Electronic Supplementary Material (ESI) for Nanoscale

On the flexibility of the gold-thiolate interface: Racemization of the $Au_{40}(SR)_{24}$ cluster

Supporting Information

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All chemicals were purchased from commercial sources and used as received. Nanopure water (> 18 MΩ) was used.

Synthesis and Isolation of $Au_{40}(SCH_2CH_2Ph)_{24}$[1,2]

Step 1. Tetrachloroauric acid trihydrate (0,5 g) was dissolved in acetone (25 mL) and glutathione (1.56 g) dispersed in acetone (25 mL) was added. The yellow brown suspension was stirred at 0 °C for 30 min. A freshly prepared solution of sodium borohydride (480 mg in 15 mL) was added rapidly resulting in a dark brown solution which was stirred at 0°C for 20 min. The clusters precipitated quickly and the supernatant suspension was decanted.

Step 2. The clusters from step 1 were dissolved in 15 mL water; 0.8 mL ethanol, 5 mL toluene and 5 mL 2-phenylethylthiol were added. The reaction mixture was heated to 80 °C for 3 h. After cooling down to room temperature, the phases were separated, the aqueous phase was discarded and the organic phase was washed with water three times. The solvents were removed by rotary evaporation. The clusters were precipitated by addition of methanol and collected by centrifugation. To remove the thiol, the clusters were repeatedly washed with large amounts of methanol, dissolved in dichloromethane and dried by rotary evaporation. Finally the clusters dissolved in dichloromethane were filtered over a PTFE syringe filter (0.2 μm) to remove insoluble by-products.

Step 3. The as-synthesized clusters were dissolved in a low amount THF (tetrahydrofuran) and passed over a gel permeation column (GPC, 90 cm in length, 2.5 cm in diameter).). The Au_{40} fraction was collected and separated from other sizes by size permeation chromatography until the UV-VIS spectra were constant over the whole band. The GPC column was prepared with 45 g of BioRad BioBead S-X1 which was suspended in 400 mL THF and allowed to swell for 3h. The gel was filled into a column and the bed was rinsed several times with THF until the eluting solvent was clear. Between two separations, the column was washed with ca. 1 bed volume of THF.

Characterization

UV-vis spectra were recorded on a Varian Cary 50 spectrometer, (pathlength 2 mm, DCM). CD spectra were recorded on a JASCO J-815 spectrometer (pathlength 5 mm, DCM); four scans were averaged and anisotropy factors were calculated using the UV-vis spectra measured simultaneously: $g=\Delta A/A=\theta[mdeg]/(32980\ A)$.

Mass spectra were recorded on a Bruker Autoflex mass spectrometer equipped with a nitrogen laser at near-threshold laser intensity in positive linear mode using DCTB as the matrix.

Separation[3,4]

Separation of enantiomers was conducted on a JASCO 20xx series HPLC system equipped with a semi-preparative Phenomenex Lux-Cellulose-1 column (5 μm, 250x10 mm). The detection was performed with a JASCO 2070plus UV-VIS detector at a detection wavelength of 380 nm. The samples were injected in toluene and eluted with *n*-hexane:*i*-propanol (9:1) at a flow rate of 3 mL / min.

Larger amounts of the enantiomers were collected and dried by rotary evaporation while keeping the temperature below 25 °C to avoid racemization before characterization.

Racemization[5]

A stock solution was prepared from the enantiomers of the cluster and split for racemization experiments at different temperatures. For time course measurements the variation of the CD-signal at 418 nm was followed on a JASCO J-715 spectrometer at six different temperatures (80, 90, 100, 110, 120, 130 °C, Specac temperature control, pathlength 5 mm, m-xylene) and the signal of blank *m*-xylene at the according temperature was subtracted. CD spectra of the stock solution as well as of the solutions after racemization were recorded for comparison. HPLC was performed for all samples after heating in order to observe changes in the composition of the samples. The values obtained from the time-course measurement at 90 °C were discarded in the determination of activation parameters, due to a technical problem within the measurements. A similar problem was observed in other measurements on the same setup.[6]

