

# Racemization of a chiral Nanoparticle evidences the Flexibility of the Gold-Thiolate Interface

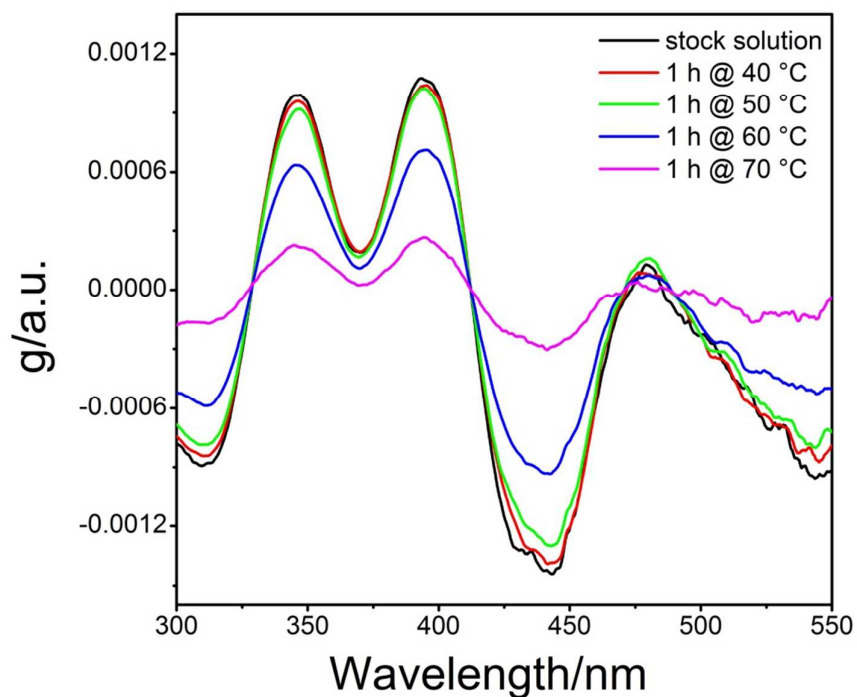
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## Supporting Information

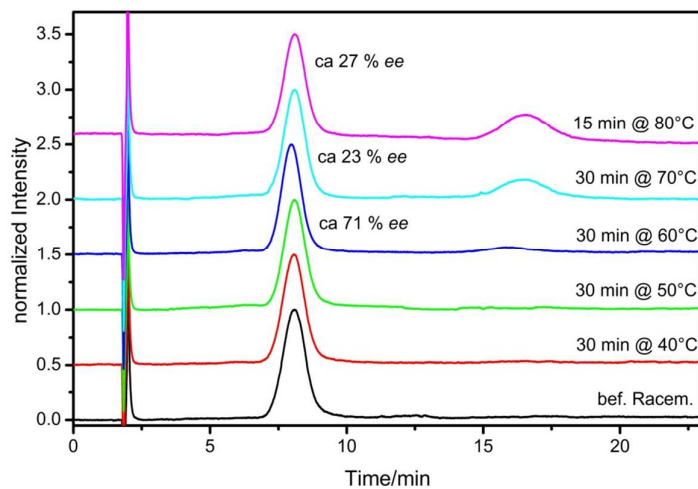
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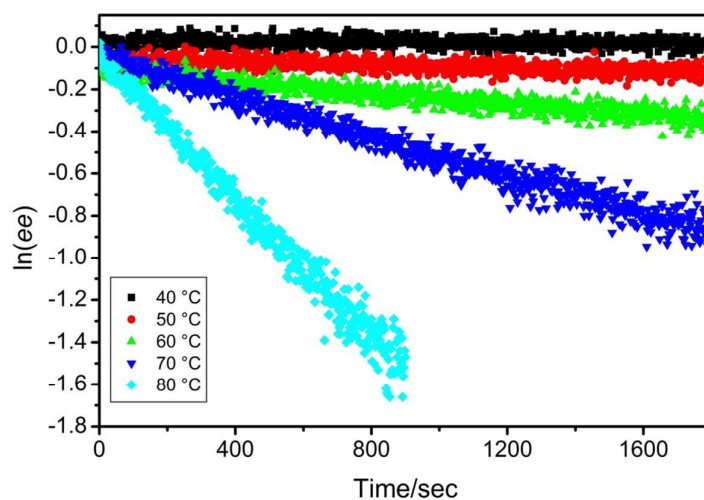


**Figure S-1.** Anisotropy factors  $\Delta A/A$  of the racemization of enantiomer **2** at different temperatures. For the 60 and 70 °C sample, a significant decrease is observed.



