

# Ultrafast Intersystem Crossing in Isolated Ag<sub>29</sub>(BDT)<sub>12</sub><sup>3-</sup> Probed by Time-Resolved Pump-Probe Photoelectron Spectroscopy

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**ABSTRACT:** The photophysics of the isolated trianion  $Ag_{29}(BDT)_{12}^{3-}$  (BDT = benzenedithiolate), a ligand-protected cluster comprising BDT-based ligands, terminating a shell of silver thiolates and a core of silver atoms, was studied in the gas phase by femtosecond time-resolved, pump-probe photoelectron spectroscopy. UV excitation at 490 nm populates one or more singlet excited states with significant charge transfer (CT) character in which electron density is shifted from shell to core. These CT states relax on an average time scale of several hundred femtoseconds by charge recombination to yield either the vibrationally excited singlet ground state (internal conversion) or a long-lived triplet (intersystem crossing). Our study is the first ultrafast spectroscopic probe of a ligand-protected coinage metal cluster in isolation. In the future, it will be interesting to study how cluster size, overall charge state, or heteroatom doping can be used to tune the corresponding relaxation dynamics in the absence of solvent.



A tomically precise, ligand-stabilized ("protected") coinage metal clusters are of great present interest due to their size-tunable electronic structure, which has stimulated applications in fields ranging from electrocatalysis to optical sensing.<sup>1–13</sup> While protected gold clusters have been explored most extensively, there has also been much recent interest in preparing and characterizing ligand-stabilized silver clusters<sup>14</sup> as well as protected nanoalloy clusters comprising mixed coinage metal cores.<sup>15</sup> Several thiolate-protected silver clusters ranging up to Ag<sub>374</sub> have been crystallized.<sup>16</sup>

Like some thiolated organosoluble gold clusters, many silver clusters show visible and near-infrared (NIR) emission. A prototypical ligand-protected silver cluster with known X-ray crystal structure is  $Ag_{29}(BDT)_{12}(TPP)_4$ , first prepared and characterized in solid state and liquid solution by Bakr et al. (BDT, 1,3-benzenedithiolate; TPP, triphenylphosphine).<sup>17</sup> Upon near-UV excitation of  $Ag_{29}(BDT)_{12}(TPP)_4$ , long-lived near-IR photoluminescence (PL) has been observed, which is attributed to phosphorescence. It has also been reported that this PL can be efficiently quenched by codissolved molecular oxygen.<sup>10</sup> Also, ultrafast intermolecular electron transfer occurs upon UV photoexcitation of  $Ag_{29}(BDT)_{12}(TPP)_4$  when methylviologen is added to the solution.<sup>18</sup>

Electrospray mass spectrometry of  $Ag_{29}(BDT)_{12}(TPP)_4$ solutions yields *trianions* as the predominant negative charge state in isolation  $(Ag_{29}(BDT)_{12}(TPP)_{4-x}{}^3)$ , where x = 0-4). Bakr et al. have proposed that these trianions all reflect eight valence electron species in a closed-shell  $1s^21p^6$  superatom configuration  $(29 - (12 \times 2) + 3 = 8)$ .<sup>17</sup> Density functional theory (DFT) calculations have established that such a "superatom" grouping of valence orbitals is a characteristic of particularly stable coinage metal clusters.<sup>7</sup> Correspondingly, solid  $Ag_{29}(BDT)_{12}(TPP)_4$  has been proposed to consist of  $Ag_{29}(BDT)_{12}(TPP)_4^{3-}$  units surrounded by countercations (which remain to be assigned)<sup>19</sup> and as a corollary, the corresponding solutions are thought to comprise predominantly solvated  $Ag_{29}(BDT)_{12}(TPP)_4^{3-}$ .

Time-dependent density-functional theory (TDDFT) calculations of the  $Ag_{29}(BDT)_{12}(TPP)_4$  cluster suggested that the UV excitation giving rise to photoluminescence is of charge transfer type—transferring negative charge from the shell toward empty d-like superatom orbitals mainly associated with the silver cluster core.<sup>17</sup> A more recent linear response (LR)-TDDFT calculation of  $Ag_{29}(BDT)_{12}(TPP)_4^{3-}$  comes to the conclusion that UV excitation mainly involves ligand-to-metal charge transfer.<sup>10</sup> At this stage, the accuracy of TDDFT excited-state predictions for this compound class, the relaxation mechanism following photoexcitation (in particular, the route to the PL emitting state) and the role of the molecular environment in modulating these processes all remain unclear.

We therefore studied this problem by removing the solvent entirely. Specifically, we used femtosecond time-resolved, two-

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color, pump-probe photoelectron spectroscopy (tr-PES) to examine the corresponding isolated multianions. These are the first ultrafast spectroscopic measurements of ligand stabilized coinage metal clusters in the gas phase. Previously, one-photon PES of isolated multianionic ligand-protected coinage metal clusters with pulsed nanosecond lasers has yielded information on electron affinities (EA), repulsive Coulomb barrier heights (RCB), as well as overall electronic structure.<sup>12,13,20,21</sup> However, accessing fast decay dynamics following electronic excitation requires tr-PES.

