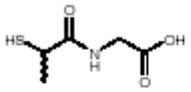
Self-Assembled Monolayers Protected Metal Nanoparticles

3-D SAMs 2

Water soluble nanoparticles

tiopronin



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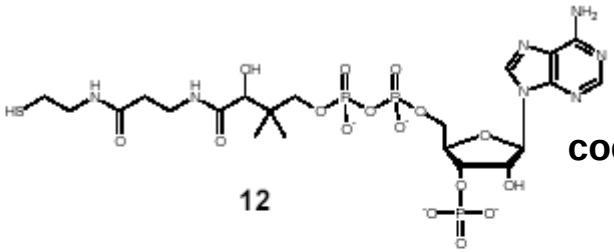
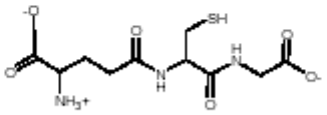


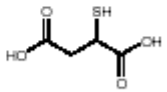
12

coenzyme A

13



14 glutathione



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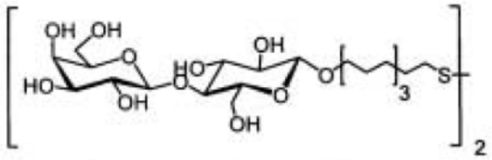
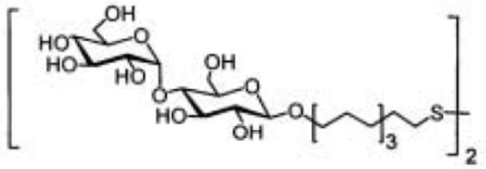
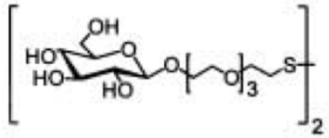


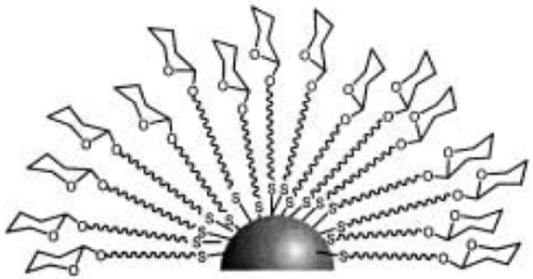
Lactose neoglycoconjugate



Maltose neoglycoconjugate



Glucose neoglycoconjugate

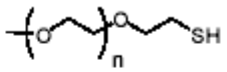


lacto-GNP
malto-GNP
gluco-GNP

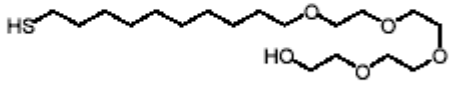
Water soluble nanoparticles

$PEG_{5000}SH$

21



22a n = 1
22b n = 2
22c n = 3



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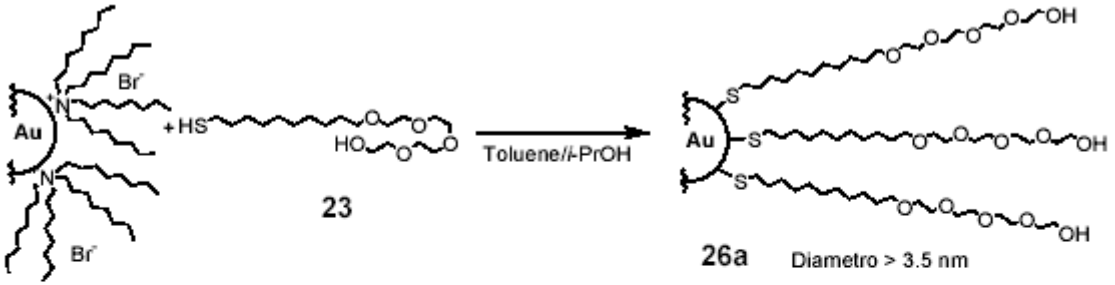
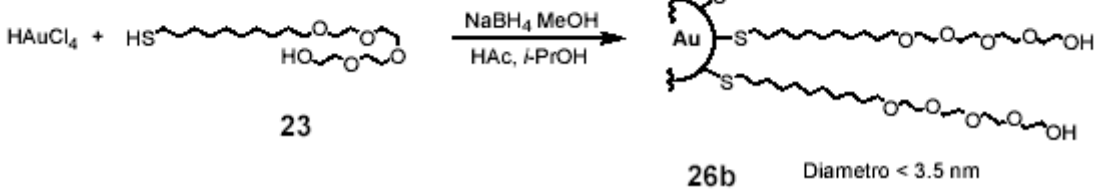


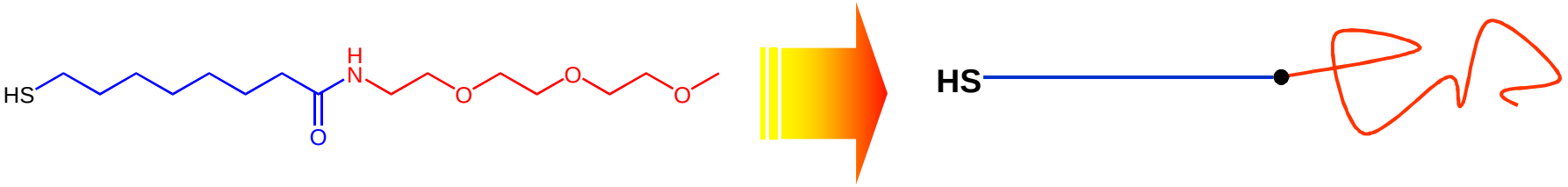
25

23



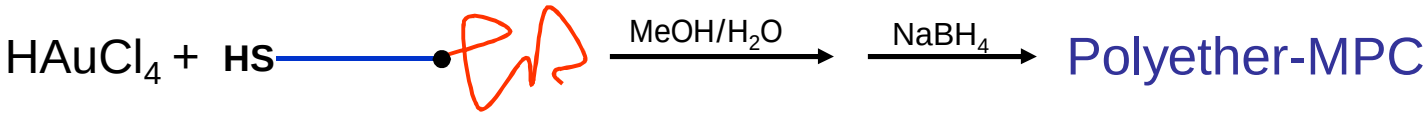
23

Water soluble nanoparticles



The hydrocarbon chain ensures the formation of a compact and tidy monolayer near the surface of the nanoparticle metal core

The polyether chain, even of short length, ensures MPCs solubility in water and polar solvents



