Supporting Information

Anion–Anion Chemistry with Mass-Selected Molecular Fragments on Surfaces
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SI 1. Estimation of layer thickness

It has been shown in a previous study that in deposited layers the ratio of phthalates (main organic component of the layer) to [B_{12}X_{12}]^{2-} ions is nearly 2:1.\textsuperscript{[1]} An optimized structure of two di-\textit{n}-octyolphthalates wrapped around a [B_{12}I_{12}]^{2-} ion is shown in Figure SI1. The volume of this unit is estimated to 2 nm\textsuperscript{3}. The volume of a deposition containing 2 \cdot 10^{14} ions may therefore be estimated to 4 \cdot 10^{14} nm\textsuperscript{3}. Based on the spot size visible for high coverages, the deposition area is roughly estimated to 10 mm\textsuperscript{2} = 1 \cdot 10^{13} nm\textsuperscript{2}. The layer thickness is therefore roughly estimated to be (4 \cdot 10^{14} nm\textsuperscript{3}/1 \cdot 10^{13} nm\textsuperscript{2}) 40 nm. Therefore, the individual layers (Figure 2g of the main text) have an estimated thickness of one or two ionic units shown in Figure SI1.

\textbf{Figure SI1.} A space-filling model of (C_{24}H_{38}O_{4})_{2}[B_{12}I_{12}]^{2-}. The calculated dimension is 2.0 × 1.3 × 1.0 nm.
SI 2. Soft-landing experiments

SI 2.1 General description

Two electrospray ionization (ESI) sources were used to transfer the anions from a 10^{-4} M solution a K_2[B_{12}I_{12}] into the gas phase. High- and low-pressure ion funnels collimated the ion beam and transferred the gaseous [B_{12}I_{12}]^{2-} precursor ions from ambient pressure to a chamber with a lower background pressure. Downstream of the ion funnels CID of the precursor ions was carried out by applying a large voltage difference to ion optics elements. Multiple collisions with background gas molecules lead to fragmentation reactions. The use of a 90° bent ion guide enabled to get rid of remaining neutral molecules. The fragment ions [B_{12}I_{11}]^{1-} (m/z = 1526) were selected by a quadrupole mass filter and guided to the surface placed directly behind the quadrupole. The latter consisted of a silicon wafer (1×1 cm²) covered with gold and a fluorinated alkane thiol self-assembled monolayer (FSAM). For more experimental details see section SI 2.3. The conductive gold surface was grounded via a picoammeter, which measured the current during the deposition. The amount of deposited ions was derived by integrating the ion current over time. The ion soft-landing instrument and its technical details are very similar to a previously described setup.[2] The ion optics are powered and controlled by the MIPS control system developed by GAA Custom Electronics, LLC and were adjusted to obtain a maximum ion current after mass selection. Applied RF voltages were adjusted to the resonance frequency of the electric LC circuit. Table SI1 gives an example of settings used during an ion deposition.

SI 2.2 Deposition parameters

Ion source
The ion source responsible for high ion currents contains two electrospray inlets and the double ion-funnel system, which have been described earlier.[3] Here, a 1.7 × 10^{-4} mol/L CH_3CN solution of the salt K_2[B_{12}I_{12}] was propelled through PEEK tubings (Techlab, O.D. 1.59 mm, I.D. 0.130 mm) at a flow rate of 2 μL/min using two syringe pumps (Harvard Apparatus 11 Plus) and electrosprayed by applying a high voltage U(ESI) of ~3400 V to a stainless steel ESI capillary tube, Waters, P/N 700000341. Charged droplets were transferred using heated stainless capillaries (Techlab, O.D. 1.59 mm, I.D. 1.000 mm) at approx. 140°C through orthogonal-inlets into the first ion funnel. For [B_{12}I_{12}]^{2-} deposition, voltages U(Inlet) of about −300 V were applied to the capillaries.

Ion funnel
In the first ion funnel, a set of four DC voltages (U_1 = −350 V, U_2 = −201 V, U_3 = −195 V, and U_4 = −103 V) generates a voltages gradient over each pair of electrodes towards the exit of the ion funnel. This gradient is superimposed by an RF voltage (f = 556 kHz, U_{RF} = 180 V) to collimate the ions and transmit them into the second ion funnel. The first funnel is operating at a background pressure of about 11.0 mbar. In the second ion funnel, also a DC voltages gradient from U_1 = −100 V to U_2 = −12 V is superimposed by an RF voltage (f = 897 kHz, U_{RF} = 120 V) to transfer the ions further into the next stage of the instrument. The second ion funnel is operating at a background pressure of about 0.73 mbar. The vacuum chambers of the two ion funnels are each pumped by a Leybold, ECODRY 65.

Ion guide
Next, the ions are separated from the neutral molecules by a 90° bent quadrupole ion guide operated at a frequency of 2096 kHz with an amplitude of 650 V. The background pressure in this vacuum chamber is
at $1.3 \times 10^{-2}$ mbar and is achieved by a Pfeiffer Vacuum, HiPace 80. Following the ion guide, ions pass through a small aperture (2.25 mm dia.) to enter the high vacuum region of the instrument. For intact deposition of the electrosprayed $[\text{B}_{12}\text{I}_{12}]^{2-}$ ions, $U_{\text{bias}} = -3$ V was applied as a bias to the ion guide. Note, that the bias determines the kinetic energy of the ions, since in the subsequent sample vacuum chamber collisions with background gas are greatly reduced (mean free path of about a meter). For the generation of fragment ions, the voltage difference between the exit of the low pressure ion funnel and the bias of the ion guide was substantially increased.

**Mass selection and deposition**

After passing the exit aperture of the ion guide, the ions were mass selected by an Extrel quadrupole mass filter (9.5 mm rod diameter). The voltages provided by the MIPS system allow to select masses in a range from 150 to 3000 amu with a maximum mass resolution of 300. Depositions were performed with a mass window of about 15 amu to ensure deposition of all ions possessing a broad isotopic pattern. The background pressure in the deposition chamber is at $3.8 \times 10^{-5}$ mbar and is achieved by a Pfeiffer Vacuum, TMH 261. The turbomolecular pump is backed with the Leybold, ECODRY 65 used to evacuate the chamber of the low pressure funnel. We do not use the entrance lens of the quadrupole; it has been removed from the machine. The voltages of the pre-filter ($U_{\text{pre}} = 0$ V) and post-filter ($U_{\text{post}} = 15$ V) of the resolving quadrupole were adjusted to maximize the ion current collected on the sample. The ion current on the target is measured with a picoammeter (RBD Instruments, 9103 USB Picoammeter). It should be noted that during ion deposition (taking typically 8-12 hours), several voltages had to be adjusted slightly over time in order to compensate for losses of the ion current. The deposition parameters for the other anions are also shown in Table SII for comparison.
Table S11: Comparison of the settings used during an ion deposition.