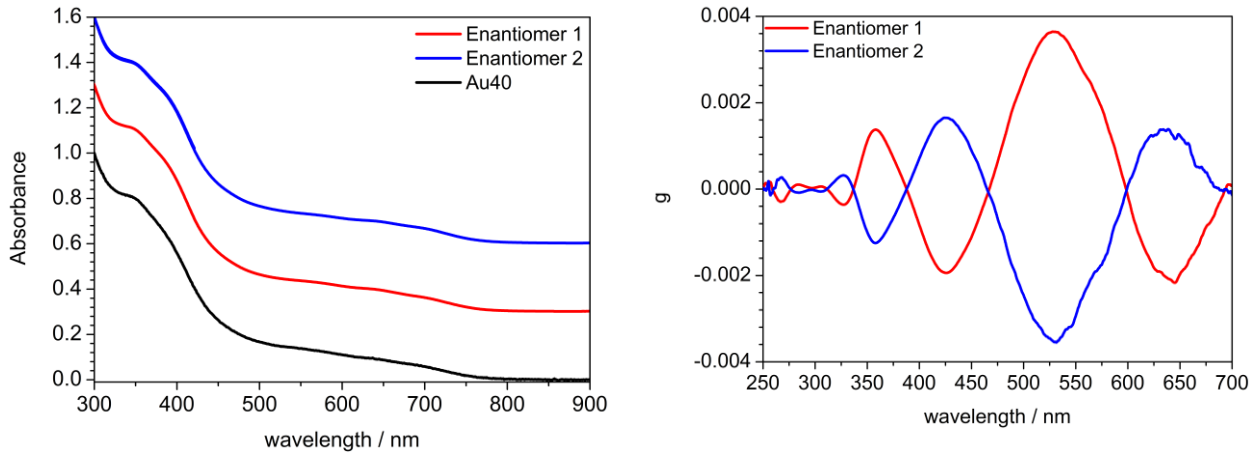


Fig. S - 1 Left: UV-vis spectra of the separated enantiomers and the crude product show the same profile. Right: g-values calculated from CD and UV-vis Spectra show a perfect mirror-image relationship.

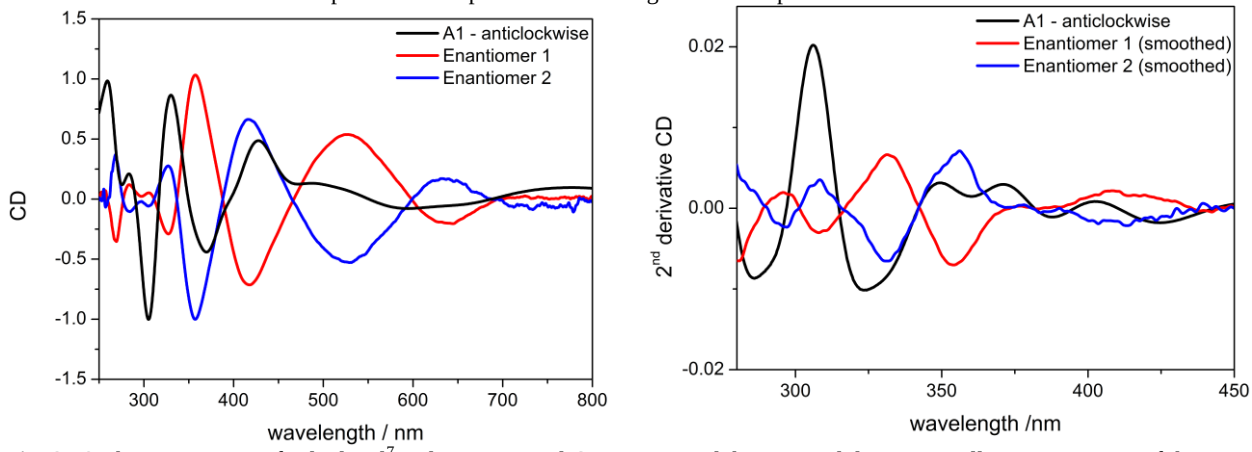


Fig. S - 2 The comparison of calculated[7] and experimental CD spectra and their second derivatives allows assignment of the configuration. The enantiomer eluting first in the HPLC is clockwise, the second enantiomer is anticlockwise with respect of the arrangement of the long units at the poles.

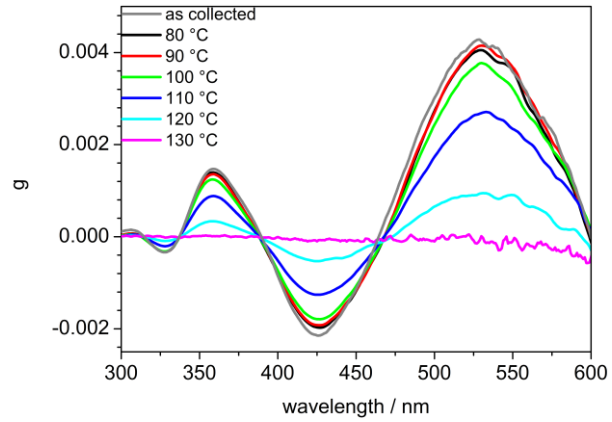


Fig S - 3 The CD signal of the initially enantiopure solution (enantiomer 1) decreases at high temperatures, indicating racemization. The samples were heated to the respective temperature for 40 min. Note, that measurements for the sample heated at 90 °C are presented here. However they were discarded for the analysis due to a technical problem at this temperature.

