Supplementary Material (ESI) for Journal of Materials Chemistry

Thiol-Containing Microspheres as Polymeric Ligands for the Immobilisation of Quantum Dots

Supplementary Information

Effect of Varying Thiol Content on QD-Loading: Fluorescence Assay

For each sample of thiol microspheres **6** (0.5, 1.0, 1.5 and 2.0 % 4-VBTU): a sample (mass was calculated as 60 mg based on a 250 μL aliquot from the bulk suspension in 50 mL) was resuspended in methanol (6 mL) and a 1 mL aliquot of this suspension was centrifuged and the microspheres isolated and dried *in vacuo* to calculate the accurate mass of microspheres in the remaining 5 ml of the suspension. The remaining 5 mL suspension was centrifuged (5 minutes, 6000 rpm) and the supernatant removed by decantation. Following 2 wash/centrifugation cycles with toluene (2 x 5 mL), the microspheres were pre-swollen by resuspending in chloroform (2 mL). A solution of QD4 (10 mg) in toluene (4 mL) was added to the microsphere suspension, which was then shaken at room temperature for 16 hours. The suspension was centrifuged (5 minutes, 6000 rpm) and the supernatant was removed by decantation and collected. The resultant QD-microspheres were washed by resuspending in a further 1.5 mL of toluene and centrifuging and the supernatant was again removed by decantation and added to the previous wash solution. After one further repeat of this wash/centrifuge process, the combined supernatants were transferred to a 10 mL volumetric flask and additional toluene was added until the total volume was 10 mL. The washed QD-microspheres, wet with toluene, were collected and their QY was measured using a Horiba Fluoromax-4 with integrating sphere attachment.

In order to calculate an extinction coefficient ε by which to correlate the mass of QDs in solution to their observed fluorescence, 10 mg of QD4 were dissolved in 10 mL of toluene and this solution was diluted; x5, x10 and x15. The relative fluorescence of the initial solution and the diluted solutions was measured using a SpectraMax GeminiXS (Molecular Devices) fluorescence plate reader. This data was plotted against the QD concentration of each solution, and the gradient of the line of best fit was taken to be the value for ε. Fluorescence readings were measured in a similar manner for each supernatant solution, containing the excess of non-immobilised QDs from each reaction and the following formula was used to calculate the QD loading for each sample of thiol microspheres **6**:

$$\text{QD-loading (\%)} = [\text{mass of immobilised QDs}/(\text{mass of microspheres} + \text{mass of immobilised QDs})]*100$$

$$\text{Mass of immobilised QDs} = \text{initial mass of QDs} - \text{mass of non-immobilised QDs}$$

$$\text{Mass of non-immobilised QDs} = (\text{fluorescence}/\varepsilon)*V$$

Data: Initial mass of QDs = 10 mg, V = volume = 10 mL

The value referred to as QD-loading is essentially the wt. % of QDs that contribute to the total mass of the QD-microsphere conjugates.

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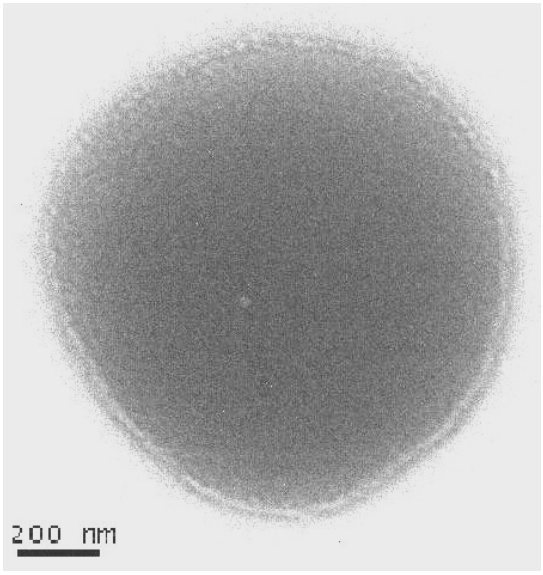
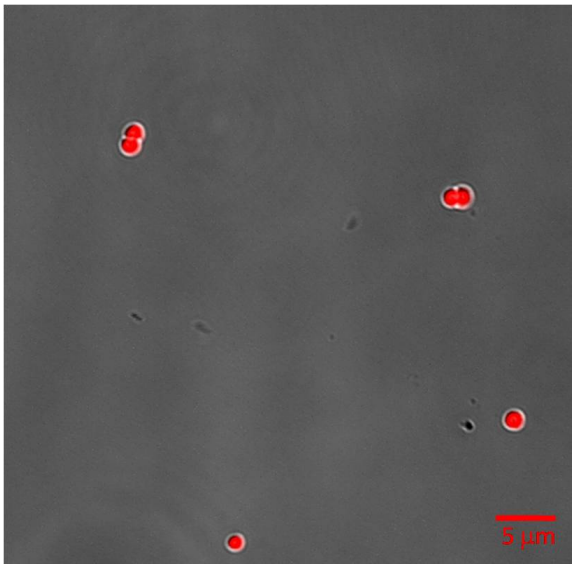
TEM Image of a Single QD-Microsphere



Confocal Microscope Image of PVP-QD-Microspheres in Water



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