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Post-synthetic functionalization and ligand exchange reactions in gold(1) phenylthiolate-based coordination polymers†

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Gold thiolate coordination polymers (CPs) are anisotropic materials with 1D or 2D networks exhibiting a large palette of photoluminescence properties. In this paper, we show that, from both lamellar acid and ester, $[Au(p-SPhCO_2X)]_n$ CPs (X = H, Me), it is possible to perform post-synthesis esterification or saponification reactions. Three new 2D phases with X = Na, K and Cs were isolated. In addition, ligand exchange reactions were carried out from 1D $[Au(p-SPh)]_n$ CP and 2D $[Au(p-SPhCO_2X)]_n$ CPs (X = H, Me) and the transformations from 1D to 2D structures and *vice versa* point out a mechanism of dissolution and recrystallization that is governed by the nature of the ligands and the presence of weak interactions. The obtained compounds exhibit solid state and RT photoemission characteristic of their structure.

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Introduction

Hybrid organic/inorganic materials offer the advantage of designing multifunctional compounds where each part brings its own properties.¹ The inorganic component can be a metal, a cluster or a nanoparticle with its own physical properties (magnetic, electric, optic, catalytic, etc.) and the organic part acts as a linker in the case of coordination polymers or protecting agent for nanoparticles and it can also exhibit some intrinsic properties (optic, conductivity) or chemical functionality (hydrophobicity, external reactive organic groups). The control of the external functionalization of hybrid nanoparticles or clusters is of tremendous importance for molecular recognition in the medical domain.² The addition of specific organic molecules or functions in coordination polymers can bring additional properties and preferential affinity for gas adsorption or generate a catalytic centre.³ There are two synthetic approaches to obtain new and complex functionalized hybrid materials: (i) by direct reaction to form the target compound and functionalize it at the same time, with the advantage being a one-step reaction but the drawback being the difficulty to

predict the structure of the resulting compound or the size of the nanoparticle; (ii) by ligand exchange reaction from a preformed material, where it is assumed that the structure of the starting compound is preserved but it requires a two-step pathway.⁴ Two mechanisms are proposed for ligand exchange reactions: (i) the associative mechanism or topotactic process, where the ligand exchange does not involve the rearrangement of the inorganic part, and (ii) the dissociative mechanism or the dissolution/recrystallization process which consists of the total or partial dissolution of the compound, followed by the coordination of the new incoming ligand, this process can either give an isostructural phase or a new one.⁵ Knowing the difficulty to control the size of nanoparticles, many reports use ligand exchange with preformed gold nanoparticles. In the case of gold thiolate clusters, $Au_n(SR)_m$, that are atomically well defined particles and for some of them structurally known, the ligand exchange offers the possibility to bring about a new external functionality.⁶ By determining their formula, it has been shown that ligand exchange reactions involved the same composition through an associative substitution mechanism.⁷ Partially exchanged ligand species have also been isolated for Au₁₀₂(SR)₄₄, Au₂₅(SR)₁₈, or Au₂₄Pd(SR)₁₈ clusters and confirm that the gold core remains the same.8 Nevertheless, depending on the incoming thiol molecule, some ligand exchange mechanisms can also be dissociative. This has been shown for $Au_{38}(SR)_{24}$ clusters that transform into $Au_{36}(SR')_{24}^{9}$ or Au25(SR)18 clusters that generate Au28(SR')20,10 and also Au₁₄₄(SR)₆₀ that change into Au₁₃₃(SR')₅₂.¹¹ In parallel to these two associative and dissociative exchange mechanisms occurring in gold thiolate clusters, we study here the post-functionalization and ligand



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Fig. 1 Representations of the structures of $[Au(p-SPhCO_2H)]_n$ (a), $[Au(p-SPhCO_2Me)]_n$ (b) and $[Au(SPh)]_n$ (c). Pink, Au(i); yellow, S; red, O; gray, C. Hydrogen atoms are omitted for clarity.