Specifically, we generated isolated  $Ag_{29}(BDT)_{12}^{3-}$  as the system for tr-PES study by electrospray ionization of  $Ag_{29}(BDT)_{12}(TPP)_4$  solutions (with associated loss of all four weakly bound monodentate phosphines). The probable  $Ag_{29}(BDT)_{12}^{3-}$  molecular structure (based on the X-ray structure of  $Ag_{29}(BDT)_{12}(TPP)_4$  and DFT calculations—see the Supporting Information) is illustrated in Figure 1. Using tr-



**Figure 1.** Molecular structure of  $Ag_{29}(BDT)_{12}^{3-}$  based on the X-ray crystal structure of  $Ag_{29}(BDT)_{12}(TPP)_4$  as reported in ref 17 (after removal of four TPP ligands and DFT structure reoptimization of  $Ag_{29}(BDT)_{12}^{3-}$  without symmetry constraints (see the Supporting Information)). Color scheme: core comprising 13 silver atoms (orange); shell comprising 12 fully coordinated (light purple) and 4 partially coordinated silver atoms (green–after TPP removal), 24 sulfur atoms (blue), and 12 terminating benzyl-derived ligands (gray).

PES we find that resonant pulsed laser excitation of this species at 490 nm (2.53 eV) can lead to rapid population of a long-

lived excited state, which we identify as the carrier of the photoluminescence observed under similar irradiation conditions in solution.

The Ag<sub>29</sub>(BDT)<sub>12</sub>(TPP)<sub>4</sub> solid was synthesized following a previously reported method and used without further purification.<sup>22</sup> Approximately 5  $\mu$ M of clusters in dimethylformamide (DMF) was electrosprayed and probed using an ion beam apparatus—parts of which have been previously described.<sup>23–25</sup> It has recently been modified to incorporate a velocity map imaging (VMI) setup and a new femtosecond laser system.

In brief, after transfer into the high-vacuum machine, electrosprayed multianions were accelerated into a time-offlight (TOF) mass spectrometer and selected therein by their mass-to-charge ratio. The selected ions entered a perpendicularly oriented VMI spectrometer mounted within the TOF flight tube. There the trianions interacted with either one (onecolor) or two femtosecond laser pulses (two color pumpprobe) leading to photoelectron detachment. Three open electrodes in an Eppink-Parker like<sup>26</sup> design (pulsed) accelerated the photoelectrons toward an imaging microchannel plate detector (MCP) equipped with a phosphor screen. The corresponding electron impacts were recorded with a charge-coupled device (CCD) camera. Angle-resolved one-color photoelectron (PE) spectra (as well as two-color, time-resolved pump-probe PE spectra (tr-PES)) were obtained from these raw data using the polar onion peeling algorithm developed by the Verlet group.<sup>27</sup> The VMI setup was calibrated using one-color, one-photon photodetachment of I<sup>-</sup> at several different wavelengths.

The femtosecond laser system consisted of a Ti:sapphire pump laser (Astrella, Coherent) with a fundamental output wavelength of 800 nm (1.55 eV), generating 35 fs pulses at a repetition rate of 1 kHz and pulse energy of 7 mJ. This pumped a wavelength tunable TOPAS Prime (Light Conversion) optical parametric amplifier (OPA), which delivered the 490 nm pump pulses (and also UV wavelengths for one-photon detachment). We used an optical delay line to vary the pump-probe timing. The instrument response function in the vacuum chamber was  $50 \pm 5$  fs. The full width at half-maximum (fwhm) bandwidths of pump and probe pulses were ~56 and ~51 meV, respectively. Further details, including laser pulse energies, polarization and focusing



**Figure 2.** One-photon PES spectra of  $Ag_{29}(BDT)_{12}^{3-}$  at various UV detachment wavelengths as indicated (at photon energies of 3.81 (black), 4.20 (red), and 4.68 (blue) eV. Normalized photoelectron counts are plotted vs EKE for determination of the RCB height and vs electron BE toward determination of the third electron affinity, EA(3).



Figure 3. (left) One-color PE spectrum recorded at a detachment wavelength of 490 nm (2.53 eV). Note the presence of two EKE components. Gaussian deconvolution yields features centered at EKEs of  $2.66 \pm 0.02$  and  $3.41 \pm 0.02$  eV. (right) The integral intensities of these features scale quadratically with laser intensity indicating that both originate from two-photon processes taking place within the same laser pulse.

conditions, OPA wavelength range, data acquisition, and deconvolution procedures used to obtain either "stationary" one-photon spectra or time-resolved pump-probe PES measurements are described in the Supporting Information.

