Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Designing sterically demanding thiolate coated gold nanoparticles as a base for metal-molecule nanojunctions

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Synthesis:

DMF and THF were dried and distilled under nitrogen prior to use and THF was stored over 3 Å molecular sieves. Starting materials, such as alkane thiols, triethylsilane, DIAD, triphenylphosphine, 11–bromoundecan-1-ol, $HAuCl_4$, $3H_2O$, potassium thioacetate, ethanol and other solvents were purchased (Alfa and Aldrich) were used without further purification. ^1H, ^{13}C NMR spectra were recorded on Brucker AC 400. Chemical shifts (δ in ppm) were referenced to TMS using $CHCl_3$ (δ = 7.26 ppm) and $CDCl_3$ (δ = 77.16 ppm) as internal standards for 1H and ^{13}C NMR spectra, respectively. IR spectra were recorded on a Perkin Elmer 1000 spectrophotometer and absorption spectra on a Hewlett Packard 8453 spectrophotometer. Mass spectrometry was carried out with a Thermo Finnigan MAT 95 apparatus using electronic impact ionisation mode and on a Qtof Waters apparatus using electrospray ionisation mode.

Tris(para-tert-butylphenyl)(4-hydroxyphenyl)methane was prepared according to the literature.

Mono-p-[tris(p-tert-butylphenyl)methyl]phenyl Ether of ω-bromo-undecane (**SI-3**). Equimolar amounts of tris(para-tert-butylphenyl)(4-hydroxyphenyl)methane (3.0 g, 5.9 mmol), 11–bromoundecan-1-ol (1.49 g, 5.9 mmol), and triphenylphosphine (1.56 g, 5.9 mmol) were introduced under nitrogen in a dried 100 mL two-necked round bottom flask equipped with a magnetic stirrer. The mixture is stirred and diluted in 40 mL of dried THF and then cooled in an ice-water bath. At 0 °C, diisopropyl azo dicarboxylate (DIAD) (1.2 g, 5.9 mmol) is added dropwise to the medium over 30 minutes and the reaction mixture is stirred for 18 hours at room temperature. The solvent was removed under reduced pressure and the residue was filtered over a short silica gel plug with cyclohexane/ether (7/3) as eluent. The collected solution was concentrated and **SI-3** was obtained as a white powder in 65% yield (2.84 g) and used without further purification for the next step.

^{1}H NMR (400 MHz, CDCl$_3$, 297 K, δ): 7.26-7.22 (m, 6H, HPh), 7.11-7.07 (m, 8H, HPh), 6.77-6.75 (m, 2H, HPh), 3.92 (t, J=6.5Hz, 2H, O-CH$_2$), 3.41 (t, J=6.9 Hz, 2H, Br-CH$_2$), 1.90-1.83 (m, 2H, Halk), 1.80-1.73 (m, 2H, Halk), 1.47-1.41 (m, 6H, Halk), 1.36-1.31 (m, 35H, Halk);^{13}C NMR (101 MHz, CDCl$_3$, 297 K, δ): 157.1, 148.4, 144.3, 139.6, 132.4, 130;9, 124.2, 113.1,67.9, 63.2, 34.4, 34.2, 32.9, 29.6 (2C), 29.5(2C),28.9, 28.3, 27.1, 26.3; IR (KBr): ν = 2958, 2927, 2856, 1606, 1504,1362, 1248, 1182, 1017, 823, 705, 625; MS (EI) m/z 738 (30) [M$^+$+H] , 605 (100), 411 (25); HRMS (EI) m/z calcd for $C_{48}H_{65}BrO$:736.4213 ; found 736.4219.

Mono-p-[tris(p-tert-butylphenyl)methyl]phenyl Ether of ω-thioacetateundecane (**4**). In a dried 50 mL round bottom two-necked flask equipped with a magnetic stirrer, 300 mg (0.41 mmol) of **SI-3** and 232 mg (2.03 mmol) of potassium thioacetate were introduced under nitrogen and diluted in 15 mL of freshly distilled, dried and degassed DMF. The mixture is stirred at 80 °C overnight. After cooling, the organic phase is extracted with ether (3x 50 mL), washed with brine, dried over magnesium sulfate and concentrated under vacuum. The crude product was purified through a 25 g flash chromatographic silica gel column (cyclohexane/ CH$_2$Cl$_2$, 100/0-60/40) to give **4** as a white solid in 58% yield (172 mg).

^{1}H NMR (400 MHz, CDCl$_3$, 297 K, δ) 7.25-7.21 (m, 6H, HPh), 7.11-7.06 (m, 8H, HPh), 6.77-6.74 (m, 2H, HPh), 3.92 (t, J=6.6 Hz, 2H, O-CH$_2$), 3,41 (t, J=7.3 Hz, 2H, S-CH$_2$), 2.62 (s, 3H, HAc), 1.8-1.73 (m, 2H, Halk), 1.6-1.53 (m, 4H, Halk), 1.46-1.40 (m, 4H, Halk), 1.39-1.25 (m, 35H, Halk);^{13}C NMR (101 MHz, CDCl$_3$, 297 K, δ) 195.9, 156.9, 148.2, 144.1, 139.3, 132.1, 130;7, 123.9, 112.9, 67.8, 62.9, 34.2, 31.3, 31.1, 30.6, 29.5, 29.4(2C), 29.3 (2C), 29.1, 28.7, 26.0; IR (KBr): ν = 3031, 2958, 2927, 2856, 1738, 1692, 1606, 1504, 1644, 1362, 1247, 1183, 1130, 1108, 1017, 953, 823, 705, 624; MS (ESI) m/z:755 (100) [M$^+$+Na]; HR-MS (ESI) m/z calcd for $C_{50}H_{68}O_2SNa$:755.4832; found 755.4808.

