Lighting up the nanoscale: new photophysical observations in gold nanoclusters

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Among the more than 100 structurally resolved metal nanoclusters (NCs) with ultra-small cores (<2 nm), $Au_{25}(SR)_{18}$ (SR = PET, 2-phenylethanethiol) is the most studied, typically existing in three oxidation states (−1, 0, +1). However, systematic photophysical investigations remain scarce, largely due to incomplete spectral coverage, insufficient NIR sensitivity in commercial fluorometers, and the lack of accurate measurements [1]. Using a custom home-built setup capable of measurements beyond the reach of standard instrumentation, our results reveal a low-energy absorption band at ~9 kK (fig. 1), not reported in the literature [2], and a strong excitation-energy dependence of both emission profile and peak position (fig. 2), representing the first observation of such behavior in gold nanoclusters. Time-resolved emission data show distinct temporal evolution for each excitation energy. Compared with the closed-shell anion, the neutral cluster displays clear deviations from Kasha's and Vavilov's rules and highly distributed, strongly non-monoexponential photoluminescence decays. These observations support a working hypothesis involving dark states and delayed fluorescence to explain the unconventional emission pathways of the neutral species.

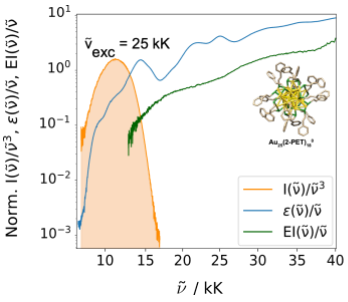

Figure 1. Normalized lineshapes of absorption, excitation and emission of $[Au_{25}(PET)_{18}]^0$ in dichloromethane.

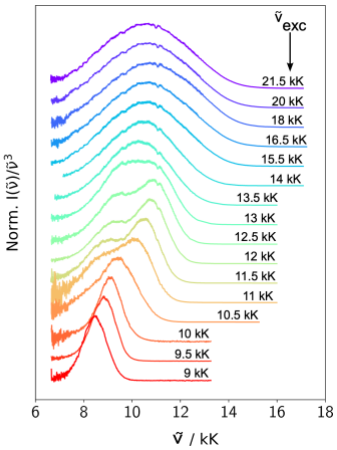

Figure 2. Normalized excitation-dependent emission spectra of $[Au_{25}(PET)_{18}]^0$ in dichloromethane.

[1] Chakraborty, I., Pradeep, T. Chem. Rev., **2017**, 117 (12), 8208–8271.

[2] Green, T.; Jin, R.; Knappenberger, K. L., Jr. et. al. J. Phys. Chem. A **2014**, 118, 10611–10621.