Electronic Supplementary Information for:

Excited state localisation cascades in inorganic semiconductor nanoparticles

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ESI-1 Typical ground and excited state charge differences for the different excited state minima

For the *N-II* minima we typically find two sulphur atoms with a S_1-S_0 NBO charge difference of ~ +0.3 each (i.e. both atom has 0.3 units of electrons less in the excited state compared to the ground state at the same geometry). There is also typically a number of zinc atoms with a S_1-S_0 NBO charge difference of ~ -0.03 - -0.06 each (i.e. both atom has 0.03-0.06 units of electrons more in the excited state compared to the ground state at the same geometry). There might also be occasionally a small number of nitrogen atoms with a similar magnitude and sign S_1-S_0 NBO charge difference. For the *I-II* minima we typically find two sulphur atoms with a S_1-S_0 NBO charge difference of ~ +0.2 each and one zinc atom with a S_1-S_0 NBO charge difference of ~ -0.4. There is more inherent variation for the *I-I minima/CX*. Typically we find a relatively large positive S_1-S_0 NBO charge difference on the 2-coordinated sulfur atom (~ +0.4 for the T_1 minima and ~ +0.8 - +1.0 for the S_1 CXs) and a relatively large negative S_1-S_0 NBO charge difference on the 2-coordinated zinc atom (~ -0.4 for the T_1 minima and ~ -0.7 - -0.8 for the S_1 CXs). Other atoms in the direct neighbourhood can also have, however, in this case a significant S_1-S_0 NBO charge difference, especially for the CXs. In these cases the S_1-S_0 NBO charge difference are typically the opposite of what normally finds for the particular type of atom (i.e. zinc atoms having less electrons in the excited state than the ground state or sulfur atoms having more) and the maximum magnitude is less than half that found for the 2-coordinated atoms.

ESI-2 PLE and ESSE values for *N-II* and *I-II* minima

Tables ST-1 and ST-2 summarise the PLE and Excited State Stabilisation Energy (ESSE, the difference in excited state energy between the ground state minimum energy geometry and the geometry in question) for the most energetically stable (i.e. lowest energy) version found of the *N-II* and *I-II* minima on the S_1 and T_1 energy landscape of each particle. Most data is taken from table 1 of my previous paper (data marked by an asterisk)[1]. In some cases a slightly more stable version of a type of minimum previously reported in reference 1 was found and then data for this new more stable minimum is included in table ST-1 and ST-2 rather than the original one. Table ST-1 also includes never before published data for the *I-II* S_1 minima of $Zn_{22}S_{22}$ and $Zn_{26}S_{26}$.

Table ST-1 PLE and ESSE values for *N-II* and *I-II* S_1 minima

S_1	*N-II*		*I-II*	
	PLE	ESSE	PLE	ESSE
$Zn_{12}S_{12}$	--	--	0.98*	0.76*
$Zn_{16}S_{16}$	--	--	0.96*	0.81*
$Zn_{22}S_{22}$	2.55*	0.44*	0.85	0.80
$Zn_{26}S_{26}$	2.61*	0.51*	0.92	0.80

Table ST-2 PLE and ESSE values for *N-II* and *I-II* S_1 minima

T_1	*I-II*		
	PLE	ESSE	ESSE-S
$Zn_{12}S_{12}$	0.91*	0.86*	0.93
$Zn_{16}S_{16}$	0.86*	0.92*	0.99
$Zn_{22}S_{22}$	0.77*	0.91*	0.97
$Zn_{26}S_{26}$	0.82*	0.92*	0.98

ESI-3 Example 10 K Born-Openheimer molecular dynamics run

Fig. S-1 and S-2 below display an example of a 10 K Born-Openheimer molecular dynamics run on the S_1 energy landscape of the $Zn_{12}S_{12}$ nanoparticle. Fig. S-1 plots the S_0 and S_1 energies as a function of the simulation progress while Fig. S-2 plots the S_1-S_0 energy difference (i.e. the excitation energy) as a function of the simulation progress.

