Rational size control of gold nanoparticles employing an organometallic precursor [Au-C \equiv C- *t*-Bu]₄ and tunable thiolate-functionalized ionic liquids in organic medium

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Abstract: Gold nanoparticles (Au NPs) stabilized with six different thiolate-functionalized ionic liquids (TFILs) were synthesized in an organic solvent. The size and optical properties of the TFIL-stabilized Au NPs can be rationally controlled by altering the *N*-alkyl chain length and (or) the counteranion of the TFIL-stabilizing ligand. Au NPs were prepared from the reduction of a gold precursor (HAuCl₄ or [Au-C \equiv C-*t*-Bu]₄) employing NaBH₄ in the presence of the different disulfide precursors. A model, based on Israelachvili theory, is proposed to account for the dependence of NP size on the *N*-alkyl chain length and the counteranion of the surfactantlike TFIL stabilizers.

Key words: gold nanoparticles, functionalized ionic liquids, gold(I) complexes, surface plasmon band, imidazolium salts.

Résumé : Des nanoparticules d'or (NPAu) stabilisées par six ioniques liquides fonctionnalisés par un thiolate (ILFT) ont été synthétisées dans un solvant organique. La taille et les propriétés optiques de ces NPAu stabilisées par des ILFT peuvent être contrôlées rationnellement en modifiant la longueur de la chaine *N*-alkyle et (ou) le contre-anion du ILFT. Les NPAu ont été préparées par réduction d'un précurseur d'or, HAuCl₄ ou [Au-C=C-t-Bu]₄, à l'aide de NaBH₄, en présence de chacun des six précurseurs de disulfure. Un modèle, basé sur la théorie de Israelachvili, est avancé pour rendre compte de la relation entre la taille des NPAu et la longueur de la chaine *N*-alkyle et la taille du contre-anion du ILFT, qui agit comme stabilisant de la NP et surfactant.

Mots-clés : nanoparticules d'or, liquides ioniques fonctionnels, complexe d'or(I), bande plasmon de surface, sels d'imidazo-lium.

Introduction

Gold nanoparticles (Au NPs) are subject to intensive research because of their application in optical sensing,¹ surface-enhanced Raman spectroscopy,² and catalysis.^{3,4} Optical¹ and catalytic⁴ properties are governed by various factors including, among others, the size and shape of the NPs and the nature of the stabilizing ligand. Correlations between NP size and the properties of NPs are challenging to establish as different ligands are most often employed to achieve variance in the NP size,⁵ which alter not only the size but also the electronics of the metal core. To establish such a relationship, it would be desirable to develop a family of stabilizing ligands, employed under identical reaction conditions,^{6,7} that can control particle size. To reach this goal, we synthesized Au NPs of tunable size using the same class of ligand, thiolate-functionalized ionic liquids (TFILs), based on an imidazolium structure. This class of Au NP ligand was first proposed by Itoh et al.8 and used for anion sensing. They were chosen here as (i) TFILs provide both electrostatic and covalent stabilization to metal NPs increasing their longterm stability^{9–11} and (*ii*) alterations to the TFIL structure can be accomplished that do not involve changing the metalbinding moiety (i.e., N-alkyl chain length or counteranion), and thus preserve the electronic nature of the NP. Kim et al.¹² previously employed TFILs in the synthesis of Au and Pt NPs and demonstrated that the position and number of thiol moieties present in either the cation or anion of the TFIL ligands impacted the size of the Au and Pt NPs. Such ligand alterations dramatically influence both the electronic properties of the metal core and the organization of the ligand sphere, parameters that are proposed to remain constant in this study. Recent reports on Au NP synthesis have featured novel gold precursors (e.g., AuX (for X = Cl or Br),¹³ [AuN(SiMe₃)₂]₄,¹⁴ and $[NMe_4][Au(CF_3)_2]^{15}$ in an effort to complement the well-established methodologies based on HAuCl416 and to provide insight into the Au NP formation mechanism.¹⁷ $[AuN(SiMe_3)_2]_4$ and $[NMe_4][Au(CF_3)_2]$ are interesting precursors as they eliminate the presence of halides in the reaction mixture, which have been shown to affect the properties of NPs.18 For instance, a recent DFT study by Janiak and coworkers¹⁹ demonstrated that the interaction between chloride anions and Au clusters possesses a large binding energy and thus Cl- will play a role in stabilizing Au NPs if present in

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the synthetic mixture. Furthermore, in the context of IL chemistry, it was even more important to select a metal precursor that does not produce any ionic by-products that can undergo ion exchange with either of the IL ions.

