ELSEVIER

Contents lists available at ScienceDirect

Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

Research paper

Binuclear organometallic Pt(II) complexes as stabilizing ligands for gold and silver metal nanoparticles

Sara Cerra^a, Laura Fontana^a, Enrico Rossi^b, Mauro Bassetti^{b,*}, Chiara Battocchio^c, Iole Venditti^c, Laura Carlini^c, Roberto Matassa^d, Giuseppe Familiari^d, Ilaria Fratoddi^{a,*}

^a Dipartimento di Chimica, Università La Sapienza, P.le A. Moro 5, 00185 Rome, Italy

^b CNR-ISB, Istituto per i Sistemi Biologici – Sede di Roma, Sezione Meccanismi di Reazione, c/o Dipartimento di Chimica, Università La Sapienza, P. le A. Moro 5, 00185

Rome, Italy

^c Dipartimento di Fisica, Unità INSTM and CISDiC, Università Roma Tre, Via della Vasca Navale 85, 00146 Rome, Italy

^d Department of Anatomical, Histological, Forensic and Orthopaedic Sciences, Section of Human Anatomy, Sapienza University of Rome, Via A. Borelli 50, 00161 Rome, Italy

ARTICLE INFO

Dedicated to Maurizio Peruzzini, on the occasion of his 65th birthday

Keywords:

Fluorene-bis-acetylide bimetallic complexes Stilbene-bis-acetylide bimetallic complexes Noble metal nanoparticles Organometallic bifunctional thiols Nanoparticle networks

ABSTRACT

The bifunctional hybrid thioester ligands containing square planar Pt(II) centers 2,7-bis[2-(*trans*-acetylthio-bis-(tributylphosphine)platinum^{II})ethynyl]-9,9-didodecyl-9*H*-fluorene (1) and *trans*-4,4'-bis[2-(*trans*-acetylthio-bis-(tributylphosphine)platinum^{II})ethynyl]stilbene (2) have been prepared in a four-step procedure and used as stabilizing and interconnecting ligands for gold and silver nanoparticles (MNPs), formed *in-situ* upon deacylation of the MeCOS-Pt(II)-terminal groups. The metallic surface is linked to the Pt(II) centers of the ligands via M-S-Pt (II) bridges. The size of the AuNPs and AgNPs which aggregate into a bi-dimensional network through hybrid metal-organic bridges was controlled by careful choice of synthetic parameters. The morpho-structural features of the nanoparticles, investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and synchrotron radiation induced X-ray photoelectron spectroscopy (SR-XPS), highlighted the linkage between the nanoparticles, featuring diameters below 10 nm.

1. Introduction

Noble metal nanoparticles (MNPs) and related organometallic precursors with narrow and controlled size distributions are at present one of the most advanced nanomaterials, with potential applications in various fields among which catalysis, biomedicine and drug delivery, molecular electronics and plasmonics [1–10]. Chemical reactions performed under suitable conditions from selected molecular entities allow for the preparation of MNPs of desired composition, size, shape and distribution, under atomic precision control [11–13]. Moreover, 2D or 3D networks showing collective physico-chemical properties can be obtained by the easy manipulation of colloidal MNPs when allowed to self-assemble into complex structures [14,15]. MNPs assemblies exhibit bulk properties that are controllable through a bottom up approach and have prompted systematic studies of electronic and solid-state phenomena.

A fundamental role in properties and potential applications is played by the stabilizing ligands, as in the case of hydrophilic organic or organometallic thiols and polymers in core-shell structures that can make NPs based colloids easy to handle in either organic or aqueous media [16]. In presence of bifunctional terminal groups at the end of the ligand molecular chain, extended networks of interconnected NPs can be obtained. Dimers, oligomers, and polymer-like gold nanoparticle chains can be prepared by varying the ratio of alkane dithiols to metal precursors [17]. In this context, fluorene and stilbene units with terminal thiol groups have been employed as organic bridges due to their extended π -conjugated electronic system allowing for the synthesis of covalently linked MNPs with tunable interparticle distances. Among these, platinum-containing fluorenyl-polyynes and metallopolyynes have been reported as promising materials for organic electronic devices [18-23]. It is also known that Pt(II) centers in MNPs can induce a synergistic effect at the electronic level in the modulation of their physicochemical properties [24]. Within the class of bifunctional ligands, we previously reported on synthesis and properties of biphenyl based NPs linked by a Pt-containing organometallic dithiol bridge [25], and more recently of silver and gold NPs stabilized by fluorene-based dithiol

* Corresponding authors. *E-mail addresses:* mauro.bassetti@cnr.it (M. Bassetti), ilaria.fratoddi@uniroma1.it (I. Fratoddi).

https://doi.org/10.1016/j.ica.2020.120170

Received 19 October 2020; Received in revised form 28 November 2020; Accepted 29 November 2020 Available online 3 December 2020 0020-1693/© 2020 Elsevier B.V. All rights reserved. ligands in which the distance between the NPs varies as a function of the interconnecting conjugated organic bridge (Chart 1) [26]. MNPs linked by bifunctional thiols were tested in electrical measurements showing a non-ohmic behavior, suitable, for example, in sensor applications [27,28].

It is worth mentioning that transition metal complex (TMC)/AuNP hybrids, i.e. gold NPs stabilized by organometallic linkers, represent a continuously growing field of investigation due to the diversity of properties and applications with respect to those of conventional organic compounds/AuNP hybrids [29].

In the present work, we have extended the study on the properties of Pt(II) bifunctional thiol ligands and related MNPs by addressing the synthesis of bimetallic complexes 1 and 2 and of the corresponding gold and silver NPs. The trans-stilbene organic bridge allows for an extension of the conjugated carbon chain with respect to its biphenyl analog, while the alkyl chains in the 9-position of the fluorene system are expected to bring improved solubility of both complex and MNPs in organic solvents, thus extending the array of tunable properties of such systems. These ligands are characterized by an extended π -system that can enhance the plasmon resonance effect of the linked nanoparticles and introduce specific absorption and emission optical features in the MNPs [30–32]. Furthermore, their bifunctional structure allows the formation of an interconnected system of nanoparticles with extensive delocalization of the electrical charge. Both gold and silver NPs have been obtained (i.e. AuNPs-1, AuNPs-2 and AgNPs-1, AgNPs-2) upon deprotection of the thiol end groups.

The preparation methods of the MNPs focused on providing highquality uniform aggregates of network assemblies. The structural and optical properties of the functionalized nanoparticles were determined by FTIR, NMR and UV–Vis spectroscopies. Synchrotron radiation spectroscopy (SR-XPS) was used to obtain detailed information on MNPs network assemblies at the nanoscopic scale. Moreover, Scanning Electron Microscopy has been employed to characterize the morphological surface, while structural identification on the bulk has been gathered by Transmission Electron Microscopy supported by selected area electron diffraction (SAED) techniques. Image processing with statistical analysis have been exploited to perform an accurate quantitative measurement of size, shape and location of the individual MNPs forming the bidimensional network.

