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Gold nanoparticles modified with coordination compounds of metals: synthesis and application

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Abstract. The data on the preparation methods and applications of gold nanoparticles with coordinated metal ions on the surfaces are generalized. The currently available data on the interaction of metal ions with gold nanoparticles modified with organic (particularly, sulfur-containing) ligands comprising terminal chelating groups are considered in detail as well as the applications of such modified nanoparticles. The bibliography includes 141 references.

I. Introduction

Due to their unique chemical, optical and electronic properties, which differ from the properties of the metal both in the macroscopic state and as individual atoms,[1,2] the gold-based nanostructures find application in different fields of modern chemistry, technology and material science,[3] in the development of optical,[1,4–6] nanoelectronic[7–9] and photonic[10,11] devices, chemical and biological sensors[12–14] and catalysts.[14,15] In addition, the nanoparticles (NP) can be used in medicine (for drug delivery[16] and as the markers in clinical diagnostics[17,18]) and also as the colouring agents that change the reflection and absorption properties of coloured glass.[19]

The main problem in the preparation of metal nanodispersions is that nanoparticles are unstable in solutions and tend to form large aggregates. To obtain stable nanoparticles of definite size and shape in the form of colloidal solutions, the presence of stabilizing agents that adsorb on the particle surface thus preventing further association is required.[1,20,21]

As such stabilizers, different sulfur-containing organic substances (thiols, sulfides, disulfides, thiourea derivatives, xanthates, dithiocarbamates, *etc.*) are often used.[1,2,20,22–26] For functionalization and stabilization of gold nanoparticles, compounds of other classes such as amines, thiocyanates, carboxylates, *etc.* can be employed. Polypyridine compounds, especially terpyridines and bipyridines, were also used in the modification of gold nanoparticles.[1,15,27]

Modifying gold nanoparticles with various organic ligands makes it possible to impart the desired properties to them. At present, the attention is focused on ligands containing a functional group (fluorophore, chromophore, receptor or electrochemically active group) bound to a sulfur-containing group through a linker.[15,28]

The targeted and controlled synthesis of ensembles based on metal nanoparticles with a definite size, shape and degree of aggregation is a challenge of modern nanochemistry. Such ensembles can form as a result of synthesis of complex compounds of metal cations with ligands attached to the nanoparticle surface and containing terminal donor groups. Modification of nanoparticles with metal complexes gives rise to new properties: optical, chemical, electrochemical or catalytic properties. These nanoparticles may serve for the design of new functional hybrid materials and supramolecular structures.[29,30]

To date, two reviews were devoted to gold nanoparticles modified with coordination compounds and their use in sensor-based diagnostics and catalysis.[31,32] However, both reviews are small in volume and in the number of cited publications.

The present review generalizes the data on the synthesis and practical use of gold nanoparticles bearing metal ions coordinated on their surface to the terminal donor groups of organic ligands that stabilize the NP. The methods of synthesis of these ligands are surveyed as well and the methods of their immobilization on the nanoparticle surface and the interaction of modified gold nanoparticles with metal ions. The information is grouped according to the

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application fields of these nanoparticles and corresponding nanomaterials. Insofar as the determination of the size, the chemical composition and the structure of NP and molecules on their surface is a separate and often difficult task, Section III presents a concise list of physicochemical methods conventionally used to elucidate the structures of nanoparticles.

II. Methods of synthesis of gold nanoparticles

The use of metal nanoparticles in the development of optical and nanoelectronic devices, chemical and biological sensors, catalysts, *etc*. requires new methods for synthesizing monodisperse nanoparticles with the controlled size and shape, because these parameter determine many physical and chemical characteristics of synthesized materials.[3, 33]

As was mentioned in the Introduction, sulfur-containing organic compounds are used most often as the stabilizers of gold nanoparticles. It deserves note that there is still no general agreement on the mechanism of interaction of thiols with the gold surface. At present, most researchers believe that this interaction is accompanied by the S–H bond cleavage in the thiol molecule and the resulting alkanethiolate becomes bound to the metal surface. The reaction on the NP surface can be considered as the oxidative addition of a thiol to the gold surface with the reductive elimination of hydrogen.[34, 35]

$$RSH + (Au^0)_n \longrightarrow RS^-Au^+(Au^0)_{n-1} + \frac{1}{2}H_2.$$

For monolayers, the formation of a thiolate on the gold surface was confirmed by FT IR spectroscopy and FT mass spectrometry. It was found[34] that the thiolate–gold bond in very strong with the energy of $\sim$40 kcal mol^{-1}.

Molecular hydrogen is apparently evolved when the process is carried out in vacuum, as confirmed by the corresponding calculations.[36] However, for thiolate layers formed in solution in the presence of oxygen, the eliminated hydrogen atoms can transform into water molecules.[37]

At the same time, according to the data of Nuzzo *et al*.,[38] methanethiol is adsorbed on the gold surface in vacuum without S–H bond dissociation. Brust and coworkers[39] noted that the adsorption of thiols on gold can proceed by different mechanisms depending on whether there exists a sufficiently easy way of hydrogen removal. Moreover, according to these authors, in the thiol layer, a hydrogen atom that remains bonded to sulfur can hardly be distinguished from a hydrogen atom adsorbed on the gold surface.

The introduction of functional groups capable of polymerization or groups capable of forming three-dimensional hydrogen bonds on the surface (*e.g*., amine derivatives of thiols) into alkanethiols as well as the formation of monolayers on substrates made of copper or silver atoms electrochemically deposited on the gold surface under 'underpotential' conditions enhances the stability of the resulting monolayer.[40]

The adsorption of disulfides on the gold surface is accompanied by the S–S bond cleavage to afford gold thiolate, like the reaction with thiols.[34, 41] Moreover, mixed monolayers are formed for asymmetric dialkyl disulfides.[41]

$$RS-SR + (Au^0)_n \longrightarrow (RS^- Au^+)_2(Au^0)_{n-2}.$$

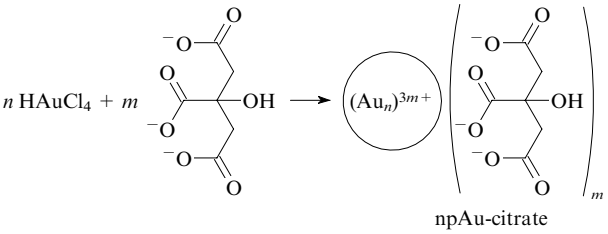
The adsorption of dimethyl sulfide on the gold surface was studied.[38] It was found that the resulting layer has a high thermal stability, particularly, the desorption peak maximum is at the temperature of >170 °C. At the same time, a secondary-ion mass spectrometric study has shown that the adsorption of dialkyl sulfides on the gold surface proceeds without the C–S bond dissociation.[42]

Currenlty, in the quest for stabilizers of gold nanoparticles, the researchers' attention is focused on thiols and disulfides containing additional functional groups. Of considerable interest are gold nanoparticles stabilized by organic ligands containing additional donor groups; these allow the synthesis of nanoparticles modified by metal complex compounds.[43] However, the direct reaction between the reactive molecular fragment and the gold NP surface is undesirable because this can lead to the loss of activity of the adsorbed compound (blocking of the active functional group) or even to irreversible aggregation of nanoparticles.[1, 28, 44]

The simplest and most widely used approach to the synthesis of gold nanoparticles is the reduction of $HAuCl_4$ in solution in the presence of stabilizing ligands. Reduction both in aqueous solutions and in organic solvents has been reported.[1] The reducing agents used include hydrogen,[45] sodium borohydride,[46] or, more rarely, aminoboranes (Me_2NHBH_3),[47] aluminium hydrides, superhydride ($LiEt_3BH$),[48] hexadecylaniline,[49] hypophosphites, formaldehyde,[50] *N*,*N*-dimethylformamide,[51] citric[52] and ascorbic acids,[53] hydroxylamine.[54] The reduction can also proceed under the action of glucose formed upon the saccharose hydrolysis.[55]

The strong reducing agents (for example, aluminium hydrides and borohydrides) quickly reduce noble metal ions; hence, they can be used only if the reaction medium contains efficient surface stabilizers preventing the coarsening of particles. Carboxylic acids (citric, tartaric, ascorbic) and their salts are weak reducing agents which slowly reduce noble metal ions. The advantage of these reducing agents consists of the possibility of finely tuning the size and the composition of the nanoparticles formed.

One of the first and most convenient methods of synthesis of nanoparticles in aqueous solutions is the method proposed by Turkevich[56] in which sodium citrate is used as the reducing agent.†



npAu-citrate

The size of nanoparticles formed in this reaction can be controlled by varying the reactant ratio. With the decrease in the citrate content in solution, nanoparticles of the larger diameter are formed. In this case, citrate ions serve as a stabilizing agent that easily forms a negatively charged

† From hereon, the homoligand gold NP with simple ligands are designated by conventional terms, for instance, npAu-citrate, npAu-SC_5H_{11}, *etc*. For intricate ligands and heteroligand gold NP, the numbers are used: npAu-**1**, npAu-**2**, *etc*.

coating on the nanoparticle surface thus inducing the electrostatic repulsion and preventing the interaction of nanoparticles.[56]

A classical way of synthesizing gold nanoparticles in organic solvents is the method proposed by Brust, Schiffrin and co-workers.[57,58] They were the first to use the well known ability of tetraalkylammonium halides to carry metal ions from the aqueous phase to the organic phase in the synthesis of gold nanoparticles in nonaqueous media. This method includes the transfer of tetrachloroaurate from an aqueous solution to an organic solvent (*e.g.*, toluene, tol) followed by the reduction of the gold salt by sodium borohydride in the presence of alkanethiols as the stabilizers.

$$AuCl_4^- \text{ (aq)} + (\text{n-}C_8H_{17})_4N^+ \text{ (tol)} \longrightarrow$$
$$\longrightarrow (\text{n-}C_8H_{17})_4N^+AuCl_4^- \text{ (tol)},$$
$$m\,AuCl_4^- \text{ (tol)} + n\,(\text{n-}C_{12}H_{25})SH \text{ (tol)} + 3m\,e^- \longrightarrow$$
$$\longrightarrow 4m\,Cl^- \text{ (aq)} + (Au_m)(\text{n-}C_{12}H_{25}SH)_n \text{ (tol)}.$$

This method allows one to synthesize virtually monodisperse nanoparticles stable in solution. As in the Turkevich method, the nanoparticle size depends on the ligand-to-tetrachloroaurate concentration ratio; the higher this ratio, the smaller the diameter of particles formed. The reactant supply rate and the temperature also affect the nanoparticle size. Thus the fast supply of the reducing agent and cooling of the reaction mixture provided NP with the diameter of $\sim$2 nm.[57,58] Based on X-ray photoelectron spectroscopy (XPS) data, it was concluded[58] that gold atoms in nanoparticles are in the Au^0 state. This is why the thiol adsorption was assumed to involve no S–H bond cleavage, as reflected in the equation of this reaction.

There are two main methods for the preparation of gold nanoparticles modified with complex ligands. One of them is based on the ligand-exchange reaction between the nanoparticles stabilized with a non-functionalized alkanethiol (*e.g.*, dodecanethiol) and a new ligand.[59] The second method consists of modifying the already adsorbed ligand which contains structural fragments necessary for its further transformations.[57,60]

Yet another method of synthesis of gold nanoparticles is their growth on the nuclei. In this case, the precursor ions are reduced on the surface of preliminarily prepared nanoparticle nuclei. Weak reducing agents are preferred, for instance, hydroxylamine, ascorbic acid, *etc*. The latter agents should reduce the precursor ions only on the surface of nuclei without forming new nucleation sites.[53]

A new combined two-step method of synthesis of gold nanoparticles of the desired size (5–110 nm) was proposed[61] which involved the use of UV irradiation and the particle growth from nuclei. In the first stage, under the action of UV radiation, spherical nanoparticles (nuclei) with the size of 5–20 nm depending on the concentration ratio between $HAuCl_4$ and the stabilizing agent (polyoxyethylene isooctylphenyl ether) were formed. The nanoparticle formation took several minutes in air at room temperature. Then, new portions of tetrachloroaurate and the reducing agent (*e.g* ., ascorbic acid) were added to the system. Nanoparticles of the larger size (25–110 nm) were formed in several minutes. This method affords gold nanoparticles of a definite size quickly and with good reproducibility.[61]

III. Methods of investigation and elucidation of the nanoparticle structure

Elucidation of the size, the chemical composition and the structure of NP and the molecules on their surface is a rather complicated problem, which is usually solved by using a combination of physicochemical analytical methods both conventional and specific.

The most information-rich and widely accepted methods used for finding the structure of modified nanoparticles and also of metal complexes attached to their surface are transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic-force microscopy (AFM), scanning tunnelling microscopy (STM), UV-Vis electronic spectroscopy, different versions of IR spectroscopy and Raman spectroscopy, dynamic light scattering (DLS), electrochemistry, X-ray diffraction (XRD), small-angle X-ray scattering (SAXS), X-ray photoelectron spectroscopy, fluorescence analysis, mass spectrometry, NMR spectroscopy, elemental analysis, phase-contrast microscopy (PCM) and thermogravimetry.

Among the methods used in determination of the size of gold nanoparticles synthesized in solution, electronic spectroscopy is the simplest, fastest and the most convenient method. Solutions of gold nanoparticles exhibit an intense absorption band at $\sim$520 nm, the so-called surface plasmon resonance (SPR) band, the appearance of which is associated with collective oscillations of conduction electrons in the near-surface layer of nanoparticles. The position and the intensity of the SPR band depend on the size and shape of particles, the extent of their interaction, the dielectric properties of the medium, *etc*. With the increase in the nanoparticle size, the SPR band shifts to longer wavelengths which is associated with mutual interference of plasmon levels for neighbouring NP and points to gradual aggregation. Thus, variations of the position and the intensity of the SPR band serves as evidence for changes in the nanoparticle structure.[62–64]

The size of synthesized nanoparticles is usually independently determined by the TEM method.[1,62]

Among the most comprehensive methods for determination of the structure of molecules on the surface of modified nanoparticles, the Raman spectroscopy deserves special mention. For gold nanoparticles modified with either individual organic ligands or coordination compounds, the surface Raman scattering is markedly enhanced. This effect is called surface-enhanced Raman scattering (SERS) and occurs for molecules adsorbed on the nanoparticle surface.[62]

So far, there is no agreement on the mechanisms of surface enhancement; however, the majority of scientists assume that the predominant contribution is due to the local enhancement of the electric field near a rough metal surface exposed to the light resonant with the localized surface plasmons.[65,66] In this case, the characteristic sizes of particles (surface irregularities) should be much smaller than the incident light wavelength. The degree of enhancement depends strongly on the size and shape of nanoparticles, their orientation and aggregation. For molecules that form chemical bonds with the surface, the chemical mechanism of enhancement is possible, which is associated with the temporary transition of electrons from the Fermi level of the metal to the vacant molecular orbital of the adsorbate.[67]

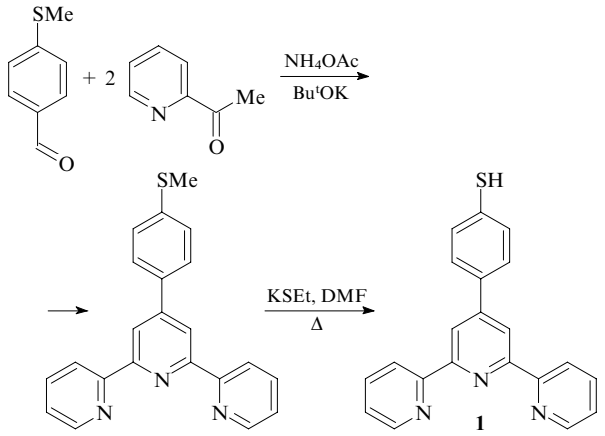
It is well known that the SERS effect exhibited by nanoparticles of gold, silver or copper may serve as an extremely sensitive analytical signal.[68] In recent years, the SERS method was used in solving various microanalytical problems as an exceptionally potent and advanced instrumental analytical method that provides high resolution, allows one to acquire large body of information and makes it possible to determine ultralow amounts of the analyte down to individual molecules.[69, 70]

IV. Synthesis and application of gold nanoparticles with metal complexes attached to the surface

1. Synthesis of gold nanoparticles modified with metal ions

For gold nanoparticles stabilized with ligands containing additional chelating groups, the interaction with metal ions is another way to prevent the nanoparticle aggregation. Complexation blocks the chelating fragment in the molecule thus preventing the irreversible aggregation of nanoparticles.[30, 43]

The stabilization of nanoparticles modified with a terpyridine derivative due to the formation of a complex with Zn^{2+} was described.[28] As the ligand, thiol **1** was used, which was synthesized as follows:

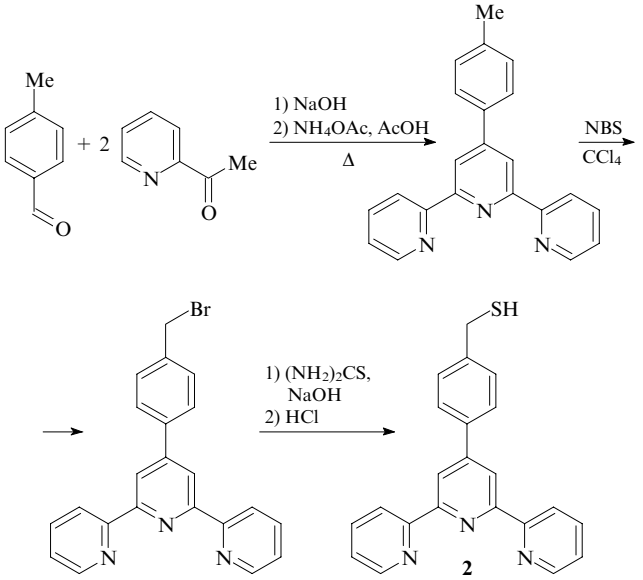


Gold nanoparticles were synthesized by the Brust method, *i.e.*, by the reduction of chloroauric acid with sodium borohydride in the presence of tetraoctylammonium bromide.[57] The stabilized nanoparticles were made to react with thiol **1**.

The addition of ligand **1** in a low concentration (up to 2×10^{-6} mol litre^{-1}) to a solution of nanoparticles results in an increase in SPR band intensity and its shift to longer wavelengths (from 520 to 580 nm), which points to the formation of small aggregates. With the increase in the ligand concentration (up to 3.0×10^{-6} mol litre^{-1}), strong aggregation occurs; for thiol concentrations above the critical value (3.5×10^{-6} mol litre^{-1}), very quick irreversible aggregation of particles and their almost immediate precipitation occurred.[28] This was explained by the fact that thiol **1** can serve as a cross-linking agent, being capable of coordinating to nanoparticles not only with its sulfur atom but also with the nitrogen atoms of its terpyridine ring. This initiates fast aggregation of NP in the presence of thiol in sufficient concentrations.

The resulting gold nanoparticles were studied in their complexation with Zn^{2+} ions. With the addition of zinc salts, an intense band at 465 nm typical of $[L \cdot ZnBr_2]$ complexes (L is a neutral ligand) appeared in the fluorescence spectra. This suggests that in this case, anions play an important role in stabilization of nanoparticles: the formation of the neutral complex $[L \cdot ZnBr_2]$ prevents the possible aggregation of nanoparticles *via* the formation of $[2\,L \cdot Zn]^{2+}$ complexes. Thus, in this case, the formation of a coordination compound on the surface of NP prevents the irreversible aggregation of NP.

The use of complexation for synthesizing ensembles of nanoparticles of definite sizes and shapes was demonstrated.[30] As the ligand, terpyridine derivative **2** was synthesized



NBS is *N*-bromosuccinimide.