| Parameter                  | [B$_{12}$I$_{11}$]$^{1-}$ | [B$_{12}$Cl$_{11}$]$^{1-}$ | [B$_{12}$I$_{12}$]$^{2-}$ |
|----------------------------|----------------------------|----------------------------|----------------------------|
| c(solution) in mol/L       | $1.7 \times 10^{-4}$       | $2.0 \times 10^{-4}$       | $1.7 \times 10^{-4}$       |
| flow rate in µL/min        | 2.0                        | 2.0                        | 2.0                        |
| U(ESI) in V                | −3400                      | −3400                      | −3400                      |
| T(Inlet 1&2) in °C         | 140                        | 140                        | 140                        |
| U(Inlet 1) in V            | −330                       | −350                       | −300                       |
| U(Inlet 2) in V            | −370                       | −350                       | −300                       |
| $U_1$(Funnel 1) in V       | −400                       | −370                       | −350                       |
| $U_2$(Funnel 1) in V       | −265                       | −320                       | −201                       |
| $U_3$(Funnel 1) in V       | −260                       | −300                       | −195                       |
| $U_4$(Funnel 1) in V       | −229                       | −180                       | −103                       |
| $f$(Funnel 1) in kHz       | 556.0                      | 556.0                      | 556.0                      |
| $U_{pp}$ (Funnel 1) in V   | 170                        | 290                        | 180                        |
| $p$(Funnel 1) in mbar      | 11.0                       | 11.0                       | 11.0                       |
| $U_1$(Funnel 2) in V       | −260                       | −160                       | −100                       |
| $U_2$(Funnel 2) in V       | −93                        | −50                        | −12                        |
| $U_{lens}$(Funnel 2) in V  | −92                        | −50                        | −8                         |
| $f$(Funnel 2) in kHz       | 897.0                      | 897.0                      | 897.0                      |
| $U_{pp}$ (Funnel 2) in V   | 120                        | 160                        | 120                        |
| $p$(Funnel 2) in mbar      | 0.73                       | 0.73                       | 0.73                       |
| $f$(Guide) in kHz          | 2096.0                     | 2096.0                     | 2096.0                     |
| $U_{pp}$ (Guide) in V      | 620                        | 1000                       | 680                        |
| $U_{bias}$ (Guide) in V    | −20                        | −20                        | −3                         |
| $U_{ext}$ (Guide) in V     | −15                        | −23                        | 0                          |
| $p$(Guide) in mbar         | $1.3 \times 10^{-2}$       | $1.3 \times 10^{-2}$       | $1.3 \times 10^{-2}$       |
| $f$(Quadrupole) in kHz     | 649.0                      | 649.0                      | 649.0                      |
| $U_{ref}$ (Quadrupole) in V| 0                          | 0                          | 0                          |
| $U_{bias}$ (Quadrupole) in V| 10                        | 0                          | 0                          |
| $U_{post}$ (Quadrupole) in V| 0                        | 0                          | 15                         |
| $U_{ext}$ (Quadrupole) in V| 0                          | 0                          | 0                          |
| $m/z$(Quadrupole) in amu   | 1489.0                     | 547.5                      | 800.0                      |
| $p$(Quadrupole) in mbar    | $3.8 \times 10^{-5}$       | $3.8 \times 10^{-5}$       | $3.8 \times 10^{-5}$       |
| $U_{bias}$ (Target) in V   | 0.0                        | 0.0                        | 0.0                        |
| $I_{ion}$ in nA            | 0.2                        | 0.3                        | 1.5                        |
**Surface preparation**

Several sample surfaces were prepared for ion deposition using a silicon substrate, which is covered with gold and coated with different self-assembling monolayers (SAM). As a standard procedure, we store surfaces in the dark, because SAMs may be damaged by longer exposure to daylight.

**Substrate**

The Si substrates (dimension: $10 \times 10$ mm$^2$, thickness: 460 to 530 µm, resistance: 1 to 30 Ohm) were purchased from *Ted Pella Inc.*

**Conductive surface**

The substrates were covered with a 100 Å Cr adhesion layer and a 1500 Å Au layer using a sputtering apparatus at *IOM Leipzig* (Leibniz Institute of Surface Engineering).

**Cleaning process**

The gold substrates were washed repeatedly in methanol (UHPLC, LiChrosolv), and dried under nitrogen. The influence of using Ozone cleaning (with a Novascan model PSD-UV4 UV-Ozone cleaner) as an additional cleaning step was investigated as well in this study, see below.

**Coating with SAM**

The cleaned gold substrates were immersed for 12 hours in glass scintillation vials containing a 1 mM methanol solution of the corresponding thiol for formation of the SAM: 1H,1H,2H,2H-Perfluorodecanethiol for FSAM and 1-Undecanethiol for HSAM. These were purchased from Sigma-Aldrich.

**Mounting in the deposition instrument**

Then, the surfaces were rinsed with methanol, dried with a flow of nitrogen, and mounted in the sample holder of the soft-landing instrument.

**Contact angle of SAM-surfaces**

As already mentioned, some samples were subjected to an additional Ozone cleaning procedure. In order to evaluate the impact of this step on SAM surfaces, the free surface energy, calculated according to the model by Owens, Wendt, Rabel and Kaelble[4], was accessed through the measurement of contact angles (Table SI2). The results shown only a negligible influence of the Ozone cleaning on the free surface energy and should not hence affect the outcome of the soft-landing experiments.

**Table SI2**: Contact angle measurements of SAM surfaces with different SAMs and preparation methods.

| Surface         | Angle of water (°) | Angle of diiodomethane (°) | Surface free energy (mN/m) |
|-----------------|--------------------|-----------------------------|---------------------------|
| FSAM (with O$_3$) | 113.6 ± 0.6        | 90.8 ± 7.0                  | 12.2                      |
| FSAM (without O$_3$) | 115.9 ± 0.1       | 95.9 ± 1.4                  | 10.1                      |
| HSAM (with O$_3$)  | 106.0 ± 0.1        | 51.5 ± 0.7                  | 35.3                      |
| HSAM (without O$_3$) | 102.6 ± 1.2       | 47.3 ± 5.0                  | 37.1                      |
**SI 2.4 Nano-ESI MS Analysis (LESA-MS)**

A TriVersa Nanomate (Advion) for Liquid Extraction Surface Analysis was used for Nano-ESI Analysis. A small portion of the layer (1 to 2 mm²) was dissolved in 2 µL of (90:10 CH₃CN:H₂O) and subjected to a subsequent chip-based nanoelectrospray analysis. This procedure not only minimized the required sample volume but resulted in a substantial increase of sensitivity in comparison to our previous ESI-MS analysis of soft-landed ions.[1,5] Mass spectra were acquired on Bruker Impact II (Bruker Daltonik, Bremen, Germany).

**SI 3. Ruling out the possibility of the direct deposition of the precursor \([B_{12}I_{12}]^{2−}\) together with \([B_{12}I_{11}]^{1−}\)**

The ion \([B_{12}I_{12}]^{2−}\) was detected within the layer after deposition of the mass selected \([B_{12}I_{11}]^{1−}\). The following considerations clarify that the detected \([B_{12}I_{12}]^{2−}\) ions are not co-deposited due to a low quality mass selection: The sample used for deposition experiments contains roughly 10% K₂[B₁₂I₁₁Cl]. While fragmentation was initiated within the ion deposition instrument and no mass selection was applied (quadrupole operates in RF only mode), reaction products of the fragment \([B_{12}I_{10}Cl]^{1−}\) (\(m/z = 1434\)) were found at the surface in post-deposition analysis. Once the fragment \([B_{12}I_{11}]^{1−}\) \(m/z = 1526\) was mass selected and deposited, no reaction products of the fragment at \(m/z = 1434\) were found in post-deposition analysis. In other words, the mass resolution is high enough in order to separate the two ionic species in the mass filter. This will be even more valid in the case of \([B_{12}I_{12}]^{2−}\) at \(m/z = 826\). The co-deposition of \([B_{12}I_{12}]^{2−}\) and \([B_{12}I_{11}]^{1−}\) can then be safely disregarded.
SI 4. Deposition of [B_{12}I_{12}]^{2−} with different kinetic energies

SI 4.1 Deposition of [B_{12}I_{12}]^{2−} with 6 eV (U_{bias} = −3 V)

The mass selected precursor [B_{12}I_{12}]^{2−} was soft-landed on the surface and no reaction products were found on the target by LESA-MS analysis (Figure SI2).

