Toward an Enhancement of the Photoactivity of Multiphotochromic Dimers Using Plasmon Resonance: a Theoretical Study

Supporting Information

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Computational details

In the DIM/QM scheme, developed by Jensen and coworkers[1] one accesses the imaginary part of the polarizability of the system, that is directly related to the optical absorption. The polarizabilities of the QM part (the molecule) are obtained through linear-response TD-DFT and those of the DIM part (the gold NP) are calculated with a classical electrodynamic method based on a frequency-dependent dielectric function. In this work an analytical Drude-Lorentz dielectric function with one oscillator is used, that is well suited for the description of the LSPR of the gold NP under study.[2] This function is built to reproduce the experimental optical properties of gold bulk[3] and contains a size-correction term that makes it adequate for the description of the plasmon band of gold NPs with a diameter in the range of 3 to tens of nanometers. Definition and value of the different parameters for this Drude function are to be found elsewhere.[2] We use the Polarisability Interaction Model (PIM) variant of the DIM/QM approach; i.e., a dipole is associated to each gold atom of the NP. This method is suited for such large NP encompassing thousands of atoms. An alternative scheme, the Capacitance Polarizability Interaction Model (CPIM) model, adding the representation of atomic charges for gold at the price of a higher calculation burden.

Au$_{4501}$ is a 5 nm large NP constituted of successive (111) FCC layers of different sizes. The cuboctahedron structure of the gold Au$_{4501}$ is cut from the FCC bulk structure with a fixed interatomic distance of 2.88 Å, so that the shape of the NP follows Wulff's rules.[4] The DIM description of the LSPR for such gold NP has been detailed previously.[2] The plasmon band is found at 500 nm in gas phase, and shows agreement with other electrodynamics calculations and experimental spectra.[5]

Interactions between the QM and the DIM part take place through two distinct phenomena, namely the so-called "Local Field" effect giving the locally exalted electric field around the NP (the LSPR) due to the external perturbation, and the "Image Field" effect related to the creation of induced dipoles in the NP due to the presence of the molecule. These two parts are discussed in more details in other works by Jensen *et al.*[1,6] The consideration of

dipoles only (PIM), rather than both partial charges and dipoles (as in the CPIM), leads to a weak Image Field and leaves the Local Field as the main effect in the calculations presented here.

Concerning the optical properties of the QM part under the influence of the DIM part, the Linear-Response equations gives the first-order change in the density due to the external potential, for a given frequency:

$$\rho'(r,\omega) = \sum_{i,a} P'_{ia}(\omega)\phi_i(r)\phi_a^*(r) + P'_{ai}(\omega)\phi_a(r)\phi_i^*(r) \tag{1}$$

where ϕ_i et ϕ_j are occupied orbitals, ϕ_a et ϕ_b unoccupied ones, and ϕ_s et ϕ_t are any orbitals.

The first-order density matrix is expressed as:

$$P'_{st}(\omega) = \frac{\Delta n_{st}}{\omega - \omega_{st} + i\Gamma} V_{st}^{\prime\mathrm{eff}}(\omega) \tag{2}$$

with Δn_{st} being the occupation difference of the ϕ_s et ϕ_t orbitals, Γ a damping factor excited state, and ω_{st} the frequency corresponding to the $\phi_s \rightarrow \phi_t$ transition. The change in the effective potential corresponding to this density variation is written as:

$$V_{st}^{\prime\mathrm{eff}}(\omega) = V_{st}^{\prime\mathrm{pert}}(r,\omega) + V_{st}^{\prime\mathrm{Coul}}(r,\omega) + V_{st}^{\prime\mathrm{xc}}(r,\omega) + V_{st}^{\prime\mathrm{DIM}}(r,\omega) \tag{3}$$

In this potential are embedded the Coulomb and XC potential from the Kohn-Sham formalism, as well as potentials traducing the influence of the DIM part: $\hat{V}^{\mathrm{DIM}}$, traducing the Image Field effect, and $\hat{V}^{\mathrm{pert}}$:

$$\hat{V}^{\mathrm{pert}} = \hat{V}^{\mathrm{ext}} + \hat{V}^{\mathrm{loc}} \tag{4}$$

the perturbation potential containing the external potential and the Local Field effect, i.e., the plasmon ($\hat{V}^{\mathrm{loc}}$).

Table S1: Comparison between BP86 and other functional results for the optical properties of 1-o and 1-c (with the 6-31G(d) atomic basis set). λ is the wavelength (in nm) and f the oscillator strength of the electronic transition.

