Visible Luminescence of Water-Soluble Monolayer-Protected Gold Clusters

Tao Huang and Royce W. Murray*

Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Received: November 8, 2000; In Final Form: August 14, 2001

A highly efficient, visible wavelength (λ_{MAX} = 700 to 800 nm) fluorescence is reported for four water-soluble monolayer-protected gold clusters (MPCs). For 451 nm excitation, the quantum yield of the luminescence of MPCs with 1.8 nm diameter cores and protected by monolayers of tiopronin thiolate is estimated as 0.003 ± 0.001. The efficiency and wavelength of the luminescence vary with the ligands of the monolayer around the gold core. The mechanism for the luminescence is hypothesized to be associated with interband transitions between the filled $5d^{10}$ band and $6(sp)^1$ conduction band.

Introduction

Luminescence from roughened metal surfaces has received increasing attention.[1−5] The overall quantum efficiency of the visible photoluminescence from copper and gold films is very low (∼10^{-10}), as observed by Mooradian[1] several decades ago. Recently, several groups have observed that orders-of-magnitude higher quantum efficiencies are seen when the metal specimen is in the nanometer dimension.[6−9]

The recent work[6,8,9] explained the luminescence by nanosized noble metals according to a previous theoretical paper,[3] as electronic transitions between occupied d bands and states above the Fermi level (usually the sp bands). Whetten et al.[8] attribute the near-infrared luminescence from small gold nanocrystals[8] to HOMO−LUMO electron transitions of lower energy than that of the d-sp interband transition model.

This paper describes the visible luminescence of several water-soluble, monolayer-protected gold clusters (MPCs).[10,11] The ligands of the monolayers are the thiolates of tiopronin (*N*-2-mercaptopropionylglycine), 3-mercapto-1-propanesulfonic acid, mercaptosuccinic acid, and glutathione. Based on excitation at 451 nm and detection at 770 nm, and using a $[Ru(bpy)_3]^{2+}$ standard, the efficiency of the tiopronin-MPC nanoparticle's luminescence is very high, about 0.3%. This is higher than previous observations[6−9] on the luminescence of gold nanocrystals and may offer advantages in applications in optical devices and biosensors. The luminescence efficiency varies substantially with the monolayer ligand and is less for the other ligands.

The experiments here report the preparation of the four water-soluble MPCs (two of which are new MPCs), their emission and excitation spectra, and the emission pH dependence for the tiopronin-MPC case. Additionally, a tiopronin-MPC core-etching experiment is described that brings out a possible core size dependence of the emission energy.

Experimental Section

Chemicals. $HAuCl_4 \cdot xH_2O$ was either purchased (Aldrich, 99.99%) or synthesized according to the literature.[12] *N*-(2-mercaptopropionyl)glycine (tiopronin, 99%), sodium 3-mercapto-1-propanesulfonate (tech., 90%), mercaptosuccinic acid (97%), and sodium borohydride (99%) were purchased from Aldrich, and glutathione (reduced form, free acid, 98%) was from Sigma. House-distilled water was further purified with a Barnstead NANOpure system (≥18 MΩ). All other chemicals were reagent grade and used as received. Tiopronin-MPCs were prepared as described previously using a 3:1 mole ratio ("3×") of the thiol and $AuCl_4^-$;[13] they are somewhat polydisperse with an average composition $Au_{201}Tiopronin_{85}$ and average core diameter 1.8 nm. Glutathione-MPCs were prepared as described previously using a 3:1 mole ratio of the thiol and $AuCl_4^-$;[14] the crude product was purified by dialysis.