2. Experimental section

General. UV-Vis absorption spectra were obtained on a Varian Cary 100 Scan UV-Vis spectrophotometer, using 1 cm quartz cells. The molar extinction coefficients (ϵ , M⁻¹ cm⁻¹) were measured in the concentration range of 5.0×10^{-6} – 1.8×10^{-4} M, and the values are given with a $\pm 5\%$ experimental error. Photoluminescence measurements were performed on a Horiba Jobin Yvon Fluoromax-4 instrument. Both absorption and emission spectra were acquired on freshly prepared samples in CH₂Cl₂ solutions. Elemental Analyses were carried out on an EA 1110 CHNS-O instrument. FTIR and Far-IR (FIR) spectra were recorded on cast deposited films from chloroform solutions using KRS-5 cells with a Bruker Vertex 70 spectrophotometer, in the range 4000–400 cm^{-1} and 600–200 cm⁻¹, respectively. NMR spectra were recorded on a Bruker AvanceII 300 MHz instrument in CDCl₃ solutions; chemical shifts are reported in δ values calibrated with solvent peaks at 7.26 ppm for ¹H NMR and 77.1 ppm for ¹³C NMR, or vs H₃PO₄ as external standard for ¹³P NMR. Mass spectra were acquired on a triple quadrupole mass spectrometer API 365 (SCIEX) with ESI ion source, provided with a second ion source APCI (atmospheric pressure chemical ionization) suitable for substances less easily ionizable. Pure samples were prepared in dilute solutions (2 mL, at least 1 mg/mL) in methanol solvent. Small amounts of formic acid, acetic acid, or ammonia were added to favor the ionization process and increase the sensitivity of the instrument. The samples were filtered through microfiber glass with 0.2 µm porosity before injection.

Materials. All reagents and analytical grade solvents were purchased from commercial sources and used as received unless otherwise stated. Disopropylamine and dichloromethane were distilled over CaH₂ under nitrogen atmosphere. Reactions were performed under Argon using standard Schlenk-line techniques. Column chromatography was carried out on silica gel Merck (70–230 mesh), and thin-layer chromatography (TLC) on aluminum sheets precoated with silica gel 60 F254 (Merck). Platinum and palladium complexes *cis*-[Pt(PBu₃)₂Cl₂] and *trans*-[Pd



Chart 1. Previous examples of organic dithiol/MNPs from our group and proposed Pt-complexes/MNP hybrids.

(PPh₃)Cl₂ [33], and the ligand precursors ((9,9-didodecylfluorene-2,7-diyl)-bis(ethyne-2,1-diyl))bis(trimethylsilane) (1a) [16] and *trans*-1,2-bis((4-(trimethylsilyl)ethynyl)phenyl)ethene (1b) [34] were prepared as previously described. Synthetic procedures and characterization of compounds 1a-c and 2a-c are reported in the Supporting Information (Fig. SI_1).

2,7-Bis[2-(trans-acetylthio-bis-(tributylphosphine)platinum^{II})ethynyl]-9,9-didodecyl-9H-fluorene (1). 2,7-Bis[2-(trans-bis-(tributylphosphine)chloride-platinum^{II})ethynyl]-9,9-didodecyl-9H-fluorene (1c) (0.500 g, 0.275 mmol) and potassium thioacetate (0.100 g, 0.875 mmol) were stirred in a mixture of ethanol (25 mL) and CH₂Cl₂ (100 mL) under Argon atmosphere at 50 °C for 3 days. Upon filtration through a pad of Celite, the solution was treated with brine (2 \times 50 mL) and the organic phase dried over Na₂SO₄ to give 1 as a yellow oil (0.496 g, 95% yield). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 7.52–7.41 (m, 2H, H-4, H-5), 7.25-7.14 (m, 4 H, H-3, H-6, H-1, H-8), 2.35 (s, 6 H, COCH₃), 2.21-1.94 (m, PCH₂, 24H), 1.94-1.78 (m, C(CH₂-)₂, 4 H), 1.75-1.51 (m, PCH₂CH₂-, 24H), 1.51–1.37, (m, PCH₂CH₂CH₂CH₃, 24H), 1.35–0.98 (m, CH2 on fluorene, 36H), 0.98-0.81 (m, CH3, 42H), 0.70-0.55 (m, 4 H, CH_2CH_3 on fluorene). ¹³C NMR (CDCl₃, 75.5 MHz): δ (ppm) = 3.8 (CH₃), 14.0 (CH₃), 22.6 (t, J_{P-C} = 17.3 Hz, PCH₂CH₂), 23.9 (CH₂), 24.3 (t, J_{P-C} = 6.7 Hz, PCH₂CH₂), 26.1, 26.2, 26.3, 29.3, 29.4, 29.5, 29.56, 29.58, 29.7 (CH₂), 30.3 (COCH₃), 31.9, 33.0, 40.6 (CH₂), 54.5 (C-9), 96.6 (t, J_P. $_{\rm C} = 15.2$ Hz, C C-Ar), 106.7 (t, J = 2.0 Hz, Pt-C C, 118.9, 124.9, 126.7, 129.3, 138.4, 150.4 (Ar), 204.3 (COCH₃). ³¹P NMR (CDCl₃, 121 MHz): δ (ppm) = 3.87 (J_{P-Pt} = 2391.8 Hz). FT-IR (film from CH₂Cl₂), $\sqrt{}$ (cm⁻¹): 2957, 2927, 2871, 2857, 2112 (C≡C), 1632 (C≡O), 1462, 1416, 1378, 1343, 1304, 1260, 1210, 1148, 1108, 1052, 1005, 944, 905, 819, 722, 648. FIR (film from CH_2Cl_2), ν^- (cm⁻¹): 577 (Pt-C), 446 and 394 (Pt-P), 326 (Pt-S). UV–Vis (CHCl₃), λ_{max} (nm) (log ε): 372 (5.1) nm. Elemental analysis (%) calcd. for C₉₃H₁₇₀O₂P₄Pt₂S₂ (1898.52): C 58.83, H 9.03, S 3.38; found: C 58.56, H 9.18, S 3.22. HRMS (ESI, CH₃OH): cluster centered at *m/z* 1897.70 (calcd. 1898.52 uma).

trans-4,4'-Bis[2-(trans-thioacetyl-bis-(tributylphosphine)platinum^{II}) ethynyl]-stilbene (2). trans-4,4'-Bis[2-(trans-bis-(tributylphosphine) chloride-platinum^{II})ethynyl]-stilbene (2c) (0.623 g, 0.416 mmol), and potassium thioacetate (0.153 g, 1.248 mmol) were stirred in a mixture of ethanol (25 mL) and CH₂Cl₂ (100 mL) under an Argon atmosphere at 50 °C for 3 days. The solvents were removed by rotary evaporation and the mixture was purified by column chromatography (alumina, petroleum ether/CH₂Cl₂ = 1/1) to give product **2** as a vellow oil (0.622 g, vield 95%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.40–7.10 (m, 8H Ar), 6.45 (H-9, H-10), 2.31 (s, COMe), 2.01 (m, CH₂), 1.35 (m, CH₂), 0.98 (m, CH₃). ¹³C NMR (75.5 MHz, CDCl₃): δ (ppm) = 204.1 (CO), 134.2 (C-1, C-1'), 130.4 (C-3, C-3', C-5, C-5'), 129.4 (C-9, C-10), 128.5 (C-2, C-6, C-2', C-6'), 126.0 (C-4, C-4'), 105.6 (C-7, C-7'), 98.0 (C-8, C-8'), 34.9 (COCH₃), 26.2, 24.3, 22.3 (m, CH₂), 13.8 (CH₃). ³¹P NMR (121 MHz, CDCl₃): δ (ppm) = 4.12, J_{P-Pt} = 2398.3 Hz. FT-IR (film from CH_2Cl_2), ν^- (cm⁻¹): 2959, 2918, 2868 (CH aliphatic), 2111 (C \equiv C), 1624 (C=O). FarIR (film from CH₂Cl₂), ν^{-} (cm⁻¹): 548 (Pt-C), 450 and 395 (Pt-P), 325 (Pt-S). UV–Vis (CH₂Cl₂), λ_{max} (nm): 373. Fluorescence (CH₂Cl₂), λ_{em} (nm): 415, 441. HR-MS (ESI, CH₃OH): cluster centered at m/z = 1573.73 (calcd. 1574.73).