In the targeted synthesis of gold nanoparticles, compound **2** was made to react with $KAuCl_4$ in ethanol, which was followed by reduction with $NaBH_4$. This led to the formation of large aggregates, as indicated by the results of TEM and electronic spectroscopy studies (in the electronic spectrum, a wide band at 615 nm was observed). However, the aggregation was irreversible as evidenced by the formation of free monodisperse nanoparticles (diameter < 3 nm) upon the addition of DMF to the solution.[71]

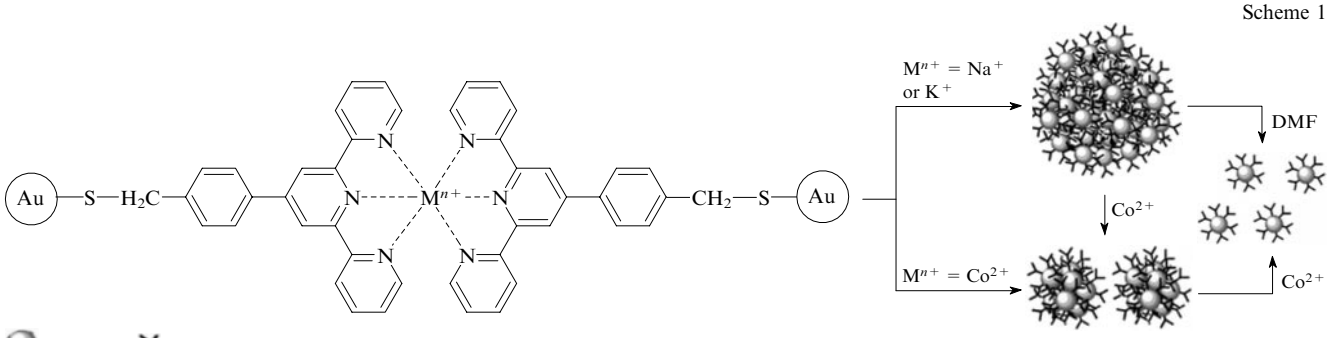
The effect of the nature of added metal ions on the properties of formed complex ensembles (Scheme 1) was studied.[30] It was found that for alkali metal ions (Na^+, K^+) as the complexing agents, strong aggregation occurred due to the weak coordination interactions between the terpyridine fragments of the ligand and the alkali metal ions to afford aggregates comprising large numbers of fine nanoparticles measuring 1.6 ± 0.2 nm.

The introduction of Co^{2+} ions, which can form stable 1 : 2 complexes with terpyridine ligands,[72, 73] afforded small spherical aggregates with the diameter of 100 – 200 nm.

Thus, by varying the nature of metal centre, one can obtain complicated three-dimensional nanostructures of different size. It deserves mention that in this example, the aggregation – disaggregation is also reversible, which opens up the possibility of transforming one three-dimensional structure into another.

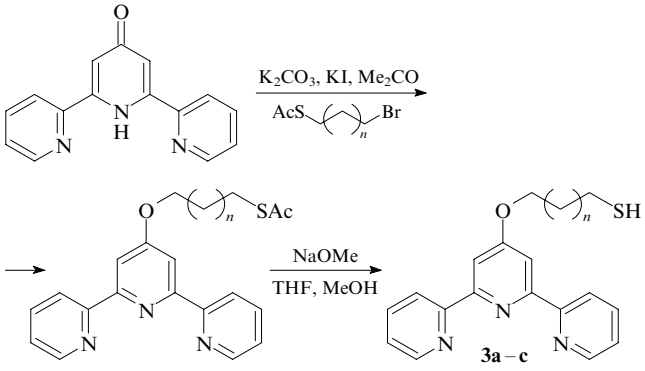
Gold nanoparticles modified with terpyridine derivatives were also studied.[74] Their interaction with Fe^{II}, Zn^{II}, Cu^{I} and Ag^{I} ions was considered. Thiols **3a** – **c** containing

Scheme 1



— npAu, is ligand **2** attached to the NP.

terpyridine groups were synthesized based on substituted 4-pyridone and bromoacetates.



n = 3 (**a**), 6 (**b**), 9 (**c**).

The starting gold nanoparticles measuring 2.0 nm and stabilized with pentanethiol (npAu-SC_5H_{11}) were synthesized according to the Brust method.[58] Nanoparticles modified with octanethiol (npAu-SC_8H_{17}), undecanethiol (npAu-$SC_{11}H_{23}$) and also nanoparticles npAu-**1a**–**c** containing terpyridine fragments on their surface were synthesized by the method of ligand exchange[75] with the use of corresponding thiols and terpyridine derivatives **3a**–**c** (Scheme 2).‡

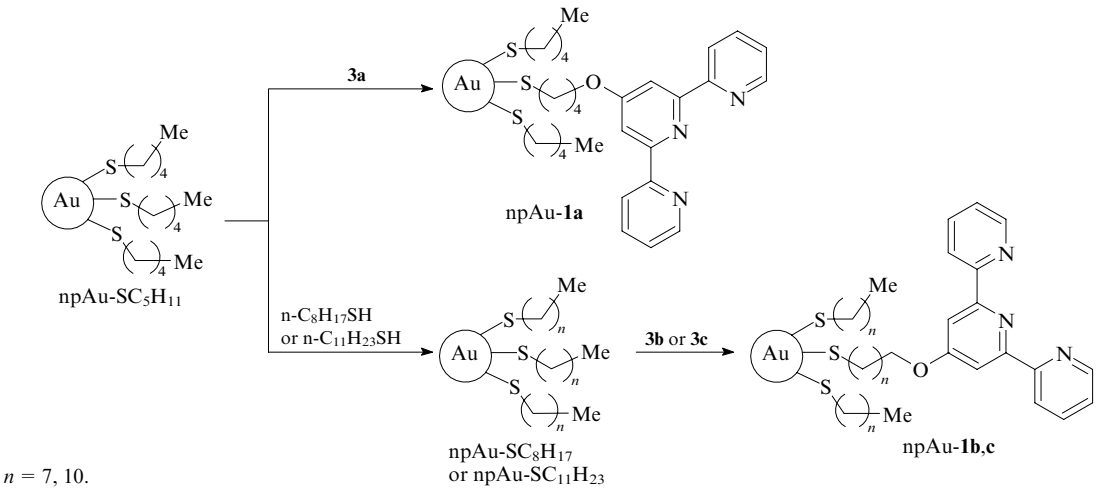
‡ Nanoparticles were uniformly covered on all sides with the adsorbed ligands; however, to save room, hereafter we show only several ligands.

The reaction between the terpyridine fragments attached to the nanoparticle surface and the metal ions leads to some aggregation of nanoparticles. In the case of $Fe(H_2O)_6(BF_4)_2$ at a low concentration of Fe^{II} ions, no apparent aggregation of nanoparticles was observed, *i.e.*, small soluble aggregates were formed. With the increase in Fe^{II} concentration, the aggregate size increased and their precipitation at high Fe^{II} concentrations was observed. According to the data of phase contrast microscopy, the resulting aggregates had a porous structure with a lot of voids and cavities. Additional experiments have shown that in the absence of Fe^{II} ions or on the addition of Fe^{II} ions to gold nanoparticles unmodified with the terpyridine ligand, no aggregation occurred.

Similar aggregates were prepared based on Ag^{I}, Zn^{II} and Cu^{I} salts. For Ag^{I} and Cu^{I}, more compact aggregates containing smaller numbers of cavities than the aggregates based on Fe^{II} and Zn^{II} were formed. The explanation lies in the fact that more stable six-coordinate complexes of Fe^{II} or Zn^{II} ions are formed quickly and virtually irreversibly to afford structures with higher porosity. On the other hand, the less stable four-coordinate complexes of Ag^{I} and Cu^{I} afford denser aggregates as a result of thermodynamically controlled aggregation. Aggregates based on Ag^{I}, Cu^{I} and, to the lesser extent, Zn^{II} can be destroyed by the addition of a large excess of the original terpyridine-containing ligand, which confirms the reversibility of complexation in these cases.

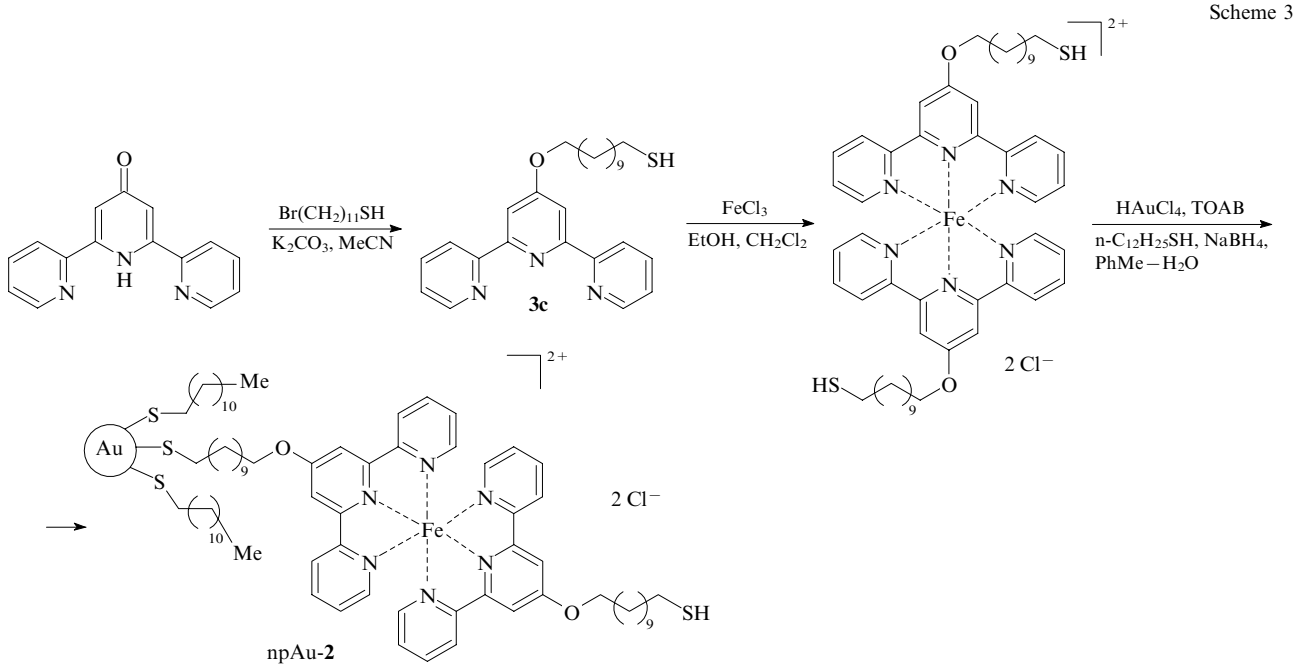
The photochemical properties of gold nanoparticles modified with a Fe^{II} terpyridine complex were studied.[76] Ligand **3c** was synthesized through the alkylation of 4-pyridone with 11-bromoundecanethiol (Scheme 3). Gold nano-

Scheme 2



n = 7, 10.

Scheme 3

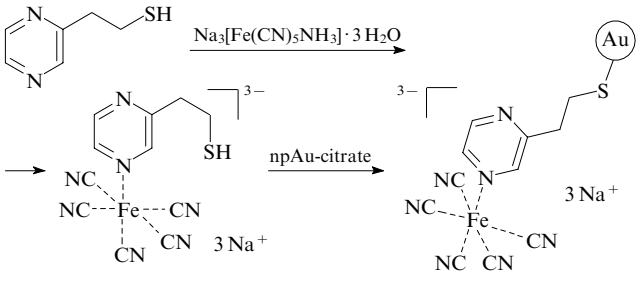


TOAB is tetraoctylammonium bromide.

particles with the average size from 3 to 5 nm were synthesized by the Brust method with the use of a mixture of dodecanethiol and the $[Fe(\mathbf{3c})_2]Cl_2$ complex as the stabilizing additives.

It was shown that the photochemical excitation of npAu-**2** gives long-lived intermediates as a result of electron transfer from the excited iron complexes to a nanoparticle. For these intermediates, absorption signals in the UV and visible regions were detected. Such systems can be used in the development of photocatalysts of hydrogen generation on water decomposition.

The controlled stabilization and flocculation of nanoparticles under the action of 2-(pyrazin-2-yl)ethanethiol and its complexes with pentacyanoferrate(II) were described.[65] Sodium citrate-stabilized nanoparticles were synthesized by the method of Turkevich[56] and then they were made to react with a Fe^{II} 2-(pyrazin-2-yl)ethanethiol complex. This yielded a solution of stable fine nanoparticles non-susceptible to further aggregation.



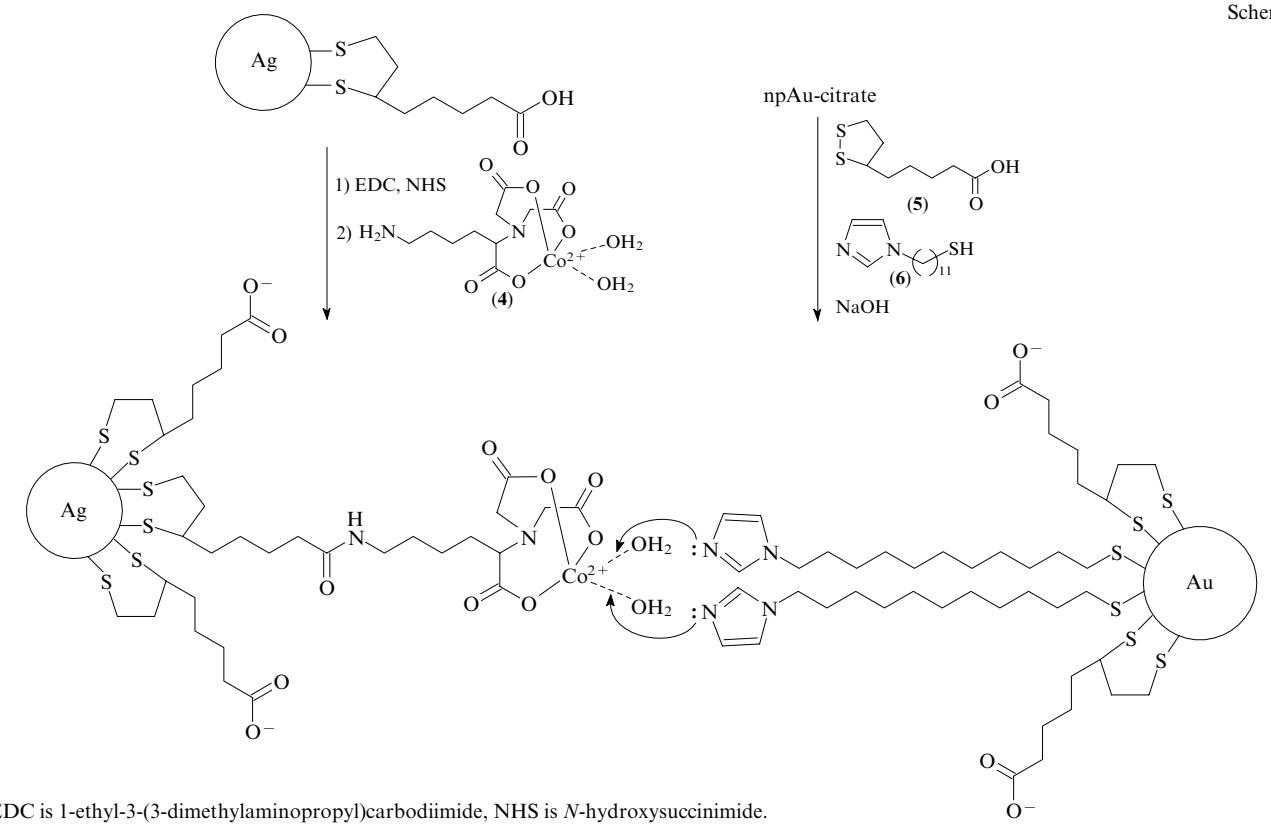
The reaction of pyridine-2- and pyridine-4-thiols with gold nanoparticles was reported;[61] studying the products by means of IR spectroscopy demonstrated considerable difference in their aggregation behaviours. The use of pyridine-2-thiol led to the formation of stable nanoparticles, whereas the addition of pyridine-4-thiol resulted most often in the aggregation of particles, which was associated with the ligand interaction with neighbouring nanoparticles *via* the nitrogen atom of the pyridine ring.[61]

Complexes of pyridine-2- and pyridine-4-thiol (2PyT and 4PyT) with pentacyanoferrate(II) ions ($[Fe(CN)_5]^{3-}$) were described.[43] The formation of $[Fe(CN)_5PyT]^{3-}$ complexes was observed; however, for pyridine-2-thiol, the iron ions were coordinated to the sulfur atom, whereas for pyridine-4-thiol, their coordination was to the nitrogen atom.

When these complexes were adsorbed on the nanoparticle surface, the aggregation occurred only for the highly labile 2PyT complex, namely, $[Fe(CN)_5(2PyT)]^{3-}$. The latter can be considered as a carrier of pyridine-2-thiol molecules to the nanoparticle surface, which, in turn, initiates the aggregation. The adsorption of the Fe^{II} complex with 4PyT led to stabilization of nanoparticles due to the formation of strong coordination bonds between the nitrogen atoms of pyridine fragments and Fe^{II}, as a result of which a negatively charged layer was formed on the NP surface.

An approach based on the coordination interactions between imidazole fragments and a Co^{II} complex with N_a,N_a-bis(oxycarbonylmethyl)-L-lysine (aminoalkylnitrilotriacetate) (**4**) was used[77] in the development of bimetallic structures involving gold and silver nanoparticles. Silver nanoparticles stabilized with thioctic acid (**5**) and modified with complex **4** were synthesized. Their synthesis was similar to the Brust synthesis of gold nanoparticles, namely, they were prepared by the reduction of silver nitrate with sodium borohydride (in the presence of tetradecylammonium bromide as the phase transfer catalyst), followed by a reaction between the resulting nanoparticles and thioctic acid (**5**) (Scheme 4). In the course of this reaction, the disulfide fragment of thioctic acid was split to afford two Ag−S bonds. Thioctic acid-modified silver nanoparticles were introduced into the amidation reaction with cobalt(II) aminonitrilotriacetate in the presence of *N*-hydroxysuccin-

Scheme 4

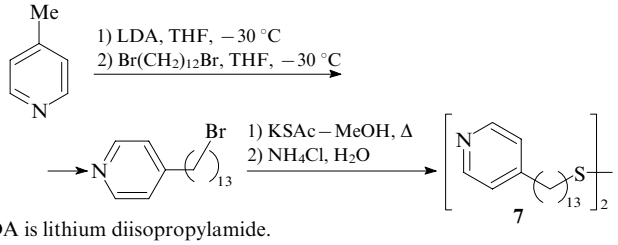


EDC is 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, NHS is *N*-hydroxysuccinimide.

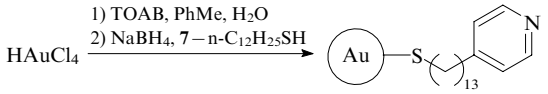
imide and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide as the activating agents. Furthermore, gold nanoparticles modified with mixed monolayers of thioctic acid (**5**) and 1-(11-mercaptoundecyl)imidazole (**6**) were prepared. These nanoparticles were synthesized by the Turkevich method by the reactoin of citrate-stabilized gold nanoparticles (measuring 13 ± 1 nm) with the corresponding sulfur-containing derivatives in the presence of sodium hydroxide. For high concentrations of imidazole derivative **6**, the nanoparticles proved to be unstable and precipitated. Furthermore, the reaction of Co^{II} complex-modified silver nanoparticles with gold nanoparticles containing free imidazole fragments on their surface afforded a mixed bimetallic structure in which, according to TEM studies, the coarse gold nanoparticles were surrounded by finer silver NP.

