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ARTICLE TYPE

Is the regulation of the electronic properties of organic molecules by polynuclear superhalogens more effective than that by mononuclear superhalogens? A high-level *ab initio* case study†

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Abstract

The regulation of the electronic properties of organic molecules induced by polynuclear superhalogens is theoretically explored here for sixteen composite structures. It is clearly indicated by the higher vertical electron detachment energy (VDE) that polynuclear superhalogens are more effective in regulating the electronic properties than mononuclear structures. However, this enhanced regulation is not only determined by superhalogens themselves but also related with the distribution of the extra electron of the final composites. The composites, of which the extra electron is mainly aggregated into the superhalogen moiety, will possess higher VDE values, as exampled in the case of **C1'**, 7.12 eV at CCSD(T) level. This is probably due to the fact that, compared with organic molecules, superhalogens possess stronger attraction towards the extra electron and thus should lead to lower energies of the extra electrons and to higher VDE values eventually. Compared with CCSD(T), Outer Valence Green's Function (OVGF) method fails completely for composite structures including Cl atom while MP2 results are generally consistent in the aspect of relative order of VDEs. Actually if the extra electron distribution of the systems could be approximated by HOMO, the results at OVGF level will be consistent with the CCSD(T) results. Conversely, the difference of VDEs between OVGF and CCSD(T) is significantly large. Besides superhalogen properties, the structures, relative stabilities and thermodynamic stabilities with respect to various fragmentation channels were also investigated for all the composite structures.

INTRODUCTION

Superhalogen is a kind of clusters consisted of central atoms and high electronegative ligands.[1, 2] Its main characteristic is the strong capability of binding the extra electron,[1-4] reflected in both the neutral forms having extremely high electron affinity (EA) and anionic forms possessing quite high vertical electron detachment energy (VDE). Owing to this character, on one hand, superhalogens possess strong oxidation ability and application potentials in the field of synthesis[3, 5, 6] and preparation of new materials.[2-7] On the other hand, the anionic forms of superhalogens are highly stable and thus could be utilized as dopants to increase the electrical conductivity of polymers.[1, 3] In fact, some superhalogen anions are commonly found as promising candidates of building blocks in both condensed phase materials and gas phase molecules.[4, 8, 9]

It is well known that some organic molecules (ethane, ethylene, benzene) are formed metastable anions only.[10-12] Albeit the F, Cl, and CN species are considered relatively effective oxidizing agents (due to their large electron affinities spanning the 3.40~3.90 eV range)[13-15] the resulting C_2H_3X, C_2H_5X, and C_6H_5X molecules (X = F, Cl, CN) do not bind an excess electron to form electronically stable anions.[11, 12] Recent works reported by Skurski and co-workers have indicated that introducing a superhalogen-like substituent into organic molecules, e.g., hydrocarbon and amino acid,[16-18] would regulate these molecules electronic properties. These composite structures,[19] generated from the combination of organic molecules of small or even negative VDE with superhalogens, possess VDE values apparently higher than their organic parents. That is to say, the organic molecules, of which the anionic forms are unstable,[10-12, 20-22] will produce stable anions after introducing superhalogen-like substituent.[16-18] Therefore the electronic properties of the organic species could be regulated by superhalogens. This type of regulation of the electronic properties of organic molecules may probably broaden the application potentials of superhalogens[16, 18] and thus it is highly worth of subsequently systematic investigation.

Previous studies have shown that, compared with mononuclear superhalogens,[23-26] the properties of polynuclear superhalogens are more prominent, their VDE values are higher and the corresponding electronic stabilities are stronger.[9, 27-38] Therefore, studying polynuclear superhalogens have become a valuable new

research direction. Among the reported works of superhalogens regulating the properties of organic molecules, they are all mononuclear structures.[16-18] Can polynuclear superhalogen regulate the electronic properties of organic molecules too? What will the effects of the regulation induced by polynuclear superhalogens be? Are the characteristics and laws of the regulation of polynuclear structures different from those of mononuclear structures? These are all urgent and untouched questions need to be explored by further study.

Therefore, we report here theoretical study of a series of composite structures formed by mononuclear ($[MgF_3]^{-1}$, $[MgCl_3]^{-1}$)[24] and binuclear ($[Mg_2F_5]^{-1}$, $[Mg_2Cl_5]^{-1}$)[27, 28] superhalogens combined with typical hydrocarbons i.e., ethylene, ethane and benzene, based on high-level *ab initio* calculations. We focus on the difference from mononuclear substitution to polynuclear substitution and on the characteristics of the regulation of the electronic properties induced by polynuclear superhalogens.

THEORETICAL METHODS AND COMPUTATIONAL DETAILS

The equilibrium geometries of the species studied here were optimized at MP2[39] level with the 6-311+G* basis set.[40, 41] The obtained structures are confirmed to be local minima by the nonexistence of imaginary frequency.[42]

Outer Valence Green's Function (OVGF)[43-45] method, which has become the most popular *ab initio* method for various superhalogen systems,[17, 18, 23, 28, 30, 32, 43-51] was used here to directly predict the VDE values of the composite structures. Although the accuracy of OVGF has been examined in many mononuclear superhalogens,[16, 28, 46-48, 50, 52-56] its capability for other superhalogen-related systems is not a matter free of debate since large deviation of OVGF results from high-level CCSD(T) calculations has been reported for superhalogen systems.[29, 57]

Therefore, to provide more reliable results of VDEs, we have also performed indirect calculations with MP2, CCSD and CCSD(T)[58-60] methods. The indirect approach consists of subtracting the anion energies from those of the neutral at the same level.[37, 48, 49, 51, 57, 61]

An enlarged basis set, AUG-CC-PVTZ,[62] is also used for OVGF. Besides 6-311+G*, CCSD and CCSD(T) calculations were also performed with a larger basis set, consisting of Def2-TZVP[63] for Mg and TZVP[64] augmented with the diffuse function[65] from 6-311+G* for all the other elements. However, the increased size of basis set provides near negligible change for OVGF, CCSD and CCSD(T) results. Therefore the results with basis sets other than 6-311+G* are only included in ESI (Table S1).

