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# Star-like superalkali cations featuring planar pentacoordinate carbon

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Superalkali cations, known to possess low vertical electron affinities (VEAs), high vertical detachment energies, and large highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps, are intriguing chemical species. Thermodynamically, such species need to be the global minima in order to serve as the promising targets for experimental realization. In this work, we propose the strategies of polyhalogenation and polyalkalination for designing the superalkali cations. By applying these strategies, the local-minimum planar pentacoordinate carbon (ppC) cluster CBe<sub>5</sub> can be modified to form a series of star-like superalkali ppC or quasi-ppC  $CBe_5X_5^+$ (X = F, Cl, Br, Li, Na, K) cations containing a CBe<sub>5</sub> moiety. Polyhalogenation and polyalkalination on the CBe<sub>5</sub> unit may help eliminate the high reactivity of bare CBe<sub>5</sub> molecule by covering the reactive Be atoms with noble halogen anions and alkali cations. Computational exploration of the potential energy surfaces reveals that the star-like ppC or quasi-ppC  $CBe_5X_5^+$  (X = F, Cl, Br, Li, Na, K) clusters are the true global minima of the systems. The predicted VEAs for  $CBe_5X_5^+$  range from 3.01 to 3.71 eV for X = F, Cl, Br and 2.12–2.51 eV for X = Li, Na, K, being below the lower bound of the atomic ionization potential of 3.89 eV in the periodic table. Large HOMO-LUMO energy gaps are also revealed for the species: 10.76-11.07 eV for X = F, Cl, Br and 4.99-6.91 eV for X = Li, Na, K. These designer clusters represent the first series of superalkali cations with a ppC center. Bonding analyses show five Be–X–Be three-center two-electron (3c-2e)  $\sigma$  bonds for the peripheral bonding, whereas the central C atom is associated with one 6c-2e  $\pi$  bond and three 6c-2e  $\sigma$  bonds, rendering  $(\pi \text{ and } \sigma)$  double aromaticity. Born-Oppenheimer molecular dynamics simulations indicate that the CBe<sub>5</sub> motif is robust in the clusters. As planar hypercoordination carbon species are often thermodynamically unstable and highly reactive, the superalkali cation characters of these ppC species should be highlighted, which may be suitable for experimental realization. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4954658]

## I. INTRODUCTION

Superalkalies with an ionization potential (IP) lower than that of the cesium atom (3.89 eV),<sup>1</sup> the lowest of any element in the periodic table, were first proposed by Gutsev and Boldyrev in 1982.<sup>2</sup> Currently, besides the IP criterion, for a species to be considered as a superalkali cation, it should be a global minimum with a large energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), a large vertical detachment energy (VDE), and a considerably high dissociation energy. With these criteria being satisfied, a superalkali cation generally means a very stable cluster, which is promising for experimental realization.

The bonding of carbon beyond the traditional tetrahedral concept has been a fascinating subject of pursuit for the past decades. However, two kinds of instabilities are routinely found for species with such nonclassical bonding. First, as relevant species do not obey the valence shell electron pair repulsion (VSEPR) theory, there is a strong tendency for the species to rearrange the positions of atoms to a traditional tetrahedral structure, that is, most of these species are not the global minima on the potential energy surfaces. Second, to maintain the nonclassical bonding, some reactive elements such as B, Al, and Be are often utilized in the design. However, exposure of these elements generally leads to high chemical reactivity, which deters the corresponding species from being synthesized. Introduction of superalkali or superalkali cation character to such nonclassical bonding systems is an interesting idea. It may be argued that superalkali character should help improve the stability of the nonclassical bonding species and thus make them more promising for experimental detections.

The most studied species with nonclassical bonding is the planar hypercoordination. It was originated from the studies on planar tetracoordinate carbon (ptC), that is, a carbon atom with four in-plane ligands. The ptC was first introduced by Monkhorst in 1968 as a transition state.<sup>3</sup> Two years later, Hoffmann *et al.*<sup>4</sup> proposed the strategies

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for stabilizing the ptC species in equilibrium structure. In 1976, 1,1-dilithiumcyclopropane ( $C_3H_4Li_2$ ) was theoretically predicted as the first stable ptC molecule by Schleyer and coworkers.<sup>5</sup> Since then, considerable efforts have been devoted to the design, prediction, and production of planar ptC and planar hypercoordinate carbon (phC) complexes.<sup>6–10</sup> Notably, a series of pentaatomic ptC clusters (Al<sub>4</sub>C<sup>-</sup>, CAl<sub>3</sub>Si<sup>-</sup>, CAl<sub>3</sub>Ge<sup>-</sup>, and C<sub>2</sub>Al<sub>4</sub>) were experimentally observed in the gas phase, primarily using the technique of photoelectron spectroscopy (PES).<sup>11–13</sup> Theoretical studies suggested that the ptC arrangement of relevant molecular species can be detected because they are the global minima on the potential energy surfaces.<sup>14,15</sup>