Bimetallic structures were formed due to the specific binding of imidazole fragments localized on the gold nanoparticle surface to the Co^{II} complexes immobilized on the silver nanoparticle surface and having vacant coordination positions originally occupied by water molecules. No aggregation occurred when silver nanoparticles modified by only thioctic acid interacted with gold nanoparticles containing imidazole groups. Nor the aggregation occurred when Ag nanoparticles modified with Co^{II} complexes interacted with Au nanoparticles modified by only thioctic acid (containing no imidazole fragments).

Approaches to the synthesis of gold nanoparticles modified with bis[13-(4-pyridyl)tridecyl] disulfide (**7**) by the Brust methods were discussed.[78] A mixture of ligand **7** with dodecanethiol in the 2 : 1 ratio was used, the average size of resulting particles was 2.2 nm, according to the TEM data.



LDA is lithium diisopropylamide.



Comparing the IR spectra of individual ligand **7** and gold nanoparticles modified with this ligand demonstrates that nitrogen atoms are not involved in the ligand adsorption on the nanoparticle surface, because the overall spectrum in the range of 3500 – 1400 nm experienced virtually no changes upon adsorption. The IR spectra of both ligand **7** and gold nanoparticles modified with this ligand (pressed as KBr pellets) demonstrated C=N bands at 1602 and 1604 cm^{-1}, respectively.

The complexation between Cu^{II} or Co^{II} ions and gold nanoparticles modified with disulfide **7** was studied.[78] According to the TEM data, the reaction with an excessive amount of the $Cu(ClO_4)_2 \cdot 6H_2O$ solution in the toluene – acetonitrile mixture afforded spherical aggregates with the average size of 100 nm. Under analogous conditions, the reaction of nanoparticles with $Co(ClO_4)_2 \cdot 6H_2O$ also afforded coarse aggregates which, however, had an irregular shape. This difference is probably due to the different coordinating ability of pyridyl-containing ligands with

respect to different transition metal ions. The aggregation of gold nanoparticles modified with ligand **7**, which proceeded in the presence of copper(II) perchlorate, was additionally confirmed by UV-Vis spectroscopic data. The electronic spectrum of a solution of modified gold nanoparticles demonstrated a characteristic SPR band at 512 nm. With the addition of a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in an acetonitrile–toluene mixture, the SPR band broadened and shifted to longer wavelengths, which confirms the formation of coarser aggregates.

2. Sensors based on modified gold nanoparticles

The existing literature contains examples of design of highly sensitive and selective sensor systems based on self-assembled thiol monolayers on the gold surface.[12] There is information on the use of modified electrodes in the determination of metal ions (Cu^{2+}, Cr^{3+}, Na^+, K^+, Ba^{2+}, *etc.*),[79,80] anions (Cl^-, Br^-, NO_3^-, SO_4^{2-}, $H_2PO_4^-$, ClO_4^-, PF_6^-, *etc.*),[80,81] and low-molecular-weight compounds.[82]

A topical trend in this field is the development of similar systems based on gold nanoparticles modified with ligand monolayers. Particularly, the use of gold NP stabilized with sulfur-containing organic compounds comprising various functional terminal groups in the determination of DNA molecules, proteins and peptides was described[83] as well as the use of gold NP modified with DNA molecules in the targeted sequencing of oligonucleotides.[84,85] Gold nanoparticles are attractive objects for grafting various markers, for instance, chromophore and fluorescence groups, to their surface, which open up the possibility of using the nanoparticles as chemical and biological sensors.[86,87]

Insofar as solutions of gold nanoparticles show an intense SPR band in the visible region and this band has a sufficiently high molar absorption coefficient and is sensitive to changes in the ligand coating of NP, these solutions can be used as highly sensitive sensors in the determination of solution components by optical methods.[63,64]

Upon the adsorption of fluorescent ligands on the surface of gold nanoparticles, the fluorescence is quenched, which also opens up the possibility of using modified nanoparticles as highly sensitive sensors.[87]

A promising trend in this field is adsorption, on the nanoparticle surface, of the ligands containing donor groups capable of interacting with different metal ions to afford complex compounds; this serves as an analytical signal in the determination of these ions.

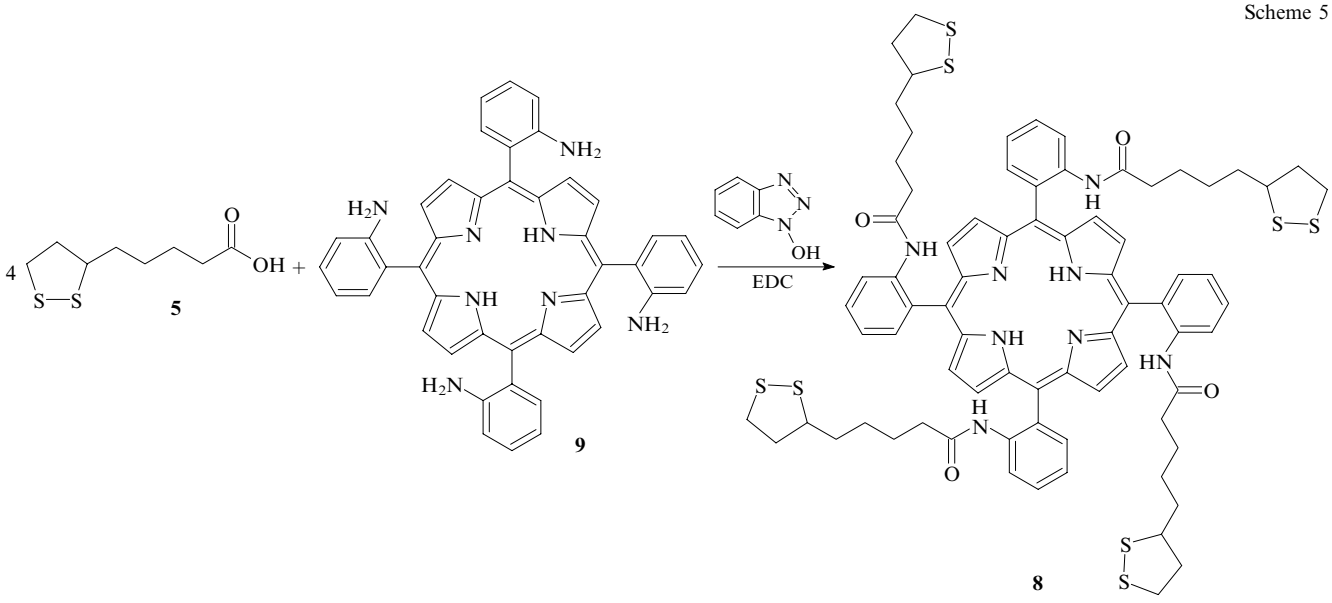
A porphyrin derivative containing disulfide groups and its complex with zinc were synthesized.[88] The complex was adsorbed on the surface of gold NP, which were tested as the optical sensors for determination of inorganic anions. Porphyrin derivative **8** was synthesized from 5,10,15,20-tetrakis(2-aminophenyl)porphyrin (**9**) and thioctic acid (Scheme 5).

Complexes of ligand **8** with $Zn(OAc)_2$ were prepared. Gold nanoparticles modified with the Zn^{2+} complex were synthesized by the Brust method, where a mixture of dodecanethiol and the synthesized complex served as the stabilizer. According to the TEM and elemental analysis data, the average number of molecules of the porphyrin derivative per nanoparticle varied from 30 to 80 depending on the NP size (3–4 nm).

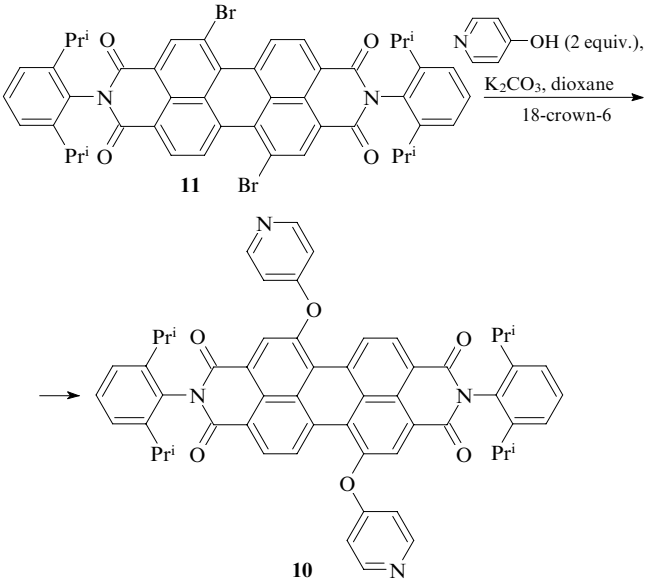
Further, the same authors studied the interaction between the zinc porphyrin-modified nanoparticles and various anions (Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, ClO_4^-). Binding of anions was due to their interaction with zinc as Lewis acids and also due to hydrogen bonding with the ligand amide groups. The strongest interaction was observed for Cl^- and $H_2PO_4^-$ anions. The main drawback of the proposed method is associated with the fact that it can be applied only to determination of anions in non-aqueous media (in methylene chloride or DMSO). This prevents the use of thus modified nanoparticles as sensors for anions in biological fluids.

The use of modified gold nanoparticles in the fluorimetric and colorimetric determination of Cu^{II} ions was described.[87] This method is based on the changes in the efficiency of photoluminescence quenching of chromophore-containing ligands in the presence of gold nanoparticles and Cu^{II} ions. The model system contained chromophore groups (pyridine) connected to the nanoparticle surface by weak coordination N–Au bonds. As the ligand, bis[*N*-(2,6-diisopropylphenyl)imide] of 1,7-bis(4-

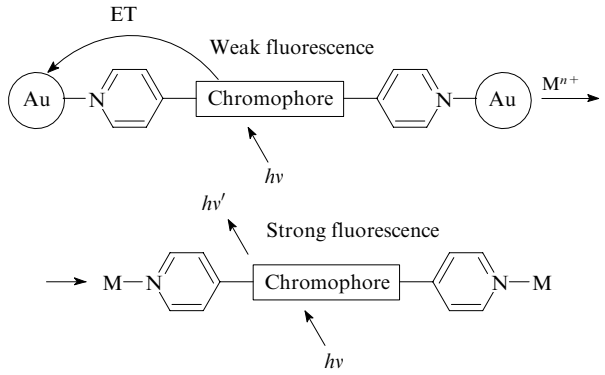
Scheme 5



pyridyloxy)perylene-3,4,9,10-tetracarboxylic acid (**10**) was synthesized by the reaction of bisimide **11** with 4-hydroxypyridine in the presence of potassium carbonate in dioxane and also 18-crown-6 as the phase transfer catalyst.



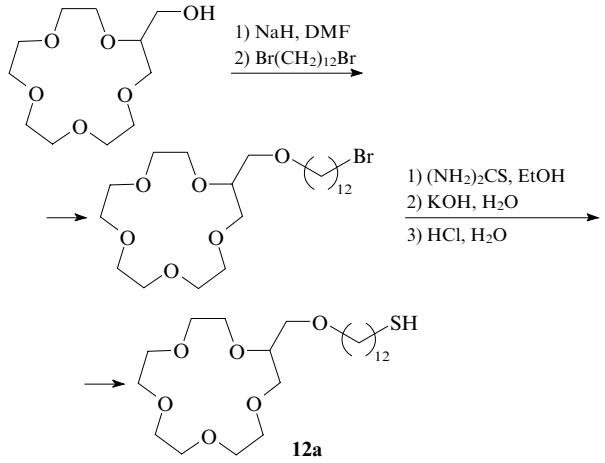
Modified gold nanoparticles were synthesized by the reduction of chloroauric acid with tetrabutylammonium borohydride in the presence of dodecylamine as the stabilizer and subsequent substitution of the desired ligand for dodecylamine. According to TEM data, the average size of nanoparticles non-modified with bisimide was 3 nm. Upon the modification, the nanoparticles aggregated due to weak coordination interactions between the pyridine nitrogen atoms and gold atoms of the neighbouring nanoparticles to induce quenching of fluorescence of chromophore groups. With the introduction of a stronger complexing agent (Cu^{II} ions), the N–Au bonds dissociate, the ligands are desorbed from the gold surface to give complexes between the ligand under study and Cu^{II} ions in the solution. This is accompanied by the appearance of a spectral band typical of the complex of bisimide **10** with Cu^{II}.



ET is energy transfer.

In systems of this type, the colorimetric determination of Cu^{II} ions is possible, because the formation of copper complexes with bisimide **10** is accompanied by liberation of individual nanoparticles and the appearance of the SPR band at 515 nm in absorption spectra, which is typical of unmodified NP. In the process, the solution changes its colour from purple to orange. Furthermore, the selectivity of the reaction of synthesized ligand **10** with Cu^{II} ions was studied. No fluorescence signal was observed in the presence of Li^+, Na^+, K^+, Ca^{2+}, Ag^+ or Al^{3+} ions; upon the addition of Cu^{2+}, the signal intensity was 2–3 times higher than after the introduction of Co^{2+}, Ni^{2+}, Fe^{3+} or Zn^{2+}.

The possibility of using crown ether-functionalized nanoparticles in the selective determination of K^+ ions in aqueous solutions was reported.[89] Chromoionophore sensors were considered as the most important class of ion-selective compounds back at the time of Pedersen, Lene and Cram works (see a review [90]). Gold nanoparticles modified with thiol **12a**-containing terminal crown-ether groups (15-crown-5) and their interaction with potassium ions was studied.[89] Ligand **12a** was synthesized as follows:

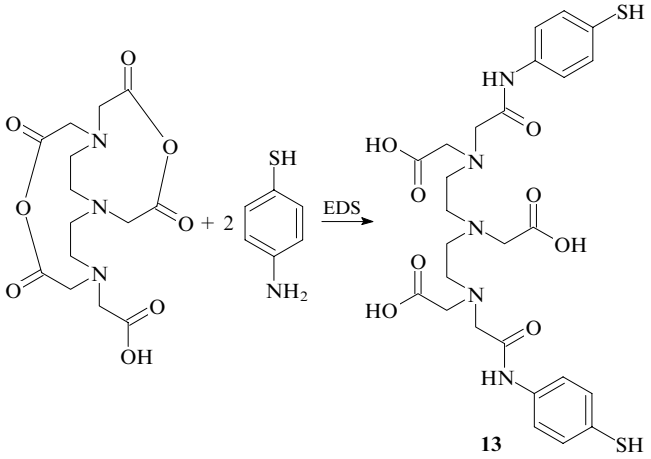


Modification of gold nanoparticles was carried out by the Turkevich method. It is noteworthy that these nanoparticles proved to be insensitive to Na^+ ions present in solution (from sodium citrate). Nor any analytical signal was observed upon the addition of excess Na^+, although it is well known that molecules of 15-crown-5 preferentially form complexes with Na^+ ions.

Upon the addition of potassium ions to a solution of modified nanoparticles, the NP aggregated due to the formation of sandwich complexes containing 15-crown-5 and K^+ ions in the 2 : 1 ratio. The solution immediately changed its colour from red to blue. This phenomenon was observed even in the presence of an excess of Na^+ ions, although 18-crown-6 is regarded as the most suitable reagent for complexation with potassium ions. To completely eliminate the possibility that Na^+ ions are responsible for the formation of aggregates and colour changes, experiments using lithium salts instead of sodium salts were carried out. All the effects observed earlier were retained. Hence, the described method of K^+ ion recognition is selective with respect to many other ions such as Na^+, Li^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+} and allows for detection of potassium ions starting from the concentration of 7.6 μmol litre^{-1} for the nanoparticle concentration of 7.1 nmol litre^{-1}.

For the development of nanoparticle-based sensors, the ligands containing photoactive groups were also used for nanoparticle modification. For example, complexes of organic ligands with lanthanides can serve as luminophores. The 1 : 1 complex of ligand **13** based on diethylenetriamine-

pentacarboxylic acid with Eu^{III} was synthesized.[91] Ligand **13** was prepared by the condensation of 4-aminobenzenethiol with diethyltriaminepentacarboxylic bisanhydride.



13

The Eu^{III} complex was prepared by the reaction of ligand **13** with $EuCl_3 \cdot 6H_2O$. The addition of a solution of this complex to a solution of NP stabilized with citrate ions (the NP average diameter was 10–15 nm) produced modified monodisperse spherical particles without any aggregation.[91]

Interesting photochemical properties were exhibited by nanoparticles modified with luminophore groups.[91,92] In particular, in certain cases, photoactive groups were observed to retain their luminescence properties after the ligand adsorption on the NP.[92]

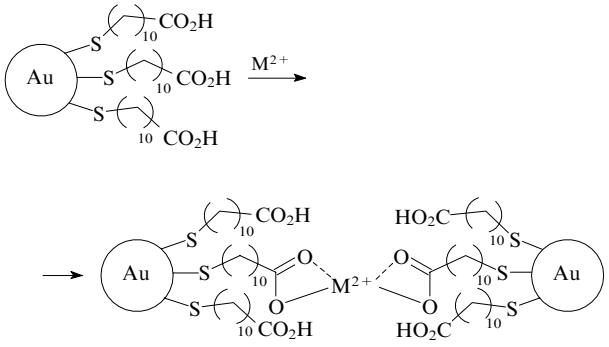
As a model compound for studying photochemical properties, the ruthenium complex $[Ru(bipy)_3]^{2+}$ (bipy is 2,2′-bipyridine) was chosen.[92] The photochemical and photophysical properties of polypyridine compounds and their complexes (including complexes with ruthenium) attract special attention because compounds of this class can be used in solar energy utilization systems.[93] Tris(bipyridine) ruthenium complexes sitting on the nanoparticle surface were synthesized according to Scheme 6.

According to the results of TEM, the average number of $[Ru(bipy)_3]^{2+}$ chromophore molecules on a single npAu-**3** particle is 145. The synthesized NP were studied by the method of nanosecond laser flash photolysis, which demonstrated the possibility of charge transfer over the NP surface. Presumably, the $[Ru(bipy)_3]^{3+}$ and $[Ru(bipy)_3]^{+}$ complexes were formed on the nanoparticle surface as a result of electron transfer between the excited and ground-state $[Ru(bipy)_3]^{2+}$ molecules. Such NP can be used in photocatalysis and also as chemical and biological sensors.[92]

In the field of sensor-based diagnostics and molecular recognition, the effect of considerable enhancement of Raman scattering by gold nanoparticles modified with organic ligands, the so-called SERS effect (see Section III), has been developed in recent years.

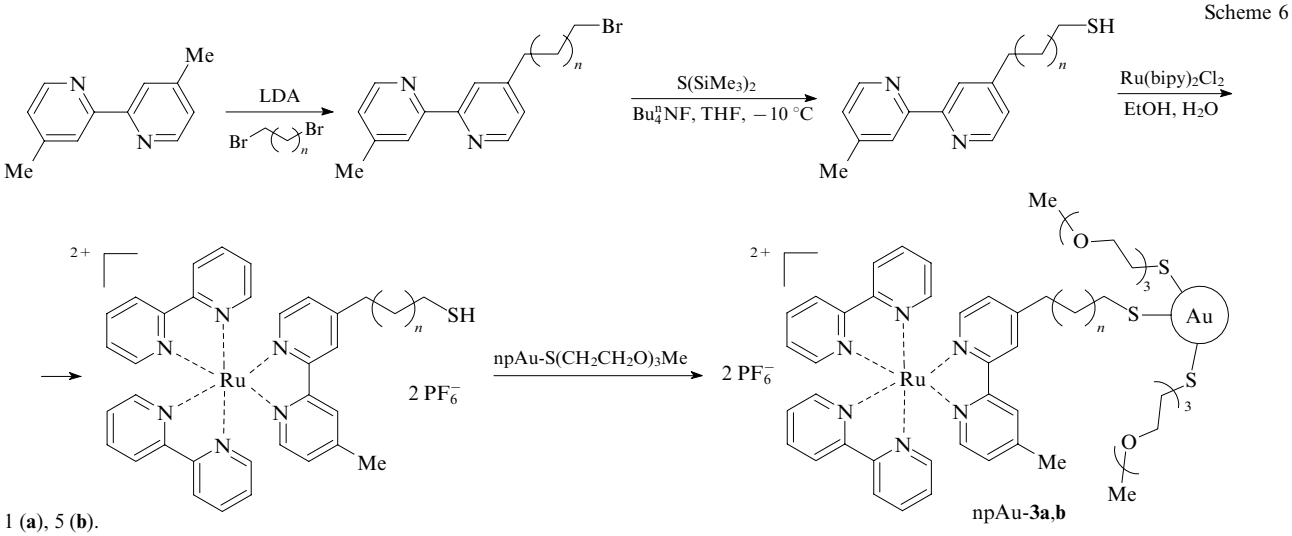
Lately, strong surface enhancement of Raman scattering has been found for gold nanoparticles modified with triazinetrithiol,[94] considerable changes being induced by the interaction of these nanoparticles with transition metal ions. It is known that the SERS effect exhibited by gold, silver and copper nanoparticles can serve as an extremely sensitive analytical signal.[68]

One of the first examples of the use of SERS effect in the determination of metal ions on their interaction with gold nanoparticles was described by Kim *et al.*,[63] who used this method to determine mercury, lead and cadmium ions. Gold nanoparticles (measuring 13.6 ± 0.6 nm) modified with 11-mercaptoundecanoic acid were synthesized.



