


# Doping Silver Increases the $\text{Au}_{38}(\text{SR})_{24}$ Cluster Surface Flexibility

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 Supporting Information

# Capillary Liquid Chromatography Mass Spectrometry Analysis of Intact Monolayer-Protected Gold Clusters in Complex Mixtures

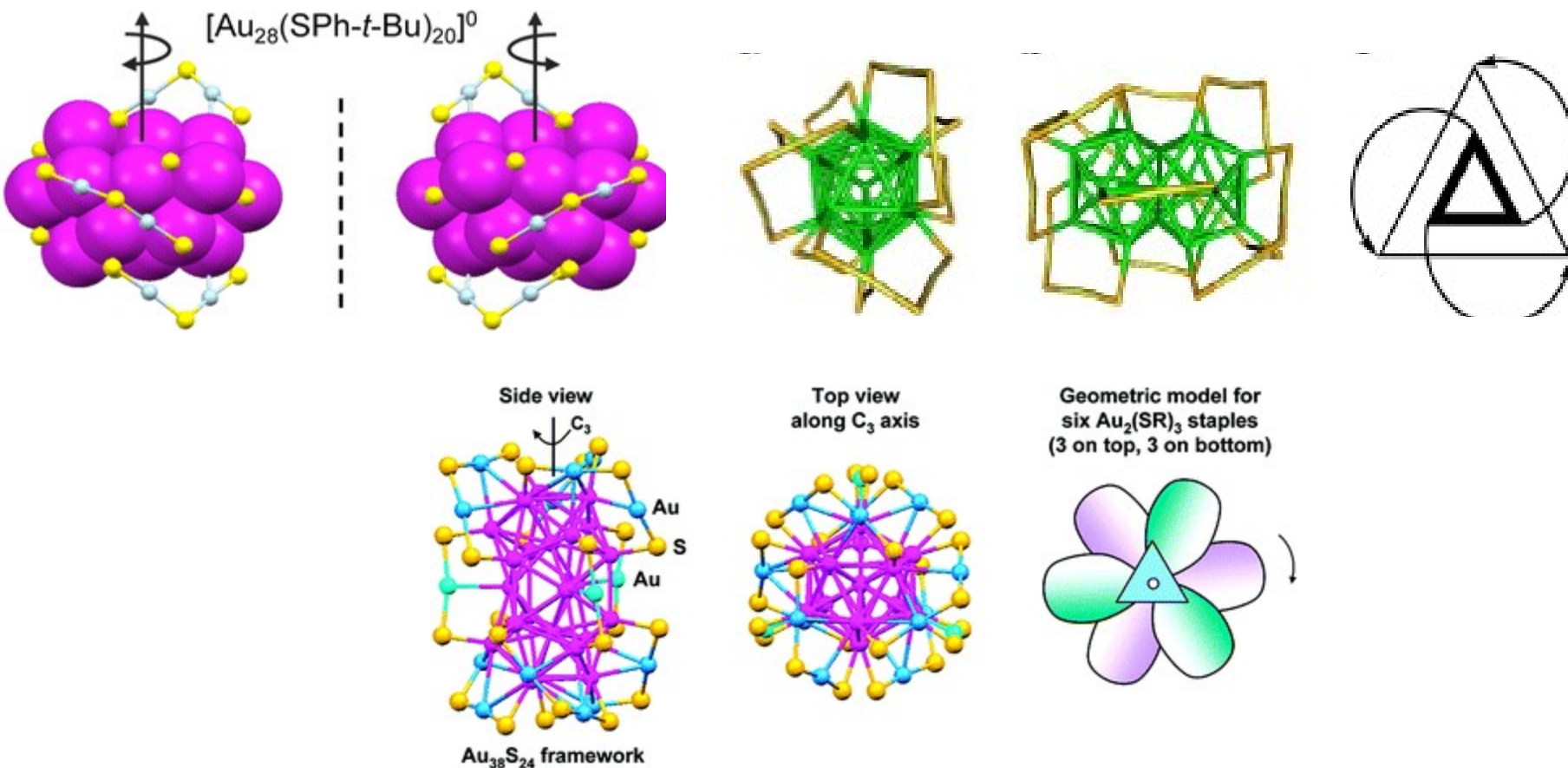
David M. Black,<sup>\*,‡</sup> Stephan B. H. Bach,<sup>†</sup> and Robert L. Whetten<sup>‡</sup>

<sup>‡</sup>Department of Physics and Astronomy, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249, United States

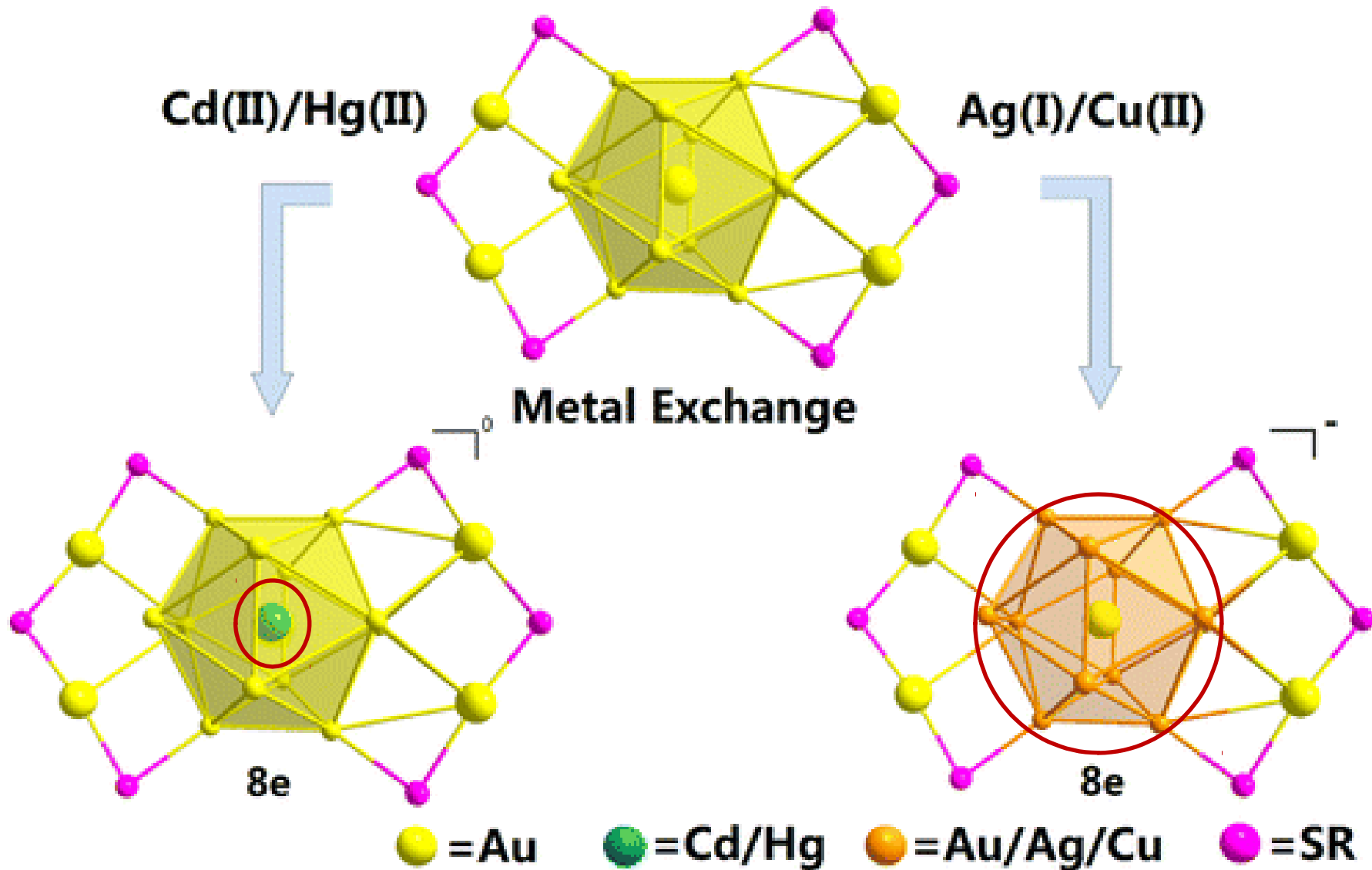
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 Supporting Information

# Chiral gold clusters



**$\text{Au}_{28}$ ,  $\text{Au}_{38}$ ,  $\text{Au}_{40}$ ,  $\text{Au}_{102}$ ,  $\text{Au}_{133}$  and  $\text{Au}_{144}$**



