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# Heptacoordinate transition-metal-decorated metallo-borospherenes and multiple-helix metallo-boronanotubes<sup>†</sup>

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The recent discovery of lanthanide-metal-decorated metallo-borospherenes  $LM_3B_{18}^{-}$  (LM = La, Tb) marks the onset of a new class of boron-metal binary nanomaterials. Using the experimentally observed or theoretically predicted borospherenes as ligands and based on extensive first-principles theory calculations, we predict herein a series of novel chiral metallo-borospherenes  $C_2 \operatorname{Ni}_6 \in \operatorname{B_{39}^-}(1)$ ,  $C_1 \operatorname{Ni}_6 \in \operatorname{B_{41}^+}$ (3),  $C_2 \operatorname{Ni}_6 \in \operatorname{B}_{42}^{2+}$  (4),  $C_2 \operatorname{Ni}_6 \in \operatorname{B}_{42}$  (5), and  $C_2 \operatorname{Ni}_8 \in \operatorname{B}_{56}$  (6) as the global minima of the systems decorated with quasi-planar heptacoordinate Ni (phNi) centers in  $\eta^7$ -B<sub>7</sub> heptagons on the cage surfaces, which are found to be obviously better favoured in coordination energies than hexacoordinate Ni centers in previously reported  $D_{2d}$  Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2). Detailed bonding analyses indicate that these phNi-decorated metalloborospherenes follow the  $\sigma + \pi$  double delocalization bonding pattern, with two effective  $(d-p)\sigma$  coordination bonds formed between each phNi and its  $\eta^7$ -B<sub>7</sub> ligand, rendering spherical aromaticity and extra stability to the systems. The structural motif in elongated axially chiral Ni<sub>6</sub>  $\in$  B<sub>42</sub><sup>2+</sup> (4), Ni<sub>6</sub>  $\in$  B<sub>42</sub> (5), and  $Ni_8 \in B_{56}$  (6) can be extended to form the metallic phNi-decorated boron double chain (BDC) doublehelix Ni<sub>4</sub>  $\in$  B<sub>28</sub> (2, 0) ( $P\bar{4}m2$ ) (**8**), triple-helix Ni<sub>6</sub>  $\in$  B<sub>42</sub> (3, 0) ( $P\bar{3}m1$ ) (**9**), and quadruple-helix Ni<sub>8</sub>  $\in$  B<sub>56</sub> (4, 0) (P4mm) (10) metallo-boronanotubes, which can be viewed as guasi-multiple-helix DNAs composed of interconnected BDCs decorated with phNi centers in  $\eta^7$ -B<sub>7</sub> heptagons on the tube surfaces in the atomic ratio of Ni : B = 1 : 7.

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## Introduction

Boron as a prototypical electron-deficient element exhibits a strong propensity to form multi-center-two-electron (*mc*-2e) bonds to compensate for its electron deficiency.<sup>1,2</sup> Persistent joint photoelectron spectroscopy (PES) and first-principles theory investigations in the past two decades have indicated that size-selected boron clusters  $B_n^{-/0}$  in an unexpectedly wide size range (n = 3-42, 48) possess planar or quasi-planar ( $B_3^--B_{38}^-$ ,  $B_{41}^-$ , and  $B_{42}^-$ ),<sup>3-5</sup> sea-shell-like ( $C_2 B_{28}^{-/0}$  and  $C_s B_{29}^-$ ),<sup>6,7</sup> cage-like ( $D_{2d} B_{40}^{-/0}$  and  $C_3/C_2 B_{39}^-$ ),<sup>8,9</sup> and bilayer ( $D_{2h} B_{48}^-$ ) structures<sup>10</sup> featuring  $\sigma + \pi$  double delocalization bonding patterns. The experimentally observed cage-like  $B_{40}^{-/} {}^{0}/B_{39}^-$  borospherenes have been extended to the  $B_n{}^{q}$  borospherene family (n = 36-42, q = n - 40) at the first-principles theory level and are all composed of twelve interwoven boron double

