

Surface Chemistry

Anion–Anion Chemistry with Mass-Selected Molecular Fragments on Surfaces

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Abstract: While reactions between ions and neutral molecules in the gas phase have been studied extensively, reactions between molecular ions of same polarity remain relatively unexplored. Herein we show that reactions between fragment ions generated in the gas phase and molecular ions of the same polarity are possible by soft-landing of both reagents on surfaces. The reactive $[B_{12}I_{11}]^{1-}$ anion was deposited on a surface layer built up by landing the generally unreactive $[B_{12}I_{12}]^{2-}$. Ex-situ analysis of the generated material shows that $[B_{24}I_{23}]^{3-}$ was formed. A computational study shows that the product is metastable in the gas phase, but a charge-balanced environment of a grounded surface may stabilize the triply charged product, as suggested by model calculations. This opens new opportunities for the generation of highly charged clusters using unconventional building blocks from the gas phase.

The chemistry of highly reactive ions is intrinsically difficult to investigate in the condensed phase.^[1] The lifetime of reactive ions is usually short because uncontrolled reactions with the surrounding medium occur. Therefore, reactions of highly reactive charged intermediates can usually only be studied within the gas phase using mass spectrometers.^[2,3] “Ion–ion chemistry”^[4,5] (referring to the reaction of an anion

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with a cation) has also been addressed using mass spectrometry^[6] resulting in important applications, e.g., sequencing of peptides by electron transfer dissociation (ETD).^[7] In contrast, reactions between ions of equal polarity inside a mass spectrometer usually do not occur.^[8] In solution, reactions between equally charged ions in the presence of counterions and solvent molecules are possible.^[9,10] However, in the gas phase, the unshielded electrostatic repulsion inside of ion traps and quadrupole mass analyzers usually results in ion distances of more than 10^4 Å.^[11] This means that ion–ion reactions between ions of same polarity face inherent difficulties.

Herein, we provide solid evidence that chemical reactions between a molecular fragment anion generated in the gas phase and an intact doubly charged anion can occur in layers on surfaces. The observed products are stable under ambient conditions, but would be virtually inaccessible by classical synthetic methods. The reactive anion is soft-landed^[12,13] from the gas phase onto a surface layer containing the anionic reaction partner. The possibility of covalently binding mass-selected reactive ions to ions of the same polarity on top of a surface opens new perspectives for the precisely controlled formation of larger, highly charged clusters with tailored electronic properties at functional interfaces. This may be relevant to emerging research fields, including energy storage and molecular electronics.^[14–17]

Suitable gaseous anions for a proof-of-concept study should be highly reactive and able to form stable products with other anions. The chemistry of the $[B_{12}X_{11}]^{1-}$ fragment anions (generated by collision-induced dissociation (CID) from *closo*-dodecaborate anions $[B_{12}X_{12}]^{2-}$ (with $X = Cl, Br,$ and CN)) has been recently investigated. Despite their negative charge, $[B_{12}X_{11}]^{1-}$ anions are strongly electrophilic as experimentally demonstrated by the spontaneous binding of noble gases.^[18–21] Therefore, $[B_{12}X_{11}]^{1-}$ anions seem to be ideal candidates to probe anion–anion reactions because these ions are prone to react with electron-donating compounds. In this study, we use the $[B_{12}I_{11}]^{1-}$ anion.

For the investigation described here, a high-throughput electrospray source coupled to an ion soft-landing instrument was built. A schematic drawing is shown in Figure 1. The design is similar to that recently introduced by Su et al.^[22] A gold surface was used as deposition target and was covered with a fluorinated alkane-thiol self-assembled monolayer (FSAM), which dissipates the collisional energy of the deposited ions efficiently and provides a thin insulating layer between deposited ions and conductive surface. A picoammeter measured the current during the deposition. We were able to generate mass-selected $[B_{12}I_{11}]^{1-}$ ion currents of

