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PAPER

Synthetic strategies for the surface functionalisation of gold nanoparticles with metals and metal clusters

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The reaction of the new ditopic thiol-phosphine compound $HS(CH_2)_{11}OOCC_6H_4PPh_2$ (**L**) with an excess of dodecanethiol-protected gold nanoparticles gave the asymmetric gold complex $[CH_3(CH_2)_{11}SAuPPh_2C_6H_4COO(CH_2)_{11}SH]$ (**4**), but no phosphine-protected gold nanoparticles were formed. However, by blocking the phosphine function in **L** with metal fragments, we have been able to produce gold nanoparticles functionalised with AuCl- and cluster $[Fe_2(CO)_7Au]$ units on the surface by the method of ligand-place exchange reaction.

Introduction

The functionalisation of gold nanoparticles with metal complexes on the outermost surface is an area of increasing interest due the potential use of these materials in catalysis,[1] chemical sensors[2] or medicine[3] among others. The advantage of these nanoparticles resides in the possibility of combining their stability with the wealth of reactivity offered by metal species. Gold nanoparticles functionalised by thiol-tethered transition metal moieties of Ru, Ti, Cu, Rh, Fe, Co, Eu and Tb have been described along with their properties in some cases.[4] Although no systematic strategy to access these nanoparticles is known, very recently a dithiocarbamated-based methodology has facilitated the formation of gold nanoparticles containing ruthenium[5] or nickel[6] on the surface.

The aim of the present paper has been to explore the possibility of establishing a general method for the synthesis of functionalised gold nanoparticles having metal fragments at the periphery. Although we first focused our attention on the formation of gold nanoparticles peripherally functionalised with free phosphine, the impossibility of obtaining such kind of derivatives prompted us to investigate new strategies and as a result we describe here the first gold nanoparticles displaying an heterometallic cluster on the surface.

Results and discussion

The formation of the free-phosphine functionalised gold nanoparticles required the previous synthesis of a molecule containing a terminal thiol function and a phosphine ligand at the opposite site of the chain. $HS(CH_2)_{11}OOCC_6H_4PPh_2$ (**L**) was chosen for this purpose since the aryl protons could provide additional spectroscopic information.

Synthesis of $HS(CH_2)_{11}OOCC_6H_4PPh_2$ (L)

L was obtained according to Scheme 1. The first step involved the oxidation of the commercially available alkanethiol $HS(CH_2)_{11}OH$ (**1**) with iodine in methanol, to give the corresponding disulphur compound **2**. Next, this product was reacted with $Ph_2PC_6H_4COOH$ in the presence of DCC and DMAP in CH_2Cl_2 at room temperature giving the di-ester **3**. Finally, reduction with PEt_3 in THF/H_2O (9 : 1) allowed us to isolate the target phosphinethiol compound **L**. The global yield was about 60.0%. This reagent was characterized by elemental analysis, ^1H, ^{13}C and ^{31}P NMR, and MALDI-TOF-MS spectrometry.

Reaction of gold nanoparticles with L

With **L** in our hands, we decided to carry out the ligand-exchange reaction with dodecanethiol-protected gold nanoparticles in an attempt to promote the exchange of dodecanethiol units for **L**. However we were fully aware that this reaction could also proceed through the phosphine group of **L**. In fact, although thiolate for thiolate ligands replacement are the ligand-exchange reactions more widely studied,[7] phosphine for thiolate ligands replacements are well documented in the literature.[8] Consequently, the proposed reaction could illustrate the behaviour of the alkanethiol-protected gold nanoparticles in front of the two potential active groups, thiol and phosphine.

The starting dodecanethiol-protected gold nanoparticles were obtained by using the protocol described by Brust.[9] A sample of these nanoparticles was dissolved in CH_2Cl_2 and reacted with **L** in a 1 : 0.3 molar ratio at room temperature. We specifically chose this molar ratio in order to avoid that excess of phosphine could interchange with the resulting nanoparticles and mask the ^{31}P NMR spectrum with broad bands. After 48 h of reaction,