Au<sub>25</sub>- 13 Ag atom doping  
 Au<sub>38</sub>- 5 Ag atom doping

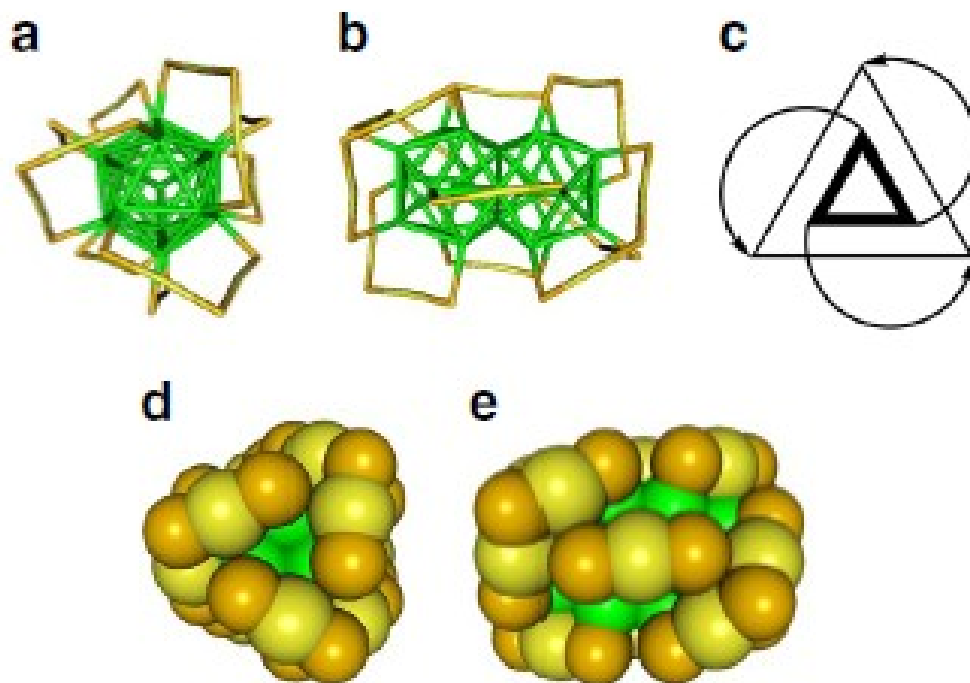
# Background...

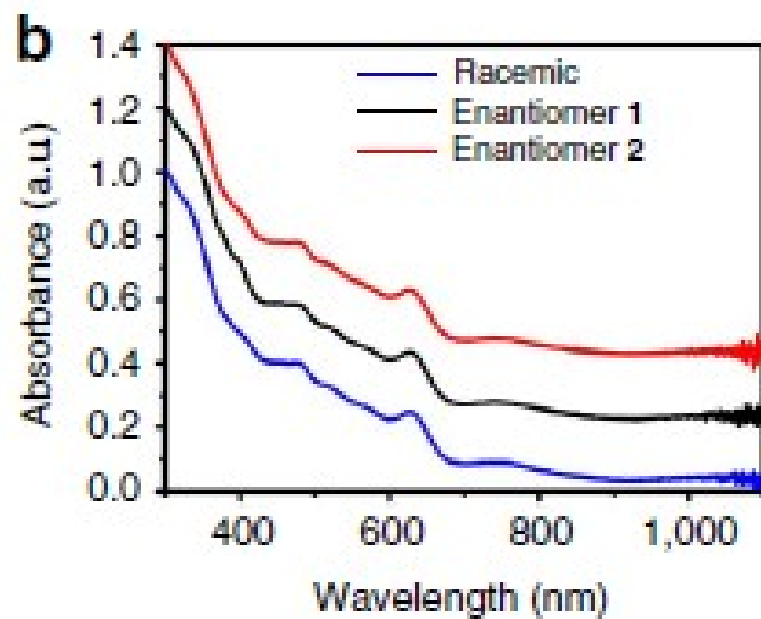
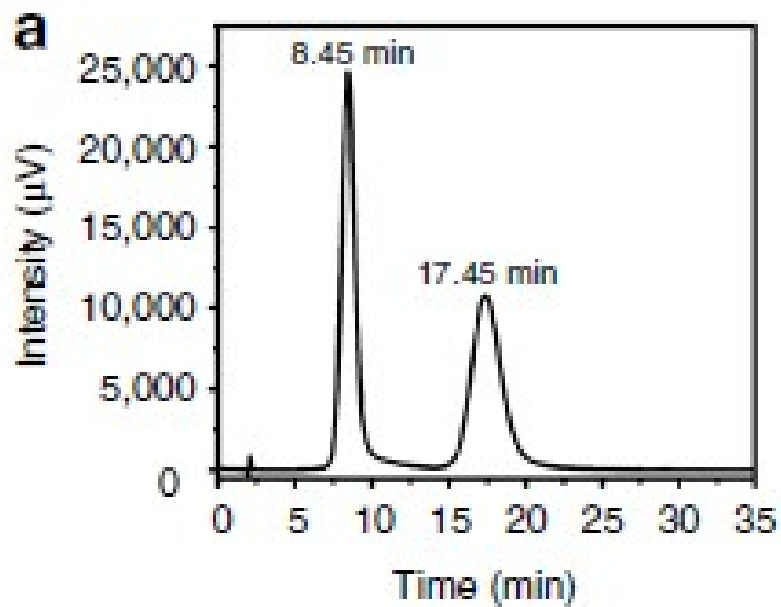
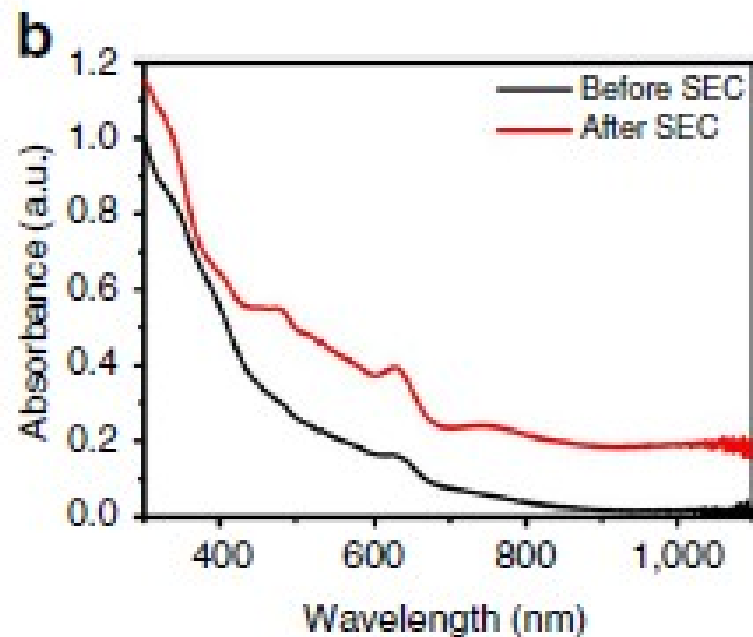
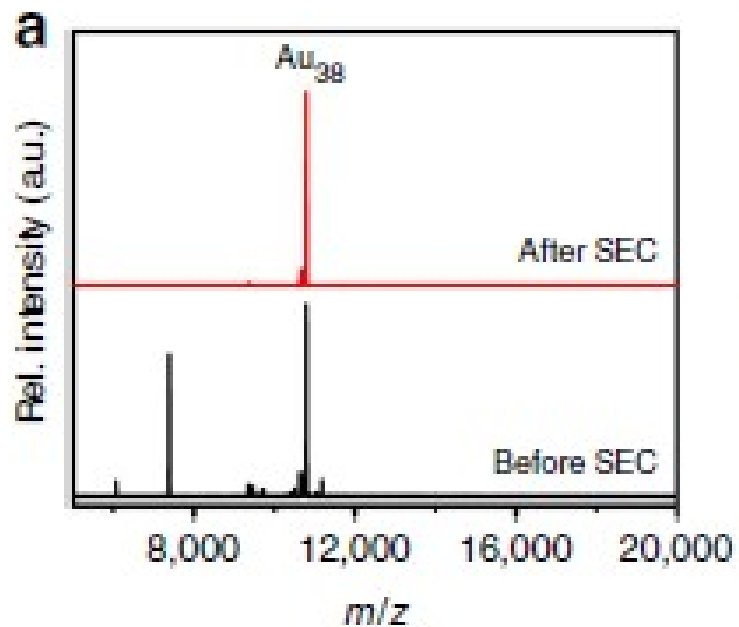
## ARTICLE

