

# Racemization of Chiral Pd<sub>2</sub>Au<sub>36</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub>: Doping Increases the Flexibility of the Cluster Surface

Noelia Barrabés,\* Bei Zhang, and Thomas Bürgi\*

Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

**S** Supporting Information

**ABSTRACT:** Pd<sub>2</sub>Au<sub>36</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> clusters have been prepared, isolated and separated in their enantiomers. Compared to the parent Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster, the doping leads to a significant change of the circular dichroism spectrum; however, the anisotropy factors are of similar magnitude in both cases. Isolation of the enantiomers allowed us to study the racemization of the chiral cluster, which reflects the flexibility of the ligand shell composed of staple motifs. The doping leads to a substantial lowering of the racemization temperature. The change in activation parameters due to the doping may be solely due to modification of the electronic structure.

Thiolate-protected gold clusters Au<sub>n</sub>(SR)<sub>m</sub> have been widely studied since the first synthesis work in 1994 by Brust et al.<sup>1</sup> Progress in atomically precise synthesis, separation and characterization revealed atomically precise nanostructures.<sup>2–6</sup> Particularly stable clusters were found to be Au<sub>25</sub>(SR)<sub>18</sub>,<sup>3,7</sup> Au<sub>38</sub>(SR)<sub>24</sub>,<sup>8</sup> Au<sub>40</sub>(SR)<sub>24</sub>,<sup>9,10</sup> Au<sub>102</sub>(SR)<sub>44</sub><sup>11</sup> and Au<sub>144</sub>(SR)<sub>60</sub>,<sup>12</sup> but other compositions were also reported.<sup>13–18</sup> These clusters consist of a symmetric metal core protected by multiple gold–thiolate staples –SR–(Au–SR–)<sub>n</sub> (*n* = 1, 2). Properties of these nanomaterials such as photoluminescence,<sup>2</sup> optical activity<sup>10,19</sup> and catalytic activity<sup>20–23</sup> are size-dependent and not observed in the bulk, which makes them attractive for applications.<sup>6,24–26</sup>

An outstanding property of certain thiolate-protected clusters (Au<sub>38</sub>, Au<sub>40</sub>, Au<sub>28</sub> and Au<sub>102</sub>) is their intrinsic chirality.<sup>27–33</sup> Recently, enantiomers of several chiral clusters have been separated.<sup>10,19,34,35</sup> The chirality is related to the arrangement of the staples on the cluster surface. Separation of the enantiomers enabled the study of their racemization.<sup>36–38</sup> The Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster takes about half an hour at 80 °C.<sup>36</sup> From the known structure of this cluster racemization must involve a drastic reorganization of the Au–S interface. The introduction of one rigid dithiol into the cluster surface leads to a significant increase of the racemization temperature possibly because the dithiol bridges neighboring staple units.<sup>39</sup>

Doping of thiolate-protected gold clusters with other metals is an interesting avenue to tune the properties of the clusters and increase their stability against etching processes and thermal treatments. In 2009 Murray et al.<sup>40</sup> synthesized PdAu<sub>24</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub>, doping the gold cluster core with one atom of Pd. Several works by Jin et al.,<sup>41</sup> Negishi et al.,<sup>42,43</sup> Dass et al.<sup>44–46</sup> and others have been performed doping the magic number Au<sub>n</sub>(SR)<sub>m</sub> clusters by metals (Pd,<sup>41,42,47,48</sup> Pt,<sup>49</sup>

Ag,<sup>44,50–53</sup> Cu<sup>46,54,55</sup>). Doping with Ag or Cu changes the electronic structure and optical properties.<sup>50,54</sup> Doping with Pd has been reported to increase the stability<sup>41,47</sup> and enhance reactivity in catalytic processes<sup>56</sup> and in ligand exchange reactions,<sup>57</sup> in comparison with the corresponding parent Au<sub>n</sub>(SR)<sub>m</sub> clusters.

