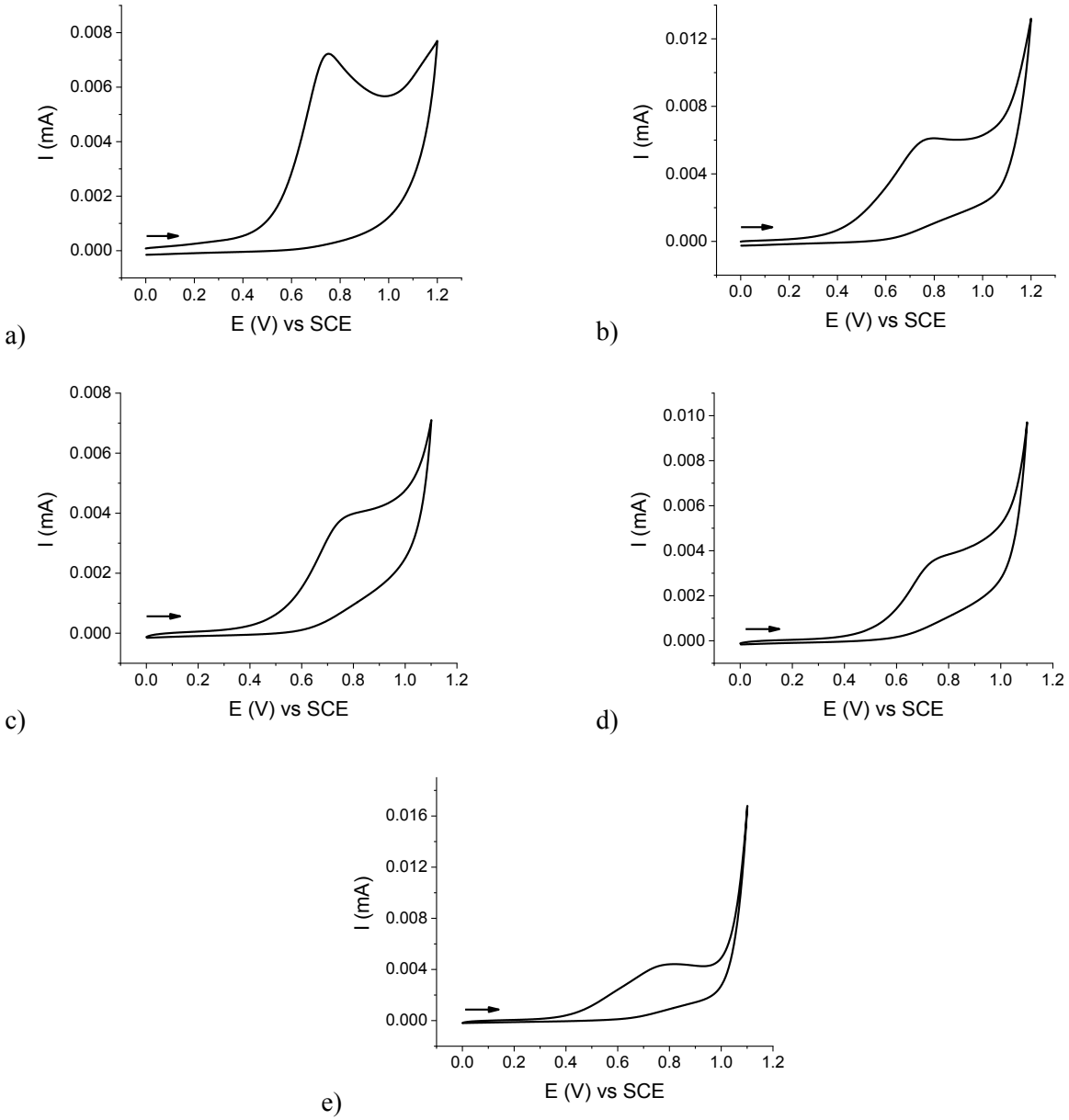


Figure S12. Cyclic voltammetries of **MPA**-capped QDs (2.6-8.9 μM) with different size (a) d = 1.7 nm, b) d = 2.4 nm, c) d = 2.8 nm, d) d = 3.1 nm, and e) d = 3.3 nm. Experimental conditions: aqueous solutions with 0.1 M $LiClO_4$, scan rate of 20 mV/s, GC as the working electrode, SCE as the reference, and Pt as the counter electrode, the arrow indicates the direction of the scan.

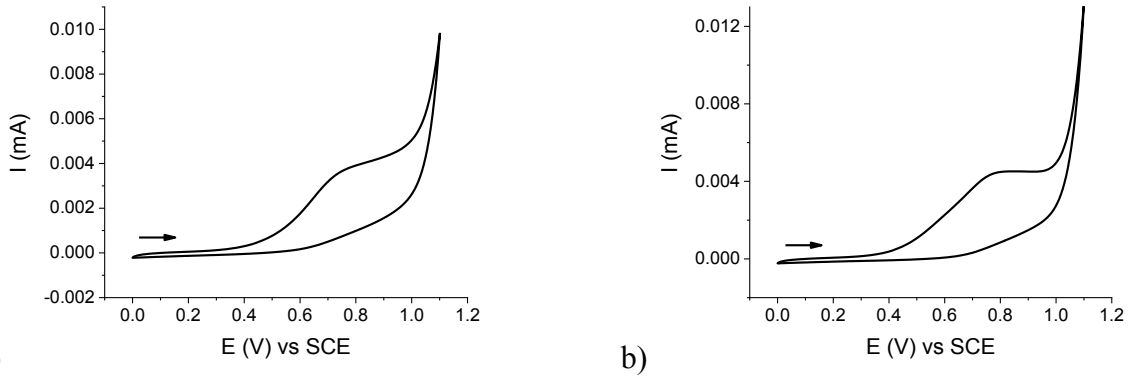


Figure S13. Cyclic voltammetries of **MSA**-capped QDs with different size (a) d = 2.8 nm (2.9 μM) and f) d = 3.4 nm (1.3 μM). Experimental conditions: aqueous solutions with 0.1 M $LiClO_4$, scan rate of 20 mV/s, GC as the working electrode, SCE as the reference, and Pt as the counter electrode, the arrow indicates the direction of the scan.

