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# Lead-enhanced gas-phase stability of multiply charged EDTA anions: a combined experimental and theoretical study

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Besides their fundamental importance, multiply charged anions (MCAs) are considered as promising molecular capacitors for which their intrinsic stabilities are of great significance. Herein, the gas-phase stabilities of ethylenediaminetetraacetic acid (EDTA) anions (i.e. [EDTA-nH]<sup>n</sup>, n = 1-4) and their Pb(II) complexes (i.e. [EDTA+Pb-nH]<sup>(2-n)-</sup>, n = 3, 4) have been investigated using an approach that combines extractive electrospray ionization mass spectrometry (EESI-MS) measurements, Car-Parrinello molecular dynamics simulations and density functional theory/Tao-Perdew-Staroverov-Scuseria calculations. The EESI-MS data showed that the doubly charged EDTA anions in the form of [EDTA-2H]<sup>2-</sup> and [EDTA+Pb-4H]<sup>2-</sup> were much more abundantly observed than the singly charged species such as [EDTA-H]<sup>-</sup> and [EDTA+Pb-3H]<sup>-</sup>, respectively. The calculation results indicated that [EDTA-2H]<sup>2-</sup> and [EDTA+Pb-4H]<sup>2-</sup> anions were thermodynamically more stable than the [EDTA-H]<sup>-</sup> and [EDTA+Pb-3H]<sup>-</sup> species in the gas phase, respectively. The [EDTA+Pb-3H]<sup>-</sup> anions preferred five-coordinated structure, whereas [EDTA+Pb-4H]<sup>2-</sup> anions formed either five-coordinated or six-coordinated structures. The calculations further revealed that significant electron clouds drifting from the ligand EDTA to the metal Pb(II) ions and the large distances between the carboxylic groups reduced the Coulomb repulsion among the excess electrons of these MCAs. Our data demonstrated that EESI-MS combined with theoretic calculations were able to provide a deep insight into the fundamental behavior of stability of MCAs in the gas phase and, thus, might be useful tools for studying MCAs for potential molecular capacitors. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: multiply charged anions; EDTA–Pb(II) complexes; molecular capacitor; gas-phase stability; extractive electrospray ionization mass spectrometry

# INTRODUCTION

Characterized by high energy content and other specific properties, multiply charged atomic and molecular ions are of fundamental and practical importance in many disciplines such as physical chemistry<sup>[1–5]</sup> and molecular capacitor design.<sup>[4,6–9]</sup> As a key for potential applications, the stability of multiply charged ions has been intensively studied.<sup>[4,7,10–13]</sup> Particularly, researches on the gas-phase stability of multiply charged anions (MCAs) are of increasing importance because some MCAs, especially those of moderate electron-binding energy, can be viewed as an electrostatic energy storage medium in the gas phase or promising molecular capacitors because multiple electrons can be stored and easily released from the molecule with less energy.<sup>[4,6,7]</sup>

Many aspects<sup>[3,5]</sup> such as molecular structures, sizes and geometry affect the stability and, thus, the electron capacitance of MCAs. To improve their stability in the gas phase, both theoretical<sup>[2,3,5,14]</sup> and experimental studies<sup>[4,5,7,10–12]</sup> have been carried out for in-depth understanding of MCAs. Early theoretical works<sup>[2,3,5]</sup> reported that gaseous MCAs are too unstable to be observed by experimental measurements because the Coulomb repulsion among excess electrons is too strong to make the MCAs are strongly dependent on theoretical calculations. Major theoretical advances in our understanding of MCAs have been made by the groups of Cederbaum and Simons. Cederbaum and co-workers investigated a series of gaseous MCAs<sup>[13,15]</sup> and proposed a construction principle for predicting the stability of gaseous MCAs.<sup>[1]</sup> Simons and co-workers performed the *ab initio* method to study the structure, bonding and stability of gas-phase MCAs and even presented a theoretical method to determine the stability of MCAs in the gas phase.<sup>[3]</sup>

The development of electrospray ionization allows the production of organometallic complexes in the gas phase from aqueous solutions.<sup>[14,16]</sup> Until now, electrospray mass spectrometry (ESI-MS) is the most widely used technique for estimating the gas-phase stability of MCAs for metal–ligands complexes,<sup>[16–18]</sup> in that it can

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provide much rich information regarding the structure, stoichiometry and metal oxidation state of dissolved metal ion complexes. Extractive electrospray ionization mass spectrometry (EESI-MS) has been demonstrated to be even softer than ESI-MS for characterization of compounds in complex liquid matrixes.<sup>[19–23]</sup> In the EESI-MS, the analytes are first nebulized by a nitrogen gas to form uncharged microdroplets, which are then ionized via collisions with the charged droplets generated by ESI spray. The separation of sample from the ESI high voltages enables the EESI-MS to become a much 'softer' ionization technique than ESI-MS,<sup>[21]</sup> and thus, it is of interest to be used for the detection of metastable or unstable gas-phase MCAs because most MCAs are difficult to obtain using electrochemical or spectroscopic, even ESI-MS, techniques.