The addition of heavy metal salts (Hg^{II}, Pb^{II}, Cd^{II}) to a solution of these nanoparticles results in their aggregation and a long-wavelength shift of the SPR band. The solution

Scheme 6



n = 1 (**a**), 5 (**b**).

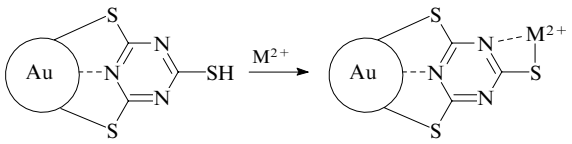
npAu-**3a**,**b**

colour changes from pink to blue. In this case, the aggregation is reversible so that the addition of EDTA to the aggregated nanoparticles results in the recovery of the original non-coordinated gold NP. For a common colorimetric determination with the use of synthesized nanoparticles, the detection limits of metal ions are rather high, for instance, 400 μmol litre^{-1} for Pb^{II} ions. It was assumed that the detection limit can be somewhat lowered down by decreasing the number of chelating fragments capable of binding to the metal on the nanoparticle surface. This can be achieved by synthesizing coarser nanoparticles. A more efficient method consists in the adsorption of ligands capable of specific and selective binding to certain metal ions on the gold surface.

Considerably lower detection limits were observed for the use of the gold nanoparticles for determining metal ions on the basis of the highly sensitive SERS effect. For instance, the detection limit for Pb^{II} ions was 25 μmol litre^{-1}. The solution did not change its colour in the process, which pointed to a higher sensitivity of this analysis as compared with the spectrophotometric method.

Using the Turkevich method, the gold nanoparticles modified with 1,3,5-triazine-2,4,6-trithiol (**14**) were synthesized.[94] Although the ligand molecule had three SH groups and three nitrogen atoms capable of binding to the gold surface by covalent and coordination bonds, respectively, no substantial aggregation of nanoparticles was observed as evidenced by the results of electronic spectroscopy and dynamic light scattering studies. However, the Raman spectra indicated that the ligand was bound to the gold surface by two sulfur atoms and a nitrogen atom of the heterocyclic ring. The third sulfur atom and two nitrogen atoms remained free and could interact with transition metal ions.

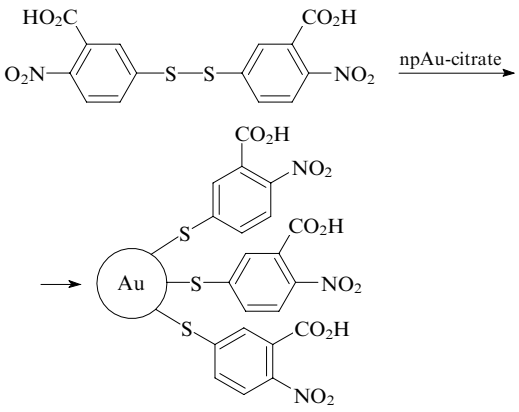
Nanoparticles modified with ligand **14** were studied in the complexation with Hg^{II} and Cd^{II} ions, because triazinethiol fragments often prove to be capable of selective interaction with heavy metal ions.



M = Hg, Cd.

According to the results of Raman spectroscopy, Hg^{II} ions are coordinated to the sulfur atom in the ligand; in addition, the triazine ring is also involved in the complex formation. The Cd^{II} ions are bound to the sulfur atom much more weakly. Hence, cadmium ions preferentially interact with the nitrogen atom of the triazine ring. This is why gold nanoparticles modified with ligand **14** can be used as selective and sufficiently sensitive sensors for determination of mercury and cadmium ions.

The use of gold nanoparticles modified with 5,5′-dithiobis(2-nitrobenzoic acid) in the selective determination of Cr^{III} ions in aqueous solutions was described.[95] These nanoparticles were synthesized by the method of Turkevich from sodium citrate-stabilized NP with the average size of 13 nm.



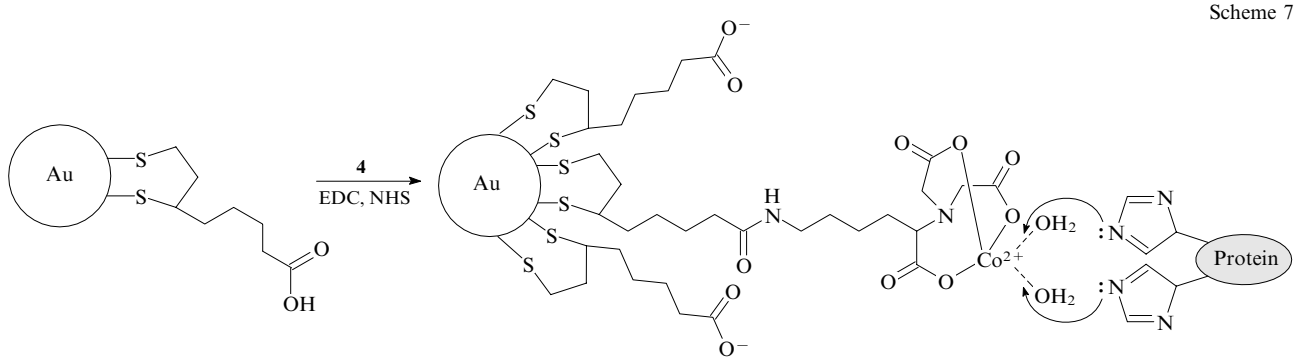
The effect of solution pH on the properties of synthesized nanodispersions was investigated. For pH > 6.0, the solutions of modified nanoparticles were stable for a long time (over a week). For pH < 5.0, their gradual aggregation was observed, as evidenced by the long-wavelength shift of the SPR band. According to TEM data, in the presence of Cr^{III} ions, coarse aggregates were formed as a result of coordination interactions between the ligands adsorbed on the nanoparticle surface and Cr^{III} ions. For other metal ions such as Pb^{II}, Al^{III}, Fe^{II}, Hg^{II}, Co^{II}, Ni^{II}, Cu^{II}, K^{I}, Cd^{II}, Mg^{II}, Ca^{II}, Zn^{II}, Mn^{II}, Fe^{III}, virtually no SPR band shift was observed. Thus, the synthesized gold nanoparticles can be used as highly sensitive sensors in the determination of Cr^{III} in solutions in the presence of other metals.

A new efficient method of protein immobilization on the surface of gold nanoparticles due to coordination interactions between complex **4** adsorbed on the nanoparticle surface and histidine residues of proteins was proposed.[96] The authors used horse-radish peroxidase and redoxin-$NADP^+$-reductase containing histidine residues introduced by methods of genetic engineering. The initial gold nanoparticles with the average size of 2.9 ± 0.9 nm were synthesized by the Brust method with thioctic acid (**5**) as the stabilizing agent. The resulting nanoparticles were modified with complex compound **4** by the amination reaction (as in Ref. 77) (Scheme 7).

In complexes **4** adsorbed on the surface of gold nanoparticles, some donor groups can be substituted for the water molecules that initially occupy two positions in the metal coordination sphere. In the final stage of this work, the synthesized nanoparticles were studied in the reaction with modified proteins containing histidine residues. The immobilization was shown to have virtually no effect on the activity of proteins studied, *i.e.*, the latter totally retained their biological functions. Independent experiments with the use of peroxidase without histidine fragments pointed to the absence of its binding to the modified nanoparticles. This confirms the fact that immobilization proceeds as a result of coordination interactions rather than non-specific adsorption of a protein on the gold surface due to electrostatic or hydrophobic interactions or hydrogen bonding. The developed procedure was also successfully employed for the surface immobilization of ferredoxin-$NADP^+$-reductase.

Darbha *et al.*[97] proposed a new fast and highly sensitive method for the determination of mercury ions in soil, water and fish, which is based on the near-surface transfer of

Scheme 7

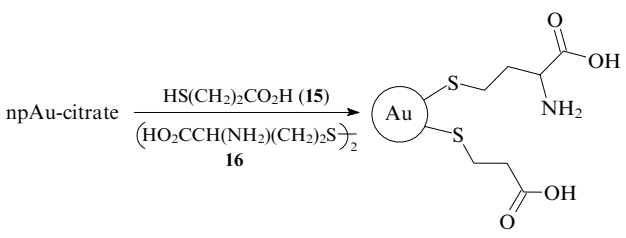


energy referred to as nanomaterial surface energy transfer (NSET) in modified gold nanoparticles. The nanoparticle surface acts as an electron acceptor and the organic ligand acts as an electron donor, which allows using such systems in the highly selective determination of metal ions. This is based on quenching of the fluorescence of chromophores upon the adsorption as a result of the energy or electron transfer. Rhodamine B, which shows strong fluorescence (the fluorescence quantum yield is 0.70) in aqueous solutions was employed as the stabilizer of gold nanoparticles. The modified gold particles were prepared by the Turkevich method.

The adsorption of rhodamine B on the nanoparticle surface totally quenches the fluorescence (static quenching) due to the efficient nonradiative transfer of energy to the nanoparticle surface. In the presence of Hg^{II} ions, rhodamine molecules are liberated from the surface of gold nanoparticles, which is accompanied by the appearance of an emission band in the fluorescence spectra. The 800-fold increase in the fluorescence intensity was observed as soon as several seconds after Hg^{II} ions in concentration of 130 ppb were added to the modified nanoparticles.

The described method makes it possible to determine Hg^{II} ions in their solutions with the concentration down to 2 ppt, *i.e.*, four orders of magnitude lower than their maximum permissible concentration in drinking water. To enhance the selectivity, gold nanoparticles were modified with mercaptopropionic acid, homocystine (covalently binds to the gold surface) and a specific chelating agent, pyridine-2,6-dicarboxylic acid. In this version, the method proved to be highly selective and made it possible to determine Hg^{II} ions in the presence of alkali and alkaline earth metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) and also heavy metal ions (Pb^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} , Cd^{2+}) without loss of sensitivity.

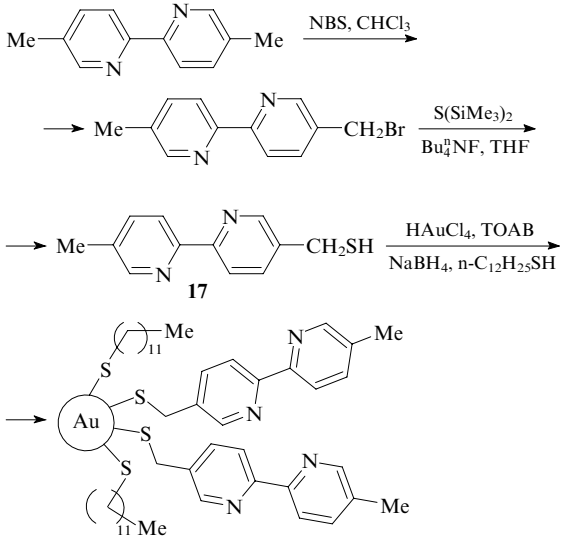
A method of determination of Hg^{II} ions in aqueous solutions based on non-linear-optical properties of gold nanoparticles modified with mercaptopropionic acid (**15**) and homocystine (**16**), was proposed.[98] The modified nanoparticles were prepared by the Turkevich method from citrate-stabilized NP with the diameter of 15 nm. The system also contained pyridine-2,6-dicarboxylic acid as the chelating agent by analogy to the method described in Ref. 97.



The addition of Hg^{II} salts to the solution induces pronounced aggregation of NP due to the coordination interactions between the mercury ions and the chelating ligands adsorbed on the nanoparticle surface. In the process, the solution colour changes from red to blue. In this case, visible changes in the solution colour occur only when the Hg^{II} ion concentration of 10 ppm has been reached.

The selectivity of binding the synthesized NP to mercury ions was additionally examined. Gold nanoparticles modified with only mercaptopropionic acid and homocystine proved to weakly interact with Fe^{II}, Mn^{II}, Zn^{II}, Ni^{II}, Cr^{III}, K^{I} and Sr^{II} ions; noticeable interaction accompanied by the SPR shift to longer wavelengths was observed in the presence of Hg^{II}, Pb^{II} and Cd^{II} ions. When pyridine-2,6-dicarboxylic acid was used as the chelating agent, the method proved to be highly sensitive with respect to Hg^{II} ions in the presence of alkali, alkaline earth (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) and heavy metal ions (Pb^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}).

Gold nanoparticles with the average size of 4 nm modified with complexes formed by a bipyridine derivative with Eu^{III} and Tb^{III} were described;[99] such particles can be used as phosphorescent materials and sensors. Thiol-group-containing 2,2′-bipyridine derivative **17** was synthesized.



These modified gold nanoparticles were introduced into complexation reactions with Eu^{III} and Tb^{III} ions. It is

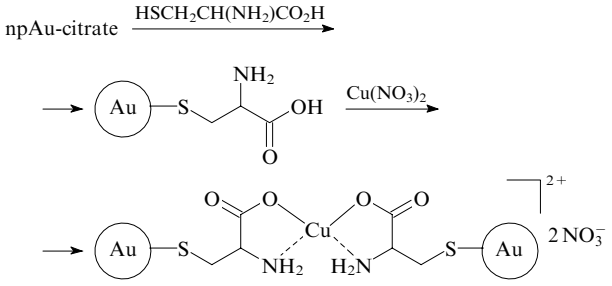
known that lanthanide ions are capable of long-term emission; however, they are characterized by low luminescence quantum yields as a result of the low absorption coefficients of ions, because the f – f-transitions are forbidden. However, phosphorescence of lanthanide ions can be considerably enhanced upon the formation of coordination compounds with organic ligands.

Among the most important advantages of the gold nanoparticles synthesized in the study cited[99] is their high absorption coefficient due to the presence of ~340 molecules of a bipyridine derivative on the surface of each nanoparticle (as evidenced by TEM and electronic spectroscopy). The adsorbed ligands were shown to interact with metal ions in the 3 : 1 ratio, the interaction involving ligands adsorbed on different nanoparticles. The latter fact was confirmed by TEM data. In the absence of lanthanide ions, individual gold nanoparticles are randomly dispersed. At the same time, in the presence of Eu^{III} or Tb^{III} ions, aggregates are formed as a result of formation of complex compounds adsorbed on the gold surface. Studying luminescent properties of these gold NP has shown that in the presence of lanthanide ions, the emission intensity sharply increases. A possible application of these systems based on bipyridine complexes with lanthanide ions is their use as the highly sensitive sensors for the ions of Group 2 metals (Ca^{2+} and Mg^{2+}) and transition metals (Cu^{2+}, Zn^{2+}, Ni^{2+}) in the presence of which the luminescence intensity decreases due to the isomorphous displacement of Eu^{III} ions from the surface-adsorbed complexes. Moreover, for Group 2 and transition metals, the luminescence was observed to considerably weaken, which is attributable to their stronger binding ability as compared with Eu^{III} ions. On the other hand, in the presence of alkali metal ions (Na^+, K^+), no changes were observed in the luminescence intensity.

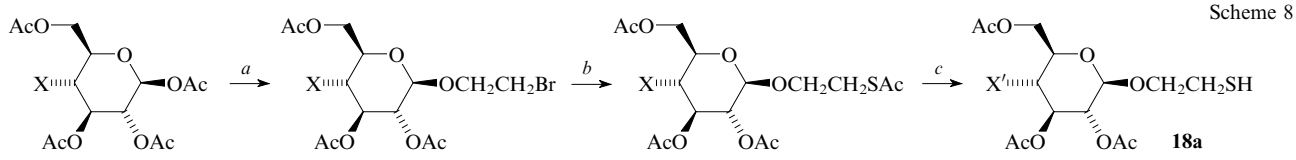
Gold nanoparticles modified with lactose derivatives were described and their interaction with calcium ions was studied.[100] For stabilizing gold nanoparticles, lactose derivatives **18a – d** containing different-length oxyethylene bridges that connect the thiol and the carbohydrate groups were synthesized (Scheme 8). In control experiments, glucose derivative **19** was used. The original gold nanoparticles measuring 16.0 ± 1.5 nm were prepared by the Turkevich method.

Upon the addition of Ca^{2+} ions to the gold nanoparticles modified by the lactose derivative, the aggregation takes place, as evidenced by TEM and electronic spectroscopic studies. The aggregates can be destroyed by the addition of EDTA to the solution; this gives the initial monodisperse nanoparticles. This confirms that aggregation proceeds due to interaction of Ca^{2+} ions with the carbohydrate residues rather than with the citrate anions also present on the surface. With the increase in the Ca^{2+} concentration in solution, the degree of aggregation increases. The degree of aggregation and the analytical sensitivity with respect to Ca^{2+} ions were shown to depend on the linker length. For the shortest linker ($m = 0$, compound **18a**), the highest sensitivity with the minimum detection limit (0.8 mmol litre^{-1} Ca^{2+}) was observed, whereas for the maximum chain length ($m = 3$), the detection limit was 10 – 35 mmol litre^{-1}. Such nanomaterials can find application in the detection of carbohydrate – carbohydrate interactions in various biological objects.

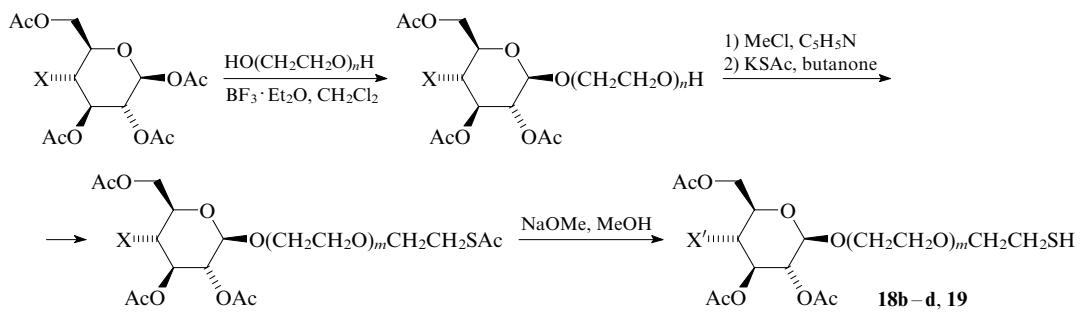
A new highly sensitive colorimetric method of cysteine determination with the use of gold nanoparticles was reported.[101] The method relies on the coordination interaction of cysteine molecules adsorbed on the gold surface with Cu^{II} ions and also on the dependence of optical properties of nanoparticles on their size and the distance between them. Modified gold nanoparticles measuring ~13 nm were synthesized by the Turkevich method.



