

Second- and Third-Order Nonlinear Optical Properties of Size-Selected Au:SR Clusters

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Thiolate-protected gold clusters have gained considerable attention in recent years, which is due to their good stabilities in solution and the solid state, and single crystal x-ray diffraction enables determination of their geometric structures.[1]–[4] This allows detailed studies on very defined ultrasmall nanoparticles. The properties of gold:thiolate clusters do not scale with size and are molecule-like.

Little is known about the nonlinear optical properties of Au:thiolate clusters. We studied the second- and third-order nonlinear optical (NLO) properties of a series of Au_m(SR)_n clusters by means of second-order nonlinear scattering,[5] multiphoton-excited fluorescence and third-harmonic generation. The second-order NLO properties are strongly symmetry-dependent and do not scale with the superatomic electron count of the clusters. This is evidenced by DFT calculations of the static first hyperpolarizability of model clusters.[6] We experimentally determined the first hyperpolarizability of Au₂₅(SR)₁₈ and Au₃₈(SR)₂₄ clusters using the Hyper-Rayleigh Scattering technique. We investigated the effect of chiral ligands and foreign metal doping in symmetry-breaking of the Au₂₅(SR)₁₈ cluster. Both strategies yield comparable first hyperpolarizabilities.

All investigated clusters show two-photon excited fluorescence. We also studied the Au₁₃₀(*p*-MBA)₅₀ cluster (*p*-MBA: *para*-mercaptobenzoic acid), which is assumed to show intrinsic chirality. In this case, a very strong first hyperpolarizability was determined. In addition, the cluster exhibits three-photon excited fluorescence. Three-photon absorption has not been observed in Au:SR clusters before. Potential applications of gold:thiolate clusters lie in multimodal deep tissue imaging, in which several detection modes can be used for readout. A striking advantage is the possibility of conjugating the clusters with biomolecules.[7]

References

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