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Supplementary Materials

Water soluble thin coated CdTeS alloyed Quantum Dots for improved FRET applications

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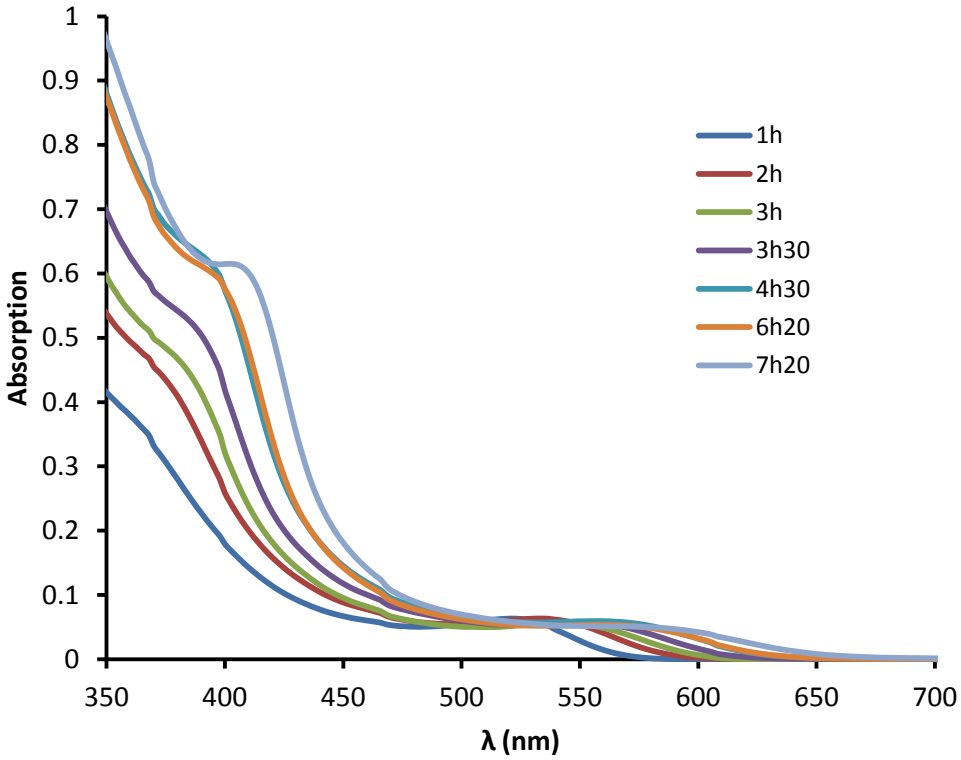
a)



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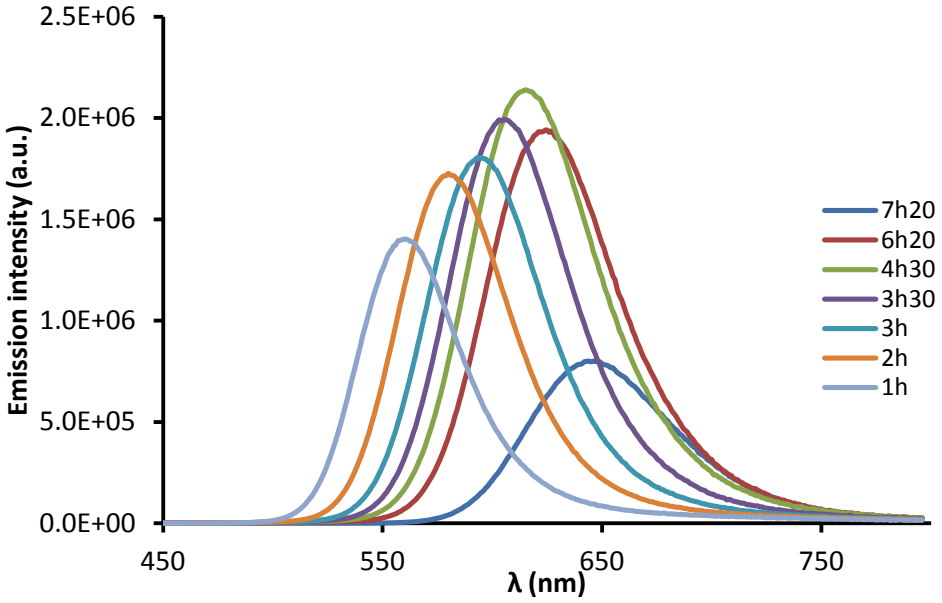

Figure S1: Temporal evolution of the UV-Vis spectra (a) and the corresponding emission spectra (upon excitation at 430 nm) (b) upon refluxing at 100°C the reaction mixture in a 4:0.5:4 Cd:Te:GSH stoichiometry.

