Tunning Linear and Non-linear Optical Properties of Ligated Silver Clusters by Synergistic Role of Subunits

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Non-linear Light – Matter interaction

Motivation

- Design of ligated silver clusters with large two-photon absorption (TPA) cross sections for potential application in two-photon biological imaging, nanolithography... based on understanding of interplay between cluster core and ligand. Ultrasmall clusters exhibit strong optical behavior (flourescence, photoluminiscence, nonlinear optical properties...)
- Find systems with desired properties for experimental preparation and characterization
- Therefore, we compare linear and non-linear optical properties of thiolate-protected low nuclearity silver clusters

Theory

In the presence of strong external field, response of the medium to the excitation is no longer linear with the exciting amplitude and processes involving more than one photon simultaneously are possible.
Two-photon absorption (TPA) – molecular excitation by simultaneous absorption of two photons

TPA cross section for excitation from ground $|0\rangle$ to final state $|f\rangle$: $\sigma_{TPA} = \frac{(2\pi e)^4 \omega_v \omega_\mu}{c^2} g(\omega_v + \omega_\mu) |T^{\omega_\mu \omega_v, f}|^2$

TPA transition amplitude tensor: $T_{ab}^{2\omega,f} = \sum_{k>0} \left[\frac{\langle 0|\hat{\mu}_a|k\rangle\langle k|\hat{\mu}_b|f\rangle}{\omega_k - \omega_f/2} + \frac{\langle 0|\hat{\mu}_b|k\rangle\langle k|\hat{\mu}_a|f\rangle}{\omega_k - \omega_f/2} \right] \quad (a,b = x,y,z)$

Use of this formula limited by: (i) sumation over all excited states (ii) computation of matrix elements of the dipole moment operator μ between excited states

RESPONSE THEORY – solution of set of coupled equations instead of sumation over all excited states.

TD-DFT is based on the response of one-electron density matrix to an external field:
- Solution of equations of motions in the first order in an external field yields the excitation energies and ground to excited state dipole moments. This is linear response (LR).
- Inclusion of terms describing response up to the second order in the external field (QR) yields permanent dipole moments of excited states as well as the state-to-state transition dipoles.

In QR–DFT formalism, the single residue (SR) and double residue (DR) of the QR function at the resonant frequencies can be used to determine the TPA matrix elements directly [1,2]

$$\lim_{\omega_c \to \omega_f} (\omega_c - \omega_f) \langle\langle \hat{\mu}_a; \hat{\mu}_b, \hat{\mu}_c \rangle\rangle_{\omega_f/2, \omega_C} = -T_{ab}^{2\omega,f} \langle f|\hat{\mu}_c|0\rangle$$

or via SOS. In the case that both photons have the same energy (E_λ), the orientationally averaged expression for two-photon matrix elements for linearly polarized photons with parallel polarization is: Sums over j and k include the ground and all excited states. The damping factor for each one-photon transition (Γ) serves to prevent the TPA cross section from blowing up near a one-photon resonance.[3]

$$\sigma \approx |S_{fg}|^2 = \frac{4}{15} \sum_j^N \sum_k^N \left(\frac{(\langle k|\mu|0\rangle \cdot \langle f|\mu|k\rangle)(\langle j|\mu|0\rangle \cdot \langle f|\mu|j\rangle)}{[(E_k - E_\lambda)(E_j - E_\lambda) + \Gamma^2]} + \frac{(\langle k|\mu|0\rangle \cdot \langle j|\mu|0\rangle)(\langle f|\mu|k\rangle \cdot \langle f|\mu|j\rangle)}{[(E_k - E_\lambda)(E_j - E_\lambda) + \Gamma^2]} + \frac{(\langle k|\mu|0\rangle \cdot \langle f|\mu|j\rangle)(\langle f|\mu|k\rangle \cdot \langle j|\mu|0\rangle)}{[(E_k - E_\lambda)(E_j - E_\lambda) + \Gamma^2]} \right)$$

Contributions to TPA:
- difference between dipole moments between the ground and excited states
- from transition moments between the excited states mediated by the intermediate state

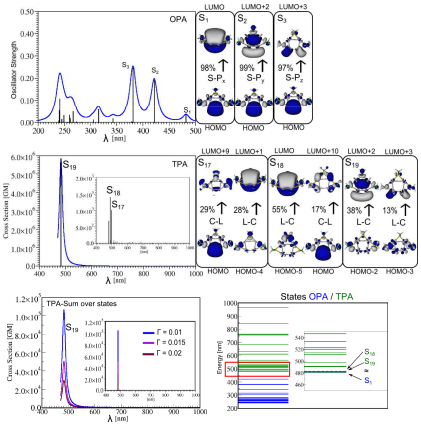
Results on thiolate-protected Ag clusters as model systems: 4Ag 3L⁻ vs. 5Ag 4L⁻ two confined core electrons

Model systems where glutation was replaced by SCH_3 group

OPA spectrum:
s-p excitations within the core; S_1 at ~480 nm

QR-SR TPA spectrum:
- Too large cross section σ of S_{19} due to resonance with S_1 state of OPA (~480nm)
- Leading excitations involve ligands
- Dominant transition dipole moment $\langle S_1|\mu|S_{19}\rangle$ = 5 Debye

SOS TPA:
through damping Γ, σ can be substantially lowered for several orders of magnitude, eg. from 10^6 to 10^4 GM, thus predicting TPA of approximately 10 000 GM