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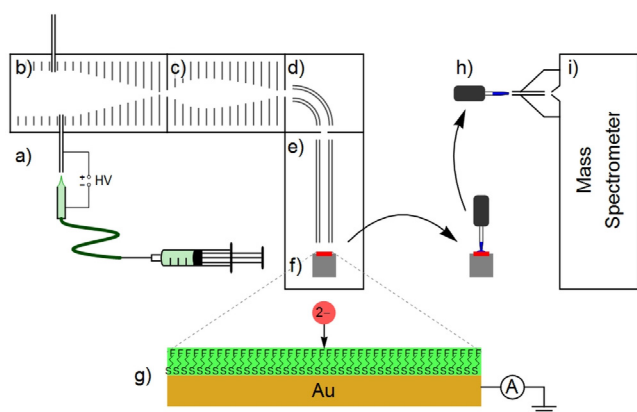


Figure 1. Schematic representation of the experimental setup with a) an electro spray source, b) a high pressure ion funnel, c) a low pressure ion funnel, d) a bent ion guide, e) a resolving quadrupole, f) a sample holder with deposition target, g) a magnification of the surface (ions are deposited on FSAM on gold, which is grounded via a picoammeter), h) a LESA setup (solvent: 90:10 CH₃CN:H₂O), and i) an analytical mass spectrometer.

0.3 nA to 0.5 nA, which is significantly higher than that previously reported for CID-generated fragment ions in similar setups.^[21] As a consequence, it was possible to fabricate layers on surfaces visible by bare eye in an area of 3 × 3 mm² within the time frame of one day by delivering approximately 2 × 10¹⁴ ions. An average layer thickness of 40 nm is estimated (section SI1). After deposition, the surface was removed from the vacuum chamber. Mass-spectrometric analysis of the reaction products formed by [B₁₂I₁₁]¹⁻ deposition on the surface was carried out using Liquid Extraction Surface Analysis (LESA).^[23] Experimental details can be found in the supporting information (section SI2).

Figure 2 shows mass spectra in the *m/z* range from 700 to 1100 obtained in the negative ion mode. The doubly charged ionic species labeled **1** to **4** are in good agreement with the results obtained from previous deposition experiments with similar reactive anions,^[21] and can be assigned to products resulting from reactions of [B₁₂I₁₁]¹⁻ with neutral organic molecules present in the vacuum chamber (Table 1). Specifically, ions **1** and **2** result from hydride and methanide abstraction from reaction partners on the surface, and ions **3** and **4** originate from binding of [B₁₂I₁₁]¹⁻ to phthalates, common plasticizers often present in mass spectrometers,^[24] which tend to accumulate with anions on surfaces during ion deposition.^[25] Formally, a H⁺ within the phthalate molecule is

Table 1: Reactions associated with the formation of ions 1–9.

[B ₁₂ I ₁₁] ¹⁻	+	H–R	→	R ⁺	+	[B ₁₂ I ₁₁ H] ²⁻	(1)
[B ₁₂ I ₁₁] ¹⁻	+	CH ₃ –R	→	R ⁺	+	[B ₁₂ I ₁₁ CH ₃] ²⁻	(2)
[B ₁₂ I ₁₁] ¹⁻	+	C ₂₄ H ₃₈ O ₄	→	H ⁺	+	[(B ₁₂ I ₁₁)C ₂₄ H ₃₇ O ₄] ²⁻	(3)
[B ₁₂ I ₁₁] ¹⁻	+	C ₁₆ H ₂₂ O ₄	→	H ⁺	+	[(B ₁₂ I ₁₁)C ₁₆ H ₂₁ O ₄] ²⁻	(4)
[B ₁₂ I ₁₁] ¹⁻	+	[(B ₁₂ I ₁₁)C ₂₄ H ₃₇ O ₄] ²⁻ (3)	→	H ⁺	+	[(B ₁₂ I ₁₁) ₂ C ₂₄ H ₃₆ O ₄] ⁴⁻	(5)
[B ₁₂ I ₁₁] ¹⁻	+	[I–Y] ²⁻ *	→	[Y] ¹⁻	+	[B ₁₂ I ₁₂] ²⁻	(6)
[B ₁₂ I ₁₁] ¹⁻	+	[B ₁₂ I ₁₁ H] ²⁻ (1)	→		+	[B ₁₂ I ₁₁ H–B ₁₂ I ₁₁] ³⁻	(7)
[B ₁₂ I ₁₁] ¹⁻	+	[B ₁₂ I ₁₁ CH ₃] ²⁻ (2)	→		+	[B ₁₂ I ₁₁ CH ₃ –B ₁₂ I ₁₁] ³⁻	(8)
[B ₁₂ I ₁₁] ¹⁻	+	[B ₁₂ I ₁₂] ²⁻	→		+	[B ₁₂ I ₁₂ –B ₁₂ I ₁₁] ³⁻	(9)

