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Linear Tetraphenylmethane-Based Thioether Oligomers Stabilising an entire Gold Nanoparticle by Enwrapping

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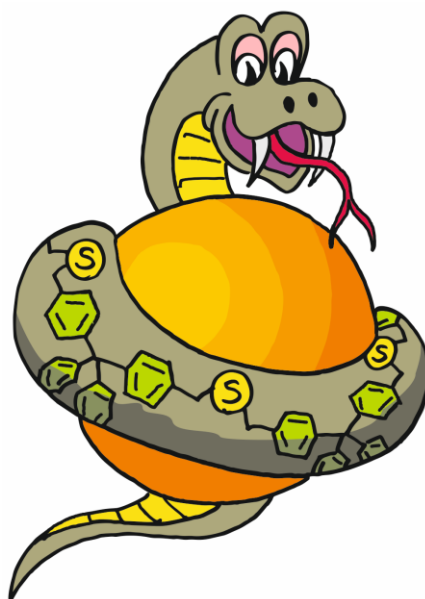
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[†] Electronic supplementary information (ESI) available: synthetic procedures and analytical data of the compounds **1-17**, details on nanoparticle formation, purification and analysis (UV-vis, ¹H-NMR and thermogravimetric analysis).

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4 **Abstract**
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7 The design and synthesis of a novel, linear thioether-based ligand subunit with a tetraphenylmethane core
8 for the stabilisation of gold nanoparticles (AuNPs) are presented. Mono-, tri, penta- and heptamers of the
9 ligand have been synthesised and successfully used to stabilise AuNPs by enwrapping. With the exception
10 of the monomer, all ligands proved to provide reliable long-term stability and re-dispersability for the
11 coated nanoparticle in common organic solvents. Despite variation of the oligomer length, all stable
12 coated nanoparticle in common organic solvents. Despite variation of the oligomer length, all stable
13 particles were of the same size within error tolerance (1.16 ± 0.32 nm for the trimer, 1.15 ± 0.30 nm for
14 the pentamer, 1.17 ± 0.34 nm for the heptamer) as investigated by transmission electron microscope
15 (TEM) imaging. These findings suggest that not solely the number of sulphurs in the ligand, but as well its
16 bulkiness play a crucial role in stabilising the AuNPs. These findings are supported by thermogravimetric
17 analysis (TGA), showing that AuNPs stabilised by the penta- or heptamer are passivated by a single ligand.
18 From Thermal stability measurements a correlation between ligand-coverage and thermal stability could
19 be found, further supporting these findings.
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32 **Table of Contents Graphic**
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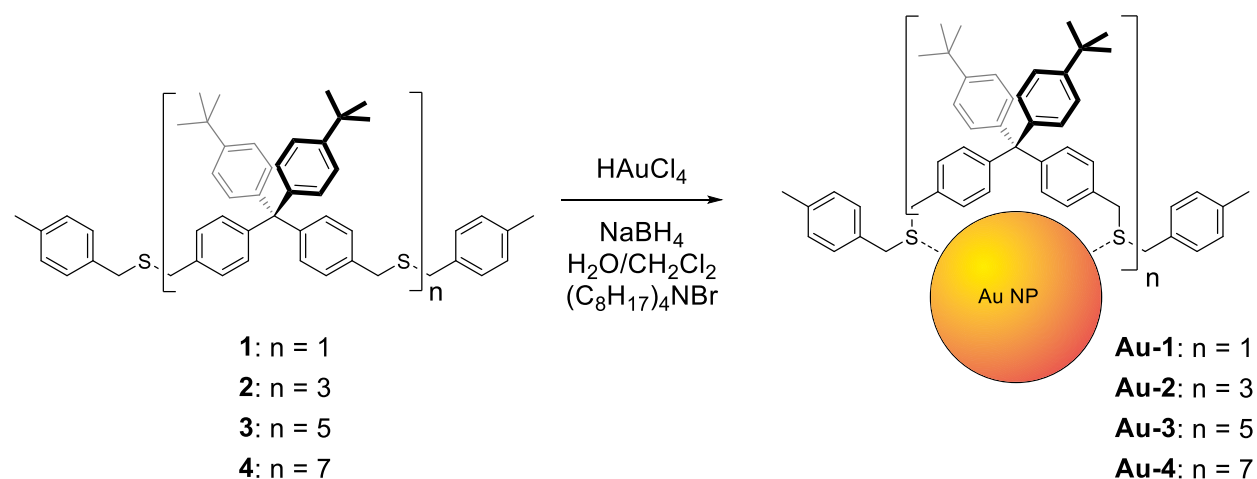