We begin with the stationary measurements (one-color photodetachment with fs laser pulses), which were recorded at detachment wavelengths of 325, 295, and 265 nm as indicated in Figure 2 (corresponding to photon energies of 3.81, 4.20, and 4.68 eV, respectively). In all cases, isotropic angular distributions were observed. The corresponding PE spectra show essentially only one component. Plotted versus electron binding energy (BE), the data allow to determine the third electron affinity (EA(3)) of  $Ag_{29}(BDT)_{12}^{3-}$  as 0.9 ± 0.1 eV (with hv - EA(3) = electron kinetic energy (EKE)). The estimated error is a result of the experimental noise, the extrapolation procedure used to determined EA(3), and the spectral width of the laser pulses. Plotted versus electron kinetic energy, the spectra also allow to determine the repulsive Coulomb barrier (RCB) height (as measured from the dianion ground state) to be  $1.7 \pm 0.1$  eV.

It is of interest to compare RCB and EA(3) with the predictions of classical electrostatics for charging a metallic sphere of radius corresponding roughly to that of the molecule in question (see structure in Figure 1).  $Ag_{29}(BDT)_{12}^{3-}$  can be thought of as consisting of a central 13-atom silver icosahedron (of radius ca. 2.8 Å), surrounded by a silver sulfide shell (of outside radius ca. 5.1 Å), which is capped by terminating ligands (to yield a total radius of 9.1 Å). Assuming a polycrystalline silver work function (WF) of 4.26 eV, classical electrostatics predicts that a third electron affinity of 0.9 eV is obtained for a conducting sphere of radius R = 10.7 Å (WF – 2.5 e<sup>2</sup>/4 $\pi e_0 R = 0.9$  eV), that is, larger than the actual molecular dimensions.

Similarly, the RCB height can be contrasted with a classical electrostatic calculation of the Coulomb repulsion between a single negative and a twofold negative point charge at distance R. This reaches a value of 1.7 eV at a separation of 17 Å—well outside the actual molecule. The RCB can also be compared to the height of a Coulomb barrier associated with charging a metallic sphere of radius R, from 2<sup>-</sup> to 3<sup>-</sup>. According to eq 5 in ref 28 an RCB of height 1.7 eV requires an R of ca. 16 Å, that

is, again a radius significantly outside the perimeter of  $Ag_{29}(BDT)_{12}^{3-}$ .

We conclude that the electronic ground state of  $Ag_{29}(BDT)_{12}^{3-}$  is not well-described by a classical metallic sphere, implying that "metallic" valence electron delocalization does not extend uniformly throughout the ligand-stabilized cluster. This is consistent with the previous TDDFT calculation<sup>17</sup> already alluded to. This ascribes the first strong UV absorption band at ca. 450 nm (see solution absorption and PL excitation spectra in the Supporting Information) to a charge-transfer excitation from *localized* electron orbitals on the silver sulfide shell to D-like, superatom lowest unoccupied molecular orbital (LUMO+1) orbitals on the silver cluster core.

We next explored the relaxation dynamics associated with 490 nm (2.53 eV) excitation. This wavelength was chosen as a compromise between TOPAS emission intensity and cluster absorption cross section in an overall range attributable to charge transfer excitations.<sup>17</sup> We first performed one-color photoelectron spectroscopy (PES) measurements at 490 nm at a number of different laser intensities. A typical PE spectrum (at an intermediate laser intensity of  $5 \times 10^9 \text{ W/cm}^2$ ) is shown in Figure 3. Again, the corresponding velocity map image on which it is based was found to be isotropic (over the full intensity range probed). In contrast to the UV measurements shown in Figure 2, the PE spectrum now manifests at least two components. This is highlighted by a corresponding twocomponent Gaussian deconvolution. Systematically varying the laser intensity and recording the corresponding PE spectra shows that both Gaussian components (centered at 2.66  $\pm$ 0.02 and 3.41  $\pm$  0.02 eV, respectively) manifest a two-photon intensity dependence. This is consistent with the above determination of EA(3) and RCB. One 490 nm photon (2.53 eV) alone cannot surmount the RCB, which lies at 2.6  $\pm$ 0.2 eV (RCB + EA(3)) when referred to the trianion ground state.

The two different electron kinetic energy (EKE) components that are fit to the 490 nm one-color PE spectra can be interpreted as deriving from two separate excited electronic states, each of which is accessed *during the same ca.*  $54 \pm 5$  *fs wide laser pulse* (ion packets spend ca. 50 ns in the VMI extraction zone; the next laser pulse arrives 1 ms later). Most

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Figure 4. Two-color pump probe measurements (490 nm (2.53 eV)/800 nm (1.55 eV)) recorded for parallel (a), magic angle (b), and perpendicular (c) relative (linear) laser polarizations as indicated. Shown are contour plots of the transient photoelectron counts vs electron kinetic energy and pump-probe delay. The three data sets look very similar indicating that they are not influenced by rotational dephasing. The expanded scale insert in (a) highlights the dynamics during the first 400 fs following 490 nm excitation.

likely, only the higher-lying state is initially (photo)-populated and can relax very rapidly to the lower state within the laser pulse. The lower electron kinetic energy component then results upon electron detachment from this state with an additional photon. By contrast, the higher electron kinetic energy feature derives from direct photoionization of the initially populated excited state.