Dynamic Light Scattering

Table S1. DLS data of AUNPs according to the entries given in table S4.

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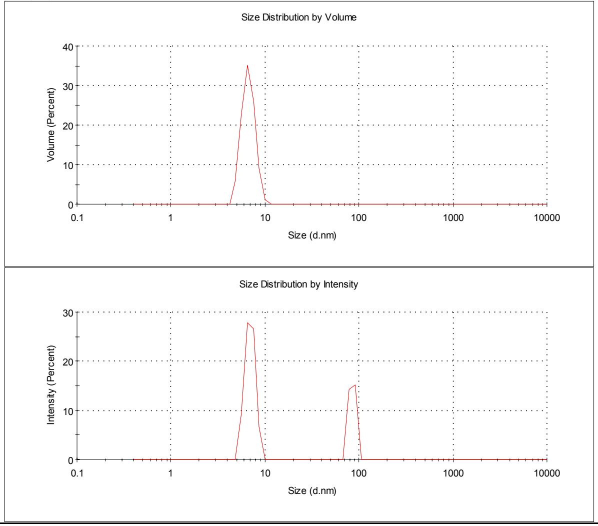

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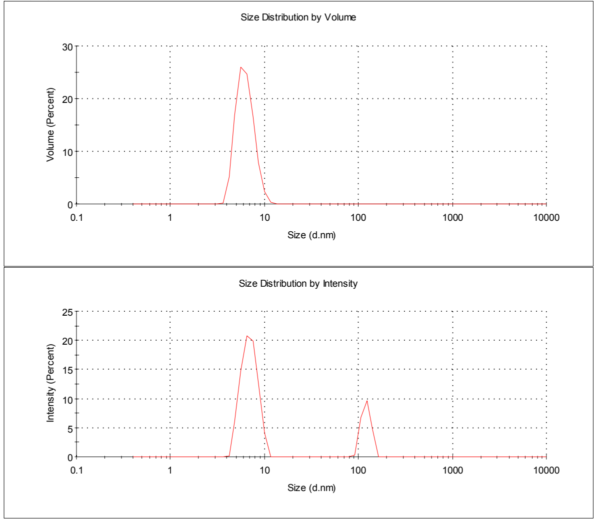

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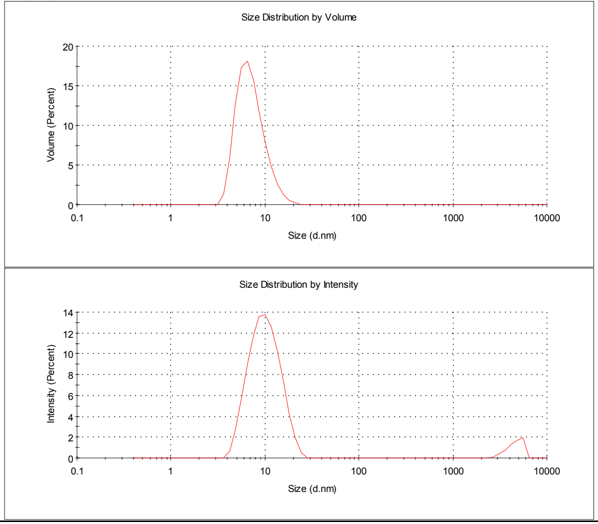

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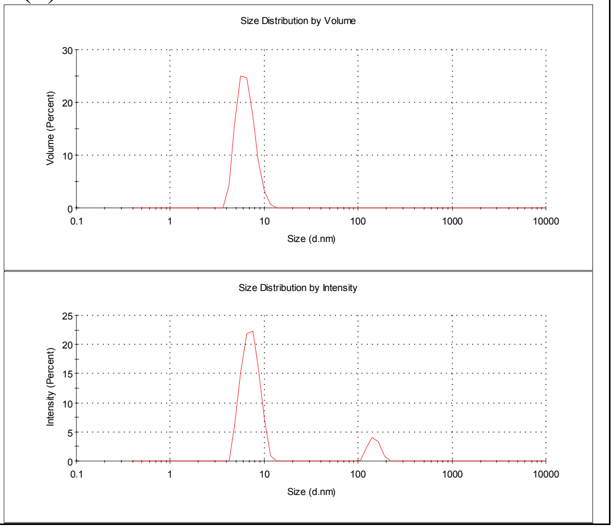

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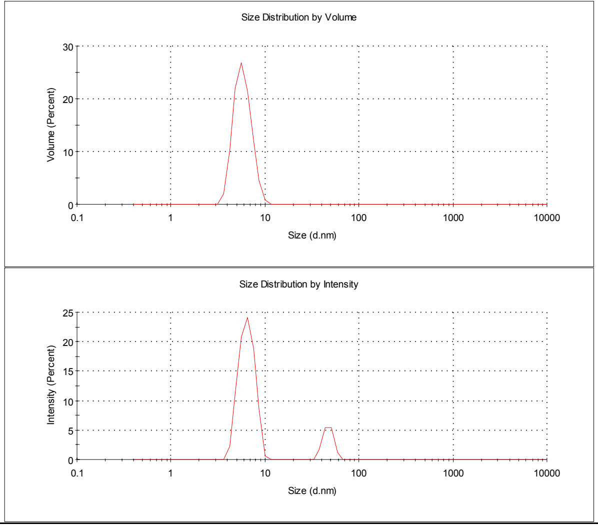
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Intensity (Percent)
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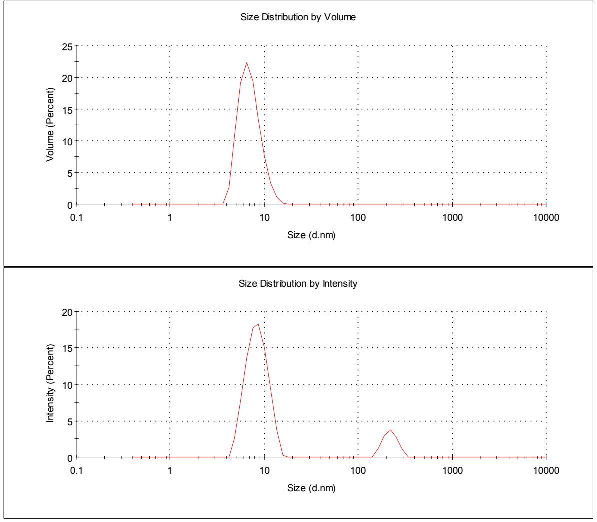
Size (d.nm)