Syntheses of 3-Mercapto-1-Propanesulfonic Acid and Mercaptosuccinic Acid Monolayer-Protected Gold Clusters. In a typical reaction, 0.31 g of $HAuCl_4 \cdot xH_2O$ (0.80 mmol) and 0.43 g of sodium 3-mercapto-1-propanesulfonate were codissolved in 35 mL of 6:1 methanol/acetic acid. $NaBH_4$ (0.6 g, 16 mmol) in 15 mL of H_2O was added with rapid stirring. The black suspension was stirred for an additional 30 min, and the solvent was then removed under vacuum at temperatures <40 °C. The pH of the crude product dissolved in 75 mL of Nanopure water was adjusted to 1 by dropwise addition of concentrated HCl; this solution was purified by dialysis. The solution was loaded into 8 in. segments of cellulose ester dialysis membrane (Spectra/Por RC, MWCO = 5000), placed in 4 L beakers of Nanopure water, and stirred slowly, recharging with fresh water ca. every 10 h over the course of 72 h. The 3-mercapto-1-propanesulfonic acid-MPC solutions were collected from the dialysis tubes, and the solvent was removed under vacuum at <40 °C. The product was found to be spectroscopically clean by NMR (absence of peaks due to unreacted thiol or disulfide and acetate byproducts). The synthesis of mercaptosuccinic acid-MPC is the same as above, using 0.36 g of mercaptosuccinic acid in the first step.

Etching of Tiopronin-MPCs. Following a previous report,[15] 25 mg 3x tiopronin-MPCs were codissolved with 0.2 g of tiopronin in 10 mL of Nanopure water and heated at 65 °C under nitrogen overnight.

Transmission Electron Microscopy (TEM). TEM samples were prepared by placing a droplet of a ca. 1 mg/mL aqueous MPC solution on Formvar-coated (200−300 Å) copper grids (200 mesh), waiting 5 min, and removing excess solution by touching a small piece of filter paper to the edge of the grid. The grid was dried under N_2 flow or in air for 30 min. Phase-contrast images of the MPCs were obtained with a side-entry Phillips CM12 electron microscope operating at 120 keV. Three

10.1021/jp0041151 CCC: $20.00
Published on Web 11/27/2001

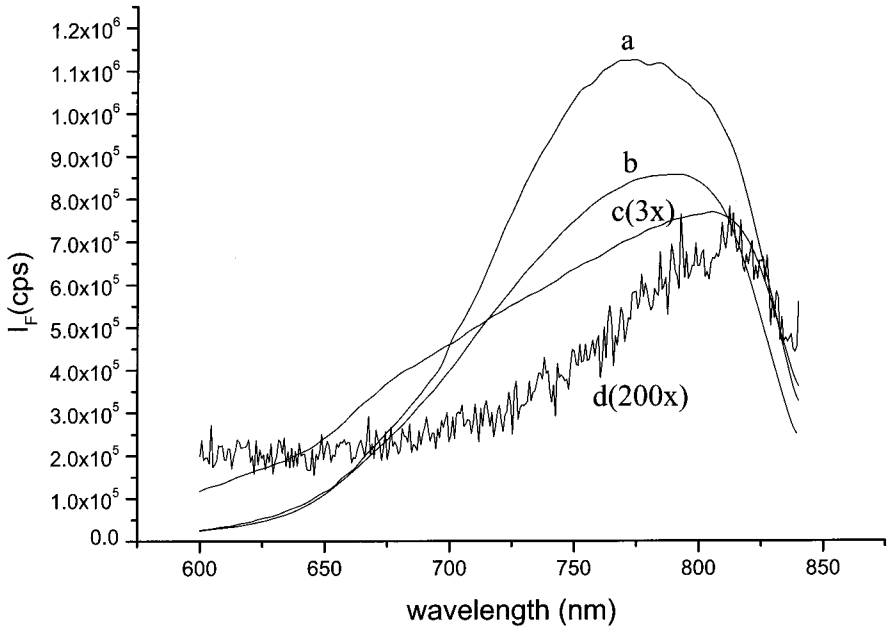

Figure 1. Emission (a) from tiopronin-MPC solution, (b) from mercaptosuccinic acid MPC solution, (c) from 3-mercapto-1-propanesulfonic acid MPC solution, and (d) from glutathione MPC solution. All excited at 451 nm and all at 1 μM concentration.