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chains (BDCs) with six hexagonal or heptagonal faces as effective ligands to coordinate metal centers.<sup>11–13</sup> Inspired by the previously reported icosahedral-B<sub>12</sub> stuffed amorphous B<sub>74</sub>, B<sub>84</sub>, B<sub>101</sub>, and B<sub>102</sub> clusters<sup>14–16</sup> and based on extensive density functional theory (DFT) calculations, our group recently predicted a series of approximately electron sufficient  $C_{\rm s}$  B<sub>111</sub>,  $C_{\rm s}$  B<sub>112</sub>,  $C_{\rm s}$  B<sub>113</sub>, and  $C_{\rm s}$  B<sub>114</sub> structures, which are the most stable neutral core-shell borospherenes with a superatomic icosahedral-B<sub>12</sub> core at the center reported to date in the size range between B<sub>68</sub> and B<sub>130</sub>, with  $C_{\rm s}$  B<sub>112</sub> being the thermodynamically most favorable species in the series.<sup>17</sup> We also proposed a bottom-up approach from the theoretically predicted medium-sized bilayer BL- $\alpha^+$  borophene on an Ag (111) substrate.<sup>18–22</sup>

Metal-doping is proved to introduce interesting structural and bonding changes to boron clusters. Exohedral  $C_{\rm s} \, {\rm M} \in {\rm B}_{40}$ (M = Be, Mg) with a quasi-planar heptacoordinate metal center in an  $\eta^7$ -B<sub>7</sub> heptagon on the cage surface were the first metallo-borospherenes predicted in theory.<sup>23</sup> The doping metal centers and the polygonal ligands around them must match both geometrically and electronically to form stable metallo-borospherenes. The recent observation of the first

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spherical trihedral metallo-borospherenes  $D_{3h} LM_3 \in B_{18}^-$  (LM = La and Tb) with three equivalent decacoordinate metal centers in three  $\eta^{10}$ -B<sub>10</sub> decagons on the cage surface in photoelectron spectroscopy (PES) experiments marks the onset of metallo-borospherene chemistry.<sup>24</sup> La<sub>3</sub>  $\in$  B<sub>18</sub><sup>-</sup> was later theoretically extended to the smallest core-shell metallo-borospherene  $D_{3h}$  La<sub>3</sub>B<sub>20</sub><sup>-</sup> (La<sub>3</sub>  $\in$  [B<sub>2</sub>@B<sub>18</sub>]<sup>-</sup>), which contains a B<sub>2</sub> unit at the center along the  $C_3$  molecular axis at the coupled cluster theory with triple excitation (CCSD(T)) level.<sup>25</sup> A perfect spherical trihedral metallo-borospherene  $D_{3h}$  Ta<sub>3</sub>  $\in$  B<sub>12</sub><sup>-</sup> with three equivalent octacoordinate Ta centers and a perfect spherical tetrahedral metallo-borospherene  $Ta_4 \in B_{18}$  with four equivalent nonacoordinate Ta centers as integral parts of the cage surface were proposed recently in theory.<sup>26,27</sup> Based on the structural motif of the first experimentally observed neutral borospherene  $D_{2d} B_{40}$ ,<sup>8</sup> a series of metallo-borospherenes Ni<sub>m</sub>  $\in$  B<sub>40</sub> (*m* = 1-6) with 1-4 quasi-planar heptacoordinate Ni (phNi) centers and 1-2 hexacoordinate Ni centers on the cage surface and two nearly degenerate two-dimensional (2D) metallo-borophenes Ni<sub>2</sub>  $\in$  B<sub>14</sub> (P2<sub>1</sub>/m) and Ni<sub>2</sub>  $\in$  B<sub>14</sub> (P1) with two phNi centers in each unit cell have also been predicted.<sup>28</sup> PhNi centers in  $\eta^7$ -B<sub>7</sub> pentagons on the cage surface of B<sub>40</sub> were found to be better favoured in thermodynamics than their hexacoordinate Ni counterparts in  $\eta^6$ -B<sub>6</sub> hexagons due to size effects. However, metallo-borospherenes smaller or larger than  $Ni_6 \in B_{40}$  and one-dimensional (1D) metallo-boronanotubes decorated exclusively with the thermodynamically most favoured heptacoordinate transition-metal (phTM) centers have still remained unknown to date in both experiments and theory.