![Mass spectra of the products formed from [B_{12}I_{12}]^{2−} deposition with U_{bias} = −3 V in the m/z range from 761.5 to 1066.5.](image)

**Figure SI2.** Mass spectra of the products formed from [B_{12}I_{12}]^{2−} deposition with U_{bias} = −3 V in the m/z range from 761.5 to 1066.5, only the [B_{12}I_{12}]^{2−} ions were observed on the surface in this m/z range, see the ×400 magnification of the isotopic patterns of ions in the m/z range from 761.5 to 1066.5.

SI 4.2 Deposition of [B_{12}I_{12}]^{2−} with 120 eV (U_{bias} = −60 V) and reactivity of the fragment [B_{12}I_{11}]^{2−}

Deposition of [B_{12}I_{12}]^{2−} was also performed with a significantly higher kinetic energy on the FSAM surface. In subsequent LESA-MS analysis the triply charged species [B_{12}I_{11}+B_{12}I_{11}]^{3−} was also found on the target by LESA-MS analysis (Figure SI3). However, the reaction is much less selective because dissociation of [B_{12}I_{12}]^{2−} does not only generate the intended [B_{12}I_{11}]^{1−}, but also the radical [B_{12}I_{11}]^{2−}. In addition, traces of the reaction products of [B_{12}I_{10}]^{−} are observed.
**Figure SI3.** Mass spectra of the products formed from $[\text{B}_{12}\text{I}_{12}]^{2-}$ deposition with $U_{\text{bias}} = -60$ V in the $m/z$ range from 698.5 to 1066.5, the additional reaction products of $[\text{B}_{12}\text{I}_{10}]^{1-}$ were observed on the surface in the $m/z$ range from 698.5 to 711.5. The triply charged species $[(\text{B}_{12}\text{I}_{11}\text{H})-(\text{B}_{12}\text{I}_{11})]^{3-}$ (7), $[(\text{B}_{12}\text{I}_{11}\text{CH}_{3})-(\text{B}_{12}\text{I}_{11})]^{3-}$ (8) and $[(\text{B}_{12}\text{I}_{12})-(\text{B}_{12}\text{I}_{11})]^{3-}$ (9) were observed, see the ×50 magnification of the isotopic patterns of ions in the $m/z$ range from 1013.5.5 to 1066.5.

**SI 4.3 Deposition of $[\text{B}_{12}\text{I}_{11}]^{2-\ast}$ with 6 eV ($U_{\text{bias}} = -3$ V)**

The deposition of mass selected $[\text{B}_{12}\text{I}_{11}]^{2-\ast}$ results predominantly in the reaction product $[\text{B}_{12}\text{I}_{11}\text{H}]^{2-}$ as shown in Figure SI4. This explains the high abundance of 1 in Figure SI3.

**Figure SI4.** Mass spectrum of the products formed from $[\text{B}_{12}\text{I}_{11}]^{2-\ast}$ deposition with $U_{\text{bias}} = -3$ V in the $m/z$ range from 761.5 to 1066.5, none of the triply charged species $[(\text{B}_{12}\text{I}_{11}\text{H})-(\text{B}_{12}\text{I}_{11})]^{3-}$ (7), $[(\text{B}_{12}\text{I}_{11}\text{CH}_{3})-(\text{B}_{12}\text{I}_{11})]^{3-}$ (8) and $[(\text{B}_{12}\text{I}_{12})-(\text{B}_{12}\text{I}_{11})]^{3-}$ (9) were observed on the surface in this $m/z$ range, see the ×50 magnification of the isotopic patterns of ions in the $m/z$ range from 858.5 to 1066.5.
SI 5. Deposition of [B\textsubscript{12}I\textsubscript{11}]\textsuperscript{1−} followed by [B\textsubscript{12}I\textsubscript{12}]\textsuperscript{2−}

[B\textsubscript{12}I\textsubscript{11}]\textsuperscript{1−} was soft-landed on the surface followed by [B\textsubscript{12}I\textsubscript{12}]\textsuperscript{2−} deposition in similar amounts. The spectrum of the LESA-MS analysis (Figure SI5) appeared as a simple addition of the spectra acquired for the individual [B\textsubscript{12}I\textsubscript{11}]\textsuperscript{1−} and [B\textsubscript{12}I\textsubscript{12}]\textsuperscript{2−} depositions.

**Figure SI5.** Mass spectra of the products formed from [B\textsubscript{12}I\textsubscript{11}]\textsuperscript{1−} (U\textsubscript{Bias} = −20 V) and [B\textsubscript{12}I\textsubscript{12}]\textsuperscript{2−} (U\textsubscript{Bias} = −3 V) deposition in the m/z range from 761.5 to 1066.5. None of the triply charged species [(B\textsubscript{12}I\textsubscript{12})-(B\textsubscript{12}I\textsubscript{11})]\textsuperscript{3+} were observed, see the ×100 magnification of the isotopic patterns of ions in the m/z range from 858.5 to 1066.5.
SI 6. Electrostatic model

SI 6.1 Current measurement during deposition of ions, which stay charged: The model of electrostatic induction

If an ion is located near the surface of a conductor, then the electric field of the ion will induce a displacement of electron density within the metal surface. The surface polarizes oppositely to the ion until the electric field lines are oriented perpendicularly to the surface so that no force along the surface on the electron density is present, see Figure SI6a. If the conductor is grounded, the metal charges oppositely to the ion. The total charge within the metal induced by the ion is calculated by evaluating the electric field flux through the surface of the conductor (Gauss law). The electric field above the surface can be modeled using a point charge of opposite polarity positioned within the metal, see Figure SI6b. The metal surface constitutes a mirror plane in this model. The integral of the positive surface charge (=the induced charge or mirror charge $Q_i$) becomes almost identical to the negative charge of the ion $Q$, if the lateral dimension $R$ is very large in comparison to the distance $h$ between surface and ion (see Figure SI6b and Eq.1). This can be derived from equations given in Purcell, E. M.: Berkeley physics course. Vol. 2, electricity and magnetism. McGraw-Hill Book Company, New York 1965, p. 92f.

$$Q_i = -Q \cdot \left(1 - \frac{1}{\sqrt{1 + \left(\frac{R}{h}\right)^2}}\right)$$  
(Eq.1)

In our experiment, the used metal target has a size in the cm range. The ions are deposited on a nm-thick SAM. Therefore, the current measured during deposition due to electrostatic induction is almost identical to the ion current, which reaches the surface.

