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Supporting Information:

Impact of vibronic coupling effects on light-driven charge transfer in pyrene-functionalized middle and large-sized Metalloid Gold Nanoclusters from Ehrenfest dynamics.

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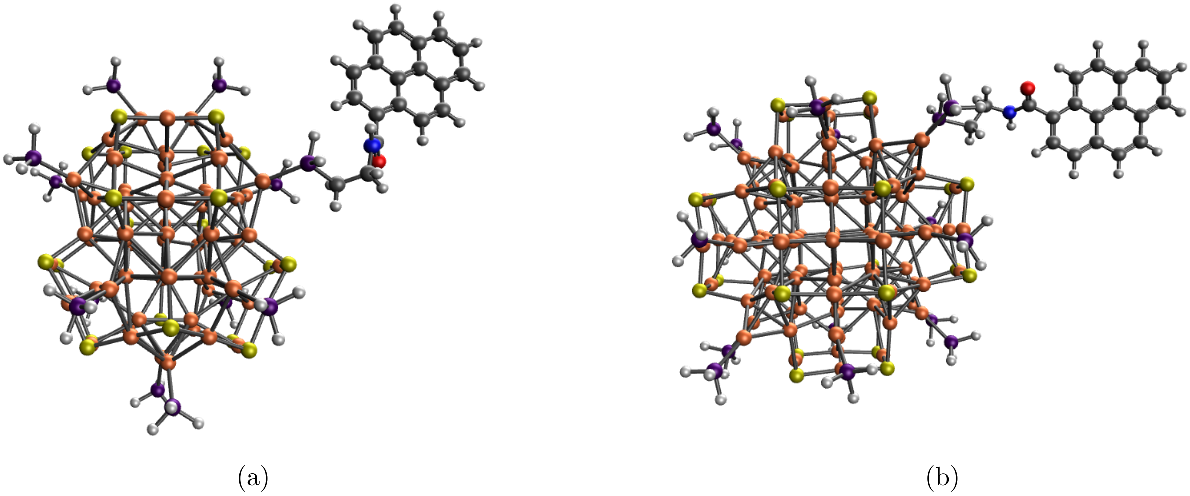
1 Systems under study



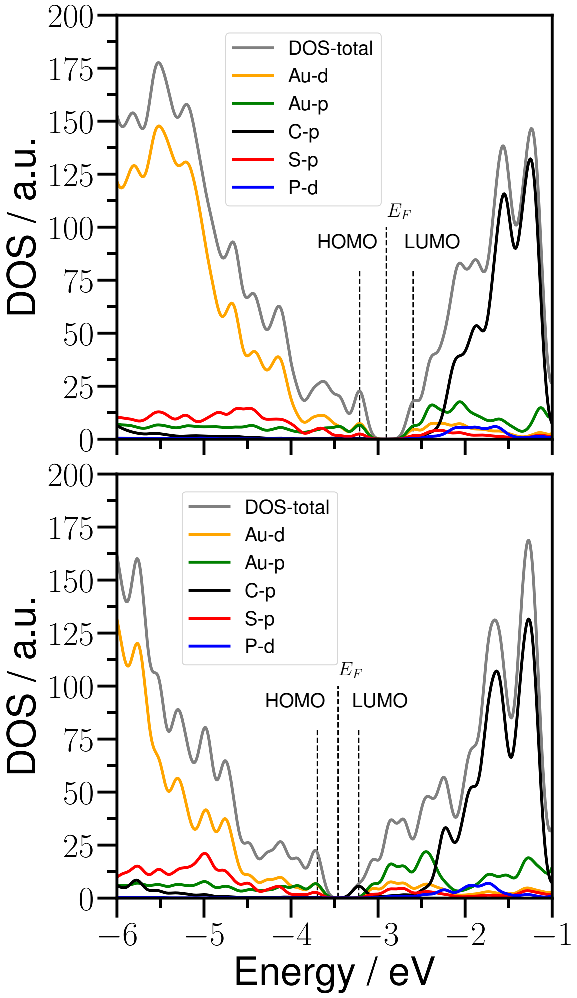
(a) (b)

S 1: Molecular structure for: (a) neutral $Au_{70}S_{20}(PH_3)_{15}PH_2Pyr$ system. (b) neutral $Au_{108}S_{24}(PH_3)_{15}PH_2Pyr$ system. The orange, yellow, purple, red, blue and white represent the Au, S, P, O, N and H atoms, respectively. For simplicity and clarity the graphical representation of the rest of the systems under study are omitted.