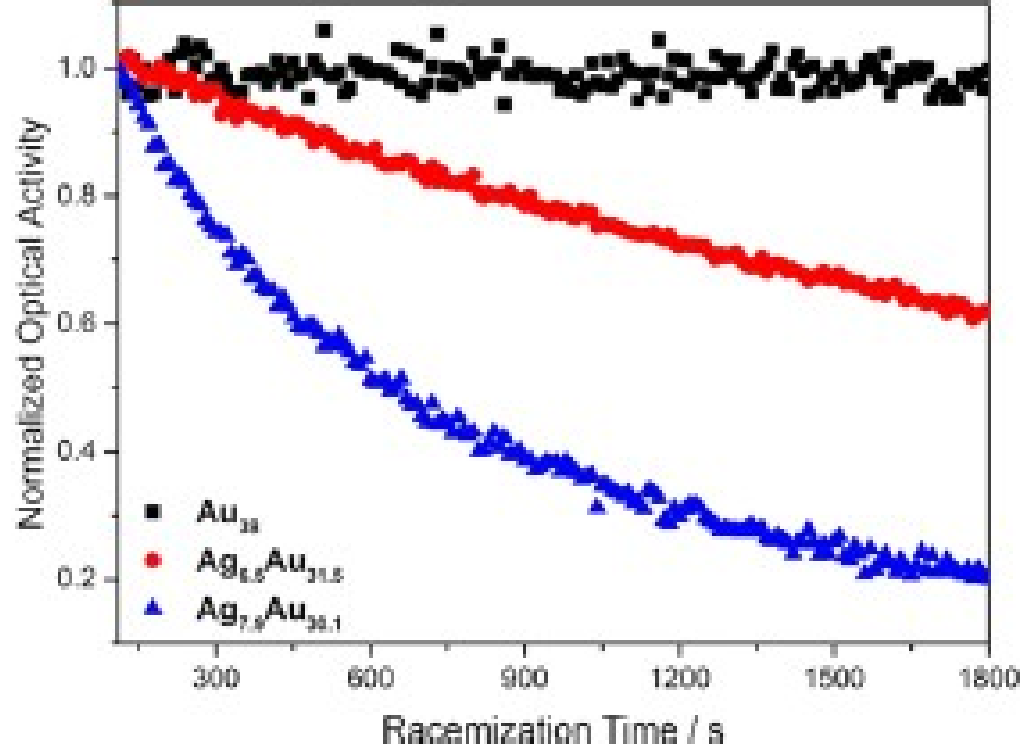
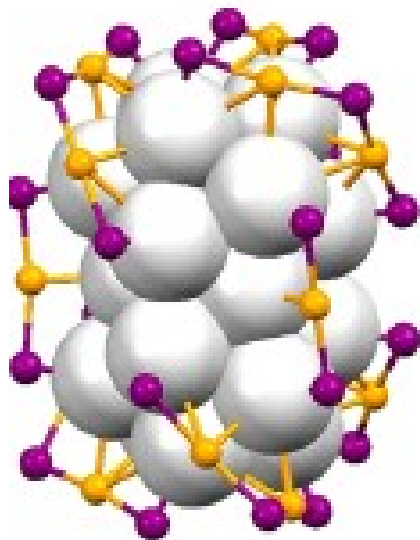
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First enantioseparation and circular dichroism spectra of  $\text{Au}_{38}$  clusters protected by achiral ligands





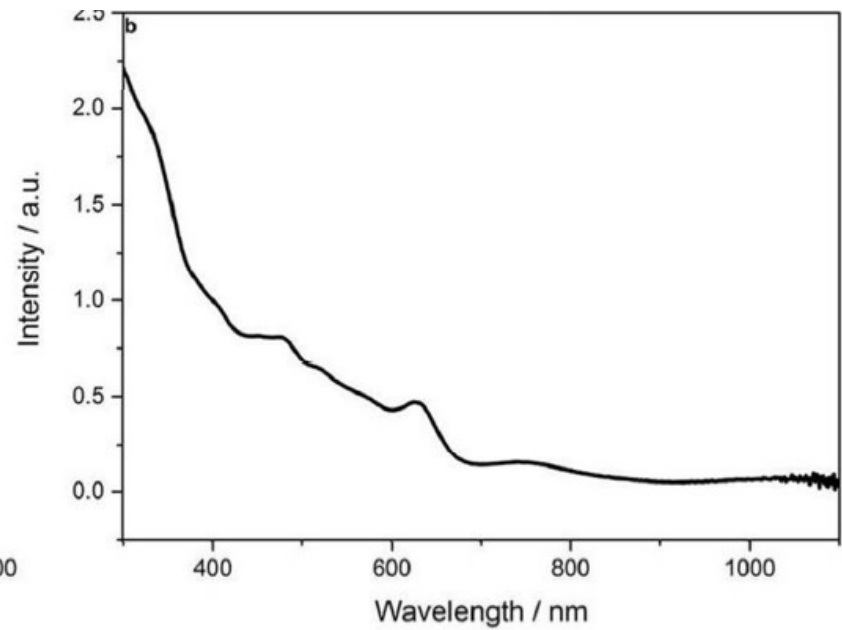
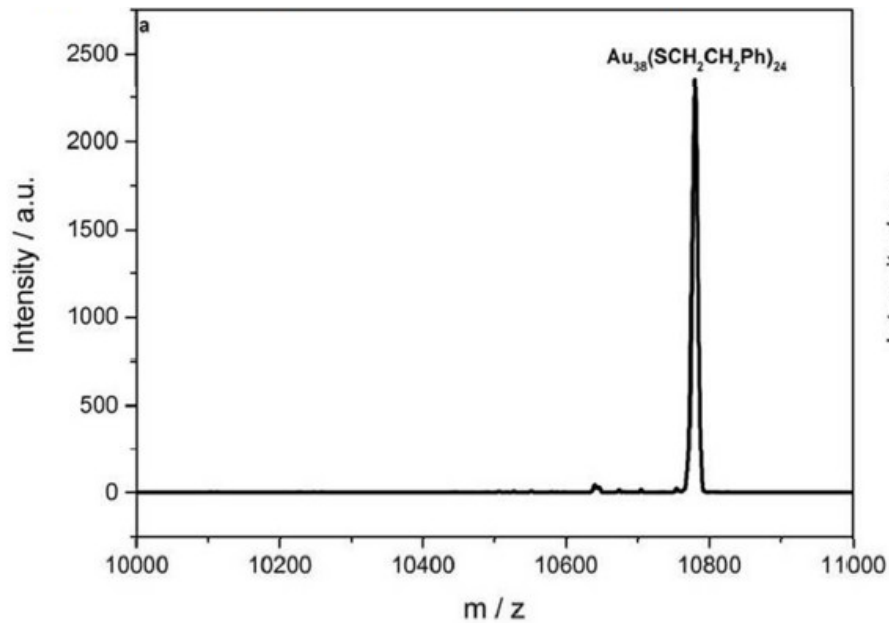


Synthesis of  $Ag_xAu_{38-x}(SCH_2CH_2Ph)_{24}$ .

Separation of  $Ag_xAu_{38-x}(SCH_2CH_2Ph)_{24}$  using HPLC.

