

ELECTRONIC SUPPLEMENTARY INFORMATION

Routes to the preparation of mixed monolayers of fluorinated and hydrogenated alkanethiolates grafted on the surface of gold nanoparticles

Maria Şologan,^a Cristina Cantarutti,^a Silvia Bidoggia,^a Stefano Polizzi,^b Paolo Pengo,^a and Lucia Pasquato^{*,a}

^a Department of Chemical and Pharmaceutical Sciences and INSTM Trieste Unit, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy. E-mail: lpasquato@units.it

^b Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venezia, Via Torino 155/b, I-30172 Venezia-Mestre, Italy

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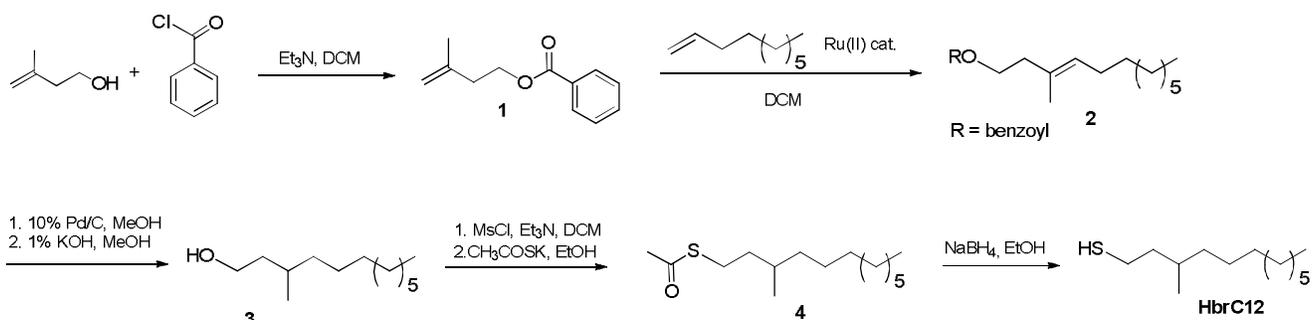
General Information

All commercially available reagents were from Aldrich and Alfa Aesar, and used without purification unless otherwise mentioned. Solvents were purchased from Aldrich and VWR, deuterated solvents from Cambridge Isotope Laboratories and Aldrich. Dry solvents were obtained from Aldrich and Alfa Aesar. Chlorinated solvents were kept over K_2CO_3 with occasional shaking for at least 24 h prior to use. All other solvents were reagent grade and used as received. Reactions were monitored by TLC on Merck silica gel plates (0.25 mm) and visualized by UV light, I_2 , or by $KMnO_4-H_2SO_4$. Chromatography was performed on Merck silica gel 60F-254 (230–400 mesh).

NMR spectra were recorded on a Varian 500 spectrometer (operating at 500 MHz for proton, at 125 MHz for carbon), or on a Jeol GX-400 MHz (operating at 400 for proton). 1H NMR spectra were referenced to the residual protons in the deuterated solvent. ^{13}C NMR spectra were referenced to the solvent chemical shift. Chemical shifts (δ) are quoted in ppm and the multiplicity of each signal is designated by the conventional abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dd, doublet of doublets. Coupling constants (J) are quoted in Hz. Mass spectra were obtained by electrospray ionization (ESI) with a Perkin Elmer APIII at 5600 eV and recorded by Dr Fabio Hollan, Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy. UV-Visible spectra were recorded on a Shimadzu UV-1800 spectrophotometer. TGA analyses were performed on TGA Q-500 V6.3 Build 189 using platinum pans and a heating rate of 10 °C/min up to 1000 °C or on a Netzsch STA 409 using alumina crucibles and a heating rate of 10 °C/min up to 650 °C. TEM images were obtained with either a Philips EM 208 operating at 100 kV or with a Joel 3010 high resolution electron microscope (1.7 nm point-to-point) operating at 300 keV using a *Gatan* slow-scan CCD camera (mod. 794). TEM samples of the gold nanoparticles were prepared by deposition of a single drop of nanoparticles solution, 0.5 mg/mL or less, onto 200-mesh copper or nickel grids coated with an amorphous carbon film. The solvent used were: chloroform, hexane or hexafluorobenzene according to the nanoparticles solubility. The diameters of the nanoparticles core were measured manually using *Gatan* software Digital Micrograph on at least 300 particles.

