## Review Article

# Nanogold-Bound Copper Complexes and Their Various Applications: A Review Article

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## Abstract

The term "nano gold," also known as "gold nanoparticles," is commonly used. These particles are extremely small, with a diameter of less than 100 nm, which is only a fraction of the width of a human hair. Due to their tiny size, nano gold particles are often found in a colloidal solution, where they are suspended in a liquid stabilizer. This colloidal gold is essentially another name for nano gold. The main method for producing gold nanoparticles in a colloidal solution is the citrate synthesis technique, which involves combining different solutions to precipitate the gold nanoparticles[1-5]. In biological systems, copper complexes play a significant role at the active sites of many metalloproteins. These complexes have potential applications in various catalytic processes that occur in living organisms, such as electron transfer reactions and the activation of specific antitumor substances. These processes are relevant in the fields of medicinal chemistry and bioinorganic chemistry. The interaction of copper chelates with biological systems and their noteworthy activities against neoplastic, bacterial, fungal, and cancerous cells are also important. Many copper (II) N, S, O / N, N-donor chelators function as effective anticancer agents due to their ability to bind with DNA base pairs[6-10]. Using hydrophilic gold nanoparticles (AuNPs) as carriers for copper complexes is a novel and purposeful strategy that Could raise these compounds' stability and solubility in $H_2O$ aqueous., thus enhancing their bioavailability. The regulated release of Cu-complexes made possible by this method also creates the possibility for fruitful in vivo and in vitro tests. The definition, significance, and numerous applications of copper complexes in connection to nanogold are presented in this review study[11-15].

**Keywords:** Nano gold, Copper Complexes, Applications.

## Introduction

A variety of frameworks, comprising nanorods, bipyramids, gold nanoshells, nanobowls, spiky nanoshells, terahedra, octahedra, cubes, and cages, could be generated through synthesizing nanogold. A silica nanoparticle core may occasionally be encased in gold, and gold nanoparticles may occasionally have a silver coating. The size and form that are chosen must match the intended use since they have a direct impact on light interacts with the material (Fig. 1)[16-20].

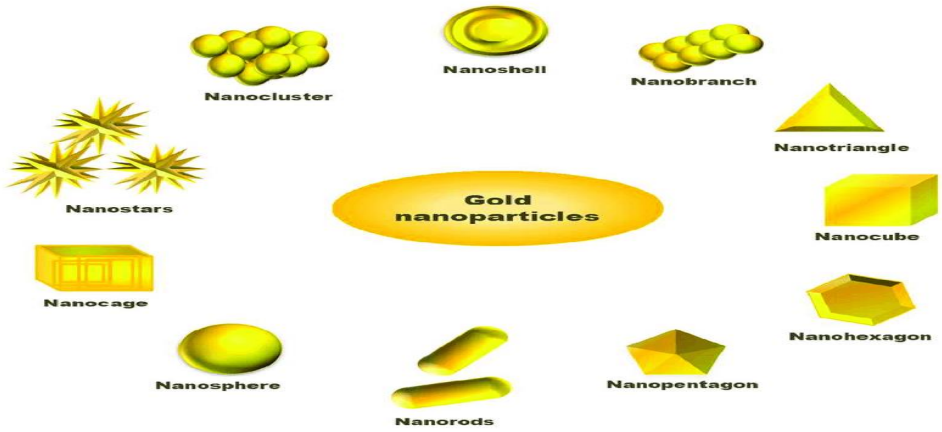



**Fig.(1): Different forms of Gold nanoparticles**

Copper complexes may possess a variety of geometry with different types and numbers of ligands, ranging from square planar, octahedral, tetrahedral, trigonal planar, and square pyramidal geometry. Despite the fact that an extensive variety of complexes have been accomplished, the synthesis and design of novel copper complexes by varying the nature of the reactants and synthetic conditions is still under investigation (Fig. 2)[21-25].