Interestingly, there is no clear indication of excited-state electron tunneling detachment (ESETD) in this multianion system. ESETD has been previously observed by some of us and others in tr-PES measurements of a wide variety of different organic and inorganic multianions (having both negative and positive electron affinities).<sup>23–25,29–32</sup> For  $Ag_{29}(BDT)_{12}^{3-}$ , ESETD should give rise to PE spectral features at EKE  $\leq 1.63$  eV (=2.53–0.9 eV), which are not observed. Perhaps, tunneling barriers (also contributed to by the ligands) are so wide that ESETD in this system occurs on much longer time scales that are inaccessible by our tr-PES setup.<sup>33</sup>

To further explore the ultrafast decay implied by the 490 nm one-color PES data, we performed time-resolved pump-probe measurements (490 (2.53 eV pump) and 800 nm (1.55 eV probe)). The results are shown in Figure 4, which plots pump-probe transients (i.e., after subtraction of the pure pump contributions to the corresponding PE spectra). Specifically, we present contour plots of electron signal versus electron kinetic energy as a function of pump-probe delay for three different relative laser polarizations: perpendicular, parallel, and magic angle. Again, the corresponding velocity map images showed no significant anisotropy, that is, all three contour maps show essentially the same time-dependent behavior. Consequently, the transients are not significantly contributed to by rotational dephasing.<sup>34</sup> Note that the freerotor orientational correlation time of  $Ag_{29}(BDT)_{12}^{3-}$  at 300 K is expected to be ~13 ps based on the DFT-derived groundstate structure.<sup>35</sup> Apparently, excitation anisotropy is not conserved over this time scale.

Two further qualitative observations from the pump-probe measurements are also noteworthy. (i) Consistent with the 490 nm (2.53 eV) one-color PE spectra, we observe ultrafast decay of the initially populated state on an average time scale of less than 100 fs. This is associated with a systematic decrease in EKE during the course of this decay from 3.0 to ca. 2.1 eV (slope of ca. 0.01 eV/fs; see inset in Figure 4a). (ii) Within less than 150 fs after the initial 490 nm excitation, we clearly see a

long-lived state with characteristic EKE of 2.1 eV, which remains populated at probe delay times greater than 100 ps that is, beyond the delay time range accessible to our experiment. Given the EA(3) determination, this translates to an excitation energy of ca. 1.45 eV (2.1 + 0.9-1.55 eV) relative to the trianion ground state. This is roughly consistent with the photoluminescence spectroscopy of Ag<sub>29</sub>(BDT)<sub>12</sub>(TPP)<sub>4</sub>, in condensed phase, which shows an NIR emission maximum at ca. 1.61 eV for the roomtemperature solid, which has been assigned as phosphorescence on the basis of its greater than microsecond lifetime (see also the Supporting Information). Conceivably, the longlived pump-probe feature observed in tr-PES can be assigned to detachment from a vibrationally excited triplet state.

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The gas-phase absorption spectrum of  $Ag_{29}(BDT)_{12}^{3-}$  is not (yet) available. However, on the basis of our inference that triplet-state energies are comparable in gaseous and condensed phases we also expect comparable absorption spectra. The solution measurement (see the Supporting Information) in DMF shows an absorption peak at 450 nm and a shoulder at 520 nm. Bakr et al. have performed TDDFT calculations of  $Ag_{29}(BDT)_{12}(TPP)_4$  in an attempt to assign these features. They come to the conclusion, that there are nine separate singlet excited states in this (unscaled) absorption energy range from 1.87 (663 nm) to 2.60 eV (480 nm), all of which have significant charge-transfer character (with corresponding shifts of electron density from shell to core). The systematic temporal decay of EKE from ca. 3.0 to 2.1 eV observed over several hundred femtoseconds following photoexcitation may reflect a cascade of rapid internal conversion (IC) (also involving intramolecular vibrational redistribution) through several such states. Note that our tr-PES transients show no clear indication of "mechanical" low-frequency breathing-like vibrational modes (observed in many time-resolved pumpprobe transient absorption spectroscopic probes of gold nanoparticles and clusters<sup>36</sup>), which for  $Ag_{29}(BDT)_{12}^{3-}$  are calculated by DFT to have a period of ca. 400 fs.

We deconvoluted the transient PES measurements using the Glotaran global analysis package<sup>37</sup> assuming sequential decay of the initially excited state through a detectable intermediate to a detectable long-lived final state. This yields rate constants of greater than 10, ~2, and less than 0.01 ps<sup>-1</sup>, respectively. The corresponding decay-associated difference spectra are shown in the Supporting Information. Such a sequential decay process would, for example, correspond to population of one

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or more singlet excited states, which can rapidly decay (>10  $ps^{-1}$ ) to a "doorway" singlet state (presumably S1) from which intersystem crossing (~2  $ps^{-1}$ ) to the long-lived triplet can occur—as indicated schematically in the Jablonski diagram shown in Figure 5.