Homogeneous phase synthesis

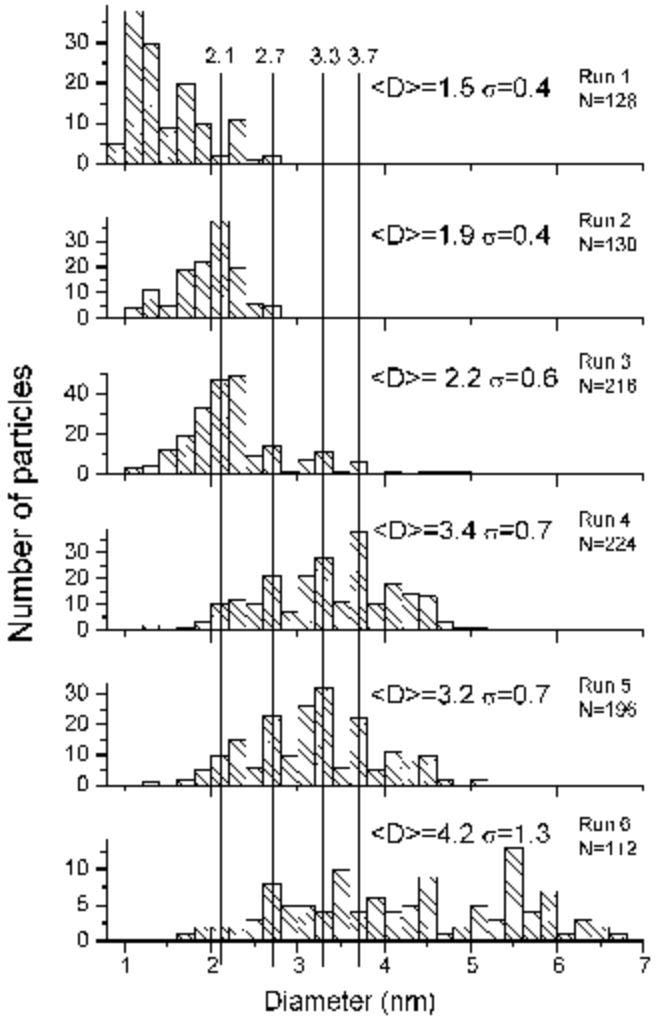
Quantitative conversion of $HAuCl_4$

Diameter of the gold core 1.5 - 4.2 nm

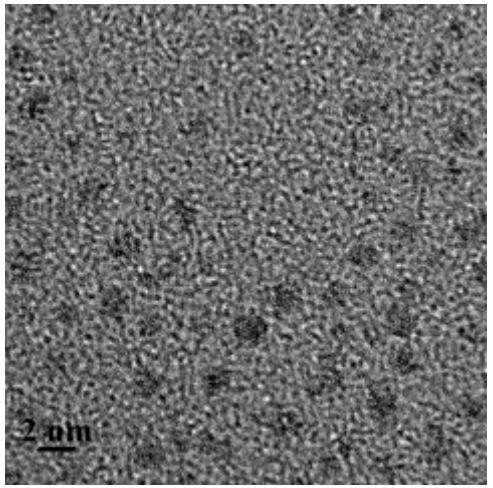
Strong influence of the reduction rate

Pengo, P; Polizzi, S.; Battagliarin, M.; Pasquato, L.; Scrimin, P. *J. Mater. Chem.* **2003**, *13*, 2471-2478.

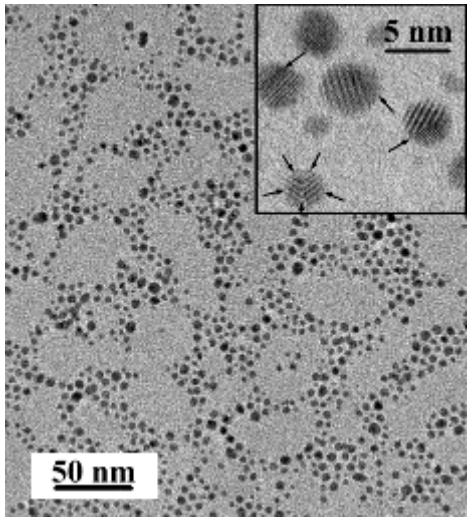
MPC-C8-TEG Characterization



Increasing Gold / thiol ratio



TEM image of MPCs obtained with a 1/3 gold/thiol molar ratio, $NaBH_4$ added in 10 sec.



TEM image of MPCs obtained with a 3/1 gold/thiol molar ratio, adding $NaBH_4$ in 30 minutes

Thiolate Ligands for Synthesis of Water-Soluble Gold Clusters

C. J. Ackerson, P. D. Jadzinsky, R. D. Kornberg **J. AM. CHEM. SOC. 2005**, 127, 6550-6551

Table 1. Water-Soluble Thiolates and Their Ability to Passivate Gold Clusters

compound name	published synthesis	diameter (nm)[k]	soluble product	stability	synthetic method[a]	behavior in HD–PAGE gel
3-mercaptopropionic acid	ref 21	undetermined[j]	yes	days to weeks	Brust	did not enter matrix in HD or LD−PAGE[i]
4-mercaptobutyric acid	no	4.0 ± 1.2	yes	weeks	Brust	not tested
3-mercapto-1,2-propanediol	ref 14[b]	4.7 ± 1.2	yes	days	Brust	single diffuse band in HD−PAGE
cysteine	ref 12[c]	1.6 ± 0.3	yes	days	Brust[f]	entered gel matrix as single band; stalled; single band in LD−PAGE
methionine	no	2.4 ± 1.0	yes	weeks	Hutchison	did not enter matrix in HD or LD−PAGE
thiomalate	ref 13[d]	2.1 ± 1.4	yes	weeks	Brust	single tight band surrounded by large halo
2-mercaptobenzoic acid	no	2.1 ± 0.9	yes	minutes	Brust	did not enter matrix in HD or LD−PAGE
3-mercaptobenzoic acid	no	1.6 ± 0.6	yes	days	Brust	did not enter matrix; single band in LD−PAGE
4-mercaptobenzoic acid	ref 7[e]	1.8 ± 0.4	yes	months	Brust	2 tight bands
tiopronin	ref 9	1.9 ± 0.7	yes	months	Brust[f]	single diffuse pink band in HD or LD−PAGE
selenomethionine	no	1.6 ± 0.4	yes	days	Hutchison	did not enter matrix in HD or LD−PAGE
1-thio-β-D-glucose	no	2.1 ± 0.5	yes[g]	months	Brust[f]	single band in LD−PAGE
glutathione	ref 8	1.4 ± 0.4	yes	months	Brust	5 bands
ITCAE pentapeptide[h]	no	1.4 ± 0.4	yes	days	Hutchison	not tested

[a] Brust synthesis was in 1:1 water:methanol with a 3:1 thiolate:gold ratio. Typical concentrations were 10 mM gold and 30 mM thiolate. A 5-fold molar excess of $NaBH_4$ in a volume of water ~10% of the reaction volume was added to complete the cluster formation. Reactions denoted Hutchison were performed as described (ref 5). [b] A 1:1 ratio of thiolate:Au(III) and a 9-fold BH_4^- excess. [c] Cystine was used as the starting material to create cysteine MPCs. [d] Highest organothiolate:Au(III) ratio used was 5:2, with equimolar $NaBH_4$ to $HAuCl_4$, likely resulting in incomplete reduction. [e] A 1.8:1 thiolate:Au(III) ratio was used. [f] These compounds failed to form soluble products in 1:1 water:methanol, but did so under similar conditions in 6:1 methanol:acetic acid. [g] This compound formed product that remained in suspension following low-speed centrifugation, indicating cluster formation, but failed to redissolve after methanol precipitation; this product was not repeatably precipitable in methanol, but could be purified from starting materials by gel filtration and, otherwise, behaved as a stable water-soluble MPC. [h] The pentapeptide had the sequence Ile-Thr-Cys-Ala-Glu. [i] LD−PAGE was a standard 12% SDS−PAGE gel. [j] Particles form aggregates within which individual particle diameters cannot be measured. [k] See Supporting Information for images, histograms, and further analysis.