As an extension, planar pentacoordinate carbon (ppC) molecules have attracted widespread attentions in recent years. In 2001, Wang and Schleyer predicted the ppCcontaining "hyparenes."<sup>16</sup> Subsequently, ppC species such as  $D_{5h}$  Cu<sub>5</sub>H<sub>5</sub>C, CBe<sub>5</sub> and CBe<sub>5</sub><sup>4-</sup>, CW<sub>5</sub><sup>2+</sup>, and Si<sub>10</sub>C<sub>2</sub> were also predicted.<sup>17-20</sup> However, almost all of these are only local minima on their potential energy surfaces, and it is unclear whether  $D_{5h}$  Cu<sub>5</sub>H<sub>5</sub>C is the global minimum or not. Thus, it has remained a desirable goal for theoretical chemists to design phC complexes that are the global minima of the systems, which can in turn facilitate the experimental explorations in the gas phase. In 2008,  $D_{5h}$  CAl<sub>5</sub><sup>+</sup> was predicted by Zeng, Schleyer, and coworkers as the first ppC global miminum.<sup>21</sup> Motivated by this finding, a series of ppC species as global minima, including CAl<sub>4</sub>Be,  $CAl_3Be_2^-$ ,  $CAl_2Be_3^{2-}$ , and  $ECBe_5^-$  (E = Al, Ga), were predicted.<sup>22-24</sup> These planar carbon species as global minima are promising for forthcoming gas-phase synthesis and spectroscopic characterization.

However, the higher electronegativity of Al and Be (relative to alkali metals) in these global phC species often results in high IP or vertical electron affinity (VEA), and thus these phC species cannot be considered as superalkali or superalkali cations. With the aim to design experimentally viable species with phC, we wonder if the phC species can also possess the superalkali character. Such species would be attractive in chemistry. And the answer appears to be "yes."

Superalkalies are commonly designed using an electronegative main-group element as the center and several alkali metal atoms as ligands, following the formula  $ML_{k+n}$ , where M represents an electronegative atom or functional group, L is an alkali metal atom, k is the maximum formal valence of atom M, and  $n \ge 1$ . Over the past 30 years, a number of mononuclear, binuclear, and polynuclear superalkalies with considerably low VDEs, or their cations with low VEAs, were theoretically designed or experimentally characterized. These include  $Li_2X$  (X = F, Cl, Br, I), OM<sub>3</sub> (M = Li, Na, K), NLi<sub>4</sub>, BLi<sub>6</sub>, M<sub>2</sub>Li<sub>2k+1</sub><sup>+</sup> (M = F, O, N, C, B for k = 1, 2, 3, 4, 5, respectively), and  $YLi_3^+$  (Y = CO<sub>3</sub>, C<sub>2</sub>O<sub>4</sub>, C<sub>2</sub>O<sub>6</sub>).<sup>25-29</sup> A recent study also found that the mono-halogenation of superalkaline-earth dications  $M^{2+}$  (M = OLi<sub>4</sub>, NLi<sub>5</sub>, CLi<sub>6</sub>, BLi7) is a valid strategy to design superalkali cations  $MF^{+}.^{30}$ 

We propose that polyhalogenation and polyalkalination are also valid strategies for the design of superalkali cations. In this work, taking the previously reported local-minimum ppC CBe<sub>5</sub> as an example, we demonstrate that the polyhalogenation and polyalkalination of CBe<sub>5</sub> successfully lead to a new series of star-like ppC or quasi-ppC species, CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> (X = F, Cl, Br, Li, Na, K), which possess large HOMO-LUMO gaps, low VEAs, high VDEs, and presumably improved thermodynamic and kinetic stabilities. The species satisfy the requirements of being superalkali cations and suggest high possibility for experimental realization. To the best of our knowledge, there have been no studies to date on ppC species with superalkali properties. The present results build an interesting link between the planar hypercoordinate carbons and the superalkalies.

