

SYNTHESIS AND CHARACTERIZATION OF BISMERCAPTO (2, 2':6', 2''-terpyridine) Ru(II)-COMPLEXES STABILIZED GOLD NANOPARTICLES AND THEIR ELECTRO CATALYTIC REDUCTION OF NITRITE

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ABSTRACT

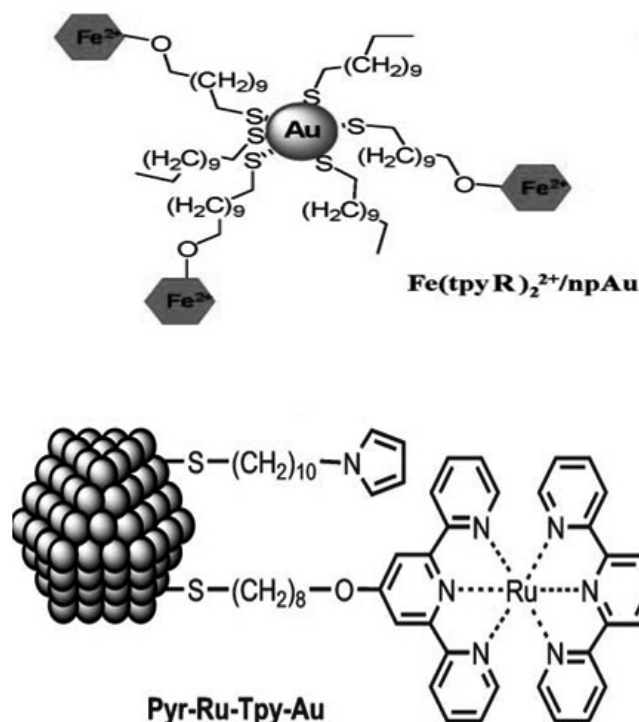
Inorganic-organic hybrid structures based on metal-complexes particularly, octahedral bis-2,2':6',2''- terpyridine metal complexes provide an advantages of increased symmetry and in the case of ruthenium(III)/ruthenium(II) complexation an entrance to a directed complexation Method. The Ru (II) terpyridine methane thiolate protected gold nanoparticle was synthesized through covalent bonding of Ru terpyridine methane thiolates over gold nanoparticles surfaces. The ligand terpyridine methanethiolate was synthesized successfully in good percentage of yield. The structures were confirmed and characterized by different physical, analytical, spectral data like FTIR, UV, SEM and Cyclic voltammetry. All the data are shown the expected results.

Keywords: Ru(II) terpyridine, Au nanopartcles, thiolates, electro catalytic reduction of nitrite

1. INTRODUCTION

2, 2'-bipyridine (bpy) has been announced to be "the most used ligand in coordination chemistry"¹, 2, 2':6', 2''-terpyridine (tpy) also has a rich chemistry. The coordination chemistry of the substituted terdentate ligand has attracted many chemists. 2, 2':6', 2''-terpyridine has been reacted with very many metals to prepare complexes. The kinetics and mechanism of formation of metal complexes and their stability have also been studied²⁻⁶. 2,2'-bipyridyl has take part in an important role in building many mixed-ligand complexes for their desired predictable co-ordination behavior and their photophysical and electrochemical properties⁷⁻⁹. The 2,2'-bipyridyl and ligands derived from it also extensively used in different areas, such as supramolecular assemblies, molecular scaffolding, electrochemistry catalysis, biochemistry, and biochemistry, ring-opening metathesis polymerization¹⁰⁻¹⁵, biologically

photoredox reactions¹⁶, synthetic, medicinal chemistry, biotechnology¹⁷ and solar cell¹⁸. Synthesis of TiO₂-Al₂O₃-SiO₂ nanopowder composite, as well as composite coating on soda lime glass and Si (100) by sol-gel method is reported¹⁹. We demonstrate here the application of this approach to the formation of stable inorganic nanocomposites featuring systematic control of interparticle spacing. Metal-mediated nanoparticle assembly was studied using mixed monolayer protected gold clusters (MMPCs). In these nanoparticles, the distance of the terpyridine functionality to the metal core was systematically varied by altering the chain lengths of the terpy ligand and the supporting monolayers. The comparison of interparticle spacing as a function of monolayer thickness required uniform cluster core size for MMPCs. The control of core size was achieved by using the pentane thiol stabilized monolayer protected cluster (MPC) as the nanoparticles source for the fabrication of all MMPCs. MPC was prepared following a previously reported protocol.



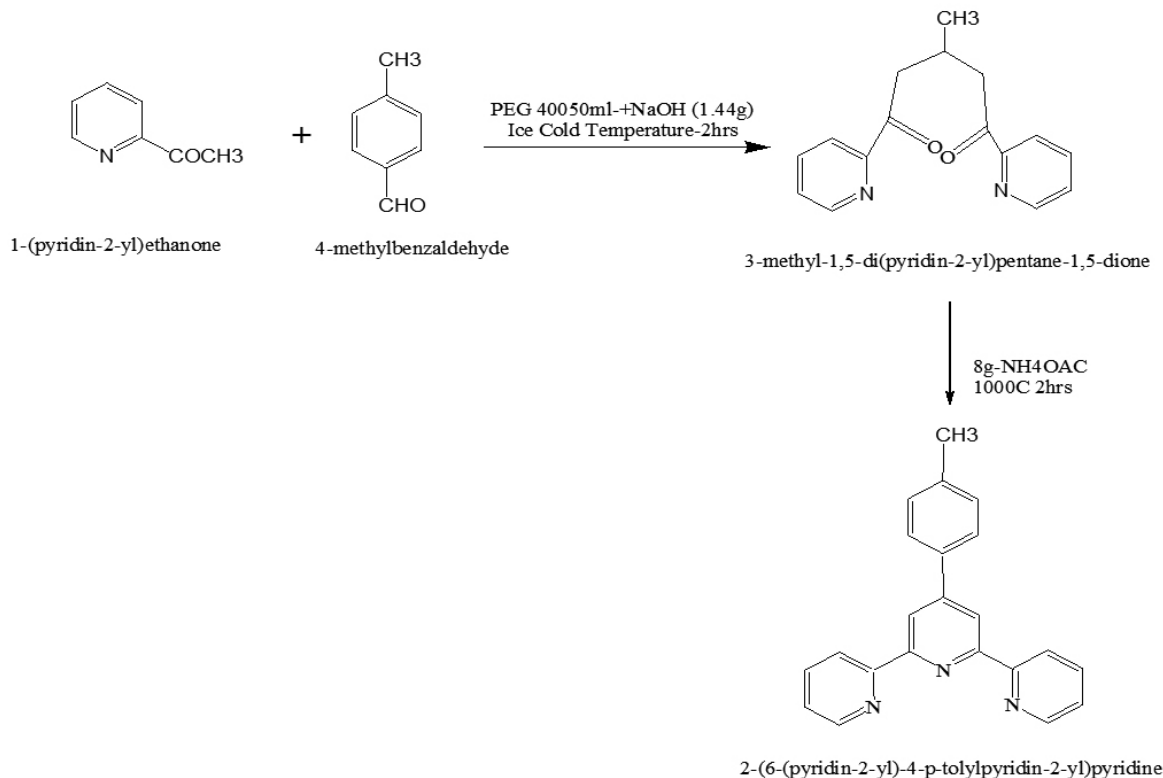
In present investigation, is to synthesized metal terpyridine complex protected with Au nanoparticle. The characterization of that nanoparticle is also tested.

