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A current project in metal-metal bonding chemistry is to achieve the ultrashort metal-metal distances (USMMDs, denoting the  $d_{M-M} < 1.900$  Å) between main group metal beryllium and a valid way for achieving such USMMDs was the substitution of carbon atom in planar pentacoordinate environment with the isoelectronic Be<sub>2</sub> moiety. In the present work, we report our recent findings that similar substitution can be applied to the carbon atom in planar hexacoordinate environment. Using species CN<sub>3</sub>Be<sub>3</sub><sup>+</sup> and CO<sub>3</sub>Li<sub>3</sub><sup>+</sup> as the template and in combination with the reasonable extension, the Be<sub>2</sub>N<sub>3</sub>M<sub>3</sub><sup>+</sup> (M = Be, Mg, Ca) and Be<sub>2</sub>O<sub>3</sub>M<sub>3</sub><sup>+</sup> (M = Li, Na, K) species with the axial ultrashort Be-Be distances of 1.627–1.870 Å had been designed computationally. The ultrashort Be-Be distances in these species represented the balance between lengthening effect of axial Be-Be electrostatic interactions and shortening effect concerning the strong X-Be bonding and repulsive X-X-X X electrostatic interactions. In addition, the shorter axial Be-Be distances were determined firstly by the smaller size of bridging electronegative X atoms and secondly by the lower electronegativity of peripheral M atoms, while the stability of newly designed species was closely related to the types of their valence electron pairs, where the localized two-center two-electron bonds were more desired for the stabilization than non-bonding valence lone pairs. In the newly designed species, Be<sub>2</sub>N<sub>3</sub>Be<sub>3</sub><sup>+</sup> and Be<sub>2</sub>N<sub>3</sub>Mg<sub>3</sub><sup>+</sup> were characterized to be the kinetically stable global minima, thereby providing the promising target for experimental realization of species with USMMDs between main group metals.

## Introduction

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Metals are generally big in atomic size. Hence, it is understandable that the metal-metal distances are commonly very long in chemical structures. As a consequence, it is natural to quest "how short a metal-metal distance can become?".<sup>1</sup> For transition metals, since the d orbitals can participate in the bonding, they possess the superior priority in forming the homonuclear high-order bonds, which can significantly shorten the intermetal distances. In particular, the Cr-Cr distances in their homonuclear quintuple or septuple bonds <sup>2</sup> are so short (1.650-1.835 Å) that were commonly called "the ultrashort metal-metal distances" (USMMDs, *i.e.*  $d_{M-M} < 1.900$  Å).<sup>1a,2b</sup>

For main group metals, however, the homonuclear bond orders higher than three-fold are impossible due to limitation of electronic shell structure. Moreover, it is rather difficult for main group metals even to form the homonuclear triple bonds because the s-block alkali and alkali earth metals don't have enough valence electrons, while the p-block metals normally suffer from the so-called "inert pair" effect, *i.e.* their outermost *s* electrons are very inert.<sup>3</sup> As a result, most main group metals cannot support the USMMDs. Nevertheless, the alkali earth metal beryllium is particular for this purpose because it is the smallest metal and sometimes because it shows the typical electron deficient properties.

With the aid of peripheral monocyclic boron rings, the Be-Be distances can be shortened unusually to 1.901 and 1.910 Å in  $Be_2B_7^-$  and  $Be_2B_8$ , respecitvely, which approach the upper limit of USMMD.<sup>4</sup> Encouraged by such pioneering work, the ultrashort Be-Be distances of 1.692–1.829 Å had been achieved covalently by forming three bonding orbitals between two beryllium atoms <sup>5</sup> and those of 1.729-1.866 Å can be realized electrostatically by enhancing the Coulomb attractions between the positively charged beryllium atoms and the negatively charged bridging atoms.<sup>5a,6</sup> In addition, the ultrashort Be-Be distances of 1.770-1.810 Å can be attained through the combinations of both covalent and electrostatic effects. <sup>7</sup>

