Supplementary Material (ESI) for Chemical Communications

How to Very Efficiently Functionalize Gold Nanoparticles by "Click" Chemistry

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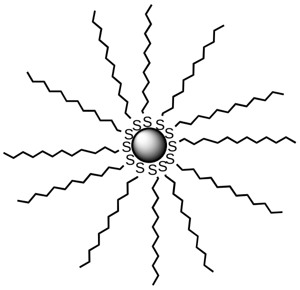
SUPPLEMENTARY INFORMATION

Page

1. Synthesis of dodecanthiolate-AuNPs …………………………………………… 1
2. Ligand exchange with bromoundecanethiol …………………………………… 2
3. Azidation of the AuNPs………………………………………………………. 3
4. General procedure for "click" reactions………………………………………… 4
5. Click chemistry with phenylacetylene…………. ………………………………. 5
6. Click chemistry with ferrocenylacetylene……………………………………… 6
7. Click chemistry with the tetraethyleneglycol derivative……………………….. 8
8. Click chemistry with the triallyl aryl dendron……….…………………………. 9
9. Click chemistry with the short polyethyleneglycol (PEG) containing dendron… 10
10. Click chemistry with the long PEG containing dendron………..……………… 12
11. Calculations of the diameters and molar masses of AuNPs…………………….. 14

1. Synthesis of dodecanethiolate-AuNPs



An aqueous solution of hydrogen tetrachloroaurate (30 mL, 30 mmol dm^{-3}, 0.9 mmol) was mixed with a toluene solution of tetraoctylammoniumbromide (80 mL, 50 mmol dm^{-3}, 4 mmol). The two-phase mixture was vigorously stirred until all the hydrogen tetrachloroaurate was transferred into the organic layer, and dodecanethiol ($C_{12}H_{25}SH$, 0.9 mmol) was then added to the organic phase. A freshly prepared solution of sodium borohydride (25 mL, 0.4 mol dm^{-3}, 10 mmol) was slowly added with vigorous stirring. After further stirring for 3 h, the organic phase was separated, evaporated to 10 mL in a rotary evaporator and mixed with 400 mL ethanol to remove excess thiol. The mixture was kept for 4 h at –18°C, and the dark brown precipitate was filtered off and washed with ethanol and acetone. The crude product was dissolved in 10 mL toluene and again precipitated with 400 mL ethanol.

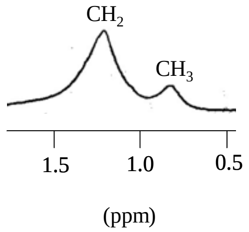


Fig. S1: ^1H NMR spectrum of dodecanethiolate-AuNPs in $CDCl_3$ (δ ppm)

^1H NMR ($CDCl_3$, 250MHz): 1.22 (22H, CH_2), 0.83 (3H, CH_3)

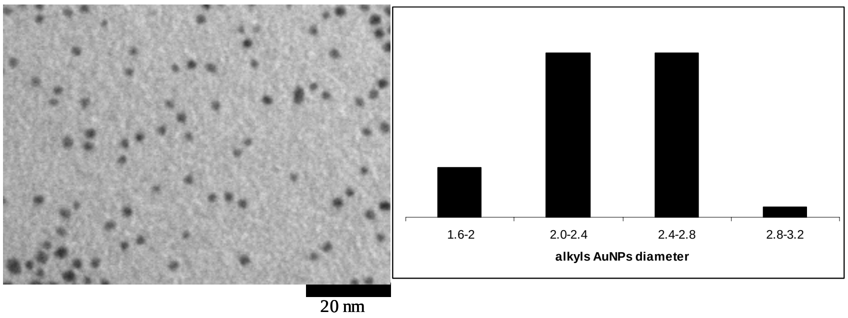


Fig. S2: TEM image of dodecanethiolate-AuNPs

diameter = 2.5 nm (± 0.3 nm)

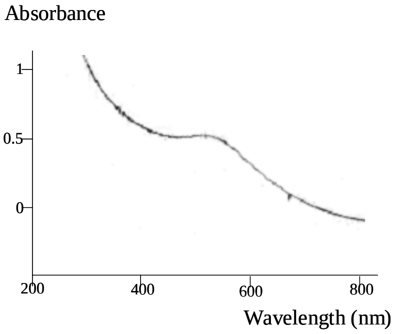
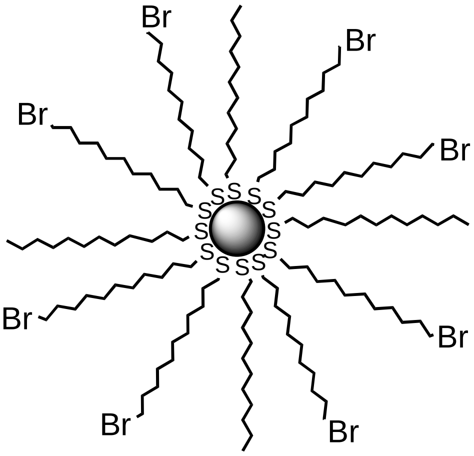


Fig. S3: UV-vis. Spectrum of dodecanethiolate-AuNPs in CH_2Cl_2

Plasmon band of the AuNPs at 520 nm

2. Ligand exchange with bromoundecanethiol



Dodecanethiolate-AuNPs (130 mg) were dissolved in distilled CH_2Cl_2 and bromoundecanethiol (500 mg) was added to the solution. After stirring for 5 days under N_2 at room temperature, AuNPs was evaporated and precipitated with acetone and ethanol to remove the excess thiol (m = 130 mg, yield = 94%).