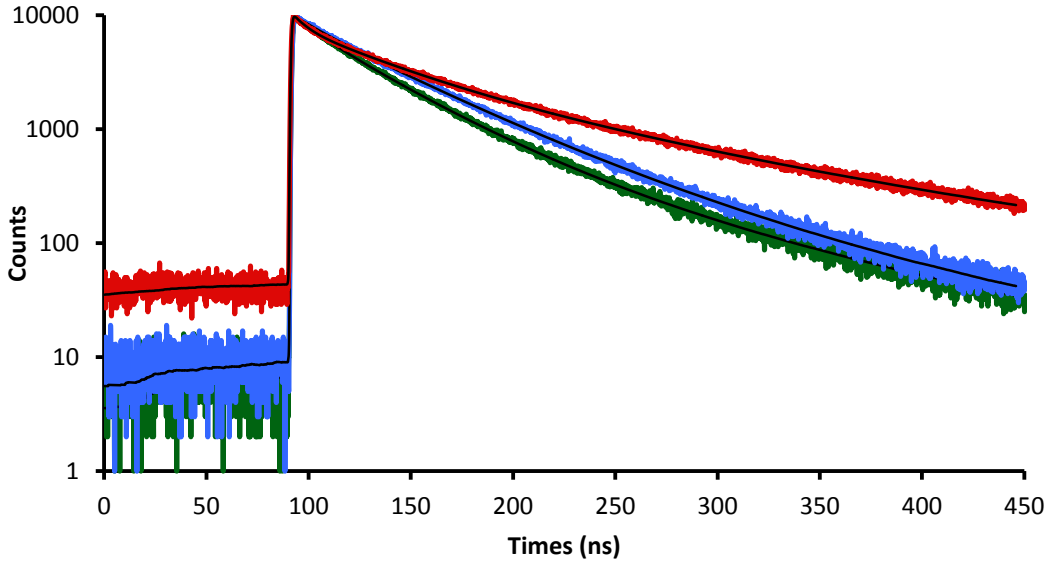

Figure S2: Time-resolved luminescence decay profiles of **QD540** (green), **QD600** (blue), **QD650** (red) in 0.01 M TRIS-HCl pH 7.4, λ_{ex} =370 nm and λ_{em} = 550 nm and the corresponding fitting according to the values given in the text (back).

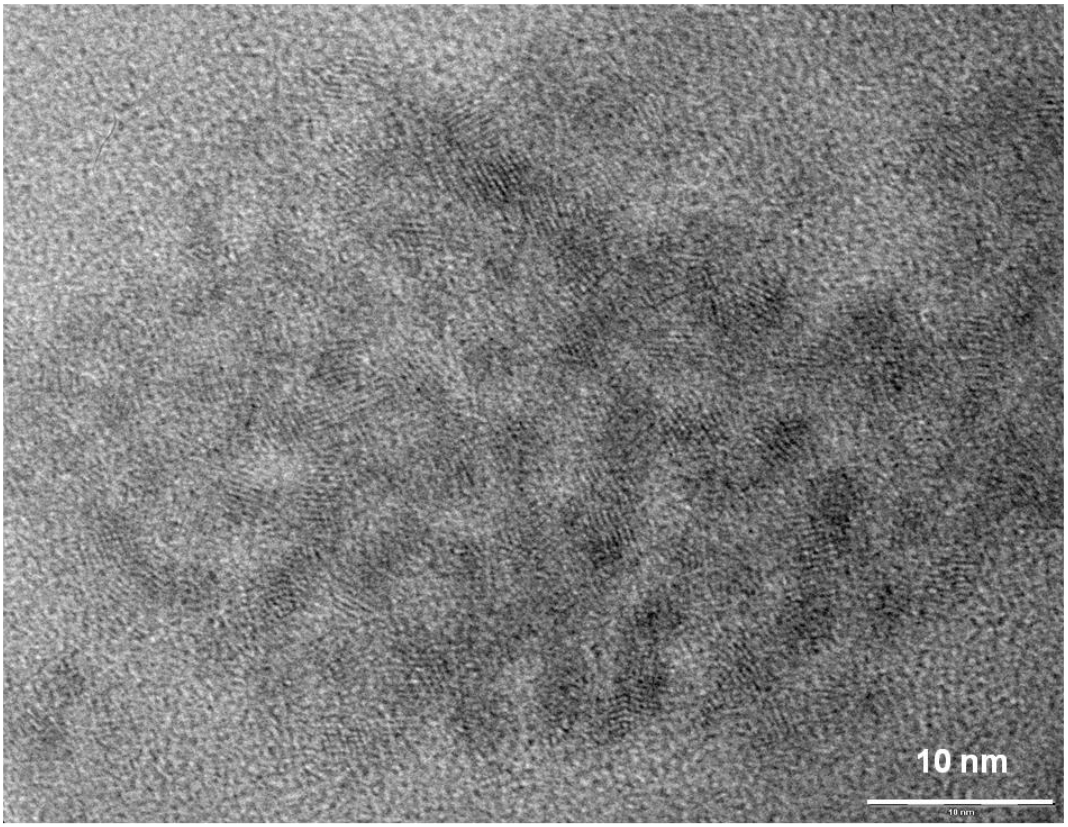

Figure S3: TEM image of **QD540**.

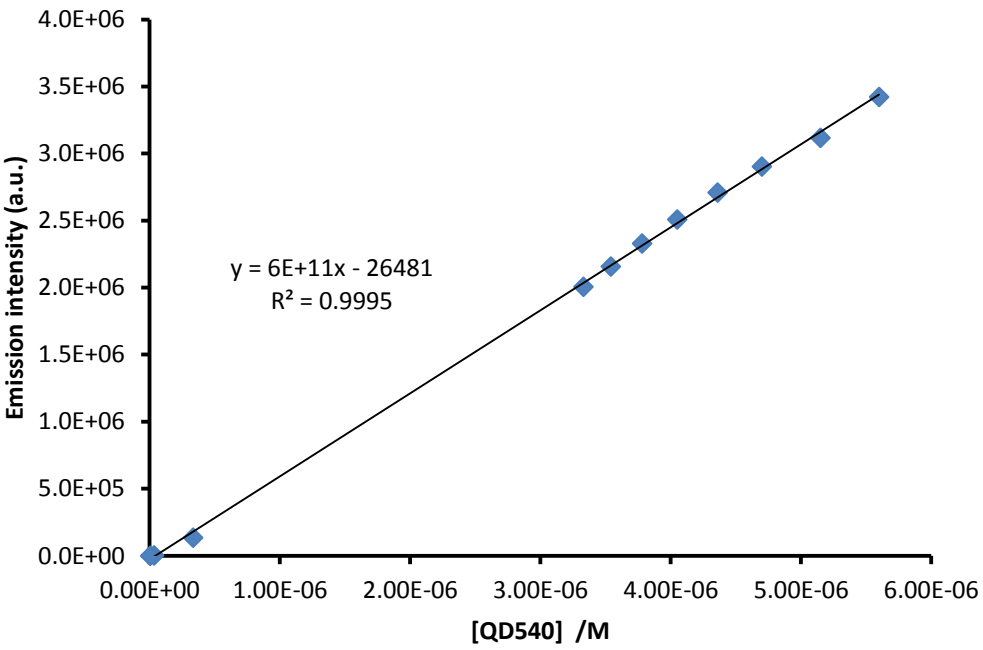

Figure S4: Emission intensity of **QD540** in TRIS/HCl 0.01M, pH 7.3 (λ_{ex} = 430 nm, λ_{em} = 540 nm) as a function of the concentration.