Interestingly, a pentagonal 3D star Be<sub>2</sub>Be<sub>5</sub>H<sub>5</sub><sup>+</sup> with an axial Be-Be distance of 1.776 Å <sup>5a</sup> was derived from CBe<sub>5</sub>H<sub>5</sub><sup>+</sup>,<sup>8</sup> a species with a planar pentacoordinate carbon (ppC). During the design of Be<sub>2</sub>Be<sub>5</sub>H<sub>5</sub><sup>+</sup>, the isoelectronic relationship (having 4 valence electrons) between carbon and beryllium dimer was utilized. Thermodynamically, Be<sub>2</sub>Be<sub>5</sub>H<sub>5</sub><sup>+</sup> was not stable because beryllium dimer is too big to match the Be<sub>5</sub>H<sub>5</sub> ring. Nevertheless, replacing the Be<sub>5</sub>H<sub>5</sub> ring in Be<sub>2</sub>Be<sub>5</sub>H<sub>5</sub><sup>+</sup> with a little larger Be<sub>6</sub>H<sub>6</sub> ring can lead to the global energy minimum Be<sub>2</sub>Be<sub>6</sub>H<sub>6</sub><sup>2+</sup> with an axial ultrashort Be-Be distance of 1.802 Å.<sup>5a</sup>

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<sup>\*</sup>Electronic Supplementary Information (ESI) available: The AdNDP results of 1 and 4–9, the electron density distribution analysis of 4–9, the pictures of optimized structures and relative energies of lowest isomers of 4–9, and the Cartesian coordinates of structures shown in the figures in the text and ESI. See DOI: 10.1039/x0xx00000x

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Fig. 1. Structures of template phC species and their isoelectronic molecules with an axial Be<sub>2</sub> moiety, in which 4 and 5 are optimized at the B3LYP/BS1 level, while other species are all optimized at the CCSD(T)/BS1 level. The axial Be-Be distances, other interatomic distances, and natural charges are shown in red, black, and italic blue fonts, respectively.

Although the isoelectronic planar hexacoordinate carbon (phC) species  $CBe_6H_6^{2+}$  was not an energy minimum due to the size mismatch between the small carbon atom and relatively large  $Be_6H_6$  ring, the feasibility of  $Be_2Be_6H_6^{2+}$  still inspired us to wonder whether the species having ultrashort Be-Be distance can be designed by replacing the carbon atom in planar hexacoordinate environment with isoelectronic  $Be_2$  moiety? The answer is turned out to be positive. In the following, we will demonstrate that the species with ultrashort Be-Be distances ranging from 1.627 to 1.870 can be achieved through such isoelectronic substitution and followed expansion using phC species  $CN_3Be_3^+$  and  $CO_3Li_3^+$  as the templates. Note that two of newly designed species are global minima with good kinetic stability, which are suitable for gas-phase generation and spectroscopic characterization.

#### **Results and discussion**

#### 1. Isoelectronic substitution

In 2012, the phC species  $D_{3h} C_4 B_3^+$ ,  $D_{3h} CN_3 Be_3^+$ , and  $D_{3h} CO_3 Li_3^+$  (see first column in Fig. 1) <sup>9</sup> had been designed as the isoelectronic species of milestone phC species  $CB_6^{2-.10}$  In 2014,

