4.1. Abstract

Mechanistic investigations on the end-to-end assembly of gold nanorods to nanochains, in the presence of \( \alpha, \omega \)-alkanedithiols, were studied. A decrease in the longitudinal plasmon absorption was observed along with a concomitant formation of a new red shifted band above a critical concentration of dithiol, which is attributed to the interplasmon coupling in assembled nanorods. However, no noticeable spectral changes were observed below the critical concentration and the TEM studies indicate that the nanorods remain isolated and randomly distributed. This step is ascribed as an incubation step wherein one of the thiol groups of \( \alpha, \omega \)-alkanedithiol preferentially binds on to the edges of nanorods, leaving the other thiol group free. Above the critical concentration, a chain up process proceeds through the interlocking of nanorods, initially to dimers and subsequently to oligomers, which results in longitudinal interplasmon coupling. Dimerization step follows a second order kinetics that deviates with time due to oligomerization. The rate constants for dimerization of nanorods possessing various dithiols and their energy of activation were determined. The large temperature dependence on
the dimerization rate constants further confirms that the process is diffusion mediated.

4.2. Introduction

There is a great deal of multidisciplinary research in recent years on the design of one dimensional (1-D) nanomaterials such as nanorods and nanowires. The scientific quest for the synthesis of these nanomaterials arises from their potential use as "interconnectors" in nanoscale devices, waveguides and catalytic motors. Over the years, chemists have achieved excellent control on the design of metal and semiconductor nanomaterials of specific dimensions. Among these, one of the well explored systems is the design of gold nanorods of various aspect ratios by adopting electrochemical, photochemical and seed mediated methods.

Dithiols have been extensively used as linkers for bridging spherical Au nanoparticles and for assembling nanoparticles on to surfaces. Such organizations result in ordered two- and three-dimensional structures. Isotropic nature of spherical Au nanoparticles prevents the selective binding of molecules on surfaces, which restricts the possibility of designing 1D nanomaterials. In contrast, the anisotropic features of Au nanorods allow their assembly in various orientations and several attempts have been made for organizing nanorods using physical methods and electrostatic/supramolecular/covalent approaches.
This includes the (i) linear organization of gold nanorods using biotin-streptavidine connectors and lateral organization through electrostatic interactions by varying the pH of the medium, (ii) longitudinal assembly through cooperative intermolecular hydrogen bonding/electrostatic interaction by using molecules such as 3-mercaptopropionic acid, cysteine and glutathione; (iii) end-to-end electrostatic assembly of Au nanorods on multiwall carbon nanotubes; (iv) selective anisotropic growth of Au tips on the edges of CdSe quantum rods and their linear organization using hexanethiol.

Gold nanorods possess two distinct surface plasmon absorption bands associated with the transverse and longitudinal oscillations of electrons. Interestingly, the former band absorbs at 520 nm whereas the later one at a longer wavelength, which undergoes a bathochromic shift with increase in aspect ratio. Interplasmon interactions in nanoparticles originate from the electric dipole coupling which results in the shift of surface plasmon absorption band. Such assembled nanomaterials may have potential applications in plasmonics and waveguides. Theoretical aspects dealing with the electrodynamic responses of assembled nanoparticles of various size and shape have been discussed, in detail, by Schatz and coworkers. Using Au nanorods as specific examples, Gluodenis and Foss have proposed the effect of mutual orientation of nanorod-nanorod on the plasmon resonance spectra at different distances by involving a simple quasistatic treatment. According to this model, the longitudinal
interaction of Au nanorods may result in the formation of a red shifted absorption band, which was experimentally verified by us and these results are presented in Chapter 3.

The growth mechanism of Au nanorods and the characterization of their crystallographic facets were investigated using electron diffraction analysis and HRTEM studies.\textsuperscript{2,38-41} Based on these investigations, it is concluded that the end facets of Au nanorods are dominated by \{111\} planes and the side facets by \{100\} and \{110\} planes. It is reported that the thiol derivatives preferentially bind to the \{111\} planes of the Au nanorods\textsuperscript{27-29} and this specific interaction can be further exploited for the organization of Au nanorods through covalent linkages. A pictorial representation of some of the possible end-to-end assemblies of Au nanorods is shown in Scheme 4.1.