2. Experimental Details

Step 1: 2-(6-pyridin-2-yl)-4-p-tolylpyridin-2-yl pyridine

2-acetylpyridine (4 ml, 35.6 mmol) was added to a suspension of crushed NaOH (1.44 g, 0.036mmol) in PEG400 (50 ml), and stirred at ice cold temperature for 10 minutes. 4-methylbezaldehyde (2.2 ml, 18mmol) was

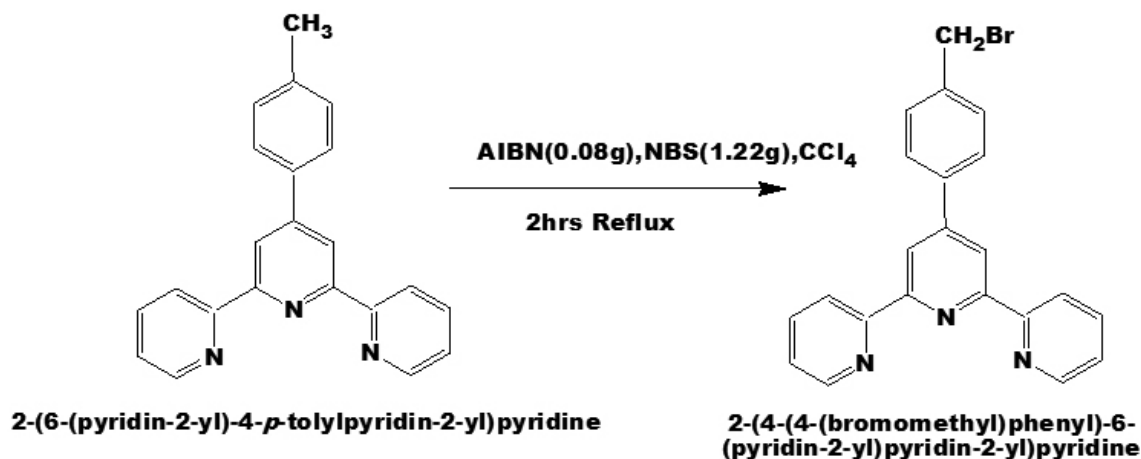
then added by syringe and the suspension left standing at ice cold temperature for 2 hrs. Stirred with magnetic stirrer, the solution became red and high viscous. After 2 hrs, NH_4OAc (8g, excess) was added and the suspension heated at 100°C for 2 hrs. During this time, the colour of the mixture changed from red to brown, and accompanied by formation of a fine brown precipitate of the product ²⁶⁻³⁰. Water (50 ml) was added and the pasty precipitate of 2-(6-pyridin-2-yl)-4-p-tolylpyridin-2-yl) pyridine isolated, washed with water (50 ml) and cold EtOH (50 ml). Light yellow massive powder yield: 1.902g.



Step: 2

4'-(4-Bromomethylphenyl)-[2,2':6',2'']terpyridine.

A mixture of 4'-(methyl phenyl)-2,2':6',2''-terpyridine (1.6g, 4.8mmol), *N*-bromsuccinimide (NBS, 1.22 g, 7.4 mmol), and *R,R'*-azoisobutyronitrile (AIBN, 0.08g, 0.48 mmol) in dry CCl_4 (60 ml) was refluxed for 2 hrs. The warm reaction mixture was filtered to remove the succinimide, and the solvent was evaporated by Rota vapor. The crude product was pale-yellow solid yield: 1.1611 g. ³¹



