# Silver migration between Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> and doped Ag<sub>x</sub>Au<sub>38-x</sub> (SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> nanoclusters

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**Supporting Information** 

## Chemicals

Tetrachloroauric acid trihydrate (Aldrich, 99.9+ %), *L*-glutathione (reduced, Sigma-Aldrich, > 99 %), sodium borohydride (Fluka, > 96 %), 2-phenylethanethiol (Aldrich, 98 %), methanol (VWR, > 99.8 %), acetone (Fluka, > 99.5 %), methylene chloride (Sigma-Aldrich, > 99.9 %), toluene (Sigma-Aldrich, 99.9 %), PTFE syringe filters (0.2  $\mu$ m, Carl Roth, Karlsruhe/Germany), recovered cellulose membranes (0.2  $\mu$ m, Sartorius) and BioBeads S-X1 (BioRad) were used as purchased if not mentioned otherwise. Nanopure water (> 18 MΩ) was used.

## Characterization

UV-vis spectra were recorded on a Varian Cary 50 spectrometer. Quartz cuvette of 10 mm path length was used (solvents: methylene chloride and toluene).

Mass spectra were obtained using a Bruker Autoflex mass spectrometer equipped with a nitrogen laser at near threshold laser fluence in positive linear mode. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile was used as the matrix with a 1:1.000 analyte:matrix ratio. A volume of 2  $\mu$ l of the analyte/matrix mixture was applied to the target and air-dried.

NMR spectra were recorded on AM-500 Bruker Advance spectrometers. <sup>1</sup>H NMR chemical shifts are given in ppm relative to SiMe<sub>4</sub>, with the solvent resonance used as internal reference.

## Synthesis of Ag<sub>x</sub>Au<sub>38-x</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub>

 $Ag_{x}Au_{38-x}(SC_{2}H_{4}Ph)_{24}$  were obtained from metal exchange between  $Au_{38}(SC_{2}H_{4}Ph)_{24}$  and  $AgSC_{2}H_{4}Ph$ , which were prepared according to a previously reported method.<sup>1</sup> Three different batches of  $Ag_{x}Au_{38-x}(SC_{2}H_{4}Ph)_{24}$  were synthesized and were employed in the following studies. Figure S1 shows slightly different silver distribution in batches A, B and C.

## Silver migration in solution

*Batch A*: As a preliminary test, 0.2 mg  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  were mixed with 0.2 mg  $Au_{38}(SC_2H_4Ph)_{24}$  in 2 mL of DCM and samples from the reaction were collected after 10 minutes and 1 hour and analysed by MALDI.

*Batch B*: In order to probe the migration process,  $1 \text{ mg } Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  and  $1 \text{ mg } Au_{38}(SC_2H_4Ph)_{24}$  were mixed in 3mL of DCM and the UV-vis spectra of the mixture were recorded immediately after mixing the two clusters and every minute over a reaction period of 30 minutes.

*Batch C*: Two reactions were performed with  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}:Au_{38}(SC_2H_4Ph)_{24}$  mass ratio of 1:1 (0.05 mg in 3 mL of DCM for both clusters) and 2:1 (0.05 mg of  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  and 0.025 mg of  $Au_{38}(SC_2H_4Ph)_{24}$  in 3 mL of DCM). The mixture was stirred at 500 rpm for 30 minutes. The composition of migration products was characterized by MALDI.

## **Dialysis experiments**

The dialytic experiments were performed using 10 cm pre-treated regenerated cellulose membrane (MWCO: 1kD). The beaker, where the dialysis experiments were performed, was always covered with parafilms to avoid contamination form the environment.  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  employed for these experiments was taken from batch B (vide supra).

*2-PET/DCM*: Dialysis membrane was tested with 2-phenylethanethiol (2-PET), which is the ligand used to stabilize the clusters. A dialysis membrane, containing 2-PET (100 mg in 1 mL of DCM) was immerged in DCM (250 mL) and let stirring for 3 hours at 500 rpm. In order to control if 2-PET was able to pass through the membrane during the reaction time, the solution outside the membrane was evaporated completely. After evaporation, 0.7 mL of deuterated DCM were added to re-dissolve the species contained in the outside solution. <sup>1</sup>H-NMR was taken and showed the presence of 2-PET, see Figure S4.

 $Ag_{x}Au_{38-x}(SC_{2}H_{4}Ph)_{24}/DCM$ : inside the membrane a solution of  $Ag_{x}Au_{38-x}(SC_{2}H_{4}Ph)_{24}$  (1 mg in 1 mL of DCM) was inserted. On the outside pure DCM (250 mL) was added. The system was stirred for 3 hours at 500 rpm. After the reaction time the inside solution was dried and MALDI spectra were collected, see Figure 2.