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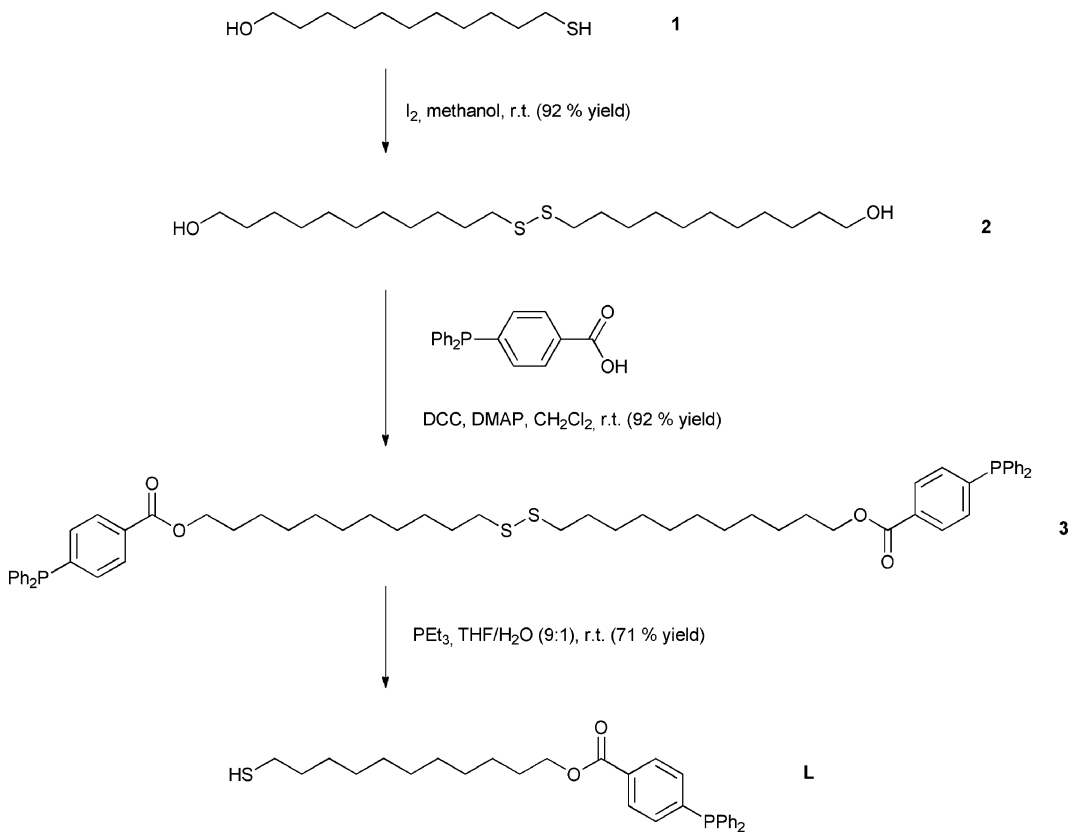


Scheme 1 Synthesis of **L**.

the ^{31}P NMR spectrum of the solution showed that the peak at −5.0 ppm due the PPh_2- group was not present and instead, a new signal appeared at 39 ppm, along with another at 29 ppm which was attributed to **L** oxide. The lack of the peak at −5.0 ppm unambiguously revealed that **L** had reacted with gold nanoparticles *via* phosphine. The key point was to know the nature of the species responsible for the peak at 39.0 ppm. Taking into account the paper by Foos,[10] in which the asymmetric complex $[CH_3(CH_2)_5SAuPPh_3]$ was reported to show a peak at 38 ppm, it was thought that our unknown compound could be the similar species $[CH_3(CH_2)_{11}SAuPPh_2C_6H_4COO(CH_2)_{11}SH]$ (**4**) (Scheme 2). To confirm this assumption, in a separate experiment we synthesized **4** by reaction of [AuCl(tht)][11] (tht = tetrahydrothiophene) with **L**, followed by treatment with dodecanethiol in presence of NEt_3. The ^{31}P NMR spectrum revealed the rapid appearance of a unique resonance at 39 ppm, thus confirming that reaction of the nanoparticles with **L** follows the previously proposed scheme in which rapid formation of an asymmetric S–Au–P compound takes place.

In the literature dealing with thiolate for phosphine ligand-exchange processes it has been proposed proposed that after formation of the asymmetric gold complexes, a fraction of phosphine ligands was incorporated on the surface of the gold nanoparticle.[10,12] In order to test the incorporation of **L** onto our gold nanoparticles, these were carefully washed, recrystallised and analyzed by ^1H and ^{31}P NMR spectroscopy. Contrarily to that reported, no signals in the ^{31}P NMR spectrum were detected. The region at about 50–65 ppm, in which the resonances of ^{31}P attached to the gold nanoparticles are expected,[13] was carefully examined and no traces of bands were present nor at room temperature neither at low temperature. In addition, in the ^1H NMR spectrum of this solution no peaks appeared in the region of 7.0–8.0 ppm (where the aryl protons of **L** are present) dismissing the attachment of **L** on the surface of the nanoparticle. These results permit therefore to establish that the reaction of **L** with gold nanoparticles causes the release of gold atoms from the nanoparticle in the form of the asymmetric gold thiolate/phosphine compound as already proposed, but attachment of the phosphine ligand onto the surface of the nanoparticle does not take place. A direct consequence of this process is that the new gold nanoparticles should be smaller than their parents. To check this point, both types of nanoparticles were analyzed by high-resolution transmission electron microscopy (HRTEM) (Fig. 1a and 1b).

