Supporting Information

Enhanced spin lifetime in colloidal quantum dots by growth from singly Mndoped molecular cluster seeds

Julian Schneider^a, Chris Page^a, James Harris^a, Nigel L. Pickett^a, Nathalie C. Gresty^a, Christopher Waby^a, Charles Biddlecombe^a, Rachel M. Barrett^b, Adam Brookfield^c, Patrick Parkinson^b, Floriana Tuna^c, Simon M. Fairclough^d and David J. Binks^{*b}

a. Nanoco Technologies Ltd, The Heath Business & Technical Park, Runcorn, Cheshire, WA7 4QX, United Kingdom.

b. Department of Physics and Astronomy & Photon Science Institute, University of Manchester, Manchester M13 9PL, United Kingdom.

c. Department of Chemistry and Photon Science Institute, University of Manchester, Manchester, M13 9PL, United Kingdom.

d. Department of Material Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

1. Synthetic Method:

All reactions required the use of anhydrous solvents, which were stored in N_2 atmosphere over activated molecular sieves to minimise moisture contamination.

1.1 Central Manganese Complex

Following a procedure reported by Khadka *et al.*¹, we synthesised a four coordinated Mn-S₄ complex that offers reactive sites (-SiMe₃) for further reactions with metal cations. The structure of the complex is shown in Schematic 1 below.



Schematic 1. Initial Mn-containing cluster.

6.75 mL of *bis*(trimethylsilyl)sulphide (TMSS) was mixed with 25.25 mL of THF to prepare a 1 M TMSS solution. A dry three-necked flask was placed under a nitrogen atmosphere, charged with TMSS solution (1 M; 10 mL) and tetrahydrofuran (THF) (84 mL) and cooled to 0°C. n-BuLi (1.6 M in THF; 6.25 mL) was then added at a rate of 1.25 mL/min, after which the reaction was maintained at a temperature of 0°C for 30 minutes. The solvent was then removed under vacuum to obtain LiS(TMS) as a white solid.

In a second dry flask MnCl₂ (0.31 g) was dissolved in dichloromethane (DCM) (40 mL), tetramethylethylenediamine (TMEDA) (0.95 mL) was added and the mixture stirred for 1 to 2 hours. The LiS(TMS) was cooled to 0°C and the mixture added over a period of 30 minutes, the temperature of 0°C was maintained for 30 minutes following completion of the addition. The solvent was then removed under vacuum to leave a light pink precipitate. The precipitate was dissolved in 20 mL of

hexane and filtered over Celite, with the reaction vessel and solids being washed with hexane (3 x 10 mL). The filtrate was collected and the solvent evaporated under vacuum to form a light pink precipitate. The powder is washed with cold hexane (2 x 1.5 mL) and the residual solvent extracted by syringe.

1.2 Zinc-capped Manganese Complex

 $ZnCl_2(TMEDA)$ (0.21 g) is dissolved in THF (5 mL), placed in a dry three necked flask under an atmosphere of N₂, and cooled to 0°C. The $[Li(TMEDA)]_2Mn[SSi(Me)_3]_4$ from Stage 1 (0.15 g) is dissolved in DCM (4 mL) in a N₂ filled glovebox and then added to the cooled solution of $ZnCl_2(TMEDA)$ over a period of 30 min, after which the mixture is allowed to return to room temperature. The resulting solution is filtered over Celite before being layered with pentane and left to crystallise.

The target complex has the formula $[Li(TMEDA)]_2Mn[SZnCl(TMEDA)]_4$ and the structure shown in Schematic 2:



Schematic 2. Zn-S cluster.

The absorbance spectrum showed no peak, but a steep onset at around 300 nm and the photoluminescence spectrum showed clear Mn(II) emission at around 620 nm (see Fig. 2a).