Based on extensive global minimum (GM) searches augmented with first-principles theory calculations, we predict in this work a series of chiral metallo-borospherenes  $C_2$  Ni<sub>6</sub>  $\in$  B<sub>39</sub><sup>-</sup> (1),  $C_1$  Ni<sub>6</sub>  $\in$  B<sub>41</sub><sup>+</sup> (3),  $C_2$  Ni<sub>6</sub>  $\in$  B<sub>42</sub><sup>2+</sup> (4),  $C_2$  Ni<sub>6</sub>  $\in$  B<sub>42</sub> (5), and  $C_2$  Ni<sub>8</sub>  $\in$  B<sub>56</sub> (6) as the global minima (GMs) of the systems and double-helix Ni<sub>4</sub>  $\in$  B<sub>28</sub> (2, 0) ( $P\bar{4}m2$ ) (8), triple-helix Ni<sub>6</sub>  $\in$  B<sub>42</sub> (3, 0) ( $P\bar{3}m1$ ) (9), and quadruple-helix Ni<sub>8</sub>  $\in$  B<sub>56</sub> (4, 0) (P4mm) (10) metallo-boronanotubes, which are exclusively decorated with phNi centers in  $\eta^7$ -B<sub>7</sub> heptagons on the cage or tube surfaces. Such highly stable phNi-doped metalloborospherenes and metallo-boronanotubes composed of interconnected BDCs follow the  $\sigma + \pi$  double delocalization bonding pattern and are spherically aromatic in nature.

## Computational details

The global minimum (GM) searches of  $Ni_6B_n{}^q$  (n = 39-42, q = n - 40),  $Ni_6B_{42}$ , and  $Ni_8B_{56}$  were performed using a Basin-Hopping algorithm implanted in the TGMin 2.0 package.<sup>29</sup> Over 1000 trial structures were probed on the potential energy surface for each species in both singlet and triplet states at the PBE/TZVP level. Candidate low-lying structures were then fully optimized with vibrational frequencies checked at both PBE0<sup>30</sup> and TPSSh<sup>31</sup> levels with the 6-311+G(d) basis set<sup>32</sup> using the Gaussian 09 program.<sup>33</sup> Natural bonding orbital (NBO) analyses were performed using the NBO 6.0 program<sup>34</sup> and detailed bonding analyses were carried out utilizing the adaptive natural density partitioning (AdNDP)<sup>35,36</sup> approach. Born– Oppenheimer molecular dynamic (BOMD) simulation was implemented employing the CP2K code<sup>37</sup> with the GTH-PBE pseudopotentials and the TZVP-MOLOPTSR-GTH basis sets. Iso-chemical shielding surfaces (ICSSs) were generated with the Multiwfn 3.7 code.<sup>38</sup> The visualization for the isosurfaces of various functions was realized with VMD software.<sup>39</sup>

First-principles calculations on 1D boron double-chain metallo-boronanotubes were performed using the Vienna *ab initio* simulation package (VASP),<sup>40,41</sup> within the framework of the projector augmented wave (PAW)<sup>42,43</sup> pseudopotential method and PBE generalized gradient approximation (GGA).44,45 The Coulomb-corrected local spin density approximation (LSDA+U) was utilized for both structural optimizations and static calculations and the Hubbard U value for Ni was 6 eV.<sup>46-49</sup> The energy cutoff of plane waves was set to 450 eV. Atomic structures were fully relaxed using the conjugate gradient (CG) method until the maximum force on each atom was less than 0.01 eV  $Å^{-1}$  and the energy precision was set to 10<sup>-5</sup> eV. To avoid mirror interactions, the minimum distance between the atoms in neighbouring mirrors is larger than 15 Å. The Brillouin zones were sampled with a 0.1 Å<sup>-1</sup> spacing in the reciprocal space by the Monkhorst–Pack scheme.