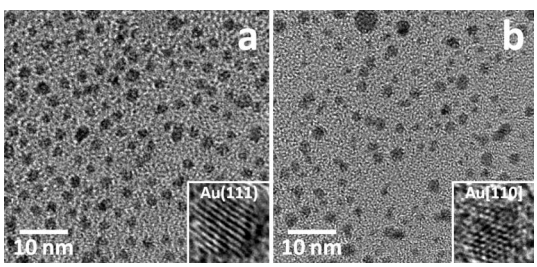
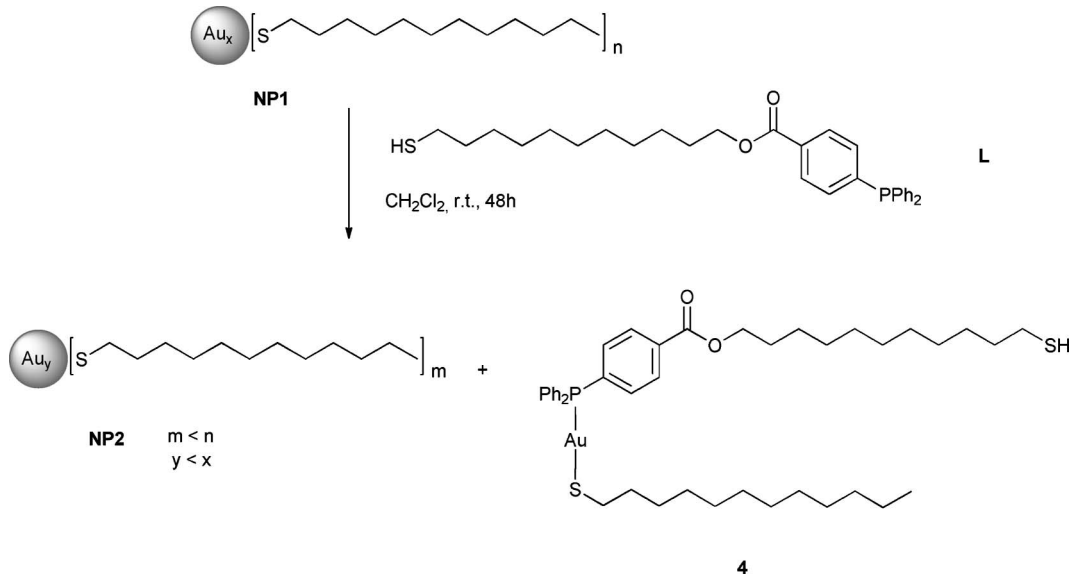


Fig. 1 (a) HRTEM of the parent gold nanoparticles. (b) nanoparticles after reaction with **L**.



Scheme 2 Reaction of gold nanoparticles with **L**.

In the first case, the starting dodecanethiol-protected Au nanoparticles (NP1) were well-dispersed and reasonably homogeneous in size (~2.4 nm), whereas the new Au particles (NP2) exhibited an average size of about 1.8 nm, and appeared to be much less homogeneous. In addition to smaller particles, a few larger nanoparticles were also present due to aggregation phenomena. In all cases, lattice spacing (see insets) confirmed the nature of gold nanoparticles. Fig. 2 shows core-size distribution histograms for both samples.

The final confirmation of the lack of compatibility between the alkanethiol-protected gold nanoparticles and the phosphine-thiol **L** in solution arises from the complete degradation of the gold nanoparticles after reaction with excess of **L** (1 : 1.5 molar ratio). Consequently, our attempts to prepare phosphine functionalized-alkanethiols protected gold nanoparticles were not successful and a new synthetic strategy for such species was needed.

New synthetic strategies

Our last results suggested that the phosphine group in **L** should be blocked to prevent reaction with gold nanoparticles. With this in mind, we made **L** to react with AuCl(tht) and the new metal complex ClAuPPh$_2$C$_6$H$_4$COO(CH$_2$)$_{11}$SH (**5**) was spectroscopically characterized, showing only one resonance at 33.0 ppm in the ^{31}P NMR spectrum. Then, **5** was reacted with a sample of hexanethiol-protected gold nanoparticles (formed by the Brust's method) which was chosen in order to promote facile thiol exchange ligands reaction. After 24 h in dichloromethane, new gold nanoparticles (NP3) were obtained and recrystallized in a mixture of CH$_2$Cl$_2$ and hexane and purified by gel permeation chromatography using thf as eluent. By integrating the methyl group signal of the hexanethiol and the two α aromatic protons of **L** in the ^{1}H NMR it was deduced that the hexane-thiol/**5** ligand ratio on the periphery of the nanoparticle was about 2 : 1. Furthermore,

