Preparation and Photoluminescent Properties of Gold(I)−Alkanethiolate Complexes Having Highly Ordered Supramolecular Structures

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Au(I)–alkanethiolates (Au(I)–SRs, R = –$(CH_2)_nH$, $n = 2-10$, 12, 14, 16, and 18) are synthesized by mixing gold salt, $HAuCl_4$, and *n*-alkanethiols in tetrahydrofuran. Au(I)–SRs show a highly ordered layer structure, and the ordering increases as the length of the alkyl chain increases. Au(I)–SRs with $n \geq 4$ emit a bright orange-red light ($\lambda_{em} \sim 610$ nm) visible to the naked eye upon irradiation with UV light, and the emission intensity increases with increasing length of the alkyl chain. We also found that noticeable aurophilic interactions between Au(I)–Au(I) exist for the Au(I)–SRs with longer alkyl groups having highly ordered layer structures.

Introduction

There has been a growing interest in the study of the luminescent properties of gold(I) complexes because of the applications in photoactive reagents, biosensors, optoelectronics, and so forth.[1,2] In particular, the studies of the gold(I) complexes containing phosphine and/or sulfur which can have a wide range of emission wavelengths have aroused much attention.[3–5] The origin of such emission behavior has been ascribed to the ligand-to-metal charge transfer (LMCT) which is mainly affected by the types of ligands as well as the ligand-to-metal-metal charge transfer (LMMCT). The luminescent properties of gold complexes induced by LMMCT have been attributed to gold–gold interactions resulted from a relativistic effect that originates from the minimum value of the ratio between the relativistic radius and the nonrelativistic one, relativistic contraction, in the 6s orbitals of the heavy elements.[6] Such attractive interactions, commonly referred to as aurophilic interactions, are generally found when the adjacent Au$\cdots$Au distances are less than 3.6 Å[7] and their bonding forces are about 29–46 kJ mol^{-1}, comparable to hydrogen bonding forces.[8]

Several factors, including the types of neighboring nucleophilic molecules, solvents, and temperature, were found to influence the optical properties of gold(I) complexes through the subsequent change of aurophilic interaction.[9–13] For example, the colorless dimeric gold(I) complex $[Au(S_2CN(C_5H_{11})_2)]_2$ displayed luminescence when exposed to vapors of volatile organic solvents such as acetone, CH_3CN, CH_2Cl_2, and $CHCl_3$ because the interactions between the solvent vapors and the complexes in the solid state change the intermolecular Au$\cdots$Au distances of the complexes.[14] In other studies, Fackler and co-workers reported the triboluminescence of [[1,3,5-triaza-7-phosphaadamantane]$_2$Au][Au(CN)$_2$], a transient emission after the grinding of the sample.[15] They found that the aggregation type via aurophilic interaction was an important factor in determining the luminescent properties of gold(I) complexes.

Recently, we reported a new synthetic route for gold nanoparticles through electron beam irradiation with gold(I)–alkanethiolates (Au(I)–SRs) having supramolecular structures.[16] By chance, we also found that these Au(I)–SRs have the luminescent properties upon UV irradiation. In this study, we synthesized and characterized the complete series of Au(I)–SRs with different alkyl lengths [R = $(CH_2)_nH$, $n = 2-10$, 12, 14, 16, and 18] to investigate the correlation between the luminescent properties and the supramolecular structures of these gold complexes.

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Experimental Section

Materials. Gold salt, hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$), and *n*-alkanethiol [$HS(CH_2)_nH$, $n = 2, 3, 4, 5, 6, 8, 9, 10, 12, 16, 18$] were purchased from Aldrich. *n*-Heptanethiol and *n*-tetradecylmercaptan were purchased from TCI. Tetrahydrofuran was dried by refluxing it with sodium and benzophenone followed by distillation. All other reagents were used as received.

Synthesis of Au(I)–SRs. The following procedure was used to synthesize all Au(I)–SRs. The synthesis is exemplified in the case of Au(I)–SC18 which has 18 carbons in the alkyl group. A solution of *n*-octadecanethiol ($C_{18}H_{37}SH$, 0.5 mmol, 144 mg) in tetrahydrofuran (THF, 5 mL) was dropped into a solution of $HAuCl_4 \cdot 3H_2O$ (0.1 mmol, 39.4 mg) in THF (5 mL) at room temperature. A brown precipitate formed immediately and then became a white solid after stirring the mixture for 1 day. The product was purified by washing it several times with THF, ethanol, and acetone and driyng under vacuum overnight. The yield was 39.4 mg (82%). Other Au(I)–SRs were prepared by the same procedure for the Au(I)–SC18 by using other *n*-alkanethiols, respectively, and the yields were always above 80%.