 $Ag_{x}Au_{38-x}(SC_{2}H_{4}Ph)_{24}|Au_{38}(SC_{2}H_{4}Ph)_{24}$ : inside the membrane a solution of  $Ag_{x}Au_{38-x}(SC_{2}H_{4}Ph)_{24}$  (1 mg in 1 mL of DCM) was inserted. On the outside  $Au_{38}(SC_{2}H_{4}Ph)_{24}$  (1 mg in 250 mL of DCM) were added. The system was stirred for 3 hours at 500 rpm. After the reaction time both the inside and outside solution were evaporated and MALDI spectra were collected, see Figure 2 and 3. Following, the outside sample was re-dissolved in 1 mL of DCM and stirred for 3 hours to concentrate all the species and favour a possible interaction between them. After the reaction time MALDI spectra was again collected, see Figure S5.

*Control experiments* 1: 1 mg of  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  and 1 mg of  $Au_{38}(SC_2H_4Ph)_{24}$  were mixed in 1 mL of DCM and stirred for 3 hours. Without the presence of the membrane, Ag migration was observed (by MALDI) as in the previous experiments, see Figure 3.

*Control experiments 2*: 1 mg of  $Ag_{x}Au_{38-x}$  ( $SC_{2}H_{4}Ph$ )<sub>24</sub> was dissolved in 1 mL of DCM and stirred for 3 hours. No sign of decomposition for  $Ag_{x}Au_{38-x}(SC_{2}H_{4}Ph)_{24}$  in MALDI spectra



Figure S1. Comparison between the MALDI spectra of  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  batch A, B and C. The vertical lines highlight the numbers of silver atoms.



Figure S2. **a**. in-situ UV-vis spectra of  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$ ,  $Au_{38}(SC_2H_4Ph)_{24}$  and their mixture. **b**. From bottom to top: UV spectra of  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  and  $Au_{38}(SC_2H_4Ph)_{24}$  after mixing at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20 and 30 minutes. **c**. UV-vis spectra at 2, 3, 4, 5, 6, 7, 8, 9, 10, 20 and 30 minutes after subtracting the spectrum measured at 1min (difference spectra).



Figure S3. Top: UV-vis spectrum measured of a mixture of  $Ag_{x'}Au_{38-x'}$  and  $Au_{38}$  (red) and spectrum obtained from a fit of this spectrum to a linear combination of the individual spectra of the original  $Ag_{x}Au_{38-x}$  and  $Au_{38}$  cluster according to f=c+ax+by, where f is the measured spectrum, x is the spectrum of the original  $Ag_{x}Au_{38-x}$  and y is the spectrum of  $Au_{38}$ . a, b and c are parameters of the fit. Bottom: residual of the fit. The residual is very small and the fitted function is close to the target function, which shows that the measured spectrum of the clusters, after metal exchange, can be well synthesized by a linear combination of the individual spectra of the species before mixing. Therefore UV-vis spectroscopy is not very sensitive to the metal exchange.



Figure S4. MALDI spectra of  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$  and  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}/Au_{38}(SC_2H_4Ph)_{24}$  reaction mixture with the starting mass ratio  $Ag_xAu_{38-x}(Au_{38} = 1:1 \text{ and } 2:1.$ 



Figure S5. MALDI spectra of  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}$ : **a**. fresh sample, **b**. after stirring in DCM solution for three hours.



Figure S6: Binomial probability distribution for (top) n=38, p=0.17 and (bottom) n=9, p=0.7.

Binomial distribution: 
$$f(x) = \frac{n!}{x!(n-x)!} p^x (1-p)^{n-x}$$

X is a random variable which denotes the number of successes in n trials each with probability p.

In the distributions above p was chosen such that the average number of incorporated Ag atoms corresponds to the one measured (Figure S6), i.e. about 6.4

Note that strict binomial distribution would be expected if for each accessible site the probability to find a Ag atom is equal. Dass and coworkers found that this is not the case but the probabilities were quite similar.<sup>3</sup>



Figure S7. **a.** <sup>1</sup>H-NMR spectra of 2-PET in DCM- $d_2$ . **b.** <sup>1</sup>H-NMR spectra in DCM- $d_2$  of the solution outside the dialysis membrane (after evaporation of the non-deuterated solvent). The black arrows indicated the signal of 2-PET.



Figure S8. MALDI spectra of  $Au_{38}(SC_2H_4Ph)_{24}$  and of concentrated  $Ag_xAu_{38-x}(SC_2H_4Ph)_{24}|Au_{38}(SC_2H_4Ph)_{24}$  outside solution. The fragmentation peaks shown here are consistent with former report.<sup>2</sup>

#### References

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