Isomer	method	λ	f	Composition
1-o				
	BP86	313	0.81	HOMO-1→LUMO+1 (51%)
				HOMO→LUMO+2 (24%)
	B3LYP	295	0.45	HOMO→LUMO+2 (91%)
		281	0.96	HOMO-1→LUMO+1 (68%)
				HOMO-2→LUMO (28%)
	PBE0	284	0.82	HOMO→LUMO+2 (90%)
		272	0.65	HOMO-1→LUMO+1 (48%)
				HOMO-2→LUMO (49%)
	CAM-B3LYP	266	1.00	HOMO-1→LUMO+1 (38%)
				HOMO→LUMO+2 (53%)
	ωB97XD	265	1.00	HOMO-1→LUMO+1 (40%)
				HOMO→LUMO+2 (51%)
1-c				
	BP86	695	0.34	HOMO→LUMO (98%)
	B3LYP	596	0.42	HOMO→LUMO (100%)
	PBE0	585	0.42	HOMO→LUMO (100%)
	CAM-B3LYP	529	0.43	HOMO→LUMO (96%)
	ωB97XD	528	0.42	HOMO→LUMO (95%)

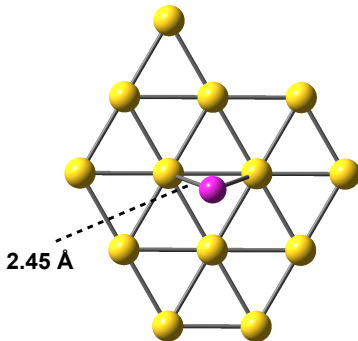**Comparison between BP86 and CAM-B3LYP results for the optical properties of 1-o and 1-c**

Figure S1: Representation of the binding site of the sulfur atom on the Au_{13} cluster.
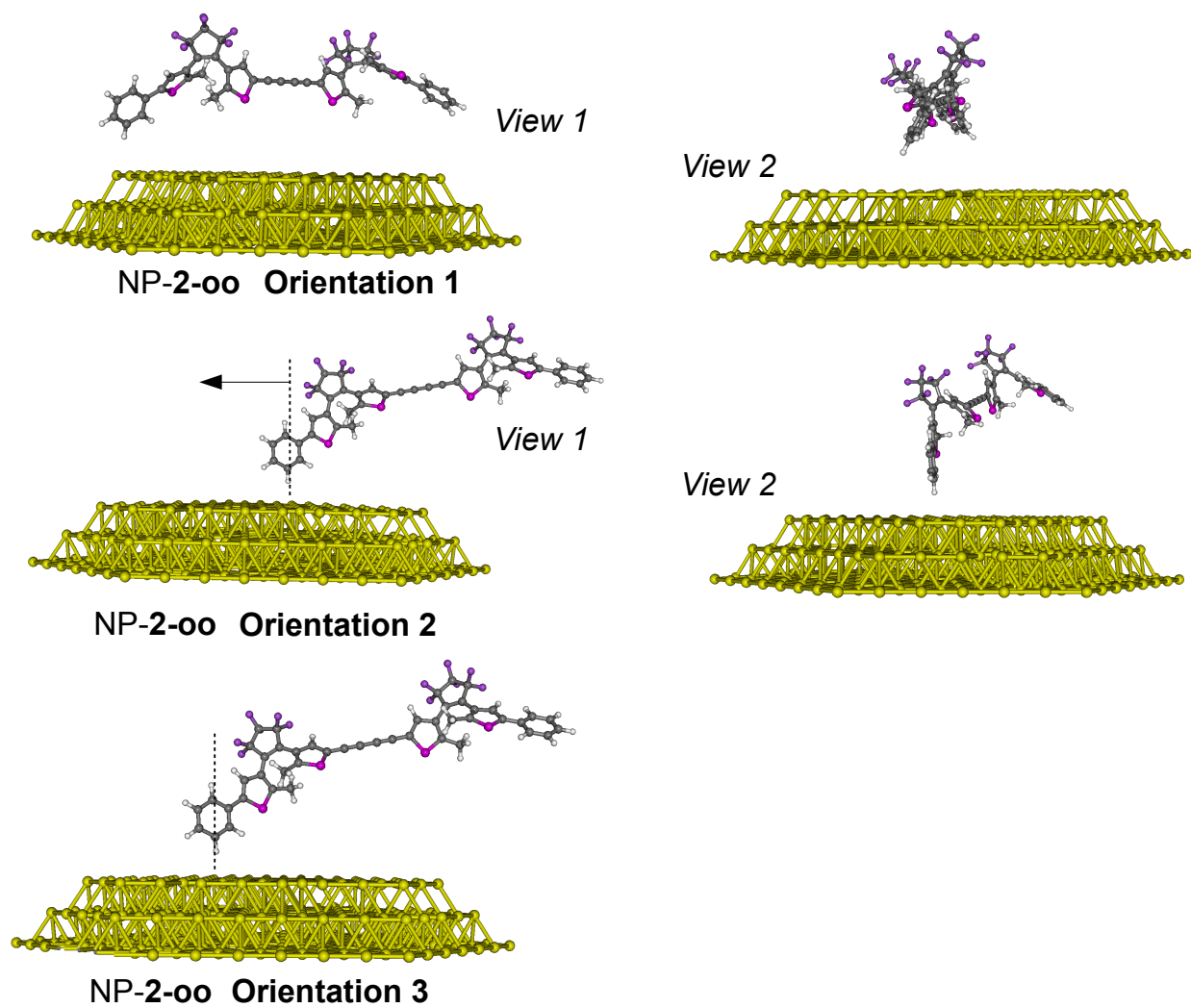
Binding site on Au_{13}

View 1

NP-2-oo Orientation 1

View 2

View 1

NP-2-oo Orientation 2

View 2

NP-2-oo Orientation 3

Figure S2: Geometries of NP-**2-oo** hybrid system under study. For the sake of clarity only the top part of the gold NP is sketched.

