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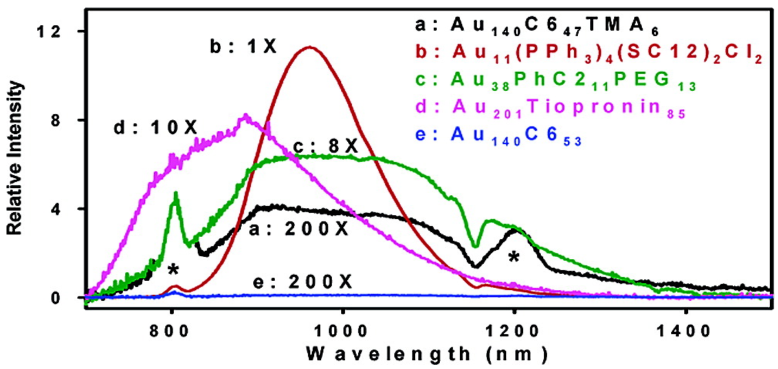

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Near-IR Luminescence of Monolayer-Protected Metal Clusters

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Stable, isolable, monolayer-protected Au clusters (MPCs) prepared by the Brust reaction with thiolate ligands are of great research interest.[1] Redox-like and "quantized double layer (QDL)" charging voltammetry has been observed for MPCs with alkanethiolate ligands.[2] Luminescence from Au MPCs has also been reported. Tiopronin-coated MPCs (av composition $Au_{201}Tio_{85}$)[3] show a broad emission from 650 to 1250 nm,[4] and emission from a glutathione passivated Au_{28} MPC was reported at 840 and 1080 nm by Whetten and co-workers.[5] The emission quantum efficiencies were roughly similar (ca. 10^{-3}) in these reports. Several possible mechanisms were discussed.

Key issues in the study of very small nanoparticles are the size effect and contributions from surface characteristics. These issues are interrelated, since the surface-to-volume ratio increases as size decreases. Here, we report visible−near-IR luminescence spectra of gold MPCs (all <2 nm diameter) that are similar, irrespective of a 20-fold range of core atoms and different monolayers. Further, luminescence can be induced by introducing polar or charged ligands into nonpolar MPC monolayers and by galvanic exchange of Au atoms onto Ag MPC core surfaces, with intensities quantitatively proportional to the number of introduced ligands and Au metal atoms. The emission intensities depend on both the nanoparticle core metal and the ligands attached to it and are proposed to result from localized electronic surface states.

Figure 1 shows the luminescence spectra[6] of five different MPCs. While the emission intensities/quantum efficiencies vary widely (see caption), as do the band shapes (which will be discussed in a separate report[7]), all of these MPCs emit over a *common* range of energies, from ca. 700 nm (1.8 eV) to 1.3 μm (0.9 eV). In organic solvents, purified, nonpolar $Au_{140}(C6)_{53}$ MPCs do not display luminescence of comparable intensity (curve e, quantum efficiency $< 10^{-6}$), but luminescence appears[7] if TMA ligands (*N*,*N*,*N*-trimethyl-(mercaptoundecyl)ammonium) are incorporated (curve a) into the hexanethiolate monolayer by ligand exchange.[8] Similarly, the weak luminescence of PhC2-coated Au_{38} MPCs is enhanced in mixed monolayer poly(ethylene glycol) ($PEG_{135}SH$)/PhC2 MPCs but still occurs at the same energy (curve c).[9] The Au_{11} MPCs were prepared by a partial ligand exchange of the dodecanethiol onto a triphenylphosphine/halide cluster.[10] Their luminescence is less broad and quite intense. Figure 1 also shows tiopronin-coated Au MPC luminescence in aqueous solution; with our current NIR detection capacity, we now know that the previously reported red-visible luminescence spectrum was truncated.[4a] It is worth mentioning that similar emission is seen for quaternary ammonium salts of 1.8 nm core diameter tiopronin-coated MPCs in organic solvents.

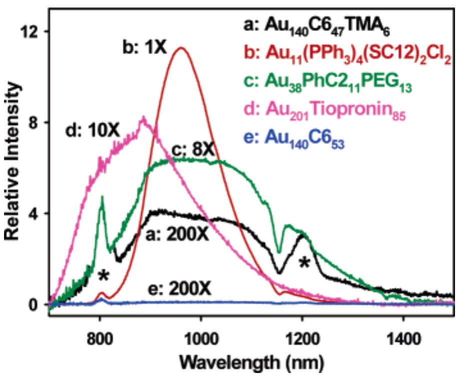

Figure 1. Au MPCs with different core sizes and monolayers. C6, C12, PhC2, PEG, and PPh_3 represent hexanethiolate, dodecanethiolate, phenylethanethiol, poly(ethylene glycol) (MW 350) thiolate, and triphenylphosphine, respectively. The spectrum of tiopronin MPC was measured in D_2O; the others were measured in methylene chloride. All spectra were excited at 400 nm. The quantum efficiencies (relative to Q-switch 5 and DTTC[11]) of the Au_{11},[10] Au_{38}, Au_{140}TMA, and Au_{201} MPCs are 0.08, 1.2×10^{-2}, 1.8×10^{-4}, and 9×10^{-3}, respectively. Asterisks indicate artifacts from second- and third-order excitation peaks (800 and 1200 nm); the dip at 1165 nm is partly due to solvent/ligand absorption.