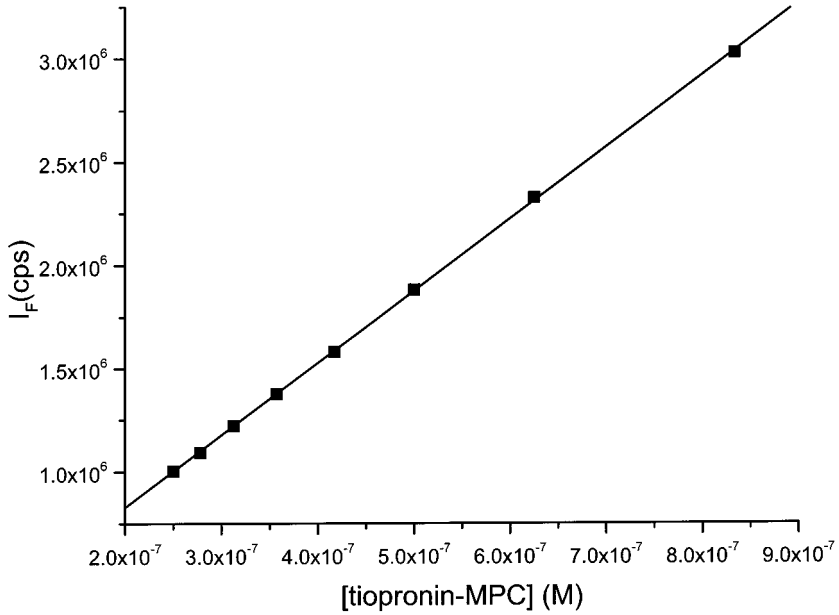

Figure 2. Emission intensity from tiopronin-MPC vs concentration. The linear fit equation is $I_F = 3.49 \times 10^{12}$[tiopronin-MPC] + 1.31×10^5, $R = 0.999$.

typical regions of each sample were obtained at either 300kx or 560kx. Size distributions of Au cores were obtained from at least two digitized photographic enlargements with Scion Image Beta Release 2 (available at www.scioncorp.com).

Spectroscopic Measurements. Proton NMR spectra were recorded at 200 MHz on a Bruker AC200 NMR spectrometer at room temperature in concentrated D_2O solutions. A line broadening factor of 1 Hz was used to improve NMR signal-to-noise (S/N) and a relaxation delay of 5 s was used to allow adequate signal decay between pulses. UV−vis spectra (200−800 nm, 1 nm resolution) were collected with an ATI UNICAM UV4 spectrometer. Fluorescence spectra were taken at a standard right angle (RA) configuration on an ISA Instruments Jobin Yvon-Spex Fluorolog model FL3-21 spectrometer, using a Hamamatsu R928 photomultiplier detector. The emission spectra are corrected for variation in the PMT spectral sensitivity. The PMT sensitivity falls about 3-fold from 600 to 800 nm, then ca. 10-fold to 850, and ca. 10^3-fold to 900 nm, so the PMT sensitivity correction can be expected to lose quality above the 800 to 850 nm range.

Results and Discussion

Emission and Excitation Spectra of Aqueous Solutions of the Four MPCs. Most of our experiments have focused on the tiopronin-MPCs since we discovered its luminescence first, in the course of exploring[16] its ability to quench the luminescence of other fluorophore solutes. With excitation at 451 nm, the emission of a 1 μM solution of tiopronin-MPCs (made using a 3:1 mole ratio of the thiol and $AuCl_4^-$) occurs in a broad peak centered at about 770 nm, as shown in Figure 1a. (The 451 nm excitation relates to our quantum yield comparison to [Ru(bpy)$_3$]$^{2+}$; see below.) The possibility of the emission arising from some adventitious impurity from the reagents or synthesis