**Figure 5.** Jablonski diagram illustrating the proposed relaxation mechanism. The 490 nm (2.53 eV) irradiation populates a singlet charge transfer state,  $S_n$ , which rapidly relaxes via a cascade of IC steps to  $S_1$  (also involving intramolecular vibrational redistribution). From there, either rapid ISC to a long-lived triplet state ( $T_1$ ), or internal conversion to the vibrationally excited ground state can occur—mediated by charge recombination. Singlet excited states ( $S_1 - S_n$ ) as well as the triplet state  $T_1$  are selectively detected via their characteristic EKE features in the transient pump–probe PES measurements (using 800 nm (1.55 eV) probe photons). For a brief discussion of final state energetics see the Supporting Information.

In the absence of higher-level calculations, we speculate that the triplet state is localized near the "surface" of the cluster. PL in solution can be quenched by  $O_2$  (which is expected to be able to diffuse within the ligand shell).<sup>10</sup> This would imply that the initial excitation involving charge transfer from shell to the cluster core is rapidly followed by charge recombination to yield either a vibrationally hot ground state or a triplet state localized on the cluster shell. Charge recombination induced intersystem crossing is known for coupled organic chromophores photoexcited to a charge transfer state. 38,39 Charge recombination is also thought to mediate ultrafast ISC in certain transition-metal complexes.<sup>23,40–46</sup> However, in such cases the sequential relaxation steps usually invoked *following* singlet excitation are (symmetry breaking) charge transfer and then charge recombination to either triplet or ground states. For the silver clusters studied here, the initial singlet excitation is already of charge transfer type; no further symmetry breaking step is needed to rationalize the observations.

Previous ultrafast spectroscopy of protected coinage metal clusters—comprising almost exclusively gold clusters—has been confined only to condensed phase. Such studies are subject to environmental effects, which cannot occur in isolation (e.g., quenching of cluster-surface localized excitations by the solvent).<sup>47–49</sup> Here we have for the first time measured what we interpret to be an intrinsic ISC rate for free  $Ag_{29}(BDT)_{12}^{3-}$ . Should ultrafast ISC via charge transfer excitation followed by charge recombination be a common relaxation mechanism for other protected coinage metal clusters in gas-phase, it will be of interest to see how tuning cluster size, overall excess charge, and composition can affect the corresponding triplet quantum yields.

In summary, we have studied the photophysics of isolated  $Ag_{29}(BDT)_{12}^{3-}$  by pump-probe photoelectron spectroscopy. UV excitation (at 490 nm) populates one or more singlet

charge transfer states in which electron density is shifted from silver sulfide moieties on the shell to the silver cluster core. We suggest that the charge transfer states can relax very rapidly (on an overall time scale of several hundred fs) by charge recombination mediated intersystem crossing to yield a longlived triplet state on the cluster shell.

# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00482.

Discussion of pump-probe photoelectron spectroscopy, schematic diagram of experimental apparatus, DFT calculations, condensed-phase spectroscopy, electronic absorption spectrum, photoluminescence emission and excitation spectra, global analysis of tr-PES measurements, dianion state energetics (PDF)

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## Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. Synthesis of Thiol-Derivatized Gold Nanoparticles in a 2-Phase Liquid-Liquid System. *J. Chem. Soc., Chem. Commun.* **1994**, 0 (7), 801–802.

(2) Chen, S. W.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. Gold nanoelectrodes of varied size: Transition to molecule-like charging. *Science* **1998**, *280* (5372), 2098–2101.

(3) Negishi, Y.; Nobusada, K.; Tsukuda, T. Glutathione-protected gold clusters revisited: Bridging the gap between gold(I)-thiolate complexes and thiolate-protected gold nanocrystals. *J. Am. Chem. Soc.* **2005**, 127 (14), 5261–5270.

(4) Gautier, C.; Burgi, T. Chiral Gold Nanoparticles. *ChemPhyschem* 2009, 10 (3), 483-492.

(5) Natarajan, G.; Mathew, A.; Negishi, Y.; Whetten, R. L.; Pradeep, T. A Unified Framework for Understanding the Structure and Modifications of Atomically Precise Monolayer Protected Gold Clusters. J. Phys. Chem. C 2015, 119 (49), 27768–27785.

(6) Tlahuice-Flores, A.; Whetten, R. L.; Jose-Yacaman, M. Ligand Effects on the Structure and the Electronic Optical Properties of Anionic  $Au_{25}(SR)_{18}$  Clusters. *J. Phys. Chem. C* **2013**, *117* (40), 20867–20875.

(7) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Gronbeck, H.; Hakkinen, H. A unified view of ligand-protected gold clusters as superatom complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105* (27), 9157–9162.