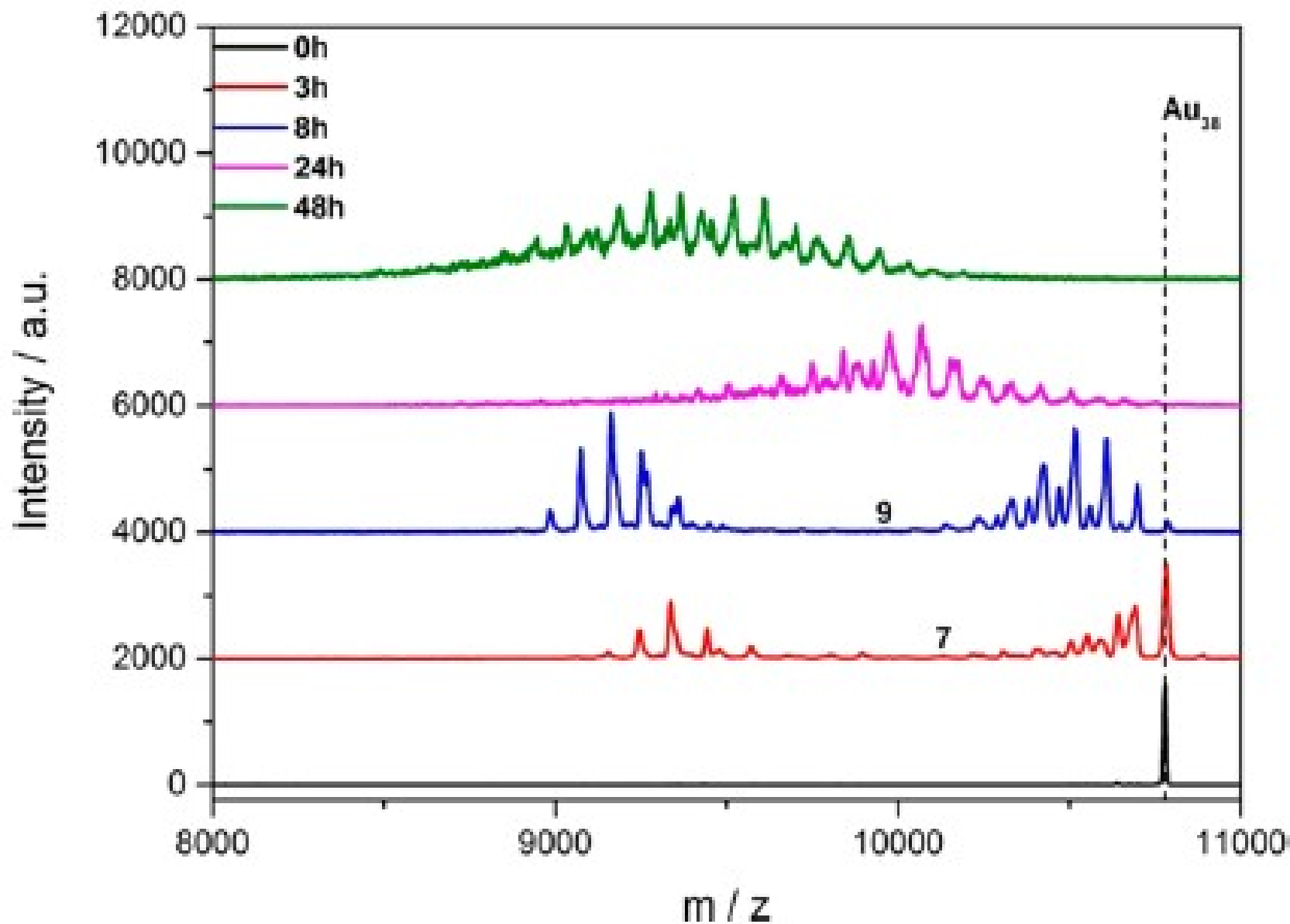
Characterization

Discussion of the results

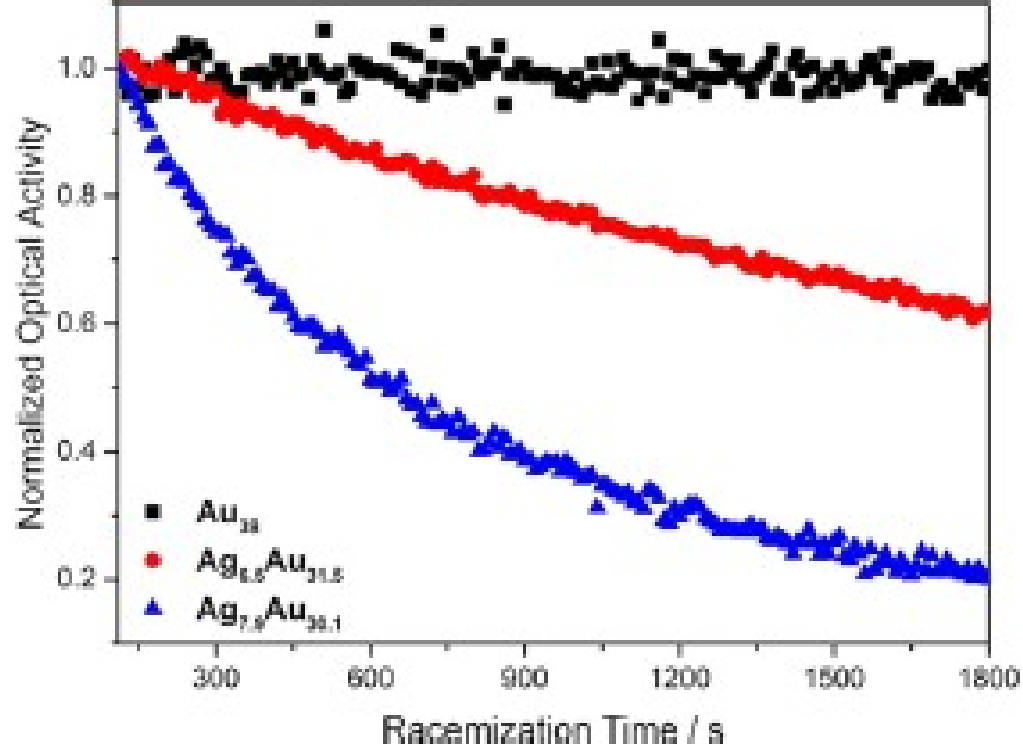
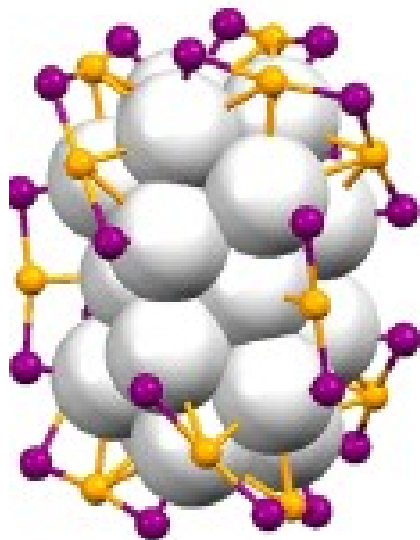


Racemic  $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$  was synthesized by thermal etching of polydispersed  $\text{Au}_n(\text{SG})_m$  nanoclusters

$\text{Ag}_x\text{Au}_{38-x}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$  was synthesized by metal exchange of  $\text{AgSCH}_2\text{CH}_2\text{Ph}$  and  $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ .





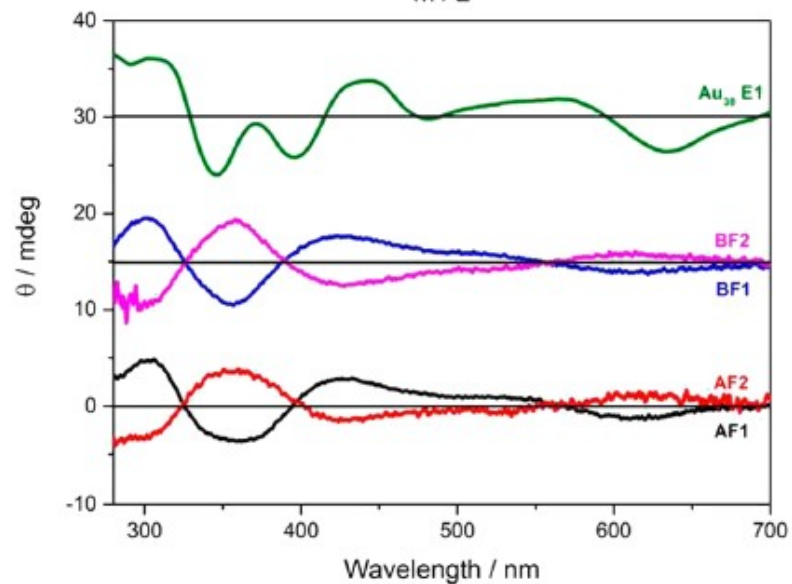
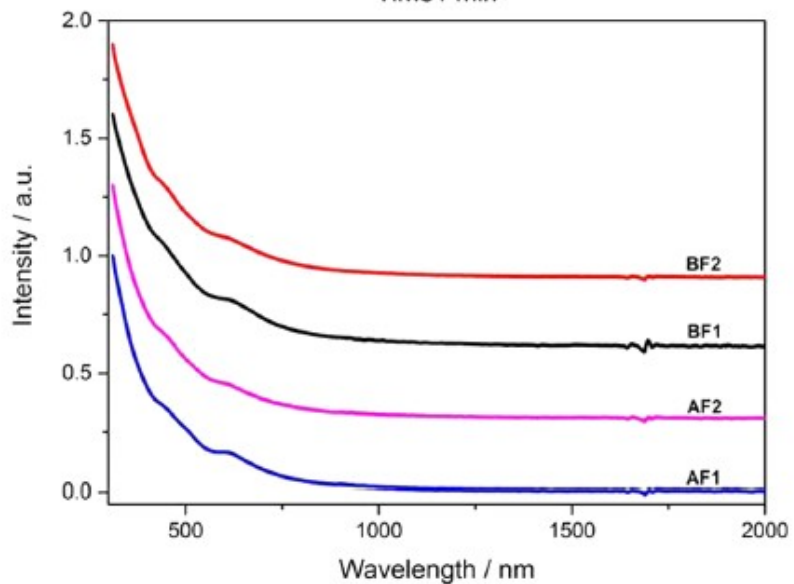
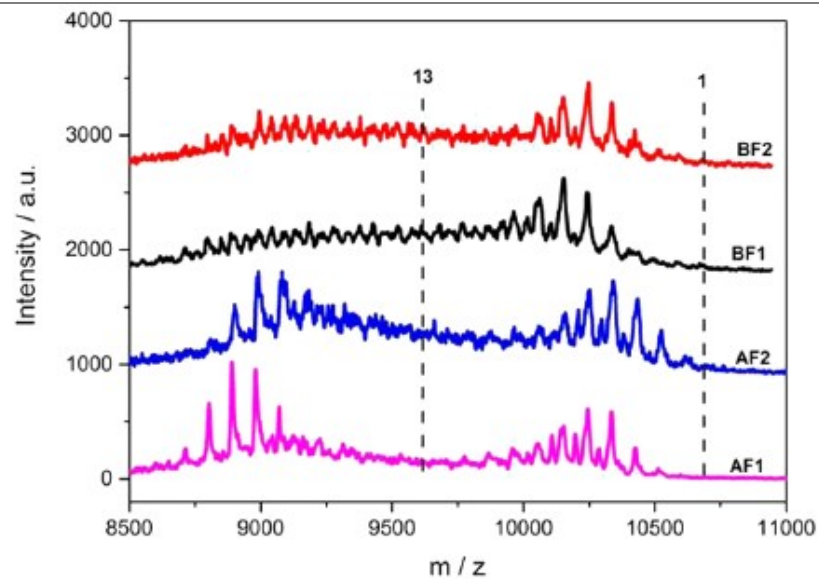
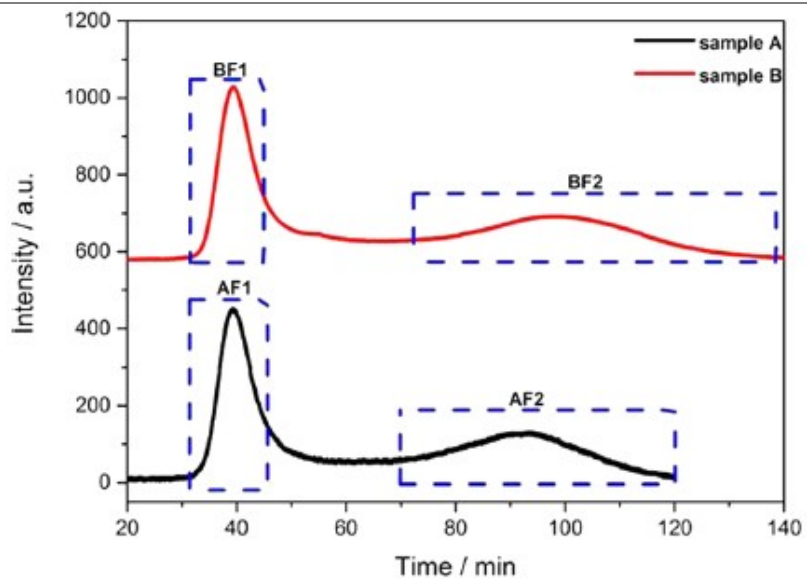