* With [I–Y]²⁻ being predominantly one of the ions **1**, **2**, **3** and **4**.

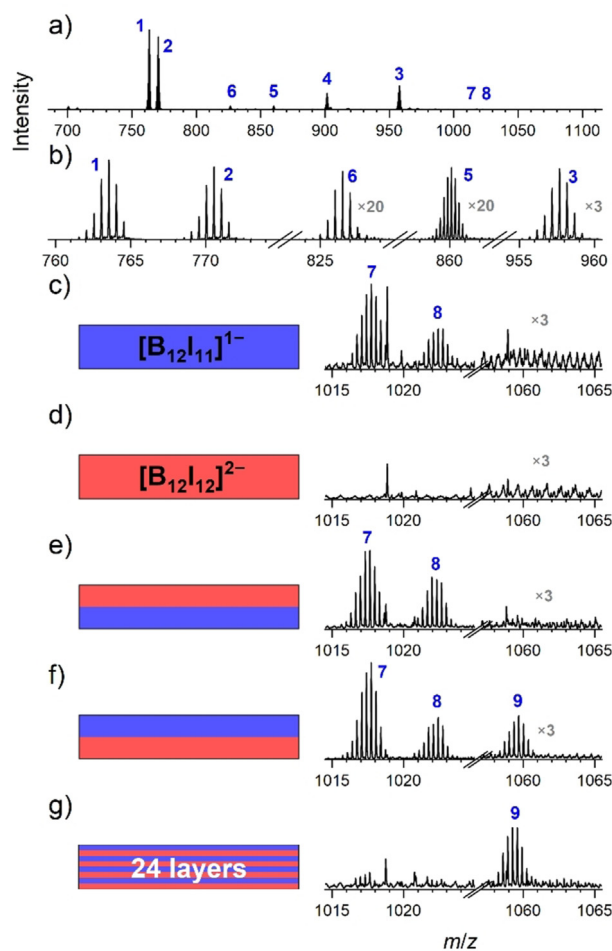


Figure 2. a) Overview of the mass spectrum of the products formed from [B₁₂I₁₁]¹⁻ deposition in the *m/z* range from 700–1100. For assignments see Table 1. b) Magnification of the isotopic patterns of ions **1**–**3**, **5**, and **6**. c–g) *m/z* Range of spectra showing the formation of triply charged ions. The scheme on the left visualizes the order of deposition (blue: [B₁₂I₁₁]¹⁻, red: [B₁₂I₁₂]²⁻). Ion **9**: [(B₁₂I₁₂)–(B₁₂I₁₁)]³⁻ only forms if [B₁₂I₁₂]²⁻ is present at the layer interface in significant amounts during [B₁₂I₁₁]¹⁻ deposition.

substituted by [B₁₂I₁₁]¹⁻ (binding via the electrophilic vacant boron atom), which results in a doubly charged anion.^[21] The ions **5** to **8** observed at lower abundances are most remarkable. These ions can unambiguously be assigned to the products of chemical reactions of two anions occurring during the deposition process. The ion **5** has the charge state of 4– (see isotopic pattern in Figure 2b) and can be attributed to the reaction of ion **3** with the [B₁₂I₁₁]¹⁻ anion (formally, two protons of the phthalate are substituted by two [B₁₂I₁₁]¹⁻ units). The organic phthalate “spacer” with long alkyl chains is supposed to separate the two negatively charged units.

