

UDC 615.277.3.015:546-022.53

## FUSED RING HETEROCYCLE FUNCTIONALIZED GOLD NANOPARTICLES: SYNTHESIS AND SELF-ASSEMBLY

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Received 21.09.2022

Accepted 06.06.2023

**Abstract:** Self-assembled nanoparticles are an area of great research prospect as they offer switchable element for designing and creating micro-scale constructs. Self-assembly of nano-hybrids through some non-covalent interactions such as electrostatic,  $\pi$ - $\pi$  and van der Waal interactions in different classes of composite materials provide a great prospect of utilization of these functional properties in tailor-made device applications. In this work gold nanoparticle functionalized with coumarin based fused-ring heterocyclic thiol exhibiting self-assembly is reported. The present work has been designed giving prior to  $\pi$ -stacking mediated self-aggregation of nanoparticles resulting formation of larger superstructures. The work reports the coumarin-based heterocyclic fused ring having a thiol anchoring group grafted to the gold nanoparticle surface for easier electron flow between the metal nanoparticle and the aromatic ligand and study their self-assembly nature.

**Keywords:** self-assembly, gold NPs, fused ring, thiazole, composites

**DOI:** 10.32737/2221-8688-2023-2-188-196

### Introduction

Recently nano-science is of great interest that shifted gradually from mere synthesis and applications of discrete nanocomponents to larger nanostructured systems. Self-assembly phenomenon can be one of the most promising routes to attain such high-ordered systems [1]. The phenomenon provides a simple, efficient and cost-effective pathway for controllable assembling of nanomaterials [2]. Self-assembled nanoparticles are an area of great research prospect as they offers switchable element for the design and creation of microscale constructs [3, 4]. Nanoparticles ensembles are often found to show different types of new electronic, magnetic and optical properties due to the interactions occurring between the excitons and surface plasmons of individual nanoparticles. Self-assembly of nano-hybrids through some non-covalent interactions (electrostatic,  $\pi$ - $\pi$  and

van der Waal interactions, for instance) in different classes of composite materials have a great impact on functional properties in various tailored miniaturized devices [2, 5, 6]. There are many routes to organization of nanoparticles in an assembly as reported in different journals. This self-organisation of nanoparticles can be through charge transport [7], electroless deposition [8], phase separation [9], anisotropy in ligand attachment [10], grafting complementary DNA [11, 12], etc. Self-assembled nanoparticle systems are also applied as chemical and biochemical sensors [13, 14], plasmon rulers [15], nanolength pH and thermometers [16], etc. A nanoscale reversible thermometer was built by Lee and co-workers using exciton-plasmon interactions mechanism by connecting a polymer, poly(ethyleneglycol) derivatised with tert-butoxycarbonyl and N-

hydroxysulfosuccinimide, as a molecular spring between two types of nanoparticles, viz. gold nanoparticles and CdTe nanoparticles [16]. Clusters of gold nanoparticles are widely applied in various areas of nanotechnology. However, the extent of functionalizing surfaces of gold nanoparticles remains quite challenging. Worden and co-workers reported an efficient controlled functionalization of the gold nanoparticles surface with a single functional group using solid phase synthesis strategy [17]. J-aggregation of cyanine dyes reported by Chen *et al.* on gold nanoparticles of two different sizes via non covalent interactions [18]. Tao and co-workers developed temperature responsive self-organization of nanoparticles, which is basically a polymer-solvent interactions using a polymer ligand with upper critical solution temperature (UCST), i.e., polystyrene, grafting in gold nanoparticles. It was observed that when the temperature rises above the transition temperature of the polystyrene grafted gold nanoparticles, the nanoparticles dispersed in solution whereas the nanoparticles aggregate into clusters below that transition temperature. [19].

In order to use self-organization of nanoparticles successfully in recent technologies and also to ensure its high efficiency a controlled and directional assembly of nanoparticles is required. Grzelczak *et al.* reported about the directed self-organization of nanoparticles. For this directional self-assembly to occur, a template is necessary which can be any object that serves as a scaffold wherein different particles are arranged with a morphological structure such that they become complementary to the template that has been used. The templates can be single molecules,

some microstructures or block copolymers [20].