Monolayer packing

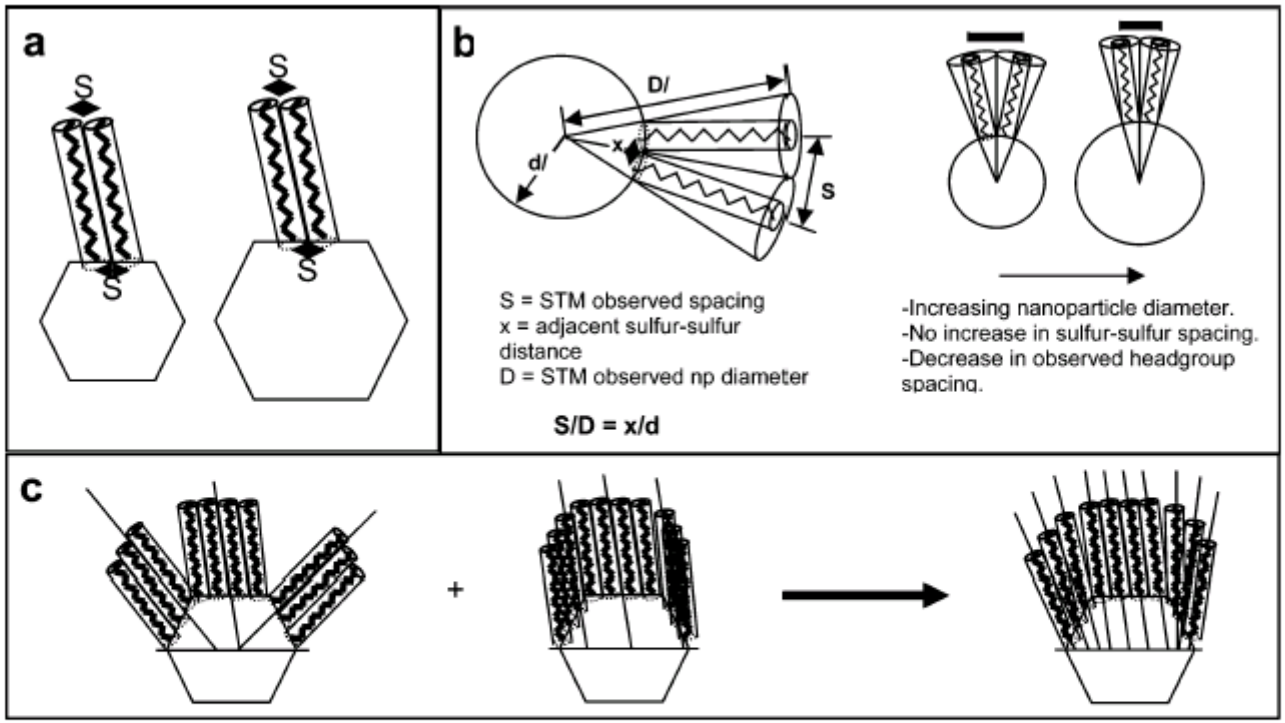
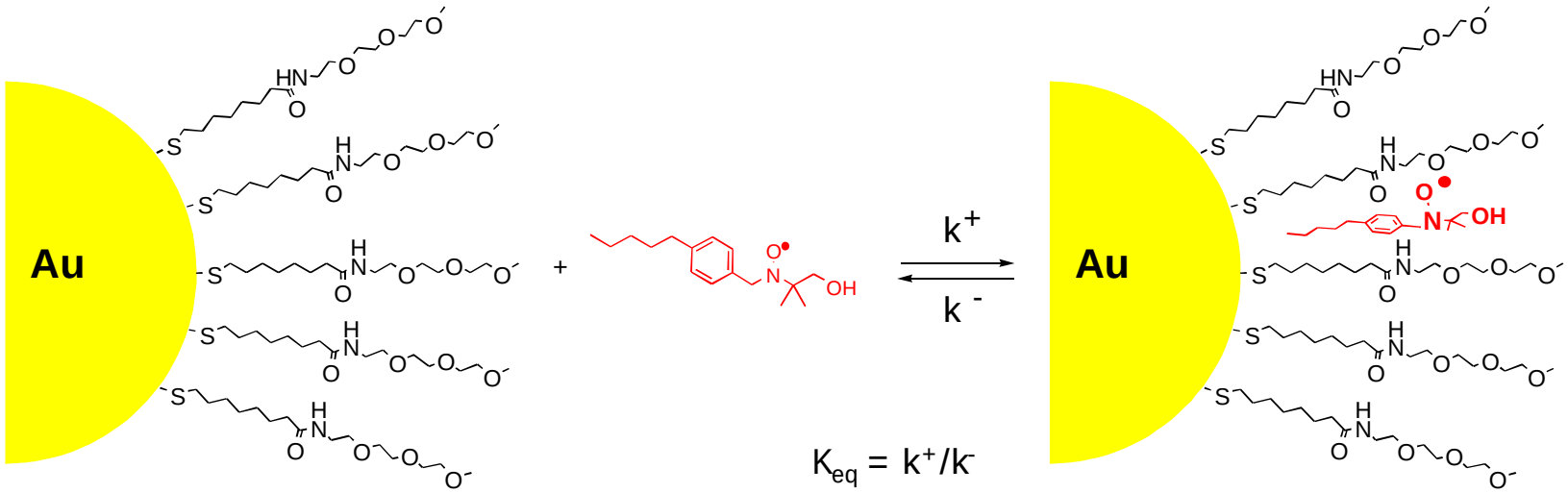


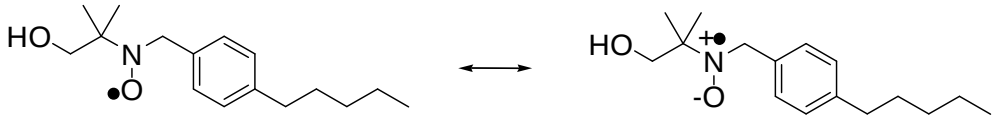
Figure 16. (a) Simplest representation of ligand packing for homoligand nanoparticles. Ligands pack on each nanoparticle facet as they would on a crystallographically equivalent flat 2-D gold surface, with a headgroup spacing corresponding exactly to the sulfur−sulfur spacing of the ligands at the nanoparticle core. (b) Schematic illustration of a ligand-coated nanoparticle relating the STM-observed headgroup spacing (S) at the periphery to the corresponding sulfur−sulfur spacing (x) at the nanoparticle core. (c) Ligands have essentially two configurations that they can assume on the faceted core: (i) they can assume their optimal tilt angle with regard to each facet (left), or (ii) they can assume a global tilt angle (middle). The first configuration leads to high-energy defects at the crystal edges, while the second does not take advantage of the particle curvature. Hence, the true configuration is likely a compromise between the two, with the ligands roughly conforming to a global tilt angle, but relaxing, and splaying outward as shown in the rightmost drawing in (c).