Approximation of the area covered by the GSH from a space filing MM2 model (ChemBio3D Ultra):

The required space for one GSH molecule on the surface of the QD was estimated from a space-filling MM2 model, in which the surface of the CdTedS quantum dot was modelled as a CdS cluster. The area covered by the ligand was approximated modelled as a conical form, with maximum height z_{max} and radius r.

$$z_{max} = \sqrt{(a^2 - r^2)} = 9.59 \text{ Å}$$
$$A_{Ligand} = \pi r^2 = 77.0 \text{ Å}^2$$

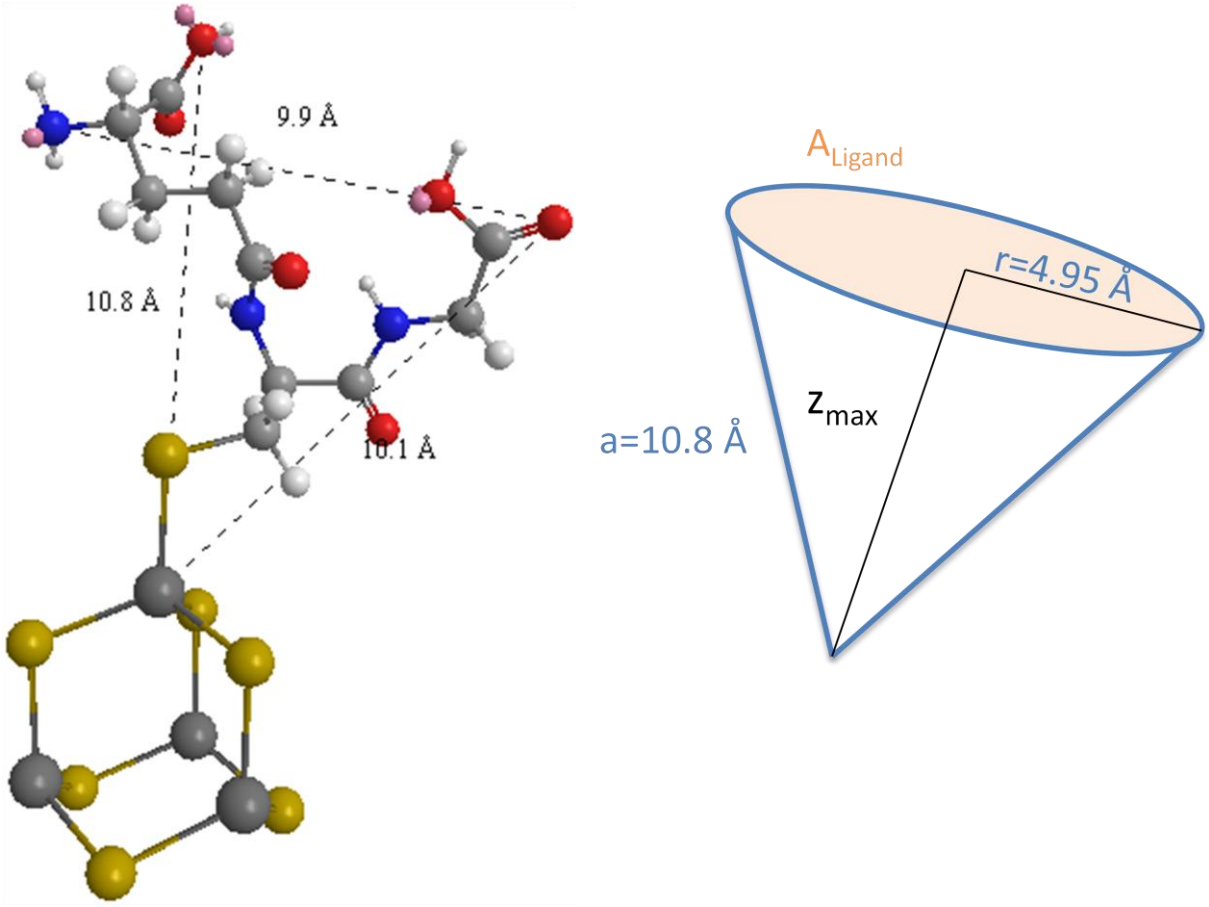

Figure S5: Approximation of the area covered by the GSH from a space filing MM2 model (ChemBio3D Ultra).

Table S1 Optical properties as well as chemical formulae of the $CdTe_xS_y$-GSH QDs at seven different reaction timesand the corresponding density (ρ), diameters (D, Th = obtained from Equation 3 and Exp = measured by TEM), volumes (V), as well as their molecular weights: MW (total molecular weight), MW_{core} (of the $CdTe_xS_y$ core only) and total number of GSH per QD.

