Detection of $[Au_{25}(PET)_{18}(O_2)_n]^-$ (n = 1, 2, 3) Species by Mass Spectrometry

Shridevi Bhat, Raghu Pradeep Narayanan, Ananya Baksi, Papri Chakraborty, Ganesan Paramasivam, Rabin Rajan J. Methikkalam, Abhijit Nag, Ganapati Natarajan, and Thalappil Pradeep*

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

S Supporting Information

ABSTRACT: [Au₂₅(SR)₁₈]⁻ nanoclusters have been tested as a model catalyst in multiple oxidation reactions involving CO, alkenes, cyclohexane, and alcohols. Oxygen is used as an oxidizing agent in most of the reactions. Hence, O2 activation is of great interest in catalysis. The mechanism of these reactions, the role of intact nanoclusters as catalytically active species, and the utility of such nanoclusters as homogeneous catalysts are not completely clear. Herein, we investigate the interaction of $[Au_{25}(SR)_{18}]^{-}$ in solution with O₂ using electrospray ionization mass spectrometry and density functional theory (DFT) calculations. Up to three O₂ molecules attach to an $[Au_{25}(SR)_{18}]^-$ in dichloromethane (DCM) when O₂ gas is passed through a solution of the former. Oxygen addition to the nanocluster leads to its decomposition. The nanocluster is most stable in toluene and least stable in tetrahydrofuran when kept under a continuous flow of O₂, where no O₂ adduct peaks are observed. It shows intermediate stability in DCM in the presence of O_{21} and the decomposition products, in this case, are of a different type compared to the



former solvents. The appearance of O_2 adducts and the variation in the stability of the nanocluster in different solvents is assumed to be due to the difference in oxygen solubility in these solvents. DFT calculations suggest that the first two O_2 molecules interact with the surface Au atoms through the cavities formed by the ligands and staples in the nanocluster and the third O₂ interacts only with 2-phenylethane thiol ligands.

1. INTRODUCTION

Developments in the field of heterogeneous and homogeneous catalysis by gold trace back to the early work of Haruta¹⁻⁴ and Hutchings.^{5,6} They established the low-temperature catalytic oxidation of CO and selective oxidation of hydrocarbons by supported gold nanoparticles and nanoclusters. Subsequently, scientists started checking out the possibility of application of monolayer-protected nanoclusters in catalysis because of the unique structure and properties of the latter.⁷⁻⁹ Advances in the mass spectrometry (MS) of nanoclusters have tremendously helped in gaining molecular level understanding of such systems.^{10,11} Computational methods have backed the experiments significantly in this regard.^{12,13} Among the thiolateprotected nanoclusters, [Au₂₅(SR)₁₈]⁻ has emerged as a widely researched model catalyst,^{8,14} owing to its highly reproducible synthetic protocols with a variety of ligands,^{15,16} well-defined structure and properties,^{17–19} and its stability in various conditions.^{20–22}

Activation of molecular O2 is of great interest in catalysis because of its utility in a number of oxidation reactions.^{8,14} There is an added advantage in using molecular O2 as an oxidant from the point of view of Green chemistry.²³ The first indirect evidence²⁴ for the interaction of $[Au_{25}(SR)_{18}]^-$ with O2 was the aerial oxidation of the nanocluster in dichloromethane (DCM) at room temperature. In this process, inherently negatively charged [Au₂₅(SR)₁₈]⁻ interacts with O₂ present in the air and gets oxidized into neutral species when its solution is exposed to air.²⁴ On the basis of this observation, $[Au_{25}(SR)_{18}]^-$ was checked for its catalytic activity in various oxidation reactions. Lopez-Acevedo et al. suggested the possibility of O_2 adsorption on $[Au_{25}(SR)_{18}]^$ upon removing one of the $Au_2(SR)_3$ units. However, they proposed a mechanism for CO oxidation reaction by removing two $Au_2(SR)_3$ units, which rendered two nearest neighboring Au atoms free for binding with CO and O₂ molecules.²⁵ Nie et al. investigated the application of oxide-supported $[Au_{25}(SR)_{18}]^{-}$ as a catalyst for the CO oxidation.²⁶ They conducted several experiments with various oxide supports and O2 pretreatment conditions to understand the effect of the same on this catalytic reaction. They concluded that intact nanoclusters on oxide surface catalyze the reaction. They also suggested that the interface positions between the nanocluster and the oxide support are the catalytically active sites. The experiments by Zhu et al. revealed that [Au₂₅(SR)₁₈]⁻ can act as a homogeneous catalyst in solution phase oxidation of styrene by O_2 .²⁷ Xie et al. examined the aerobic oxidation of