exchange reactions for their analogues: the gold thiolate coordination polymers (CPs), $[Au(SR)]_n$.¹² One article reports the dynamic ligand exchange processes occurring in gold thiolate colloidal species.¹³ Here, a series of crystalline solids of gold para-substituted phenylthiolate CPs are studied to evaluate the effect of the para-substituent on the structure and photoluminescence properties of CPs. Thus, the first part concerns the esterification and saponification of $[Au(p-SPhCO_2H)]_n$ and $[Au(p-SPhCO_2Me)]_n$ CPs, respectively. $[Au(p-SPhCO_2H)]_n$ (Fig. 1a) has been reported as a lamellar CP forming helical -Au-S-Au-S- chains with para-mercaptobenzoic acid in the interlamellar space interacting with each other through catemeric hydrogen bonds.¹⁴ This CP exhibits low emission centered at 665 nm at RT. $[Au(p-SPhCO_2Me)]_n$ (Fig. 1b) is also described as a lamellar compound, but in this case the gold-sulfur chains are in a zig-zag shape and there is neither interpenetration nor weak interactions between the linker molecules.¹⁵ This esterified CP shows bright emission at 645 nm at RT due, in part, to the presence of short aurophilic interactions. In the second part, ligand exchange between these two 2D CPs and the 1D [Au(SPh)], CP (Fig. 1c) is presented to probe the associative and/or dissociative mechanisms that are involved. The structure of $[Au(SPh)]_n$ is made of two interdigitated helical -Au-S-Au-S- chains and the CP displays moderate photoemission at RT centered at 684 nm.16 The different reactions carried out are presented in Scheme 1.



Scheme 1 Pathways of the different esterification, saponification and ligand exchange reactions carried out. The numbers correspond to the obtained compounds after reactions.

Experimental

Chemicals

Tetrachloroauric acid trihydrate (HAuCl₄·3H₂O, \geq 49% Au basis) and methanol (Chromasolv[®]) were purchased from Sigma-Aldrich Company. 4-Mercaptobenzoic acid (>95%) was purchased from TCI. The glassware used in the synthesis were cleaned with aqua regia (aqua regia is a very corrosive product and should be handled with extreme care), then rinsed with copious amounts of deionised water and dried overnight prior to use. All reactions were carried out under atmospheric conditions.

The syntheses of the CPs $[Au(p-SPhCO_2H)]_n$ ¹⁴ $[Au(p-SPhCO_2Me)]_n$ ¹⁵ and $[Au(SPh)]_n$ ¹⁶ were performed following the procedures reported previously. The ligand *p*-HSPhCO₂Me has been obtained *via* the esterification of *p*-mercaptobenzoic acid.¹⁷

Synthetic procedures

Esterification of $[Au(p-SPhCO_2H)]_n$ (1). The insoluble powder of $[Au(p-SPhCO_2H)]_n$ (50 mg) was stirred in an acidic mixture of 60 ml of MeOH with few drops of H_2SO_4 under reflux (set temperature: 120 °C) for 2 days (1') and 7 days (1). The resulting white powder was thoroughly washed with MeOH and dried under vacuum.

Saponifications of $[Au(p-SPhCO_2Me)]_n$ (2, 3 and 4). The insoluble powder of $[Au(p-SPhCO_2Me)]_n$ (50 mg) was stirred in an aqueous solution of NaOH (60 ml, 145 equiv.) at 80 °C for one week. The resulting white powder, compound 2, was thoroughly washed with water and dried under vacuum. The same reactions were carried out with KOH aqueous solution (60 ml, 145 equiv.) under reflux for 72 h and CsOH aqueous solution (60 ml, 145 equiv.) under reflux for 72 h. The resulting white powders, compounds 3 and 4, respectively, are thoroughly washed with water and dried under vacuum.

Exchange reactions

Compound 5. In a 20 ml vial, 40 mg of $[Au(p-SPhCO_2Me)]_n$ (0.110 mmol, 1 equiv.) was mixed with 3 ml of HSPh (29 mmol, 263 equiv.). The vial is closed and heated at 120 °C for 6 h. Published on 29 September 2020. Downloaded by University of New Mexico on 5/15/2021 6:51:09 PM.

