One–pot Synthesis of Coordination Polymer 2,5–Dimercapto–1,3,4–thiadiazole–Gold and its Application in Voltammetric Sensing of Resorcinol

2.1   Introduction

In recent years the study of coordination polymers (CPs) has emerged as a vibrant area of research. Coordination polymers are the family of compounds which are considered as metal–organic frameworks (MOFs) exhibiting synergism of more than two physical/chemical properties in one framework. CPs are formed by incorporation of metal building blocks in multi–dentate organic or inorganic bridging ligands [Hu et al., 2012; Wu et al., 2012]. The design of efficient coordination polymer encapsulated with noble metal ion has made significant interest over the past two decades. Coordination polymers have been widely used for a number of applications including hydrogen fuel storage, sensing, water purification, heterogeneous catalysis or catalyst supporting energy–storage devices such as lithium ion batteries and double layer capacitors [Fang et al., 2009; Ghosh et al., 2004; Xiao et al., 2006; Wang et al., 2006; Gao et al., 2010; Wang et al., 2010; Sun et al., 2010]. Therefore, it is becoming more demanding for synthesis of such coordination polymer in commercial purposes through shorter route without catalyst at room temperature [Bisht et al., 2012; Ma et al., 2011; Carne et al., 2011].

In this scenario, 2,5–dimercapto–1,3,4–thiadiazole (DMTD) may be of great interest for constructing CPs with interesting topologies and facinating properties due to its four possible bonding sites (diazole nitrogen atoms and sulfydryl sulfur donors) which provide feasibility for metal ion to be linked with ligand and thus expending lower dimensional chain into multi–dimensional ones. Furthermore, azole rings are

superior in terms of hydrogen bonding and π–π stacking [Xie et al., 2011]. We explore the possibility of synthesizing coordination polymer DMTD–Au under optimal conditions without using catalyst or extra control of other experimental condition and pH etc. Simple design reaction process is employed, in which the concentration of Au(III), DMTD and reaction conditions are systematically varied with progress of reaction and product, selectivity being monitored by several instrumental techniques. This compound is also compared with the Au(0)–DMTD composite in order to evaluate the difference in the coordination polymer and composite of the two components [Kannan et al., 2008]. Ultimately, this reaction process leads to an enhanced practical utility of synthesized coordination polymer DMTD–Au, thereby providing a platform for production of such polymers with physical properties competitive with all those of the existing coordination polymers.

It is first time to use gold salt for synthesis of coordination polymer, establish the structural features and its application in voltammetric sensing of resorcinol (RS) up to nanomolar level. Phenolic compounds which are extensively used in tanning, cosmetic, dye, pesticides, flavoring agents, medicines, antioxidants and photography chemicals, are highly toxic and low degradable in ecological environment therefore they have listed as environmental pollutants by the US Environmental Protection Agency (EPA) and European Union (EU) [Wang et al., 2003; Peng et al., 2006; Hu et al., 2012; Mobin et al., 2010]. Resorcinol is one of the phenolic compounds having high toxicity, it can be easily absorbed through the gastric tract and human skin, which can cause dermatitis, catarrh, convulsion and cyanopathy [Kang et al., 2000; Yang et al., 2006]. In recent years, various methods have been applied for determination of RS such as spectrophotometry, high–performance liquid

chromatography, quartz crystal microbalance, surface plasmon resonance and fluorescence spectroscopy [Mirmohseni et al., 2004; Wright et al., 1998; Vilchez et al., 2000]. However these methods require expensive and sophisticated instrumentation or complicated sample preparation with a moderate limit of detection. Further electrochemical technique has always offered simple instrumentation, low cost and portability. In this process, the concept of modified electrode is one of the exciting fields of electro analytical chemistry [Gupta et al., 2014]. Several existing electrochemical methods for RS sensing are based on immobilization of enzyme on modified electrode however we have demonstrated a simple non–enzymatic, highly accurate and rapid voltammetric method with DMTD–Au modified carbon past electrode for ultra trace level sensing of RS within a wide range of concentration.

2.2   Experimental

2.2.1   Materials

2,5–Dimercapto–1,3,4–thiadiazole (DMTD), and $HAuCl_4$ were purchased from Sigma Aldrich. Ethanol, resorcinol, sodium dihydrogen phosphate and disodium hydrogen phosphate from SRL, India were used as received unless otherwise mentioned. The electrode body used for construction of carbon paste electrode was obtained from Bioanalytical Systems. The glassware used in the synthesis of polymer was cleaned with freshly prepared aqua regia (3:1, HCl/HNO_3) and rinsed comprehensively with ultrapure water (Merck India).