Characterization. IR spectra were recorded on a JASCO FT/IR-200 over the range 4000–500 cm^{-1} using KBr pellets. ^1H NMR spectra were obtained on a JEOL LNM-LA 300 spectrometer at 300 MHz with chemical shifts indicated relative to $SiMe_4$ in $CDCl_3$ solution. Elemental analysis was performed using the CE1110 from CE instrument. X-ray scattering experiments were performed at the 3C2 beam line at the Pohang Accelerator Laboratory (PAL) at room temperature. Thermogravimetric analysis (TGA) was carried out on a TA instrument TGA-2050. The heating rate of TGA was 10 °C min^{-1}. The solid-state photoluminescence spectra were acquired on a HORIBA FluoroMax-3 spectrofluorometer with pressed KBr pellets at room temperature. For comparison of the emission intensities of Au(I)–SRs, we used the same molar amount, 0.025 mmol, of the samples in the preparation of the KBr pellets. The transparent KBr pellets with uniform diameter, 13.13 (±0.05) mm, and thickness, 0.143 (±0.015) mm, were obtained under the same pressure using the fixed total weight of the mixture of KBr and Au(I)–SRs (60 mg).

Results and Discussion

The Au(I)–SRs were prepared simply by mixing gold salt with excess *n*-alkanethiol in THF. The number of carbons in the *n*-alkanethiol (*n*) was varied from 2 to 18. After stirring the mixture for 24 h, the yellowish color that originated from $HAuCl_4$ completely disappeared, and the Au(I)–SRs were obtained as a white solid precipitate through the well-known chemical reaction shown in the following equation.[17]

$$HAuCl_4 + 3RSH \rightarrow Au(I)\text{–}SR + RS\text{–}SR + 4HCl \quad (1)$$

We found that these white solids were insoluble in common solvents ranging from very polar H_2O to nonpolar *n*-hexane. Similar insoluble nature of gold complexes was already reported by others[18] and was ascribed to the cross-linked polymeric structures due to aurophilic interactions between gold atoms.[19] Therefore, characterization of Au(I)–SRs was only possible in the solid state of these compounds. Figure 1 shows the solid-state ^{13}C NMR result of Au(I)–SC18 along with the carbon site assignments. The chemical shifts of C1 and C2, closest to the sulfur headgroup, are observed at 40.8 ppm as a shoulder and at 39.4 ppm, respectively, where two peaks are shifted downfield by more than 10 ppm compared to those of *n*-octadecanethiol. Badia et al. reported similar large downshifts in the Au(I)–alkylthiolate system and mentioned that the origin of this shift was the gold–thiolate interaction.[20] The chemical shift value of the midchain methylenes around at 34.3 ppm for the alkyl groups in Au(I)–SC18 indicates that these alkyl groups have a trans conformation. In a solution of *n*-alkanes, the peaks of midchain carbons are observed at 29–30 ppm indicating a mixture of trans and gauche forms, whereas they are shifted downfield to 33–34 ppm in the crystalline state for the all-trans chain conformation.[21] The all-trans conformation of the alkyl group in Au(I)–SC18 and other Au(I)–SRs were further confirmed by Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) studies shown in the later part of this article. The ^1H NMR results of the remaining organic compounds in the reaction mixture after the collection of the Au(I)–SRs precipitate are shown in Figure 2. When the reactant molar ratio of gold salt and *n*-octadecanethiol, 1:3, was used as shown in the above chemical reaction (eq 1), the only triplet peak was found at 2.7 ppm, which originated from the protons adjacent to sulfur in disulfide, $–CH_2–CH_2–S–S–$ (Figure 2a). Therefore, the formation of di-*n*-alkyl disulfide compounds from reaction 1 was confirmed. On the other hand, a new quartet peak from the $–CH_2–CH_2–SH$ at 2.5 ppm coexisted in the case that 10 times excess *n*-octadecanethiol was used (Figure 2b); this result indicated that unreacted *n*-octadecanethiol remained. Although eq 1 has been used to express the reaction between the gold salt and the alkanethiols many times,[22,23] we believe that this is the first time that this reaction has been proven stoichiometrically.

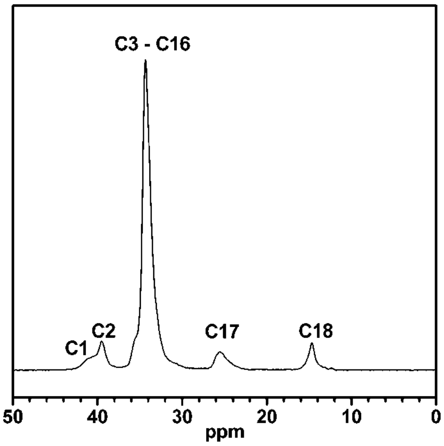

Figure 1. Solid-state (7 kHz) cross-polarization/magic angle spinning ^{13}C NMR spectrum of Au(I)–SC18.