View 1

View 2

NP-**2-cc** **Orientation 1**

NP-**2-cc** **Orientation 2**

View 1
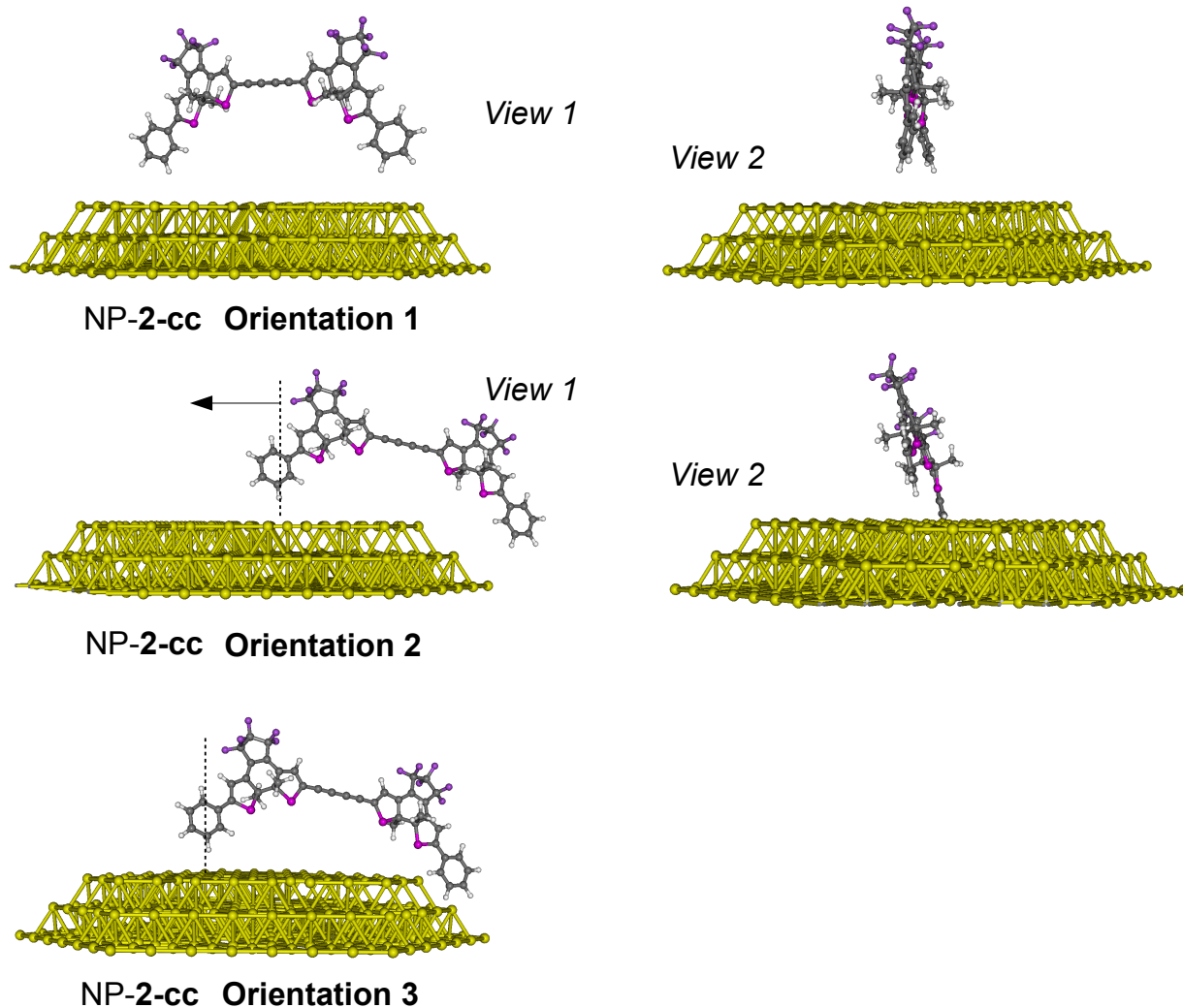
View 2

NP-**2-cc** **Orientation 3**

Figure S3: Geometries of NP-**2-cc** hybrid system under study. For the sake of clarity only the top part of the gold NP is sketched.

Conformations of 2-oo and 2-cc

References

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