2.2.2   Synthesis of coordination polymer (DMTD–Au)

In a typical synthesis of coordination polymer (DMTD–Au), ethanolic solution of $HAuCl_4$ (5.95 mM) was added to 2,5–dimercapto–1,3,4–thiadiazole (17.7 mM,

prepared in ethanol solution) under vigorous stirred condition for 18 h at room temperature under a thin stream of nitrogen gas as shown in reaction scheme (Figure 2.1). A pale yellow precipitate was obtained and then purified by filtration and washed several times with water ethanol mixture (30:70 v/v) to remove un–reacted DMTD and gold salt thereafter dried in vacuum for 15 h.
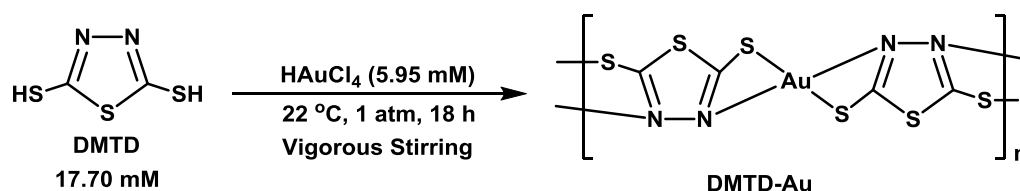
Figure 2.1 Reaction scheme for the synthesis of coordination Polymer DMTD–Au.

2.2.3   Instrumentation

Infrared spectra in KBr pellets were recorded with a Fourier transform infrared (FT–IR) spectrometer scanning from 2500 to 400 cm^{-1}. Raman spectra were measured with a micro Raman spectrometer at 180° scattering geometry (Renishaw, Germany) with a 514.5 nm line of an Ar+ laser at 50 mW at room temperature. TEM measurements were performed with Jeol Jem 2010 electron microscope operating at a voltage 200 kV on a carbon–coated copper grid modified with 5 μL of polymer solution in ethanol. ^{13}C NMR spectra of resulting polymers were recorded on a JEOL AL300 NMR (300 MHz) in DMSO–d_6 solvent and are reported in parts per million (δ) from residual solvent peak. Thermogravimetric analysis (TGA) was performed on a NETZSCH, STA 409 PC analyzer with a heating rate of 20 °C min^{-1} under a flow of N$_2$–gas. X–ray diffraction pattern for powder samples of coordination polymer DMTD–Au was carried out with 18 kW rotating anode powder X–ray diffractometer from 10°

to 80°, Rigaku, Japan with Cu–Kα radiation operating in Bragg–Brentano geometry and fitted with a graphite monochromator in diffracted beam with 3°min^{-1} scan rate. UV–Vis absorption spectra were recorded using Perkin Elmer Lambda–25 spectrophotometer by using a quartz cuvette with optical path length of 1 cm. Elemental analysis was recorded with X–ray photoelectron, Kratos Analytical Instrument, Shimadzu group company Amicus XPS, UK. The number–average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by Youglin ACME 9000 gel permeation chromatography in DMF at 40 °C with flow rate 0.5 mL/min on two polystyrene gel columns [PL gel 5 μm 10E 4 Å columns (300 x 7.5 mm)] connected in series to Gradient Pump and a RI detector. The columns were calibrated against seven poly(methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M–M–10). Electrochemical workstation (mode l700C), CH–Instrument Inc., USA is used for electrochemical measurement using three electrodes assembly consisting DMTD–Au carbon paste modified electrode as a working electrode, Pt foil as counter electrode and Ag/AgCl as reference electrode for all electrochemical measurements. Neutral phosphate buffer (pH 7.0) was used as a supporting electrolyte and scan rate was fixed 50mV/sec for each measurement.

2.2.4   Modified carbon paste electrode preparation

The active carbon paste was made by mixing known amount of DMTD–Au (2.5 %w/w) with graphite powder (67.5% w/w) in a mortar pestle followed by addition of Nujol oil (30%w/w). The absence and presence of DMTD–Au in active paste resulted into the formation of unmodified CPE and modified CPE/DMTD–Au systems. The mixture was thoroughly homogenized and filled manually in the cavity (1mm diameter)

of electrode body. Electrode surface was smoothed on clean butter paper applying pressure to get better electrical contact.

2.3   Results and Discussion

2.3.1 Structural, Morphological and Molecular weight studies of synthesized coordination polymer DMTD–Au

The FT–IR spectra of DMTD–Au and DMTD have been recorded in region 400–2500 cm^{-1} as shown in figure 2.2. In case of DMTD, region from 2450–2350 cm^{-1} contains several weak bands that derived from C–H stretching overtones and fermi resonances. Peaks appearing in the region 1300–1205 cm^{-1} are assigned to ring modes coupled to (exocyclic) C–C stretch and a ring stretching mode. The most prominent of these are the asymmetric stretches (ν_{as}) at 1500 cm^{-1} and symmetric stretch (ν_s) at 1407 cm^{-1} of C=N respectively, ν_{as} and ν_s modes of C–S–C stretches have been assigned to peaks at 718 and 658 cm^{-1} respectively. Further a strong IR–absorbing band at 1075 cm^{-1} is assigned due to an out of phase combination of N–N and symmetric C–S–C stretches which get reduced to 1049 cm^{-1} in DMTD–Au. DMTD–Au shows C=N band at 1384 cm^{-1}. Diminution in intensity of C=N bond and reduction in stretching frequency of C=N in DMTD–Au indicates interaction of nitrogen atom with gold which is also confirmed by Raman Spectroscopy. Raman spectrum of DMTD–Au (Figure 2.3) exhibit band at 380 and 546 cm^{-1} which arises due to Au–S and Au–N linkage respectively ensuring the metal–sulphur and metal–nitrogen linkage [Zaidi et al., 1977]. Further a band at 660 cm^{-1} in Raman spectrum is due to symmetric C–S–C stretch while absence of absorption peak near 522 cm^{-1} clearly indicates absence of S–S bond in coordination polymer DMTD–Au. The results from FT–IR and Raman spectroscopy