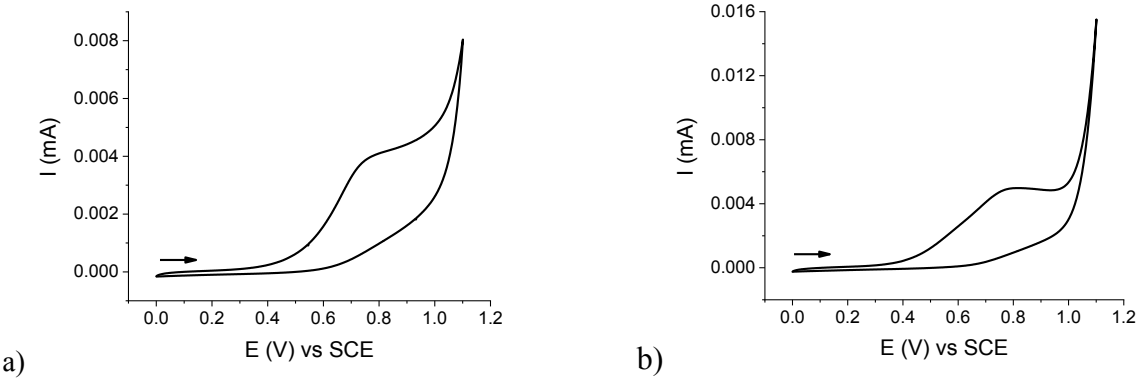
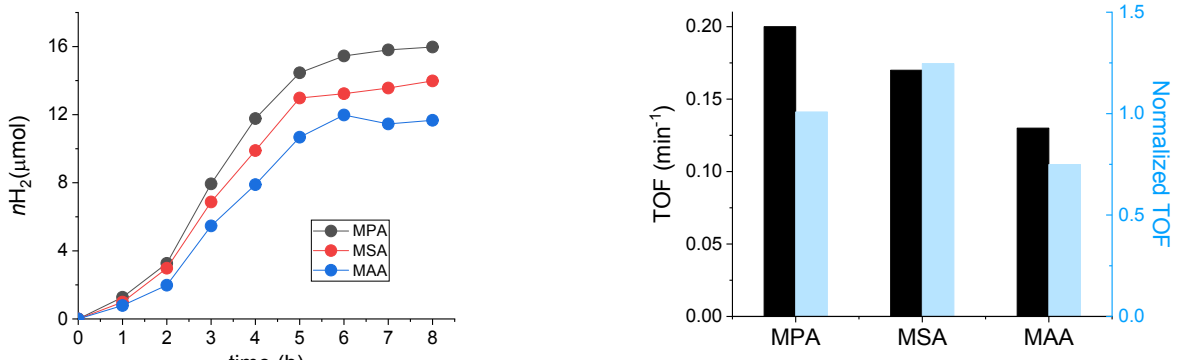
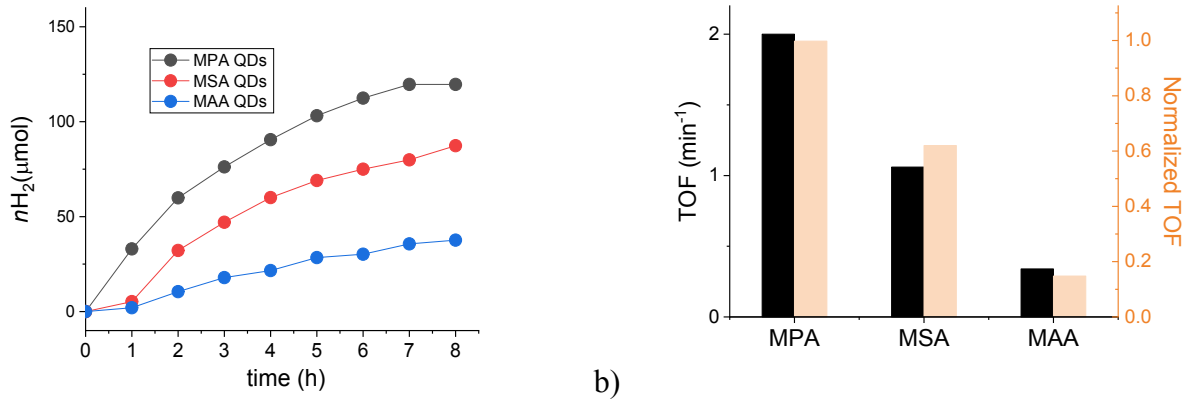


Figure S14. Cyclic voltammetries of **MAA**-capped QDs with different size (a) d = 2.6 nm (5.8 μM) and f) d = 3.2 nm (3.2 μM). Experimental conditions: aqueous solutions with 0.1 M $LiClO_4$, scan rate of 20 mV/s, GC as the working electrode, SCE as the reference, and Pt as the counter electrode, the arrow indicates the direction of the scan.



a) b)

Figure S15. (a) Moles of H_2 produced vs time at pH = 5 for d = 2.7(±0.1) nm QDs (4.7 μM for **MPA**, 5.8 μM for **MAA**, 2.9 μM for **MSA**) with different stabilizing agents (aqueous solution, buffer ascorbate = 1.68 M, [**1**] = 50 μM); maximum TOFs normalized with respect to the fraction of photons absorbed.



a) b)

Figure S16. (a) Moles of H_2 produced vs time at pH = 5 for d = 3.3(±0.1) nm QDs (2.6 μM for **MPA**, 3.2 μM for **MAA**, 1.3 μM for **MSA**) with different stabilizing agents (aqueous solution, buffer ascorbate = 1.68 M, [**1**] = 50 μM); (b) maximum TOFs normalized with respect to the fraction of photons absorbed.