2 Computational details

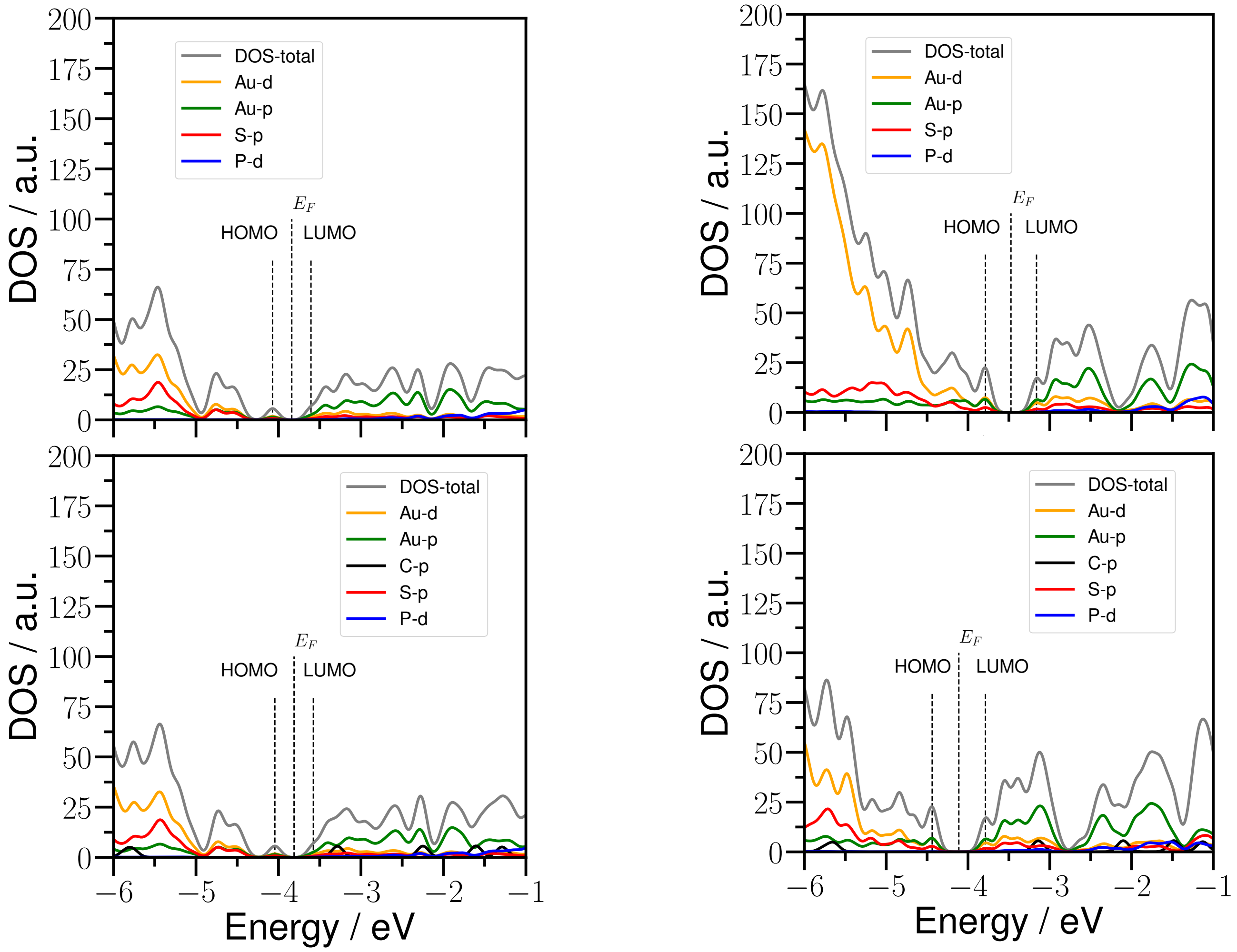
The metalloid GNC structures used were taken from the literature.[1, 2] For the pyrene labeling, an R group was substituted by the pyrene derivate (-$CH(O)NHCH_2CH_3$ linker with the pyrene ring) and attached to a phosphine group. The geometries were relaxed at the DFTB level of theory. All the calculations were performed using the DFTB+ code.[3] The set of DFTB parameters recently published for the description of the interactions of gold-phosphine[2] have been used. The quantum dynamics simulations based on the Ehrenfest approach in the RT-TDDFTB framework start from an electronic ground-state configuration, following the entire photodynamics (photoexcitation process and charge transfer dynamics) In this semi-classical method, the nuclei are driven by the instantaneous expectation value of the force at each time for the moving electron density. A perturbation to the Hamiltonian is added in the form of a laser pulse for the corresponding excitation, imitating pump-probe experiments. An extensive discussion can be founded in previously published papers.[3–5] In the computation of the absorption spectra, an electric field intensity of 0.001 V/Å is employed with the propagation of 82684 steps using a time step of 0.0024 fs, in the linear response regime. For the Ehrenfest dynamics, an electromagnetic wave, a $\sin^2$ shaped pulse is employed describing the electron dynamics during the light absorption with an electric field of 0.1 V/Å and an energy laser of 400 nm (expressed in eV units equal to 3.09). The total duration of the pulse is 100 fs in all cases. For the nuclei evolution in the Ehrenfest dynamics based on the Verlet algorithm, a Temperature of 300 K is used.

