

## Electronic Supplementary Information

### On transient absorption and dual emission of the atomically precise, DNA-stabilized silver nanocluster $\text{Ag}_{16}\text{Cl}_2$

Sami Malola<sup>a</sup> and Hannu Häkkinen<sup>a,b,\*</sup>

<sup>a</sup> Department of Physics, Nanoscience Center, University of Jyväskylä, FI-40014 Jyväskylä, Finland

<sup>b</sup> Department of Chemistry, Nanoscience Center, University of Jyväskylä, FI-40014 Jyväskylä, Finland

\* hannu.j.hakkinen@jyu.fi

### Computational methods

The calculations were done using the density functional theory (DFT) as implemented in the GPAW software.[1] GPAW is a real-space grid based DFT-code which includes scalar-relativistic corrections for metal atoms. The starting structure of  $(\text{DNA})_2\text{-Ag}_{16}\text{Cl}_2$  cluster was based on the crystal structure published by the Vosch group [2] which was updated recently when Cl ligands were found in the structure. [3,4] Based on the previous studies the structure was confirmed to include 16 Ag, 2 Cl and 2 DNA strands with 16 phosphates. The implicit total charge in the solvent is 10-, which makes the system a 6 electron superatom, as expected experimentally. This takes into account that in addition to negatively charged phosphate groups and chlorides there are two deprotonated  $\text{G}_9^-$  bases in the strands.[4] We started the calculations by optimizing the ground state  $S_0$  structure as a spin-paired calculation using real-space grid with 0.2 Å grid spacing and the Perdew-Burke-Ernzerhof (PBE) xc-functional [5] until maximum forces of atoms were below 0.05 eV/Å. In all the calculations, an implicit water solvent model was used that is already published and tested earlier.[4,6]

The next step was to optimize the lowest excited  $S_1$  and  $T_1$  state structures, for which we used Maximum Overlap Method (MOM)[7] and spin polarization. Excitations were constructed by promoting an electron from the HOMO to LUMO state either into Singlet (alpha spin) or Triplet (beta spin) form. The same optimization criteria were used for the excited state structures as for the ground state. Structural changes during optimization were visualized as magnified vectors for the selected group of atoms: Ag- and Cl-atoms and the atoms of  $\text{G}_9^-$  bases. The vectors were constructed on atoms by comparing the aligned atomic coordinates before and after optimization. After optimization, the xc-functional was changed to GLLB-sc,[8] which was used to describe the wavefunctions and to study electronic and optical properties. GLLB-sc was previously shown to reproduce much better the optical gap and the experimental absorption spectrum than PBE. [4] Note also that the GLLB-sc functional can not provide (in the current implementation) the energy gradients, hence we have used the PBE functional for the parts that require them in the calculations (structure optimization, Ir-TDDFT kernel).

The electronic structure of  $S_0$ ,  $S_1$  and  $T_1$  states was analyzed by projecting the density of states to atoms, for which the symmetries of the electron states were projected to spherical harmonics functions centered at the individual atoms.[9]