All the calculations were performed with Gaussian 09 code[66] with the exception of CCSD and CCSD(T) results which were obtained with ORCA 3.0.2 program.[67, 68]

RESULTS AND DISCUSSIONS

1. Structures and relative stabilities of the $C_2H_3Y^-$, $C_2H_5Y^-$, and $C_6H_5Y^-$ (Y=MgF_2, $MgCl_2$, Mg_2F_4, Mg_2Cl_4) anions

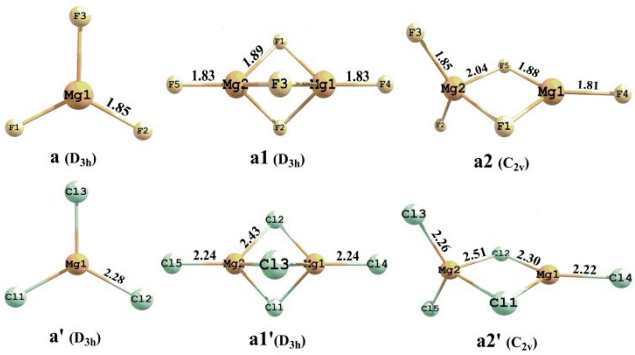

Fig. 1. Optimized structures and selective bond lengths of the mononuclear and binuclear superhalogen anions.

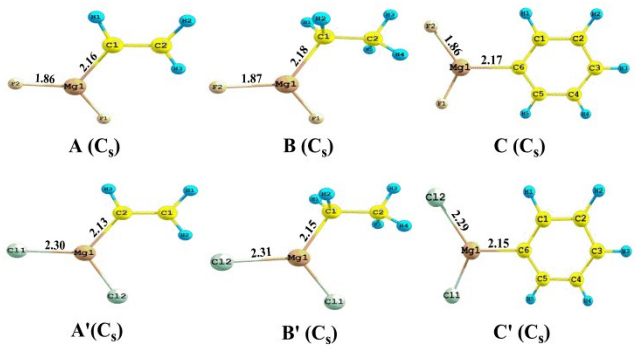

Fig. 2. Optimized structures and selective bond lengths of the mononuclear superhalogen composite structures.

The superhalogen-like substituents are formed by removing one halogen atom from the mononuclear and polynuclear superhalogens here.[16] These substituents are employed to obtain composite structures by replacing one hydrogen atom of the organic molecules (ethylene, ethane and benzene). Since all the hydrogen atoms are equivalent in these organic molecules, each organic species has only one replaced position when certain superhalogen-like substituent is used. The mononuclear superhalogens $[MgX_3]^{-1}$（X=F, Cl）(**a**, **a'** in Fig. 1), all the halogen atoms are equivalent, can only form one type of mononuclear superhalogen-like substituent. Therefore, there is only one composite structure when a mononuclear superhalogen-like substituent is combined with an organic molecule. For three organic molecules (ethylene, ethane and benzene), there are surely three composite structures (**A**, **B**, **C**) including F atom and corresponding three composite structures (**A '**, **B '**, **C '**) with Cl atom (in Fig. 2).

Based on previous work,[16, 17] we only consider here the binuclear superhalogen-like substituents obtained from the detachment of one terminal halogen atom. For triple-bridge structures(**a1, a1'** in Fig.1), the two terminal halogen atoms are equivalent to each other and thus there is only one type of superhalogen-like substituent, we call it type I substituent. For double-bridged structures(**a2, a2'** in Fig. 1), there are two types of superhalogen-like substituent because of the existence of two types of terminal halogen atoms. Taking $[Mg_2F_5]^{-1}$ (**a2** in Fig. 1) as an example, Mg_1 atom binds with only one terminal F_4 atom and Mg_2 atom links with two equivalent terminal atoms F_2 and F_3. This double-bridged superhalogen $[Mg_2F_5]^{-1}$ removes F_4 atom to

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form the type II substituent and it removes F_2 or F_3 atom to form the type III substituent. Finally, for binuclear superhalogens, there are totally three types of superhalogen-like substituent, type I, II, III.