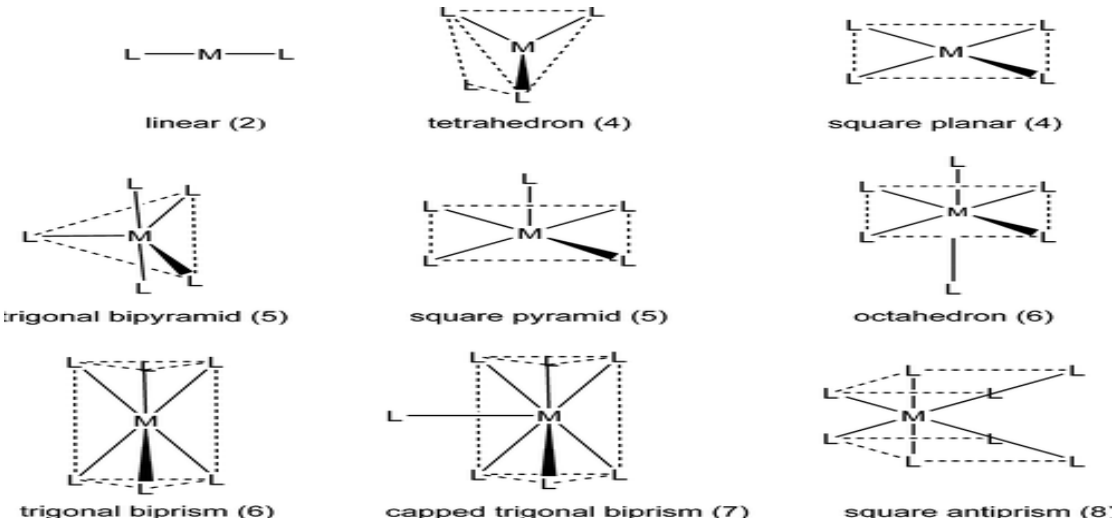



**Fig.(2): Geometric structures of copper complexes**

Recently, biomedical research has been concentrating on developing novel metal-based anticancer medicines that can be used in place of Pt(II) compounds. Significant emphasis has been paid to the research of new Cu-based antitumor agents using diverse metals such as gold, ruthenium, silver, and copper. This strategy is motivated by the assumption intrinsic metals may be less hazardous for regular cells than malignant cells. Furthermore, copper(II) complexes containing hexyl bis(pyrazol-1-yl) acetate ligands have recently been investigated as prospective catalysts for improving the efficiency of the Kharasch-reaction, which involves the oxidation of alkenes at the allyl position. The synthesis technique encompasses the utilization of soft donor atom-containing ligands, such as the aromatic $sp^2$ hybridized nitrogen that exists in pyrazolyl derivatives[26-29]. Given the restricted solubility of these coordination compounds in aqueous environments, a strategic strategy is required for effective administration of medicines. Conjugating copper complexes with hydrophilic gold nanoparticles provides a strategy for improving their solubility, stability in water, and eventually, their bioavailability. Furthermore, this drug delivery method allows for the regulated and progressive release of copper complexes. In this sense, we utilized SR-XPS and NEXAFS spectroscopy to investigate the molecular and electronic structures of selected Cu(II)-coordination complexes. The investigation involved examining the metal ion's oxidation state and local coordination chemistry employing Cu K-edge XAFS in both near-edge (XANES) and extended (EXAFS) regions. To create a comparison, we additionally glanced at the pristine ligands[30-33]. The deployment of complementary probes, namely XPS-NEXAFS-XAFS, has provided a precise and dependable understanding of the local coordination chemistry and electronic structure of Cu(II)-coordination complexes. Through coupling with hydrophilic AuNPs, these compounds can serve as vital components for the assembly of nanoassemblies. Some members of our team have previously successfully tested this strategy utilizing model systems[34-38]. In this paper, we indicate the outcomes of a multidisciplinary assessment of Cu(II)-coordination compounds, in addition to preliminary observations about interactions between coordination compounds and AuNPs. We additionally emphasize future research directions (Fig. 3).

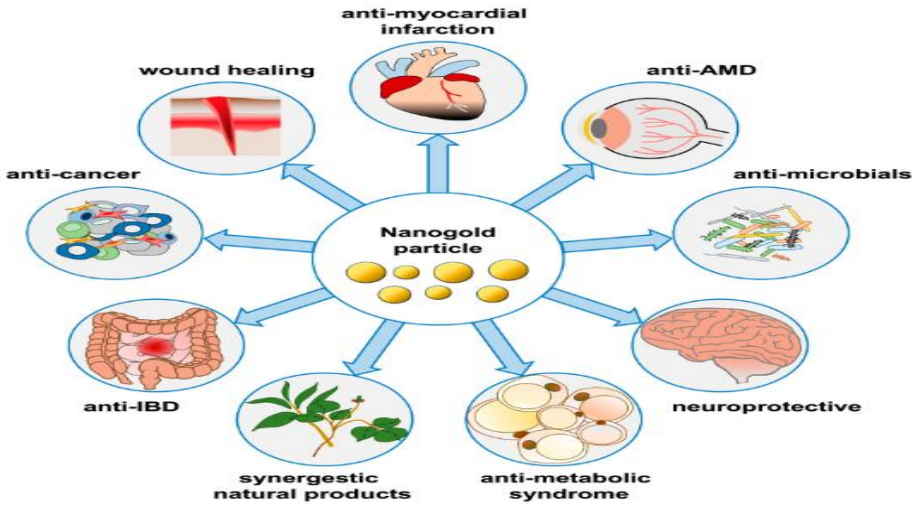
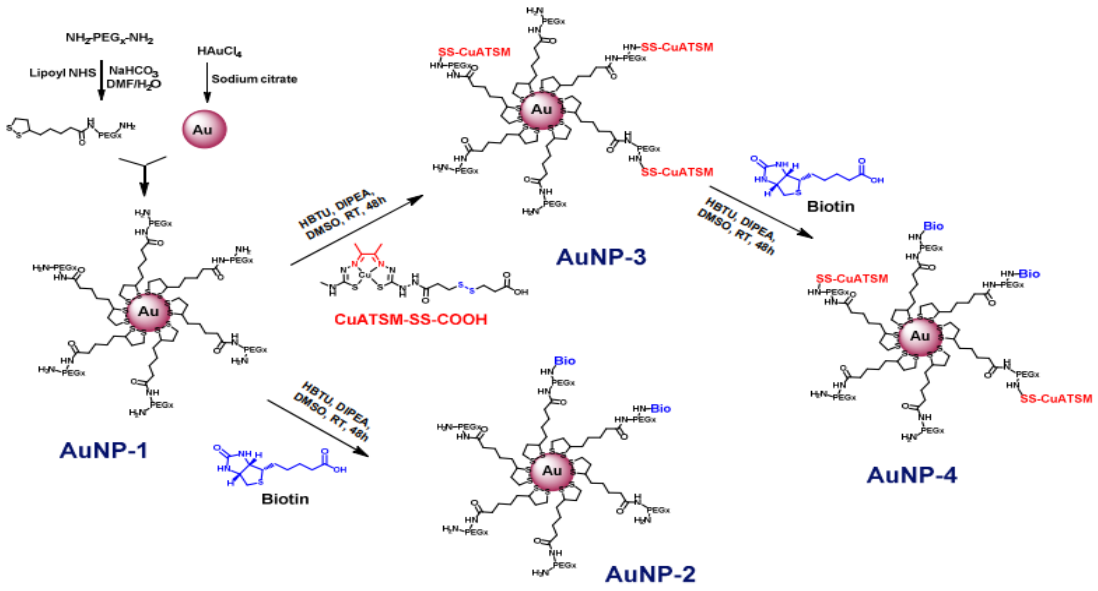



