ChemComm

COMMUNICATION

Check for updates

Cite this: Chem. Commun., 2025, 61, 6482

Received 11th February 2025, Accepted 24th March 2025

DOI: 10.1039/d5cc00757g

rsc.li/chemcomm

Ultraviolet photoactivation perturbs the metal-ligand interface of atomically precise nanoclusters †:

Anagha Jose, ^(b)^a Jada N. Walker, ^(b)^b Maya Khatun, ^(b)^c Sami Malola,^c B. S. Sooraj, ^(b)^a Hannu Häkkinen, ^(b)*^c Jennifer S. Brodbelt ^(b)*^b and Thalappil Pradeep ^(b)*^{ad}

This study investigates the use of ultraviolet (UV) photoactivation to structurally characterize atomically precise clusters in the gas phase. UV photoactivation of negatively charged precursor ions generates electron photodetachment species in lower charge states. These ions dissociate through single ligand losses, a mechanism that differs notably from the well known dissociation pathways of 8-electron cluster ions caused by collisional activation with implications to photo-chemistry. Computations show that the photodetachment induced by UV photoactivation perturbs the metal-ligand interfaces, providing a mechanistic understanding of UV based dissociation processes across different cluster systems.

Atomically precise clusters (APCs) of noble metals protected with ligands are an important family of materials in contemporary science.^{1–5} Over 500 APCs are known today, and about 350 of them have crystal structures.⁶ The structure of APCs consists of an inner metal core connected by metal-metal bonds, a metal-ligand interface, and an outer ligand shell.² The stability of the metal-ligand interface is crucial for the functionality, and tunability of clusters. Additionally, the metalligand interface protects the metal core from oxidation and aggregation, and it determines the size, shape, and electronic structure of the APCs. Modulating the surface reactivity, active site accessibility, and charge distribution enhances the catalytic, optical, and sensing properties of APCs.^{7–14} The structure



Individual cluster ions have gained significant attention in the past decade owing to their promising structural properties.¹⁵ For instance, Black *et al.* investigated the application of ultraviolet photodissociation mass spectrometry for analyzing gold nanoclusters, specifically $Au_{25}(pMBA)_{18}$ and $Au_{36}(pMBA)_{24}$, protected with *para*-mercaptobenzoic acid (*pMBA*) ligands.^{16,17} UVPD was shown to cause extensive fragmentation of the monolayer-protected cluster (MPC) ions using a single 193 nm UV pulse, uncovering unique structural insights not achieved with conventional methods like collision induced dissociation (CID).

Absorption of UV photons by negatively charged ions in the gas phase can induce electron photodetachment of nanocluster systems.¹⁸ Photodetachment produces ions of reduced charge that can be subsequently mass selected for supplemental collisional activation. Termed activated-electron photodetachment (a-EPD), this dissociation strategy effectively unravels the structural and electronic properties of nanoclusters. Additionally, ions excited by UV photons can produce unique fragment ions that provide further insights into the stability of the metal-ligand interfaces of APCs. Mass-selected photodetachment spectroscopy can also reveal the ionization potentials of cluster ions, providing information on their photophysical properties.^{19,20}

In this work, we present the UV photoactivation mass spectrometric investigation of two model APCs, $[Ag_{29}(BDT)_{12}]^{3-}$ and $[PtAg_{24}(DMBT)_{18}]^{2-}$, abbreviated as Ag_{29} and $PtAg_{24}$, revealing a perturbation of their metal-ligand interfaces. Isolation and activation of the charge-reduced precursors generated by UV photoactivation cause the loss of a single ligand, distinctly different from the dissociation channel usually observed upon CID of these superatomic clusters. The computational analysis demonstrates that the metal-ligand interface has perturbed upon photodetachment in both cluster systems.

The clusters Ag_{29} and $PtAg_{24}$ were synthesized in solution, with counter ions, as discussed in the experimental section.^{21,22}

View Article Online

^a DST Unit of Nanoscience (DST UNS) & Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras (IITM), Chennai 600036, India. E-mail: pradeep@iitm.ac.in

^b Department of Chemistry, University of Texas at Austin, Texas 453552, USA. E-mail: jbrodbelt@cm.utexas.edu

^c Departments of Chemistry and Physics, Nanoscience Center,

University of Jyväskylä, FI-40014 Jyväskylä, Finland.