The present study illustrates, the end to end organization of Au nanorods using various \(\alpha,\omega\)-alkanedithiols namely 1,3-propanedithiol (C\textsubscript{3}-DT), 1,5-pentanedithiol (C\textsubscript{5}-DT), 1,6-hexanediol (C\textsubscript{6}-DT), 1,8-octanedithiol (C\textsubscript{8}-DT) and 1,9-nonanedithiol (C\textsubscript{9}-DT). Although there are several reports on the organization of Au nanorods, no attempts have been made to understand the mechanistic aspects dealing with the nanochain formation. Details of various steps involved in the Au nanochain formation using alkanedithiols and their interplasmon interaction were investigated. These results were compared with 1-alkylmercaptans of varying alkyl chain lengths.
4.3. Results and Discussion

Gold nanorods of aspect ratios 2.2 and 2.9 were synthesized by following the modified photochemical method as discussed in Chapter 2, section 2.3.1. A shift in the absorption maximum of their longitudinal plasmon band was observed from 620 nm to 700 nm, with increase in aspect ratio (Figure 4.1). Unless otherwise specified, all studies were carried out using nanorods of average aspect ratio 2.9 in a mixture (1:4) of water and acetonitrile. The spectral properties of gold nanorods were unaffected on increasing the composition of acetonitrile and
the rods were quite stable for several hours\textsuperscript{28} (details in section 3.3.1). Recently it is reported that the plasmon resonance of Au nanorods, synthesized by seed mediated methods, drift to shorter wavelength and authors have reported methods for arresting this by adding millimolar quantities of Na\textsubscript{2}S.\textsuperscript{42} However, in the present case we have adopted the photochemical method for the synthesis of Au nanorods and no such drift was observed in a mixture (1:4) of water and acetonitrile.

The concentrations of Au nanorods used in various studies were determined from their extinction coefficients ($\varepsilon$). Extinction coefficient of the transverse and longitudinal plasmon absorption bands of Au nanorods (aspect ratio 2.9) were estimated in conjunction with Transmission Electron Microscopy (TEM) and

\begin{center}
\includegraphics[width=\textwidth]{figure4.1.png}
\end{center}

\textbf{Figure 4.1.} Absorption spectrum and TEM images of gold nanorods of two different aspect ratios: trace ‘a’ of A and image in B corresponds to nanorod of aspect ratio 2.2; and trace ‘b’ of A and image in C corresponds to nanorod of aspect ratio 2.9. Inset shows the magnified images.
Inductively Coupled Plasma (ICP) analysis ($\varepsilon_{515\text{nm}} = 0.27 \times 10^{10} \text{ M}^{-1} \text{cm}^{-1}$ and $\varepsilon_{700\text{nm}} = 0.53 \times 10^{10} \text{ M}^{-1} \text{cm}^{-1}$), details given in Chapter 2. Further the interaction of nanorods with various $\alpha,\omega$-alkanedithiols were investigated by following the changes in their plasmon absorption band.

### 4.3.1. Organizing Gold Nanorods Using $\alpha,\omega$-Alkanedithiols

Au nanorods of aspect ratio 2.9 (~0.12 nM) were suspended in a mixture (1:4) of water and acetonitrile and microlitre quantities of $\alpha,\omega$-alkanedithiols were added so that volume change is negligible. In the case of C9-DT, both the transverse as well as longitudinal plasmon absorption bands of Au nanorods were found to be unaffected on the addition of lower concentrations (up to 1.0 $\mu\text{M}$) of dithiol (Figure 4.2). Interestingly, further increase in the concentration of C9-DT led to a decrease in the intensity of the longitudinal surface plasmon band centered at 700 nm with a concomitant formation of a new band in the near-infrared (NIR) region. The absorption spectral changes of Au nanorods on addition of 2.0 $\mu\text{M}$ of C9-DT, recorded at various time intervals, are presented in Figure 4.3. The newly formed band shifts to longer wavelength with increase in time and found to be more intense and broad.

