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DOI

[10.1021/acs.jpcc.9b05638](https://doi.org/10.1021/acs.jpcc.9b05638)

Publication date

2019

Document Version

Final published version

Published in

Journal of Physical Chemistry C

License

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[Link to publication](#)

Citation for published version (APA):

Sels, A., Azoulay, R., Buma, W. J., Koenis, M. A. J., Nicu, V. P., & Bürgi, T. (2019). Vibrational Circular Dichroism of Thiolate-Protected Au₂₅ Clusters: Accurate Prediction of Spectra and Chirality Transfer within the Mixed Ligand Shell. *Journal of Physical Chemistry C*, 123(36), 22586-22594. <https://doi.org/10.1021/acs.jpcc.9b05638>

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Vibrational Circular Dichroism of Thiolate-Protected Au₂₅ Clusters: Accurate Prediction of Spectra and Chirality Transfer within the Mixed Ligand Shell

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Supporting Information

ABSTRACT: We have prepared Au₂₅(PET)_{18–2x}((R)-FBINAS)_x (PET = 2-phenylethylthiol, (R)-FBINAS = (R)-5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-dithiol) mixed ligand shell clusters via ligand exchange. Two fractions with different composition of the ligand shell were separated using size-exclusion chromatography and studied by infrared (IR) spectroscopy and vibrational circular dichroism (VCD). Both IR and VCD spectra are dominated by FBINAS vibrations although PET is more abundant on the cluster. Calculated VCD spectra on a model cluster Au₂₅(SH)₁₆(FBINAS)₁ depend on the charge state of the cluster, and the anion is in excellent agreement with the experimental spectra of the Au₂₅(PET)_{18–2x}(FBINAS)_x samples. Calculations of Au₂₅(SH)₁₄(FBINAS)₂ furthermore show very similar spectra for different adsorption isomers with one exception, where the two ligands share a SR–Au–SR–Au–SR staple motif. Model calculations show that it is not necessary to consider the entire cluster for obtaining reliable VCD and IR spectra, but the staple motifs cannot be neglected. A band that is assigned to PET shows significant vibrational optical activity, and an anisotropy factor that depends on the composition of the ligand shell. This shows that the FBINAS molecules can transfer chirality to achiral PET within the ligand shell of the cluster.

INTRODUCTION

Monolayer-protected metal clusters have attracted researchers for their physical properties and their potential applications.^{1,2} These nano-objects allow one to study fundamental physical phenomena related to quantum confinement and the transition from molecular to bulk behavior. Many applications of these clusters (and of nanoparticles) have been proposed based on their optical,^{3,4} magnetic,⁵ thermal,⁶ and catalytic⁷ properties but also their molecular recognition features. Application fields include sensing,^{8–10} delivery,¹¹ imaging,^{12,13} and cancer therapy.¹⁴ In many of these applications, the surface properties of the monolayer-protected clusters are of crucial importance, because it is the outermost layer of the clusters that interacts with the environment.¹⁵ The ligand exchange reaction is a simple and efficient method to change surface properties of clusters and to introduce functionality.^{16–21}

Factors that affect the properties of the cluster surface are the nature of the thiolates in the protecting layer and, for mixed thiolate layers, the composition and the distribution of the different thiolates (phase separation versus mixing of thiolates).²² In addition to these factors the structure, i.e., conformation of the adsorbed molecules plays a crucial role.

Elucidating the structure of adsorbed molecules is therefore an important issue, but at the same time, it is a challenging task. The structure of numerous thiolate protected clusters has been determined in the recent past by single-crystal X-ray crystallography.²³ However, the conformation of an adsorbed molecule may be different in the crystal compared to the solution state,²⁴ similar to what has been observed for other compounds.^{25,26} In fact, the forces acting on the molecules due to crystal packing may very well overrule the subtle factors that determine the conformation of the molecules in solution. Methods are therefore required that can provide structural information on dissolved clusters. Nuclear magnetic resonance (NMR), for example, is a powerful tool to get structural information on monolayer-protected clusters in solution.^{27,28} For clusters, the resonances are however broadened, which complicates the interpretation and diminishes the information content. Vibrational spectroscopy is another technique that is sensitive to structure.^{24,29–35} The effect of conformation on

Received: June 13, 2019

Revised: July 30, 2019

Published: August 20, 2019

infrared and Raman spectra can be subtle, and in addition, the interpretation is often not straightforward.

