

Electronic Supporting Information for

Aqueous-phase synthesized CdTe quantum dots: an insight into nanoparticle architecture-quantum yield relationship, characterization, and computational study of small clusters

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Table of Contents	Pages
1 Calculations for ZnS monolayers generation	S2
2 Measurement of relative QY for Rhodamine (B and 6G) and synthesized QDs	S3
3 Distribution size DLS analysis for synthesized QDs obtained after 4 h of reaction.	S6
4 cLog and QY correlation for each ligand in QDs synthesis.	S7
5 Tauc plots and E_g calculations	S7

1. Calculations for ZnS monolayers generation

The ZnS/CdTe ratio was taken from reference [1]. The first excitation peak from medium to an aqueous solution of QDs composed of CdTe wishing to be surface modified with ZnS. Once this value is determined, the absorbance at this wavelength is measured. As an example, a solution of QDs (200 mL) composed of CdTe-TGA shows the absorbance of $A = 0.0626$ (a.u.) when measured at 540 nm (first excitation peak). With this last value, the size of the QDs is calculated using equation S1 (section 5.6), resulting in 3.11 nm.

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7174 \times 10^{-3})\lambda^2 - (1.0064 \times 10^{-7})\lambda - (194.84)$$

$$D = (9.8127 \times 10^{-7})(540)^3 - (1.7174 \times 10^{-3})(540)^2 - (1.0064 \times 10^{-7})(540) - (194.84)$$

$$D = 3.11 \text{ nm}$$

The size is used to calculate the molar absorption coefficient (ϵ) from the relationship:

$$\epsilon = 10043(D)^{2.12}$$

$$\epsilon = 10043(3.11)^{2.12}$$

$$\epsilon = 1.12 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$$

Using Beer's Law ($A = \epsilon \cdot l \cdot C$), the concentration is calculated, resulting in 5.61×10^{-7} M. Therefore, for the total volume (200 mL), there is 0.112 μmol . The average thickness of ZnS monolayers has a value of 0.335 nm, so the generation of the first monolayer generates an increase of 0.670 nm in the diameter of the QDs. Assuming spherical particles, the first monolayer volume (V_{ml1}) is given by:

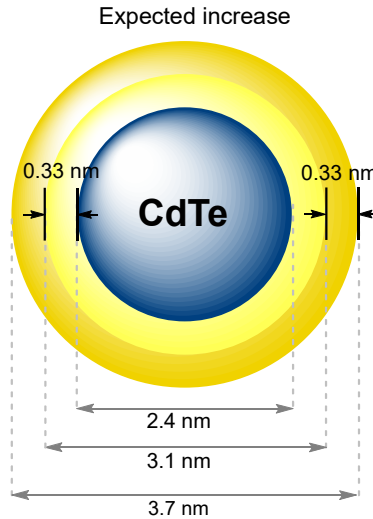


Fig. 1S. QDs core-shell and ZnS monolayer arrangement.

$$V_{ml1} = \frac{\pi}{6}(R_1^3 - r_1^3) = \frac{\pi}{6}((3.11 + 0.670)^3 - (3.11)^3) \text{ nm}^3 = 12.55 \text{ nm}^3$$

The volume of the second monolayer (V_{ml2}) will be:

$$V_{ml2} = \frac{\pi}{6}(R_2^3 - r_2^3) = \frac{\pi}{6}((3.78 + 0.670)^3 - (3.78)^3)nm^3 = 17.88 nm^3$$

If the density of ZnS is 4.09 g/mL or 4.09×10^{-21} g/nm³, the mass of the first ZnS monolayer (M_{ml1}) will be:

$$\begin{aligned} M_{ml1} &= V_{ml1} \cdot \rho_{ZnS} \\ M_{ml1} &= 12.55 nm^3 \cdot 4.09 \times 10^{-21} g/nm^3 \\ M_{ml1} &= 5.13 \times 10^{-20} g \end{aligned}$$

The molar ratio CdTe:ZnS: TGA is 1:1.1:2, so the amount of ZnS for 200 mL of a solution containing 0.112 μ mol will be:

$$\begin{aligned} ZnS_{ml1} &= 1.1 \cdot 5.13 \times 10^{-20} g \cdot 0.112 \times 10^{-6} mol \cdot 6.023 \times 10^{23} \frac{g}{mol} = 3.28 \times 10^{-3} g \\ ZnS_{ml1} &= 3.28 \times 10^{-3} g \cdot /136.28 \frac{g}{mol} = 3.92 \times 10^{-5} mol \text{ de Zns} \end{aligned}$$

If the solutions that serve as a source of Zn, S, and TGA have a concentration of 200 mM, the amount that must be added corresponds to 196, 196, and 392 μ L, respectively. Calculations for the second and third monolayers are performed in the same way. For the second monolayer: 279 μ L of Zn solution, 279 μ L of S solution, and 558 μ L of TGA solution. For the third monolayer: 377 μ L of Zn solution, 377 μ L of S solution, and 754 μ L of TGA solution.