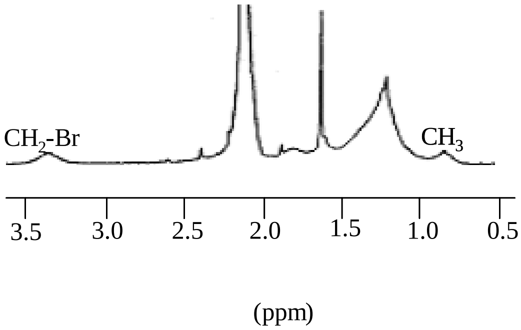


Fig. S4: ^{1}H NMR spectrum of mixed dodecanethiolate-1-bromoundecanethiolate AuNPs in $CDCl_3$ (δ ppm)

^{1}H NMR ($CDCl_3$, 250MHz): 3.40 (2H, CH_2-Br), 1.22 (22H, CH_2), 0.83 (3H, CH_3)

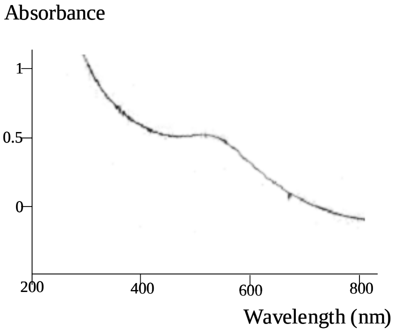
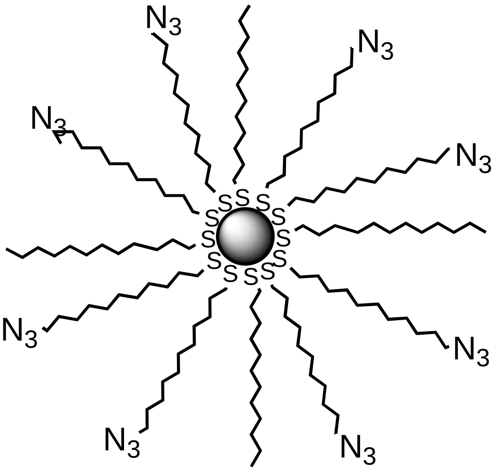


Fig. S5: UV-vis. Spectrum of mixed dodecanethiolate-1-bromoundecanethiolate

Plasmon band of mixed AuNPs at 520 nm

3. Azidation of the AuNPs



The mixed AuNPs (10 mg/mL, 150 mg) were dissolved in CH_2Cl_2 (15 mL) and added to an equal volume of 0.25 M NaN_3 (244 mg) in DMSO. The solution was stirred for 48 h under N_2 at rt, water was added, and the black organic layer was isolated. The organic layer was dried over sodium sulfate, the solvent was evaporated, and the AuNPs were washed with ethanol and dried (m = 140mg, yield = 98%).

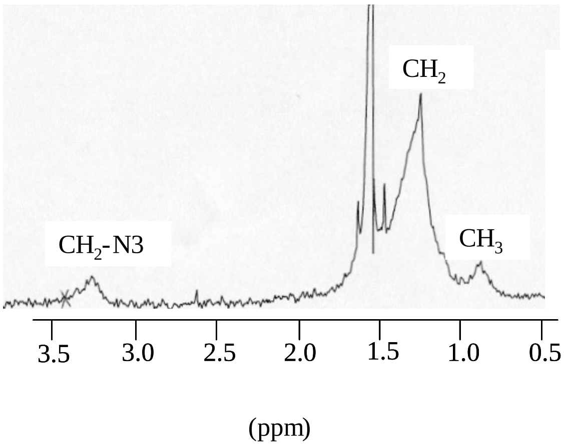


Fig. S6: ^1H NMR spectrum of mixed dodecanethiolate-1-azidoundecanethiolate AuNPs in $CDCl_3$ (δ ppm)

^1H NMR ($CDCl_3$, 250MHz): 3.26 (2H, CH_2-Br), 1.22 (22H, CH_2), 0.83 (3H, CH_3)

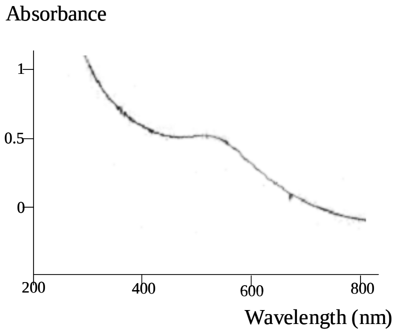


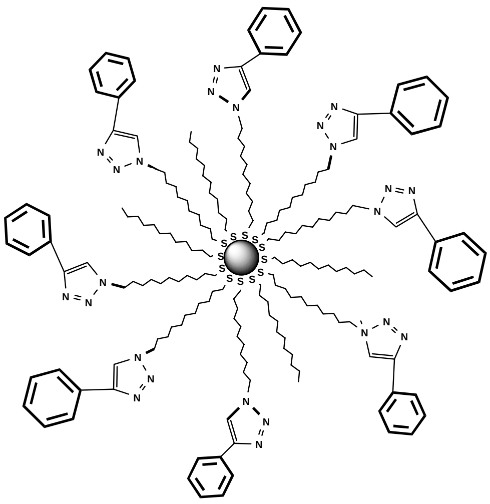
Fig. S7: UV-vis. spectrum of mixed dodecanethiolate-1-azidoundecanethiolate AuNPs in CH_2Cl_2

Plasmon band of mixed AuNPs at 520 nm

4. General procedure for “click” reactions

The azidoalkylthiolate-AuNPs (50 mg) and the alkyne (0.1 mmol) were dissolved in THF. At 0°C, $CuSO_4$ was added (2 eq. *per* alkyne, 1M water solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (4 eq. *per* branch, 1M water solution) in order to set a 1:1 (THF/water) ratio. The solution was allowed to stir for 2 days at rt under N_2. After removing THF under vacuum, CH_2Cl_2 and water solution of ammonia were added. The mixture was allowed to stir for 10 min. in order to remove all the Cu^{II} trapped inside the AuNPs as $Cu(NH_3)_6$. The organic phase was washed twice with water, dried with sodium sulfate, and the solvent was removed under vacuum. In order to remove the excess alkyne, the product was precipitated with MeOH/ether for the PEG ligand, with CH_2Cl_2/MeOH for the triallyl dendron, and with CH_2Cl_2/ether for the ferrocenyl and phenyl derivatives.