Besides experimental measurements, theoretic tools are also important for MCA studies because the calculations can reveal a deep insight into the fundamental behavior of the stability of MCAs. Classical molecular simulations of organic and bio-organic molecules are firmly established and allow thorough dynamic investigations, but their applications in organometallic chemistry are complicated to be readily used. However, ab initio molecular dynamic simulations have been employed to successfully investigate the structures and conformations of ethylenediaminetetraacetic acid (EDTA)-metal ion species,<sup>[24,25]</sup> especially for the systems having strong intermolecular hydrogen-bonding interactions. In this work, Car-Parrinello molecular dynamics (CPMD) simulations, density functional theory (DFT)/Tao-Perdew-Staroverov-Scuseria (TPSS) calculations and EESI-MS<sup>[19-23]</sup> were employed together to investigate the structures and stability of the multiply charged EDTA anions and their Pb(II)-coordinated complexes in the gas phase. The theoretical results showed that both  $[EDTA-2H]^{2-}$  and  $[EDTA + Pb-4H]^{2-}$  anions were stable, even thermodynamically more stable than [EDTA-H]<sup>-</sup> and [EDTA + Pb-3H]<sup>-</sup> species, respectively, in the gas phase.

## **MATERIALS AND METHODS**

## **Material and reagents**

The monoclinic crystalline crystal of lead(II) acetate (Pb(Ac)<sub>2</sub>·3H<sub>2</sub>O) (AR grade) was bought from Damao Chemical Reagent Factory (Tianjin, China), and the disodium salt of EDTA (Na<sub>2</sub>H<sub>2</sub>Y.2H<sub>2</sub>O) was obtained from Xilong Chemical Plant (Shantou, China). Chemicals such as methanol (AR grade) were bought from Chinese Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were directly used without any pretreatment, unless dissolution and dilution with deionized water were necessary. A 500-µL of lead(II) acetate solution with a concentration of 0.02 mg/g was directly infused at a flow rate of 5 µL/min for EESI-MS analysis, without any further pretreatment. The same volume of EDTA/water solution with a concentration of 0.005 mg/g was delivered at a flow rate of 5 µL/min into the ESI emitter, by using a syringe pump, for generation of the primary ions and simultaneous extraction of the Pb(II) ions from the lead acetate compounds.

## Instrumental setup

Under the negative-ion detection mode, experiments were carried out using a commercial linear ion trap mass spectrometer (LTQ-XL, Finnigan, San Jose, CA) coupled with a homemade EESI source.<sup>[19–23]</sup> The principle and basic configuration of an EESI source were previously illustrated for rapid analysis of liquid<sup>[23]</sup> and metal uranyl species in natural water samples.<sup>[26]</sup> In this study, the EESI source described here was employed for identification

and characterization of the stability of doubly charged metalligands as well as multiply charged anions of [EDTA-nH]<sup>n-</sup> in the gas phase. In the EESI source, the neutral analytes underwent numerous collisions with the charged particles generated by the electrospray using a negative high voltage (-3.5 kV). During the collisions, online droplet-droplet extraction occurred between the neutral sample droplets and the charged droplets, allowing continuous extraction of interesting compounds and subsequent ionization of neutral analytes. The analyzed ions were then introduced into the linear trap quadrupole (LTQ) mass analyzer for mass analysis through the ion guide system of the LTQ-MS instrument. The distance (a) between the end tips of the two sprays and the distance (b) between the spray tips of the EESI source and the MS inlet were 2 and 5 mm, respectively. The angle (a) between the electrospray beam and the MS inlet of the LTQ-MS instrument and the angle (b) between the two spray beams were 150° and 60°, respectively. The LTQ-MS instrument was running in the negative-ion detection mode. The temperature of the heated capillary of the LTQ-MS was maintained at 180 °C, and the pressure of both spray ESI and sample nebulization was optimized to be 1 MPa. The default values of voltages were used for the heating capillary, the tube lenses, the conversion dynodes, the detectors and so on. Further optimization was not performed. All full-scan mass spectra were recorded using the Xcalibur software of the LTQ-MS instrument with an average time of 30 s. The precursor ions of interest were isolated using a mass window of 1.4 mass/charge (m/z) unit. Collision-induced dissociation (CID) experiments were performed by applying 15%–30% collision energy for 30 ms to the precursor ions. MS<sup>n</sup> spectra were collected with a recording time of more than 30 s if necessary.

## **Theoretical calculations**

There are three types of stability including electronic, geometrical and thermodynamical stability that should be considered<sup>[3,5]</sup> when we discuss the stability of MCAs. The first is electronic stability of the anion. If  $A^{n-}$ , at its own optimal geometry, is more stable than the corresponding  $A^{(n-1)-}$  at the same geometry, we consider  $A^{n-}$  to be vertically electronically stable. If  $A^{n-}$  at its optimal geometry is more stable than  $A^{(n-1)-}$  at its own optimal geometry, we consider  $A^{n-}$  to be adiabatically electronically stable. In addition, there is the issue of geometrical stability. If  $A^{n-}$  has all real vibrational frequencies at its optimal geometry, it is locally geometrically stable. Finally, if  $A^{n-}$  is more stable than any possible dissociation fragment, it is thermodynamically stable. Clearly, if an anion is thermodynamically stable, it must also be electronically and geometrically stable.