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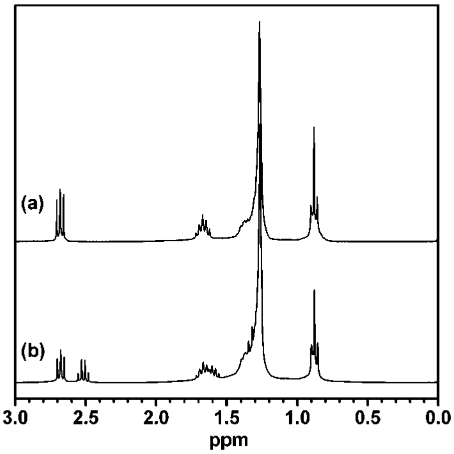

Figure 2. ^{1}H NMR spectra of the supernatants after the reaction of $HAuCl_4$ and *n*-octadecanethiol in the molar ratio of (a) 1:3, (b) 1:10.

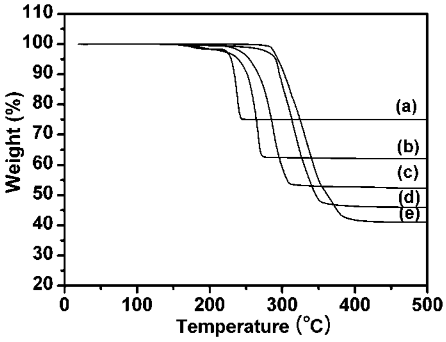

Figure 3. Representative thermogravimetric profile of Au(I)–SRs (a) Au(I)–SC2; (b) Au(I)–SC6; (c) Au(I)–SC10; (d) Au(I)–SC14; (e) Au(I)–SC18.

The thermal stability of the Au(I)–SRs was examined by TGA. Representative TGA curves are shown in Figure 3; the decomposition temperatures are summarized in Table 1. All Au(I)–SRs show similar single-stage weight loss behavior, while the decomposition temperature increases as the number of the carbon in the alkyl group increases. For example, Au(I)–SC2 shows the lowest onset decomposition (T_{onset}) and complete decomposition temperatures (T_{cd}) at 229 and 244 °C, respectively, while Au(I)–SC18 has the highest T_{onset} and T_{cd} values at 295 and 390 °C, respectively. Obviously, the longer alkyl chains of Au(I)–SRs can provide additional stabilization energy by cohesive interactions between the alkyl groups. Similar phenomena, the increase of the thermal stability of the materials with longer alkyl groups, were found in the case of gold nanoparticles stabilized with various alkanethiols.[24] As expected, the amount of residue decreases as the carbon number in Au(I)–SRs increases with a maximum value for Au(I)–SC2. The residue was clarified as gold metal from the selected-area electron diffraction pattern observed during transmission electron microscopy (not shown in here) and also from the golden color of the material. Also, the amount of residue for each sample was found to be almost the same as the content of unknown component from elemental analysis within experimental error (Table 1). For example, the contents of C, H, S, and an unknown component of Au(I)–SC18 were 45.30, 7.87, 6.61, and 40.22%, respectively, and the amount of residue from TGA was 40.96%. Therefore, Au(I)–SC18 and the other Au(I)–SRs prepared in this study were composed of one alkanethiolate group per one gold atom.