## **Results and discussion**

#### PhNi-decorated metallo-borospherenes

Using the previously reported borospherenes  $B_n^q$  (*n* = 39–42, *q* = n - 40<sup>8,9,11-13</sup> as ligands to coordinate six Ni atoms in  $\eta^7$ -B<sub>7</sub> heptagons or  $\eta^6$ -B<sub>6</sub> hexagons, we obtained the global minima of their metallo-borospherenes Ni<sub>6</sub>  $\in$  B<sub>n</sub><sup>q</sup> (n = 39-42, q = n -40) as shown in Fig. 1a, with more alternative low-lying isomers depicted in Fig. S1.† The axially chiral global minimum (GM)  $C_2$  Ni<sub>6</sub>  $\in$  B<sub>39</sub><sup>-</sup> (1, <sup>1</sup>A) with six phNi centers in six  $\eta^7$ -B<sub>7</sub> heptagons on the cage surface has the same symmetry as its parent borospherene  $C_2$   $B_{39}^{-,9}$  with the smallest vibrational frequency of 113.1 cm<sup>-1</sup>. It is the first metallo-borospherene reported to date with only phTM centers as the integral parts of the cage surface. The two original B<sub>6</sub> hexagons on the top and bottom of the parent borospherene  $C_2 B_{39}^{-}$  have been enlarged to two equivalent  $\eta^7$ -B<sub>7</sub> heptagons in  $C_2$  Ni<sub>6</sub>  $\in$  $B_{39}^{-}$  (1) to host two Ni atoms more comfortably on the cage surface, further demonstrating that phNi centers are better favoured over their hexacoordinate Ni counterparts in thermodynamics due to size effects, which is similar to the situation observed in Ni<sub>6</sub>  $\in$  B<sub>40</sub>.<sup>28</sup> The second lowest-lying isomer  $C_1$  Ni<sub>6</sub>  $\in B_{39}^{-}$  (1b, <sup>1</sup>A) with six phNi centers lies 0.17 eV higher, while its triplet counterpart  $C_2$  Ni<sub>6</sub>  $\in$  B<sub>39</sub><sup>-</sup> (**1c**, <sup>3</sup>A) appears to be 0.24 eV less stable (Fig. S1a<sup>†</sup>). With the same symmetry as the GM of  $C_3 \operatorname{B_{39}}^{-,9}$  the fourth lowest-lying isomer  $C_3 \operatorname{Ni}_6 \in \operatorname{B_{39}}^{-}$  (1d, <sup>1</sup>A) with three phNi centers and three hexacoordinate Ni centers on the cage surface along the C3 molecular axis lies 0.44 eV higher in energy than  $C_2 \operatorname{Ni}_6 \in \operatorname{B}_{39}^-(1)$ .



Fig. 1 (a) Optimized structures of the Ni-decorated metallo-borospherenes  $C_2 \operatorname{Ni}_6 \in \operatorname{B}_{39}^{-1}$  (1),  $D_{2d} \operatorname{Ni}_6 \in \operatorname{B}_{40}$  (2),  $C_1 \operatorname{Ni}_6 \in \operatorname{B}_{41}^+$  (3),  $C_2 \operatorname{Ni}_6 \in \operatorname{B}_{42}^{2+}$  (4),  $C_2 \operatorname{Ni}_6 \in \operatorname{B}_{42}$  (5), and  $C_2 \operatorname{Ni}_8 \in \operatorname{B}_{56}$  (6) at the PBE0/6-311+G(d) level. (b) Calculated average coordination energies ( $E_c$ ) of the  $\operatorname{Ni}_m \in \operatorname{B}_n^q$  metallo-borospherenes with respect to  $\operatorname{Ni}_m \operatorname{B}_n^q = \operatorname{Ni}_{m-1} \operatorname{B}_n^q + \operatorname{Ni}$ . The black and red dots stand for the heptacoordinate and hexacoordinate Ni centers on the cage surfaces, respectively.

