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Review

Coordination compounds built on metal surfaces

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ABSTRACT

The vigorous development of Nanotechnology and Nanoscience has induced a more intense study on coordination compounds built on metal surfaces of different types, such as flat surfaces, electrodes and nanoparticles. Both self-assembled coordination compound and metal surface tend to modify their properties in such a degree that even new ones can arise. In this review the state-of-art of this new field in Coordination Chemistry is analyzed. Especial attention has been given to the general procedures used to build coordination compounds on metal surfaces.

1. Introduction

At the end of the last century a new era for Coordination Chemistry started with the birth and development of Nanoscience and Nanotechnology. The applications found for coordination compounds in Supramolecular Chemistry permitted their fast and spontaneous incorporation to nanosystems [1].

The possibility of building coordination compounds on solid surfaces has made possible the preparation of nanoscaled devices with new properties. In this review we will only address our attention on coordination compounds built on metal surface although practically the same type of constructions is possible on metal oxides, nanotubes, graphite, etc. This decision is due to two main reasons: (1) this is the first review completely dedicated to coordination compounds built on different types of metal surfaces and a necessary delimitation is unavoidable and (2) the electron transfer

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(ET) processes using two different pathways: between neighboring coordinated metal ions or between them with the metal surface through self-assembled ligands, may perhaps be the main distinguishing property in this new area [2,3].

The construction of coordination compounds on metal surfaces is possible using two main approaches:

1. Form the complex and then self-assemble it on the metal surface as a whole.
2. Build the complex using the layer-by-layer (LbL) procedure starting from the self-assembly of an appropriate ligand.

In both cases, the selection of the ligand through which the coordination compound will be attached to the metal surface is very important.

"Self-assembly" is a term of Supramolecular Chemistry [1] and is generally used to define repeated supramolecular interactions among molecules in solution or solid state to give special arrangements or architectures. This term is especially used for the formation of micelles and others systems formed by surfactants. Here we will use the term "self-assembled monolayer (SAM) (or multilayer)" to define the adsorption (better chemisorption) of molecules on solid surfaces. The interaction between the molecules that form a monolayer and the metallic surface is more than a simple adsorption but cannot by analyzed as a typical coordination or covalent bond. It has its own specificities as we will analyze below.

2. Formation of self-assembled mono- and multilayers on metal surfaces

Until now, coordination compounds have been mainly built on soft metal surfaces. Gold has been the metal most studied for self-assembly processes, generally using alkanethiols.

The main characteristics of the formation of SAM of alkanethiols on gold can be summarized as following:

1. Au(1 1 1) presents the best characteristics for the formation of SAMs.
2. The thiolate group (formed by deprotonation as a consequence on the interaction) is associated with three gold atoms on the surface.
3. The Au–SR interaction is reversible which permits the alkanethiolate anions to interact among themselves in order to achieve the formation of a highly compact monolayer.
4. Alkanethiolates with about 10–20 carbon atoms achieve the highest organized monolayer.
5. Alkanethiolates self-assemble on the gold surface with a tilt of about 30° from the normal to the surface.

The most common (and simplest) procedure to form a SAM consists in dipping an extremely clean unoxidized gold sheet into an ethanol solution of the corresponding alkanethiol. Other volatile organic solvents can also be used. The concentration of the thiol may vary between 1 mM and 1 μM. SAM must be completely formed after 12–18 h of interaction at room temperature. Actually, the molecules are self-assembled within the first seconds or minutes but the rest of the time is required in order to achieve a highly organized and compact monolayer containing about 5 nmoles of thiol cm^{-2} of surface. A more detailed analysis of the factors that affect the formation of a SAM can be found in the excellent reviews of Ulman [4], Finklea [5] and Whitesides and coworkers [6].

Similar SAM have been built on silver, copper, nickel, palladium and platinum [7]. Silver, nickel and copper are less inert and can easily oxidize. Since copper can oxidize extremely easily it is difficult to obtain organized and compact SAM on this metal. The most stable SAM on platinum have been obtained using isocyanide [8].

SAM of thiols or other types of sulfur-containing molecules (xanthates, dithiocarbamates, dithiocarboxylates, etc.) that present a terminal functional group permit the construction of a second monolayer through the formation of a covalent bond. The most common reaction used in the formation of a second monolayer corresponds to the formation of an amide group by the condensation (using a carbodiimide) between carboxylate and amine groups. The second monolayer can also be self-assembled electrostatically or by means of non-covalent interactions (van der Waals forces, hydrogen bonding, etc.) or metal–ligand bonding [6]. A simple physical adsorption also permits self-assembly but with a non-specific character for which a relatively thick film is formed instead of a monolayer.

The self-assembly of one monolayer on top of another, no matter the force applied to maintain them together, is called "layer-by-layer" (LbL) procedure. In the LbL procedure once the first monolayer is formed and identified the modified metal surface is dipped into a solution containing the compound to form the second monolayer and so on. Therefore, LbL is a stepwise procedure.

This review is mainly dedicated to the self-assembly of additional monolayers through the formation of coordination bonds. As mentioned above, a coordination compound can be formed and self-assembled on a metal surface in one step, i.e. self-assembling the coordination compound as a whole. Obviously, the coordination compound must contain a functional group able to self-assemble

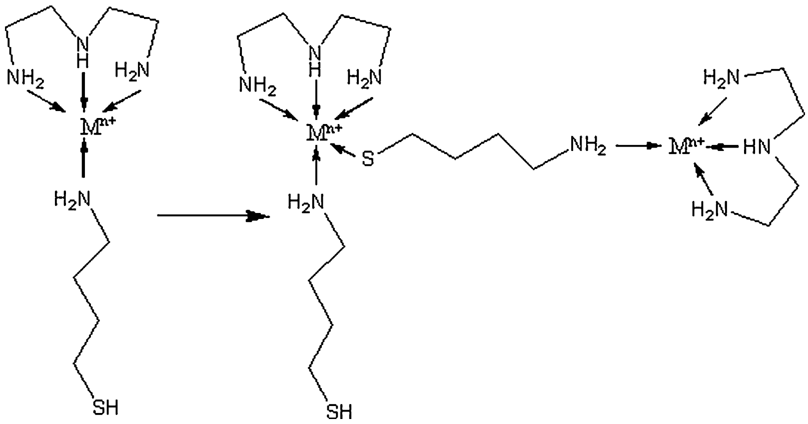

Fig. 1. Schematic representation of a hypothetical complex in which the thiol pendant group can coordinate to the metal center.

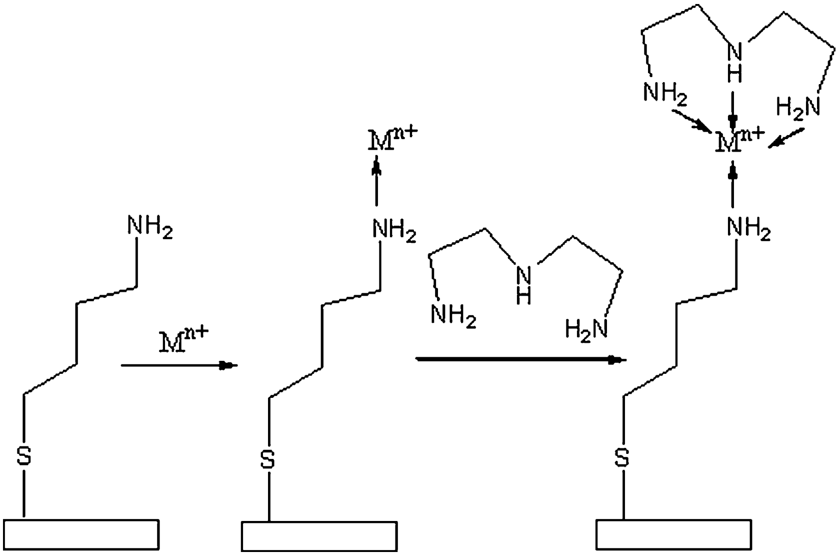

Fig. 2. Schematic representation of a hypothetical complex built LbL on a metal surface.

to the metal surface. This requisite defines the procedure to be selected: one-step self-assembly or layer-by-layer procedure. If the functional group (e.g. thiol) to be used in the self-assembly to the metal surface is also able to coordinate to the metal center only the LbL procedure can by used in order to an avoid additional (unwanted) coordination. In Fig. 1 we have represented a hypothetical situation in which the thiolate pendant group of a coordination compound is able to coordinate to the metal center and, therefore, is no longer disposable for the self-assembly process. In such case, the complex cannot be self-assembled as a whole and the LbL procedure should be used. Fig. 2 shows the LbL formation of the same hypothetical coordination compound in three steps: (1) the aminoalkanethiolate, named "base monolayer", (2) the coordination of M^{n+} that will behave as a "coordinating linker" and, (3) the coordination of *trien*, the terminal ligand.