Hybrid nanoparticles which are self-assembled via surface modifications explore mainly co-valent or electrostatic bonding. Because of the existence of strong non-covalent interactions between the self-assembled composite nanoparticles they are being extensively explored in optoelectronics [21]. To utilize such materials, the size of optoelectronic devices as well as other components like optical switches, focusing lenses, light generators, etc. [22] is reduced.

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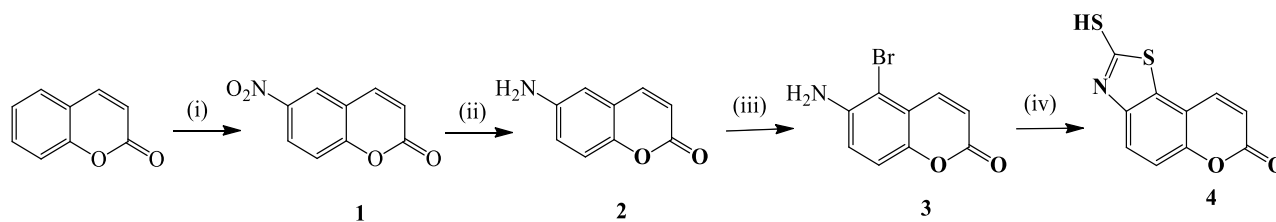
In our earlier report we observed that coumarin thiazole fused ring system was capable to induce long range self-assembly in silver nanoparticles upon surface functionalization [23]. As coumarin and its derivatives are reported to exhibiting  $\pi$ -stacking behavior [24], it may be effective in inducing self-assembly of the functionalized metal nanoparticles mediated via  $\pi$ -stacking and other non-covalent interactions. Thus, to explore the potential of pi-stacking on the self-aggregation of nanoparticles, the present work reports on the synthesis of 2-mercapto-7H-chromeno [5, 6-d] thiozole-7-one functionalized gold nanoparticles and the study into their self-assembly.

## Experimental

### Synthesis of the ligand

The coumarin-thiazole fused ring ligand has been synthesized following a previously reported method by our group [23]. The synthesized ligand has been characterized by comparing the melting point, FT-IR and NMR

spectroscopy with the previous report [23] and found to be in very good agreement. The detailed synthetic procedure and the spectral information have been incorporated in the supplementary information.



i) Nitration mixture, 0°C; ii) Fe dust / NH<sub>4</sub>Cl, 80-90°C, 2Hrs; iii) NBS, CH<sub>3</sub>CN; iv) CS<sub>2</sub>, DBU

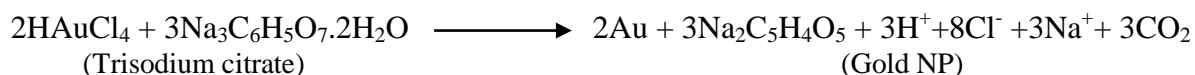
**Scheme 1.** Synthetic scheme of the Coumarin-thiazole fused ring system

Color: pale yellow, MP: 108-110 °C (reported 110°C [23]), FTIR (ATR mode, cm<sup>-1</sup>): 2750 (S-H stretching vibration), 3072 (=C-H), 1745 (C=O stretching of ester)

#### Preparation of gold nanoparticle (AuNP)

The gold nanoparticles were prepared by reduction using trisodium citrate at 100 °C. In a 50 ml deionized water chloroauric acid was

added and shaken followed by heating to boiling state, to the boiled solution of chloroauric acid preheated citrate solution was rapidly introduced into the round bottom flask with drastic agitation and stirring. The mixtures were constantly heated until a ruby-red color appeared. The formation of AuNP were monitored using UV-Vis spectroscopy.