The solid was then filtered, washed with acetone and dried under an ambient atmosphere.

Compound 6. In a 20 ml vial, 28 mg of $[Au(SPh)]_n$ (0.091 mmol, 1 equiv.) was mixed with 46 mg of *p*-HSPhCO₂Me (0.275 mmol, 3 equiv.) in 10 ml of water. The vial was closed and heated at 120 °C for 20 h. The solid was then filtered, washed first with water and then with acetone, and dried under an ambient atmosphere.

Compound 7. In a 20 ml vial, 44 mg of $[Au(p-SPhCO_2Me)]_n$ (0.120 mmol, 1 equiv.) was mixed with 126 mg of p-HSPhCO₂H (0.817 mmol, 7 equiv.) in 10 ml of water. The vial was closed and heated at 100 °C for 20 h. The solid was then filtered, washed with acetone and dried under an ambient atmosphere.

Compound 8. In a 20 ml vial, 31 mg of $[Au(SPh)]_n$ (0.101 mmol, 1 equiv.) was mixed with 90 mg of *p*-HSPhCO₂H (0.584 mmol, 6 equiv.) in 10 ml of water. The vial was closed and heated at 120 °C for 20 h. The solid was then filtered, washed first with water and then with acetone, and dried under an ambient atmosphere.

Materials and methods

Powder X-ray diffraction (PXRD) experiments were carried out on a Bruker D8 Advance A25 diffractometer using Cu K α radiation equipped with a 1-dimensional position-sensitive detector (Bruker LynxEye). XR diffraction patterns were recorded between 4° and 90° (2 θ) with 0.02° steps and 0.5 s per step (28 min for the scan). The divergence slit was fixed to 0.2° and the detector aperture to 189 channels (2.9°).

The infrared spectra were obtained from a Bruker Vector 22 FT-IR spectrometer with KBr pellets at room temperature and registered from 4000 to 400 cm⁻¹.

Thermo-gravimetric analyses (TGA) were performed with a TGA/DSC 1 STARe System from Mettler Toledo. Around 2 mg of the sample was heated at a rate of 10 $^{\circ}$ C min⁻¹, in a 70 µl alumina crucible, under an air atmosphere (20 ml min⁻¹).

Shining droplets of bulk gold were observed at the end of the experiments.

SEM images were obtained with an FEI Quanta 250 FEG scanning electron microscope in the microscopy centre of Lyon 1 University. Samples were mounted on a stainless pad and sputtered with carbon to prevent charging during observation.

The photoemission studies were performed on homemade apparatus. The sample was illuminated using an EQ99X laser driven light source filtered using a Jobin Yvon Gemini 180 monochromator. The exit slit from the monochromator was then reimaged on the sample using two 100 m focal length, 2 inch diameter MgF₂ lenses. The whole apparatus was calibrated by means of a Newport 918D Low power calibrated photodiode sensor over the range of 190–1000 nm. The resolution of the system is 4 nm. The emitted light from the sample was collected using an optical fiber connected to a Jobin-Yvon Triax 320 monochromator equipped with a cooled CCD detector. At the entrance of the monochromator different long pass filters can be chosen in order to eliminate the excitation light. The resolution of the detection system is 2 nm.

Results and discussion

Esterification reaction

In order to study the post-functionalization of gold(i) thiophenolatebased compounds, the esterification of the 2D layered $[Au(p-SPhCO_2H)]_n$ coordination polymer was tested first. Its interlayer distance of 1.48 nm corresponds to two noninterpenetrated *p*-SPhCO₂H molecules interacting through catemeric hydrogen bonds (Fig. 1a).¹⁴ To esterify the carboxylic acid groups, the insoluble $[Au(p-SPhCO_2H)]_n$ solid was stirred in a solution of methanol under reflux in the presence of sulphuric acid acting as a catalyst. After two days of reaction, compound 1' was isolated and new peaks on the PXRD pattern appear with predominant 00*l* reflections characteristic of a lamellar compound (Fig. 2a). The first peak was localized at 4.75° (2 θ) which corresponds to an interlamellar distance of