5. Click chemistry with phenylacetylene



yield = 81%

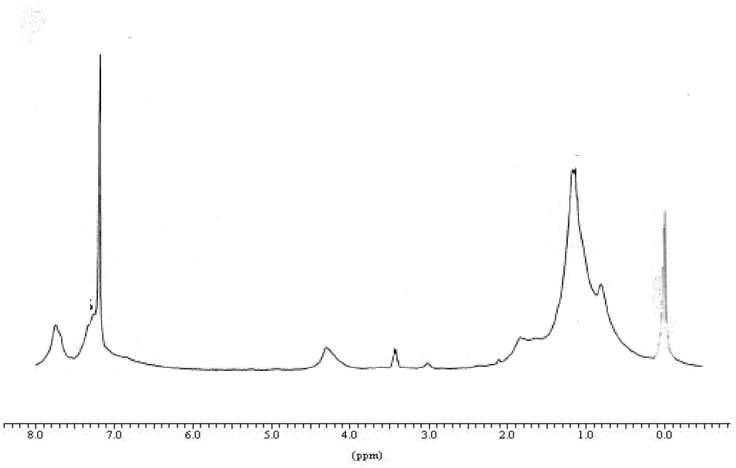


Fig. S8: ^{1}H NMR spectrum of phenyltriazolylakanethiolate AuNPs in $CDCl_3$ (δ ppm)

^{1}H NMR ($CDCl_3$, 250MHz):7.74 (2H, C-C*H*-phenyl) 7.60 (1H, C*H*-triazole), 7.33 (3H, C*H*-CH-C), 4.36 (2H, triazole-CH_2), 1.25 (18H, $CH_2C\mathit{H}_2CH_2$), 0.87 (3H, $CH_2C\mathit{H}_3$)

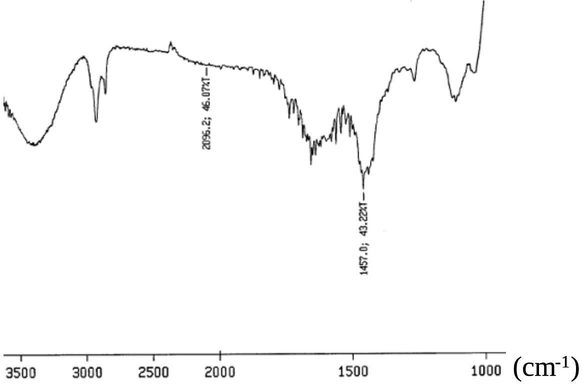


Fig. S9: IR spectrum of phenyltriazolylakanethiolate AuNPs

Disappearance of the ν_{N_3} band at 2094 cm^{-1}

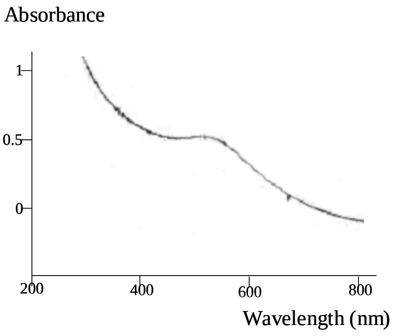
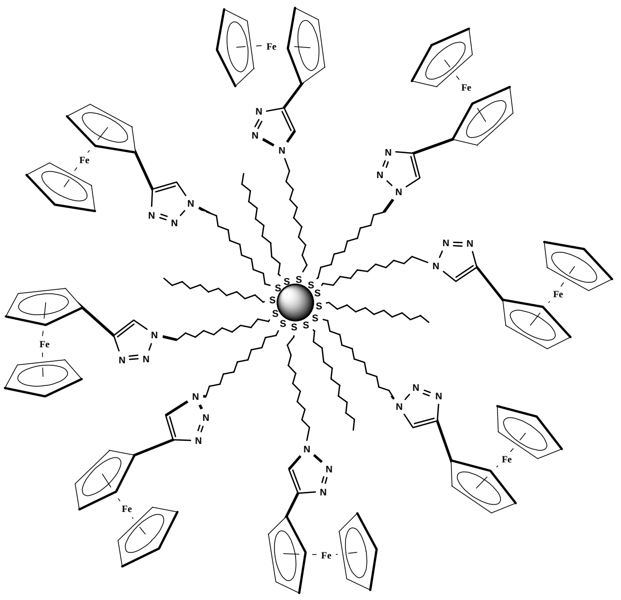


Fig S10: UV-vis. spectrum of phenyltriazolylakanethiolate AuNPs in CH_2Cl_2

Plasmon band of the AuNPs at 520 nm

6. Click chemistry with ferrocenylacetylene



yield = 80%

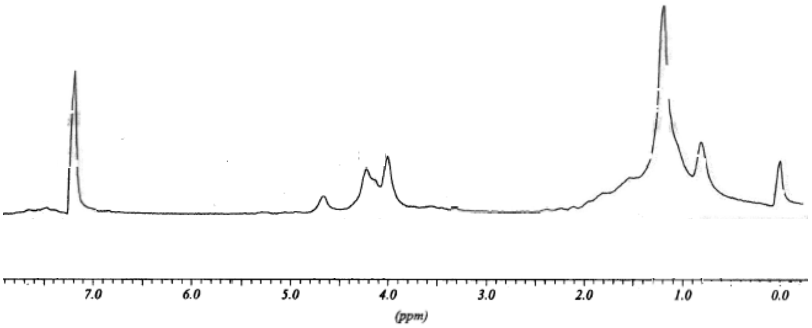


Fig. S11: ^{1}H NMR spectrum of ferrocenyltriazolylakanethiolate AuNPs in CDCl$_3$ (δ ppm)

^{1}H NMR (CDCl$_3$, 250MHz): 7.54 (1H, C*H*-triazole), 7.33 (3H, C*H*-CH-C), 4.73, 4.28, 4.07 (9H, Cp), 4.19 (2H, triazole-CH_2), 1.25 (18H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 0.87 (3H, $\mathrm{CH_2C}\mathit{H}_3$)

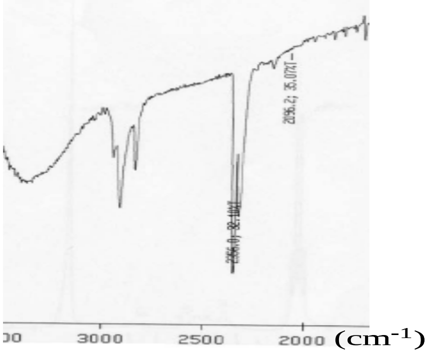


Fig. S12: IR spectrum of ferrocenyltriazolylakanethiolate AuNPs

Disappearance of the ν_{N_3} band at 2094 cm^{-1}

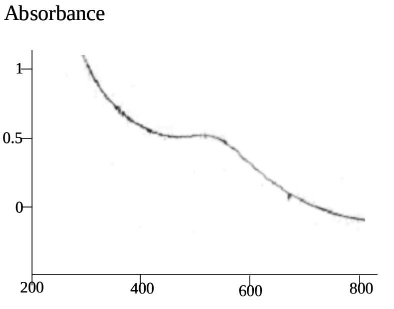


Fig. S13: UV-vis. spectrum of ferrocenyltriazolylakanethiolate AuNPs in CH$_2$Cl$_2$