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4 Gold nanoparticles (AuNPs) have fascinated mankind ever since the fourth century *a.d.*¹ and
5 unambiguously still do nowadays. Because of their unique multifaceted properties, AuNPs are used in
6 numerous fields of research. They find applications in medical therapeutics², catalysis³, chemical and
7 biological sensing^{4,5}, molecular electronics⁶⁻⁸, and recently also as functional subunits of hybrid materials⁹.
8 AuNPs were also considered as molecule-like building blocks^{10,11} integrated in larger architectures by wet
9 chemical protocols⁶. In order to use AuNPs as functional subunits, the following features move into the
10 focus of interest: 1) the particle's size and shape controlling its physical properties. Thus in an ideal sample,
11 these dimensional and structural features should be as uniform as possible. 2) The chemical nature, the
12 number and the spatial arrangement of functional groups exposed at the particles surface as connecting
13 points addressed by wet chemistry. 3) The stability of the particle determining the harshness of applicable
14 reaction conditions applied for their integration/decoration by wet chemistry protocols. And finally, 4) the
15 NPs synthetic availability and purity.

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17 While there is a whole plethora of reports on NPs stabilised by various thiolates¹², stabilisation of NPs by
18 thioether-based structures has only been reported on rare occasions. The weakness of the interaction
19 between the sulphur atom of a thioether motive and the NPs metal surface is particularly appealing, as 1)
20 it can sum-up to a considerable contribution by using multidentate oligothioether systems, and 2) it might
21 even allow for optimization of the arrangement of the coating structure by reversible ligand particle
22 interactions. Inspired by the concept, we explored the potential of linear¹³ as well as dendritic¹⁴
23 multidentate thioether systems as passivating surface coatings of small AuNPs. The integer ratios between
24 coating ligands and AuNPs even paved the way to stable, coated particles exposing an integer number of
25 functional groups. In particular, the use of ligands comprising a central acetylene unit yielded in coated
26 AuNPs exposing two ethynyl groups on opposed sides in the case of linear oligomeric thioether ligands,^{15,16}
27 and even in AuNPs with a single ethynyl handle in the case of the dendritic ligand system.^{17,18} Oxidative
28 acetylene homo coupling protocols enabled the assembly of organic-inorganic hybridmaterials as "pearl
29 necklace"-type arrays in the case of the bifunctionalised AuNPs,^{15,16} and as dumbbell-type structures in
30 the case of monofunctionalised AuNPs.¹⁷ The scope of wet-chemical protocols profiting from these AuNPs
31 as artificial molecules were further widened by applying azide-acetylene click-reaction protocols to
32 decorate oligoazide linkers with particles resulting in dumbbell-, trike- or squad-like superstructures.¹⁸ In
33 all these thioether ligand structures the sulphur atoms were interlinked by a 3-*tert*.butyl- α,α' -*meta*-xylene
34 motive and the importance of having a sterically demanding ligand shell covering the rather reactive
35 surface of a AuNP became obvious during stabilising studies with various dendritic systems.¹⁴ While the
36 2nd generation dendrimer stabilising an entire particle and thereby providing mono-functionalised AuNPs