E-mail: hannu.j.hakkinen@jyu.fi

^d International Centre for Clean Water, 2nd Floor, B-Block,

IIT Madras Research Park, Kanagam Road, Taramani, Chennai 600113, India

[†] Dedicated to Prof. G. Ranga Rao on his 65th birthday.

[‡] Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1020/dc.e007577

^{10.1039/}d5cc00757g



Fig. 1 (a) Electrospray ionization mass spectra (ESI MS) of $[Ag_{29}(BDT)_{12}]^{3-}$. (b) HCD of $[Ag_{29}BDT_{12}]^{3-}$ at NCE 5, NCE 15, and NCE 20. (c) UV photoactivation of $[Ag_{29}BDT_{12}]^{3-}$ at 2 pulses at 2 mJ per pulse. Photodetachment of $[Ag_{29}(BDT)_{12}]^{3-}$ produced $[Ag_{29}(BDT)_{12}]^{2-}$ and $[Ag_{29}(BDT)_{$

The protecting ligands of Ag₂₉ and PtAg₂₄ are 1,3-benzenedithiol (BDT) and 2,4-dimethylbenzenethiol (DMBT), respectively. These clusters were characterized by various spectroscopic and diffraction studies (presented in ESI‡). The optical absorption spectrum of Ag₂₉ exhibited the characteristic features at 447 nm and 513 nm (Fig. S1, ESI‡). Time-dependent optical absorption spectra of Ag₂₉ were measured to confirm the stability of the cluster (Fig. S2, ESI‡). High-resolution electrospray ionization mass spectrometry (HRESI-MS) of the cluster generated an ion of m/z 1603, corresponding to the 3- charge state ($[Ag_{29}(BDT)_{12}]^{3-}$), as shown in Fig. 1a. The cluster exists as $[Ag_{29}(BDT)_{12}]^{3-}$ as the principal charge species under these electrospray conditions. The observed isotopic distribution pattern is in good agreement with the simulated pattern of $[Ag_{29}(BDT)_{12}]^{3-}$, confirming the purity of the synthesized samples. The structure of the cluster determined by single crystal X-ray diffraction (SCXRD) is shown in the inset of Fig. 1a. We compare the higher energy collisional dissociation (HCD) and ultraviolet photoactivation of Ag₂₉ at different normalized collision energy (NCE) and pulse energy, respectively. Systematic fragmentation is seen upon collisional activation of $[Ag_{29}(BDT)_{12}]^{3-}$; fragments obtained were assigned as $[Ag_{19}(BDT)_6]^-$ (m/z 2888),

 $[Ag_{24}(BDT)_9]^{2-}$ (*m*/*z* 1924), and $[Ag_5(BDT)_3]^{-}$ (*m*/*z* 960) as reported previously (Fig. 1b).²³ However, upon UV photo-activation of $[Ag_{29}(BDT)_{12}]^{3-}$, we see the emergence of $[Ag_{29}(BDT)_{12}]^{2-}$ and $[Ag_{29}(BDT)_{12}]^{1-}$ species in the mass spectrum (Fig. 1c). Simulated and experimental isotopic distributions are shown as insets in Fig. 1c. DFT calculations have shown the first and second ionization potentials of $[Ag_{29}(BDT)_{12}]^{3-}$ to be 0.46 eV and 2.76 eV, respectively. The 1- and 2-species observed in the mass spectrum are justified, as these energies are lower than the accessible energies generated from a single 193 nm UV photon (6.44 eV). We conducted similar experiments using the same number of laser pulses and different laser energies (i.e., 1 pulse at 1 mJ per pulse, 1 pulse at 2 mJ per pulse, and 1 pulse at 3 mJ per pulse) (Fig. S3a, ESI[‡]). Also, we performed experiments with different numbers of laser pulses and the same laser energy (i.e., 1 pulse at 2 mJ per pulse, 2 pulses at 2 mJ per pulse, and 3 pulses at 2 mJ per pulse) (Fig. S3b, ESI[‡]). The abundances of $[Ag_{29}(BDT)_{12}]^{2-}$ and $[Ag_{29}(BDT)_{12}]^{1-}$ species increase with increasing laser pulses and laser energies. Activated-electron photodetachment dissociation (a-EPD) experiments were performed using UV photoactivation (1 pulse at 2 mJ per pulse) to generate