Fig. 2 (a) Powder X-ray diffraction patterns of the starting $[Au(p-SPhCO_2H)]_n$ solid (black), compounds **1**' (orange) and **1** (red) furnished from the esterification of $[Au(p-SPhCO_2H)]_n$ after 2 and 7 days of stirring, respectively. The asterisks correspond to a second lamellar phase of $[Au(p-SPhCO_2Me)]_n$. The diagrams are compared to the simulated pattern of $[Au(p-SPhCO_2Me)]_n$ (grey). (b) PXRD patterns of $[Au(p-SPhCO_2Na)]_n$ (**2**, blue), $[Au(p-SPhCO_2K)]_n$ (**3**, purple) and $[Au(p-SPhCO_2Cs)]_n$ (**4**, pink) compounds furnished from the saponification of the $[Au(p-SPhCO_2Me)]_n$ solid (black).

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1.86 nm; this increase of 0.38 nm is in good accordance with the replacement of hydrogen atoms by methyl groups. In addition the new peaks match the reflections of the simulated structure of $[Au(p-SPhCO_2Me)]_n$ (Fig. 2a).¹⁵ From the PXRD diagram of 1', it is clear that after 2 days the esterification is not complete and the major product remains $[Au(p-SPhCO_2H)]_p$. Therefore, the reaction time has been extended to 7 days. In that case, $[Au(p-SPhCO_2Me)]_n$ becomes the major product, but still approximately 15% (as deduced from the PXRD pattern) of $[Au(p-SPhCO_2H)]_n$ is present (Fig. 2a). Besides, small peaks corresponding to another lamellar compound with a first reflection at 4.98° (2 θ) start to appear (<5%), which could correspond to another $[Au(p-SPhCO_2Me)]_n$ phase (Fig. 2a). The mixture of the two acidic and esterified phases in 1 was also confirmed by FT-IR spectroscopy (Fig. S1 and S2, ESI⁺). Indeed, on the spectrum of 1, both the antisymmetric vibrations of the carbonyl for the ester and the carboxylic acid groups are present at 1720 and 1690 cm⁻¹, respectively. In addition, hydrogen bonds between the acids are still present with large bands at 2555 and 2670 cm⁻¹. Different synthetic conditions have been attempted in order to generate a complete esterification of $[Au(p-SPhCO_2H)]_n$, but with harsher conditions the formation of bulk gold was observed and water removal by the use of a Dean Stark did not allow complete esterification either. This observation indicates that $[Au(p-SPhCO_2Me)]_n$ is more easily obtained by direct synthesis from HAuCl₄ and p-HSPhCO₂H in methanol, when redox reaction and esterification take place simultaneously.¹⁵ Also the presence of hydrogen bonds between the carboxylic acids generating a 3D network increases the stability of $[Au(p-SPhCO_2H)]_n$. In addition, compound 1 exhibits bright yellow emission with a maximum band centered at 660 nm (λ_{ex} = 320 nm at room temperature and in the solidstate) (Fig. S3, ESI[†]). This intense luminescence is related to the compound $[Au(p-SPhCO_2Me)]_n$, which shows a quantum yield (QY) of ~70% compared to $[Au(p-SPhCO_2H)]_n$ having a QY of less than 1% at RT.14,15

Saponification reactions

Saponification of $[Au(p-SPhCO_2Me)]_n$ was carried out with several alkali hydroxide solutions used as a base: NaOH, KOH and CsOH. From PXRD (Fig. 2b), the saponification of the ester-based compound with NaOH and KOH leads to new and highly crystalline compounds $[Au(p-SPhCO_2Na)]_n$ (2) and $[Au(p-SPhCO_2K)]_n$ (3) with interlamellar distances of 1.76 and 1.77 nm, respectively. In the case of $[Au(p-SPhCO_2Cs)]_n$ (4), the compound exhibits also a layered structure with an interlayer distance of 1.93 nm, but it is poorly crystalline. The slight increase of the interlamellar distances for the three compounds is in accordance with the ionic radii of Na⁺, K⁺ and Cs⁺ (116, 152 and 181 pm, respectively) (Fig. S4, ESI†). These new interlamellar distances obtained after saponifications are close to the one of $[Au(p-SPhCO_2Me)]_n$ (1.86 nm) and suppose that the ligands are not interpenetrated. From PXRD the three phases are pure without the presence of the starting material or bulk gold (Fig. 3). The full conversion of the ester into the alkali carboxylate salt was also confirmed by FT-IR spectroscopy