the kinetically viable phC species  $D_{3h}$  CN<sub>3</sub>Mg<sub>3</sub><sup>+</sup> was further derived from CN3Be3+ via isoelectronic substitution of Be atoms with Mg atoms.<sup>11</sup> In this work, as described in the Introduction section, we attempted to design the species with ultrashort Be-Be distances using these phC structures as the templates. Delightfully, as shown in Fig. 1, replacing the central phC in  $C_4B_3^+$ ,  $CN_3Be_3^+$ , and  $CO_3Li_3^+$  with a  $Be_2$  moiety led to  $Be_2C_3B_{3^+}$  (1),  $Be_5N_{3^+}$  (4), and  $Be_2O_3Li_{3^+}$  (7) species with  $D_{3h}$ symmetry, which were examined to be the genuine energy minima at both B3LYP/BS1 and MP2/BS1 levels (see Computational Methods section for details of mixed basis sets BS1). The axial Be-Be distance in 1 is 2.162 Å in the CCSD(T)/BS1-optimized geometry, obviously longer than the threshold of 1.900 Å for determining the USMMD. As a comparison, those in 4 and 7 are 1.870 and 1.678 Å, respectively, being the eligible USMMDs. Notably, the experimentally known shortest metal-metal distance is also 1.678 Å, which was found in the Cr-Cr multiple bond in chromium dimer Cr2.21 Here, our attention was paid to the essential differences for Be-Be distances in these three isoelectronic species. Stoichiometrically, the peripheral six atoms in each species compose of three relatively high electronegative X atoms (X = C, N, and O) and three relatively

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low electronegative M atoms (M = B, Be, and Li). Since X atoms bound axial  $Be_2$  moiety more tightly than M atoms in **1**, **4**, and **7**, respectively, we speculate that the shorter axial Be-Be distance may be related first to the smaller size of X atoms.

If our speculation is valid, the isoelectronic substitution of M atom in 1, 4, and 7 with their heavier congeners will not influence the order for Be-Be distances regarding the X atoms. Therefore, to prove such speculation, we tried to replace the M atoms in 1-3 with their heavier congeners Al/Ga, Mg/Ca, and Na/K, leading to the isoelectronic species  $Be_2C_3Al_3^+$  (2),  $Be_2C_3Ga_{3^+}$  (3),  $Be_2N_3Mg_{3^+}$  (5),  $Be_2N_3Ca_{3^+}$  (6),  $Be_2O_3Na_{3^+}$  (8), and  $Be_2O_3K_3^+$  (9). It is worth of note that 2 and 3 adopt the openshell singlet state and  $C_{2\nu}$  symmetry at both B3LYP/BS1 and MP2/BS1 levels. The CCSD(T)/BS1 optimization of 2 and 3 encountered some difficulties, so their B3LYP/BS1-optimized structures with Be-Be distances of 1.973 and 2.110 Å for 2 and 3, respectively, are given in Fig. 1. The Be-Be distances found in CCSD(T)/BS1-optimized geometries <sup>12</sup> for 5, 6, 8, and 9 are 1.733, 1.698, 1.648, and 1.627 Å, respectively. As expect, the variation of Be-Be distances in these analogue molecules is consistent with that in 1, 4, and 7, i.e. the longest axial Be-Be distances are found in 2 and 3 with bridging C atoms, the significant shorter values can be found in 5 and 6 with bridging N atoms, while the shortest values will be found in 8 and 9 with bridging O atoms. In addition, it becomes clear through the presence of 2, 3, 5, 6, 8, and 9 that the shorter axial Be-Be distances are related to the lower electronegativity of M atoms. Specifically, B, Al, and Ga have the electronegativity of 2.05, 1.61, and 1.81 (Pauling scale),<sup>13</sup> which corresponds the axial Be-Be distances of 2.162, 1.973, and 2.108 in 1, 2, and 3, respectively. It is remarkable that the Be-Be distance of 1.627 Å in 9 is even shorter than the Cr-Cr distance of 1.650 Å in linear F-Cr-Cr-F molecule and should be chemically the shortest metal-metal distance known to date.