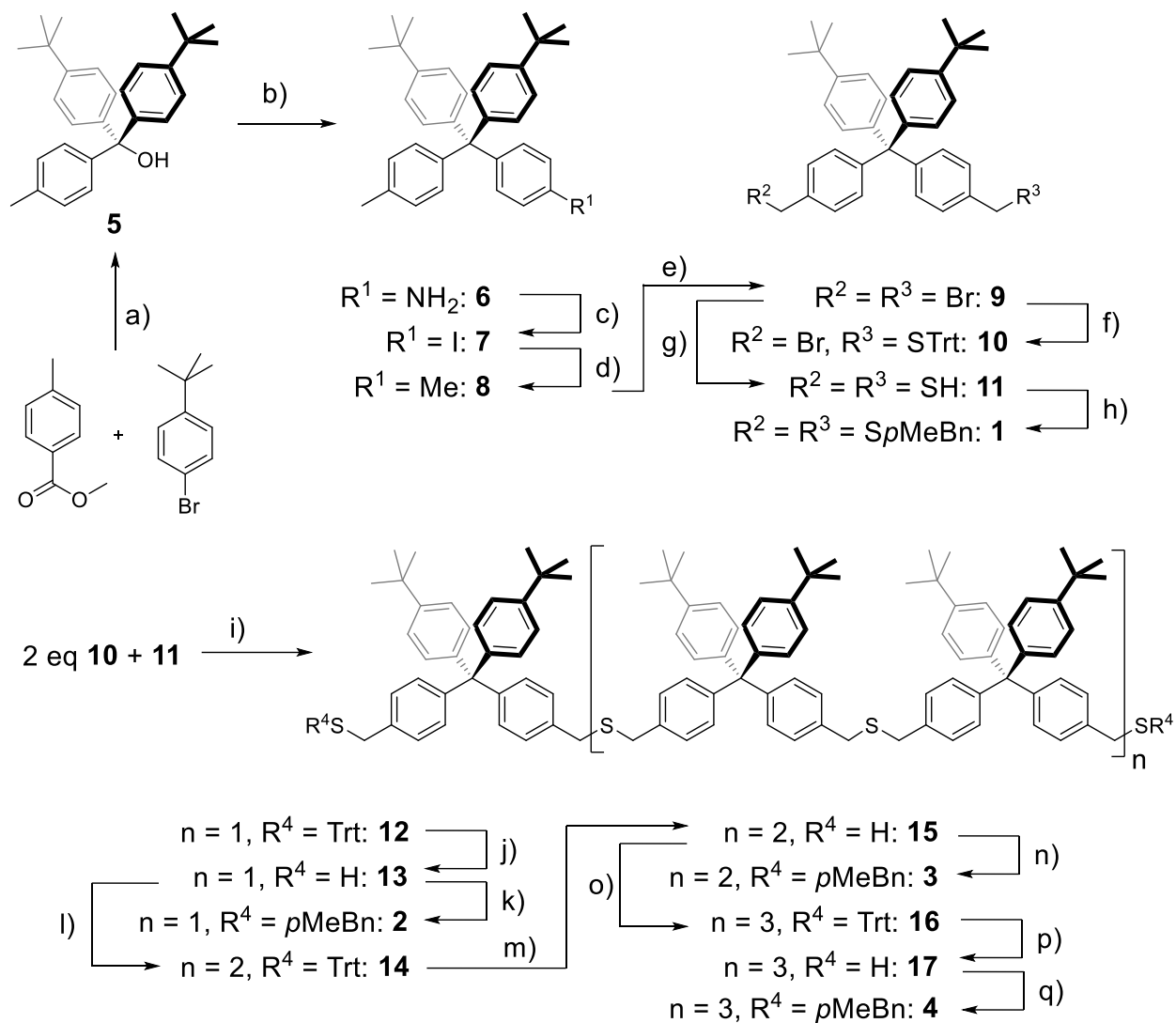
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4 were ideally suited for most of the applications we had in mind, the limited synthetic availability of the
5 macromolecular ligand handicapped the further exploration of the system. We thus kept on seeking for
6 alternative ligand motives combining coordinating benzylic thioethers with bulkiness sterically protecting
7 the coated ligand.
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11 Here we report our new bulky tetraphenylmethane-based ligand theme and its excellent AuNPs stabilising
12 properties (Scheme 1). In particular, the obtained linear oligomers not only provide stable AuNPs with
13 very good processability features, but also the pentamer (**3**) and heptamer (**4**) are both able to stabilise
14 an entire particle and thus are interesting lead structures towards mono-functionalised AuNPs. The
15 molecular design combines an increased bulkiness of the parent building block due to both, the two *tert*-
16 butyl decorated phenyl rings and the three dimensional tetraphenylmethane core structure, with an
17 increased spacing between both sulphur atoms compared to the *meta*-xylene motive. While the bulkiness
18 is likely to provide solubility to both, the bare ligand as well as the coated particle, the increased spacing
19 between neighbouring sulphur atoms results in further remote contact points on the AuNPs, which should
20 be reflected in the ligand/particle interactions. Either the increased spacing influences the particle's size
21 or it alters the arrangement of the ligand at the particle's surface, which holds the potential for new
22 packing motives and ligand/particle ratios. As final optimization, the terminal sulphur atoms were masked
23 by 4-methylbenzyl-groups instead of the benzyl groups used so far, mainly to provide an easy to detect
24 NMR signature of the subunit.
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55 **Scheme 1:** Linear tetraphenylmethane-based thioether oligomers **1-4** and concept of their Au
56 nanoparticle stabilisation by surface coating.
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4 For the synthesis of ligands **1-4** (see scheme 2), the core-precursor **8** was first synthesised, following a
5 marginally modified literature protocol¹⁹: triphenylmethanol derivative **5** was obtained via a twofold
6 *Grignard* reaction of the *Grignard* reagent obtained from 1-bromo-4-*tert*-butylbenzene and solid
7 magnesium in tetrahydrofuran (THF) and methyl *p*-toluate. Subsequent electrophilic aromatic
8 substitution with aniline in glacial acetic acid and hydrochloric acid as catalyst led to compound **6**. A one-
9 pot *Sandmeyer*-type reaction delivered compound **7** by substitution of the amine by an iodine atom
10 through preliminary *in situ* formation of its diazonium salt. Subsequent methylation with methyl lithium
11 in THF yielded compound **8** with the completed carbon skeleton of the target structure in a yield of ~50
12 % over the four steps. The key-precursors **9-11** were synthesised with slight modification of the protocol
13 reported by Peterle¹³: mild radical bromination of compound **8** upon illumination with a halogen lamp
14 with N-bromosuccinimide (NBS) as bromine source in methyl formate gave the bis-benzylbromide
15 derivative **9**. The bis-mercapto derivative **11** was obtained by treatment of the bromine precursor **9** with
16 thiourea in dimethyl sulfoxide (DMSO) during 15 hours to form its thiouronium salt, which was
17 precipitated by an excess of dichloromethane (DCM). The precipitate was re-dissolved in MeOH and
18 treatment with aqueous sodium hydroxide (1 M), followed by reprotonation with aqueous hydrochloric
19 acid (1 M) provided the desired bis-methylenemercapto tetraphenylmethane derivative **11**. Continuous
20 degassing of all solvents, aqueous solutions, and reaction mixtures in a steady stream of argon turned out
21 to be crucial in order to avoid polymerisation due to disulfide formations.
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Scheme 2: Molecular structures and synthesis of ligands **1-4**.[†] a) 1) Mg, THF, reflux, 22 h, 2) H₂O, sat. NH₄Cl, 87 %; b) aniline, HCl, AcOH, 140 °C, 15 h, 71 %; c) 1) BF³·OEt₂, ^tBuNO₂, DCM, -30 °C, 3 h, 2) KI, I₂, -30 °C → room temperature, 15 h, 84 %; d) MeLi, THF, -60 °C, 15 h, quant.; e) NBS, AIBN, methyl formate, hv, reflux, 15 h, 60 %; f) TrtSH, NaH, THF, room temperature, 15 h, 48 %; g) 1) thiourea, DMSO, 40 °C, 15 h, 2) DCM, 3) 1 M aq. NaOH, 1 M aq. HCl, MeOH, 3 h, 51-93 %; h) 4-methylbenzyl bromide, NaH, THF, 5 h, 91 %; i) NaH, THF, room temperature, 5 h, 88 %; j) SiEt₃H, TFA, DCM, room temperature, 1 h, quant.; k) 4-methylbenzyl bromide, NaH, THF, 15 h, 89 %; l) **10**, NaH, THF, room temperature, 5 h, 83 %; m) SiEt₃H, TFA, DCM, room temperature, 1 h, quant.; n) 4-methylbenzyl bromide, NaH, THF, 15 h, 77 %; o) **10**, NaH, THF, room temperature, 5 h, 79 %; p) SiEt₃H, TFA, DCM, room temperature, 1 h, quant.; q) 4-methylbenzyl bromide, NaH, THF, 15 h, 72 %. Me = Methyl, Bn = benzyl, Trt = trityl.