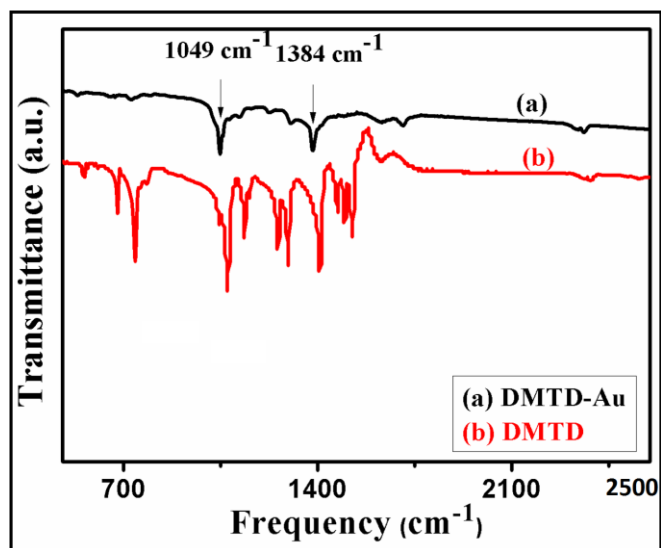reveal that gold ions are coordinated between DMTD molecules throughout the polymer chain.

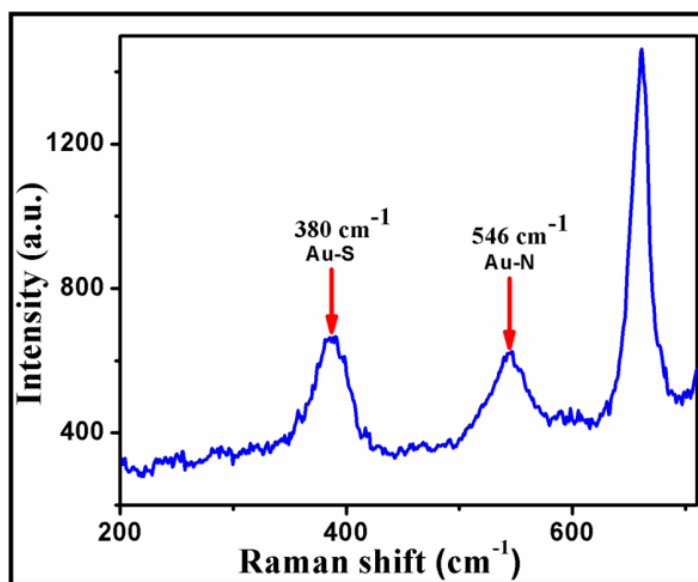**Figure 2.2** FT–IR spectra of (a) DMTD–Au and (b) DMTD.

Figure 2.3 Raman spectra of (a) DMTD–Au and (b) DMTD.

The architecture of DMTD–Au was investigated by powder X–ray diffraction (XRD) (Figure 2.4). The diffraction pattern of DMTD–Au and DMTD are stacked with

diffraction pattern of fully reduced gold (Figure 2.4) taken from JCPDS file CAS number 7440–57–5. Indexing for the diffraction peaks of DMTD–Au was performed by Dicvol software, which showed that the diffraction features are appearing at 2θ values of 28.28º, 40.44º, 50.10º, 58.58º, 66.30º and 73.56º corresponding to the (100), (110), (112), (200), (202) and (114) planes, respectively, for the tetragonal system. Sharp diffraction peaks confirm the crystalline characteristics of the polymer DMTD–Au. The present study reveals not only the crystalline nature of coordination polymer but also it demonstrates the absence of fully reduced gold within coordination sphere supporting XPS results.
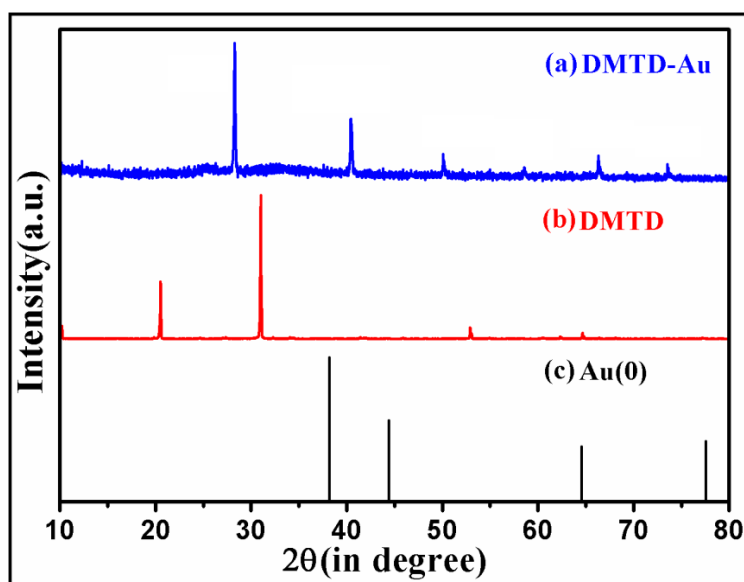

Figure 2.4 XRD of (a) DMTD–Au, (b) DMTD and (c) Au(0), taken from JCPDS file CAS number 7440–57–5.