Synthesis

Synthesis of the branched thiol, HbrC12. 3-methyldodecane-1-thiol (**HbrC12**) was prepared according to Scheme S1.



Scheme S1

3-methylbut-3-enylbenzoate, 1. Benzoyl chloride (700 μL , 6 mmol) was added to a solution of 3-methylbut-3-en-1-ol (608 μL , 6 mmol) in dry DCM (8 mL) at 0-5°C under argon. Triethylamine (1.69 mL, 12 mmol) was added in 15 minutes and the reaction mixture was stirred 15 minutes. The mixture was diluted with 2 mL of DCM and stirred at room temperature for 3.5 hours. The reaction mixture was diluted with 10 mL of DCM and washed with 10% HCl (2 x 15 mL); saturated NaHCO_3 (15 mL) and brine (15 mL). The solvents were removed under reduced pressure and the crude product was purified by flash chromatography using hexane to hexane/diethyl ether 96/4. Yield 78%. The $^1\text{H-NMR}$, ^{13}C NMR and Mass-spectra are in agreement with the literature.¹

(3E)-3-methyldodec-3-en-1-yl benzoate, 2. 1-decene and 3-methylbut-3-enylbenzoate, **1** were simultaneously added *via* a syringe to a stirring solution of dichloro[1,3-bis(2,6-isopropylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene) ruthenium(II) in dry deoxygenated DCM. The reaction was refluxed under argon atmosphere for 24 hours. The reaction mixture was then reduced in volume to 0.5 mL and purified directly on silica gel column, eluting with hexane. ^1H NMR (500 MHz, CDCl_3): δ 8.05 (d, 2H, Bz), 7.43-7.55 (m, 3H, Bz), 5.26- 5.35 (m, 1H, $\text{CH}_2\text{-CH=}$), 4.36 (t, 2H, CH_2O), 2.46 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-O}$), 2.00 (m, 2H, $\text{CH}_2\text{-CH}_2\text{=CH}$), 0.87-1.78 (m, 20H, CH_2). ^{13}C NMR (500 MHz, CDCl_3): δ 166 (C=O), 128.2-132.7 (Bz), 121.25 ($\text{CH}_2\text{-CH=}$), 63.6 (CH_2O), 38.7 ($\text{CH}_2\text{-CH}_2\text{-O}$), 13.8-30 (CH_2).

3-methyldodecan-1-ol, 3. 1. Pd/C (0.018 g) was added to 0.045 g (0.1488 mmol) of compound **2** dissolved in 2 mL of MeOH. The reaction was left under hydrogen atmosphere for 1 day. Then the reaction was stopped and the mixture was centrifuged. The supernatant was separated and the solvent was evaporated under reduced pressure obtaining a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 8.05 (d, 2H, Bz), 7.43-7.55 (m, 3H, Bz), 4.36 (t, 2H, $\underline{\text{CH}_2\text{O}}$), 2.46 (m, 2H, $\underline{\text{CH}_2\text{-CH}_2\text{-O}}$), 0.87-1.78 (m, 20H, $\underline{\text{CH}_2}$). ^{13}C NMR (500 MHz, CDCl_3): δ 166 (C=O), 128.2-132.7 (Bz), 63.6 ($\underline{\text{CH}_2\text{O}}$), 38.7 ($\underline{\text{CH}_2\text{-CH}_2\text{-O}}$), 13.8-30 ($\underline{\text{CH}_2}$).

2. A 1% solution of KOH in methanol (1 mL) was added to 0.037 g (0.115 mmol) of the compound obtained in the preceding step, the reaction mixture was stirred at room temperature for 1 day. The solvent was removed under reduce pressure and the residue was dissolved first in 30 mL water and then 30 mL of hexane were added. The aqueous layer was extracted with hexane (4 x 30 mL) and ethyl acetate (4 x 30 mL). The pure product was obtained in a 56% yield. ^1H NMR (500 MHz, CDCl_3): δ 3.6 (m, 2H, $\underline{\text{CH}_2\text{-OH}}$), 0.87-1.78 (m, 25H, $\underline{\text{CH}_2}$).