When Au(I)–SRs with $n \geq 4$ were irradiated with UV light (thin-layer chromatography lamp, $\lambda_{\mathrm{ex}} \sim 360$ nm), a bright emission of orange-red light was observed. The emission intensity of the Au(I)–SR powders was found to increase with increasing carbon number in the alkyl group on the basis of primitive observations with the naked eye. Because Au(I)–SRs were not soluble in any solvent, clear solutions of Au(I)–SRs for fluorescence spectroscopy could not be obtained. However, the Au(I)–SRs could be well dispersed in several organic solvents, including THF, for several minutes without any precipitation. Figure 4 shows the luminescent behavior of Au(I)–SRs dispersed in THF. For relatively direct comparison, the same molar amount of Au(I)–SRs, 0.05 mmol, was dispersed in 10 mL of THF for each sample. It is certain that the emission intensity increased as the carbon number increased. For a more detailed quantitative study of this luminescent behavior, we tried to observe the emission spectra of the Au(I)–SRs using fluorescence spectroscopy. Unfortunately, we could not get reproducible emission data from either the Au(I)–SR powders or the Au(I)–SR dispersed in THF solution; (1) uniform films of Au(I)–SRs for spectroscopy measurements could not be prepared from the Au(I)–SR powders, and (2) the emission intensity from the powdery dispersion state of the Au(I)–SR complexes varied, possibly because of the light scattering from the powders. Instead, we obtained reasonably reproducible emission intensity data using pressed KBr pellets containing 0.025 mmol repeating units of each Au(I)–SR. Because the same molar amount of Au(I)–SRs and the same size of pressed KBr pellet were used in this emission study, we believe that a relatively quantitative comparison of the emission intensities of the sample is possible.[25,26] However, because each sample pellet contains different amounts of KBr molecules and the ordered structure of the samples is not the same, these emission data can not be as good as those obtained from liquid solution samples reported by others.[27,28] Figure 5 shows the emission spectra of Au(I)–SRs in KBr pellet upon excitation at 310 nm; a broad high-energy (HE) emission band at about 410−440 nm and a low-energy (LE) emission band with the peak maximum ranging from 610 to 620 nm are observed. The selection of the excitation wavelength at 310 nm was based on the most intensive LE emission at around 610 nm for Au(I)–SRs with $n \geq 4$. Bachman et al. observed an HE emission band at 463 nm and a LE emission band at 643 nm from Au(I)–phenylthiolate [Au(I)–SPh] complexes with a supramolecular structure prepared from PhSNa and EtNCAuCl with the LE emission

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Table 1. Summary of Thermogravimetric and Elemental Analysis Data of Au(I)–SRs in this Study[a]

	TGA results			elemental analysis results			
Au(I)–SRs	T_{onset} (°C)	T_{cd} (°C)	amount of residues (%)	content of C (%)	content of H (%)	content of S (%)	content of unknown (%)
Au(I)–SC2	229.49	247.63	75.02	11.34 (9.31)	2.11 (1.94)	13.41 (12.43)	73.14 (76.32)
Au(I)–SC4	231.52	253.76	66.87	18.11 (16.79)	3.19 (3.15)	12.21 (11.21)	66.49 (68.85)
Au(I)–SC6	252.48	274.80	62.05	23.65 (22.94)	4.08 (4.14)	10.90 (10.21)	61.37 (62.71)
Au(I)–SC8	253.25	279.60	57.11	29.45 (28.09)	5.09 (4.97)	9.33 (9.37)	56.13 (57.57)
Au(I)–SC10	265.71	313.09	52.32	33.91 (32.45)	5.92 (5.67)	8.77 (8.66)	51.40 (53.22)
Au(I)–SC12	269.15	335.50	48.27	36.74 (36.20)	6.27 (6.28)	8.01 (8.05)	48.98 (49.47)
Au(I)–SC14	287.83	355.85	45.91	40.01 (39.45)	6.81 (6.80)	7.96 (7.52)	45.22 (46.23)
Au(I)–SC16	294.93	383.39	42.95	43.47 (42.31)	7.09 (7.27)	7.13 (7.06)	42.31 (43.36)
Au(I)–SC18	295.45	390.25	40.96	45.30 (44.83)	7.87 (7.67)	6.61 (6.65)	40.22 (40.85)

[a] Calculated values in parentheses.

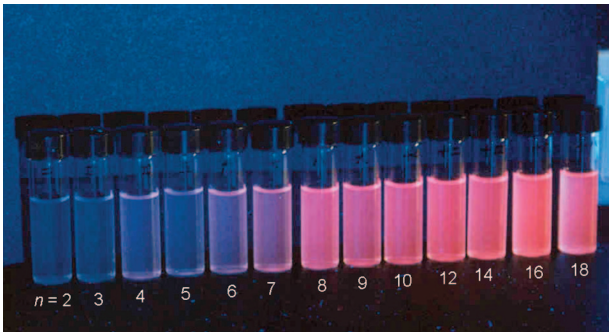

Figure 4. Photograph of the luminescence of the Au(I)–SRs (excited by longwave UV ≳ 350 nm, Black Ray longwave ultraviolet lamp model B100 AP, UVP Inc.) dispersed in THF.

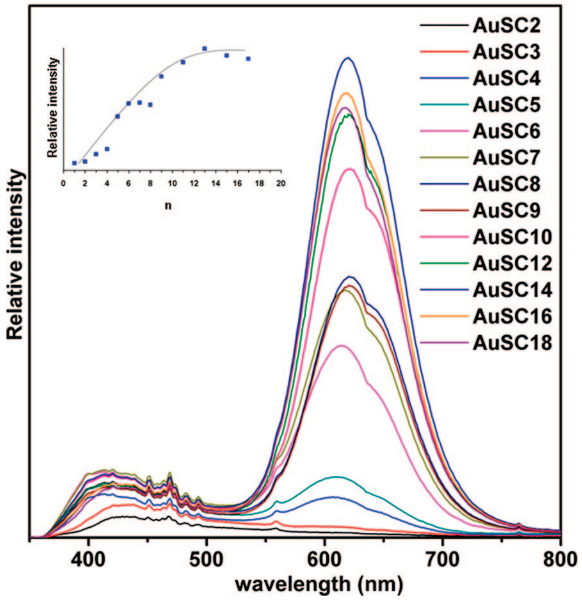

Figure 5. Room temperature photoluminescence (PL) spectra of Au(I)–SRs with various alkyl chain lengths (excited at 310 nm) in a solid KBr pellet. Inset shows the PL intensity versus *n*.