Extensive GM searches indicate that  $D_{2d}$  Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2, <sup>1</sup>A) with four phNi centers and two hexacoordinate Ni centers on the cage surface is indeed the true GM of the system, with the boron skeleton of the experimentally observed D<sub>2d</sub> B<sub>40</sub> remaining basically unchanged (Fig. S1b<sup>+</sup>), in line with the previously predicted results.<sup>28</sup>  $C_1$  Ni<sub>6</sub>  $\in$  B<sub>41</sub><sup>+</sup> (3, <sup>1</sup>A) with six phNi centers as the GM of the monocation appears to be 0.08 and 0.15 eV more stable than the second lowest-lying isomer  $C_1$  Ni<sub>6</sub>  $\in B_{41}^+$ with five phNi and one hexacoordinate Ni at the PBE0 and TPSSh levels, respectively (Fig. S1c<sup>†</sup>), again supporting the thermodynamic favorability of a phNi center over its hexacoordinate Ni counterpart. The two close-lying isomers may coexist in experiments. As shown in Fig. 1a and Fig. S1d,† as the welldefined GM of the di-cation, the axially chiral  $C_2$  Ni<sub>6</sub>  $\in$  B<sub>42</sub><sup>2+</sup> (4, <sup>1</sup>A) composed of twelve interwoven BDCs possesses six phNi centers on the cage surface in six  $\eta^7$ -B<sub>7</sub> heptagons, with the same symmetry as its parent borospherene  $C_2 \operatorname{B_{42}}^{2+,11}$  The high-symmetry second lowest-lying isomer  $D_3$  Ni<sub>6</sub>  $\in$  B<sub>42</sub><sup>2+</sup> (4b, <sup>1</sup>A<sub>1</sub>), which also contains six phNi centers on the cage surface lies 0.28 and 0.25 eV higher than the  $C_2$  GM at PBE0 and TPSSh, respectively. The obtained core-shell and bilayer isomers of Ni<sub>6</sub>B<sub>n</sub><sup>q</sup> (n = 39-42, q = n - 40) (Fig. S1a–S1d<sup>†</sup>) are found to be at least 2.50, 4.03, 2.44, and 4.29 eV less stable

than their metallo-borospherene GMs **1**, **2**, **3**, and **4** at PBE0, respectively. **1**–**4** have the calculated large HOMO–LUMO energy gaps of  $\Delta E_{\text{gap}} = 1.51 \text{ eV}$ , 2.26 eV, 2.14 eV, and 2.42 eV at PBE0, respectively, well supporting their high chemical stabilities.

The axially chiral triplet  $C_2 \operatorname{Ni}_6 \in \operatorname{B}_{42}(5, {}^3\mathrm{B})$  as the GM of the neutral cage appears to have the same structural motif as the singlet  $\operatorname{Ni}_6 \in \operatorname{B}_{42}{}^{2+}(4)$ , with four close-lying isomers within 0.1 eV (Fig. S1e†). More interestingly, the elongated  $\operatorname{Ni}_6 \in \operatorname{B}_{42}{}^{2+}(4)$  and  $\operatorname{Ni}_6 \in \operatorname{B}_{42}(5)$  can be extended along the  $C_2$  molecular axis to form the axially chiral metallo-borophenes  $C_2 \operatorname{Ni}_8 \in \operatorname{B}_{56}(6, {}^1\mathrm{A}), C_2 \operatorname{Ni}_{10} \in \operatorname{B}_{70}({}^1\mathrm{A}),$  and  $C_2 \operatorname{Ni}_{12} \in \operatorname{B}_{84}({}^1\mathrm{A})$  composed of interwoven BDCs, which contain eight, ten, and twelve phNi centers as integral parts of the cage surface, respectively, with  $C_2 \operatorname{Ni}_8 \in \operatorname{B}_{56}(6)$  as the true GM of the system lying at least 0.29 eV more stable than other low-lying isomers at PBE0 (Fig. S1f†), while  $C_2 \operatorname{Ni}_{10} \in \operatorname{B}_{70}({}^1\mathrm{A})$  and  $C_2 \operatorname{Ni}_{12} \in \operatorname{B}_{84}({}^1\mathrm{A})$  are true minima on the potential energy surfaces of the corresponding neutral cages (Fig. S2†).