Fig. 2 a-EPD experiments of charge-reduced radical species $[{\rm Ag}_{29}({\rm BDT})_{12}]^2-$ at NCE 10, NCE 30 and NCE 40.

charge-reduced radical species, followed by isolation and collisional activation of the primary charge-reduced precursor ion, $[Ag_{29}(BDT)_{12}]^{2-}$ (MS³) (Fig. 2). For a-EPD of $[Ag_{29}(BDT)_{12}]^{2-}$ the fragments observed were $[Ag_{24}(BDT)_9]^-$ (*m*/*z* 3852), $[Ag_{24}(BDT)_8]^-$ (*m*/*z* 3712), $[Ag_{29}(BDT)_{11}]^{2-}$ (*m*/*z* 2336), and $[Ag_5(BDT)_3]^-$ (*m*/*z* 960). We find that the emergence of $[Ag_{29}(BDT)_{11}]^{2-}$, the one ligand loss feature, is increasingly prominent with increasing collisional energy.

This fragmentation pattern is distinctly different from the collisional activation of $[Ag_{29}(BDT)_{12}]^{3-}$, as reported earlier (Fig. 1b).

We also synthesized a bimetallic PtAg24 nanocluster using a previously reported protocol,²² and it exhibited prominent absorption features at 450 and 580 nm (Fig. S4, ESI‡). Timedependent optical absorption measurements confirmed the stability of the PtAg₂₄ cluster (Fig. S5, ESI[‡]). Fig. 3a presents the ESI MS of $PtAg_{24}$, which exhibits a peak at m/z 2626 with a 2- charge state corresponding to $[PtAg_{24}(2,4-DMBT)_{18}]^{2-}$. The inset of Fig. 3a shows the overlay of experimental and simulated isotopic distributions. The structure of $[PtAg_{24}(2,4-DMBT)_{18}]^{2-}$ was determined by SCXRD, which is shown in the inset (Fig. 3a). Experiments have been conducted on the PtAg₂₄ system, which ionizes in the 2- state, and upon UV photoactivation, it produces the $[PtAg_{24}(2,4-DMBT)_{18}]^{-}$ species. In Fig. 3b and c, we compare the HCD and UV photoactivation mass spectra of $[PtAg_{24}(2,4-DMBT)_{18}]^{2-}$ at different collisional and laser pulse energies. The compositions of the fragment ions are assigned in the mass spectra. Systematic



Fig. 3 (a) Electrospray ionization mass spectrum of $[PtAg_{24}(DMBT)_{18}]^{2-}$. Simulated and experimental isotopic distributions of $[PtAg_{24}(DMBT)_{18}]^{2-}$ are shown in the inset. (b) HCD of $[PtAg_{24}(DMBT)_{18}]^{2-}$ at NCE 0 and NCE 5. (c) UV photoactivation of $[PtAg_{24}(2.4-DMBT)_{18}]^{2-}$ at different energies, 2 pulses at 1 mJ per pulse, 2 pulses at 2 mJ per pulse, and 2 pulses at 3 mJ per pulse.

fragmentation occurs upon collisional activation, resulting in several fragments, all of which are 8e-species (Fig. 3b).²⁴ For the UV photoactivation spectra, ions corresponding to $[PtAg_{24} (2,4-DMBT)_{18}]^-$ and $[PtAg_{24}(2,4-DMBT)_{17}]^-$ are observed along with other fragments. Photodetachment calculations have shown that the first ionization potential of $[PtAg_{24} (2,4-DMBT)_{18}]$ is 1.68 eV. The abundance of the ion corresponding to a single ligand loss increases with an increase in the laser energy per pulse.

