On the Incorporation Mechanism of Hydrophobic Quantum Dots in Silica Spheres by a Reverse Microemulsion Method

Supporting Information

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Calculation of the relative affinity and quenching rate of TEOS versus NP-5.

For the calculations it is assumed that in case NP-5 or TEOS is added only, the QDs are fully (or at least equally) covered by these ligands because of the large excess as compared to the original coating.

The initial QE of the QDs (QE_I) before addition of NP-5 or TEOS can be written as

$$QE_I = \frac{\Gamma_{rad}}{\Gamma_{rad} + \Gamma_{nonrad}} = \frac{\Gamma_{rad}}{\Gamma_{tot}}, \qquad (1)$$

where Γ_{rad} and Γ_{rad} are the radiative and non-radiative decay rates respectively, and Γ_{tot} is the total decay rate. It is further assumed that the quenching rate per TEOS or NP-5 molecule is constant, and that the total quenching rate is thus the product of the quenching rate per molecule and the number of molecules attached. The total QE of the QDs (QE_T) after addition of TEOS can then be written as

$$QE_T = \frac{\Gamma_{rad}}{\Gamma_{tot} + n \cdot \Gamma_{TEOS}}, \qquad (2)$$

where n is the number of TEOS molecules (in percentage, 100 is full coverage), and Γ_{TEOS} is the quenching rate per percent TEOS coverage. Since the emission intensities in Figure 4 of the article are relative emission intensities (compared to the initial intensity), we define the relative QE (QE_R) as

$$QE_R = \frac{QE_T}{QE_I} = \frac{\Gamma_{tot}}{\Gamma_{tot} + n \cdot \Gamma_{TEOS}}. \qquad (3)$$

Similarly, the relative QE of the QDs (QE_T) after addition of NP-5 can be written as

$$QE_R = \frac{QE_T}{QE_I} = \frac{\Gamma_{tot}}{\Gamma_{tot} + n \cdot \Gamma_{NP-5}}. \tag{4}$$

When TEOS or NP-5 are added only, the coverage is assumed to be 100 %, hence n = 100. The QE_R in those cases are 0.16 and 0.84 respectively. Filling in these numbers in equations 3 and 4, yields that

$$\Gamma_{tot} = 19 \cdot \Gamma_{TEOS} = 525 \cdot \Gamma_{NP-5}. \tag{5}$$

This implies that the quenching rate per TEOS molecule is 525/19 = 28 times higher than for NP-5. When both TEOS and NP-5 are added, the relative QE (QE_R) is defined as

$$QE_R = \frac{QE_T}{QE_I} = \frac{\Gamma_{tot}}{\Gamma_{tot} + n \cdot \Gamma_{TEOS} + (100 - n) \cdot \Gamma_{NP-5}}. \tag{6}$$

It was found that QE_R is 0.34 on average when both TEOS and NP-5 are added (Figure 4A and 4B). Filling in this number in equation (6) and by defining Γ_{NP-5} and Γ_{tot} as a function of Γ_{TEOS} (equation (5)), the value for n can be calculated. In this manner we obtain a value of 36 for n, which means that 36 % of the surface is covered by TEOS, and 64 % by NP-5.

Table S1. Number of molecules X (rows) relative to molecule Y (column) in a standard reverse microemulsion system. 1 ML DDT stands for 1 monolayer of DDT molecules. It is estimated that one monolayer DDT around a 6.4 nm QD contains approximately 650 DDT molecules assuming a surface area of 20 Å^2 per DDT molecule. One can also calculate the number of thiols that may attach to the QD surface by calculating the number of ZnS unit cells on the surface of a 6.4 nm QD, which gives approximately the same number (540).

	1 ML DDT	TEOS	NH_3	NP-5	H_2O
QDs	650	3.6×10^5	2.1×10^6	2.9×10^6	5.6×10^6
1 ML DDT	1	550	3200	4500	8600
TEOS		1	6	8.2	16
NH_3			1	1.4	2.7
NP-5				1	1.9