S-(3-methyldodecyl) ethanethioate, 4. 1. Triethylamine (0.125 mL, 1.24 mmol) was slowly added to an aliquot of alcohol **3** (0.050 g, 0.249 mmol) diluted in 7 mL of hexane. The reaction mixture was left stirring at room temperature for 30 minutes. The solution was cooled in an ice bath and MsCl (0.085 mL, 0.747 mmol) was added dropwise. The reaction mixture was stirred for 4 hours at room temperature and afterwards, excess MsCl was destroyed by adding 20 mL of water. The organic layer was separated and the aqueous layer was extracted with diethyl ether (8 x 30 mL). The combined organic layers were washed with 0.1 M HCl (3 x 30 mL), saturated aqueous NaHCO_3 (3 x 30 mL) and brine (3 x 30 mL). The organic solution was dried, filtered and brought to dryness to give 80 mg of crude product which was used in the next step without further purification. ^1H NMR (270 MHz, CDCl_3): δ 4.28 (m, 2H, $\underline{\text{CH}_2\text{-OMs}}$), 3.00 (s, $\text{CH}_3\text{-O}$) (0.87-1.78 (m, 25H, $\underline{\text{CH}_2}$).

2. Under argon atmosphere, potassium thioacetate (65 mg, 0.498 mmol) was dissolved in 20 mL of degassed absolute ethanol. The crude mesylate, obtained in the preceding step (80 mg, 0.249 mmol) diluted with degassed ethanol (1 mL) was added over 5 minutes to the stirring solution of potassium thioacetate. The mixture was brought to reflux and kept at this temperature for 4 hours. After cooling, the precipitate was filtered off and rinsed with ethanol. The solvent was removed and the residue was taken up with a mixture of hexane (50 mL) and water (50 mL). The aqueous layer was extracted with hexane (3 x 30 mL) and the combined organic layers were washed with brine (4 x 30 mL), dried over anhydrous Na_2SO_4 , and brought to dryness. The crude product was purified by column chromatography

on silica gel using hexane as eluent. ^1H NMR (500 MHz, CDCl_3): δ 2.84-2.92 (m, 2H, $\underline{\text{CH}_2\text{-S}}\text{Ac}$), 2.32 (s, 3H, $\text{CH}_3\text{-CO}$), 1.56, 1.4 (m, $\underline{\text{CH}_2\text{-CH}_2\text{-S}}$), 1.48 (m, 1H, CH), 1.1-1.35 (m, 14 H, CH_2), 0.89 (6H, CH_3). ^{13}C NMR(500 MHz, CDCl_3): δ 196.09 (CO), 36.47 ($\underline{\text{CH}_2\text{-CH}_2\text{-S}}$), 32.26 (CH), 30.56 ($\text{CH}_3\text{-CO}$), 29.04-29.8 (CH_2), 27.04 ($\underline{\text{CH}_2\text{-S}}\text{Ac}$), 22.59 ($\text{CH}_2\text{-CH}_3$), 19.16 (CH_3), 14.02 ($\text{CH}_3\text{-CH}_2$).

3-methyldodecane-1-thiol, HbrC12. NaBH_4 (6.74 mmol) was added to a solution containing 0.087 g (0.337 mmol) of thioacetate **4** in 5 mL of deoxygenated ethanol. The reaction mixture was stirred at room temperature for 4 hours and afterwards, the reaction mixture was treated with 20 mL of water and 20 mL of AcOEt. The phases were separated and the organic layer was extracted with water (1 x 30 mL) and dried over Na_2SO_4 . The solvent was removed *in vacuo* to give 0.054 mg of colorless oil. ^1H NMR (500 MHz, CDCl_3): δ 2.50 (m, 2H, $\underline{\text{CH}_2\text{-SH}}$), 1.1-1.65 (m, 14 H, CH_2), 0.89 (6H, CH_3). ^{13}C NMR (500 MHz, CDCl_3): δ 41.56 ($\underline{\text{CH}_2\text{-CH}_2\text{-S}}$), 31.947 (CH), 30.56 ($\text{CH}_3\text{-CO}$), 29.34-29.91 (CH_2), 22.79 ($\underline{\text{CH}_2\text{-SH}}$), 22.77 ($\text{CH}_2\text{-CH}_3$), 19.22 (CH_3), 14.10 ($\text{CH}_3\text{-CH}_2$).

Analysis of the monolayer composition. At least 1 mg of nanoparticles was decomposed by overnight treatment with 3 mL of an iodine (2 mg/mL) solution in chloroform. The solvent and the excess iodine were left evaporating under a fume cupboard; the mixture of disulfides was dried under vacuum and analysed by ^1H NMR. The ratio between the ligands was determined by integration of the methylene groups in the alpha position with respect to the sulfur atom.