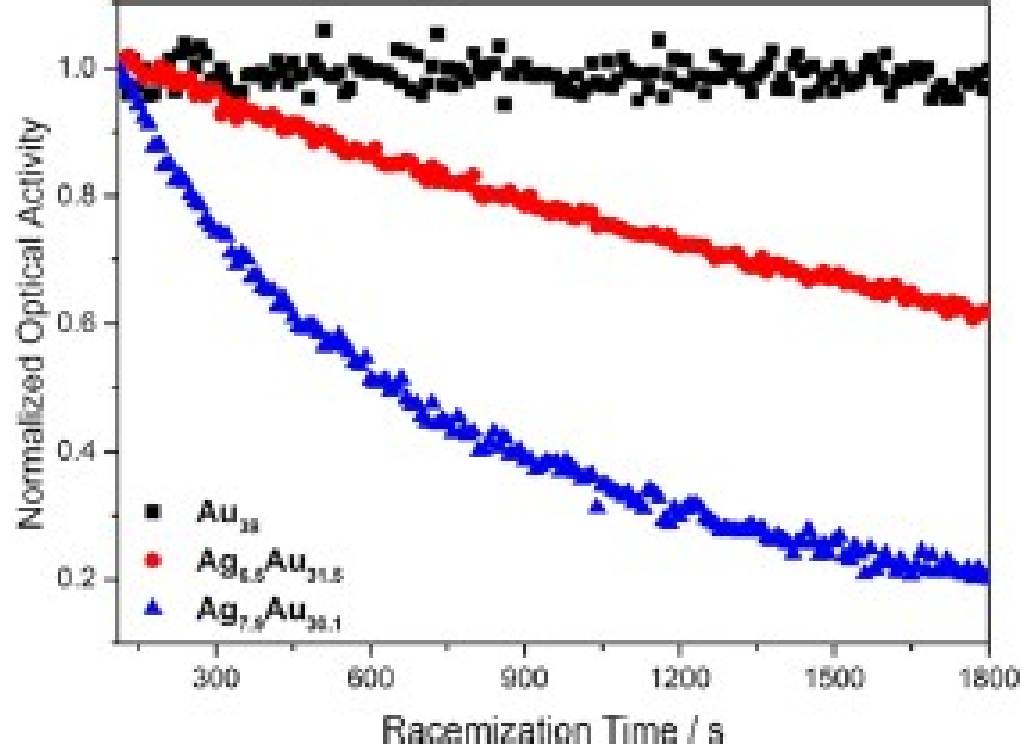
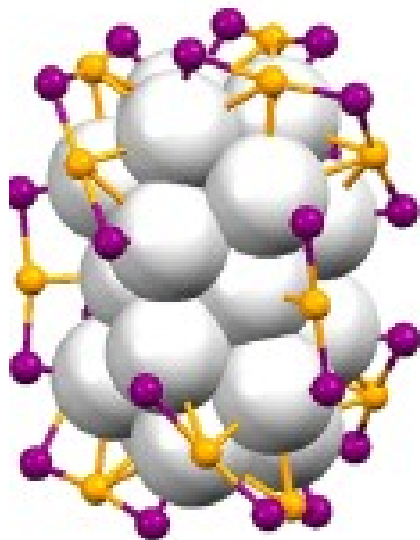
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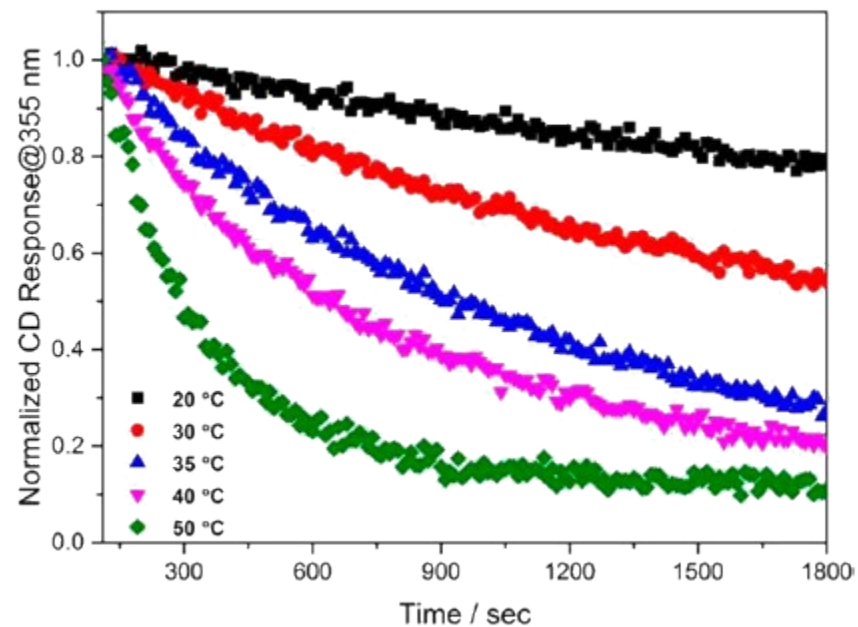
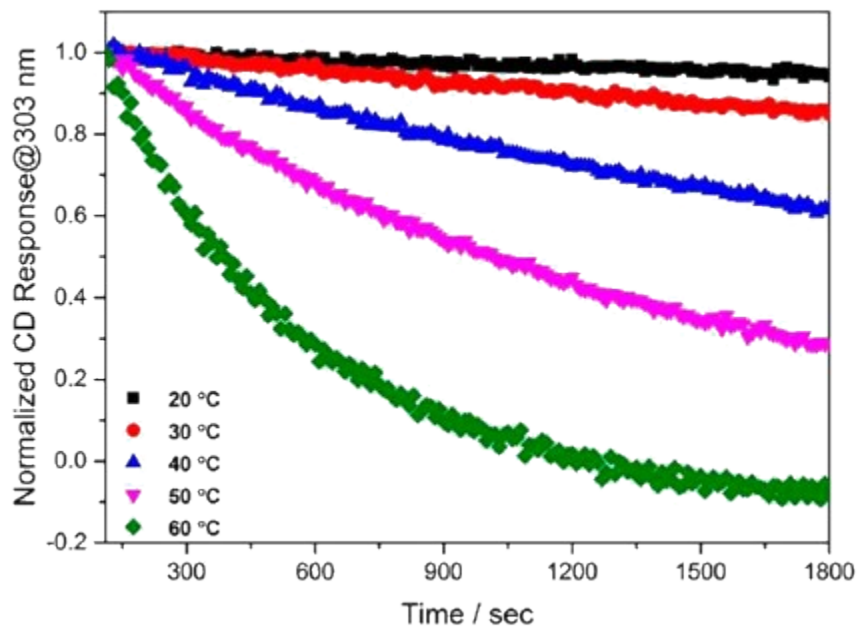
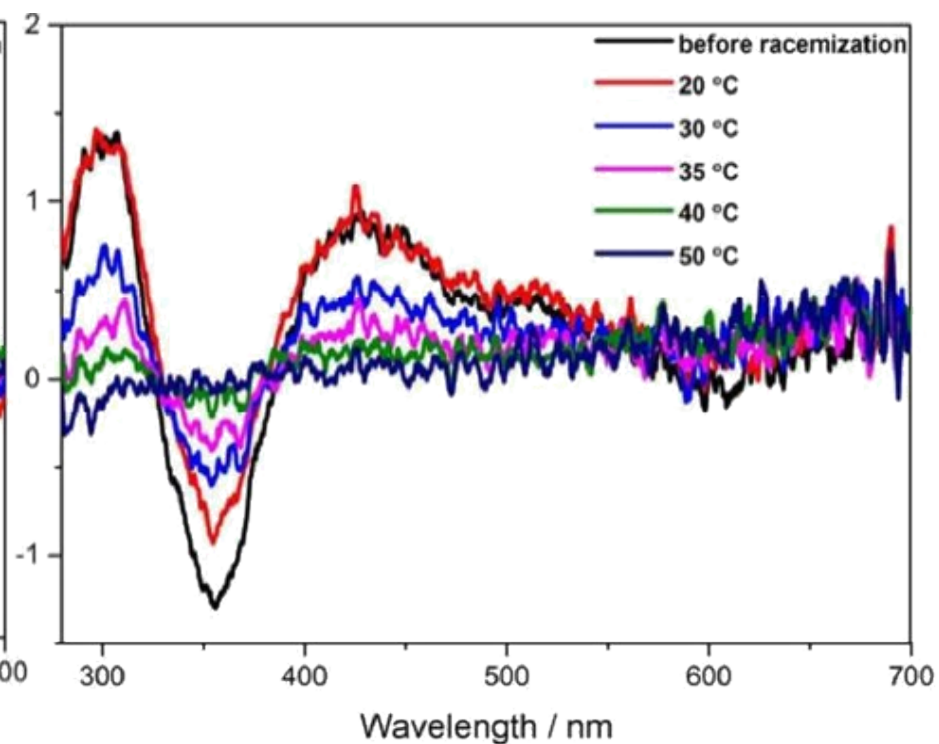
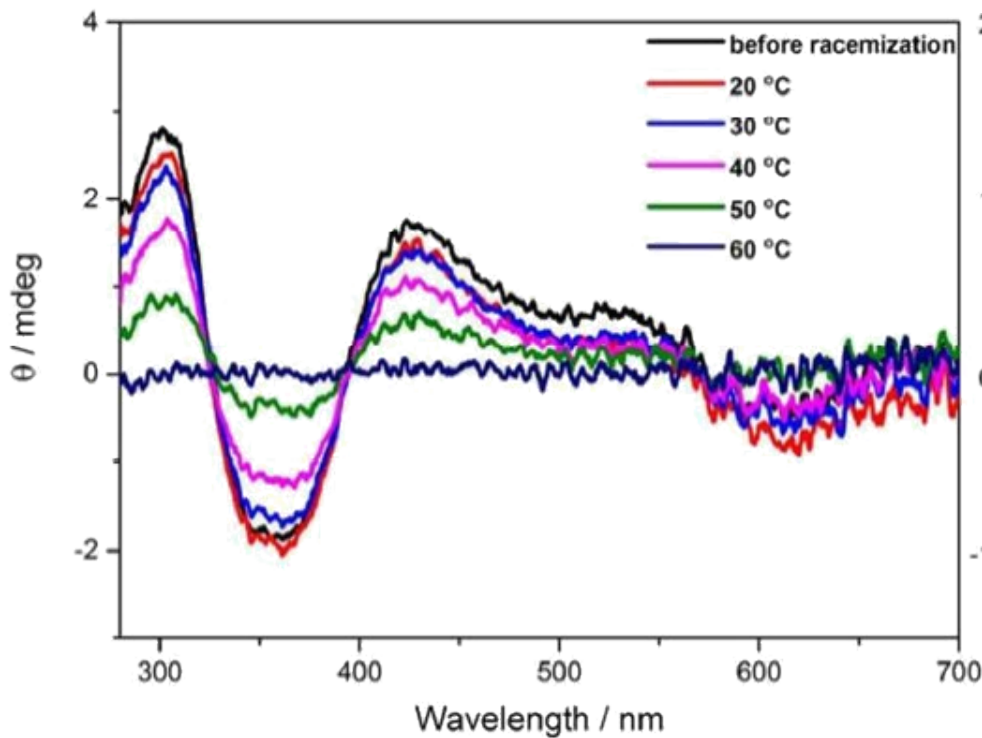


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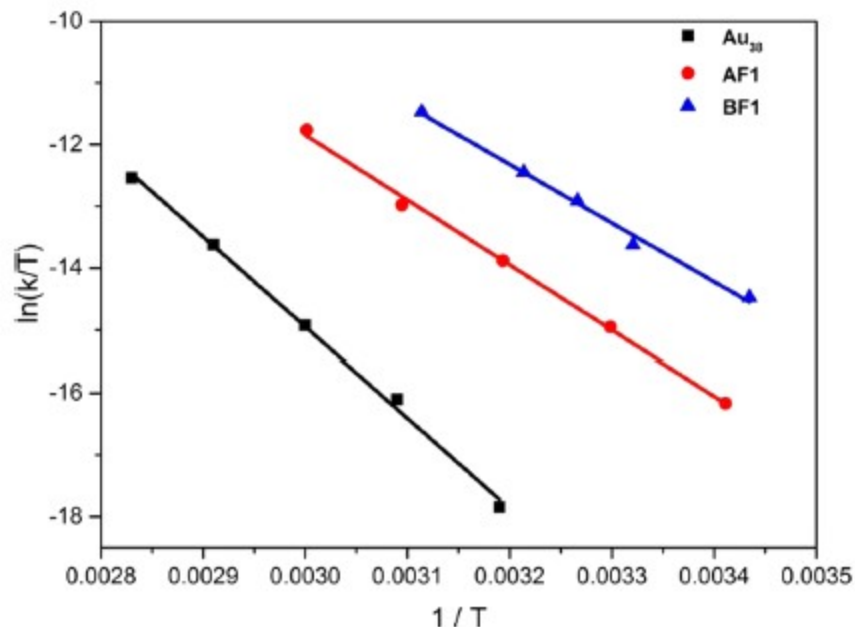
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# Eyring analysis

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{R} \times \frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R}$$



sample	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kcal mol <sup>-1</sup> )	$E_a$ (kcal mol <sup>-1</sup> )
Au <sub>38</sub>	28.8	9.7	25.6	29.5
AF1	20.9	-8.1	23.4	21.5
BF1	18.9	-11.3	22.4	19.5

# Future perspective.....

Intercluster reaction product of  $\text{Au}_{25}\text{PET}_{18}$   
and  $\text{Ag}_{25}\text{DMBT}_{18}$ .

