Electronic supplementary information for:

Optical excitations in stoichiometric uncapped ZnS nanostructures

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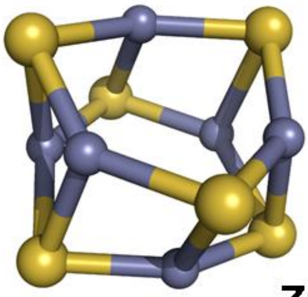
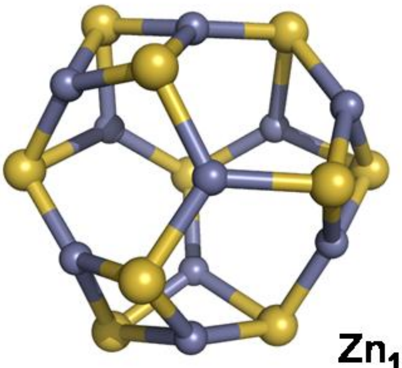
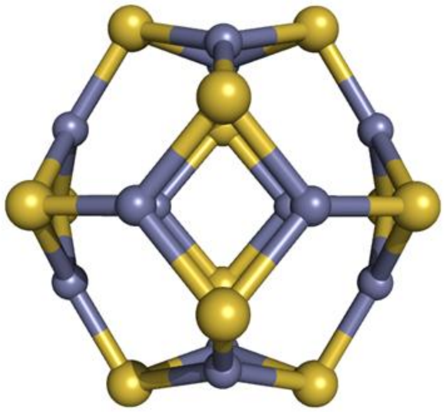
ESI1 *Pictures of other ground state candidates*