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4 The monomeric parent ligand **1** was isolated in good yields by column chromatography after treating the
5 bis-mercapto precursor **11** with α -bromo *para* xylene and sodium hydride as base in THF at room
6 temperature. The bifunctional compound **10**, made from the bis-bromine precursor **9** via a S_N2 reaction
7 with trityl mercaptan and sodium hydride as base in THF, comprises one trityl masked thiol and a benzylic
8 bromide as leaving group, and is therefore an ideal building block for the stepwise assembly of the longer
9 oligomers **2-4**. Elongation of the dithiol derivative **11** on both sides with **10** in THF at room temperature
10 using sodium hydride as base gave the terminally trityl protected trimer **12** in a good isolated yield of 88%.
11 Deprotection of **12** by treatment with TFA and SiEt₃ in DCM gave quantitatively the trimer **13** exposing
12 terminally free thiols. A similar elongation protocol enabled the transformation from the trimer **13** to the
13 pentamer **14**, and from the free thiol pentamer **15** to the heptamer **16**. With 83% for **14** and 79% for **16**,
14 the isolated yields decreased slightly the longer the oligomers became. Deprotections using the conditions
15 described above for **12** provided the corresponding free dithiol trimer **13**, pentamer **15**, and heptamer **17**
16 almost quantitatively. Subsequent end-capping of the dithiol oligomers was performed with similar
17 conditions described above for the assembly of **1** and provided the end-capped oligomers **2-4** in good
18 isolated yields. All new ligand structures **1-4** as well as their precursors were fully characterised by ¹H- and
19 ¹³C-NMR spectra, and MALDI-ToF mass spectrometry. The small molecule type precursors were further
20 analysed by elemental analysis, while the more precious oligomers were characterized by high resolution
21 MALDI-ToF mass spectrometry instead.

