

Electronic Supplementary Information for:

Photoluminescence in semiconductor nanoparticles; an atomistic view of excited state relaxation in ZnS

Martijn A. Zwijnenburg

Department of Chemistry, University College London, 20 Gordon Street, WC1H 0AJ, UK. Email address: m.zwijnenburg@ucl.ac.uk.

Content:

ESI1 *Pictures of additional structures considered (p2)*

ESI2 *Comparison of DZ(D)P and def2-TZVP results (p2)*

ESI3 *Effect of amount of Hartree-Fock exchange on results obtained (p2-4)*

ESI1 Pictures of additional structures considered

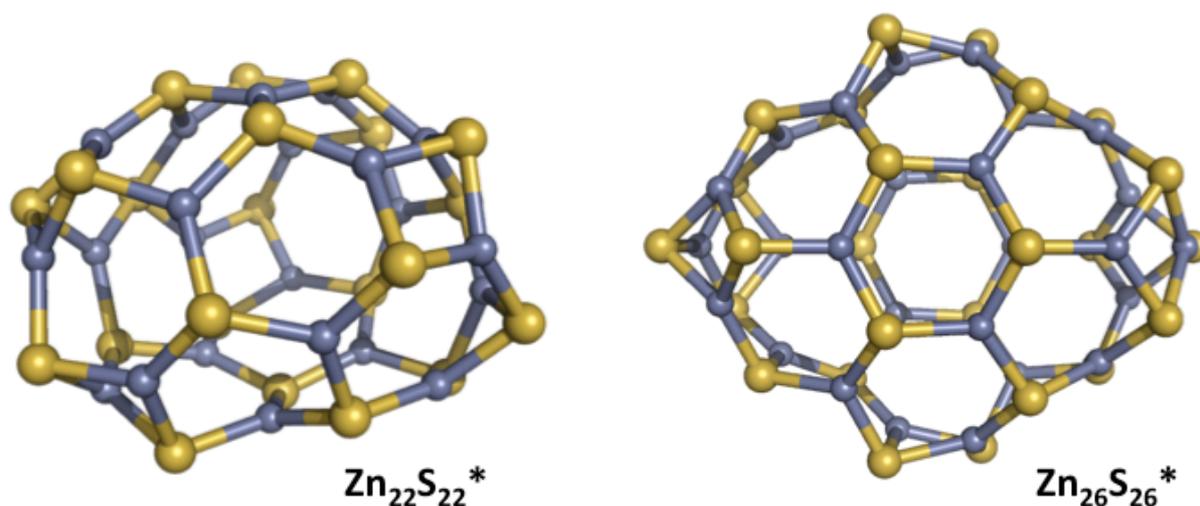


Fig. S1 Structures of $\text{Zn}_{22}\text{S}_{22}^*$ and $\text{Zn}_{26}\text{S}_{26}^*$

ESI2 Comparison of DZ(D)P and def2-TZVP results

For selected nanoparticles we have also optimized the S1 excited state with the larger triple-zeta def2-TZVP basis-set¹. A comparison between these results and those obtained with the DZ(D)P basis-set² used in the main paper can be found in table S1 below (in both cases when using the B3LYP XC-functional). From the data in table ESI4-1 it is clear that, just as we previously observed for absorption energies at the ground state minimum energy geometry **Error! Bookmark not defined.**, that both basis-sets lead to very similar results with the difference being typically less than 0.1 eV.

Table S2 Comparison of S1 photoluminescence energies for selected nanoparticles calculated with the DZ(D)P and def2-TZVP basis-sets

	DZ(D)P	Def2-TZVP
$\text{Zn}_{12}\text{S}_{12}$	0.98	1.03
$\text{Zn}_{16}\text{S}_{16}$	0.96	0.95
$\text{Zn}_{22}\text{S}_{22}^*$	2.56	2.65
$\text{Zn}_{22}\text{S}_{22}$	2.55	2.66

ESI3 Effect of amount of Hartree-Fock exchange on results obtained

As discussed in the main paper TD-B3LYP provides the best match with CASPT2 excitation energies calculated with large-basis-sets and a large-active-space for both the ground state and excited state (*I-I*) minima of Zn_4S_4 and Zn_6S_6 ³. We believe therefore the TD-B3LYP results to be the most realistic (fulfilling criteria (i) outlined in the paper) and use TD-B3LYP throughout to make predictions. We feel further supported in this assessment by the fact that, as shown in the

paper, the TD-B3LYP calculated luminescence energies for $\text{Zn}_{22}\text{S}_{22}$ and $\text{Zn}_{26}\text{S}_{26}$ lie in the same range as the experimentally measured luminescence signals for 1-2 nm ZnS nanoparticles.

Notwithstanding the apparent success of TD-B3LYP, we wanted to explore the sensitivity of our obtained results on the percentage of Hartree-Fock exchange (HFE) in the employed XC-functional. To achieve this aim, we performed additional excited state energy minimisations besides those with B3LYP (20% HFE) reported in the main paper with the PBE⁴ (0% HFE), B3LYP⁵ (50% HFE) and a modified version of B3LYP with 100% HFE (which we will refer to as B₁₀₀LYP) XC-functionals for $\text{Zn}_{12}\text{S}_{12}$ and $\text{Zn}_{22}\text{S}_{22}^*$. We furthermore explored TD-HF, the time-dependent version of Hartree-Fock. In line with our previous work³ on absorption and luminescence in Zn_4S_4 and Zn_6S_6 and absorption in larger nanoparticles^{Error! Bookmark not defined.} we find that using TD-PBE gives lower absorption and luminescence energies than when TD-B3LYP is used, while using XC-functionals with a higher percentage of HFE than B3LYP (i.e. TD-B3LYP and B₁₀₀LYP) and TD-HF yields higher absorption and luminescence energies. Fig. S3 shows that the shift in energies with percentage HFE obtained is approximately linear.