Received: April 5, 2018 **Revised:** July 28, 2018 Published: August 5, 2018 alcohols catalyzed by $[Au_{25}(SR)_{18}]^-$ calcinated on carbon nanotubes.²⁸ Liu et al. found that the Au_{25} supported on hydroxyapatite catalyzes aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone.²³

The mechanism of catalysis of oxidation reactions by Au₂₅ nanoclusters is still unclear even though there are a significant number of investigations of the applications of these nanoclusters as a model catalyst for these reactions. It is crucial to get a deeper understanding of the stability of the nanocluster under these reaction conditions, catalytically active centers, nature of binding between the cluster and the reactant and product species, and influence of reaction conditions. Recently, Dreier et al. carried out a reinvestigation of the homogeneous catalysis of styrene oxidation by t-butyl hydrogen peroxide (TBHP) using [Au₂₅(SR)₁₈]^{-.29} They established that the nanoclusters are unstable in the presence of TBHP and undergo oxidative decomposition. Au(I)-thiol precursors and decomposition products are equally effective in catalyzing styrene oxidation.²⁹ Such investigations show that there is a need to conduct fundamental research to understand the catalysis by nanoclusters, which would help in designing selective catalysts for various chemical processes.

In spite of several existing studies on the catalytic activity of the cluster in oxidation reactions, there is no clear understanding of the interaction of molecular O_2 with the nanocluster. In all the investigations conducted so far, interaction with oxygen was suggested but there is no evidence for an oxygen bound cluster. Such an adduct would be the central species responsible for the oxidation of the cluster in atmospheric conditions and in other processes too. In this regard, our objective has been to answer a fundamental question, that is, whether $[Au_{25}(SR)_{18}]^-$ reacts with O_2 in ambient conditions.

In this paper, the interaction between $[Au_{25}(PET)_{18}]^-$, where PET is 2-phenylethane thiol, and molecular O_2 in solution phase was examined using electrospray ionization (ESI) MS and UV/vis absorption spectroscopy. Up to three O_2 attachments to $[Au_{25}(PET)_{18}]^-$ were detected in the mass spectra. This gives a direct evidence for the interaction of $[Au_{25}(PET)_{18}]^{-}$ with molecular O₂. Oxygen attachment to the nanocluster leads to its decomposition to smaller polymer-like products. Adduct formation between [Au₂₅(PET)₁₈]⁻ and O₂ was observed only in the case of DCM and not in toluene and tetrahydrofuran (THF). However, the nanoclusters were stable in the case of toluene for long time, in the presence of O_2 . Density functional theory (DFT) calculations suggested that the interaction sites for the first and the second O₂ are surface Au atoms of the nanocluster and the third O2 interacts with only PET ligands.

2. EXPERIMENTAL SECTION

2.1. Materials. Chloroauric acid trihydrate (HAuCl₄· $3H_2O$), PET, tetraoctylammonium bromide (TOAB), and sodium borohydride (NaBH₄) were purchased from Sigma-Aldrich. Toluene, THF, DCM, and methanol were purchased from RANKEM and were of analytical grade. All the chemicals were used as such without any further purification.

2.2. Instrumentation. A PerkinElmer LAMBDA 25 instrument with a range of 200–1100 nm and a band pass filter of 1 nm was used for measuring UV/vis absorption spectra of the samples.