2. Measurement of relative QY for synthesized QDs

The QY measurement was performed using the procedure described in references 1 and 2 as a model. It is necessary to mention that the measured QY corresponds to the relative efficiency using the UV-vis and fluorescence spectra. The other type of efficiency, the absolute QY, involves integrating spheres and delicate calculations to know the contributions of all the radiative processes after the fluorophore excitation. In this document, the mention of QY always refers to the relative QY. Rhodamine 6G and B were used as reference fluorophores. To validate the response of the equipment used, the QY measurement was carried out by comparative method for Rhodamine B using Rhodamine 6G as a reference, which reports a value of 0.95 (95 %). The comparative method consists of measuring the absorbance and fluorescence for various solutions of the reference and the sample or analyte, where the relationship:

$$QY_m = QY_R \cdot \left(\frac{m_m}{m_R}\right) \cdot \left(\frac{n_m^2}{n_R^2}\right)$$

where m_m and m_R are the slope of the line obtained by the plot of normalized fluorescence intensity vs. absorbance for each case. n is the refractive index of the solvent in which the sample and reference are dissolved. The normalized mention refers to eliminating the contribution to the fluorescence of the solvent used (ethanol).

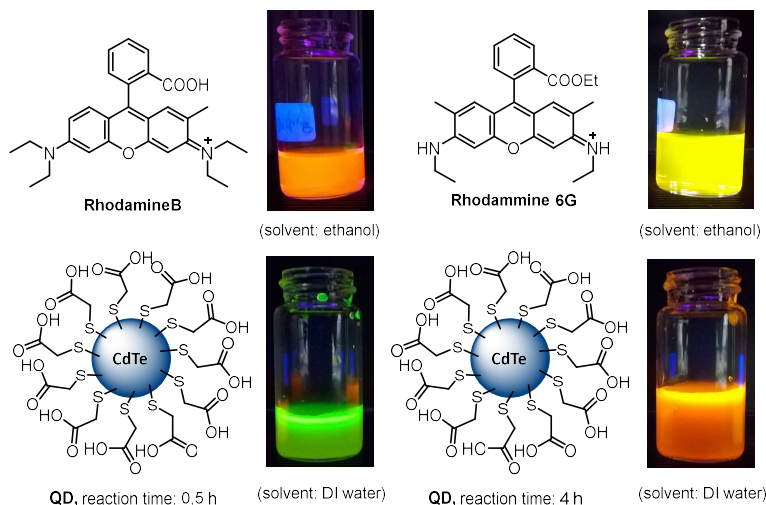


Fig. 2S. The physical aspect of Rhodamines (B and 6G) and synthesized QDs under UV-VIS light (365 nm).