Self-assembled monolayers of 1 and 2 on gold. Gold coated silica wafers prepared by growing Au film 4000 Å thick onto Si(111) substrates were cut into slices (ca 1 cm²) and washed repeatedly with acetone, ethanol and chloroform, then blown dry under nitrogen. Compound 1 (0.035 g,

0.019 mmol) dissolved in 20 mL of THF and aqueous NH₄OH (30%, 260 μ L, 6.5 mmol) were allowed to react for 2 h at 30 °C. The mixture was filtered on Celite and freshly washed gold substrates were dipped into the solution for 4 h. The obtained multilayers were rinsed with different solvents (ethanol, THF and acetone) and then dried under vacuum in order to achieve the formation of SAM films in the monolayer thickness regime. An analogous procedure was followed using compound **2**.

Synthesis of gold nanoparticles AuNPs-1 and AuNPs-2. An aqueous solution of HAuCl₄·3H₂O (0.0237 g, 0.0602 mmol) in deionized water (5 mL) was mixed with a solution of tetraoctylammonium bromide (TOAB) (0.040 g, 0.0734 mmol) in toluene (9.5 mL). The two-phase mixture was vigorously stirred until all the tetrachloroauric acid was transferred into the organic layer, then a solution of thioester 1 (0.114 g, 0.0602 mmol, Au/S molar ratio 1/1) in toluene (9.5 mL) was added. A freshly prepared aqueous solution of sodium borohydride (0.0228 g, 0.6020 mmol) in deionized water (5 mL) was rapidly added under vigorous stirring and the reaction mixture allowed to react for 3 h. At the end, the organic phase was separated and washed with water. The organic phase was reduced to 2 mL in a rotary evaporator, and 20 mL of ethanol were added. The mixture was kept overnight at -18 °C and then centrifuged at 5000 rpm for 15 min to remove excess of reagents, TOAB and byproducts. The supernatant was rinsed out and the precipitate was washed by centrifugation (5000 rpm for 5 min) with ethanol (\times 2) and then with dichloromethane ($\times 10$). After removal of the supernatant, a red ruby solution of AuNPs-1 nanoparticles was obtained by taking up with 10 mL of toluene. Gold nanoparticles stabilized with ligand 1 were also prepared using the starting materials in Au/S molar ratios: 1/2 and 1/1.43. Gold nanoparticles (AuNPs-2) stabilized with ligand 2 were prepared according to an analogous procedure with Au/S molar ratios 1/1, 1/2, 2/1 and 3/1. AuNPs-1: (yield 30%, 0.007 g). UV-Vis (CH₂Cl₂): $\lambda_{max} = 570$ nm. Fluorescence (CH₂Cl₂): $\lambda_{em} = 540$ nm ($\lambda_{exc} = 520$ nm). FT-IR (film from CH₂Cl₂), ν^{-} (cm⁻¹): 580 (Pt-C), 446 and 394 (Pt-P), 326 (Pt-S); 227 (Au-S). AuNP-2: (yield 21%, 0.0062 g). UV-Vis (CH₂Cl₂), $\lambda_{max} = 515$ nm. Fluorescence (CH_2Cl_2): $\lambda_{em} = 590$ nm ($\lambda_{exc} = 500$ nm).

Synthesis of silver nanoparticles AgNPs-1 and AgNPs-2. Silver nanoparticles (AgNPs-1) stabilized with ligand 1 were prepared by using the Ag/S molar ratios 1/0.5, 1/1, 1/2, as herein described for the 1/1 case. Silver nanoparticles (AgNPs-2) stabilized with ligand 2 were prepared by an analogous procedure using the Ag/S molar ratios 1/1, 3/1 and 1/12. The AgNO₃ salt (0.0243 g, 0.143 mmol) was dissolved in deionized water (5 mL) and mixed with a solution of tetraoctylammonium bromide (TOAB) (0.0954 g, 0.1745 mmol) in toluene (10 mL). The two-phase mixture was vigorously stirred until all the silver salt was transferred into the organic layer and a solution of ligand 1 (0.1307 g, 0.143 mmol) in toluene (10 mL) was then added. A freshly prepared aqueous solution of sodium borohydride (0.0541 g, 1.43 mmol) in deionized water (5 mL) was rapidly added under vigorous stirring. After further stirring for 4 h the organic phase was separated, washed with water and the organic solution was reduced to 2 mL in a rotary evaporator. Ethanol (40 mL) was added and the nanoparticles allowed to precipitate when kept overnight at -18 °C. The suspension was separated by centrifugation at 5000 rpm for 15 min, the supernatant was removed, and the precipitate was carefully washed with ethanol (5000 rpm for 15 min, two times) and with dichloromethane (5000 rpm for 5 min, ten times). AgNPs-1: (0.063 g, yield 26%). UV–Vis (CH₂Cl₂), $\lambda_{max} = 460$ nm. Fluorescence (CH₂Cl₂): $\lambda_{em} = 544$ nm ($\lambda_{exc} = 400$ nm). AgNPs-2: (0.0064 g, yield 15%). UV–Vis (CH₂Cl₂): $\lambda_{max} = 400$ nm. Fluorescence (CH₂Cl₂): $\lambda_{em} = 460$ nm ($\lambda_{exc} =$



380 nm). During the centrifugation procedure the sample showed a tendency to aggregate giving a dark solution.

TEM analysis. TEM images and Electron Diffraction Patterns (EDP) were captured using a FEI-Titan operating at 80 keV, whereas low voltage experiments were performed using a ZEISS EM10 TEM operating at 60 keV. Measurements were carried out on cast deposited samples obtained from CH₂Cl₂ or DMF solutions on Cu grids coated with amorphous carbon [35]. XPS analysis was performed with a homemade instrument consisting of a preparation and analysis UHV chamber (resolution of 1.0 eV as measured at the Ag 3d_{5/2} core level). The used Xray radiation is a non-monochromatized Mg-Ka (1253.6 eV). The spectra were energy referenced to the C1s signal of aliphatic C atoms having a binding energy BE = 284.70 eV. Atomic ratios were calculated from peak intensities by using Scofield's cross section values and calculated λ factor [36]. Curve-fitting analysis of the C1s, Au4f, S2p, spectra was performed using Voigt profiles as fitting functions, after subtraction of a Shirley-type background [37]. For quantitative data, the BE values were referred to NIST data. The spectra have been acquired on films cast or spin deposited from CHCl₃ and CH₂Cl₂ solvents on TiO₂/Si (111) wafers.

SR-XPS characterization. SR-XPS experiments were carried out at the PM4-LowDosePES beamline at Helmholtz-Zentrum Berlin (BessvII Synchrotron Radiation facility). The PM4 bending magnet beamline is equipped with a Plane Grating Monochromator operating in collimated light (collimated PGM). The LowDose PES end-station is equipped with a SES100 hemispherical analyzer, whose Energy Resolution was estimated as 0.2 eV. XPS data were collected in fixed analyzer transmission mode (pass energy = 30 eV), with the monochromator entrance and exit slits fixed at 30 µm. Photon energy of 380 eV and 600 eV were used for C1s, S2p, Pt4f, Au4f, Ag3d and O1s spectral regions with energy resolution 0.22 eV. Calibration of the energy scale was made referencing the spectra to the gold Fermi edge of an Au reference sample, and the $Au4f_{7/}$ 2 was always found at 83.96 eV. Curve-fitting analysis of the C1s, O1s, S2p, Pt4f, Au4f and Ag3d spectra was performed using Gaussian curves as fitting functions. S2p_{3/2,1/2}, Au4f_{7/2,5/2}, Ag3d_{5/2,3/2}, P2p_{3/2,1/2} and Pt4f7/2,5/2 doublets were fitted by using the same full width at halfmaximum (FWHM) for each pair of components of the same core level, a spin-orbit splitting of, respectively, 1.2 eV, 6.0 eV and 3.3 eV and branching ratios $S2p_{3/2}/S2p_{1/2} = 2/1$, $Ag3d_{5/2} / Ag3d_{3/2} = 3/2$, $Au4f_{7/2}/Au4f_{5/2}\,{=}\,4/3 and\,Pt4f_{7/2}/Pt4f_{5/2}\,{=}\,4/3.$ When several different species were individuated in a spectrum, the same FWHM value was used for all individual photoemission bands.