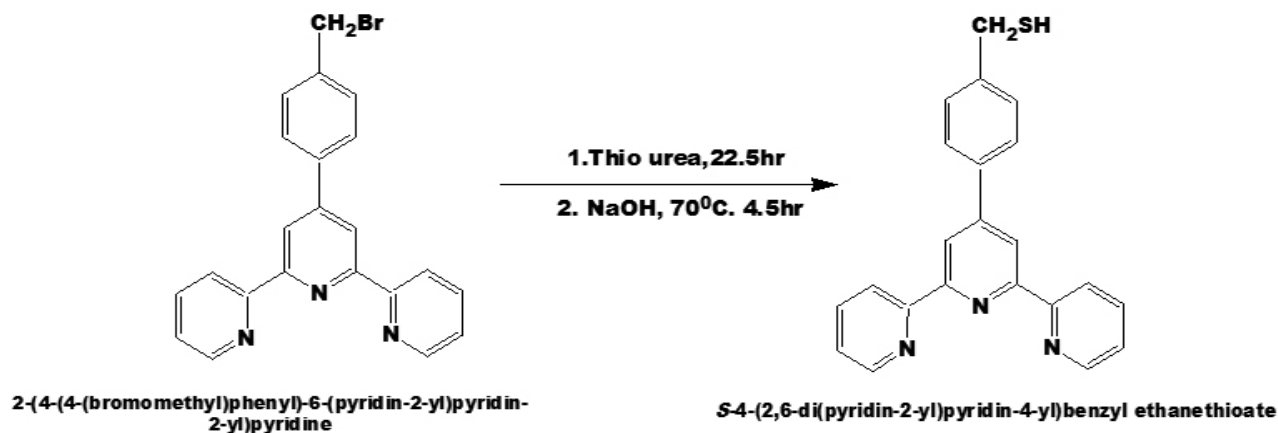
Step: 3

4'-(4-mercaptomethylphenyl)-2, 2':6, 2''-terpyridine

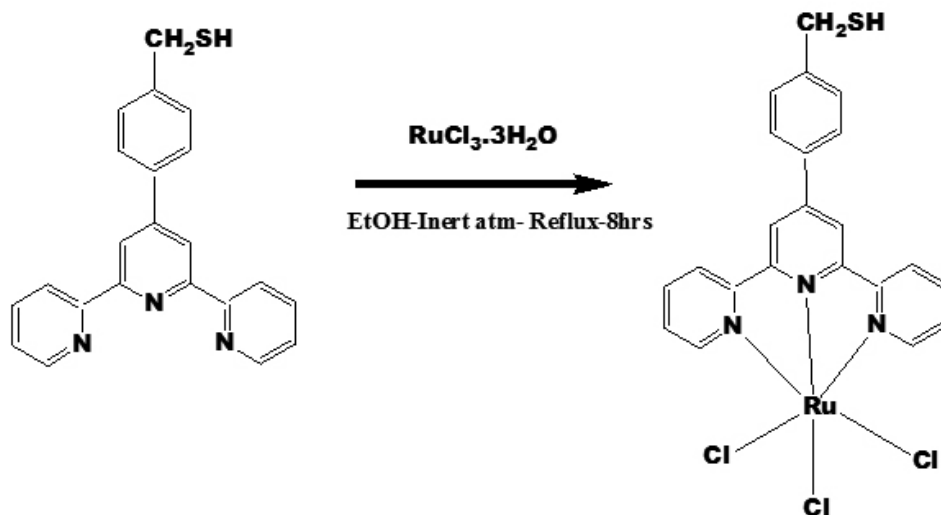
A solution of 4'-(4-bromomethylphenyl)-2, 2':6, 2''-terpyridine (0.5212 g, 1.24 mmol) and 0.048 g (1.34 mmol) of thiourea in 130 ml of ethanol-acetone mixture (1:1, v/v) was heated at reflux for 22.5 h. After cooling, the precipitate was filtered, washed with acetone, and dried to give 0.481g (89%). A mixture of (0.481g, 1.21mmol) and NaOH (0.42g, 1.1 mmol) in 40 ml of water was heated at 70°C for 4.5 h. After cooling, the precipitate was filtered and washed with water, and then dried under vacuum at room temperature overnight to give 4'-(4-mercaptomethylphenyl)-2, 2':6, 2''-terpyridine (1.324 g). ^{32,33}

Step: 4. Synthesis of terpyridine Ruthenium (III) Complexes.

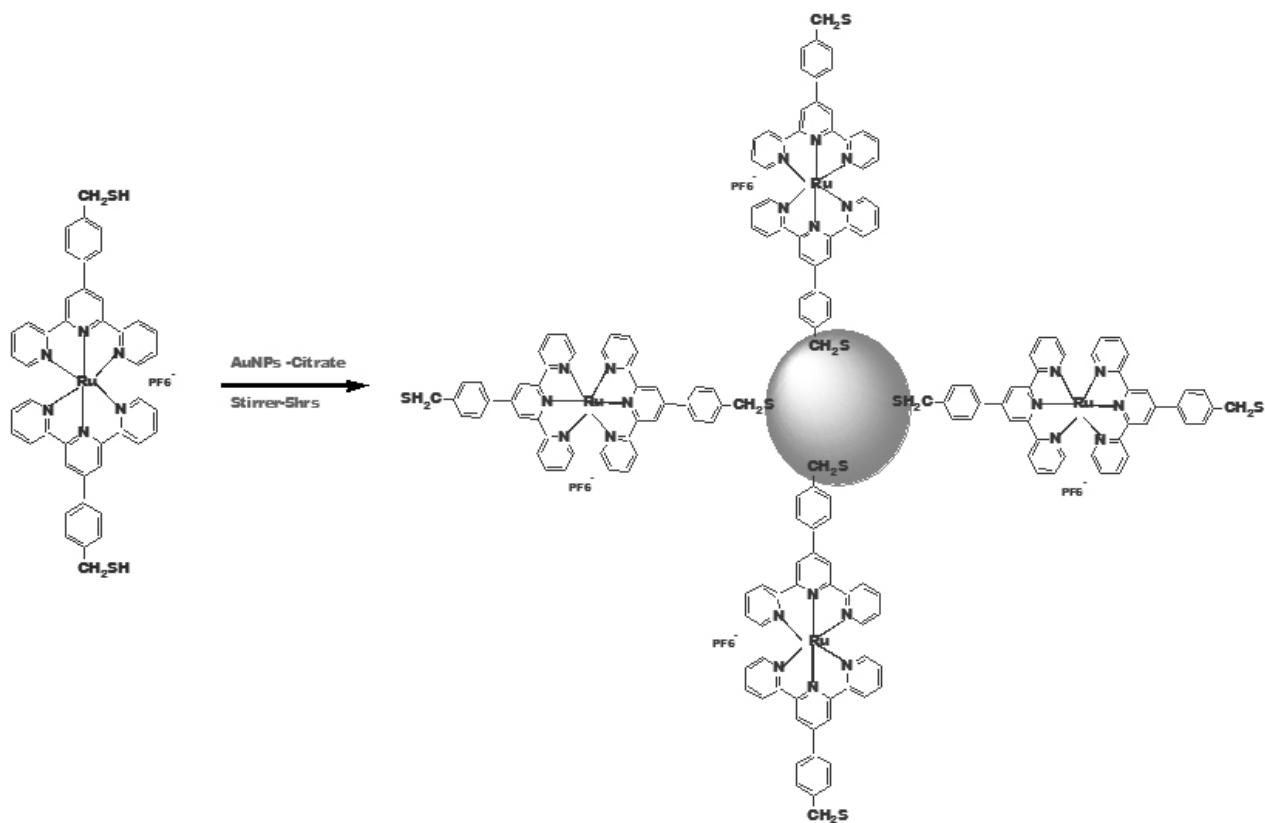
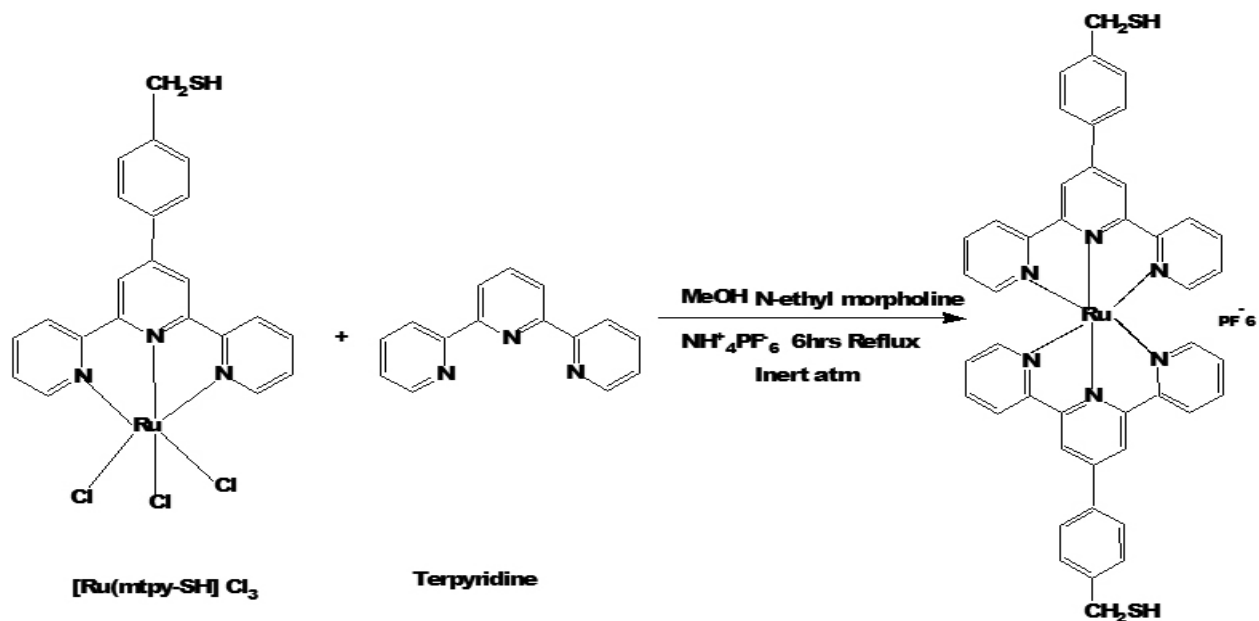
2, 2':6'2'-terpyridine (mterpy-SH) (0.20 g, 1.23 mmol) was added to $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (100 mg, 1.23 mmol) in ethanol and refluxed for 8 hrs under an inert atmosphere. The mixture was cooled and the dark brown precipitate was collected by filtration, washed thoroughly with methanol, water and diethyl ether and dried under vacuum. Yield: 0.20 g.