The ESI MS measurements were done by a Waters' Synapt G2Si high definition MS instrument, consisting of an

electrospray source, quadrupole ion guide/trap, ion mobility cell, and time-of-flight detector. Nitrogen gas was used as the nebulizer gas. The measurements were done in negative ion mode as $[Au_{25}(SR)_{18}]^-$ is intrinsically negatively charged. In the case of toluene samples, acetonitrile was added to facilitate the ion detection. The optimized conditions used to obtain a well-resolved MS spectrum were as follows:

| sr. no. | parameters | value |
|---------|----------------------|-----------------------|
| 1 | sample concentration | $10 \ \mu g/mL$ |
| 2 | solvents | DCM or toluene or THF |
| 3 | flow rate | $30 \ \mu L/min$ |
| 4 | capillary voltage | 3.5 kV |
| 5 | cone voltage | 120–150 V |
| 6 | source offset | 80–120 V |
| 7 | desolvation gas flow | 400 L/h |
| 8 | trap gas flow | 5 mL/min |

2.3. Synthesis of [Au25(PET)18]-. A modified Brust-Schiffrin single-phase procedure was used for the synthesis of $[Au_{25}(PET)_{18}]^{-.30}$ Approximately 40 mg of HAuCl₄·3H₂O was taken in 7.5 mL of THF, and ~65 mg of TOAB was added and stirred for ~15 min to get a deep-red-colored solution. Following this, 5 mol equivalents (with respect to gold) of PET was added, and the reaction mixture was stirred for approximately 2 h to get a colorless solution of Au-SR thiolate mixtures. These thiolates were reduced by \sim 39 mg of NaBH₄ taken in 2.5 mL of ice-cold water. The reaction mixture was stirred at a constant speed of 1500 rpm at room temperature for another 6 h to get a reddish-brown-colored solution. To remove excess thiol and other impurities, THF was evaporated by vacuum drying and the nanocluster was precipitated by methanol addition. The supernatant solution containing excess thiol was discarded. This step was repeated 2-3 times followed by extraction of the nanocluster in acetone leaving behind bigger particles. The acetone was vacuum-dried, and the pure nanocluster was extracted in DCM.

2.4. Interaction of $[Au_{25}(PET)_{18}]^-$ with O_2 , CO_2 , N_2 , and Ar. All the gases used were of high purity (99.99%). These reactions were performed in two ways. In one, the nanocluster solution in DCM was kept under O_2 environment created by an O_2 -filled balloon. The samples for time-dependent UV/vis spectroscopy and ESI MS were withdrawn at different time intervals using a syringe. The same procedure was followed for other gases as well. In another method, O_2 gas was passed through the solution of the nanocluster in DCM with continuous stirring. The samples were withdrawn using a syringe at different time intervals and monitored using UV/vis spectroscopy and ESI MS. To check the effect of solvents on $Au_{25}(PET)_{18}-O_2$ adduct formation, the same procedure was repeated with toluene and THF.

2.5. Molecular Docking Studies. In order to obtain further insights into the molecular level interactions of O_2 with $[Au_{25}(PET)_{18}]^-$, molecular docking studies were performed using AutoDock 4.2.1. The DFT-optimized $[Au_{25}(PET)_{18}]^-$ structure was used for this investigation. Oxygen was used as the "ligand" and $[Au_{25}(PET)_{18}]^-$ as the "receptor" molecule. The output for ligand was saved in PDBqt format. DFT-optimized charges were used for the receptor. Receptor grids were generated using $126 \times 126 \times 126$ grid points in *xyz* with grid spacing of 0.375 Å and map types were created using AutoGrid-4.2. The grid parameter file (.gpf) was saved using MGL Tools-1.4.6.50 and docking was

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performed using AutoDock 4.2. The results of AutoDock generated an output file (.dlg), and the generated conformers were scored and ranked as per the interaction energy keeping the 10 lowest energy conformers. The output files generated by Lamarckian genetic algorithm were analyzed using MGL Tools-1.4.6. The conformer with lowest binding energy (BE) of the interacting molecules was used as an initial structure for DFT optimization. We sequentially docked one to three O₂ molecules to $[Au_{25}(PET)_{18}]^-$ by combining the output coordinates of the last docked O₂ molecule and $[Au_{25}(PET)_{18}]^-$ to be the new receptor and the next O₂ to be docked as the ligand. The binding free energy of the $[Au_{25}(PET)_{18}O_2]^-$ was -3.26 kcal/mol.