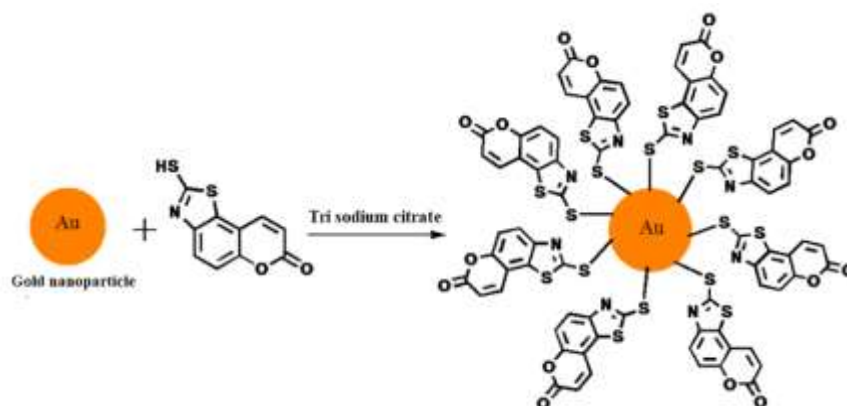


**Scheme 2.** Synthesis of AuNPs

#### Synthesis of functionalized gold nanoparticles (functionalized AuNPs)

In this process the modified Turkevich method was used. In a 50 mL conical flask the thiol ligand was dissolved in water-alcohol-acetone mixture (7:2:1). In another 50 mL conical flask sodium citrate solution was prepared (50 mL 1% solution). Chloroauric acid solution is kept stirring at 60° C on another RB

flask. To the chloroauric acid solution the thiol ligand solution was added, followed by addition of sodium citrate solution. The reaction mixture was continued to be stirred for about 2hrs until a dark color solution appeared. The solution is taken out of centrifuge to remove larger particles and suspension obtained thereafter is used for further analysis.

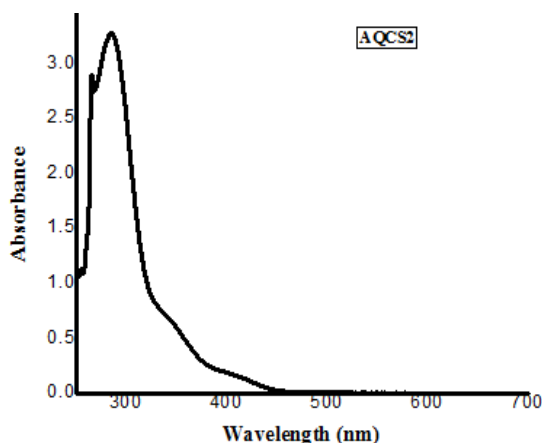


**Scheme 3.** Schematic representation of surface functionalization of AuNPs with the synthesized ligand

## Results and discussion

### UV-Visible Studies

From Fig. 1 it has been observed that the UV-Vis spectrum of synthesized organic ligand



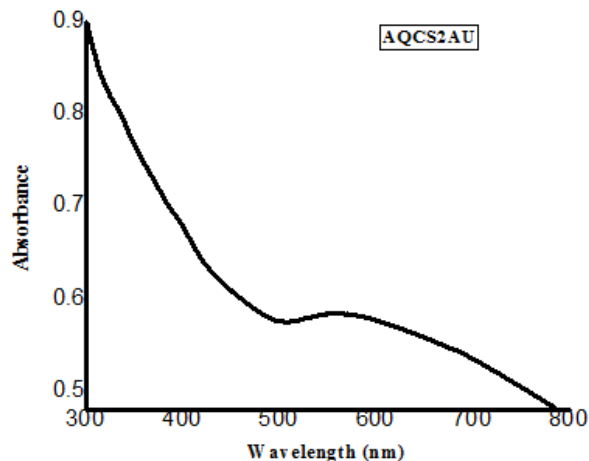
**Fig. 1.** UV-Vis Spectrum of ligand

UV-Vis spectrum of thiol functionalized gold nanoparticles shows characteristic absorption band due to Surface Plasmon Resonance (SPR) at 562 nm (Fig. 2) suggesting the successful formation of gold nanoparticles (AuNP).