	Rq (%)	D_{Th}(nm)	FWHM	Em	T (min)	V_{Th}(nm3)	ρ (kg/m3)	GSH (mmol)	Chemical Formula	MW_{core} (g/mol)	MW (g/mol)
E107 3	15.2	2.85	55	555	60	12.1	5.28	1.55	$CdTe_{0.13}S_{0.15}(GSH)_{0.69}$	38314	99100
E107 5	19.9	3.1	61	575	120	15.6	5.13	1.41	$CdTe_{0.14}S_{0.32}(GSH)_{0.47}$	48069	97169
E107 7	21.7	3.2	62	591	180	17.1	5.2	1.35	$CdTe_{0.12}S_{0.33}(GSH)_{0.44}$	53578	107880
E107 8	24.7	3.28	64	601	210	18.5	5.05	1.03	$CdTe_{0.15}S_{0.58}(GSH)_{0.35}$	56351	95466
E107 9	28	3.32	69	612	270	19.2	5.01	0.92	$CdTe_{0..12}S_{0.55}(GSH)_{0.22}$	57779	86262
E107 10	25.7	3.35	72	624	375	19.7	5.01	0.82	$CdTe_{0.11}S_{0.54}(GSH)_{0.21}$	59435	86868
E107 11	11.4	3.37	77	647	435	20.03	4.94	0.31	$CdTe_{0.11}S_{0.55}(GSH)_{0.09}$	59586	71130

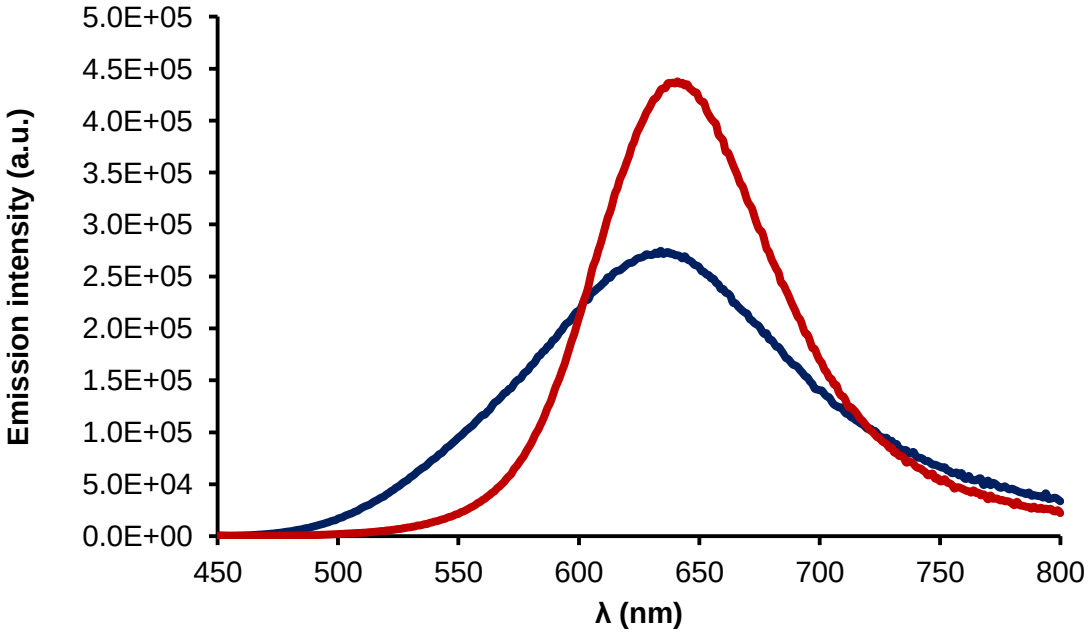

Figure S6: Emission spectra of quantum dots emitting at 636 nm before (blue) and after addition of GSH at room temperature (red, Citrate buffer, pH 8.5).

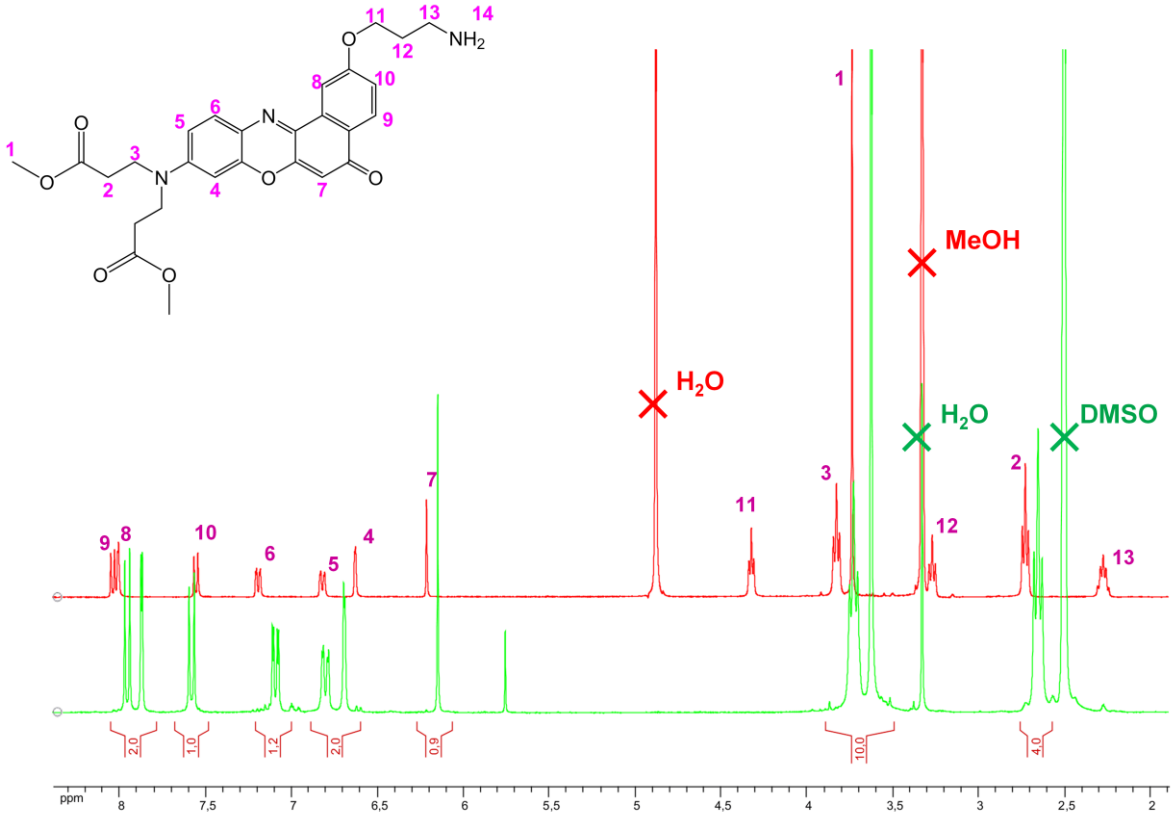

Figure S7: ^{1}H NMR spectrum of functionalized Nile-Red dyes (**1** in *d6*-DMSO, green and **3** in MeOD, red), 300 MHz.