**Figure SI6.** a) Polarization of a grounded metal surface due to electrostatic induction by an ion. The field lines stand perpendicular on the surface (otherwise further displacement of the electron density would occur), b) The electric field outside the metal plate can be modeled using the mirror charge concept.
SI 6.2 Estimation of the influence of a grounded surface on the addition of [B$_{12}$I$_{11}$]$^{1-}$ to [B$_{12}$I$_{12}$]$^{2-}$

The model discussed in the following allows a qualitative rationalization how thermochemistry and barrier height change for the addition of [B$_{12}$I$_{11}$]$^{1-}$ to [B$_{12}$I$_{12}$]$^{2-}$ near a grounded surface compared to the gas phase. We do not claim any quantitative meaning regarding the real experiment discussed in the manuscript.

Figure 3 in the main text represents the potential energy surface for the addition of [B$_{12}$I$_{11}$]$^{1-}$ to [B$_{12}$I$_{12}$]$^{2-}$ in the gas phase. To evaluate the influence of a conductive surface on the energetics of the reaction, we use the mirror charge model, explained in sections SI 6.1. With respect to the self-assembled monolayer (alkanethiol), the distance between the center of deposited [B$_{12}$I$_{12}$]$^{2-}$ and the gold surface (mirror plane) was estimated to 13 Å. For quantum chemical calculation of the potential, point charges were used, which are derived from the mirroring of the atomic coordinates at the gold surface and using the opposite Mullikan charges of the respective atoms. It has to be considered that mirror charges constitute a model to describe the electric field and electrostatic potential near the grounded surface due to the polarization of the surface. Mirror charges are not actual localized point charges present at these positions within the surface and the calculated potential energy which result from their interaction with each other was subtracted from the calculated total energy of the system. Figure SI7 shows the result of the quantum chemical calculation and the potential energy, which results from a simple point charge model, which is a reasonable approximation at large distances of the ions.

**Figure SI7.** a) Potential energy surface of the reaction between [B$_{12}$I$_{11}$]$^{1-}$ to [B$_{12}$I$_{12}$]$^{2-}$ in the gas phase (red dots) and at a grounded conductive surface (blue dots) derived from quantum chemical calculations B3LYP/def2-svp using mirror charges to model the influence of the grounded surface.
The solid curves in (a) and (b) show the potential of the system if \([B_{12}I_{12}]^{2-}\) and \([B_{12}I_{11}]^{1-}\) are approximated by a 2− and 1− point charges.

**SI 6.3 The force on an ion approaching the surface (sub-monolayer regime)**

According to Gauss’s law, a uniformly charged infinite plate gives rise to a constant electric field with field lines perpendicular to the plate. Arrangement of two infinite parallel plates charged with opposite but equal charges results in a homogeneous electric field between the plates and vanishing of the field (zero electric field) above and below the plates.

For a finite ion distribution (e.g., soft-landed ion deposit), fringing effects as well as inhomogeneous ion distribution make a difference with respect to the (ideal) case just considered. Specifically, Ref\(^{[6]}\) provides an equation for the force exerted on an ion approaching two circular homogeneously oppositely charged plates of finite radius. While on the axis of symmetry only a force perpendicular to the plate is acting on the ions, ions approaching the plate out of axis experience also forces in plane parallel to the charged plate. Repulsion at the borders of the charged plates is significantly larger as also discussed in detail in Ref\(^{[6]}\). Most models discussed in the literature consider the force on an ion, which approaches a homogenously charged plate and not ions at discrete positions. In the following model we consider a sub-monolayer of equally charged ions on the surface (Figure SI8a). If the distance between the incoming ion and the surface is similar to the distance between the deposited ions, the force on the incoming ion can no longer be approximated by that caused by a homogeneously charged surface. For the sake of simplicity, a two-dimensional distribution of equally spaced point charges will be examined. Specifically, an array of 50 x 49 point charges \((-2)\) was defined so that the symmetry center lies exactly between two point charges. The electric field originating from permanently charged particles near a conductive, grounded surface can be calculated using the mirror charge model (Figure SI8b). Corresponding countercharges were defined by an array of +2 point charges of equal size with a distance of two grid points below the \((-2)\) point charge grid. Note that possible effects of co-adsorbed organic molecules are not considered within this electrostatic model. In Figure SI8c the force on a negative test charge is visualized by black/grey arrows.
Figure SI8. a) Ball and stick model for a sub-monolayer coverage of deposited dianions, b) Electric field lines according to the image charge model, c) visualization of the force vectors on a negative test charge in the “free space” above the layer. The force on a test charge approaching in the direction of the blue arrows is discussed in Figure SI9.

The one-dimensional force in z-direction (perpendicular to the surface) for two different positions (see arrows in Figure SI8c) are depicted in Figure SI8. Figure SI8a shows the force on an ion which approaches directly another ion on the surface, dependent on the grid size n. Figure SI8b shows the force on an ion, which approaches the interspace between two ions dependent on the grid size n. It can be seen that after a small increase in repulsive force, the ion is attracted before reaching its final position within the layer. The strength of repulsion is strongly dependent on the size of the model array and can therefore be attributed to fringing effects. Considering a very large grid, almost no repulsion force acts on an ion approaching a central region of the deposit. The approaching ion is hardly influenced because the electric field is almost zero. However, close to the surface, the ion is directed towards the interspace and even attractive forces are present in proximity of the surface. This rationalizes that ions of same polarity can come in close contact on the surface because substantial Coulomb barriers are absent.
**Figure SI9.** Development of the force on a point charge approaching the central region of a grid (negative and positive point charges in parallel arrangement) for different grid sizes, a) the point charge approaches directly a grid point. The repulsive force of two point charges of same polarity is indicated by a dotted line, b) the point charge approaches the position between two grid points. The grey area (FSAM thickness) is equal to the distance of two grid points in the applied model.
SI 6.4 Reaching the multilayer: The role of additional charge balancing processes

As long as the ion coverage on top of the SAM is in the sub-monolayer range, the continuous charging of the surface oppositely to the deposited anions may be considered. Charge balancing of the deposited anions is rationalized by the positively charged gold surface. A potential difference between the layer on top of the SAM and the gold surface builds up. Breakdown potentials for fluorinated SAMS have been investigated by Whiteside and coworkers,\textsuperscript{[7]} and show that potential differences in the order of 1-10 V result in electron transfer. Using an estimated charge density of 2e/2nm\textsuperscript{2} per monolayer (see model in section SI1), we estimate that this breakdown potential is reached if a full monolayer is deposited. Note that only orders of magnitude can be estimated here due to several uncertainties (exact ion density in a monolayer, permittivity, fringing effects of the layer). Therefore, as soon as the ion coverage reaches the multilayer region, redox reactions may be considered. These result in electron transfer from the deposited layer to the gold surface and may reduce the potential difference. The electrons apparently do not originate from the deposited electronically highly stable anions as previous studies on redox reactions indicate strongly that organic solvents (here the organic components of the layer and contaminations present in the vacuum chamber) are oxidized before the anions do.\textsuperscript{[8]} This may generate cations in the layer, which may act as counterions for the deposited anions. Further studies will be conducted to obtain a detailed understanding of these processes or to identify other possible processes which contribute to the charge balance in multilayer deposits.
SI 7 Influence of the organics

For the formation of the triply charged $[\text{B}_{12}\text{I}_{11}-\text{I-B}_{12}\text{I}_{11}]^{3-}$, a B-I bond needs to be formed. If the highly reactive $[\text{B}_{12}\text{I}_{11}]^{1-}$, prior to interaction with $[\text{B}_{12}\text{I}_{12}]^{2-}$, reacts with an organic molecule, then a very stable B-C bond is formed. This B-C bond is shielded by five iodine substituents. Therefore, a nucleophilic attack, in the frame of which the B-C bond is broken and the $[\text{B}_{12}\text{I}_{11}]^{1-}$ unit is transferred to $[\text{B}_{12}\text{I}_{12}]^{2-}$, must be considered to have an energetically high lying transition state. In contrast, direct addition of $[\text{B}_{12}\text{I}_{11}]^{1-}$ to $[\text{B}_{12}\text{I}_{12}]^{2-}$ without involvement of an organic molecule is a reaction with a significantly lowered barrier if it occurs in a charge-balanced environment instead of the gas phase (see Figure 3 of the main text and Figure SI7).

