

Supplemental Information for “Efficient Emission from Core / (Doped) Shell Nanoparticles: Applications for Chemical Sensing”

Rahul Thakar, Yingchuan Chen, Preston T. Snee

Chemicals Used:

BODIPY 577/618 maleimide (Invitrogen), Diethyl zinc (Strem, 95%), Hexamethyldisilathiane (TMS_2S , Fluka, purum), N-hexylphosphonic acid (HPA, Alfa Aesar) Manganese Chloride (Sigma Aldrich, 99+%), Oleylamine (Fluka, technical grade), Selenium (Alfa Aesar, 99+%), Sodium Hydroxide (Fisher, ACS Certified), Stearic Acid (Fluka, purum), Trioctylphosphine (TOP, Strem, 97%), Trioctylphosphine Oxide (TOPO, Aldrich, 90%, purified by distillation at 220 °C at 200 mTorr), Methanol, Isopropanol, Hexane (Fisher, ACS Certified)

Synthesis of Manganese Stearate:

Manganese stearate was prepared using manganese chloride and stearic acid. A 1.0 g portion of MnCl_2 was added to 40 mL methanol which was heated to reflux. Next, 4.52 g of stearic acid was added. After the stearic acid melted and mixed with the hot methanol solution, 0.636 g NaOH in methanol was added. The manganese stearate precipitate thus obtained was washed with hot methanol, centrifuged at 3.9×10^3 RPM, and washed again for several cycles. The final solution was dried *in vacuo*. The sample was characterized by NMR.

Synthesis of ZnSe and ZnSe/ZnMnS:

The core NCs were synthesized according to a modification of a previously published procedure [1]. First, 12.0 g of oleylamine was degassed at 110 °C at ~200 mTorr in a 4 necked round bottom flask. The system was flushed with dry N₂ and the temperature was raised to 310° C. A solution of 0.099 g diethyl zinc, 0.67 mL of 1.5mM trioctylphosphine selenide (synthesized from Se shot and trioctylphosphine) and 4mL trioctylphosphine were mixed in a vial and injected into the pot while stirring rapidly. Immediately after the solution was annealed for 45 minutes at 270° C and then lowered to 170° C. A solution of 0.042g manganese stearate, 6.0 mL trioctylphosphine, 160 mg hexamethyldisilathiane and 76 mg diethyl zinc was prepared in the glove box in a vial and allowed to stir until a turbid but homogenous mixture was obtained. This was loaded into a syringe and added into the pot at 170° C using an addition funnel. A constant flow (~1 drop / sec) was maintained. The temperature was allowed to cool to room temperature at which point a faint orange emission ($\lambda = 570\text{nm}$) was visible. The ZnSe/ZnMnS NCs were extracted with additional hexane and then precipitated with excess methanol using isopropanol as a co-solvent. A control sample was prepared by addition of manganese stearate in trioctylphosphine to the ZnSe cores without zinc or sulfur precursors.

Synthesis of ZnSe/ZnMnS/ZnS:

In a 4 necked 50 mL round bottom flask 10 g trioctylphosphine oxide with 0.4 g n-hexylphosphonic acid and degassed at 160° C at ~200 mTorr. The precipitated ZnSe/ZnMnS NCs were solubilized in hexane and injected into the pot at 80° C upon which hexane was removed. At this point the manganese emission from the ZnSe/ZnMnS NCs became considerably more emissive, which seemed to brighten further as the hexane

was removed. Separate solutions of 80 mg diethyl zinc in 3 mL trioctylphosphine and 160 mg hexamethyldisilathiane in 3ml trioctylphosphine were prepared and loaded into separate 3 mL syringes inside a glove box. These solutions were injected using a syringe pump into the round bottom flask at 170° C through a capillary tube over the course of 2 hours.

Water solubilization and dye conjugation:

ZnSe/ZnMnS/ZnS NCs were precipitated from ~1 mL of growth solution with excess isopropanol with a small amount of methanol and centrifuged into a pellet. The pellet was dried and weighed after which a 5× excess (by weight, typically 50-100 mg) of neutralized octylamine modified RAFT synthesized polyacrylic acid was added.[2,3] Next, ~3mL of chloroform was mixed with the solution with ~1 or two drops of methanol to help solubilize the polymer. Care must be used not to add too much methanol. The solution was dried under vacuum upon which pH 7 buffered water was added. The solution was stirred for ~1 hour, filtered with 450 nm Millipore filters and then centrifuged in 50K MW dialysis filters from Millipore. Several portions of pH 7 water were added to the centrifuge filters to remove excess polymer. The solution was filtered again, and separated into equal portions. A small portion of BODIPY 577/618 maleimide was dissolved in dimethylformamide which was then added to the test solution. The NC / dye couple was stirred for two days, dialyzed in 50K MW centrifuge filters to remove excess dye, after which they were characterized using UV/VIS spectrophotometry and steady-state fluorometry. The dye conjugated to the polymers by the natural thiol functionality of the polymers.