## **II. COMPUTATIONAL METHODS**

The global-minimum structures of  $CBe_5X_5^+$  (X = F, Cl, Br, Na, K) clusters were explored using the stochastic search algorithm<sup>31</sup> at the B3LYP/lanl2dz level.<sup>32</sup> For each  $CBe_5X_5^+$ cluster, about 3000 structures were generated (1500 for both the singlet and triplet states). In total, 15 000 structures were explored for the five species. The top ten low-lying isomers for each  $CBe_5X_5^+$  cluster were subsequently optimized at the B3LYP/6-311+G(2df) level,<sup>33</sup> and their nature as stationary points was ascertained via vibrational frequency analyses. The global-minimum structure of  $CBe_5Li_5^+$  and three lowest isomers were constructed based on the literature<sup>34</sup> and fully reoptimized at the B3LYP/6-311+G(2df) level.

Single-point CCSD(T) calculations<sup>35</sup> were performed for the global minima and three lowest-energy isomers of CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> (X = F, Cl, Br, Li, Na, K) at the B3LYP/6-311 + G(2df) geometries. Their relative energies were determined at the CCSD(T)//B3LYP/6-311+G(2df) level, plus zeropoint energy (ZPE) corrections at B3LYP/6-311+G(2df). In addition, the global-minimum structures of the species were also optimized at the MP2/6-311+G(2df) level,<sup>36</sup> followed by vibrational frequency calculations. The MP2 method produced essentially the same structures as those at B3LYP, with the bond distances being slightly elongated (within 0.02 Å).

Natural bond orbital (NBO) and adaptive nature density partitioning  $(AdNDP)^{37}$  analyses were performed at the B3LYP/6-311+G(2df) and B3LYP/6-31G(d) levels, respectively, to gain insight into the bonding of the species. To assess aromaticity, the nucleus independent chemical shifts (NICS)<sup>38</sup> were calculated at the centers of three-membered rings and at 1 Å above these centers, as well as 1 Å above the ppC or quasi-ppC centers. The VEAs and VDEs for CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> were calculated using the outer valence Green's function (OVGF) method<sup>39</sup> at both B3LYP and MP2 geometries. The HOMO-LUMO gaps were obtained based on MP2/6-311+G(2df) calculations.

The stochastic searches of the potential energy surfaces were run using the Coalescence Kick (CK)<sup>31</sup> program, the AdNDP analyses were carried out using the AdNDP program,<sup>37</sup> and all other calculations were performed using the Gaussian 09 package.<sup>40</sup> Molecular structures, canonical molecular orbitals (CMOs), and AdNDP partitioned orbitals were visualized using the CYLview and Molekel 5.4 programs.<sup>41,42</sup>

#### III. THE DESIGN STRATEGIES

To design the superalkali cations containing planar pentacoordinate carbon, two conditions should be satisfied. First, the species should have lower VEAs than 3.89 eV of Cs. Second, the species should be the global minima on their potential energy surfaces. Here, we use CBe<sub>5</sub> as the elementary unit. CBe<sub>5</sub> has an IP of 6.52 eV at the CCSD(T)/6-311+G(2df) level. In addition, the ppC motif of CBe5 was known to be a true minimum, albeit not the global minimum.<sup>17</sup> How to design superalkali cations based on the CBe5 unit? To decrease the IP of CBe<sub>5</sub>, we will demonstrate two complementary strategies: polyhalogenation and polyalkalination. As an added bonus, polyhalogenation and polyalkalination can also eliminate the reactivity with regard to the bare Be atoms, passivating the whole CBe5 unit via closed-shell halogen anions or alkali cations. Our extensive calculations reveal that halogenation or alkalination on each Be-Be edge of the CBe<sub>5</sub> ppC motif results in star-like superalkali cations with a ppC or quasippC:  $CBe_5X_5^+$  (X = F, Cl, Br, Li, Na, K). We will discuss the structures, stability, and bonding of these species. Note that the strategy of polyalkalination was employed previously for designing the superalkali cations, whereas the strategy of polyhalogenation is proposed for the first time in this work.

#### **IV. RESULTS AND DISCUSSION**

### A. Star-like ppC or quasi-ppC complexes, $CBe_5X_5^+$ (X = F, Cl, Br, Li, Na, K)

Polyhalogenation and polyalkalination with five X ligands readily generate a series of star-like complexes,  $CBe_5X_5^+$ 

(X = F, Cl, Br, Li, Na, K), whose global-minimum structures **1A–6A** as identified from the CK searches are illustrated in Fig. 1. Their three alternative low-lying structures are shown in Fig. S1 in the supplementary material.<sup>43</sup> Structures **1A–6A** are reasonably well-defined global minima, being at least 10–31 kcal/mol more stable than their nearest isomers at the single-point CCSD(T) level. We stress that **1A–6A** appear to be the first planar pentagonal star-like species as the global minima. Beautiful, global three-dimensional molecular pentagonal stars were reported by Merino *et al.*, but the previously reported planar pentagonal star-like clusters are at most local minima.