The formation of the new red shifted band can be explained on the basis of interplasmon coupling in assembled nanorods. In the case of gold nanorods there are two modes of plasmon oscillations (transverse and longitudinal) and each of
these modes can couple with plasmon oscillations of the neighboring rods. In the present study, we observe a selective coupling of longitudinal plasmon band whereas the transverse plasmon band remains more or less unaffected. These results suggest that the addition of C9-DT leads to the coupling of the longitudinal plasmon oscillation, resulting from an end to end assembly of gold nanorods as described in Chapter 3 using bifunctional ligands such as thioalkyl carboxylic acids, cysteine and glutathione. Interplasmon interaction have been recently also observed by Liz-Marzan and coworkers by linearly assembling Au nanorods on multiwall carbon nanotubes.

![Graph](image)

**Figure 4.2.** Absorption spectral changes of Au nanorods of aspect ratio 2.9 [~0.12 nM] on addition of 0.5 µM of 1,9-nonanedithiol.
Figure 4.3. Absorption spectral changes of Au nanorods of aspect ratio 2.9 [~0.12 nM] on addition of 2.0 μM of 1,9-nonanedithiol at time interval of a) 0, b) 18, c) 24, d) 30 and e) 48 min.

One of the interesting observations in the present case is the decrease in the longitudinal plasmon band and the formation of a red shifted band above a critical concentration of dithiol. The interaction between Au nanorods and other α,ω-alkanedithiols (C8-DT, C5-DT and C3-DT) was further investigated and the spectral changes are presented in Figures 4.4 to 4.6. An isosbestic point is observed in the case of α,ω-alkanedithiols with long alkyl chains (C9-DT and C8-DT) which gradually shifts to longer wavelength with time (~ 1 h). In contrast, the intensity of the longitudinal plasmon band decreases rapidly in the case of C5-DT and C3-DT (Figures 4.5 and 4.6) and these fast changes were monitored using a diode array spectrophotometer (upper limit is 1000 nm).
Figure 4.4. Absorption spectral changes of Au nanorods of aspect ratio 2.9 [~0.12 nM] on addition of 2.0 μM of 1,8-octanedithiol at time interval of a) 0, b) 6, c) 9, d) 12, e) 15, f) 18, g) 21, h) 24, i) 36 and j) 48 min.

Figure 4.5. Absorption spectral changes of Au nanorods of aspect ratio 2.9 [~0.12 nM] on addition of 2.0 μM of 1,5-pentanedithiol, with a time interval of 6 seconds.
The capping agents at the edges of Au nanorods can play a major role in the linear organization. Most of the reports on the synthesis of Au nanorods involve the presence of a cationic surfactant, cetyltrimethylammonium bromide (CTAB) and a co-surfactant in certain cases. Several mechanisms have been suggested for explaining the seed mediated growth of Au nanorods.\textsuperscript{2,38,41,43,44} A surfactant-directed metal nanorod growth mechanism was proposed by Murphy and coworkers which involves the differential blocking of certain crystallographic facets of Au nanorod (\{100\} or \{110\}) by CTAB which promotes the anisotropic growth of \{111\} edges.\textsuperscript{2} An alternate mechanism involving the electric field directed growth of Au nanorods was proposed by Perez-Juste et al. which suggests

\[ \text{C3-DT} \]

\[ 0 \rightarrow 55 \text{ s} \]

\[ \begin{array}{cccc}
0.6 & 0.4 & 0.2 & 0.0 \\
600 & 800 & 1000 & \text{Wavelength, nm}
\end{array} \]

**Figure 4.6.** Absorption spectral changes of Au nanorods of aspect ratio 2.2 [\textasciitilde 0.12 nM] on addition of 2.0 \textmu M of 1,3-propanedithiol, with a time interval of 5 seconds.
that the Au\textsuperscript{III} ions were initially bound to CTAB which upon reduction to Au\textsuperscript{I} ions interact more strongly with CTAB micelle.\textsuperscript{41} According to this mechanism the slow collision frequency of Au\textsuperscript{I} bound CTAB and the enhanced electric field at the tips allows the reduction of Au\textsuperscript{I} at the termini. In the present case we have adopted a photochemical method for the synthesis of Au nanorods by using CTAB as surfactant and tetraoctylammonium bromide as co-surfactant.\textsuperscript{15} At the growing edges of nanorods, the capping agents may be loosely bound and the $\alpha,\omega$-alkanedithiols possessing short alkyl chains may diffuse faster and more efficiently into the micellar shell resulting in the rapid organization of Au nanorods.