The vertical electron detachment energy (VDE) of a dianion can be determined as the difference in total energy between the optimized dianion complex and the singly charged anion calculated at the dianion geometry. The adiabatic electron detachment energy (ADE) of a dianion can be calculated as the difference in energy between the optimized geometries of the dianion and singly charged anion complexes. The VDE and ADE of a singly charged anion are defined in a similar way between the anion and the corresponding neutral. The same ways can be used to obtain the VDE and ADE of triply and quadruply charged anions. All complexes with single-spin states correspond to the lowest energy, which are used to calculate the ADE and VDE corrected by zero-point vibrational energy (ZPE), without anharmonic scaling.

Ab initio molecular dynamics (MD) simulations were performed to investigate the structures of EDTA and its complexes with Pb(II) in the gas phase. Trajectories of 10 ps CPMD simulation<sup>[27]</sup> of each species were generated, the potential energy profiles were plotted and examined to determine the local minimals, and then configurations at those local minimals of potential energy were extracted from the trajectory for further study. DFT with plane-wave basis set at kinetics cutoff of 70 Rydberg and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional<sup>[28]</sup> combined with Troullier-Martin norm-conserving pseudopotentials<sup>[29]</sup> were used to calculate the potential energy. The exchange-correlation energy of Pb(II) atom was calculated with a nonlinear core correction.<sup>[30]</sup> To generate the trajectories, an 11-ps-duration CPMD for each species was performed, and the last 10 ps was used for conformational search. The time step for the simulation was set to 5 a.u. (0.12 fs), and the fictitious electronic mass was set to 500 a.u. Configurations were sampled at each MD step. The initial configurations of the clusters of  $[EDTA-3H+Pb]^{-}$  and  $[EDTA-4H+Pb]^{2-}$  were based on the experimental crystal structure of K<sub>2</sub>Pb(EDTA). 2H<sub>2</sub>O<sup>[31]</sup>and were optimized with plane-wave DFT method. The initial conformations of the  $[EDTA-nH]^{n-}$  (n = 1-4) ions were based on the initial geometry structure of neutral EDTA from the NIST (National Institute of Standards and Technology) Standard Reference Database Number 69 (http://webbook.nist.gov/cgi/cbook.cgi?Name=EDTA&Units=SI). Then, wavefunction was determined by self-consistent calculation converged at 1.0 D-6 a.u. followed by CPMD simulations. To simulate the gas-phase system, that is, to eliminate the interaction of the system with its periodic images, a large periodical box with side length of 1.5 nm was used, and Tuckerman Poisson solver method was also used to diminish the self-interaction.<sup>[32]</sup> The CPMD code, version 3.5, was used.<sup>[27]</sup>

The first 10 lowest energy structures for each anion species archived from CPMD then undergo geometrical optimization without any symmetry constraints by using DFT with the TPSS functional,<sup>[33]</sup> as implemented using the Gaussian 03 package.<sup>[34]</sup> Harmonic vibrational frequencies were estimated at the same level to ensure the stationary points as local minima. ZPE and thermal corrections obtained at 298.15 K and 1 atm without scale were included in all calculations. The 6-311 + G(d, p) basis set was used for the ligand atoms, whereas for the metals, the effective core potential of Wadt and Hay (Los Alamos effective core potential (ECP)) included in the LanL2DZ basis set was applied.<sup>[35-37]</sup> This ECP has been demonstrated to provide reliable results for a variety of transition metal complexes<sup>[38,39]</sup> and Pb(II) coordination compounds. Compared with the all-electron basis sets, the use of ECPs can be capable of achieving a comparable level of accuracy to all-electron basis set of double-zeta split-valence polarization (DZVP),<sup>[40]</sup> accounting for its relativistic effects to some extent. It is believed that relativistic effects will become especially important for the heavy metal atoms. The natural bond order (NBO) analysis<sup>[41]</sup> was performed to gain insight into the nature and stability of the metal-ligand bonds in the metal complexes. The NBO method estimates the stabilization energy associated with the electron donor-acceptor interactions, E(2), by using second-order perturbation theory. The transfer of electron density from the ligands to the Pb ions was characterized by the natural atomic charges using the natural population analysis (NPA) by the NBO 3.0 program incorporated into the Gaussian 03 package, on the basis of the optimized structures at the TPSS/6-311 + G (d, p) level. Different values of the spin multiply were considered for the calculations of  $[EDTA + Pb-3H]^{-}$  and  $[EDTA + Pb-4H]^{2-}$  species. The electronic states with the lowest spin number (ns = 1) were found to be energetically more favorable for all complexes.