Calculation of the Dye/QD ratios of QD-NR1, QD-NR2, QD-NR3, QD-NR4, QD-NR5, and QD-NR6 from their UV-absorption spectra:

The UV-absorption spectra ($A(\lambda)$) of the conjugated QDs have been fitted to a linear combination of the absorption of the Nile-Red ($A_{NR}(\lambda)$) and of the QD540 ($A_{QD}(\lambda)$):

$$A(\lambda) = a\, A_{NR}(\lambda) + b\, A_{QD}(\lambda)$$

The corresponding Dye and QD concentrations were obtained from the populations *a* and *b*, by taking into account the respective extinction coefficients, *i.e.* 16600 L. $mol^{-1}.cm^{-1}$ for the dye at 535 nm and 70 130 L. $mol^{-1}.cm^{-1}$ for the QD 540 at 400 nm.
Values are summarized in Table S1.

Sample	*Eq.*	*b*	*a*	*[QD]*	*[NR]*	*[NR]/[QD]*
QD-NR1	5	1.68	0.18	9.60616E-06	7.67711E-06	0.79918599
QD-NR2	9	3.11	0.55	1.77828E-05	2.34578E-05	1.31912799
QD-NR3	13	2.5	0.49	1.42949E-05	2.08988E-05	1.46197756
QD-NR4	18	2.2	0.45	1.25795E-05	1.91928E-05	1.5257187
QD-NR5	23	2.16	0.46	1.23508E-05	1.96193E-05	1.58850548
QD-NR6	37	2.09	0.52	1.19505E-05	2.21783E-05	1.85584497

Table S2: Factors *a* and *b*, and corresponding NR and QD concentrations as well as NR/QD ratios for **QD-NR1**, **QD-NR2**, **QD-NR3**, **QD-NR4**, **QD-NR5**, and **QD-NR6** upon addition of 5 to 3 eq. of Nile-Red dye.

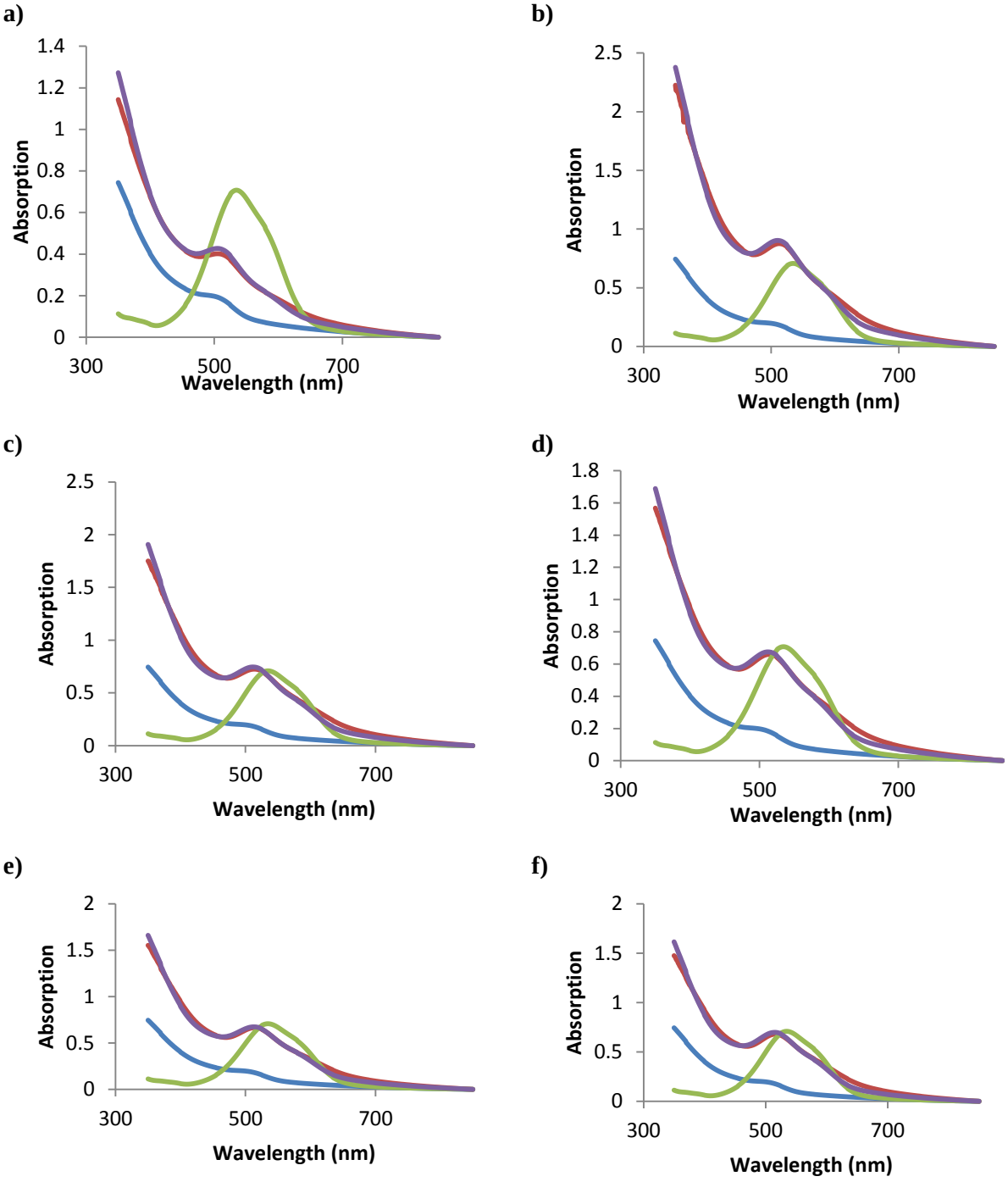

Figure S8: Experimental absorption spectra of Nile-red (green), **QD540** (blue) and for conjugated QDs (red) with increasing dye/QD molar ratio as well as calculated spectra (purple) : a) **QD-NR1**, b) **QD-NR2**, c) **QD-NR3**, d) **QD-NR4**, e) **QD-NR5**, and f) **QD-NR6**.