(6)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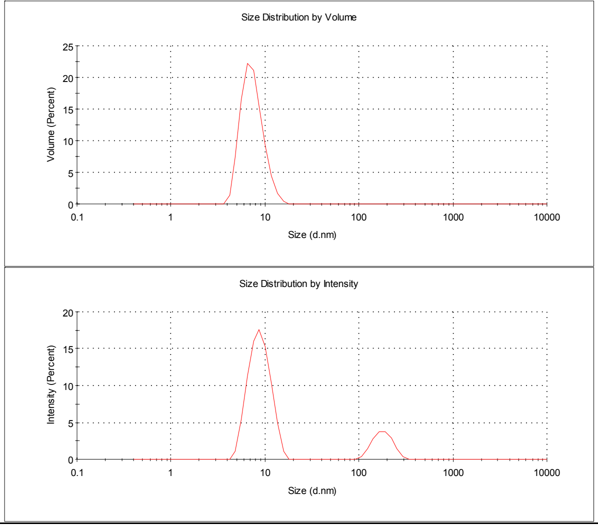
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Volume (Percent)
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Size (d.nm)

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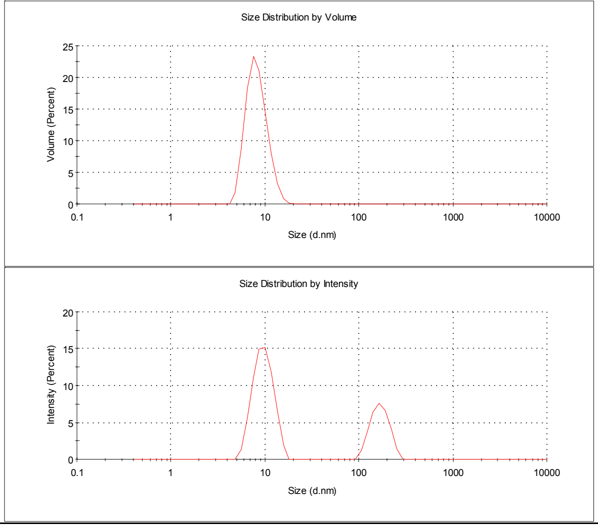
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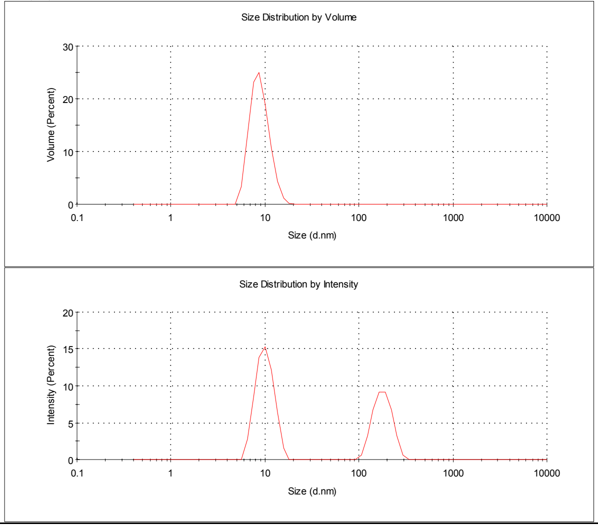
Size (d.nm)

(9)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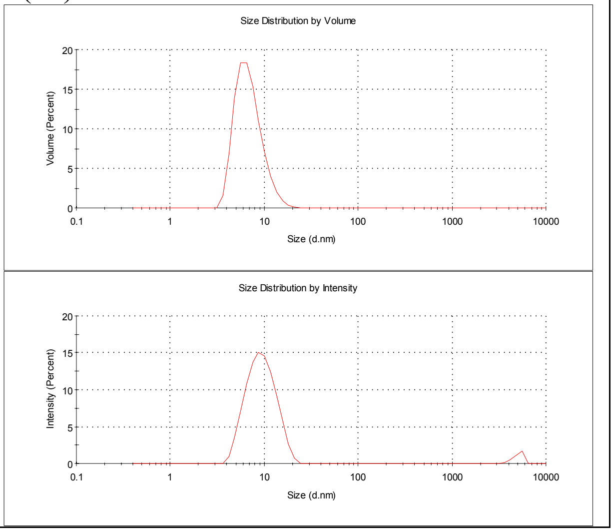
Size (d.nm)