# **RESULTS AND DISCUSSION**

#### Extractive electrospray mass spectrometry observations

In the full-scan EESI-MS spectrum recorded using EDTA water solutions, the doubly charged [EDTA-2H]<sup>2-</sup> anions (*m*/*z* 145) were much more intensively observed than the singly deprotonated [EDTA-H]<sup>-</sup> species (*m*/*z* 291), as shown in Fig. 1(a). Similarly, in the mass spectrum obtained using EDTA-Pb(II) water solutions, higher abundances of doubly charged [EDTA + Pb-4H]<sup>2-</sup> species were also observed compared with the singly charged [EDTA + Pb-3H]<sup>-</sup> anions, as shown in Fig. 1(b). Note that no triply and quadruply charged negative ions such as [EDTA-3H]<sup>3-</sup> and [EDTA-4H]<sup>4-</sup> could be found in the mass spectra recorded using either EDTA or EDTA-Pb water solutions, probably because the Coulomb repulsion between excess electrons made such multiply charged anions unstable in the gas phase.

The two excess electrons in the doubly charged negative ions  $[EDTA-2H]^{2-}$  (m/z 145) were rigidly survived during the CID experiments. For example, the neutral loss of water and CO<sub>2</sub> species were preferably observed than to detach electrons from the precursor ions of [EDTA-2H]<sup>2–</sup> (m/z 145) in the MS/MS experiment. This resulted in a major peak of the doubly charged product ions of m/z 127 in the MS/MS spectrum (Fig. 2(a)). More interestingly, the product ions of two electrons were predominantly detected at m/z 109 in the MS<sup>3</sup> spectrum (Fig. 2(b)). These data provided solid experimental evidences for that; in comparison with the singly charged species, the [EDTA-2H]<sup>2-</sup> ions were unusually stable in the gas phase. These findings stimulated similar CID measurements on anions such as [EDTA + Pb-4H]<sup>2-</sup>. As expected, neutral loss of water and CO<sub>2</sub> from the [EDTA + Pb-4H]<sup>2-</sup> anions was also detected in the MS/MS experiments, and the major fragments maintained the negative charges without electron detachment. The same fragmentation pattern was observed using various EDTA-Pb complexes labeled with lead isotopes including <sup>208</sup>Pb, <sup>207</sup>Pb and <sup>206</sup>Pb (Fig. 3). Generally, because of the Coulomb repulsion between two electrons, the stability of doubly charged anions should be much lower than the corresponding singly charged anions. The experimental observations indicated that the anions of EDTA and EDTA-Pb complexes should have deep insights into the fundamental behavior that accounts for the unusual stability in the gas phase. Therefore, to interpret these experimental observations, ab initio MD simulations and DFT calculations were carried out.

## Geometrical stability study

The stability and thermodynamics of a compound depend heavily on the molecular geometry.<sup>[3,5]</sup> MCA is geometrically stable on the condition that all the vibrational frequencies are real at its locally optimal geometry. To obtain these local minimal structures, the accuracy of the chosen theory was first justified with a test of the [EDTA + Pb-4H]<sup>2–</sup> complex. The results showed that TPSS density functional gives much more consistent results with experimental values compared with those of the B3LYP, BP86 or PBE functionals (Table S1 in the supporting information). Thus, the TPSS functional was then chosen for further geometrical optimization and frequency calculation after achieving several local minimum structures obtained by CPMD simulations. Results



Figure 1. Ethylenediaminetetraacetic acid (EDTA) anion signals recorded using extractive electrospray ionization mass spectrometry with different EDTA solutions: (a) disodium salt of EDTA water solutions, (b) Pb(II)–EDTA water solutions.



Figure 2. The fragmentation pathways of  $[EDTA-2H]^{2-}$ : (a)  $MS^2$  mass spectrum of m/z 145, (b)  $MS^3$  mass spectrum of m/z 127.

showed that different local minimum structures obtained from the CPMD simulations gave very similar configuration after geometrical optimization by TPSS functional. In this study, the two structures are assumed to belong to the same family when the difference of Gibbs energies between very similar structures is within 0.05 kJ/mol. Figures S1–S4 in the supporting information show the several low-energy isomers of  $[EDTA-nH]^{n-}$  (n = 1-4) calculated at TPSS/6-311+G (d, p) level. The minimum energy geometry structures of [EDTA + Pb-3H]<sup>-</sup> and [EDTA + Pb-4H]<sup>2-</sup> complexes are shown in Figs S5 and S6, respectively. Note that Figs S1(a)-S6(a) correspond to the lowest energy structures for each species. All really vibrational frequencies for these anionic species were calculated at their optimized structures at the same level (Table S2), demonstrating that all these MCAs are locally geometrically stable. The application of ab initio MD (CPMD) simulation method plays important roles in the modeling of these systems with strong intermolecular hydrogen-bonding interactions, which is difficult to obtain using the static quantum chemical calculations or classical molecular simulations. The calculated results show that the relative stable isomer for each type of anionic species usually possesses large numbers of

hydrogen bonds. The lowest energy isomer for each  $[EDTA-nH]^{n-}$ , (n = 1-3) has 17 hydrogen bonds, whereas the relative stable  $[EDTA-4H]^{4-}$  anions has 14 hydrogen bonds.