Recently, the groups of Roucoux,²⁰ Hou,²¹ and Dyson²² studied the influence of various structural parameters of functionalized ionic liquid (FIL)-stabilized Rh and Pd NPs. Specifically, the concept of "supramolecular" arrangement of FILs at the surface of stabilized NPs was explored and evoked to rationalize such NP properties as catalytic activity.

Herein, we propose the use of a family of disulfide TFIL precursors 1-6 (Scheme 1) in the formation of stable Au NPs with control of the NP size (Scheme 2) by reduction of gold precursors using NaBH₄. The TFILs act as surfactants, which stabilize the NPs through the anchoring of the thiol moiety to the metal surface. We also introduce a model to rationalize this control and study the impact of the ligands 1-6onto the optical properties of the synthesized Au NPs. We also introduced a novel organometallic Au NP precursor, [Au-C=C-t-Bu]4,23 to avoid the presence of halides during the NP synthesis and compared its performance with the more commonly used halide-based precursor, HAuCl₄. $[Au-C \equiv C-t-Bu]_4$ is expected to decompose under reducing conditions into Au(0) and volatile organic by-products, thus leaving the NP surface and the IL free of unwanted contaminants. Overall, our study suggests that FILs can act as surfactants to stabilize metal NPs and exert some level of size control over the final NP size.

Results and discussion

Synthesis of TFILs

Compounds 1-6 are characterized by four parameters: (1) a thiolate function that binds to the Au particle, (2) an imidazolium unit, (3) an alkyl chain playing the role of spacer between the metal binding and imidazolium moiety, and (4) a counteranion (Scheme 2). In this study we altered both components (3) and (4) to impact the size of the particle while preserving (1) and (2) to have constant electronic and molecular structure, respectively. The procedure employed for the synthesis of 1-6 was adapted from that reported by Itoh et al.⁸ (R₁ = H, n = 5, and X = Cl⁻; Scheme 1) to prepare a series of TFIL precursors having differing N-alkyl chains (n =5, 8, and 10) and counteranions $(X^- = -OTf \text{ and } -NTf_2)$ (Scheme 3). Synthesis of the disulfide precursors 1-6 was achieved through the quaternization of ω -bromodisulfides with 1,2-dimethylimidazole, followed by an ion exchange of Br- with either -OTf or -NTf2. 1,2-Dimethylimidazole was selected here instead of 1-methylimidazole, to ensure the stabilization of the NPs was provided solely by the TFILs 1-6. NPs stabilized by 1-alkyl-3-methylimidazolium ILs may involve the formation of N-heterocyclic carbenes, which primarily occur at the C2 position on the imidazolium ring.²⁴⁻²⁶ Thus, TFILs based on the 1-alkyl-2,3-dimethylimidazolium moiety were employed in this study to restrict the formation of carbene stabilizing species. Furthermore, ion exchange of Br- to form disulfides 1-6 prior to NP synthesis allows for a better control of the properties of both the TFIL stabilizers and the resulting Au NPs. This contrasts with the work of Itoh et al.8 as anion exchange was performed directly on the Au NPs. Their technique led Scheme 1. Ionic liquid disulfides 1–6 employed as precursors in the synthesis of thiolate-stabilized gold nanoparticles.⁸



$$\begin{array}{l} {\sf R}_1 = {\sf H}; \ {\sf X} = {\sf CI}; \ n = 5 \ ({\sf Itoh \ et \ al. \ precursor}) \\ {\sf R}_1 = {\sf CH}_3; \ {\sf X} = {}^\circ {\sf OSO}_2 {\sf CF}_3 \ ({}^\circ {\sf OTf}); \ n = 5 \ ({\sf 1}), \ n = 8 \ ({\sf 2}), \ n = 10 \ ({\sf 3}) \\ {\sf R}_1 = {\sf CH}_3; \ {\sf X} = {}^\circ {\sf N} ({\sf SO}_2 {\sf CF}_3)_2 \ ({}^\circ {\sf NTf}_2); \ n = 5 \ ({\sf 4}), \ n = 8 \ ({\sf 5}), \ n = 10 \ ({\sf 6}) \end{array}$$

Scheme 2. Synthesis of thiolate-stabilized gold nanoparticles.



to the development of a useful anion sensor; however, the extent of the full counteranion replacement within the NP ligand sphere, as well as the anion's impact during the synthesis of the NPs, was not determined. The present work used TFIL precursors composed of a known counterion and explored their influence on the properties of the resulting Au NPs.