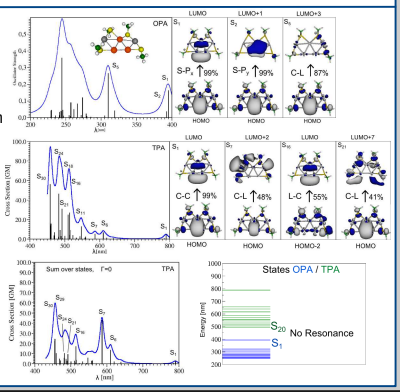
These findings show that small HOMO-LUMO gap indicates low lying S_1 state that can be resonant with two-photon states, resulting in large σ

Example where resonance is not present and therefore σ is low: 5Ag 4L⁻

OPA spectrum:
s-p excitations within the core; but S_1 above 400 nm

TPA spectra:
- No large σ in TPA spectra because there is no resonance with S_1 state of OPA (~400nm)
- Since HOMO-LUMO excitation characterizes S_1 state, larger gap gives rise to higher energy of S_1

- Wavelengths of OPA S_1 state indicate orientationally if TPA σ will be large or not



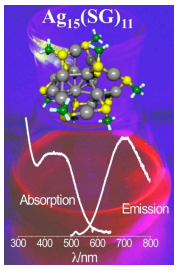
Linear and non-linear optical properties of thiolated silver clusters with 4 confined electrons

I. 15Ag 11L⁻ for which large flourescence has been measured

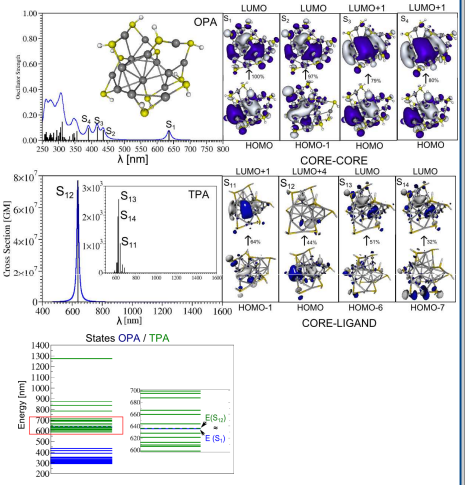
OPA spectrum:
excitations within the core; S_1 at ~635 nm

QR-SR TPA spectrum:
- Too large cross section σ of S_{12} due to resonance with S_1 state of OPA (~635nm)
- Leading excitations involve ligands
- Dominant transition dipole moment $\langle S_1|\mu|S_{12}\rangle$ = 23 Debye

SOS TPA through damping Γ, σ can be substantially lower towards realistic values of 200 000 GM [5]



[4] Nanoscale 5, 5637 (2013)



The leading excitations in states with large TPA involve core and ligands

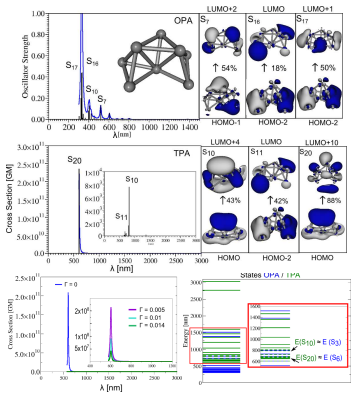
8Ag core from 15Ag 11(SH)⁻

OPA spectrum:
excitations within the core; S_6 at ~600nm

QR-SR TPA spectrum:
Too large cross section σ due to resonance of S_{20} with S_6 state of OPA (~600nm)

SOS TPA through damping Γ, σ can be substantially lower towards realistic values

Metallic core can have large TPA, thus synergy between core and ligands has significant influence on TPA

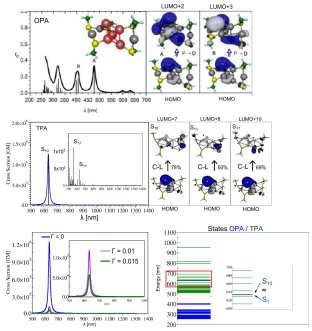


II. Thiolate-protected silver clusters as model systems 8Ag 5L⁻

OPA spectrum:
p-d excitations within the core; S_1 at ~635 nm

QR-SR TPA spectrum:
Too large cross section σ of S_{10} due to resonance with S_1 state of OPA (~635nm)
Leading excitations involve ligands

SOS TPA through damping Γ, σ can be substantially lowered from 10^6 to 10^4 GM



Conclusions and Prospectives

- **Large TPA cross section at low wavelengths are expected when resonance of TPA with S_1 state of OPA occurs. Since S_1 state is usually dominated by HOMO-LUMO excitation, low HOMO-LUMO gap indicates that S_1 is located at low wavelengths.**
- **The leading excitations in states with large TPA involves always ligands, not only core; ligand choice plays key role.**
- **Can we classify ligands as "donors" or "acceptors" for which is known to invoke large TPAs ?**
- **The aim is to design systems with large TPAs at the given wavelength by synergistic role of subunits which are experimentally possible to realize**

References

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[2] Masunov, Tretiak et al. *J.Phys.Chem C*, 2013, 117, 18170-18189
[3] P.N.Day et al. *J.Chem.Theory Comput.* 2010, 6, 2809-2821
[4] F Bertorelle, R Hamouda, D Rayane, M Broyer,R Antoine,PhDugourd, L Gell, A Kulesza, R Mitrić, V Bonačić-Koutecký, *Nanoscale* 5, 5637 (2013)
[5] Z Sanader, M Krstić, V Bonačić-Koutecký, in preparation