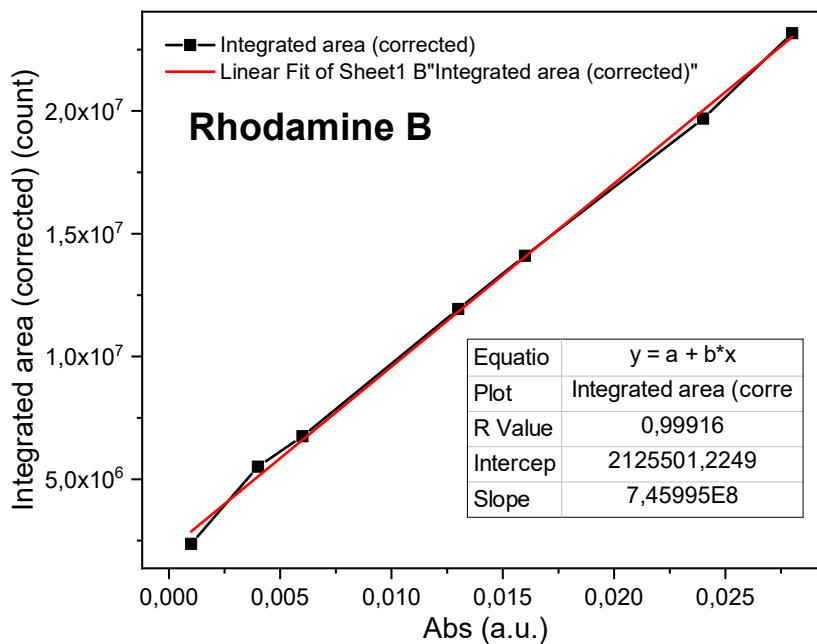
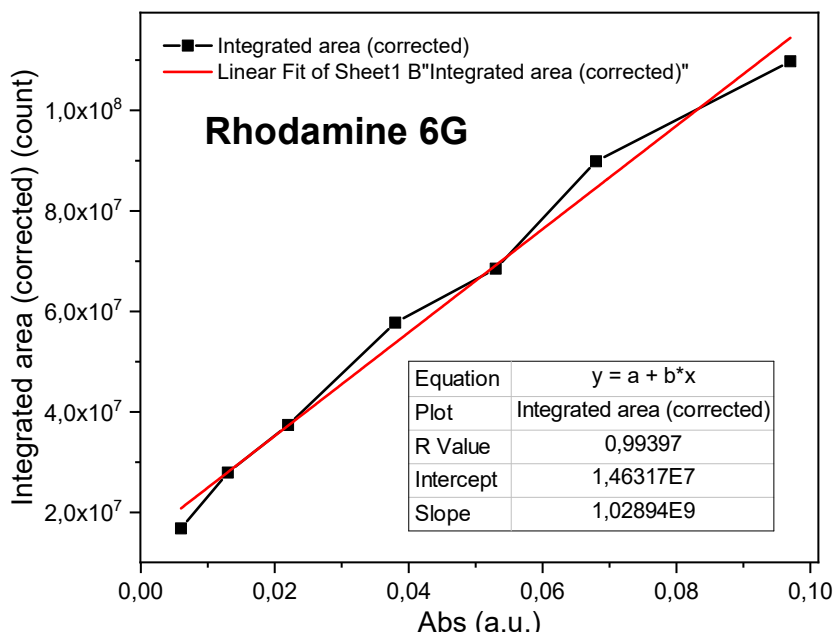
Sample	Fluorophore (μmol/L)	Abs	Integrated area (corrected)
Rho6G1	8,62E-08	0,006	16814262,1
Rho6G2	1,72E-07	0,013	27928212,6
Rho6G3	2,59E-07	0,022	37388352,3
Rho6G4	4,31E-07	0,038	57755905,2
Rho6G5	5,17E-07	0,053	68499268,2
Rho6G6	6,90E-07	0,068	89865831,4
Rho6G7	8,62E-07	0,097	109764294
		Slope -m _R	1,029 E+09