Table S1. Synthetic details for the preparation of nanoparticles **NP-C12/F6**, obtained by place exchange from **NP-C12**, and characterisation data.

Nanoparticles	Mass NP-C12 (mg) ^a	HF6 (mmol)	HC12/HF6 initial ratio	Diameter ^e (nm)	Composition ^f	X _{F6} ^g	Solubility Score ^h
NP-C12/F6-a	30.6	0.0023 ^b	10.3/1.0	3.4 ± 0.4	Au ₁₃₄₀ (C12) ₂₁₃ (F6) ₂₆	0.106	1
NP-C12/F6-b	36.5	0.0018 ^c	15.0/1.0	3.3 ± 0.3	Au ₁₃₁₀ (C12) ₂₁₀ (F6) ₃₀	0.125	1
NP-C12/F6-c	31.9	0.0059 ^d	4.0/1.0	3.4 ± 0.6	Au ₁₃₄₀ (C12) ₂₀₈ (F6) ₃₀	0.126	1
NP-C12/F6-d	30.0	0.0032 ^b	7.0/1.0	3.2 ± 0.4	Au ₁₂₈₉ (C12) ₁₉₄ (F6) ₃₅	0.154	1
NP-C12/F6-e	30.5	0.0045 ^d	5.0/1.0	3.2 ± 0.3	Au ₁₂₈₉ (C12) ₁₉₀ (F6) ₃₅	0.156	1
NP-C12/F6-f	31.9	0.0029 ^d	8.0/1.0	3.3 ± 0.6	Au ₁₃₄₀ (C12) ₁₇₄ (F6) ₄₀	0.188	1
NP-C12/F6-g	15.0	0.0054 ^d	3.0/1.0	3.2 ± 0.4	Au ₁₂₈₉ (C12) ₁₈₅ (F6) ₄₆	0.200	1
NP-C12/F6-h	31.3	0.0038 ^d	4.8/1.0	3.8 ± 0.3	Au ₂₂₆₇ (C12) ₂₃₂ (F6) ₆₈	0.227	1
NP-C12/F6-i(C)	23.9	0.0079 ^d	2.0/1.0	3.6 ± 0.6	Au ₁₈₃₀ (C12) ₁₉₇ (F6) ₇₃	0.270	1
NP-C12/F6-i(H)				3.6 ± 0.6	Au ₁₈₃₀ (C12) ₁₈₀ (F6) ₁₀₀	0.357	0.5
NP-C12/F6-j	23.2	0.0060 ^d	2.7/1.0	3.6 ± 0.6	Au ₁₈₃₀ (C12) ₂₀₉ (F6) ₈₅	0.286	1
NP-C12/F6-k(C)	24.1	0.0105 ^d	1.6/1.0	3.6 ± 0.6	Au ₁₈₃₀ (C12) ₂₀₆ (F6) ₈₆	0.294	1
NP-C12/F6-k(H)				3.6 ± 0.6	Au ₁₈₃₀ (C12) ₁₈₄ (F6) ₁₂₃	0.400	0.5
NP-C12/F6-l	26.0	0.0213 ^b	1.2/1.0	2.5 ± 0.7	Au ₄₈₈ (C12) ₈₁ (F6) ₄₈	0.370	1
NP-C12/F6-m	44.7	0.0345	1.0/1.0	3.2 ± 0.8	Au ₁₂₈₉ (C12) ₁₂₃ (F6) ₁₁₂	0.478	0
NP-C12/F6-n	33.3	0.1231 ^c	1.0/4.6	3.0 ± 0.8	Au ₉₇₆ (C12) ₇₄ (F6) ₁₀₈	0.600	0
NP-C12/F6-o	37.0	0.0274 ^d	1.0/10.0	3.1 ± 0.4	Au ₁₂₀₀ (C12) ₇₃ (F6) ₁₆₀	0.720	0

^a Dissolved in deoxygenated DCM to a concentration of 2.0 mg/ml. ^b Added as a 26.3 mM solution in deoxygenated DCM. ^c Added as a 131.5 mM solution in deoxygenated DCM. ^d Added as a 13.15 mM solution in deoxygenated DCM. ^e Average diameters and standard deviation obtained by analysis of a population of at least 300 particles. ^f Calculated on the basis of the TGA and TEM and ^1H NMR analyses of decomposed nanoparticles. ^g Molar fraction of the fluorinated ligand in the monolayer of nanoparticles **NP-C12/F6** determined by ^1H NMR analysis of decomposed nanoparticles. ^h The solubility scores are defined arbitrarily as follows: score 1 is assigned to nanoparticles fully soluble in chloroform; score 0.5 is assigned to nanoparticles fully soluble in hexane; score 0 is assigned to nanoparticles fully soluble in hexafluorobenzene.