F. Stellacci et al. *J. AM. CHEM. SOC.* **2006**, *128*, 11135-11149.

Properties of the Monolayer

EPR Spectroscopy as a tool to investigate the monolayer properties

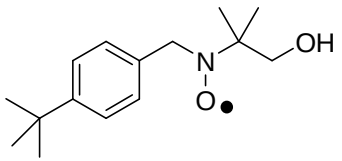




- the hyperfin coupling constants *a*(N) and *a*(2H$_\beta$) are larger in polar media

M. Lucarini, P. Franchi, G. F. Peduli, P. Pengo, P. Scrimin, L. Pasquato, *J. Am. Chem. Soc.*, **2004**, *126*, 9326.

Properties of the Monolayer

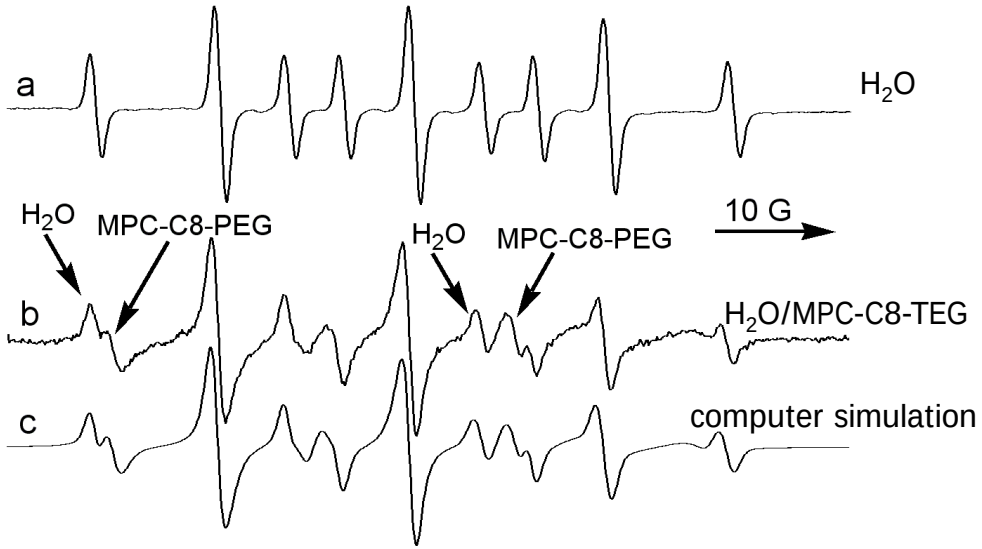


$1 \div 2 \times 10^{-5}$ M

k^+ $7.7\ 10^9\ M^{-1}s^{-1}$

k^- $1.9\ 10^6\ s^{-1}$

K_{eq} $5.683\ M^{-1}$

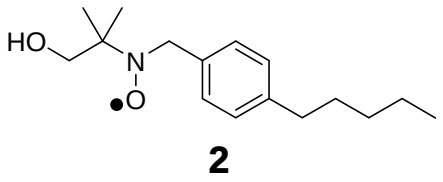


MPC-C8-TEG, d = 3.4 nm, σ 0.7 nm

- rapid exchange of the probe between the aqueous phase and the monolayer
- the nitroxide group is located in a less polar environment shielded from the aqueous solvent

M. Lucarini, P. Franchi, G. F. Peduli, P. Pengo, P. Scrimin, L. Pasquato, *J. Am. Chem. Soc.*, **2004**, *126*, 9326.

Monolayer packing



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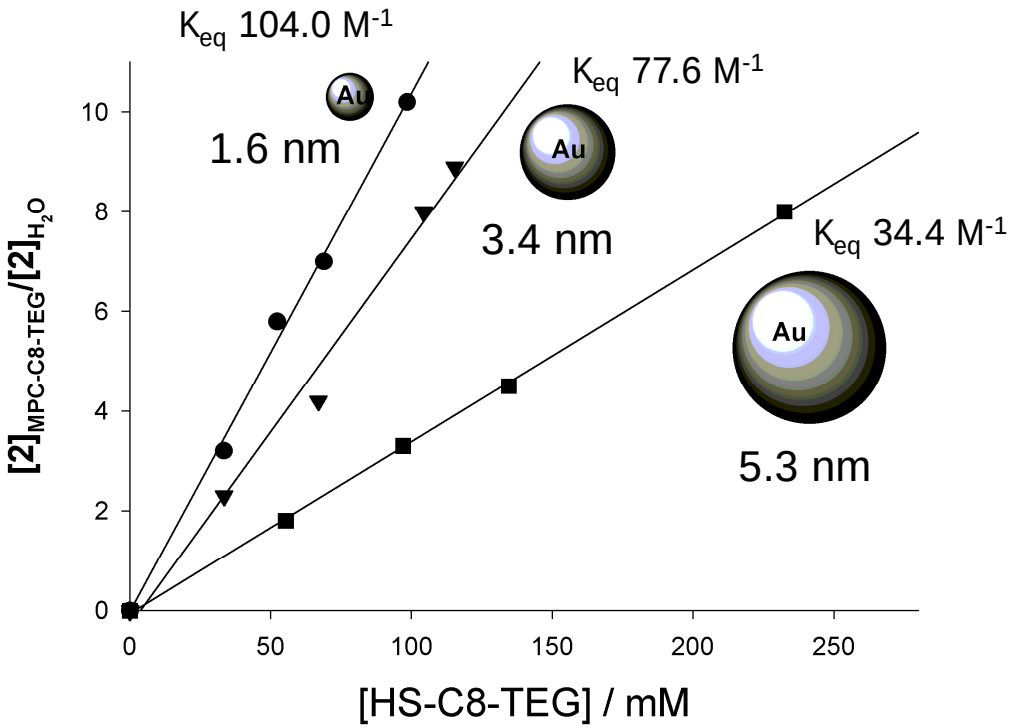
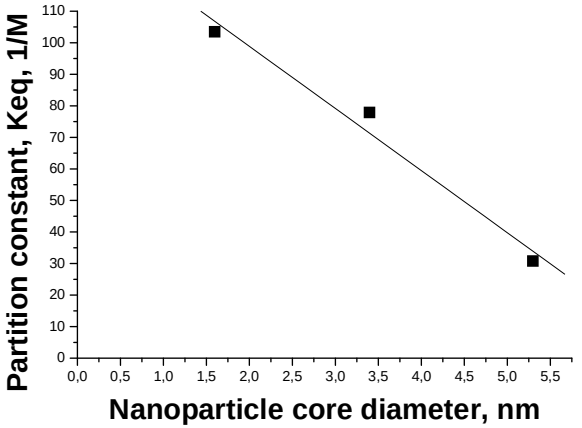
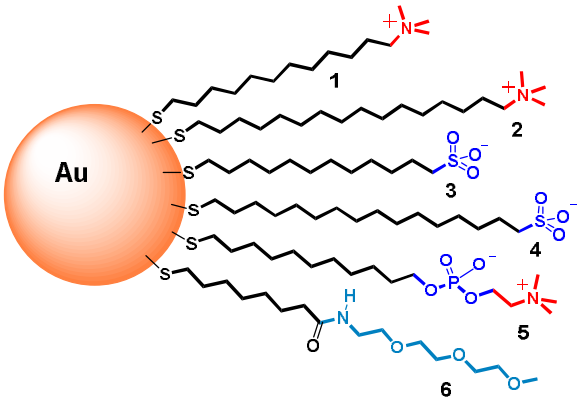




M. Lucarini, P. Franchi, G. F. Pedulli, C. Gentilini, S. Polizzi, P. Pengo, P. Scrimin, L. Pasquato, *J. Am. Chem. Soc.* **2005**, *127*, 16384.