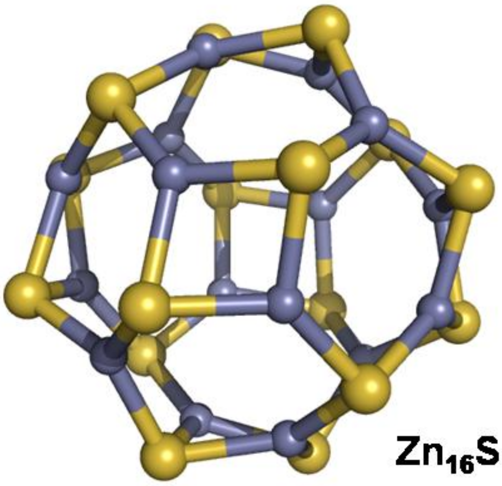
Zn_6S_6



$Zn_{10}S_{10}$



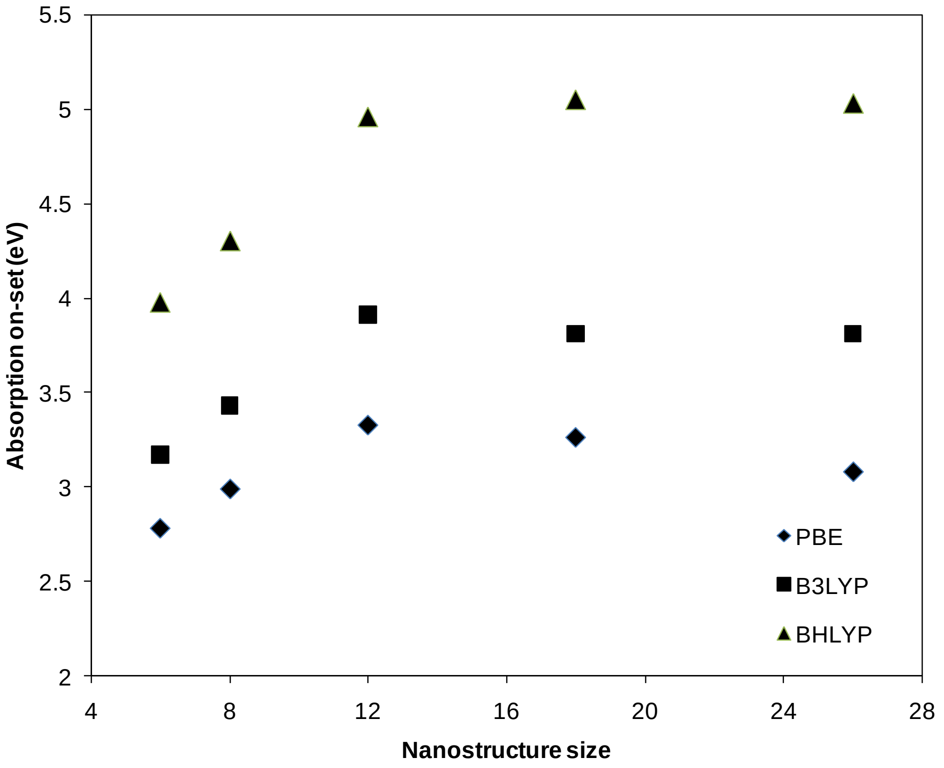
$Zn_{12}S_{12}$



$Zn_{16}S_{16}$

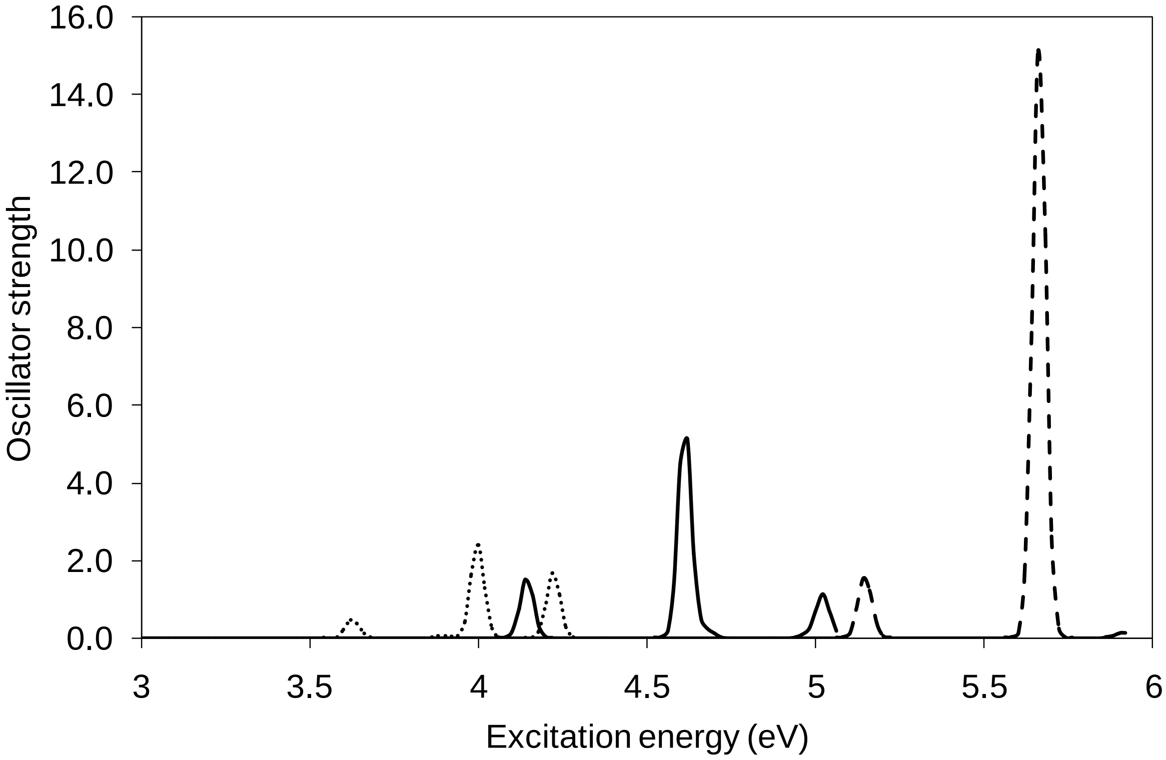
ESI2 *Absorption on-set values calculated with TD-PBE and TD-BHLYP*

The figure below gives the energy of the lowest singlet excitation (i.e. S0 -> S1, the absorption on-set) for the global minimum geometries for Zn_6S_6, Zn_8S_8, $Zn_{12}S_{12}$, $Zn_{18}S_{18}$ and $Zn_{26}S_{26}$, calculated with TD-PBE, TD-B3LYP and TD-BHLYP. From the data presented it is clear that all XC-potentials yield similar trends for changes in the absorption on-set values with increasing nanostructure size, where the TD-PBE values consistently lie below the TD-B3LYP values and the TD-BHLYP values always lie higher in energy. The increase of amount of Fock exchange in the XC-potential thus leads to a consistent shift of the absorption on-set values to higher energy.



ESI3 *Optical absorption spectra calculated with TD-PBE and TD-BHLYP*

The figure below gives the optical absorption spectra (30 lowest excitations) of the $Zn_{12}S_{12}$ global minimum candidate calculated with TD-PBE (····), TD-B3LYP (uninterrupted) and TD-BHLYP (---). We find all XC-potentials to yield similar spectra that are in-line with ESI2 shifted to lower energy relative to the B3LYP spectra for TD-PBE and shifted to higher energy for TD-BHLYP. Another effect of increasing the amount of Fock exchange that can be observed is a consistent rise in the oscillator strengths of the peaks.



ESI4 *Comparison with previous work by Maxtain and co-workers*

The table below presents the two lowest excitations for both the Zn_6S_6 and Zn_8S_8 global minimum candidates calculated using TD-B3LYP/def2-TZVP (values in parentheses are calculated with the smaller DZ(D)P basis-set) and TD-MPW1PW91/SKBJ(d). The latter are the results reported by Maxtain and co-workers[1]. Excitations highlighted in bold are dipole allowed and carry finite intensity, oscillator strengths of allowed transitions given in italics. As can be seen the TD-MPW1PW91 excitation energies are shifted upwards in energy relative to the TD-B3LYP values by approximately 0.3 eV, while the oscillator strengths obtained with both XC-potentials agree very well.