band being considerably more intense.[29] These HE and LE bands were ascribed to an LMCT-derived state and a triplet metal-centered state, respectively. Because the chemical and supramolecular structures of Bachman's Au(I)–SPh are very close to those of Au(I)–SRs, as discussed later in this paper, we can apply the same explanation for the HE and LE bands. From the large Stokes shift, 3.3×10^4 cm^{-1} in our case, between the excitation and the emission bands, which means that a significant geometrical distortion exists, we believe that the LE emission of Au(I)–SRs is phosphorescence while more detailed studies including lifetime measurements are needed to elucidate the origin of these bands.[30] For the LE band, the emission peak starts to appear in Au(I)–SC4, and then the intensity increases as the chain length increases (see the inset in Figure 5). This result agrees well with the photographic picture shown in Figure 4. The emission intensity might level off when the carbon number (*n*) is 14, but we cannot conclude this yet because we do not have data for Au(I)–SRs with $n > 18$. The luminescent properties of gold complexes are known to be affected by gold–gold interactions, and these interactions depend on the nature of the ligands, that is, electron donating power, size, and energy level of the frontier orbital.[31–33] In our case, the length of the ligands seems to affect the degree of gold–gold interactions, resulting in different emission intensities. From the X-ray studies, we found that different degrees of ordered structures were obtained from Au(I)–SRs having different alkyl group lengths as shown in the next paragraph. On the other hand, the emission profile of the HE band is somewhat different from that of the LE band. The growth in intensity with a slight blue-shift of the maximum wavelength was observed for the Au(I)–SRs with $n \leq 7$ as the carbon number increased, whereas both the emission intensity and the wavelength did not change much, if any, for Au(I)–SRs with $n \geq 8$. In general, the emission maxima derived from the S → Au LMCT of gold(I)–thiolate complexes are in the range of 480 to 520 nm when the LMCT is mainly affected by the electron-donating properties of the ligands, not by the aurophilic interaction. When the aurophilic interaction exists in the gold(I) complexes, the peak position and intensity of the LMCT emission band can be changed.[34] In our case, the X-ray results from the Au(I)–SRs show that the aurophilic interaction increases to a certain degree with longer alkyl chain groups. It was also reported that the electron donating ability of the alkyl chain increases with increasing length of

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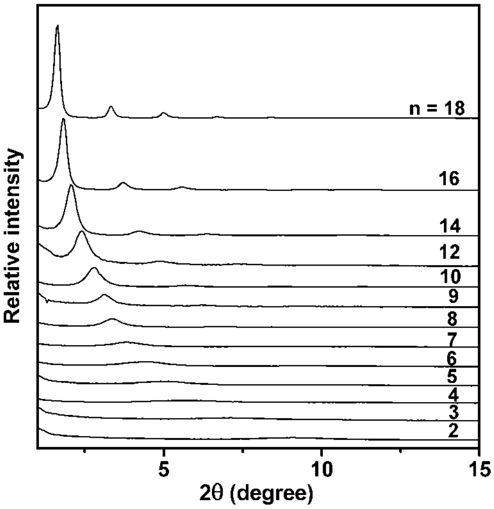

Figure 6. Powder XRD patterns of the Au(I)–SRs in the small angle region.

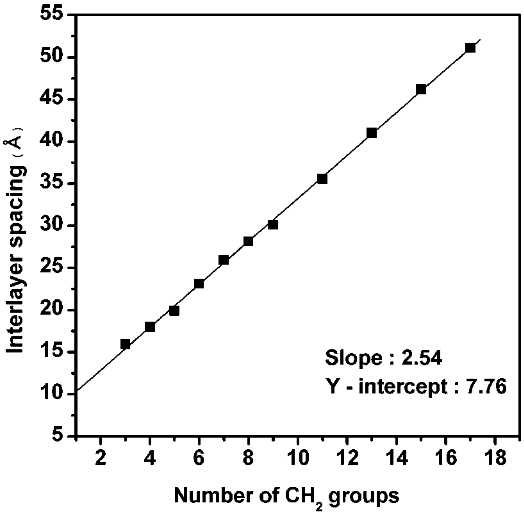

Figure 7. Measured layer spacing of the complexes as a function of the number of methylene groups. The slope and *Y*-intercept calculated by a linear regression method are shown.