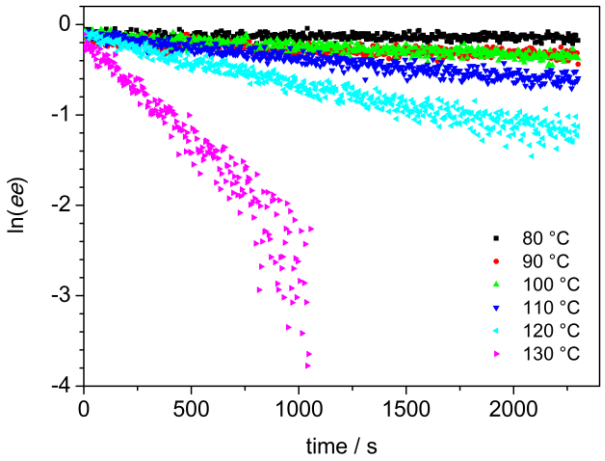


Fig. S - 4 The linear dependence of ln(*ee*) as a function of time supports a first-order reaction.

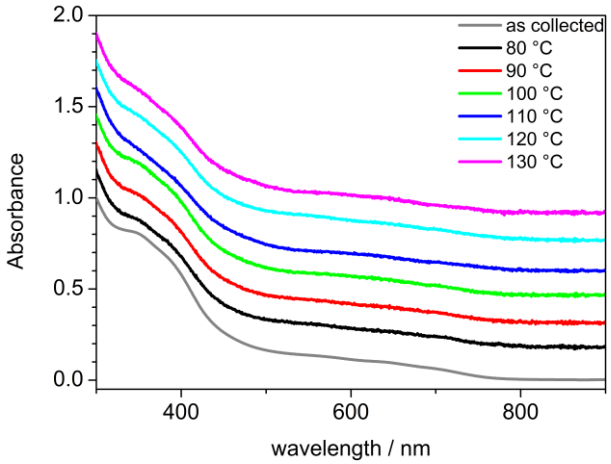


Fig. S - 5 Heating of Enantiomer 1 up to 130 °C does not change the UV-VIS spectrum, indicating that no decomposition takes place.

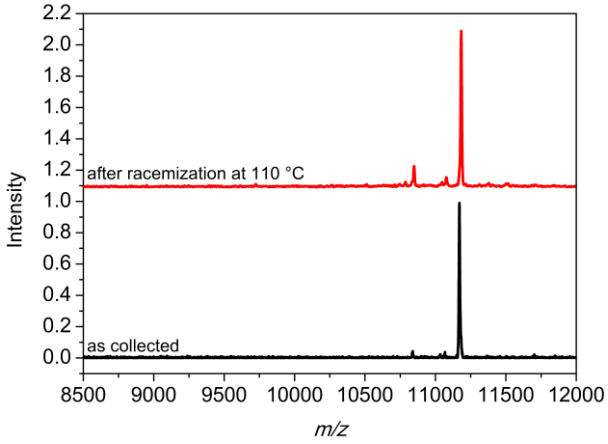
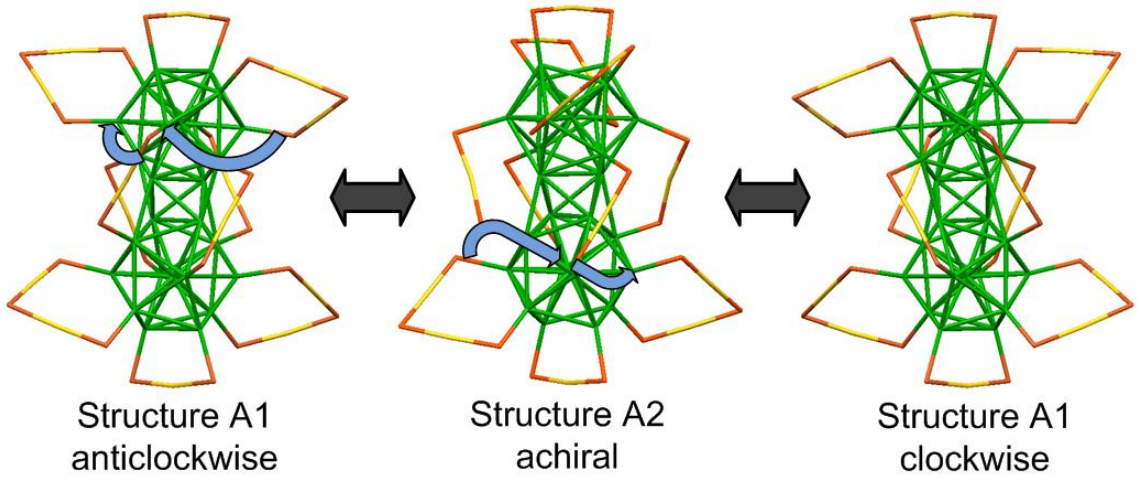