Zn_6S_6

	TD-B3LYP	TD-MPW91
E_g	3.08 (3.17)	3.37
A_{2u}	**3.34 (3.41)** *2.92E-2*	**3.60** *2.9E-2*

Zn_8S_8

	TD-B3LYP	TD-MPW91
e	**3.36 (3.43)** ***1.6E-2***	**3.65** ***1.8E-2***
a	3.62 (3.68)	3.94

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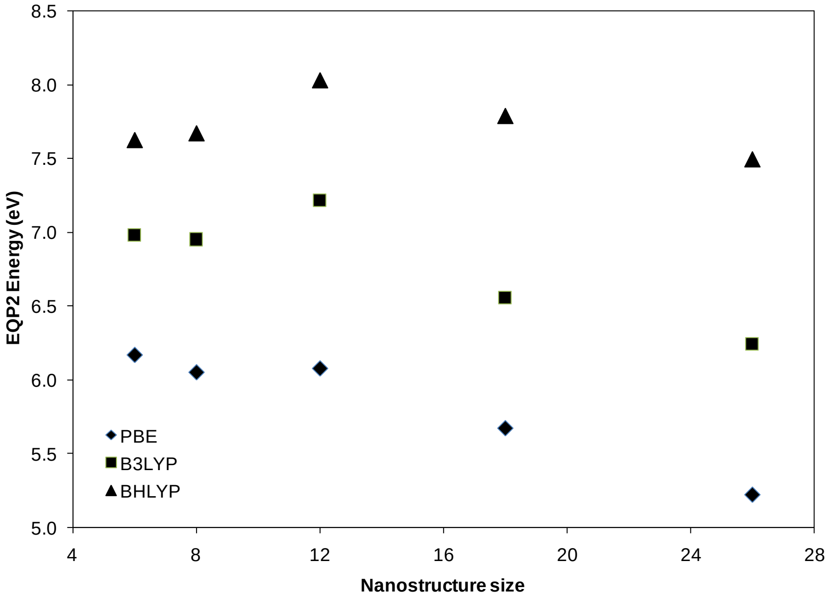
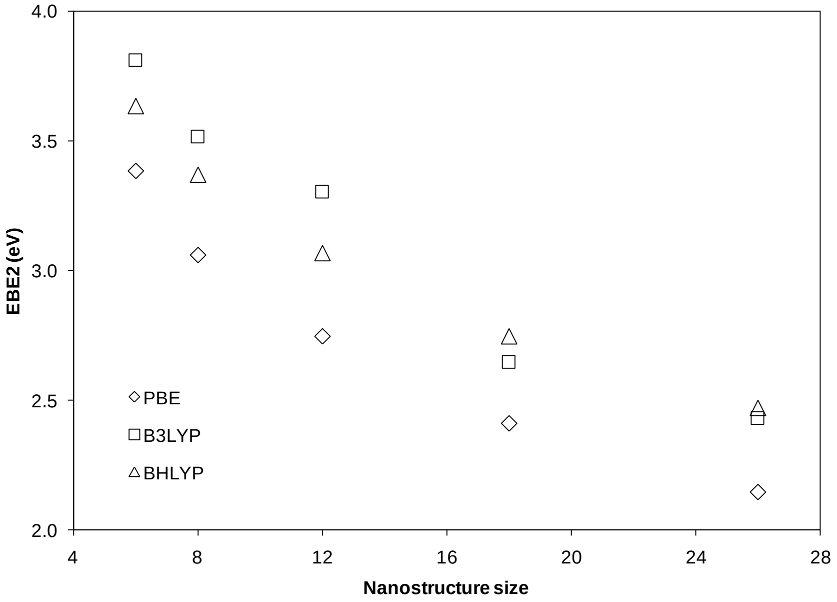
[1] J.M. Matxain, A. Irigoras, J.E. Fowler and J.M. Ugalde, Phys. Rev. A, 2001, **64**, 013201.

ESI5 *Quasiparticle gaps and exciton binding energies calculated with PBE and BHLYP*

The figures below show how the quasiparticle gap and exciton binding energy vary with the nanostructure size, when calculated with TD-PBE, TD-B3LYP and TD-BHLYP. We find all XC-potentials to give similar results. For the quasiparticle gap, the PBE values lie below the B3LYP calculated values while the BHLYP derived values lie higher in energy. In case of the exciton binding energy all XC-potentials give very similar results.





ESI6 *Electron density difference plot for* $Zn_{14}S_{14}$

Below is given a plot for the electron density difference between S0 and S1 for $Zn_{14}S_{14}$. In line with the analysis based on Mulliken charge differences the plot shows that the difference between S0 and S1 is predominantly localised on the fused 4-membered ring. Especially the now empty *p*-like orbital on the sulfur atom in the middle of the fused 4-membered ring is clearly visible in the electron density difference.