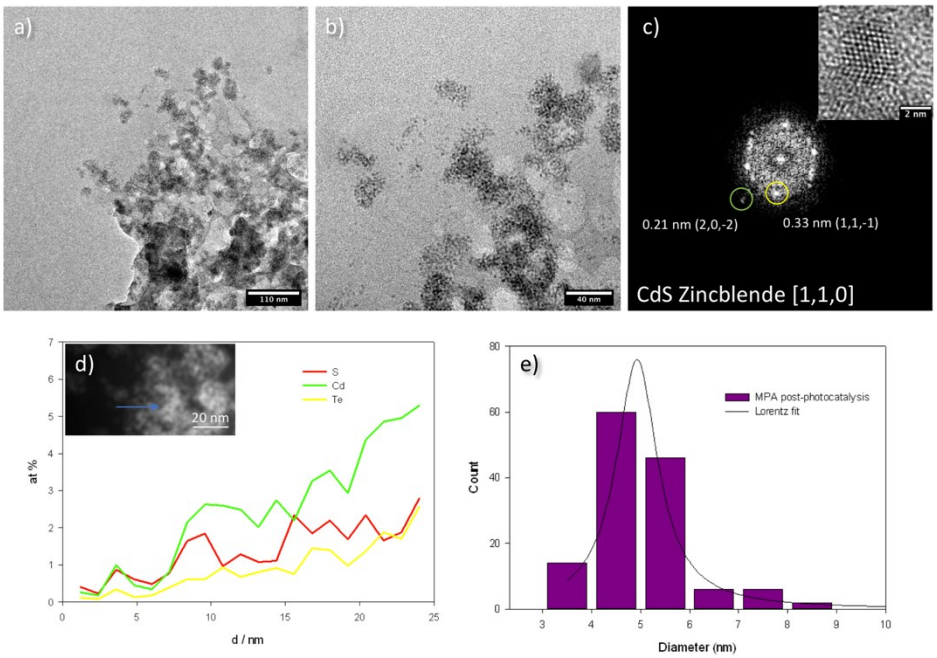


Figure S17. (a,b) Low magnification TEM image of **MPA**-capped QDs after photocatalysis experiment; (c) high magnification HR-TEM detail of a single quantum dot (inset) and relative Fast Fourier Transformate for **MPA**-capped QDs after photocatalysis experiment; d) elemental distribution along a linear profile of a QDs aggregate in the same sample, displayed in the reference STEM-HAADF micrograph in the inset; g) size distribution analysis and Lorentzian fitting of **MPA**-capped QDs obtained in STEM-HAADF mode, displaying an evident increase in average size and polydispersity.

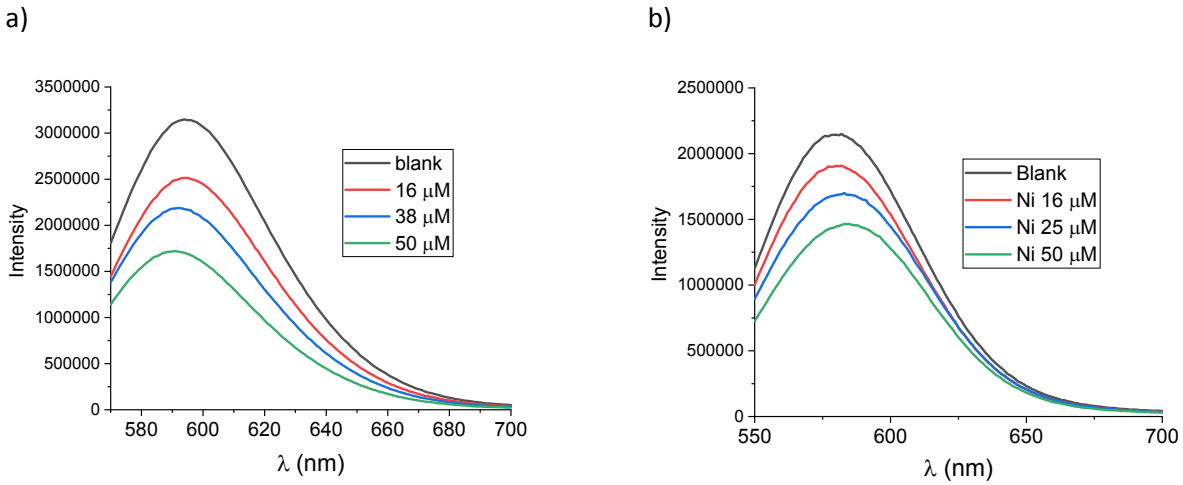


Figure S18. Emission spectra in water recorded at increasing catalyst concentration of **MPA** QDs with (a) d = 3.3 nm (2.6 μM) and (b) d = 2.8 nm (4.7 μM).

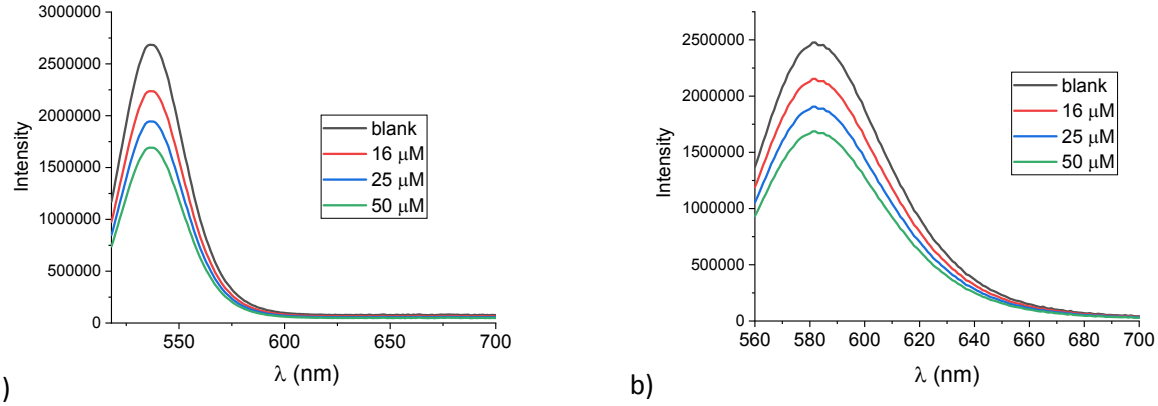


Figure S19. Emission spectra in water recorded at increasing catalyst concentration of **MAA** QDs with (a) d = 3.2 nm (3.2 μM) and (b) d = 2.6 nm (5.8 μM).

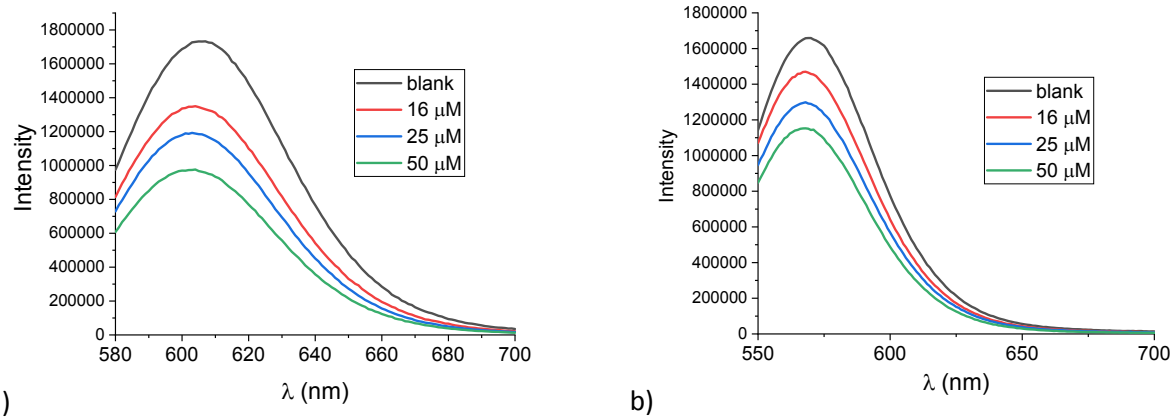


Figure S20. Emission spectra in water recorded at increasing catalyst concentration of **MSA** QDs with (a) d = 3.4 nm (1.3 μM) and (b) d = 2.8 nm (2.9 μM).