**Fig.(3): Application of Nano gold particle**

## Literature review

In order to assess the anticancer effectiveness of a copper(II) diacetyl-bis(N4-methylthiosemi carbazone) complex and its nano conjugates, Anup Kumar Pramanik and associates carried out a study in 2016,[39]. A cleavable disulfide bond that the researchers used to connect the copper(II) complex to a carboxylic acid group allowed for effective distribution. They created highly soluble gold nanoparticles (AuNPs) by mixing copper with amine-terminated lipoic acid and polyethylene glycol (PEG) to increase their solubility in water. To enable focused activity, biotin was added to the gold nanoparticle carrier's surface. The researchers tested HeLa and HaCaT cells to determine the anticancer potency of the copper complex and its conjugates. Surprisingly, whereas the conjugates completely eliminated cancer in HeLa cells, which are derived from cervical carcinoma, they only showed limited effectiveness against HaCaT cells. Due to the breakdown of the disulfide linker in the presence of glutathione (GSH), a reducing chemical frequently present in cancer cells, the conjugates displayed a progressive and controlled release of the complex. It's interesting to note that when tested against HeLa cells, the biotin-added conjugates did not perform better. This conclusion was reinforced by drug uptake tests that demonstrated similar in vitro uptake characteristics for both types of conjugates. The tumor volume of the biotin-conjugated nanoparticle group was shown to be reduced by 3.8 times when compared to the control group, whereas it was only reduced by 2.3 times in the case of the non-biotin conjugates in in vivo study employing a HeLa cell xenograft tumor model. This indicates significant targeting effects.




**Scheme (1): A demonstration in which PEG stabilized gold nanoparticles and nano-conjugates are made.**

In 2016, Nguyễn Hoàng Ly et al., [40] introduced a novel technique for detecting $Cu^{2+}$ ions in environmental and biological solutions. This technique demonstrated high selectivity and sensitivity. The researchers utilized gold nanoparticles (AuNPs) coated with glycine (GLY) in a hydrazine buffer. The dissociative adsorption of GLY on the AuNPs resulted in distinctive CN stretching peaks at approximately 2108 $cm^{-1}$. X-ray photoelectron spectroscopy confirmed the presence of Cu species on the AuNPs, while UV-Vis spectra indicated aggregation of the Au particles. Interestingly, the formation of the GLY-$Cu^{2+}$ complex caused a noticeable color shift, indicating destabilization. The synthesis of CN variety from GLY on the surface of hydrazine-covered AuNPs was evident from the CN stretching band at around 2108 $cm^{-1}$. Importantly, further ions, including $Fe^{3+}$, $Fe^{2+}$, $Hg^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cr^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Ca^{2+}$, $NH^{4+}$, $Na^{+}$, and $K^{+}$ at concentrations as high as 50 µM, did not lead to similar spectral vagaries. The revealing limit for $Cu^{2+}$ ions using the CN band was found to be as low as 500nM in distilled water and 1M in river water. Furthermore, the researchers also explored the potential application of this technique for intracellular ion detection in cancer cells, highlighting its practicality (Fig. 4).

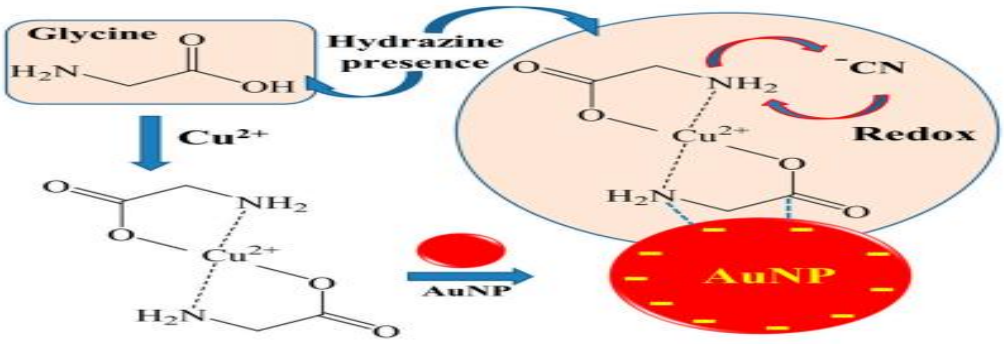



**Fig. (4): The diagram illustrates the detection process of $Cu^{2+}$ ions, which occurs through the redox assets that cause the dissociation of GLY into CN groups on the surfaces of Au-NPs in the occurrence of hydrazine.**

In 2023, Minako Oshima et al. [41] synthesized supramolecular systems that contained chiral Schiff base complexes of Ni(II), Cu(II), Zn(II), and colloidal gold nanoparticles (AuNPs) with diameters of 10 nm in 2017. They were able to recognize different induced CD spectra, indicating direct adsorption of chiral Schiff base metal complexes onto the surface of AuNPs. The purpose of the study was to evaluate and clarify the induced CD bands displayed by chiral Schiff base complexes of Ni(II), Cu(II), and Zn(II) on AuNPs, as illustrated in Fig. (5).