Table S2. Synthetic details for the preparation of nanoparticles **NP-C12/F10**, obtained by place exchange from **NP-C12**, and characterisation data.

Nanoparticles	Mass NP-C12 (mg) ^a	HF10 (mmol)	HC12/HF10 initial ratio	Diameter ^f (nm)	Composition ^g	X _{F10} ^h	Solubility Score ⁱ
NP-C12/F10-a(C)	43.0	0.0032 ^b	10.0/1.0	3.2 ± 0.3	Au ₁₂₈₉ (C12) ₁₉₄ (F10) ₃₁	0.139	1
NP-C12/F10-a(H)				3.2 ± 0.3	Au ₁₂₈₉ (C12) ₁₆₁ (F10) ₆₀	0.272	0.5
NP-C12/F10-b(C)	47.0	0.0069 ^b	5.0/1.0	3.2 ± 0.3	Au ₁₀₈₉ (C12) ₁₈₇ (F10) ₃₅	0.157	1
NP-C12/F10-b(H)				3.2 ± 0.3	Au ₁₂₈₉ (C12) ₁₃₆ (F10) ₇₈	0.366	0.5
NP-C12/F10-c	28.1	0.0009 ^c	21.0/1.0	3.6 ± 0.6	Au ₁₈₃₀ (C12) ₁₇₆ (F10) ₄₃	0.200	1
NP-C12/F10-d(C)	27.4	0.0045 ^d	4.2/1.0	3.6 ± 0.6	Au ₁₈₃₀ (C12) ₂₁₁ (F10) ₇₃	0.258	1
NP-C12/F10-d(H)				3.6 ± 0.6	Au ₁₈₃₀ (C12) ₁₇₀ (F10) ₁₁₂	0.400	0.5
NP-C12/F10-e	30.0	0.0517 ^e	1.0/4.0	4.0 ± 0.6	Au ₂₄₀₆ (C12) ₁₂₆ (F10) ₂₀₀	0.615	0
NP-C12/F10-f	23.4	0.1053 ^d	1.0/6.0	3.2 ± 0.5	Au ₁₂₈₉ (C12) ₂₇ (F10) ₁₈₆	0.873	0

^a Dissolved in deoxygenated DCM to a concentration of 2.0 mg/ml. ^b Added as a 15.8 mM solution in deoxygenated DCM. ^c Added as a 22.8 mM solution in deoxygenated DCM. ^d Added as a 22.4 mM solution in deoxygenated DCM. ^e Added as a 100 mM solution in deoxygenated DCM. ^f Average diameters and standard deviation obtained by analysis of a population of at least 300 particles. ^g Calculated on the basis of the TGA and TEM and ¹H NMR analyses of decomposed nanoparticles. ^h Molar fraction of the fluorinated ligand in the monolayer of nanoparticles **NP-C12/F10** determined by ¹H NMR analysis of decomposed nanoparticles. ⁱ The solubility scores are defined arbitrarily as follows: score 1 is assigned to nanoparticles fully soluble in chloroform; score 0.5 is assigned to nanoparticles fully soluble in hexane; score 0 is assigned to nanoparticles fully soluble in hexafluorobenzene.

Table S3. Synthetic details for the preparation of nanoparticles **NP-brC12/F6**, obtained by direct synthesis.

Nanoparticles	HAuCl ₄ (mmol) ^a	TOAB (mmol) ^b	Au/(total thiols) ^c	HbrC12/HF6 Initial ratio	NaBH ₄ (mmol) ^{d,e}
NP-brC12/F6-a	0.150	0.373	4.0/1.0	10.0/1.0	1.50
NP-brC12/F6-b	0.162	0.405	4.0/1.0	3.0/1.0	1.62
NP-brC12/F6-c	0.122	0.304	4.0/1.0	1.0/1.0	1.22
NP-brC12/F6-d	0.066	0.1645	4.0/1.0	1.0/1.0	0.66
NP-brC12/F6-e	0.082	0.205	5.0/1.0	1.0/1.0	0.82
NP-brC12/F6-f	0.137	0.338	3.0/1.0	1.0/1.0	1.37
NP-brC12/F6-g	0.115	0.287	4.0/1.0	1.0/3.0	1.15
NP-brC12/F6-h	0.127	0.318	4.0/1.0	1.0/7.0	1.27
NP-brC12/F6-i	0.123	0.308	4.0/1.0	1.0/5.0	1.23