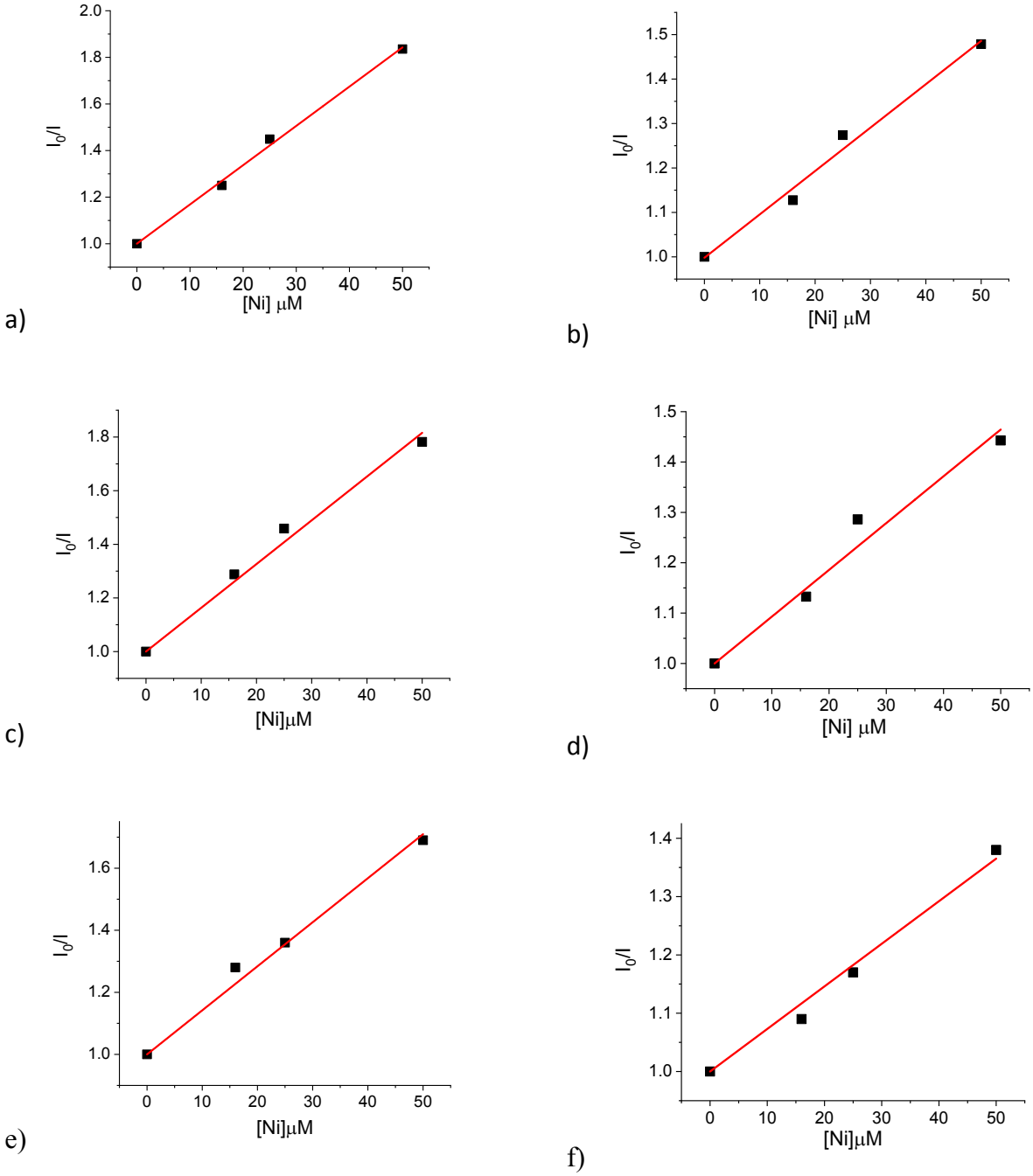


Figure S21. Stern-Volmer plots of (a) d = 3.3 nm (2.6 μM), (b) d = 2.8 nm (4.7 μM) **MPA** QDs; (c) d = 3.4 nm (1.3 μM), (d) d = 2.8 nm (2.9 μM) **MSA** QDs; (e) d = 3.2 nm (3.2 μM), (f) d = 2.6 nm (5.8 μM) **MAA** QDs.

Table S2: K_{SV} and k_Q values of **MPA, MSA** and **MAA** QDs

	K_{SV} M^{-1}	k_Q
MPA QDs, d = 2.8 nm	9760	2.9×10^{11}
MPA QDs, d = 3.3 nm	16850	3.8×10^{11}
MSA QDs, d = 2.8 nm	9290	3.8×10^{11}
MSA QDs, d = 3.4 nm	16430	4.6×10^{11}
MAA QDs, d = 2.6 nm	7530	5.4×10^{11}
MAA QDs, d = 3.2 nm	14190	8.2×10^{11}

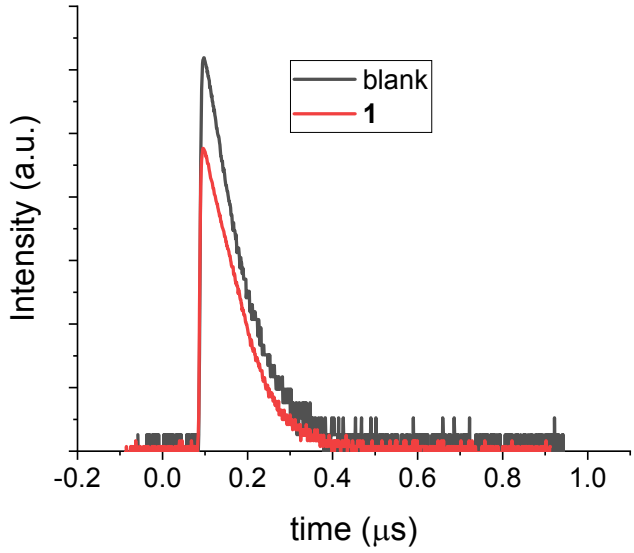
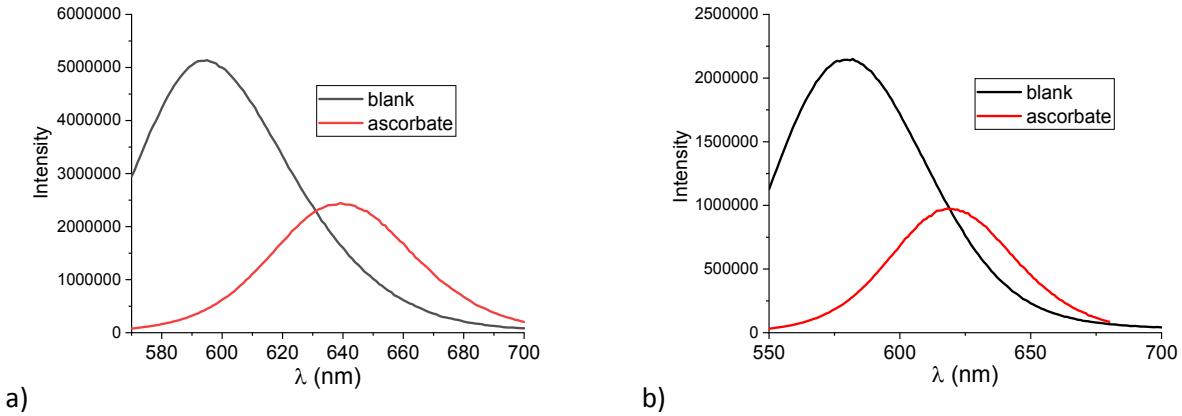


