Photo-induced intramolecular charge migration on gold nanoclusters passivated by a chromophore ligand: a computational study

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Stoichiometric gold nanoclusters functionalized by a ligand shell are the subject of intensive research efforts, both experimentally and theoretically.[1,2] Inspired by the work of Devadas et al.,[3] we designed model systems based on the experimentally characterized gold nanoclusters $Au_{11}(PR_3)_7Cl_3$,[4] $Au_{20}(SR)_{16}$[5] and $[Au_{25}(SR)_{18}]^{1-}$[6] that we functionalized by a methyl bipyridine moiety through substitution of one ligand in their passivation shell. We theoretically investigated the ultrafast charge migration triggered by the excitation of these model systems by an ultrashort strong optical pulse, before the onset of nuclei motion. The basis of field-free electronic excited states were computed at the TD-DFT level of theory (with a tuned CAM-B3LYP functional) and its results were confirmed by using the explicitly correlated CAS-SCF method. We show that a significant amount of charge is transferred from the bipyridine chromophore to the metallic core after photoexcitation on the three model systems, accompanied by the beating of the electron density between the two subunits of the cluster, see Fig. 1.[7] We discuss the influence of the superatomic[8] character of the nanocluster on the amplitude of charge migration.
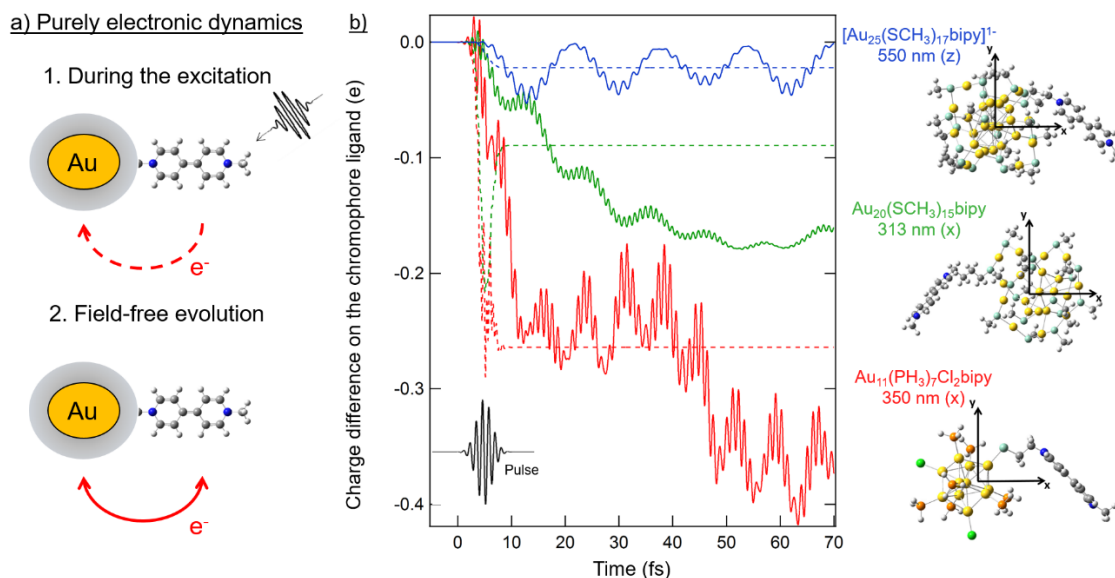

Figure 1. a) Schematic representation of the purely electronic dynamics on the model systems. b) Time-evolution of the electron density difference on the chromophore subunit with respect to its initial electron density in the electronic ground state. Solid lines: total electron density difference, dashed lines: permanent charge transfer. Please note that the pulse, indicated by the black curve, is not at scale.

References:

[1]   H. Qian, M. Zhu, Z. Whu and R. Jin, *Acc. Chem. Res.,* **2012,** 45, 1470

[2]   G. Lugo, V. Schwanen, B. Fresh, and F. Remacle, *J. Phys. Chem. C.,* **2015**, 119, 10969

[3]   M. Devadas, K. Kwak, et al., *J. Phys. Chem. Lett.*, **2010**, 1, 1497

[4]   B. S. Gutrath, U. Englert, Y. Wang and U Simon, *Eur. J. Inorg. Chem.*, **2013**, 2002

[5]   C. Zeng, C. Liu, Y. Chen, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.*, **2014**, 136, 11922

[6]   C. A. Fields-Zinna et al., *J. Am. Chem. Soc.*, **2013**, 135, 15585

[7]   V. Schwanen and F. Remacle, to be submitted.

[8]   M. Walter, J. Akola, et. al., *PNAS*, **2008,** 105, 9157