**Step: 5. Synthesis of ruthenium (II) complexes**

terpy (0.131 g, 0.812 mmol) was added to $[\text{Ru}(\text{mterpy-SH})\text{Cl}_3]$ (0.20 g, 0.813 mmol) in methanol along with *N*-ethylmorpholine (5 drops). The mixture was refluxed for 6hrs and an inert atmosphere. The resulting deep red solution was filtered and a three-fold excess of methanolic ammoniumhexafluorophosphate was added to the filtrate. The resulting red precipitate was filtered off and recrystallized from acetone-acetonitrile solution and dried under vacuum. Yield: 0.750 g

**Step: 6. Synthesis of Ru-Terpyridinethiolates functionalized AuNPs nanoparticles.**

The ligand-exchange reaction of Ru-Terpy-Au with a Citrate capped AuNPs was carried out as follows. A mixture of $[\text{Ru}(\text{TerpySH})_2]^{2+}$ (50 mg) and AuNPs (5ml) were added in MeCN (10 mL) was stirred at room temperature for 48 hrs. To the mixture was added EtOH (200 mL) and then the resulting precipitate was collected by filtration and washed several times with EtOH. The nanoparticles were dissolved in MeCN to purify and precipitated with EtOH, and then the particles were isolated by filtration.



3. RESULT AND DISCUSSION

3.1 UV-Visible Spectrum

The grafting of terpy SH is confirmed by the presence of a peak at 276 nm, attributed to $\pi-\pi^*$ transitions from the aromatic groups. The terpyridine groups of terpy SH molecules were exposed and provide sites for the coordination of ruthenium ions. Addition of ruthenium ions to the terpy SH functionalized

Au-NPs led to a further decrease of the intensity. Moreover, the presence of a shoulder at 520 nm, attributed to the metal to ligand charge transfer (MLCT) of $[Ru(terpySH)_2]^{2+}$, confirmed the in situ formation of the bis-terpyridine ruthenium complex. This feature is already observed after complexation of pre-functionalized spherical gold nanoparticles²⁴. Functionalization of Au-NRPs by preformed $[Ru(terpySH)_2]$ the spectra were recorded upon excitation at 280 nm. The result is shown in fig. 4a and 4b.