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37 The ability of these oligothioether type structures **1-4** to stabilise AuNPs was analysed using the protocol
38 already applied successfully for linear and dendritic multidentate ligand structures¹³⁻¹⁸ and is sketched in
39 scheme 1. It basically consist of a variation of the AuNP synthesis reported by Brust *et al.*²⁰ in the presence
40 of the multidentate ligand structure of interest. In a two phase water/DCM system comprising tetra-*n*-
41 octylammonium bromide (TOAB) as phase transfer catalyst, equal amounts of gold and sulphur atoms
42 were dissolved. In other words, 2 equivalents of the gold salt HAuCl₄ were used for the bidentate ligand
43 **1**, 4 equivalents for the tetra-dentate ligand **2**, and 6 respectively 8 equivalents were used for the hexa-
44 respectively the octa-dentate ligands **3** and **4**. After complete transfer of the gold salt to the organic phase,
45 the two phase reaction mixture was vigorously stirred while an aqueous NaBH₄ solution was added. After
46 another 10 minutes stirring at room temperature, the phases were allowed to separate and the intense
47 dark brown coloured DCM phase indicated the presence of AuNPs dissolved in the organic phase. Addition
48 of excessive amounts of ethanol caused the precipitation of the AuNPs, which were centrifuged and dried
49 *in vacuo*, before being re-dissolved in DCM. Interestingly, some of these particles were not only formed
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4 almost quantitatively (in fact the AuNPs were the only detectable form of gold), but also displayed very
5 promising stability features, which depended on the length of the oligomer used to stabilise the AuNP.
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9 Already with the monomeric ligand **1**, no precipitation of gold was observed during the synthesis pointing
10 at superior AuNPs stabilising properties compared to the *meta*-xylene motive used before, which caused
11 precipitation of gold already during the particles synthesis.¹³ In spite of these promising behaviour during
12 the synthesis, the ligand **1** coated AuNPs (**Au-1**) did not display suitable stability features agglomerating
13 to larger AuNPs within hours in solution. The initially intense brown AuNPs solution already turned
14 gradually reddish during work up, pointing at the formation of larger particles. To our delight, the AuNPs
15 **Au-2**, **Au-3** and **Au-4** stabilised by the trimer **2**, the pentamer **3** and the heptamer **4** displayed considerably
16 improved stability features. These particles turned out to remain stable and soluble over several days
17 without alteration of the UV spectra pointing at constant particle sizes. In the dried state the particles
18 were even stored over months without losing their redispersability. These particles were easily re-
19 dispersed in DCM allowing for repeated precipitation (with ethanol), centrifugation and re-dispersion
20 cycles without loss of material. Furthermore, these particles were stable enough to allow for purification
21 by gel permeation chromatography, providing AuNPs samples of excellent purity. The extensively purified
22 and *in vacuo* dried coated particles **Au-2**, **Au-3** and **Au-4** were analysed by UV-Vis- and ¹H-NMR-
23 spectroscopy, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA).
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36 The ¹H-NMR spectra of the AuNPs **Au-2**, **Au-3** and **Au-4** displayed broadening of all signals characteristic
37 for particles due to reduced tumbling motion of the ¹H-labels in comparison to the free ligands **2-4** (see
38 figures S1-3 in the ESI). In spite of the reduced resolution of the ¹H-NMR signals, the spectra document
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clearly the successful separation of the AuNPs from both, the phase transfer catalyst TOAB and excess of oligomeric ligand due to purification by gel permeation chromatography.