Among the global minima, **1A**, **4A**, **5A**, and **6A** adopt perfectly planar, highly symmetric  $D_{5h}$  (<sup>1</sup>A'<sub>1</sub>) structures, whereas **2A** and **3A** undergo a slight non-planar distortion as  $C_2$  (<sup>1</sup>A) structures. The  $D_{5h}$  structures of CBe<sub>5</sub>Cl<sub>5</sub><sup>+</sup> and CBe<sub>5</sub>Br<sub>5</sub><sup>+</sup> are second-order stationary points with two small imaginary frequencies (e<sub>2</sub>" mode), yet they turn out to lie only 0.04 and 0.43 kcal/mol higher in energy (including ZPE corrections) than their corresponding  $C_2$  structures, respectively. Thus the energetic gain from  $D_{5h}$  to  $C_2$  structures is negligible, suggesting that the non-planar  $C_2$  distortion is a relatively minor issue for the species. The ∠BeClBe and ∠BeBrBe bond angles change from 62.37°/57.74° in  $D_{5h}$  CBe<sub>5</sub>Cl<sub>5</sub><sup>+</sup>/CBe<sub>5</sub>Br<sub>5</sub><sup>+</sup> to 62.57°/58.45° in **2A/3A**, which are also quite small.

In terms of bond distances, the Be–Be distances in **4A–6A** are similar (1.98–2.00 Å), whereas those in **1A–3A** span a range from 1.99 to 2.08 Å. The C–Be distances appear to be more uniform in the six species (1.69–1.73 Å). Interestingly, the evolution of C–Be and Be–Be distances in **1A–3A** closely correlates to the trend of X–Be distances (or the atomic radii of X), hinting that these structures are primarily dominated



FIG. 1. Optimized global-minimum structures 1A-6A of  $CBe_5X_5^+$  (X = F, Cl, Br, Li, Na, K) at the B3LYP/6-311+G(2df) level. Bond distances are indicated in Å.

by the bridging halogen atoms (X = F, Cl, Br). In contrast, the C–Be and Be–Be distances in 4A-6A are relatively rigid, suggesting that alkali atoms (X = Li, Na, K) only play a secondary role therein.

# B. Peripheral Be–Be and Be–X bonds: Charge transfers versus covalent bonding

In order to understand the nature of bonding in the starlike 1A-6A complexes, we performed the AdNDP analyses, as well as NBO charge and Wiberg bond index analyses. AdNDP is an extension of the NBO analysis. It represents the electronic structure of a molecular system in terms of *n*-center two-electron (nc-2e) bonds, with the value of *n* ranging from one to the total number of atoms in the molecule. The AdNDP analysis thus recovers not only the classical Lewis bonding elements (such as lone-pairs and 2c-2e bonds) but also nonclassical, delocalized *n*c-2e bonds. For the sake of clarity, only the AdNDP results of 1A and 4A are presented in Fig. 2, and those of 2A, 3A, 5A, and 6A are shown in Fig. S2.<sup>43</sup> The majority of the occupation numbers (ONs) for the bonds are close to the ideal value of 2.0 |e|, suggesting that 1A-6A are well-behaved bonding systems.

For **1A**,  $\text{CBe}_5\text{F}_5^+$ , fifteen lone-pairs of the F atoms are readily recovered in AdNDP, with the ON values of 1.86–1.98 |e| (Fig. 2(a), the first row). Note that the  $np_x$  lone-pairs in **1A–3A** have the ONs of 1.74–1.86 |e| , which are the lowest of all ON values in **1A–6A**, hinting that the  $np_x$  atomic orbitals (AOs) of X, in particular X = Cl and Br, are markedly involved in the covalent Be–X interactions, despite the large difference in electronegativity between Be and F/Cl/Br; see below for an interpretation of this observation. The remaining bonding elements of **1A–3A** appear to be similar to those of **4A–6A**, at least formally. The peripheral Be–Be or X–Be bonding in **1A–6A** is described as five 3c-2e Be–X–Be  $\sigma$  bonds according to the AdNDP results, which hold together the star-like Be<sub>5</sub>X<sub>5</sub> motif. Discernible difference in the spatial distribution of electron clouds is observed between **1A–3A** and **4A–6A**. The Be–X–Be  $\sigma$  clouds in **4A–6A** are predominantly located on the Be–Be edge, whereas they are shifted to the X center in **1A–3A**. This trend is understandable, because in **1A–3A** complexes the X center (X = F, Cl, Br) is more electronegative than Be, whereas in **4A–6A** the Be atom is more electronegative than X (X = Li, Na, K).