The XPS study of DMTD–Au (Figure 2.5) reveals binding energy values 85.41 eV and 89.11 eV corresponding to Au(I) $4f_{7/2}$ and Au $4f_{5/2}$ respectively [Bourg et al., 2000; Li et al., 2012]. The Au $4f_{7/2}$ binding energy in DMTD–Au is shifted. The direction of this shift clearly corresponds to Au being oxidized in DMTD–Au and its

magnitude is similar to that observed for Au(I). The experimental photoemission curve of S(2p) signal (Figure 2.5b) can be fitted with two doublets i.e., two different atomic sulfur environments with $2p_{3/2}$ components peaking at 161 and 162.5 eV. The first one can be assigned due to aromatic sulphur, while the second is related to sulphur attached to gold ions [Bastus et al., 2009; Cui et al., 2011; Cai et al., 2012]. Nitrogen 1s binding energy 400.0 eV in figure 2.5c corresponds to N–N binding energy [Yang et al., 2010; Soylemez et al., 2013]. The binding energy is referenced to C(1s) of C=N at 287 eV [Yang et al., 2010] in figure 2.5d since the electronegative substituents decrease electron density of carbon atom causing a small increase in C(1s) binding energy.
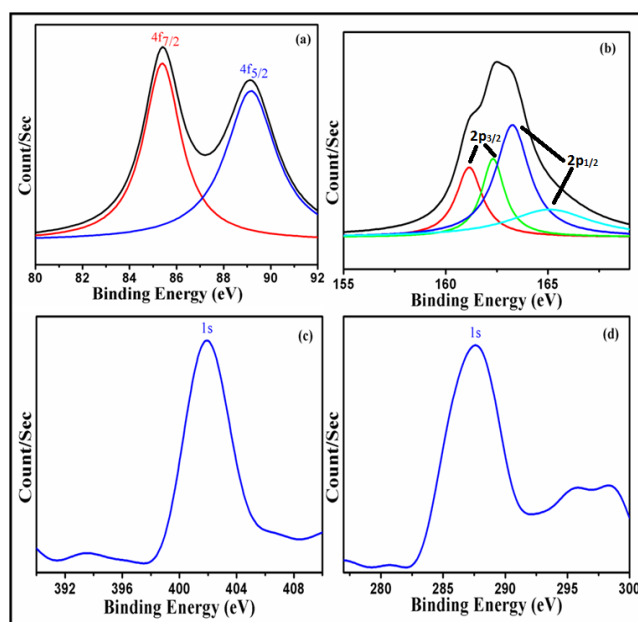
Figure 2.5 XPS spectra of DMTD–Au for Au(4f) (a), S(2p) (b), N(1s) (c) and C(1s) (d) regions.

The HR–TEM image (Figure 2.6) demonstrates that the rigid molecules of coordination polymer, DMTD–Au are arrayed in the coordination polymer sphere with an average diameter of about 170 nm having parallel porous nanospheres. It is reasonable to assume that the rigid coordination polymer DMTD–Au molecules are

arrayed due to the π–π stacking of adjacent molecular chains in the same plane. Corresponding SAED pattern clearly shows that synthesized coordination polymer has crystalline characteristics which support the XRD results.
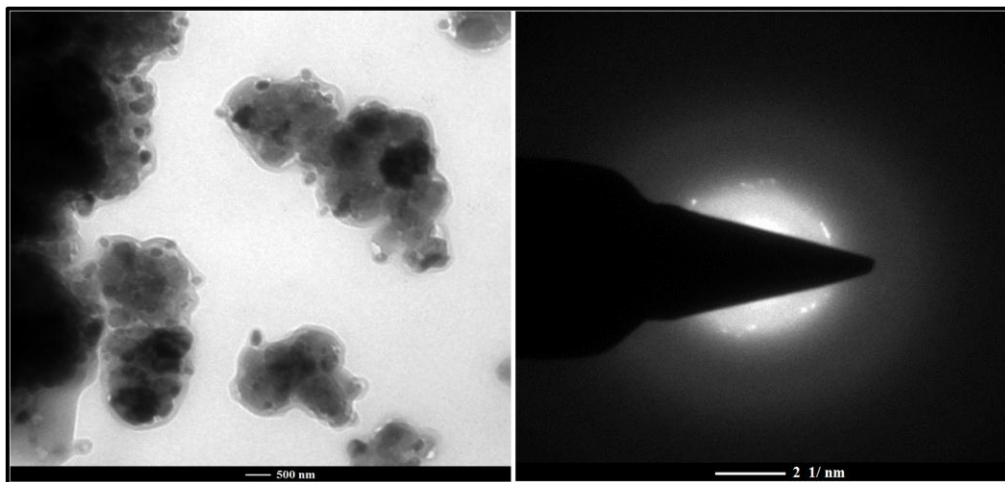

Figure 2.6 HR–TEM image (left) and corresponding SAED pattern (right) of DMTD–Au.