(10)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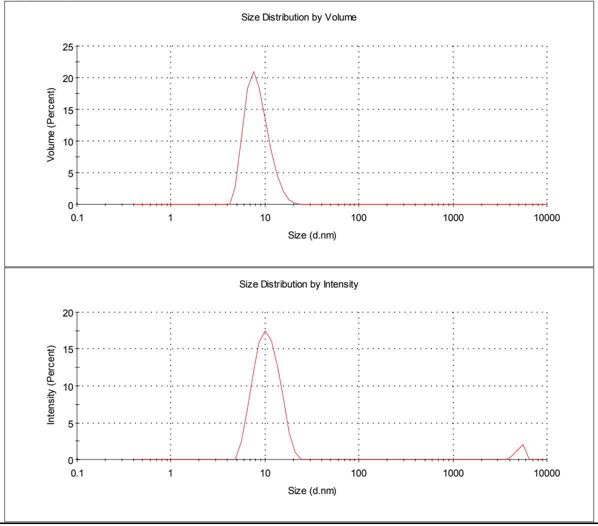
Size (d.nm)

(11)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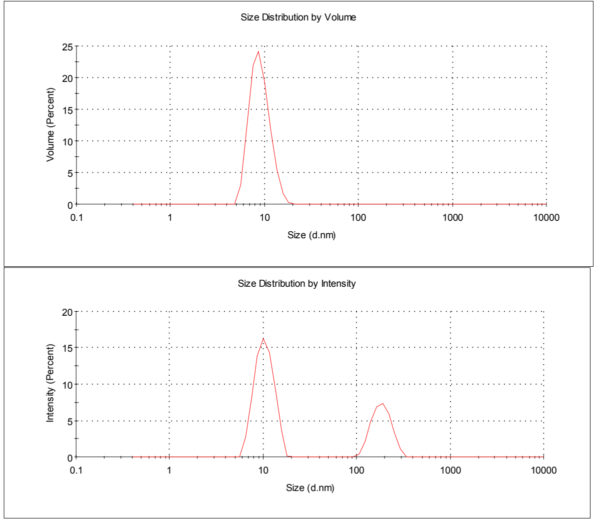
Size (d.nm)

(12)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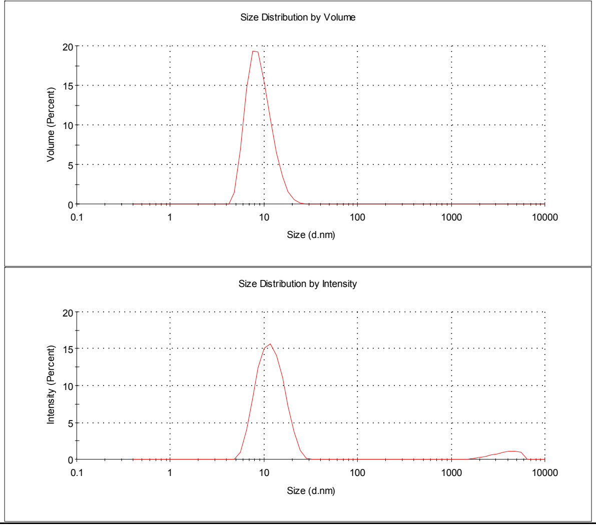
Size (d.nm)

(13)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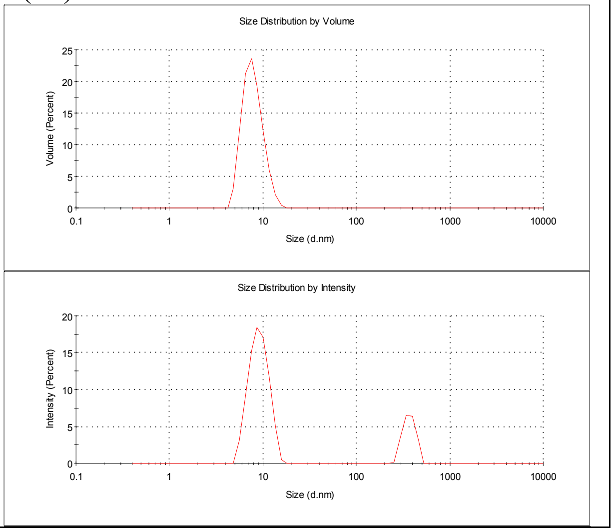
Size (d.nm)

(14)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Size (d.nm)
Size Distribution by Intensity
Intensity (Percent)
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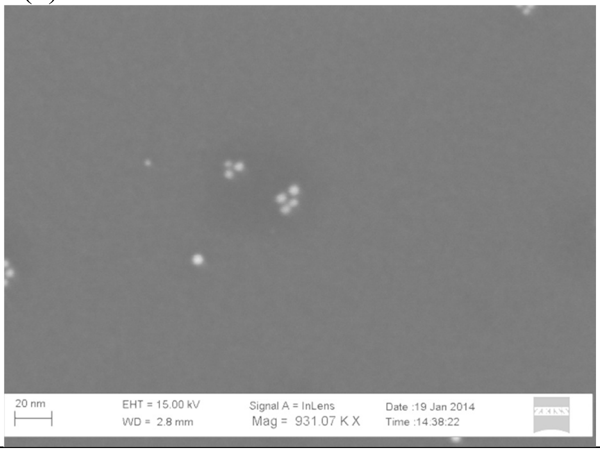
Size (d.nm)

Scanning Electron Microscopy:Table S2. SEM images of AUNPs according to the entries given in table S4.