3. Results and discussion

Synthesis of organometallic bifunctional ligands. The objectives of this

work were the preparation and characterization of Au or Ag nanoparticles stabilized with organometallic bifunctional thiol ligands, in order to obtain MNPs with fine controlled structural and optical properties. Ligands 2,7-diethynyl-(9,9-didodecyl)-fluorene and *trans*-4,4'bis-(2-ethynyl)-stilbene were chosen as the conjugated π -systems and coordinated to -Pt(II)(PBu₃)₂SCOCH₃ end groups by formation of acetylide-platinum bonds. The overall synthetic pathway to form the Ptbimetallic complexes **1** and **2** consisted of a four-step procedure, which is summarized in Scheme 1.

The trimethylsilyl protected diynes **1a** or **2a**, obtained by Sonogashira-Hagihara coupling of the corresponding dibromide precursors, were allowed to react under basic conditions to afford the bisethynyl derivatives **1b** or **2b**. In the third step, the organometallic compounds **1c** or **2c** were obtained by means of a dehydrohalogenation reaction involving the diynes **1b** or **2b** and the square planar platinum (II) complex *cis*-[Pt(PBu₃)₂Cl₂], according to a reported procedure [38]. An accurate control of the stoichiometry between the platinum complex and **1b** or **2b** was necessary to avoid polymerization reactions and favor the formation of the dinuclear complexes **1c** or **2c** (details in **Supporting Information**). In the final step, the ligand exchange reaction of -Cl by $-SCOCH_3$ allowed the isolation of the bifunctional organometallic compounds **1** and **2** featuring terminal thioacetate groups.

Spectroscopic characterization of platinum complexes 1c, 1, 2c, 2. The Far-IR spectrum of the fluorene complex 1c has shown the stretching signals due to the Pt bonds: ν (Pt-P) at 447 cm⁻¹ and 396 cm⁻¹, ν (Pt-C) at 577 cm⁻¹ and ν (Pt-Cl) at 309 cm⁻¹ [39]. The formation of the *trans*isomer is evidenced by the ³¹P NMR spectrum where the phosphorous signal falls at 4.10 ppm with coupling constant $J_{31P-195Pt}$ equal to 2391 Hz [40]. The Far-IR spectrum of 2c has shown the stretching modes of the Pt bonds at $\nu(Pt-P) = 450 \text{ cm}^{-1}$ and 395 cm⁻¹, $\nu(Pt-C)$ at 548 cm⁻¹ and ν (Pt-Cl) at 307 cm⁻¹, giving evidence of Pt-C bond formation. Upon formation of the platinum complex, the stretching of the $C \equiv C$ triple bond is shifted at a lower frequency (2c, 2111 cm^{-1}) as expected for the introduction of the metal center. In the ¹³C NMR spectrum the signals associated to the triple bond were observed at 98.0 ppm (-C=C-Ar) and 105.6 ppm (Pt–C=C, tr). The ³¹P NMR spectrum showed a signal at 7.02 ppm with $J_{P-Pt} = 2365$ Hz, typical for the *trans* isomer. The formation of the trans isomer is evidenced by the ³¹P NMR spectrum where the peak associated to phosphorous is found at 4.10 ppm with coupling constant $J_{31P-195Pt} = 2391$ Hz. The presence of the thiocarbonyl group is indicated by the stretching band in the FT-IR spectrum at 1630 cm⁻¹, by the methyl signal at 2.44 ppm in the ¹H NMR spectrum and 204.3 ppm in the ¹³C NMR spectrum. The FTIR spectrum of complex 2 showed the stretching frequency of the carbonyl group at 1624 cm⁻¹, shifted from the typical value due to the presence of the platinum centers. The presence of the acetyl group has been confirmed by the ¹H NMR with a



Scheme 1. Synthetic routes to bimetallic complexes 1 (FL) and 2 (ST).

peak at 2.31 ppm, while the carbonyl and the methyl groups were found at 204.3 and 35.0 ppm in the ¹³C NMR spectrum. Concerning the Far-IR characterization, products **1** and **2** highlighted the stretching of the new introduced Pt-SCOCH₃ bonds: ν (Pt-S) at ca. 325 cm⁻¹ [41,42]. The ³¹P NMR spectrum showed the signal associated with the phosphine groups at 4.19 ppm with a coupling constant J = 2398 Hz. The FTIR and FIR spectra of compounds **1** and **2** are reported in Fig. SI_2 whereas NMR spectra are reported in Fig. SI_3 for compounds **1** and **2**, respectively.

The compounds **1**, **1a–c**, **2**, **2a–c** were characterized by absorption and fluorescence spectroscopy. The UV–Vis spectra of each series of compounds highlighted a progressive red-shift of the absorption maximum going from the dibromide precursors, FL or ST, to the diethynyl derivatives and then to the dichloride or dithioacetate Pt(II) complexes, due to increased electron density within the conjugated system (Fig. SI_4). Excitation of the platinum complexes at the wavelength of their absorption maxima (373 nm) gave rise to the corresponding photoluminescence spectra, characterized by vibronic structures with emission peaks at 558 nm and 587 nm for the fluorene complex **1** and at 416 nm and 440 nm for the stilbene complex **2** (Fig. 1).

Functionalized Noble metal nanoparticles: synthesis and characterization of AuNPs and AgNPs based networks. The Brust's synthesis of thiolderivatized metal nanoparticles in a two-phase liquid-liquid system to obtain colloidal MNPs is a commonly used procedure [43,44], which we followed in this work starting from the Au³⁺ or Ag⁺ ion precursors (tetrachloroauric acid or silver nitrate). The reduction of the metal ions by sodium borohydride was carried out in wet conditions in presence of the bis-thioacetate Pt^{II} ligand 1 or 2 and of the phase transfer agent tetraoctylammonium bromide (TOAB) (Scheme 2). During the synthesis, the thioester is subjected to an *in situ* deacetylation that allows the formation of the S-metal bond [45]; subsequently the addition of NaBH₄ causes the reduction of the Au³⁺ or Ag⁺ ions to the corresponding atomic metal clusters.

The introduction of thiols as stabilizing outer layers on the MNP surface allows to control the size and morphology of the nanoparticles. Different thiol/metal molar ratios have been used in the synthetic procedure for manufacturing nanoparticles with a reproducible and controlled diameter. Therefore, appropriate stoichiometric ratio of reactants and the subsequent purification steps are crucial [46]. AuNPs and AgNPs stabilized with the two novel bifunctional organometallic thioesters, 1 and 2, were obtained. After purification, the nanoparticles were characterized by both spectroscopic (FTIR, UV–Vis, SR-XPS) and electron microscopy techniques (FESEM, TEM, and SAED) in order to investigate their morpho-structural properties.

The UV–Vis characterization carried out on the metal nanoparticles in dichloromethane solution revealed the presence of broad surface plasmon resonance (SPR) bands. Fig. 2a and b shows typical UV–Vis spectra in CH₂Cl₂ of AuNPs and AgNPs functionalized with fluorene and stilbene platinum complexes.