Nanoparticle synthesis and characterization

Synthesis of Au NPs was achieved by combining an organic solution of an Au precursor (HAuCl₄ or [Au-C=C-t-Bu]₄, 0.100 and 0.025 mmol, respectively) with a methanol solution of one of disulfides 1-6 (0.20 mmol) and reducing the mixture with $NaBH_4$ (Scheme 2). The solution instantly changed colour from pale yellow to purple, indicating the formation of Au NPs. TEM analysis of the reaction mixtures showed the presence of well-dispersed Au NPs having mean diameters ranging from 3.0 to 4.3 nm depending on nand X^{-} (Fig. 1 and Table 1; see the Supplementary data for size and distribution data, Figs. S1 and S2). X-ray photoelectron spectrometry (XPS) analysis of the Au NPs (for HAuCl₄ and disulfide 1) indicated the presence of gold, sulfur, carbon, nitrogen, oxygen, and fluorine, which signified the TFIL stabilization of the NPs (Supplementary data Figs. S3–S7). The S2 $p_{(3/2)}$ binding energies (BEs) for disulfide 1 and the corresponding stabilized Au NPs are 163.7 and 162.3 eV respectively; a shift (-1.4 eV) that was in agreement with the binding of the thiolate functionality to the surface of the Au NPs.²⁷ Additional evidence for the presence of an Au–S bond was provided by the BEs of Au $(4f_{(7/2)} =$ 84.0 eV and $4f_{(5/2)} = 87.7$ eV).^{27,28} The Au:disulfide ratio was optimal at 1:2, affording small and well-dispersed NPs, whereas a smaller ratio (1:1) formed large Au aggregates and a larger ratio (1:4) produced clusters of small Au NPs that were not monodispersed. This ratio (1:2) was kept constant in all of the subsequent studies.

Size analysis and supporting model

The nature of the disulfide precursor, in terms of n and X⁻, was found to influence the size of the Au NPs synthesized from $[Au-C=C-t-Bu]_4$ (Table 1, entries 1–6). These results showed an increase in the NP size with an increase in the length of the *N*-alkyl chain (*n*) and a decrease in the NP size with an increase in the molecular volume of the counteranion

Scheme 3. Synthetic pathway for the preparation of disulfide ionic liquids 1–6 (for n = 5, 8, and 10 and $X^- = -OTf$ and $-NTf_2$).



Fig. 1. Transmission electron micrograph of thiolate-stabilized gold nanoparticles, employing $[Au-C \equiv C-t-Bu]_4$ and disulfide 6.



 (X^{-}) . The dependence of *n* and X^{-} on the size of the Au NPs can be justified by adapting the geometric theory proposed by Israelachvili²⁹ for the formation of spherical micelles (Scheme 4). This theory was adapted because of the intrinsic surfactant nature of the TFILs and their ability to bind strongly to the Au surface through their thiolate functionality. For a conventional micelle, (Scheme 4A) the radius (R) of a spherical micelle is dependent on the properties of the surfactant molecule such that $R = 3v/a_0$, where v is the volume of the hydrocarbon chain and a_0 is the area of the headgroup. This relationship can be extended to the formation of spherical NPs stabilized by TFILs **1–6** such that $R \propto v/a_0$, where R is now the radius of the structure containing the particle and the ligand shell, v is the volume of the hydrocarbon chain, including the thiolate moiety, and a_0 is the area of the imidazolium headgroup, including both the cation and the anion (Scheme 4B). According to this relationship, an increase in nwould increase v, thus increase R, and ultimately the NP size. The TEM data obtained for Au NPs stabilized by thiolate ligands 1-6 (Table 1, entries 1-6) showed an increase in NP size when comparing n = 5, 8, and 10. In terms of the influence of X⁻, this relationship predicts that an increase in a_0 would decrease the diameter of the NP. The molecular volume of the counteranions employed here are 0.131 and 0.232 nm³ for \neg OTf and \neg NTf₂, respectively.³⁰ Therefore, the larger \neg NTf₂ anion would increase a_0 and thus decrease the NP size. A comparison of the TEM data for thiolate-stabilized NPs with \neg OTf (Table 1, entries 1–3) and \neg NTf₂ (Table 1, entries 4–6) counteranions showed a consistently smaller size for the \neg NTf₂ species.