**Figure S-2.** HPLC chromatograms of  $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$  (Enantiomer **1**) before (bottom trace) and after racemization at elevated temperatures. No additional peaks of significant intensity are visible. The broadening of the peak for enantiomer **2** makes determination of

enantiomeric excesses by comparison of peak areas impossible for the 40 and 50 °C samples. The *ee* for the 70 °C sample is lower than expected which may be related to improper cooling of the reaction after 30 min (‘after-burning effect’).



**Figure S-3.** Linear dependence of  $\ln(ee)$  versus reaction time for the racemization of  $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$  at different temperatures. This supports a first-order reaction.

**Table S-1.** Activation parameters derived from Arrhenius-type plot for the racemization of  $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ . The values for  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  are calculated for 20 °C (293.15 K).

$E_a$	$117.72 \pm 2.2 \text{ kJ mol}^{-1}$	$28.14 \pm 0.53 \text{ kcal mol}^{-1}$
$A$	$(3.32 \pm 3.89) \cdot 10^{14} \text{ s}^{-1}$	
$\Delta H^\ddagger = E_a - RT$		$25.70 \pm 0.53 \text{ kcal mol}^{-1}$
$\Delta S^\ddagger = R \ln \left( \frac{hA}{kT} \right)^{-1}$		$0.50 \pm 0.08 \text{ cal mol}^{-1} \text{ K}^{-1}$
$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$		$25.55 \pm 0.55 \text{ kcal mol}^{-1}$

## Determination of the errors of activation parameters

The rate constants  $k$  were determined for each reaction temperature by linear fits.  $\Delta k$  is then given by the standard deviation of the determined slope. Since the error for  $k$  is different at each reaction temperature, the fit in the Arrhenius-plot ( $\ln(k)$  vs  $1/T$ ) was slightly modified by applying a weighted linear regression. Errors  $\Delta \ln(k)$  were calculated from  $k$  and  $\Delta k$  as follows:

$$\Delta \ln(k) = [\ln(k + \Delta k) - \ln(k - \Delta k)]/2$$

In the Arrhenius-plot, the weighted linear regression gives  $E_a \pm \Delta E_a$  (slope, via slope =  $-E_a/R$ ) and  $\ln(A) \pm \Delta \ln(A)$ . The error for  $A$  is then calculated from  $\Delta \ln(A)$  as:

$$\Delta A = \exp(\ln(A) + \Delta \ln(A)) - A$$

The Activation Enthalpy is  $\Delta H^\ddagger$ , its error is  $\Delta \Delta H^\ddagger = \Delta E_a$ . The activation entropy is calculated as:

$$\Delta S^\ddagger = R[\ln(hA/kT)]^{-1}$$

And the corresponding error:

$$\Delta \Delta S^\ddagger = R[\ln\{h(A + \Delta A)\}/kT]^{-1} - R[\ln(hA/kT)]^{-1}$$

By applying the approximation  $\Delta y \approx y(x + \Delta x) - y(x)$ .