As it can be observed, both AuNPs exhibit a broad peak with maximum near 580 nm, which is red shifted with respect to the typical resonance at about 520 nm found in spherical AuNPs [47]. Usually, the red shift of the SPR band is correlated to increasing volume, size dispersity and aggregation of the NPs system [48]. The shift of the plasmonic resonance is probably related to interparticle electro-magnetic coupling effects [14,49]. In the case of AuNPs-1 and AuNPs-2, particles with small diameter and with a good degree of monodispersity have been observed by morphological studies. The SPR bands of the silver nanoparticles AgNPs-1 and AgNPs-2 were found at about 470 and 400 nm (λ_{max}), respectively. Fluorene based AgNPs-1 show a trend similar to that observed in AuNPs.

SR-XPS studies. In order to probe the local chemistry occurring at the head group/metal interface as well as the ligand molecular structure stability and intermolecular interactions, High Resolution Synchrotron Radiation-induced XPS measurements were carried out on AuNPs-1, AuNPs-2, AgNPs-1 and AgNPs-2, as well as, for comparison, on the ligands 1 and 2 deposited onto "flat" polycrystalline gold surfaces. These studies have been carried out on the sample obtained using a metal to sulfur molar ratio of 1/1. Data collected at S2p and Au4f and Ag3d core levels, respectively, allowed the assessment of the local chemistry at the metal/thiol interface, and Pt4f spectra were extremely useful to probe metal-aromatic rings intermolecular interactions, as observed for analogous systems [50]. S2p, Pt4f, Au4f and Ag3d XPS data (BE, FWHM, atomic ratio values and assignments) are summarized in Table S1 of the Supporting Information. S2p spectra of AuNPs-1, AgNPs-1 and 1 are reported in Fig. 3. It is noteworthy that in the spectrum of complex 1 (Fig. 3a-bottom), two pairs of spin-orbit components can be observed, whereas in AuNPs-1 and AgNPs-1, S2p spectra show one spin-orbit pair only. The S2p signal that can be observed in all three spectra has a S2p3/ 2 main component BE of about 162 eV, as expected for sulfur atoms covalently bonded to metals. This signal is usually observed in self assembled monolayers (SAMs) of thiols anchored on metal surfaces as well as on metal nanoparticles stabilized by thiols [51].

The organometallic thioester ligands **1** and **2** were deprotected by hydrolysis under basic conditions in order to isolate the free thiol derivative and to prepare SAMs on gold surfaces for HR-XPS studies. The signal at higher BE values ($S2p_{3/2}$ BE = 164 eV) that appears in the spectrum of **1** is attributed to free thiol or thiolate end groups. The two sulfur signals are of the same intensity, suggesting that **1** molecules anchor to the gold surface only with one terminal group, as expected for rigid π -conjugated molecules showing an attitude to stack, attaining an uprising position on the surface. For complex **2**, the S2p spectrum, reported at the bottom of Fig. 3b, is similar. On the other hand, in **AuNPs-2** and **AgNPs-1** scales S2p signal is observed (similarly to **AuNPs-1** and **AgNPs-1**), coherently with the hypothesized formation of



Fig. 1. Normalized UV–Vis absorption (red line) and emission spectra (blue line) of complex 1 (a) and of complex 2 (b) in dichloromethane. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. a) Schematic representation of two-phase synthesis of gold and silver nanoparticles. b) Structures of the obtained AuNPs and AgNPs.



Fig. 2. UV-Vis spectra (CH₂Cl₂). a) AuNPs-1 and AuNPs-2 in Au/S 1/1 M ratio. b) AgNPs-1 and AgNPs-2 in Ag/S 1/0.5 M ratio samples.

networks with all thiol terminal groups involved in S-Metal bonds, as driven by the deacylation reaction above described.

Au4f and Ag3d XPS spectra of **AuNPs-1** and **AgNPs-2** are reported in Fig. SI_5. Both spectral regions show two couples of spin-orbit pairs, as expected for functionalized nanoparticles. The main signals, at lower BE values (Au4f_{7/2} 83.80 eV; $Ag3d_{5/2}$ 367.66 eV) are attributed to metallic atoms of respectively gold and silver, in the nanoparticles core. The low intensity signals at higher BE values (about 20% of total metal signal for all four samples) are due to positively charged metal atoms on the nanoparticles surface, chemically bonded to sulfur atoms of the thiol end groups. The same behavior is observed for **AuNPs-2** and **AgNPs-1** Au4f and Ag3d spectra, as summarized in Table SI_1.

Pt4f spectra of **AuNPs-1**, **AgNPs-1** and ligand 1 are reported in Fig. 4 and are representative for the analogous **AuNPs-2**, **AgNPs-2** and ligand **2** systems; the main Pt signal has $Pt4f_{7/2}$ BE = 73.00 eV for all samples, as expected for binuclear compounds analogous to Pt-polyynes [38]. A small component at lower BE values is also observed in all Pt4f spectra, and attributed to Pt atoms electronically interacting with the ethynylbiphenyl groups of adjacent molecules, as expected for rod-like polyynes giving rise to metal-to-ligand (MLCT) intra and inter-molecular charge transfer [52]. In fact, binuclear π -conjugated molecules like ligands **1** and **2** are well known to give rise to self-assembling structures, due to the highly favorable interchain interactions arising between metal centers and adjacent acetylene moieties and aromatic rings. Some of us already observed and reported this behavior in a study about the self-assembling organization of dinuclear Pt(II) and Pd(II)-based complexes anchored on silver nanoparticles, on gold surfaces and on organometallic polymetallaynes [53].

Electron microscopy study. Detailed morpho-structural investigations of the MNPs directly linked by organometallic bifunctional thiol ligands **1** or **2** have been performed. Electron microscopy images of the AuNPs bridged by ligand **1** are shown in Fig. 5. The surface morphology of **AuNPs-1** sample obtained with molar ratio Au/S 1/1 evidence different bright nanometric regions of aggregate nanoparticles. The brightest area is related to the high density of NPs, forming a quasi-domo islands with dimension of more than hundred nanometers (marked by white dot line)



Fig. 3. XPS S2p spectra: a) S2p core level spectra of AuNPs-1 (top), AgNPs-1 (middle) and complex 1 (bottom); b) S2p core level spectra of AuNPs-2 (top), AgNPs-2 (middle) and complex 2 (bottom).



Fig. 4. XPS Pt4f spectra collected on **AuNPs-1** (top) and **AgNPs-1** (middle) and ligand **1** (bottom); spin-orbit components associated to Pt(II) atoms are in blue (Pt 4f_{7/2} component) and cyan (Pt 4f_{5/2}); the signal attributed to Pt atoms acting as electron-acceptors from fluorene electron-rich moieties of adjacent molecules is in red (Pt4f_{7/2}) and orange (Pt4f_{5/2}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 5a). A magnified region shows the presence of stacked polydispersed NPs (Inset). The electron diffraction pattern (EDP) in Fig. 5b exhibits diffraction rings produced by a randomly orientation of the polycrystalline nanoparticles. Measuring the d-spacing of the diffraction rings, we were able to establish the typical pattern of the face-centeredcubic (fcc) Au crystallites of space group *Fm*-3 m (yellow dot arcs). Furthermore, very few extra diffraction spots selected by red dot circles can be noticed, and not evaluated because of the poor number and crystalline organization. The corresponding Bright Field (BF) TEM image clearly shows well separated AuNPs with approximately spherical shape (Fig. 5c). The morphometric analysis of the AuNPs identified an average diameter of 4.42 ± 0.31 nm. The estimated neighbor-distance distribution is centered around 2.17 ± 0.41 nm which could correspond to the length of organometallic linker [14,54,55].