Vibrational circular dichroism (VCD) is more sensitive toward structure (conformation and configuration) than conventional infrared spectroscopy,^{36,37} but it has been applied only rarely in the field of monolayer-protected clusters.^{24,38–41} The structural information contained in VCD spectra emerges from the comparison between measured and theoretical spectra, and the quality of the latter is therefore essential. Several factors are important, including the method (quantum chemical approach, basis set), treatment (or not) of solvent and structure model used. In particular for thiolate-protected clusters, the structure models used for the calculations up to now were not sufficiently accurate.

Here we investigate the influence of structure elements of a thiolate-protected cluster on the VCD spectrum of the adsorbed ligand. We also study the influence of the charge state of the cluster and adsorption isomerism on the VCD spectra. For our studies we use the $\text{Au}_{25}(\text{PET})_{18}$ cluster (PET = 2-phenylethylthiolate), which is achiral. This cluster was ligand-exchanged with chiral (R)-FBINAS ((R)-5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-dithiol) to form $\text{Au}_{25}(\text{PET})_{18-2x}((\text{R})\text{-FBINAS})_x$ clusters. Overall, the comparison between experimental and theoretical spectra is excellent, which shows the potential of VCD spectroscopy to elucidate the structure of adsorbed molecules in solution. Careful analysis of the spectra provides evidence for chirality transfer from the chiral FBINAS to achiral PET within the mixed ligand shell of the cluster.

EXPERIMENTAL METHODS

The synthesis of (R)-5,5',6,6',7,7',8,8'-octafluoro-[1,1'-binaphthalene]-2,2'-dithiol ((R)-FBINAS. Scheme 1) was done according to known procedures^{42–44} with some modifications and is described in the Supporting Information.

Scheme 1. (R)-5,5',6,6',7,7',8,8'-Octafluoro-[1,1'-binaphthalene]-2,2'-dithiol ((R)-FBINAS)

Synthesis and Characterization of Clusters.

$\text{Au}_{25}(\text{PET})_{18}^0 \cdot \text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (1.0 g) and TOABr (1.642 g) were dissolved in tetrahydrofuran (250 mL). PET (1.62 mL) was added to the solution and stirred for 1 h at room temperature. Next, an aqueous solution of NaBH_4 (0.917 g, 50 mL) at 0 °C was added to the mixture. After 3 days of stirring the aqueous phase was removed and the organic phase dried by rotary evaporator and washed with methanol (three times) to remove free thiol and other byproducts. The clusters were dissolved in a minimum amount of toluene and passed over a size exclusion column (SEC, SX1 biobeads, toluene) in order to isolate pure $\text{Au}_{25}(\text{PET})_{18}^0$. Oxidation of $\text{Au}_{25}(\text{PET})_{18}^0$ was performed by passing the cluster over a silica column (DCM).

Pure $\text{Au}_{25}(\text{PET})_{18}^0$ clusters were obtained after washing with MeOH, acetonitrile and extraction with diethyl ether. UV–vis, MALDI–TOF, and NMR analysis confirmed the purity of the sample (see Supporting Information).

Ligand exchange reactions were performed by mixing a solution of $\text{Au}_{25}(\text{PET})_{18}^0$ (0.6 mg/mL, DCM) with a 25-fold molar excess of (R)-FBINAS for 48 h. After the reaction, the mixture was dissolved in a minimum amount of toluene and passed over a SEC column. Five different fractions were separated and analyzed by UV–vis and MALDI. Only two fractions were used in the experiments, called fraction 1 and fraction 2 in the following. The UV–vis spectra of the two fractions are provided in the Supporting Information.