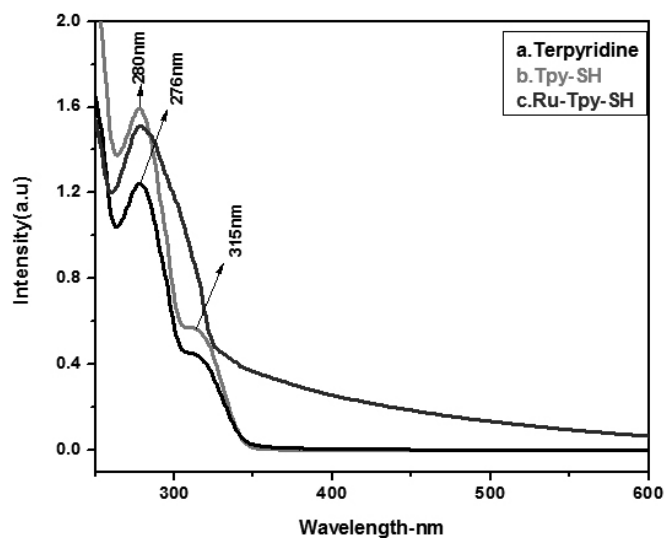
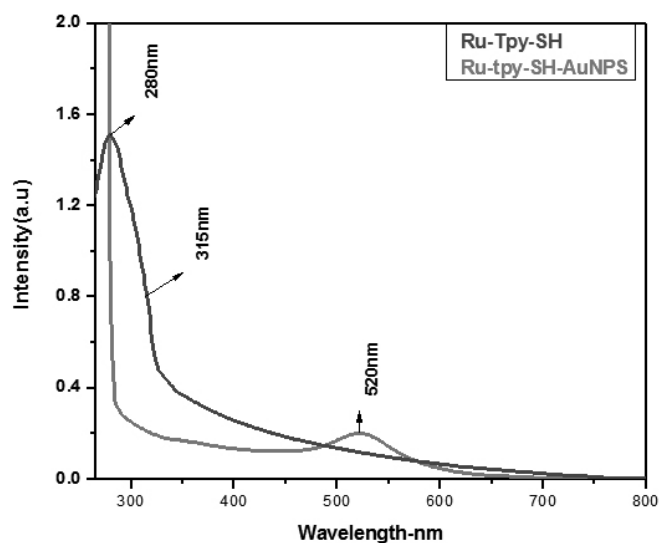
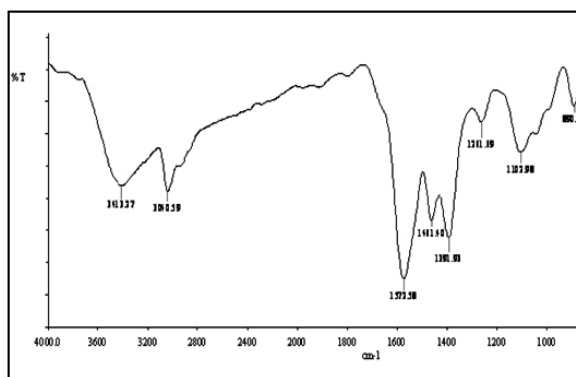


Fig. 4a and 4b.

3.2 FT-IR Spectrum.

FT-IR spectrum showed characteristic absorption bands at 3052, 1602 and 1466 cm^{-1} (aromatic); 1584, 1566 cm^{-1} (C=C and C=N stretching vibration of pyridine); 824, 792 cm^{-1} (C-H deformation vibration of pyridine); 740 cm^{-1} . terpyridine ligands and their complexation deformation of pyridine; 2926, 2854 cm^{-1} (C-H stretching of aliphatic) and 962 cm^{-1} . FT-IR-Spectrum of $[\text{Ru}(\text{terpy-SH})_2]^{2+}$, $[\text{Ru}(\text{terpy-SAuNPs})_2]^{2+}$ are shown below.



The result shows in fig. 5a, 5b, 5c.

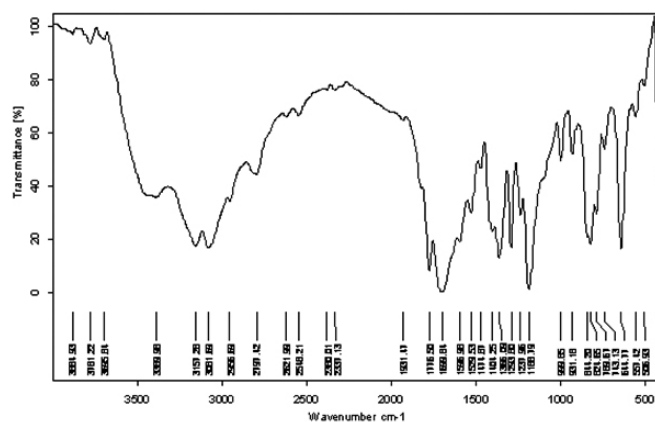


Fig. 5a Terpyridine.

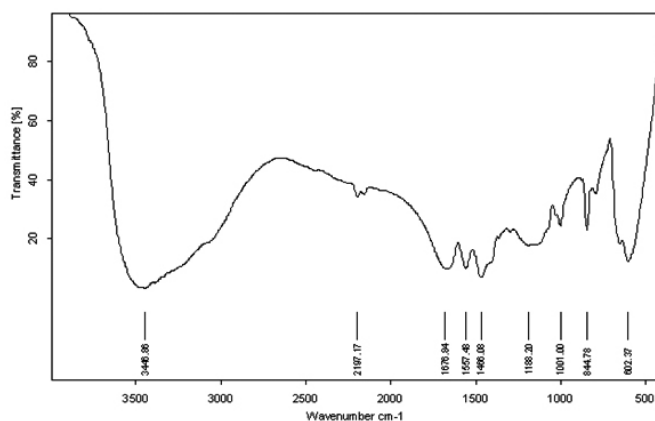


Fig. 5b (Bromomethyl)terpyridine.

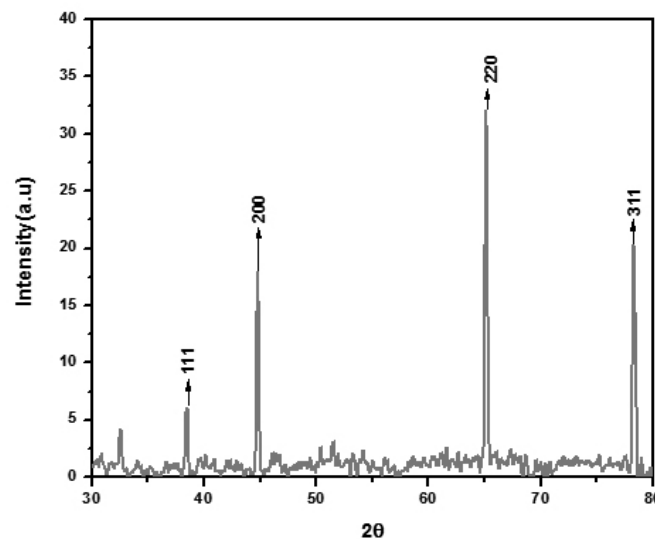


Fig. 5c Ru-Terpyridinethiolates.