Another important factor to take into consideration, when defining the procedure to follow when building a coordination compound on a metal surface, is the steric effect that can be introduced by the terminal self-assembled ligands. A bulky terminal ligand affects the surface coverage. If a LbL is used, as that represented in Fig. 2, actually only part of M^{n+} coordinated to the self-assembled aminoalkanethiolate will sterically be able to associate *trien*. Therefore, when using the LbL process what should actually be expected to happen is the formation of a mixed multilayer, as represented in Fig. 3. Depending on how bulky the second ligand is, it can coordinate to only 60–70% or less of self-assembled M^{n+} (coordinated to the aminoalkanethiolate). Therefore, the final product is a mixed layer.

When using the LbL procedure it may happen that when the metal ion is coordinated to the terminal group of the base monolayer (second step) some ligands may dissociate in order to fulfill the coordination sphere of the metal ion. Of course, this event only takes place when the strength of metal–amino group bond is greater than the S–metal surface association. This dissociation process logically affects the surface coverage of the metal surface and the organization and stability of the monolayer. In order to avoid the undesirable dissociation process of the base ligand the metal ion can be coordinated by weak ligands, easily removable when forming the next monolayer of strong ligands.

The self-assembly of mono- and multilayers on metals can be carried out on flat surfaces, electrodes, nanoparticles and channels or pores. Metal electrodes can present different shapes (flat, bead, disk-like, etc.) but in order to simplify the terms used in this Review we will only refer to "flat surface" for metals with no additional connection or use. Coordination compounds can also be built on the same types of surfaces. In this review we will only address our attention to the first three types of metal surfaces. Channels and pores, especially those of nanodimensions, present serious steric restrictions to build coordination compounds of different types. Practically no work has been reported for these last two cases.

Two aspects of a surface are flatness and roughness (or smoothness). We will not further analyze the roughness of metal surfaces (flat or not) although it may affect the formation of multilayers, especially when more than three monolayers are involved in a LbL procedure.

Roughness is a very important factor to consider when selecting the technique to characterize the modified surface. For example, when using atomic force microscopy (AFM), scanning electron microscopy (SEM) or scanning tunneling microscopy (STM), techniques that characterizes the topology of surfaces, the minimization of the roughness of a surface to be analyzed defines the possibility of achieving acceptable results. On the contrary, in surface enhanced Raman spectroscopy (SERS), FTIR and X-ray

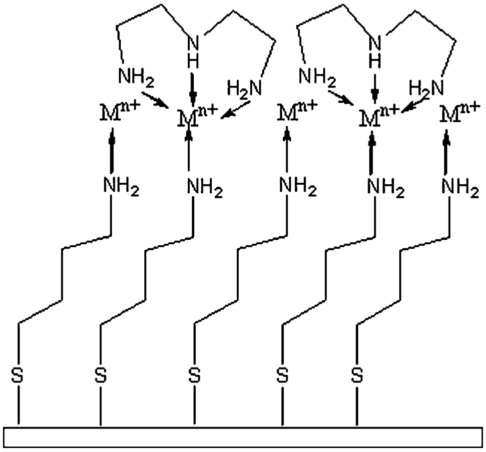

Fig. 3. Representation of how in the LbL process represented in Fig. 2 the *trien* ligands can only coordinate to part of the terminal metal ions due to steric restrictions.

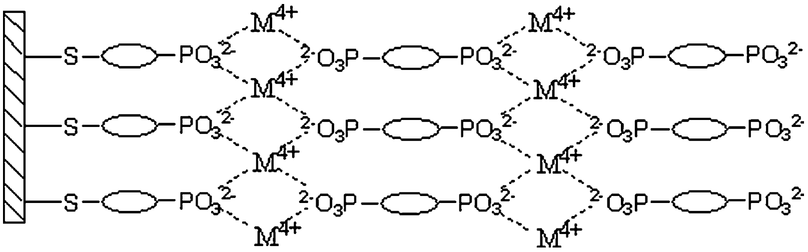

Fig. 4. Schematic representation of M(IV)-bis(alkanephosphonate) multilayers.

photoemission spectroscopy (XPS), among many others, the roughness mainly affects the cleanness of the studied surface.

3. Self-assembly on flat surfaces

3.1. Bis(phosphonates) and M(IV) of group 4

The first report on construction of coordination compounds on solid surfaces corresponded to a short communication on the formation of a multilayer of zirconium(IV) with decanephosphonate derivatives on a silicon wafer [9]. Thereon, several reports appeared devoted to similar multilayer systems but mainly on gold surfaces. Hf(IV) and Ce(IV) were also used as linkers of bis(alkanephosphonates), mainly 1,10-decanediylbis(phosphonate) [10–13]. In all these reports very similar systems were studied as that depicted in Fig. 4. Since in this type of system a M(IV) ion is alternating, as coordinating linker, with organic ligands they are sometimes called “hybrid” multilayers.

A mercaptoalkanephosphonate has been mostly used to form the base SAM on gold (and in some cases other surfaces were used) leaving the phosphonate terminal group to coordinate the first metal ion, M(IV). An exception in this sense was the use of 11-hydroxyundecanethiol [10]. The terminal hydroxyl group was phosphonated *in situ* with phosphorous oxychloride and further on 11-hydroxyundecylphosphonate was used a ligand. A similar procedure was reported but introducing a copolymer [14].

Each M(IV) ion links two successive bis(alkanephosphonates) (Fig. 4) and, at the same time, coordinates neighboring chains. This characteristic guarantees the formation of a robust multilayer system. The main and exclusive role of M(IV) is as a coordinating linker. Another property that reinforces the stability of the multilayer system is that the formed complex is neutral. This type of multilayer system was built using a LbL procedure.

An interesting approach consisted in using Zr(IV) as linker of alternating 1,10-decanediylbis(phosphonate) and 4,4′-azobis[(*p*-phenylene)methylene]bis(phosphonate) monolayers [15]. Varying the ratio between both monolayers and the thickness of the resulting film the authors were able to control the index of refraction of the modified surface. With a terminal azo-monolayer the system could have served as a photosensor but this application was not studied.

3.2. Bis- tetrakis- and hexakis(hydroxamate) and M(IV) of group 4

Rubinstein and coworkers used bis(hydroxamate) derivatives and Ti(IV), Zr(IV), Hf(IV) and/or Ce(IV) as coordinating linkers to form multilayers on gold surfaces. They selected a cyclic disulfide bound to a bis(hydroxamate) moiety (Fig. 5a) to form the base monolayer on gold. The S–S bond disrupted opening the cycle and the two thiolate groups self-assembled to the gold surface. This way, a highly compact base monolayer could be obtained. The bis(hydroxamate) groups pointing outward from the surface were used to coordinate Ti(IV), Zr(IV) and Ce(IV). To complete the coordination sphere of these metal cations the same ligand was used leaving its cyclic disulfide moiety pointing outward. If the system was formed stepwise the resulting bilayer could be symmetric or asymmetric [16]. After that report, the authors worked on a multilayer system using the same cyclic disulfide bound to a bis(hydroxamate) moiety for the preparation of the base monolayer on a gold surface. A second ligand, a tetrakis(hydroxamate) (Fig. 5b) was used to form the additional layers. Ti(IV) or Ce(IV) were used to link, through the formation of coordination bonds, one tetrakis(hydroxamate) with the following one. The multilayer system was built stepwise with up to 10 ligand–M(IV) layers [17].

The tetrakis(hydroxamate) system presents some similarities with the above-mentioned bis(phosphonates) but with the advantage of using two terminal bidentate groups linked through a double chain (Fig. 5b). Rubinstein and coworkers further reported a combined multilayer system built on gold using the ligand represented in Fig. 5a to form the base monolayer and the tetrakis (hydroxamate) ligand (Fig. 5b), now alternating with an alkanebis(phosphonate) ligand and Zr(IV) as the coordinating linker. The authors claimed that the construction of this hybrid system permitted a more rational manipulation since tetrakis(hydroxamate) is acid-sensitive while alkanebis(phosphonate) is acid-resistant [18]. This type of system was further studied but using alkanebis(phosphonate) only to form the terminal monolayer. The effect of the metal ion linker (Zr(IV) or Ce(IV)) was analyzed in detail. They confirmed that with Zr(IV) a greater thickness could be achieved, with a large excess of the cation evenly distributed between the organic layers. This excess of Zr(IV) was transformed through time into ZrO_2 to make the multilayer system become a robust composite organic–ceramic multilayer [19]. Rubinstein and coworkers also reported the use of a hexakis(hydroxamate) ligand (Fig. 5c). This way, a branched multilayer was obtained using Zr(IV) as coordinating linker. This multilayer system behaved as an excellent dieletric with self-repair properties [20]. The branched nature of hexakis(hydroxamate) ligand used (Fig. 5c) allowed the construction (using a divergent approach) of 2–11 generation “coordination dendrimers” on gold surfaces [21].