Interestingly, it was found that the  $[EDTA-3H+Pb]^{-}$  system prefers a five-coordinated configuration in the gas phase (Scheme 1(a)) because all the first three low energy isomers (Fig. S5(a)-(c)) have five coordinations. For these three isomers, the long Pb–N<sub>2</sub> bond (distances ranging from 2.70 to 2.85 Å) in proximity of the hydroxyl group and the relatively short Pb-N<sub>15</sub>  $(Pb-N_{15} = 2.47-50 \text{ Å})$  and  $Pb-O_{21}$   $(Pb-O_{21} = 2.27-2.30 \text{ Å})$  bonds in the opposite suggest that they are in hemidirected coordination,<sup>[42]</sup> with a stereochemically active lone pair of electrons in the proximity of the hydroxyl group. The isomer, as shown in Fig. S5(d), can be regarded as six-coordinated by two nitrogen and three oxygen atoms from carboxylic group, as well as by an irregular coordinated bond from the oxygen of the hydroxyl group. However, the bond length Pb-O<sub>8</sub> (L) of hydroxyl group in  $[EDTA + Pb-3H]^ (Pb-O_8 = 2.91 \text{ Å})$  is longer than a normal ionic radii ( $R_1 = 2.60$  Å) but shorter than a typical van der Waals radii  $(R_2 = 3.54 \text{ Å})$ .<sup>[43]</sup> The relatively long Pb–O<sub>8</sub> bond in the hydroxyl group would suggest the presence of an active lone pair in the





**Figure 3.** Validation of fragmentation pathways of  $[EDTA + Pb-4H]^{2-}$  by the different isotopes of Pb: MS<sup>2</sup> mass spectrum of m/z 248 (a), 247 (b) and 246 (c), respectively.



Scheme 1. Significantly increased stabilities of (a) [EDTA-3H]<sup>3-</sup> and (b) [EDTA-4H]<sup>4-</sup> by complexing lead(II).

proximity of the hydroxyl group, and the very short Pb–O<sub>21</sub> bond (Pb–O<sub>21</sub> = 2.25 Å) opposite indicates that the lone pair should be located opposite to the Pb–O<sub>21</sub> bond (Scheme 1(a)).

For the  $[EDTA-4H + Pb]^{2-}$  complex, the calculated Gibbs free energy of five-coordinated complex is slightly smaller (about 0.04 KJ/mol) than that of six-coordinated isomer, indicating that two configurations nearly have the same possibility for an existence in the gas phase in contrast to only six coordinates found in crystal structure<sup>[31]</sup> or in previous study.<sup>[38,39]</sup> The differences of calculated Gibbs free energies between the two isomers are so small (within the calculated errors) that they can be ignored in the present study. Note that all calculations related to  $[EDTA + Pb-4H]^{2-}$  complex in the following are based on the structure with six-coordinated isomers. The six-coordinated  $[EDTA + Pb-4H]^{2-}$  isomer has C<sub>2</sub> symmetry, for which there are two pairs of equivalent carboxylate rings (two G and R glycinate rings) (Scheme 1(b)), together with one ethylenediamine ring (E ring). The highly symmetric geometry of  $[EDTA + Pb-4H]^{2-}$ 

enhances its stability to some extent and, hence, shows much more abundant than the [EDTA + Pb-3H]<sup>-</sup> ions in the EESI-MS spectrum (Fig. 1(a)). Similar to [EDTA + Pb-3H]<sup>-</sup>, [EDTA + Pb-4H]<sup>2-</sup> also has the hemidirected structure. The natural bond orbital analysis shows that the Pb(II) lone pair orbital is predominantly 6s but is slightly polarized by a small 6p contribution, about 4.72% and 2.98% for complexes of [EDTA + Pb-3H]<sup>-</sup> and [EDTA + Pb-4H]<sup>2-</sup>, respectively (Table S3). This further confirms that these two EDTA-Pb(II) ions ([EDTA + Pb-4H]<sup>2-</sup> and [EDTA + Pb-3H]<sup>-</sup>) are hemidirectly structured.<sup>[42]</sup> On the other hand, the data provide evidences that the relatively large fraction of polarized 6p is responsible for better stability of the [EDTA + Pb-4H]<sup>2-</sup> rather than the [EDTA + Pb-3H]<sup>-</sup> ions.