VCD Spectroscopy. IR and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at $\lambda/4$ retardation (central frequency at 1400 cm^{-1}) was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter ($<1800\text{ cm}^{-1}$) in front of the photoelastic modulator was used to enhance the signal/noise ratio. Solutions of 2–3 mg of cluster in 200 μL of CD_2Cl_2 were prepared and measured in a transmission cell equipped with CaF_2 windows and a 200 μm spacer. For the measurements of (R)-FBINAS, 2 mg was dissolved in 200 μL of CD_2Cl_2 . CD_2Cl_2 served as reference. For both the sample and the reference, 24000 scans at 4 cm^{-1} resolution were averaged. The reference was subtracted from the sample spectrum.

Quantum Chemical Calculations. Density functional theory (DFT) as implemented in Gaussian09⁴⁵ was used to study the geometry of FBINAS and $\text{Au}_{25}(\text{SH})_{16}(\text{FBINAS})_1$ and to calculate the corresponding IR and VCD spectra. The calculations were performed using the B3PW91^{46,47} functional and a 6-31G** basis set⁴⁸ for H, C, F and S and a Lanl2MB⁴⁹ for Au. Prior to the calculation of the spectra all degrees of freedom were completely relaxed in order to reach equilibrium geometries. IR and VCD spectra were constructed from calculated dipole and rotational strengths assuming a Gaussian band shape with a half-width at half-maximum of 5 cm^{-1} . Frequencies were scaled by a factor of 0.966. This factor was chosen to have a good match between experimental and calculated infrared spectra of the aromatic ring vibrations in the range $1400\text{--}1550\text{ cm}^{-1}$. All calculations were performed for the gas phase species. Following the work in refs 50–54 we have performed VCD calculations also for the neutral cluster, which is an open shell system. We note, however, that the computational procedures currently available for computing VCD spectra are not able to fully capture the physics of open shell systems.⁵⁵

To elucidate the origin of the intense VCD bands observed experimentally, additional calculations have been performed using the ADF software suite^{56–59} using the BP86 exchange-correlation functional^{60,61} and a TZP basis set.⁶² This has allowed us to perform a generalized coupled oscillator VCD analysis.⁶³ No frequency scaling was done for these calculations.

RESULTS AND DISCUSSION

IR and VCD of (R)-FBINAS. Figure 1 compares the experimental and calculated IR and VCD spectra of (R)-FBINAS. The calculations almost quantitatively reproduce the experimental spectra. The prominent band in the VCD

Figure 1. IR and VCD spectra of (R)-FBINAS: experiment, black; calculation, red.

spectrum at 1516 cm^{-1} is due to an in-plane ring deformation mode of the naphthyl rings with strong C–C stretching components at C_6 and C_7 . This band shows a strong bisignate shape due to the in- and out-of-phase combinations of the mode located on the two naphthyl parts of the molecule. Interestingly, the ring deformation modes above 1550 cm^{-1} are almost completely silent in the VCD spectra. In contrast to the band at 1516 cm^{-1} , these modes are located mostly within one naphthyl part of the molecule, according to the calculations.

Characterization of Clusters. FBINAS is structurally similar to BINAS (1,1'-binaphthyl-2,2'-dithiol), and the adsorption of the latter on thiolate-protected gold clusters through ligand exchange has been studied in the past.^{64–67} MALDI mass spectrometry showed that one BINAS molecule displaces two monothiolates originally adsorbed on the cluster. Ligand exchange leads to a complex mixture of species differing in composition and adsorption sites (isomers). For the $\text{PdAu}_{24}(\text{PET})_{18-2x}(\text{BINAS})_x$ cluster, species with different x and different isomers (for the same x) could be separated using chromatography (HPLC).⁶⁷ Interestingly, for $x = 1$, only one isomer has been found, indicating that there is a preferred adsorption site. In fact, calculations are in agreement with this. On the Au_{25} (or PdAu_{24}) cluster the BINAS molecule fits perfectly on the adsorption site that bridges two long staples (see Figure 2) because the corresponding S–S distances in the cluster and in the unperturbed free molecule match perfectly. This also holds for FBINAS.