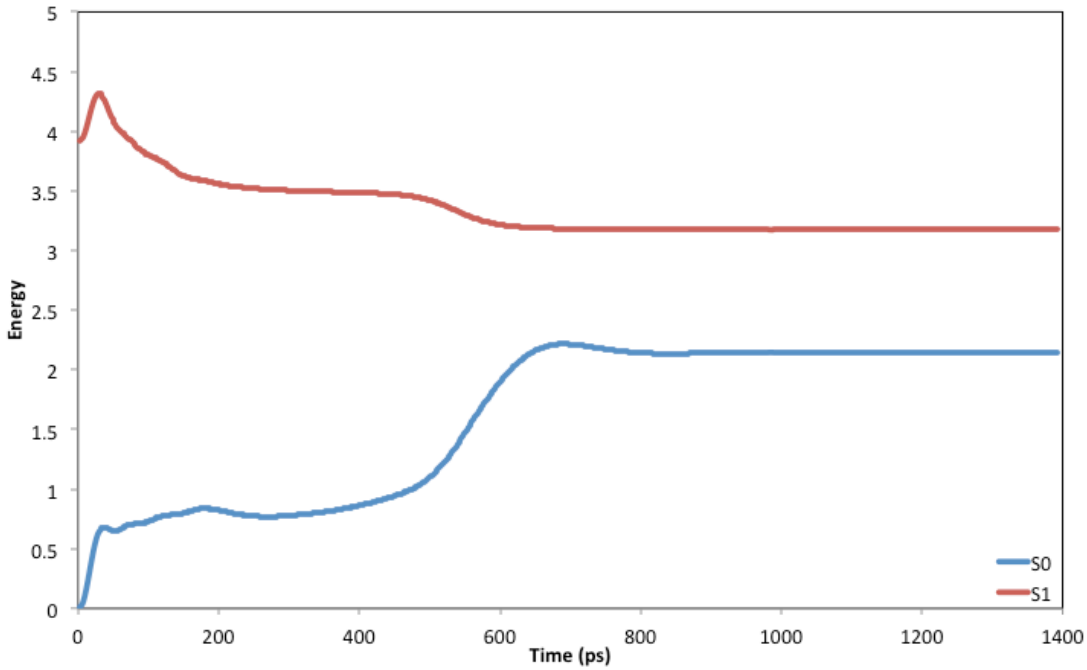

Fig. S-1 Plot of the S_0 and S_1 energies as a function of the simulation progress for a typical BOMD calculation on $Zn_{12}S_{12}$.

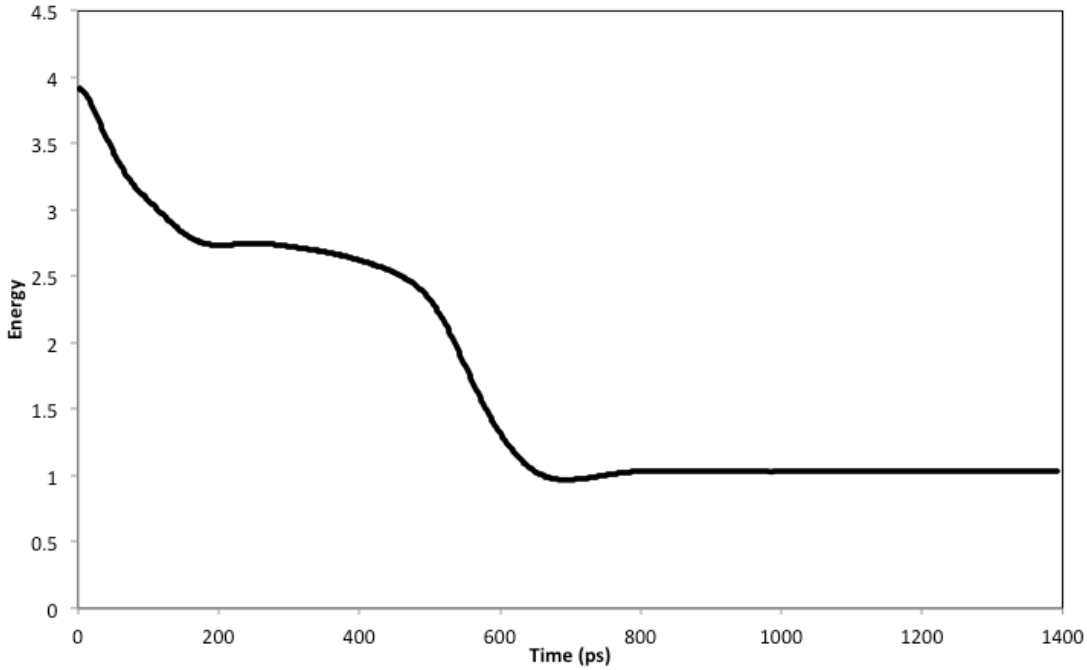

Fig. S-2 Plot of the S_1-S_0 energy difference (i.e. the excitation energy) as a function of the simulation progress for a typical BOMD calculation on $Zn_{12}S_{12}$.