2.6. DFT Optimization. The interaction of a few oxygen molecules with [Au₂₅(PET)₁₈]⁻ was computationally studied by considering the $[Au_{25}(PET)_{18}(O_2)_n]^-$ (n = 1, 2, and 3) and using DFT with the projector augmented wave (PAW) method as implemented in the GPAW software package.^{31,32} The calculations were performed in linear combination of atomic orbitals mode of GPAW which efficiently utilizes the given basis set to form the wave function for atomic species, and thus, the computational time could be greatly reduced even for larger structures. The exchange-correlation functional and basis set were the Perdew-Burke-Ernzerhof (PBE) functional³³ and a double- ζ plus polarization basis set,³⁴ respectively. The calculations for $[Au_{25}(PET)_{18}(O_2)]^-$ were also done using vdW-DF2 functional, and the results obtained were compared with those obtained using PBE functional. The valence electrons of atoms in the PAW setups were Au (5d¹⁰6s¹), S (3s²3p⁴), O (2s²2p⁴), C (2s²2p²), and H (1s¹) and the other electrons were kept in a frozen core, with scalarrelativistic effects for Au atoms. The most favorable conformers obtained from molecular docking simulations were taken as the initial structures for geometry optimizations. Furthermore, the electron density was calculated using a real-space grid spacing of 0.2 Å and the relaxation criterion was that the forces on all atoms were <0.05 eV/Å, without applying any symmetry constraints. The BE of $(O_2)_n$ molecules was calculated as the energy difference of $[Au_{25}(PET)_{18}(O_2)_n]^-$ and the sum of isolated $[Au_{25}(PET)_{18}]^-$ and $(O_2)_n$ molecules. The average BE was obtained by dividing the total BE by the number of O₂ molecules. The visual molecular dynamics software³⁵ was used to create the visualization of all the optimized structures.

3. RESULTS AND DISCUSSION

We chose $[Au_{25}(PET)_{18}]^{-}$ as a model system for the experiments. These nanoclusters were synthesized by the modified Brust–Schiffrin synthetic protocol³⁰ and characterized by UV/vis absorption spectroscopy and ESI MS. The UV/ vis absorption spectrum of the nanocluster in DCM, given in Figure S1A, showed the characteristic features of $[Au_{25}(PET)_{18}]^{-}$. The mass spectrum of the sample, presented in Figure S1B,C, also gave the characteristic peak of $[Au_{25}(PET)_{18}]^{-}$, thus confirming the quality of our synthesis. The experiments were conducted in DCM as $[Au_{25}(SR)_{18}]^{-}$ oxidizes in it upon interaction with atmospheric O₂.²⁴

Initially, the stability of the nanocluster in the presence of O_2 was checked by keeping the nanocluster solution in a continuous flow of O_2 and monitoring the time-dependent UV/vis absorption spectra. These spectra are shown in Figure S2. As expected, oxidation of the nanocluster was evident in the presence of O_2 , as indicated by the increase in the intensity of the 400 nm peak with time and the disappearance of hump

at 800 nm. Oxidation started occurring within 45 min of introduction of O_{22} and it was faster than in air. In Figure S3, the UV/vis absorption spectrum of the nanocluster kept in the O_2 environment for 4 h is compared with that of $[Au_{25}(PET)_{18}]^-$ and air-oxidized $[Au_{25}(PET)_{18}]^0$. We observed the increase in intensity of 400 and 450 nm features (indicated as peaks 1 and 2 in Figure S3) as compared to both $[Au_{25}(PET)_{18}]^-$ and $[Au_{25}(PET)_{18}]^0$. This spectrum corresponds to the reaction mixture consisting of parent nanocluster, its O_2 adducts as well as the decomposition products (discussed later). The increase in intensity of peaks 1 and 2 could be attributed to the presence of O_2 adducts and the decomposition products in the solution.

Figure 1 shows a comparison of ESI MS spectra of $[Au_{25}(PET)_{18}]^-$ with a sample of the same kept under O₂



Figure 1. ESI MS spectra of $[Au_{25}(PET)_{18}]^-$ in DCM before (black trace) and after (red trace) introducing O₂. The O₂ atmosphere was created using an O₂-filled balloon. Two assignments, that is, $[Au_{25}(PET)_{18}O_3]^-$ or $[Au_{25}(PET)_{18}(CHCl)]^-$, are possible for the peak highlighted with an asterisk. The blue trace shows ESI MS spectrum of $[Au_{25}(PET)_{18}]^-$ after bubbling O₂ continuously for a period of 540 min through its solution. Inset "i" shows experimental (red trace) and simulated (dark-blue trace) mass spectra of $[Au_{25}(PET)_{18}(O_2)]^-$.