(8) Chakraborty, A.; Fernandez, A. C.; Som, A.; Mondal, B.; Natarajan, G.; Paramasivam, G.; Lahtinen, T.; Hakkinen, H.; Nonappa; Pradeep, T. Atomically Precise Nanocluster Assemblies Encapsulating Plasmonic Gold Nanorods. *Angew. Chem., Int. Ed.* **2018**, 57 (22), 6522-6526.

(9) Chakraborty, P.; Nag, A.; Paramasivam, G.; Natarajan, G.; Pradeep, T. Fullerene-Functionalized Monolayer-Protected Silver Clusters:  $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$  (n = 1–9). ACS Nano **2018**, 12 (3), 2415–2425.

(10) Khatun, E.; Ghosh, A.; Chakraborty, P.; Singh, P.; Bodiuzzaman, M.; Ganesan, P.; Nataranjan, G.; Ghosh, J.; Pal, S. K.; Pradeep, T. A thirty-fold photoluminescence enhancement induced by secondary ligands in monolayer protected silver clusters. *Nanoscale* **2018**, *10* (42), 20033–20042.

(11) Zhang, B.; Garcia, C.; Sels, A.; Salassa, G.; Rameshan, C.; Llorca, J.; Hradil, K.; Rupprechter, G.; Barrabes, N.; Burgi, T. Ligand and support effects on the reactivity and stability of  $Au_{38}(SR)_{24}$  catalysts in oxidation reactions. *Catal. Commun.* **2019**, *130*, 105768.

(12) Hirata, K.; Tomihara, R.; Kim, K.; Koyasu, K.; Tsukuda, T. Characterization of chemically modified gold and silver clusters in gas phase. *Phys. Chem. Chem. Phys.* **2019**, *21* (32), 17463–17474.

(13) Kim, K.; Hirata, K.; Nakamura, K.; Kitazawa, H.; Hayashi, S.; Koyasu, K.; Tsukuda, T. Elucidating the Doping Effect on the Electronic Structure of Thiolate-Protected Silver Superatoms by Photoelectron Spectroscopy. *Angew. Chem., Int. Ed.* **2019**, *58* (34), 11637–11641.

(14) Jin, R. C.; Zeng, C. J.; Zhou, M.; Chen, Y. X. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chem. Rev.* **2016**, *116* (18), 10346–10413.

(15) Baksi, A.; Schneider, E. K.; Weis, P.; Krishnadas, K. R.; Ghosh, D.; Hahn, H.; Pradeep, T.; Kappes, M. M. Nanogymnastics: Visualization of Intercluster Reactions by High-Resolution Trapped Ion Mobility Mass Spectrometry. *J. Phys. Chem. C* **2019**, *123* (46), 28477–28485.

(16) Yang, H. Y.; Wang, Y.; Chen, X.; Zhao, X. J.; Gu, L.; Huang, H. Q.; Yan, J. Z.; Xu, C. F.; Li, G.; Wu, J. C.; Edwards, A. J.; Dittrich, B.; Tang, Z. C.; Wang, D. D.; Lehtovaara, L.; Hakkinen, H.; Zheng, N. F. Plasmonic twinned silver nanoparticles with molecular precision. *Nat. Commun.* **2016**, 7. DOI: 10.1038/ncomms12809

(17) AbdulHalim, L. G.; Bootharaju, M. S.; Tang, Q.; Del Gobbo, S.; AbdulHalim, R. G.; Eddaoudi, M.; Jiang, D. E.; Bakr, O. M.  $Ag_{29}(BDT)_{12}(TPP)_4$ : A Tetravalent Nanocluster. J. Am. Chem. Soc. **2015**, 137 (37), 11970–11975.

(18) Aly, S. M.; AbdulHalim, L. G.; Besong, T. M. D.; Soldan, G.; Bakr, O. M.; Mohammed, O. F. Ultrafast static and diffusion-controlled electron transfer at  $Ag_{29}$  nanocluster/molecular acceptor interfaces. *Nanoscale* **2016**, *8* (10), 5412–5416.

(19) Soldan, G.; Aljuhani, M. A.; Bootharaju, M. S.; AbdulHalim, L. G.; Parida, M. R.; Emwas, A. H.; Mohammed, O. F.; Bakr, O. M. Gold Doping of Silver Nanoclusters: A 26-Fold Enhancement in the Luminescence Quantum Yield. *Angew. Chem., Int. Ed.* **2016**, *55* (19), 5749–5753.

(20) Hirata, K.; Kim, K.; Nakamura, K.; Kitazawa, H.; Hayashi, S.; Koyasu, K.; Tsukuda, T. Photoinduced Thermionic Emission from  $[M_{25}(SR)_{18}]^-$  (M = Au, Ag) Revealed by Anion Photoelectron Spectroscopy. J. Phys. Chem. C **2019**, 123 (20), 13174–13179.