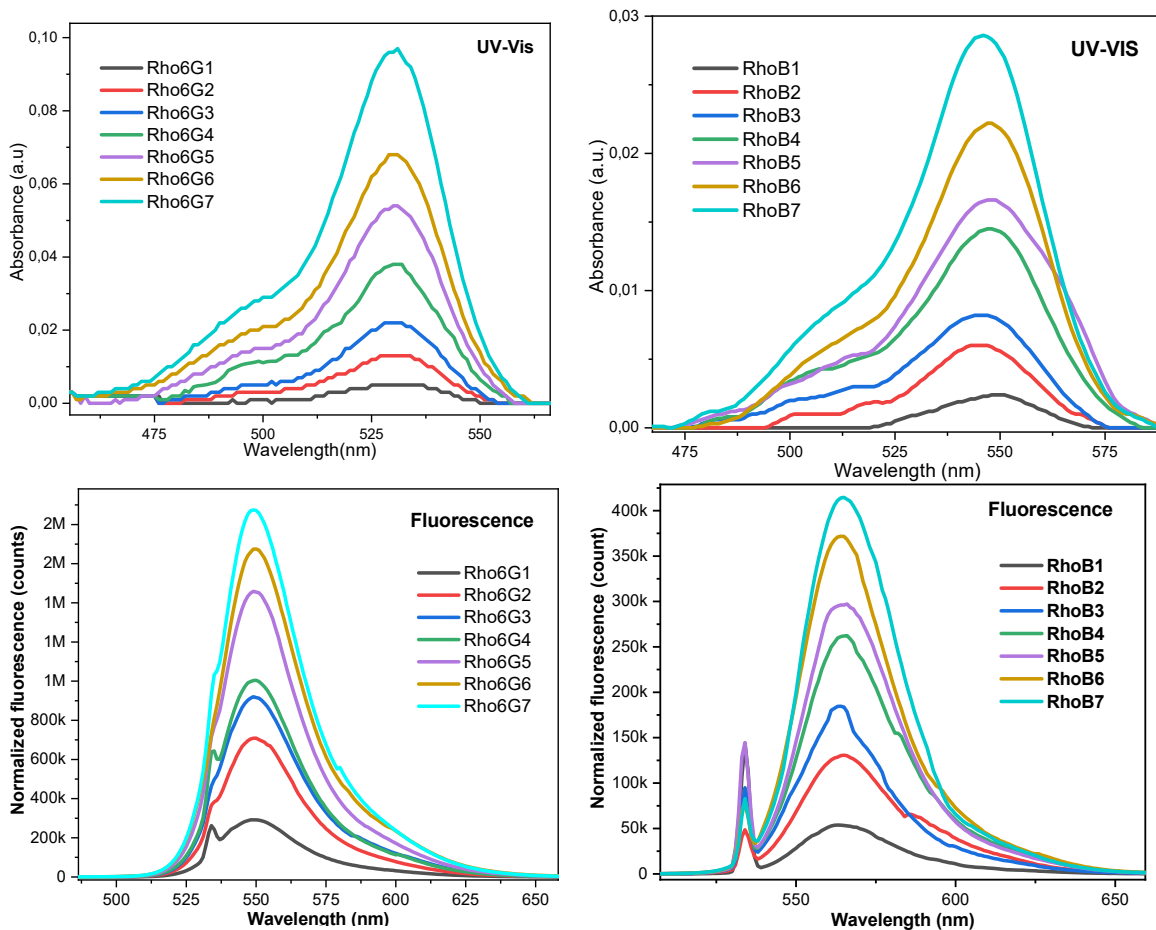
RhoB1	9,43E-08	0,0010	2367324,4
RhoB2	1,89E-07	0,0040	5552901,3
RhoB3	2,83E-07	0,0060	6746844,3
RhoB4	4,72E-07	0,0130	11930565,5
RhoB5	5,66E-07	0,0160	13802772,1
RhoB6	7,55E-07	0,0240	19486598,7
RhoB7	8,49E-07	0,0280	23163001,1
		Slope -m _m	7,460 E+08

$$QY_m = 0,95 \cdot \left(\frac{7,46 \times 10^8}{1,029 \times 10^9} \right) \cdot \left(\frac{1,35}{1,35} \right) = 0,689 \text{ (68,9\%)}$$

As a result, the fluorescence QY of Rhodamine B is obtained as 0,689 (68,9%), which is very close to the reported QY (0.7). This method provides good accuracy by calculating the slope of the line generated by plotting the integrated fluorescence intensity against the

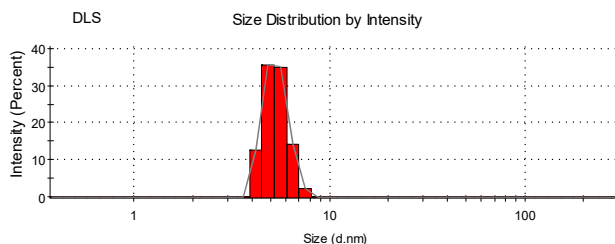
absorption for multiple concentrations of each fluorophore. The QY for synthesized QDs was measured in the same way. To avoid self-aggregation problems of QDs solutions, the absorbance values were always between 0.1 and 0.03.