#### 2. Electronic structure analysis

We had performed the electronic structure analysis to gain more insight into relationship between the axial Be-Be distances and the bonding. As an extension of natural bond orbital (NBO),14 the adaptive natural density partitioning (AdNDP)<sup>15</sup> can describe the bonding in a molecule using *n*c-2e bonds, where *n* ranges from 1 to the total number of atoms in the molecule. In general, the AdNDP orbital are generated with n values as small as possible, thus AdNDP can provide much more explicit bonding patterns than the traditional canonical molecular orbitals (CMOs). The AdNDP results of 1, 4, and 7 are shown representatively in Fig. 2, those of 5, 6, 8, and 9 are given in Fig. S1 in the †ESI, while the AdNDP analyses were not applied to 2 and 3 since the AdNDP program for open-shell system is not available. As the first row of Fig. 2 shows, in twelve pairs of valence electrons of 1, six of them form the peripheral localized C-B 2c-2e  $\sigma$  bonds with the occupation number (ON) of 1.96 |e| and the rest six pairs are involved in the delocalized B-C-Be-B 4c-2e  $\sigma$  bonds with ON of 1.95 |e|. Interestingly, though the peripheral N-Be 2c-2e  $\sigma$  bonds (ON = 1.97 [e]) in 2 (see the second row in Fig. 2) are not different in essential from those of C-B bonds in 1, the bonding between N



atoms and axial Be atoms in **2** is best described as six localized N-Be 2c-2e  $\sigma$  bonds with ON of 1.96 |e|, *i.e.* in comparison with the 4c-2e  $\sigma$  bonds found in **1**, the bonding around the axial Be<sub>2</sub> moiety in **2** is localized. Moreover, the bonding pattern is further changed in **3**, where not only the bonding concerning axial Be<sub>2</sub> moiety is localized (six 2c-2e O-Be  $\sigma$  bonds with ON of 1.99 |e|), but the peripheral six 2c-2e  $\sigma$  bonds found in **1** and **2** are replaced by six 1c-2e *s* and *p* lone paris of O atoms with ONs of 1.97 and 1.95 |e|, respectively, in **3**. The AdNDP analyses indicate that the shorter Be-Be distance may be related to more localized interatomic bonding.

It is interesting that no AdNDP orbital having axial Be-Be bonding character is observed in 1 and 4-9. Our analysis suggested that the Be-Be distances represent balance between the lengthening and shortening effects. The former effect came from the repulsion between two positively charged axial Be atoms, which the later effect includes strong covalent and ionic bonding interaction between Be and X atoms as well as the electrostatic repulsion among three X atoms. As a result, we performed the traditional NBO analyses and the Wiberg bond index (WBI, a kind of covalent bonding index) are given in Table 1, while the natural charges are shown in Fig. 1 in italic blue font. As the Table 1 shows, WBI<sub>Be-Be</sub> values range from 0.05 to 0.13, suggesting the negligible Be-Be covalent bonding. Simultaneously, the natural charges on axial atoms are largely positive, indicating that the direct electrostatic effect between two axial Be atoms is obviously repulsive. Therefore, both covalent and electrovalent bonding characters for Be-Be bonding are consistent with the AdNDP results that no orbital having axial Be-Be bonding character can be observed.

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View Article Online Table 1. The numbering (#) lowest vibrational frequencies (v<sub>min</sub> in cm<sup>-1</sup>), the HOMO–LUMO gaps (Gap in eV), and the Wiberg bond indices (WBIs) of Delta 10.1039/C9DT00630C

	#	V <sub>min</sub>	Gap	WBI						
				Be	х	М	Be-Be	Be–X	Be–M	X-M
$Be_2C_3B_3^+$	1	581	3.79	1.65	3.83	3.55	0.05	0.33	0.20	1.48
$Be_2C_3AI_3^+$	2	212	1.79	2.25	3.22/3.10	1.69/1.80	0.12	0.64/0.64	0.08/0.07	0.69/0.65/0.68
$Be_2C_3Ga_3^+$	3	110	1.93	2.11	3.14/2.97	1.32/1.43	0.10	0.58/0.62	0.08/0.04	0.64/0.39/0.50
$Be_2N_3Be_3^+$	4	435	3.81	1.85	2.37	1.46	0.08	0.51	0.08	0.62
$Be_2N_3Mg_3^+$	5	232	2.55	2.04	1.98	0.72	0.12	0.62	0.02	0.30
$Be_2N_3Ca_3^+$	6	179	2.27	2.07	2.07	0.92	0.13	0.61	0.04	0.38
Be <sub>2</sub> O <sub>3</sub> Li <sub>3</sub> +	7	282	4.92	1.58	1.17	0.16	0.08	0.49	0.01	0.07
Be <sub>2</sub> O <sub>3</sub> Na <sub>3</sub> +	8	143	3.77	1.60	1.12	0.08	0.09	0.50	0.01	0.03
$Be_2O_3K_3^+$	9	95	3.40	1.64	1.13	0.07	0.09	0.51	0.01	0.03



