

## Supporting information

### Highly Luminescent Glutathione-Capped ZnS:Mn/ZnS

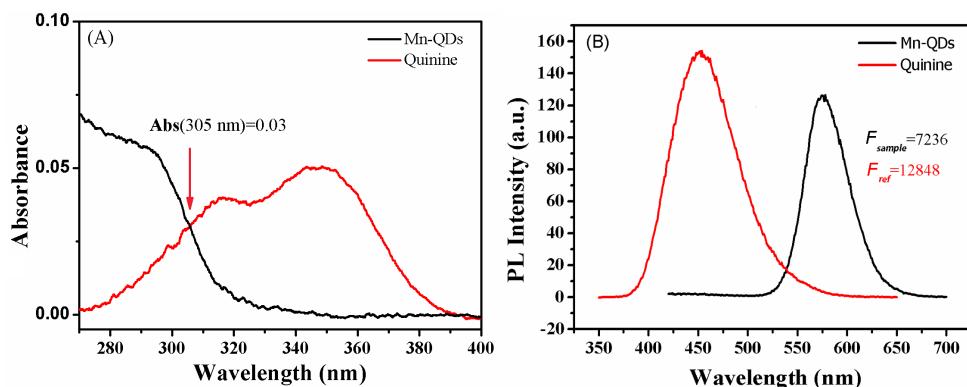
### Core/Shell Doped Quantum Dots for Targeted Mannosyl Groups Expression on the Cell Surface

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**Figure S1.** (A) Absorbance spectra and (B) photoluminescence emission spectra of the standard quinine sulfate and a sample of GSH capped ZnS:Mn d-dots with excitation at 305 nm, where the absorbance values of the two samples are equal.

The quantum yield of the GSH capped ZnS:Mn d-dots was calculated using the following equation, by referencing to the standard quinine sulfate (QY = 55%, in 0.5-M H<sub>2</sub>SO<sub>4</sub>)<sup>S1, S2</sup>:

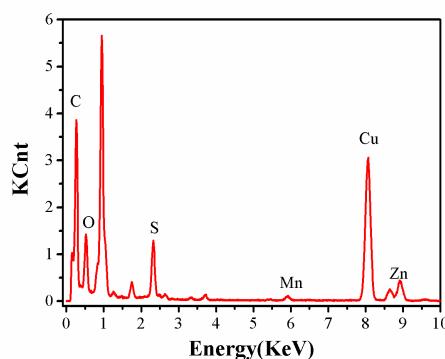
$$\text{QY}(\text{sample}) = (F_{\text{sample}}/F_{\text{ref}})(A_{\text{ref}}/A_{\text{sample}})(n_{\text{sample}}^2/n_{\text{ref}}^2)\text{QY}(\text{ref})$$

where  $F$ ,  $A$ , and  $n$  are the measured fluorescence (area under the emission peak), absorbance at the excitation wavelength and refractive index of the solvent respectively.

**Table S1.** The QY and reaction conditions of the ZnS:Mn d-dots have been reported by aqueous-phase synthetic method.

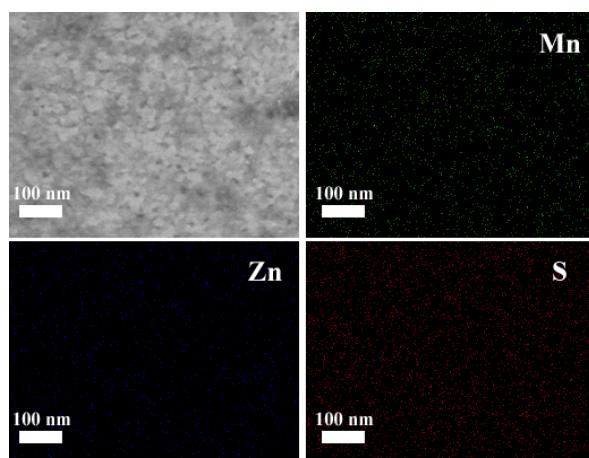
<i>Ligand</i>	<i>QY</i>	<i>Reaction conditions</i>		<i>Pure dopant emission</i>	<i>Ref</i>
		<i>Temperature</i>	<i>Time</i>		
MPA	12.1	microwave	5 min	NO	[32]
MPA	8.2	50 °C	2 h	NO	[50]
Thioglycerol	13.2	reflux	20 h	Yes	[42]
GSH	27.4	70 °C	3 h	Yes	This work

- [32] W. Jian, J. Zhuang, W. Yang and Y. Bai, *J. Lumin.*, 2007, **126**, 735-740.  
[42] M. Geszke-Moritz, H. Piotrowska, M. Murias, L. Balan, M. Moritz, J. Lulek and R. Schneider, *Journal of Materials Chemistry B*, 2013, **1**, 698-706.  
[55] P. Wu, L.-N. Miao, H.-F. Wang, X.-G. Shao and X.-P. Yan, *Angew. Chem. Int. Ed.*, 2011, **50**, 8118-8121.