Plasmon band of the AuNPs at 520 nm

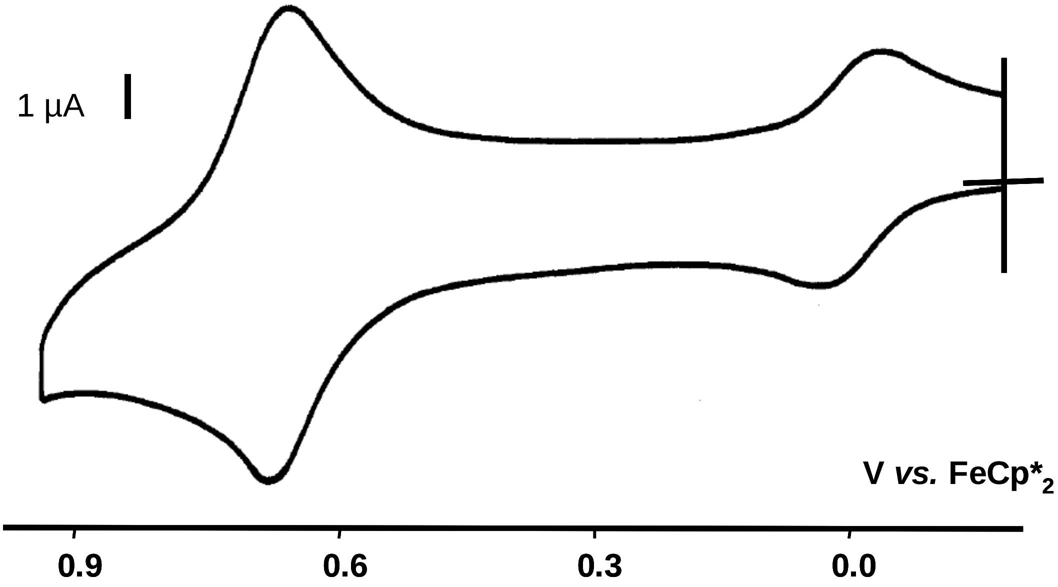
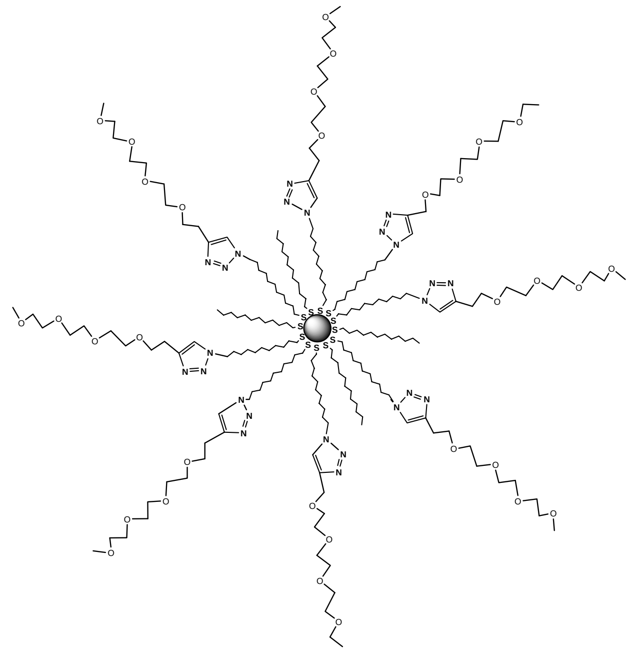


Fig. S14: Cyclic voltammetry of AuNPs with ferrocenyl termini obtained by “click” chemistry

$E_{1/2}$ 0.67 V. Solvent :CH_2Cl_2; temperature: 20ºC; supporting electrolyte: [*n*Bu_4N][PF_6] 0.1M; working and counter electrodes: Pt; reference electrode: Ag; scan rate: 0.200 V.s^{-1} ; internal reference: decamethylferrocene.

7. Click chemistry with the tetraethyleneglycol derivative



yield = 82%

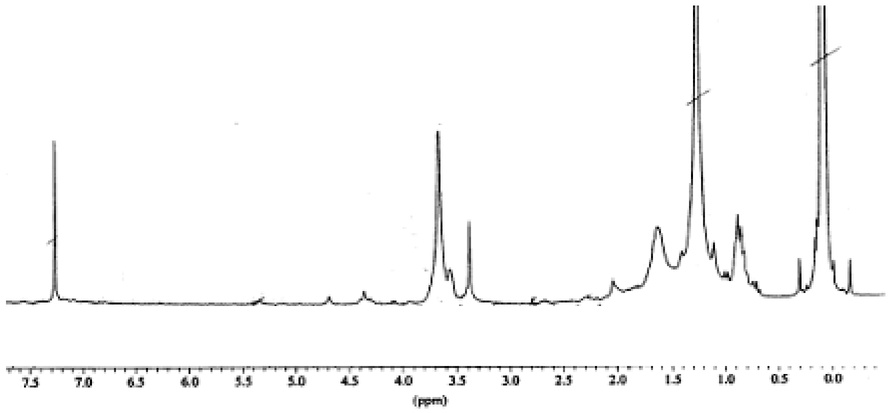


Fig. S15: ^{1}H NMR spectrum of AuNPs with tetraethyleneglycol termini in CDCl$_3$ (δ ppm)

^{1}H NMR (CDCl$_3$, 250MHz): 7.53 (1H, CH-triazole), 4.69 (2H, triazole-CH_2-0), 4.35 (2H, CH$_2$-CH_2-triazole), 3.66 (12H, OCH_2CH_2O), 3.37 (3H, CH_3O), 2.66 (2H, CH_2S), 1.25 (18H, CH$_2$CH_2CH$_2$), 0.87 (3H, CH$_2$CH_3).