Figure S22. Emission decays of **MPA** QDs (2.6 μM) in aqueous solution measured by laser flash photolysis (excitation at 532 nm) in the presence and in the absence of 50 μM **1**.



a) b)

Figure S23. Emission spectra of (a) **MPA** QDs with d = 3.3 nm (2.6 μM) and (b) **MPA** QDs with d = 2.8 nm (4.7 μM) in aqueous solution in the absence and in the presence of 1.68 M ascorbate (pH 5).

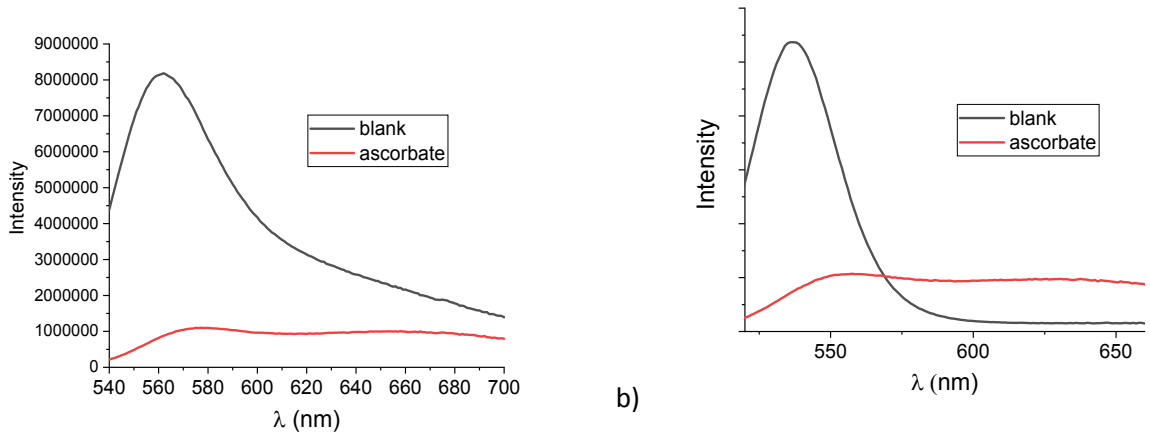
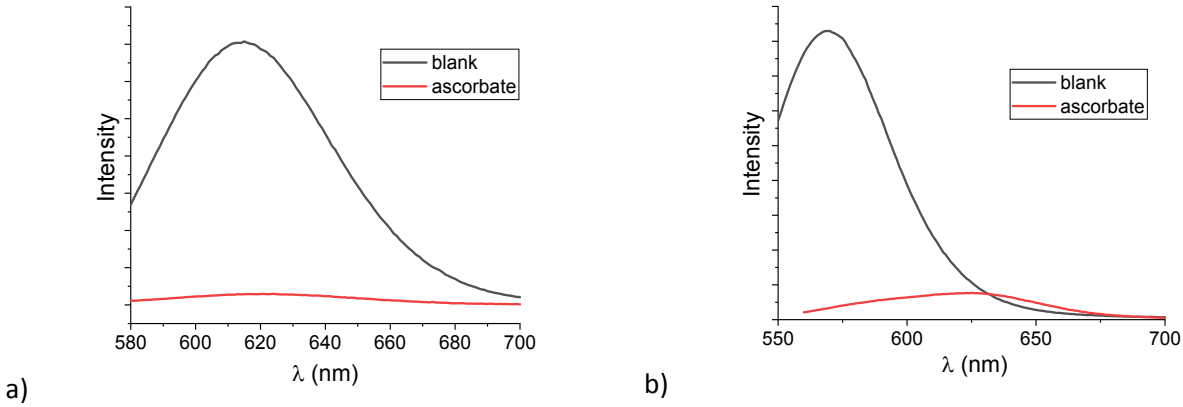


Figure S24. Emission spectra of (a) **MAA** QDs with d = 3.2 nm (3.2 μM) and (b) **MAA** QDs with d = 2.6 nm (5.8 μM) in aqueous solution in the absence and in the presence of 1.68 M ascorbate (pH 5).



a) b)

Figure S25. Emission spectra of (a) **MSA** QDs with d = 3.4 nm (1.3 μM) and (b) **MSA** QDs with d = 2.8 nm (2.9 μM) in aqueous solution in the absence and in the presence of 1.68 M ascorbate (pH 5).

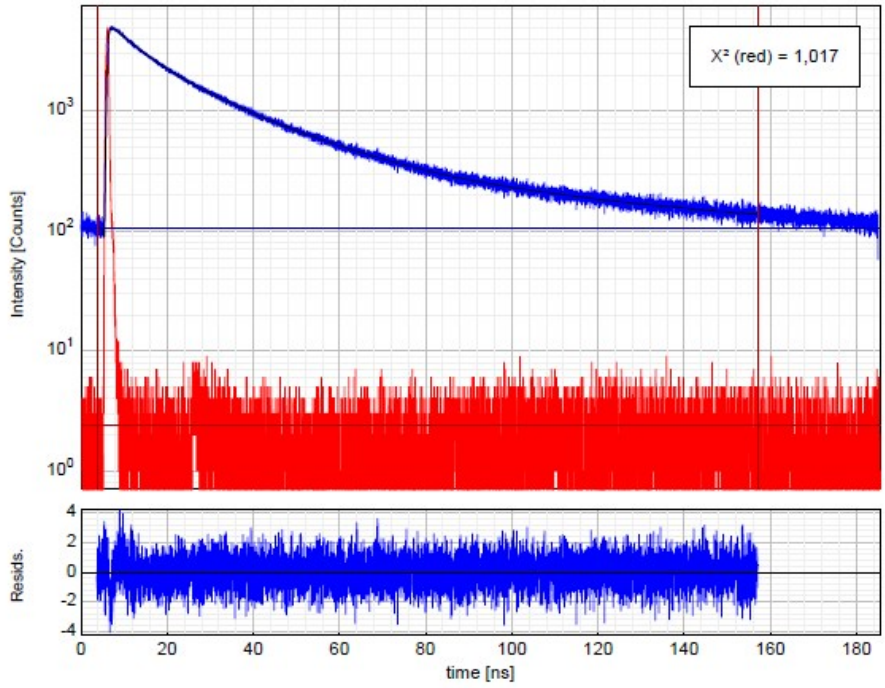


Figure S26. Fluorescence decay of **MPA** QDs with d = 3.3 nm in water in the presence of 1.68 M ascorbate (pH 5) measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 58 ns (10%), τ_2 = 22 ns (46%), τ_3 = 8 ns (44%), the average lifetime is $<\tau>$ = 19 ns.