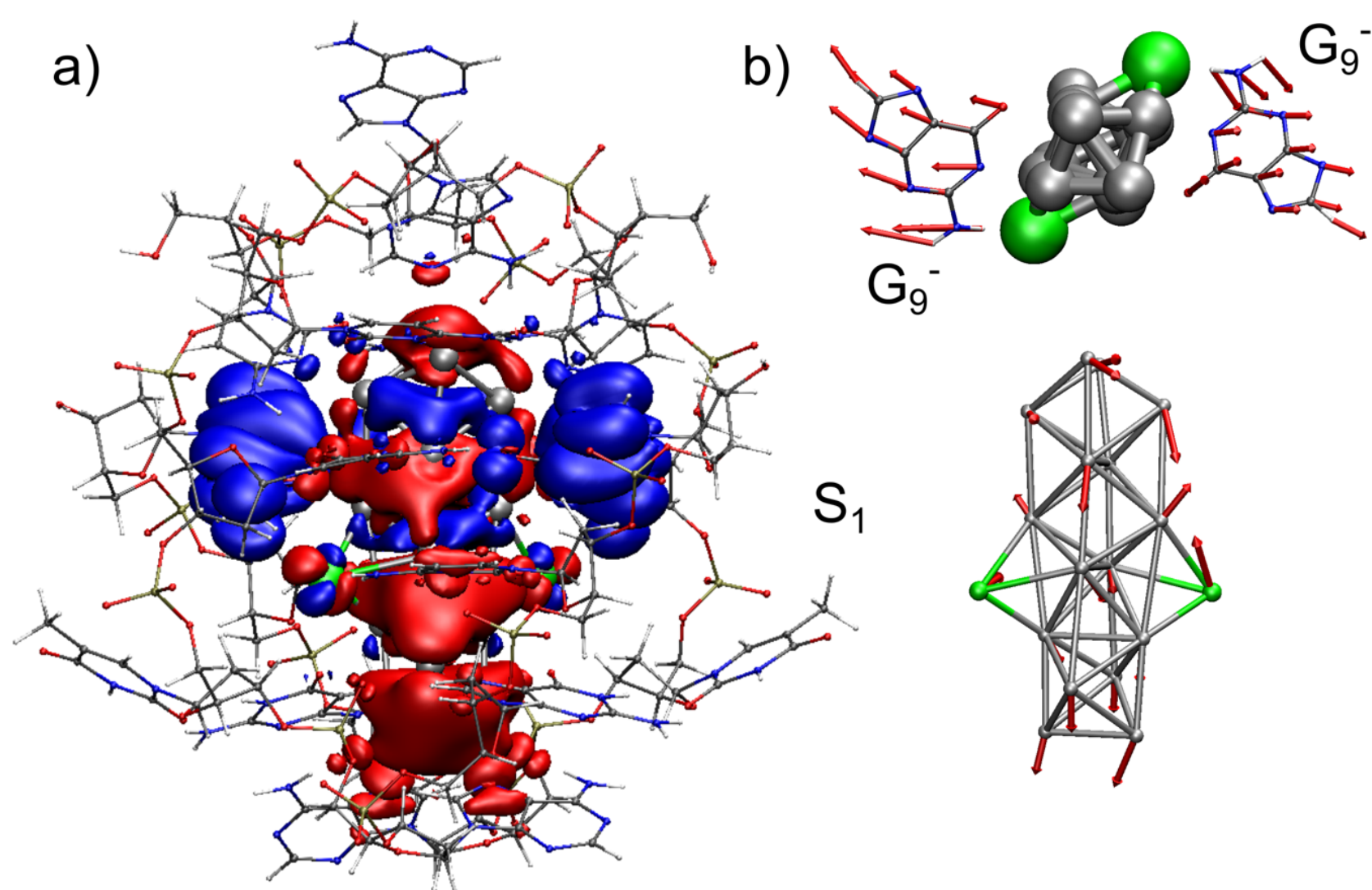
Characteristics of the lowest excitations from the ground state were visualized by forming a density difference of HOMO and LUMO states which is interpreted here as difference of hole and electron densities, respectively. The emission energies were estimated with respect to the ground state using excited state total energies in spin purified form. In general, for a singlet state the emission energy  $E_{em} = 2E_S - E_T - E_{GS}$ , where  $E_S$  is the singlet state energy,  $E_T$  a triplet and  $E_{GS}$  a ground state energy, and the triplet state emission energy is simply  $E_{em} = E_T - E_{GS}$ . [7]

Optical absorption spectra were calculated using the linear response density-functional theory (lr-TDDFT)[10] with PBE functional as a kernel. For the excited state structures the calculated absorption spectra are plotted as difference spectra to the ground state which mimics the experimentally measured transient absorption spectra. In lr-TDDFT calculations all possible electron-hole pairs with positive energies were taken into account. Further analysis of the selected long wavelength absorption peaks of the calculated spectra of  $S_1$  and  $T_1$  excited states was done based on the decomposition of the solved single excitations into Kohn-Sham electron-hole state pairs. Energy eigenvalues, oscillator strengths and relative contributions of Kohn-Sham electron-hole pairs were processed to create approximate electron-hole densities from the weighted difference of Kohn-Sham state densities participating into the most important transitions. The weights were formed from the oscillator strengths and relative contributions of electron-hole pairs. The set of single excitations were selected to be the strongest in oscillator strength and the closest in energy to the maximum of the analyzed peak which meant one excitation in the case of  $S_1$  and two for  $T_1$ .