Additionally, we explored the influence of phthalate binding to $[\text{B}_{12}\text{I}_{12}]^{2-}$. Figure SI10 shows an optimized dioctylphthalate-$[\text{B}_{12}\text{I}_{12}]^{2-}$ unit, which is used as a model. The dianion is fully saturated and only non-covalent interactions with the organic molecules are possible. For the required B–I bond formation, iodine must act as a nucleophile, which reacts with the electrophilic boron atom of $[\text{B}_{12}\text{I}_{11}]^{1-}$. However, the nucleophilicity of accessible iodine substituents is apparently not influenced by complexation with the organic molecule. Only a negligible difference in the atomic charge (natural population analysis (NPA)) was found. The atomic NPA charges of the iodine atoms in the free $[\text{B}_{12}\text{I}_{12}]^{2-}$ was calculated (B3LYP-GD3BJ/def2SVPP) to be +0.014. With one coordinated dioctylphthalate, the atomic NPA charge changes by +0.017 at maximum.

Figure SI10. Molecular structure of the dioctylphthalate-$[\text{B}_{12}\text{I}_{12}]^{2-}$ adduct, optimized on a B3LYP-GD3BJ/def2SVPP level.
SI 8. Details computational investigations

Electronic structure calculations were performed using the Gaussian 16 rev. C.01 program\textsuperscript{[9]}. Geometries were optimized with subsequent frequency analysis using the B3LYP\textsuperscript{[10]} functional in combination with the basis set family introduced by Weigend and Ahlrichs\textsuperscript{[11,12]}. The influence of dispersion interactions was considered by using the D3 version of Grimme's dispersion correction with Becke-Johnson damping\textsuperscript{[13,14]}.

All given values should be considered within an uncertainty range of 5 kJ/mol and have been rounded accordingly.

The potential energy surface (PES) for the association of $[\text{B}_{12}\text{I}_{12}]^{2-}$ and $[\text{B}_{12}\text{I}_{11}]^{1-}$ (correspond to the dissociation of $[\text{B}_{12}\text{I}_{11}-\text{I}-\text{B}_{12}\text{I}_{11}]^{3-}$) was modeled using different approaches visualized in Figure SI11a-c, with the goal to find a good starting geometry for a high level transition state search. The obtained PES are shown in Figure SI11d and visualize the energy of the system dependent on the separation of the two fragments defined as the distance between the center of the $\text{B}_{12}$ scaffolds. The equilibrium distance for the triply charged anion is 7.578 Å. The three different approaches are described in the following: (i) The two fragments were separated in a fixed orientation towards each other as shown in Figure SI11a (atoms on the straight line remain on this line during separation). Relaxation and reorientation of the structures is not considered, i.e., a rigid PES scan was performed using B3LYP-GD3BJ/def2SVP. Obtained energies are plotted red in Figure SI11d; (ii) The fragments were separated using a defined z-matrix, which fixes the geometry in a $\sigma_v$ symmetry by stepwise increasing the marked boron-boron distance (red) in Figure SI11b. Under these constrains, geometry optimization using B3LYP-GD3BJ/def2SVP was performed for each step. Obtained energies are shown in green in Figure SI11d; (iii) A relaxed PES scan was performed by a stepwise increase of the distance between the marked iodine atoms in Figure SI11d on B3LYP-GD3BJ/def2SVP level of theory. The energies are shown in blue in Figure SI11d. The geometry obtained at 9.66 Å was used to perform a high-level transition state search (B3LYP-GD3BJ/def2QZVPP) which was found at an BSSE-corrected 0 K enthalpy of $+204.5$ kJ/mol with respect to the separated reagents calculated on the same level. For comparison, the potential energy of two negative point charges (one doubly charged, one singly charged) is shown in grey.
Figure SI11. a)-c) Visualization of the geometry constrains used for different PES scans to find the transition state for the association/dissociation of $[B_{11}I_{12}]^{2-}$ and $[B_{12}I_{11}]^{3-}$. The results are shown in Figure d). For details, see text above.
The PES for the association/dissociation of neutral $[\text{H}_2\text{B}_{12}\text{I}_{12}]$ and $[\text{B}_{12}\text{I}_{11}]^{1-}$ was calculated equivalently to the data-set visualized in blue in Figure SI11c. The result is shown in Figure SI12. The coordination of to cations eliminates the Coulomb barrier. The results show that the B-I bond formation is without barrier in the absence of the Coulomb repulsion.

**Figure SI12.** Results of a relaxed PES scans for the association/dissociation of $\text{H}_2[\text{B}_{12}\text{I}_{12}]$ and $[\text{B}_{12}\text{I}_{11}]^{1-}$. 
SI 9. influence of the parameters

SI 9.1 Chemical influence of the surface (SAM Exchange)

The reported experiments for the \([B_{12}I_{12}]^{1-}\) and \([B_{12}I_{12}]^{2-}\) deposition on gold surfaces covered with FSAM was repeated with modified surfaces: (1) The experiments were repeated using the HSAM, (2) an unmodified gold surface was used for the deposition experiments. Figure S13 shows that the key results (formation of \([(B_{12}I_{12})-(B_{12}I_{11})]\)\(^{3-}\) by deposition of the two ions in the right order is independent of the surface.

![Diagram](image)

**Figure S13.** Mass spectrum (LESA-MS negative mode) of the triply charged ions \([(B_{12}I_{12})-(B_{12}I_{11})]\)\(^{3-}\) formed from a-d) different deposition experiments indicated on the left (Blue: \([B_{12}I_{11}]^{-}\) deposition, red: \([B_{12}I_{12}]^{2-}\), green: HSAM, yellow: gold) in the m/z range from 1014.5-1065.5.

SI 9.2 Influence of the kinetic energy of \([B_{12}I_{11}]^{1-}\) deposition

A multilayer was produced by switching 12 times between deposition of \([B_{12}I_{12}]^{2-}\) \((U_{\text{Bias}} = -3 \, \text{V})\) and \([B_{12}I_{11}]^{1-}\) \((U_{\text{Bias}} = -10 \, \text{V})\). The triply charged product \([(B_{12}I_{12})-(B_{12}I_{11})]\)\(^{3-}\) can also be observed in the layer by decreasing the kinetic energy of \([B_{12}I_{11}]^{1-}\) from 20 eV to 10 eV. The result from LESA-MS (Figure S14) analysis doesn't differ from the previous layer by layer deposition \(([B_{12}I_{11}]^{-} \text{ with } 20 \, \text{eV kinetic energy})\).
Figure SI14. Nano-ESI Spectrum of the products formed from \([\text{B}_{12}\text{I}_{12}]^{2-}\) \((U_{\text{Bias}} = -3 \text{ V})\) and \([\text{B}_{12}\text{I}_{11}]^{1-}\) \((U_{\text{Bias}} = -10 \text{ V})\) layer by layer deposition in the \(m/z\) range from 1013.5 to 1066.5, the triply charged product \(([\text{B}_{12}\text{I}_{12}]\cdots[\text{B}_{12}\text{I}_{11}])^{3-}\) were observed on this FSAM deposition surface. No significant influences on the result could be observed by decreasing the kinetic energy of \([\text{B}_{12}\text{I}_{11}]^{1-}\).