3 Electronic structure - Density of states



S 2: (a) Density of States (DOS) and Partial Density of States (PDOS) analysis for: (top) neutral $Au_{108}S_{24}(PPh_3)_{16}$ system (bottom) neutral $Au_{108}S_{24}(PPh_3)_{15}PPh_2Pyr$ system.

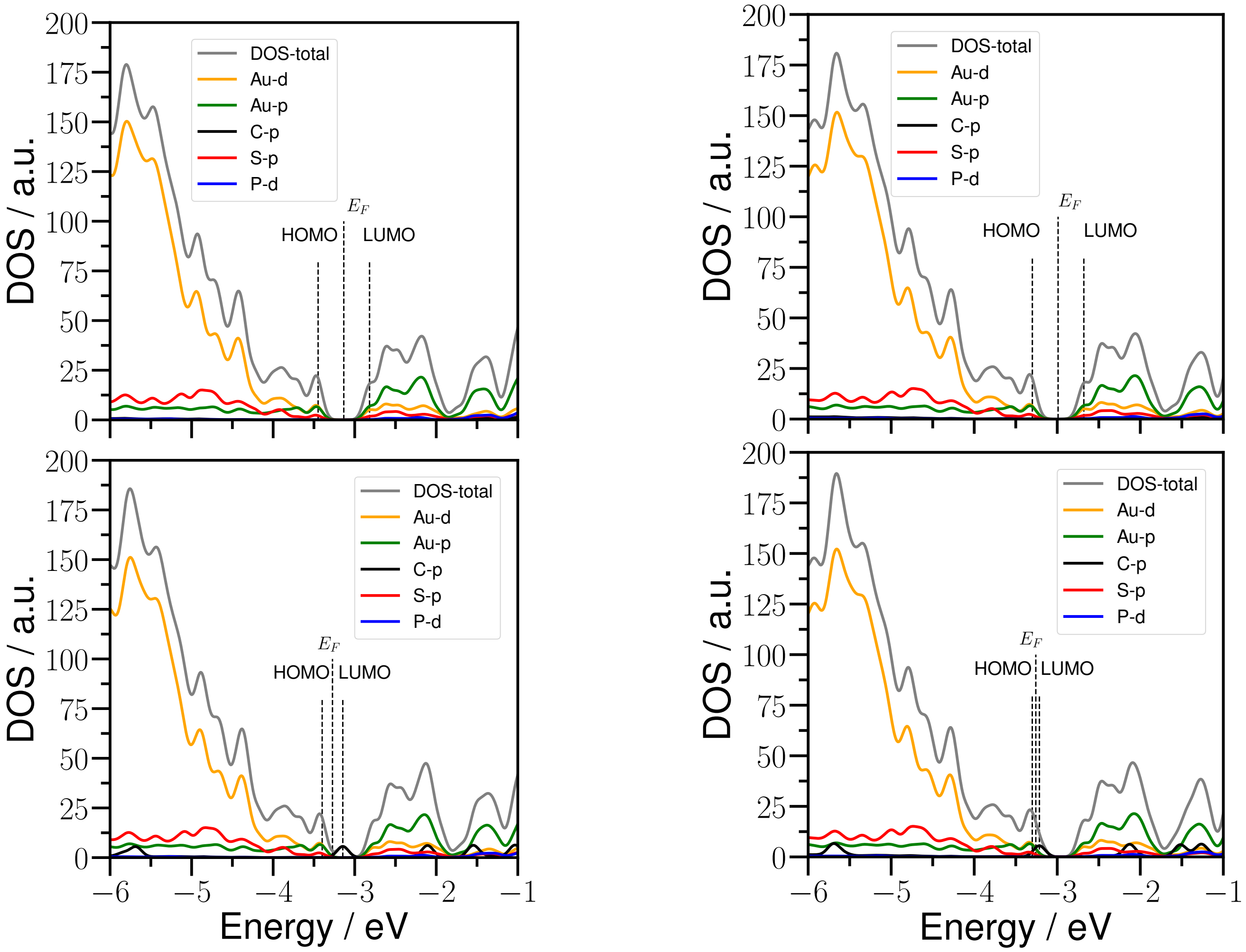
Figure S2 shows the calculated density of states (DOS) and partial density of states (PDOS) for $Au_{108}S_{24}(PPh_3)_{16}$ system (on top) and $Au_{108}S_{24}(PPh_3)_{15}PPh_2Pyr$ system (on bottom). The HOMO-LUMO gap (ΔHLG) for $Au_{108}S_{24}(PPh_3)_{16}$ system is -0.62 eV, in consonance with the validated result obtained by Irle et al.[2] The ΔHLG for $Au_{108}S_{24}(PPh_3)_{15}PPh_2Pyr$ system is -0.47 eV. From the DOS and PDOS analysis in Figure S2, the Fermi level is decreased resulting in the introduction of an electron acceptor dye as the pyrene derivative, from -2.90 eV for $Au_{108}S_{24}(PPh_3)_{16}$ to -3.46 eV for $Au_{108}S_{24}(PPh_3)_{15}PPh_2Pyr$ system, a shift of -0.56 eV. A reduction if compared with the value of $Au_{108}S_{24}(PPh_3)_{16}$ system. The Gold d and orbitals and Sulfur p orbital contribution to the bonding is clearly denoted in both cases. While