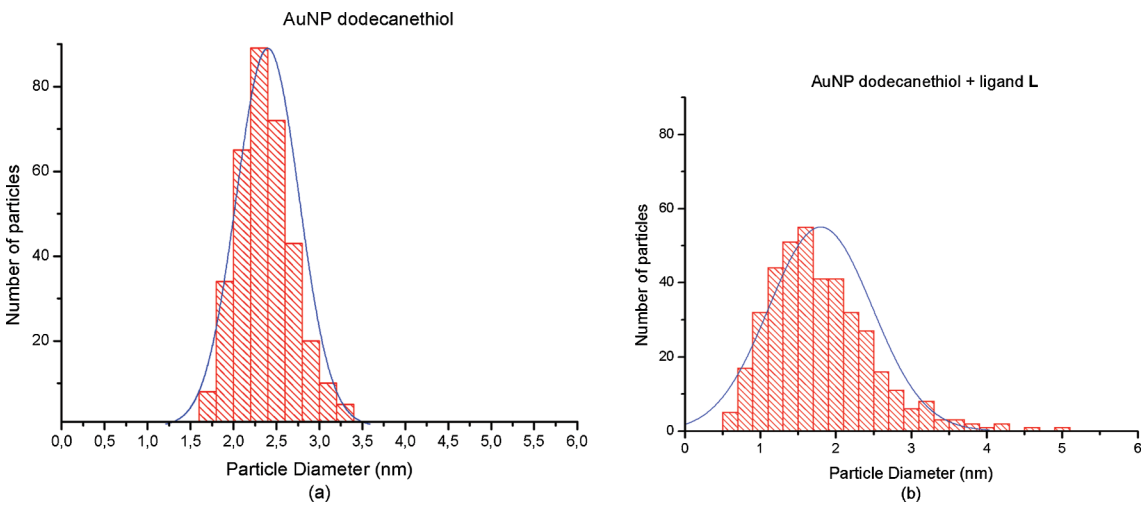


Fig. 2 Size distribution histogram of gold nanoparticles before reaction with **L** (NP1) (a) and after reaction (NP2) (b).

two broad triplets assigned to the -CH_2S group of both ligands could be observed at 2.66 and 3.08 ppm, in agreement with the proposed structure for NP3. The next step for the synthesis of gold nanoparticles functionalised with transition metals was to treat the bilayer gold nanoparticles with the binuclear iron cluster $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$[19] in the presence of $TlBF_4$ salt as chloride abstractor, in thf. The purpose of this reaction was to displace the chloride by the iron anion to form the expected trinuclear Fe_2Au cluster. However, we obtained a very insoluble black residue resulting from the aggregation of the gold nanoparticles. Consequently, a new strategy was attempted, consisting in the partial replacement of hexanethiolate ligands of preformed gold-hexanethiol nanoparticles for the new cluster-functionalised thiolate **6** which previous synthesis was made according to Scheme 3.

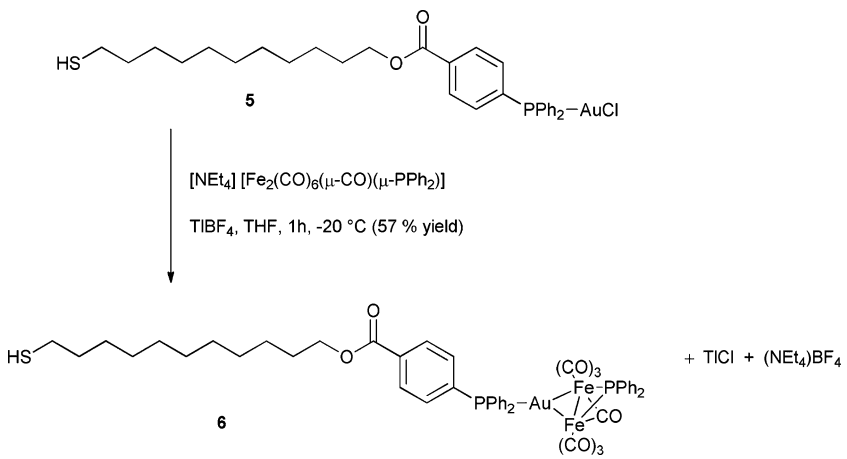
The two doublets at 52.0 and 130.5 ppm (^3J(P–P) = 25.1 Hz) in the ^{31}P NMR spectrum of **6** in thf are relevant for monitoring the formation of the gold nanoparticles. The reaction of hexanethiol-gold nanoparticles and **6** in a 1 : 0.3 molar ratio was performed in thf at room temperature for 15 h. After this period, the new nanoparticles NP4 were precipitated by adding hexane and purified by gel permeation chromatography (Scheme 4). The most interesting spectroscopic feature is the shifting of the two doublets of the cluster to 57.1 and 117. 5 ppm (^3J(P–P) = 22.9 Hz) indicating that the reaction proceeded. The ^{1}H NMR spectrum was consistent with the presence of two different layers and the thiol-hexane : **6** ratio of 2.7 : 1.0 was obtained by integrating the methyl protons of hexanethiol and the α-aromatic protons of **6**. The presence of the trinuclear Fe_2Au cluster was also corroborated by the IR spectrum, for which the pattern in the carbonyl region was almost identical to that exhibited by the cluster $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(AuPPh_3)]$.[14]

It is interesting to note that the same reaction carried out in a molar ratio higher than 1 : 0.3 (gold-hexanethiol : **6**) affords much less soluble gold nanoparticles due the high polarity of the cluster-functionalised thiolate. For the same reason attempts to prepare directly the mixed thiolate gold nanoparticles were discarded.