**Fig. 3.** Plots of the Laplacian  $\nabla^2 \rho(r)$  as well as bond paths and critical points of **4** in two different molecular planes. **A**: The plane contains the two axial Be atoms and one N and one Be atoms, which bisects the peripheral N<sub>3</sub>Be<sub>3</sub> ring. **B**: the plane of N<sub>3</sub>Be<sub>3</sub> ring. The blue dashed lines denote the areas of charge concentration ( $\nabla^2 \rho(r) < 0$ ), while the solid red lines indicate the areas of charge depletion ( $\nabla^2 \rho(r) > 0$ ). The brown sticks between pairs of atoms are bond paths. Brown dots are bond critical points, yellow dots are ring critical points, and green dots between axial beryllium atoms are cage critical points.

It would be interesting that the Be-Be distance in **4–9** are ultrashort but there is no bond between two Be atoms. Thus, to further confirm such conclusion, the electron density distribution in **4–9** are analyzed using QTAIM (quantum theory of atoms in molecules) method.<sup>16</sup> The Laplacian distribution  $\nabla^2 p(r)$  as well as the bond paths and critical points of **4** are

shown in Fig. 3, the electron concentration areas distributed around the electronegative N atoms, while the electron depletion areas appear in the region close to Be atoms. There are twelve bond paths between N atoms and their adjacent Be atoms, which consistent with the AdNDP results that the N-Be interactions are 2c-2e bonds. The ring critical points (yellow dots) can be found between each N-N-Be combination and at the molecular center, while the cage critical points (green dots) can be found between two axial Be atoms. It is remarkable that no bond path and bond critical point can be found between two axial Be atoms, which is also consistent with the AdNDP analysis results. The results for 5-9 are similar to that for **4**, so they are given in Fig. S2 and S3 in †ESI.

The WBI<sub>Be-X</sub> values range from 0.33 to 0.64, signifying the substantial Be-X covalent bonding character. In addition, the natural charges on X atoms and the Be atoms are largely negative and positive, respectively, indicating the solid Coulomb attractions. Therefore, both covalent and electrovalent bonding between Be and X atoms are strongly attractive. Such effect can significantly shorten the Be-X distances, which contributes to shorten the axial Be-Be distances. Except for WBIBe-B value of 0.20 in 1, other WBIBe-M values range from 0.01 to 0.08, suggesting the negligible Be-M covalent bonding. The WBI<sub>X-M</sub> in **1** is 1.48, indicating the partial double bonds, which collaborates the formation of a C-B 2c-2e bond and two C-B-Be-C 4c-2e bonds. The WBI<sub>X-M</sub> in 2-6 range from 0.30 to 0.69, revealing the significantly X-M (X = C and N) covalent characters, which are consistent with the presence of AdNDP-viewed X-M 2c-2e bonds. In contrast, the WBIO-M values in 7–9 are all 0.01. Such negligible value is in line with the 1c-2e O valence lone pairs rather than 2c-2e bonds.