The synthesized coordination polymer DMTD–Au has a prominent peak at chemical shift value 206.95 (Figure 2.7) caused by strong deshielding of aromatic carbon (chemical shift value 177 is reported for DMTD) [Yamaguchi et al., 1999]. Down field shielding in chemical shift value for DMTD–Au signifies the interaction of metal with DMTD molecule. It displays that aromatic carbon atoms are in strong electronegative environment and are same in nature throughout architecture.

On account of various characterization techniques, possible chemical structure of DMTD–Au has been proposed as shown in figure 2.8 which supports the ^{13}CNMR, FT–IR, RAMAN, GPC, HR–TEM and XPS results.
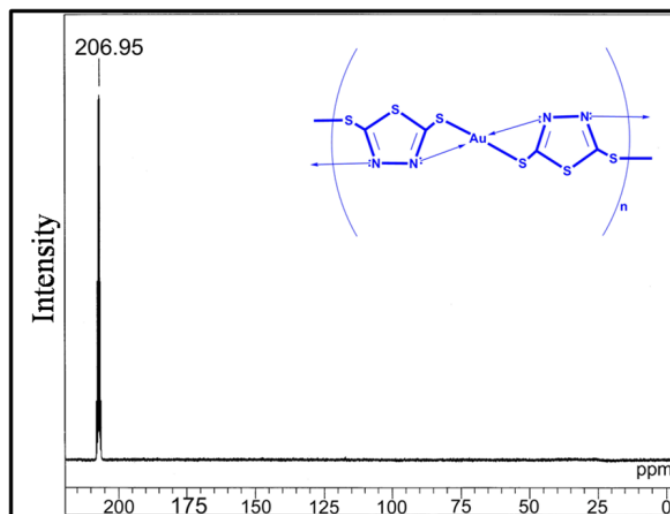
Figure 2.7 ^{13}CNMR spectra of DMTD–Au in DMSO–d_6 at room temperature.
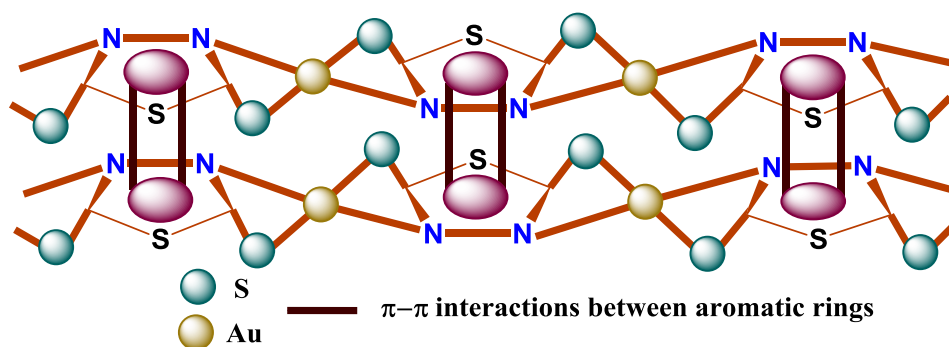
Figure 2.8 Proposed structure of synthesized coordination Polymer DMTD–Au.

The molecular weight distribution of coordination polymer DMTD–Au was determined by gel permeation chromatography. The figure 2.9 shows the chromatogram which clearly indicate that molecular weight of dominant fraction is located around Mn = 376655 gmol^{-1} (PDI–2.32). The minuscule humps are due to fragmentation of polymeric chains and traces of lower molecular weight polymeric fragments. The UV–Vis spectrum of DMTD–Au (Figure 2.10) exhibit the maximum absorption peak at about 433 nm with a shoulder at 323 nm are attributed due to π–π* and MLCT (Au→π*) transition respectively [Roberts et al., 2012]. Thermal analysis of polymeric

sample was examined by TGA (Figure 2.11) under N_2 atmosphere by varying the temperature to 800 °C at heating rate of 20 °C min^{-1}. The first weight loss (2%) occurred in the temperature range of 40–140 °C accounts for the uncoordinated water molecules which includes the lattice and adsorbed water molecules. Degradation of DMTD–Au starts at 260 °C which may be due to cleavage of metal–sulphur and metal–nitrogen linkage indicating a good extent of thermal stability of synthesized coordination polymer. It exhibits two sharp exothermic peaks near 280 °C, 600 °C and two endothermic peaks at 510 °C, 730 °C.