the character of the unocupied states is mainly of a Carbon p orbital nature. In the case of the LUMO orbital of the $Au_{108}S_{24}(PPh_3)_{15}PPh_2Pyr$ system the Carbon p orbital nature is remarkable. The barrier for excitations is decreased and the pyrene-labeled system can be more easily excited. For alkyl phosphine ligands , the ΔHLG calculated for $Au_{108}S_{24}(PCH_3)_{16}$ and $Au_{108}S_{24}(PC_2H_5)_{16}$ systems is -0.63 eV and -0.62 eV, respectively. For the pyrene-labeled complexes with methyl and ethyl groups, a ΔHLG of -0.25 eV and -0.08 eV is computed. The study for the $Au_{70}S_{20}(PH_3)_{12}$ and $Au_{108}S_{24}(PH_3)_{16}$ systems, and the corresponding pyrene-labeled cases, there are no significative changes for ΔHLG values, presenting -0.46 eV and -0.47 eV for the middle-sized GNC composed systems and -0.63 eV and -0.65 eV for the large-sized systems, respectively. Clearly, the complexes with H as protecting ligands (phosphines) pointed the hypothesis that the shorter ΔHLG value for the middle-sized GNC complexes is responsible for a better photoexcitation properties in comparison to the similar large-sized GNC complexes.