SI 10. Formation of \([\text{B}_{12}\text{I}_{11}\text{I}-\text{B}_{12}\text{Cl}_{11}]^{3-}\)

Deposition of \([\text{B}_{12}\text{I}_{12}]^{2-}\) was performed on the surface followed by \([\text{B}_{12}\text{Cl}_{11}]^{1-}\) deposition and the corresponding \([\text{B}_{12}\text{I}_{11}\text{I}-\text{B}_{12}\text{Cl}_{11}]^{3-}\) was found on the target by LESA-MS analysis (Figure SI15). Thus, we demonstrated that formation of such highly charged clusters is not limited to the particular case of \([\text{B}_{12}\text{I}_{11}]^{1-}\).

Figure SI15. Mass spectrum (LESA-MS) of the products formed from \([\text{B}_{12}\text{I}_{12}]^{2-}\) \((U_{\text{Bias}} = -3 \text{ V})\) and \([\text{B}_{12}\text{Cl}_{11}]^{1-}\) \((U_{\text{Bias}} = -20 \text{ V})\) layer by layer deposition in the \(m/z\) range from 543.5 to 831.5, the triply charged species \(([\text{B}_{12}\text{I}_{12}\text{I}-\text{B}_{12}\text{Cl}_{11}]^{3-}\) were observed in small traces, see the 3200× magnification of the isotopic patterns of \([\text{B}_{12}\text{I}_{12}\text{I}-\text{B}_{12}\text{Cl}_{11}]^{3-}\) in the \(m/z\) range from 718.5-726.5.
SI 11. Current traces of $[\text{B}_{12}\text{I}_{12}]^{2-}$ deposition on Au and FSAM-coated Au

The current measurements were performed during the deposition of $[\text{B}_{12}\text{I}_{12}]^{2-}$ on a gold surface and a FSAM-coated gold surface (Figure SI16). In both cases, no significant difference in the ion currents could be observed, and the measured currents were constant over the time. Fluctuations of the current observed are due to spray instabilities of the ESI source. Also, the current is highly sensitive to the spray parameters like the sprayer position.

![Figure SI16](image)

**Figure SI16.** Ion current measurements for a $[\text{B}_{12}\text{I}_{12}]^{2-}$ deposition ($U_{\text{Bias}} = -3$ V) on a) FSAM-coated gold surface and b) a gold surface, each measurement with a constant current around 1.5 and 1.3 nA over 6000 s. The difference in total ion current is due to the high sensitivity of the current towards the spray conditions.

SI 12. Current decays of $[\text{B}_{12}\text{I}_{12}]^{2-}$ deposition on thin borosilicate glass above a metal surface

The current measurements were performed during the deposition process of $[\text{B}_{12}\text{I}_{12}]^{2-}$ on borosilicate plates (insulators) with different thicknesses (100 and 600 µm). Figure SI17 shows that the induced current drops to almost zero within minutes during the ion deposition on such insulators on top of a metal sample holder. This current decay originates from the buildup of an electric field above the sample. The charge balancing effect due to induced countercharges within the metal is less effective (see Eq.1 in section SI6.1) because the borosilicate plate is much thicker than the SAM surface. With a higher kinetic energy of the ion beam, more ions can be deposited (see insert in Figure SI17, after 60 s) but also the repulsive electric field increases and the current approaches zero again after some time.
**Figure SI17.** Ion current measurements of \([\text{B}_{12}\text{I}_{12}]^{2−}\) deposition \((U_{\text{Bias}} = -3 \text{ V})\) on a borosilicate plate with a thickness of 100 µm (red) and 600 µm (blue) over 100 s. In all cases, the DC voltage and radio frequency were applied to the quadrupole at 10 s. After 60 s, \(U_{\text{Bias}}\) was increased to \(-5 \text{ V}\) for all measurements.

**SI 13. Synthesis**

\(\text{K}_2[\text{B}_{12}\text{I}_{12}]\) and \([\text{t-Bu}_4\text{N}][\text{B}_{12}\text{Cl}_{12}]\) salts were prepared according to previously reported literature procedures.\(^{[15,16]}\)

**SI 14. Cartesian Coordinates**

*Table SI3:* Cartesian coordinates (in Å) of \([\text{B}_{12}\text{I}_{12}]\) optimized with B3LYP-GD3BJ/def2TZVPP. 
\(E = -3574.91869433\) Ha

| Atom | X    | Y    | Z    |
|------|------|------|------|
| B    | 0.05710000 | -1.545679000 | -1.004628000 |
| B    | 0.000120000 | 0.000286000 | -1.700859000 |
| B    | -0.9546860000 | 1.217084000 | -1.004236000 |
| B    | -0.000079000 | -0.000349000 | 1.430157000 |
| B    | 0.944441000 | -1.204061000 | 0.507693000 |
| B    | 1.436854000 | 0.526233000 | 0.508120000 |
| B    | 0.862465000 | 1.284420000 | -1.004118000 |
| B    | -1.452477000 | -0.531925000 | -1.004305000 |
| B    | -0.853135000 | -1.270585000 | 0.507689000 |
| B    | -1.472076000 | 0.418634000 | 0.508036000 |
| B    | -0.056623000 | 1.528924000 | 0.507992000 |
Table SI4: Cartesian coordinates (in Å) of $[B_{12}I_{12}]^{2-}$ optimized with B3LYP-GD3BJ/def2TZVPP. $E = -3872.88583139$ Ha

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| B    | 1.032695000 | 1.005624000 | 0.890862000 |
| B    | -1.032752000 | -1.005734000 | -0.890916000 |
| B    | 1.644011000 | -0.411269000 | 0.000000000 |
| B    | 0.621562000 | -0.638339000 | 1.441548000 |
| B    | -0.621521000 | 0.638257000 | 1.441466000 |
| B    | -0.367516000 | 1.654700000 | 0.000000000 |
| B    | 1.032695000 | 1.005624000 | -0.890862000 |
| B    | 0.621562000 | -0.638339000 | -1.441548000 |
| B    | -0.621521000 | 0.638257000 | -1.441466000 |
| B    | -1.643888000 | 0.411203000 | 0.000000000 |
| B    | -1.032752000 | -1.005734000 | 0.890916000 |
| B    | 0.367465000 | -1.654650000 | 0.000000000 |
| I    | 2.360330000 | 2.298574000 | 2.036093000 |
| I    | -2.360382000 | -2.298601000 | -2.036140000 |
| I    | 3.757297000 | -0.939815000 | 0.000000000 |
| I    | 1.420525000 | -1.458788000 | 3.294704000 |
| I    | -1.420498000 | 1.458783000 | 3.294642000 |
| I    | -0.839809000 | 3.781196000 | 0.000000000 |
| I    | 2.360330000 | 2.298574000 | -2.036093000 |
| I    | 1.420525000 | -1.458788000 | -3.294704000 |
| I    | -1.420498000 | 1.458783000 | -3.294642000 |
| I    | -3.757224000 | 0.939801000 | 0.000000000 |
| I    | -2.360382000 | -2.298601000 | 2.036140000 |
| I    | 0.839781000 | -3.781096000 | 0.000000000 |