The $\text{Au}_{25}(\text{PET})_{18-2x}((R)\text{-FBINAS})_x$ sample was prepared by ligand exchange. Using size exclusion chromatography several fractions were collected and two fractions were subsequently used for measurements. MALDI mass spectrometry revealed a mixture of species with different composition x in the two fractions (Figure 3). Fractions 1 and 2, respectively, have an average number of (R)-FBINAS x of 2.6 and 1.7.

Figure 2. Model $\text{Au}_{25}(\text{SH})_{16}((R)\text{-FBINAS})_1$ cluster. FBINAS bridges two SR–Au–SR–Au–SR staples (marked in green). Each SR–Au–SR–Au–SR staple contains two “inner positions” and one “outer position”. The FBINAS is attached on the inner position of one staple and the outer position of a second staple. Color code: orange is gold, yellow is sulfur, gray is carbon, blue is fluorine, and white is hydrogen.

Figure 3. MALDI mass spectra of $\text{Au}_{25}(\text{PET})_{18-2x}((R)\text{-FBINAS})_x$ sample. Two fractions collected in size exclusion chromatography are shown.

Experimental IR and VCD Spectra. Figure 4 shows the IR and VCD spectra of the two samples. In the IR spectra, the relative intensity of the bands associated with FBINAS is identical for the two samples. However, small differences can be observed in the spectra at 1263 , 1458 and 1488 cm^{-1} . These bands are due to adsorbed PET, as will be discussed below. Concretely, the bands are associated with CH_2 wagging (1263 cm^{-1}), CH_2 scissoring (1458 cm^{-1}) and in plane phenyl ring vibrations (1488 cm^{-1}). Interestingly, the IR spectra are largely dominated by the FBINAS bands, although the cluster contains more PET than FBINAS. In fact the PET:FBINAS ratio is 4.9 for fraction 1 and 8.6 for fraction 2. This shows that the oscillator strength of most of the FBINAS vibrations are larger compared to the ones of PET. Further, the comparison of the two VCD spectra shows that, although the average composition (FBINAS vs PET) is different in the two samples,

Figure 4. IR and VCD of fraction 1 (red) and fraction 2 (blue) of the $\text{Au}_{25}(\text{PET})_{18-2x}((\text{R})\text{-FBINAS})_x$ sample. Spectra of fraction 2 were multiplied by a factor of 1.8 to compensate for the different concentrations and to facilitate the comparison.

the spectra are almost identical to within the noise. A slight shift (2 cm^{-1}) of the band at 1263 cm^{-1} can be observed. Since the benzyl moiety is expected to yield weak VCD bands,⁶⁸ one would expect that also the VCD spectra are determined by bands associated with the FBINAS ligands. However, as can be seen, the shape of the VCD spectra is not much affected by the number of FBINAS ligands on the cluster.

Calculated IR and VCD Spectra of FBINAS Adsorbed on Au_{25} . The calculation of IR and VCD spectra of $\text{Au}_{25}(\text{PET})_{18-2x}(\text{FBINAS})_x$ is a complex task since each PET ligand can adopt several conformations (gauche +, gauche −, anti), and in addition, there are two possible positions of the molecule with respect to the staple, corresponding to different absolute configurations at the sulfur atom (see Figure 2). This results in a tremendous number of possible conformers. Calculating a mean spectrum by considering all of these possible conformations is unpractical. Alternatively, only one conformation could be chosen, for example, the one found in the crystal structure. However, this is also not a valid option since the conformation of PET on the cluster in the solid state and in solution may not be the same.²⁴ On the basis of the experimental observation that the infrared spectra are largely dominated by the FBINAS ligand, we therefore chose a model for the calculations that completely neglects PET, replacing it by hydrogen (S–H groups, see Figure 2). The S–H vibrations are out of the spectral range considered here. Therefore, all the calculated VCD signals in the spectral range shown in the

figures below are associated with adsorbed FBINAS. In this context, it is interesting to note that the benzyl moiety in a chiral molecule has been shown to be VCD inactive.⁶⁸