3.3. X-ray diffraction of Ru-Terpy-SAuNPs.

XRD spectrum measurements confirm that the crystal structures of the nanoparticles are face-center-cubic (fcc) (Joint Committee for Powder Diffraction Standards (JCPDS). Moreover, XRD pattern of the gold sample with the Ru-Terpy-S-Au nanoparticles synthesized indicating that crystalstructure of the nanoparticles was FCC (JCPDS 4-0783).

Fig. 7: X-ray diffraction of Ru-Terpy-SAuNPs.

3.4 SCANNING ELECTRON MICROSCOPE.

This result indicates that the Ru-(terpy)²⁺ complexes are present. Field emission scanning electron microscopy (FESEM) indicates a rather smooth and homogeneous surface structure with few aggregates distributed statistically over the substrate (Fig. 8a, 8b) shows a FESEM micrograph of the same diluted sample with isolated Au nanoparticles of spherical shape and of an average apparent size of about 100 nm. The SEM pictures evidence the existence of nanoparticles with EDAX. The results shows in fig. 9.

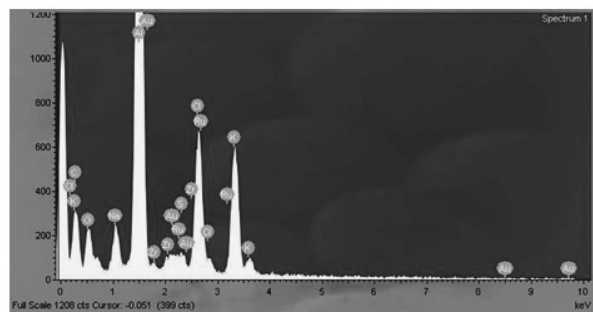
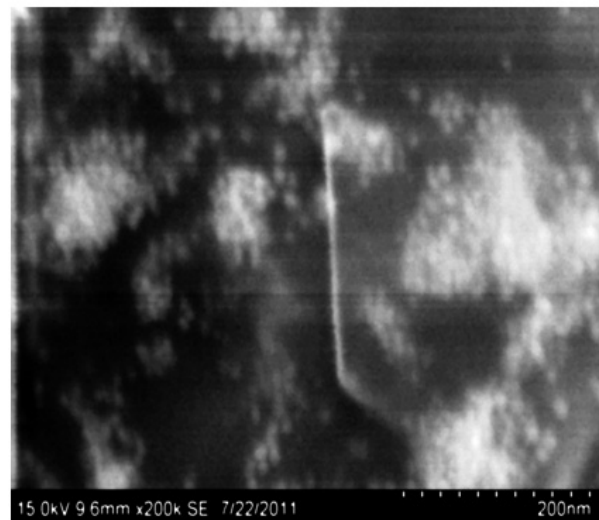
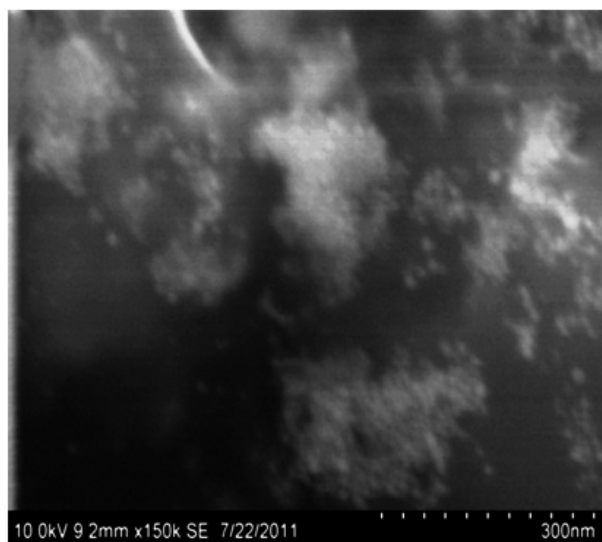


Fig. 8a, 8b and 9 SEM- Ruthenium- Terpyridine-S-AuNPs-Complexes and EDAX.

3.5 Electrochemical Studies- Terpyridine Complexes-Ru-Terpy-AuNps

The complex is electrochemically active and exhibits a reversible (83 mV) ruthenium (II/III) process at +0.9 V in MeCN solution of interest for potential applications of this type of complex in electrochemical devices, is the observation of a second quasi-reversible process at +1.08 V assigned to the oxidation of the thioether sulfur. This second process is absent in the model complex [Ru(terpySH)₂][PF₆]₂ (terpy = 2,2':6',2''-terpyridine) and is characteristic of the thioether-functionalised compounds.

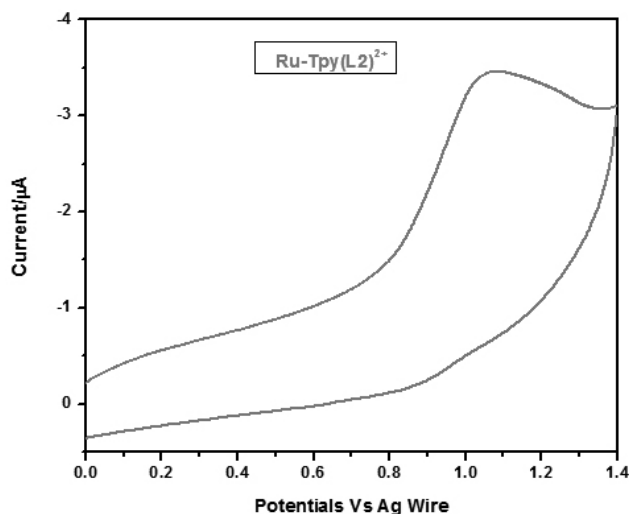


Fig. 10: Terpyridine complexes -Ru-Terpy-AuNPs.