Even more intriguing are the product anions **6**, **7**, and **8**. Ion **6** can be identified as [B₁₂I₁₂]²⁻ and triply charged anions **7** and **8** result

from addition of $[\text{B}_{12}\text{I}_{11}]^{1-}$ to the doubly charged anions **1** ($[\text{B}_{12}\text{I}_{11}\text{H}]^{2-}$) and **2** ($[\text{B}_{12}\text{I}_{11}\text{CH}_3]^{2-}$), respectively. Unlike compound **5** with an intercalated phthalate alkyl chain, in the cases of **7** and **8**, the center of charge of a dianion and a singly charged anion must approach each other on a sub-nanometer scale (around 8 Å) in order to form the detected products. In the gas phase, a repulsive barrier of more than 2 eV would have to be overcome.

We have ruled out the possibility of the direct deposition of the precursor $[\text{B}_{12}\text{I}_{12}]^{2-}$ together with $[\text{B}_{12}\text{I}_{11}]^{1-}$ (see section SI3). Moreover, possible interferences coming from MS detection or the formation of the products after exposing the surface to ambient conditions must be excluded. To this end, the mass-selected precursor $[\text{B}_{12}\text{I}_{12}]^{2-}$ was soft-landed on the surface. No reaction products were found as shown in Figure 2d and section SI4. Next, deposition of $[\text{B}_{12}\text{I}_{11}]^{1-}$ was performed followed by $[\text{B}_{12}\text{I}_{12}]^{2-}$ deposition in similar quantities. LESA-MS analysis revealed that the spectrum appeared as a simple addition of the spectra obtained for the individual $[\text{B}_{12}\text{I}_{11}]^{1-}$ and $[\text{B}_{12}\text{I}_{12}]^{2-}$ depositions (Figure 2e and section SI5). Apparently, the products of highly reactive $[\text{B}_{12}\text{I}_{11}]^{1-}$ form almost instantaneously on the surface and subsequent $[\text{B}_{12}\text{I}_{12}]^{2-}$ deposition has virtually no influence on the formation of ions **1–5**, **7**, and **8**. In contrast, if the sequence is reversed and $[\text{B}_{12}\text{I}_{12}]^{2-}$ is deposited first followed by $[\text{B}_{12}\text{I}_{11}]^{1-}$, a new product **9** is observed (see Figure 2f) and could be identified as $[\text{B}_{12}\text{I}_{12}-\text{B}_{12}\text{I}_{11}]^{3-}$. This particular experiment (compare Figure 2e,f) excludes the influence of post-deposition treatment of the surface on the formation of the triply charged ions. It strengthens the hypothesis that the fragment anion $[\text{B}_{12}\text{I}_{11}]^{1-}$ generated in the gas phase forms stable reaction products with doubly charged ions of the same polarity in a direct addition reaction on the surface. Notably, the ions **7** and **8** were still observed in this experiment with higher abundances than **9**, although an excess of $[\text{B}_{12}\text{I}_{12}]^{2-}$ is present at the surface during $[\text{B}_{12}\text{I}_{11}]^{1-}$ deposition. This indicates that $[\text{B}_{12}\text{I}_{11}]^{1-}$ ions cannot penetrate deep into the layer of previously deposited $[\text{B}_{12}\text{I}_{12}]^{2-}$ and ions **9** form only at the interface between the two layers. As soon as the underlying layer generated by $[\text{B}_{12}\text{I}_{12}]^{2-}$ deposition is fully covered by the layer formed by $[\text{B}_{12}\text{I}_{11}]^{1-}$ and co-adsorbed hydrocarbons, the incoming $[\text{B}_{12}\text{I}_{11}]^{1-}$ can still react with the ions **1** and **2** yielding **7** and **8**, but no $[\text{B}_{12}\text{I}_{12}]^{2-}$ for the formation of **9** is available. Based on this finding, a multilayer structure was produced by switching 12 times between deposition of $[\text{B}_{12}\text{I}_{12}]^{2-}$ and $[\text{B}_{12}\text{I}_{11}]^{1-}$. A similar number of ions was deposited in each sub-layer. The corresponding LESA-MS spectrum clearly shows that under these conditions, ion **9** forms with significantly higher abundance in comparison to ions **7** and **8** (Figure 2g). Exchange of the fluorinated SAM by a hydrogenated SAM or preparing samples without a SAM on a non-modified gold surface did not change the results shown in Figure 2. Therefore, a chemical influence of the sample surface can be excluded. Also, reducing the kinetic energy of the $[\text{B}_{12}\text{I}_{11}]^{1-}$ ion from 20 eV to 10 eV did not change the result (section SI9).