For further establishing the linear organization, the morphology of the gold nanorods in the absence (Figure 4.1B) and presence (Figure 4.7) of C3-DT were examined by using Transmission Electron Microscopy (TEM), under identical conditions. TEM samples were prepared by drop casting the same solution used for spectroscopic investigation on to a formvar coated copper grid. The nanorods before the addition of C3-DT are randomly distributed throughout the grid (Figure 4.1B), whereas in the presence of C3-DT, Au nanorods were found as nanochain (Figure 4.7) and accumulated in a few locations in the grid. In an earlier report, Banin and coworkers have obtained a linear assembly of CdSe nanorods possessing Au tips using hexanethiol.\textsuperscript{5} In this system, the thiol groups bind strongly on to the Au tips and the bifunctional molecules allow the preferential
organization of CdSe nanorods as nanochains. Although several types of end-to-end organization were observed (Figure 4.7), majority of the rods were aligned in a slightly tilted fashion. A tilted geometry, similar to that shown in Scheme 4.1 (type III), may be more favored for dithiols such as C3-DT possessing short alkyl chains. Longitudinal organization of nanorods in the presence of various α,ω-alkanedithiols results in interplasmon coupling and the mechanistic aspects of nanochain formation were investigated by following the absorption-time changes.24,28,32

![Image A](image.png)  
![Image B](image.png)

**Figure 4.7.** Transmission electron micrographs of nanochains formed on addition of C3-DT to Au nanorods of aspect ratio 2.2.

### 4.3.2. Mechanism in the Nanochain Formation

In order to gain a better understanding on the mechanism in the nanochain formation, the time dependent changes of the longitudinal plasmon absorption
band were investigated by varying the concentration of C3-DT and C9-DT (Figures 4.8 and 4.9). An incubation period was observed for all α,ω-alkanedithiols followed by a decrease in the intensity of the longitudinal plasmon absorption band. It is clear from Figure 4.8 and 4.9 that the concentration of α,ω-alkanedithiols plays a decisive role in initiating the linear organization of the nanorods. In the case of C3-DT the linear organization is complete in almost two minutes and the absorption spectra recorded at different concentrations are presented in Figure 4.10. The absorption maximum of the newly formed band shifts to longer wavelengths with increase in concentration of dithiol (Figure 4.10).

![Graph](image)

**Figure 4.8.** Absorption-time changes in the longitudinal absorption band (620 nm) of Au nanorods [~0.12 nM] on addition of 1,3-propanedithiol; [C3-DT]: a) 0.58, b) 0.66, c) 0.74, d) 0.83 μM.
Further the time dependent changes in the longitudinal absorption band of Au nanorods on addition of 2.0 μM of various dithiols (Figure 4.11) were investigated. In all the cases, an incubation period was observed, which increases with alkyl chain length of ω-ω-alkanedithiols. The critical concentration of dithiol for nanochain formation was elucidated by plotting the absorbance of the longitudinal plasmon band at 700 nm (and the newly formed band around 1000 nm) against the concentration of ω-ω-alkanedithiols added. Solutions were kept sufficiently long for ensuring the completion of the reaction (for example, in the case of C9-DT, Au nanorod solution was kept for 30 min). A sigmoidal plot was

![Figure 4.9](image)

**Figure 4.9.** Absorption-time changes in the longitudinal absorption band of Au nanorods [0.12 nM] on addition of 1,9-nonanedithiol: [C9-DT]: a) 0.99 b) 1.33, c) 1.66, d) 2.0 μM.
Figure 4.10. Absorption spectral changes on addition of different concentrations of 1,3-propanedithiol, recorded after 4 minutes; [C3-DT]: a) 0, b) 0.58, c) 0.66, d) 0.74 and e) 0.83 μM.