Although the emission spectra in Figure 1 lie in a common energy range, the MPC optical absorbance energetics differ widely. Using a molecular viewpoint of these nanoparticles, we found the optical band gaps of the Au_{140}, Au_{38}, and Au_{11} MPCs to increase with decreasing size and to have values of ≤ 0.4,[2] 1.3,[9] and 1.6 eV,[10] respectively. The luminescence energy is clearly not controlled by a simple excited-state HOMO−LUMO transition, where the emission energy must equal or exceed the energy gap. We propose that the core size-independence of the emission energy reflects a participation of localized core surface states that have size-independent energetics. The results of ligand place exchanges with polar ligands and galvanic exchange of silver core atoms with gold ones provide quantitative evidence for such states.

Figure 2A shows that luminescence intensity increases linearly (with near zero intercept) with the average number of TMA ligands exchanged onto (relatively nonluminescent) Au_{140} MPCs. The ratio of TMA and hexanethiolates in the mixed monolayer was determined by NMR, using the methylammonium (3−4 ppm) and terminal methyl (0.8−1.0 ppm) resonances, respectively. Since the metal core size is unchanged by the ligand place exchange reaction, confirmed by UV absorbance and TEM,[7] the luminescence appears to be localized to the specific surface sites occupied by the TMA ligands. This is qualitatively a general effect; luminescence results from insertion of polar ligands into MPC monolayer shells, as will be detailed in the full report.[7]

A similar quantitative dependence (Figure 2B) was observed[12] in core metal galvanic exchange reactions of tiopronin-coated Ag MPCs with Au(I) [p-$SCH_2(C_6H_4)C(CH_3)_3$], at various mole ratios of the two. The exchange reaction was allowed to proceed until further luminescence changes were insignificant. The MPC emission spectrum changes from that of an Ag MPC (∼500 nm) to that of

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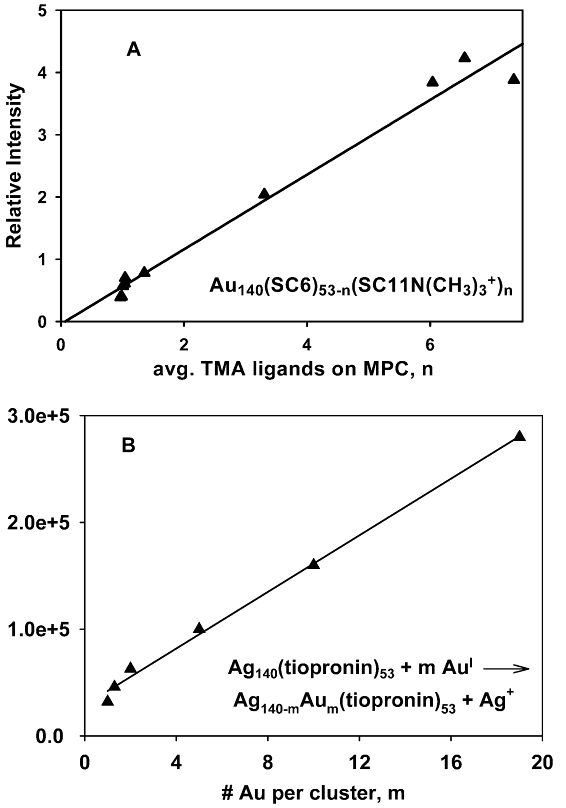

Figure 2. (A) Luminescence intensity (at 1000 nm) vs number of TMA ligands exchanged onto $Au_{140}(C6)_{53}$ MPCs. Five data points at ca. 1 TMA ligand exchanged are partially overlapped. Solid line is a least-squares fit. Emission intensities were normalized using UV absorbance at 400 nm to account for concentration differences. (B) Luminescence at 690 nm (PMT detector) of products of core metal Galvanic exchange reaction of Ag tiopronin MPCs (av 1.6 nm core diameter) with Au(I) [p-$SCH_2(C_6H_4)C(CH_3)_3$].[4a,12] The number of Au atoms incorporated per cluster was obtained by elemental analysis.

a Au MPC as the reaction proceeds. The galvanic exchange reaction is effectively a "titration" of surface Ag atoms by Au^I. The final Au MPC-like emission increases linearly[12] with the reactant ratio of Au(I)[*p*-$SCH_2(C_6H_4)C(CH_3)_3$] to silver MPCs; analysis of the products reveals that the increase is linear with the number of incorporated gold atoms per MPC core. Considering that one gold atom replaces one silver surface atom, the fluorescence intensity result shows that the surface gold atoms act as discrete surface-state emitters, whose population systematically changes during the exchange reaction. This result is parallel to the ligand exchange results of Figure 2A and reinforces our proposal that the NIR emission is an electronic surface-state phenomenon. The chemical nature of these states remains to be determined.

It is well-known for semiconductor quantum dots that surface states (trap states) can localize carriers, slowing their recombination and causing a red-shift in band edge luminescence.[13] The long lifetime (μs) of the luminescence from Au_{28} glutathione MPCs[5] is in that sense consistent with a surface-state origin. Unfortunately, we have no lifetime information for the MPCs described here.

Polynuclear Au(I)−sulfido complexes[14] can be luminescent. However, the Au(I) thiolate complex used in this paper is not luminescent in the NIR, so its adsorption onto the nanoparticle surface and fluorescence enhancement by metal surfaces and particles[15] is an improbable source of the luminescence reported here.

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