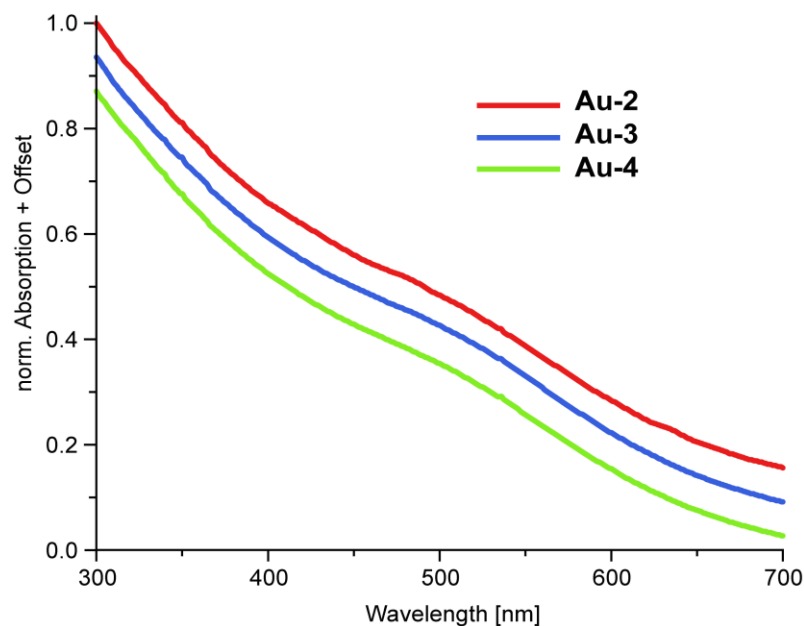


Figure 1: Normalised UV-VIS spectra of the oligomer stabilised nanoparticles **Au-2**, **Au-3** and **Au-4** recorded in CH_2Cl_2 . Their individual absorption spectra are shifted vertically for clarity (offset).

The UV-Vis absorption spectra **Error! Reference source not found.** of the ligand stabilised particles **Au-2**, **Au-3** and **Au-4** are very similar and are displayed in figure 1. Eye-catching is the absence of a distinct surface plasmon resonance (SPR) band at around 520 nm pointing at AuNPs with diameters smaller than 2 nm.²¹ To gain further information about the particles' sizes, TEM micrographs were recorded from samples spread over a carbon network covered TEM grid. Typical sections of the TEM micrographs for all particles are displayed in figure 2 (top) and larger areas are displayed in the ESI. The gold particles observed in the TEM micrographs were analysed using the software *ImageJ* for particle counting and measuring, resulting in the size distributions displayed at the bottom of figure 2. In agreement with the observations made in the UV-VIS spectra, all three ligands **2-4** stabilise particles with diameters below 2 nm. The AuNPs obtained are very comparable for all three ligands even with very comparable size distributions. In particular average particle sizes of 1.16 ± 0.32 nm were recorded for **Au-2**, of 1.15 ± 0.30 nm for **Au-3**, and of 1.17 ± 0.34 nm for **Au-4** respectively. Thus the particle sizes obtained are comparable to the ones already reported using *meta*-xylene interlinked thioether oligomers (~ 1.1 nm).¹³⁻¹⁶