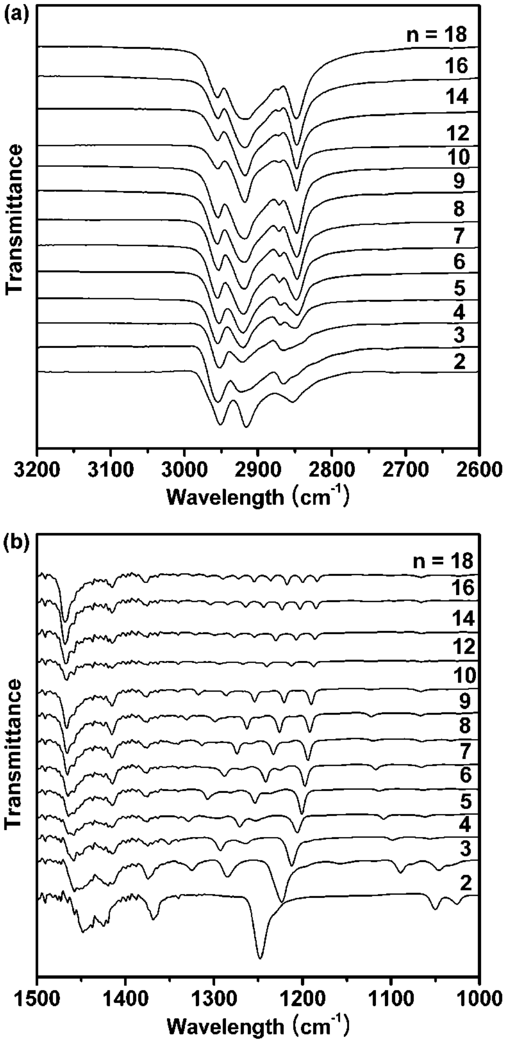

Figure 8. Infrared spectra of Au(I)–SRs (a) in the high frequency (2600–3200 cm^{-1}) region indicating the symmetric (d$^+$) and antisymmetric (d$^-$) bands from the CH$_2$ C−H stretching and (b) in the low frequency (1000–1500 cm^{-1}) region containing the methylene wagging (W*x*) progressions.

the alkyl groups.[35] The origin of change in the HE band around 420 nm according to the variation of alkyl groups in this study is not yet completely understood; however, it seems to be affected by changes of the electron donating power and the strength of the aurophilic interaction with increasing chain length in alkanethiolate.

The XRD curves in a small angle region of Au(I)–SRs are shown in Figure 6. Au(I)–SRs with $n \leq 7$ exhibit only one broad small-angle reflection with the resolution we can achieve, while the intensity increases as n increases. Au(I)–SRs with $n \geq 8$ show a series of ordered reflections that can be assigned to (0*k*0) planes, indicating that these samples have highly ordered layer structures. Both the intensity and the number of peaks for Au(I)–SRs with $n \geq 8$ increased where even (050) and (060) planes were observed in Au(I)–SC18. Therefore, the Au(I)–SRs with longer alkyl groups have higher ordering and higher emission intensity. The linear relationship between the interlayer spacing of the (010) plane for Au(I)–SRs with $n \geq 4$ and the number of CH$_2$ groups is shown in Figure 7. The data for AuSC2 and AuSC3 are not included here because their small angle peak is very broad with very low intensity, indicating a lack of well-ordered structures. The slope of about 2.54 Å per methylene unit in Figure 7 indicates that the alkyl group is fully extended, having an all-trans conformation, and it is perpendicular to the plane structure of the Au(I)–SRs. This is also supported by the strong symmetric (d$^+$) and antisymmetric (d$^-$) CH$_2$ stretching bands with peak maxima around 2847 and 2916 cm^{-1} in FT-IR that are correlated to the extremely high percentage of all-trans conformations.[36] It is well known that these trans peaks at 2847 and 2916 cm^{-1} shifted to around 2855 and 2926 cm^{-1}, respectively, when the population of gauche form in the alkyl chain increases.[37] In this regard, the position of each d$^+$ and d$^-$ band of Au(I)–SRs with $n \geq 4$ is another strong evidence that the dominant structure of the alkyl group of Au(I)–SRs is all trans (Figure 8a). Additionally, the well-resolved progression bands between 1175 and 1350 cm^{-1}, which are attributed to wagging vibrations (W*x*), have been known to be the markers of trans