3.6 Electro Modification Of Complexes Studies Of Ru-Terpy-Au.

The electro activity of Ru-Terpy-Au was performed by cyclic voltmetry (CV). The first scan of the CV of Ru-Terpy-Au in 0.1 M TBAP-MeCN at a GC electrode exhibited a single irreversible oxidation wave at E_p = +1.16 V(vs. Ag/0.1 M AgNO₃) which seems to overlap the oxidation peaks of the ruthenium(II)/(III) couple. Repeat scans showed an increase in the redox-peak currents. After fifty scans, the electrode was rinsed copiously with solvent and dipped into fresh 0.1 M TBAP-MeCN solutions. The CV of the Ru-Terpy-Au modified GC electrode showed two irreversible peaks due to terpyridine at 21.58 and 21.91 V and one reversible redox peak due to the Ru(II)/(III) couple at +0.95 V (ΔE_p = 114 mV). Thus metal nanoparticles bearing a Ru-terpyridine complex are readily immobilized on metal electrode surfaces.

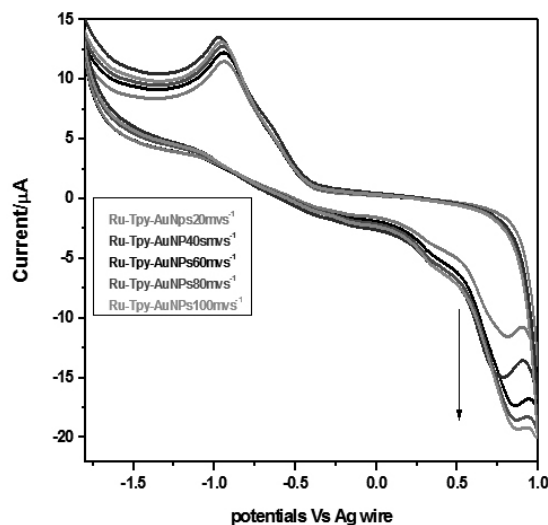


Fig. 11: Electro modification of complexes studies of Ru-Terpy-Au.

3.7 Electrocatalysis Of Nitrite Reduction By Using Ru-(Terpys)²⁺Au Nps/GC Modified

At a bare GC and at the modified GC in 0.1 M phosphate buffer solution pH 7. This fig. 12 shows the GC bare electrode no cathodic reduction current, and modified GC electrode reduction of nitrite cathodic negative potential is high compare than GC electrode. Increasing the cathodic peak current increases with different scan rate by using [Ru (terpyS-AuNPs)₂]²⁺/GC modified electrode. The reduction of Nitrite Ru^(II) [(terpyS-AuNPs)₂]²⁺/GC modified electrode at reduction potential range -0.68V compare than GC electrode reduction potentials of nitrite fig. 13.

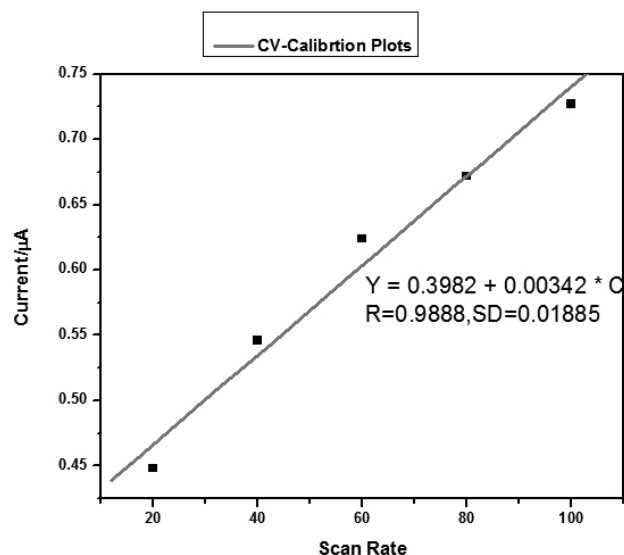
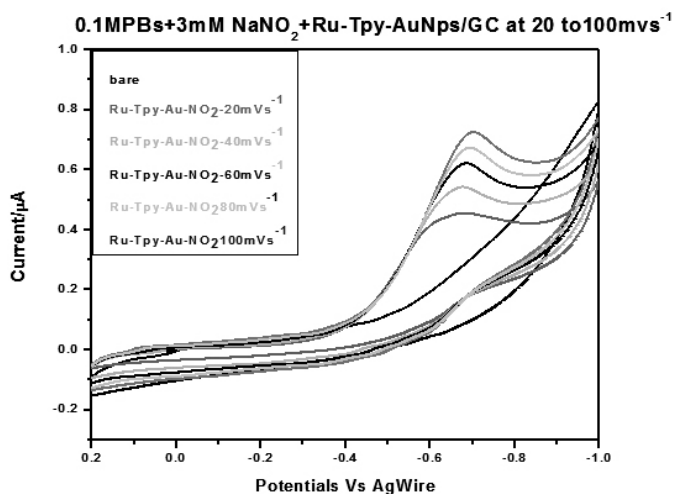
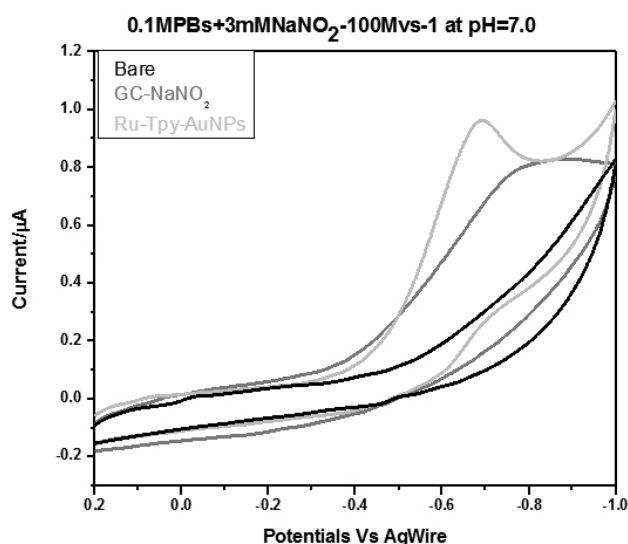
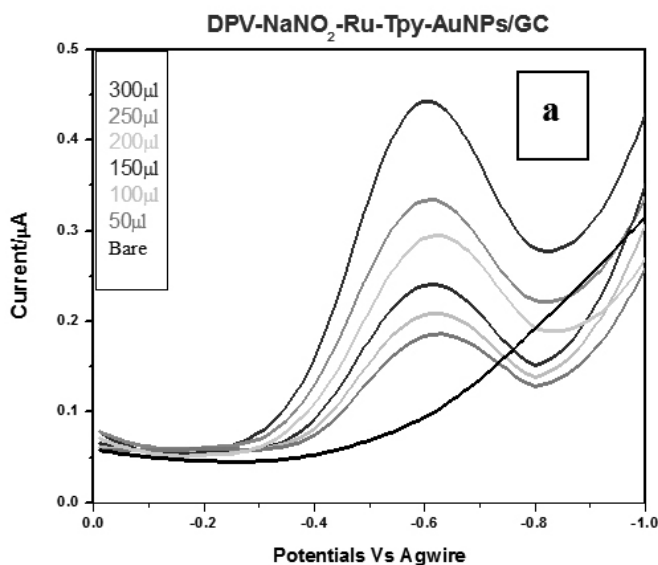