By increasing the Au/S molar ratio to 1/2 (AuNPs-1 1/2 mol/mol sample), the surface roughness decreased (Fig. 5d, white arrowed) and separated nanoaggregates of dozens nanometer are shown in the Inset. EDP analysis still confirms the presence of a gold face-centered-cubic (fcc) (yellow dot arcs) with increasing of extra diffraction spots (Fig. 5e, red dot circles). The polygonal white lines drawn on Fig. 5f evidence well-separated nanoaggregates with some overlapping nanoparticles. Further, narrow dark lines connecting two Au-NPs can be observed with possible relation to the organometallic linkers (blue arrows). Indeed, the statistical imaging analysis of the neighbor-distances exhibits a decreasing in polydispersity distribution with an estimated distance of 2.31 \pm 0.33 nm and an average diameter of 4.21 \pm 0.42 nm of the NPs.

By reaching an Au/S molar ratio of 1/1.43 (AuNPs-1 1/1.43 mol/ mol sample), the 2D-network shows a better uniformity in dimension and distribution of the AuNPs in Fig. 5g, showing well-separated nanoparticles in the Inset. EDP provided similar results of the previously crystalline gold samples (yellow dot arcs of Fig. 5h), whereas the increasing extra diffraction signal allowed to determine its crystallographic composition at nanometric scale (indicated by red dot arcs). Two different d-spacings of about 0.256 nm and 0.172 nm were estimated in agreement with crystalline phase of gold sulfide (Au₂S), corresponding to the crystalline plane oriented on (002) and (022) of a



Fig. 5. Morphological and structural study of self-assembled AuNPs of the AuNPs-1 1/1 mol/mol (a–c), AuNPs-1 1/2 mol/mol (d–f), and AuNPs-1 1/1.43 mol/mol (g–i) samples. (a) SEM image illustrating quasi-dome islands. Inset: magnification of a single quasi-dome island. (b) EDP taken from Figure (c) belonging to face-centered cubic (fcc) gold structure (yellow dot arcs) and extra diffraction spots marked by red dot circles. (c) BF-TEM image of gold nanoparticles 2D-network. (d) SEM image illustrating smallest quasi-dome islands. Inset: magnification of void surrounded by AuNPs. (e) EDP taken from Figure (f) belonging to crystalline gold structure (yellow dot arcs) and extra diffraction spots are marked by red circle dots. (f) BF-TEM image of gold nanoparticles 2D-network. (g) SEM image illustrating the surface morphology. Inset: magnification of nano-islands with flat and smooth surface. (h) EDPs taken from Figure (i) belonging to crystalline gold structure (yellow dot arcs) and to crystalline gold sulfide (Au₂S) are marked by red dot arcs. (i) BF-TEM image of gold nanoparticles 2D-network. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cubic space group Pn3m, as reported by Ishikawa et al. [56].

A 2D-network of spatially separated AuNPs is shown in Fig. 5i. Aligned quasi-spherical nanoparticles can be observed (white lines), and dark lines NPs are still evident (blue arrowheads). The morphometric analyses provide an average diameter of 4.05 ± 0.53 nm of the NPs separated by surface-to-surface nearest-neighbor distance at 2.43 ± 0.24 nm similar to the length of the organometallic linker distance. By increasing the thiol/gold molar ratio, the surface morphology of the 2D-networks changes from quasi-dome islands of hundreds of nanometers to a smooth surface. Also, bulk investigations show a slight decrease in size of the nanoparticles followed by an increase in the ordered organization among the interparticle distances (Table SI_2). The behavior of the spatial distribution, related to an increase of the sulfur amount, shows a slight increase in distance followed by an improvement in the mono-dispersity. Therefore, the dimensions of the AuNPs are inversely

proportional to the spatial distribution among the surface-to-surface nearest-neighbor of the distances.

Fig. 6 displays the morpho-structural characterization of the silver nanoparticles bridged by ligand **1**, varying the M/S molar ratio. SEM observations clearly show clusters of **AgNPs-1** 1/1 mol/mol with irregular organizations and high polydispersed in dimension (Fig. 6a, Inset). SAED measurements identified the pure crystalline characters of silver nanoparticles with a face-centered cubic (fcc) structure, (silver dot arcs of Fig. 6b). The corresponding BF-TEM image in Fig. 6c shows large and small silver nanoparticles. High magnification image of a selected region (blue dot square) was acquired (Inset of Fig. 6c), showing silver nanoparticles of irregular or polygonal shape with a dimension of about 10 nm. An improvement in uniformity of the morphological features has been obtained by reaching an Ag/S molar ratio of 1/2 (**AgNPs-1**-1/2 sample). Fig. 6d evidences a smooth surface area with NPs uniformly



Fig. 6. Morphological and structural study of silver nanoparticles self-assembled in a monolayer network of the AgNPs-1 $1/1 \mod/mol$ (a–c), AgNPs-1 $1/2 \mod/mol$ (d–f), and AgNPs-1 $1/0.5 \mod/mol$ (g–i) samples. (a) SEM image illustrating the surface morphology. Inset: magnification of NPs high polydispersed in dimension (blue rectangle). (b) EDP taken from Figure (c) showing distinct diffraction rings corresponding to polycrystalline face-centered cubic (fcc) silver structure (silver dot arcs) and extra diffraction spots are marked by red dot circles. (c) BF-TEM image of silver nanoparticles network. (d) SEM image illustrating the smooth surface. Inset: magnification of single nanoparticles uniformly distributed (blue rectangle). (e) EDP taken from Figure (f) belonging to the previously crystalline silver structure (silver dot arcs) and extra diffraction spots are marked by red dot circles. (f) BF-TEM image of silver nanoparticles 2D-network. (g) SEM image illustrating large NPs surrounded by smallest one. (h) EDP taken from Figure (i) belonging to the previously crystalline silver structure (silver dot arcs) and crystalline silver nanoparticles network. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

distributed (Inset). The electron diffraction pattern of Fig. 6e still exhibits face-centered-cubic (fcc) structure of the silver nanocrystal (silver dot arcs) with very few extra diffraction spots (red dot circles). The BF-TEM image of Fig. 6f shows a self-assembled micro-aggregate with a nano-mosaic shape. Since the NPs are well-separated, it was possible to estimate the surface-to-surface nearest-neighbor distances (2.25 ± 0.28 nm), with an average diameter of 7.33 ± 0.62 nm (Inset). The latest **AgNPs-1**-1/0.5 shows a surface with large nanoparticles surrounded by small ones (Fig. 6g). The image in Fig. 6i still confirms the crystalline silver features (silver dot arcs, Fig. 6h). EDP images show enough extra diffraction spots to determine the presence of a monoclinic Ag₂S crystalline phase with d₀₂₂ = 0.267 nm and d₀₄₁ = 0.166 nm yy [57]. The presence of silver sulfide phase is also evident in Fig. 6i characterized by the bright halo surrounding the surface of the dark silver nanoparticles

with average diameter of about 20 nm. The sulfur amount grew homogeneously on the existing Ag nanocrystals, resulting in core-shell Ag@S of shell thickness of about 5 nm. The silver nanoparticles are also well-aligned like a chain and separated by a distance of about 2.2 nm less than the shell thickness. By comparing the length of 2.4 nm for the ligand and the thickness of the shell (of about 5 nm), it is possible to assume that the Ag@S surface is covered by a first shell of chemisorbed thiol plus a second shell of physisorbed one in agreement with the SR-XPS characterization. The amount of physisorbed/free thiol should be very low respect to the chemisorbed thiol, indeed the S2p spectra show only the spin-orbit component associated to the sulfur atom covalently bonded to the AgNPs surface and not that one associated to the –SH group. NPs are separated by surface-to-surface nearest-neighbor distance of 2.3 nm (Inset in Fig. 6i), similar to the length of the organometallic linker **1**. Similarly, to the growth of the Au organometallic nanoparticles, the increase of the Ag/S molar ratio promote a decreasing size of the AgNPs.