Figures 5 and 6 show the IR and VCD spectra, respectively, of the cluster in different charge states: anionic, neutral and

Figure 5. Calculated IR spectra of $\text{Au}_{25}(\text{SH})_{16}((\text{R})\text{-FBINAS})_1$ in different charge states (anion (green), neutral (blue), cation (black)). The experimental IR spectrum of dissolved $\text{Au}_{25}(\text{PET})_{18-2x}((\text{R})\text{-FBINAS})_x$ (fraction 1) in CD_2Cl_2 is shown in red. The spectrum of $\text{Au}_{25}(\text{PET})_{18}$ dissolved in CD_2Cl_2 is shown in brown. The dashed lines indicate dominant bands associated with PET. The yellow line highlights the shift of the band at around 1580 cm^{-1} .

cationic. Note that the anionic cluster is an eight electron “super atom” and thus has a closed $1\text{S}^21\text{P}^6$ electronic shell.⁶⁹ The neutral cluster, on the other hand, is an $1\text{S}^21\text{P}^5$ open shell system. The cationic cluster is a $1\text{S}^21\text{P}^4$ closed shell system.⁷⁰

The IR spectra of the cluster in the different charge states are very similar. Minor differences in (relative) band intensities can be observed. Also, there is a shift to higher wavenumbers of the band at 1580 cm^{-1} in the series cation–neutral–anion. This vibration is a naphthyl in-plane deformation mode with a large amplitude at C_1 and C_2 , which are in close proximity to the cluster core. Vibrational bands of PET are visible at 1263, 1458, and 1488 cm^{-1} in the experimental spectra, as a comparison with the IR spectrum of $\text{Au}_{25}(\text{PET})_{18}$ shows (Figure 5).

The calculated VCD spectra are more sensitive to the charge state than the IR spectra (Figure 6). Whereas the band at 1602 cm^{-1} is visible for all three charge states (positive band), the two bands at 1650 and 1580 cm^{-1} are hardly visible in the VCD spectrum of the anion. The strong bisignate band around 1512 cm^{-1} changes relative intensity depending on the charge state of the cluster. In the anion, the lower wavenumber band is stronger than the higher wavenumber counterpart. For the neutral and cationic clusters, the situation is reversed, the lower wavenumber band being weaker than the higher wavenumber band. Further significant spectral changes are visible for the bands at 1449 cm^{-1} (single band for anion, double band for neutral and cation), at 1390 cm^{-1} (very low intensity for cation), and at 1346 cm^{-1} (very low intensity for cation, single peak for anion, double peaks for neutral and cation).

The experimental VCD spectrum of the $\text{Au}_{25}(\text{PET})_{18-2x}((\text{R})\text{-FBINAS})_x$ sample fits very well with the calculations for the $\text{Au}_{25}(\text{SH})_{16}((\text{R})\text{-FBINAS})_1$ cluster. The calculated spectrum for the cluster anion fits particularly well

Figure 6. Calculated VCD spectra of $\text{Au}_{25}(\text{SH})_{16}((\text{R})\text{-FBINAS})_1$ in different charge states (anion (green), neutral (blue), cation (black)). The experimental VCD spectrum of dissolved $\text{Au}_{25}(\text{PET})_{18-2x}((\text{R})\text{-FBINAS})_x$ (fraction 1) in CD_2Cl_2 is shown in red. The labels refer to the wavenumbers of the corresponding bands in the experimental spectrum (where visible).

(see green and red spectra in Figure 6). For example, there is only one clear band visible above 1550 cm^{-1} in the experiment and the calculation of the anion, whereas three bands are observed for the calculated spectra of the neutral and cationic cluster. Note that for the free FBINAS molecule, none of these bands are visible in the VCD spectrum both in the experiment and in the calculation (see Figure 1). Also the bisignate band around 1512 cm^{-1} of the cluster has the same relative intensity in the experiment and calculation for the anion. For the other two charge states the relative intensity is inverted. Furthermore, the intensity and shape of the bands at 1346 , 1390 , and 1449 cm^{-1} fit best with the calculated spectra of the anion.