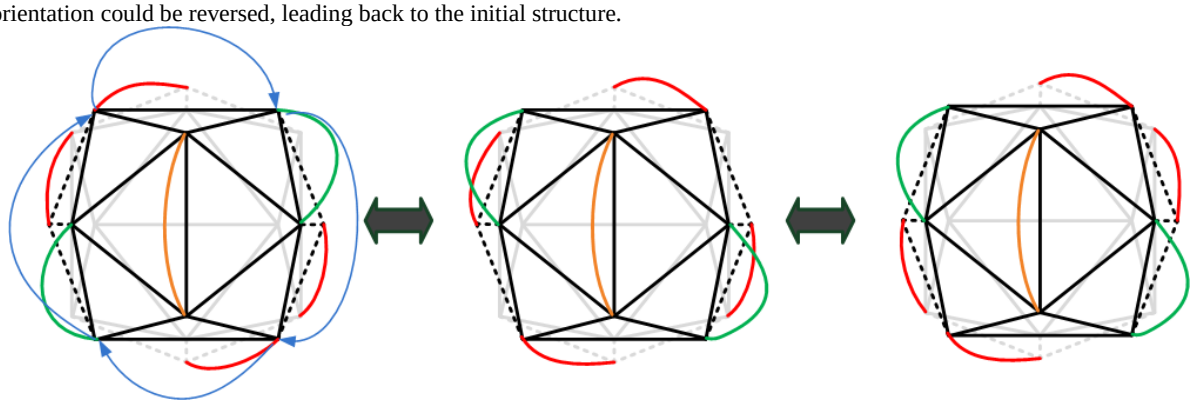
Fig. S - 6 MALDI Spectra of Enantiomer 1 as collected and after racemization. Besides fragments no other masses are observed.

Table S - 1 Activation parameters obtained from the Eyring plot for the racemization of $Au_{40}(2\text{-PET})_{24}$. Practically the same values were obtained for both enantiomers. Errors were calculated from the standard error of the slope and intercept of the Eyring fits.

	Enantiomer 1	Enantiomer 2
E_a	24.7 ± 1.6 kcal/mol	25.5 ± 0.8 kcal/mol
$\Delta H^{\ddagger}$	24.0 ± 1.6 kcal/mol	24.7 ± 0.8 kcal/mol
$\Delta S^{\ddagger}$	-12.7 ± 4.1 cal/mol/K	-11.0 ± 2.1 cal/mol/K
$\Delta G^{\ddagger}$	28.8 ± 3.1 kcal/mol	28.8 ± 1.6 kcal/mol



Scheme S - 1 Graphical presentation of a possible mechanism for the inversion of the anticlockwise (with respect to the long units) enantiomer to the clockwise enantiomer (and vice versa) via an achiral transition structure. The inversion of the orientation takes place via a cyclic transition state in which the thiol ligands attached to one hemisphere exchange places. The staples stay intact. Only movements on the "front" of the cluster are indicated by arrows, the same movements need to take place at the same time at the backside. This exchange of places leads to an asymmetric structure in which the orientation of the ligands on the both hemispheres is opposite. Inversion can also take place at the second hemisphere leading to the second enantiomer or the first reorientation could be reversed, leading back to the initial structure.



Scheme S - 2 Schematic projection of the proposed $Au_{40}(2\text{-PET})_{24}$ structure seen from the top. The upper hemisphere of the core is drawn black; the lower hemisphere is drawn grey. Dotted lines present those edges of the icosahedra lying beneath other edges in this projection. The short gold-thiolate unit at the pole is presented in orange, those at the equator in red and the long units in green. The long units and the short end unit of the lower sphere are omitted for clarity.

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