Figure 4.11. Absorption-time changes in the longitudinal absorption band of Au nanorods [0.12 nM] on addition of 2.0 μM α,ω-alkanediathiols.
obtained (Figure 4.12) from which the critical concentration of dithiol for nanochain formation was estimated as \( \sim 0.6 \) \( \mu \)M in all cases. The spectral changes are relatively slower in the case of \( \alpha,\omega \)-alkanedithiols with long alkyl chain (for example, C9-DT, in Figure 4.11) and various steps in the nanochain formation were investigated using absorption spectral studies and TEM analysis (*vide infra*).

We have estimated the number of thiol groups per nanorods for obtaining quantitative information on the chain up process. The total surface area of Au nanorod (length of 54.2 nm and diameter of 18.5 nm) is estimated as 4070 nm\(^2\) which includes the lateral surface area of \( \sim 2470 \) nm\(^2\) and both edges together occupying a surface area of \( \sim 1600 \) nm\(^2\). The footprint of thiol is reported as 0.214 nm\(^2\) which indicate that each edges of the Au nanorods can accommodate a
maximum of ~3740 thiol moieties. The critical concentration of dithiol at which dimerization occurs was estimated as ~0.6 μM (for ~0.12 nM of Au nanorods) which corresponds to a nanorod to dithiol ratio of 1:5000 (Figure 4.12). Absorption spectral studies indicate that during the incubation period nanorods are mainly isolated and the number of thiol moieties that may be bound on each edge of nanorods is less than 2500. These results indicate that the edges of nanorods are not thickly packed with thiolate groups in the incubation step, which allows interlocking of nanorods during dimerization step.

Incubation period and the stepwise formation of nanochains (chain up process) were investigated by recording TEM images by drop casting the solution on to a formvar coated copper grid during the course of the kinetic experiments and by varying the concentration of dithiol. After the addition of C9-DT, the changes in the absorbance of the surface plasmon band were followed as a function of time (Figure 4.13). TEM samples were prepared simultaneously by drop casting 75 μL of solution from the cuvette at different time intervals. The TEM images shown in Figure 4.14 clearly indicate that the nanochains were formed only after the incubation period (>500 s in the case of C9DT, see Figure 4.9). After the incubation period a preferential end-to-end organization of nanorods, initially to dimers and finally to oligomers/nanochains were observed.

We have analyzed the statistical distribution of the Au nanorods per chain as a
**Figure 4.13.** Absorption-time changes in the longitudinal absorption band of Au nanorods [-0.12 nM] on addition of [2.0 μM] 1,9-nonanedithiol. Disturbance at 500, 1000, 1500, and 2500 seconds due to the withdrawal of 75 μL of solution from the cuvette for drop casting it to grid.

function of time (Figure 4.15), which indicates the gradual organization of nanorods.

Further the stepwise assembly of nanorods to nanochain was followed by varying the concentration of **C9-DT**. After the addition of **C9-DT**, solutions were kept for 30 min for ensuring the completion of nanochain formation and TEM images were recorded by following the same procedure. Rod assemblies of different chain lengths were obtained by varying the concentration of **C9-DT**.
Figure 4.14. TEM micrographs of Au nanorods (aspect ratio 2.9) recorded in presence of C9-DT [2.0 μM] at time intervals of (A) 500, (B) 1000 and (C) 1500 s (TEM samples were prepared by drop casting 75 μL of solution from the cuvette).
4.3.3. Effect on Addition of 1-Alkylmercaptans

From the TEM studies, it is evident that during the incubation period nanorods remain isolated and then nanorods are brought together as nanochains through dithiol linkage, resulting in interplasmon coupling. Control experiments were carried out by investigating the effect of addition of monothiol derivatives (1-alkylmercaptans) on plasmon absorbance of Au nanorods. Both the transverse as well as longitudinal plasmon absorption bands of Au nanorods (~0.12 nM) were found to be unaffected on addition of 10 μM of 1-alkylmercaptans (Figure 4.16) such as 1-pentylmercaptan (C₅T), 1-octylmercaptan (C₈T) and 1-nonylmercaptan.
Figure 4.16. (A,B,C) Absorption spectral features of Au nanorod [-0.12 nM] in presence of 1-alkylmercaptans [10 µM] at time interval of 30 min. (D) Absorption spectra of gold nanorods (aspect ratio 2.9) in (1:4) water - acetonitrile recorded immediately after the addition of 1-propylmercaptan. a) 0, b) 1, c) 2, d) 3, e) 4, f) 5, g) 6 µM