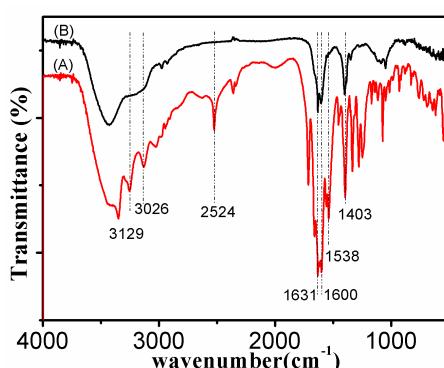
**Figure S2.** EDS spectrum of the GSH capped ZnS:Mn/ZnS core/shell d-dots.

The result indicated the presence of S (2.3 keV) Zn (8.6 keV), Mn (5.9 keV) and O (0.5 keV).

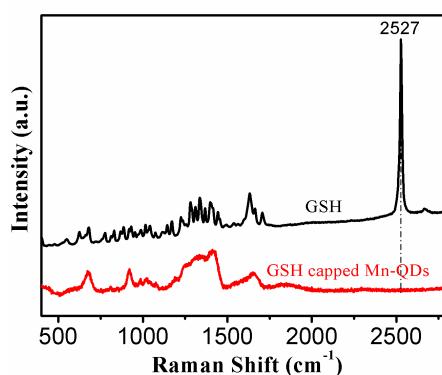


**Figure S3.** Element mapping images of the GSH capped ZnS:Mn/ZnS core/shell d-dots.

Element mapping (Figure S3) of the as-prepared ZnS:Mn/ZnS d-dots further disclosed that manganese, zinc, and sulfur were uniformly distributed in the semiconductor NCs, and confirmed the formation of nearly monodisperse NCs.



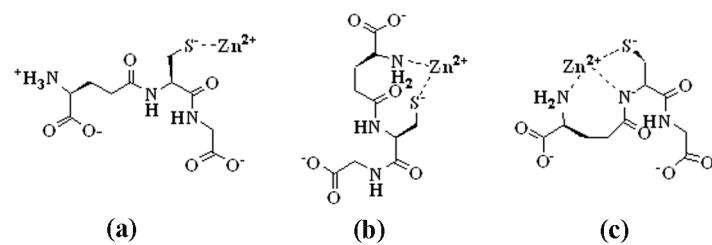
**Figure S4.** FT-IR spectra of (A) GSH and (B) GSH capped ZnS:Mn/ZnS core/shell d-dots.



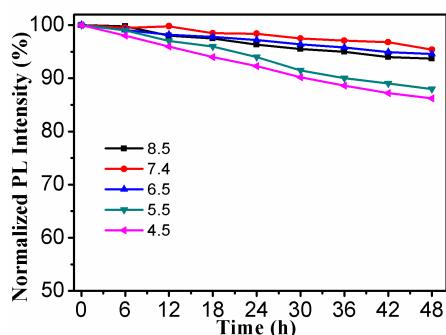
**Figure S5.** Raman spectra of GSH and GSH capped ZnS:Mn/ZnS core/shell d-dots.

**Table S2.** The concentration of Zn and Mn element in the samples were determined by ICP-AES spectra and the quantum yields of ZnS:Mn/ZnS with different doped concentration.

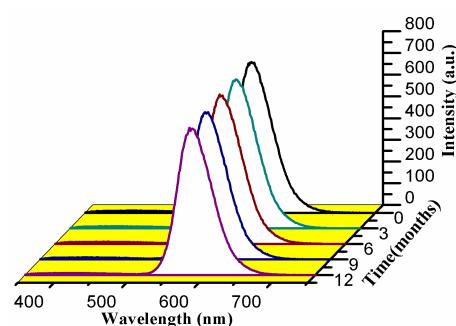
Sample NO.	Initial Mn/Zn concentration (mol %)	ICP results in Mn/Zn (mol %)	quantum yield (%)
QDs1	0	0	0
QDs2	0.5	0.59	0.3
QDs3	1	1.2	6.5
QDs4	2	1.8	21.0
QDs5	4	4.3	27.4
QDs6	6	6.5	24.4
QDs7	8	8.6	14.2
QDs8	10	9.7	12.1



**Figure S6.** Zn-GSH complexes at different pH values: (a) complex I, pH 6.5–8.3; (b) complex II, pH 8.3–10.3; (c) complex III, pH 10.3–11.5.<sup>S3</sup>



**Figure S7.** The stability of GSH capped ZnS:Mn/ZnS d-dot under the pH value 4.5-8.5.



**Figure S8.** Solid fluorescence spectra of GSH capped ZnS:Mn/ZnS powder keep for months under normal atmospheric conditions.

## References

- S1. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.
- S2. M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmuller and U. Resch-Genger, *Anal. Chem.*, 2009, **81**, 6285-6294.
- S3. J. Zhang, J. Li, J. Zhang, R. Xie and W. Yang, *J. Phys. Chem. C*, 2010, **114**, 11087-11091.