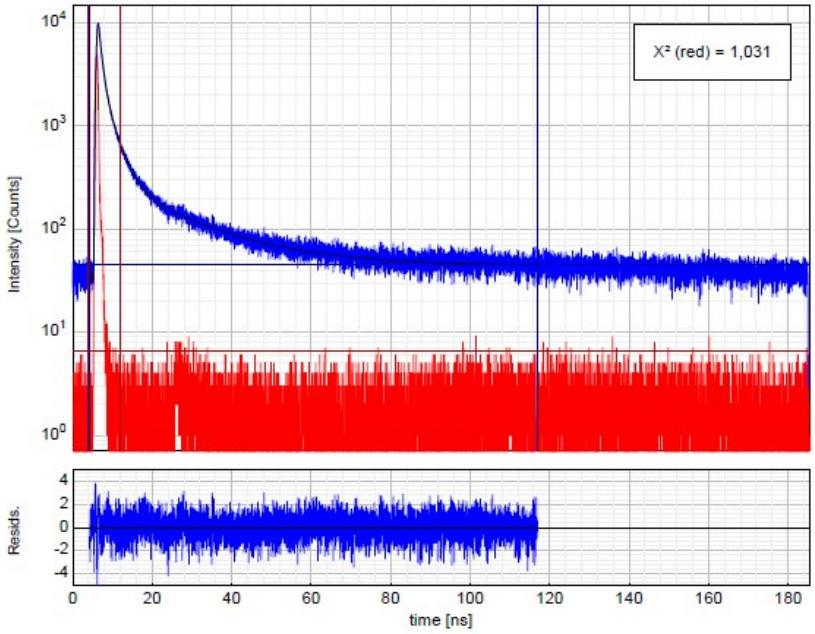


Figure S27. Fluorescence decay of **MSA** QDs with d = 3.4 nm in water in the presence of 1.68 M ascorbate (pH 5) measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 18 ns (2%), τ_2 = 2.7 ns (22%), τ_3 = 0.7 ns (76%), the average lifetime is $<\tau>$ = 1.44 ns.

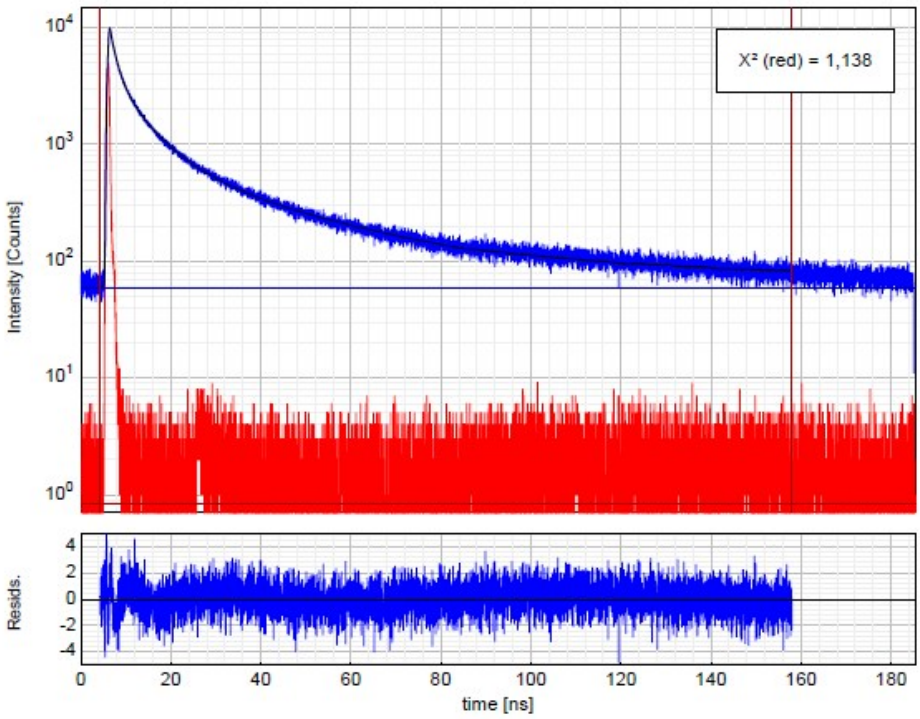


Figure S28. Fluorescence decay of **MAA** QDs with d = 3.2 nm in water in the presence of 1.68 M ascorbate (pH 5) measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 31 ns (6%), τ_2 = 7 ns (28%), τ_3 = 1.3 ns (66%), the average lifetime is $<\tau>$ = 4.7 ns.

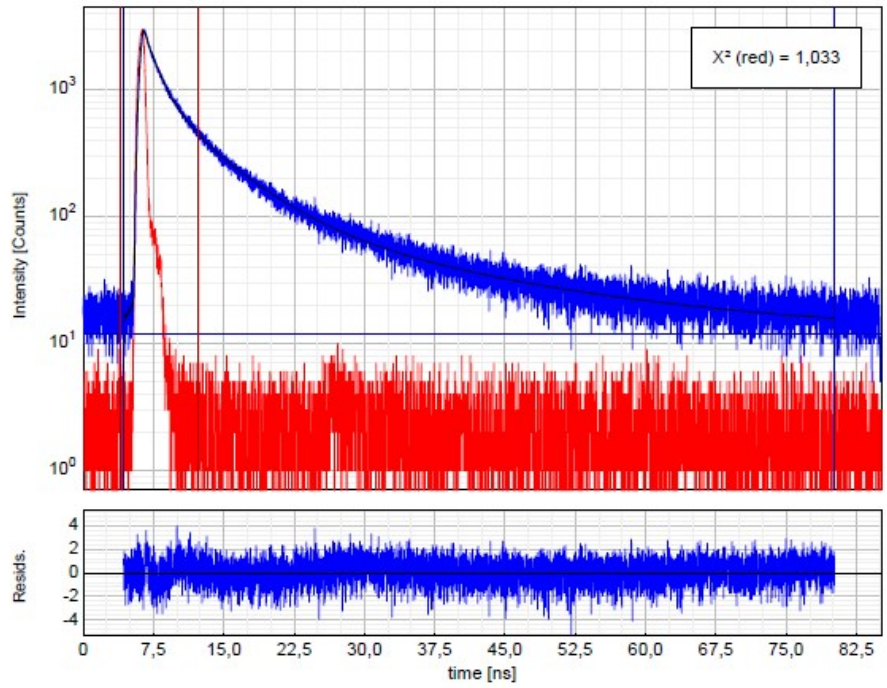


Figure S29. Fluorescence decay of **MAA** QDs with d = 2.6 nm in water in the presence of 1.68 M ascorbate (pH 5) measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 22.7 ns (12%), τ_2 = 5 ns (39%), τ_3 = 1.4 ns (49%), the average lifetime is $<\tau>$ = 5.3 ns.