^a Used as a 32 mM solution in deoxygenated milliQ water. ^b Added as a 34 mM solution in deoxygenated DCM. ^c The thiols were added as a solution in deoxygenated DCM, the solution was prepared with the specified **HbrC12/HF6** ratio, the total concentration of the thiols (**HbrC12+HF6**) was adjusted in order to add exactly 2.0 ml of the solution to the mixture containing HAuCl₄ and TOAB. ^d Added as a 0.4 M solution. ^e Added all at once.

Table S4. Characterisation data for nanoparticles **NP-brC12/F6**.

Nanoparticles	Diameter (nm) ^a	Composition ^b	X _{F6} ^c	Solubility score ^d
NP-brC12/F6-a	3.7 ± 0.6	Au ₂₂₃₀ (brC12) ₃₀₅ (F6) ₂₂	0.068	1
NP-brC12/F6-b	3.6 ± 0.7	Au ₁₈₃₀ (brC12) ₂₅₀ (F6) ₄₃	0.147	1
NP-brC12/F6-c	3.4 ± 0.8	Au ₁₃₄₀ (brC12) ₂₀₂ (F6) ₄₇	0.192	1
NP-brC12/F6-d	2.1 ± 0.6	Au ₂₇₀ (brC12) ₆₈ (F6) ₁₇	0.198	1
NP-brC12/F6-e	3.1 ± 0.9	Au ₉₇₆ (brC12) ₁₄₈ (F6) ₆₂	0.294	1
NP-brC12/F6-f	1.6 ± 0.5	Au ₂₀₈ (brC12) ₃₀ (F6) ₂₄	0.446	1
NP-brC12/F6-g	2.8 ± 0.6	Au ₈₀₇ (brC12) ₇₆ (F6) ₉₂	0.545	0
NP-brC12/F6-h	2.7 ± 0.9	Au ₅₀₀ (brC12) ₂₈ (F6) ₁₃₉	0.833	0
NP-brC12/F6-i	1.9 ± 0.9	Au ₂₀₁ (brC12) ₁₁ (F6) ₆₃	0.851	0

^a Average diameters and standard deviation of a population of at least 300 particles. ^b Calculated on the basis of the TGA and TEM and ¹H NMR analyses of decomposed nanoparticles. ^c Molar fraction of the fluorinated ligand in the monolayer of nanoparticles **NP-brC12/F6** determined by ¹H NMR analysis of decomposed nanoparticles. ^d The solubility scores are defined arbitrarily as follows: score 1 is assigned to nanoparticles fully soluble in chloroform; score 0.5 is assigned to nanoparticles fully soluble in hexane; score 0 is assigned to nanoparticles fully soluble in hexafluorobenzene.

Table S5. Synthetic details for nanoparticles **NP-C8/F6**, obtained by direct synthesis.

Nanoparticles	HAuCl ₄ (mmol) ^a	TOAB (mmol) ^b	Au/(total thiols) ^c	HC8/HF6 Initial ratio	NaBH ₄ (mmol)	Addition time
NP-C8/F6-a	0.140	0.360	3.0/1.0	7.0/1.0	1.43	all at once
NP-C8/F6-b	0.146	0.360	3.0/1.0	5.0/1.0	1.46	all at once
NP-C8/F6-c	0.183	0.450	3.0/1.0	3.0/1.0	1.80	3'30"
NP-C8/F6-d	0.128	0.315	3.0/1.0	1.5/1.0	1.28	3'30"
NP-C8/F6-e	0.154	0.382	3.0/1.0	2.0/1.0	1.54	3'30"
NP-C8/F6-f	0.288	0.712	3.0/1.0	1.0/1.5	1.33	30'
NP-C8/F6-g	0.139	0.348	3.0/1.0	1.0/1.0	1.39	5"
NP-C8/F6-h	0.124	0.307	3.0/1.0	1.0/1.0	1.39	3'30"
NP-C8/F6-i	0.133	0.330	3.0/1.0	1.0/2.0	1.33	3'45"
NP-C8/F6-j	0.178	0.444	3.0/1.0	1.0/5.0	1.78	30'

^a Used as a 32 mM solution in deoxygenated milliQ water. ^b Added as a 35 mM solution in deoxygenated DCM. ^c The thiols were added as a solution in deoxygenated DCM, the solution was prepared with the specified **HC8/HF6** ratio, the total concentration of the thiols (**HC8+HF6**) was adjusted in order to add exactly 1.0 ml of the solution to the mixture containing HAuCl₄ and TOAB. ^d Added as a 0.42 M solution.