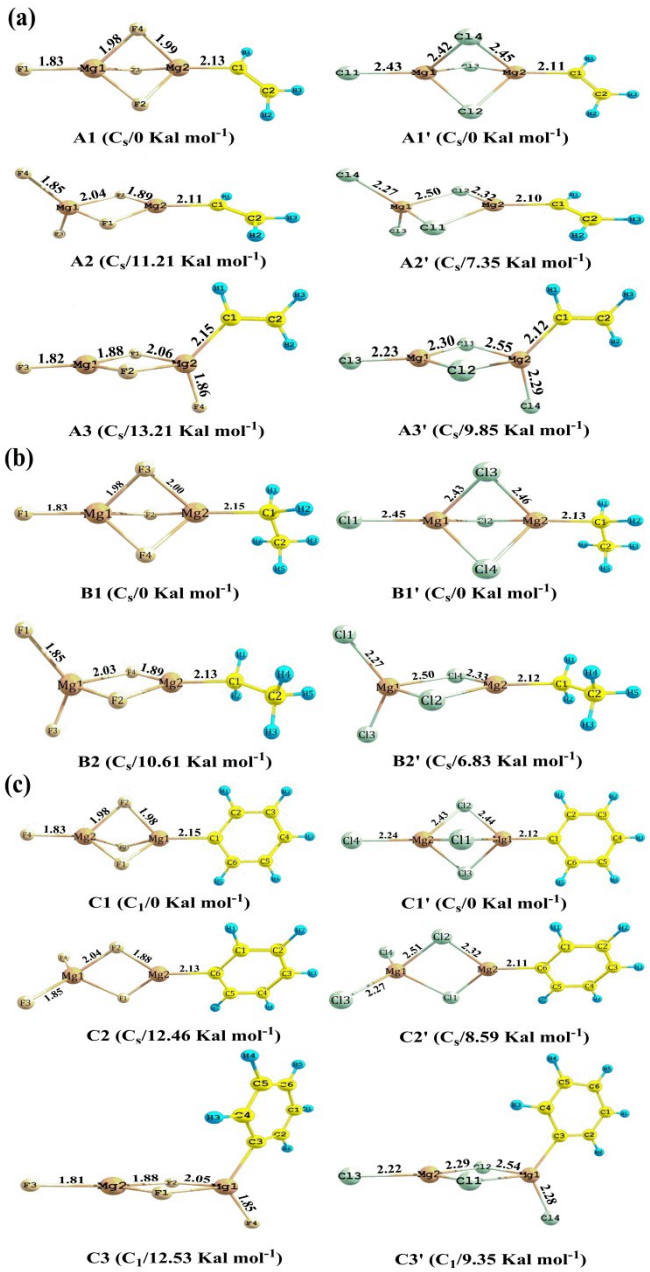

Fig. 3. Optimized structures, selective bond lengths, and relative energy (corrected with zero point vibration energy) of the binuclear superhalogen composite structure anions. (a) $[C_2H_3Mg_2X_4]^{-1}$, (b) $[C_2H_5Mg_2X_4]^{-1}$, (c) $[C_6H_5Mg_2X_4]^{-1}$ (X=F, Cl).

Therefore, for a certain organic molecule, there are at most three composite structures when combined with above three types of binuclear superhalogen-like substituent. In fact, for ethylene and benzene molecules, a total number of six composite clusters including F atom are finally obtained from the geometry optimizations, **A1-A3** in Fig. 3(a) and **C1-C3** in Fig. 3(c). However, for ethane molecule, there are only two composite structures **B1** and **B2**, formed with the type I and type II substituent respectively. Since the optimization of the initial structure, formed with the type III substituent, leads to the composite structure **B2** eventually. Similar situation takes place in the composite structures with Cl atom too as shown in Fig. 3.

Among all the composite structures obtained from binuclear superhalogen-like substituents, the most stable ones are those formed with type I substituent, i.e., the triple-bridged superhalogens. For example, among **A1**, **A2** and **A3**, obtained from the combination of ethylene and $[Mg_2F_5]^{-1}$ superhalogen, **A1** is the most stable one and the relative energies of **A2** and **A3** are 11.21 and 13.21 Kcal mol^{-1} respectively. In the corresponding structures of Cl atoms, **A1'** is again the most stable one and the relative energies of **A2'** and **A3'** are 7.35 and 9.85 Kcal mol^{-1} respectively. Similar situation occurs in structures including ethane and benzene molecules too (Fig. 3(b), (c)). In addition, for a certain organic molecule (ethylene, ethane, or benzene), we have found that the relative energies of composite structures are decreased from F to Cl atom.

2. Electron detachment energies of the $C_2H_3Y^-$, $C_2H_5Y^-$, and $C_6H_5Y^-$ (Y=MgF_2, $MgCl_2$, Mg_2F_4, Mg_2Cl_4) anions

For organic molecules, it is very difficult to bound extra electron.[10-12] However, this ability will be significantly improved by introducing a superhalogen-like substituent. That is to say, superhalogens could regulate the electronic properties of organic molecules. According to Table 1, firstly, the VDE values of all the composite structures studied here are positive, secondly, their VDEs are significantly larger than the maximum atomic value (3.60 eV)[14] of the halogen element. Therefore the extra electrons of these composites are very stable and they could be considered to be strongly bound anions.

In detail, at CCSD(T) level, compared with the mononuclear superhalogen composites, the VDE values of binuclear composites are higher. For example, for ethylene-based composites, the VDEs of binuclear structures **A1**, **A2**, and **A3** are larger than that of monuclear composite **A** by 0.30~1.80 eV. In the cases of ethane-based composites, the VDEs are increased by 0.89~1.81 eV from mononuclear structure **B** to binuclear composites **B1** and **B2**. Similarly, for benzene-based composites, the VDEs also increase by 0.17~1.09 eV from **C** to **C1**, **C2** and **C3**. The composite structures including Cl atom occur similar situations. Therefore, compared with the mononuclear structures, polynuclear superhalogens are clearly more effective in regulating the electronic properties of typical organic small molecules and they could possess larger potentials in application.

As shown in Table 1, for all the composite structures, the

VDEs at MP2 level are generally larger than those at CCSD(T) level and the overestimation remains within the range of 0.05~0.88 eV. However, the relative order of the VDE values at MP2 level are generally consistent with that of CCSD(T) results as shown in Fig. 4.

Table 1. Calculated VDEs of the composite structure anions under study at various theoretical levels (in eV).

	MP2	OVGF	CCSD	CCSD(T)
A	5.05	5.31(0.91)[a]	4.61	4.63
B	3.88	3.89(0.92)	3.79	3.83
C	5.69	5.00(0.89)	5.24	5.32
A'	5.31	5.59(0.91)	4.83	4.84
B'	4.19	4.18(0.91)	4.06	4.09
C'	6.43	5.20(0.89)	6.32	6.24
A1	5.97	6.00(0.92)	5.51	5.55
A2	6.84	6.77(0.92)	6.40	6.43
A3	5.35	5.51(0.91)	4.90	4.93
A1'	7.28	6.22(0.91)	7.13	7.01
A2'	6.64	6.88(0.91)	6.53	6.45
A3'	6.62	5.87(0.90)	6.50	6.51
B1	4.78	4.77(0.92)	4.68	4.72
B2	5.69	5.68(0.92)	5.60	5.64
B1'	7.04	5.01(0.91)	7.08	6.92
B2'	5.74	5.74(0.91)	5.61	5.64
C1	5.90	5.58(0.89)	5.81	5.85
C2	6.79	6.19(0.89)	6.33	6.41
C3	5.87	5.17(0.89)	5.43	5.49
C1'	7.51	5.74(0.89)	7.22	7.12
C2'	6.74	6.26(0.89)	6.57	6.56
C3'	7.57	5.42(0.89)	6.66	6.69
Mg_2F_5(T)[b]	9.06	7.45(0.86)	8.96	8.86
Mg_2F_5(D)[c]	8.42	6.41(0.87)	8.03	7.97
Mg_2Cl_5(T)	7.48	7.34(0.89)	7.54	7.38
Mg_2Cl_5(D)	6.83	6.50(0.91)	6.72	6.64
MgF_3	8.03	8.56(0.98)	7.65	7.66
$MgCl_3$	6.29	6.34(0.92)	6.31	6.17

[a] Pole strength is shown in parenthesis.