Table SI5: Cartesian coordinates (in Å) of $[B_{12}I_{11}-I-B_{12}I_{11}]^{3-}$ optimized with B3LYP-GD3BJ/def2TZVPP. $E = -7447.77787657$ Ha

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| B    | -1.593612000 | -3.227277000 | 0.000000000 |
| B   |      |      |      |      |
|-----|------|------|------|------|
|     | -0.181897000 | -2.135091000 | 0.000000000 |
| B   | 1.136422000  | -2.878677000 | 0.899507000  |
| B   | 0.213321000  | -5.465558000 | 0.000000000  |
| B   | -1.118259000 | -4.690113000 | -0.892530000 |
| B   | 0.561811000  | -4.481159000 | -1.442746000 |
| B   | 1.136422000  | -2.878677000 | -0.899507000  |
| B   | -0.553160000 | -3.093090000 | 1.450738000  |
| B   | -1.118259000 | -4.690113000 | 0.892530000  |
| B   | 0.561811000  | -4.481159000 | 1.442746000  |
| B   | 1.601871000  | -4.348195000 | 0.000000000  |
| I   |     |      |      |      |
| I   | -3.655286000 | -2.522951000 | 0.000000000  |
| I   | 2.558081000  | -1.735488000 | 2.053086000  |
| I   | 0.479850000  | -7.627219000 | 0.000000000  |
| I   | -2.565269000 | -5.845150000 | -2.036706000 |
| I   | 1.274489000  | -5.374588000 | -3.294413000 |
| I   | 2.558081000  | -1.735488000 | -2.053086000 |
| I   | -1.270781000 | -2.176890000 | 3.281918000  |
| I   | -2.565269000 | -5.845150000 | 2.036706000  |
| I   | 1.274489000  | -5.374588000 | 3.294413000  |
| I   | 3.652855000  | -5.073485000 | 0.000000000  |
| I   | -1.270781000 | -2.176890000 | -3.281918000 |
| I   | -0.980488000 | 0.000883000  | 0.000000000  |
| B   | -0.187417000 | 2.137264000  | 0.000000000  |
| B   | -1.309121000 | 3.197927000  | -0.895370000 |
| B   | 1.425343000  | 2.836840000  | 0.000000000  |
| B   | 0.375967000  | 2.971884000  | 1.450978000  |
| B   | 0.375967000  | 2.971884000  | -1.450978000 |
| B   | -1.309121000 | 3.197927000  | 0.895370000  |
| B   | -0.360752000 | 4.599261000  | -1.443065000 |
| B   | -1.399920000 | 4.734109000  | 0.000000000  |
| I   | -3.000230000 | 2.444906000  | -2.038800000 |
| B   | 1.317683000  | 4.380189000  | 0.893369000  |
| B   | 1.317683000  | 4.380189000  | -0.893369000 |
| I   | 3.238434000  | 1.671556000  | 0.000000000  |
| B   | -0.360752000 | 4.599261000  | 1.443065000  |
| I   | 0.815495000  | 1.893562000  | 3.274543000  |
| I   | 0.815495000  | 1.893562000  | -3.274543000 |
| I   | -3.000230000 | 2.444906000  | 2.038800000  |
| B   | 0.223132000  | 5.465392000  | 0.000000000  |
| I   | -0.835184000 | 5.636806000  | -3.296163000 |
| I   | -3.207272000 | 5.947463000  | 0.000000000  |
| I   | 2.999500000  | 5.145112000  | 2.042227000  |
| I   | 2.999500000  | 5.145112000  | -2.042227000 |
| I   | -0.835184000 | 5.636806000  | 3.296163000  |
| I   | 0.500647000  | 7.625699000  | 0.000000000  |
Table S16: Cartesian coordinates (in Å) of the TS for[B$_2$I$_{11}$-I-B$_2$I$_{11}$]$^2_2$ formation optimized with B3LYP-GD3BJ/def2QZVPP. $E = -7447.787877$ Ha

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| B    | -4.906516000 | 0.196896000 | 1.773733000 |
| B    | -3.534080000 | 0.006805000 | 0.784254000 |
| B    | -3.571538000 | -1.059627000 | -0.533516000 |
| B    | -6.251457000 | -0.005734000 | -0.767380000 |
| B    | -6.010865000 | 1.043271000 | 0.656583000 |
| B    | -5.131800000 | 1.380885000 | -0.874356000 |
| B    | -3.462006000 | 0.754195000 | -0.735131000 |
| B    | -4.465346000 | -1.396320000 | 1.017147000 |
| B    | -6.116201000 | -0.738594000 | 0.854657000 |
| B    | -5.303348000 | -1.503145000 | -0.553908000 |
| B    | -4.693883000 | -0.192698000 | -1.621860000 |
| I    | -4.883280000 | 0.432964000 | 3.920554000 |
| I    | -1.915621000 | -2.291787000 | -1.128983000 |
| I    | -8.135949000 | -0.014170000 | -1.844444000 |
| I    | -7.545086000 | 2.370625000 | 1.419297000 |
| I    | -5.543829000 | 3.141689000 | -2.063099000 |
| I    | -1.671069000 | 1.620332000 | -1.543269000 |
| I    | -3.902020000 | -3.071111000 | 2.254395000 |
| I    | -7.784189000 | -1.680289000 | 1.869416000 |
| I    | -5.935431000 | -3.421267000 | -1.333339000 |
| I    | -4.542946000 | -0.439598000 | -3.764170000 |
| I    | -3.518755000 | 3.348560000 | 1.541356000 |
| I    | 8.240295000 | 0.175040000 | -1.356150000 |
| B    | 6.210819000 | 0.076535000 | -0.568058000 |
| B    | 5.660048000 | -1.290375000 | 0.433135000 |
| B    | 4.814030000 | 0.674753000 | -1.497844000 |
| B    | 5.342239000 | 1.536846000 | -0.031680000 |
| B    | 5.010369000 | -1.072099000 | -1.210540000 |
| B    | 5.866177000 | 0.322450000 | 1.161811000 |
| B    | 3.922305000 | -1.536339000 | 0.122279000 |
| B    | 4.452608000 | -0.674424000 | 1.589190000 |
| I    | 6.981073000 | -2.949509000 | 0.931760000 |
| B    | 3.604594000 | 1.290164000 | -0.342545000 |
| B    | 3.399551000 | -0.322381000 | -1.072551000 |
| I    | 5.045936000 | 1.542223000 | -3.481186000 |
| B    | 4.256056000 | 1.073084000 | 1.302139000 |
| I    | 6.254118000 | 3.512534000 | -0.131590000 |
| I    | 5.495707000 | -2.450412000 | -2.824940000 |
| I    | 7.450318000 | 0.736827000 | 2.596538000 |
| B    | 3.053329000 | -0.075715000 | 0.660131000 |
| I    | 2.998357000 | -3.503116000 | 0.217989000 |
| I    | 4.222301000 | -1.541980000 | 3.572039000 |
| I    | 2.276130000 | 2.939548000 | -0.838910000 |
Table SI7: Cartesian coordinates (in Å) of [H\(^+\)]\([B_{24}I_{23}]^{3-}\) optimized with B3LYP-GD3BJ/def2TZVPP. \(E = -7448.79727343\) Ha