for 1 h using an O2-filled balloon, in DCM. We observed a peak corresponding to one O2 adduct of the nanocluster, that is, $[Au_{25}(PET)_{18}(O_2)]^-$, at m/z = 7425. The inset "i" of the Figure 1 shows the match between experimentally observed (red trace) and simulated (dark-blue trace) mass spectra for $[Au_{25}(PET)_{18}(O_2)]^-$ species, which are in good agreement with each other. The peak at higher mass highlighted with an asterisk could be given two assignments, that is, $[Au_{25}(PET)_{18}O_3]^-$ or $[Au_{25}(PET)_{18}(CHCl)]^-$. The peak could be the result of overlap between these two species as well. However, because of the poor intensity and poorly resolved isotopic pattern of the peak, we were unable to provide an exact assignment for the same. Though there have been indirect results for the interaction of $[Au_{25}(PET)_{18}]^{-1}$ with O_{2i} for the first time we have observed the adduct species $[Au_{25}(PET)_{18}(O_2)]^-$ in the mass spectrum. As mentioned earlier, the aerial oxidation of $[Au_{25}(PET)_{18}]^-$ to

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Figure 2. (A) (i) Time-dependent ESI MS spectra, up to 90 min, upon exposure of $[Au_{25}(PET)_{18}]^-$ to a continuous flow of O₂ in DCM. In (ii), mass spectra are enlarged to show the region corresponding to the $[Au_{25}(PET)_{18}(O_2)_n]^-$ species. (B) (i) Time-dependent ESI MS spectra beyond 90 min in the presence of O₂. In (ii), mass spectra are expanded to show the region corresponding to the $[Au_{25}(PET)_{18}(O_2)_n]^-$ species. (B) (i) Time-dependent ESI MS spectra beyond 90 min in the presence of O₂. In (ii), mass spectra are expanded to show the region corresponding to the $[Au_{25}(PET)_{18}(O_2)_n]^-$ species. Intensity of $[Au_{25}(PET)_{18}]^-$ is normalized. The intensity of the parent nanocluster also decreases in this time window.

 $[Au_{25}(PET)_{18}]^0$ in DCM is a strong evidence for the interaction of the nanocluster with molecular O_2 . This interaction takes place when the nanocluster dissolved in DCM is exposed to air for several hours.²⁴ We were not able to detect the O_2 adducts of the nanocluster in mass spectra in the case of aerial oxidation process. In our experiments, pure O_2 was supplied continuously and therefore the oxidation occurs within ~45 min. Hence, we presume that the adduct formation takes place significantly only when O_2 is passed directly into the solution of the nanocluster and when a large amount of O_2 is present in the solution.

We did an experiment by taking cluster solution in DCM and bubbling O2 gas continuously through the solution, to check the effect of amount of O_2 in the reaction mixture on O_2 addition. The mass spectrum of the nanocluster after 540 min of continuous flow of O_2 is shown in Figure 1 (blue trace). Up to three molecules of O2 were attached to the cluster in this case. This experiment proved that the amount of O_2 present in solution has an effect on adduct formation. The match between the experimental and simulated mass spectra for $[Au_{25}(PET)_{18}(O_2)_2]^-$ and $[Au_{25}(PET)_{18}(O_2)_3]^-$ species is given in Figure S4. They are in good agreement with each other. The intensity of the peak corresponding to $[Au_{25}(PET)_{18}(O_2)]^-$ was the highest compared to other O_2 adduct peaks. This could be due to the higher stability of the species compared to others. It is also possible that the different species react with each other in the reaction mixture and an equilibrium is established between them with time.

Time-dependent ESI MS measurements were done to check the variation of the relative abundance of different species in the reaction mixture with time. The spectra are presented in Figure 2. It could be noted that initially, that is, within 15 min, $[Au_{25}(PET)_{18}(O_2)]^-$ and $[Au_{25}(PET)_{18}(O_2)_2]^-$ were observed. $[Au_{25}(PET)_{18}(O_2)_3]^-$ started appearing in about 60 min of reaction and its intensity increased relatively with time up to 120 min, then started decreasing, and finally disappeared in the spectrum of 630 min. Thus, the reaction between the nanocluster and O_2 is highly dynamic in nature.