[b]Triple-bridge structure

[c] Double-bridge structure

As shown in the second column of Table 1, the pole strengths, which are all larger than 0.85, verify the OVGF approximation. For composite structures with F atom, the relative order of VDE values at OVGF level agrees with CCSD(T) even though OVGF either overestimates or underestimates the VDEs as shown in Fig. 5(a). For example, compared with CCSD(T) results, the VDE value is overestimated by 0.68 eV for **A** but is underestimated by 0.32 eV for **C**. In the case of composite structures with Cl atom, the relative order of VDE values at OVGF level is apparently different from that of CCSD(T) as shown in Fig. 5(b). Besides that, the deviation of OVGF values from CCSD(T) level is significantly larger in the composites with Cl atom. For example, the VDE values of **B1'**, **C1'** and **C3'** are underestimated by 1.91, 1.38 and 1.27 eV, respectively.

Although OVGF has become one of the most popular *ab initio* methods for superhalogen-related systems, its performance here is not good. MP2 method may be acceptable here since it provides the right trend of the relative VDE values. However, it seems that sufficient reliability of the theoretical values could be ensured only from high-level calculations, e.g., CCSD(T).

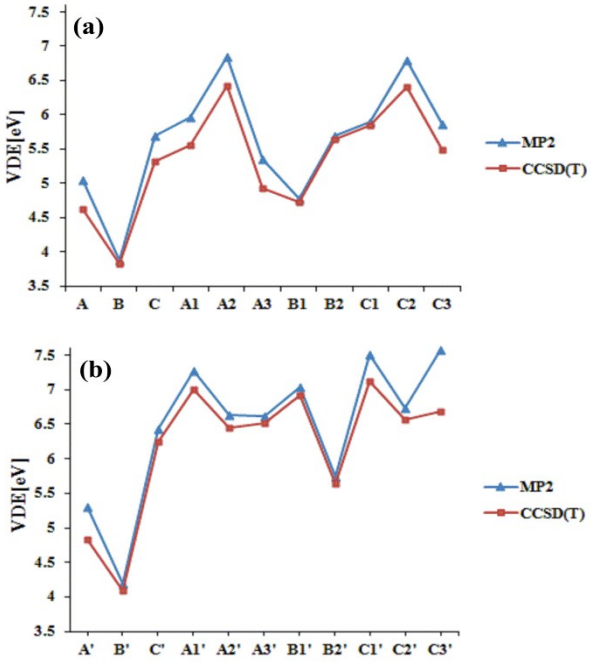

Fig. 4. The comparison between VDE values at MP2 and CCSD(T) level, (a) composite structures with F atom, (b) composite structures with Cl atom.

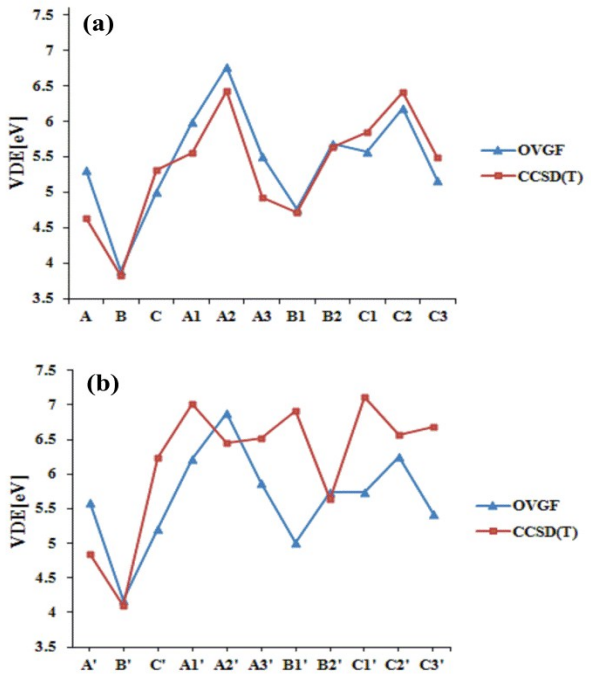

Fig. 5. The comparison between VDE values at OVGF and CCSD(T) level, (a) composite structures with F atom, (b) composite structures with Cl atom.

3. Analysis on the distribution of the extra electron of the $C_2H_3Y^-$, $C_2H_5Y^-$, and $C_6H_5Y^-$ (Y=MgF_2, $MgCl_2$, Mg_2F_4, Mg_2Cl_4) anions under study

The above results demonstrate that the electronic properties of organic molecules could be regulated by polynuclear superhalogens too. Furthermore, the VDE values of the resulted composites are higher than those of corresponding mononuclear composites. However, this increased effect of the regulation, from mononuclear superhalogen to polynuclear superhalogen, is not entirely determined by superhalogens themselves. As shown by high-level CCSD(T) results, the VDE values of $[Mg_2F_5]^{-1}$ are higher than those of $[Mg_2Cl_5]^{-1}$ by 1.33 and 1.48 eV (Table 1), but binuclear composite structures with Cl atom usually have VDE values higher than those of corresponding composites with F atom. For example, the VDE of **B1'** is higher than that of **B1** by 2.20 eV. Therefore, some other factors, which also influence the effect of the regulation, must exist.