Broido demonstrated a method to evaluate the activation energy related with thermal decomposition. The equation developed for calculation of activation energy (E_a) is as follows:

$$lnln\ (1/Y) = - (E_a/R)\ 1/T + constant\ \ \dots\dots Eq(1)$$

$$Where\ Y = W_t - W_\infty / W_0 - W_\infty$$

Y is fraction of number of initial molecules not yet decomposed; W_t – weight at anytime t, W_∞ – weight at infinite time (= zero) and W_0 – initial weight. A plot of lnln (1/Y) *vs.* 1/T gives an excellent approximation to a straight line. The slope is related to activation energy for thermal decomposition. Activation energy using Broido model as shown in figure 2.12 is measured as 25.20kJ/mol with R^2 value 0.984 [Broido, 1969].
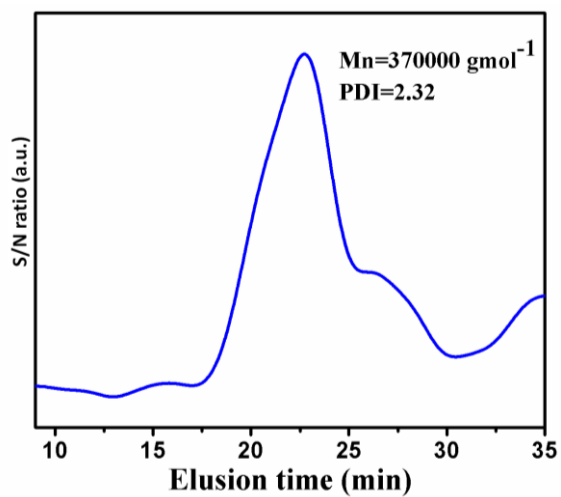
Figure 2.9 Gel permeation chromatogram of DMTD−Au.
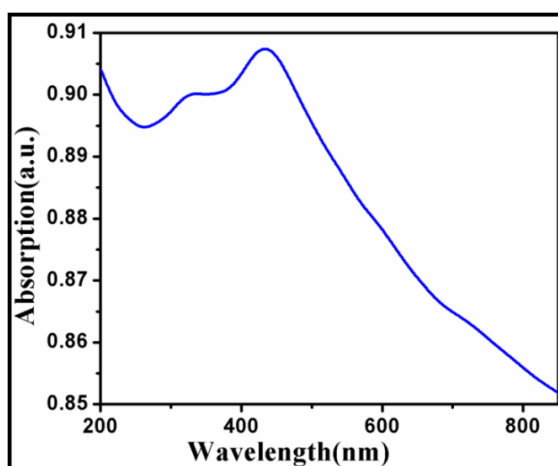
Figure 2.10 UV−Vis spectrum of coordination polymer DMTD−Au.
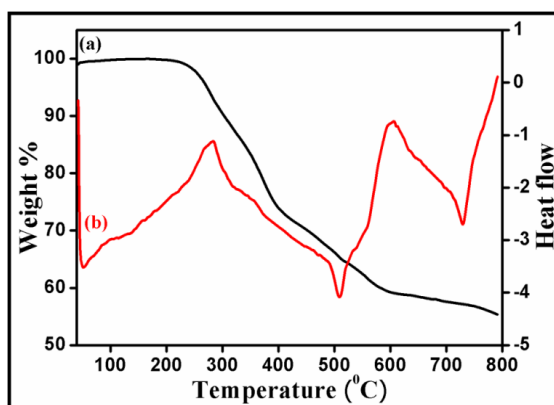
Figure 2.11 TGA (a) and DTA (b) plot of DMTD−Au.

2.3.2 Electroanalysis of CPE/DMTD–Au modified electrode

The cyclic voltammetry of DMTD–Au modified carbon paste electrode was examined in presence of 0.02 M Fe(II) /Fe (III) redox couple in 0.1 M phosphate buffer solution (PBS) pH 7. Significant increase in peak current of Fe(II) /Fe (III) redox couple was observed with DMTD–Au modified carbon paste electrode as compared to unmodified carbon paste electrode for the same amount of Fe(II) /Fe (III) redox couple (Figure 2.13), which reveals that DMTD–Au polymeric material facilitates electron transfer and can be used as an excellent electrocatalytic material.
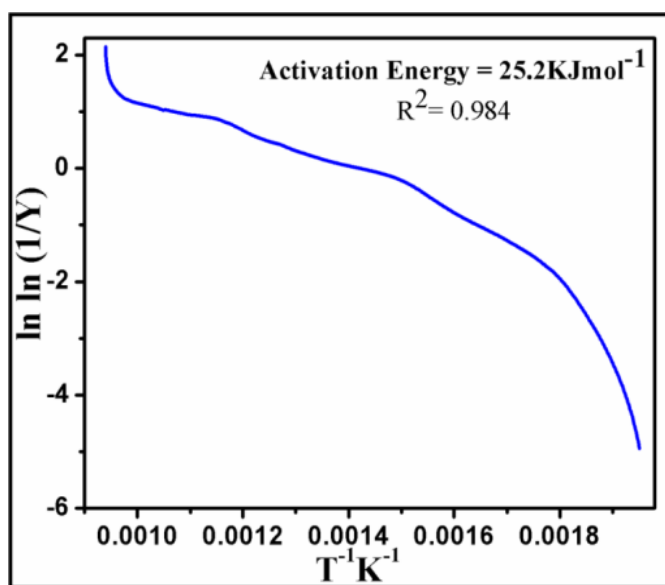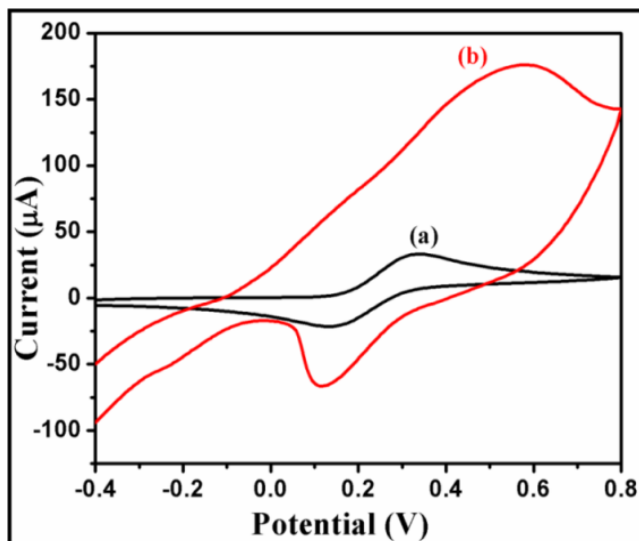