### FT-IR Studies

The FT-IR spectra of the thiol ligand (AQCS2) and the functionalized Gold nanoparticle were recorded (Fig. 3). The FT-IR of the thiol ligand shown in Fig. 3(a) exhibited weak band at  $2750\text{ cm}^{-1}$  for S-H stretching vibration along with stretching band at  $3072\text{ cm}^{-1}$  ( $=\text{C-H}$ ), and  $1745\text{ cm}^{-1}$  ( $\text{C=O}$  stretching of ester),  $628\text{ cm}^{-1}$  ( $\text{C-S}$  stretching). Presence of common stretching features of the ligand in the IR spectrum of functionalized gold nanoparticle (Figure 3b) around  $3072\text{ cm}^{-1}$  (aromatic  $=\text{C-H}$ ),  $1602\text{ cm}^{-1}$  ( $\text{C=N}$ ),  $1534\text{ cm}^{-1}$  (aromatic  $\text{C=C}$ ) indicate the association of the ligand with gold nanoparticle. However, in the spectrum of the AQCS2 the functionalized Gold nanoparticle the S-H stretching vanishes indicating attachment of the ligand on the gold nanoparticle surface through Au-S linkage. Further, the stretching band of  $\text{C=O}$  at  $1747\text{ cm}^{-1}$  of the ligand has got merged with the band at  $1708\text{ cm}^{-1}$  in the functionalized system to give a

exhibited absorbance at wavelength 289 nm and the absorption is attributed to the  $\pi\rightarrow\pi^*$  transition for ( $\text{C=O}$ ).



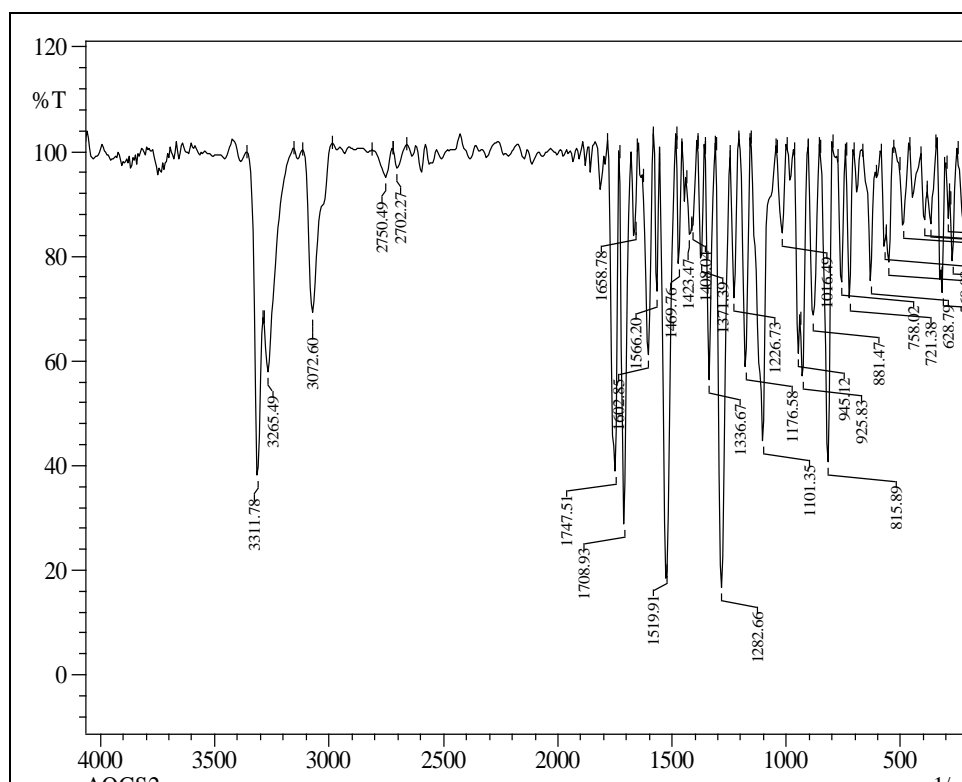
**Fig. 2.** UV-Vis Spectrum of functionalized AuNPs

broader band at  $1745\text{ cm}^{-1}$ .