Monolayer packing



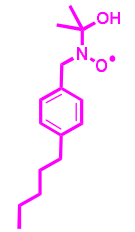
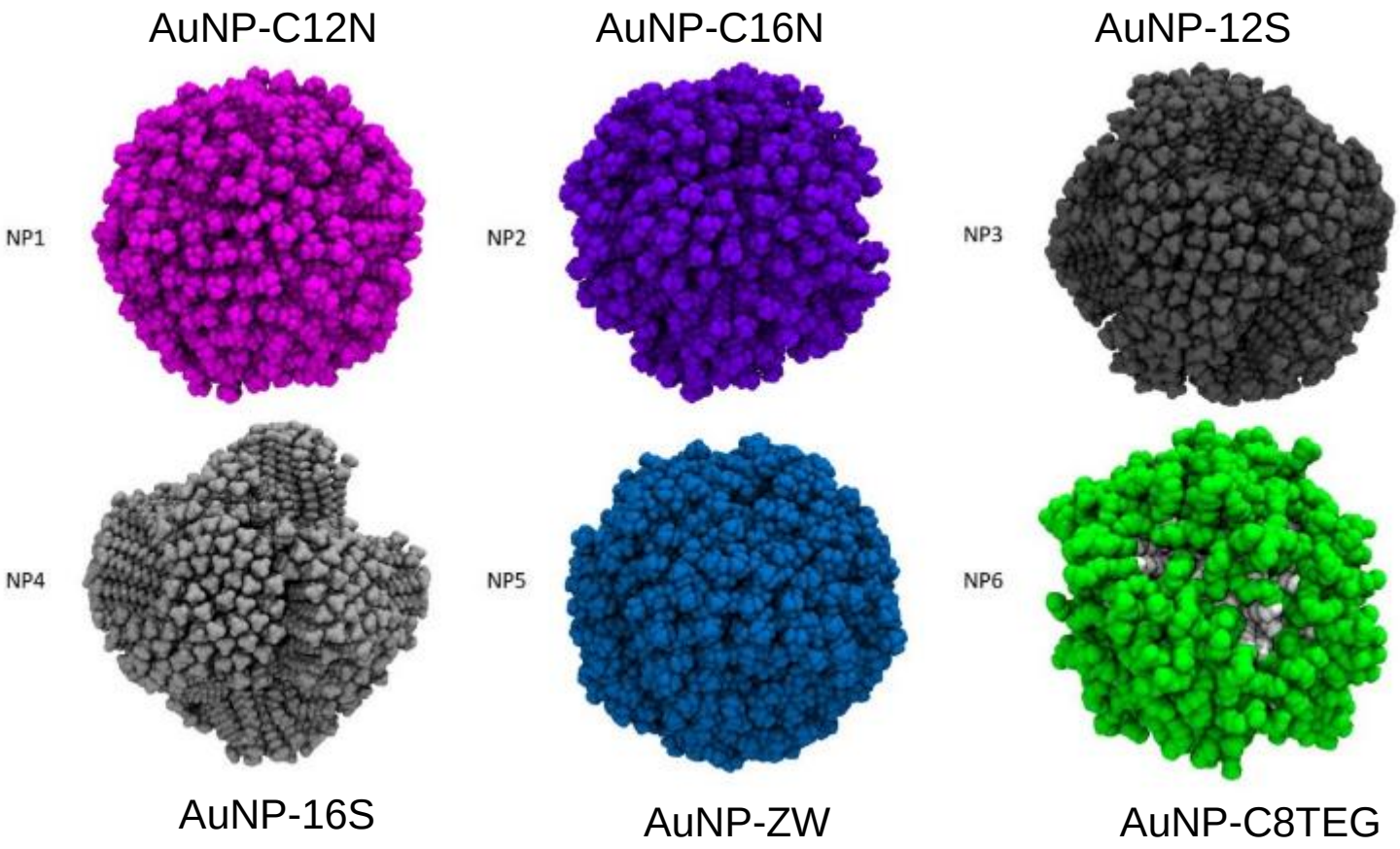


Table 1. Spectroscopic parameters for the radical probe and partition equilibrium (K_{eq}) constants.

NP	T (K)	a_N (G)	a_{2H} (G)	K_{eq} (M^{-1})
-	300	16.25	10.14	
-	340	16.22	9.80	
NP-1	300	15.20	8.50	131
NP-1	340	15.35	8.46	20
NP-2	300	14.50[a]	8.45[a]	
		15.18	8.58	
NP-2	340	15.15	8.50	320
NP-3	300	15.15	8.40	133
NP-3	340	15.40	8.48	26
NP-4	300	14.40[a]	8.38[a]	
		15.23	8.30	
NP-4	330	14.58[a]	8.40[a]	
		15.33	8.33	
NP-4	340	15.32	8.40	98
NP-5	300	15.25	8.35	550
NP-6[b]	298	15.70	9.00	77

M. Lucarini, P. Posocco, L. Pasquato et al. submitted manuscript 2020.

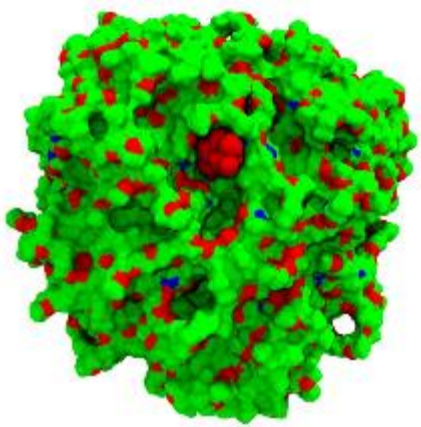
Monolayer packing



M. Lucarini, P. Posocco, L. Pasquato et al. submitted manuscript 2020.

Monolayer packing

AuNP-C8TEG



b)

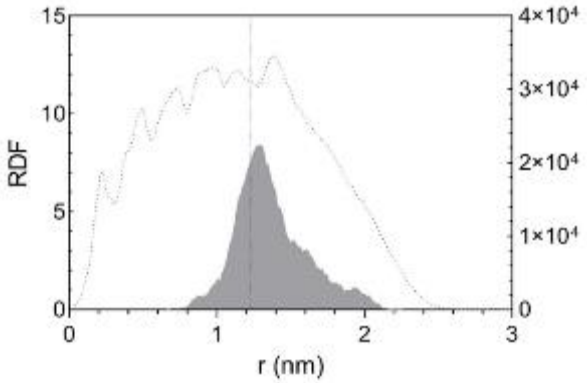
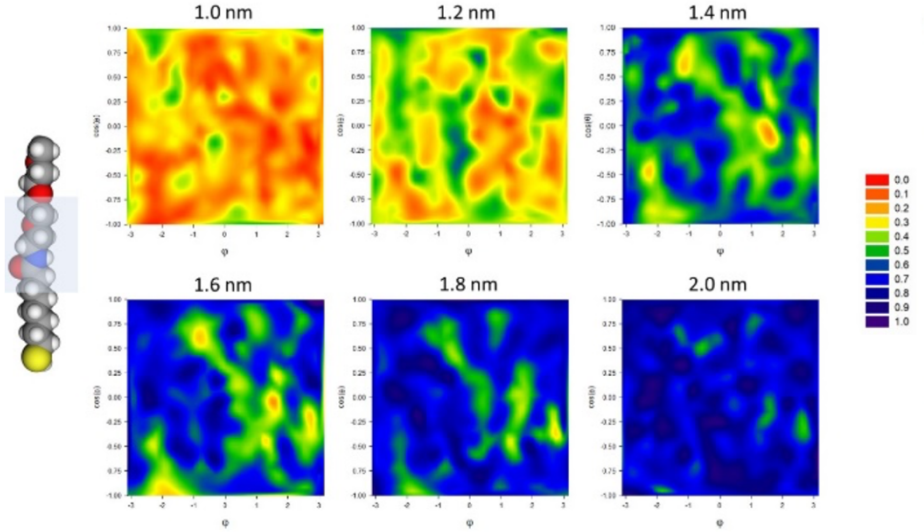