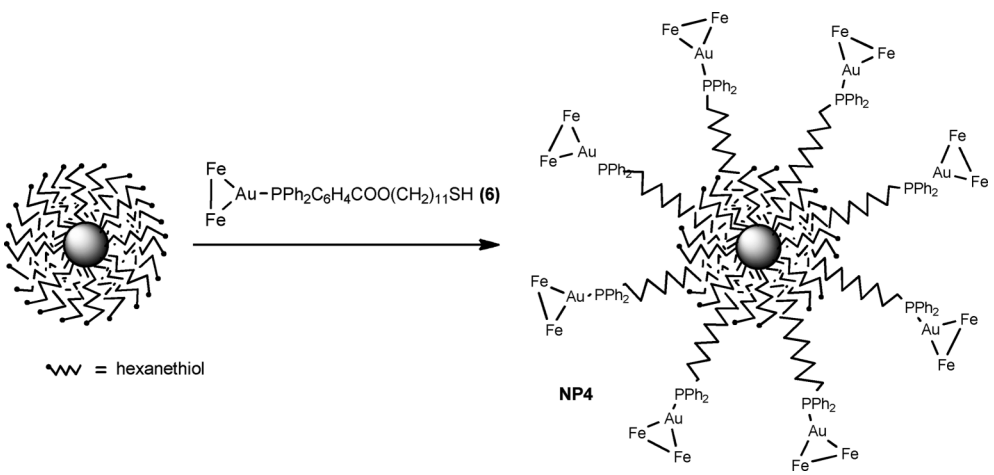
The UV-vis spectrum of NP4 shows a continuous absorption, which gradually disappears at higher wavelengths, and a weak surface plasmon (SP) resonance at about 499 nm that confirms that the diameter of the gold nanoparticles is larger than 2 nm.[15]

Nanoparticles NP4 were analysed by high-resolution transmission electron microscopy (HRTEM) and appeared well-dispersed (Fig. 3). Fig. 4 shows the core-size distribution histogram.

Their average diameter is 2.89 nm so that the approximate number of Au atoms in the core is 742.[16] Taking into account the



Scheme 3 Synthesis of **6**.



Scheme 4 Synthesis of NP4.

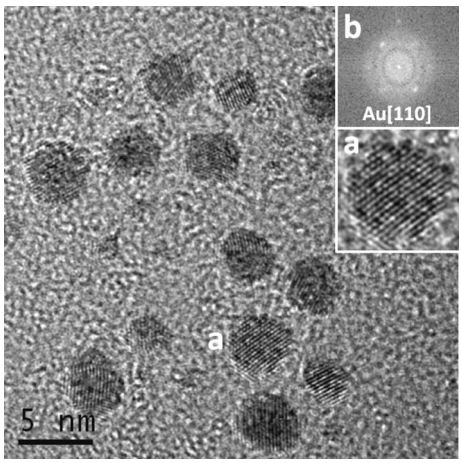


Fig. 3 HRTEM of the cluster-functionalised gold nanoparticles NP4.

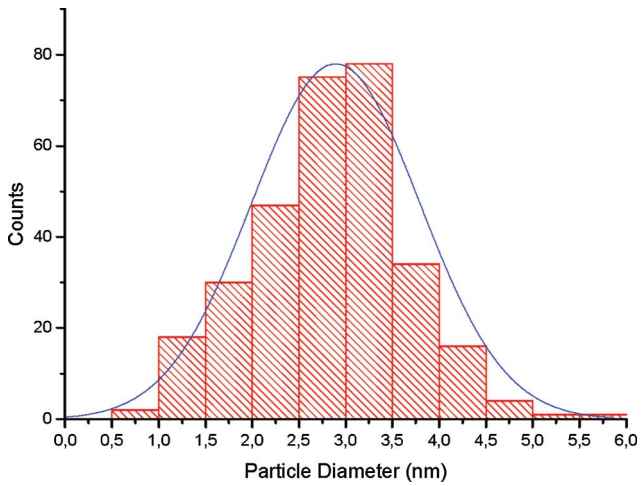


Fig. 4 Size distribution histogram of NP4.

elemental analysis of C, H and S and the thiolate hexane/**6** ratio, obtained by integrating the methyl protons of hexanethiol and the α-aromatic protons of **6** it is deduced that the total number of ligands is 242, including 65 ligands of **6**. Similar results are obtained by applying the size core model.[17] To the best of our knowledge this is the first heterometallic cluster grafted on the periphery of gold nanoparticles. It should be noted that a similar species containing the homometallic iron cluster $[Fe(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)]_4$ has been recently reported by Astruc.[18]

Conclusions

Free phosphine derivatives and alkanethiolate-protected gold nanoparticles are not compatible in solution. However, thiol molecules containing the phosphine function previously blocked with metal units such as AuCl or the metal cluster fragment $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(AuPPh_2)]$ have shown to be suitable for the surface functionalisation of gold nanoparticle through ligand-place exchange reactions. We believe that this strategy can be extended to other metal fragments to give new gold nanoparticles functionalised with a plethora of metals and/or transition metal clusters on the periphery.