A multilayer system based on hexakis(hydroxamate) ligand and Zr(IV) as coordinating linker was used to immobilize gold nanoparticles (AuNP) capped with 6-mercaptohexanol and also a cyclic disulfide bound to a bis(hydroxamate) moiety. This same ligand was used to form the base monolayer. The coordinated AuNP films grew in a true LbL way, adding one AuNP monolayer at a time. Using conductive AFM, an increase in ohmic resistance with the number of AuNP layers was observed [22].

The multilayer systems analyzed above used one or two ligands with a M(IV) coordinating linker in all cases. The main goal was to obtain robust systems with an appreciable thickness. We will now analyze other types of constructions of coordination compounds on flat metal surfaces with new properties.

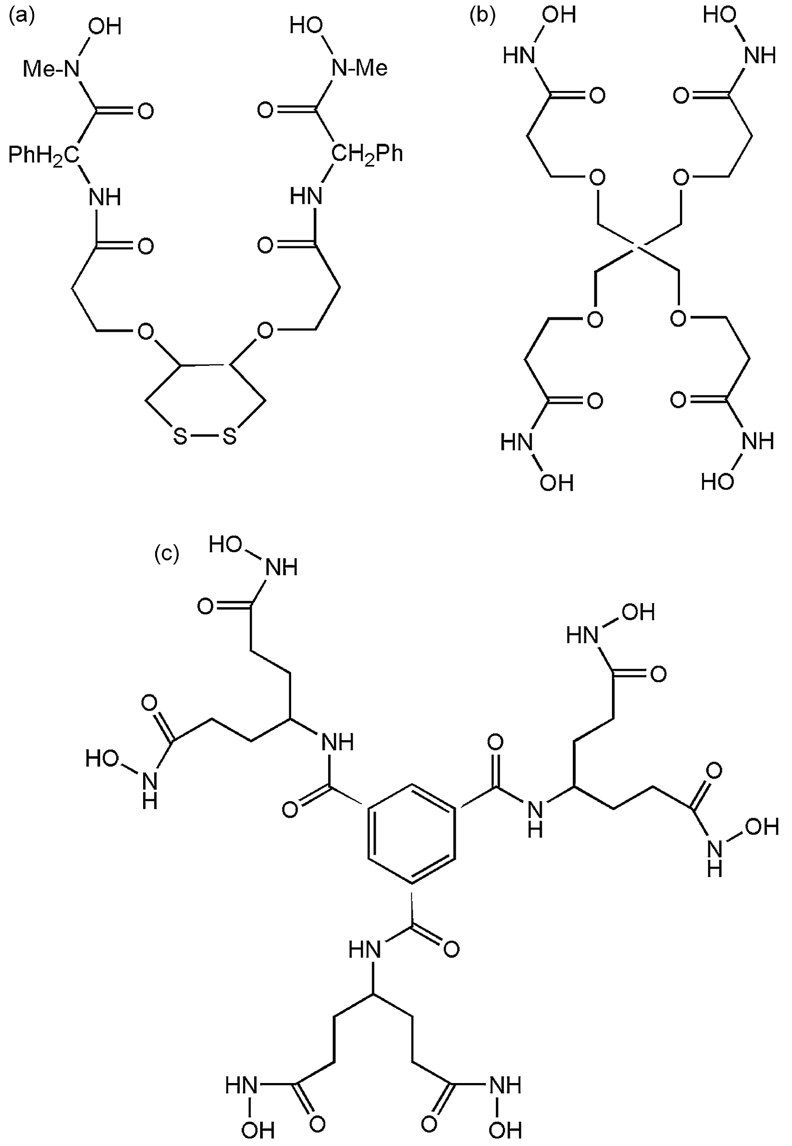

Fig. 5. Different hydroxamate ligands used to build M(IV) coordination compounds on gold surfaces.

3.3. Ruthenium coordination compounds

As mentioned in Section 2, the intermolecular interactions among the components of each monolayer are important in order to achieve a stable and compact system. When the molecules that form the base monolayer present a terminal bulk functional group, this can affect the preorganization process and compactness of the monolayer. From a coordination point of view, bulk terminal groups containing donor atoms are practically indispensable to build a coordination compound on a metal surface. An interesting approach to minimize this problem consisted in preparing a mixed base monolayer. Licciardello and coworkers reported the formation of a mixed base monolayer using thiophenol and 4′(4-mercaptophenyl)-2,2′:6′,2″-terpyridine in a 1:1 molar ratio [23,24]. The terpyridine (tpy) moiety pointing out from the modified gold surface served to coordinate $Ru(tpy)^{2+}$ to the self-assembled mixed base monolayer [25]. A similar base monolayer was used to immobilize lactoferrin, which will be analyzed further on. A terpyridine thiolated derivative was first used to immobilize cobalt, chromium and osmium complexes (forming multilayer systems) on gold electrodes [26].

Evidently, the use of mixed base monolayers is very important to take into consideration when designing the way to build coordination compounds on metal surfaces. Moreover, it is essential to analyze which compound, and in what molar ratio, will the base ligand accompany in the mixed monolayer in order to reduce to a minimum the steric restrictions introduced by the terminal moiety of the base ligand, by the metal ion and also by the terminal ligand. Additionally, the “accompanying” compound should enhance the stability of the mixed base monolayer.

Ruthenium coordination compounds have been mainly built on electrodes, however, some have also been built on simple flat gold surfaces. $[Ru(CN)_5]^{3-}$ moiety has been coordinated to a SAM of 4-mercaptopyridine through the nitrogen atom of the pyridine moiety. The back-donation of $[Ru(CN)_5]^{3-}$ played an important role in the stabilization of the formed multilayer [27,28]. This system was also compared with a similar one using a $[Fe(CN)_5]^{3-}$ moiety. As expected, the ruthenium complex exhibited a greater back-donation [29].

11-Mercaptoundecanoic acid (MUA) was coupled to *p*-methylamine-pyridine to form a base monolayer to which a trinuclear ruthenium complex, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(bpy)_2(CO)]$

(bpy: 2,2′-bipyridyl), was coordinated. CO was liberated electrochemically and its coordination site was used to coordinate the second trinuclear unit, and so on (up to five units) [30].

A mixed multilayer system, based on two ruthenium complexes, $[Ru(NH_3)_5Cl]^{2+}$ and $[Ru(CN)_6]^{4-}$, was built on a gold surface. Both ruthenium complexes were linked together through a cyano bridge, $[(CN)_5Ru–CN–Ru(NH_3)_5]^-$. This mixed-valence dimeric anionic complex was electrostatically immobilized on a gold surface, previously modified with a disulfide derivative monolayer containing quaternary ammonium terminal groups [31]. The stability of this system was not analyzed.

Most of the ruthenium complexes analyzed here are not neutral and, therefore, the mono- or multilayers they form require the presence of counterions. Other complexes mentioned in this review also present this same characteristic which is very important especially in the case of modified electrodes.

3.4. First row transition metal compounds

The first report on the construction of a first row transition metal compound on a flat metal surface corresponded to the use of 11-mercaptoundecanoic acid and 16-mercaptohexadecanoic acid as ligands with Cu(II) as the coordinating linker. These ligands were used indistinctly to form the base monolayer with the carboxylic moiety pointing outward from the gold surface, which served to coordinate Cu(II). A second monolayer (and so on) was attached through coordination of the mercapto group to Cu(II). Unexpectedly, the authors reported that according to XPS determinations the metal ion was not reduced to Cu(I). Up to six layers of mercaptocarboxylate were self-assembled this way [32]. A similar, but much simpler system was built consisting in the formation of a base monolayer of mercaptoundecanoic acid and Cu(II) coordinated to the terminal carboxylate groups. The coordinatively unsaturated Cu(II) ions served to detect organophosphorus compounds as a selective surface acoustic wave device [33].

As mentioned above, the preparation of a mixed base monolayer using thiophenol and 4′(4-mercaptophenyl)-2,2′:6′,2″-terpyridine in a 1:1 molar ratio was reported [23,24]. The authors used the terminal terpyridine moiety to coordinate Fe(II) to SAM but containing free coordination sites. This mixed monolayer was patterned by a lithographic technique on a SAM of 11-mercaptoundecanol that served as "blackboard". To this SAM lactoferrin, a glycoprotein that contains two iron-binding sites (His-253, Tyr-92, Tyr-192 and Asp-60 of the N-lobe and Hys-253, Tyr-435, Tyr-528 and Asp-395 of the C-lobe), was associated through direct coordination with immobilized Fe(II). The presence of 11-mercaptoundecanol (as blackboard) was necessary to avoid unspecific adsorptions of the protein to the gold surface [34].

Two approaches, completely different from the others mentioned up to now, were used to build coordination compounds on metal surfaces. One consisted in synthesizing a ligand directly on a gold surface. 4-Piperidinemethanethiol was synthesized and self-assembled on a Au(1 1 1) surface. The NH group of the piperidine moiety was then transformed into a dithiocarbamate group through condensation of CS_2. This was, an amphiphilic ligand with thiolate and dithiocarbamate terminal anionic groups was formed, with the latter pointing outward from the surface. Nevertheless, the amphiphilic ligand was able to make a "flip" and self-assemble through the dithiocarbamate group but with less stability than the Au–thiolate interaction. Copper(II) was coordinated to the free dithiocarbamate group and its coordination sphere was completed with the addition of morpholyldithiocarbamate anion. This way, a bis(dithiocarbamato)copper(II) complex was self-assembled on a gold surface in three steps [35].