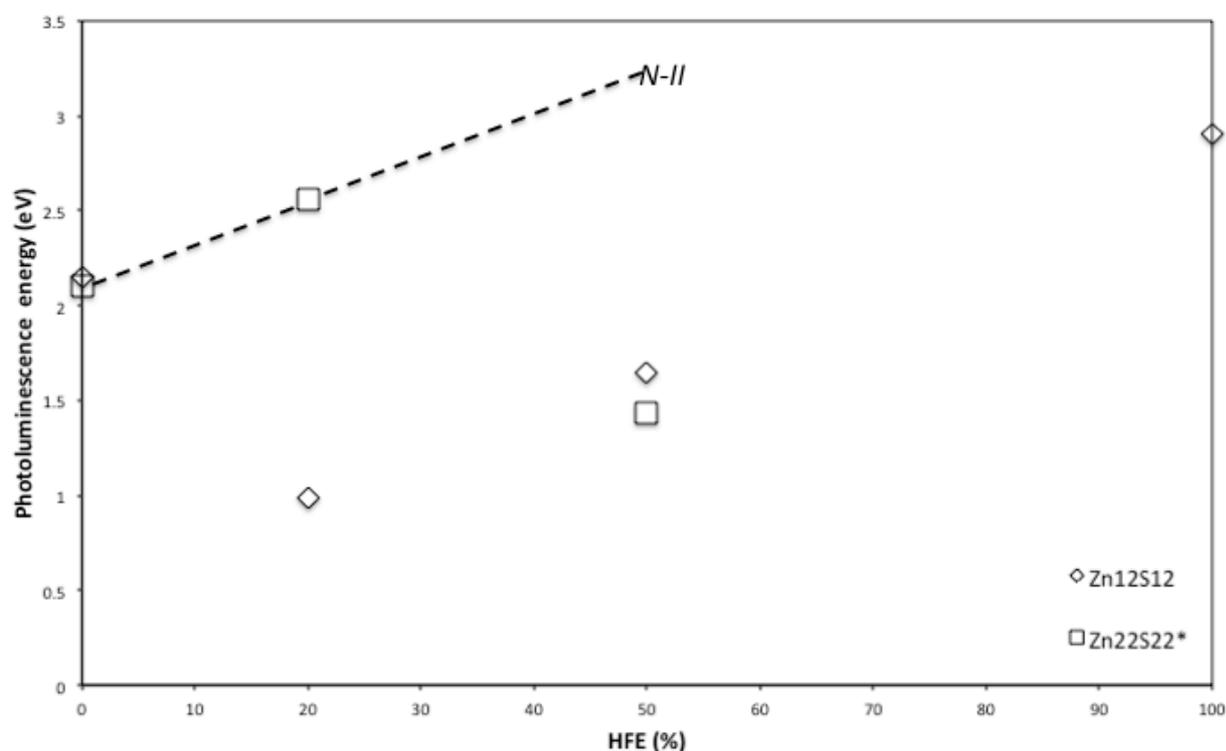


Fig. S3 Photoluminescence energies of $\text{Zn}_{12}\text{S}_{12}$ and $\text{Zn}_{22}\text{S}_{22}^*$ S1 minima found plotted versus the percentage of HFE in the XC-functional.

For $\text{Zn}_{12}\text{S}_{12}$ we obtained the same S1 minimum (in terms of excited state localization) with any XC-functional considered, except for TD-PBE where for $\text{Zn}_{12}\text{S}_{12}$ a *N-II* instead of an *I-II* minimum was found. For $\text{Zn}_{22}\text{S}_{22}^*$ we obtain a transition with increasing amount of HFE from a *N-II* minimum (for TD-PBE and TD-B3LYP) to an *I-II* minimum (TD-B3LYP). Increasing the percentage of HFE thus leads one to find minima in which the excited state is more localized. Having said that for both nanoparticles considered as examples here the localization of the hole never changes when increasing or decreasing the percentage of HFE (always localized over two adjacent sulfur atoms forming a S_2^{3-} molecular anion like species). Moreover, increasing the percentage of HFE merely seems to push the transition between *I-II* and *N-II* to larger nanoparticles (i.e. for PBE $\text{Zn}_{12}\text{S}_{12}$ is the

first particle with a *N-II* minimum, for B3LYP this is $\text{Zn}_{22}\text{S}_{22}$ and for TD-BHLYP it will be most likely a particle slightly larger than those studied here). Finally, linear extrapolation of the $\text{Zn}_{22}\text{S}_{22}^*$ results in Fig. S3 (dashed line) would suggest that for such larger nanoparticles TD-BHLYP *N-II* minima would display luminescence at approximately 3.3 eV (375 nm), a much lower wavelength than that measured experimentally. At the same time the TD-BHLYP predicted luminescence energies of the *I-II* minima in Fig. S3 (approximately 1.5 eV, 820 nm) lie at much longer wavelengths than experiment. As a result, short of finding a completely different type of excited state minimum for TD-BHLYP, there appears to be no way that TD-BHLYP can match the experimental spectra.

References

- ¹ A. Schafer, H. Horn, R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571.
- ² F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.
- ³ M.A. Zwijnenburg, C. Sousa, F. Illas, S.T. Bromley *J. Chem. Phys.* 2010, **134**, 064511.
- ⁴ K. Burke, M. Ernzerhof, J.P. Perdew, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- ⁵ A.D. Becke, *J. Chem. Phys.* 1993, **98**, 1372.