Experimental

Materials. Hydrogen tetrachloroaurate (III) (Johnson Matthey), sodium borohydride (Sigma–Aldrich), tetraoctylammonium bromide (TOAB; Aldrich), 1-dodecanethiol, 98 +% (Aldrich), 1-hexanethiol, 95% (Aldrich), 11-mercapto-1-undecanol, 97% (Aldrich), iodine (Panreac), sodium bisulfite (Aldrich), 4-(diphenylphosphino)-benzoic acid, 97% (Aldrich), *N*,*N*′-dicyclohexylcarbodiimide (DCC, Fluka), 4-dimethylaminopyridine (DMAP, Aldrich), triethylphosphine, 99% (Aldrich), triethylamine (Aldrich), $MgSO_4$ anhydrous (Panreac) were all used as received without further purification. The materials [AuCl(tht)],[11] $TlBF_4$ and $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$[19] were synthesized as reported in the literature. Sephadex LH-20 (GE Healthcare Bio-Sciences AB) was swollen in suitable solvents and loaded into a glass column. Chromatographic purifications were performed by flash chromatography using silica gel (Fluka 0.063–0.2 mm). All solvents were distilled from appropriate drying agents. Deionised water was obtained from Millipore Milli-Q water purification system. All manipulations were performed under purified nitrogen using standard Schlenk techniques.

Instrumentation. ^1H, $^{13}C\{^1H\}$ and ^{31}P NMR spectra were obtained on Bruker DXR 250 and Varian Mercury 400 instruments. Bidimensional NMR spectra (HSQC ^1H-^{13}C) were recorded on a Varian Mercury 400 apparatus. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for ^1H and ^{13}C, H_3PO_4 for ^{31}P), and coupling constants are given in Hz. MS MALDI-TOF spectra were recorded in a VOYAGER-DE-RP (Applied Biosystems) spectrometer. UV-visible samples were placed in quartz cuvettes (Suprasil, Hellma; path length of 1 cm) and analyzed using a spectrophotometer (Cary 100 SCAN, Varian). Infrared spectra were carried out in a spectrophotometer FT-IR NICOLET Impact 400 or on a NICOLET 520 FT-IR in the region between 4000 and 400 cm^{-1} and KBr has been used as dispersing medium. To designate the intensity of the bands of spectrum have used the following abbreviations: s, strong; m, medium; w, weak and vs, very strong. It is noteworthy that only IR bands which give us information about the structure of the compounds have been assigned. Elemental analyses were carried out on Thermo Finnigan-1108 instrument. High-resolution transmission electron microscopy (HRTEM) measurements were performed at 200 kV with a JEOL 2100 microscope (point-to-point resolution of 0.21 nm). Samples were prepared by placing a drop of toluene solution on a holey-carbon-coated Cu grid and allowing the solvent to evaporate in air.

Synthesis of ditopic ligand $HS(CH_2)_{11}OOCC_6H_4PPh_2$ (L). (0.165 g, 60.0%). This ligand was synthesized in three steps. *First step*: Synthesis of compound **2** (0.924 g, 92.2%). A methanol solution (80 mL) containing 11-mercapto-1-undecanol (1.002 g, 4.90 mmol) (**1**) was titrated by 1 M iodine methanol solution until the solution turned light yellow, and then the reaction was quenched with sodium bisulfite. The reaction mixture was evaporated to dryness under reduced pressure at room temperature and then the product, 11-hydroxyundecyldisulfide (**2**) was extracted in CH_2Cl_2 as a white solid. *Second step*: Synthesis of compound **3** (0.232 g, 91.8%). To a stirred solution of **2** (0.253 g, 0.62 mmol) in 40 mL CH_2Cl_2 was added 4-(diphenylphosphino)-benzoic acid (0.377 g,