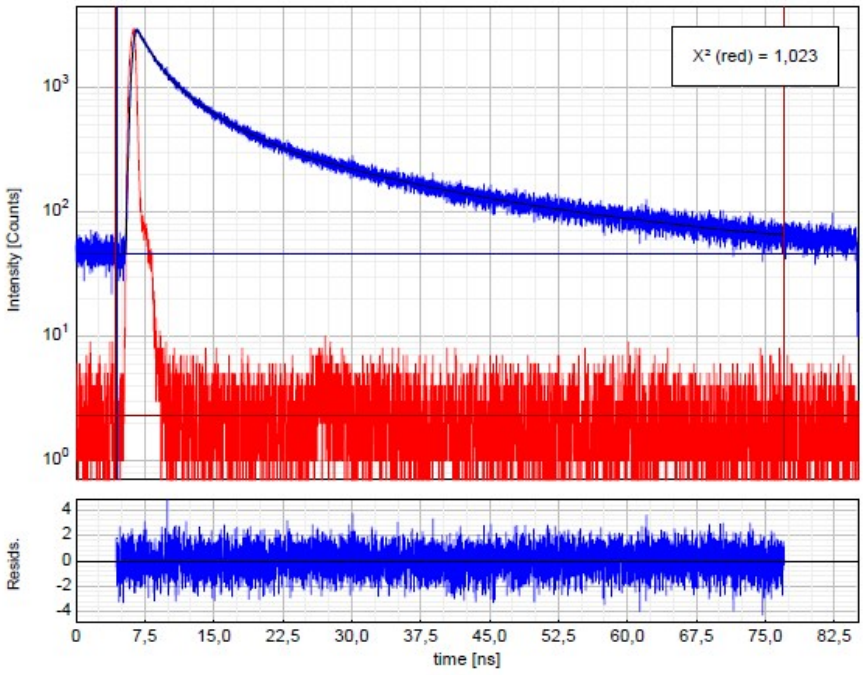


Figure S30. Fluorescence decay of **MPA** QDs with d = 2.8 nm in water in the presence of 1.68 M ascorbate (pH 5) measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 22 ns (12%), τ_2 = 5 ns (39%), τ_3 = 1.4 ns (49%), the average lifetime is $<\tau>$ = 5.5 ns.

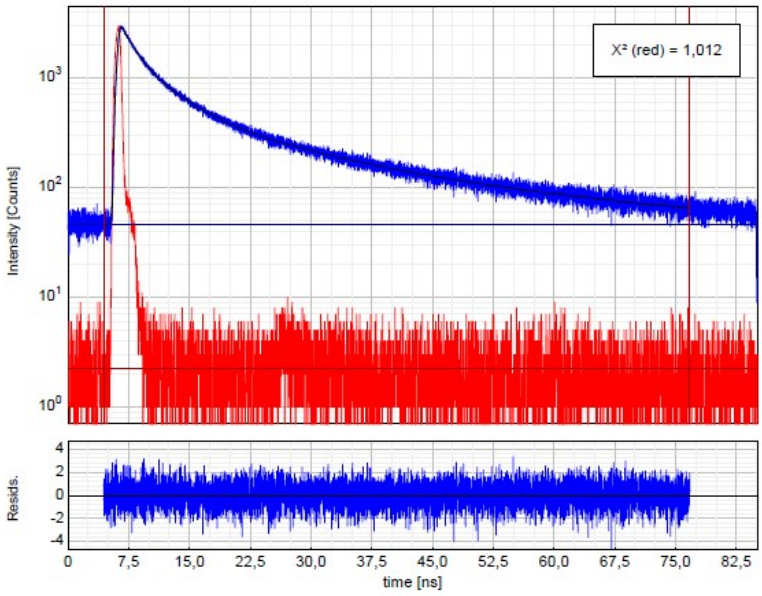


Figure S31. Fluorescence decay of **MSA** QDs with d = 2.8 nm in water in the presence of 1.68 M ascorbate (pH 5) measured by TC-SPC (excitation at 460 nm, analysis at 600 nm). Triexponential fitting leads to three time-constants: τ_1 = 22 ns (4%), τ_2 = 5.6 ns (26%), τ_3 = 1.3 ns (70%), the average lifetime is $<\tau>$ = 3.1 ns.

Table S3. lifetime of QDs in the presence and in the absence of 1.68 M ascorbate (pH 5), along with quenching efficiency.

	τ_0 (ns)	τ_{buffer} (ns)	Quenching efficiency	k (s^{-1})
MPA QDs, d = 2.8 nm	33	5.5	83 %	1.5×10^8
MPA QDs, d = 3.3 nm	44	19	57 %	3.0×10^7
MAA QDs, d = 2.6 nm	14	5.3	62 %	1.1×10^8
MAA QDs, d = 3.2 nm	17	4.7	73 %	1.5×10^8
MSA QDs, d = 2.8 nm	24	3.1	87 %	2.8×10^8
MSA QDs, d = 3.4 nm	35	1.4	95 %	6.8×10^8

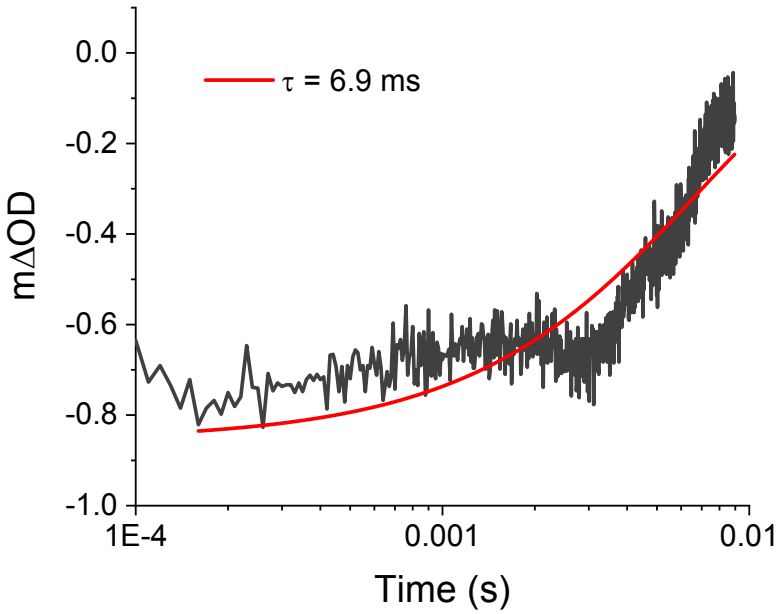


Figure S32: Kinetic decay at 580 nm of **MPA** QDs (2.6 μM) in aqueous solution followed by laser flash photolysis (excitation at 532 nm).