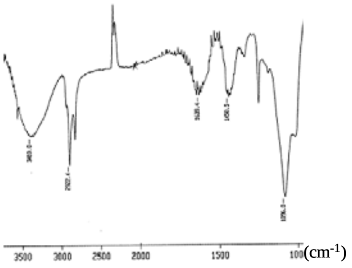


Fig. S16: IR spectrum of AuNPs with tetraethyleneglycol termini

Disappearance of the ν_{N_3}band at 2094 cm^{-1}

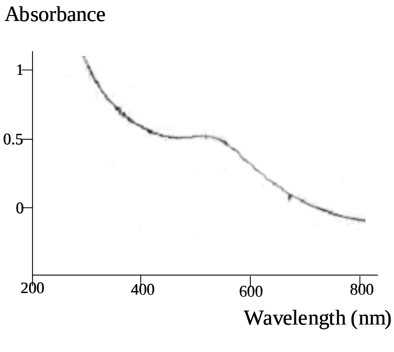
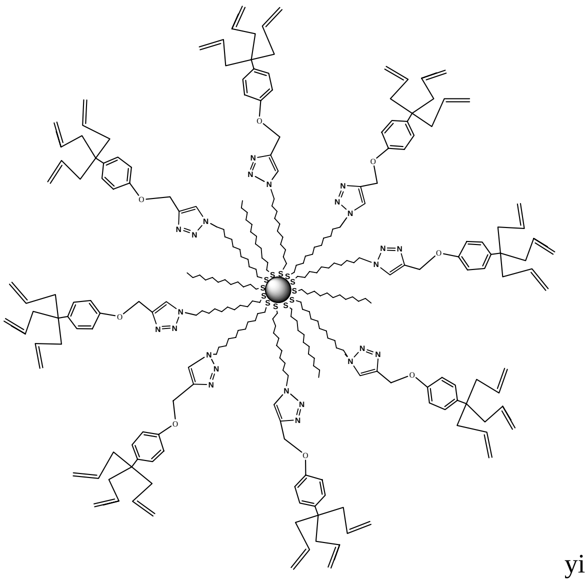


Fig. S17: UV-vis. spectrum of AuNPs with tetraethyleneglycol termini in CH$_2$Cl$_2$

Plasmon band of the AuNPs at 520 nm

8. Click chemistry with the triallyl aryl dendron



yield = 81%

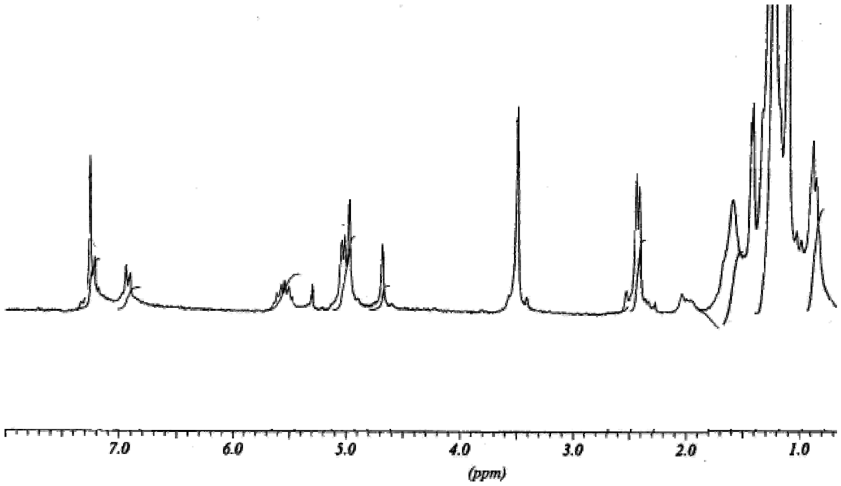


Fig. S18: ^{1}H NMR spectrum of AuNPs with triallyl aryl dendron termini in $CDCl_3$ (δ ppm)

^{1}H NMR ($CDCl_3$, 250MHz): 7.53 (1H, C*H*-triazole), 7.21 and 6.94 (4H, C*H* aromatic), 5.54 (3H, C*H* allyl), 5.01 (6H, CH-CH_2-allyl), 4.69 (2H, triazole-CH_2-0), 2.44 (2H, CH_2 allyl), 1.25 (18H, $CH_2CH_2CH_2$), 0.87 (3H, CH_2CH_3)