The NBO charges and Wiberg bond orders (Table I) are fully consistent with the above analysis. For the peripheral Be–Be or X–Be bonding, major positive charges in **1A–3A** are situated at the Be centers (+0.61 to +1.19 |e|) and the X centers are almost neutral, except for **1A**. Consequently, the peripheral covalent bonding in **1A–3A** is dominated by X–Be, with Wiberg bond orders of 0.37–0.73. On the other hand, the positive charges in **4A–6A** are located on the X (X = Li, Na, K) centers, +0.81 to +0.85 |e|, and the Be centers are almost neutral. Thus Be–Be covalent bonds dominate the peripheral bonding in **4A–6A**, with Wiberg bond orders of 0.77–0.79. Simple arithmetic on the basis of data shown in Table I reveals that the overall positive charge in the CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> complexes is located on Be in **1A–3A** and on X (X = Li, Na, K) in **4A–6A**, as anticipated.

The above results suggest that, in an ionic picture, the Be and Cl/Br centers in **2A** and **3A** are in the formal charge states of Be<sup>+</sup> positive and Cl/Br neutral, whereas the Be and X centers in **4A–6A** are formally Be neutral and Li<sup>+</sup> positive. The C–Be interaction in **1A–6A** involves both covalent and ionic components. The Be<sup>+</sup>–X–Be<sup>+</sup> 3c-2e  $\sigma$  bond in **2A** and **3A** appears to be covalent despite the difference in



FIG. 2. AdNDP bonding patterns of 1A and 4A with the occupation numbers (ONs).

TABLE I. Nature charges (Q, in |e|) and Wiberg bond indices (WBIs) for the global-minimum structures **1A–6A** of CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> (X = F, Cl, Br, Li, Na, K) at the B3LYP/6-311+G(2df) level.

	$Q_{\rm C}$	$Q_{ m Be}$	Qx	WBI <sub>C-Be</sub>	WBI <sub>Be-Be</sub>	WBI <sub>X-Be</sub>	WBIC	WBI <sub>Be</sub>	WBIX
1A	-2.11	1.19	-0.57	0.55	0.06	0.37	2.83	1.46	0.79
2A	-1.90	0.70-0.71	-0.12 to -0.13	0.57	0.10	0.67-0.68	3.02	2.17-2.18	1.45
3A	-1.98	0.61-0.64	-0.0 to -0.04	0.54-0.55	0.11	0.71-0.73	2.94	2.26-2.29	1.55-1.57
<b>4</b> A	-2.08	-0.22	0.84	0.57	0.79	0.13	2.87	2.65	0.31
5A	-2.20	-0.17	0.81	0.54	0.77	0.16	2.76	2.63	0.37
6A	-2.27	-0.20	0.85	0.53	0.78	0.13	2.69	2.62	0.31

electronegativity: 1.57 for Be versus 3.16/2.96 for Cl/Br at the Pauling scale. The key to understand this phenomenon lies in the fact that the Be centers in 2A and 3A are in the formal Be<sup>+</sup> charge state (Table I), which are more electronegative than Be neutral, making the Be<sup>+</sup>-Cl and Be<sup>+</sup>-Br bonding rather covalent. For 1A, the Be centers can be considered to be in formal Be<sup>2+</sup> charge state and the F centers in F<sup>-</sup> charge state, due to the extreme electronegativity of F (3.98). As already pointed out in Section IV A, the structural distortion for 2A and **3A** species from planar  $D_{5h}$  to non-planar  $C_2$  is a relatively minor issue in terms of energetics. Nonetheless, we would like to comment briefly on the distortion. The 2A and 3A species differ from 1A and 4A-6A in that (i) 2A/3A have formal Be<sup>+</sup> centers and hence sort of covalent Be<sup>+</sup>-X-Be<sup>+</sup> bonding and (ii)  $D_{5h}$  CBe<sub>5</sub>Cl<sub>5</sub><sup>+</sup> and CBe<sub>5</sub>Br<sub>5</sub><sup>+</sup> show longer C-Be distances, 1.72(9) and 1.73(8) Å, as compared to 1.69–1.71 Å in 1A, 4A, 5A, and 6A. Since the delocalization of C  $p_z$  AO to peripheral  $\pi$ -accepting ligand atoms is crucial to the stability of the ppC species, the C-Be distance and the degree of coplanarity interplay in the 2A/3A systems. The slightly longer C–Be distances make the planar  $D_{5h}$  CBe<sub>5</sub>Cl<sub>5</sub><sup>+</sup> and  $CBe_5Br_5^+$  disadvantageous, which undergo distortion to  $C_2$  to shorten the C-Be distances: from 1.729 to 1.725 Å in 2A and 1.738 to 1.729 Å in **3A**. The  $C_2$  distortion may also optimize the  $Be^+-X-Be^+$  covalent bonding in 2A/3A. Our analysis shows that the delocalized  $\pi$  orbital in 2A and 3A (that is, the HOMO) benefits most in the structural distortion, whose orbital energy is lowered from -11.18 and -10.96 eV in  $D_{5h}$ to -11.23 and -11.09 eV in  $C_2$ , respectively.