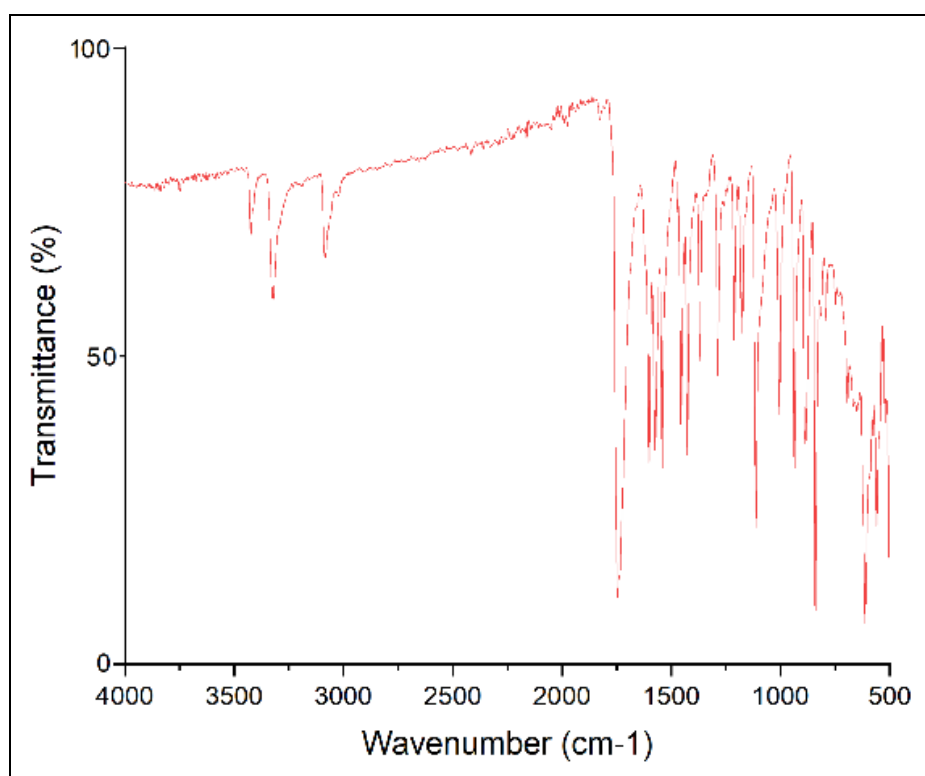
### TEM Study

Transmission Electron Microscopy (TEM) of AuNPs as well as the fused ring thiol functionalized AuNPs allows the imaging of individual crystallites and also help in developing the geometric depiction of the size and shape of the particles present in a sample.

TEM image of Au nanoparticles clearly shows that the particles are spherical in shape and the average size of Au nanoparticle lies in the range of 5 to 20 nm (Fig. 4a). The selected area electron diffraction (SAED) pattern of an area containing some uncoated nanoparticles (Fig. 4b) shows a set of spots due to the single crystalline nature of the nanoparticles. The TEM image shows that the functionalized AuNPs are spherical in shape with size in the range of 20 nm (Fig. 4c) and the presence of ligand shell around the AuNPs which confirms the successful encapsulation of the AuNPs with the synthesized fused ring thiol. The changes in the crystalline lattice of the functionalized AuNPs as distinct from those in the lattice of uncoated AuNPs, are clearly noticeable from the SAED pattern of functionalized AuNPs (Fig. 4d).