(1)



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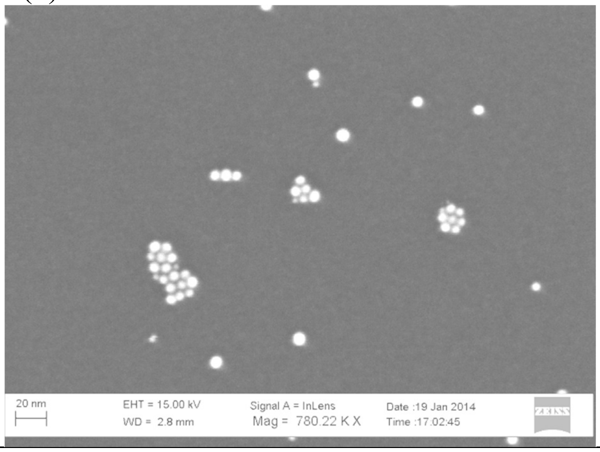

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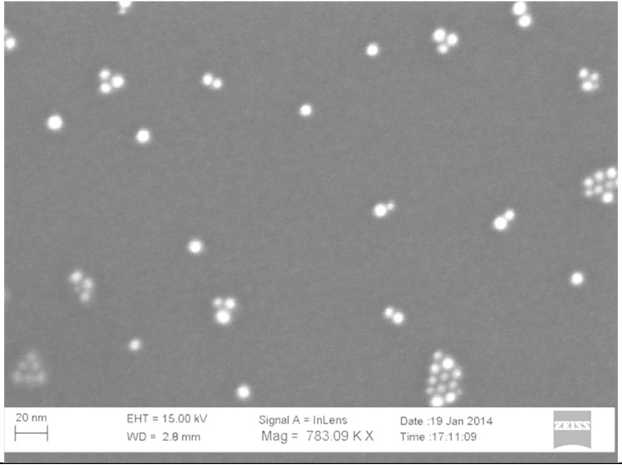

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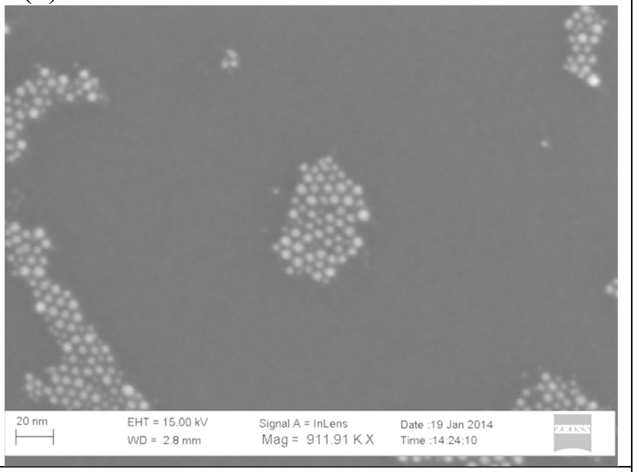

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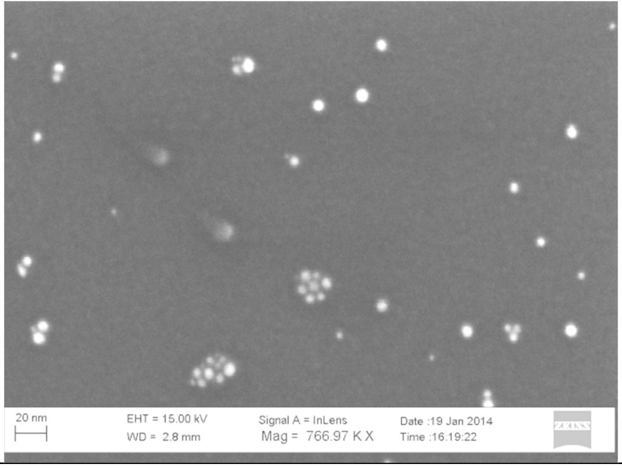

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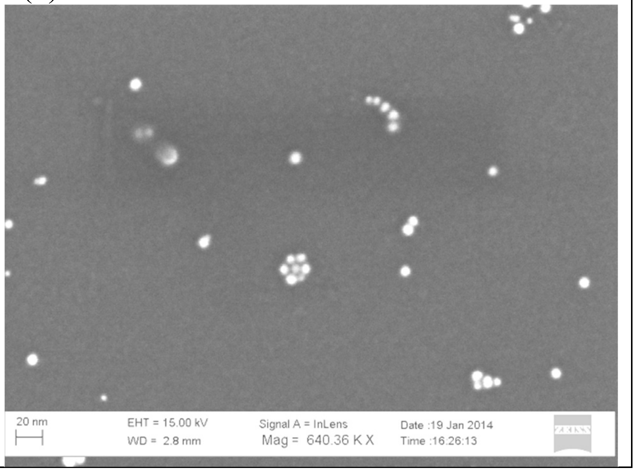