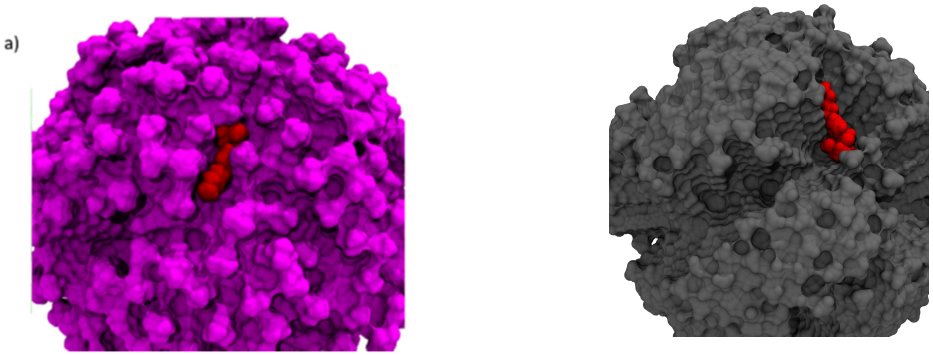
Figure S2. a) Binding of the radical probe (in red) within **NP6**. Solvent is omitted for clarity, oxygen atoms are in red and nitrogen atoms in blue, all the others atoms of the ligand are in green.
b) Radial distribution function (RDF) of nitrogen atom of the radical probe (solid line, left axis) and thiolate of **6** (dotted line, right axis) reported from the gold surface



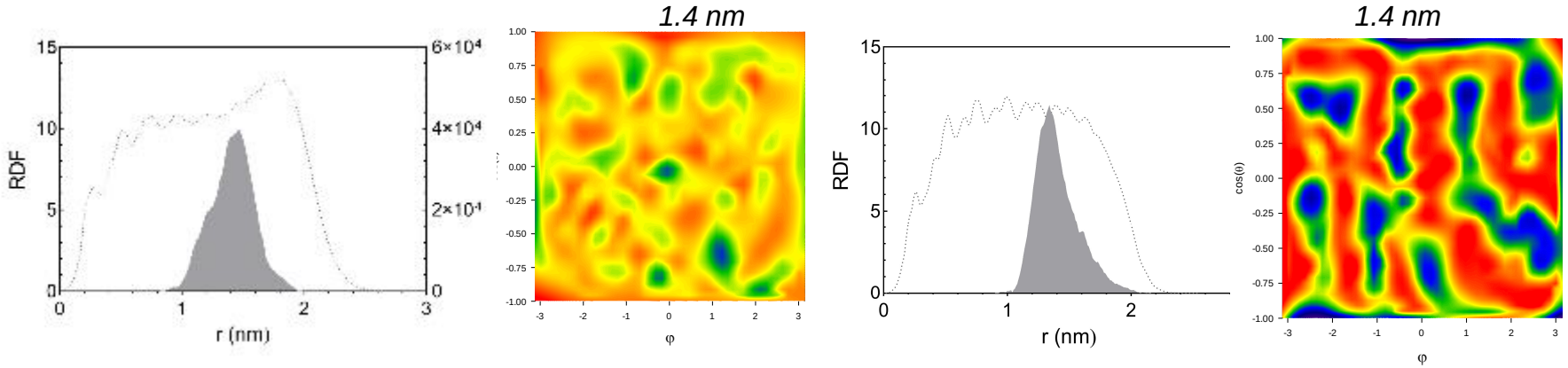
M. Lucarini, P. Posocco, L. Pasquato et al. submitted manuscript 2020.

Monolayer packing

end group: ammonium ion solfonate



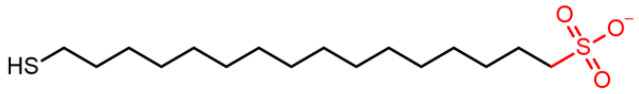
NP1 **NP3**

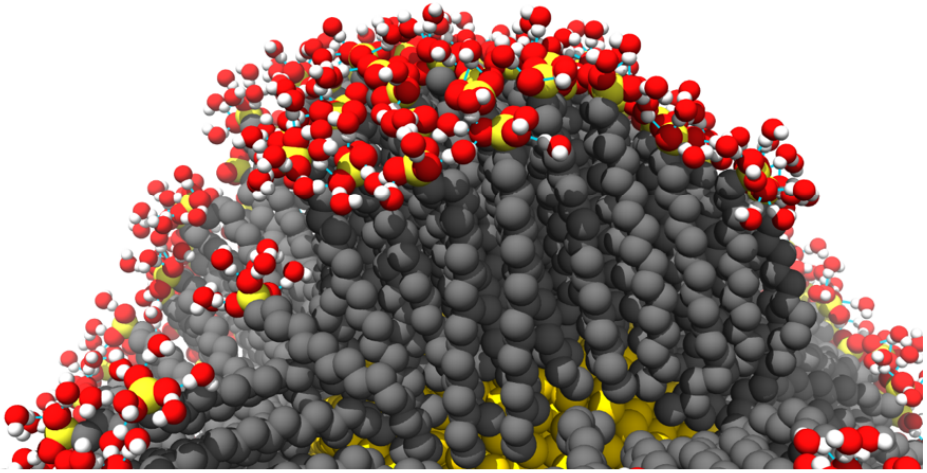


normalized water distribution at 1.4 nm from the gold surface

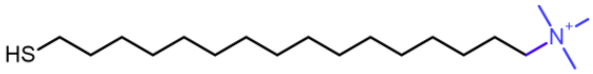
M. Lucarini, P. Posocco, L. Pasquato et al. manuscript submitted.

