The two enantiomers of the Au$_{40}$(2-PET)$_{24}$ cluster were collected using HPLC and analyzed by MALDI-TOF mass spectrometry, UV-vis- and CD-spectroscopy. The flexibility of the cluster surface allows racemization of the intrinsically chiral cluster at elevated temperatures (80–130 °C) which was monitored following the optical activity. The determined activation energy (25 kcal mol$^{-1}$) lies in the range of previously reported values for Au$_{38}$ nanoclusters whereas the activation entropy deviates significantly from the one in Au$_{38}$. The latter may indicate that the racemization can take place via different mechanisms.

Normally, such rearrangements on the cluster surface are very difficult to probe experimentally. However, in the case of chiral structures, where the rearrangement leads to racemization, optical activity is a sensitive probe. Besides the Au$_{38}$(2-PET)$_{24}$ cluster, racemization experiments were conducted with Au$_{38}$(2-PET)$_{24}$(R-BINAS)$_{1}$ (BINAS = 1,1′-binaphthyl-2,2′-dithiol). In this cluster two 2-PET ligands are replaced by one BINAS ligand. The incorporation of this dithiolate ligand leads to a stabilization of the cluster toward racemization, i.e. it takes place only at higher temperatures compared to Au$_{38}$(2-PET)$_{24}$. The question arises if such rearrangements of the gold–thiolate interface are a characteristic of the Au$_{38}$ cluster and if not: do other clusters rearrange at similar temperatures?

We herein present results of the racemization of Au$_{40}$(2-PET)$_{24}$. This is until now the second thiolate-protected cluster, besides Au$_{38}$(2-PET)$_{24}$, which could be separated into its enantiomers. We were able to follow the racemization over time at different temperatures by CD-spectroscopy and to calculate the activation parameters which we compared with those known for Au$_{38}$(2-PET)$_{24}$.

In contrast to Au$_{38}$(2-PET)$_{24}$ (ref. 12) the structure of Au$_{40}$(2-PET)$_{24}$ is yet not confirmed experimentally. However, model structures of Au$_{40}$SR$_{24}$ were presented and the corresponding CD spectra match well the experimental one. The calculated structure of Au$_{40}$SR$_{24}$ shown in Fig. 1 describes the cluster to have a Au$_{26}$ core consisting of two Au$_{13}$ icosahedra which are connected by four short staple units. Each end is capped by one monomeric and two dimeric gold–thiolate units; the latter are arranged in a helical manner. Several closely
related structures with slightly different energies are described. Another structure was recently also proposed but no calculated CD spectra were reported.

The synthesis of Au₄₀(2-PET)₂₄ was described earlier. Large amounts of the enantiomers could be separated with an improved HPLC method. Details can be found in the ESI. Characterization with UV-vis and MALDI-TOF-MS were in accordance with data reported earlier.

CD spectra and calculated g-values (ΔA/A) of the enantiomers match with those reported earlier. Slightly smaller values for enantiomer 2 are observed due to the contamination with enantiomer 1 as seen in the HPL chromatogram (Fig. 2). The enantiomer eluting second in the HPLC shows a good match of its CD spectrum with the calculated one published for a model structure which is left-handed (or anti-clockwise, A) with respect to the dimeric Au–thiolate units at the poles (Fig. S2†).

For racemization experiments aliquots were taken from a stock solution of an enantioenriched material. For both enantiomers, the CD signal at 418 nm was followed over the course of 40 min at five temperatures (Fig. 3). For clarity only the results of the racemization of enantiomer 1 (C-Au₄₀(2-PET)₂₄) are presented graphically. The racemization of enantiomer 2 gives the same results. A significant decrease of the CD signal with conservation of the shape of the spectrum can be observed for high temperatures (Fig. S3†). Importantly, the unchanged UV-vis spectra and the MALDI-TOF spectra of the heated samples show that the cluster is stable under these conditions (Fig. S5 and S6†). HPLC (Fig. 4) confirms these findings. CD signal and enantiomeric excess are related linearly and the ee is obtained from the normalized CD signal by multiplication with the initial value of the ee which is estimated from the HPL chromatograms. At temperatures higher than 100 °C a relatively fast decrease of the CD signal (thus ee) can be seen. After 40 min at 130 °C saturation is reached at about ee = 0, i.e. the sample contains a racemate.