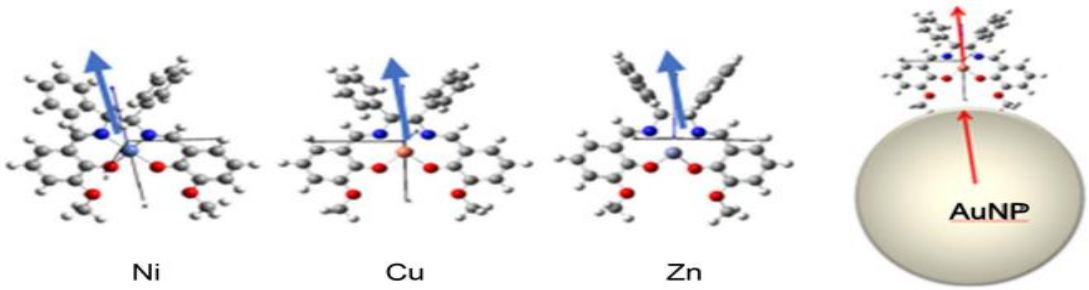
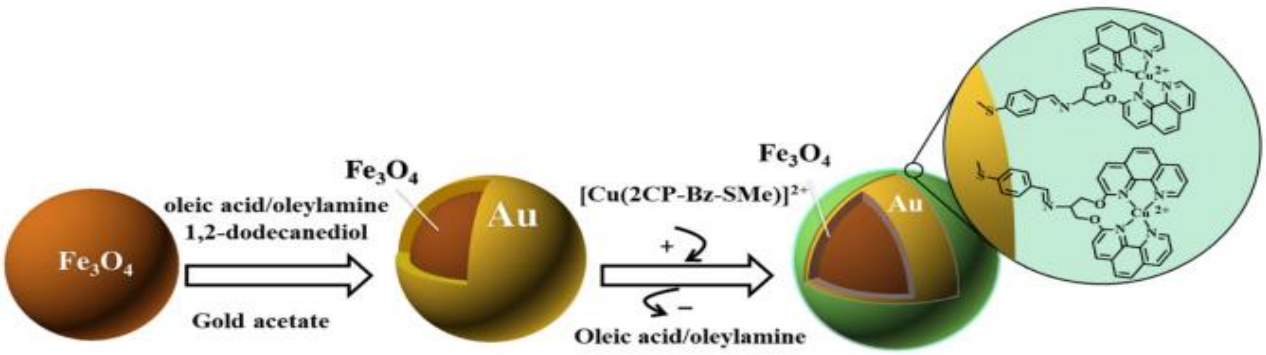



**Fig. (5): [Left] Calculated electric dipole moments for compounds 1a, 1b, and 1c of optimal structures (blue arrows in comparable directions with somewhat different magnitudes). Supramolecular hybrid systems comprising chiral complex and AuNP, as proposed (right).**

In 2018, Maria A.S. Silvaa et al. [42] conducted an in-depth investigation of magnetic nanoparticles for their prospective utilization for medication administration and imaging probes in 2018. The research focuses on the creation of a magnetic platform utilizing a modular capping technique. Magnetic gold-coated $Fe_3O_4$ nanoparticles ($Fe_3O_4$@Au) were produced and subsequently functionalized using a clip-phen thioether derivative complex of copper (II) ($Fe_3O_4$@Au@Cu).

[Cu(2CP-Bz-SMe)] is a copper compound. binds DNA and possesses nuclease activity. Raman scattering investigation validated the functionalization of $Fe_3O_4$@Au with the copper complex through the sulfur atom of the thioether molecule. Despite the gold shell dilution and functionalization with the copper complex, magnetic studies suggested that $Fe_3O_4$@Au@Cu retained its magnetic characteristics. Nuclease studies with $Fe_3O_4$@Au@Cu indicated that the nanomaterial's plasmid DNA nuclease activity was mediated through an oxidative route mediated by $H_2O_2$ species in a Fenton-like reaction. The nuclease activity was primarily derived from the HO% species, as indicated by electron paramagnetic resonance spectra (aN = 15.07 G, aH = 14.99 G), highlighting the successful transfer of radical production properties from [Cu(2CP-Bz-SMe)] core-shell Au-coated $Fe_3O_4$ nanoparticles require. This is the first instance of a Cu-complex immobilized on a Au-coated magnetic nanoparticle producing reactive oxygen species, to the best of our knowledge., as illustrated in Scheme (2).




**Scheme (2): Representative illustration showing the formation of $Fe_3O_4$@Au and its functionalization with $[Cu(2CP\text{-}Bz\text{-}SMe)]^{2+}$.**

In a study conducted in 2019, Ilaria Fratoddi et al., [43] investigated the use of hydrophilic gold nanoparticles (AuNPs) for medication delivery. The researchers focused on loading and releasing two copper(I)-based anticancer compounds: compound A ([Cu(PTA)4]+[BF4]), and compound B ([HB(pz)3Cu(PCN)]). Compound A is a water-soluble compound composed of a chemical A is a neutral chemical with a mixed ligand combination that is soluble in water, whereas Compound B is a metal organized in a cationic structure. The study's goal was to evaluate the effectiveness of loading chemicals A and B onto AuNPs in order to increase bioavailability and achieve controlled release. Several methods, including dynamic light dispersion (DLS), UV-Vis, FT-IR, and extreme-resolution X-ray photo-electron spectroscopy (HR-XPS), were used to look into the non-covalent interactions between the chemicals and the surface of AuNPs. According to the findings, the AuNPs-A system outperformed the AuNPs-B system in terms of dependability and efficiency. AuNPs-A had a 90% drug loading effectiveness compared to AuNPs-B's 65%. A four-

day release study employing AuNPs-A was also conducted. conjugated systems in a water solution demonstrated a gradual release of up to 10%, as shown in Fig. 6.