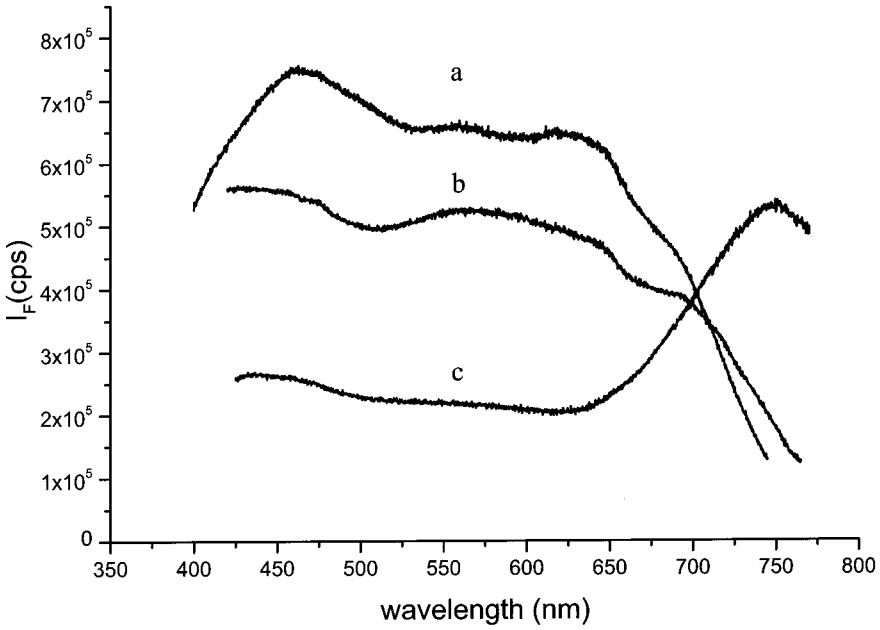

Figure 3. Excitation spectra (a) of tiopronin-MPC solution (1 μM, emission at 770 nm), (b) of mercaptosuccinic acid MPC solution (1 μM, emission at 787 nm), and (c) of 3-mercapto-1-propanesulfonic acid MPC solution (1 μM, emission at 802 nm).

was carefully scrutinized. None of the solutions used during the sequence[13] of synthetic steps exhibited fluorescence emission (including solutions of tiopronin, of $AuCl_4^-$/tiopronin mixtures, and of pH 1 solutions that, without MPCs present, had contacted dialysis membrane for 2−3 days). The crude tiopronin-MPC product is much less luminescent than following purification by dialysis (72 h); the tiopronin-MPC luminescence seems partly quenched by byproducts of the synthesis (quencher identity unknown). Overall, the evidence is firm that the emission definitely originates from the tiopronin-MPC itself. Additionally, we point to previous[8] observations of Au nanoparticle luminescence (at a lower energy) where the nanoparticles had been prepared and purified by a different route.

At low tiopronin-MPC concentrations (<1 μM), the fluorescence intensity changes linearly with concentration, as shown in Figure 2. At higher concentrations, the emission intensity rolls over and actually decreases (not shown). In a 1 mM solution, no fluorescence can been seen. The high-concentration effect is certainly associated with excessive absorption of the exciting beam by the dark MPC solution (this has been seen[17]); there is also the possibility of self-quenching by the tiopronin-MPCs themselves.

The intensity of the luminescence of the tiopronin-MPC is comparable to those of solutions of the $[Ru(bpy)_3]^{2+}$ metal complex (as the chloride salt, bpy is 2,2′-bipyridine) and the cyanine laser dyes LDS750 and DTTC, at similar ranges of concentration. The complex and dyes have[18] respectively quantum yields of 0.042,[18a] 0.004,[18b] and 0.21[19] when excited at 451, 572, and 763 nm. Their emission maxima lie at 630, 700, and 810 nm, respectively, which are not far from and bracket the tiopronin 770 nm maximum in Figure 1a (and the maxima of etched and place-exchanged MPCs; vide infra Figure 5). We have used the Ru complex and the LDS750 and DTTC dyes as comparative standards to estimate the quantum yield for the nanoparticles at 770 nm (correcting for the spectral response of the spectrometer's PMT detector and for the relative absorbances of metal complex and of dyes to MPC). The results for quantum yields of 1.8 nm average core diameter tiopronin-MPCs are in reasonable agreement, being 0.003 ± 0.001, 0.0024, and 0.001, respectively. This quantum yield is approximately 7 orders of magnitude greater than that of gold films and larger than a recent observation[8] of the (integrated band) NIR luminescence of dodecanethiolate-coated MPCs.

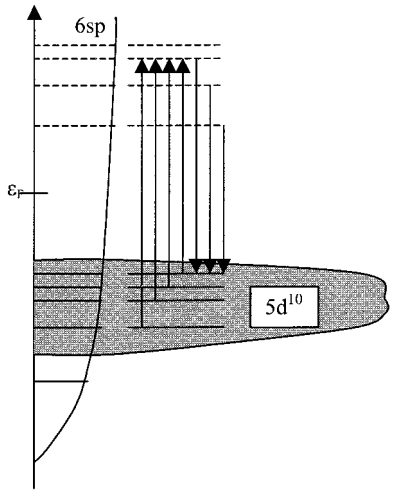

Figure 4. Schematic model of interband excitation and emission.