The relationship between NP size and the TFIL counteranion was investigated already by Janiak and co-workers³⁰⁻³² in metal NPs synthesized directly in IL solvents. In their system, the relationship is opposite to what we observe, with an increase in NP diameter when the molecular volume of the anion was increased. Their results provided evidence that the NPs were stabilized by a classical electric double layer where anionic species stabilize the metal surface and thus govern the size of the NPs.30 For our system, the size variation trends observed and the XPS measurements are both consistent with a covalent binding of the thiolate to the metal surface (as suggested by Itoh et al.⁸ and shown in Scheme 2) and a global arrangement where the IL anion and cation pair are localized at the periphery of the ligand shell. These results, and especially the compliance to the Israelachvili model, suggest that there is a high level of organisation in the ligand shell resulting from the surfactant nature of the TFIL stabilizers. This is in accordance to what is expected from both imidazolium moieties³³ through electrostatic interactions and the N-alkyl chains through van der Waals interactions; the later being a similar phenomenon to that observed in the formation of self-assembled monolayers (SAMs) of long-chain alkanethiol on Au NPs.34

Influence of the gold precursor

Au NPs synthesized from $[Au-C \equiv C-t-Bu]_4$ were compared with NPs prepared employing HAuCl₄. [Au-C \equiv C-t-Bu]₄²³ is expected to decompose under reducing conditions to Au(0)and volatile organic by-products. TEM analysis of the thiolate-stabilized Au NPs showed well-dispersed NPs for the syntheses with either precursor, although slightly larger NPs were obtained from HAuCl₄ (Table 1, entries 7-12) compared with those from $[Au-C \equiv C-t-Bu]_4$ (Table 1, entries 1–6). This difference was attributed to the presence of Cl- ions in the Au precursor, which may exchange with the counteranion of the TFIL stabilizer. According to our proposed model (Scheme 3), exchange of either -OTf or -NTf₂ with the smaller Cl⁻ species would decrease a_0 and increase the size of the resulting Au NPs. It was also observed that the trend between NP size and the properties of the disulfide ligand (*n* and X^{-}) were not as clear for particles synthesized from HAuCl₄. This discrepancy was most pronounced when 148

Table 1. Influence of the gold and disulfide precursors on the size and size distribution of thiolate-stabilized gold nanoparticles (Au NPs).

		Stabilizing ligand			Au NP size
Entry	Au precursor	Disulfide	п	X-	(nm) (standard deviation σ) ^{<i>a</i>}
1	[Au-C≡C- <i>t</i> -Bu] ₄	1	5	⁻ OTf	2.9(±0.6)
2		2	8	⁻ OTf	$3.2(\pm 0.6)$
3		3	10	⁻ OTf	3.3(±0.6)
4		4	5	⁻ NTf ₂	$2.7(\pm 0.5)$
5		5	8	⁻ NTf ₂	$2.9(\pm 0.4)$
6		6	10	⁻ NTf ₂	$3.2(\pm 0.6)$
7	HAuCl ₄	1	5	[–] OTf	3.3(±0.6)
8		2	8	[–] OTf	$4.2(\pm 0.7)$
9		3	10	⁻ OTf	4.3(±0.7)
10		4	5	⁻ NTf ₂	3.0(±0.4)
11		5	8	⁻ NTf ₂	3.0(±0.3)
12		6	10	⁻ NTf ₂	3.1(±0.5)

Note: Reaction conditions: [Au] = 0.1 mmol, disulfide = 0.2 mmol (2 equiv), NaBH₄ = 1.0 mmol (10 equiv), solvent = CH₃OH (for HAuCl₄), CH₃OH–CH₂Cl₂ (3:2, for

 $[Au-C\equiv C-t-Bu]_4).$

^aDetermined by TEM, measurement of >200 spherical particles.

comparing disulfides **2** (4.2 nm) to **3** (4.3 nm) (Table 1, entries 8 and 9) and **4** (3.0 nm) to **5** (3.0 nm) (Table 1, entries 10 and 11) as very little difference in size was observed for these NPs. The lack of correlation within the HAuCl₄ data was again accredited to anion exchange of the TFIL anion and thus emphasizes the importance of having well-defined systems in the synthesis of nanomaterials, including the use of halide-free metal precursors such as $[Au-C\equiv C-t-Bu]_4$.