Extensive molecular dynamics (MD) simulations indicate that 1-6 are dynamically stable at certain temperatures, as is evident from their calculated small root-mean-square-deviations, RMSD = 0.05, 0.05, 0.08, 0.10, 0.08, and 0.08 Å, and

their maximum bond length deviations, MAXD = 0.15, 0.16, 0.27, 0.37, 0.27, and 0.29 Å at 200, 200, 300, 800, 500, and 800 K, respectively. No higher-energy isomers are observed during the simulations in 30 ps (Fig. S3<sup>†</sup>).

Fig. 1b demonstrates the variation of coordination energy  $(E_c)$  with the number (m) of Ni atoms in metallo-borospherenes 1-6 with respect to  $Ni_m B_n^q = Ni_{m-1} B_n^q + Ni$  (referring to triplet Ni and singlet  $B_n^q$ ). The coordination energies  $E_c$  of Ni<sub>6</sub>  $\in B_{39}^{-}(1)$ , Ni<sub>6</sub>  $\in B_{41}^{+}(3)$ , Ni<sub>6</sub>  $\in B_{42}^{2+}(4)$ , Ni<sub>6</sub>  $\in B_{42}(5)$ , and Ni<sub>8</sub>  $\in B_{56}$  (6) increase almost perfectly linearly with the number (m) of Ni atoms in the systems in the relationship of  $E_{\rm c}$  =  $E_{c/atom}m$  (where  $E_{c/atom}$  is the averaged coordination energy per Ni), while the two hexacoordinate Ni centers in Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2) clearly depart the  $E_{\rm c} \sim m$  linear relationship with lower coordination energies, indicating that  $\eta^7$ -B<sub>7</sub> heptagons are better ligands to coordinate the Ni centers than  $\eta^6$ -B<sub>6</sub> hexagons in Nidoped metallo-borospherenes due to size effects. The  $E_{\rm c} \sim m$ linear relationships in Fig. 1b show that  $Ni_6 \in B_{39}^-$  (1),  $Ni_6 \in$  $B_{41}^{+}(3)$ ,  $Ni_6 \in B_{42}^{-2+}(4)$ ,  $Ni_6 \in B_{42}(5)$ , and  $Ni_8 \in B_{56}(6)$ , with only phNi centers on the cage surfaces, have the average coordination energies per phNi atom of  $E_{c/atom}$  = 93.72, 94.51, 96.51, 96.75, and 98.09 kcal mol<sup>-1</sup> at PBE0, respectively, while in Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2), the four phNi centers have an average  $E_{c/atom}$  = 95.04 kcal mol<sup>-1</sup> and the two hexacoordinate Ni centers highlighted in red have a lower average  $E_{c/atom} = 77.16 \text{ kcal mol}^{-1}$ , indicating quantitatively that phNi centers are obviously better favoured in thermodynamics over their hexacoordinate Ni

counterparts in Ni-doped metallo-borospherenes. The  $E_{\rm c} \sim m$  linear relationship also indicates that the phNi centers and hexacoordinate Ni centers on the cage surfaces can be practically viewed as independent coordination sites in metalloborospherenes.