Overall, there are three regions of specific charge states in **1A–6A**: the inner C center is negatively charged, the Be centers in middle Be<sub>5</sub> ring can be in the Be<sup>2+</sup>, Be<sup>+</sup>, or Be charge state, whereas the X centers in outer X<sub>5</sub> span from F<sup>-</sup> to Cl/Br to Li<sup>+</sup>/Na<sup>+</sup>/K<sup>+</sup>. The electrostatic interactions between the three regions help stabilize the star-like clusters.

#### C. Double ( $\pi$ and $\sigma$ ) aromaticity

The nature of bonding associated with the ppC center in **1A–6A** is critical in understanding these unique star-like clusters. According to the AdNDP data (Fig. 2 and Fig. S2),<sup>43</sup> the ppC center is stabilized via four 6c-2e bonds: three  $\sigma$  bonds versus one  $\pi$  bond. The  $\pi$  bond is totally delocalized and completely bonding, whose  $2\pi$  electrons conform to the (4*n* + 2) Hückel rule, rendering  $\pi$  aromaticity to the **1A–6A** clusters. The three  $\sigma$  bonds for each **1A–6A**  species are similar in shape to the  $\pi$  sextet in typical aromatic hydrocarbon molecules, such as benzene or cyclopentadienyl anion (C<sub>5</sub>H<sub>5</sub><sup>-</sup>), suggesting that the **1A–6A** clusters possess  $\sigma$ aromaticity as well. In short, the star-like **1A–6A** species possess both  $\pi$  and  $\sigma$  aromaticity, which underlies the structural and electronic stability of these ppC or quasi-ppC clusters.

Aromaticity in **1A–6A** is confirmed independently using the NICS calculations, performed on the center of certain three-membered rings (NICS(0)) and at 1 Å above the center (NICS(1)), as well as at 1 Å above the carbon center. It is generally believed that NICS(0) can reflect  $\sigma$  aromaticity, whereas NICS(1) probes  $\pi$  aromaticity. As shown in Fig. S3,<sup>43</sup> the NICS(0) and NICS(1) values at the B3LYP/6-311+G(2df) level are all negative, suggesting that **1A–6A** indeed possess double ( $\pi$  plus  $\sigma$ ) aromaticity, in consistent with the AdNDP analyses.

#### D. Thermodynamic and kinetic stability

Star-like ppC or quasi-ppC cations **1A–6A** are the global minima on their potential energy surfaces, which mean they are thermodynamically the most stable isomers. We further examine the thermodynamic stability by considering two dissociation reactions,

$$CBe_5X_5^+ \rightarrow CBe_4X_4 + BeX^+ (X = F, Cl, Br), \qquad (1)$$

$$CBe_5X_5^+ \rightarrow CBe_5X_4 + X^+ (X = Li, Na, K).$$
(2)

As shown in Fig. 3, using 2A and 4A as examples, there are large differences between reactions (1) and (2) owing to the different electronegativity of the X atoms. We calculated the dissociation energies of reactions (1) and (2) at the single-point CCSD(T)//B3LYP/6-311+G(2df) level. With ZPE corrections at B3LYP included, both reactions (1) and (2) have large positive total energy changes, 119.37–129.51 kcal/mol for 1A-3A and 63.89-82.39 kcal/mol for 4A-6A, indicating that these star-like complexes are very stable against decomposition. Note that the previously reported superalkali  $CO_3Li_3^+$ ,<sup>29</sup> which possesses a planar hexacoordinate carbon structure,<sup>46</sup> was calculated with a total energy change of 132.90 kcal/mol for the reaction  $CO_3Li_3^+ \rightarrow CO_3Li_2 + Li^+$ . The Li<sup>+</sup> cation is dissociated from two O atoms in  $CO_3Li_3^+$  and from two Be atoms in  $CBe_5Li_5^+$  (Reaction (2)). Considering the huge difference between O and Be in terms of electronegativity, the present endothermicity for CBe<sub>5</sub>Li<sub>5</sub><sup>+</sup> (82.39 kcal/mol) is quite substantial. To investigate