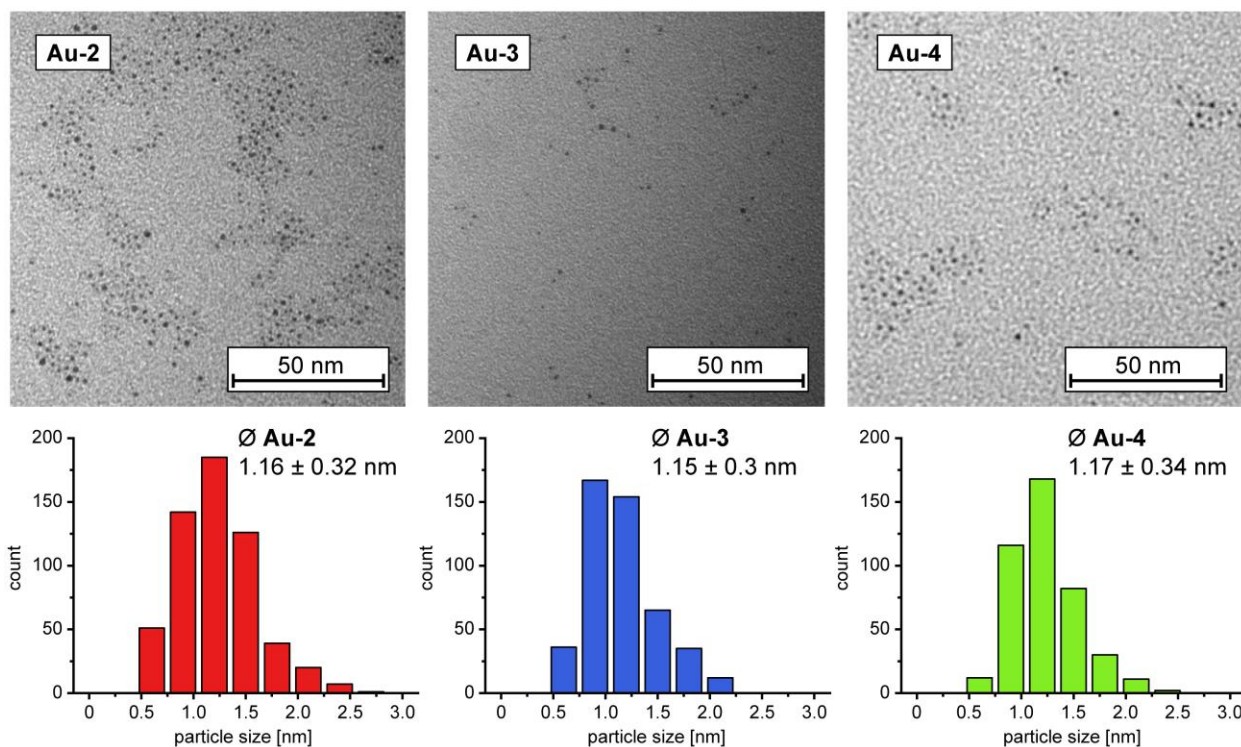


Figure 2: *Top:* Representative sections of the TEM micrographs for samples of the oligomer-stabilised nanoparticles **Au-2**, **Au-3** and **Au-4**; *bottom:* Size distribution of the particles observed in the TEM micrographs.

The purity of the coated AuNPs makes the thermogravimetric analysis (TGA) particularly interesting, allowing conclusions with respect of the ratio of organic ligand coating the AuNPs' surface. For all three AuNPs nanoparticles **Au-2**, **Au-3** and **Au-4** the weight loss attributed to the decomposition of the organic coating starts at about 200°C and levels out at about 600°C (TGAs are displayed in the ESI). Weight losses of 26.5 %, 24.5 % and 32.1 % were recorded for **Au-2**, **Au-3** and **Au-4** respectively. As the lost weight must arise from the coating ligands **2-4**, the remaining weight must belong to the Au atoms forming the AuNPs. As the molecular weights of both, the coating ligand and of the Au atoms are known, the data even allow to determine the number of Au atoms per coating ligand (see ESI).