Figure 1b−d shows emission spectra of 1 μM solutions of the other three MPCs, all excited at 451 nm. That of Figure 1c shows that 3-mercapto-1-propanesulfonic acid-MPC (1 μM) has a peak at about 802 nm and a shoulder at about 700 nm, while the mercaptosuccinic acid-MPC (Figure 1b) exhibits an emission peak at ca. 787 nm. The emission of glutathione-MPC is much weaker than the others, and all are less emissive than the tiopronin-MPC. The common drop-off of the emission intensity of all four MPCs above about 820 nm reflects degradation of the spectrometer performance at lower energies. Because of this, the emission maxima in Figure 1, curves c and d, may actually lie at higher wavelengths than we are able to access. Those for curves a and b on the other hand can be expected to be reasonably accurate; for example, the nominal lower energy 815 nm emission maximum[19] of the reference laser dye DTTC was observed at 810 nm. Likewise, the emission intensities of 3-mercapto-1-propanesulfonic acid-MPC and glutathione-MPC may be underestimated. Nonetheless, the obvious variation of

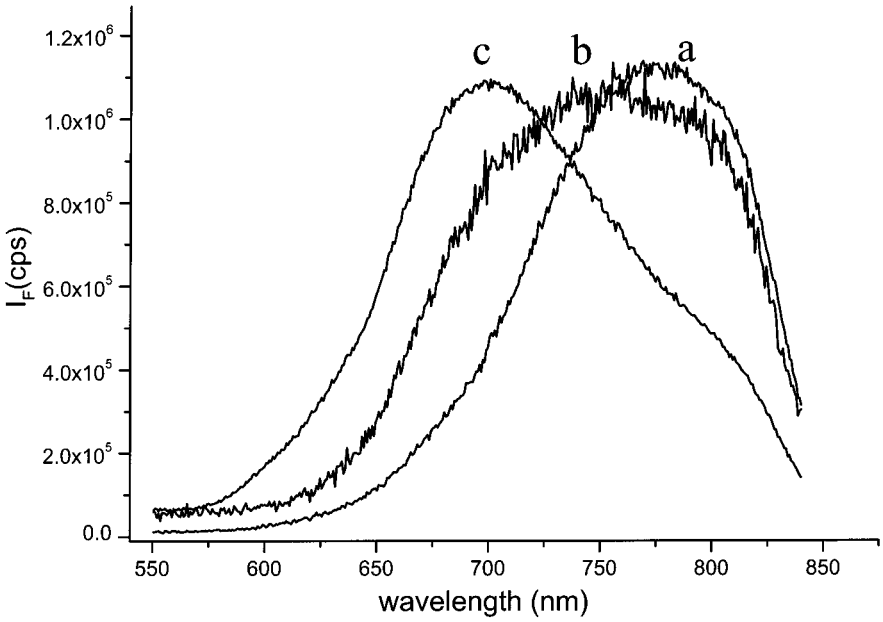

Figure 5. Emission from tiopronin-MPC solution (1 μM), before (a) and after (b) etching. (c) Emission from 1 μM solution of tiopronin-MPC that had been place-exchanged (feed ratio 2:1) with 3-mercapto-1-propanesulfonic acid (relative number of the two ligands expected to be ca. 2:1).