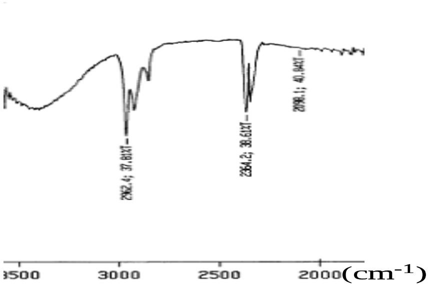


Fig. S19: IR spectrum of AuNPs with triallyl aryl dendron termini

Disappearance of the ν_{N_3}band at 2094 cm^{-1}

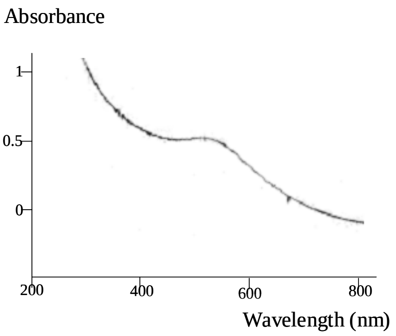
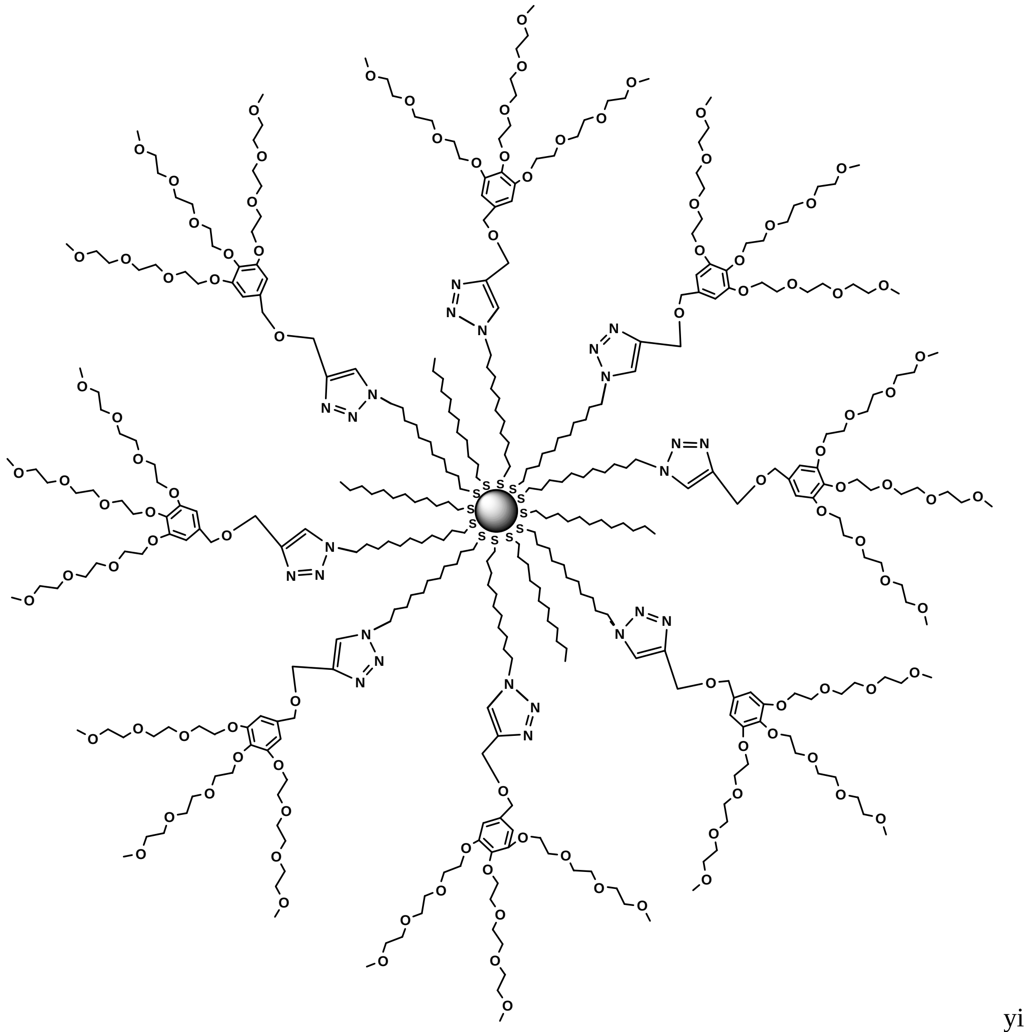


Fig. S20: UV-vis. spectrum of AuNPs with triallyl aryl dendron termini in CH_2Cl_2

Plasmon band of the AuNPs at 520 nm

9. Click chemistry with the short polyethyleneglycol (PEG) containing dendron



yield = 85%

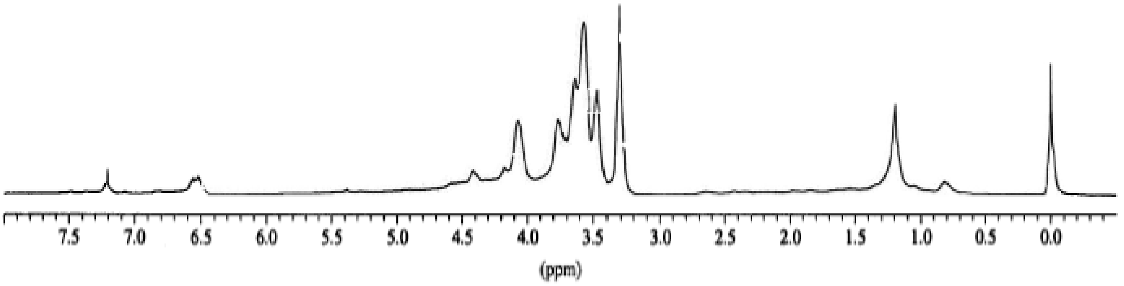


Fig. S21: ^{1}H NMR spectrum of AuNPs with short dendronic PEG termini in CDCl$_3$ (δ ppm)

^{1}H NMR (CDCl$_3$, 250MHz): 7.53 (1H, CH-triazole), 6.58 (2H, CH-arom.), 4.60 (2H, triazole-CH_2-0), 4.49 (2H, CH$_2$-CH_2-triazole), 4.14 (8H, OCH_2-arom. and arom-OCH_2CH$_2$), 3.66 (30H, OCH_2CH_2O), 3.37 (9H, CH_3O), 2.47 (2H, CH_2S), 1.25 (18H, CH$_2$CH_2CH$_2$), 0.87 (3H, CH$_2$CH_3).

Microanalysis: S (1.47%) ; Au (18.86%)

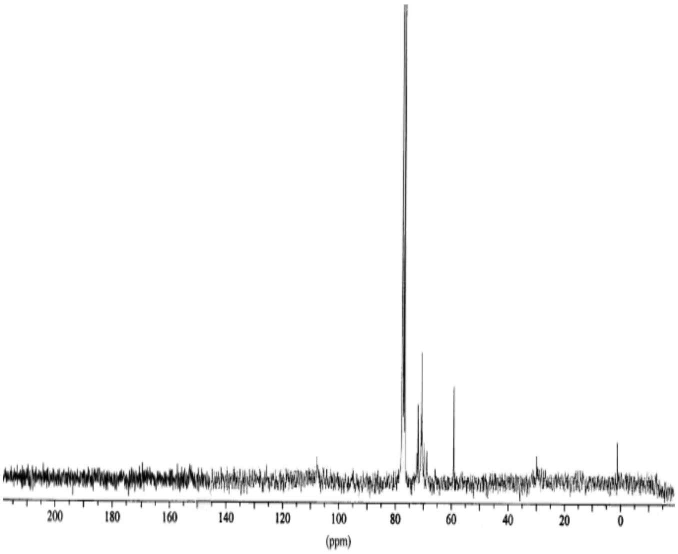


Fig. S22: ^{13}C NMR spectrum of AuNPs with short dendronic PEG termini in $CDCl_3$ (δ ppm)