Influence of Isomerism. The results presented above demonstrate that the calculations of $\text{Au}_{25}(\text{SH})_{16}(\text{FBINAS})_1$ are in excellent agreement with experimental spectra of $\text{Au}_{25}(\text{PET})_{18-2x}(\text{FBINAS})_x$ samples. This shows that the vibrational spectra are dominated by FBINAS rather than

PET. It furthermore means that a single FBINAS molecule on Au_{25} is a good model for the description of vibrational spectra for the complex mixture of $\text{Au}_{25}(\text{PET})_{18-2x}(\text{FBINAS})_x$ species differing in x ($x = 1, \dots, 4$) and containing isomers (for the same x). To better understand the reason for this we performed further calculations of the six possible isomers of $\text{Au}_{25}(\text{SH})_{14}((\text{R})\text{-FBINAS})_2$ shown in Figure 7. A comparison of the calculated VCD spectra is shown in Figure 8. The

Figure 8. Calculated VCD spectra for isomers of $\text{Au}_{25}(\text{SH})_{14}((\text{R})\text{-FBINAS})_2$. The structures of the isomers are shown in Figure 7. The experimental spectrum of $\text{Au}_{25}(\text{PET})_{18-2x}((\text{R})\text{-FBINAS})_x$ (fraction 1) is also shown for comparison.

corresponding IR spectra are given in the Supporting Information (Figure S3). Both the calculated VCD and IR spectra are very similar for the different isomers with the exception of isomer 3 and to a lesser extent isomer 5. In

Figure 7. Isomers of $\text{Au}_{25}(\text{SH})_{14}((\text{R})\text{-FBINAS})_2$ used for the calculations of IR and VCD spectra.

isomers 3 and 5, the two ligands on the cluster share a common staple (see Figure 7), where one ligand is in the “inner position” and the other ligand in the “outer position” (see Figure 2 for the definition of “inner” and “outer”). Note that also in isomer 1 the two FBINAS ligands share one staple, but in this case, both ligands are located in the two “inner” positions.

To further study the influence of various structural elements on the VCD spectra, we compared the calculated spectra of the $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$ cluster with spectra (i) of the two $(R)\text{-FBINAS}$ ligands including the staples motifs, (ii) of $\text{Au}_{25}(\text{SH})_{16}((R)\text{-FBINAS})_1$ (only one ligand), (iii) of the two isolated ligands, and (iv) of one isolated ligand. These calculations were performed for isomers 3 (Supporting Information, Figure S6) and 6 (Figure 9). The corresponding

Figure 9. Calculated VCD spectra of different structural elements for isomer 6 of $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$: black, entire $\text{Au}_{25}(\text{SH})_{14}(\text{FBINAS})_2$ cluster; red, staple plus two FBINAS molecules; orange, $\text{Au}_{25}(\text{SH})_{16}(\text{FBINAS})_1$ cluster; blue, two isolated FBINAS molecules; green, one single FBINAS molecule.

structures and IR spectra are shown in the Supporting Information (Figures S4 and S5). Note that for these calculations the structural elements were “extracted” from the optimized structure of the $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$ cluster and the spectra were calculated without further optimization, in order to retain the relative orientation of the relevant groups. This is a crucial detail, viz., all intense VCD bands are the result of exciton coupling interactions between the electric dipole transition moments associated with the two halves of the FBINAS ligand (see Supporting Information Figures S7 and S8). Consequently, unless the relative orientation of the interacting dipoles is the same in the two sets of calculations, the VCD spectrum predicted by a full calculation cannot be reproduced from fragment calculations.

As can be seen in Figure 9, in the case of isomer 6, the calculations performed for the perturbed FBINAS structures in the cluster yield a VCD spectrum (in green) that exhibits most of the characteristics of the $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$.