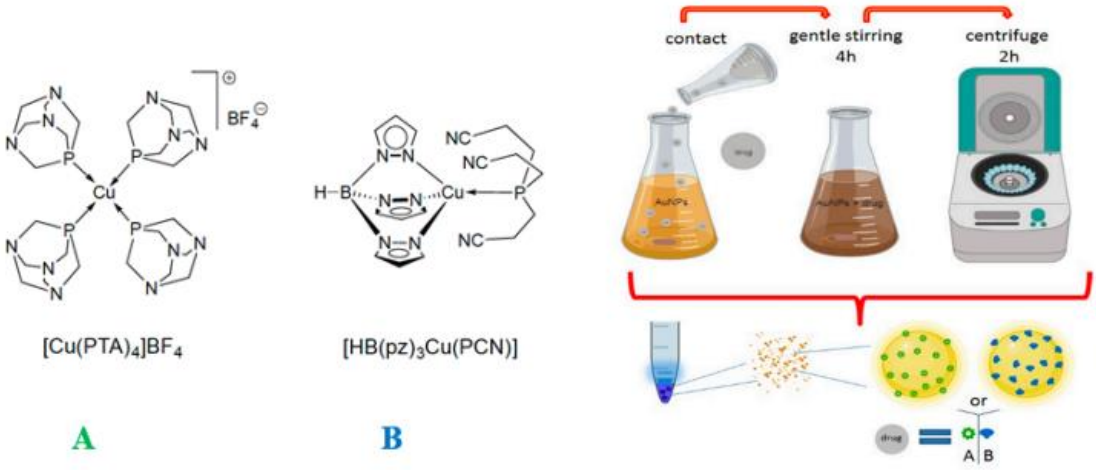



**Fig. (6): Chemical compositions of the anticancer Cu(I)-complexes retained in this investigation are shown in (a); a loading technique schematic is shown in (b) to produce the conjugated AuNPs-A and AuNPs-B.**

During the year 2019, a team of researchers led by Shifan Zhao et al., [44] colleagues introduced a novel type of biofuel cells called non-enzymatic biofuel cells (NEFCs) that do not rely on compartments for their functioning. These NEFCs employ an electrografted copper complex of 3,5-diamino-1,2,4-triazole and nanoporous gold nanoparticles as catalysts. What makes these cells remarkable is their ability to operate in a neutral solution and enable self-powered pyrophosphate sensing. This sensing is made possible by the stronger coordination of $Cu^{2+}$ with oxygen (O) rather than nitrogen (N) at the cathode. Refer to Figure 7 for a visual representation.

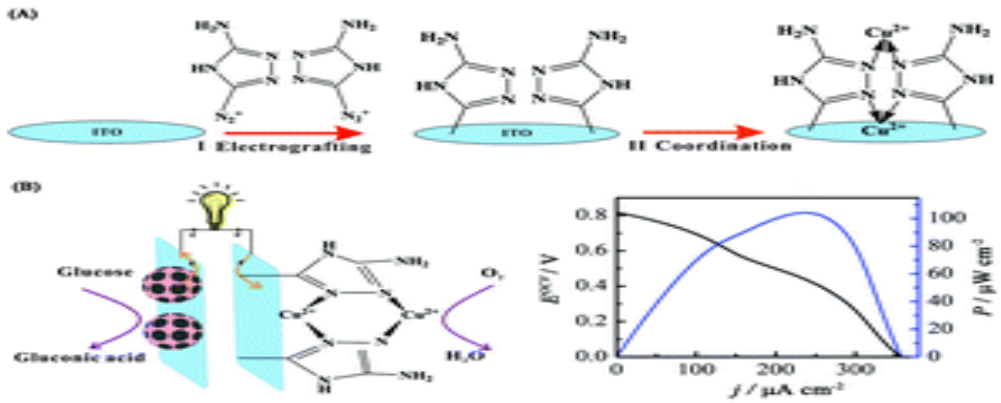



**Fig. (7): 5-diamino-1,2,4-triazole and nanoporous gold nanoparticles as catalysts**

In a paper published in 2020, Gennaro Picardi et al., [45] used a mixture of Cu(I) compounds to functionalize gold colloidal nanoparticles (NPs) in acetonitrile. The Bipyridyl ligand with a

thioctic acid moiety and the 2,9-dimesithylene-1-10-phenanthroline ligand made up the Cu(I) compounds. Several methods, including UV electronic absorption, inductively coupled plasma atomic emission spectroscopy, scanning transmission electron microscopy with energy dispersive X-ray analysis, and surface distribution and coverage analyses, were used to confirm the metallic complex's attachment to the Au NPs through the formation of an Au-S bond. The outcomes showed that the imbedding of the metallic complex onto the Au-NPs had been effective. Interestingly, the quantity of the metallic complex was only around four times that of compact alkanethiols, which are substantially smaller. monolayers that self-assembled on related gold nanoparticles. By measuring the frequency of a specific marker band at roughly 1000 $cm^{-1}$, Surface Enhanced Raman Spectra (SERS) were utilized to determine the complexation state of the surface-bound bipyridine molecules. Figure 8 illustrates how the bigger substituted phenanthroline ligand was found to be more peripheral. In contrast, the evaluation of the powders' normal Raman spectra, and SERS data revealed that the two polycyclic ligands were aligned perpendicular to the surface.