Fig. 3 SEM pictures of (a) $[Au(p-SPhCO_2Na)]_n$ (2) and (b) $[Au(p-SPhCO_2K)]_n$ (3) compounds issued from the different saponification reactions of $[Au(p-SPhCO_2Me)]_n$. The scale bar represents 5 μ m.

(Fig. S5 and S6, ESI[†]). Indeed, on the three spectra, the antisymmetric vibrations of CO are shifted from 1720 cm⁻¹ to 1540 cm⁻¹. The small difference between the anti- and symmetric stretching bands of CO₂ ($\Delta \nu = 140 \text{ cm}^{-1}$) is characteristic of cations chelated by carboxylate groups.18 The three compounds present also intense and large bands of O-H stretching due to the solvation and hydration of the samples. From SEM pictures (Fig. 3), the crystallites of the compounds furnished from the saponification reactions are thin plates of around 1-5 µm size for 2 and 3 corresponding to the morphology of the starting material $[Au(p-SPhCO_2Me)]_n$, which may indicate that their lamellar structures are isoreticular. The TGA results show that the three compounds start to decompose from 350 °C (Fig. S7, ESI⁺). In addition, compounds 2 and 3 are photoluminescent showing their emission maxima at 670 and 648 nm, respectively (Fig. 4). The brighter emission of 3 is really close to that of the starting solid $[Au(p-SPhCO_2Me)]_n$, suggesting similarities in the gold-containing inorganic layer.¹⁵

The possibility of performing esterification and saponification reactions proves the remarkable stability of gold(1) thiophenolatebased compounds under extreme conditions of acidic and basic media under reflux for several days.

Exchange reaction

To gain more insights into the mechanism of post-functionalization, ligand exchange reactions between the three structurally different



Fig. 4 Emission spectra of $[Au(p-SPhCO_2Na)]_n$ 2 (blue) and $[Au(p-SPhCO_2K)]_n$ 3 (purple) recorded in the solid state at room temperature with λ_{ex} = 320 nm.



Fig. 5 PXRD patterns of compounds **5** $([Au(SPh)]_n)$, **6** $([Au(p-SPhCO_2Me)]_n)$, **7** $([Au(p-SPhCO_2H)]_n)$ and **8** $([Au(p-SPhCO_2H)]_n)$ obtained by ligand exchange reactions. The simulated PXRD diagrams of the associated compounds are also shown.

gold(i)-phenylthiolate-based coordination polymers, $[Au(p-SPhR)]_n$ with R = H, CO₂H and CO₂Me, were carried out (Fig. 1).

For this purpose, an excess of an incoming thiol ligand was used (*p*-HSPhR with R = H, CO_2H and CO_2Me). When the lamellar $[Au(p-SPhCO_2Me)]_n$ compound was mixed with thiophenol, the formation of a crystalline compound, 5, was observed via PXRD, with a diagram corresponding to the structure of $[Au(SPh)]_n$ with doubly interpenetrated helical Au-S chains (Fig. 5). The formation of this phase was confirmed by SEM pictures, showing that the pellets of the starting materials are transformed into long curved fibers (Fig. 6a) in good accordance with the 1D structure of [Au(SPh)]_n.¹⁹ The complete ligand exchange and purity of compound 5 were also confirmed by FT-IR showing the disappearance of the CO band of the ester (Fig. S8, ESI[†]) and the expected gold content obtained from the decomposition of the organic part during TGA (Au calculated: 64.3%, measured: 63.1%) (Fig. S9, ESI⁺). The transformation of a 2D CP into a 1D CP clearly points out



Fig. 6 SEM pictures of compounds **5** (a), **6** (b), **7** (c) and **8** (d) obtained by ligand exchange reactions.

that this ligand exchange reaction involves a complete rearrangement of the atoms and implies a dissolution/recrystallization mechanism.