Optical properties analysis

The optical properties of the synthesized Au NPs were analyzed using UV-vis spectroscopy. A surface plasmon band (SPB) was observed for Au NPs stabilized by TFILs 1-6 $(\lambda_{max}(MeOH) = 535-650 \text{ nm})$ and was dependent on the nature of the thiolate employed (Fig. 2). The length of the alkyl chain was observed to influence the SPB as the longer chain thiolates, n = 8 and 10 (Fig. 2, curves b, c, e, and f), showed λ_{max} = 535 nm, whereas Au NPs synthesized from the shorter chain disulfides, n = 5 (Fig. 2, curves a and d), caused the λ_{max} to red shift to >535 nm. For TFIL 1 and 4 (n = 5) stabilized NPs, the distance between the particle surface and the IL environment is smaller than in the case of the longer chain TFIL-stabilized NPs. This shorter distance resulted in the NP perceiving a more polar environment and thus a globally higher dielectric medium at its surrounding. The theory predicts that the position of the SPB shifts toward the lower energy region as the surrounding medium refractive index increases,1,35 which is consistent with the observed trend. A shorter chain disulfide (n = 2) was desired to further test this hypothesis; however, the synthesis of this disulfide could not be achieved. Aggregation of the NPs in solution could also be envisaged as the cause of this shift, in which case a red-shift is expected when the mean distance between particles decreases;^{1,36} however, the TEM images obtained for all NPs are not consistent with significant aggregation in solution (Supplementary data Figs. S1 and S3). These results **Scheme 4.** Schematic representation of (A) the size dependence of micelles on surfactant properties and (B) the size dependence of gold nanoparticles (Au NPs) on thiolate-functionalized ionic liquids (TFIL) properties.²⁹

(A) Formation of Spherical Micelles: $R = 3_v/a_0$



(B) Formation of Thiolate Stabilized Au NPs: R α v/a₀



are supporting the idea that TFILs organize around the particle. Indeed, in the case of the longest alkyl spacers (n = 8and 10), the respective blue-shift observed proves that the alkyl portion of the TFIL resides close to the surface of the particle, whereas the imidazolium cation and anion are maintained at the periphery of the ligand sphere. Moreover, the results obtained for n = 8 and 10 are virtually identical. This can be explained by the fact that changes happening far from the surface will not impact the perceived dielectric medium of the particle significantly. When the alkyl spacer is short (n = 5), the dielectric medium perceived by the Au NP is altered by the presence of the imidazolium cation and anion.

Conclusions

In conclusion, this report has outlined the synthesis of stable, well-dispersed Au NPs employing an organometallic Au precursor $[Au-C \equiv C-t-Bu]_4$ and TFIL stabilizers in a molecular solvent. This halogen-free Au complex allowed for the recognition of a relationship between the properties of the Au NPs, in terms of NP size and SPB, and two properties of the thiolate-stabilizing ligand, namely the length of the N-alkyl chain and the counteranion. A model, based on Israelachvili theory, was employed to explain the correlation between the size of Au NPs and the properties of the thiolate ligands. This model and XPS data evidenced a high level of organization inside these NPs where the TFILs interact with the particle surface through their thiolate functionalities. Functionalized ionic liquids act as surfactants for the synthesis of metal NPs with controlled properties leading to a novel bottomup approach to the design of functional nanomaterials, as well as models to measure the influence of small size changes on the properties of NPs. Furthermore, $[Au-C \equiv C-t-Bu]_4$ has been shown to be an effective precursor in the synthesis of NPs featuring increased compositional purity and opens new opportunities for gaining an understanding in the role various stabilizing ligands play in the formation of Au NPs.

Experimental section

General remarks

All syntheses of ILs and NPs were carried out under an argon atmosphere employing Schlenk techniques. 6-Mercapto-1-hexanol,^{37,38} 9-mercapto-1-nonanol,^{37,39,40} 11-mercapto-1undecanol,^{37,41,42} bis(6-hydroxyhexyl)disulfide,⁴¹ bis(11hydroxyundecyl)disulfide,^{37,41} bis(6-bromohexyl)disulfide,^{42,43} and $[Au-C \equiv C-t-Bu]_4^{23,44}$ were prepared following known literature procedures. Tetrahydrofuran (distillation over Na and benzophenone) and acetonitrile (dried over 4 Å molecular sieves) were purified prior to use. All other chemicals and solvents were purchased from commercial sources and used without further purification. Melting points (mp) were determined on a Gallenkamp melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Varian Mercury spectrometer. Mass spectra (MS) were recorded in positive electrospray mode with an IonSpec 7.0 tesla FTMS (IonSpec Corp., Lake Forest, California). TEM was performed on a Phillips CM 200 microscope. UVvis spectra were recorded on a Jasco V-660 spectrophotometer. XPS was performed on a VG ESCALAB 3 MKII spectrometer (VG, Thermo Electron Corporation, UK) equipped with an Mg Ka source.