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| B    | -2.861041000 | 0.815938000 | 1.275108000 |
| B    | -2.014292000 | -0.284563000 | 0.147292000 |
| B    | -3.139632000 |-1.578275000 |-0.354715000 |
| B    | -5.306571000 | 0.301460000 | -0.153178000 |
| B    | -4.200326000 | 1.570730000 | 0.350909000 |
| B    | -4.166689000 | 0.937684000 | -1.337966000 |
| B    | -2.800763000 |-0.222274000 | -1.469690000 |
| B    | -3.183292000 | -0.937302000 | 1.335640000 |
| B    | -4.530247000 | 0.228706000 | 1.455951000 |
| B    | -4.660606000 |-1.217428000 | -0.441904000 |
| B    | -4.471640000 |-0.810685000 | -1.268824000 |
| I    | -1.836048000 | 1.832905000 | 2.866484000 |
| I    | -2.533073000 | -3.610995000 | -0.763174000 |
| I    | -7.477174000 | 0.520982000 | 0.441904000 |
| I    | -4.873764000 | 3.592465000 | 0.770970000 |
| I    | -4.816876000 | 2.153165000 | -3.003650000 |
| I    | -1.738558000 | -0.512277000 | -3.307769000 |
| I    | -2.645816000 |-2.179560000 | 3.022820000 |
| I    | -5.661785000 | 0.493973000 | 3.280786000 |
| I    | -6.135825000 | -2.753103000 | 0.997080000 |
| I    | -5.530056000 | -1.854963000 | -2.838787000 |
| I    | -1.432657000 | 2.978794000 | -1.015791000 |
| I    | 0.082831000  | -1.061819000 | 0.594685000 |
| B    | 2.120048000  | -0.244906000 | 0.167726000 |
| B    | 2.834418000  | 1.309806000 | 0.572098000 |
| B    | 2.996588000  | -1.019942000 | -1.156560000 |
| B    | 3.255396000  | -1.552157000 | 0.533358000 |
| B    | 2.739057000  | 0.749315000 | -1.123424000 |
| B    | 3.149122000  | -0.114881000 | 1.601226000 |
| B    | 4.225633000  | 1.519590000 | -0.521551000 |
| B    | 4.484377000  | 0.979896000 | 1.161481000 |
| I    | 1.711009000  | 3.008147000 | 1.306098000 |
| B    | 4.643698000  | -1.338810000 | -0.557238000 |
| B    | 4.324839000  | 0.084879000 | -1.584452000 |
| I    | 2.013950000  | -2.293693000 | -2.608525000 |
| B    | 4.737729000  | -0.784713000 | 1.142158000 |
| I    | 2.608050000  | -3.515079000 | 1.214831000 |
| I    | 1.466796000  | 1.721641000 | -2.590142000 |
### Table SI8: Cartesian coordinates (in Å) of [H⁺][B₂₄I₂₃]³⁻ optimized with B3LYP-GD3BJ/def2TZVPP. E = -7449.22101124 Ha

| Atom | X    | Y    | Z    |
|------|------|------|------|
| B    | 2.869549000 | 0.717686000 | -1.330827000 |
| B    | 2.046331000 | -0.290357000 | -0.113539000 |
| B    | 3.168319000 | -1.546405000 | 0.472643000 |
| B    | 5.330734000 | 0.312560000 | 0.106816000 |
| B    | 4.217389000 | 1.536808000 | -0.479956000 |
| B    | 4.203983000 | 1.037351000 | 1.253892000 |
| B    | 2.838792000 | -0.106898000 | 1.481631000 |
| B    | 3.193103000 | -1.035304000 | -1.264275000 |
| B    | 4.537709000 | 0.119358000 | -1.487169000 |
| B    | 4.681866000 | -1.248891000 | -0.366943000 |
| B    | 4.507392000 | -0.712607000 | 1.313801000 |
| B    | 2.683969000 | 1.258458000 | 0.361659000 |
| I    | 1.821618000 | 1.611862000 | -2.982037000 |
| I    | 2.559830000 | -3.538844000 | 1.041655000 |
| I    | 7.499410000 | 0.541660000 | 0.198619000 |
| I    | 4.848669000 | 3.536848000 | -1.047549000 |
| I    | 4.868359000 | 2.372907000 | 2.814926000 |
| I    | 1.774347000 | -0.247455000 | 3.339657000 |
| I    | 2.626124000 | -2.395510000 | -2.845919000 |
| I    | 5.641865000 | 0.256474000 | -3.338277000 |
| I    | 6.155330000 | -2.815856000 | -0.819255000 |
| I    | 5.572081000 | -1.634095000 | 2.949207000 |
| I    | 1.503379000 | 3.071056000 | 0.796317000 |
| I    | -0.003432000 | -1.123793000 | -0.455283000 |
| B    | -2.076767000 | -0.274771000 | -0.111491000 |
| B    | -2.790067000 | 1.250588000 | -0.635246000 |
| B    | -2.977755000 | -0.951090000 | 1.264323000 |
| B    | -3.213661000 | -1.614878000 | -0.388562000 |
| B    | -2.711574000 | 0.816148000 | 1.105102000 |
| B    | -3.096764000 | -0.258973000 | -1.565260000 |
| B    | -4.187478000 | 1.538227000 | 0.434006000 |
| B    | -4.413704000 | 0.848995000 | -1.195193000 |
Table SI9: Cartesian coordinates (in Å) of \([H^+I_2B_{12}I_2]^{2-}\) optimized with B3LYP-GD3BJ/def2TZVPP. \(E = -3873.81411045\) Ha

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| B    | 1.122618000 | 1.287914000 | 0.038911000 |
| B    | 0.850924000  | 0.262377000  | 1.485400000  |
| B    | -0.849765000 | -0.265429000 | 1.485510000  |
| B    | -0.838387000 | -0.259105000 | -1.402410000 |
| B    | 0.837298000  | 0.262011000  | -1.402547000 |
| B    | 0.399617000  | -1.397705000 | -0.868362000 |
| B    | 0.412410000 | -1.395987000 | 0.926955000  |
| B    | -0.411681000 | 1.394082000  | 0.930154000  |
| B    | -0.400289000 | 1.399460000  | -0.865154000 |
| B    | -1.572081000 | 0.426216000  | 0.039833000  |
| B    | -1.122573000 | -1.287986000 | 0.037130000  |
| B    | 1.572115000  | -0.426296000 | 0.037727000  |
| I    | 2.578298000  | 2.883998000  | 0.025970000  |
| I    | -1.991248000 | -0.570222000 | 3.290926000  |
| I    | -2.062934000 | -0.525964000 | -3.187206000 |
| I    | 2.060305000  | 0.532637000  | -3.187838000 |
| I    | 0.933287000  | -3.135974000 | -2.037915000 |
| I    | 1.011660000  | -3.149510000 | 2.032706000  |
| I    | -1.010058000 | 3.145325000  | 2.039981000  |
| I    | -0.934871000 | 3.140173000  | -2.030700000 |
| I    | -3.704438000 | 0.952787000  | -0.114842000 |
| I    | -2.578254000 | -2.884048000 | 0.022041000  |
| I    | 3.704428000  | -0.952644000 | -0.119470000 |
| I    | 1.993823000  | 0.563436000  | 3.290544000  |
| H    | -3.457970000 | 0.343255000  | -1.747295000 |
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