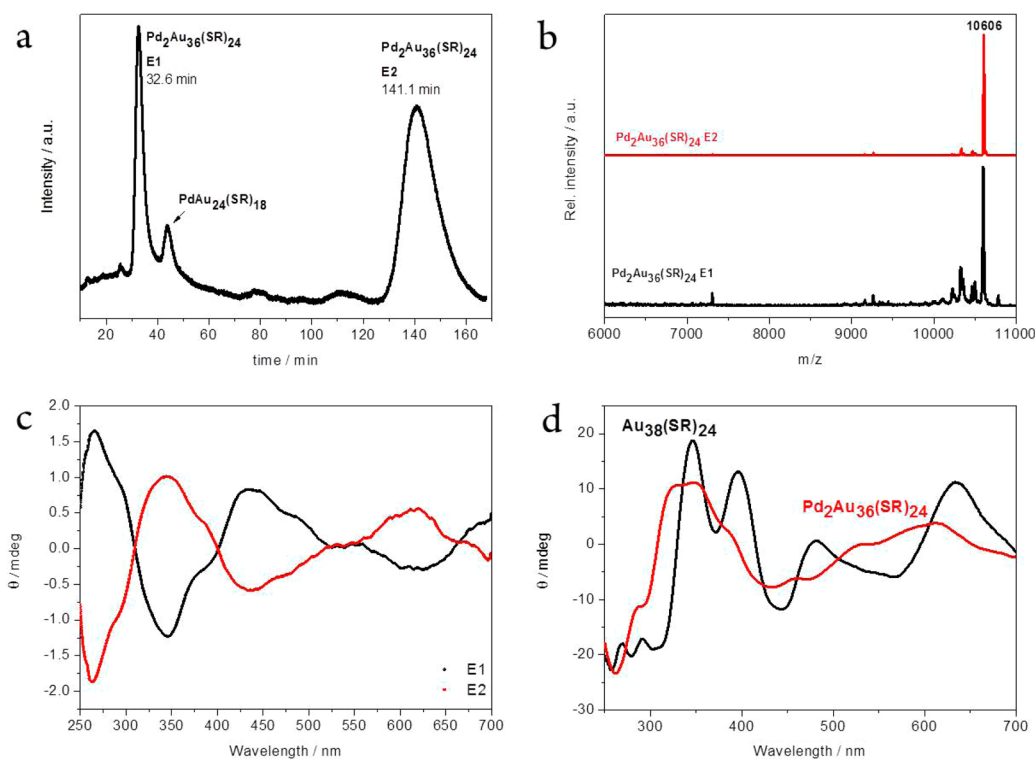
The effect of doping on the chiroptical properties of Pd doped gold clusters protected by chiral thiolates has been addressed by Yao et al.<sup>58</sup> Clusters with atomic Au:Pd ratios between (7.9–8.8) and (4.7–5.4) were isolated and a relatively weak optical activity was found. We report herein the first separation of the enantiomers of a Pd doped gold cluster, Pd<sub>2</sub>Au<sub>36</sub>(SR)<sub>24</sub>, protected by achiral thiolates (SR = SC<sub>2</sub>H<sub>4</sub>Ph), achieved by chiral high-performance liquid chromatography (HPLC). The cluster has a different CD spectrum compared to the parent Au<sub>38</sub> compound, however with comparable anisotropy factors. The racemization of the doped cluster proceeds at significantly lower temperature, showing that doping of the cluster strongly affects the flexibility of the protecting staples at its surface.

Pd<sub>x</sub>Au<sub>38–x</sub>(SR)<sub>24</sub> (*x* = 1, 2) clusters were synthesized following an adapted protocol based on a previous report (for details see Supporting Information).<sup>47</sup> The main difference to the synthesis reported by Negishi et al.<sup>47</sup> concerns the purification steps. After extraction of the crude product with acetonitrile (separation of PdAu<sub>24</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> clusters), a second extraction with acetone is performed in order to completely remove Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub>. Then the nanoclusters were isolated in a gel permeation column (GPC/SEC).<sup>9</sup> The fraction containing Pd<sub>2</sub>Au<sub>36</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> was collected and refined several times until the UV–vis absorption properties were stable. Despite the numerous separations through the SEC column, MALDI spectra (S2) show the presence of PdAu<sub>24</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub>, Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub>, Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub>, PdAu<sub>37</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> besides Pd<sub>2</sub>Au<sub>36</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> in the obtained sample. Further purification and separation of pure enantiomeric forms of Pd<sub>2</sub>Au<sub>36</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub> was performed using HPLC in several steps.