Synthesis of TFILs

The synthesis of disulfide ILs 1-6 followed a similar pathway to that reported by Itoh et al. (Scheme 1).⁸ The synthesis and characterization data for all novel compounds are reported.

Bis(9-hydroxynonyl)disulfide

9-Mercapto-1-nonanol (7.81 g, 58.2 mmol) was dissolved in 12 mL MeOH and titrated with 0.5 mol/L methanolic iodine until the reaction turned from colourless to a persistent yellow colour. The mixture was allowed to stir at room temperature (rt) for 1 h. The reaction was quenched with 10% **Fig. 2.** UV–vis spectra of λ_{\max} (MeOH) for gold nanoparticles (Au NPs) synthesized employing (A) HAuCl₄ and (B) [Au-C \equiv C-*t*-Bu]₄ as gold precursors stabilized by thiolates (a) n = 5, $X^- = -OTf$; (b) n = 8, $X^- = -OTf$; (c) n = 10, $X^- = -OTf$; (d) n = 5, $X^- = -NTf_2$; (e) n = 8, $X^- = -NTf_2$; and (f) n = 10, $X^- = -NTf_2$.



NaHSO₃(aq) and extracted with CH₂Cl₂ (3 × 50 mL). The organic phase was washed with 10% NaHSO₃(aq) and H₂O and dried over MgSO₄. The solvent was removed and the product was dried in vacuo to yield a white solid. Yield: 7.09 g (92%); mp 65–66 °C. ¹H NMR (300 MHz, CDCl₃, ppm) &: 3.61(t, J = 6.2 Hz, 4H), 2.65 (t, J = 7.3 Hz, 4H), 1.64–1.28 (m, 30H). ¹³C NMR (75.5 MHz, CDCl₃, ppm) &: 63.2, 39.4, 33.0, 29.7, 29.6, 29.4, 29.4, 28.7, 25.9. MS (ESI+) m/z: 351.2386 (M⁺ = [C₁₈H₃₉O₂S₂]⁺ requires 351.2385).

Bis(9-bromononyl)disulfide

Bis(9-hydroxynonyl)disulfide (3.55 g, 10.1 mmol) and PPh₃ (5.56 g, 21.2 mmol) were dissolved in 100 mL of distilled THF under an argon atmosphere. NBS (4.50 g, 25.3 mmol) was added in portions over 30 min. The mixture was stirred at rt for 1 h then heated to 50 °C for 18 h. The solvent volume was reduced, EtO₂ was added, and the mixture was cooled for 30 min to cause the precipitation of white solids. Upon filtration and solvent evaporation, the crude mixture was purified on silica employing EtOAc–hexanes. Bis(9-bromononyl)disulfide was obtained as a colourless liquid. Yield: 3.56 g (74%). ¹H NMR (300 MHz, CDCl₃, ppm) δ : 3.38 (t, *J* = 6.8 Hz, 4H), 2.65 (t, *J* = 7.4 Hz, 4H), 1.82 (pentet, *J* = 7.4 Hz, 4H), 1.64 (pentet, *J* = 7.1 Hz, 4H),

1.46–1.22 (m, 20H). ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ: 39.3, 34.2, 33.0, 29.7, 29.3, 29.3, 28.9, 28.6, 28.3.

Bis(11-bromoundecyl)disulfide

Bis(11-bromoundecyl)disulfide was obtained as a white solid. Yield: 2.93 g (52%). ¹H NMR (300 MHz, CDCl₃, ppm) δ : 3.39 (t, J = 6.9 Hz, 4H), 2.66 (t, J = 7.5 Hz, 4H), 1.83 (pentet, J = 7.2 Hz, 4H), 1.65 (pentet, J = 7.2 Hz, 4H), 1.45–1.21 (m, 28H). ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ : 39.4, 34.3, 33.0, 29.7, 29.7, 29.6, 29.4, 29.4, 29.0, 28.7, 28.4.