3. Distribution size DLS analysis for synthesized QDs obtained after 4 h of reaction.

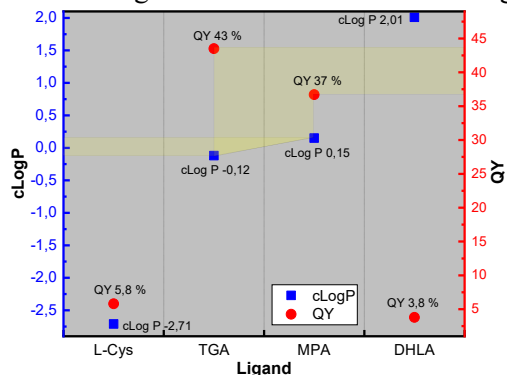
The previous report³ allowed the assessment of particle size distribution through intensity distribution of particle sizes using DLS. The analysis gave information about the polydispersity index (PDI), a dimensionless value that classifies dispersed solutions in monodisperse (PDI = 0.0-0.1) and polydisperse (PDI > 0.4). QDs sample analyzed by DLS showed a monodisperse profile (PDI = 0.045) with a d_H of 4.17 nm for NPs obtained after 4 h of reaction.



DLS analysis was performed in a Zetasizer Nano ZS (Malvern) instrument using a quartz cell (10,00 mm path).

4. cLog and QY correlation for each ligand in QDs synthesis.

We referred to the relationship between cLog and QY for QDs with a differentiated ligand on their surface. It is related to a specific cLog range, which means a required hydrophobicity to retain the QY. The following figure shows each ligand's correlation between cLog and QY.



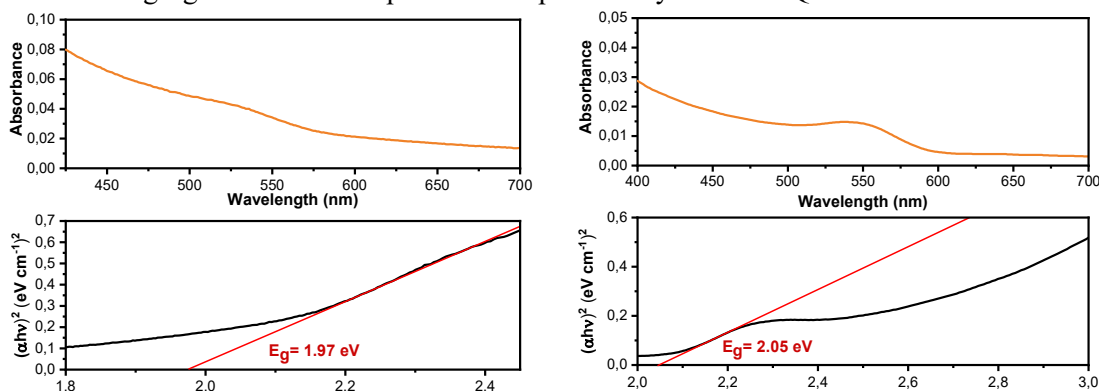
This correlation will be helpful when a ligand is selected to avoid low QYs in aqueous colloidal synthesis. In fact, it is possible to run a rapid calculation using cheminformatic platforms to know the cLog value of your selected ligand before the synthesis. The cheminformatics platforms have shown value in rapidly screening thousands of organic compounds with therapeutic purposes, so it would be interesting to have them as a toolbox in hybrid nanoparticle design.

5. Tauc plots and E_g calculations

In order to perform the Tauc plot,⁴ calculations were made from the data obtained in the UV-Vis spectra of the synthesized QDs. For this purpose, energy and photon quantity (ahv) calculations were performed using the following equations, which consider values such as absorbance and wavelength, plotted in the UV-Vis spectrum.

$$\text{Energy (eV)} = \frac{1240}{\text{Wavelength}} \quad ahv = 2,303 \cdot \text{Absorbance} \cdot (\text{Wavelength})^2$$

In the Tauc plot, the energy corresponding to the bandgap of crystalline semiconductors is extrapolated from the linear region to the abscissa, and a corresponding value of 2.17 eV is found. The following figure shows examples of Tauc plots for synthesized QDs.



References

1. S. Xu, C. Yao, J. Zhang, Z. Dai, G. Zheng, B. Sun, S. Sun, Q. Han, F. Hu y H. Hou, *Adv. Mater. Res.*, 2009, **60–61**, 165–169.
2. Allen, M. W. Measurement of Fluorescence Quantum Yields. *Thermo Sci.* 2010, 1–4.
3. C. A. M. Bonilla, M. H. T. Flórez, D. R. Molina Velasco and V. V. Kouznetsov, *New J. Chem.*, 2019, **43**, 8452–8458.
4. P. Makula, M. Pacia, W. Macyk. *J. Phys. Chem. Lett.*, 2018, 9, 6814–6817.