FIG. 3. Proposed dissociation pathways for **2A** and **4A**.

the dynamic stability of the **1A–6A** complexes, Born-Oppenheimer molecular dynamics (BOMD) simulations were performed for each species for 50 ps at B3LYP/6-31G(d) level, at the temperature of 298 K. The calculated root-meansquare deviations (RMSD) of the structures, relative to those optimized at B3LYP/6-31G(d), are shown in Fig. 4. The BOMD results reveal that the ppC CBe<sub>5</sub> motif in **1A–6A** is well maintained during the simulations, suggesting that the structures are rigid against isomerization and decomposition.



To demonstrate the accumulation and magnification effects of polyhalogenation and polyalkalination in lowering the electron binding energy of the ppC complexes, we calculated the VEAs of  $CBe_5X_n^+$  (X = F, Cl, Br, Li, Na, K; n = 1, 3, 5) at the OVGF/6-311+G(2df) level using their optimized structures at MP2/6-311+G(2df). All the  $CBe_5X_n^+$ 







FIG. 5. Calculated VEAs as a function of *n* for the  $\text{CBe}_5X_n^+$  (X = F, Cl, Br, Li, Na, K; *n* = 1, 3, 5) complexes at the MP2 level. The horizontal dashed line shows the lowest atomic ionization potential (IP) in the periodic table (3.89 eV for Cs).

TABLE II. Calculated vertical electron affinities (VEAs) and vertical detachment energies (VDEs) for the global minima **1A–6A** of CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> (X = F, Cl, Br, Li, Na, K) at the OVGF/6-311+G(2df) level, using the B3LYP and MP2 optimized structures. The HOMO-LUMO gaps at MP2/6-311+G(2df) are also listed.

	VEA	(eV)	VDE	E <sub>HOMO-LUMO</sub> (eV)	
	OVGF//B3LYP	OVGF//MP2	OVGF//B3LYP	OVGF//MP2	MP2
1A	3.70	3.71	13.74	13.65	10.76
2A	3.14	3.13	13.14	13.04	11.07
3A	3.12	3.01	12.89	12.72	11.05
4A	2.51	2.51	8.92	8.84	6.91
5A	2.35	2.36	8.03	7.94	6.19
6A	2.12	2.12	6.74	6.79	4.99

(n = 1, 3) clusters turn out to be true minima as well and the CBe<sub>5</sub> unit is maintained; see their optimized structures in Fig. S4.<sup>43</sup> As shown in Fig. 5, the VEA values of CBe<sub>5</sub>X<sub>n</sub><sup>+</sup> decrease monotonously with the number of X atoms, both for polyhalogenation and polyalkalination, indicating that the two strategies are indeed working towards lowering the VEAs of the ppC systems. From n = 1 to 5, the VEAs of CBe<sub>5</sub>X<sub>n</sub><sup>+</sup> drop by as much as 2.4, 3.2, and 3.3 eV for X = F-Br and 2.8, 2.8, and 2.7 eV for X = Li-K. Note that the most remarkable drops in VEAs are for X = Cl and Br, although the X = Li-K complexes possess the ultimately lower VEAs, suggesting that polyhalogenation is a powerful (and indeed unanticipated) approach in the design of novel species with ultra-low electron binding energies.

Upon polyhalogenation and polyalkalination, we reach the **1A–6A** global-minimum cation clusters. As discussed above, the bonding in the species consists of a peripheral framework with five 3c-2e Be–X–Be  $\sigma$  bonds, as well as a delocalized framework for the ppC enter, which features  $\pi$  plus  $\sigma$  double aromaticity (with  $2\pi$  and  $6\sigma$  electrons). Such twodimensional, 18-electron closed-shell,<sup>47,48</sup> double aromatic ppC or quasi-ppC CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> (**1A–6A**) cation clusters suggest the possibility of extremely low VEAs, that is, as superalkali cations, because their stable electronic configuration and the anticipated sizable HOMO-LUMO gap should push the extra electron to the highly energetic LUMO above the energy gap. Alternatively, the corresponding neutral complexes may possess superalkali characters. Indeed, the optimized representative  $CBe_5X_n$  neutral structures (Fig. S5)<sup>43</sup> show that the flat, star-like clusters are also highly competitive on their potential energy surfaces, albeit with structural distortions.