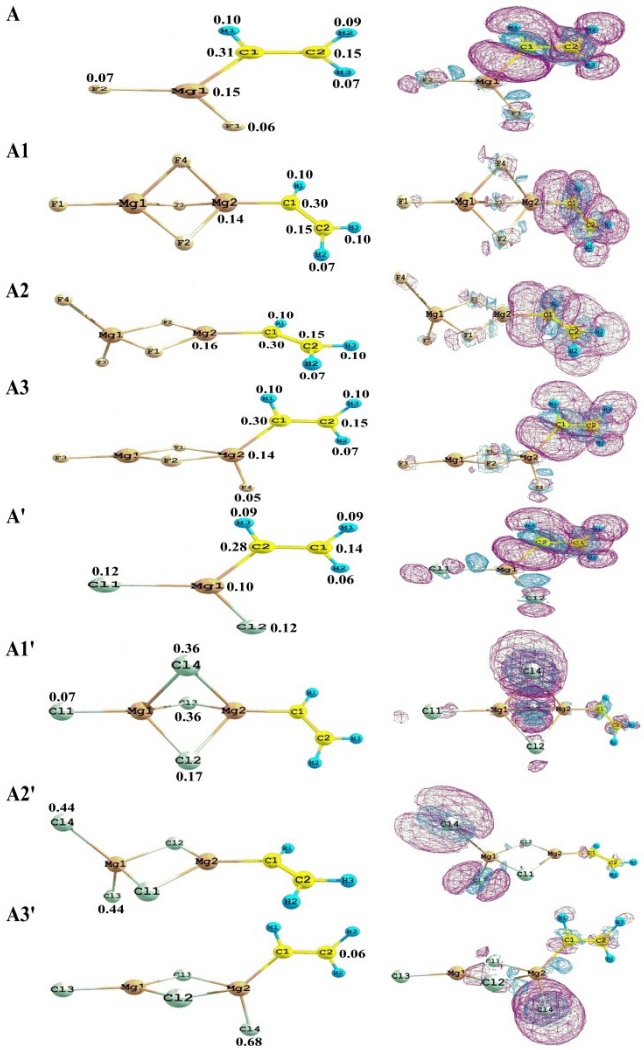

Fig. 6. 3D representation (isovalue set to be 0.002 a.u.) and condensed values (larger than 0.04 a.u. from Löwdin population) of the distribution of extra electron of the $[C_2H_3Mg_2X_4]^{-1}$ and $[C_2H_3MgX_2]^{-1}$ (X=F, Cl) composite structures based on density difference between anion and neutral forms at CCSD level.

According to previous work, analysis on the distribution of the extra electron could provide microscopic interpretation and mechanism of the properties of superhalogens.[29] Therefore, we also analyzed here the distribution of extra electron, based on linearized CCSD electron density from ORCA calculations.

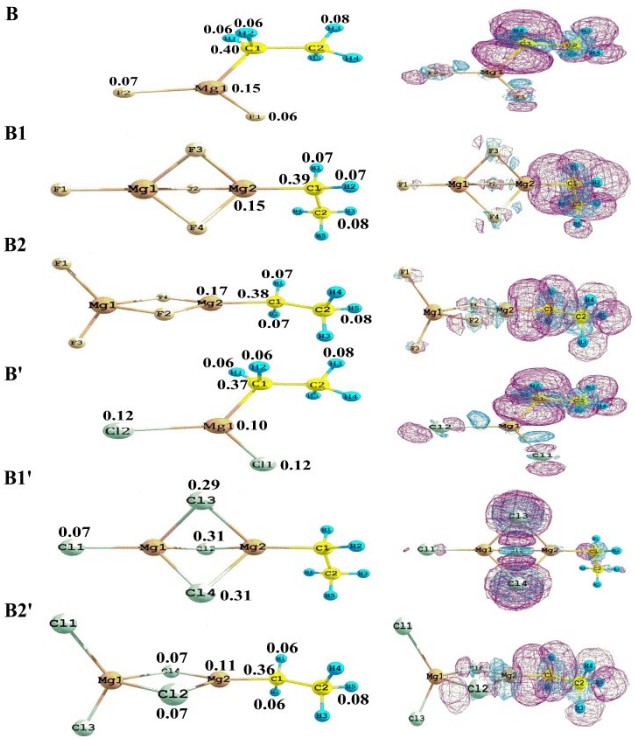

Fig. 7. 3D representation (isovalue set to be 0.002 a.u.) and condensed values (larger than 0.04 a.u. from Löwdin population) of the distribution of extra electron of the $[C_2H_5Mg_2X_4]^{-1}$ and $[C_2H_5MgX_2]^{-1}$ (X=F, Cl) composite structures based on density difference between anion and neutral forms at CCSD level.

In the cases of various composites including F atom, there is one common feature in the distribution of extra electrons, that is the main aggregation into the organic moiety (Fig.6~8). Therefore, it could be deduced that, for these composites, the reason of the increased VDE from mononuclear to polynuclear structure should be the enhancement of superhalogen properties of the substituent.

The situation of composites including Cl atom is different. The extra electrons of the mononuclear composites **A'** and **B'**, based on ethylene and ethane, are still localized at the organic moieties. However, the extra electrons of the corresponding binuclear composites are mainly aggregated into the superhalogen moieties. Compared with organic molecules, superhalogens possess stronger attraction towards the extra electron and thus should lead to lower energies of the extra electrons and to higher VDE values eventually. According to this idea, it could be inferred that the increase of the VDE from mononuclear to binuclear composites including Cl atom should be larger than that of including F atom. This prediction is actually confirmed by our ab initio results. At CCSD(T) level, the VDE values of **B1** and **B2** are higher than that of **B** by 0.89~1.81 eV while the VDEs of **B1'** and **B2'** are remarkably higher than that of **B'** by 1.55~2.83 eV. For the composites based on benzene, **C'-C3'**, the difference between VDEs of the binuclear and mononuclear structures is apparently

small (0.32~0.88 eV). The reason is that the extra electron distribution of mononuclear structure is consistent with that of binuclear structure, i.e.,localized on the superhalogen moieties (Fig. 8).