ESI-4 Evidence from charge differences for a strongly avoided crossing

The nature of the barrier between the *N-II* and *I-II* minima was analysed by calculating the S_1-S_0 and S_2-S_0 charge differences along the interpolation pathway that links both minima. Fig. S-2 plots these charge differences for the zinc atom on which an excited electron becomes localised in the *I-II* minimum. One can clearly see that

while the S_1 and S_2 energy surfaces do not cross (see Fig. 4 of the main paper) the characters of both surfaces clearly cross around the top of the barrier.

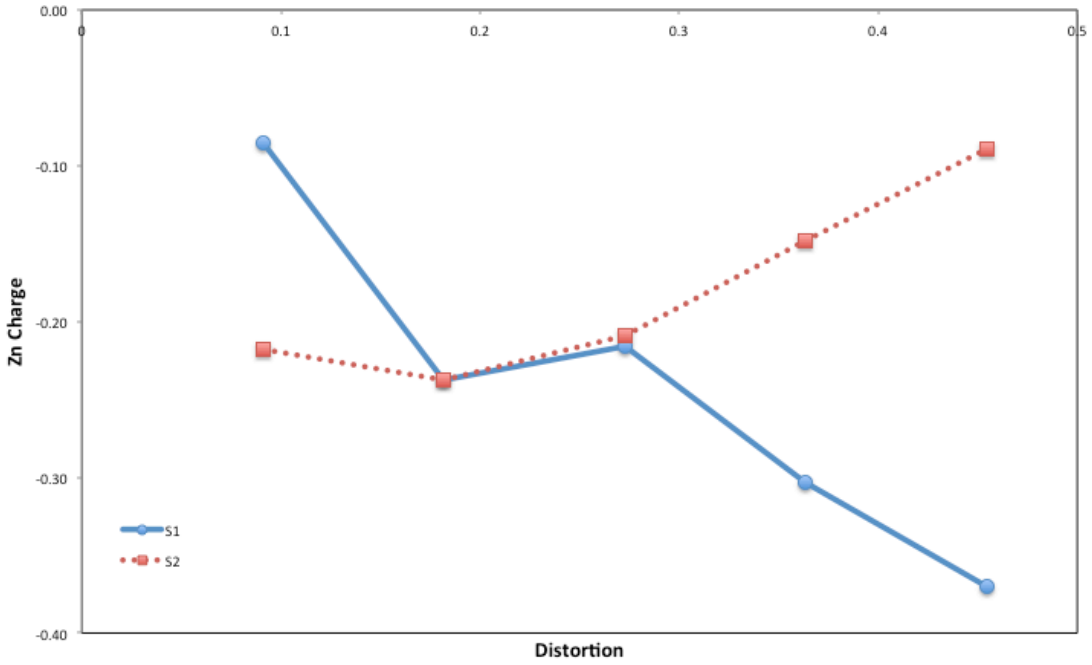

Fig. S-3 Plot of the difference in ground and excited state charge for the Zn atom on which the electron localises in the *I-II* minimum as a function of the linear distortion that links the $Zn_{22}S_{22}$ *N-II* and *I-II* minima (states labelled S_1 and S_2 after their ordering at the *N-II* minimum).