(C9T). No noticeable spectral changes were observed even after 3-4 h. In contrast, the intensity of the transverse as well as longitudinal plasmon absorption bands decreased with increase in concentration of 1-propylmercaptan (C3T). The intensity of the newly formed band is lower indicating the possibility of precipitation. 1-propylmercaptan can displace the surfactant molecules (CTAB
and TOAB) on the surface of Au nanorods, however the propyl groups of C3T may be inadequate in protecting the nanorods from precipitation. The control experiments with monothiol derivatives (C5T, C8T and C9T) for long time (Figure 4.17) thus confirm that the nanorods remain monofunctionalized during the incubation period.

![Absorbance plots](image)

**Figure 4.17.** Long time absorption spectral features of Au nanorod [~0.12 nM] in presence of 1-alkylmercaptans [2 μM] at time interval of 30 min.

### 4.3.4. Kinetic Investigations of Nanochain Formation

The mechanism of nanochain formation involves two steps (Scheme 4.2): an incubation step followed by interlinking of nanorods. During incubation period,
one of the thiol groups of \( \alpha, \omega \)-alkanediol preferentially binds on to the edges of nanorods leaving the other thiol group free. No spectral changes were observed during incubation period which is analogous to the reaction between 1-alkylmercaptans and gold nanorods (Figure 4.16 and 4.17). Above the critical concentration, nanorods possessing the anchoring thiol groups interlock to yield the nanochains. The formation of the near infrared absorption band is attributed to the selective coupling of the longitudinal plasmon oscillations in interlinked nanorods.\(^{20}\)

Although the incubation and nanochain formation steps are not clearly separated, one can obtain meaningful mechanistic insight by analyzing the second step. Two observations may be considered while discussing the nanorod chain formation step: (i) formation of a new band through a isosbestic point, observed after the incubation step, which shifts to longer wavelength with time (Figures 4.2-4.5) and (ii) the presence of dimers (with a small percentage of trimers and tetramers) distributed throughout TEM grid which accumulates as nanochains at specific locations with time (Figures 4.14). From these observations it is concluded that the nanorods initially form dimers. If the chain up process proceeds through a dimerization step (step 2a in Scheme 4.2), it should initially follow a second order kinetics, which may deviate with time due to subsequent oligomerization of dimers. The second order rate constant \((k_{\text{dimer}})\) was obtained
Scheme 4.2. Generalized scheme showing the stepwise formation of nanochains: step 1 denotes ‘incubation step’, step 2a denotes ‘dimerization step’ and step 2b denotes the oligomerization of dimers to nanochains (note: there is considerable overlap between various steps; tilting observed in the case of short alkyl chain dithiols such as C3-DT are not indicated).

by following the relationship (eq: 4.1).\(^46\)

\[
k_{\text{dimer}} = \frac{x}{a_0(a_0-x)}
\] (4.1)

where \(a_0\) is the initial concentration of nanorods, \(x\) is the concentration of nanorods reacted in time ‘\(t\)’ and \((a_0-x)\) is the concentration of nanorods
remaining at time 't'. For analyzing the kinetic parameters, concentration of isolated nanorods at a given time was obtained by dividing the absorbance of the longitudinal plasmon band at 700 nm (Figure 4.18-4.20 for C9DT, C8DT and C5DT respectively) by the extinction coefficient of the nanorod ($\varepsilon_{700\text{nm}} = 0.53 \times 10^{10} \text{ M}^{-1}\text{cm}^{-1}$). The initial concentration of the rods ($a_0$) can thus be expressed in absorbance term as $\frac{A_0}{\varepsilon}$ the concentration of nanorods reacted in time 't' as $\frac{(A_0 - A_t)}{\varepsilon}$ and the concentration of nanorods remaining after time 't' as $\frac{A_t}{\varepsilon}$ (where $A_0$ and $A_t$ corresponds to absorbance at 't0' and 't'). After the incubation period, a decrease in the intensity of the longitudinal plasmon absorption band was observed for all $\alpha,\omega$-alkanedithiols and point of inflection is assumed as the time at which the dimerization ($t_0$) starts. By substituting the concentration terms in rate equation (4.1) by absorbance terms, the following relationship was obtained.