^{13}C NMR ($CDCl_3$, 62 MHz):126.1 (*C*H of triazole and arom. core), 107.16 (C_qCH_2O), 70.39 (OCH_2CH_2O), 65.90 (triazole-CH_2-O), 58.91 (CH_3O)

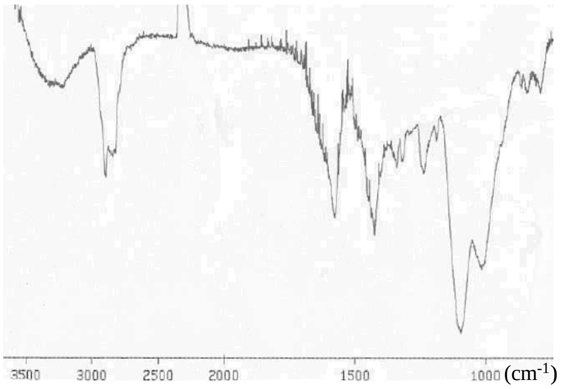


Fig. S23: IR spectrum of AuNPs with short dendronic PEG termini

Disappearance of the ν_{N_3}band at 2094 cm^{-1}

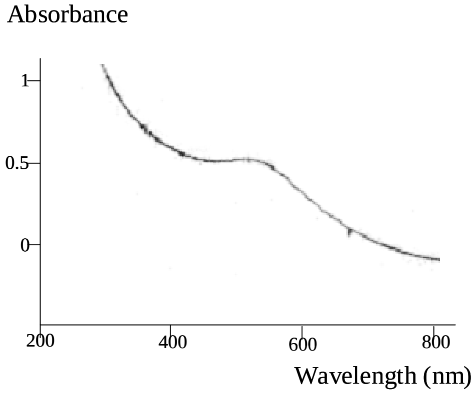


Fig. S24: UV-vis. spectrum of AuNPs with short dendronic PEG termini in CH_2Cl_2

Plasmon band of the AuNPs at 520 nm

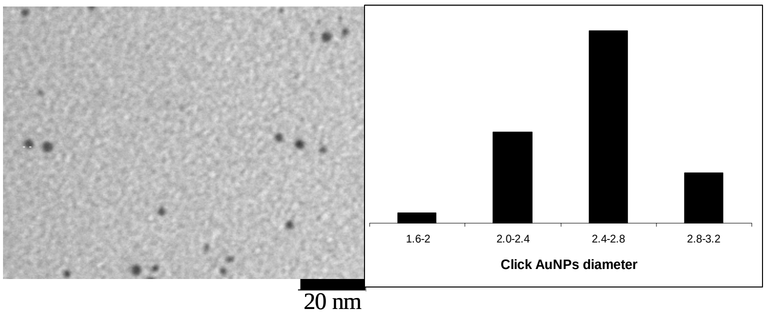
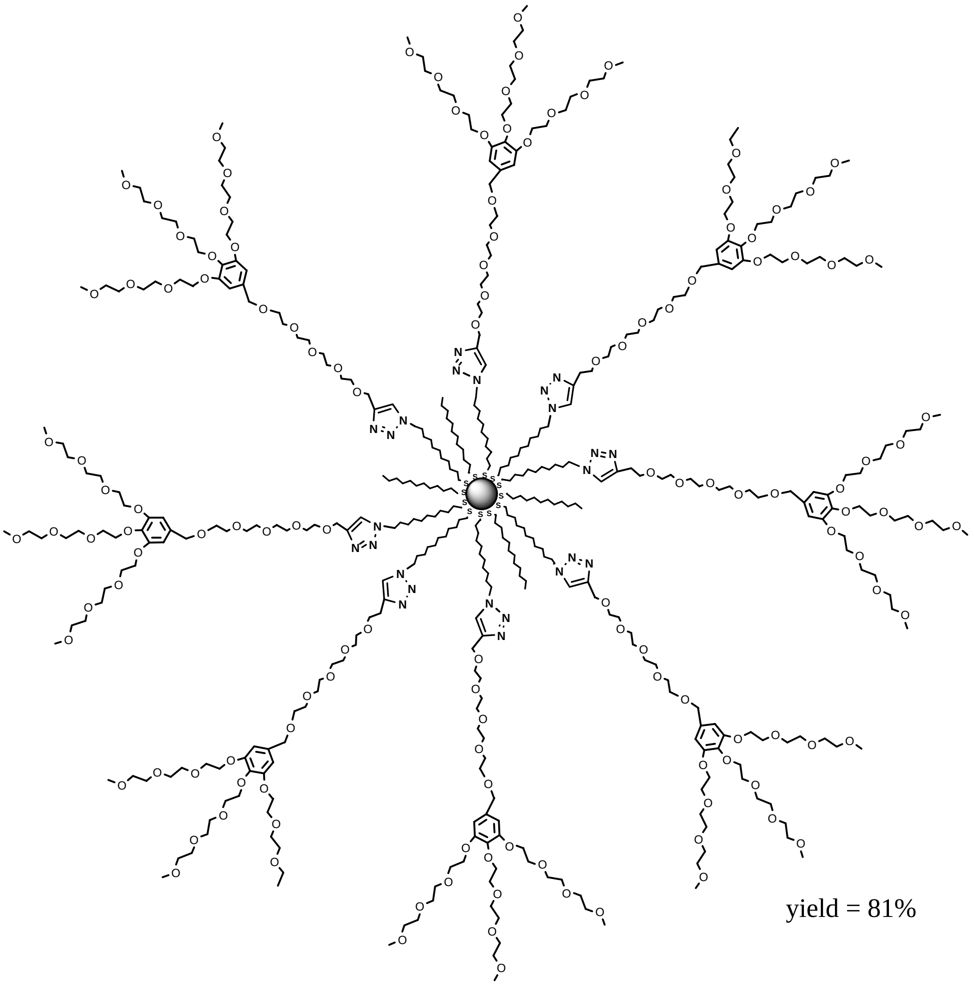


Fig. S25: TEM image of AuNPs with short dendronic PEG termini

diameter = 2.5 nm (± 0.3 nm)