(21) Hirata, K.; Yamashita, K.; Muramatsu, S.; Takano, S.; Ohshimo, K.; Azuma, T.; Nakanishi, R.; Nagata, T.; Yamazoe, S.; Koyasu, K.; Tsukuda, T. Anion photoelectron spectroscopy of free  $[Au_{25}(SC_{12}H_{25})_{18}]^-$ . Nanoscale **2017**, 9 (36), 13409–13412.

(22) Baksi, A.; Ghosh, A.; Mudedla, S. K.; Chakraborty, P.; Bhat, S.; Mondal, B.; Krishnadas, K. R.; Subramanian, V.; Pradeep, T. Isomerism in Monolayer Protected Silver Cluster Ions: An Ion Mobility-Mass Spectrometry Approach. J. Phys. Chem. C 2017, 121 (24), 13421–13427.

(23) Winghart, M. O.; Yang, J. P.; Vonderach, M.; Unterreiner, A. N.; Huang, D. L.; Wang, L. S.; Kruppa, S.; Riehn, C.; Kappes, M. M. Time-resolved photoelectron spectroscopy of a dinuclear Pt(II) complex: Tunneling autodetachment from both singlet and triplet excited states of a molecular dianion. *J. Chem. Phys.* **2016**, *144* (5), 054305.

(24) Winghart, M. O.; Yang, J. P.; Kuhn, M.; Unterreiner, A. N.; Wolf, T. J. A.; Dau, P. D.; Liu, H. T.; Huang, D. L.; Klopper, W.; Wang, L. S.; Kappes, M. M. Electron tunneling from electronically excited states of isolated bisdisulizole-derived trianion chromophores following UV absorption. *Phys. Chem. Chem. Phys.* **2013**, *15* (18), 6726–6736.

(25) Dau, P. D.; Liu, H. T.; Yang, J. P.; Winghart, M. O.; Wolf, T. J. A.; Unterreiner, A. N.; Weis, P.; Miao, Y. R.; Ning, C. G.; Kappes, M. M.; Wang, L. S. Resonant tunneling through the repulsive Coulomb barrier of a quadruply charged molecular anion. *Phys. Rev. A: At., Mol., Opt. Phys.* **2012**, *85* (6). DOI: 10.1103/PhysRevA.85.064503

(26) Eppink, A. T. J. B.; Parker, D. H. Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen. *Rev. Sci. Instrum.* **1997**, *68* (9), 3477–3484.

(27) Roberts, G. M.; Nixon, J. L.; Lecointre, J.; Wrede, E.; Verlet, J. R. R. Toward real-time charged-particle image reconstruction using polar onion-peeling. *Rev. Sci. Instrum.* **2009**, *80* (5), 053104.

(28) Stoermer, C.; Friedrich, J.; Kappes, M. M. Observation of multiply charged cluster anions upon pulsed UV laser ablation of metal surfaces under high vacuum. *Int. J. Mass Spectrom.* **2001**, 206 (1–2), 63–78.

(29) Ehrler, O. T.; Yang, J. P.; Sugiharto, A. B.; Unterreiner, A. N.; Kappes, M. M. Excited state dynamics of metastable phthalocyanine-tetrasulfonate tetra-anions probed by pump/probe photoelectron spectroscopy. *J. Chem. Phys.* **2007**, *127* (18), 184301.

(30) Verlet, J. R. R.; Horke, D. A.; Chatterley, A. S. Excited states of multiply-charged anions probed by photoelectron imaging: riding the repulsive Coulomb barrier. *Phys. Chem. Chem. Phys.* **2014**, *16* (29), 15043–15052.

(31) Horke, D. A.; Chatterley, A. S.; Verlet, J. R. R. Effect of Internal Energy on the Repulsive Coulomb Barrier of Polyanions. *Phys. Rev. Lett.* **2012**, *108* (8). DOI: 10.1103/PhysRevLett.108.083003

(32) Horke, D. A.; Chatterley, A. S.; Verlet, J. R. R. Femtosecond Photoelectron Imaging of Aligned Polyanions: Probing Molecular Dynamics through the Electron-Anion Coulomb Repulsion. *J. Phys. Chem. Lett.* **2012**, 3 (7), 834–838.

## The Journal of Physical Chemistry Letters

Letter

(33) Jager, P.; Brendle, K.; Schwarz, U.; Himmelsbach, M.; Armbruster, M. K.; Fink, K.; Weis, P.; Kappes, M. M. Q and Soret Band Photoexcitation of Isolated Palladium Porphyrin Tetraanions Leads to Delayed Emission of Nonthermal Electrons over Microsecond Time Scales. J. Phys. Chem. Lett. **2016**, 7 (7), 1167–1172.

(34) Horke, D. A.; Chatterley, A. S.; Bull, J. N.; Verlet, J. R. R. Time-Resolved Photodetachment Anisotropy: Gas-Phase Rotational and Vibrational Dynamics of the Fluorescein Anion. *J. Phys. Chem. Lett.* **2015**, *6* (1), 189–194.

(35) Schalk, O.; Unterreiner, A. N. The influence of rotational diffusion on transient anisotropy in ultrafast experiments. *Phys. Chem. Chem. Phys.* **2010**, *12* (3), 655–666.