Disulfide 1

1,2-Dimethylimidazole (1.37 g, 14.3 mmol) was dissolved in 10 mL of MeCN. Bis(6-bromohexyl)disulfide (2.74 g, 6.99 mmol) was added and the mixture was stirred at 70 °C for 48 h. The solvent was removed in vacuo and the residual solid was washed with Et₂O (3 \times 20 mL). Lithium trifluoromethanesulfonate (2.23 g, 14.3 mmol) was added in small portions to a solution of the crude product in 15 mL of H₂O. The mixture was stirred at rt for 1 h and 25 mL of CH₂Cl₂ was added. The organic phase was washed with H₂O and dried over MgSO₄. The solvent was removed and the product was dried in vacuo to yield a white solid. Yield: 3.63 g (72%); mp 104–106 °C. ¹H NMR (300 MHz, (CD₃)₂CO, ppm) δ : 7.65 (d, J = 2.0 Hz, 2H), 7.60 (d, J = 2.0 Hz, 2H), 4.28 (t, J = 7.5 Hz, 4H), 3.93 (s, 6H), 2.77 (s, 6H), 2.70 (t, J = 7.5 Hz, 4H), 1.88 (pentet, J = 7.5 Hz, 4H), 1.68 (pentet, J = 7.5 Hz, 4H), 1.52–1.28 (m, 8H). ¹³C NMR $(75.5 \text{ MHz}, (\text{CD}_3)_2\text{CO}, \text{ppm}) \delta$: 145.6, 123.4, 122.3 (q, $J_{\text{CF}} =$ 322.1 Hz), 122.0, 49.0, 38.9, 35.5, 30.4, 29.6, 28.5, 26.4, 9.8. MS (ESI⁺) m/z: 212.1342 (M²⁺ = [C₂₂H₄₀N₄S₂]²⁺ requires 212.1344).

Disulfide 2

The product was obtained as an amber oil. Yield: 3.19 g (80%). ¹H NMR (300 MHz, (CD₃)₂CO, ppm) δ : 7.65 (d, J = 2.0 Hz, 2H), 7.60 (d, J = 2.1 Hz, 2H), 4.27 (t, J = 7.5 Hz, 4H), 3.92 (s, 6H), 2.76 (s, 6H), 2.70 (t, J = 7.5 Hz, 4H), 1.86 (pentet, J = 7.5 Hz, 4H), 1.66 (pentet, J = 7.5 Hz, 4H), 1.48–1.25 (m, 20H). ¹³C NMR (75.5 MHz, (CD₃)₂CO, ppm) δ : 145.6, 123.4, 122.3 (q, $J_{CF} = 322.1$ Hz), 121.9, 49.0, 39.3, 35.5, 30.5, 30.0, 29.8, 29.8, 29.7, 29.0, 26.8, 9.8. MS (ESI⁺) m/z: 254.1811 (M²⁺ = [C₂₈H₅₂N₄S₂]²⁺ requires 254.1809).

Disulfide 3

The product was obtained as an amber oil. Yield: 2.20 g (79%). ¹H NMR (300 MHz, (CD₃)₂CO, ppm) δ : 7.64 (d, J = 2.0 Hz, 2H), 7.61 (d, J = 2.0 Hz, 2H), 4.28 (t, J = 7.5 Hz, 4H), 3.93 (s, 6H), 2.77 (s, 6H), 2.71 (t, J = 7.5 Hz, 4H), 1.87 (pentet, J = 7.2 Hz, 4H), 1.67 (pentet, J = 7.2 Hz, 4H), 1.45–1.25 (m, 28H). ¹³C NMR (75.5 MHz, (CD₃)₂CO, ppm) δ : 145.6, 123.4, 122.3 (q, $J_{CF} = 322.1$ Hz), 121.9, 49.1, 39.3, 35.5, 30.5, 30.2, 30.2, 30.2, 29.8, 29.8, 29.1, 26.9, 9.8. MS (ESI⁺) m/z: 282.2124 (M²⁺ = [C₃₂H₆₀N₄S₂]²⁺ requires 282.2128).

Disulfide 4

The product was obtained as an amber oil. Yield: 2.91 g (90%). ¹H NMR (300 MHz, (CD₃)₂CO, ppm) δ : 7.60 (d, J = 2.1 Hz, 2H), 7.56 (d, J = 2.1 Hz, 2H), 4.27 (t, J = 7.5 Hz, 4H), 3.92 (s, 6H), 2.76 (s, 6H), 2.70 (t, J = 7.2 Hz, 4H), 1.89

(pentet, J = 7.4 Hz, 4H), 1.68 (pentet, J = 7.1 Hz, 4H), 1.54–1.30 (m, 8H). ¹³C NMR (75.5 MHz, (CD₃)₂CO, ppm) δ : 145.5, 123.3, 121.8, 120.9 (q, $J_{CF} = 321.6$ Hz), 49.1, 38.8, 35.5, 30.3, 29.5, 28.5, 26.4, 9.7. MS (ESI+) m/z: 212.1342 (M²⁺ = [C₂₂H₄₀N₄S₂]²⁺ requires 212.1345).