There is a continuous formation and conversion of different species with different relative concentrations. This behavior could be explained in two ways: either three O_2 attachment to the nanocluster might be resulting in the decomposition of the nanocluster or different species in the reaction mixture might be interacting with each other to form other species. It is even possible that both these processes are occurring simultaneously.

The lower mass regions of the time-dependent ESI MS data are shown in Figure 3. Decomposition of the cluster was



Figure 3. (A) Lower mass range (m/z = 1200-5000) ESI MS spectra of $[Au_{25}(PET)_{18}]^-$ upon exposure to a continuous flow of O₂. (B) Data after 90 min. Peak highlighted with the asterisk corresponds to $[Au_4(PET)_5]^-$, a commonly observed fragment in the mass spectrum of $[Au_{25}(PET)_{18}]^-$.

observed because of the interaction with O_2 . Initially, lower mass thiolates were formed which were shifted into higher mass with time. A common fragment of the cluster, $[Au_4(PET)_5]^-$, was observed throughout. Apart from this, a series of peaks similar to polymer-like species were observed. These polymer-like thiolate peaks start at m/z = 1412.3 and spacing between the consecutive peaks is 74. The isotopic



Figure 4. Time-dependent ESI MS spectra upon exposure of $[Au_{25}(PET)_{18}]^-$ to a continuous flow of O_2 in toluene. Spectra in different regions are presented in (A-C). Intensity of $[Au_{25}(PET)_{18}]^-$ is normalized.

pattern indicates that these are singly charged species. All the peaks correspond to singly charged species, which implies that the leaving group is a neutral species with a mass of 74. The width of the peaks increases as we move from lower mass to higher mass. There is another set of peaks, which is at a constant spacing of 27 units from the previous set of peaks. The spacing between consequent peaks in this series too is 74 units.

To check the effect of solvent on the interaction, we carried out the same reaction in toluene keeping all other conditions the same and the interaction was monitored using timedependent UV/vis spectroscopy and ESI MS. Time-dependent UV/vis spectra of the nanocluster in toluene kept under a continuous flow of O₂ are given in Figure S5A. No O₂ adducts of the nanocluster were observed in time-dependent ESI MS spectra shown in Figure 4. Degradation of the nanocluster was observed but to a lesser extent compared to that in the case of DCM. In the case of THF, the nanocluster was unstable in the presence of O₂ and degraded completely within 2 h. The timedependent UV/vis absorption spectra are shown in Figure S5B. No O2 attached species were observed in time-dependent ESI MS spectra (shown in Figure S6) of the nanocluster in THF in the presence of O₂. The degradation of the nanocluster within 2 h was observed here too. The degradation products are composed of thiolates of smaller masses. No polymer-like thiolate peaks were observed in the mass spectra in the case of THF.

The solvent variation experiments show that the cluster is more stable in toluene in the presence of O_2 . In DCM, oxidation of the nanocluster happens faster than in the case of toluene and it degrades into lower mass polymeric thiolates which grow to larger polymeric species with time. The peak corresponding to the nanocluster was also present up to 6 h in the time-dependent experiments. Thus, the solution consisted of a complex mixture composed of the nanocluster, its O_2 adducts, and the nanocluster degradation products. Predicting the catalytic efficiency of the nanocluster and catalytically active species involved is a difficult task in such scenarios. We note here that Dreier et al.²⁹ reported oxidative decomposition of $[Au_{25}(SR)_{18}]^-$ during styrene oxidation. They concluded that the Au(I) species resulting from the oxidative decomposition of the cluster are the catalytically active species in the styrene oxidation reaction and not the nanocluster itself. The nanocluster is unstable in the case of THF in the presence of O₂ and degraded within 2 h. Variation in the stability of the nanocluster in different solvents in the presence of O_2 could be due to the difference in O₂ solubility of the solvents. It could be noted that O₂ solubility is the least in the case of toluene and the highest in the case of THF. In DCM, O2 has an intermediate solubility. Our experiments indicate that the difference in the solubility of O_2 in these three solvents might affect the interaction of the nanocluster with O2. We could detect the O2 adducts of the nanocluster only in DCM which has an intermediate value of O2 solubility. Thus, variation in the interaction of the nanocluster with O_2 as well as difference in the stability of the nanocluster in different solvents could be the consequences of different O₂ solubility of the solvents. Hence, in cluster catalysis, choice of the solvent or reaction medium also plays an important role.