The linearity of the plot of ln(ee) vs. time shows that the reaction is of first-order kinetics (Fig. S4†). The initial reaction rate at each temperature was determined from a linear fit of the initial slope. The activation parameters of the reaction were obtained from a linear least square fit of the Eyring plot. The activation energy $E_a$ is calculated to be 24.7 ± 1.6 kcal mol⁻¹ (standard error) and the activation enthalpy 24.0 ± 1.6 kcal mol⁻¹. These values are slightly lower than those for Au₃₈(2-PET)₂₄. However, the racemization still takes place at higher temperatures for Au₄₀(2-PET)₂₄ due to the different activation entropies in the two cases. The relatively low negative value of −12.7 ± 4.1 cal mol⁻¹ K⁻¹ for the activation entropy indicates an inner-molecular mechanism without intermediate release of ligands, possibly via a cyclic state with concerted bond breaking and formation. The low value of the activation enthalpy also indicates that the Au–S bonds are not completely broken during the process.

The energy and enthalpy of activation obtained for the racemization of Au₄₀(2-PET)₂₄ are of the same magnitude as those reported earlier for Au₃₈(2-PET)₂₄ and for C/Au₄₀[R-BINAS]₂(2-PET)₂₂. Strikingly, the racemization of Au₄₀ takes place at a
similar temperature as that of Au38 clusters stabilized by BINAS, as can be seen in Fig. 5. Only for the Au38 cluster with exclusively 2-PET ligands the entropy is positive. For the other investigated clusters a negative entropy of activation of about the same magnitude (ca. –10 to –20 cal mol⁻¹ K⁻¹) is obtained. The fact that for different clusters the activation enthalpy is in the same range whereas the activation entropy differs significantly for the Au38(2-PET)₂₄ and Au40(2-PET)₂₄ clusters highlights the importance of the activation entropy in these rearrangements. The racemization may take place via different mechanisms for different clusters.

Considering the proposed structure for Au40(2-PET)₂₄ one would expect that the racemization is more difficult compared to Au38(2-PET)₂₄ since the dimeric gold-thiolate units at the poles as well as the monomeric units at the equator are oriented chirally (Fig. 1). A possible mechanism for the racemization is presented graphically in the ESI (Scheme S1†). The orientation of the short units at the equator as well as that of the long units needs to be reversed in order to obtain the other enantiomer. The short staples at the poles are not involved. The inversion may take place independently at both hemispheres of the cluster. The proposed mechanism is a concerted sliding mechanism with a cyclic transition state which fits well to the negative activation entropy. When the orientation of the gold-thiolate units at only one hemisphere is inverted, the cluster is achiral, corresponding to the calculated structure A2 in ref. 25. From this point on, the re-arrangement can be inversed leading back to the initial enantiomer or can take place as well at the second hemisphere, leading to the other enantiomer. No other structures were observed in the HPL chromatograms of the racemized samples, indicating that the supposed achiral intermediate is unstable and converts rapidly to one of the enantiomers.

It should be further noted that this follows the same principle as the proposed mechanism of the racemization of Au38(2-PET)₂₄ where an achiral intermediate (Pei intermediate) is suggested.† The proposed mechanisms for the racemization of Au40(2-PET)₂₄ requires only one (concerted) step per hemisphere to obtain the inversed orientation contrary to the proposed mechanism of Au38(2-PET)₂₄ in which two steps are needed. However, the whole cluster surface, except the short units at the pole, is involved as four staple motifs located at the poles and the equator (two monomer units and two dimer units) need to move for the rearrangement for each hemisphere of Au40(2-PET)₂₄. Only the dimer units at the poles move in the case of Au38(2-PET)₂₄; the monomer units at the equator remain in their position.†

Conclusion

We have shown that the surface of Au40(2-PET)₂₄ is flexible and can undergo racemization. Compared to Au38(2-PET)₂₄ higher temperatures are required for racemization, which is due to the negative activation entropy for Au40(2-PET)₂₄. The higher temperatures required for the racemization of Au40 compared to Au38 makes it potentially a better candidate for applications such as asymmetric catalysis where maintenance of enantio-purity is required at elevated temperatures.

Acknowledgements

We thank Dr Sophie Michalet (SMS, UniGE) for the MALDI measurements, Sami Malola (University of Jyväskylä, Finland) for providing the calculated CD data and the structural information. We thank further Profs Stefan Matile and Jérôme Lacour (UniGE) for providing their CD spectrometer. We are grateful to the Swiss National Foundation and the University of Geneva for financial support. S.K. is grateful to the German Academic Exchange Service.
Notes and references