# A DFT study of a new class of Gold Nanocluster-Photochrome multi-functional switches

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# I. $Au_{25}(SH)_{17}$ -DTE- systems: Molecular Dynamics procedure

Simulations were run with the DL\_POLY\_MD package.<sup>1,2</sup> Force Field parameters for C, H, S atoms were those of the General Amber Force Field (GAFF).<sup>3</sup> Parameters for the gold atoms were taken from the work of Ayappa and coworkers.<sup>4</sup> The atomic charges used for the Dynamics are Mulliken charges obtained at the DFT level, with the PBE0 functional. A 6-31G(d) basis set was chosen for C, S and H, and the LANL2DZ basis set and effective core potential was used for Au atoms. The simulation was run in vacuum at T = 298 K on a single hybrid system (no periodic conditions), and a Verlet leapfrog algorithm was chosen to integrate the equation of motion. We ran our simulations in the NVT ensemble with a Hoover thermostat (coupling constant = 0.5 ps), for 10 ns, with an equilibration phase of 1 ns. During these simulations, only the atoms of the DTE and the alkanethiol chains are allowed to move and the nanocluster structure is kept fixed, in the geometry obtained at the DFT level.

## II. Molecular orbitals of the isolated DTEs.



Figure S-1: Molecular orbitals involved in the electronic transitions described in Table 1 (threshold: 0.02 a.u.).



Figure S-2: Bonding interaction between the two reactive carbon atoms in the LUMO of the **1o** (threshold: 0.02 a.u.) and **2o** (threshold: 0.01 a.u.) compounds.

#### **III.** Bond Length Alternation calculation

The Bond Length Alternation is calculated as follows:

 $BLA = \sqrt{\frac{1}{N}\sum_{i}(d_i - d_M)^2}$ 

where N is the number of C-C bonds,  $d_M$  is the mean bond length and  $d_i$  is the  $i^{th}$  bond length. In DTEs, the bonds taken into account are sketched in the following figure:



Figure S-3: C-C bonds taken into account for the calculation of the BLA. Simple bonds are in red and double bonds are in green.

IV. Absorption spectra of the GNC : comparison of different pseudopotentials.



Figure S-4: Theoretical convoluted absorption spectra and stick spectra of the  $[Au_{25}(SH)_{18}]^-$  GNC, obtained with the CAM-B3LYP functional with different pseudopotentials and associated basis sets. Top to bottom: Lanl2DZ, Lanl2TZ, Lanl2TZ(f) and SDD (MWB60).

# V. Absorption spectra of GNC-10 and GNC-20.



Figure S-5: Theoretical absorption spectra of GNC-10 (left) and GNC-20 (right). DTE spectrum is in green, the gold cluster spectrum is in dotted black line, and the hybrid system spectrum is in red. The stick spectra are also represented.

VI. Effect of the conformation on the optical properties of GNC-20.



Figure S-6: UV theoretical absorption spectra of GNC-**20** for two different conformation the UV region. The stick spectra are also represented.

#### VII. Förster energy transfer

In Förster energy transfer mechanism, the energy transfer rate  $k_F$  can be written as:

$$k_F = \frac{1}{\tau_0} \frac{R_0^6}{|r_A - r_D|^6}$$

where  $R_0$  is the Förster radius,  $\tau_0$  is the excited lifetime,  $r_A$  and  $r_D$  are the position vectors of the donor and the acceptor. The Förster radius is the distance between the donor and the acceptor for which the energy transfer occurs with a 50 percent probability:

$$R_0^6 = \frac{9000 \times ln(10)\kappa^2 Q_D}{128\pi^5 n^4 N_A} \int F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda$$

This radius is obtained with  $Q_D$  (the donor luminescence efficiency), the overlap between the donor and the acceptor spectra, and  $\kappa^2$ , the orientation factor defined as follow:

$$\kappa^2 = (\cos \gamma - 3\cos \alpha \cos \beta)^2$$

The angles  $\alpha$ ,  $\beta$  and  $\gamma$  are geometrical parameters representing the orientation between the two dipole transition moments, the donor emission dipole and the acceptor absorption dipole.

![](_page_8_Figure_8.jpeg)

Figure S-7: Orientation of the transition dipoles moments and representation of the angles  $\alpha$ ,  $\beta$  and  $\gamma$ .

Table S-I: Orientation of the transition dipole moments of the donor (10) and the acceptor (GNC), and orientation factor  $\kappa^2$ . The number of the GNC excited state is given (for instance S24 is the 24th GNC excited state).

dipoles	α	β	$\gamma$	$\kappa^2$
$1o(S1) \rightarrow GNC(S24)$	57.4	135.04	99.12	0.97
$1o(S1) \rightarrow GNC(S25)$	39.27	135.04	171.89	0.43
$1o(S1) \rightarrow GNC(S30)$	110.75	135.04	46.05	0.00
$1o(S1) \rightarrow GNC(S34)$	33.23	135.04	129.2	1.31

### VIII. Redox potentials

![](_page_10_Figure_1.jpeg)

Figure S-8: Born-Haber thermodynamic cycle used for the computation of the oxidation potential.

IX. IR spectra of GNC-10 (in black) and GNC-1c (in red) compounds.

![](_page_11_Figure_1.jpeg)

Figure S-9: IR theoretical spectra of GNC-1o and GNC-1c. A FWHM of 3  $\rm cm^{-1}$  is used, with a scaling factor of 1.

The IR spectra may be useful to probe the state of the photochrome without altering the system. The superimposition of the GNC-1o and GNC-1c spectra reveals a non-common area around 3000 cm<sup>-1</sup>. There is more precisely a couple of intense bands at 2980 cm<sup>-1</sup> only present for the open isomer and not for the closed one, which could thus be used as a fingerprint to probe the photochromic state. The displacement mode corresponding to this frequency is represented in Figure S-10.

![](_page_12_Picture_0.jpeg)

Figure S-10: Representation of the 2980  $\rm cm^{-1}$  mode.

#### References

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