To check the interaction of other commonly used gases such as CO₂, N₂, and Ar with the cluster, we did similar experiments by keeping the $[Au_{25}(PET)_{18}]^-$ solution in DCM in the environments of these gases using respective gas-filled balloons. The time-dependent UV/vis spectra of $[Au_{25}(PET)_{18}]^-$ in DCM in the presence of CO₂, N₂, and Ar are shown in Figure S7. CO2 and N2 caused gradual oxidation of the $[Au_{25}(PET)_{18}]^{-}$, but in the Ar environment, the nanocluster was unchanged and was stable. The ESI MS spectra of the nanocluster before and after keeping in the respective gas environments are shown in Figure S8. In the case of CO_{2} , the intensity of the nanocluster peak was reduced drastically within 10 min and it disappeared within 15–20 min (note that the intensity of the peak corresponding to the nanocluster is normalized in Figure S8). However, the nanocluster features were intact up to 4 h in time-dependent UV/vis absorption spectra of it kept under a CO₂ environment. Therefore, the disappearance of the nanocluster peak in the mass spectrum could be due to the change in ionizability of the nanocluster upon exposure to CO₂ and not because of the degradation of the nanocluster. In the cases of N₂ and Ar, the nanocluster was intact and no variation in the mass spectrum was observed. However, no adduct species of the nanoclusters were observed in these cases in the mass spectra.



Figure 5. DFT-optimized structures of (A) $[Au_{25}(PET)_{18}]^-$, (B) $[Au_{25}(PET)_{18}(O_2)]^-$, (C) $[Au_{25}(PET)_{18}(O_2)_2]^-$, and (D) $[Au_{25}(PET)_{18}(O_2)_3]^-$ along with the energies of the structures and BEs. Color codes: golden yellow—Au, green—S, red—O, and blue stick models represent PET ligands.

To get an insight into the structure and nature of the bonding between the [Au₂₅(PET)₁₈]⁻ and O₂ molecules, DFT calculations were conducted. First, we determined the most favorable interaction sites for the first, second, and third O₂ molecules with the cluster using molecular docking studies. The most favorable structure for each adduct given by molecular docking was then optimized using the DFT method. The DFT-optimized geometrical structures of $[Au_{25}(PET)_{18}(O_2)]^-$, $[Au_{25}(PET)_{18}(O_2)_2]^-$ and $[Au_{25}(PET)_{18}(O_2)_3]^-$ are shown in Figures 5 and S9. As $[Au_{25}(PET)_{18}]^{-}$ has a cavity-like structure on both sides formed by the ligands and the three staples around the C_3 axis of the cluster, 36 it is possible for the O_2 molecule to interact with Au atoms on the surface of the nanocluster. The interaction of O_2 with Au atoms at the surface is a weak supramolecular one, involving electrostatic and van der Waals interactions with an average Au-O bond distance of 3.33 Å, and we also observed that there is a slight distortion at the base of the cavity formed by the three gold atoms on the surface of the icosahedral core because of the average contraction of Au-Au bond distance (\sim 0.02 Å). Moreover, the O₂ molecule was elongated slightly by the distance of 0.029 Å because of the interaction with Au atoms. The changes in the Au-S bonding interactions were found to be negligible. The calculated BE per O_2 for the interaction of O_2 with $[Au_{25}(PET)_{18}]^-$ is -11.34 kcal/mol. The calculations for $[Au_{25}(PET)_{18}(O_2)]^-$ were also performed using vdW-DF2 functional including dispersion corrections to account for van der Waals forces. The bonding parameters obtained using PBE and vdW-DF2 functionals are compared in Table S1 (see Supporting Information). The structure of the molecule remained the same after including the dispersion corrections, and there were no significant differences in bonding parameters. We also noticed that the energy of the structure wherein the first O₂ interacts with the PET ligand (-1981.85 eV) is higher than the energy of structure B in Figure 5. This clearly confirms the interaction of O₂ with the surface Au atoms of the nanocluster. The BE values of atomic and molecular oxygen on various surfaces of Au and bare clusters of Au obtained from the literature are listed in the Table S2, for comparison.