ESI-5 Alternative ground state structure found by DFT optimisation of the $Zn_{22}S_{22}$ *I-I* T_1 minimum or S_1 CX

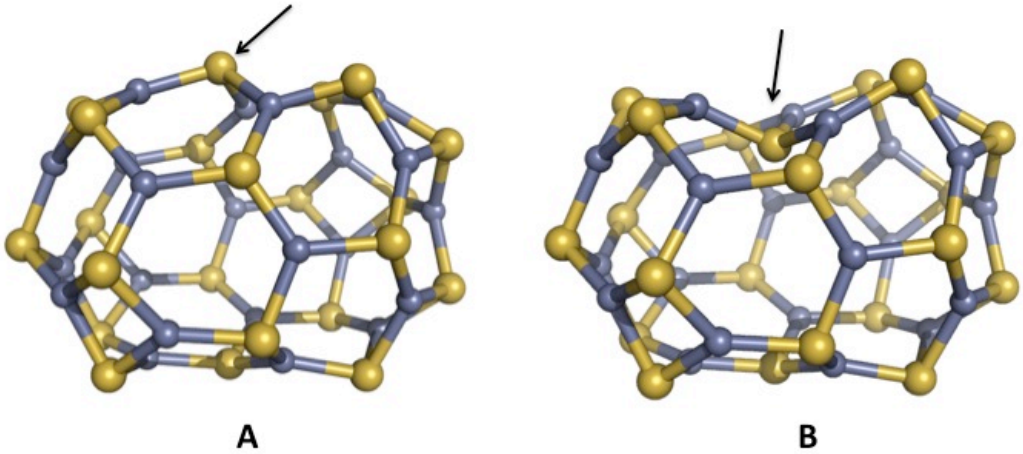

Fig. S-4 Comparison of the geometries of the $Zn_{22}S_{22}$ global minimum (A) and the alternative ground state structure obtained by a DFT optimisation starting from the $Zn_{22}S_{22}$ *I-I* T_1 minimum or S_1 CX (B). An arrow highlights the sulfur atom that is inverted in structure B.

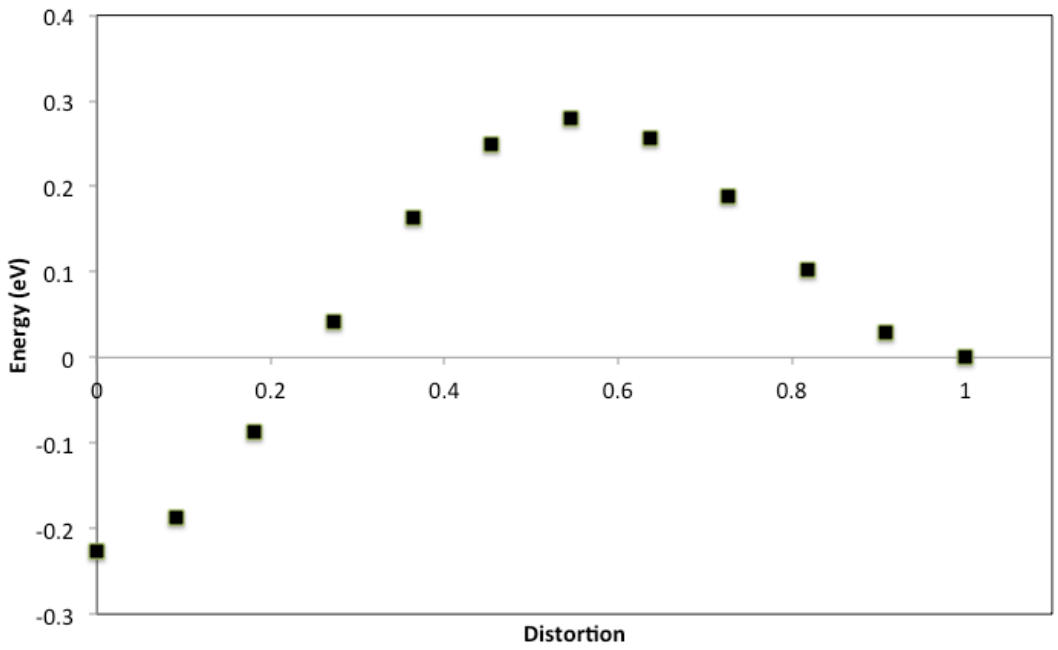

Fig. S-5 Energy profile along the interpolated path that connects the $Zn_{22}S_{22}$ global minimum (left, 0) and the alternative ground state structure obtained by a DFT optimisation starting from the $Zn_{22}S_{22}$ *I-I* T_1 minimum or S_1 CX (right, 1).

References

[1] M.A. Zwijnenburg, Nanoscale, 2012, **4**, 3711.