Disulfide 5

The product was obtained as an amber oil. Yield: 3.90 g (79%). ¹H NMR (300 MHz, (CD₃)₂CO, ppm) δ : 7.62 (d, J = 2.1 Hz, 2H), 7.58 (d, J = 2.1 Hz, 2H), 4.27 (t, J = 7.5 Hz, 4H), 3.93 (s, 6H), 2.77 (s, 6H), 2.70 (t, J = 7.2 Hz, 4H), 1.83 (pentet, J = 7.4 Hz, 4H), 1.66 (pentet, J = 7.2 Hz, 4H), 1.50–1.24 (m, 20H). ¹³C NMR (75.5 MHz, (CD₃)₂CO, ppm) δ : 145.6, 123.4, 121.9, 121.0 (q, $J_{CF} = 321.4$ Hz), 49.1, 39.2, 35.5, 30.5, 30.0, 29.8, 29.8, 29.7, 29.1, 26.9, 9.8. MS (ESI⁺) m/z: 254.1811 (M²⁺ = [C₂₈H₅₂N₄S₂]²⁺ requires 254.1813).

Disulfide 6

The product was obtained as a pale yellow oil. Yield: 3.39 g (58%). ¹H NMR (300 MHz, (CD₃)₂CO, ppm) δ : 7.62 (d, J = 2.1 Hz, 2H), 7.58 (d, J = 2.1 Hz, 2H), 4.27 (t, J = 7.5 Hz, 4H), 3.93 (s, 6H), 2.77 (s, 6H), 2.71 (t, J = 7.5 Hz, 4H), 1.88 (pentet, J = 7.2 Hz, 4H), 1.67 (pentet, J = 7.2 Hz, 4H), 1.45–1.25 (m, 28H). ¹³C NMR (75.5 MHz, (CD₃)₂CO, ppm) δ : 145.6, 123.4, 121.9, 121.0 (q, $J_{CF} = 321.6$ Hz), 49.1, 39.3, 35.5, 30.5, 30.2, 30.2, 30.2, 30.2, 29.8, 29.8, 29.1, 26.9, 9.8. MS (ESI⁺) *m/z*: 282.2124 (M²⁺ = [C₃₂H₆₀N₄S₂]²⁺ requires 282.2128).

Synthesis of gold nanoparticles

From $[Au-C \equiv C-t-Bu]_4$

[Au-C≡C-*t*-Bu]₄ (27 mg, 0.025 mmol) was dissolved in 10 mL of degassed CH₂Cl₂ and the disulfide IL (0.20 mmol) was dissolved in 10 mL of degassed MeOH. Upon addition of the disulfide solution, the mixture was stirred for 30 min to form a light yellow solution. NaBH₄ (38 mg, 1.0 mmol) in 5 mL MeOH was added dropwise and stirred for 1 h. The precipitate was isolated via centrifugation (7500 rpm for 10 min), washed with acetone–pentane (2:1) (3 × 10 mL), and dried in vacuo. The crude mixture was employed for UV–vis and TEM analyses, while purified NPs were used for XPS.

From HAuCl₄

HAuCl₄·3H₂O (34 mg, 0.10 mmol) and the disulfide IL (0.20 mmol) were separately dissolved in 10 mL of degassed MeOH. Upon addition of the disulfide, the mixture was stirred for 30 min to form a light yellow solution. NaBH₄ (38 mg, 1.0 mmol) in 5 mL MeOH was added dropwise and stirred for 1 h. The precipitate was isolated via centrifugation (7500 rpm for 10 min), washed with acetone–pentane (2:1) (3 × 10 mL), and dried in vacuo. The crude mixture was employed for UV–vis and TEM analyses, while purified NPs were used for XPS.

Transmission electron microscopy

TEM of Au NPs was obtained on a Phillips CM 200 microscope operating at an accelerating voltage of 200 kV with a point resolution of 0.24 nm. Sample preparation included dilution of 10 drops of the Au NP solution in 20 drops of *i*-PrOH, followed by deposition on a carbon-coated copper grid (400 mesh) at rt. The NP size distribution was determined from the measurement of >200 spherical particles chosen in arbitrary areas of enlarged micrographs.

UV-vis spectroscopy

Spectra were recorded on a Jasco V-660 spectrophotometer. Sample preparation included the dilution of 0.1 mL of the crude Au NP solution in 4.0 mL of MeOH. A correction of the raw data was employed to normalize the background.

Supplementary data

Supplementary data are available with the article through the journal Web site (http://nrcresearchpress.com/doi/suppl/ 10.1139/v11-146).

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