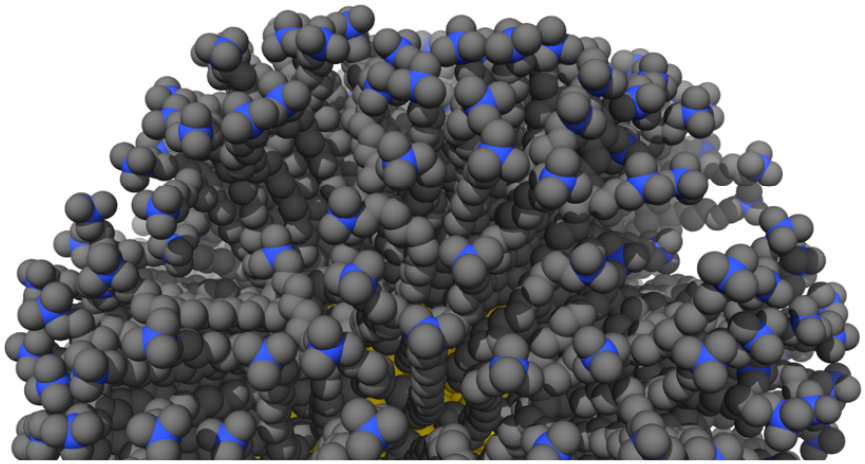
Monolayer packing





bundled self-assembled monolayer





urchin-like self-assembled monolayer

M. Lucarini, P. Posocco, L. Pasquato et al. manuscript submitted.

Monolayer packing

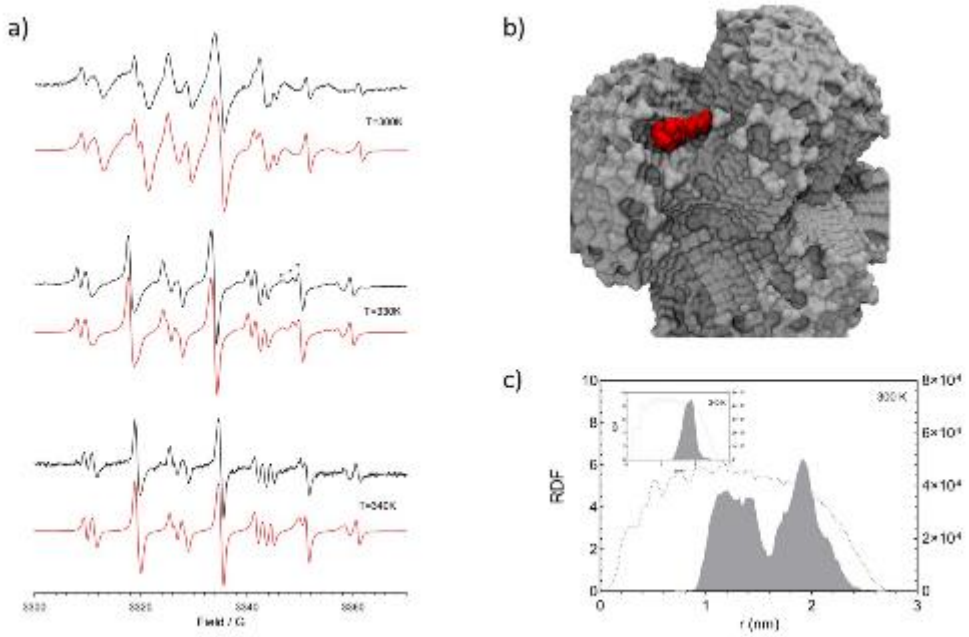
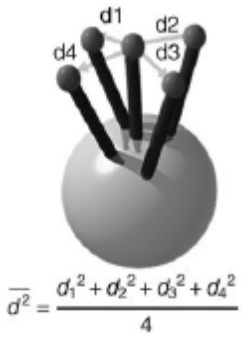


Figure 5. a) EPR spectra of the radical probe recorded in the presence of **NP4** (13.3 mg/0.1mL) at 300 K (top), 330 K (middle) and 340 K (bottom). Stars refer to the three different radical species (see text). In red are reported the corresponding theoretical simulations; b) Binding of the radical probe (in red) within **NP4**. Solvent is omitted for clarity. c) Radial distribution function (RDF) of nitrogen atom of the radical probe in the monolayer of **NP2** (solid line, left axis) and ligand **2** (dotted line, right axis) reported from the gold surface. Insert: same RDFs as in panel c), but predicted at 340 K.

M. Lucarini, P. Posocco, L. Pasquato et al. submitted manuscript 2020.

Monolayer packing

Dynamics of Thiolate Chains on a Gold Nanoparticle



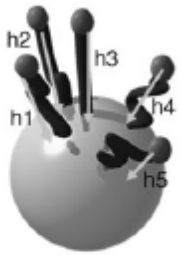
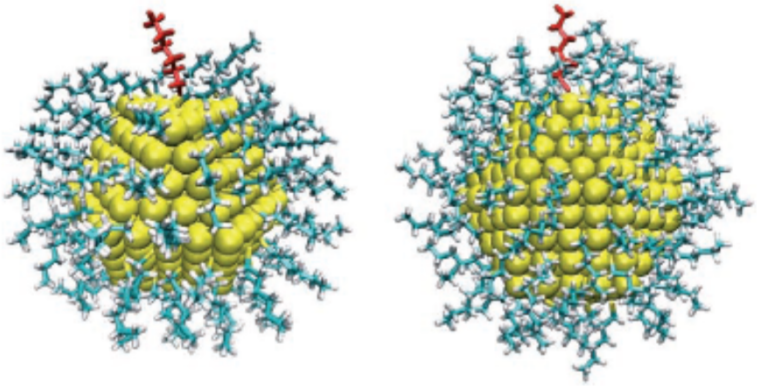


Figure 2. Cartoons illustrating how terminal chain atoms become more available to the external environment. Left: increase of the "horizontal" distance from the neighbors. Right: increase of the height from the particle surface.

$Au_{309}(SC_6H_{13})_{80}$

diametro 2.3 nm
shape: CO



Schematic representation of the molecular-dynamics simulations.
The red thiolate represents the least crowded (left) and the most linearly extended (right) thiolate.

hair-whorl

Hairy-ball theorem: it is know that one cannot comb the hair on a ball smootly so that there is no bald spot.

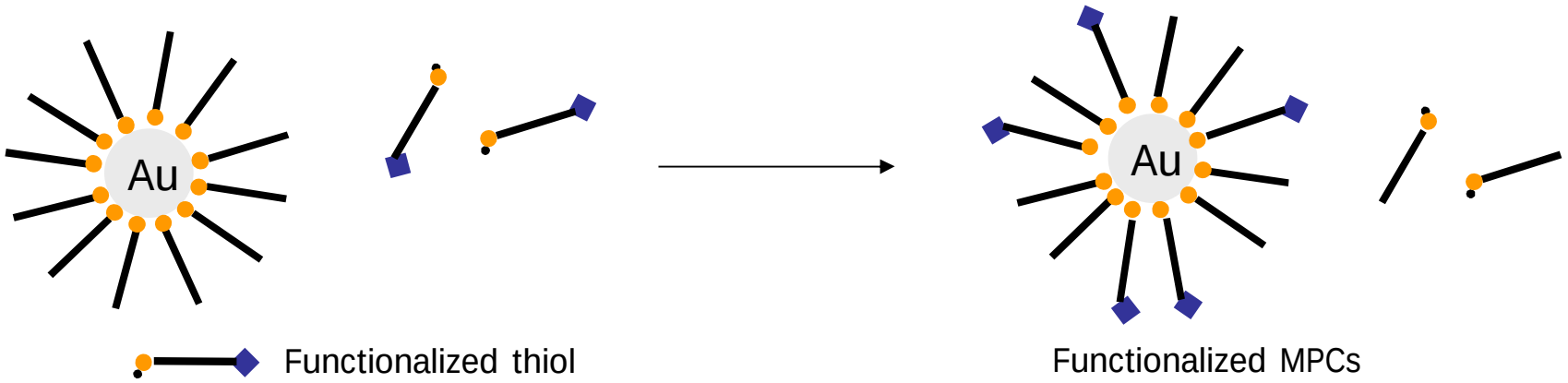
S. Rapino and F. Zerbetto, *Small,* 2007, **3**, 386-388.