Table S6. Characterisation data for nanoparticles **NP-C8/F6**.

Nanoparticles	Diameter (nm) ^a	Composition ^b	X _{F6} ^c	Solubility Score ^d
NP-C8/F6-a	3.0 ± 0.6	Au ₉₇₆ (C8) ₂₂₉ (F6) ₁₁	0.045	1
NP-C8/F6-b	3.3 ± 0.8	Au ₁₃₄₀ (C8) ₂₄₆ (F6) ₁₈	0.068	1
NP-C8/F6-c	3.8 ± 0.7	Au ₁₆₃₄ (C8) ₂₈₃ (F6) ₂₉	0.093	1
NP-C8/F6-d	2.7 ± 0.5	Au ₅₂₇ (C8) ₁₃₉ (F6) ₃₈	0.213	1
NP-C8/F6-e	3.0 ± 0.6	Au ₉₇₆ (C8) ₁₆₆ (F6) ₄₆	0.217	1
NP-C8/F6-f(C)	2.8 ± 0.6	Au ₇₈₀ (C8) ₁₁₄ (F6) ₆₇	0.370	1
NP-C8/F6-g(C)	2.6 ± 0.5	Au ₄₇₅ (C8) ₇₅ (F6) ₅₃	0.417	1
NP-C8/F6-h	3.1 ± 0.6	Au ₉₇₆ (C8) ₁₂₆ (F6) ₉₀	0.417	1
NP-C8/F6-g(H)	2.4 ± 0.5	Au ₄₆₅ (C8) ₅₇ (F6) ₅₇	0.500	0.5
NP-C8/F6-i(C)	2.3 ± 0.5	Au ₄₅₉ (C8) ₅₇ (F6) ₅₇	0.500	1
NP-C8/F6-f(F)	2.4 ± 0.5	Au ₄₅₉ (C8) ₅₃ (F6) ₅₉	0.522	0
NP-C8/F6-f(H)	2.9 ± 0.5	Au ₈₀₇ (C8) ₈₆ (F6) ₉₈	0.533	0.5
NP-C8/F6-i(F)	2.4 ± 0.4	Au ₄₅₉ (C8) ₃₂ (F6) ₈₀	0.717	0
NP-C8/F6-j	2.5 ± 0.4	Au ₄₆₀ (C8) ₁₆ (F6) ₇₈	0.830	0

^a Average diameters and standard deviation of a population of at least 300 particles. ^b Calculated on the basis of the TGA and TEM and ¹H NMR analyses of decomposed nanoparticles. ^c Molar fraction of the fluorinated ligand in the monolayer of nanoparticles **NP-C8/F6** determined by ¹H NMR analysis of decomposed nanoparticles. ^d The solubility scores are defined arbitrarily as follows: score 1 is assigned to nanoparticles fully soluble in chloroform; score 0.5 is assigned to nanoparticles fully soluble in hexane; score 0 is assigned to nanoparticles fully soluble in hexafluorobenzene.

TableS7. Synthetic details for nanoparticles **NP-C16/F6**, obtained by direct synthesis.

Nanoparticles	HAuCl ₄ (mmol) ^a	TOAB (mmol) ^b	Au/(total thiols) ^c	C16/F6 ^c Initial ratio	NaBH ₄ (mmol)	Addition time
NP-C16/F6-a	0.129	0.322	3.0/1.0	7.0/1.0	1.29	all at once
NP-C16/F6-b	0.129	0.322	3.0/1.0	5.0/1.0	1.29	all at once
NP-C16/F6-c	0.152	0.375	3.0/1.0	3.0/1.0	1.52	3'50"
NP-C16/F6-d	0.167	0.418	3.0/1.0	3.0/1.0	1.68	3'30"
NP-C16/F6-e	0.190	0.472	3.0/1.0	2.0/1.0	1.90	3'40"
NP-C16/F6-f	0.248	0.615	3.0/1.0	1.0/1.0	2.48	4'30"
NP-C16/F6-g	0.152	0.375	3.0/1.0	1.0/10.0	1.52	30'
NP-C16/F6-h	0.165	0.412	3.0/1.0	1.0/8.0	1.65	30'
NP-C16/F6-i	0.123	0.307	3.0/1.0	1.0/1.5	1.23	35'
NP-C16/F6-j	0.138	0.345	3.0/1.0	1.0/2.5	1.38	31'
NP-C16/F6-k	0.098	0.240	3.0/1.0	1.0/5.0	0.99	35'