Scheme 8



X = *O*-D-(GalAc$_4$), X′ = *O*-D-Gal (Gal is galactose residue);
(*a*) $HOCH_2CH_2Br$, $BF_3 \cdot Et_2O$, CH_2Cl_2; (*b*) KSAc, butanone; (*c*) NaOMe, MeOH.



X = *O*-D-(GalAc$_4$) or OAc; for compounds **18**: X′ = *O*-D-Gal: $m = 1$ (**b**), 2 (**c**), 3 (**d**); for compound **19**: X′ = OH, $m = 3$; $n = m + 1$.

Solutions of cysteine and Cu^{II} salt were sequentially added to sodium citrate-stabilized NP.

The aggregation of NP is due to the interaction of a copper atom with carboxyl and amino groups of cysteine to form complex compounds adsorbed on the gold surface. Each Cu^{II} ion binds together two ligand molecules localized on neighbouring nanoparticles. The system sensitivity proved to be much lower when a pre-synthesized Cu^{II} cysteine complex was added to the solution of gold nanoparticles. This was explained by the fact that aside from the complexation of cysteine, the Cu^{II} ions can be involved in the oxidation of the thiol moiety of the amino acid, which affects their binding to gold nanoparticles. For the procedure developed in the above studies, the cysteine detection limit was 10 nmol litre^{-1}. This method is extremely selective with respect to other α-amino acids, glutathione, thioglycolic acid and 2-mercaptoethanol.

Gold NP were modified with a 1,10-phenanthroline derivative which can selectively interact with Li^+ ions.[102] The primarily prepared citrate-modified gold nanoparticles measuring 4 nm were used as the nuclei for the subsequent synthesis of nanoparticles with the size of 32 nm. The nanoparticles measuring 4 and 32 nm were modified with phenanthroline derivative **20** (Scheme 9).

The ligands present on the gold surface react with Li^+ ions to form 2 : 1 metal complexes, and this leads to nanoparticle aggregation. The modified gold nanoparticles measuring 4 nm were found to be more sensitive with respect to lithium ions. Presumably, this is associated with their relative surface areas. Assuming that in both cases the ligands occupy the whole surface of a particle, the formation of complexes requires less Li^+ ions for smaller particles (4 nm) (surface area $\sim$50 nm^2) than for 32 nm particles (surface area $\sim$3200 nm^2). In the study cited, the gold nanoparticles modified with this ligand were shown to be selective with respect to Li^+ ions in the presence of small amounts of K^+ and Na^+ ions.

A new method of synthesis of gold nanoparticles containing crown-ether groups on their surfaces was proposed.[103] Modified nanoparticles were used as selective sensors for K^+ ions.

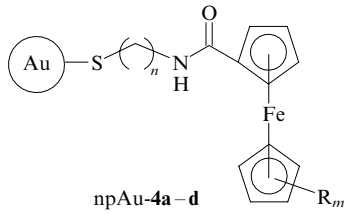
The addition of potassium ions to a NP solution gives coarser aggregates due to the coordination interaction of crown-ether moieties on the nanoparticle surface with K^+ ions to form sandwich complexes with the ratio ligand : metal = 2 : 1. It was mentioned that such complexes may incorporate crown-ether moieties of ligands adsorbed on either one nanoparticle or on different nanoparticles. Gold nanoparticles modified with crown ether derivatives are highly sensitive with respect to K^+ ions; the selective determination of K^+ in the presence of other cations such as Na^+, Li^+, Cs^+, Rb^+, NH_4^+, Mg^{2+} and Ca^{2+} is possible. The detection limit of potassium ions was shown to be 0.05 – 0.95 mmol litre^{-1}.

Gold nanoparticles modified with alkanethiols containing ferrocene moieties are described.[104] The synthesized nanoparticles were tested as the redox sensors for oxoanions. The development of new sensors for anions is a topical research area because many inorganic anions play an important role in biological and biochemical processes. Sensors for anions often represent redox systems usually based on ferrocene derivatives.[105, 106]

Ligands based on thiols containing terminal ferrocenecarboxamide moieties with methylene chain-linkers of different length were synthesized.[104] To study how the stereoelectronic properties affect the oxoanion recognition, ligands in which the unsubstituted cyclopentadienyl ring (Cp) was replaced by completely methylated (η^5-C_5Me_5, Cp*) or monosubstituted (η^5-C_5H_4Ac) rings were also synthesized. The target gold NP npAu-**4a** – **d** were synthe-

Scheme 9

sized by the ligand exchange with dodecanethiol-stabilized nanoparticles prepared by the Brust method (the size 2.0 nm).

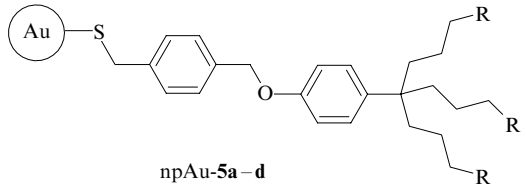


npAu-**4a**–**d**

R_m = H: n = 1 (**a**), 6 (**b**); R_m = Me_5, n = 11 (**c**); R_m = Ac, n = 11 (**d**).

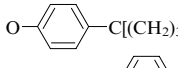
Depending on the linker length and the dodecanethiol to ligand ratio, gold nanoparticles with various ratios of dodecanethiol and ferrocene derivatives on the surface were formed. These nanoparticles were studied by cyclic voltammetry (CV) on a platinum electrode. As expected, the voltammograms demonstrated a single reversible wave of ferrocene oxidation with the shape dependent of the nature of ferrocene complex. Upon the addition of tetrabutylammonium dihydrogenhosphate to the solution, the voltammogram demonstrated a new electrochemically less reversible (with partial adsorption) wave at a less positive potential (220 ± 20 mV) as compared with original nanoparticles. The intensity of this new wave increased with the increase in the anion concentration. The initial wave disappeared upon the addition of 1 equivalent of the anion. Its shift depended on neither the ligand concentration on the nanoparticle surface nor the chain length; however, it decreased upon replacement of one Cp ring by the Cp* moiety and increased upon its replacement by η^5-C_5H_4Ac. This pointed to the important role of the hydrogen bond formed between an amide NH group and the terminal oxygen atom in the oxoanion. The addition of tetrabutylammonium hydrogensulfate to a solution of modified gold nanoparticles resulted in the wave being shifted (30 mV) from its initial position. This makes it possible to use these modified NP in the determination of HSO_4^- ions in solution. Moreover, a possibility of selective determination of $H_2PO_4^-$ ions in the presence of both $Bu^n_4NHSO_4$ and Bu^n_4NCl was demonstrated.

Yet another example of the use of ferrocene derivatives adsorbed on the gold surface in the determination of $H_2PO_4^-$ and HSO_4^- anions and also of adenosine 5′-triphosphate anion (ATP^{2-}) was described.[107] Tri- and nonaferrocenyl-containing dendrimers with terminal thiol groups containing linkers of different nature were synthesized; these ligands were used in the synthesis of modified gold nanoparticles npAu-**5a**–**d**.

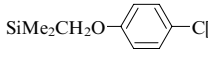


npAu-**5a**–**d**

R = $SiMe_2Fc$ (**a**), $SiMe_2CH_2NHC(O)Fc$ (**b**),

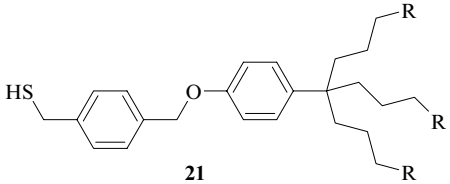


(**c**),

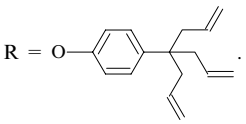


(**d**); Fc is ferrocenyl.

The following two approaches to the synthesis of modified gold nanoparticles were used: the method of ligand exchange with dodecanethiol-modified gold nanoparticles (for triferrocenyl-containing dendrimers) and the direct synthesis of nanoparticles by the Brust method with the use of ready ligands as the stabilizers (for nonaferrocenyl-containing dendrimers). The scope of application of the first approach is limited by the size of dendrimers used in modification. Thus the introduction of model nonaallyl derivative **21** into the ligand-exchange reaction led to the adsorption of a very small number of dendrimer molecules on the gold surface (less that one molecule per particle).



21

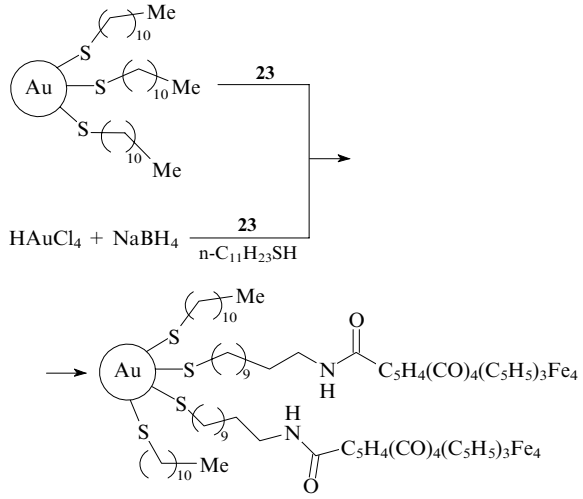


Hence, to obtain such NP, the direct Brust method (using dodecanethiol–dendrimer mixture in different ratios) was employed. According to TEM results, the average size of the thus synthesized nanoparticles was 2.9 nm.

Using CV, it was shown that nanoparticles npAu-**5c**,**d** modified with dendrimers containing nine ferrocenyl fragments can selectively recognize anions such as $H_2PO_4^-$ and ATP^{2-} in solutions (a new wave appears in the CV curve at the less positive potential). Such nanoparticles can be used in titration of the mentioned anions owing to the shift that appears in the voltammograms even in the presence of other anions (Cl^- and HSO_4^-). Nanoparticles npAu-**5b** with ferrocenylamide moieties can be used in the recognition and titration of HSO_4^- anions; this was also confirmed by electrochemical studies. Furthermore, the synthesized dendrimer gold nanoparticles can be used in the modification of platinum electrodes through the formation of nanoparticle films on the electrode surface. Moreover, the thus modified platinum electrodes exhibited the sensor activity with respect to $H_2PO_4^-$, HSO_4^- and ATP^{2-} ions. After washing, the electrode can be used again.

A more recent study [108] presents another example of the synthesis of gold nanoparticles modified with derivatives of the tetrahedral cluster $[Fe(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)]_4$ (**22**) covalently bound to the surface to be used as sensors for $H_2PO_4^-$ and ATP^{2-} oxoanions. Like ferrocene, cluster **22** is an example of a strong reducing system (Fe_4/Fe_4^+) in which a neutral cluster is oxidized to a cationic cluster, the process being completely reversible and proceeding at moderate potentials. In the non-adsorbed state, the amide-containing derivative of complex **22** fails to recognize oxoanions. The authors of the study cited have shown that in the latter case, gold nanoparticles serve as templates for self-assembling of nanostructured fragments. Such nanoparticles can recognize the anions mentioned above. The thiol $[Fe_4(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_4(\eta^5\text{-}C_5H_4C(O)NH(CH_2)_{11}SH]$ (**23**) with the terminal metal complex group was synthesized. The modified gold NP were synthesized by two

methods, namely, the ligand exchange with undecanethiol-stabilized nanoparticles and directly by the Brust method with participation of ligand **23**.



The resulting NP were studied by cyclic voltammetry method. As compared with the aforementioned gold nanoparticles modified with dendrimer derivatives of ferrocene, the redox recognition of anions with the use of the derivative of cluster **22** proceeds more easily; moreover, the shift of the voltammogram wave for ATP^{2-} anions was larger than for $H_2PO_4^-$ anions (in contrast to the case of ferrocene-based receptors).

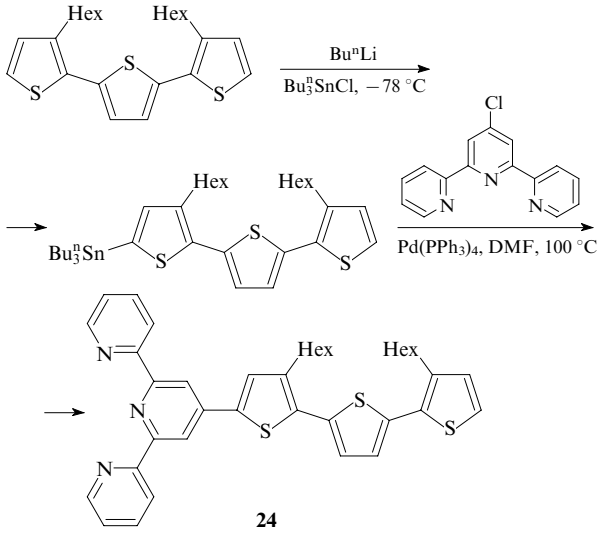
3. The adsorption of modified gold nanoparticles on different supports

The literature contains examples of the synthesis of films of gold nanoparticles immobilized on various supports.[109–112] Particularly, to prepare such films, the formation of specific hydrogen bonds between the ligands attached to the nanoparticle surface is used.[109] Dendrimers based on nanoparticles bonded *via* amino groups were synthesized.[110] Gold nanoparticles modified with appropriate ligands can be used as the 'initiators' of the formation of metal films and aggregates of certain sizes and shapes.[111, 113, 114]

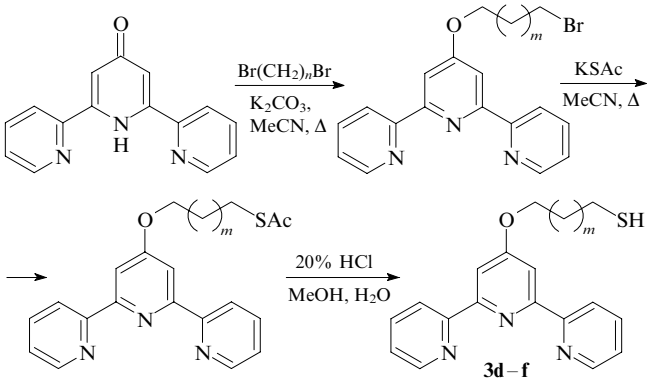
The chemical and thermal stability of hybrid nanoparticles and nanoparticle layers immobilized on a silicon support and also their resistance to sonication were studied.[115] The preparation of multilayer 'films' is based on the formation of hydrogen bonds between ligands adsorbed on the gold surface and containing carboxyl groups and polymers containing terminal amine groups. Moreover, films were synthesized by the reaction of Cu^{II} ions with the carboxyl groups of 11-mercaptoundecanoic acid adsorbed on the surface of nanoparticles.[112, 115] The electronic spectra of such films featured the broadening and a considerable long-wavelength shift of the SPR band as compared with the initial nanoparticles (>600 nm). The sonication of such films induced only a small SPR shift (<5 nm) and no changes in the band intensity, which points to the absence of any morphological changes or aggregation in the latter case.

Nanoparticles modified with thiols containing carboxyl terminal groups can be used in the development of multilayer networks of nanoparticles due to formation of bridges between carboxyl groups and metal ions, *e.g.*, Cu^{II} (see Refs 111 and 112). Such self-assembled films exhibit high stability and can be studied by different methods, namely, gravimetry (quartz crystal microbalance), spectroscopy, conductivity measurements.[112, 116] However, despite the high stability of such films, there are limitation on their use, *e.g.*, in solutions, because the films are unstable in strongly acidic media and cannot be studied by electrochemical methods if electrochemically active metal linkers (*e.g.*, Cu^{II}) have been used for their preparation.[117]

Keen attention is attracted to ligand-modified gold nanoparticles that are capable of forming nanoscale networks on different supports due to formation of metal–ligand–metal coordination bonds. A new method of network formation from gold nanoparticles and complex compounds adsorbed on the surface was described.[118] As the ligands, terpyridine compounds **3d–f**, **24** were synthesized.



Hex = n-C_6H_{13}.



$n = 3, 6, 9$; $m = 1$ (**d**), 4 (**e**), 7 (**f**).

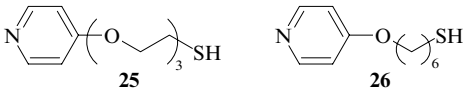
Gold nanoparticles (average diameter 4.7 ± 1.1 nm) were modified with terpyridine derivatives and then used in the synthesis of monolayers by the Langmuir–Blodgett method on the surface of gold electrodes supported by Si/SiO_2. The synthesized monolayers were studied in the complexation with $Fe(H_2O)_6(BF_4)_2$.

Based on electrochemical studies, the number of complex molecules per unit surface area of the gold electrode was calculated to be 3.7×10^{-11} mol cm^{-2}, *i.e.*, >10 complex molecules per nanoparticle.

The conductivity of all terpyridine derivatives was calculated from the results of electrochemical studies. As

expected, for conjugated thiophene ligand **24**, the conductivity proved to be 4–5 orders of magnitude higher than for its non-conjugated analogues. The conductivity of layers formed by ligands **3d**–**f** depended linearly on the methylene chain length and decreased with its elongation. Thus, the nature of the linker (conjugated or non-conjugated groups) that connect the chelating fragment with the group bound to the nanoparticle surface has the crucial effect on the electrochemical properties of modified NP.

A method of preparation of nanoparticle films on the gold surface by the formation of complex compounds between Cu^{II} ions and terminal pyridine groups of thiols adsorbed on the gold surface was proposed.[119] As the ligands, compounds **25**, **26** were synthesized.

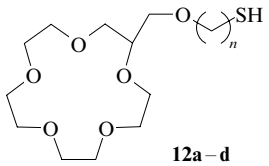


25 **26**

Modified nanoparticles were synthesized by ligand exchange with octanethiol-stabilized nanoparticles prepared by the Brust method. Nanoparticle layers adsorbed on the gold electrode surface were formed due to coordination bonding between the pyridine groups of the ligands and Cu^{II} ions. This was accomplished by alternating immersion of the tested plates into a $Cu(NO_3)_2$ solution containing the modified nanoparticles. The monolayer formation was reversible and the layers could be completely destroyed by the introduction of EDTA into the system.

The authors of the study cited have also shown that the use of Zn^{II}, Mn^{II} and Ni^{II} salts as the complexing agents failed to produce sequential adsorbed layers on the electrode surface.

Films of nanoparticles modified with crown ether-based ligands and their interaction with metal ions were described.[117] As the ligands for nanoparticle stabilization, crown ether derivatives **12a**–**d** with different length of the methylene chain connecting the ionophore groups with sulfur-containing groups were synthesized (by the method analogous to that proposed in Ref. 89).



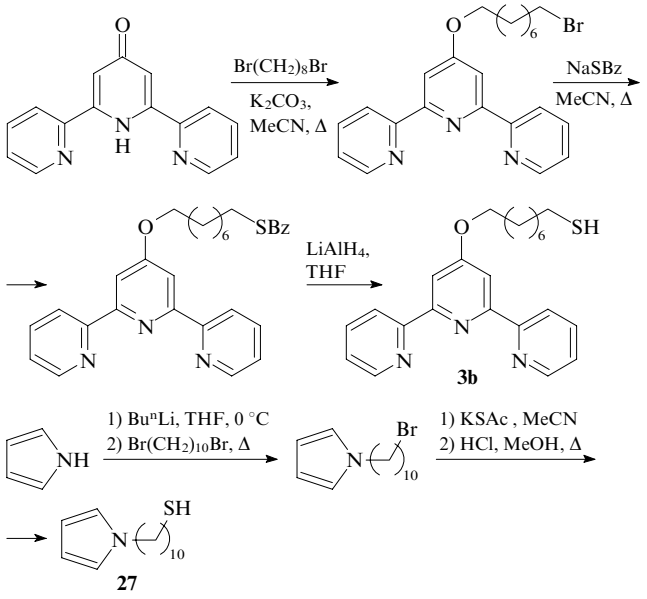
12a–**d**

n = 12 (**a**), 10 (**b**), 8 (**c**), 6 (**d**).