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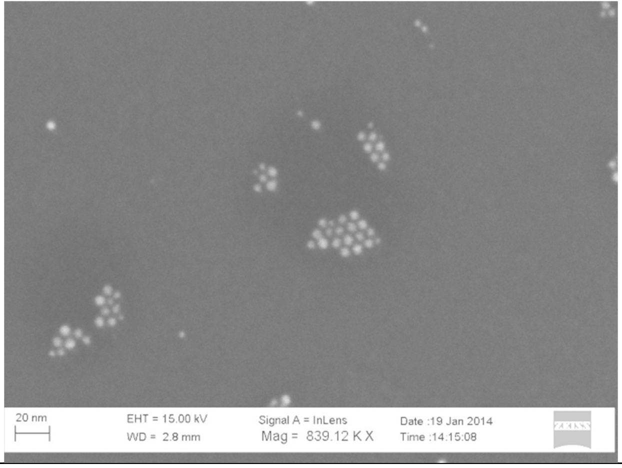
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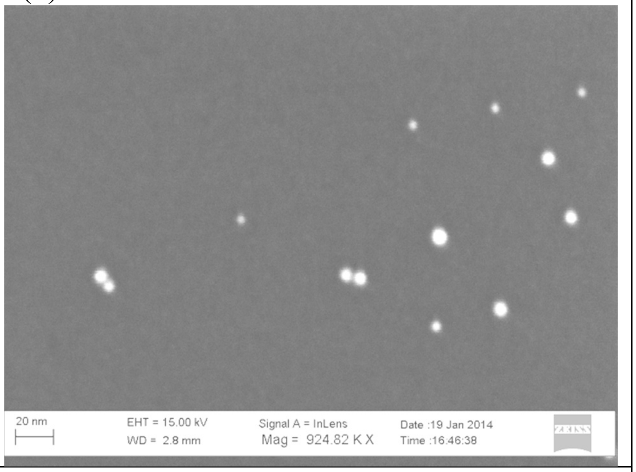
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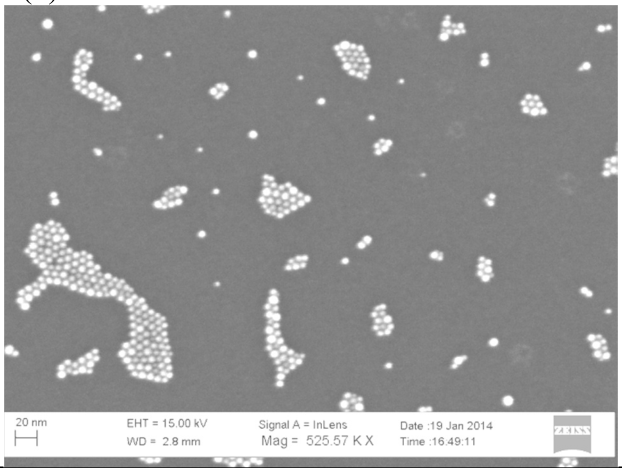
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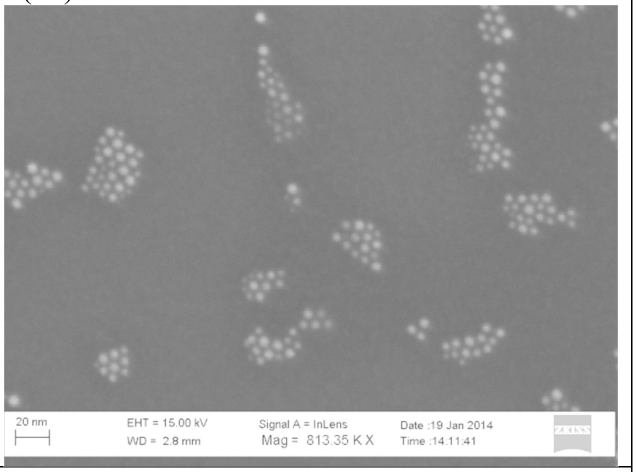
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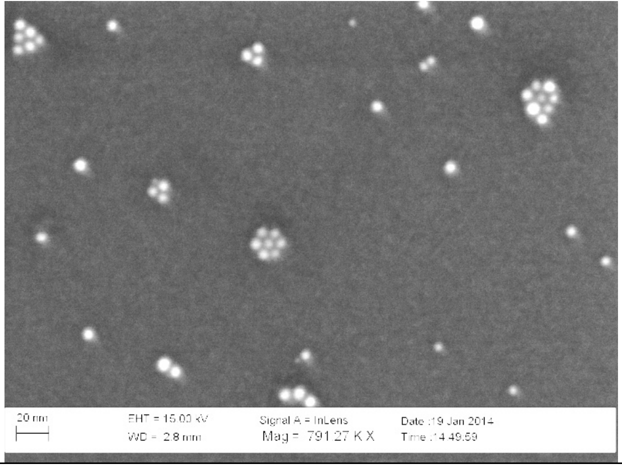
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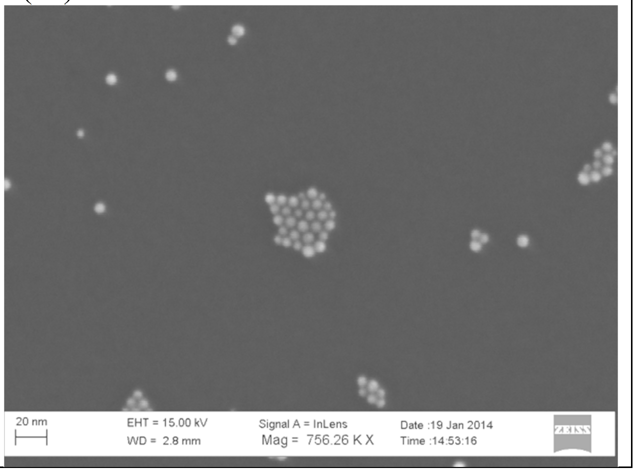
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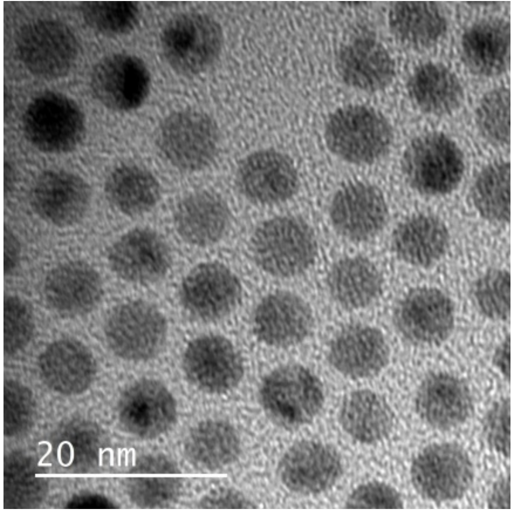
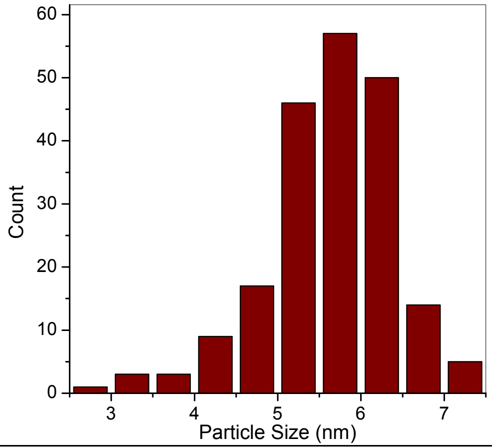
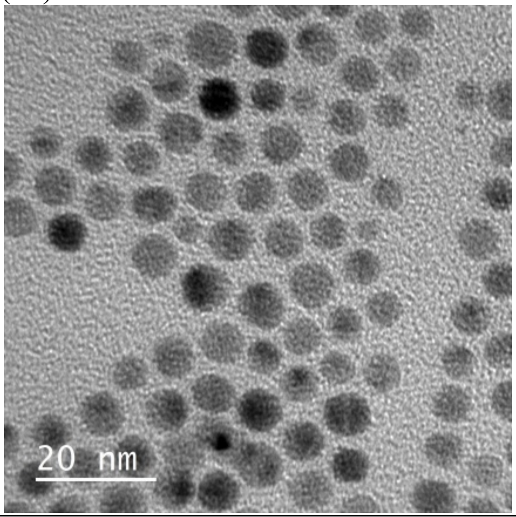
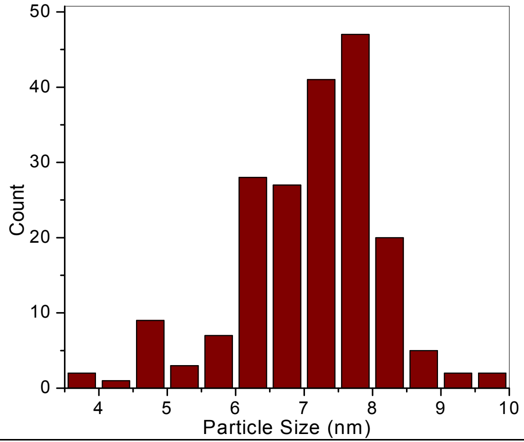
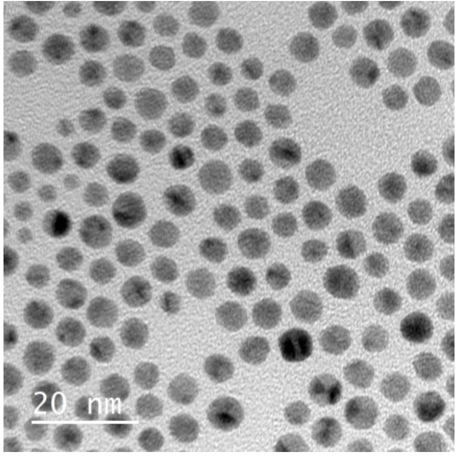
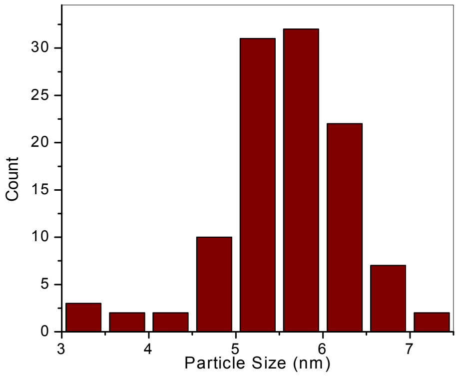
Table 3. Transmission Elecron Microspy