**Figure 2.12** Thermal activation energy plot of DMTD–Au.

Figure 2.13 CV for 0.02 M Fe(II) /Fe(III) in 0.1 M PBS (pH 7) at unmodified carbon paste electrode (a) and (DMTD–Au) modified carbon paste electrode (b).

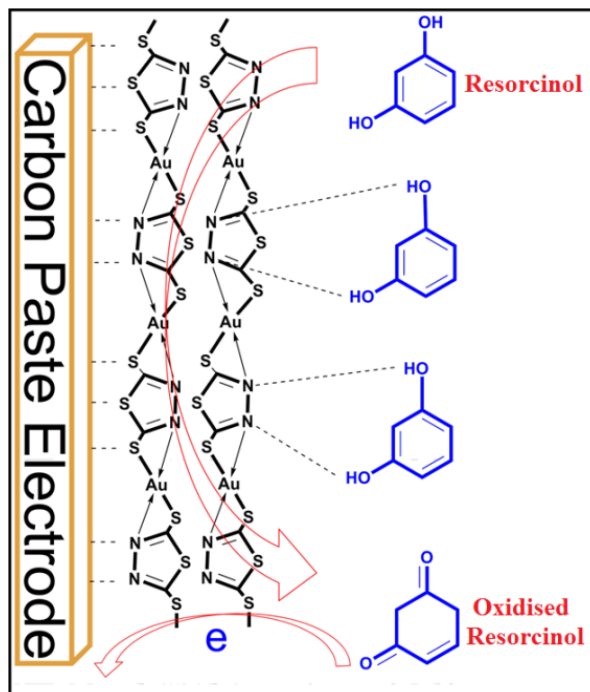### 2.3.3   Voltammetric Sensing of Resorcinol

The synthesized coordination polymer has been further utilized for voltammetric sensing of resorcinol by DMTD–Au modified carbon paste electrode in phosphate buffer solution. We have selected potential window region 0 to 0.9 V for voltammetric sensing of resorcinol as oxidation of resorcinol is expected in this region. Resorcinol did not show any peak at bare carbon paste electrode in PBS at trace concentration; also the characteristic peak of modified carbon paste electrode was absent in the selected potential range. Resorcinol addition shows anodic peak at potential 0.55 V *vs* Ag/AgCl over modified electrode (Figure 2.14). The electrochemistry behind this electro–sensing of resorcinol is probably because of the catalytic effect of DMTD–Au which exhibit faster electron transfer kinetics *via* interaction of diazole nitrogen with hydroxyl group of resorcinol through hydrogen bonding as shown in schematic representation (Figure 2.15). The potential utility of present modified electrode was further examined by recording the voltammetric response on successive addition of resorcinol in PBS