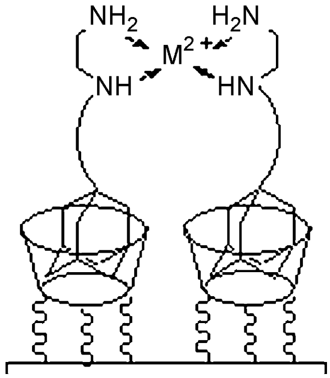

Fig. 6. $M(en)_2{}^{2+}$ formed by adamantanoyl ethylenediamine derivatives supramolecularly associated with β-cyclodextrin dodecylthioether derivatives self-assembled on a gold surface. Adapted from Ref. [37].

The other novel approach was completely based on supramolecular interactions. For this, a β-cyclodextrin [36] dodecylthioether derivative was self-assembled on a gold surface and an adamantanoyl ethylenediamine derivative was supramolecularly associated with it. Once the adamantanoyl moiety was included in the cyclodextrin cavity two ethylenediamine terminal groups coordinated Cu(II) or Ni(II) to form a $M(en)_2{}^{2+}$ unit for each two self-assembled cyclodextrins as depicted in Fig. 6 [37].

3.5. Metalloporphyrins and metallophthalocyanines

Metalloporphyrins and metallophthalocyanines are highly stable coordination compounds that generally present one or two free coordination sites. They have been recently used in the development of sensors when modifying metal electrodes. These results have been possible thanks to previous studies on the self-assembly of these types of compounds on flat surfaces.

Both porphyrins and phthalocyanines are bulky planar macrocycles. This characteristic requires a different way to self-assemble them on a metal surface. Two approaches have been used: (a) self-assemble an alkanethiol with a terminal donor atom able to coordinate apically the metal ion inserted in the macrocycle; (b) link thiol derivatives to one or more positions of the macrocycle to be used for the self-assembly. If process (a) is used the plane formed by the macrocycle should stay held parallel (approximately) to the metal surface. With process (b) a horizontal orientation can be achieved only if more than one thiol pending moiety is linked (more or less symmetrically) to the macrocycle. Only one pending group provokes a perpendicular orientation of the macrocycle [38]. Process (b) has been scarcely used [39], perhaps due to synthetic difficulties. Nevertheless, Lindsey's group succeeded in synthesizing different zinc(II) porphyrins monosubstituted with pending thiol derivatives [40–43].

When the macrocycle is associated perpendicularly to the metal surface the access of any external substrate is sterically restricted. Nevertheless, such geometric arrangement of the self-assembled macrocycles favors the achievement of a compact SAM that could be highly stable due to π–π interactions.

Zinc(II) porphyrins monosubstituted with thiol derivatives and ferrocene (Fc) were used to study the effect of the spacer length on the photoelectrochemical properties when self-assembled on gold. The authors observed that as the length of the spacers increased, the SAM tended to form a highly ordered structure and the photocurrent also increased [44].

Isothiocyano [45] and isocyano [46] moieties have also been used to self-assemble porphyrins and phthalocyanines on gold surfaces.

The horizontal position of the immobilized macrocycle is important when using it to develop a sensor since it offers a high accessibility to the substrate. Nevertheless, the horizontal position reduces the surface coverage (a negative effect), with many empty spaces under the "macrocyclic umbrella". If the macrocyclic monolayer is prepared mixed with another thiolated derivative, the latter should present a much shorter chain than that used to immobilize the macrocycle. If this requirement is not fulfilled, the second thiol present can affect the position adopted by the macrocycle [47]. That is the reason for which no second thiol is generally used to form a mixed SAM for macrocyclic immobilization.

A metalloporphyrin has been self-assembled perpendicularly to a gold surface through a cyclic disulfide base monolayer, similar to that represent in Fig. 5a, but containing two hydroxamate groups plus two imidazolyl terminal groups. The two imidazolyl moieties served to associate to the axial coordination positions of iron tetraphenylporphyrin forcing the perpendicular position of the macrocycle [48]. According to electrochemical determinations when the layer was self-assembled in one step a higher coverage was achieved than when the process was carried out in two steps (LbL self-assembly of cyclic disulfide followed by the coordination of iron tetraphenylporphyrin). Due to steric factors not all the imidazolyl moieties of the base monolayer were able to coordinate the metallomacrocycle.

Imidazolyl-terminated linkers have also been used to self-assemble different metalloporphyrins through the apical coordination to the metal ion [49]. Additional monolayers were reported to be self-assembled to this base monolayer of metalloporphyrin by using bidentate pyrazine as a bridging ligand [50]. A similar system was reported but using a diimidazole binder to anchor cobalt and iron tetraphenylporphyrins to an ultrathin film of gold deposited on mica. The advantage of this latter system consisted in its transparency, which permitted to study it by UV–vis spectroscopy [51].

Thiophenol derivatives are convenient to immobilize metalloporphyrins. 4-Pyridinethiol has been used to self-assemble octaethylporphyrinatozinc(II) by the apical coordination of pyridine nitrogen. This Zn–N(Py) bond is not characterized by a high stability but, nevertheless, was expressed with a significant shift in some signals recorded by SERS [52].

An apical coordination was also used to form a layer of a ruthenium phthalocyanine on gold but using pyridine carboxaldehyde as linker. Actually, the ligand was condensed through the carboxaldehyde moiety to a base monolayer containing terminal amine groups. Pyridine moieties served to axially coordinate to ruthenium and an additional condensation permitted the apical coordination of a cobalt tetraphenylporphyrin as terminal monolayer [53].

4. Metal electrodes modified with coordination compounds

Modification of metal (mainly gold, platinum, silver and copper) electrodes with coordination compounds follows the same two approaches already mentioned in the introduction: the self-assembly of the metal complex as a whole on the metal electrode and the LbL procedure. When the LbL procedure is used the best alternative seems to consist in preparing a mixed base monolayer in order to avoid direct interactions between neighboring coordinated metal ions. As expected, a mixed base monolayer, where one of the constituents should be electrochemically inactive, results in a relatively low surface coverage but the resulting average effect is positive.

The main characteristic of modifying metal electrodes is that acceptable electrochemical signals have to be achieved. Therefore, the experimental conditions in the preparation of SAM on metal electrodes (electrode pretreatment, immobilization technique, surface coverage, surfactants, electrolytes, solvents and temperature) are very important [54–57]. Additionally, rate and mechanism of ET between the coordinated metal ion and the metal surface have to be taken into consideration since they can affect the sensibility of the modified electrode [2,3,5].

Metal electrodes modified with coordination compounds are studied electrochemically, including electrochemical impedance spectroscopy (EIS) [58,59], in order to characterize the stability of the formed SAM, define surface coverage, possible formation of defect structures, stability of the SAM bonding, orientation of the terminal groups, etc. It is also very convenient to characterize the modifying surface with a quartz crystal microbalance (QCM) [57].

Building coordination compounds on electrode surfaces does not only permit one to analyze their new electrochemical properties and ET rates. Most importantly, metal electrodes modified with coordination compounds have found applications as sensors and as supports for building biosensors.

4.1. First row transition metal compounds

One of the first reports on gold electrodes modified with coordination compounds described the formation of a mixed monolayer of 2,2′-thiobis(ethyl acetoacetate) and *n*-octadecyltrichlorosilane. The acetoacetate terminal groups served to coordinate Cu(II) and Pb(II) to produce an electrochemical response, which disappeared in the presence of Fe(II), Fe(III) or VO^{2+} [60]. Earlier than that, gold electrodes modified with several types of sulfur-containing carboxylic acids were reported. The terminal carboxylate groups served to coordinate $Co(NH_3)_5{}^{3+}$ and the ET kinetics were studied [61]. From then on, the construction of first row transition metal complexes on metal electrodes have been reported but with no transcendent applications.

Gold electrodes modified with a thiol-modified terpyridine ligand, 4′-(5-mercaptopentyl)-2,2′:6′,2″-terpyridinyl Cr(III), Co(II) and Os(II) complexes were self-assembled on gold surface as a whole although the LbL procedure was also analyzed [26]. In this second case, part of the ligands forming the base monolayer dissociated to complete the coordination sphere of the metal ion (see Section 2). The modified electrode containing Cr(III) was able to detect NO but no quantitative information was offered.

The only report found on a copper(II) complex built on a gold electrode with a certain applicability was that used as NO sensor. Ribose bis(thiosemicarbazonato)copper(II) built LbL on a gold electrode was able to detect NO concentrations down to 6 μM [62].