The proposed structure of ion **9** contains a bridging hypervalent iodine as shown in Figure 3 and is denoted by $[\text{B}_{12}\text{I}_{11}-\text{I}-\text{B}_{12}\text{I}_{11}]^{3-}$. The CID of **9** resulted in the observation of

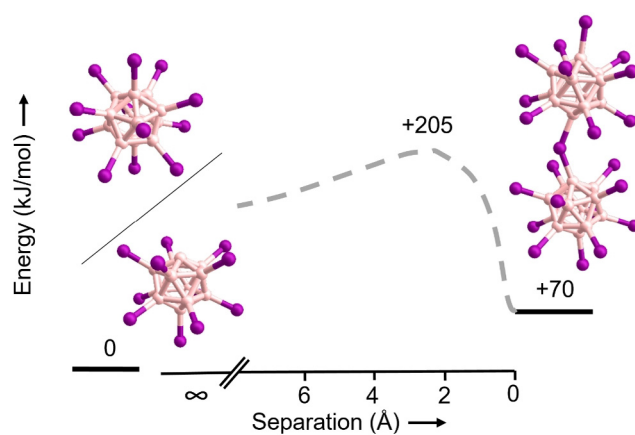


Figure 3. B3LYP energetics for the reaction of $[\text{B}_{12}\text{I}_{11}]^{1-}$ with $[\text{B}_{12}\text{I}_{12}]^{2-}$ in the gas phase, see details in section SI8.

the fragments $[\text{B}_{12}\text{I}_{12}]^{2-}$ and $[\text{B}_{12}\text{I}_{11}]^{1-}$, which is indeed consistent with the assumed structure. It is worth noting that some bridged *closo*-borate anions were successfully synthesized under strongly acidic and annealing conditions or in electrochemical experiments,^[26–28] but the sterically demanding periodinated ion **9** has not been reported yet. Our attempts to generate **9** from $[\text{B}_{12}\text{I}_{12}]^{2-}$ salts using thermal decomposition or electrochemical oxidation generated free iodine and resulted in black, mostly insoluble products in agreement with previous literature reports.^[29,30] The sole anion detected in the soluble residues was $[\text{B}_{12}\text{I}_{12}]^{2-}$. It appears that the highly unstable intermediate $[\text{B}_{12}\text{I}_{11}]^{1-}$, if formed in the condensed phase at all, decomposes further. However, a direct gas phase reaction between $[\text{B}_{12}\text{I}_{12}]^{2-}$ and $[\text{B}_{12}\text{I}_{11}]^{1-}$ appears virtually impossible. Quantum chemical calculations (B3LYP/def2-TZVPP) predict a large barrier of 205 kJ mol⁻¹, mainly due to the repulsive Coulomb force, and an unfavorable reaction enthalpy of 70 kJ mol⁻¹ for the formation of the product (Figure 3).