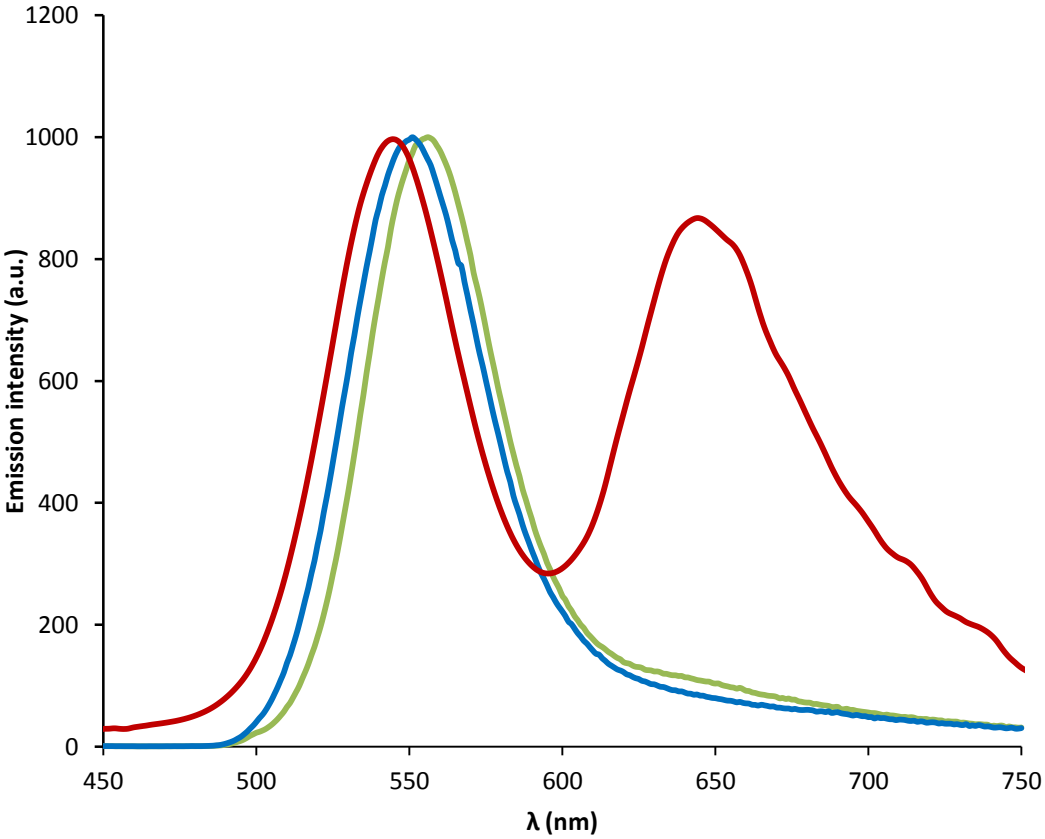

Figure S9: Normalized emission spectra of unconjugated QDs in absence of Nile-Red (blue), after mixing with of 23 equivalents of Nile-Red (green) and of conjugated QDs (NR/QD = 2.40, red), 0.01 M TRIS-HCl pH 7.4, λ_{ex} = 375 nm.

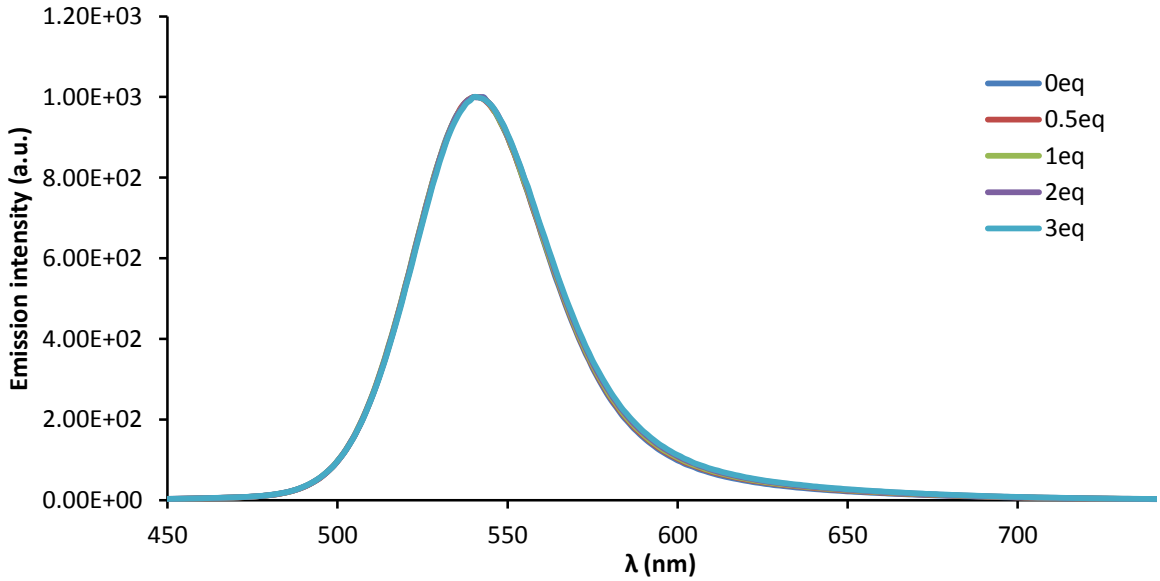

Figure S10: Normalized emission spectra of **QD540** (blue) and after mixing with of 0, 0.5, 1,2 and 3 equivalents of Nile-Red in 0.01 M TRIS-HCl pH 7.4, λ_{ex} = 375 nm.