First, the mixture of the clusters was separated at room temperature using a chiral cellulose-based analytical HPLC column and hexane/isopropanol (90:10) as eluent. The eluting solutions were monitored by an UV detector at 620 nm. Several peaks were collected (S1). MALDI analysis was performed of each collected fraction (S2). The first peaks in the chromatogram (P1, see Supporting Information) correspond to small

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**Figure 1.** Characterization of  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ ; (a) HPLC chromatogram of the enantioseparation; this sample is one fraction (P5) of a previous crude HPLC separation (see text for more details); (b) MALDI spectra of enantiomers; (c) CD spectra of enantiomers of  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  (about  $6 \times 10^{-6}$  mol/L); and (d) comparison CD spectra of E2 of  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  ( $\times 10$ ) and  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ .

clusters with mass below 5500. The fraction between 30 and 68 min (P2) contains several species identified by MALDI (S2) and CD (S3) as first enantiomeric form of  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ ,  $\text{PdAu}_{37}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  and  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  mixed with  $\text{PdAu}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  clusters. The following fractions P3 and P4 consist mainly of second enantiomeric form of  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  and  $\text{PdAu}_{37}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ , respectively.

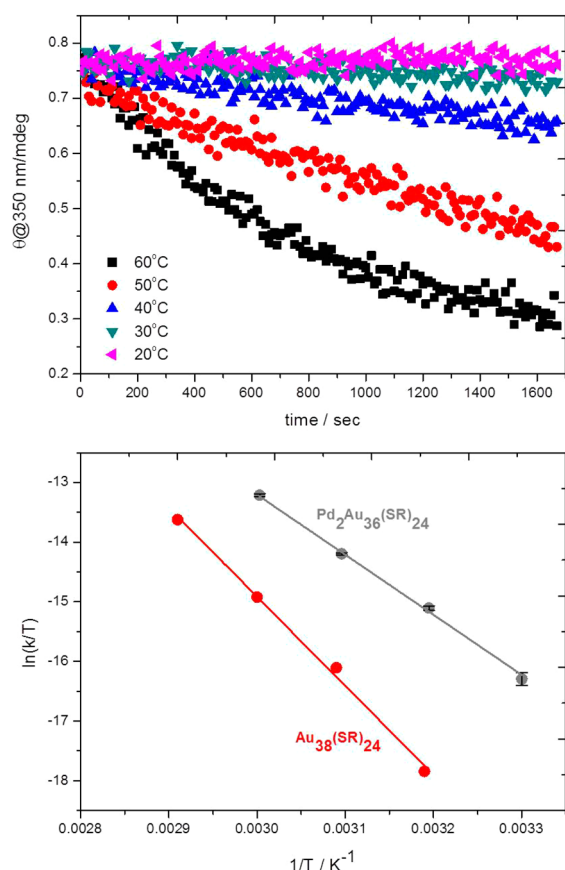
Finally, a broad peak P5 from 125 to 160 min corresponds to the second enantiomer of  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ . In order to obtain highly pure enantiomeric samples, a second separation of the P5 fraction was performed (Figure 1).

The fractions corresponding to enantiomers 1 and 2 of  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  at 32.6 and 141.1 min, respectively, were collected over several HPLC runs. The first enantiomer overlaps with other clusters and could not be obtained absolutely pure, whereas the second enantiomer is pure after the second HPLC run, as confirmed by MALDI (Figure 1b). Therefore, the chiroptical characterization and racemization studies were performed with the second enantiomer (see below). The UV-vis spectra (Figure S4) show the characteristic electronic transitions of  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ , similar to previous report by Negishi et al.<sup>47</sup> The spectrum of enantiomer E2 is somewhat more defined at low wavelength (below 800 nm) compared to the one of E1 and the one reported before<sup>47</sup> underlining the purity of the sample containing the second enantiomer E2. CD spectra of the two enantiomers gives perfect mirror images with clear signals observed between 250 and 700 nm (263 (-), 293 (-), 344 (+), 386 (+), 431 (-), 474 (-) and 607 (+) nm, signs for enantiomer 2) (Figure 1c). Comparison between the CD spectra of  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  and  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  (Figure 1d) shows significant differences between the two, revealing the strong influence of the doping