Fig. 12: Electrocatalysis of nitrite reduction by using Ru- (TerpyS)²⁺AuNps/GC modifie.

3.8 Electrocatalytic detection of NaNO₂ by using GC/Ru-Terpy-AuNPs electrode.



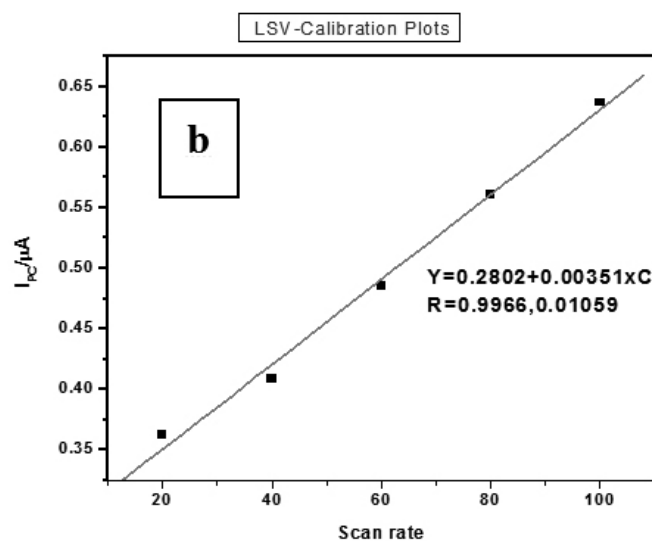
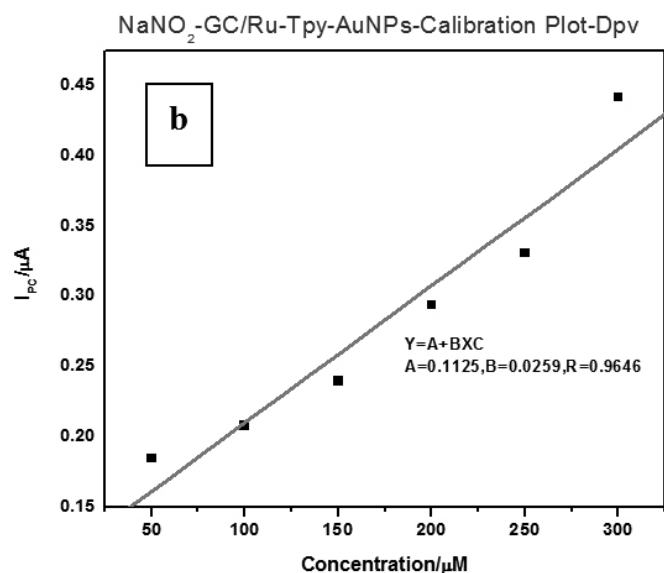
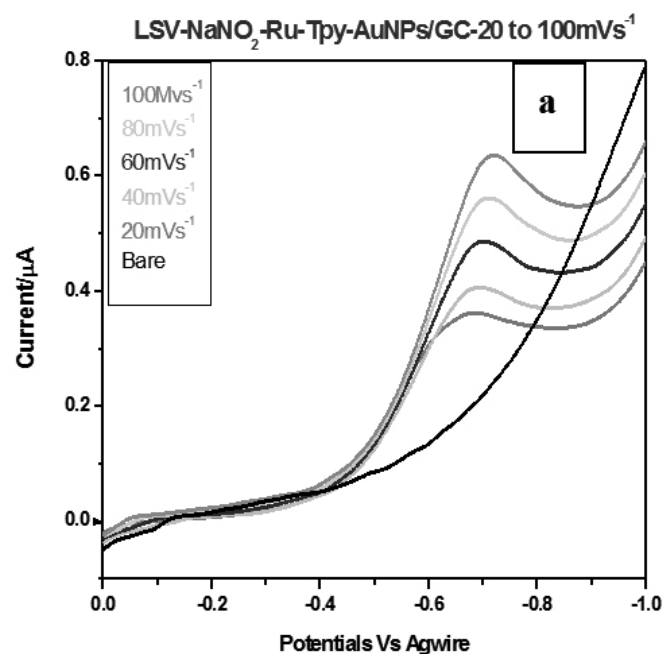


Fig. 13: Electrocatalytic detection of NaNO₂ by using GC/Ru-Terpy-AuNPs electrode.



4. CONCLUSION

The Ru (II) terpyridine methane thiolate protected gold nanoparticle was synthesized through covalent bonding of Ru terpyridine methane thiolates over gold nanoparticles surfaces. The ligand terpyridine methanethiolate was synthesized successfully in good percentage of yield. The structures were confirmed and characterized by different physical, analytical, spectral data from, ¹H NMR, FTIR, UV, SEM and Cyclic voltammetry. All the data are showing the expected results. The complexes [Ru (terpy-S-AuNPs)₂]²⁺ modified on GC electrodes at potentials negative of the nitrite reduction peak. The electrochemical response of Ru (terpy-S-AuNPs)₂²⁺-modified GC electrodes in aqueous solution was more robust than in acetonitrile solution, and the response of the nitrite reduction process was shown to be pH dependent in solutions out of the range of pH 7. Therefore [Ru (terpyS-AuNPs)₂]²⁺ complex modified GC electrodes were found to catalyze the reduction of nitrite in pH-7 phosphate buffer solution.

5. REFERENCES

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