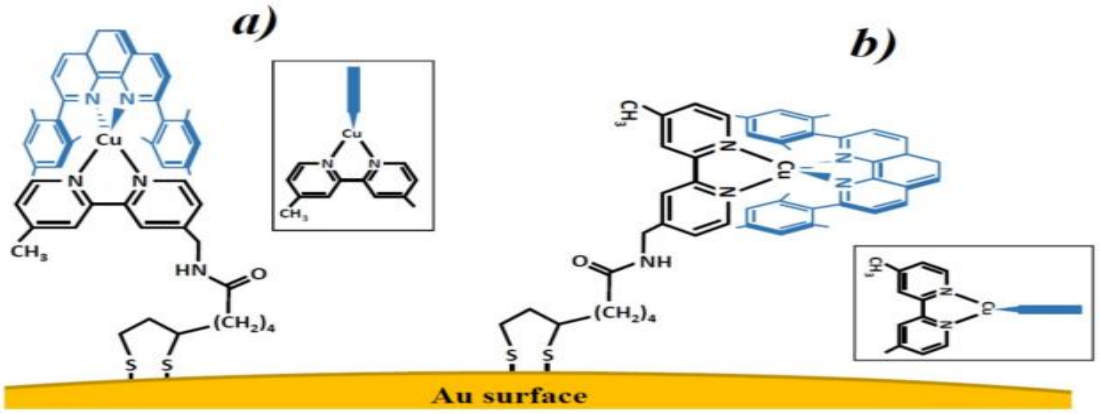
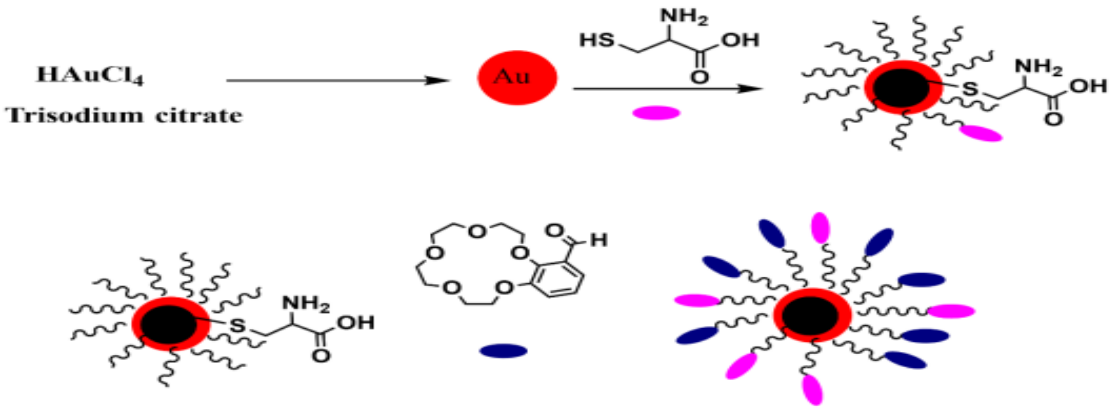



**Fig.(8): The tetrahedral Cu(I) complex is bound to the surface in two limiting directions by S-Au bonds. The phenanthrene molecular plane is shown by the thick blue line in the smaller insects. The molecular planes of the bipyridine and phenanthrene are both normal to the surface in Figure a. In b), the surface is parallel to the phenanthrene ligand.**

In 2021, Changiz Karami et al. [46] built gold nanoparticles utilising two unique functional groups, crown ether and carboxylic acid, in 2021. These nanoparticles were then tested as a copper ion sensor in an aqueous solution. Transmission electron microscopy (TEM) and Fourier-transform infrared (FTIR) spectroscopy were used to investigate the Au-crown/carboxylic nanocomposite. The UV-visible spectrum was captured before and after the injection of $Cu^{2+}$ ions to investigate the sensor's reaction to copper ions. The detection technique is based on the successful complexation of

$Cu^{2+}$ ions with Au-crown/carboxylic ions, which results in a color shift from red to blue. A linear association with a correlation value of 0.9814 was obtained at A630/A545 between the reduction in absorbance intensity and the concentration of $Cu^{2+}$ ions in the concentration range of 75 nM to 1250 nM. The detection limit was determined to be 150 nM. Notably, among other cations, this sensor assay selectively targets copper ions and provides a simple method for measuring and detecting them in aqueous solutions, as shown in Scheme (3).




**Scheme (3): Synthesis of Au-crown/carboxylic ligand.**

In 2021, Green LED plasmon excitation (525 nm) was used by Léa Gimeno et al. [47] to graft a copper(II) complex onto colloidal gold nanoparticles (NPs). In this method, nitrobenzaldehyde and nitromethane were present in DMF, resulting in the very efficient synthesis of the equivalent nitroaldol molecule. Kinetic studies employing 1H NMR and Raman spectroscopies demonstrated that when subjected to green light irradiation, the process displayed greater efficiency, particularly in close proximity to the NPs (reaching nearly 100% conversion after 100 minutes). Following the conclusion of the process, the nanocatalyst could be gathered and utilized in two subsequent reactions. Green LED stimulation of the plasmonic nanocatalyst proved to be a simple and efficient technique, dramatically improving the rate of the Henry reaction while needing less energy and shorter reaction times than characteristic applications as shown in Fig.(9).