The transition metal compound that has been most used to modify metal electrodes has been ferrocene and its derivatives. Fc constitutes a stable and excellent electron donor with well-defined electrochemical properties. As expected, metal electrodes modified with SAM containing ferrocenyl terminal groups have mainly been used to study ET kinetic processes between Fc and the electrode. The self-assembly of Fc through alkylthiol pending groups tend to form multilayers and aggregates, a problem that has been solved using a mixed base monolayer [63]. The formation of Fc multilayers is apparently controlled by hydrogen bonds and highly organized SAM have been achieved by increasing the concentration of Fc with alkythiol pending groups [64].

$FcCO_2(CH_2)_nSH$ was self-assembled on a gold electrode [65,66], which constitutes the first report on ferrocenyl moieties modifying gold electrodes. The authors detected that long chain lengths and low surface coverage caused slow ET kinetics between the electrode and the ferrocene groups. When this type of system was studied in butyronitrile/ethyl chloride solvent mixtures slow ET processes were observed, especially at low temperatures [67]. The ET kinetics of a mixed monolayer ($FcCO_2(CH_2)_nSH + CH_3(CH_2)_{n-1}SH$) on gold was studied in detail [68]. The authors were not able to explain, using the indirect-induced temperature jump method, the kinetic behavior for $n \leq 8$, which could have been attributed to the presence of poorly organized SAM. Several other reports have also been dedicated to this important issue [69–74].

The self-assembly process of $FcCO(CH_2)_5SH$ on gold electrodes with the formation of mono- and multilayers has been studied with a electrochemical quartz crystal microbalance [75]. A relatively high surface coverage ($0.75\,nmol\,cm^{-2}$) was determined, which dropped down to $0.46\,nmol\,cm^{-2}$ (corresponding to a simple monolayer) after rinsing the modified electrode with water and ethanol.

The electrochemical properties of ferrocenyl units (FcC12S-Au) are affected when forming a binary monolayer on gold electrodes [76]. In the presence of $^{+}H_3N–(CH_2)_{11}S–$ an anodic shift was observed while the contrary took place when the second self-assembled compound was $^{-}OOC–(CH_2)_{11}S–$. This result indicates the importance of the charge of the SAM in ET processes.

Ferrocenyl derivatives have not only been self-assembled on gold electrodes, but also on platinum. For this, 12-ferrocenyldodecyl isocyanide was successfully used both on gold and platinum electrodes [8]. The isocyanide derivative gave a redox peak ~300 mV more negative than its disulfide analogues.

Electrodes modified with SAM containing ferrocenyl moieties and photoactive compounds have received special attention. Mirkin and coworkers reported gold, platinum and ITO films modified with 4-(4-mercaptobutyl)-4′-ferrocenylazobenzene [77,78]. SAM of ferrocenylundecanethiol on gold electrodes was used to catalyze the chemiluminescence of luminol. This system was used for detection of glucose in the presence of glucose oxidase [79].

Gold electrode modified with ferrocenylhexanethiol was studied in aqueous and dichloromethane solutions in the presence of various anions, i.e. HSO_4^- (or SO_4^{2-}), ClO_4^-, and PF_6^-. While the redox peaks of ferrocene measured in aqueous solutions were observed to shift to more positive values in the anion order of PF_6^-, ClO_4^-, and HSO_4^-, in dichloromethane the observed shifts became more negative in this same order [80,81]. The electrochemical effect that the solvent may cause on a ferrocenyl-modified (1-(4-mercaptododecyl)-4-(2-ferrocenyl-1-ethylene) pyridinium bromide) electrode was also analyzed when studying acetonitrile solutions with varying amounts of water as can be observed in Fig. 7 [82]. The authors observed that the current decreased and the oxidation potential shifted negatively with increasing water contents in acetonitrile solutions due to changes in the dielectric constant of the solvent.

A gold electrode modified with 11-ferrocenyl(carbonyloxy) undecanethiol was used to determine egg-phosphatidylcholine lipid vesicle [83]. Once the lipid was adsorbed on the SAM a significant increase in the anodic peak current was observed. This observed variation could be attributed to Fc–peptidic bond interactions, which will be analyzed in Section 5.2.

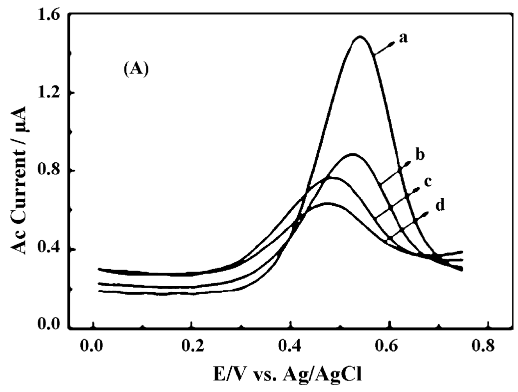

Fig. 7. Effect of water content in acetonitrile solutions on the cyclic votammograms of ferrocenyl-modified (1-(4-mercaptododecyl)-4-(2-ferrocenyl-1-ethylene) pyridium bromide) electrode: (a) pure acetonitrile; (b) 1% water; (c) 5% water; (d) 10% water content [82].

An interesting report on ferrocenyl-modified gold electrodes corresponds to those modified with a mixed monolayer of ($Fc(CH_2)_6SH/HO(CH_2)_2SH$ and $Fc(CH_2)_{16}SH/HO(CH_2)_{11}SH$). $HO(CH_2)_nSH$ was introduced in the monolayer in order to achieve a surface with low concentration of ferrocene moieties. This condition was required since the purpose was to study the effect that the inclusion of the ferrocene groups into β-cyclodextrin cavities would cause [84].

4.2. Ruthenium and osmium coordination compounds

Ruthenium and osmium are the only second and third row transition metals reported to form coordination compounds modifying metal electrodes, even forming "duets" in some reports. Pyridine chelating derivatives (mainly bpy and tpy) and NH_3 have been the ligands mostly used to form the immobilized ruthenium and osmium complexes.

ET kinetics of electrodes modified with ruthenium and osmium have been widely studied by Finklea's and Abruña's groups and by other authors [2,5,56,85–93]. The ET kinetics of the two metal ions are completely different. The electrolyte used may affect the electrochemical behavior of the metal electrodes modified with ruthenium and osmium complexes [94]. Additionally, the use of mixed monolayers, where only one of the constituents is electroactive with the other behaving as a "diluent" that reduces the steric effects of the associated bulky complexes, has proven to be convenient [95].

$[M(bpy)2(bpe)Cl]^+$ (M:Ru(II), Os(II); bpe:*trans*-1,2-bis(4-pyridyl)ethylene) complexes, both in solution and self-assembled, were studied photo- and electrochemically [96]. The authors observed that while oxidation of the osmium centers proceeded as a simple one-electron-transfer reaction, the behavior of the ruthenium aquo-compound is more complicated. The rate at which two Ru^{3+} centers disproportionated was larger for the immobilized complex than in solution phase, most likely due to a neighboring effect caused by the monolayer. A similar pair of complexes, $[M(bpy)_2(1,3\text{-bis}(4\text{-pyridyl})propane)Cl]^+$, forming a mixed monolayer was previously studied using the second ligand to form the base monolayer on platinum electrodes [97]. An exchange dynamic, controlled by the rate of desorption of each complex via a dissociative mechanism, was observed. Additionally, the presence of mixed monolayers (Os/Ru) resulted in an increased broadening of the voltammetric wave associated with the ruthenium complex relative to the case of a monolayer only containing the ruthenium complex. Abruña and coworkers also immobilized an $Os(bpy)_2^{2+}$complex on gold electrodes using a $Py–(CH_2)_n–SH$ ligand [98].

Platinum disk electrodes were modified with $[Os(bpy)_2(4,4'\text{-trimethylenedipyridine})_2]^{2+}$, with one of the 4,4′-trimethylenedipyridine ligands directly associated with the metal surface, which exhibited nearly ideal cyclic voltammetric behavior [99]. The ET kinetics of a very similar system was previously reported [100]. $[Ru(bpy)_3]^{2+}$ containing a pendant amino group was LbL self-assembled on gold sputtered silicon electrodes previously modified with thioctic acid and its electrochemiluminescent properties were studied [101]. The use of the LbL procedure permitted the formation of a compact organized layer. When $[Ru(bpy)_3]^{2+}$ electroluminescent devices were studied by MALDI-TOF mass spectrometry and micro-Raman spectroscopy $[(bpy)_2(H_2O)RuORu(OH_2)(bpy)_2]^{4+}$ dimer was identified as the performance-degrading product [102]. The formed

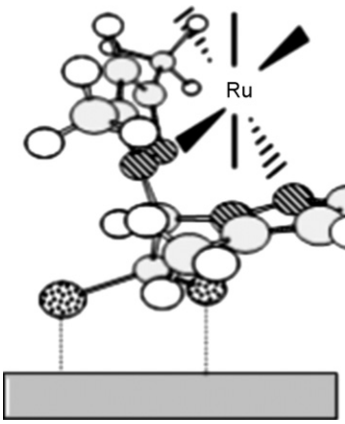

Fig. 8. Ruthenium(II) complex with bis(3,5-dimethylpyrazol-1-yl)dithioacetate was self-assembled LbL on a gold electrode [106].