#### **Electronic stability investigation**

The electronic stability of the MCAs was investigated in terms of VDE and ADE for better characterization of the stability of MCAs.<sup>[3,5]</sup> As shown in Table 1, all the singly and doubly charged anions have positive VDE and ADE, showing that all of them are electronically stable in the gas phase. On the contrary, negative VDE (-2.1593, -5.3491) and ADE (-2.7734, -5.7390) are found for the triply charged anions ([EDTA-3H]<sup>3-</sup>) and guadruply charged anions ([EDTA-4H]<sup>4-</sup>), respectively, indicating that they are not stable in the gas phase. These data are consistent with the EESI-MS spectra, where no signal of  $[EDTA-3H]^{3-}$ or [EDTA-4H]<sup>4-</sup> ions (Fig. 1(a)) was detected. For the stable gas-phase MCA species, it must overcome the strong Coulomb repulsion of excess electrons. However, the calculated Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies confirm that [EDTA-3H]<sup>3-</sup>, instead of  $[EDTA-4H]^{4-}$ , is the most unstable species, whereas the  $[EDTA+Pb-4H]^{-2}$  ion is mostly stabilized by the energy difference between its HOMO and LUMO orbits of -4.7127 eV (Table S4). Moreover, the  $[EDTA-2H]^{2-}$  and  $[EDTA + Pb-4H]^{2-}$  ions are more stable than [EDTA-H]<sup>-</sup> and [EDTA + Pb-3H]<sup>-</sup>, respectively. This is partially attributed to the large distances between their carboxylate groups, allowing the excess electrons to be widely delocalized over the carboxylate groups, and thereby notably reducing the strong Coulomb repulsion between the electrons.<sup>[4]</sup>

**Table 1.** Calculated vertical (VDE) and adiabatic (ADE) electron detachment energies for [EDTA-nH]<sup>n-</sup>, (n = 1–4) and [EDTA + Pb-nH]<sup>(n-2)-</sup>, (n = 3–4)<sup>a</sup>

Compounds	VDE (eV)	VDE (nm)	ADE (eV)	ADE (nm)
[EDTA-H] <sup>-</sup>	3.5145	353	2.4053	516
[EDTA-2H] <sup>2-</sup>	0.7295	1701	0.4177	2970
[EDTA-3H] <sup>3-</sup>	-2.1593	575	-2.7734	44
[EDTA-4H] <sup>4-</sup>	-5.3491	232	-5.7390	216
$[EDTA + Pb-3H]^{-}$	4.5619	272	4.3923	282
$[EDTA + Pb-4H]^{2-}$	1.0562	1175	0.7836	1583
	2.4738 <sup>b</sup>	501 <sup>b</sup>		

<sup>a</sup>The VDE and ADE of all MCAs were calculated on the basis of their lowest energy ground states.

<sup>b</sup>The VDE for removing electrons from second molecular orbital was obtained, on the basis of the relative energy difference between the highest and second molecular orbital energies, as well as the VDE for the first electron detachment.

<sup>c</sup>The ZPE corrections were made for all VDE and ADE energies.

<b>Table 2.</b> Natural population analysis charges calculated for [EDTA-nH] <sup><math>n-1</math></sup> and [EDTA + Pb-nH] <sup><math>(2-n)-1</math></sup> , (n = 3, 4) complexes				
Atoms (EDTA 2013- (EDTA 10) - 2013- (EDTA 4014- (EDTA 10) - 4012-				

Atoms	[EDTA-3H] <sup>3-</sup>	[EDTA + Pb-3H]	[EDTA-4H] <sup>4-</sup> [	$EDTA + Pb-4H]^{2-}$		
Pb	NA	1.423	NA	1.434		
$0_8 + 0_7$	-1.325	-1.287	-1.606	-1.499		
$O_{21} + O_{20}$	<sub>0</sub> —1.591	-1.475	-1.606	-1.499		
$0_{27} + 0_{20}$	<sub>6</sub> –1.592	-1.487	-1.613	-1.500		
$O_{33} + O_{32}$	2 -1.559	-1.477	-1.613	-1.500		
NA, not applicable.						

On the other hand, the NPA (Table 2) reveals that considerable amounts of electrons have transferred to the Pb atom from the oxygen atoms in the EDTA-Pb complexes. This phenomenon can also be intuitively seen from the highest occupied molecular orbitals for  $[EDTA + Pb-3H]^{-}$  and  $[EDTA + Pb-4H]^{2-}$  (Fig. S2). This significantly weakens the interactions between electrons, resulting in enhanced stability of the EDTA-Pb anions. Table 2 shows that the natural atomic charges of Pb in complex [EDTA + Pb-3H]<sup>-</sup> (NPA = 1.423) is smaller than that in  $[EDTA + Pb-4H]^{2-}$  (NPA = 1.434), indicating that the electron transfer is more pronounced for  $[EDTA + Pb-3H]^{-}$  species than that of  $[EDTA + Pb-4H]^{2-}$ . This is also reflected by the electron population of 6p orbital (Table S3), which is 0.66 for lead in the  $[EDTA + Pb-3H]^{-}$  and 0.61 in  $[EDTA + Pb-4H]^{2-}$ , respectively. The capability of transition metals for acceptance of electrons is heavily dependent on the nature of the accepting empty orbital. This is favored by the vacant 6p orbital of Pb<sup>2+</sup> ions in the complexes. The coordination of EDTA to Pb(II) atoms can be embodied from the strong interaction of Pb(II) atoms with the EDTA ligands by second-order perturbative energy E(2) (Table S5), in which the dominated interactions are resulted from the  $\boldsymbol{\sigma}$ donation of the lone pair electrons of the nitrogen (LP(N)) and oxygen atoms (LP(OG) or LP(OR)) to antibonding sp-hybridized orbitals (or s orbitals) on Pb ions, LP\*(Pb). Note that all NPA analyses were performed on the basis of the lowest energy structure after optimization. These data support that  $[EDTA + Pb-4H]^{2-}$ and [EDTA + Pb-3H]<sup>-</sup> are much more stable species with respect to [EDTA-4H]<sup>4-</sup> and [EDTA-3H]<sup>3-</sup> ions, respectively.