To understand the difference in the fragmentation process, we performed computational studies on Ag₂₉ and PtAg₂₄. We have computed the DFT optimized structures of Ag₂₉, with increase in charge, namely $[Ag_{29}(BDT)_{12}]^-$, $[Ag_{29}(BDT)_{12}]^{2-}$, and $[Ag_{29}(BDT)_{12}]^{3-}$ (Fig. S6a-c, ESI[‡]). While comparing the DFT-optimized structures of $[Ag_{29}(BDT)_{12}]^{3-}$, we observe a slight perturbation of the Ag–S bond in its $[Ag_{29}(BDT)_{12}]^{-}$, and $[Ag_{29}(BDT)_{12}]^{2-}$ charge states as compared to the $[Ag_{29}(BDT)_{12}]^{3-}$ parent species. The ligand detachment energy (LDE) for one ligand loss was calculated using both optimized and non-optimized structures. The values were 4.66 and 5.55 eV, respectively. Similarly, we have computed the DFT optimized structures of [PtAg₂₄(2,4-DMBT)₁₈]⁻, and [PtAg₂₄ $(2,4-\text{DMBT})_{18}$ ²⁻ (Fig. S6d and e, ESI[‡]). A comparison of the DFT-optimized structures showed slight perturbation of the Ag-S bond in [PtAg₂₄(2,4-DMBT)₁₈]⁻ as compared to the $[PtAg_{24}(2,4-DMBT)_{18}]^{2-}$ parent species. We have considered two possible DMBT ligands based on the symmetry of the metal-ligand interface. The detachment energies for the loss of ligand were calculated as 1.66 and 2.14 eV, for both these



Fig. 4 Ligand detachment energy obtained from the optimization and without optimization (italic) of the dissociated fragments (in eV) (a) $[Ag_{29}(BDT)_{12}]^{2-}$ and it's one ligand loss species $[Ag_{29}(BDT)_{11}]^{2-}$; (b) $[PtAg_{24}(2,4-DMBT)_{18}]^{-}$ and it's one ligand loss species $[PtAg_{24}(2,4-DMBT)_{11}]^{-}$. Atomic colour codes: gray: Ag, Blue: Pt, yellow: S, orange: P, grey: C, Hs are omitted for clarity.

cases using optimized structures. However, the non-optimized structures gave values of 2.35 and 2.96 eV, respectively. The ligand detachment processes of $[Ag_{29}(BDT)_{12}]^{2-}$ and $[PtAg_{24}(2,4-DMBT)_{18}]^{-}$ are shown in Fig. 4. The calculated ligand detachment energies, whether considering optimized or non-optimized dissociation structures for both the clusters were much below the accessible energies of the UV photon used, which was 6.44 eV (193 nm).

In conclusion, we have examined the UV photoactivation of two APCs, $[Ag_{29}(BDT)_{12}]^{3-}$ and $[PtAg_{24}(DMBT)_{18}]^{2-}$ in the gas phase. UV photoactivation results in the formation of the charge-reduced electron-detached species, yielding clusters in 2- and 1-charge states from the 3-precursor. These ions dissociate through single ligand losses, distinctly different from the dissociation channels seen for the same cluster ions using collisional activation. UV photoactivation of $[PtAg_{24}(DMBT)_{18}]^{2-}$ also yielded similar results. This unique pathway suggests a change in the energetics of the metal-ligand interface, as supported by calculations. These insights on the atomically precise clusters will be useful in understanding the behaviour of the clusters in the gas phase. Expanding UV photoactivation analysis into APCs could provide more insights into their structure and bonding. Such studies would help us gain insights into structures of larger nanoparticles, which may resemble proteins, on the latter UV photoactivation studies are performed routinely. These structural insights enable us to understand the behaviour of clusters in the gas phase, which could enhance their utility in catalytic (including photocatalytic) and electrochemical applications.

A. J. acknowledges the MHRD for the PMRF and IIT Madras for the IIE grant. The computational work was supported by the

Research Council of Finland and carried out during M. K.'s extended visit to IIT Madras. The simulations were performed at the Finnish National Supercomputing Center CSC. J. S. B. acknowledges funding from the Welch Foundation (F-1155). T. P. thanks the SERB, India, for funding through the research grant, SPR/2021/000439 and through a JC Bose Fellowship. T. P. also acknowledges funding from the Centre of Excellence on Molecular Materials and Functions, through the Institute of Eminence Scheme IIT Madras.

Data availability

Data supporting this article have been included as part of the ESI.[‡]

Conflicts of interest

There are no conflicts to declare.