$$k_{\text{dimer}}t = \frac{\varepsilon(A_0 - A_t)}{A_0 A_t} \quad (4.2)$$

A plot of $[\varepsilon(A_0 - A_t)]/A_0 A_t$ versus time gave a straight line in the initial period which deviate away from linearity with time for C9DT (Figures 4.21 and 4.22), C8DT (Figure 4.23) and C5DT (Figure 4.24). Indeed, the linearity in the initial period supports the dimerization of nanorods proposed in Scheme 4.2 (step2a) and the rate constant of the dimerization ($k_{\text{dimer}}$) was determined from the initial slope. The deviation from linearity may be mainly attributed to the involvement of other
Figure 4.18. Effect of temperature at a) 55, b) 45, c) 35, d) 25, e) 20, f) 15 and g) 10 °C; on absorption-time changes in the longitudinal absorption band of Au nanorods (aspect ratio-2.9) on addition of 2 μM of C9-DT.

Figure 4.19. Effect of temperature at a) 10, b) 15, c) 20, d) 25, e) 35 f) 45 and g) 53.5 °C on the absorption-time changes in the longitudinal absorption band of Au nanorods (aspect ratio-2.9) on addition of 2 μM of C8-DT.
Figure 4.20. Effect of temperature at a) 10, b) 15, c) 20 and d) 25 °C on the absorption-time changes in the longitudinal absorption band of Au nanorods (aspect ratio-2.9) on addition of 2 μM of C5-DT.

Figure 4.21. Effect of temperature at a) 55, b) 45, c) 35 & d) 25°C; on the kinetic plot of $\frac{[\varepsilon(A_0-A_t)]}{A_0A_t}$ versus time of Au nanorods (aspect ratio-2.9) on addition of 2 μM of C9-DT.
Figure 4.22. Effect of temperature at a) 20, b) 15 & c) 10°C; on the kinetic plot of $[\varepsilon(A_0-A_t)/A_0A_t]$ versus time of Au nanorods (aspect ratio-2.9) on addition of 2 μM of C9-DT.

Figure 4.23. Kinetic plot of $[\varepsilon(A_0-A_t)/A_0A_t]$ versus time at different temperatures for nanorods possessing C8-DT; a) 10, b) 15, c) 20, d) 25, e) 35 f) 45 and g) 53.5°C.
complex kinetic processes (e.g., oligomerization) and the formation of various products having absorption at 700 nm.

For investigating the activation energy of the dimerization step, the effect of temperature on the nanochain formation process was investigated by following the absorption-time plot for the dimerization of rods possessing C9DT, C8DT and C5DT. The second order rate constants were obtained from the initial slope (equation 4.1) and these plots are illustrated in Figures 4.21-4.24. The rate constants for the dimerization of rods possessing C9DT, C8DT and C5DT are summarized in Table 4.1 and the Arrhenius plots of log k versus 1/T are shown in Figure 4.25. The energy of activation for the dimerization of nanorods possessing

![Image of Figure 4.24. Kinetic plot of \([\varepsilon(A_0 - A_t)/A_0A_t]\) versus time at different temperatures for nanorods possessing C5-DT; a) 10, b) 15, c) 20, d) 25°C.](image-url)
C9DT, C8DT and C5DT were estimated from the slope as 85.9, 80.2 and 33.8 kJ mol\(^{-1}\), respectively and these results indicate that dimerization is more favored in the case of nanorods possessing C5DT. The large temperature dependence on the rate constants further confirms that the dimerization is diffusion-mediated process.

**Table 4.1. Second order rate constants\(^a\) for the dimerization\(^b\) of Au nanorods\(^b\) (aspect ratio- 2.9)**

<table>
<thead>
<tr>
<th>Temp, K</th>
<th>10(^{-7})k, M(^{-1})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C9-DT</td>
</tr>
<tr>
<td>283</td>
<td>0.11</td>
</tr>
<tr>
<td>288</td>
<td>0.34</td>
</tr>
<tr>
<td>293</td>
<td>0.81</td>
</tr>
<tr>
<td>298</td>
<td>1.36</td>
</tr>
<tr>
<td>308</td>
<td>3.90</td>
</tr>
<tr>
<td>318</td>
<td>9.44</td>
</tr>
<tr>
<td>326.5</td>
<td>-</td>
</tr>
<tr>
<td>328</td>
<td>18.6</td>
</tr>
</tbody>
</table>

\(^a\)error limit is \(\pm 10\%\); \(^b\)step 2a in Scheme 2
Figure 4.25. Arrhenius plot of log $k$ versus $1/T$ for the dimerization Au nanorods for different $\alpha,\omega$-alkanedithiols; a) C9-DT, b) C8-DT, c) C5-DT.