Nanoparticles - functionalization

- **synthesis using a mixture of thiols**

  thiols should survive under the reaction conditions

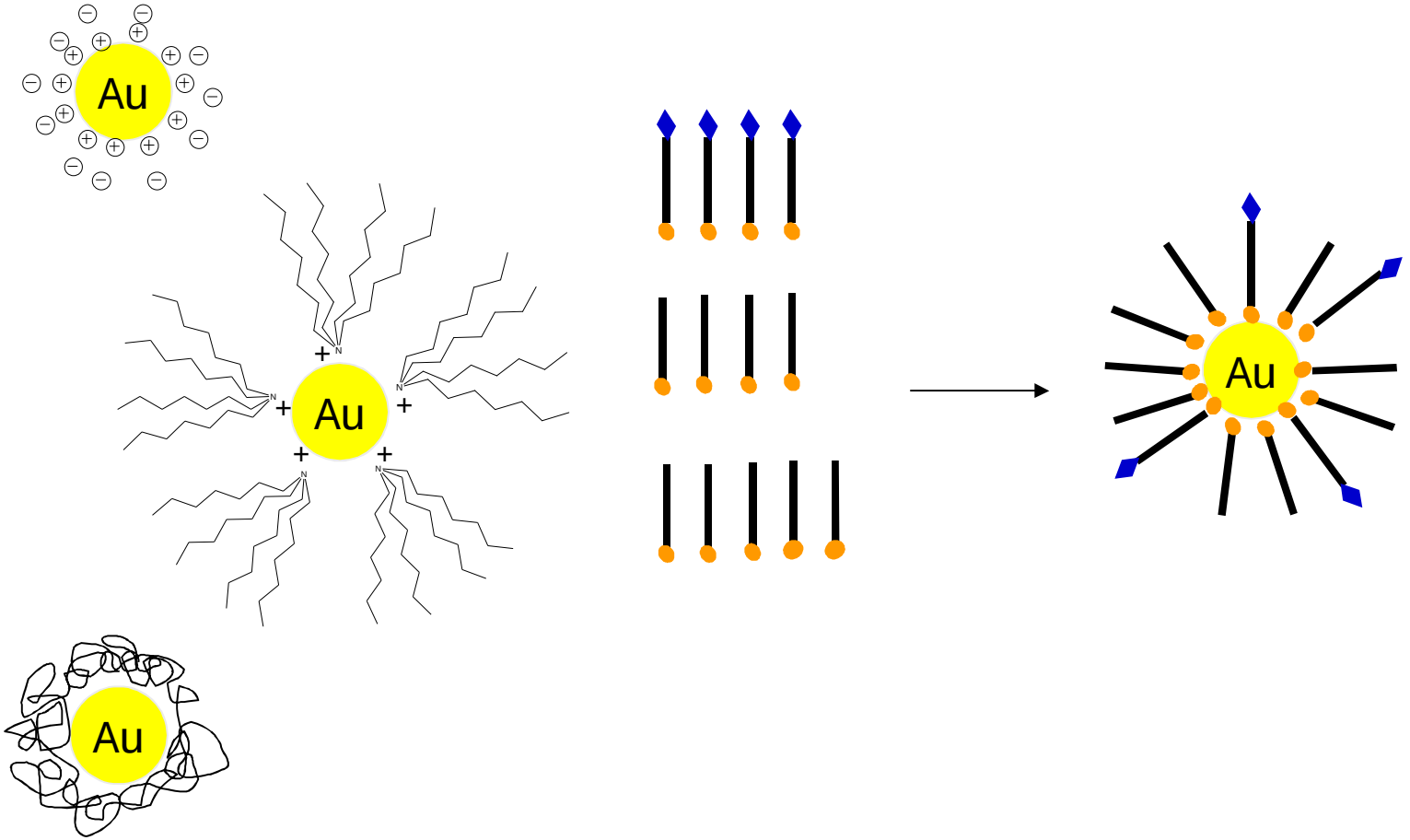
- **Ligand exchange**



Hostetler, M. J.; Green, S. J.; Murray, R. W. *J. Am. Chem. Soc.,* **1996**, *118*, 4212 - 4213.

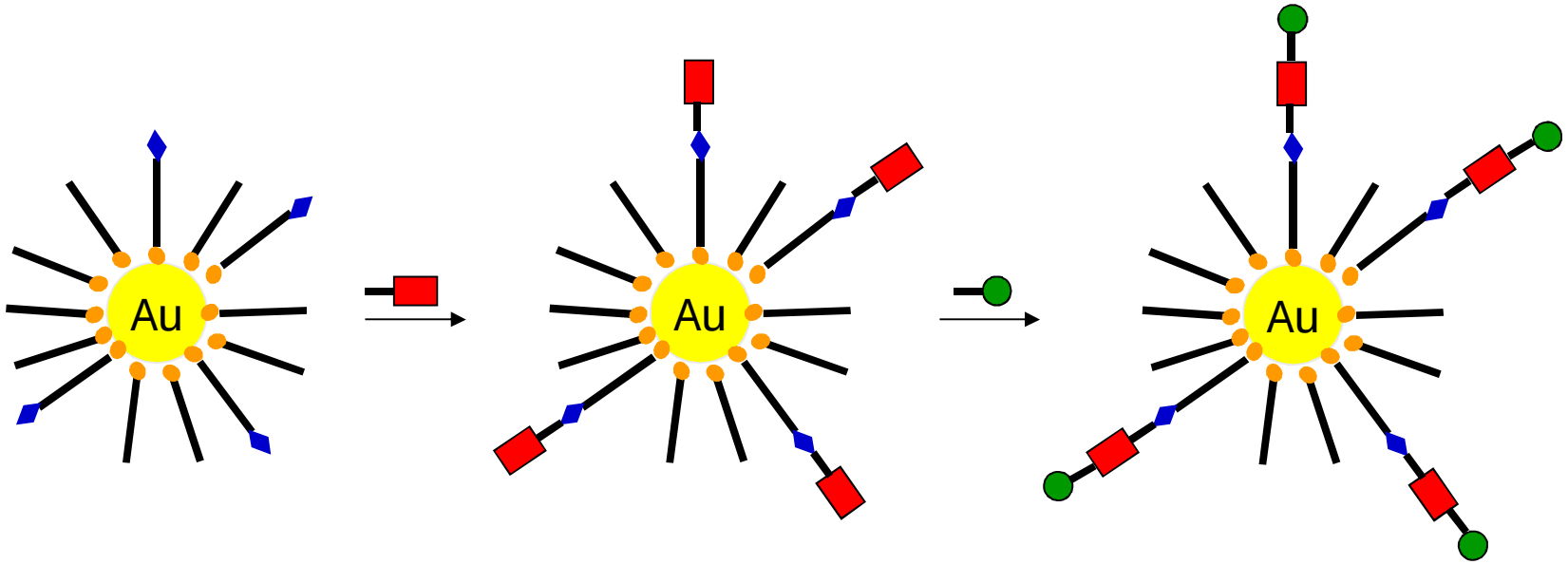
Nanoparticles - functionalization

Synthesis of the monolayer with a blend of thiols



Nanoparticles - functionalization

Covalent Modification



Templeton, A. C.; Hostetler, M. J.; *Warmoth, E. K.; Chen, S.; Hartshorn, C. M.; Krishnamurthy, V. M.; Forbes, M. D. E.; Murray, R. W. J. Am. Chem. Soc.* ***1998****, 120*, 4845-4849.