The most favorable interaction sites for the second O_2 are at the cavities formed by the three gold atoms on the surface of the $[Au_{25}(PET)_{18}(O_2)]^-$ based on the molecular docking studies. The second O_2 occupies the cavity on the opposite side of the first O_2 . However, there is a distinct difference by 0.25 Å in the Au–O bond distance of the second O_2 with the surface Au atoms of the nanocluster. The calculated BE per O_2 for this case is -10.83 kcal/mol, which is slightly lesser than

that of the one O_2 attachment. Further addition of a O_2 to give $[Au_{25}(PET)_{18}(O_2)_3]^-$ clearly showed that the interaction of the third O₂ molecule was only with PET ligands. Introduction of three O₂ significantly affected the interactions in the entire nanocluster. The bond lengths of three O2 molecules varied distinctly from 1.26 to 1.28 Å, and the largely elongated bond length of O_2 was due to the interaction with the ligands. It is worth noting that the Au–O bond length for the O₂ bound to the Au through the cavities (mentioned before) increases from 3.33 Å in $[Au_{25}(PET)_{18}(O_2)]^-$ to 3.48 Å in $[Au_{25}(PET)_{18}(O_2)_4]^-$ (DFT-optimized structure is given in Figure S10 in Supporting Information). This suggested that the addition of more than three O2 weakened the interactions of O₂ at the cavities. The calculated BE per O₂ for the case of three O_2 attachments was -10.75 kcal/mol. We also conducted an additional study, which showed that the addition of more number of O2 molecules in various positions to the cluster such as under the staples and above the core penetrating O2 into the cluster could cause larger changes in Au–S and Au–Au network and if these larger number of O₂ molecules get under the cavity-like structure formed by Au atoms and ligands, then the cluster may distort and degrade fully.

4. CONCLUSIONS

In conclusion, the interaction of $[Au_{25}(PET)_{18}]^-$ with O₂ was investigated in detail using UV/vis absorption spectroscopy and ESI MS. Direct evidence for the attachment of O₂ with the nanocluster was observed in the mass spectra for the first time. Up to three O_2 molecules can attach to a $[Au_{25}(PET)_{18}]^-$. It was also observed that O2 attachment causes decomposition of the nanocluster. The effect of solvents on the interaction was examined by conducting the experiments in different solvents, such as DCM, toluene, and THF. We observed the O₂ adducts of the nanocluster only in the case of DCM. It was noted that the nanocluster is most stable in toluene in the presence of O_2 and least stable in the case of THF. The O₂ solubility of the solvent was proposed to be a deciding factor here. DFT calculations were carried out to understand the nature of bonding between the nanocluster and O2. The first and the second O₂ interact with the nanocluster by attaching to the surface Au atoms through the cavities present in the nanocluster formed by Au and ligands. The interaction of the third O₂ was found to be with the PET ligands. The average BE was highest for the first O2 attachment and decreased with further O₂ additions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b03220.

Characterization of $[Au_{25}(PET)_{18}]^-$; monitoring stability of cluster in continuous flow of O₂ by timedependent UV/vis absorption spectroscopy; comparison of UV/vis spectra of air-oxidized and O₂-treated $[Au_{25}(PET)_{18}]^-$; effect of solvent on the interaction of $[Au_{25}(PET)_{18}]^-$ cluster with O₂; interaction of $[Au_{25}(PET)_{18}]^-$ with other common gases such as CO_2 , N₂, and Ar; structures of higher energy isomers; c o m p a r i s o n of b o n d i n g p a r a m et e r s of $[Au_{25}(PET)_{18}(O_2)]^-$ obtained using PBE and vdW-DF2 functionals; binding energy of O₂ on various surfaces of Au and bare clusters of Au from the literature; DFT-optimized structures of higher energy isomers of $[Au_{25}(PET)_{18}(O_2)]^-$; and Cartesian coordinates for DFT-optimized structures (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: pradeep@iitm.ac.in.

ORCID [©]

Thalappil Pradeep: 0000-0003-3174-534X

Notes

The authors declare no competing financial interest.

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