^a Used as a 34 mM solution in deoxygenated milliQ water. ^b Added as a 35 mM solution in deoxygenated DCM. ^c The thiols were added as a solution in deoxygenated DCM, the solution was prepared with the specified **HC16/HF6** ratio. The total concentration of the thiols (**HC16+HF6**) was adjusted in order to add exactly 1.0 ml of the solution to the mixture containing HAuCl₄ and TOAB. ^d Added as a 0.44 M solution.

Table S8. Characterisation data for nanoparticles **NP-C16/F6**.

Nanoparticles	Diameter (nm) ^a	Composition ^b	X _{F6} ^c	Solubility Score ^d
NP-C16/F6-a	2.9 ± 0.5	Au ₉₇₆ (C16) ₁₇₇ (F6) ₆	0.026	1
NP-C16/F6-b	3.2 ± 0.6	Au ₁₂₈₉ (C16) ₂₁₃ (F6) ₈	0.036	1
NP-C16/F6-c	2.6 ± 0.5	Au ₄₆₀ (C16) ₁₀₅ (F6) ₅	0.045	1
NP-C16/F6-d	3.0 ± 0.5	Au ₉₇₆ (C16) ₁₇₈ (F6) ₁₁	0.055	1
NP-C16/F6-e	3.2 ± 0.6	Au ₉₇₆ (C16) ₁₄₇ (F6) ₄₂	0.217	1
NP-C16/F6-f	2.9 ± 0.5	Au ₈₀₀ (C16) ₁₄₂ (F6) ₇₉	0.357	1
NP-C16/F6-g(C)	2.1 ± 0.4	Au ₃₀₉ (C16) ₄₂ (F6) ₃₅	0.455	1
NP-C16/F6-g(F)	2.1 ± 0.5	Au ₃₀₉ (C16) ₂₆ (F6) ₅₂	0.666	0
NP-C16/F6-h(C)	2.1 ± 0.4	Au ₃₀₉ (C16) ₄₀ (F6) ₄₄	0.524	1
NP-C16/F6-i(C)	2.6 ± 0.4	Au ₄₇₅ (C16) ₇₀ (F6) ₈₀	0.533	1
NP-C16/F6-i(H)	2.7 ± 0.6	Au ₅₂₇ (C16) ₅₅ (F6) ₈₆	0.574	0.5
NP-C16/F6-j(C)	2.5 ± 0.3	Au ₄₇₅ (C16) ₇₁ (F6) ₉₆	0.573	1
NP-C16/F6-j(H)	2.0 ± 0.4	Au ₃₀₉ (C16) ₃₁ (F6) ₄₄	0.586	0.5
NP-C16/F6-k(C)	2.3 ± 0.4	Au ₃₁₄ (C16) ₂₃ (F6) ₆₃	0.730	1
NP-C16/F6-k(F)	2.2 ± 0.5	Au ₃₁₄ (C16) ₁₈ (F6) ₇₂	0.804	0
NP-C16/F6-h(H)	2.2 ± 0.4	Au ₃₁₄ (C16) ₁₉ (F6) ₆₁	0.762	0.5
NP-C16/F6-h(F)	2.1 ± 0.3	Au ₃₀₉ (C16) ₁₉ (F6) ₆₂	0.764	0

^a Average diameters and standard deviation of a population of at least 300 particles. ^b Calculated on the basis of the TGA and TEM and ¹H NMR analyses of decomposed nanoparticles. ^c Molar fraction of the fluorinated ligand in the monolayer of nanoparticles **NP-C8/F6** determined by ¹H NMR analysis of decomposed nanoparticles. ^d The solubility scores are defined arbitrarily as follows: score 1 is assigned to nanoparticles fully soluble in chloroform; score 0.5 is assigned to nanoparticles fully soluble in hexane; score 0 is assigned to nanoparticles fully soluble in hexafluorobenzene.

References

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