The Free Activation Enthalpy  $\Delta G^\ddagger$  is calculated as:

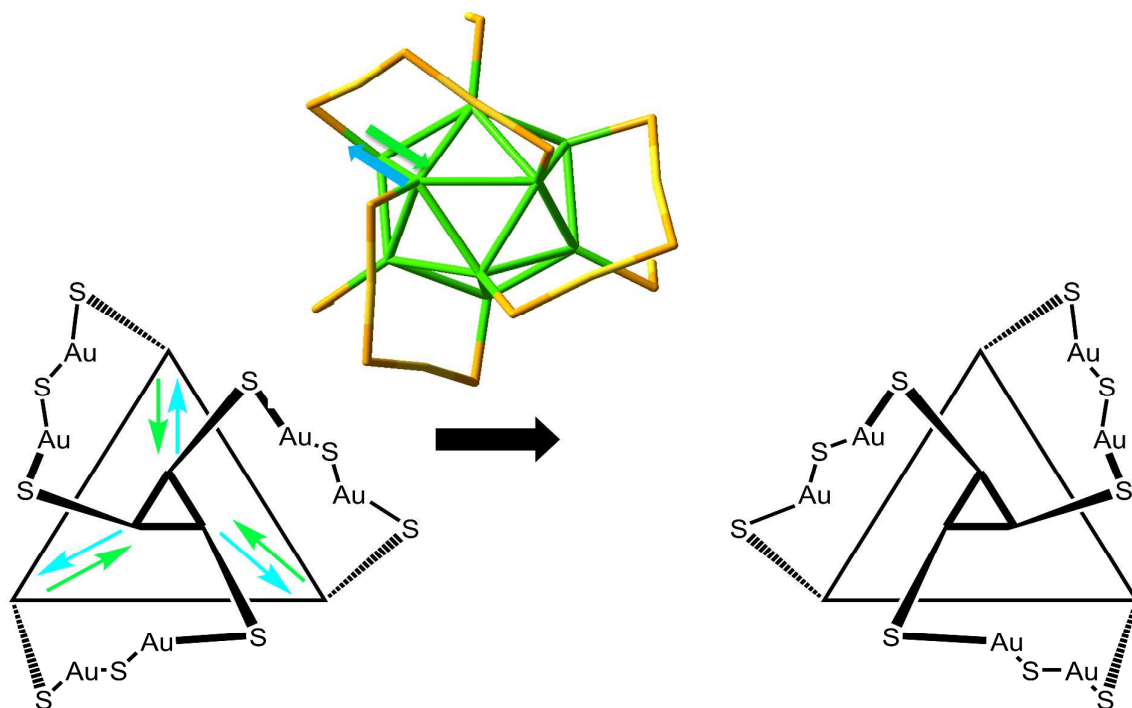
$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

With the error:

$$\Delta \Delta G^\ddagger = \Delta \Delta H^\ddagger - T\Delta \Delta S^\ddagger \text{ (since } \Delta y = dy/dx_1 * \Delta x_1 + dy/dx_2 * \Delta x_2 + \dots)$$

### A possible third mechanism for the racemization

We briefly describe a possible third mechanism in addition to the two mechanisms described in the manuscript. This is similar to the “sliding” mechanism. In principle, the sulfur atoms binding to the polar and equatorial Au surface atoms of a hemisphere exchange simultaneously with their closest counterparts. In this mechanism the staples stay intact but the sulfur atoms binding to the polar sites move to the equatorial sites and vice versa. Scheme S-1 highlights the mechanism and the movement of the atoms involved. We however assume the mechanism as unlikely since strong steric interactions (e.g. with monomeric staples or organic backbones (phenylethyl fragments)) are expected. This should lead to a drastic increase of the activation barrier.



**Scheme S-1.** Schematic highlighting a possible third mechanism for the racemization of  $\text{Au}_{38}(\text{SR})_{24}$  clusters. As in the manuscript, the cluster is represented in the top view. The

triangles represent the Au atoms to which the dimeric staples bind. In the mechanism, the end of the staple binding to the polar atoms slide towards the equatorial Au-surface atom (blue arrows). The sulfur atom initially binding to the equatorial Au-surface atom slides towards the polar Au atom (green arrows). This happens simultaneously at all three binding sites, leading to full inversion in one step. The cluster structure at the top is the involved section of the cluster, omitting the lower half of the cluster and the atom in the center of the icosahedron for clarity. The organic  $-\text{CH}_2\text{CH}_2\text{Ph}$  groups are omitted. Monomeric staples are hinted by showing the closer binding sulfur atoms and the adatoms.