Adding a second perturbed FBINAS structures in the fragment calculations yields more intense VCD signals (the blue spectrum), while the addition of the staple or of the gold cluster yields very good band positions (see the orange and red spectra). Therefore, it should be clear that (1) the VCD spectrum of $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$ is dominated by the FBINAS bands and, (2) in order to reproduce this spectrum, one only needs to consider a realistically perturbed FBINAS structure. A similar trend is seen also for isomer 3 (Figure S6). However, in this case, the fragment calculations do not reproduce the full calculations as well. This can be attributed to the fact that, in isomer 3, the two FBINAS ligands interact much more than in isomer 6 as they are situated closer together. Since also in this case a single ligand on the cluster is a good model to calculate vibrational spectra, we can conclude that in order to obtain reliable spectra from fragment calculations the minimum structural element that is required to perturb the FBINAS ligands is the staples.

Finally, we note that the calculations on $\text{Au}_{25}(\text{SH})_{14}(\text{FBINAS})_2$ and $\text{Au}_{25}(\text{SH})_{16}(\text{FBINAS})_1$ are in good agreement with the experiment, as was already the case for the calculations on $\text{Au}_{25}(\text{SH})_{16}(\text{FBINAS})_1$ using a different method as discussed above (Figure 6).

Transfer of Chirality within the Ligand Layer. Careful inspection of the VCD spectra indicates the transfer of chirality from FBINAS to coadsorbed PET within the ligand layer. PET can adopt one anti and two gauche conformations, the latter corresponding to transiently chiral enantiomeric structures. In the free molecule, all conformations are populated and the two gauche conformers are equally abundant. This situation may be different within the mixed ligand shell due to coadsorbed chiral FBINAS. If the chirality can be transferred from FBINAS to PET, the vibrations of the latter may become VCD active. Indeed, there is a significant IR and VCD signal at 1263 cm^{-1} in the cluster samples, matching exactly the strongest signal of the measured IR spectrum of $\text{Au}_{25}(\text{PET})_{18}$ (see Figures 5 and 10). This band is assigned to CH_2 vibrations of PET in the gauche conformation.²⁴ For PET in an anti conformation, two bands are observed at 1215 and 1305 cm^{-1} (Figure 10). In the experimental spectra, these bands are only weak (Figure 10). Further support for the chirality transfer within the ligand layer emerges from a comparison between the IR and VCD spectra of the two $\text{Au}_{25}(\text{PET})_{18-2x}((R)\text{-FBINAS})_x$ samples, differing in the average number x of incorporated $(R)\text{-FBINAS}$ ligands (Figure 4).

As concerns the IR spectra the (relative) intensity of bands that can be associated with FBINAS is almost identical for the two samples (Figure 4). Small differences can be observed for the PET bands at 1263 , 1458 , and 1488 cm^{-1} . The relative intensity of the 1458 and 1488 cm^{-1} bands with respect to the FBINAS bands is larger for fraction 2 compared to fraction 1, in agreement with the mass spectra, which show more PET for fraction 2. The band at 1263 cm^{-1} , in contrast, is considerably stronger for fraction 1, although this fraction contains less PET indicating a conformational change toward gauche.²⁴ In agreement with this observation, the bands associated with an anti conformation at 1215 and 1305 cm^{-1} show the opposite behavior (Figure 10). The VCD signal at 1263 cm^{-1} indicates that one of the two gauche conformations of PET prevails, due to the interaction with FBINAS within the ligand layer. The above interpretation is further supported by comparing the anisotropy factors for both samples. In fact, the anisotropy factors for bands associated with FBINAS are

Figure 10. IR (top) and VCD (bottom) spectra of fraction 1 (red) and fraction 2 (blue) of $\text{Au}_{25}(\text{PET})_{18-2x}((R)\text{-FBINAS})_x$ sample. The black IR spectrum corresponds to $\text{Au}_{25}(\text{PET})_{18}$. Spectra of fraction 2 were multiplied by a factor of 1.8 to compensate for the different concentrations.