4.3.5. FT- Raman Studies

For characterizing the surface interactions of $\alpha,\omega$-alkanedithiols on Au nanorods, Raman spectroscopic investigations were carried out. It was recently demonstrated by El-Sayed and coworkers that the Surface-Enhanced Raman Scattering (SERS) intensity of adsorbed molecules is stronger on surfaces covered with aggregated Au nanorods. The observed increase in intensity is attributed to the enhancement of the electric field between the particles in the aggregate. In the present case the FT-Raman spectrum of Au nanorods (0.12 nM) in 1:4 water/acetonitrile, recorded in the presence of C9DT (2 $\mu$M), showed a new band at 475 cm$^{-1}$, which is characteristic of $\nu_\text{Au-S}$ stretching mode (Figure 4.26). This
study confirms the formation of Au-S bond through the binding of 1,9-nonanediethiol.

![Raman Shift, cm⁻¹](image)

**Figure 4.26.** FT Raman spectra of (a) Au nanorods (0.12 nM) (b) C9-DT (2 μM) and (c) Au nanorods (0.12 nM) containing 2 μM of C9-DT. All measurements were carried out in 1:4 water/acetonitrile mixture.

### 4.4. Experimental Section

All absorption spectral studies were carried in duplicate. Stock solutions of α,ω-alkanediethiols were prepared in acetonitrile. Microlitre quantities of these
solutions were added to a 10 mm cuvette containing a mixture of 600 µL of Au nanorods in water and 2.4 mL acetonitrile (1:4 water/acetonitrile mixture; concentration of Au nanorod is ~0.12 nM). The absorption spectral changes on addition of α,ω-alkanedithiols were recorded in a Shimadzu UV 3101PC Spectrophotometer. TEM measurements were carried out in 100 kV Jeol Transmission Electron Microscope (operated at 80 kV) and the samples were prepared by drop casting the same solution used for spectroscopic investigation (75 µL) to formvar coated copper grid, then allowed to evaporate excess solvent. Raman spectrum was recorded using a Confocal Raman Spectrometer operating at a 514 nm laser excitation with a confocal (60 X) objective or (100 X) objective. ¹H NMR spectra recorded in 4:1 CD₃CN/D₂O mixture using a 300 MHz Bruker NMR Spectrometer.

4.5. Conclusions

Interaction between Au nanorods and α,ω-alkanedithiols of varying chain lengths were investigated using absorption spectroscopy and Transmission Electron Microscopy. Based on these studies, it is concluded that the nanochain formation proceeds through an incubation step followed by the dimerization and subsequent oligomerization of nanorods in a preferential end-to-end fashion. During the incubation step, nanorods remain isolated and no changes in the plasmon absorption bands were observed similar to the reaction of 1-
alkylmercaptans with Au nanorods. These results indicate that one of the thiol
groups of $\alpha,\omega$-alkanedithiol preferentially binds on to the edges of nanorods in the
incubation period, leaving the other thiol group free. After the incubation step,
nanorods were brought together as nanochains through dithiol linkage, resulting in
interplasmon coupling. The clear isosbestic point observed in time dependent
absorption spectrum and dimers observed in the TEM monographs confirm the
involvement of dimerization step in the chain up process. The spectral changes
were analyzed for a second order kinetic process and linearity in the initial period
further supports the dimerization mechanism, which deviates with time due to the
contribution of other complex processes. Based on the mechanistic understanding
on the nanochain formation presented here, it is possible to incorporate a desired
number of Au nanorods in a nanochain and such methodologies may have
applications in the design of Au nanochains as interconnectors in nanoscale devices.

4.6. References

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