pH 7.0. A systematic change in current was noticed after each addition of resorcinol into supporting electrolyte solution as shown in voltammogram (Figure 2.16a). This DMTD–Au modified carbon paste electrodes do not suffer electrode fouling and poisoning problem for resorcinol detection which is major limitation of other existing modified electrodes. Stability of the electrode is also an important factor for biosensing applications and was tested repeatedly more than 5 times by using the same modified carbon paste electrode. Calibration plot of resorcinol concentration *vs* peak current (Figure 2.16b) provides the sensitivity and limit of detection as 0.019 µA/nM and 29.77 nM respectively at R^2 0.999 and S/N (signal–to–noise ratio) 3.
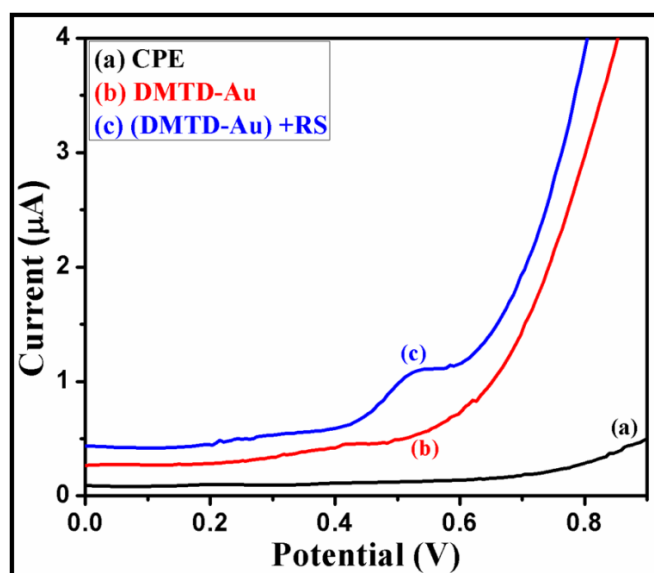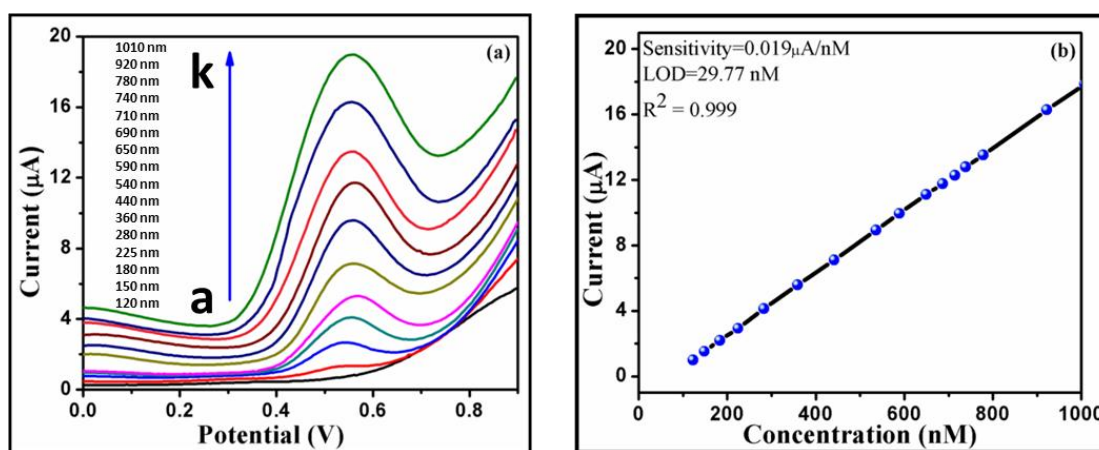

Figure 2.14 DPV response of unmodified carbon paste electrode (a), (DMTD–Au) modified carbon paste (b) and DMTD–Au modified carbon paste + RS (c) in phosphate buffer pH 7.

Figure 2.15 Schematic representation of voltammetric sensing mechanism of resorcinol.

Figure 2.16 Differential pulse voltammogram of RS at various concentrations (112.60 $\times 10^{-9}$ to 1.09 x 10^{-6} M) in 0.1 M phosphate buffer (pH 7.0) at DMTD–Au modified carbon paste electrode (a) and corresponding standard addition calibration plot of current *vs.* resorcinol concentration (b).

2.4   Conclusions

This work presents one–pot facile synthesis of coordination polymer (DMTD–Au) at room temperature. The synthetic method is very simple, requires no catalyst to initiate the polymerization which can have commercial applications in drug delivery, gas storage, catalysis and sensing applications. The molecular weight of DMTD–Au is 376655 g mol^{-1} (PDI–2.32) and activation energy of synthesized material evaluated using Broido model is 25.21 kJ/mol at R^2 value 0.984. The DMTD–Au molecules are aligned parallel and polymeric layers are stacked on account of π–π stacking and hydrophobic interaction. Further the redox activity of DMTD–Au is explored in electrochemical determination of resorcinol up to nanomolar concentration with modified carbon paste electrode. Under the optimized conditions, DMTD–Au modified carbon paste electrode (DMTD–Au/CPE) shows the anodic peak current at lower positive potential (0.55 V) than other existing methods and exhibit linear response towards resorcinol concentration with sensitivity and limit of detection 0.019 µA/nM and 29.77 nM respectively at S/N 3. The developed coordination polymer based modified electrode possesses advantageous properties of larger active surface area, stability and rapid electron transfer rate which cumulatively demonstrate the excellent performance toward the electrocatalytic oxidation and detection of resorcinol. Notable conclusions of modified electrode surface demonstrate that DMTD–Au can be used to assemble a selective and sensitive sensor for resorcinol through the formation of intermolecular hydrogen bonding *via* hetroatom. With regard to future research directions, we hope to broaden the scope for the synthesis of such thiadiazole–gold coordination polymer encapsulated with other valuable metal ion and finding their

potential application towards chemical sensors, biomedical applications, biosensors and

other electrochemical purposes.