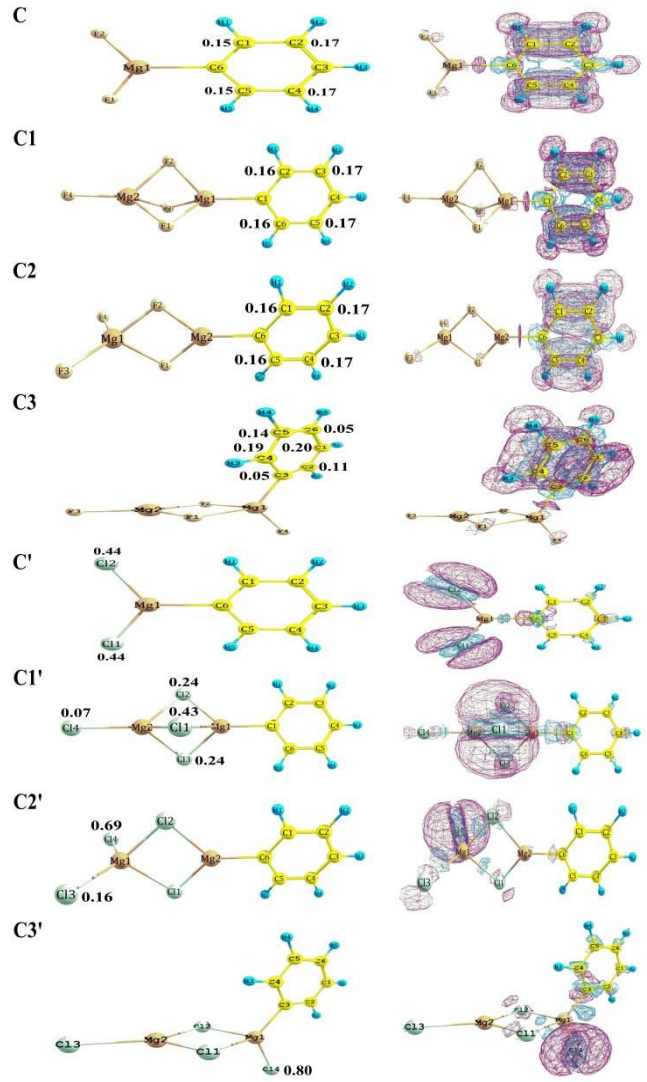

Fig. 8. 3D representation (isovalue set to be 0.002 a.u.) and condensed values (larger than 0.04 a.u. from Löwdin population) of the distribution of extra electron of the $[C_6H_5Mg_2X_4]^{-1}$ and $[C_6H_5MgX_2]^{-1}$ (X=F, Cl) composite structures based on density difference between anion and neutral forms at CCSD level.

Similar as the binuclear composite structures, the distributions of the extra electrons of mononuclear composites are different for structures including F atom from those including Cl atom. For example, the extra electron distribution of **C'**, mainly aggregated into the superhalogen part, is remarkably different from that of **C** which is localized into the benzene moiety in Fig. 8. Thus this difference will lead to higer VDE for **C'** than **C** by 0.92 eV.

According to above all, the different distributions of the extra electrons have important influence on the VDE values of the composite structures studied here.

4. Comparison of HOMO and the extra electron distribution

The highest occupied molecular orbital (HOMO) has been utilized to approximate the distribution of the extra electron of superhalogen-related systems in previous work.[16-18, 25, 26] Therefore, the comparison between HOMO and the extra electron distribution is performed in this work.

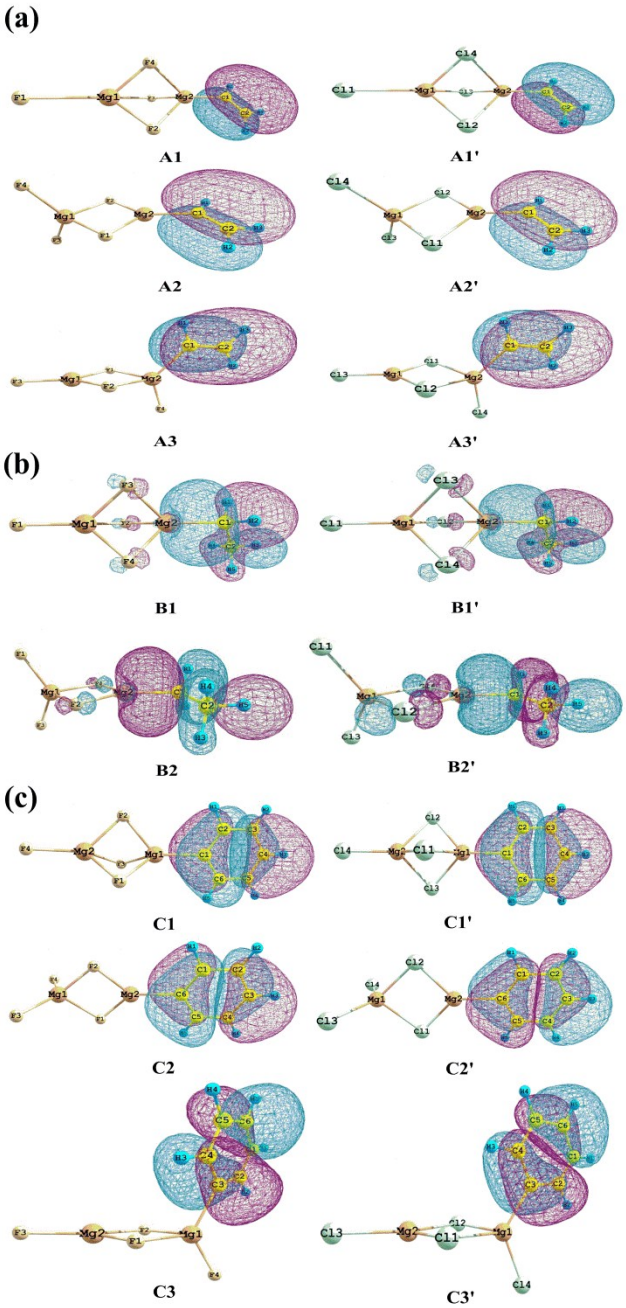

Fig. 9. The HOMO (isovalue 0.02 Å^{-3}) in the binuclear superhalogen composite structures. (a) $[C_2H_3Mg_2X_4]^{-1}$, (b) $[C_2H_5Mg_2X_4]^{-1}$, (c) $[C_6H_5Mg_2X_4]^{-1}$ (X=F, Cl).