Complexity due to both Ligand exchange  
and metal exchange.

Metal exchange can be tried to reduce the  
complexity.

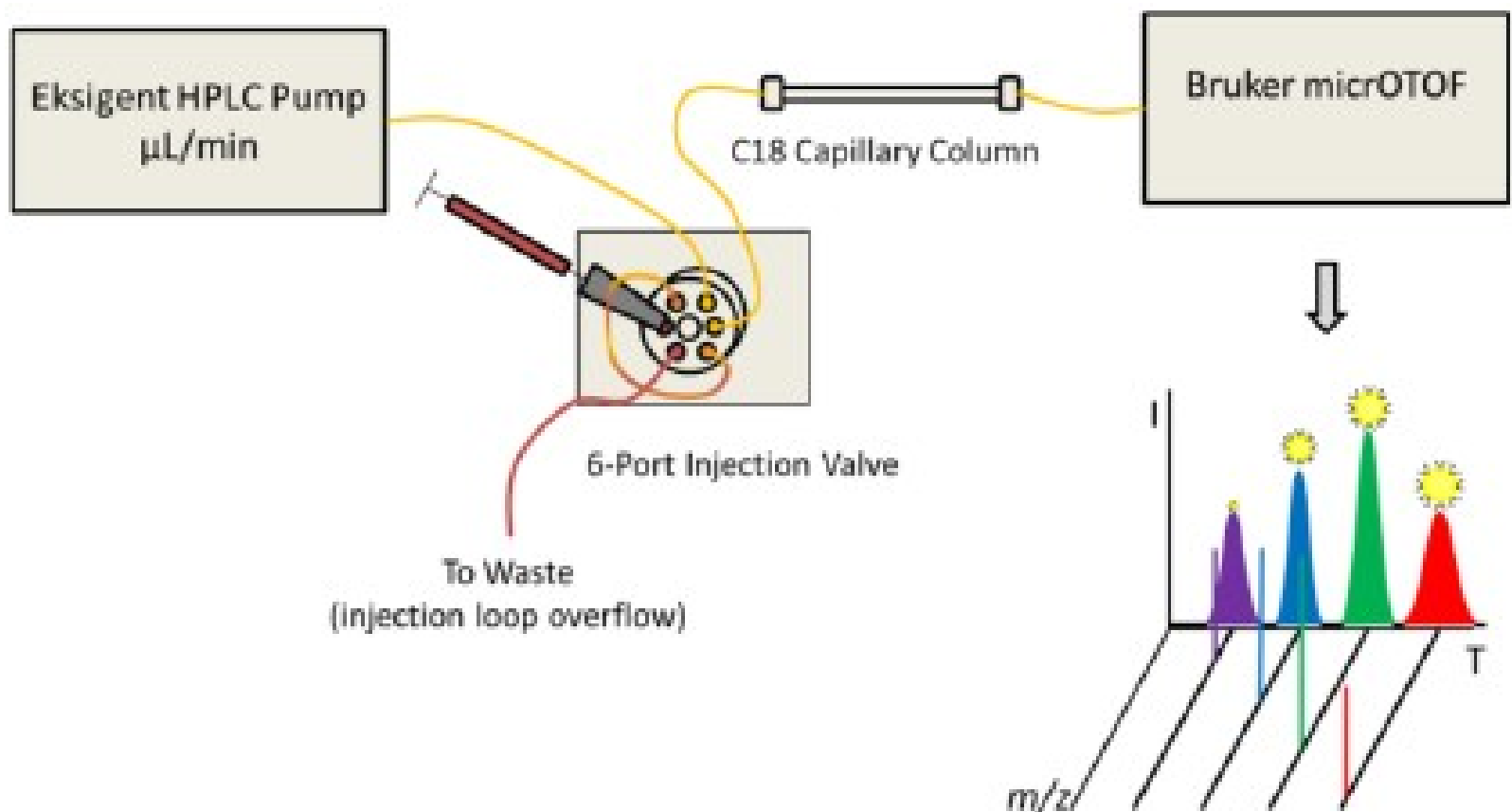
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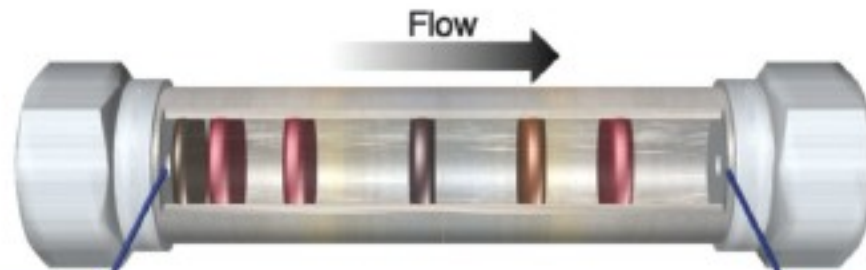
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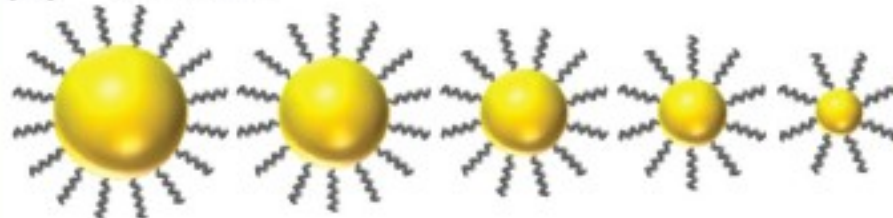
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**S** Supporting Information