Background FRET theory and equations

The overlap integral $J(\lambda)$ between the QDs emission spectrum and the Nile Red absorption spectrum has been calculated according to Equation (S1) and amounts to 1.27×10^{15} M^{-1} cm^{-1} nm^4:

$$J(\lambda) = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 \, d\lambda \qquad \text{(S1)}$$

where $F_D(\lambda)$ is the normalized emission of the donor (QD) and $\varepsilon_A(\lambda)$ is the absorption coefficient of the acceptor (Nile Red) at wavelength λ.

The Förster radius R_0 (nm), *ie.* the distance at which the efficiency of the FRET is 50%, could be calculated from the value of $J(\lambda)$ and from the value of the NHs-activated QDs (**QD540** in presence of NHS/EDCI) quantum yield (ϕ_D = 0.24) by Equation (S2):

$$R_0^6 = 8.79 \times 10^{-5} n_r^{-4} \phi_D \chi^2 J(\lambda) \qquad \text{(S2)}$$

where ϕ_D is the quantum yield of the donor in the absence of acceptor, χ^2 is the orientation factor of the donor and acceptor dipoles (assumed to be equal to 2/3 in the case of dynamic averaging of the donor and acceptor dipoles within the donor lifetime),[1] n_r is the refractive index of the solution (e.g., n_r = 1.33 for water), N_{Av} is Avogadro's number.

The energy transfer efficiencies have been calculated from the variations of the intensity of the QDs according to Equation (S3):

$$E_{FRET} = 1 - \frac{I_{DA}}{I_D} \qquad \text{(S3)}$$

where I are the intensities (I) of the donor in absence of acceptor (X_D) and for the donor-acceptor pair (X_{DA}).

The distance between the donor and the acceptor, r can be obtained from Equation (S4):

$$E_{FRET} = \frac{nR_0^6}{nR_0^6 + r^6} \qquad \text{(S4)}$$

for n donor-acceptor pairs with a Förster radius R_0 separated by a distance r.

[1] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum, New York, NY, USA, 2nd edition 1999.

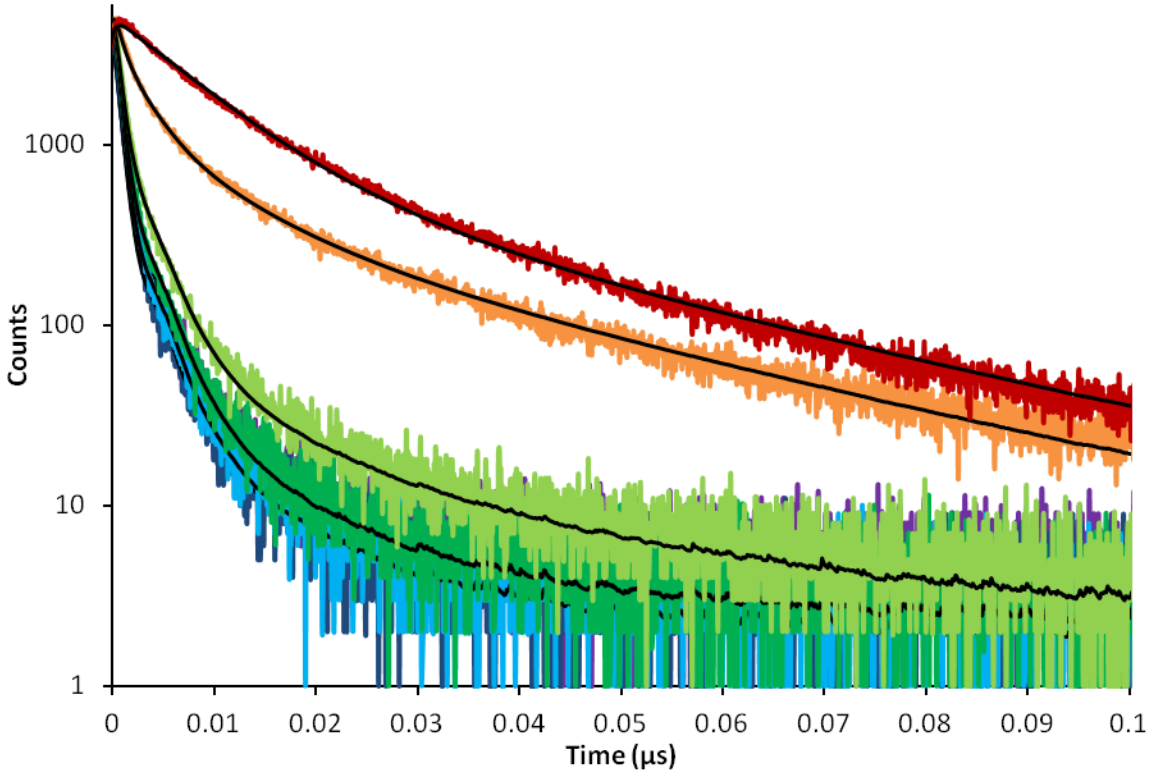

Figure S11: Time-resolved luminescence decay profiles of unconjugated (—), and of conjugated QDs with increasing dye/QD molar ratios (**QD-NR1,** —**, QD-NR2,** —**, QD-NR3,** —**, QD-NR4,** —**, QD-NR5,** —**, QD-NR6,**—) and corresponding tetra-exponential fits. 0.01 M TRIS-HCl pH 7.4, λ_{ex} =370 nm and λ_{em} = 540 nm.