For binuclear composites including F atom, the distribution of HOMO is generally consistent with that of the extra electron, i.e., mainly localized into the organic moieties as shown in Fig. 6~9. In addition, we also analyzed the increase of the VDE values, ΔVDE, from mononuclear to binuclear composites. It is found that the values of ΔVDE, at both OVGF and CCSD(T) levels are consistent with each other as shown in Fig. 10(a) where the blue solid line (OVGF results) and the red solid line (CCSD(T) results)

are extremely close to each other. For example, the ΔVDE from **B** to **B1** at OVGF level is 0.88 eV while the value at CCSD(T) level is 0.89 eV.

However, for the binuclear composite structures including Cl atom, there is apparent difference between the distributions of HOMO and those of the extra electron. HOMOs are mainly localized into organic moieties while the extra electrons are aggregated into the superhalogen part. As shown in Fig. 10(b), the ΔVDE values for composites including Cl atom at OVGF level are remarkably different from those of CCSD(T). For example, at OVGF level, the ΔVDE of from **A'** to **A1'** and that from **B'** to **B1'** is 0.63 and 0.83 eV respectively. However, the corresponding values at CCSD(T) level are 2.17 and 2.83 eV respectively.

According to above results, it may be concluded that, if the extra electron density of the systems could be approximated with HOMO orbital, the results at OVGF level will be consistent with the CCSD(T) calculations. Conversely, the difference between OVGF and CCSD(T) is significantly large.

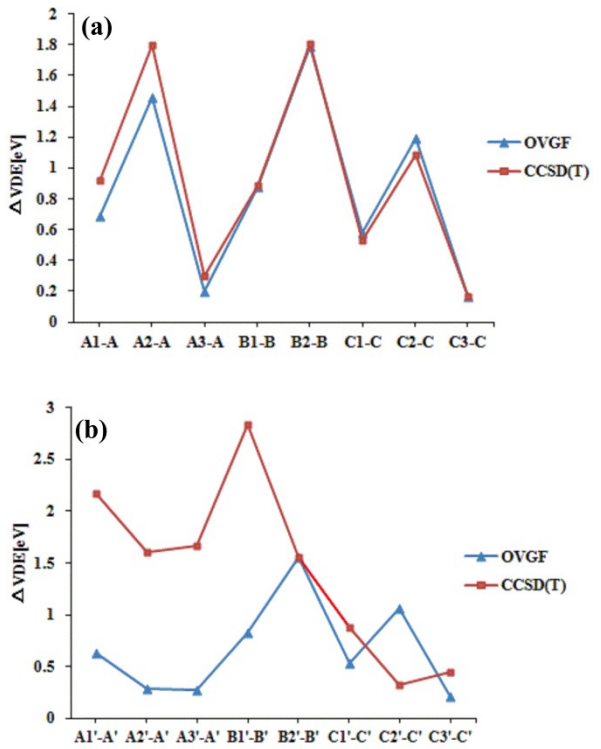

Fig. 10. The comparison between ΔVDE values at OVGF and CCSD(T) level, (a) composite structures with F atom, (b) composite structures with Cl atom.

It is well known that CCSD(T) is highly reliable in predicting VDE values since it takes into account of electron correlation sufficiently.[23, 37, 48, 50, 69, 70] In the aspect of calculating VDE values by OVGF,[43-45] this method uses only closed-shell HF single-determinant of the anionic form as reference and appromximates the electron detachment by electron propagator theory. Compared with CCSD(T), there are several defects in OVGF, e.g., the orbital relaxation arising from the electron detachment may be ignored. The incapacity of HOMO to describe the extra electron should imply that the orbital relaxation, arising from the electron detachment, gives remarkable influence on the extra electron distribution as well as VDE. Thus it is not strange that OVGF, as a method which ignores the orbital relaxation, will fail in these cases.

5. Thermodynamic stability of the $C_2H_3Y^-$, $C_2H_5Y^-$, and $C_6H_5Y^-$ (Y=MgF_2, $MgCl_2$, Mg_2F_4, Mg_2Cl_4) anions

Table 2. Mononuclear superhalogen composite structure anions MP2 (in kcal mol^{-1}) and free enthalpies (ΔG_r^{298} in kcal mol^{-1}) of the fragmentation reactions (for T = 298.15 K) considered in this work. The results are obtained at the MP2/6-311 + G* level.

Fragmentation path	MP2	ΔG_r^{298}
A$^-$ → $C_2H_3^-$ + MgF_2	85.02	77.68
A$^-$ → C_2H_3MgF + F^-	84.34	76.93
A'$^-$ → $C_2H_3^-$ + $MgCl_2$	91.98	84.82
A'$^-$ → C_2H_3MgCl + Cl^-	61.60	54.59
B$^-$ → $C_2H_5^-$ + MgF_2	89.45	82.06
B$^-$ → C_2H_5MgF + F^-	80.56	73.93
B'$^-$ → $C_2H_5^-$ + $MgCl_2$	96.92	90.27
B'$^-$ → C_2H_5MgCl + Cl^-	58.43	52.71
C$^-$ → $C_6H_5^-$ + MgF_2	79.39	71.38
C$^-$ → C_6H_5MgF + F^-	88.90	81.13
C'$^-$ → $C_6H_5^-$ + $MgCl_2$	86.97	78.83
C'$^-$ → C_6H_5MgCl + Cl^-	66.50	58.76

According to previous works,[16, 17] two of the various possible fragmentation paths are selected and investigated at MP2 level to study the thermodynamic stabilities of these composite structures. They are: (i) the detachment of the neutral superhalogen substituent (MgF_2, $MgCl_2$, Mg_2F_4, Mg_2Cl_4) and (ii) the loss of the F^- or Cl^- anion. Our previous results have demonstrated that the fragmentation energies at higher theoretical levels, MP4 and CCSD, are also quite close to those at MP2 level since the derivations are only within 2 Kcal mol^{-1}.[29]

As shown in Table. 2 and 3, the values of the fragmentation energies are all positive. For the first fragmentation channel, the values are calculated to be within the range from 81 to 130 Kcal mol^{-1} based on electronic energies. The inclusion of zero point vibration energy (ΔGr^{298}) provides the same results even though the corresponding values are lower by 6~13 Kcal mol^{-1}. Similar situation takes place in the second fragmentation channel, the values of the fragmentation energies are calculated to be within the range of 58~106 Kcal mol^{-1} based on electronic energies and that of zero point vibration energy (ΔGr^{298}) are from 5 to 15 Kcal mol^{-1}.