$[(bpy)_2(H_2O)RuORu(OH_2)(bpy)_2]^{4+}$ dimer was considered by the authors as an effective quencher of luminescence device. A similar effect will be analyzed in Section 5.2.

Mercaptoacetate modifying a gold electrode served to coordinate $Ru(NH_3)_5{}^{3+}$. The resulting electrode, modified LbL, was observed to electrochemically interact with $[Fe(CN)_6]^{3-}$, EDTA and NO. $[Fe(CN)_6]^{3-}$ formed a binuclear complex with $Ru(NH_3)_5{}^{3+}$ while EDTA subtracted Ru(III) from the bilayer coordination sphere. NO, on the contrary, formed a stable coordination bond with ruthenium which induced a higher reversibility in the Ru(III/II) redox system [103].

The interaction of metal electrodes modified with ruthenium complexes with NO has been studied and seems to be a promising topic. The first reports on this issue corresponded to platinum electrodes modified with $[Ru(bpy)_2L(NO_2)]^+$ complexes [104,105]. Reversible cyclic voltammetric peaks corresponding to the formation of coordinated nitrate and nitrosyl species were observed.

A ruthenium(II) complex with bis(3,5-dimethylpyrazol-1-yl)dithioacetate was self-assembled LbL on a gold electrode (Fig. 8). The formed layer was compact (surface coverage of 4.15 pmol cm^{-2}) and highly organized according to AFM determinations. This modified electrode was used to detect NO through coordination to one of the disposables coordination sites of ruthenium(II) [106].

4.3. Metalloporphyrins and metallophthalocyanines

The planar nature of metalloporphyrins and metallophthalocyanines requires a special approach to self-assemble them on metal electrodes, as already mentioned in Section 3.5. The method most used for the immobilization of metalloporphyrins on gold electrodes has consisted in the axial coordination to isonicotinate-, pyridine- and imidazole-terminated base monolayers. This way, the immobilized metalloporphyrin lies approximately parallel to the surface presenting its second axial position free and completely accessible. When using isonicotinate-terminated adsorbates a higher reproducibility in the formation of the base monolayer has been observed.

The formation of a base monolayer containing terminal groups able to coordinate a given metalloporphyrin eliminates the necessity of prior modification of the metalloporphyrin, and requires only a small quantity of it in the surface reaction. This permits better control of the surface coverage of the modified electrode. Moreover, axially bound metalloporphyrins exhibit sharp peaks and stable cyclic voltammetric behavior [49].

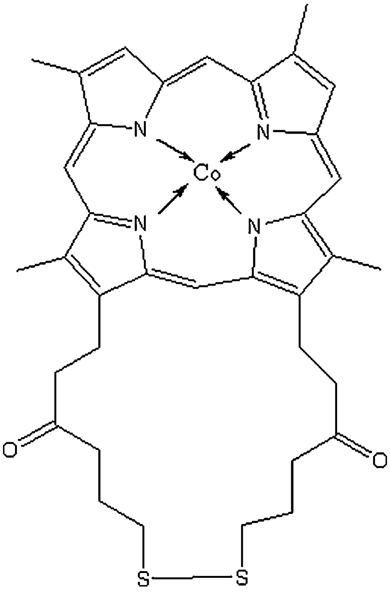

Fig. 9. Co(II) porphyrin disulfide derivative used to self-assemble on gold electrodes [112].

The importance of electrodes modified with redox active metalloporphyrins is expressed in the large number of reports on this issue [37–43,49,107–115].

An electrode modified with ruthenium phthalocyanine (using 1,4-diisocyanobenzene as base monolayer) has been studied with results similar to those obtained with metalloporphyrins [116]. Interestingly, the authors studied the formed multilayer by XPS and could observe that each macrocycle covered about 12 molecules of 1,4-diisocyanobenzene forming the base monolayer.

Montfort's group [112,113] has synthesized metalloporphyrin disulfide derivatives (Fig. 9) and self-assembled them to modify gold electrodes using a method that permitted stable and compact monolayers. The electrochemical behavior of these modified electrodes was compared with those of the metalloporphyrin in solution.

The effect of alkyl spacers in metalloporphyrins containing pendant disulfides and their photoelectrochemical properties have been analyzed. In this sense, a higher ordered structure on gold electrodes was achieved when the length of the spacers was increased. On the other hand, photochemical studies permitted one to observe that the quantum yield increased in zigzag (even–odd effect) when the spacer was increased up to six methylene groups while additional lengthening led to slight decreases [111]. The authors explained this behavior taking into consideration that: (a) two competitive deactivation pathways of the excited singlet state of the metalloporphyrin could have taken place; (b) metalloporphyrin aggregation enhanced the rate of non-radiative pathway in the excited state; and (c) ET rate from the gold electrode to the resulting metalloporphyrin radical decreased with an increase of the spacer length.

The preparation of stacked mixed multilayer of metalloporphyrin has also been reported. For example, several monolayers of bis(dinitrogen)-*meso*-tetramesitylporphyrinatoruthenium(II) were stacked one on top of the other with a high order using bidentate pyrazine-terminated ligands [49].

Interestingly, a ferrocene–porphyrin–C_{60} was synthesized and self-assembled through an alkanethiol pendant group near to the ferrocene moiety. This ingeniously designed triad contained a donor, a photoexcitable and an acceptor group linked in this order. As expected, this system was studied photoelectrochemically [117].

The intensity of the induced photocurrent is larger by two orders of magnitude than that of porphyrin–polyalkanethiol systems due to the effect of the donor–acceptor (ferrocene and C_{60}) moieties present in the SAM.

Several metalloporphyrins, such as haemoglobin and its analogues are known to coordinate nitric oxide, a radical of biological importance. For that reason, several groups have worked on modifying electrodes with metalloporphyrins (generally in polymeric form) [118,119] and metallophthalocyanines [115] in order to develop NO sensors, mainly using carbon and glassy-carbon electrodes. Covering the modifying surface with Nafion® (a cationic exchanger) eliminates the interference caused by nitrite anion. Up to now electrodes modified with metalloporphyrins are more efficient than those modified with ruthenium complexes (analyzed above) as NO sensors.

5. Coordination compounds capping metal nanoparticles

The development of noble metal nanoparticles (MNP) has attracted great attention in recent years due to their interesting and novel optical [120], as well as catalytic and electrical properties [121]. The singularity of MNP is due to the very small size of these species where a high percent of the atoms are on the surface. Due to the small size and high percent of atoms on the surface in MNP when irradiated with visible light they are able to electronically excite in a process called “surface plasmon resonance” (SPR). SPR is expressed as a maximum in the electronic spectrum with its position depending on the metal and the size of the MNP. For example, gold nanoparticles with an average diameter of 2–3 nm will present their SPR maximum at 503–507 nm (red), while for silver nanoparticles it will be at around 405 nm (yellow).

In order to avoid aggregation MNP are stabilized by capping them through the self-assembly of different species, mainly sulfur-containing molecules. AuNP capped with alkanethiols have been the most studied MNP since they are greatly resistant against oxidation and are easy to obtain. The nature of the capping agent can significantly affect the properties of MNP.

The approximately spherical form of MNP introduces a new factor to consider when analyzing the capping SAM. The curvature of the surface favors the accessibility, especially of bulky substrates, to metal ions coordinated to MNP. This specificity makes a significant difference when comparing with metal complexes self-assembled on flat or electrode surfaces as already analyzed above.

Several groups have capped MNP with metal complexes, specially to use them as catalysts and sensors [122]. Nevertheless, relatively few reports on metal complexes capping MNP have been published up to now.

5.1. Main group metal complexes

11-Mercaptoundecanoic acid (MUA) capping AuNP was used in the detection of spectroscopically silent metal ions such as lead(II), cadmium(II) and mercury(II) [123]. This type of AuNP was able to associate any of these heavy metal ions contained in an aqueous solution through the coordination to the terminal carboxylate moieties of MUA. Such coordination caused the aggregation of AuNP and, consequently, an enhancement of the hyper Raleigh scattering effect was observed. An increase of the intensity and a red shift of the SPR band were observed due to a decrease in the symmetry and also to an increase in the size of the chromophoric entity. As expected, with the addition of EDTA the effect was reversed. This way, AuNP capped with MUA served as photosensor of spectroscopically silent cadmium, mercury and lead ions.

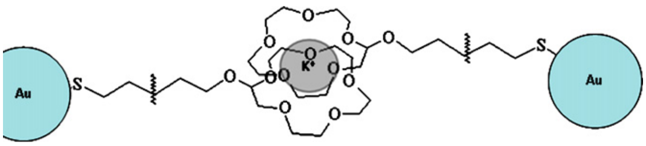

Fig. 10. Sandwich structure formed by K^+ with the two 15-crown-5 ether terminal moieties of neighboring AuNP. Adapted from Ref. [124].