AuNPs and AgNPs stabilized with ligand **2** have been investigated by TEM observations for characterizing their morphology features (Fig. 7). **AuNPs-2**-2/1 sample show well-separated and monodispersed gold nanoparticles of 3.65 ± 0.15 nm (Fig. 7a). Small chains of few nanoparticles can be noticed (white dots ellipse) separated by a distance of 2.65 ± 0.21 nm forming at least dimers of NPs, (Fig. 7b). Different silver nanoparticles show high polydispersity in dimension and in distribution (Fig. 7c). The calculated diameters correspond to 7.35 ± 0.32 nm. Some AgNPs exhibited neighbor-distance distributions 3.05 ± 0.41 with high polydispersity of the distances (Fig. 7d).

4. Conclusions

Two novel bifunctional organometallic thioesters containing Pt(II) centers have been prepared and used for the stabilization of gold and silver nanoparticles in order to obtain interconnected MNPs systems. The chemical physical properties of these materials have been investigated by optical, structural and morphological techniques. The absorption spectra of the gold and silver nanoparticles have shown a broad Plasmon Resonance absorption peak, suggesting the formation of interconnected systems of AuNPs or AgNPs thanks to the bifunctional ligands used. The structural studies carried out by means of the HR-XPS technique have confirmed the presence of the nanoparticle networks; in particular, the S2p spectra acquired for both gold and silver nanoparticles have only highlighted the sulfur component due to the S atoms being bonded on the metal surface in absence of free thiol functionality.

Also, the Au4f or Ag3d spectra have confirmed the functionalization of the metal nanoparticles surface in presence of the Au-S or Ag-S covalent bonds. The morphological evolution of the two different noble metal nanoparticles with the organometallic linker 1, related to the variation of the M/S molar ratio, shows different morphological evolution both in shape and in spatial distribution. Gold samples clearly show notuniformly spaced but monodisperse quasi-spherical shaped nanoparticles, while the mainly polygonal shaped silver nanoparticles are uniformly separated, also forming a nano-mosaic network. Using the ligand 2 to connect the noble metal nanoparticles (gold and silver), we can observe that the monodisperse nanoparticles have a uniform size with a variation of less than 2.5% compared to the synthetized noble metal nanoparticles covalently bridged by ligand 1. In conclusion, stable and monodisperse AuNPs and AgNPs based networks have been obtained. In this way, combining the optical properties of the metal nanoparticles and of the organometallic linkers, new perspectives in optoelectronic and sensing applications can be envisaged.

CRediT authorship contribution statement

Sara Cerra: Investigation, Methodology, Data curation. Laura Fontana: Investigation, Methodology, Data curation. Enrico Rossi: Methodology, Data curation. Mauro Bassetti: Conceptualization, Data curation, Supervision, Writing - original draft, Writing - review & editing. Chiara Battocchio: Investigation, Methodology, Data curation. Iole Venditti: Investigation, Methodology, Data curation. Laura Carlini: Investigation, Methodology, Data curation. Roberto Matassa: Investigation, Methodology, Data curation. Giuseppe Familiari: Investigation, Methodology, Data curation. Ilaria Fratoddi:

Fig. 7. Morphological of gold and silver nanoparticles self-assembled in a monolayer network of the AuNPs-2 2/1 mol/mol (a, b), AgNPs-2 4/1 mol/mol (c, d). (a) BF-TEM image of well-separated gold nanoparticles illustrating small aggregated of closer nanoparticles assembly indicated by white dots ellipse. (b) Magnification area still evidence dimer of AuNPs (c) BF-TEM image of silver nanoparticles network dispersed in a matrix and (d) high magnification area show disordered nanoparticle with poly-dispersed in dimension.



Conceptualization, Data curation, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the University of Rome, Ateneo projects Sapienza, 2019 RM11916B75D8FAF5 and 2017 RM11715C792D1AF3, the European Research Infrastructure EUMINA fab (under the FP7 specific program Capacities, Grant Agreement Number 226460), CNR-DISBA project NutrAge (7022) for financial support and the Advanced Microscopy Laboratory (AML) in CRANN for the provision of their facilities and expertise. The authors are also pleased to thank Ezio Battaglione of the Electron Microscopy Laboratory "Pietro M. Motta", at Sapienza University of Rome, for fruitful discussions and experimental help in TEM measurements. The authors from Roma Tre gratefully knowledge the grant of Excellence Departments, MIUR (ARTICOLO 1, COMMI 314-337 LEGGE 232/2016). We thank HZB for the allocation of synchrotron radiation beamtime; the research leading to SR-XPS results has been supported by the project CALI-PSOplus under the grant agreement no. 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020.

Associated content

Synthetic experimental procedures in the synthesis of compounds **1a,b** and **2a,b**, and spectroscopic characterization. Figures of UV-vis, FT-IR and ¹H-NMR spectra, Table of XPS data and morphometric analysis of NPs

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.120170.

References

- E.E. Elemike, D.C. Onwudiwe, L. Wei, L. Chaogang, Z. Zhiwei, Sol. Energy Mater. Sol. Cells 201 (2019).
- [2] V. Pareek, A. Bhargava, R. Gupta, N. Jain, J. Panwar, Adv. Sci. Eng. Med. 9 (2017) 527–544.
 [3] L. Wang, M. Hasanzadeh Kafshgari, M. Meunier, Adv. Funct. Mater. (2020)
- [5] L. Walig, M. Hasanzaden Kaisngari, M. Meumer, Adv. Funct. Mater. (2020) 2005400.
- [4] Q. Dong, G. Li, C.-L. Ho, M. Faisal, C.-W. Leung, P.W.-T. Pong, K. Liu, B.-Z. Tang, I. Manners, W.-Y. Wong, Adv. Mater. 24 (2012) 1034–1040.
- [5] Z. Meng, G. Li, S.-C. Yiu, N. Zhu, Z.-Q. Yu, C.-W. Leung, I. Manners, W.-Y. Wong, Angew. Chem. Int. Ed. 59 (2020) 11521–11526.
- [6] Z. Wei, D. Wang, Y. Liu, X. Guo, Y. Zhu, Z. Meng, Z.-Q. Yu, W.-Y. Wong, J. Mater. Chem. C 8 (2020) 10774–10780.
- [7] Z. Meng, F. Xiao, Z. Wei, X. Guo, Y. Zhu, Y. Liu, G. Li, Z.-Q. Yu, M. Shao, W.-Y. Wong, Nano Res. 12 (2019) 2954–2959.
- [8] Z. Meng, Z. Wei, K. Fu, L. Lv, Z.-Q. Yu, W.-Y. Wong, J. Organomet. Chem. 892 (2019) 83–88.
- [9] Z. Meng, C.-L. Ho, H.-F. Wong, Z.-Q. Yu, N. Zhu, G. Li, C.-W. Leung, W.-Y. Wong, Sci. China Mater. 62 (2019) 566–576.
- [10] Q. Dong, Z. Meng, C.-L. Ho, H. Guo, W. Yang, I. Manners, L. Xu, W.-Y. Wong, Chem. Soc. Rev. 47 (2018) 4934–4953.
- [11] C.D. De Souza, B.R. Nogueira, M.E.C. Rostelato, J. Alloys Compd. 798 (2019) 714–740.
- [12] M. Grzelczak, J. Pérez-Juste, P. Mulvaney, L.M. Liz-Marzán, Chem. Soc. Rev. 37 (2008) 1783–1791.
- [13] L. Sun, Y.A. Diaz-Fernandez, T.A. Gschneidtner, F. Westerlund, S. Lara-Avila, K. M. Poulsen, Chem. Soc. Rev. 43 (2014) 7378–7741.