For all these superhalogen composite structures, the calculated fragmentation energies are larger than 50 Kcal mol^{-1} whatever the neutral superhalogen substituent was detached or the halogen anion was lost. Therefore, these fragmentation channels here are strongly endothermic, i.e., thermodynamically stable. Thus, we believe in the stability of the superhalogen composite structure anions here as their geometrical and electronic stabilities have been verified by non-existence of imaginary frequency (see ESI) and high VDE values.

Table 3. Binuclear superhalogen composite structure anions MP2 (in kcal mol^{-1}) and free enthalpies (ΔG_r^{298} in kcal mol^{-1}) of the fragmentation reactions (for T = 298.15 K) considered in this work. The results are obtained at the MP2/6-311 + G* level.

Fragmentation path	MP2	ΔG_r^{298}
A1$^-$ → $C_2H_3^- + Mg_2F_4$	119.51	107.20
A1$^-$ → $C_2H_3Mg_2F_3+F^-$	103.36	94.22
A2$^-$ → $C_2H_3^- + Mg_2F_4$	90.32	96.00
A2$^-$ → $C_2H_3Mg_2F_3+F^-$	90.87	83.01
A3$^-$ → $C_2H_3^- + Mg_2F_4$	87.64	76.18
A3$^-$ → $C_2H_3Mg_2F_3+F^-$	88.19	81.00
A1'$^-$ → $C_2H_3^- + Mg_2Cl_4$	123.27	110.85
A1'$^-$ → $C_2H_3Mg_2Cl_3+Cl^-$	80.31	71.62
A2'$^-$ → $C_2H_3^- + Mg_2Cl_4$	114.33	103.50
A2'$^-$ → $C_2H_3Mg_2Cl_3+Cl^-$	71.37	64.27
A3'$^-$ → $C_2H_3^- + Mg_2Cl_4$	98.41	86.61
A3'$^-$ → $C_2H_3Mg_2Cl_3+Cl^-$	68.73	61.78
B1$^-$ → $C_2H_5^- + Mg_2F_4$	125.23	112.34
B1$^-$ → $C_2H_5Mg_2F_3+F^-$	101.65	92.41
B2$^-$ → $C_2H_5^- + Mg_2F_4$	113.25	101.73
B2$^-$ → $C_2H_5Mg_2F_3+F^-$	89.66	81.80
B1'$^-$ → $C_2H_5^- + Mg_2Cl_4$	129.62	116.67
B1'$^-$ → $C_2H_5Mg_2Cl_3+Cl^-$	79.28	70.38
B2'$^-$ → $C_2H_5^- + Mg_2Cl_4$	120.63	109.85
B2'$^-$ → $C_2H_5Mg_2Cl_3+Cl^-$	70.29	63.41
C1$^-$ → $C_6H_5^- + Mg_2F_4$	112.06	99.58
C1$^-$ → $C_6H_5Mg_2F_3+F^-$	105.72	96.86
C2$^-$ → $C_6H_5^- + Mg_2F_4$	98.58	87.12
C2$^-$ → $C_6H_5Mg_2F_3+F^-$	92.24	84.34
C3$^-$ → $C_6H_5^- + Mg_2F_4$	81.52	69.25
C3$^-$ → $C_6H_5Mg_2F_3+F^-$	91.87	84.30
C1'$^-$ → C_6H_5- + Mg_2Cl_4	116.61	104.32
C1'$^-$ → $C_6H_5Mg_2Cl_3+Cl^-$	82.63	74.43
C2'$^-$ → $C_6H_5^- + Mg_2Cl_4$	106.71	95.73
C2'$^-$ → $C_6H_5Mg_2Cl_3+Cl^-$	72.74	65.84
C3'$^-$ → $C_6H_5^- + Mg_2Cl_4$	92.72	80.59
C3'$^-$ → $C_6H_5Mg_2Cl_3+Cl^-$	71.98	65.11

CONCLUSIONS

According to the results provided by high-level *ab initio* calculations here, we concluded the following:

At the highest CCSD(T) level, compared with the composites from mononuclear superhalogen ($[RMgX_2]^{-1}$), the VDEs of the composites from binuclear superhalogen ($[RMg_2X_4]^{-1}$) are higher. Therefore, polynuclear superhalogens are clearly more effective in regulating the electronic properties of typical organic small molecules. However, this more effective regulation is not only determined by superhalogen themselves but also related with the distribution of the extra electron of the composites. When the extra electron aggregates on the superhalogen moiety, the composite will have high VDE since superhalogens possess strong attraction towards the extra electron.

Compared with CCSD(T), OVGF fails for the composite structures with Cl atom and thus its reliability is questionable. Although there are deviations from CCSD(T) results in the aspect of absolute value of VDE, the relative order of VDEs with MP2 is generally consistent with CCSD(T). Knowing the extremely high lost of CCSD(T) calculations, MP2 method should be at least acceptable in the relative values of VDE.

For binuclear composites including F atom, it is reasonable to approximate the distribution of the extra electron by that of HOMO. This fact may be the reason for the agreement between OVGF and CCSD(T) for these composites. Whereas, for binuclear superhalogen composites with Cl atom, this approximation is not acceptable and thus OVGF results are remarkably different from CCSD(T). Therefore, we could conclude that OVGF could be reliable only if the extra electron of the system could be approximated by HOMO.

Detachment of halogen anions (F^-, Cl^-) and neutral superhalogen-like substituents (MgF_2, $MgCl_2$, Mg_2F_4, Mg_2Cl_4) of the composite structures here are shown to be highly endothermic according to the calculated fragmentation energies. This confirms the thermodynamic stability of these composite structures.

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Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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