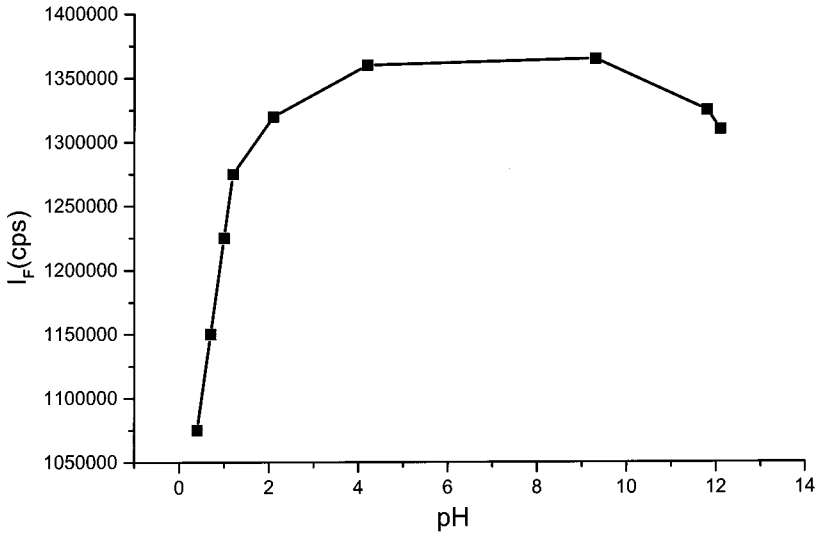

Figure 6. Emission intensity at 770 nm (excited at 451 nm) of tiopronin-MPC solution (1 μM) as a function of pH.

both emission maxima and intensities suggests that the ligands attached to the gold core have a significant influence on its luminescence.

The absorbance spectra (not shown) of the above materials all display an intense absorbance ($\epsilon_{\text{tiopronin-MPC}} > 10^5\ M^{-1}\ cm^{-1}$ at 450 nm)[13,20] that climbs steadily with decreasing wavelength. The 520 nm surface plasmon absorbance band for the 1.8 nm core diameter tiopronin-MPCs is not evident on this intense background of absorbance, and is weak even for tiopronin-MPCs with larger[13] cores. The excitation spectra of three of the four MPCs are shown in Figure 3 (that of glutathione-MPC is not shown). It is evident that the excitation spectra bear no resemblance to the absorbance profile, being all relatively flat from 400 to ca. 650 nm, and show no maxima that would be obviously associated with a surface plasmon excitation. Changes in the excitation spectra occur above ca. 650 nm, and there the excitation of 3-mercapto-1-sulfonic acid-MPC seems different from those of the other two MPCs. The emission maximum wavelength of tiopronin-MPC is also insensitive to the excitation energy (400, 451, 500 nm).

The cartoon depiction of Figure 4 shows a 5d to 6sp interband excitation. Figure 4 is a possible (and probably over-simplified) model of the emission process, showing that excitation (absorbance) occurs from relatively closely spaced electronic levels in the MPC core, such as from a broad band of occupied $5d^{10}$ states. The relatively flat excitation spectra at higher energies imply that emission is localized to transitions from unoccupied 6sp states above the Fermi level but probably at the lower edge of the sp band. The efficiencies and energies of the 6sp emitter states seem to be influenced by the nature of the thiolate ligand, and in this sense they might be regarded as a kind of surface electronic state of the MPC molecule.

Emission from Tiopronin-MPCs with Different Core Sizes. The possible dependency of the emission on MPC core size was explored in experiments in which tiopronin-MPCs with different average core sizes were made by using different mole ratios of tiopronin to $AuCl_4^-$ in the MPC synthesis.[13] The average tiopronin-MPC core diameters 1.8, 2.2, 3.1, and 3.9 nm were made by using 3:1, 1:1, 1:6, and 1:12 ratios, respectively. Only the smallest, the 1.8 nm core size MPC (that

discussed above), was observed to luminesce. We infer that the luminescence maximum moves to lower energy with increased core size (or disappears, which we view as less likely). A proportional relation between nanoparticle luminescence wavelength and size is anticipated from a recent theoretical analysis.[7,9]

The core size dependence was further explored in an experiment in which the tiopronin-MPC was subjected to etching conditions such as that previously described by the Whetten group[15] to decrease average MPC core size. Tiopronin-MPCs of 1.8 nm were incubated in a concentrated solution of tiopronin thiol at 65 °C under N_2 overnight. The result, shown in Figure 5, curves a and b, is a shift in the emission maximum of the etched material, from 770 to about 750 nm. An analogous effect was observed when an aqueous solution of the tiopronin-MPC was simply stirred at room temperature with a 2-fold molar excess of any of the four thiols for several days, as for example seen in Figure 5c. At this point we should recall that these MPCs are somewhat polydisperse in core size. While the effect seen in Figure 5c could arise from an etching process, it is also possible that the distribution of core sizes was altered by inadvertent fractionation during isolation of the MPC product, as some solid matter was formed during the incubation that was discarded. In either event, the Figure 5 results are not inconsistent with a core size-wavelength relationship.