The initial hexanethiol-stabilized nanoparticles were prepared by the Brust method; the modified NP were synthesized by the ligand exchange between the stabilized nanoparticles and thiols **12a**–**d**. The resulting NP were supported on glass and the thus modified plate was alternately immersed into solutions of the metal salt and nanoparticles in order to form alternating layers as a result of the gold–thiol and metal–crown ether interactions. The latter led to the formation of sandwich complexes with the ratio metal : ligand = 1 : 2.[117]

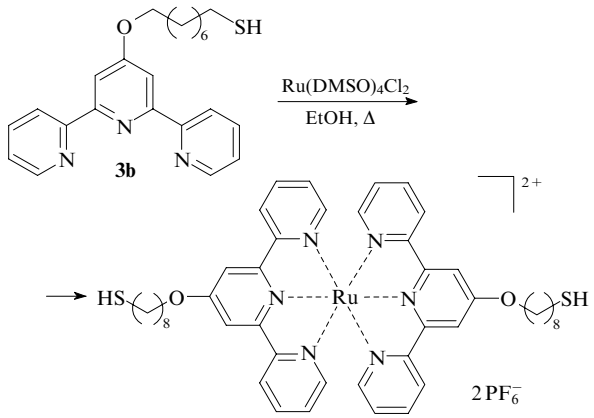
It was shown that the introduction of complexing agents other than alkali metal ions (for example, Cu^{II}) into the system fails to produce analogous films, because due to their smaller size, the copper ions cannot fill the crown-ether cavity and form a complex compound. This result confirms the hypothesis of the presence of crown ether–metal ion–crown ether interactions in the film.

A ruthenium terpyridine complex adsorbed on gold nanoparticles was synthesized.[120] Its electrochemical properties and prospects of participation in ligand exchange reactions were studied. In the first stage, ligands **3b** and **27** were prepared.



Nanoparticles synthesized by the Brust method and modified with a terpyridine derivative were introduced into the reaction with $Ru(tpy)Cl_3$ (tpy is 2,2′:6′,2″-terpyridine). This was accompanied by an increase in the nanoparticle size and their insignificant aggregation (the particle size was 5.5 ± 1.0 nm). Then, the nanoparticles modified with the adsorbed ruthenium complex were introduced into the ligand-exchange reaction with *N*-(ω-mercaptoalkyl)pyrrole to afford new multifunctional gold nanoparticles which contained free ligands (pyrrole derivatives capable of electropolymerization) and complexes (ruthenium with terpyridine). Then, the electropolymerization of resulting NP was carried out with the use of cyclic voltammetry; this was accompanied by immobilization of gold nanoparticles on the metal electrode surface. Such nanocomposite materials are very promising for the development of sensors, catalysts and in nanoelectronics.[120]

Yet another example of the formation of self-assembled monolayers of ruthenium(II) terpyridine complex on the surface of a gold electrode and gold nanoparticles was described.[121] Compound **3b** was synthesized by the same method as in the previous reference,[120] which was followed by the formation of a complex between the studied ligand and Ru^{II}.



This gave a dipolar derivative of terpyridine capable of interacting with two different nanoparticles. Next, the synthesized complex was adsorbed on the surfaces of a gold electrode and gold nanoparticles; the possibility of functionalizing a gold electrode by modified nanoparticles was also investigated.

The monolayer of nanoparticles formed on the electrode surface had a clearly pronounced morphology, consisted of domains of different shape with sizes from 20 to 60 nm; the average thickness of this layer was 2.401 nm. The layer was homogeneous due to the presence of three-dimensional clusters and their coexistence in different orientations. Thus, the synthesized dipolar complex acted as a bifunctional linker that could adsorb on the gold surface with one end and on the nanoparticle surface with the other end.[121]

Gold nanoparticles were modified with a Ru^{II} tris(bipyridine) complex.[122] As the aurophilic group, the dithiocarbamate group was chosen. The complex compound of Ru^{II} with a dithiocarbamate derivative was synthesized according to Scheme 10.

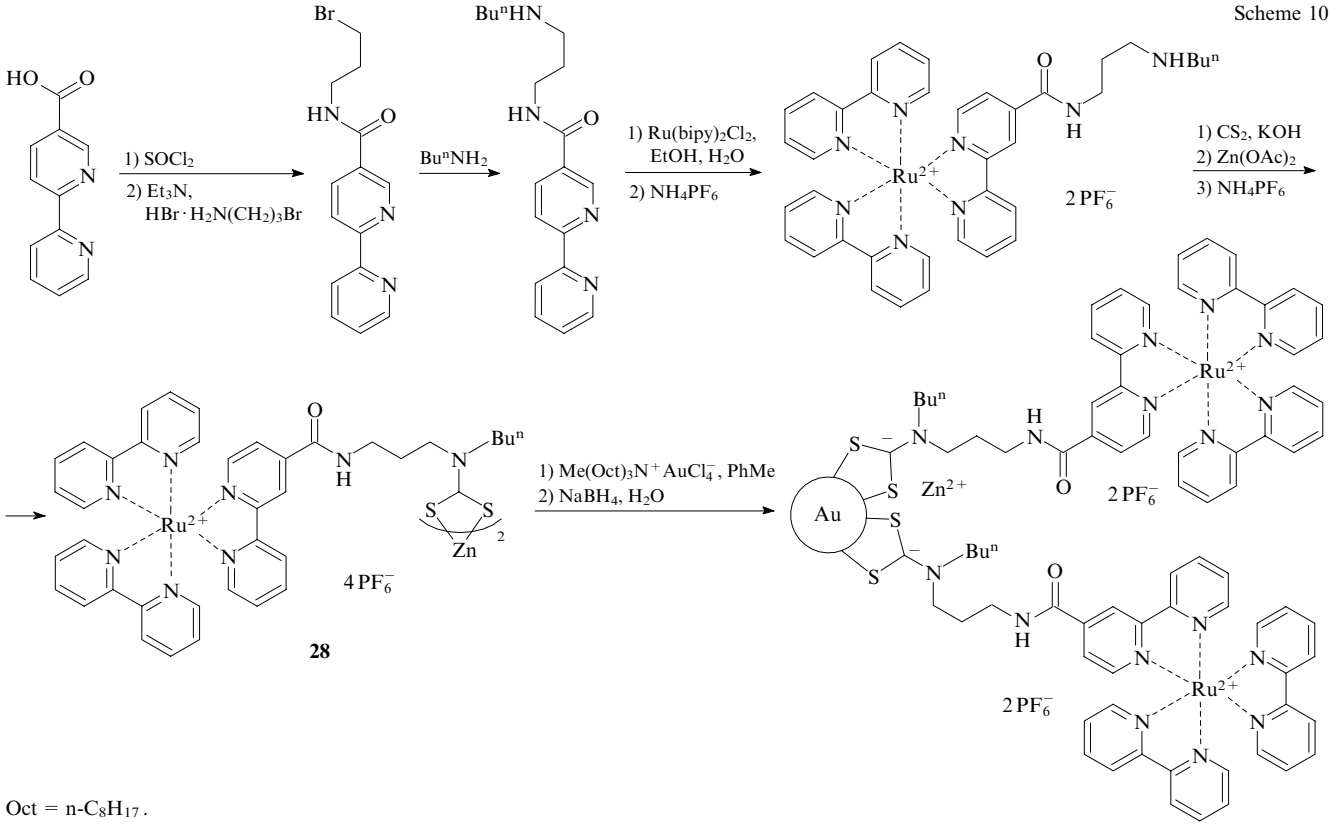
The synthesized tris(bipyridine) derivative was adsorbed on the nanoparticles upon the reaction of neutral Zn^{II} dithiocarbamate complex **28** with tetrachloroaurate followed by its reduction with $NaBH_4$. The average diameter of synthesized nanoparticles was 2.90 nm. Their luminescence spectra demonstrated no emission bands typical of the ruthenium tris(bipyridine) complex, because, as a rule, the adsorption of compounds containing luminophore groups on the nanoparticle surface quenches the luminescence.

4. Catalysts based of gold nanoparticles

The current laboratory and industrial practice widely uses catalysts immobilized on different supports, for instance, organic polymers,[123–125] activated carbon,[126] inorganic supports such as zeolites,[127] silica gel,[128] metal oxides.[129] Catalysts supported on the nanoparticle surface combine some advantages of both homogeneous and heterogeneous catalytic systems. On the one hand, immobilization on inert supports makes it possible to easily isolate the catalysts from the reaction mixtures, recover and use again in several cycles as in the traditional heterogeneous catalysts. On the other hand, the use of homogeneous catalysts allows their concentration to be maintained constant throughout the volume of the reaction mixture.[12]

There are published data on the preparation of catalysts based on self-assembled monolayers on the surface.[130, 131] The immobilization of catalysts on the surface of gold nanoparticles appears to be even more promising. The synthesized particles should have sizes comparable with certain biological molecules including proteins and nucleic acids and also various cellular substructures. Hence, these

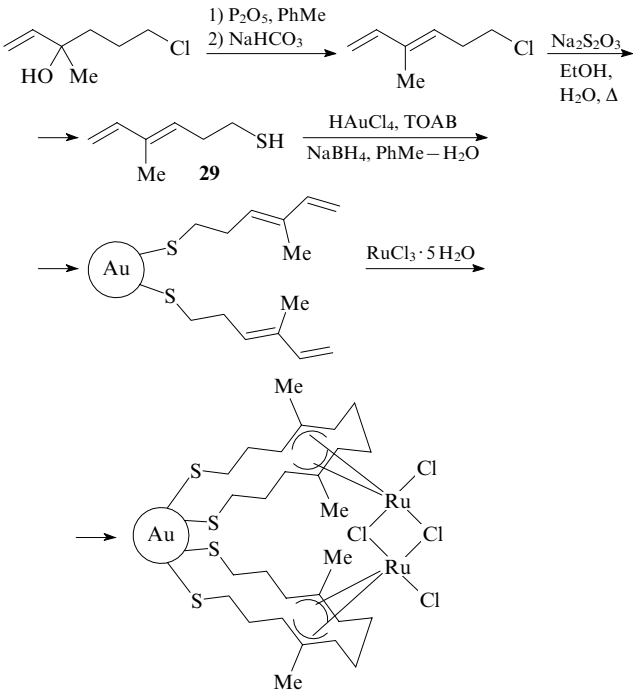
Scheme 10



Oct = n-C_8H_{17}.

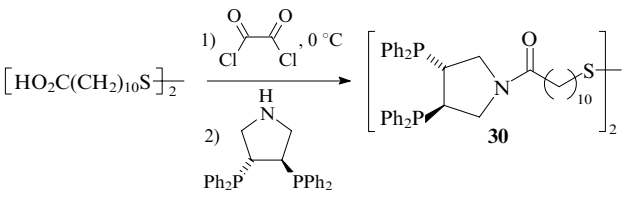
systems are promising as regards their interaction with biological molecules.[14, 32]

An early publication in this field [132] reports the synthesis of gold nanoparticles modified with binuclear ruthenium complexes with hexadiene derivatives, which proved to be active in the norbornene polymerization. As the ligand for modifying the gold surface, thiol **29** containing a hexadiene moiety was used. Modified gold NP were prepared by the Brust method and then introduced into the reaction with $RuCl_3 \cdot 5H_2O$ aimed at the synthesis of a metal complex catalyst adsorbed on the gold surface.

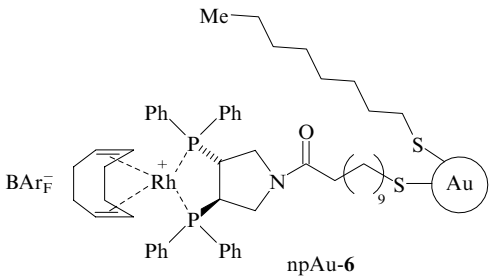


The data of NMR and IR spectroscopy indicate that binuclear coordination compounds with the central metals connected by chlorine bridges are formed on the NP surface. Note that when this reaction is carried out in methylene chloride, these nanoparticles can be considered as a heterogeneous catalyst. Moreover, such NP are well soluble in acetone, which makes it possible to carry out the polymerization under homogeneous conditions. It should be emphasized that for a catalyst immobilized on the gold surface, more catalytic cycles per unit time are possible than for the ruthenium complex in solution. Probably, this is associated with the fact that the orientation of the catalyst on the surface may appear more favourable for its reaction with the monomer and for the polymer chain propagation.

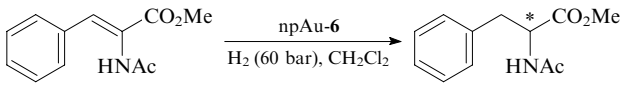
Catalysts based on a chiral complex of rhodium with diphosphine immobilized on the gold NP surface are described.[133] Chiral bis(diphosphine) ligand **30** was synthesized from 11,11′-dithiobis(undecanoic acid).



Gold nanoparticles modified with ligand **30** were obtained by the ligand exchange reaction with npAu-SC_8H_{17}-n. As a result of their interaction with $[Rh(cod)Cl]_2$ in the presence of $TlBAr_F$ (cod is cycloocta-1,5-diene, $BAr_F = [B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$), mixed monolayers involving octanethiol molecules and adsorbed complex molecules are formed on the NP surface (npAu-**6**).



In the hydrogenation of methyl α-acetamidocinnamate, the npAu-**6**-based catalyst exhibits an activity comparable with the activity of the analogous homogeneous catalyst (the yields of the product were 98% and 99%, respectively); moreover, with this catalyst immobilized on nanoparticles, the enantioselectivity of this reaction is retained (93% *ee*). Furthermore, NP could be easily removed from the reaction sphere by filtration and utilized three more times without any loss in enantioselectivity.

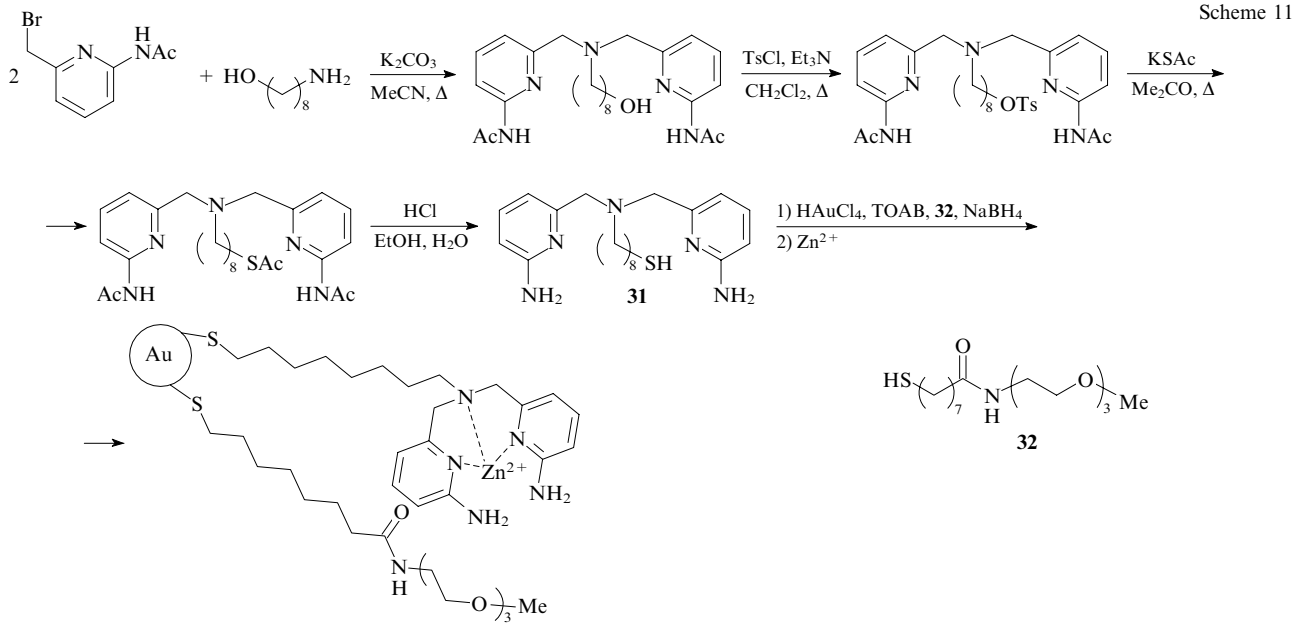


A new catalyst for the hydrolysis of phosphate diesters and DNA was proposed.[134] This catalyst was formed by the adsorption of bis(6-amino-2-pyperidylmethyl)(8-mercaptooctyl)amine (**31**) on the surface of gold nanoparticles. Gold nanoparticles were modified with mixed monolayers formed by ligand **31** and thiol **32** containing three oxyethylene units, which increased the solubility of nanoparticles in water. The gold nanoparticles were prepared by the Brust method in the presence of thiols **31** and **32** as the stabilizing agents (Scheme 11).

The reaction of bis(*p*-nitrophenyl) phosphate with gold nanoparticles modified with a zinc complex involved the hydrolysis of phosphodiester bonds to give *p*-nitrophenoxide and *p*-nitrophenyl phosphate. The reactivity of the complex adsorbed on the nanoparticle surface was higher as compared with the analogous complex in solution for the equal zinc ion concentrations. The hydrolysis on the surface was most probably favoured by the fast formation of highly reactive binuclear complexes. The interaction of the modified gold NP with DNA also involved the hydrolysis, whereas in solution, a similar Zn^{II} complex featured no catalytic activity.

A two-step method of gold NP functionalization was developed aimed at the synthesis of Ru^{II} complexes adsorbed on the surface.[135] To modify the surface, mercaptopropionic acid covalently bonded to the NP surface was made to react with dodecacarbonyltriruthenium $[Ru_3(CO)_{12}]$. The initial gold nanoparticles stabilized with sodium mercaptopropionate were synthesized by the Brust method. Then, NP were successively treated with hydro-

Scheme 11

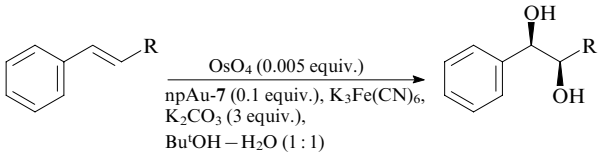


chloric acid and a solution of $Ru_3(CO)_{12}$ complex in toluene.

The reaction of the $Ru_3(CO)_{12}$ complex with carboxyl groups on the NP surface first led to the formation of the dimeric complexes $\{Ru[S(CH_2)_2COO](CO)_3\}_2$. In the absence of other donor ligands, the terminal carbonyl groups can be replaced by the neighbouring mercaptopropionic acid molecules to afford symmetrical ruthenium dicarbonyl carboxylate fragments. The primarily formed dimeric complexes can also be linked in chains with repeating $\{Ru[S(CH_2)_2COO](CO)_2\}_2$ fragments due to elimination of terminal carbonyl groups. Thus gold nanoparticles were modified with ruthenium complexes that formed a coat of ruthenium carbonyl carboxylate oligomers connected by the Ru–O–Ru bridging groups. Such hybrid nanoparticles are very promising for catalysis.

Gold nanoparticles functionalized with dihydroquinidine derivatives (npAu-**7**) that exhibited the catalytic activity in the Sharpless asymmetric dihydroxylation of aromatic alkenes were described.[136] The yields and the enantioselectivity were comparable with those obtained in catalytic reactions carried out in solution and with catalysts immobilized on polymeric supports. First, alkanethiol **33** with the terminal dihydroquinidine group was synthesized (Scheme 12).