- [14] S.K. Ghosh, T. Pal, Chem. Rev. 107 (2007) 4797-4862.
- [15] M.A. Squillaci, M.A. Stoeckel, P. Samorì, Nanoscale 11 (2019) 19319–19326.
- [16] I. Venditti, G. Testa, F. Sciubba, L. Carlini, F. Porcaro, C. Meneghini, S. Mobilio, C. Battocchio, I. Fratoddi, J. Phys. Chem. C 121 (2017) 8002–8013, and references therein.
- [17] I. Hussain, M. Brust, J. Barauskas, A.I. Cooper, Langmuir 25 (2009) 1934–1939.
- [18] C.-L. Ho, Z.-Q. Yu, W. Wong, Coord. Chem. Rev. 45 (2016) 5264–5295.
- [19] A. Haque, R.A. Al-Balushi, I.J. Al-Busaidi, M.S. Khan, P.R. Raithby, Chem. Rev. 118 (2018) 8474–8597.
- [20] C.-L. Ho, W.-Y. Wong, Coord. Chem. Rev. 257 (2013) 1614–1649.
- [21] L. Xu, C.-L. Ho, L. Liu, W.-Y. Wong, Coord. Chem. Rev. 373 (2018) 233–257.
 [22] A. Haque, L. Xu, R.A. Al-Balushi, M.K. Al-Suti, R. Ilmi, Z. Guo, M.S. Khan, W.-
- Y. Wong, P.R. Raithby, Chem. Soc. Rev. 48 (2019) 5547–5563. [23] W.-Y. Wong, C.-L. Ho, Acc. Chem. Res. 43 (2010) 1246–1256.
- [24] Z. Yang, S. Pedireddy, H.K. Lee, Y. Liu, W.W. Tjiu, I.Y. Phang, X.Y. Ling, Chem. Mater. 28 (2016) 5080–5086.
- [25] C. Battocchio, I. Fratoddi, L. Fontana, E. Bodo, F. Porcaro, C. Meneghini, I. Pis, S. Nappini, S. Mobilio, M.V. Russo, G. Polzonetti, Phys. Chem. Chem. Phys. 16 (2014) 11719–11728.
- [26] M. Quintiliani, M. Bassetti, C. Pasquini, C. Battocchio, M. Rossi, F. Mura, R. Matassa, L. Fontana, M.V. Russo, I. Fratoddi, J. Mat. Chem. C 2 (2014) 2517–2527.
- [27] I. Fratoddi, R. Matassa, L. Fontana, I. Venditti, G. Familiari, C. Battocchio, E. Magnano, S. Nappini, G. Leahu, A. Belardini, R. Li Voti, C. Sibilia, J. Phys. Chem. C 121 (2017) 18110–18119.
- [28] A. Bearzotti, P. Papa, A. Macagnano, E. Zampetti, I. Venditti, R. Fioravanti, L. Fontana, R. Matassa, G. Familiari, I. Fratoddi, J. Environ. Chem. Eng. 6 (2018) 4706–4713.
- [29] C. Quintana, M.P. Cifuentes, M.G. Humphrey, Chem. Soc. Rev. 49 (2020) 2316–2341.
- [30] Q. Wang, W.-Y. Wong, Polym. Chem. 2 (2011) 432–440.
- [31] Q. Liu, N. Zhu, C.-L. Ho, Y. Fu, W.-S. Lau, Z. Xie, L. Wang, W.Y. Wong, J. Organomet. Chem. 812 (2016) 2–12.
- [32] H. Zhan, S. Lamare, A. Ng, T. Kenny, H. Guernon, W.-K. Chan, A.B. Djurišić, P. D. Harvey, W.Y. Wong, Macromolecules 44 (2011) 5155–5167.
- [33] G.B. Kauffman, L.A. Teter, J.E. Huheey, Inorg. Synth. 7 (1963) 245-249.
- [34] M. Linseis, S. Zalis, M. Zabel, R.F. Winter, J. Am. Chem. Soc. 134 (2012) 16671–16692.
- [35] E. Kraleva, M.L. Saladino, R. Matassa, E. Caponetti, S. Enzo, A. Spojakina, J. Struct. Chem. 52 (2011) 330–339.
- [36] J.M. Scofield, J. Electron Spectr. Relat. Phenom. 8 (1976) 129-134.
- [37] D.A. Shirley, Phys. Rev. B 5 (1972) 4709-4714.
- [38] C. Battocchio, F. D'Acapito, I. Fratoddi, A. La Groia, G. Polzonetti, G. Roviello, M. V. Russo, Chem. Phys. 328 (2006) 269–274.
- [39] S.F. Parker, K. Refson, R.D. Bennett, J. Best, M.Y. Melnikov, J.A. Weinstein, Inorg. Chem. 51 (2012) 9748–9756.
- [40] I. Fratoddi, C. Battocchio, A. La Groia, M.V. Russo, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 3311–3329.
- [41] K. Nakamoto, J. Fujita, R.A. Condrate, Y. Morimoto, J. Chem. Phys. 39 (1963) 423–427.
- [42] I.R. Moraes, M. Weber, F.C. Nart, Electrochim. Acta 42 (1997) 617–625.
- [43] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R.J. Whyman, Chem. Soc., Chem. Commun. (1994) 801–802.
- [44] A. Uehara, S.G. Booth, S.Y. Chang, S.L.M. Schroeder, T. Imai, T. Hashimoto, J.F. W. Mosselmans, R.A.W. Dryfe, J. Am. Chem. Soc. 137 (2015) 15135–15144.
- [45] S. Iimura, K. Manabe, S. Kobayashi, Org. Lett. 5 (2003) 101–103.
- [46] S.F. Sweeney, G.H. Woehrle, J.E. Hutchison, J. Am. Chem. Soc. 128 (2006) 3190–3197.
- [47] M.R. Langille, M.L. Personick, C.A. Mirkin, Angew. Chem. Int. Ed. 52 (2013) 13910–13940.
- [48] A. Zuber, M. Purdey, E. Schartner, C. Forbes, B. van der Hoek, D. Giles, A. Abell, T. Monro, H. Ebendorff-Heidepriem, Sens. Actuators, B: Chem. 227 (2016) 117–127.
- [49] V. Amendola, O.M. Bakr, F. Stellacci, Plasmonic 5 (2010) 85-97.
- [50] I. Fratoddi, C. Battocchio, A. Furlani, P. Mataloni, G. Polzonetti, M.V. Russo, J. Organomet. Chem. 674 (2003) 10–23.
- [51] C. Battocchio, F. Porcaro, S. Mukherjee, E. Magnano, S. Nappini, I. Fratoddi, M. Quintiliani, M.V. Russo, G. Polzonetti, J. Phys. Chem. C 118 (2014) 8159–8168.
- [52] C. Battocchio, I. Fratoddi, M.V. Russo, G. Polzonetti, Chem. Phys. Lett. 400 (2004) 290–295.
- [53] C. Battocchio, I. Fratoddi, M.V. Russo, V. Carravetta, S. Monti, G. Iucci, F. Borgatti, G. Polzonetti, Surf. Sci. 601 (2007) 3943–3947.
- [54] I. Fratoddi, I. Venditti, C. Battocchio, G. Polzonetti, F. Bondino, M. Malvestuto, E. Piscopiello, L. Tapfer, M.V. Russo, J. Phys. Chem. C 115 (2011) 15198–15204.
- [55] R. Matassa, M. Carbone, I. Fratoddi, R. Caminiti, J. Phys. Chem. B 114 (2010) 2359–2364.
- [56] K. Ishikawa, T. Isonaga, S. Wakita, Y. Suzuki, Solid State Ion. 79 (1995) 60–66.
- [57] R. Matassa, S. Orlanducci, G. Reina, M.C. Cassani, D. Passero, M.L. Terranova, Sci. Rep. Nat. Publ. Group (2016) 31163.