## Thermodynamic stability evaluation

The thermodynamic stability is the most important property of MCAs considered as potential molecular capacitors.<sup>[4,6]</sup> Thermodynamically stable anions must be electronically and geometrically stable. However, many small MCAs that are electronically and locally geometrically stable are not certainly thermodynamically stable because they may readily undergo molecular dissociation and electron autodetachment.<sup>[3]</sup> Thus, it is critical to characterize the thermodynamic stability of EDTA anions by using both theoretic methods and experimental tools.

Neutral loss of species such as water and carbon dioxide from  $[EDTA-2H]^{2-}$ ,  $[EDTA + Pb-4H]^{2-}$  and  $[EDTA + Pb-3H]^{-}$  anions was observed in the MS/MS experiments (Figs 2–4, respectively). The CID data (Fig. 2) imply that the electron-binding energies of the doubly charged EDTA anions are larger than the corresponding energies required to cleave C–H and C–C bonds for generation of water and carbon dioxide. The energies required for production of two CO<sub>2</sub> and H<sub>2</sub>O from the EDTA dianions were precisely calculated to be 121.51 and 61.50 kcal/mol, respectively (Table 3). Thus, the electron-binding energy of the EDTA dianions was estimated to be higher than 121.51 kcal/mol.





Figure 4. Validation of fragmentation pathways of  $[EDTA + Pb-3H]^-$  by the different isotopes of Pb: MS<sup>2</sup> mass spectrum of m/z 497 (a), 496 (b) and 495 (c), respectively.

<b>Table 3.</b> Calculated dissociation energies ( $\Delta E$ ) of [EDTA-nH] <sup>n-</sup> , (n = 1–2) and [EDTA + Pb-nH] <sup>(n-2)-</sup> , (n = 3–4) in the gas phase (kcal/mol). <sup>a</sup>				
Reactants	Fragments	ΔE		
[EDTA-H] <sup>−</sup> →	$[EDTA-H-CO_2]^-+CO_2$	25.74		
	$[EDTA-H-H_2O]^- + H_2O$	48.41		
$[EDTA-2H]^{2-} \rightarrow$	[EDTA-2H-2CO <sub>2</sub> ] <sup>2-</sup> + 2CO <sub>2</sub>	121.51		
	[EDTA-2H-2H <sub>2</sub> O] <sup>2-</sup> + 2H <sub>2</sub> O	61.50		
$[EDTA + Pb-3H]^{-} \rightarrow$	$[EDTA + Pb-3H-2CO_2]^- + 2CO_2$	16.99		
	$[EDTA + Pb-3H-H_2O]^- + H_2O$	35.59		
$[EDTA + Pb-4H]^{2-} \rightarrow$	$[EDTA + Pb-4H-2CO_2]^{2-} + 2CO_2$	81.69		
	$[EDTA + Pb-4H-2H_2O_2]^{2-} + 2H_2O_2$	153.50		
<sup>a</sup> ΔE is the ZPE-corrected energy.				

Under the mild CID conditions with low collision energy (15% collision energy), no electron detachment was observed for both  $[EDTA-2H]^{2-}$  and  $[EDTA+Pb-4H]^{2-}$  anions. Charge separation was detected for  $[EDTA-2H]^{2-}$  ions with 18% CE and  $[EDTA+Pb-4H]^{2-}$  ions with 28% CE. Under such CID conditions (about 153.50 kcal/mol), singly charged negative fragments of m/z 332, 331 and 329 were detected (Fig. 3) because one of the two electrons was emitted from the  $[EDTA+Pb-4H]^{2-}$  complexes during the dissociation process. Similar fragmentation patterns were observed in the CID spectra recorded using  $[EDTA+Pb-4H]^{2-}$  labeled with Pb isotopes (Fig. 3(b) and (c)), providing that the  $[EDTA+Pb-4H]^{2-}$  ions have the most possibility of thermodynamic stability, with

electron-binding energy of about 153.50 kcal/mol. All the major products still maintain the -2 charge state for fragmentation of doubly charged ions in the MS/MS, on the other hand, indicating that there may exist a repulsive Coulomb barrier against electron detachment for  $[EDTA + Pb-4H]^{2-}$  ions. The repulsive Coulomb barrier of  $[EDTA-2H]^{2-}$  and  $[EDTA + Pb-4H]^{2-}$  anions were estimated to be approximately 70.65 and 52.71 kcal/mol, respectively, on the basis of the Coulomb's law,  $e^2/4\pi\epsilon_0 r$ , where r was the effective distance between the two excess electrons in Å,<sup>[7,11]</sup> indicating that these two doubly charged EDTA-Pb(II) species might also be dynamically stable. This is likely attributed to the molecular structures of the anions, which also play important roles for stabilization of the multiply charged anions.<sup>[4,44]</sup>