1.23 mmol), DCC (0.277 g, 1.34 mmol) and DMAP (0.014 g, 0.11 mmol) successively. The resulting mixture was allowed to stir overnight at room temperature under nitrogen. When the reaction was finished, the white solid was removed by filtration, solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica using a mixed eluent (hexane:ethyl acetate, 10 : 1), obtaining **3** as a colourless to light-yellow oil. *Third step*: Synthesis of compound **L** (0.165 g, 71.0%). Compound **3** (0.232 g, 0.24 mmol) was dissolved in THF/H_2O (9 : 1, 20 mL) and (73.1 μL, 0.50 mmol) of triethylphosphine was added to it at room temperature.[20] The mixture was stirred for 30 min and the solvent was then removed under a vacuum. CH_2Cl_2 (20 mL) was added and washed with H_2O (3 × 10 mL). The compound was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ anhydrous. Removal of solvent followed by flash chromatography on silica using a mixed eluent (hexane:ethyl acetate, 4 : 1) yielded the final product **L**. Elemental analysis: Found: C, 73.0; H, 7.5%. Calc. for $C_{30}H_{37}O_2PS$: C, 73.1; H, 7.5%. NMR: δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.02–7.96 (2H, m, CH_{Ph}), 7.37–7.30 (12H, m, CH_{Ph}) 4.32 (2H, t, $^3J_{HH}$ = 8.0, CH_2COOAr), 2.51 (2H, pq, $J \approx$ 8.0, $HSCH_2$), 1.81–1.25 (18H, m, CH_2). δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 166.4 (s, COOAr), 143.8 (d, $^1J_{CP}$ = 14.1 C_{Ph}–P), 136.2 (d, $^1J_{CP}$ = 10.0, C_{Ph}–P), 133.9 (d, $^2J_{CP}$ = 20.1, C_{Ph}), 133.2 (d, $^2J_{CP}$ = 19.1, C_{Ph}), 130.4 (s, C_{Ph}), 129.3 (d, $^3J_{CP}$ = 6.0, C_{Ph}), 129.1 (s, C_{Ph}), 128.7 (d, ^3J = 7.0, C_{Ph}), 65.2 (s, CH_2COOAr), 34.0 (s, CH_2), 29.5 (s, CH_2), 29.3 (s, CH_2), 29.1 (s, CH_2), 28.7 (s, CH_2), 28.4 (s, CH_2), 26.0 (s, CH_2), 24.6 (s, CH_2SH). δ_P (101.2 MHz; $CDCl_3$; H_3PO_4) −5.1 (s). MS (MALDI-TOF) (CH_2Cl_2): calc.: m/z = 493.23 [M + H]$^+$; found: m/z = 493.3 (100) [M + H]$^+$.

Synthesis of the compound $HS(CH_2)_{11}OOCC_6H_4PPh_2AuCl$ (5). (1.6 g, 91%). To a solution of **L** (1.2 g, 2.44 mmol) in 40 mL of CH_2Cl_2 with stirring at room temperature [AuCl(tht)][11] was added (0.764 g, 2.38 mmol). The stirring was maintained for 30 min. Thereafter, the solution was evaporated to dryness under reduced pressure obtaining a colorless to light-yellow oil that was washed with hexane to extract the tht liberated in the reaction. Elemental analysis: Found: C, 49.6; H, 5.1%. Calc. for $C_{30}H_{37}AuClO_2PS$: C, 49.7; H, 5.1%. IR: ν_{max}/cm^{-1} 3074 w (arC-H), 3052 w (CH_3), 2922 s and 2843 s (CH_2), 1717vs (C═O) and 1430 s (S–CH_2). NMR: δ_H (400 MHz; CD_2Cl_2; Me_4Si) 8.15–8.02 (2H, m, CH_{Ph}), 7.69–7.43 (12H, m, CH_{Ph}), 4.31 (2H, t, $^3J_{HH}$ = 8.0, CH_2COOAr), 2.50 (2H, s_b, $HSCH_2$), 1.82–1.18 (18H, m, CH_2). δ_C (100.6 MHz; CD_2Cl_2; Me_4Si) 165.6 (s, COOAr), 134.7 (d, $^2J_{CP}$ = 14.1, C_{Ph}), 134.4 (d, $^2J_{CP}$ = 14.1, C_{Ph}), 134.0 (s, C_{Ph}), 132.7 (s, C_{Ph}), 130.2 (d, $^3J_{CP}$ = 12.1, C_{Ph}), 129.8 (d, $^3J_{CP}$ = 12.1, C_{Ph}), 128.6 (d, $^1J_{CP}$ = 61.4, C_{Ph}–P), 66.0 (s, CH_2COOAr), 34.6 (s_b, CH_2), 29.9 (s, CH_2), 29.6 (s, CH_2), 29.2 (s, CH_2), 29.0 (s, CH_2), 28.8 (s, CH_2), 26.4 (s, CH_2), 25.0 (s_b, CH_2SH). δ_P (101.2 MHz; CD_2Cl_2; H_3PO_4) 33.6 (s).

Synthesis of the complex $CH_3(CH_2)_{11}SAuPPh_2C_6H_4COO(CH_2)_{11}SH$ (4). (0.0904 g, 0.12 mmol) of the compound **5** was dissolved in 20 mL of CH_2Cl_2. To this stirring solution was added (30 μL, 0.12 mmol) of dodecanethiol followed by (17 μL, 0.12 mmol) of Et_3N. The reaction was monitored by ^{31}P NMR and after 2 h of stirring, one only signal at 39 ppm was observed.