1.3 ZnS:Mn Molecular Cluster

The zinc capped manganese (0.5 mmol) was dissolved in DCM (5 mL), charged to a dry three necked flask, and cooled to -75° C. (TMEDA)Zn(S(TMS))₂ (0.17 M in THF; 13 mL), synthesised following the procedure from DeGroot and Corrigan², was added dropwise while maintaining the temperature at -75° C. After 5 minutes, the mixture was allowed to warm to room temperature and stirred for a further 15 minutes. The mixture was then cooled to -75° C and (TMEDA)ZnCl₂ (0.2 M in THF; 11.25 mL) was added dropwise while maintaining the temperature at -75° C. After 5 minutes, the mixture was allowed to -75° C and (TMEDA)ZnCl₂ (0.2 M in THF; 11.25 mL) was added dropwise while maintaining the temperature at -75° C. After 5 minutes, the mixture was allowed to warm to room temperature, resulting in the formation of a turbid solution. The solids were separated by centrifugation and washed with hexane, yielding the smaller cluster ahead of CQD growth.

The larger cluster was synthesised by adding alternating $(TMEDA)Zn(S(TMS))_2$ and $(TMEDA)ZnCl_2$ precursors to the crude smaller cluster solution to grow the existing clusters in a stepwise manner. This approach is similar to the successive ionic layer adsorption and reaction (SILAR) technique utilised in CQD synthesis. Successive additions were carried out until the larger cluster ceased to be soluble in DCM. The larger cluster used in this paper was synthesised from two further complete cycles on top of the smaller cluster.

1.4 Cluster based synthesis of InP Colloidal Quantum Dots

The molecular cluster (100 mg) was dissolved in DCM (5 mL) and charged to a dry three-necked flask under a nitrogen atmosphere. *Tris*(trimethylsilyl)phosphine (TMSP) (1 M in Dowtherm[®] RP; 1 mL) was added over a period of 5 minutes and the resulting mixture stirred for 15 minutes at room temperature. It was observed that the clusters are insoluble in 1-octadecene before the addition of the TMSP but are soluble afterwards, with the solution turning yellow in colour, evidencing the reaction between them.

A mixture of In carboxylate (2.71 g; 5 mmol), oleic acid (1.7 mL; 5.5 mmol), octadecylamine (0.67g, 2.5 mmol), and octadecene (23 mL) was degassed at 110°C for 1 hour and then cooled. The In-containing mixture (7.5 mL) was added to the three-necked flask containing the molecular cluster and TMSP over a period of 5 minutes and the resulting mixture stirred for 30 minutes at room temperature. The DCM was removed under vacuum and the remaining mixture was heated to 220°C and stirred at this temperature for 30 minutes before cooling to room temperature.

The quantum dots were grown further by adding a portion of the indium precursor (15 mL) to the reaction mixture, degassed at 110°C for 30 minutes, and placed under a nitrogen atmosphere. The reaction mixture was then heated to 250°C and a first portion of the zinc and phosphor precursors (0.46 M in Dowtherm[®] RP; 1 mL) was added at a rate of 4 mL/hour. The reaction mixture was then heated to 250°C and a further portion (0.46 M in Dowtherm[®] RP; 1 mL) was added. The reaction mixture was then allowed to cool to room temperature.

To confirm that the clusters nucleate the growth of the quantum dots, the absorption spectra of the QDs was compared when the initial amount of molecular cluster was varied but the other reaction parameters kept constant; the resulting absorption spectra are shown in Figure S1 below. The first absorption feature is blue-shifted for the spectrum corresponding to an initial cluster amount of 150 mg compared to the where it was for an initial cluster amount of 50 mg. A blue-shifted absorption spectrum corresponds to a smaller dot size, consistent with the smaller amount of In and P precursor available per dot when the number of clusters is greater.



Figure S1. Comparison of the absorbance spectrum for QDs synthesised using an initial amount of seed cluster of a) 50 mg, and b) 150 mg.