almost identical for the two fractions (Table 1). In contrast, the anisotropy factor for the 1263 cm^{-1} band is larger (by a

Table 1. Anisotropy Factors $\Delta A/A$ of some vibrational bands of fraction 1 and fraction 2 of $\text{Au}_{25}(\text{PET})_{18-2x}((R)\text{-FBINAS})_x$ Cluster Sample

wavenumber/ cm^{-1}	anisotropy factor fraction 1 ($\times 10^{-4}$)	anisotropy factor fraction 2 ($\times 10^{-4}$)
1602	2.6	2.3
1520	1.9	2.2
1485	3.2	3.6
1449	3.8	4.1
1390	5.6	5.5
1346	10.0	9.6
1263	2.3	4.6

factor of 2) for fraction 1, which contains less PET and more FBINAS. This shows that FBINAS transfers chirality to coadsorbed PET.

Transfer of chirality in nanoclusters has been observed before.²⁴ In that case, the origin of chirality is an intrinsically chiral cluster (Au_{38}), which transfers its chirality to the adsorbed (achiral) ligand (PET). In the current case the chirality is transferred between ligands within the cluster shell of an achiral cluster. Such chirality transfer is more difficult to detect by VCD since the signals arising from the transfer of chirality are superimposed on the VCD spectrum of the intrinsically chiral ligand (FBINAS in our case). In fact, a prerequisite for detecting chirality transfer in such a case is a careful analysis of the VCD spectrum of the cluster, also based on accurate calculations, which is the main target of this work.

CONCLUSIONS

The IR and VCD spectra of $\text{Au}_{25}(\text{PET})_{18-2x}(\text{FBINAS})_x$ have been studied. Two samples, differing in the average number of FBINAS molecules in the ligand shell, show very similar VCD spectra. Calculations taking into account only one FBINAS ligand and neglecting PET are in good agreement with experimental spectra, showing that the spectra are dominated by FBINAS. Interestingly, the charge state of the cluster has a noticeable influence on the VCD spectra. Calculations on the possible isomers of the cluster containing two FBINAS ligands are very similar with the exception of the isomers where the two FBINAS ligands share the same staple. The calculations furthermore reveal that a model considering only ligands and staples is in good agreement with the experiment. However, the staple is necessary for a reliable prediction. The VCD spectra of the free ligand is distinctly different from the one adsorbed on the cluster. Careful inspection of samples containing different FBINAS/PET ratios shows that FBINAS influences the conformation of PET. The observation of a VCD signal assigned to PET indicates that the chiral FBINAS transfers its chirality to (originally) achiral PET within the mixed ligand layer of the cluster. In general, our work demonstrates the power of VCD for the study of the structure of the ligand shell of chiral nanomaterials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b05638.

Synthesis of FBINAS; UV-vis spectrum, MALDI mass spectrum, and NMR spectrum of $\text{Au}_{25}(\text{PET})_{18}^0$; UV-vis spectra and MALDI mass spectra of $\text{Au}_{25}(\text{PET})_{18-2x}((R)\text{-FBINAS})_x$ clusters after separation by SEC; calculated IR spectra of different isomers of $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$; structure elements used for the calculations based on $\text{Au}_{25}(\text{SH})_{14}((R)\text{-FBINAS})_2$; calculated IR spectra of structure elements for isomers 3 and 6; and calculated VCD spectrum of structure elements for isomer 3 (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support by the University of Geneva and the Swiss National Science Foundation (Grant Number 200020_172511) is kindly acknowledged. V.P.N. acknowledges funding from UEFISCDI (PN-III-P1-1.1-TE-2016-1049, Contract No. 46/2018). M.A.J.K. and W.J.B. acknowledge financial support from The Netherlands Organisation for Scientific Research (NWO) in the framework of the Fund New Chemical Innovations (NWO Project No. 731.014.209). We thank Roman Lagoutte for advise concerning the synthesis of the BINAS ligand.

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