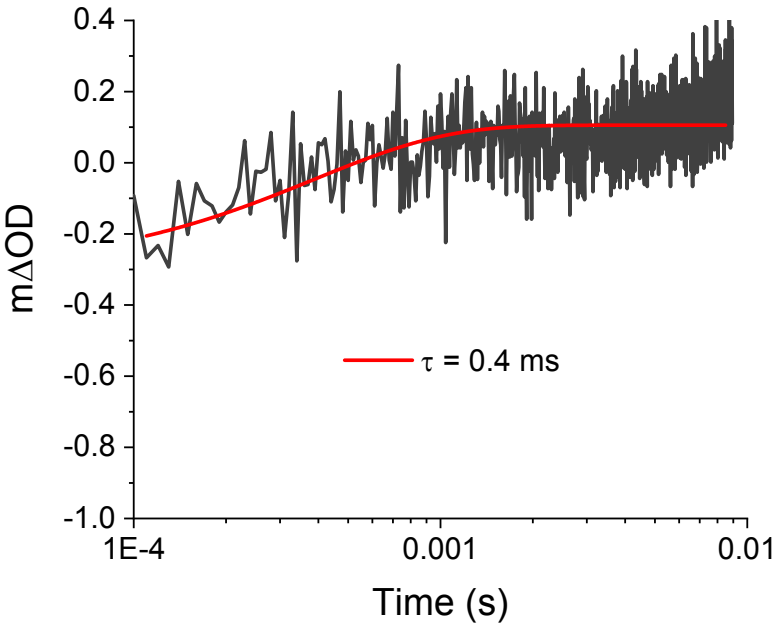


Figure S33. Kinetic decay at 580 nm of **MPA** QDs (2.6 μM) in aqueous solution in the presence of 1.68 M ascorbate buffer (pH 5) followed by laser flash photolysis (excitation at 532 nm).

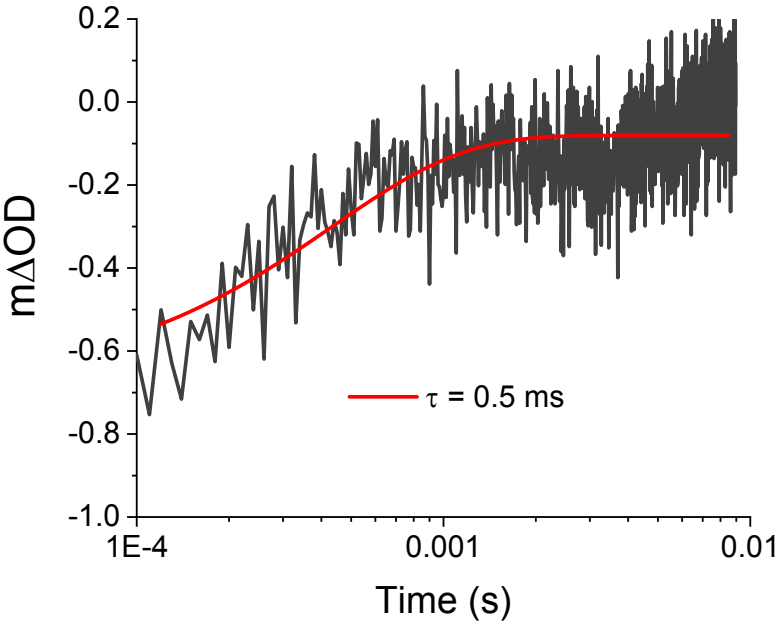


Figure S34. Kinetic decay at 580 nm of **MPA** QDs (2.6 μM) in aqueous solution in the presence of 1.68 M ascorbate buffer (pH 5) and 50 μM **1** followed by laser flash photolysis (excitation at 532 nm).

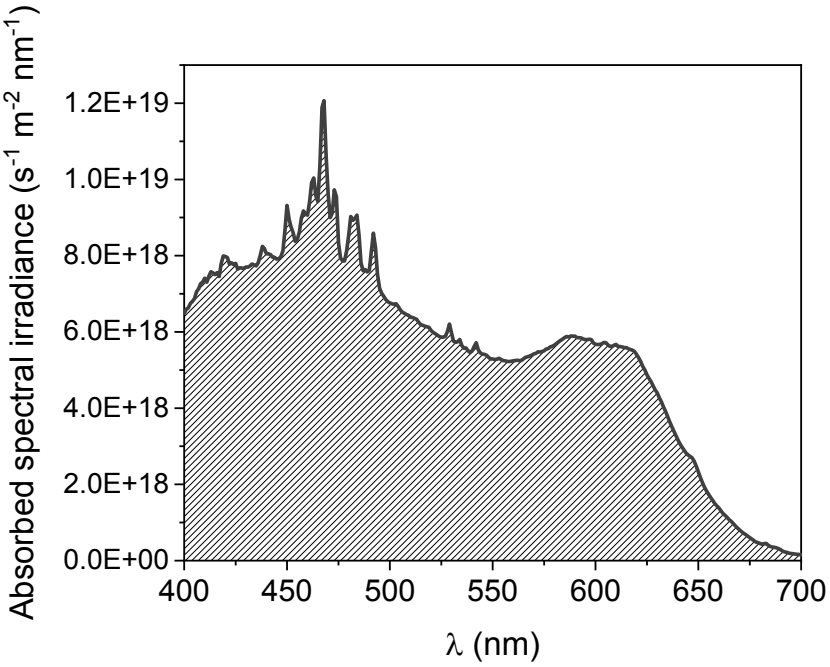


Figure S35. Absorbed spectral irradiance of a solution containing 2.6 μM QDs with d = 3.3 nm, 1.68 M buffer ascorbate at pH = 5, 50 μM **1**. Integration of the curve yields an absorbed photon flux per surface area of $1.6 \cdot 10^{21}$ photons/s·m^2, considering the irradiated surface area of 0.0005 m^2 an absorbed photon flux of $8.3 \cdot 10^{17}$ photons/s can be calculated.