(36) Jung, Y.; Shen, J.; Liu, Y. H.; Woods, J. M.; Sun, Y.; Cha, J. J. Metal Seed Layer Thickness-Induced Transition From Vertical to Horizontal Growth of MoS<sub>2</sub> and WS<sub>2</sub>. *Nano Lett.* **2014**, *14* (12), 6842–6849.

(37) Snellenburg, J. J.; Laptenok, S. P.; Seger, R.; Mullen, K. M.; van Stokkum, I. H. M. Glotaran: A Java-Based Graphical User Interface for the R Package TIMP. *J. Stat. Softw.* **2012**, *49* (3), 1–22.

(38) Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R.; Galili, T.; Levanon, H. Novel mechanism for triplet state formation in short distance covalently linked radical ion pairs. *J. Am. Chem. Soc.* 2000, 122 (40), 9715–9722.

(39) Hou, Y. Q.; Biskup, T.; Rein, S.; Wang, Z. J.; Bussotti, L.; Russo, N.; Foggi, P.; Zhao, J. Z.; Di Donato, M.; Mazzone, G.; Weber, S. Spin-Orbit Charge Recombination Intersystem Crossing in Phenothiazine-Anthracene Compact Dyads: Effect of Molecular Conformation on Electronic Coupling, Electronic Transitions, and Electron Spin Polarizations of the Triplet States. *J. Phys. Chem. C* **2018**, 122 (49), 27850–27865.

(40) Ha-Thi, M. H.; Shafizadeh, N.; Poisson, L.; Soep, B. An Efficient Indirect Mechanism for the Ultrafast Intersystem Crossing in Copper Porphyrins. J. Phys. Chem. A **2013**, 117 (34), 8111–8118.

(41) Trinh, C.; Kirlikovali, K.; Das, S.; Ener, M. E.; Gray, H. B.; Djurovich, P.; Bradforth, S. E.; Thompson, M. E. Symmetry-Breaking Charge Transfer of Visible Light Absorbing Systems: Zinc Dipyrrins. J. Phys. Chem. C 2014, 118 (38), 21834–21845.

(42) Pomarico, E.; Pospisil, P.; Bouduban, M. E. F.; Vestfrid, J.; Gross, Z.; Zalis, S.; Chergui, M.; Vlcek, A. Photophysical Heavy-Atom Effect in Iodinated Metallocorroles: Spin-Orbit Coupling and Density of States. J. Phys. Chem. A **2018**, 122 (37), 7256–7266.

(43) Frei, F.; Rondi, A.; Espa, D.; Mercuri, M. L.; Pilia, L.; Serpe, A.; Odeh, A.; Van Mourik, F.; Chergui, M.; Feurer, T.; Deplano, P.; Vlcek, A.; Cannizzo, A. Ultrafast electronic and vibrational relaxations in mixed-ligand dithione-dithiolato Ni, Pd, and Pt complexes. *Dalton* T **2014**, 43 (47), 17666–17676.

(44) Chergui, M. On the interplay between charge, spin and structural dynamics in transition metal complexes. *Dalton T* **2012**, *41* (42), 13022–13029.

(45) El Nahhas, A.; Consani, C.; Blanco-Rodriguez, A. M.; Lancaster, K. M.; Braem, O.; Cannizzo, A.; Towrie, M.; Clark, I. P.; Zalis, S.; Chergui, M.; Vlcek, A. Ultrafast Excited-State Dynamics of Rhenium(I) Photosensitizers  $[Re(Cl)(CO)_3(N, N)]$  and  $[Re-(imidazole)(CO)_3(N, N)]^+$ : Diimine Effects. *Inorg. Chem.* 2011, 50 (7), 2932–2943.

(46) Cannizzo, A.; Blanco-Rodriguez, A. M.; El Nahhas, A.; Sebera, J.; Zalis, S.; Vlcek, A.; Chergui, M. Femtosecond fluorescence and intersystem crossing in Rhenium(I) Carbonyl-Bipyridine Complexes. *J. Am. Chem. Soc.* **2008**, *130* (28), 8967–8974.

(47) Zhou, M.; Higaki, T.; Li, Y. W.; Zeng, C. J.; Li, Q.; Sfeir, M. Y.; Jin, R. C. Three-Stage Evolution from Nonscalable to Scalable Optical Properties of Thiolate-Protected Gold Nanoclusters. *J. Am. Chem. Soc.* **2019**, *141* (50), 19754–19764.

(48) Hartland, G. V. Optical Studies of Dynamics in Noble Metal Nanostructures. *Chem. Rev.* 2011, 111 (6), 3858–3887.

(49) Jin, R. C.; Cao, Y. C.; Hao, E. C.; Metraux, G. S.; Schatz, G. C.; Mirkin, C. A. Controlling anisotropic nanoparticle growth through plasmon excitation. *Nature* **2003**, *425* (6957), 487–490.