#### **Stability evaluation**

The ultrashort Be-Be distances found in Be<sub>2</sub>N<sub>3</sub>M<sub>3</sub><sup>+</sup> (M = Be, Mg, Ca) and Be<sub>2</sub>O<sub>3</sub>M<sub>3</sub><sup>+</sup> (M = Li, Na, and K) species are exciting. However, to be experimentally realized, these molecules should be stable enough. In this work, we studied thermodynamic stability and kinetic stability of concerned species. The thermodynamic stability was studied by the extensive exploration of potential energy surfaces using stochastic search algorithm.<sup>17</sup> At final CCSD(T)/BS1 level, **7** with bridging O atoms is the high energy local minimum, being 50.3 kcal/mol higher than the lowest energy isomer (see **7b** in

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Fig. S4). Substitution of Li atoms in **7b** with Na and K atoms leads to isomers **8b** and **9b**, which are 48.4 and 70.1 kcal/mol lower than **8** and **9**, respectively. Molecule **6** with bridging N atoms was identified to be the third lowest isomer and higher than corresponding global energy minimum by 10.5 kcal/mol. In general, it should very hard for **6–9** to be generated in the experiments. As a comparison, **4** and **5** were confirmed to be the global energy minima, which are 16.4 and 2.4 kcal/mol lower in energy than their second lowest isomers.

The better thermodynamic stability of **4–6** than **7–9** may be the consequence their peripheral bonding: The N-M localized 2c-2e  $\sigma$  bonding orbitals in **4–6** are more favourable to stability than the non-bonding oxygen lone pairs in **7–9**. Within **4–6**, the WBI<sub>N-Mg</sub> and WBI<sub>N-Ca</sub> values of 0.30 and 0.38 in **5** and **6** are obviously smaller than WBI<sub>N-Be</sub> value of 0.62 in **4**, which, together with the larger charge separation of +1.62/–1.82 and +1.54/–1.74 |e| in **5** and **6** than that of +1.20/–1.49 |e| in **4**, indicate the less covalent N-M bonding character in **5** and **6** than in **4**. This corresponds to the moderate stability of **5** (global minimum with adjacent isomers) and **6** (low-lying local minimum) and the high stability of **4** (deep lying global minimum). So, the stability of current systems might be related to the degree of X-M covalent properties.

Since the global minima might be kinetically unstable and the local minima can be kinetically viable,<sup>11</sup> we had performed 100 picoseconds BOMD simulations<sup>18</sup> for global minima 4 and 5, third-lowest isomer 6 and representative high-lying isomer 7 at the B3LYP/6-31G(d) level and 298 K to examine their kinetic stability. The structural evolution during the simulations was described by the root-mean-square derivations (RMSD, relative to their B3LYP/6-31G(d)-optimized structures). As shown in Fig. 4, the RMSD plot of global minima 4 and 5 have no upward jump and the fluctuation of RMSD values is very small, which indicate the kinetically very stable structure at room-temperature. Being the kinetically stable global energy minima, 4 and 5 would suitable for the gas phase generation and followed spectroscopic characterization. In contrast, the RMSD plot of 6 showed immediate upward jump when the simulation started, suggesting the significantly structural changes had happened. The detailed examination on the structure revealed that 6 underwent the rapid isomerization, generating the global minimum (6a) on Be<sub>2</sub>N<sub>3</sub>Ca<sub>3</sub><sup>+</sup> potential energy surface. Subsequently, the interchange between 6a and the second lowest isomer (6b) can be observed. Such simulation results revealed that local minimum 6 is also kinetically unstable. The RMSD plot of 7 shows the irreversible jump at about 1.5 ps, which corresponds to the isomerization. In the rest simulation time, the interchange among many lowlying isomers of 7 can be witnessed, but not structure of 7 itself can be observed again, so 7 is also kinetically unviable.