on the electronic structure of the cluster. The intensity of CD spectra depends on the concentration of the sample, and the concentration-independent anisotropy factors  $g = \Delta A/A = \theta[\text{mdeg}]/(32980 \times A)$  were calculated (Figure S5). The maximum anisotropy factor of  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  was reported to be  $4.0 \times 10^{-3}$ , which corresponds well to the value found here for  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  (Figure S5). Also, the anisotropy factor of the two clusters is about  $1.0 \times 10^{-3}$  around 300 nm. In a previous study of Pd-doped Au clusters covered by chiral thiolates anisotropy factors of  $1.0 \times 10^{-4}$  and  $4.2 \times 10^{-5}$  were found.<sup>58</sup> The relatively weak anisotropy factor was explained by the coexistence of isomers.

The possibility to separate and store enantiomers of doped clusters enabled us to study their racemization using circular dichroism (CD). For the racemization studies, the enantiopure sample (E2) was dissolved in toluene and the CD signal at 350 nm was followed over the course of 30 min at different temperatures (30, 40, 50, and 60 °C, Figure 2). After thermal treatment UV-vis spectra of the solution was recorded in order to evaluate the stability of the clusters against decomposition at slightly elevated temperatures. The heating had no influence on the UV-vis spectra (Figure S6), showing that decomposition is negligible. In contrast, increased heating leads to significant decrease of the CD responses, whereas the spectral shape is conserved (Figure S7). This is clear evidence for racemization of the cluster.

Rate constants  $k(T)$  were obtained from the racemization experiments by determining the initial reaction rates by linear fits. The Eyring plot (Figure 2) gives a linear fit, derived activation parameters  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  are summarized in Table S1. Compared to the parent  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  cluster the doping leads to a significant drop in activation enthalpy from about 29 kcal/mol to about 20 kcal/mol and a drop in the



**Figure 2.** Racemization experiment with  $\text{E2-Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ ; (top) CD response at 350 nm as a function of time at different temperatures; (bottom) Eyring plot  $\ln(k/T)$  vs  $1/T$  for the racemization of  $\text{Pd}_2\text{Au}_{36}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$  and  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ . The data of the latter was taken from the literature.<sup>36</sup> Errors on the points for  $\text{Pd}_2\text{Au}_{36}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$  derive from the fit of the rate constants (standard deviation).

activation entropy from about +10 to  $-12$  cal/mol K. The doped cluster racemizes at lower temperature compared to the parent gold cluster. At 50 °C about 50% of the Pd doped cluster has reacted after half an hour whereas for the parent gold cluster this fraction is about 10%. These activation parameters are directly related with the reaction mechanism of the racemization process. It is thought that the structure of the doped cluster is analogous to the parent  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  cluster. Furthermore, on the basis of theoretical studies,<sup>47</sup> it was proposed that the Pd atoms are located in the two central positions of the elongated cluster core. This would indicate that the significant changes observed in the racemization kinetics, which reflects the flexibility of the Au–S interface, is electronic in nature. Interestingly, the doped cluster has been reported to be more stable than the parent  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  cluster<sup>47</sup> although the latter racemizes at higher temperature. The reason for this is unclear but the decomposition of the cluster may be related to the detachment of thiolate from the cluster surface, whereas the racemization likely proceeds without complete Au–S bond breaking.

In conclusion, the isolation and separation of pure enantiomers of a Pd doped thiolate-protected gold cluster  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  was achieved for the first time. Compared to the parent  $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$  cluster the circular dichroism (CD) spectrum is significantly different. However, anisotropy

factors are of similar magnitude. Racemization of the chiral cluster proceeds at significantly lower temperature compared to the parent gold cluster, which is reflected in different activation parameters. This indicates that electronic effects due to the doping render the Au–S interface more flexible.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Details of the experimental part (synthesis and characterization). Additional HPLC, MALDI, UV–vis and CD measurements described in the text and thermodynamic activation parameters. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

noelia.barrabes@unige.ch

thomas.buergi@unige.ch

### Notes

The authors declare no competing financial interest.

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