On the basis of the EESI-MS/MS spectral data, all the fragmentation pathways were calculated to be endothermic and, thus, are not favored in the gas phase (Table 3). These theoretical results confirm that all the anions, except for  $[EDTA-3H]^{3-}$  and  $[EDTA-4H]^{4-}$  ions, are thermodynamically stable in the gas phase. Note that the  $[EDTA+Pb-4H]^{2-}$  and  $[EDTA-2H]^{2-}$  anions are more stable than their corresponding singly charged anions  $[EDTA+Pb-3H]^{-}$  and  $[EDTA+Pb-3H]^{-}$  and  $[EDTA+Pb-3H]^{-}$  and  $[EDTA+Pb-3H]^{-}$  and  $[EDTA+Pb-3H]^{-}$  and  $[EDTA+Pb-3H]^{-}$  and  $[EDTA+Pb-3H]^{-}$  in the relative highly symmetric geometry also plays a key role in the stabilization. A total amount of 81.69 and 153.50 kcal/mol are required to fragment the  $[EDTA+Pb-4H]^{2-}$  ions for generation of  $[EDTA+Pb-4H-2CO_2]^{2-}$  and  $[EDTA+Pb-4H-2H_2O]^{2-}$  species, respectively. Therefore, the  $[EDTA+Pb-4H]^{2-}$  ions are the most thermodynamically stable multiply charged anions from theoretical calculations in this work. This can also be reflected from the

EESI mass spectra (Fig. 1(b)) to some extent, in which the signal abundance of  $[EDTA + Pb-4H]^{2-}$  (*m*/*z* 248) is much higher than that of  $[EDTA + Pb-3H]^{-}$  (*m*/*z* 247).

Further calculations were performed for estimation of the energy required to release the electrons from the MCAs. As shown in Table 1, the emission of the first and the second electrons from  $[EDTA + Pb-4H]^{2-}$  is likely to be enabled by light irradiation, with the detachment photon energies (h $\gamma$ ) of 1.0562 eV (1175 nm wavelength) and 2.4738 eV (501 nm wavelength), respectively. Once the noncovalent interaction between the Pb(II) and the EDTA skelecton is broken, the rest electrons can be readily released. This promisingly makes  $[EDTA + Pb-4H]^{2-}$  anions to be considered as a potential molecular capacitor, allowing the electrons to be released under different conditions.

## CONCLUSIONS

The CPMD simulations and DFT/TPSS calculations were combined to interpret the EESI-MS measurements in which the signal intensities of doubly charged EDTA anions ([EDTA-2H]<sup>2-</sup> and [EDTA + Pb-4H]<sup>2-</sup>) were much stronger than the singly charged species ([EDTA-H]<sup>-</sup> and [EDTA + Pb-3H]<sup>-</sup>). The theoretical calculations displayed that the singly charged EDTA-Pb(II) anions preferred five-coordinated structures, whereas the doubly charged [EDTA + Pb-4H]<sup>2-</sup> complex either formed five-coordinated or six-coordinated structures in the gas phase. The complexation of Pb(II) with [EDTA-HI]<sup>n-</sup> (n=3, 4) substantially improves the stability of multiply charged EDTA anions in the gas phase.

Both [EDTA-2H]<sup>2-</sup> and [EDTA + Pb-4H]<sup>2-</sup> anions were found to be even thermodynamically more stable than [EDTA-H]<sup>-</sup> and [EDTA + Pb-3H]<sup>-</sup> species, respectively, in the gas phase. These can be reflected by the EESI-MS/MS data. The stabilization of MCAs of EDTA-Pb complexes is mainly attributed to the fact that considerable amounts of electrons are transferred from the EDTA to Pb(II) ions and the geometric symmetry of the anions. Consequently, the strong Coulomb repulsion between the excess electrons in the anions of EDTA-Pb complexes is substantially reduced. The electron-binding energy of  $[EDTA + Pb-4H]^2$  was estimated to be about 153.50 kcal/mol. The moderate binding energies make the MCAs of EDTA-Pb complexes promising molecular capacitors, allowing the electrons to be emitted in a step-by-step way when irradiated by photons of different wavelengths. The results show that forming complexes with transition metal (e.g. lead) is an alternative strategy to stabilize MCAs in the gas phase. The approach combining EESI-MS measurements and theoretical calculations can be useful to provide valuable information to build molecular capacitors.

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Supporting information may be found in the online version of

#### **Supporting Information**

this article.

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