TEM images and size determinations of selected samples (according to Entries in Table S4)

(10)  	(10) 
(12)  	(12) 
(12)  	(12) 

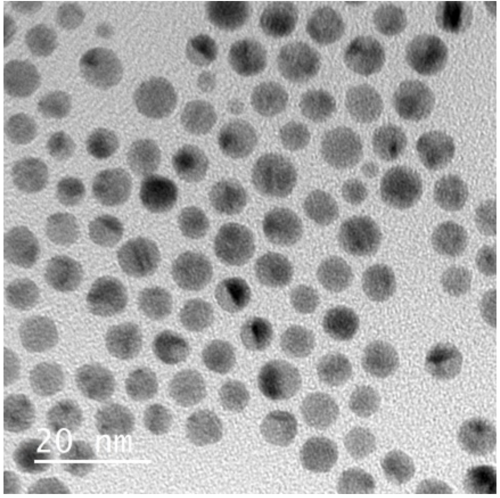
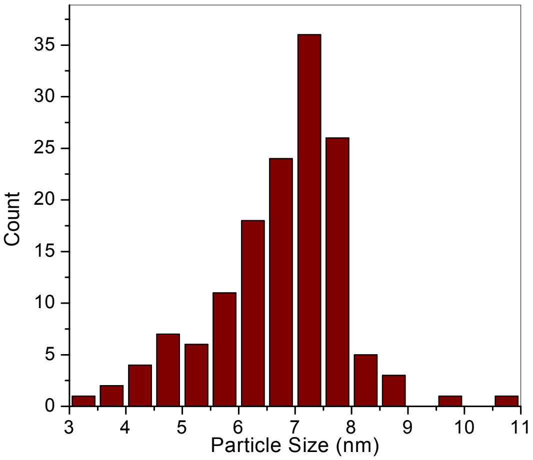
(12)  	(12) 

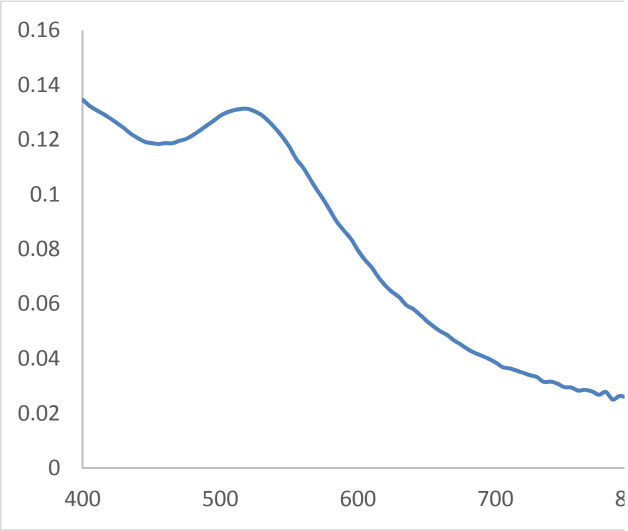
Table 4. Synthetic and spectroscopic details of synthesized gold nanoparticles.