A more elegant and selective ion detection method was developed by Chen and coworkers who used AuNP capped with a thiolate containing a 15-crown-5 ether terminal moiety for the detection of potassium in the presence of Li^+, Cs^+, $NH_4{}^+$, Ca^{2+}, and Na^+ ions [124]. As known, sodium ions form the most stable complexes with this crown ether. Nevertheless, potassium was detected through a change from red to blue color by the formation a 2:1 sandwich shape complex displacing sodium from inside two neighboring macrocyclic rings of the same or different AuNP (Fig. 10). This way, potassium was detected at concentrations between 7.6 μM and 0.48 mM.

1,10-Phenanthroline can behave as a Li^+ selective organic chromophore [125]. AuNP capped with 1,10-phenanthroline terminal moieties associated Li^+ in order to achieve a coordination number of four. This way, an aggregation of nanoparticles was induced, expressed in a change of color from red to blue, linearly proportional to lithium concentration in the range from 9 to 90 mM. An important observation was that small AuNP were more effective as chromophores than bigger ones.

5.2. Transition metal complexes

Ferrocene presents interesting redox properties, constitutes an excellent electron donor and is highly stable. This explains why MNP capped with ferrocenyl terminal moieties have been extensively studied. If the ferrocenyl terminal moieties are present in a mixed monolayer together with other electroactive derivatives multistep chemical and redox catalytic reactions can be observed [126].

Ferrocenyl termini AuNP (Fig. 11) has been obtained in two steps (LbL) through the condensation of ethylenediamine-*N*-ferrocenyl amide to about 50% of the carboxylic groups of capping mercaptoacetate. This type of AuNP was able to self-aggregate to form micro- and nanometric spheres, depending on the concentration of the solution. This effect was attributed to donor–acceptor interactions of the ferrocenyl moieties with the amido groups of neighboring nanoparticles combined with the effect produced by hydrogen bond formation with the solvent. Therefore, this type of system was

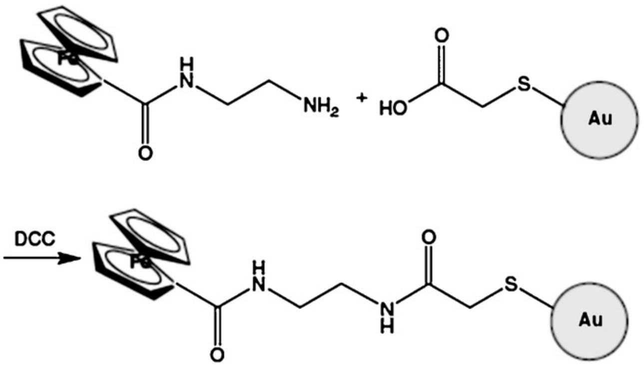

Fig. 11. Ferrocenyl termini AuNP formed LbL through the condensation of ethylenediamine-*N*-ferrocenyl amide to about 50% of the carboxylic groups of capping mercatoacetate [127].

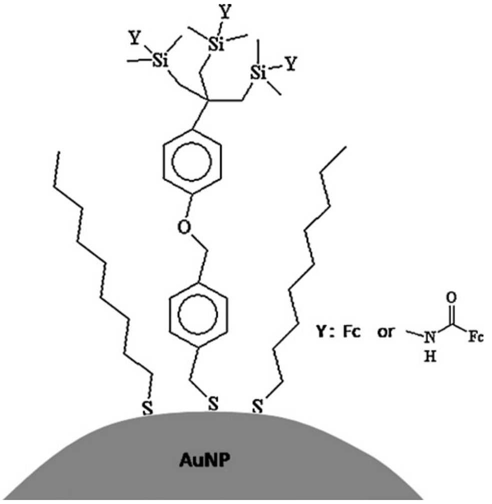

Fig. 12. AB_3 dendron-like compound with a AuNP nucleus and terminal Fc moieties. Adapted from Ref. [130].

studied as peptide sensor with positive results [127]. On the other hand, the observed interaction between the ferrocene derivatives expressed as an aggregation process of AuNP can serve to explain the formation of multilayers and aggregates when modifying gold electrodes as already mentioned above [62,63].

In a more or less similar way, a ferrocene amide derivative was also used to cap AuNP mixed in different proportions (7–38%) with alkanethiol. The AuNP capped with the mixed monolayer (obtained in one step) was employed for the selective detection of dihydrogen phosphate anion in dichloromethane [128]. The redox peaks of ferrocene moieties decreased in intensity and a new less positive pair of peaks appeared in the presence of this oxoanion. An excess of $H_2PO_4^-$ eliminated the typical ferrocene peaks and further increased the new ones. Apparently, this effect was caused by the formation of hydrogen bonds between each amide groups and negatively charged oxygen of the anions. Similar results, but with a smaller shift, were obtained in the detection of HSO_4^- [129].

The sensing property of MNP containing terminal ferrocenyl moieties can be enhanced if it is capped with a dendron-like compound, known as dendronized cluster. Using MNP as nucleus the capping thiolates can be transformed in several steps (generations) to finally achieve complex molecular species with an increasing number of ramifications. These new ramifications can improve the sensing capacity of this type of MNP. Astruc and coworkers used this idea [130] using two types of dendronized thiol ligands formed by AB_3 (Fig. 12) and AB_9 units, with nonasilylferrocenyl and amidoferrocenyl groups anchored to AuNP. Both dendronized clusters were titrated with $H_2PO_4^-$ and ATP and a shift in the redox peaks was observed. The highest shift was observed for AB_9 dendrimer showing a positive dendritic effect.

The electrochemical properties of ferrocene derivatives capping MNP have also been used in the fabrication of thin films. AuNP capped with mixed SAM of octanethiol and biferrocene thiolated derivative, AuNP-BFc, was used for the preparation of thin films by its electrodeposition on indium–tin oxide (ITO) electrodes [131]. A two-step one-electron oxidation of the biferrocene units of AuNP-BFc in CH_2Cl_2 electrolyte solution was induced, which produced the adhesive AuNP-BFc film on the ITO electrode surface. Analysis by STM and AFM of the modified surface showed that the interparticle distances were greater than expected and also the presence of solvent, anions and oxidized biferrocene units in the film.

Other complexes of iron capping MNP have been studied but in less extension. 2-Mercapto- and 4-mercaptopyridine (2-MPy and 4MPy, respectively) were set to react with $[Fe(CN)_5(H_2O)]^{3-}$ and S-coordinated $[Fe(CN)_5(2MPy)]^{3-}$ and N-coordinated $[Fe(CN)_5(4MPy)]^{3-}$ complexes were obtained [132]. Each of these two iron(III) complexes was then attached to citrate protected AuNP. AuNP capped with $[Fe(CN)_5(2MPy)]^{3-}$ dissociated the 2MPy ligand and an aggregation of the nanoparticles was observed. On the contrary, $[Fe(CN)_5(4MPy)]^{3-}$ generated very stable AuNP. Evidently, the symmetric association of 4MPy to AuNP guaranteed the formation of a SAM of the iron complex positively charged on the AuNP that repelled the neighboring nanoparticles.

Ruthenium complexes with bpy ligand are well known for their fluorescent properties and for that same reason have been used to cap MNP. Fluorescence of ruthenium complexes normally quench when associated with MNP. For example, the electrostatic interactions between tris(bipyridyl)ruthenium(II) and anionic *N*-(2-mercaptopropionyl)glycine self-assembled on AuNP produced the quenching effect [133]. As expected, this electrostatic quenching is sensitive to pH and also to the presence of electrolytes in aqueous solution. The quenching effect was also used, but in the opposite sense, to determine the attachment of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ to the surface of citrate protected AuNP and AgNP. A quenching effect proportional to the concentration of these colloids was observed [134].

A possible mechanism responsible of the quenching of $Ru(bpy)_3{}^{2+}$ associated with AuNP has been proposed [135]. A $Ru(bpy)_3{}^{2+}$ thiol derivative was self-assembled (through a spacer of seven methylene units) to AuNP capped with monothiol derivative of triethylene glycol by an exchange reaction. The resulting mixed SAM was formed with different percentages of the chromophores. For AuNP containing the highest proportions of $Ru(bpy)_3{}^{2+}$ a charge transfer in the excited state was observed. The ET products, namely $Ru(bpy)_3{}^{3+}$ and $Ru(bpy)_3{}^{+}$, were found to be stable for several nanoseconds before recombination. No ET to the gold cluster was observed.

$[Ru(bpy)_3]^{2+}$ associated with AuNP can cause a shift in the maximum of the SPR band. For example, the association of $Ru(bpy)_3{}^{2+}$ to AuNP ($d = 19$ nm) motivated an 8-fold increase in the color-change rate when the temperature was increased from 24.0 to 51.0 °C. On the contrary, for AuNP ($d = 48$ nm), after capped with the same complex, a 3-fold decrease in the color-change rate was observed for the same temperature variation [136].