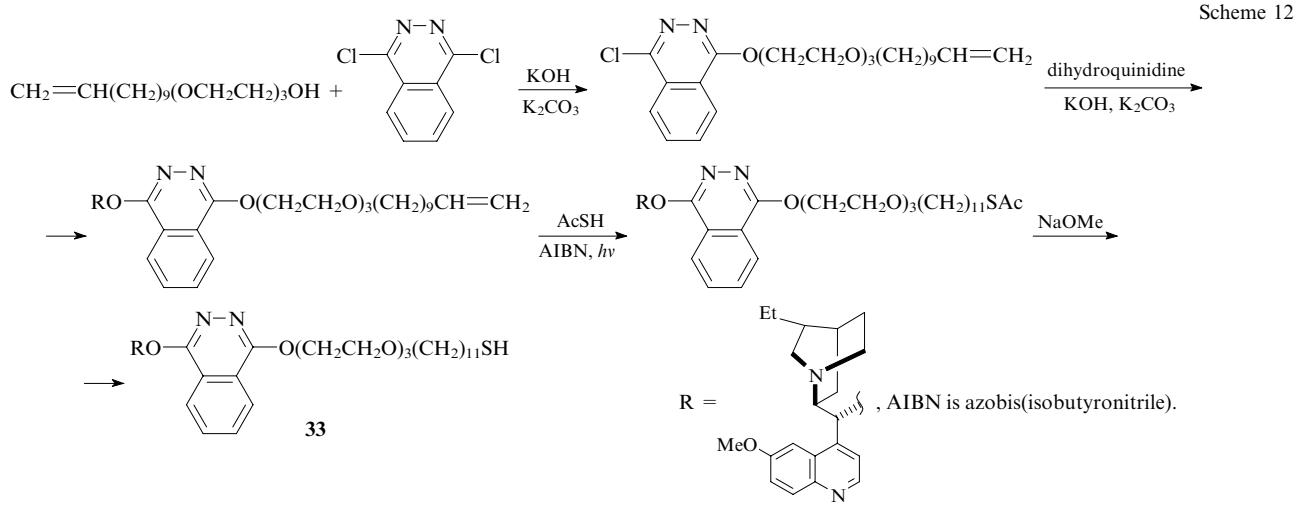
Next, the synthesized npAu-SC_8H_{17} were introduced into the ligand exchange reaction with thiol **33** in order to synthesize the target nanoparticles npAu-**7**. The resulting gold NP could catalyze asymmetric dihydroxylation of *trans*-β-substituted styrenes under the action of the $OsO_4-K_3Fe(CN)_6$ system. The corresponding diols were synthesized in 72% to 83% yields and enantiomeric excess of 79% to 90%.



R = Me, CO_2Me, Ph.

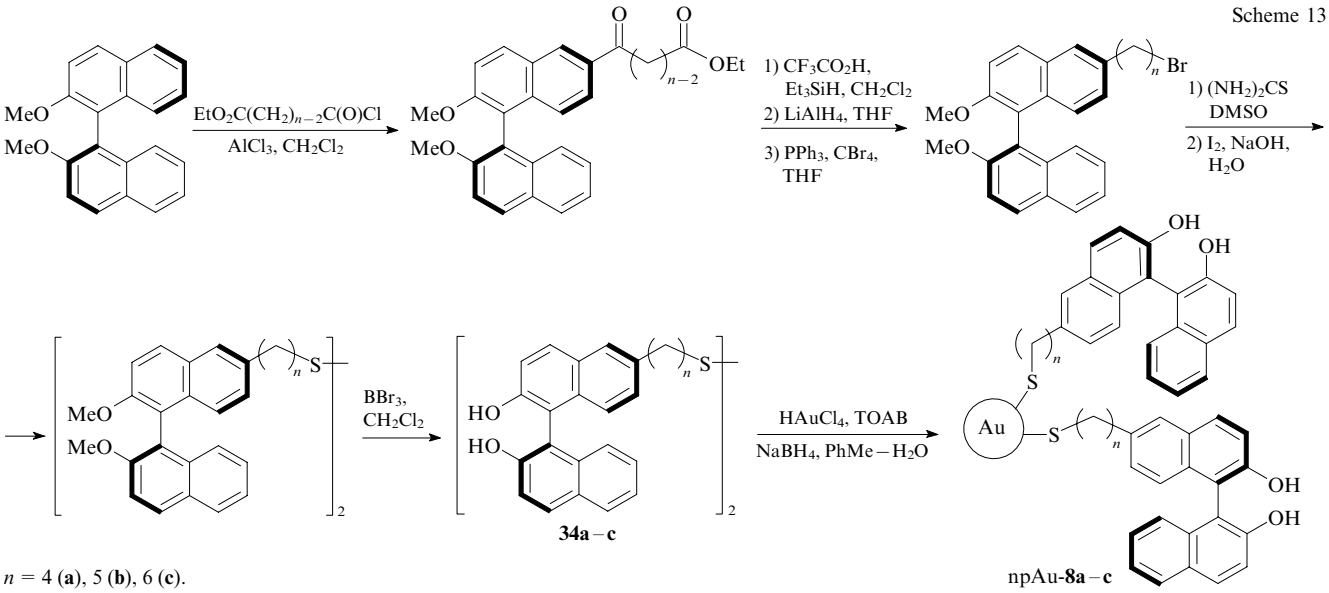
Gold nanoparticles modified with disulfide derivatives based on the BINOL ligand and its complexes with titanium, which exhibited catalytic activity in the asymmetric

Scheme 12



, AIBN is azobis(isobutyronitrile).

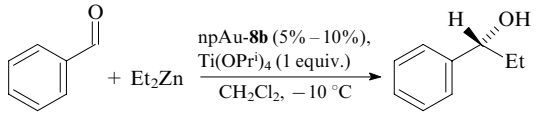
Scheme 13



n = 4 (**a**), 5 (**b**), 6 (**c**).

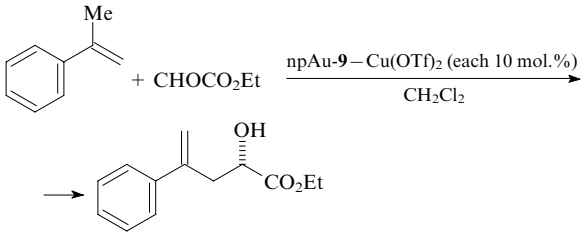
alkylation of benzaldehydes under the action of Et_2Zn, were studied.[137] Disulfides **34a**–**c** containing (*R*)-1,1′-binaphthyldiol terminal groups with different lengths of the methylene linker were prepared. Modified NP (npAu-**8a**–**c**) were synthesized by the Brust method (Scheme 13).

Nanoparticles npAu-**8b** served as the catalyst for alkylation. The yields of target products were 92%–98%, the enantiomeric excess was 72%–86%, which is comparable with the results for homogeneous catalysts containing the same complex in solution (yield >95%, 90% *ee*). Gold nanoparticles employed as the catalyst could be easily isolated from solution and reused. In the latter case, the yield of the product was 75% and the enantiomeric excess was 62%.

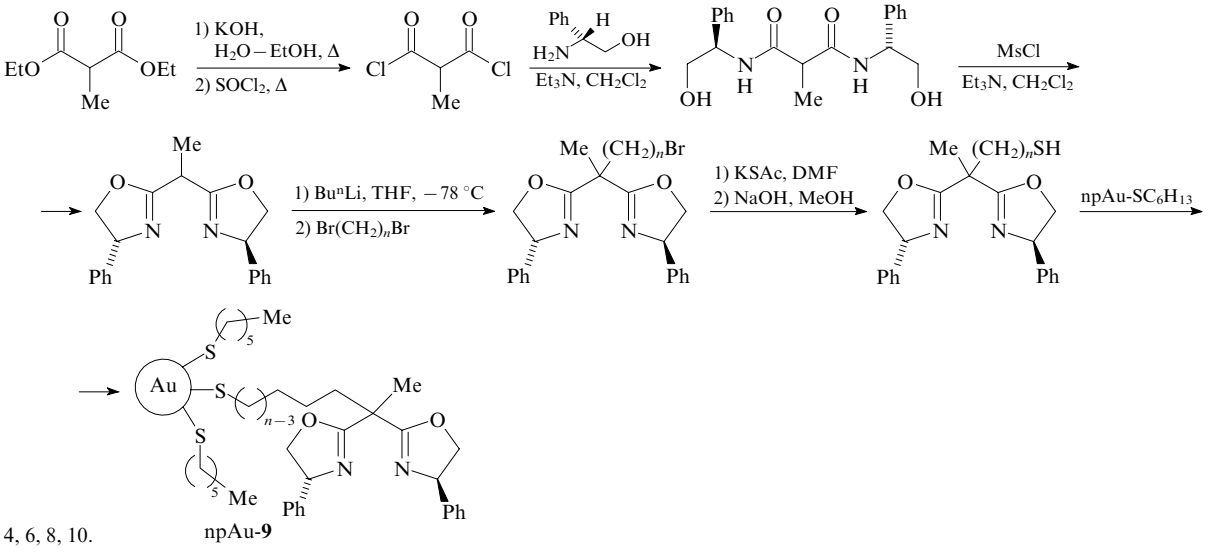


The preparation of gold nanoparticles npAu-**9** modified with copper(II) complexes with chiral bisoxazoline derivatives was described (Scheme 14).[138] The synthesized metal complexes catalyzed the ene reaction, as shown for the reaction of 2-phenylpropene with ethyl glyoxylate. Moreover, it was observed that the stability of npAu-**9** nanoparticles modified with Cu^{II} bisoxazoline complexes depended on the length of the methylene linker.

The yield of the product of the ene reaction catalyzed with modified NP was 93%–99%, the enantiomeric excess was 85%–86% depending on the stabilizing ligand and the



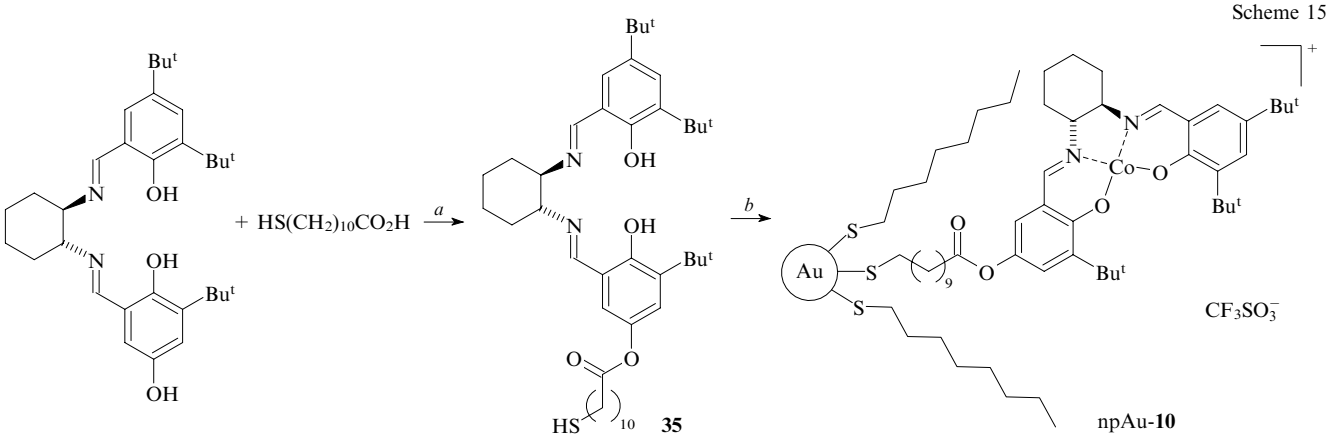
Scheme 14

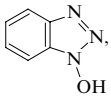


n = 4, 6, 8, 10.

npAu-**9**

Scheme 15

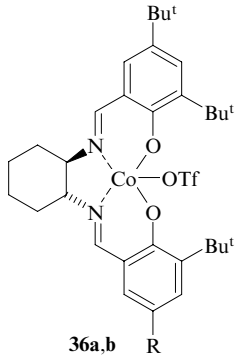


(*a*) EDC · HCl, , CH_2Cl_2, 0 °C; (*b*) 1) $Co(OAc)_2 \cdot 4H_2O$; 2) npAu-SC_8H_{17}-n, CH_2Cl_2; 3) O_2, CF_3SO_3H.

length of the methylene linker; npAu-**9** with $n = 4$ proved to be most efficient. The catalyst could be easily isolated from solution and reused.

Chiral Co^{III} salen complexes adsorbed on the surface of gold nanoparticles were synthesized.[139] They were studied as catalysts in the reaction of hydrolytic kinetic resolution of oxiranes, a widely used method of synthesis of pure optically active terminal epoxides. In the first stage, chiral alkanethiol **35** containing a salen terminal group was obtained (Scheme 15).

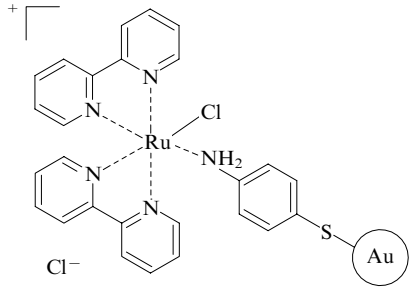
Gold NP modified with ligand **35** (npAu-**10**) were synthesized by the ligand exchange method from octanethiol-stabilized nanoparticles pre-synthesized by the Brust method. Their reaction with $Co(OAc)_2 \cdot 4H_2O$ followed by oxidation in the presence of trifluoromethanesulfonic acid produced active Co^{III} complexes immobilized on the surface of nanoparticles. The efficiency of the npAu-**10** catalyst in the hydrolytic kinetic resolution of hexene 1-oxide was compared with the efficiency of analogous non-adsorbed catalysts **36a**,**b**.

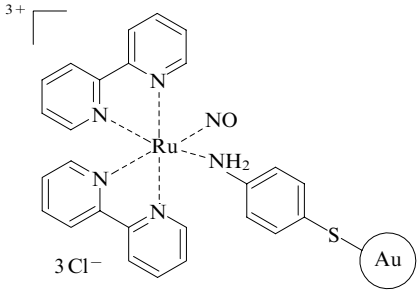


R = Bu^t (**a**), $OC(O)C_7H_{15}$-n (**b**).

Nanoparticles npAu-**10** exhibited very high catalytic activity in the mentioned reaction and afforded complete kinetic resolution with the enantiomeric purity of products of >99.9% in the presence of 0.01 mol.% of the catalyst within 5 h. Moreover, for the homogeneous analogues, much longer reaction time (52 h for compound **36b**) or a higher catalyst concentration (0.1%, 24 h for compounds **36a**,**b**) were required. The catalysts based on gold nanoparticles could be easily isolated from the reaction mixture and reused. Moreover, the enantiomeric purity of products remained at the former level at least in 7 repeated cycles.

Gold nanoparticles modified with ruthenium(II) complexes capable of coordinating nitrogen(II) oxide were studied.[140] The gold nanoparticles npAu-**11** and npAu-**12** were synthesized by the Brust method in the presence of *cis*-[RuCl(ABTh)(bipy)$_2$]Cl and *cis*-[Ru(ABTh)(bipy)$_2$.NO]Cl_3, respectively (ABTh is 4-aminobenzenethiol).

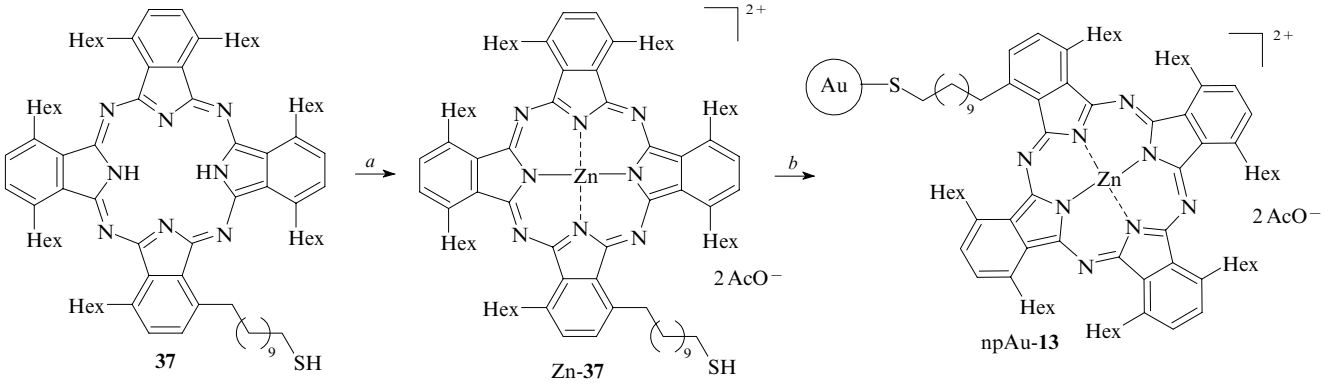




According to TEM data, in both cases, nanoparticles of virtually the same size and dispersivity (with the average diameter 24.9 ± 2.2 nm) were synthesized. It is interesting that upon illumination with visible light (430 nm), free NO evolved from the npAu-**12** complex. Hence, the ruthenium complex-modified npAu-**12** can find application as regulators of the nitrogen monoxide concentration.

The synthesis of gold nanoparticles npAu-**13** modified with a phthalocyanine derivative (Scheme 16) to be used as

Scheme 16



(*a*) $Zn(OAc)_2 \cdot 2H_2O$, n-$C_5H_{11}OH$, Δ; (*b*) $HAuCl_4$, TOAB, $NaBH_4$, PhMe – H_2O.

the sensitizers was described.[141] Particles npAu-**13** generated singlet oxygen with a high quantum yield; however, this required the presence of a phase transfer catalyst in the reaction mixture. A zinc complex with phthalocyanine **37** in which thiol is connected with the phthalocyanine moiety by a polymethylene linker was synthesized. Gold nanoparticles were synthesized by the Brust method; the average size of npAu-**13** was 2–4 nm.

Nanoparticles npAu-**13** are soluble in many polar solvents such as ethanol, methanol, DMSO, in which the original complex Zn-**37** is insoluble. The electronic spectrum of modified gold nanoparticles has an absorption peak at 695 nm, whereas the absorption peak of the non-adsorbed complex is at 688 nm. This photosensitizer with λ_{max} = 695 nm is the best choice for the photodynamic therapy of cancer as regards the depth of penetration of the radiation into human skin.

Fluorescence spectra were recorded for free and adsorbed complexes. For complex-modified gold nanoparticles, no fluorescence quenching was observed (λ_{em} = 715 nm). For free and adsorbed complexes, the quantum yields of singlet oxygen were determined. The quantum yield was 0.45 for the free complex in toluene and 056 for npAu-**13**. The higher quantum yield for nanoparticles was explained by the fact that in addition to the phthalocyanine complex, the nanoparticle surface bore TOAB molecules favourable for the oxygen generation. Thus, modified nanoparticles npAu-**13** can be used for the transport of sensitizing agents in the photodynamic therapy of cancer.

V. Conclusion

In the present review, we wished to draw attention to the results of studies of metal nanoparticles, first of all, gold nanoparticles with coordinated metal ions attached to their surface. To become capable of binding metal cations, the nanoparticles surface should be modified with sulfur-containing organic ligands containing additional terminal donor groups. The structures of such ligands are diversified, varying from the simplest amines to macrocycles. In the majority of cases, these are chelating ligands. Moreover, the formation of coordination compounds attached to the NP surface makes it possible to synthesize new materials, the properties and the subsequent use of which are determined by metals serving as complexing agents.

The most important applications of metal ion-modified nanoparticles include the controlled aggregation, in particular, reversible aggregation, catalysis of various chemical transformations, in particular, photo- and electroactive processes, the development of highly sensitive and selective sensor systems for cations, anions, low-molecular-mass compounds and biological molecules, the preparation of multilayer networks and films of nanoparticles aimed at the synthesis of conducting materials.

Summarizing the experimental data accumulated to date, the following structure–property relationships can be formulated for NP with the sulfur-containing ligands and metal complexes attached to their surface.