10. Click chemistry with the long PEG-containing dendron



yield = 81%

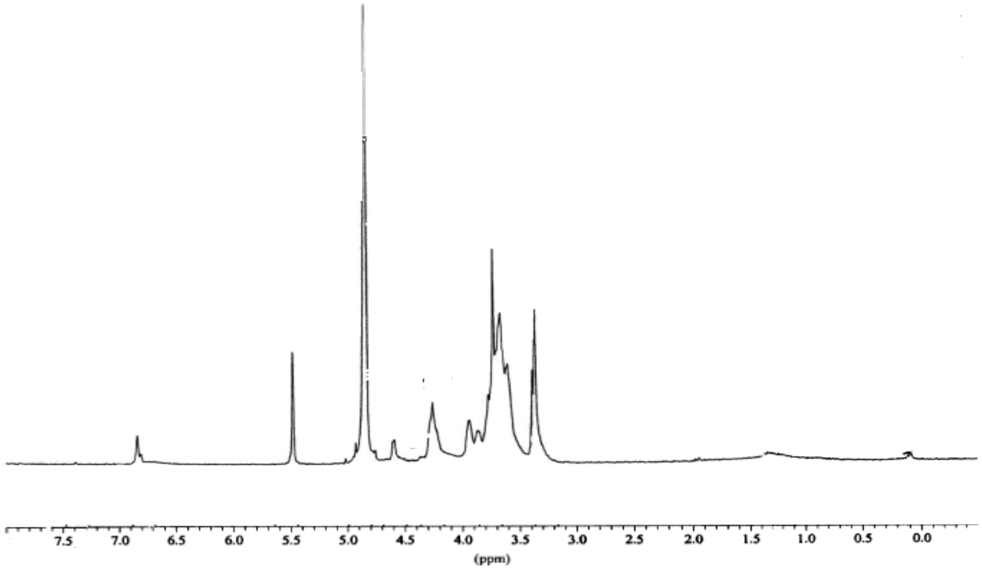


Fig. S26: ^{1}H NMR spectrum of AuNPs with long dendronic PEG termini in $CDCl_3$ (δ ppm)

^{1}H NMR ($CDCl_3$, 250MHz): 7.53 (1H, $\mathrm{C}H$-triazole), 6.58 (2H, $\mathrm{C}H$-arom.), 4.60 (2H, triazole-$\mathrm{C}H_2$-0), 4.49 (2H, $\mathrm{CH_2}$-$\mathrm{C}H_2$-triazole), 4.14 (8H, $\mathrm{OC}H_2$-arom. and arom-$\mathrm{OC}H_2\mathrm{CH_2}$), 3.66 (48H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$), 3.37 (9H, $\mathrm{C}H_3\mathrm{O}$), 2.47 (2H, $\mathrm{C}H_2\mathrm{S}$), 1.25 (18H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 0.87 (3H, $\mathrm{CH_2C}H_3$)

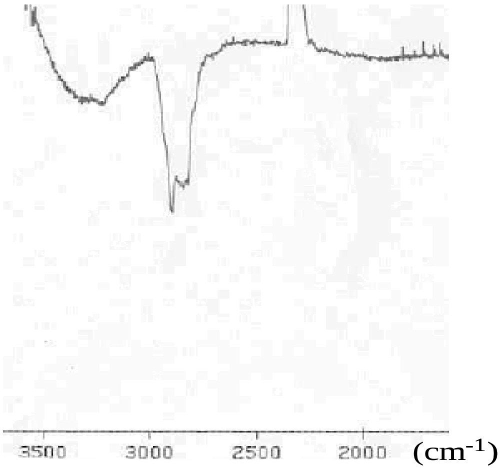


Fig. S27: IR spectrum of AuNPs with long dendronic PEG termini

Disappearance of the ν_{N_3}band at 2094 cm^{-1}

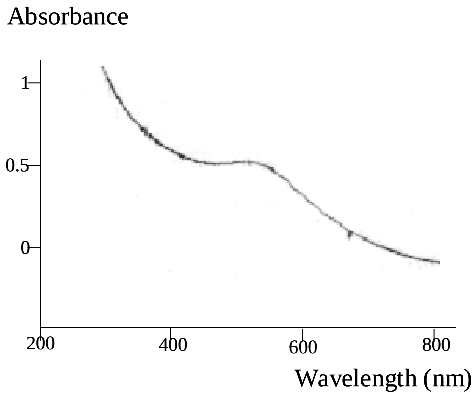


Fig. S28: UV-vis. spectrum of AuNPs with long dendronic PEG termini in CH_2Cl_2

Plasmon band of the AuNPs at 520 nm

11. Calculations of the diameters and molar masses of AuNPs

Diameter of AuNPs obtained by TEM before and after AuNP transformations: 2.5 nm (±0.3)

Number of gold atoms: $N(Au) = \frac{4\pi \text{ x } 12.5^3}{3 \text{ x} 17} =$ 481 gold atoms *per* AuNP

Elemental analysis : Au (18.86%); S (1.47%).

This leads to 230 S atoms *per* AuNP.

Each AuNP contains 72% (±3) of functionnalized ligand and 28% (±3) of alkyl thiolate ligands, i.e. 166±6 functionnal ligands (% obtained by peak integrations in the ^{1}H NMR spectrum); the molar mass (MM) of each AuNP is calculated using the following formula:

MM(AuNP) = MM(functionnalized ligand) x (230 x 0.72) + MM (alkyl ligand) x (230 x 0.28) + MM(Au) x N(Au)

	Dodecane-thiolate	Bromoundecane-thiolate	Azidoalkyl-thiolate	Phenyltriazolyl derivative	Ferrocenyltriazolyl derivative	TEG derivative	Triallyl dendronic derivative	Short PEG-containing dendron	Long PEG-containing dendron
MM (thiolate ligand) (g.mol^{-1})	201	266	228	330	438	444	494	860	1036
MM (functionnalized AuNP) (g.mol^{-1})	140000	150000	145000	160000	180000	180000	190000	250000	280000

Using these results, equivalent numbers used for the synthesis of the AuNPs are calculated: approximately 2000 bromoundecanethiol *per* AuNP were used for the ligand exchange, and approximately 20 NaN_3 molecules *per* bromoundecanethiol were used for the azidation of the AuNPs.