The inverse reaction was also possible: when *p*-HSPhCO₂Me was mixed with the 1D $[Au(SPh)]_n$ solid, the layered $[Au(p-SPhCO_2Me)]_n$ compound, **6**, was formed. The completeness of the process was again confirmed by FT-IR with the appearance of the characteristic ester vibration bands $v_{as}(CO_2)$ and $v_{s}(CO_2)$ at 1720 and 1400 cm⁻¹, respectively (Fig. S8, ESI†). It can be observed from the PXRD pattern that the solid **6** exhibits two lamellar phases with interlamellar distances of 1.85 and 1.76 nm (Fig. 5), where the first phase corresponds to the reported structure of $[Au(p-SPhCO_2Me)]_n$ and the second one may be a similar structure with a different rotation of the methyl group and/or more interpenetrated ligands. The transformation from a 1D to a lamellar structure was also confirmed by the formation of thin pellets of around 20 µm size after the ligand exchange (Fig. 6b).

Each of the two previous solids, $[Au(p-SPhCO_2Me)]_n$ and $[Au(SPh)]_n$, was also allowed to react with an excess of the *p*-SPhCO₂H ligand. In both cases the lamellar $[Au(p-SPhCO_2H)]_n$ compounds 7 and 8, respectively, were obtained. On PXRD (Fig. 5) compound 7 exhibits low crystallinity with the presence of bulk gold as an impurity and the first reflection corresponds to an interlamellar distance of 1.50 nm, close to the value expected for $[Au(p-SPhCO_2H)]_n$ (1.48 nm). When the exchange reaction was performed from $[Au(SPh)]_n$, the crystallinity of compound 8 was better, with an interlamellar distance of 1.48 nm as expected for the structure of $[Au(p-SPhCO_2H)]_n$, and more importantly no bulk gold was formed even though a slightly higher temperature was used (120 °C instead of 100 °C) (Fig. 5). From SEM images (Fig. 6c and d), compounds 7 and 8 can be described as small pellets of around 1 µm in size. The presence of the carboxylic acid groups was confirmed by FT-IR spectroscopy with $\nu_{as}(CO_2)$ and $\nu_{\rm s}({\rm CO}_2)$ at 1690 and 1400 cm⁻¹, respectively, and the formation of hydrogen bonds between the acids with the bands at 2550 and 2670 cm⁻¹ (Fig. S8, ESI[†]).

In addition, compounds **5** and **6** exhibit photoemission centered at 684 and 648 nm at RT, corresponding to the luminescence of $[Au(SPh)]_n$ and $[Au(p-SPhCO_2Me)]_n$, respectively (Fig. S10, ESI[†]), while 7 and **8** are only weakly luminescent at RT like $[Au(p-SPhCO_2H)]_n$. These photoluminescence properties confirm the success of the ligand exchange reactions and the dissolution–recrystallization mechanism.

Conversely, when starting from the $[Au(p-SPhCO_2H)]_n$ solid with an excess of HSPh or *p*-HSPhCO₂Me ligands, no transformation was observed. This suggests again that the hydrogen bonds between the carboxylic acid functions are responsible for the increased stability of this gold thiolate compound and prevent ligand exchange reactions through this mechanism.

Conclusions

This study shows that the post-functionalisation approach by either esterification or saponification reactions is possible on gold(1) phenylthiolate coordination polymers. The ligand exchange strategy shows that it implies a complete rearrangement of the gold thiolate network and proves that the mechanism involves a dissolution–recrystallization process. Additional experiments, such as *in situ* SAXS or NMR, would provide an in-depth understanding of the mechanisms and provide evidence on whether the ligand exchange occurs before or after the CP dissociation or if another process is involved.²⁰ In addition, this work highlights that the structure of gold thiolate compounds is highly dependent on the functionalisation of the organic ligands and that weak interactions such as hydrogen bonds, C–H··· π and aurophilic interactions represent the driving forces for the self-assembly.

Conflicts of interest

There are no conflicts to declare.

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