References

- 1 R. Jin, C. Zeng, M. Zhou and Y. Chen, Chem. Rev., 2016, 116, 10346-10413.
- 2 I. Chakraborty and T. Pradeep, Chem. Rev., 2017, 117, 8208-8271.
- 3 H. Hirai, S. Ito, S. Takano, K. Koyasu and T. Tsukuda, *Chem. Sci.*, 2020, **11**, 12233–12248.
- 4 J. Xie, Y. Zheng and J. Y. Ying, J. Am. Chem. Soc., 2009, 131, 888-889.
- 5 S. Knoppe and T. Burgi, Acc. Chem. Res., 2014, 47, 1318-1326.
- 6 A. Pihlajamäki, S. Malola and H. Häkkinen, *ChemRxiv*, 2024, preprint, DOI: 10.26434/chemrxiv-2024-kxjpb.
- 7 X. Du and R. Jin, ACS Nano, 2019, 13, 7383-7387.
- 8 R. Jin, Nanoscale, 2015, 7, 1549-1565.
- 9 S. Knoppe, M. Vanbel, S. Van Cleuvenbergen, L. Vanpraet, T. Bürgi and T. Verbiest, J. Phys. Chem. C, 2015, 119, 6221–6226.
- 10 B. N. S. Sooraj and T. Pradeep, *Atomically Precise Metal Nanoclusters*, Elsevier, 2022, pp. 83–101.
- 11 K. S. Sugi, A. P. Sandra, N. Nonappa, D. Ghosh, J. S. Mohanty, M. Paulthangam Kannan, B. S. Sooraj, P. Srikrishnarka, J. Roy, W. A. Dar and T. Pradeep, *Nanoscale*, 2023, **15**, 11927–11934.
- 12 Y. Chen, C. Zeng and R. Jin, Catalysis, 2016, 28, 51-85.
- 13 S. Malola and H. Häkkinen, Chem. Commun., 2019, 55, 9460-9462.
- 14 A. Jana, B. K. Spoorthi, A. S. Nair, A. Nagar, B. Pathak, T. Base and T. Pradeep, *Nanoscale*, 2023, **15**, 8141–8147.
- 15 M. Azubel, A. L. Koh, K. Koyasu, T. Tsukuda and R. D. Kornberg, ACS Nano, 2017, 11, 11866–11871.
- 16 D. M. Black, C. M. Crittenden, J. S. Brodbelt and R. L. Whetten, J. Phys. Chem. Lett., 2017, 8, 1283–1289.
- 17 Y. Zhang, X. Gu, F. K. Busari, S. Barkaoui, Z. K. Han, A. Baiker, Z. Zhao and G. Li, *Nano Res.*, 2024, 17, 9594–9600.
- 18 R. Antoine, J. Lemoine and P. Dugourd, *Mass Spectrom. Rev.*, 2014, 33, 501–522.
- 19 S. Ito, Y. Tasaka, K. Nakamura, Y. Fujiwara, K. Hirata, K. Koyasu and T. Tsukuda, J. Phys. Chem. Lett., 2022, 13, 5049–5055.
- 20 K. Hirata, K. Yamashita, S. Muramatsu, S. Takano, K. Ohshimo, T. Azuma, R. Nakanishi, T. Nagata, S. Yamazoe, K. Koyasu and T. Tsukuda, *Nanoscale*, 2017, 9, 13409–13412.
- 21 L. G. AbdulHalim, M. S. Bootharaju, Q. Tang, S. Del Gobbo, R. G. AbdulHalim, M. Eddaoudi, D. E. Jiang and O. M. Bakr, *J. Am. Chem. Soc.*, 2015, **137**, 11970–11975.
- 22 J. Yan, H. Su, H. Yang, S. Malola, S. Lin, H. Häkkinen and N. Zheng, J. Am. Chem. Soc., 2015, 137, 11880–11883.
- 23 P. Chakraborty, S. Malola, M. Neumaier, P. Weis, H. Häkkinen and M. M. Kappes, Angew. Chem., Int. Ed., 2023, 62, e202305836.
- 24 J. Yan, H. Su, H. Yang, S. Malola, S. Lin, H. Häkkinen and N. Zheng, J. Am. Chem. Soc., 2015, 137, 11880–11883.