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and gauche conformation populations in the alkyl groups; the interband spacing ($\Delta\nu$) in Wx mode depends on the average number of trans units m by the equation $\Delta\nu = 326/(m + 1)$.[38] The measured average values of $\Delta\nu$ for Au(I)–SRs in Figure 8b are as follows: $\Delta\nu = 17.7$, $n = 18$; $\Delta\nu = 19.8$, $n = 16$; $\Delta\nu = 22.3$, $n = 14$; $\Delta\nu = 26.4$, $n = 12$; $\Delta\nu = 32.0$, $n = 10$; $\Delta\nu = 35.7$, $n = 9$; $\Delta\nu = 39.7$, $n = 8$; $\Delta\nu = 45.5$, $n = 7$; $\Delta\nu = 53.0$, $n = 6$; $\Delta\nu = 65.0$, $n = 5$; and $\Delta\nu = 81$, $n = 4$. Using the above equation, we can derive the calculated number of *trans*-methylene units to be as follows: $m + 1 = 18.4$, $n = 18$; $m + 1 = 16.5$, $n = 16$; $m + 1 = 14.6$, $n = 14$; $m + 1 = 12.3$, $n = 12$; $m + 1 = 10.2$, $n = 10$; $m + 1 = 9.1$, $n = 9$; $m + 1 = 8.2$, $n = 8$; $m + 1 = 7.2$, $n = 7$; $m + 1 = 6.2$, $n = 6$, $m + 1 = 5.0$, $n = 5$; and $m + 1 = 4.0$, $n = 4$. When the experimental inaccuracies in the frequency estimates are considered, the $m + 1$ value for each Au(I)–SR is remarkably consistent with the real alkyl chain number of thiolates. Therefore, the chain conformation of the alkyl group in Au(I)–SRs with $n \geq 4$ should be all trans. Because the d spacing of each complex is about twice the length of the corresponding Au(I)–SRs with a fully extended alkyl for $n \geq 4$, these samples should have a bilayer structure as shown in Figure 9. Similar bilayer structures were found in other polymeric metal complexes such as the RNCAuCl[39] and Ag(I)−SR complexes.[40] To clarify the structure of the Au–S lattice, we studied the physical implication of the intercept, 7.76 Å (Figure 7), which might correspond to 2 times the thickness of the CH_3–S–Au residue as similar results were reported for the Ag(I)–SR complexes.[41,42] The S–C bond of an untilted all-trans chain has an angle of 35.5° to the normal to the Au–S plane.[43] When the length of the S–C bond and the van der Waals radius of the CH_3 group to be 1.82 and 1.69 Å, respectively, are considered, the theoretical thickness of the (CH_3–S) residue is $2 \times (1.69 + 1.82 \times \cos 35.5) = 6.34$ Å. Then, the difference between the Y-intercept and the thickness of the CH_3–S residue, 1.42 Å, might originate from the Au–S slab thickness and the separation (or overlap) that may exist between the methyl groups of adjacent layers. The following calculation also confirms this assumption. In the case of Au(I)–SC18, the length of the alkyl group, from the S to the end methyl group, can be calculated by summation of the entire chain length of 1.27 Å per CH_2 group and the van der Waals radius of the chain end CH_3 group as follows: $2 \times (1.69 + 1.27 \times 17 + 1.82 \times \cos 35.5) = 49.52$ Å. The layer thickness of Au(I)–SC18 obtained from the XRD result is 51.11 Å. Thus, the discrepancy, which represents the thickness of the Au–S slab and the separation (or overlap) between adjacent layers, is 1.59 Å. This value is not very different from the 1.42 Å obtained from the calculation using the intercept.

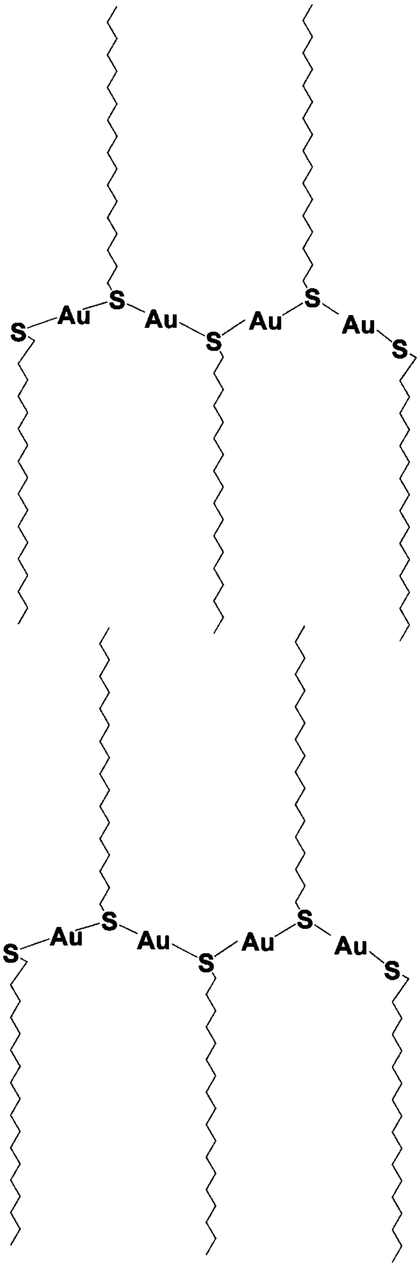

Figure 9. Proposed bilayer structure of Au(I)–SC18.