Entry	Name	Temp.	Alkyl thiol	**4**[a]	DLS[b] size±st.d.(%)	TEM[c]
1	AuNP-c(0)	0-5 °C	-	0	7.0±0.9(100) 85.2±6.2(<1)	
2	AuNP-c(2)	0-5 °C	$C_{10}H_{21}SH$ (**4c**)	2	7.0±1.4(100) 121.1±13.4(-)	
3	AuNP-c(5)	0-5 °C	$C_{10}H_{21}SH$ (**4c**)	5	10.4±3.9	
4	AuNP-c(0)	r.t.	-	0	7.2±1.5(100) 147.8±20.3(-)	
5	AuNP-c(2)	r.t.	$C_{10}H_{21}SH$ (**4c**)	2	6.5±1.2(100) 47.1±5.6(<1)	
6	AuNP-c(5)	r.t.	$C_{10}H_{21}SH$ (**4c**)	5	8.5±2.2(100) 221.8±36.9(<1)	
7	AuNP-d(0)	0-5 °C	-	0	8.9±2.3(100) 182.0± 42.0(-)	
8	AuNP-d(2)	0-5 °C	$C_{12}H_{25}SH$ (**4d**)	2	9.8±2.3(100) 169.2± 36.8(<1)	
9	AuNP-d(5)	0-5 °C	$C_{12}H_{25}SH$ (**4d**)	5	10.1±2.1(100) 181.1± 40.2(<1)	
10	AuNP-d(0)	r.t.	-	0	9.7±3.4(100)[d] -	6.3±0.3 1.8±0.4
11	AuNP-d(2)	r.t.	$C_{12}H_{25}SH$ (**4d**)	2	10.8±3.2(100)[d] -	
12	AuNP-d(5)	r.t.	$C_{12}H_{25}SH$ (**4d**)	5	10.5±2.3(100) 188.0± 43.3(<1)	6.7±0.7 2.0±0.4
13	AuNP-d(15)	r.t.	$C_{12}H_{25}SH$ (**4d**)	15	12.2±4.0(100)[d] -	5.1±0.7 1.6±0.3
14	AuNP-d(30)	r.t.	$C_{12}H_{25}SH$ (**4d**)	30	9.2±2.1(100) 369.5±53.0(<1)	6.3±0.9 1.6±0.3

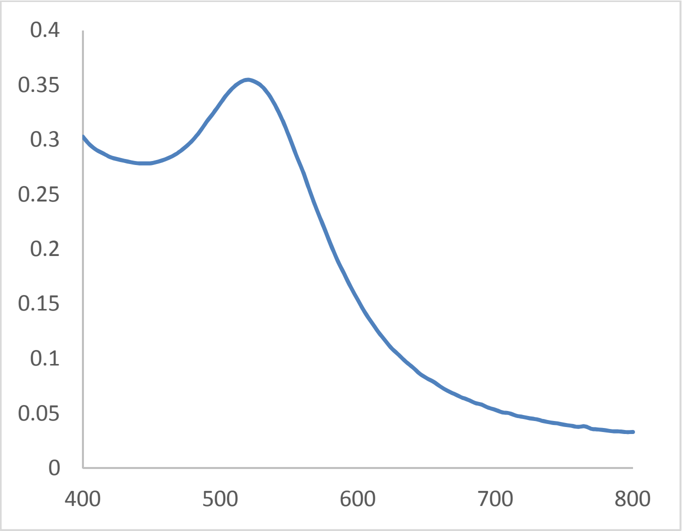
[a] concentration of 4 in [mol%] [b] size determined by intensity weighted distribution function, fractional amounts from mass weighted [c] Size and (spacing) in [nm] [d] contamination with particles > 5µm

Figure S1. UV vis data of selected samples according to entries in table S4.

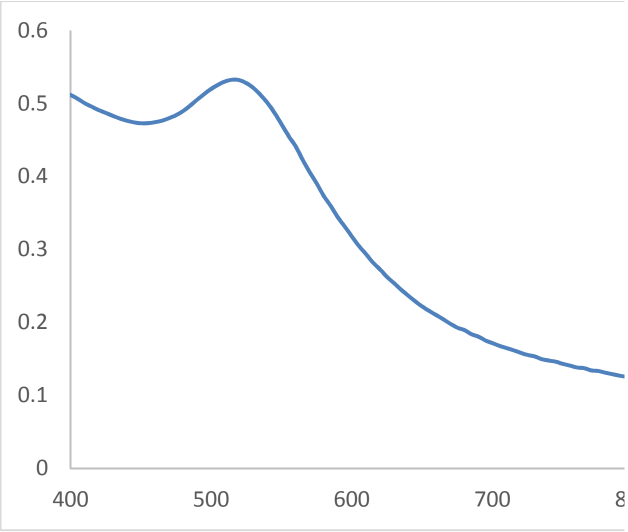
Entry 10



Entry 13



Entry 12



Entry 14