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	α_1 (%)	α_2 (%)	α_3 (%)	α_4 (%)	$<\tau>$ (ns)
QD542	5	15	49	0	29.7	53.4	16.9	0	18
QD-NR1	4	13	47	0.8*	26.3	33.2	23.7	16.8	17
QD-NR2	1	6	30	0.5*	28.6	11.9	5.2	54.3	3
QD-NR3	2	5	21	0.4*	21.0	10.3	2.7	66.0	2
QD-NR4	1	5	25	0.3*	21.6	8.8	1.6	68.0	1
QD-NR5	0.4*	2	9	0	76.2	18.0	5.8	0	1
QD-NR6	0.4*	2	10	0	77.0	18.9	4.1	0	1

*These values are given as an indication of the fitting and the estimated error is around 1 ns.

Table S3: Decay parameters for $CdTe_xS_y$ QDs with increasing dye/QD molar ratios obtained from time-resolved studies in 0.01 M TRIS-HCl pH 7.4, λ_{ex} =370 nm and λ_{em} = 540 nm.

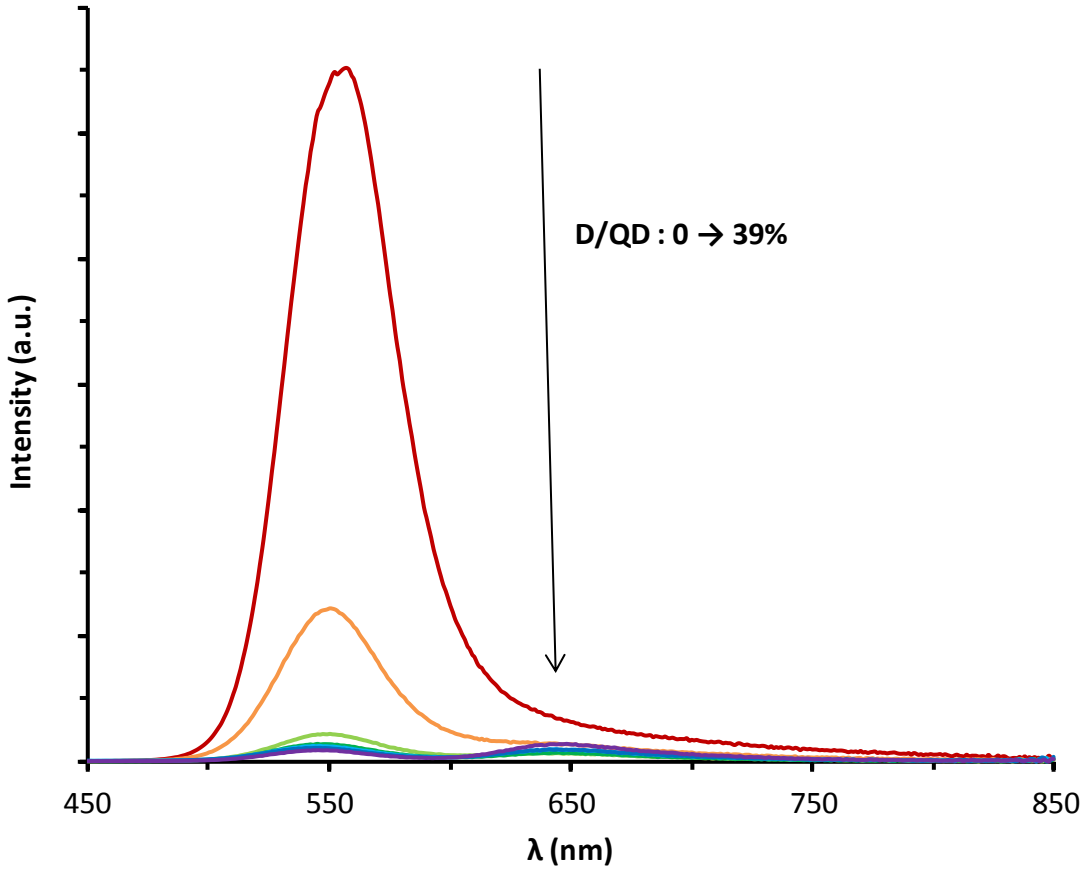

Figure S12: Emission spectra of unconjugated (—), and of conjugated QDs with increasing dye/QD molar ratios (**QD-NR1,** —**, QD-NR2,** —**, QD-NR3,** —**, QD-NR4,** —**, QD-NR5,** —**, QD-NR6,**—), 0.01 M TRIS-HCl pH 7.4, λ_{ex} = 375 nm.

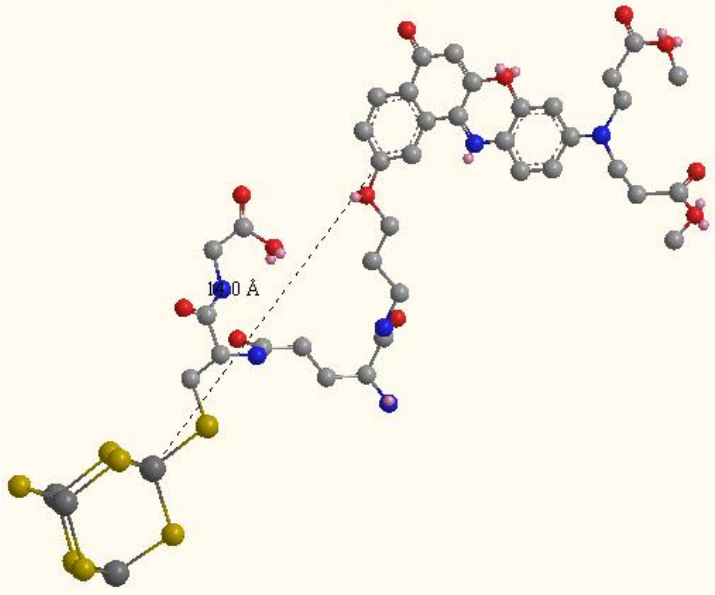

Figure S13: Space filling MM2 model of conjugated QD with a Nile-Red molecule (ChemBio3D Ultra)