The core sizes of the other three luminescent MPCs were also not larger than 2 nm. That of the glutathione-MPC sample was 1.4 ± 0.8 nm, that of mercaptosuccinic acid MPC was 1.9 ± 1.0 nm, and that of 3-mercapto-1-propanesulfonic acid MPC was 1.8 ± 1.0 nm. These results further emphasize the importance of small core size of the metal nanoparticle, specifically for the present materials smaller than 2 nm.

pH Dependence of Tiopronin-MPCs Emission. The emission at 770 nm of 1 μM tiopronin-MPCs is shown in Figure 6. The luminescence intensity drops sharply at low pH and slightly at high pH. These are not effects associated with a decomposition reaction, as far as we can tell, and are not understood At intermediate pH, the emission intensity is rather pH-independent. The pK_a of tiopronin-MPC (1.8 nm) is ca. 5.6;[13] so Figure 6 shows that the emission is not sensitive to whether the tiopronin ligands are protonated.

Acknowledgment. This work was supported in part by grants from the National Science Foundation and Office of Naval Research. We thank the UNC Dental Research Center for access to HRTEM measurements, and Professors Robert Whetten and Mostafa El-Sayed of Georgia Institute of Technology for helpful discussions.

References and Notes

(1) Mooradian, A. *Phys Rev. Lett.* **1969**, *22*, 185−187.

(2) Boyd, G. T.; Yu, Z. H.; Shen, Y. R. *Phys. Rev. B* **1986**, *33*, 7923−7936.

(3) Apell, P.; Monreal, R.; Lundqvist, S. *Phys. Scr.* **1988**, *38*, 174−179.

(4) Gimzewski, J. K.; Sass, J. K.; Schlitter, R. R.; Schott, J. *Europhys. Lett.* **1989**, *8*, 435−440.

(5) Reihl, B.; Coombs, J. H.; Gimzewski, J. K. *Surf. Sci.* **1989**, *211−212*, 156−164.

(6) Wilcoxon, J. P.; Martin, J. E.; Parsapour, F.; Wiedenman, B.; Kelley, D. F. *J. Chem. Phys.* **1998**, *108*, 9137−9143.

(7) Mohamed, M. B.; Volkov, V.; Link, S.; El-Sayed, M. A. *Chem. Phys. Lett.* **2000**, *317*, 517−523.

(8) Bigioni, T. P.; Whetten, R. L.; Dag, O. *J. Phys. Chem. B* **2000**, *104*, 6983−6986.

(9) Link, S.; El-Sayed, M. A. *Intl. Rev. Phys. Chem.* **2000**, *19*, 409−453,

(10) (a) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801−802. (b) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. *J. Chem. Soc., Chem. Commun.* **1995**, 1655−1656.

(11) (a) Hostetler, M. J.; Murray, R. W. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 42−50. (b) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.*, **2000**, *33*, 27−36. (c) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17−30.

(12) *Handbook of Preparative Inorganic Chemistry*; Brauer, G., Ed.; AP: New York, 1965; p 1054. (b) Block, B. P. *Inorg. Synth.* **1953**, *4*, 14.

(13) Templeton, A. C.; Chen, S.; Gross, S. M.; Murray, R. W. *Langmuir* **1999**, *15*, 66−76.

(14) Schaaff, T. G.; Knight, G.; Shafigullin, M. N.; Borkman, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, *102*, 10643−10646.

(15) Schaaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **1999**, *103*, 9394−9396.

(16) Huang, T. Unpublished results, University North Carolina, 2000.

(17) Aquila, A.; Murray, R. W. *Langmuir* **2000**, *16*, 5949−5954.

(18) (a) Houten, J. V.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853−4858. (b) Knorr, F. J.; Wall, M. H.; McHale, J. L. *J. Phys. Chem. A* **2000**, *104*, 9494−9499. (c) www.exciton.com.

(19) Sahyun, M. R. V.; Serpone, N. J. *J. Phys. Chem. A* **1997**, *101*, 9877−9883.

(20) Templeton, A. C.; Pietron, J. J.; Murray, R. W.; Mulvaney, P. *J. Phys. Chem. B* **2000**, *104*, 564−570.