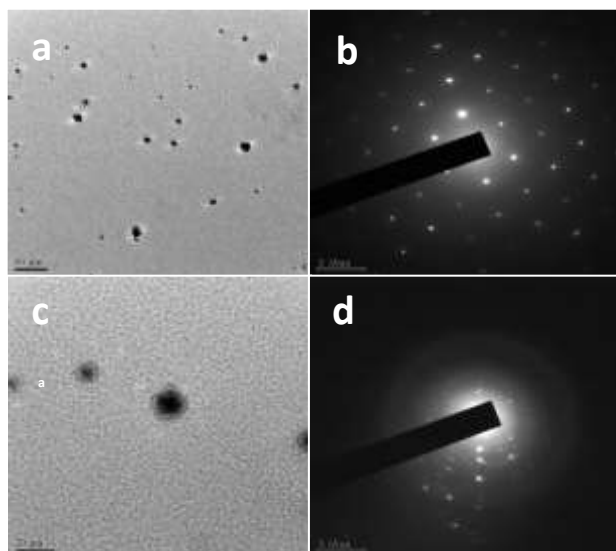


(a)

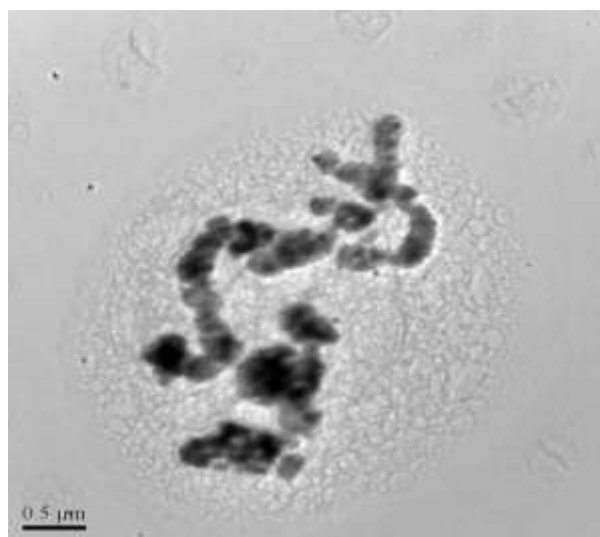


(b)

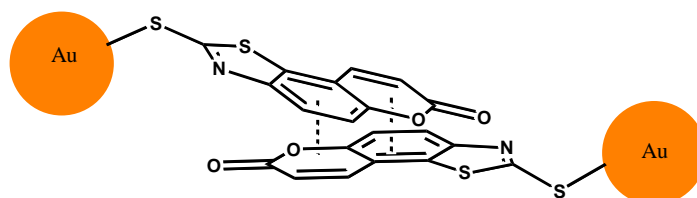
**Fig. 3.** FT-IR spectrum of (a) the thiol ligand AQCS2, and (b) AQCS2 functionalized gold nanoparticle



**Fig. 4.** (a) TEM and (b) SAED pattern of free AuNP. (c) TEM of functionalized AuNPs (d) SAED of functionalized AuNP



**Fig. 5(a).** TEM micrograph of self assembled AuNPs



**Fig. 5(b).** Representation of  $\pi$ - $\pi$  stacking of capped AuNPs

The SAED pattern of functionalized AuNPs exhibited less degree of crystallinity than the corresponding pattern of uncoated AuNPs which it is due to the coating of ligand to the Au surface through covalent functionalization. The functionalized AuNPs exhibited self-assembly (Fig. 5a) of almost small spherical AuNPs which is attributed to the formation of  $\pi - \pi$  stacking interaction between

the lactonyl ring of one coumarin system and carbocyclic ring of another coumarin system (Fig. 5b) and this kind of  $\pi - \pi$  interaction has also been found earlier in various coumarin based derivatives [24, 25]. The  $-SH$  anchoring group present on the fused-ring compound serve to graft the ligand on the gold nanoparticle surfaces.