The effect on the electrochemical and spectroscopic properties of ferrocenyl or biferrocenyl-functionalized terpyridyloctanethiolate SAM on AuNP upon the coordination of ruthenium(II) to tpy were studied [137]. Electrochemical shifts upon coordination of ruthenium(II) indicated an interaction with the iron centers. A similarly modified AuNP, but only capped with 2,2′:6′,2″-terpyridyloctanethiol (without Fc units), was used to coordinate $Ru(tpy)^{3+}$ and as a building block for the creation of new types of composites [138]. For this, AuNP capped with a mixed SAM of $[Ru(tpy)(terpyridyloctanethiol)]^{3+}$, with the thiol moiety attached to the Au surface, and 1-(10-mercaptodecyl)pyrrole was electropolymerized on a glass carbon electrode creating a film of a conductive poly(metal nanocomposite).

MNP have also been capped with organoruthenium compounds [139]. For this, AuNP capped with mercaptopropanoic acid were set to interact with $(Ru_3(CO)_{12})$ clusters. An insertion of carboxylate groups into the Ru clusters resulted in the fragmentation and formation of a shell of Ru dicarbonyl carboxylate oligomers that remained attached to AuNP through the carboxylic groups of self-assembled mercaptopropanoate.

Self-assembled metal complexes have served as junctions in the functionalization process of MNP. For example, a cobalt complex has been used for attaching proteins to AuNP [140]. A NTA amino-derivative Co(II) complex was condensed (forming an amido group) to AuNP protected with thioctic acid. The two free coordination sites of Co(II) served to associate two histidine tags introduced by genetically engineering to horseradish peroxidase and ferredoxin-NADP$^+$ reductase. These immobilized proteins kept their enzymatic activity almost entirely. Analogues of the enzymes without the histidine tag could not be immobilized on the Co(II) complex capping AuNP.

Copper(II) pyridine complexes have also been used as junctions when capping AuNP and gold disk electrode. A gold electrode modified with pyridine-terminated thiol derivative coordinated copper(II) ion and then AuNP capped with a mixed SAM of octanethiolate and pyridine-terminated thiol derivative were associated. Copper(II) served as coordinating linker. The coordination process of AuNP was done LbL and reversibly controlled by additions of EDTA. Zn(II), Mn(II) and Ni(II) were also used but a lower coverage and reproducibility were achieved. This multilayer system, in the presence of hydrophobic electrolyte anions (PF_6^-, ClO_4^-, BF_4^-, etc.), showed an enhanced ET kinetics and an increased effective capacitance, which were related to the presence of peripheral (and internal) metal ion centers [141].

Gold nanoparticles have been stabilized with a zinc(II) phthalocyanine containing a C_{11} mercaptoalkyl tether photosensitizer. This type of system was able to generate singlet oxygen with enhanced quantum yields when compared to the free phthalocyanine. Other zinc(II) macrocycles supported on AuNP have been used for sensing anions [142]. In this sense, a disulfide-functionalized zinc(II) porphyrin self-assembled on AuNP was observed to associate anions such as $H_2PO_4^-$ and Cl^- with enhanced binding affinities compared to the free zinc(II) porphyrin [143].

[Ti(O–i-Pr)$_4$] has been associated with AuNP through terminal bisnaphthol moieties (Fig. 13). This system was studied in the benzaldehyde asymmetric alkylation catalysis with an almost quantitative yield (more than 92% of conversion and an enantiomeric excess superior to 80%) [144]. Different spacers were used (4–6 methylene units) to minimize the steric repulsions between the bulky [Ti(O–i-Pr)$_4$] units. The advantage of using this known catalyst on AuNP is that it is easier to recuperate and purify.

More recently, a chiral rhodium–diphosphine complex has been incorporated into self-assembled thiolate monolayer of AuNP and studied as hydrogenating catalyst of methyl α-acetamidocinnamate [145]. The self-assembled metal nanocatalyst showed a full conversion and a 93% ee yield, the same efficiency of free catalyst. Nevertheless, this type of metal nanocatalyst is easy to recover. The main characteristic of this system is based on the bulkiness of the phenyl moieties of phosphines, which are characterized by large Tolman angles. For that reason, long spacers should have favored the access of the substrate to the metal center. Furthermore, the use of a mixed base monolayer could also have assisted the access of the substrate. As concluded by the authors, only small MNP (with diameters less than 5 nm) should be used. Larger MNP allow an easy recovery of the catalyst but require the use of greater amounts of MNP, making the process more expensive.

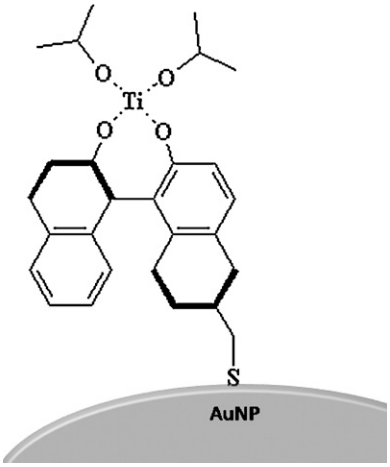

Fig. 13. AuNP capped with [Ti(O–i-Pr)$_4$]. Adapted from Ref. [144].

5.3. Lanthanide metal complexes

Europium complexes present excellent luminescent properties which have been studied when associated with AuNP. The luminescence of an Eu(III) complex of diethylenetriaminepentaacetic acid with two thiophenol moieties was slightly quenched when assembled to a AuNP, probably because of the proximity of the complex to the metal cluster [146]. In contrast, the interaction of AgNP protected with poly(vinylpyrrolidone) with an Eu(III) complex of dinicotinic acid resulted in an aggregation process and an enhancement of the luminescence properties within a limited concentration region [147].

Interesting results were obtained when a monothiolated bpy derivative served to cap AuNP and associate europium(III) or terbium(III) forming self-assembled $M(bpy)_2^{3+}$ complexes. These complexes exhibited luminescence (red-emitting for europium and green-emitting for terbium) with quantum yields greater than similar complexes formed from cryptand or calixarene derivatives with bipyridyl moieties. The luminescence of both types of AuNP decreases dramatically in the presence of Ca(II), Mg(II), Zn(II), Ni(II) and Cu(II) to serve as metal ion sensors [148].

Gadolinium compounds have been widely studied to improve the sensitivity of magnetic resonance imaging (MRI), a powerful medical imaging technique. 1,2-Mercaptoamine was condensed to two of the five carboxylic groups of diethylenetriaminepentaacetic acid. The resulting chelating ligand was associated with AuNP through the two thiol groups and to a Gd(III) metal ion by the other donor groups. Each of the resulting capped AuNP contained as average about 150 gadolinium complexes. The nanoparticles exhibited a high relaxivity ($585\,\text{mM}^{-1}$) as compared to the non-associated Gd(III) complex [149].

6. Outlook

Until now, nanocatalysis has mainly been centered on the study of new catalysts among unmodified metal nanoparticles [150]. The catalytic properties of metal complexes self-assembled on nanoparticles can harmonically combine with those of the nanosized metal forming efficient bimetallic catalysts. The combination of the catalytic properties of metal complexes with those of MNP [151] is a promising alternative, especially in enantioselective reactions [144,145].

The immobilization of metalloproteins is of practical importance. This type of biomolecule is extremely susceptible to any external factor. For that reason, when metalloproteins are chemically immobilized on any kind of support their conformation can be significantly affected, that is, they can denature. When the immobilized metalloproteins are enzymes, which have valuable industrial and medical applications, the catalytic activity decreases [36]. Even when the immobilization of an enzyme is physical in nature and takes place on a charged surface, there is a high probability that the enzymatic activity will be affected due to alterations in the conformation of the enzyme as a consequence of electrostatic interactions [152].

The simplest (and most used) way to immobilize a metalloprotein on a metal surface consists to first form a SAM with a mercaptocarboxylic acid and then conjugate the biomolecule by a condensation reaction through the amine groups of the latter [153].

Self-assembled metal complexes have served to immobilize different types of biomolecules, especially metalloproteins. For example, capped AuNP containing Co(NTA) termini served to immobilize horseradish peroxidase and ferredoxin-NADP$^+$ [140]. Ni(NTA) associated with gold surfaces has been successfully used to immobilize histidine tagged proteins [154,155].

As mentioned in Section 3.4 for lactoferrin [33], metal complexes could serve to supramolecularly immobilize metalloproteins without affecting their conformation. Metal nanoparticles with associated enzymes can serve as biosensors and detectors [156].

Probably the most promising materials are those named “hybrids” containing both inorganic and organic compounds, especially polymers. Molecular conducting polymers are receiving great attention. Recently, several types of inorganic conducting polymers have been synthesized and found different applications (sensors, light-emitting devices, solar cells, nanolithography, photonic crystal, catalysis, etc.) [157]. Among this type of polymers, a copper(I) coordinating polymer based on isonicotinic acid as ligand can be mentioned [158].

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