## Conclusions

We have demonstrated that the species  $CN_3Be_3^+$  and  $CO_3Li_3^+$  with a central planar hexacoordinate carbon (phC) are eligible template structures for designing the species with ultrashort Be-Be distances through substitution of phC with isoelectronic



Fig. 4. Plots of RMSD versus time for the BOMD simulations of  $D_{3h}$  Be<sub>5</sub>N<sub>3</sub><sup>+</sup> (4), Be<sub>2</sub>N<sub>3</sub>Mg<sub>3</sub><sup>+</sup> (5), Be<sub>2</sub>N<sub>3</sub>Ca<sub>3</sub><sup>+</sup> (6), and Be<sub>2</sub>O<sub>3</sub>Li<sub>3</sub><sup>+</sup> (7) at B3LYP/6-31G(d) level and 298 K.

Be<sub>2</sub> moiety. The enhanced Coulomb attractions between the positively charged axial Be atoms and the negatively charged N or O atoms play the crucial role in shortening the interatomic Be-Be distances. On the top of this, the relationship can be established between shorter Be-Be distances and the smaller size of bridging electronegative atoms as well as the lower electronegativity of peripheral M atoms. The stability of design species corresponds to the types of their valence electron pairs, where localized 2c-2e bonding orbitals are more favourable than the non-bonding 1c-2e valence lone pairs. Remarkably,  $Be_5N_3^+$  (4) and  $Be_2N_3Mg_3^+$  (5) are confirmed to be the kinetically stable global minima, which are suitable for experimental realization. We invite the gas-phase generation and spectroscopic characterization of these interesting species to push metal-metal bonding chemistry forward.

#### **Computational Methods**

In this work, BS1 was named to denote the mixed basis set with def2-TZVPP basis set for K, cc-pVTZ basis set for Ca, and aug-cc-pVTZ basis set for other elements. The species designed in this work

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were optimized and then their vibrational frequencies were analyzed at both B3LYP/BS1 and MP2/BS1 level, which gave the very similar results. The wavefunctions of reported species were also confirmed to be stable at the B3LYP/BS1 level. Therefore, B3LYP functional should be reliable for current system and it was employed in the electronic structure analyses and stability studies. The geometries of designed closed-shell singlet species were refined at the CCSD(T)/BS1 level and reported in the text. To better understand the electronic structures, the natural bond orbitals (NBO)<sup>14</sup> analyzed were performed at the B3LYP/BS1 level, while the adaptive natural density partitioning (AdNDP)<sup>15</sup> were carried out at the B3LYP/6-31G(d) level (AdNDP is insensitive to basis set). The electron density distribution was analyzed by Quantum Theory of Atoms in Molecules (QTAIM)<sup>16</sup> method. The potential energy surfaces of designed species were explored using the stochastic search algorithm.<sup>16</sup> During the exploration, the randomly generated structures were initially optimized at the B3LYP/6-31G(d) level and 20 lowest isomers were re-optimized at the B3LYP/BS1 level. Then ten lowest isomers will be identified and their energies will be improved at the CCSD(T)/BS1 level. The T1- and D1-diagnostic values of CCSD(T) calculations range from 0.015 to 0.027 and from 0.036 to 0.079, respectively. Though some of T1-diagnostic values are a little higher than 0.02, corresponding D1-diagnostic values are all less than 0.1, so the multi-reference characters of current systems are not obvious and the CCSD(T) calculations should be reliable enough. The final relative energies were compared based on the CCSD(T)/BS1 electronic energies plus B3LYP/BS1 zero-point energy corrections. The 100 picoseconds Born-Oppenheimer molecular dynamic (BOMD)<sup>17</sup> simulations were run at the B3LYP/6-31G(d) level and 298 K. The QTAIM analyses were performed using Multiwfn program,<sup>18</sup> the stochastic search was realized by GXYZ 2.0 program,19 the AdNDP bonding patterns were analyzed using AdNDP program,<sup>20</sup> the CCSD(T) jobs were performed using MolPro 2012.1 package,<sup>21</sup> and all other calculations were carried out using Gaussian 09 package.<sup>22</sup>

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### **Conflicts of interest**

There are no conflicts to declare.

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