(a)

(b)

S 3: DOS and PDOS analysis for:
(a) (top) $\mathbf{Au_{70}S_{20}(PH_3)_{12}}$ system ; (bottom) $\mathbf{Au_{70}S_{20}(PH_3)_{11}PH_2Pyr}$ system
(b) (top) $\mathbf{Au_{108}S_{24}(PH_3)_{16}}$ system ; (bottom) $\mathbf{Au_{108}S_{24}(PH_3)_{15}PH_2Pyr}$ system

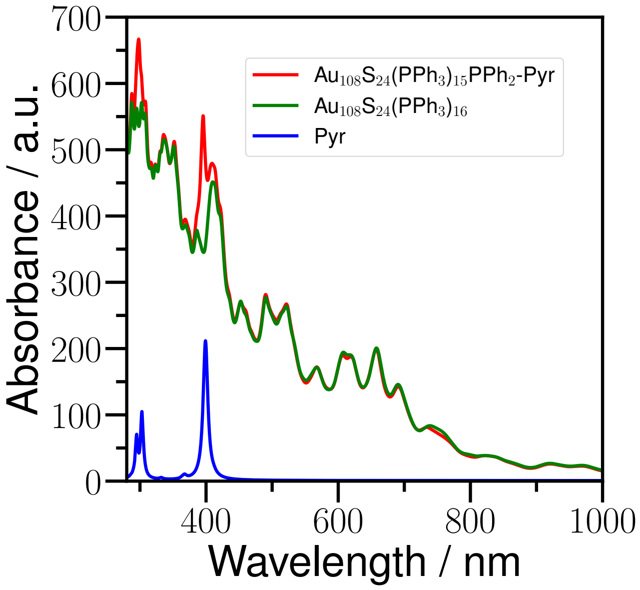


(a)

(b)

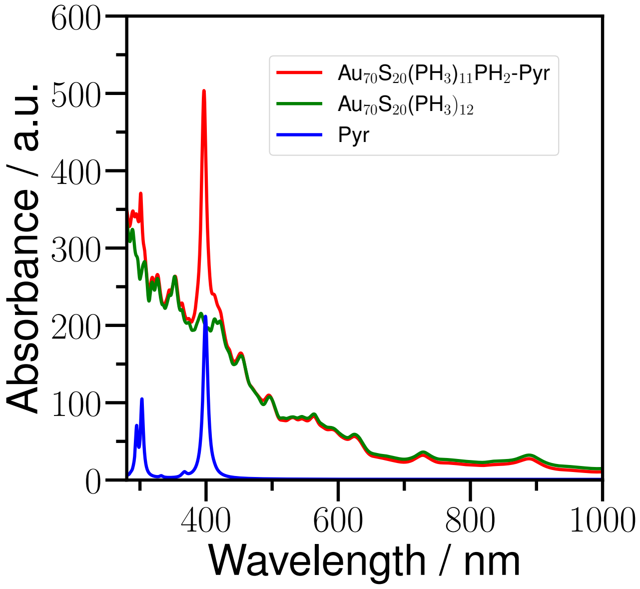
S 4: DOS and PDOS analysis for:
(a) (top) $\mathbf{Au_{108}S_{24}(PCH_3)_{16}}$ system ; (bottom) $\mathbf{Au_{108}S_{24}(PCH_3)_{15}P(CH_3)_2Pyr}$ system
(b) (top) $\mathbf{Au_{108}S_{24}(P(C_2H_5)_3)_{16}}$; (bottom) $\mathbf{Au_{108}S_{24}(P(C_2H_5)_3)_{15}P(C_2H_5)_2Pyr}$ system

4 Optical properties - Absorption spectra

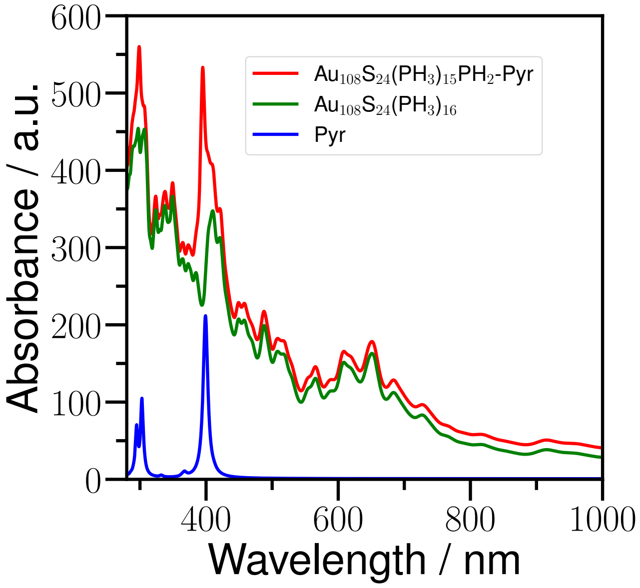


S 5: Absorption spectra for $Au_{108}S_{24}(PPh_3)_{15}PPh_2Pyr$ system.