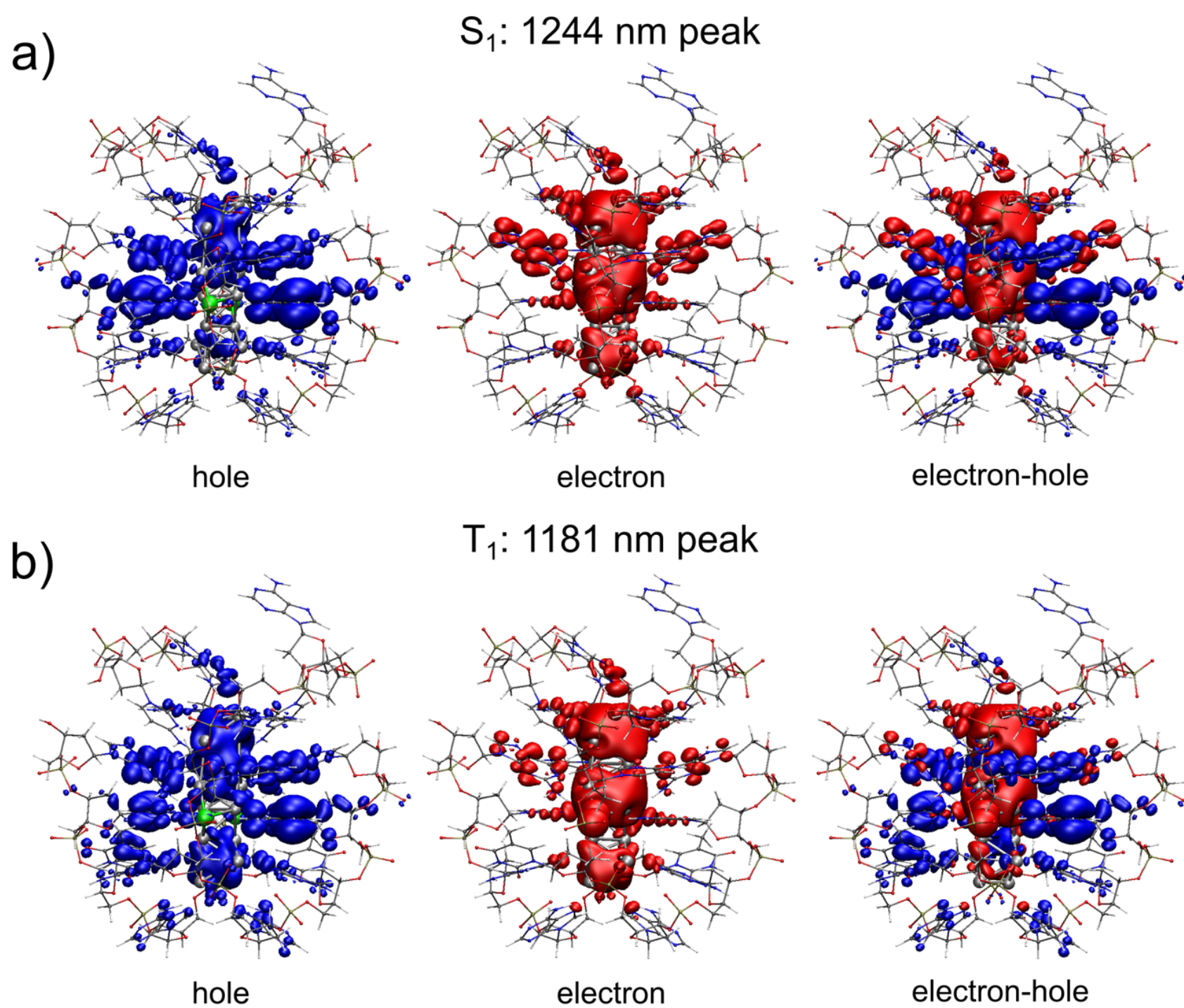
## References

1. Enkovaara, J. et al. Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method, *J. Phys. Condens. Matter* **2010**, *22*, 253202.
2. Cerretani, C.; Kondo, J.; Vosch, T., Removal of the A10 Adenosine in a DNA-Stabilized  $Ag_{16}$  Nanocluster. *RSC Adv.* **2020**, *10*, 23854–23860
3. González-Rosel A. et. al., Chloride Ligands on DNA-Stabilized Silver Nanoclusters, *J. Am. Chem. Soc.* **2023**, *145*, 19, 10721–10729
4. Malola S.; Matus M. F.; Häkkinen H., Theoretical Analysis of the Electronic Structure and Optical Properties of DNA-Stabilized Silver Cluster  $Ag_{16}Cl_2$  in Aqueous Solvent, *J. Phys. Chem. C* **2023**, *127*, 33, 16553–16559
5. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
6. Held A.; Walter M., Simplified continuum solvent model with a smooth cavity based on volumetric data, *J. Chem. Phys.* **2014**, *141*, 174108.
7. Ivanov A.V.; Levi G.; Jónsson E. Ö.; Jónsson H., Method for Calculating Excited Electronic States Using Density Functionals and Direct Orbital Optimization with Real Space Grid or Plane-Wave Basis Set, *J. Chem. Theory Comput.* **2021**, *17*, 8, 5034–5049.
8. Kuisma, M.; Ojanen, J.; Enkovaara, J.; Rantala, T. T. Kohn-Sham potential with discontinuity for band gap materials. *Phys. Rev. B* **2010**, *82*, 115106.

9. Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A unified view of ligand-protected gold clusters as superatom complexes, *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*(27), 9157–9162.
10. Walter, M. et al. Time-dependent density-functional theory in the projector augmented-wave method. *J. Chem. Phys.* **2008**, *128*, 244101.



**FIG S1.** Visualization of changes in the electronic and atomic structure of the  $(DNA)_2Ag_{16}Cl_2$  cluster under  $S_1$  (HOMO-LUMO) excitation. (a) Electron density change: blue/red denote depleted / enhanced density regions. (b) atomic displacements in the  $G_9^-$  and in the inorganic core.  $T_1$  excitation creates electron density changes and atomic displacements which are almost identical to  $S_1$  and they are not shown here. In detail, the displacements in (b) can be described as follows: in the upper part of the metal core, the Ag-Ag distances in the longitudinal direction are getting significantly shorter (up to -8%). On the other hand, Ag-Ag distances in the center of the metal core close to Cl are expanding by almost the same amount (up to +7 %) while Cl-Ag bonds are getting shorter (up to -5 %). In the perpendicular direction to the main axis, the changes are on average smaller, in the upper part of the metal core the system expands (up to +4%) and in the lower part shrinks (up to 2%).



**FIG S2.** Visualization of the hole and electron densities and their difference corresponding to NIR absorption peaks under (a)  $S_1$  and (b)  $T_1$  excitations.