Characterization:

Samples were characterized with a Cary 500 UV/VIS by Varian and a Fluorolog 3 by Jobin Yvon. Time-resolved data on the Perkin Elmer Victor3 using a Dysprosium filter set. Data was taken at 30 μ s - 4500 μ s intervals using a 30 μ s integration time. The experiment was repeated three times and averaged. All data were plotted and analyzed using Matlab scripts. TEM images and EDS elemental analysis were taken with a JEOL JEM-3010 at the UIC Research Resource Center. EPR spectra were taken with a Varian E-109E spectrometer and analyzed using the Matlab suite of software.

References

1. Hines, M.; Guyot-Sionnest, P. *J. Phys. Chem. B*, **1998**, *102*, 3655.
2. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromol.*, **1998**, *31*, 5559.
3. Wu, X.; Liu, H.; Liu, J.; Haley, K. N.; Treadway, J. A.; Larson, J. P.; Ge, N.; Peale, F.; Bruchez, M. P. *Nat. Biotech.*, **2003**, *21*, 41.

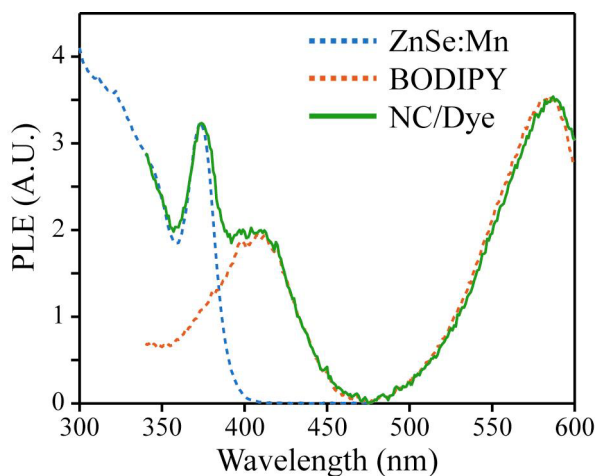


Figure S1. Photoluminescence excitation spectra of the ZnSe:Mn / BODIPY conjugated chromophore. The control NC and dye PLE spectra are scaled as a guide to the eye. PLE data was recorded by monitoring the emission at 670 nm where there is minimal overlap (~20%) of the manganese emission over the BODIPY dye, however it is not necessarily clear what percent of the PLE signal comes from the manganese emission.

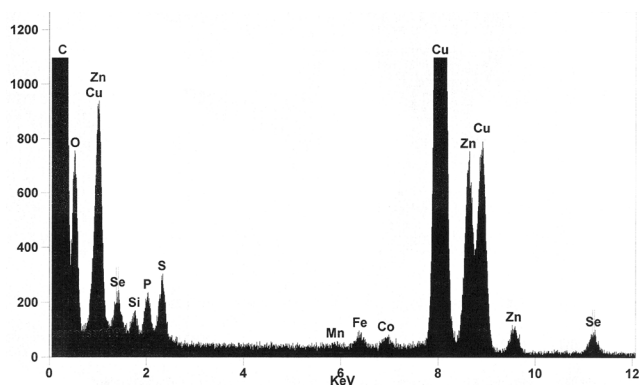


Figure S2. EDS elemental analysis of the ZnSe//ZnMnS/ZnS NCs. The presence of the elements Fe, C, Co, Cu and Si are from the microscope and TEM grids.

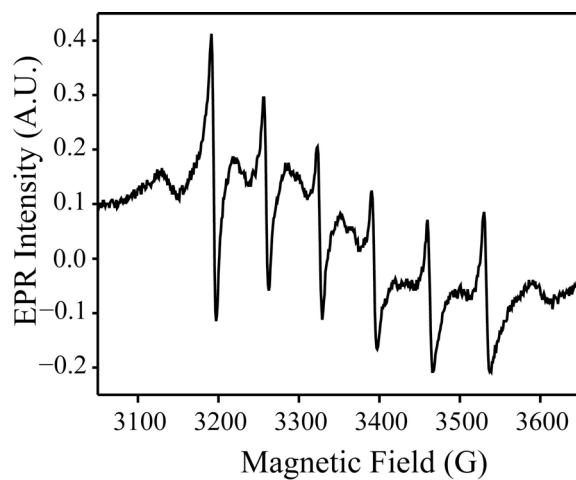


Figure S3. EPR spectra of ZnSe//ZnMnS/ZnS NCs. The hyperfine coupling constant of $63.5 \pm 1.4 \times 10^{-4} \text{ cm}^{-1}$ is indicative of manganese in a zinc sulfide layer.