Figure S5 displays a high absorption peak belong to the pyrene derivate at 400 nm. A similar peak was described before. [4] A preceding work using TD-DFT calculations of UV-Vis spectrum for gold-phosphine complexes confirms a red-shift with a discrepancy of around 100-150nm from experiments. [6] This has been considered typical for gold systems. [7, 8] The theoretical peak found at 400 nm describes a bathochromic effect due to the no presence of solute-solvent interactions in the calculations performed. This assumption is supported having in mind the findings in the comparison between the experimental work done by Devadas et al.[9] and our previous theoretical results [4] The sum of the individual contributions of the parts is the total absorption of the $Au_{108}S_{24}(PPh_3)_{15}PPh_2Pyr$ system. All these suggest that no ground-state interactions are present here. Similar conclusions are described in Figure S6 and Figure S7.

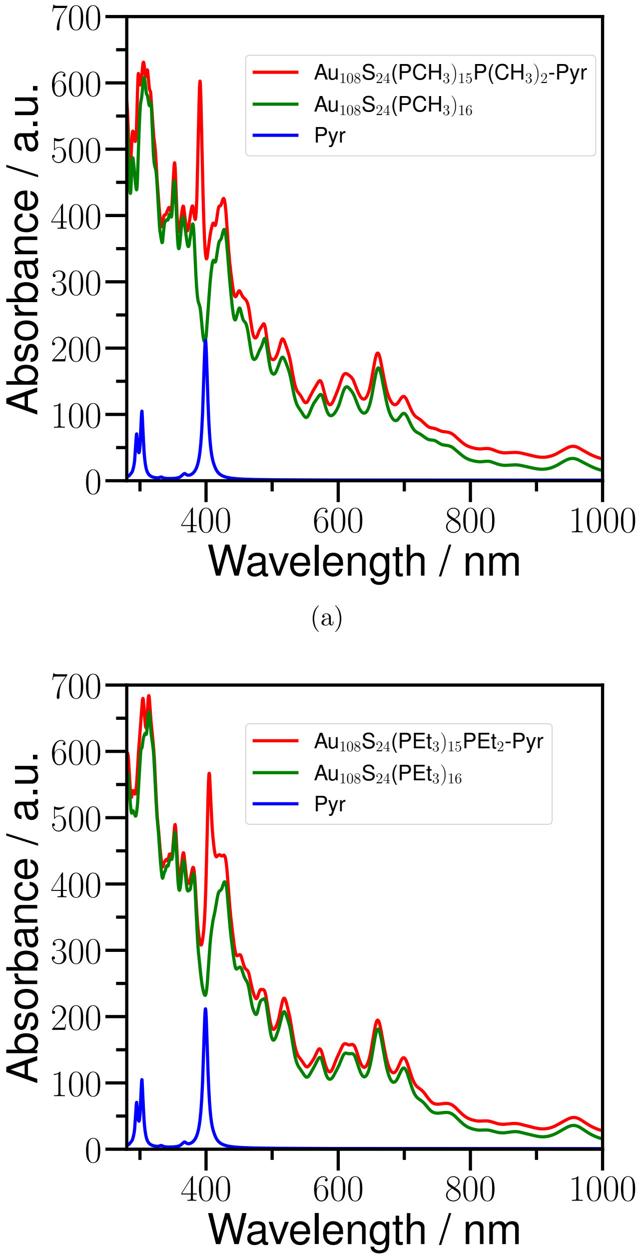


(a)



(b)

S 6: Optical properties: (a) Absorption spectra for $\mathbf{Au_{70}S_{20}(PH_3)_{11}PH_2Pyr}$ system (b) $\mathbf{Au_{108}S_{24}(PH_3)_{15}PH_2Pyr}$ system



(a)

(b)

S 7: Optical properties: (a) Absorption spectra for **$Au_{108}S_{24}(PCH_3)_{15}P(CH_3)_2Pyr$** system (b) Absorption spectra for **$Au_{108}S_{24}(P(C_2H_5)_3)_{15}P(C_2H_5)_2Pyr$** system

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