1.5 Growth of ZnSeS Shell

A dry three-necked flask was charged with CQDs (eq. 0.65 mmol [P]) and 1-octadecene (15 mL), degassed for 10 minutes, and placed under a nitrogen atmosphere. Zinc (II) acetate (1.92 g; 10.46 mmol), zinc (II) isostearate (1.31 g; 2.08 mmol), and ammonium bifluoride (0.10g; 1.75 mmol) were added and the mixture degassed at 110°C for 50 minutes. Trioctylphosphine (TOP; 1 mL) was added and the mixture degassed at 110°C for a further 10 minutes.

The reaction mixture was then heated to 190°C and held at this temperature for 10 minutes, followed by heating at 210°C for 20 minutes, and heating at 230°C for 10 minutes. Trioctylphosphine selenide (TOPSe; 2 M in TOP; 0.92 mL) was added over a period of 40 minutes. 16 minutes after addition of TOPSe was commenced, the addition of 1-dodecanethiol (DDT; 3.07 mL) began for a period of 135 minutes. After all of the DDT was added, the reaction mixture was cooled to below 100°C.

Zinc (II) chloride (1.00 g; 7.33 mmol) was then added and the mixture heated to 180°C for 60 minutes. 1-octanol (3 mL) was then added over a period of 60 minutes.

The reaction was cooled to 75°C at which point toluene (15 mL) was added. The reaction mixture was then cooled further to 40°C and acetone (70 mL) was added. The resulting precipitate was collected by centrifugation (7500 rcf, 5 minutes) and the supernatant discarded, before being redissolved in toluene (15 mL) and re-precipitated (20 mL). The precipitate was again collected by centrifugation (7500 rcf, 5 minutes) and the supernatant discarded. The solid was dissolved in toluene (10 mL), (7500 rcf, 5 minutes) and the supernatant discarded. The solid was dissolved in toluene (10 mL), (7500 rcf, 5 minutes) and filtered into a vial.

2. Average size and size distribution.



Figure S2. Size distribution of CQDs obtained from transmission electron microscopy, which has an average of 5.3 nm and a standard deviation of 16%.



Figure S3. Dynamic light scattering data showing the average size and size distribution for the CQDs before (red) and after(blue) the addition of the shell layer. Note that the CQDs sizes obtained from the dynamic light scattering measurements correspond to the hydrodynamic size and so include the surface ligands as well the CQD itself⁸. In contrast the TEM measurements correspond to the CQD only.

3. Energy Dispersive X-Ray Spectroscopy.



Figure S4. Energy Dispersive X-Ray Spectroscopy (EDS). a) HAADF image core/shell InP/ZnSeS CQDs and corresponding EDS images showing the distribution of b) indium, c) phosphorus, d) zinc, e) selenium, and f) sulphur.

4. Electron Energy Loss Spectroscopy.



Figure S5. a) Electron energy loss (*EELS*) *image of several CQDs* and EELS spectra in the region of the L_2 and L_3 Mn peaks at pixel a) (9,7), b) (13,7), c) (20,11), and d) (21.8), where pixels are counted (horizontally, vertically) from the top left corner of the image shown in part a).

5. Electron paramagnetic resonance (EPR) spectrum for CQDs grown from the large seed cluster.



Figure S6. Q-band (33.95 GHz) EPR spectrum at 3 K for CQDs grown from the large seed cluster (black) and its simulation (red) using S = 5 / 2, g = 2.007, $A(^{55}Mn) = 266$ MHz, D = 100 MHz and E=0..

References.

1 C. B. Khadka, D. G. Macdonald, Y. Lan, A. K. Powell, D. Fenske and J. F. Corrigan, *Inorg. Chem.*, 2010, **49**, 7289–7297.

2 M. W. DeGroot and J. F. Corrigan, Organometallics, 2005, 24, 3378–3385.

3 L. Pitkänen and A. M. Striegel, Analytical and Bioanalytical Chemistry, 2016, 408, 4003–4010.