The VEAs of the **1A–6A** cations are presented in Table II, as well as depicted in Fig. 5. The VEA values were calculated using the OVGF method at both the B3LYP and MP2 structures. The B3LYP and MP2 structures give rather similar VEA values, and only those at MP2 will be discussed. The VEAs of  $CBe_5X_5^+$  (X = F, Cl, Br) are 3.71, 3.13, and 3.01 eV, respectively. The values are clearly lower than the IP of the Cs atom (3.89 eV). According to definition, the  $CBe_5X_5^+$  (X = F, Cl, Br) species belong to the superalkali cations. To reach the superalkali cation complexes via halogenation is quite unusual; the only prior study is the monohalogenation by Hou and coworkers.<sup>30</sup> The fact that **1A–3A** are associated with a ppC complex makes them more interesting. Furthermore, upon polyalkalination, the ppC complexes with even lower VEAs are readily reached. The 4A-6A species are predicted with VEAs as low as 2.12–2.51 eV. For comparison, the atomic IPs of C, Be, and Li/Na/K are 11.26, 9.32, and 5.39/5.14/4.34 eV, respectively.

The calculated VDEs of the **1A–6A** cations amount to 12.72-13.65 eV for X = F, Cl, Br and 6.79-8.84 eV for X = Li, Na, K 13.65 eV (Table II). It is therefore



FIG. 6. Pictures of the HOMOs and LUMOs of 1A-6A at the MP2 level.

far more difficult for these star-like ppC or quasi-ppC superalkali cations to lose one more electron and form dications, consistent with the closed-shell nature and double aromaticity of the **1A–6A** cations. The MP2/6-311+G(2df) calculated HOMO-LUMO gaps for the **1A–6A** cations are 4.99–6.91 eV for X = Li, Na, K and 10.76–11.07 eV for X = F, Cl, Br, further indicating the electronic stability of these cations.

The calculated VEAs, VDEs, and HOMO-LUMO gaps of the 1A-6A cations are correlated with the nature of their HOMOs and LUMOs, which are depicted in Fig. 6. For example, the LUMOs of 1A-3A are primarily Be based, whereas those of 4A-6A have an increasing X (X = Li, Na, K) component. The nature of the frontier orbitals (Fig. 6) not only explains why there exists a sharp decrease in VEA values from **1A–3A** to **4A–6A** but also highlights the powerfulness of polyhalogenation in lowering the VEA of the systems. Indeed, polyhalogenation manages to decrease the VEA of Be (atomic IP: 9.32 eV) to 3.01-3.71 eV in 1A-3A (that is, by as much as 5.6-6.3 eV). For comparison, polyalkalination decreases the VEA of Li/Na/K (atomic IPs: 5.39/5.14/4.34 eV) to 2.51/2.36/2.12 eV in 4A-6A (that is, by 2.2–2.9 eV). Clearly, there is a lot more room to explore superalkali species using the strategy of polyhalogenation.

The good thermodynamic and kinetic stabilities, stable electronic structures,  $\sigma$  and  $\pi$  double aromaticity, small VEAs, large VDEs, and large HOMO-LUMO gaps of CBe<sub>5</sub>X<sub>5</sub><sup>+</sup> (X = F, Cl, Br, Li, Na, K) demonstrate that covering the bare Be atoms in CBe<sub>5</sub> motif with alkali metal cations or halogen anions may be valid in eliminating the reactivity of Be atoms in the CBe<sub>5</sub> motif and thus improving the chemical stability.

#### **V. CONCLUSIONS**

Using the strategies of polyhalogenation and polyalkalination, we have computationally designed the first series of unique star-like superalkali cations featuring the planar pentacoordinate carbon (ppC):  $CBe_5X_5^+$  (X = F, Cl, Br, Li, Na, K). Chemical bonding in the systems involves peripheral five Be–X–Be 3c-2e  $\sigma$  bonds, as well as the eight electron shell associated with the ppC or quasi-ppC center, the latter rendering ( $\pi$  and  $\sigma$ ) double aromaticity with  $2\pi$  and  $6\sigma$  electrons. This bonding pattern stabilizes the ppC- or quasi-ppC-containing  $CBe_5X_5^+$  cations. Very low vertical electron affinities are predicted for the species, 3.01-3.71 eV for X = F, Cl, Br and 2.12-2.51 eV for X = Li, Na, K, manifesting their nature as superalkali cations. Large HOMO-LUMO energy gaps are also calculated, 10.76–11.07 eV for X = F, Cl, Br and 4.99–6.91 eV for X = Li, Na, K. The ppC complexes with superalkali character or superalkali complexes containing a ppC center, were unknown in the literature. The current  $CBe_5X_5^+$  complexes invite forth-coming experimentally characterizations.

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