At the layer interface, however, this reaction becomes possible. The presence of permanent anions in the proximity to the grounded metal surface above a thin insulating layer (FSAM, see Figure 1g) induces a displacement of electrons in the conductive gold. Thus, the gold surface accumulates a charge opposite to that of the deposited ions, resulting in a measurable current during deposition. For more explanations, please see the model of electrostatic induction and mirror charges in the supporting information, section SI6. The induced positive charge balances the negative charge of the ions at the interface. Anions can approach the surface without significant long-range repulsion. Therefore, deposition in high densities becomes possible as previously rationalized employing a two-plate capacitor model.^[13,31] In order to model the influence of a grounded surface next to a deposited $[\text{B}_{12}\text{I}_{12}]^{2-}$, the potential energy surface of the reaction shown in Figure 3 was calculated in the presence of mirror charges (see details in SI6). The metastable trianion becomes thermochemically stable and the barrier height appears to be substantially reduced (as may also be rationalized by a Bell–Evans–Polanyi type of argument^[32]). Although this simple model cannot account for the complex electrostatic situation at the interface

of the multilayer deposit, it rationalizes the bond formation and stabilization of the product in a charge-balanced environment. $[\text{B}_{12}\text{I}_{11}]^{1-}$ approaches the interface with several eV of kinetic energy. The energy of the collision can be efficiently dissipated into the condensed phase resulting in a stable adduct. In LESA-MS experiments, the product $[\text{B}_{12}\text{I}_{11}-\text{I}-\text{B}_{12}\text{I}_{11}]^{3-}$ is transferred into the gas phase and dissociation into the reagents would be enthalpically favored, but the large Coulomb barrier kinetically stabilizes the triply charged ion against dissociation (see Figure 3).^[33]

With increasing anion coverage on the surface, the potential difference between the anionic layer and the gold surface increases. In multilayer coverages, additional charge balancing effects must be considered which reduce the potential difference between the deposited layer and the gold surface. Previous reports on the deposition of electronically stable anions indicate that the ions retain their charge even in multilayer coverage.^[25] Cyclic voltammetry experiments performed on $[\text{B}_{12}\text{I}_{12}]^{2-}$ solutions indicate that highly oxidizing conditions lead to decomposition of the organic solvents before neutralization of the ions occurs.^[29] The oxidation of organic molecules present in the layer (see Table 1 and Figure 1) is a possible process which may generate cations. However, the details of charge balancing in multilayer deposits of ions of one polarity still need to be unraveled. Investigations on ion-ion and ion-neutral reactions at interfaces of multilayer deposits may also contribute to the in-depth understanding of the remarkably strong electrostatic fields at liquid interfaces.^[34]

Finally, to demonstrate that formation of such highly charged cluster-ions is not unique to $[\text{B}_{12}\text{I}_{11}]^{1-}$, deposition of $[\text{B}_{12}\text{Cl}_{11}]^{1-}$ on $[\text{B}_{12}\text{I}_{12}]^{2-}$ was carried out. Indeed, the corresponding triply charged product ion $[\text{B}_{12}\text{I}_{11}-\text{I}-\text{B}_{12}\text{Cl}_{11}]^{3-}$ has been found on the surface (section S110).

In conclusion, we have performed proof-of-concept experiments showing that reactive fragment ions amenable only in the gas phase (e.g. $[\text{B}_{12}\text{I}_{11}]^{1-}$) may be chemically bound to ions of same polarity on surfaces. While a high Coulomb barrier prevents this reaction in the gas phase, close proximity of anions becomes possible on a grounded surface. The reaction is driven by saturating the highly electrophilic vacant boron atom in $[\text{B}_{12}\text{I}_{11}]^{1-}$ with a weakly nucleophilic iodine substituent of $[\text{B}_{12}\text{I}_{12}]^{2-}$. These results may set the stage for building up highly charged functional clusters and novel products using mass-selected intermediates, which would not be accessible in either gas or solution phase. Controlling the nature and amount of co-adsorbed organic molecules would be an important step aiming at unravelling the influence of competing chemical reactions. This may enable selective transformation of deposited intermediates via their reaction with chosen neutrals as well as ions of any polarity.

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Conflict of Interest

The authors declare no conflict of interest.

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