Synthesis of the compound $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Au(PPh_2C_6H_4COO(CH_2)_{11}SH)\}]$ (6). (0.291 g, 57%). The compounds $HS(CH_2)_{11}OOCC_6H_4PPh_2AuCl$ (0.314 g, 0.43 mmol), $TlBF_4$ (0.126 g, 0.43 mmol), and $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ (0.270 g, 0.43 mmol) were stirred in THF (50 mL) for 1 h at −20 °C. The solution obtained, after filtration, was evaporated to dryness under reduced pressure. Then the product was extracted in thf. Elemental analysis: Found: C, 49.75; H, 4.0%. Calc. for $C_{49}H_{47}AuFe_2O_9P_2S$: C, 49.8; H, 4.0%. IR: ν_{max}/cm^{-1} 3052 w (arC-H), 2956 w (CH_3), 2926 m and 2848 m (CH_2), 2061 m, 2043 m, 2013vs, 1974vs and 1774 m (CO), 1721 m (C═O) and 1430 m (S–CH_2). NMR: δ_H (400 MHz; THF-d_8; Me_4Si) 8.15–8.02 (2H, m, CH_{Ph}), 7.91–7.43 (12H, m, CH_{Ph}), 7.41–7.11 (10H, m, CH_{Ph}), 4.32 (2H, t, $^3J_{(HH)}$ = 8.0, CH_2COOAr), 2.46 (2H, *p*q, $J_=$ 8.0, $HSCH_2$), 1.78–1.13 (18H, m, CH_2). δ_P (101.2 MHz; THF-d_8; H_3PO_4) 130.5 (d, $^3J_{PP}$ = 25.1), 52.0 (d, $^3J_{PP}$ = 25.1).

Ligand-Exchange reaction of dodecanethiol-capped gold nanoparticles with ligand L (NP2). The gold nanoparticles stabilized with dodecanethiol were prepared using the method of Brust. A sample of these nanoparticles (0.100 g) was dissolved in 10 mL of CH_2Cl_2 and reacted with **L** in a 1 : 0.3 molar ratio at room temperature for 48 h. The reaction mixture was concentrated under a vacuum and by addition of hexane, gold nanoparticles were precipitated. The nanoparticles were washed with hexane, filtered and dried. UV-Vis: λ_{max} = 530 nm.

Ligand-Exchange reaction of hexanethiol-capped gold nanoparticles with ligand 5 (NP3). The gold nanoparticles stabilized with hexanethiol were prepared using the method of Brust. A sample of these nanoparticles (0.100 g) was dissolved in 10 mL of CH_2Cl_2 and reacted with **5** in a 1 : 0.3 molar ratio at room temperature for 24 h. The reaction mixture was concentrated under a vacuum and by addition of hexane, gold nanoparticles were precipitated. The nanoparticles were washed with hexane and then filtered and dried. Further purification was achieved by gel permeation chromatography (GPC) using thf as eluting solvent. IR: ν_{max}/cm^{-1} 3057 w (arC-H), 2948 w (CH_3), 2917 m and 2848 m (CH_2), 1717 m (C═O) and 1430 m (S–CH_2). NMR: δ_H (400 MHz; CD_2Cl_2; Me_4Si) 8.2–7.92 (2H, m, CH_{Ph}), 7.80–7.21 (12H, m, CH_{Ph}), 4.30 (2H, m, CH_2COOAr), 3.08 (0.14H*, t, $^3J_{HH}$ = 8.0, SCH_2), 2.66 (0.2H*, t, $^3J_{HH}$ = 8.0, SCH_2), 2.10–0.99 (27H*, m, CH_2), 0.96 (6H, m, CH_3). *The integrations were not the expected ones due to the environment of the nanoparticles. δ_P (101.2 MHz; CD_2Cl_2; H_3PO_4) 33.1 (s). UV-Vis: λ_{max} = 508 nm. HRTEM: The average diameter of NP3 = 2.51 nm

Ligand-Exchange reaction of hexanethiol-capped gold nanoparticles with ligand 6 (NP4). The gold nanoparticles stabilized with hexanethiol were prepared using the method of Brust. A sample of these nanoparticles (0.070 g) was dissolved in 10 mL thf and reacted with **6** in a 1 : 0.3 molar ratio at room temperature for 15 h. The reaction mixture was concentrated *in vacuo* and by addition of hexane, gold nanoparticles were precipitated. The nanoparticles were washed with hexane and then filtered and dried. Further purification was achieved by gel permeation chromatography (GPC) using THF as eluting solvent. Elemental analysis: Found: C, 20.66; H, 2.38; S, 3.08%. IR: ν_{max}/cm^{-1} 3048 w (arC-H), 2948 w (CH_3), 2913 m and 2843 m (CH_2), 2030 s, 1961 s and 1917 m (CO), 1717 m (C═O) and 1435 m (S–CH_2). NMR: δ_H (400 MHz; THF-d_8; Me_4Si) 8.24–7.98 (2H, m, CH_{Ph}), 7.96–6.79 (22H, m, CH_{Ph}), 4.32 (2H, m, CH_2COOAr), 3.08 (0.13H*, m, SCH_2), 2.68 (0.3H*, m, SCH_2), 1.61–0.98 (31H*, m, CH_2), 0.89 (9H, m, CH_3). *The

integrations were not the expected ones due to the environment of the nanoparticles. δ_P (101.2 MHz; THF-d_8; H_3PO_4) 117.5 (d, $^3J_{PP} = 22.9$), 57.1 (d, $^3J_{PP} = 22.9$). UV-Vis: $\lambda_{max} = 499$ nm.

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