### Conclusion

A large self-aggregates of gold nanoparticles being functionalized with coumarin based fused-ring organic thiol derivative, namely, *2-mercapto-7H-chromeno [5, 6-d] thiozole-7-one*, have been accomplished through a multistep reaction process mentioned above. This self-assembly formation of the

functionalized gold nano-particles needs no special arrangements such as treatments or equipment. This work exhibited the feasibility of non-covalent interactions, one of many like  $\pi$ -stacking interactions which have actively participated in the assembly formation of functional nanomaterials.

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**KONDENSƏ OLUNMUŞ HƏLQƏVİ HETEROTSİK İLƏ FUNKSIONALLAŞDIRILMIŞ QIZIL NANOHİSSƏCİKLƏRİ: SİNTEZİ VƏ ÖZ-ÖZÜNƏ YIĞILMASI****Saurav Paul<sup>1,\*</sup>, Bimal B. Çakraborti<sup>1</sup>, Kuheli Deb<sup>1</sup>, Sudip Çoudhuri<sup>1,2</sup>**<sup>1</sup> Assam Universiteti, Kimya Departamenti, Silçar-788011, Hindistan<sup>2</sup> Yumşaq Materialların Tədqiqi Mərkəzi, Kimya Fakültəsi, Assam Universiteti, Silçar-788011, Hindistan

**Xülasə:** Öz-özünə yığılan nanohissəciklər perspektivli tədqiqat sahəsini təmsil edirlər. Müxtəlif sinif kompozit materiallarda elektrostatik,  $\pi$ - $\pi$  və van der Waals qarşılıqlı təsirləri kimi bəzi qeyri-kovalent qarşılıqlı təsirlər hesabına nanohibridlərin öz-özünə yığılması bu funksional xüsusiyyətlərin individual sifarişlə hazırlanmış cihazlarda istifadəsi üçün böyük perspektivlər açır. Məqalədə kumarin əsasında kondensləşmiş halqalara malik heterosiklik tiol ilə funksionallaşdırılmış, öz-özünə yığılan qızıl nanohissəciklər haqqında məlumat verilir. Metallik nanohissəcik və aromatik liqand arasında elektron axınını asanlaşdırmaq üçün qızıl nanohissəciklərin səthinə paylanmış tiol qrupuna malik kumarin əsaslı heterosiklik kondensasiya halqası tədqiq edilmiş və onların öz-özünə yığılmasının təbiəti öyrənilmişdir.

**Açar sözlər:** öz-özünə yığılma, qızıl nanohissəcikləri, tiazol, kompozitlər

**НАНОЧАСТИЦЫ ЗОЛОТА, ФУНКЦИОНАЛИЗИРОВАННЫЕ ГЕТЕРОЦИКЛОМ С КОНДЕНСИРОВАННЫМ КОЛЬЦОМ: СИНТЕЗ И САМОСБОРКА****Саурав Паул<sup>1</sup>, Бимал Б. Чакраборти<sup>1</sup>, Кухели Деб<sup>1</sup>, Судип Чоудхури<sup>1,2</sup>**<sup>1</sup>Кафедра химии, Университет Ассама, Силчар-788011, Индия<sup>2</sup> Центр изучения мягких материалов, Химический факультет, Университет Ассама, Силчар-788011, Индия

**Аннотация:** Самособирающиеся наночастицы представляют собой перспективную область исследований. Самосборка наногбридов за счет некоторых нековалентных взаимодействий, таких как электростатические,  $\pi$ - $\pi$  и ван-дер-ваальсовы взаимодействия в различных классах композиционных материалов, открывает большие перспективы использования этих функциональных свойств в устройствах, изготовленных по индивидуальному заказу. В работе сообщается о проявляющих самосборку наночастицах золота, функционализированных гетероциклическим тиолом с конденсированными кольцами на основе кумарина. Исследуется гетероциклическое конденсированное кольцо на основе кумарина, имеющее тиольную якорную группу, привитую к поверхности наночастицы золота для облегчения потока электронов между металлической наночастицей и ароматическим лигандом, и изучается природа их самосборки.

**Ключевые слова:** самосборка, наночастицы золота, тiazол, композиты