The Au(I)–SRs with $n \geq 8$, having more intensive emission and highly ordered structures, show two wide-angle reflections at d spacings of 3.45 Å and 3.88 Å although the intensity is not large (Figure 10). The intensity of these peaks increased with increasing length of the alkyl chain, while their d spacing values remained constant. The distance between the ordered side alkyl groups of comb-like polymers has been known to be about 4.17 Å.[44] Therefore, the 3.45 Å and 3.88 Å peaks should not be from the alkyl groups. The Au•••Au distance for Au(I) complexes that have aurophilic interactions, suggested to be the origins of the luminescent properties in gold(I) complexes, has been found to be less than 3.6 Å.[7] Therefore, the wide-angle reflections at 3.45 Å possibly represent the Au•••Au distance from aurophilic interactions that cause the luminescence. However, the d

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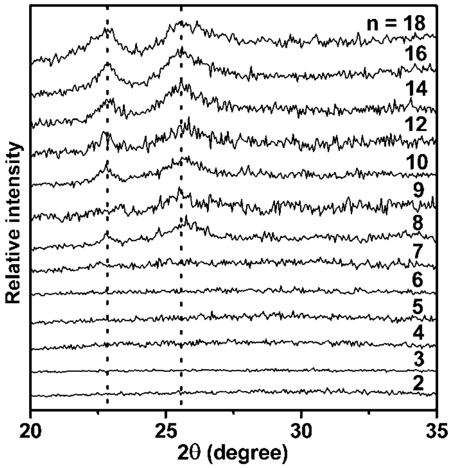

Figure 10. Powder XRD patterns of the Au(I)–SRs in the wide angle region.

spacing of the 3.88 Å peak is somewhat larger than the known range of the Au•••Au distance from aurophilic interactions. We cannot conclude whether the 3.88 Å reflection causes the luminescence or not. Still, it is quite certain that Au(I)–SRs with longer alkyl groups can have highly ordered bilayer supramolecular structures and noticeable aurophilic interactions between the Au(I)–Au(I), which in turn generates the increased LE emission.

Using multifunctional thiols, such as mercaptoalkanoic acid ($HS-R-CO_2H$), functionalized Au(I)–SRs were synthesized; these functionalized complexes also displayed luminescent properties. The functionalized Au(I)–SRs can be attached to the glass or silicon wafers and chemically reacted with other chemicals. We are currently trying to make soluble and/or more easily processed Au(I)–SRs by incorporating other organic moieties. We are also trying to attach luminescent organic moieties and/or mesogenic groups to change the supramolecular structures and the luminescent properties. The blue or red shift of the emission can be expected by changing the size or the π conjugation of the side groups. Au(I)–SRs were found to be thermally very stable in air. When Au(I)–SC18 was kept at 100 °C for one week under air, the layered structures were maintained and almost the same intensity of emission was observed.

At the beginning of this work, we believed that the luminescent property of the reaction product arose from gold nanoparticles surrounded by thiolates because the luminescent behavior of nanosized gold clusters had already been reported by others.[45] However, the elemental analysis and TGA results shown above clearly indicate that our product was composed of Au(I) and alkanethiolate in a 1:1 mol ratio. When surfactants such as tetraoctylammonium bromide (TOAB) were added to the mixture in the preparation of Au(I)–SRs, as is the general process for preparing thiolate-capped gold nanoparticles,[46] the resulting products did not show any supramolecular structure or luminescence in either solution or solid state. Possibly the existence of the surfactant prohibits formation of the polymeric ordered layer structures.

In this paper, Au(I)–SRs, which have been known to be precursors for the preparation of stabilized gold nanoparticles, were synthesized very easily by mixing $HAuCl_4$ and *n*-alkanethiols. Au(I)–SRs were found to have highly ordered polymeric supramolecular structures, and the ordering increased as the length of the alkyl group increased. The highly ordered supramolecular structures of Au(I)–SRs were found to be a key factor for the aurophilic effect, which in turn generated the luminescent property. The luminescent Au(I)–SRs have good thermal and chemical stability and can also be easily functionalized by changing the end group of the thiolates.

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