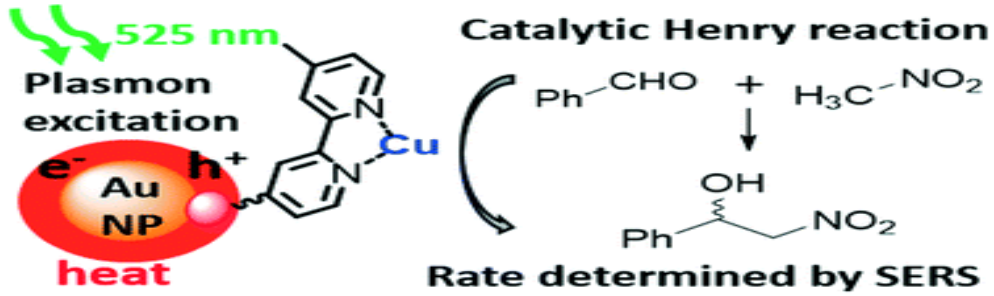


**Fig.(9): grafted green LED plasmon excitation of colloidal gold nanoparticles (NPs)**

In 2022, Ahmad Junaid et al. [48] successfully synthesized and characterized a nanogold-copper(II) complex conjugate [(Cu)(phen)(cys)($H_2O$)]$NO_3$n. This complex was subsequently investigated for its ability to inhibit the growth of both breast cancer cells (MCF7) and normal cells (MCF10A). The Turkevich technique was employed to create the nanogold solution. Two methods were used to synthesize the complex: one The first method involved the sequential reaction of gold nanoparticles with L-cysteine, Cu-(II) nitrate, and 1,10-phenanthroline, followed by the synthesis of a ternary Cu-(II) complex of 1,10-phenanthroline with L-cysteine, [(Cu)(phen) (cys)($H_2O$)]$NO_3$. FT-IR and electrospray ionization mass spectrometry were exploited to study the produced [(Cu)(phen)(cys)($H_2O$)]$NO_3$ complex, which presented that L-cysteine was connected to Cu by its carboxylic, and amino groups but not through the SH group. The free SH group linked to the nano-Au surface to create the nano-Au[(Cu)(phen)(cys)($H_2O$)]$NO_3$n conjugate. The rise in the emergencies plasmon's absorption band in the Uv-visible spectrum and the lack of a SH peak in the FT-IR analysis of the nanogold-copper complex provided evidence for this. exploited the 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfo-phenyl)-2H-tetra-zolium assay, the antiproliferative effects of the nano-Au Cu-complex conjugate and the free Cu-complex on breast cancer cells (MCF-7) and their toxicity on normal cells (MCF-10A) were evaluated. As shown in Figure 10, the nano-Au[(Cu)(phen)(cys)($H_2O$)]$NO_3$n conjugate exhibited unique antiproliferative and proapoptotic effects in breast cancer cells, demonstrating its potential as a successful anticancer therapy.

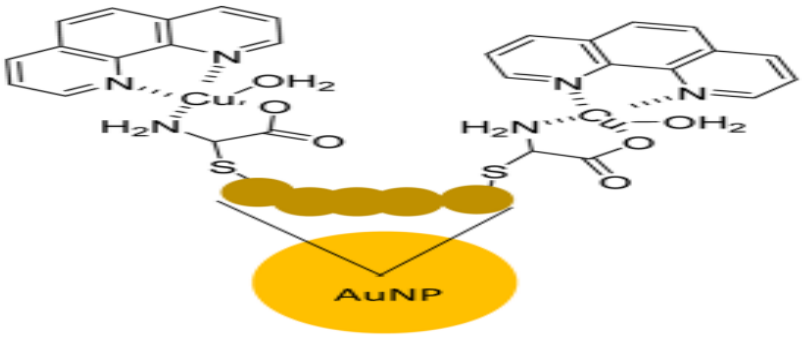



**Fig.(10): [Cu(phen)(cys)($H_2O$)]$NO_3$-functionalized gold nanoparticles**

Sammar Fathy ELhabal et al., [49] study examined the use of plant extract as an effective and eco-friendly substitute for chemical and physical techniques for the synthesis of metal nanoparticles in 2022. The scientists were able to effectively create copper (CuNPs) and gold (AuNPs)

nanoparticles by using Salvadora persica fruit extract as a reducing and stabilizing agent. Peak wavelengths for CuNPs and AuNPs were found to be 440 nm and 530 nm, respectively, according to analysis of the UV-Vis spectra. Additionally, spherical nanoparticles with diameters between 100 and 113 nm for AuNPs and 130 to 135 nm for CuNPs were revealed by transmission electron microscopy. Energy-dispersive X-ray spectroscopy was used to establish the existence of AuNPs and CuNPs in the sample. The researchers used GC-MS to find active phytochemicals in the alcoholic extract of SP fruit. The presence of SP biomolecules that served as stabilizers on the nanoparticle surface was also confirmed using Fourier-transform infrared spectra. Zeta potential tests showed that the nanoparticles were extremely stable, displaying a significant negative potential between 25.2 and 28.7 mV. According to the study, both green AuNPs and CuNPs had antibacterial activity against both gram-positive and gram-negative bacteria, with CuNPs performing better. AuNPs and CuNPs also showed potential antioxidant and anticancer activities when tested on MCF-7 and MDA-MB-231 breast cancer cells. The most prominent molecule among SP's bioactive chemicals, especially targeting methenyl tetrahydrofolate synthetase, was identified by molecular docking investigations to be beta-sitosterol (Fig. 11).