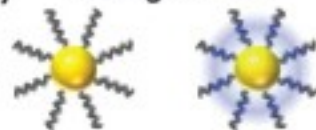




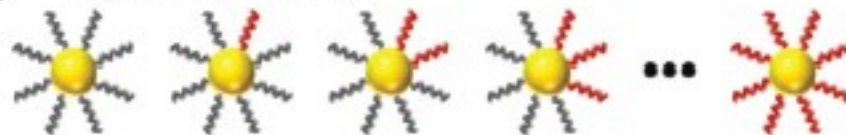
(a) Core Size



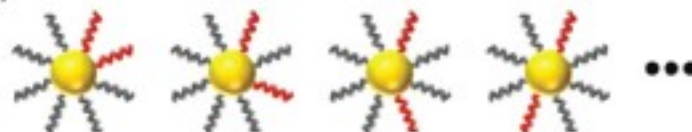
(b) Charge State



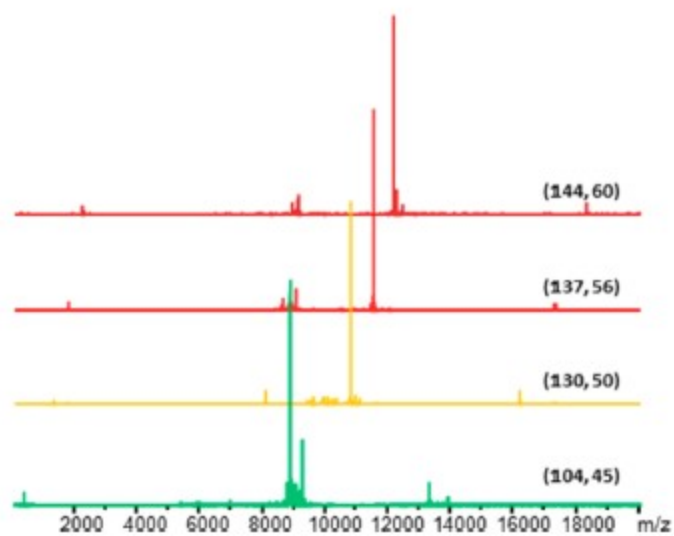
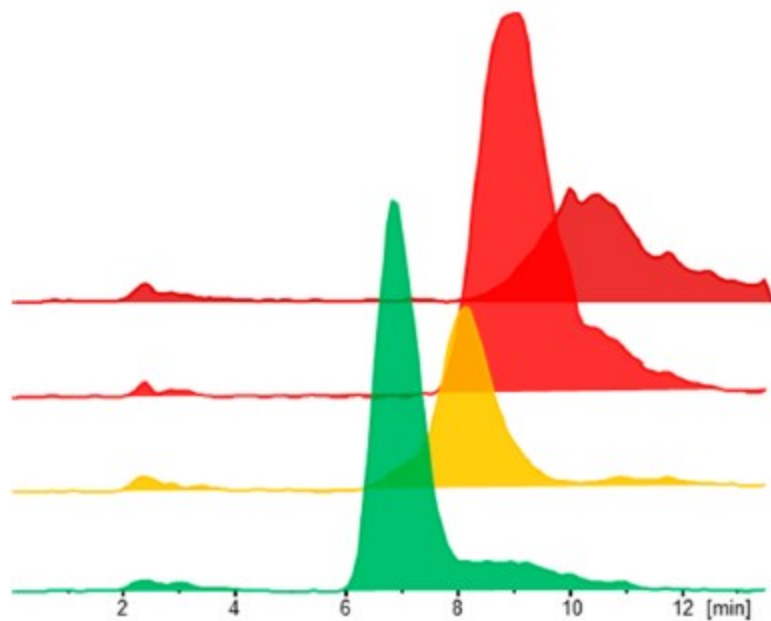
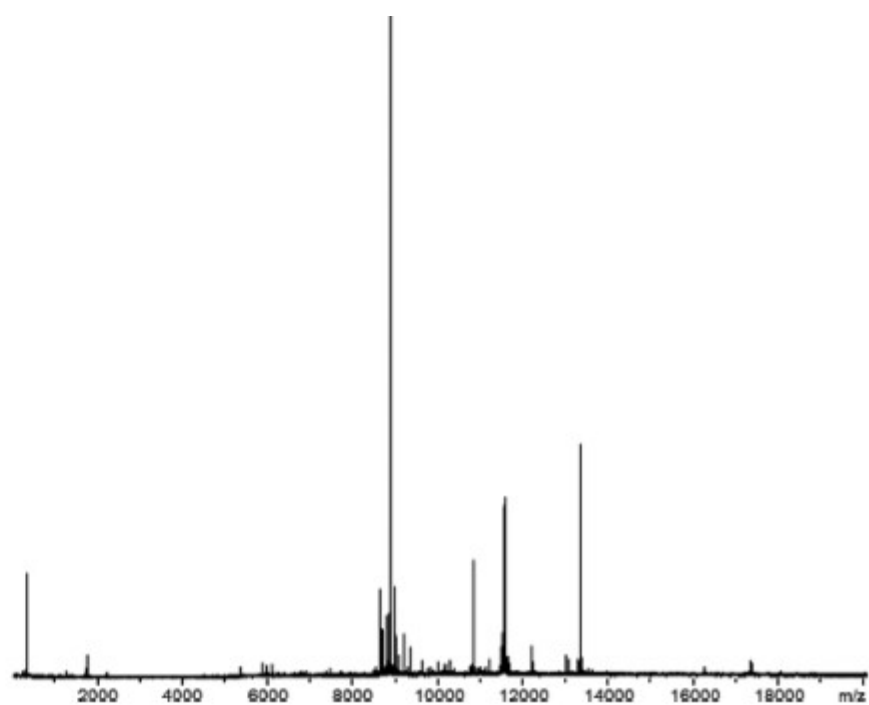
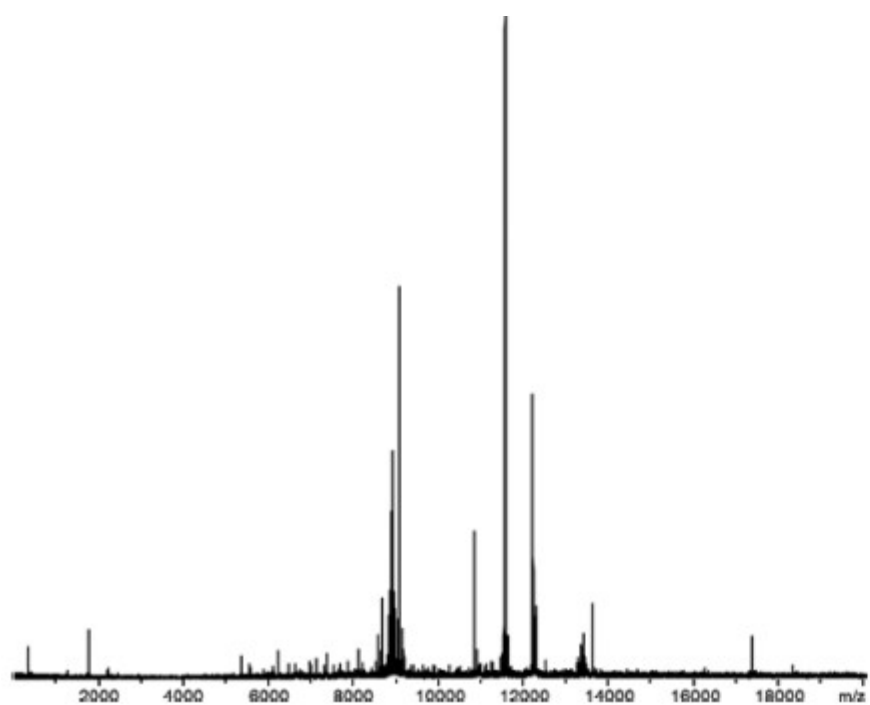
(c) Ligand Composition

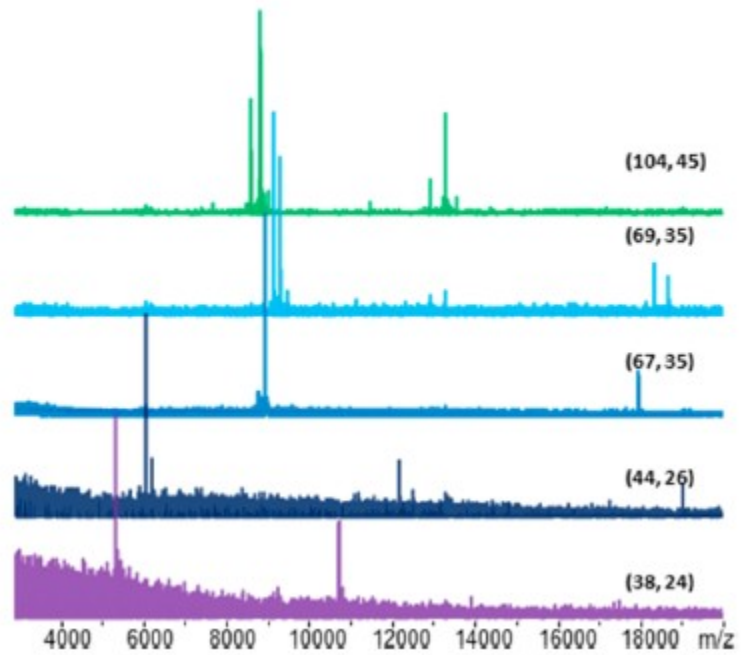
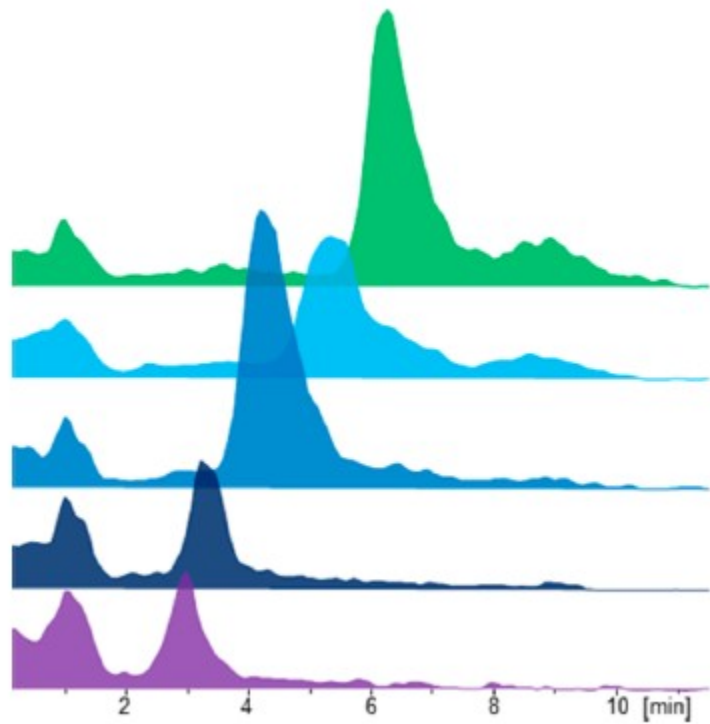


(d) Coordination Isomer









# References

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Malola, S.; Lehtovaara, L.; Knoppe, S.; Hu, K. J.; Palmer, R. E.; Burgi, T.; Hakkinen, H. Au-40(Sr)(24) Cluster as a Chiral Dimer of 8-Electron Superatoms: Structure and Optical Properties. *J. Am. Chem. Soc.* 2012, 134, 19560–19563.

**THANK YOU**