1) The linker length affects the ligand ability to stabilize gold NP. In general, for polymethylene linkers, the average length of a chain of ~6–12 carbon atoms connecting a gold NP and a sulfur atom is optimal. Thiols and disulfides with shorter or longer linkers exhibit weaker stabilizing activity. A similar dependence was also observed for the adsorption of sulfur-containing compounds on a flat surface.[34]

2) The nature of the linker is also important, especially for electrochemically active derivatives attached to the NP surface. Of critical importance for the electrochemical properties of NP is the type (conjugated or non-conjugated system) of the linker connecting the cheating agent and the group interacting with the nanoparticle surface. The conductivity of ligands with polymethylene linkers depends linearly on the chain length and decreases with its elongation.

3) For modifying the surface of gold nanoparticles, attention is focused on ligands containing a functional group (fluorophore, chromophore, receptor or electrochemically active group). However, this is often complicated by the direct interaction of this functional group with the nanoparticle surface, which can lead to undesired loss of activity of the adsorbed compound or the aggregation of NP. This problem can be solved by the preliminary preparation of a complex of the required ligand in which the donor centres of its functional group are blocked or by preparing modified NP by the ligand exchange.

4) As the complexing metals in the synthesis of coordination compounds with ligands attached to the gold NP surface, transition metals are used more often than main group metals. This is associated with the higher resistance of transition metal complexes against aggregation.

Recent yers have seen an increase in the number of studies devoted to the synthesis of metal nanoparticles modified with coordination compounds of metals, first of all, transition metals. We believe that further increase in the number of publications on this subject will be observed in the near future with the stronger trend for convergence of the fundamental studies on the synthesis of new modifying agents and the practical studies on the use of nanoparticles in the material science and chemical engineering.

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References

1. M-C Daniel, D Astruc *Chem. Rev.* **104** 293 (2004)
2. A C Templeton, W P Wuelfing, R W Murray *Acc. Chem. Res.* **33** 27 (2000)
3. G Schmid, M Bäumle, M Greekens, I Heim, C Osemann, T Sawitowski *Chem. Soc. Rev.* **28** 179 (1999)
4. F Seker, P R L Malenfant, M Larsen, A Alizadeh, K Conway, A M Kulkarni, G Goddard, R Garaas *Adv. Mater.* **17** 1941 (2005)
5. K Ai, Y Liu, L Lu *J. Am. Chem. Soc.* **131** 9496 (2009)
6. T Ung, L M Liz-Marzán, P Mulvaney *J. Phys. Chem. B* **105** 3441 (2001)
7. D Lee, R L Donkers, G Wang, A S Harper, R W Murray *J. Am. Chem. Soc.* **126** 6193 (2004)
8. S Paul, C Person, A Molloy, M A Cousins, M Green, S Kolliopoulou, P Dimitrakis, P Normand, D Tsoukalas, M C Petty *Nano Lett.* **3** 533 (2003)
9. M Caironi, E Gili, T Sakanoue, X Cheng, H Sirringhaus *ACS Nano* **4** 1451 (2010)
10. H Imahori, M Arimura, T Hanada, Y Nishimura, I Yamazaki, Y Sakata, S Fukuzumi *J. Am. Chem. Soc.* **123** 335 (2001)
11. M Yamada, A Kuzume, M Kurihara, K Kubo, H Nishihara *Chem. Commun.* 2476 (2001)
12. M T Rojas, A E Kaifer *J. Am. Chem. Soc.* **117** 5883 (1995)
13. K W Gano, D C Myles *Tetrahedron Lett.* **41** 4247 (2000)
14. L Pasquato, P Pengo, P Scrimin *J. Mater. Chem.* **14** 3481 (2004)
15. P V Kamat *J. Phys. Chem. B* **106** 7729 (2002)
16. G F Paciotti, D C I Kingston, L Tamarkin *Drug Dev. Res.* **67** 47 (2006)
17. A J Haes, R P Van Duyne *J. Am. Chem. Soc.* **124** 10596 (2002)
18. B Dragnea, C Chen, E-S Kwak, B Stein, C C Kao *J. Am. Chem. Soc.* **125** 6374 (2003)
19. X Xu, M Stevens, M B Cortie *Chem. Mater.* **16** 2259 (2004)
20. C D Bain, E B Troughton, Y T Tao, J Evall, G M Whitesides, R G Nuzzo *J. Am. Chem. Soc.* **111** 321 (1989)
21. A J Viudez, R Madueño, T Pineda, M Blázquez *J. Phys. Chem. B* **110** 17840 (2006)
22. L A Porter Jr, D Ji, S L Westcott, M Graupe, R S Czernuszewicz, N J Halas, T R Lee *Langmuir* **14** 7378 (1998)
23. K Torigoe, K Esumi *J. Phys. Chem. B* **103** 2862 (1999)
24. O Tzhayik, P Sawant, S Efrima, E Kovalev, J T Klug *Langmuir* **18** 3364 (2002)
25. R Resch, C Baur, A Bugacov, B E Koel, P M Echternach, A Madhukar, N Montoya, A A G Requicha, P Will *J. Phys. Chem. B* **103** 3647 (1999)
26. Y Tan, Y Li, D Zhu *Langmuir* **18** 3392 (2002)
27. K G Thomas, J Zajicek, P V Kamat *Langmuir* **18** 3722 (2002)
28. M Montalti, L Prodi, N Zacceroni, M Beltrame, T Morotti, S Quici *New J. Chem.* **31** 102 (2007)
29. R B Romashkina, E K Beloglazkina, A N Khlobystov, A G Majouga, D A Pichugina, V I Terenin, N V Zyk, N S Zefirov *Mendeleev Commun.* **21** 129 (2011)
30. X Zhang, D Li, X-P Zhou *New J. Chem.* **30** 706 (2006)
31. J D E T Wilton-Ely *Dalton Trans.* 25 (2008)
32. S Roy, M A Perices *Org. Biomol. Chem.* **7** 2669 (2009)
33. A Henglein *J. Phys. Chem.* **97** 5457 (1993)
34. A Ulman *Chem. Rev.* **96** 1533 (1996)
35. R C Thomas, L Sun, R M Crooks, A J Ricco *Langmuir* **7** 620 (1991)
36. F Tielens, E Santos *J. Phys. Chem. C* **114** 9444 (2010)
37. J C Love, L A Estroff, J K Kriebel, R G Nuzzo, G M Whitesides *Chem. Rev.* **105** 1103 (2005)
38. R G Nuzzo, B R Zegarski, L H Dubois *J. Am. Chem. Soc.* **109** 733 (1987)
39. M Hasan, D Bethell, M Brust *J. Am. Chem. Soc.* **124** 1132 (2002)
40. H Fukushima, S Seki, T Nishikawa, H Takiguchi, K Tamada, K Abe, R Colorado Jr , M Graupe, O E Shmakova, T R Lee *J. Phys. Chem. B* **104** 7417 (2000)
41. J Zak, H Yuan, M Ho, L K Woo, M D Porter *Langmuir* **9** 2772 (1993)
42. E M W J Beulen, B-H Huisman, P A van der Heijden, F C J M van Veggel, M G Simons, M E F Biemond, P J de Lange, D N Reinhoudt *Langmuir* **12** 6170 (1996)
43. F S Nunes, L Da Silva Bonifácio, K Araki, H E Toma *Inorg. Chem.* **45** 94 (2006)
44. S I Stoeva, F Huo, J-S Lee, C A Mirkin *J. Am. Chem. Soc.* **127** 15362 (2005)
45. A Henglein, M Giersig *J. Phys. Chem. B* **104** 6767 (2000)
46. M Brust, D J Schiffrin, D Bethell, C J Kiely *Adv. Mater.* **7** 795 (1995)
47. K Torigoe, A Suzuki, K Esumi *J. Colloid Interface Sci.* **241** 346 (2001)
48. C K Yee, R Jordan, A Ulman, H White, A King, M Rafailovich, J Sokolov *Langmuir* **15** 3486 (1999)
49. P R Selvakannan, S Mandal, R Pasricha, S D Adyanthaya, M Sastry *Chem. Commun.* 1334 (2002)
50. A B R Mayer, W Grebner, R Wannemacher *J. Phys. Chem. B* **104** 7278 (2000)
51. I Pastoriza-Santos, L M Liz-Marzán *Langmuir* **18** 2888 (2002)
52. C H Munro, W E Smith, M Garner, J Clarkson, P C White *Langmuir* **11** 3712 (1995)
53. N R Jana, L Gearheart, C J Murphy *Chem. Mater.* **13** 2313 (2001)
54. K R Brown, M J Natan *Langmuir* **14** 726 (1998)
55. Z-M Qi, H-S Zhou, N Matsuda, I Honma, K Shimada, A Takatsu, K Kato *J. Phys. Chem. B* **108** 7006 (2004)
56. J Turkevich, P C Stevenson, J Hillier *Discuss. Faraday Soc.* **11** 55 (1951)
57. M Brust, J Fink, D Bethell, D J Schiffrin, C Kiely *J. Chem. Soc., Chem. Commun.* 1655 (1995)
58. M Brust, M Walker, D Bethell, D J Schiffrin, R Whyman *J. Chem. Soc., Chem. Commun.* 801 (1994)
59. A C Templeton, M J Hostetler, E K Warmoth, S Chen, C M Harstshorn, V M Krishnamurthy, M D E Forbes, R W Murray *J. Am. Chem. Soc.* **120** 4845 (1998)
60. A C Templeton, M J Hostetler, C T Kraft, R W Murray *J. Am. Chem. Soc.* **120** 1906 (1998)
61. H-L Zhang, S D Evans, J R Henderson, R E Miles, T Shen *J. Phys. Chem. B* **107** 6087 (2003)
62. S P Gubin, G Yu Yurkov, N A Kataeva *Nanochastitsy Blagorodnykh Metallov i Materialy na ikh Osnove* (Nanoparticles of Noble Metals and Materials Based on Them) (Moscow: Azbuka-2000, 2006)

63. Y Kim, R C Johnson, J T Hupp *Nano Lett*. **1** 165 (2001)
64. K C Grabar, R G Freeman, M B Hommer, M J Natan *Anal. Chem*. **67** 735 (1995)
65. S H Toma, J A Bonacin, K Araki, H E Toma *Eur. J. Inorg. Chem*. 3356 (2007)
66. M Moskovits *Rev. Mod. Phys*. **57** 783 (1985)
67. A Otto, I Mrozek, H Grabhorn, W Akemann *J. Phys.: Condens. Matter* **4** 1143 (1992)
68. A Campion, P Kambhampati *Chem. Soc. Rev*. **27** 241 (1998)
69. R M Jarvis, R Goodacre *Anal. Chem*. **76** 40 (2004)
70. M Culha, D L Stokes, L R Allain, T Vo-Dinh *Anal. Chem*. **75** 6196 (2003)
71. J-D Grunwaldt, C Kiener, C Wögerbauer, A Baiker *J. Catal*. **181** 223 (1999)
72. T Yutaka, I Mori, M Kurihara, N Tamai, H Nishihara *Inorg. Chem*. **42** 6306 (2003)
73. N W Alcock, P R Barker, J M Haider, M J Hannon, C L Painting, Z Pikramenou, E A Plummer, K Rissanen, P Saarenketo *J. Chem. Soc., Dalton Trans*. 1447 (2000)
74. T B Norsten, B L Frankamp, V M Rotello *Nano Lett*. **2** 1345 (2002)
75. M J Hostetler, A C Templeton, R W Murray *Langmuir* **15** 3782 (1999)
76. M Alvaro, C Aprile, B Ferrer, F Sastre, H García *Dalton Trans*. 7437 (2009)
77. I E Sendroiu, D J Schiffrin, J M Abad *J. Phys. Chem. C* **112** 10100 (2008)
78. R B Romashkina, E K Beloglazkina, A G Mazhuga, N V Zyk *Ros. Nanotekhnol*. **4** (11 – 12) 110 (2009)
79. A-C Liu, D-C Chen, C C Lin, H H Chou, C-H Chen *Anal. Chem*. **71** 1549 (1999)
80. S Zhang, C M Cardona, L Echegoyen *Chem. Commun*. 4461 (2006)
81. K V Gobi, T Ohsaka *J. Electroanal. Chem*. **485** 61 (2000)
82. A Janshoff, C Steinem, A Michalke, C Henke, H-J Galla *Sens. Actuators, B* **70** 243 (2000)
83. A Verma, V M Rotello *Chem. Commun*. 303 (2005)
84. J J Storhoff, R Elghanian, R C Mucic, C A Mirkin, R L Letsinger *J. Am. Chem. Soc*. **120** 1959 (1998)
85. C A Mirkin, R L Letsinger, R C Mucic, J J Storhoff *Nature (London)* **382** 607 (1996)
86. F Stellacci, C A Bauer, T Meyer-Friedrichsen, W Wenseleers, S R Marder, J W Perry *J. Am. Chem. Soc*. **125** 328 (2003)
87. X He, H Liu, Yul Li, S Wang, Yon Li, N Wang, J Xiao, X Xu, D Zhu *Adv. Mater*. **17** 2811 (2005)
88. P D Beer, D P Cormode, J J Davis *Chem. Commun*. 414 (2004)
89. S-Y Lin, S-W Liu, C-M Lin, C-H Chen *Anal. Chem*. **74** 330 (2002)
90. G W Gokel, W M Leevy, M E Weber *Chem. Rev*. **104** 2723 (2004)
91. D J Lewis, T M Day, J V MacPherson, Z Pikramenou *Chem. Commun*. 1433 (2006)
92. P Pramod, P K Sudeep, K G Thomas, P V Kamat *J. Phys. Chem. B* **110** 20737 (2006)
93. Q Wang, S M Zakeeruddin, M K Nazeeruddin, R Humphry-Baker, M Grätzel *J. Am. Chem. Soc*. **128** 4446 (2006)
94. V M Zamarion, R A Timm, K Araki, H E Toma *Inorg. Chem*. **47** 2934 (2008)
95. Y-Q Dang, H-W Li, B Wang, L Li, Y Wu *Appl. Mater. Interfaces* **1** 1533 (2009)
96. J M Abad, S F L Mertens, M Pita, V M Fernández, D J Schiffrin *J. Am. Chem. Soc*. **127** 5689 (2005)
97. G K Darbha, A Ray, P C Ray *ACS Nano* **1** 208 (2007)
98. G K Darbha, A K Singh, U S Rai, E Yu, H Yu, P C Ray *J. Am. Chem. Soc*. **130** 8038 (2008)
99. B I Ipe, K Yoosaf, K G Thomas *J. Am. Chem. Soc*. **128** 1907 (2006)
100. A J Reynolds, A H Haines, D A Russel *Langmuir* **22** 1156 (2006)
101. L Li, B Li *Analyst* **134** 1361 (2009)
102. S O Obare, R E Hollowell, C J Murphy *Langmuir* **18** 10407 (2002)
103. G Patel, A Kumar, U Pal, S Menon *Chem. Commun*. 1849 (2009)
104. A Labande, J Ruiz, D Astruc *J. Am. Chem. Soc*. **124** 1782 (2002)
105. C M Casado, I Cuadrado, B Alonso, M Morán, J Losada *J. Electroanal. Chem*. **463** 87 (1999)
106. O Reynes, J-C Moutet, J Pecaut, G Royal, E Saint-Aman *New J. Chem*. **26** 9 (2002)
107. M-C Daniel, J Ruiz, S Nlate, J-C Blais, D Astruc *J. Am. Chem. Soc*. **125** 2617 (2003)
108. J R Aranzaes, C Belin, D Astruc *Chem. Commun*. 3456 (2007)
109. L Han, D R Daniel, M M Maye, C-J Zhong *Anal. Chem*. **73** 4441 (2001)
110. N Krasteva, I Besnard, B Guse, R E Bauer, K Müllen, A Yasuda, T Vossmeyer *Nano Lett*. **2** 551 (2002)
111. A C Templeton, F P Zamborini, W P Wuelfing, R W Murray *Langmuir* **16** 6682 (2000)
112. F P Zamborini, M C Leopold, J F Hicks, P J Kulesza, M A Malik, R W Murray *J. Am. Chem. Soc*. **124** 8958 (2002)
113. F P Zamborini, J F Hicks, R W Murray *J. Am. Chem. Soc*. **122** 4514 (2000)
114. W P Wuelfling, F P Zamborini, A C Templeton, X Wen, H Yoon, R W Murray *Chem. Mater*. **13** 87 (2001)
115. S R Isaacs, H Choo, W-B Ko, Y-S Shon *Chem. Mater*. **18** 107 (2006)
116. M C Leopold, R L Donkers, D Georganopoulou, M Fisher, F P Zamborini, R W Murray *Faraday Discuss*. **125** 63 (2004)
117. R R Pompano, P G Wortley, L M Moatz, D J Tognarelli, K W Kittredge, M C Leopold *Thin Solid Films* **510** 311 (2006)
118. D Hobara, S Kondo, M-S Choi, Y Ishioka, S Hirata, M Murata, K Azuma *Phys. Status Solidi A* **6** 1706 (2007)
119. S Chen, R Pei, T Zhao, D J Dyer *J. Phys. Chem. B* **106** 1903 (2002)
120. M Ito, T Tsukatani, H Fujihara *J. Mater. Chem*. **15** 960 (2005)
121. T-Y Dong, C Huang, C-P Chen, M-C Lin *J. Organomet. Chem*. **692** 5147 (2007)
122. M S Vickers, J Cookson, P D Beer, P T Bishop, B Thiebaut *J. Mater. Chem*. **16** 209 (2006)
123. W Dumont, J C Poulin, D T Phat, H B Kagan *J. Am. Chem. Soc*. **95** 8295 (1973)
124. N Takaishi, H Imai, C A Bertelo, J K Stille *J. Am. Chem. Soc*. **98** 5400 (1976)
125. P R Cooke, J R L Smith *J. Chem. Soc., Perkin Trans. 1* 1913 (1994)
126. S C Petrosius, R S Drago, V Young, G C Grunevald *J. Am. Chem. Soc*. **115** 6131 (1993)
127. P Sutra, D Brunel *Chem. Commun*. 2485 (1996)
128. Y V S Rao, D E De Vos, T Bein, P A Jacobs *Chem. Commun*. 355 (1997)
129. C Maillet, P Janvier, M Pipelier, T Praveen, Y Andres, B Bujoli *Chem. Mater*. **13** 2879 (2001)
130. I O Benitez, B Bujoli, L J Camus, C M Lee, F Odobel, D R Talham *J. Am. Chem. Soc*. **124** 4363 (2002)
131. M Zayatz, E Katz, I Willner *J. Am. Chem. Soc*. **124** 14724 (2002)
132. M Bartz, J Küther, R Seshadri, W Tremel *Angew. Chem., Int. Ed*. **37** 2466 (1998)

133. T Belser, M Stöhr, A Pfaltz *J. Am. Chem. Soc.* **127** 8720 (2005)
134. R Bonomi, F Selvestrel, V Lombardo, C Sissi, S Polizzi, F Mancin, U Tonellato, P Scrimin *J. Am. Chem. Soc.* **130** 15744 (2008)
135. S Wang, W-S Sim *Langmuir* **22** 7861 (2006)
136. H Li, Y-Y Luk, M Mrksich *Langmuir* **15** 4957 (1999)
137. K Marubayashi, S Takizawa, T Kawakusu, T Arai, H Sasai *Org. Lett.* **5** 4409 (2003)
138. F Ono, S Kanemasa, J Tanaka *Tetrahedron Lett.* **46** 7623 (2005)
139. T Belser, E N Jacobsen *Adv. Synth. Catal.* **350** 967 (2008)
140. A M Díaz-García, M Fernández-Oliva, M Ortiz, R Cao *Dalton Trans.* 7870 (2009)
141. D C Hone, P I Walker, R Evans-Gowing, S Fitzgerald, A Beeby, I Chambrier, M J Cook, D A Russell *Langmuir* **18** 2985 (2002)