In the case of **Au-2** the remaining 73.5 % of the weight corresponds to 24.14 Au atoms per ligand **2**. Assuming a spherical shape for the AuNP with the diameter of 1.16 nm obtained as average number by TEM analysis, the density of gold allows to calculate the average AuNP's mass and to determine the number of Au atoms involved. Applying these calculations to **Au-2**, an average number of 48.27 Au atoms

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4 per particle is obtained corresponding to twice the number of Au atoms calculated per ligand. We thus
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6 conclude that two ligands **2** are coating one particle, as it was already reported for *meta*-xylene based
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8 linear oligomers^{15,16} and first generation dendritic ligands.¹⁴ The analysis became even more exciting for
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10 the particles **Au-3** and **Au-4**: for **Au-3** the TGA gave a ratio of 42.18 Au atoms per ligand **3**, and the TEM
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12 based dimensional analysis of the particles pointed at 47.04 Au atoms per average AuNP. In the case of
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14 **Au-4**, 39.49 Au atoms per ligand **4** were calculated while the average particle was determined to consist
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16 of 49.54 Au atoms. In spite of the inaccuracy of these estimations of the number of Au atoms per ligand
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18 and particle, the obtained numbers clearly suggest that both ligand structures **3** and **4** are able to coat
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20 and stabilise an entire AuNP as single wrapping ligand.

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22 This 1/1 ratio of coating ligand per particle is particularly appealing for future developments towards
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24 particles exposing a single functional group as inorganic/organic hybrid macromolecules addressable by
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26 wet chemical protocols. Equally important for their use as “artificial macromolecules” is their thermal
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28 integrity in suspension limiting the range of potentially applicable reaction conditions. Thus suspensions
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30 of the particles **Au-2**, **Au-3** and **Au-4** dispersed in toluene were gradually heated by steps of 10 °C and
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32 kept at the elevated temperature for one hour before optical analysis (UV-VIS). For **Au-2** a colour change
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34 from brown to bluish accompanied by a black precipitation was observed above 90 °C, pointing at the
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36 thermal decomposition of the ligand coated **Au-2**. Similar behaviour at the same temperature was
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38 observed for **Au-4**, pointing at comparable thermal stability of this AuNP coated by a single ligand. For **Au-**
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40 **3** slightly lower decomposition temperatures were recorded, as the alteration in the UV VIS spectra and
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42 precipitation was already observed above 80 °C. For all three coated particles **Au-2**, **Au-3** and **Au-4**
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44 promising thermal stabilities were observed increasing their attraction as future ligand structure of
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46 inorganic/organic hybrid building blocks.

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48 In conclusion, we present a new thioether-based oligomer motive with superior AuNP stabilising
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50 properties. The 1/1 ratio between coating ligands and AuNPs in combination with the improved synthetic
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52 accessibility of the linear oligomers **3** and **4** compared with the dendritic ligands reported so far and the
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54 thermal stability of the coated particles, makes these oligomers to very promising coatings for AuNPs with
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56 controlled exposure of functional groups. We attribute the superior stabilising features mainly to the
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58 considerably enlarged bulkiness of the structure covering larger areas of the AuNPs’s surface. In addition,
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60 the increased distance between thioether subunits lifts the interlinking structure from the coated gold
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62 surface, which might support the coating as well. In spite of the reduced number of coordinating thioether
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64 subunits per organic mass, these structures display promising thermal stability features in dispersion,
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4 pointing at an inferior role of the number of coordinating thioethers in the molecules design. This
5 observation is to some extent supported by the work of McCaffrey *et al.*, who reported the stabilisation
6 of AuNPs in a rigid organic molecular cage, bearing only three thioether group as coordination point for
7 the encapsulated AuNP.²² Currently we are investigating both, ligands exposing functional groups as well
8 as more elaborated branched ligand systems based on the here reported new motive.
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