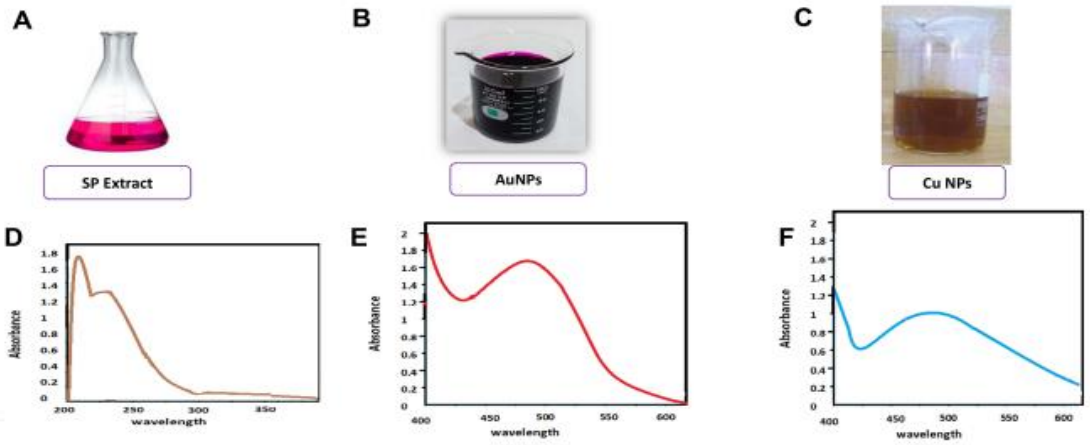
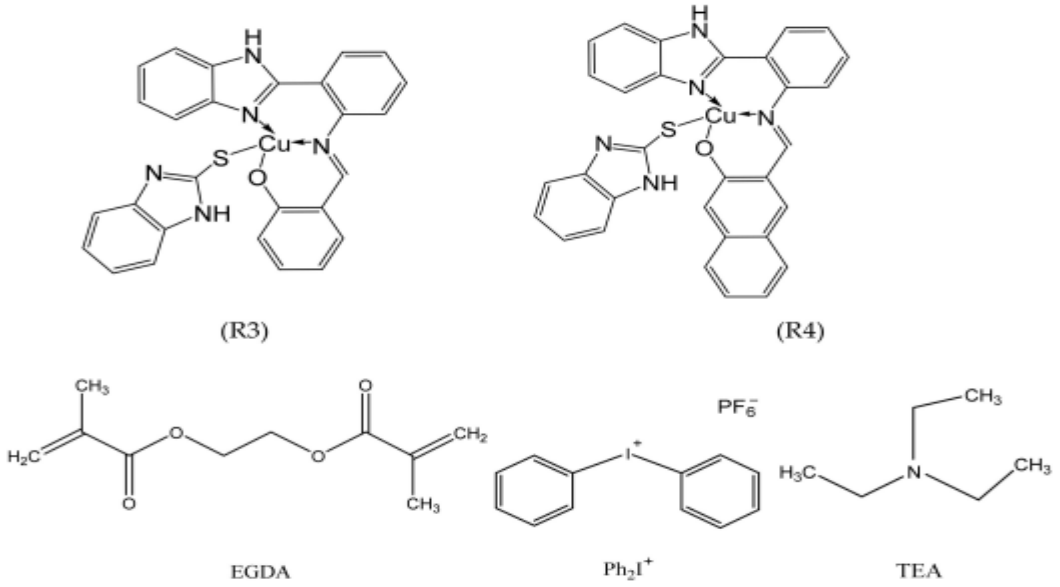



**Fig.(11). The illustrations below indicate visual confirmation of SP, AuNPs, and Cu-NPs (A), in addition to UV spectra for SP extract, Au-NPs, and Cu-NPs.**

Lama M. Alhomaidan et al., [50] produced and analyzed novel benzimidazole Schiff base ligands complexed with copper II in their investigation. These complexes were used in conjunction with triethylamine (TEA) and an iodonium salt (Iod) as photoredox catalysts/photoinitiators. The goal was to employ this catalyst system to polymerize Ethylene glycol dipropenoate while exposing the reaction to evident light from an LED-lamp. The procedure was performed at a temperature of 28°C, and the light's intensity was 543 mW/cm$^2$ with a wavelength of 405 nm. The creation of gold and silver nanoparticles, with extents varying from 1-30 nm, was the out-comes of the interaction

between the Cu(II)-complexes and the amine / Ido salt. The photopolymerization performance of the copper II complexes, including the nanoparticles, was carefully examined and reported in the study. Cyclic voltammetry was used to investigate the photochemical reactions. The researchers noticed the in-situ production of polymer nanocomposite nanoparticles during the irradiation process at 28°C utilizing the LED with a wavelength of 405 nm and a strength of 543 mW/cm$^2$. Through UV-Vis, FT-IR, and TEM analyses, the presence of Au nanoparticles (Au-NPs) and silver nanoparticles (Ag-NPs) inside the polymer matrix was verified (Scheme 4).




**Scheme (4). presented the structures of the Cu(II)-complexes $R_3$, and $R_4$ along with the monomers and additives that were utilized in their study.**

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## Conclusions

Identifying nano gold and its forms, studying copper complexes and their geometric shapes, as well as studying nano gold associated with copper complex and its various applications, including inhibition of cancer cells and in the field of adsorption, developing platforms for drug delivery, imaging investigations, and using them as photo catalysts.

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