#### Bonding analyses of metallo-borospherenes

Detailed NBO analyses show that the Ni atoms in these metallo-borospherenes possess the positive natural net atomic charges of  $q_{\rm Ni} = +0.79 \sim +0.832|e|$  and electronic configurations of  $3d^{9.00-9.04}$  4s<sup>0.15-0.18</sup>, indicating that the Ni centers on the cage surfaces donate their 4s electrons almost completely to the  $\eta^6$ -B<sub>6</sub>/ $\eta^7$ -B<sub>7</sub> ligands to form effective Ni–B coordination interactions while, in return, accept roughly one electron in their partially filled 3d orbitals from the surrounding ligands *via* effective B(2p)  $\rightarrow$  Ni(3d) back donations.

Detailed AdNDP bonding analyses performed as shown in Fig. 2 reveal the delocalized coordination bonding patterns between the Ni centers and their  $\eta^7$ -B<sub>7</sub>/ $\eta^6$ -B<sub>6</sub> ligands in both  $D_{2d}$  Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2) and  $C_2$  Ni<sub>8</sub>  $\in$  B<sub>56</sub> (6). As shown in the first row of Fig. 2a, Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2) possesses 48 3c-2e in-surface  $\sigma$  bonds on the B<sub>40</sub> ligand with the occupation numbers ON = 1.73-1.92|e| and  $4 5c-2e \pi$  bonds,  $4 6c-2e \pi$  bonds, and 4 7c- $2e \pi$  bonds over the twelve interwoven BDCs with ON = 1.73-1.89|e|, with a  $\sigma + \pi$  double delocalization bonding pattern well inherited from the parent borospherene  $D_{2d}$  B<sub>40</sub>.<sup>8</sup> More interestingly, as shown in the second row, each phNi pos-



sesses 3 1c–2e lone pairs in the radial direction  $(3d_{z^2}, 3d_{xz}, and 3d_{yz})$  with |ON| = 1.80-1.95|e| and 2 8c–2e  $B_7(\sigma)$ –Ni( $d_\delta$ ) insurface (d–p) $\sigma$  coordination bonds between its remaining tangential 3d orbitals  $(3d_{xy} \text{ and } 3d_{x^2-y^2})$  and its 2p– $\sigma$  orbitals of the  $\eta^7$ - $B_7$  ligand around it with ON = 1.87–1.88|e|. It is the two in-surface 8c–2e (d–p) $\sigma$  bonds that generate the average coordination energy of  $E_{c/atom} = 95.04$  kcal mol<sup>-1</sup> for each phNi in Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2). Each hexacoordinate Ni center in Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2) also possesses 3 1c–2e lone pairs in the radial direction, but its two in-plane 7c–2e (d–p) $\sigma$  coordination bonds (two B<sub>6</sub>( $\sigma$ )–Ni ( $d_\delta$ ) bonds) with the  $\eta^6$ -B<sub>6</sub> ligand around it are proved to have an obviously lower  $E_{c/atom} = 77.16$  kcal mol<sup>-1</sup>, showing that the  $\eta^6$ -B<sub>6</sub> hexagons are too small in size to host a Ni atom comfortably inside.

The axially chiral isomer  $C_2$  Ni<sub>8</sub>  $\in$  B<sub>56</sub> (6) possesses a similar bonding pattern, as shown in Fig. 2b. It possesses 68 3c-2e  $\sigma$  bonds on 68 B<sub>3</sub> triangles on the B<sub>56</sub> ligand and 8 5c-2e  $\pi$  bonds, 4 6c-2e  $\pi$  bonds, and 4 8c-2e  $\pi$  bonds over the B<sub>56</sub> skeleton composed of interwoven BDCs, again following the  $\sigma$  +  $\pi$  double delocalization bonding pattern. Similar to the situation in Ni<sub>6</sub>  $\in$  B<sub>40</sub> (2), each phNi in Ni<sub>8</sub>  $\in$  B<sub>56</sub> (6) also forms 3 1c-2e lone pairs (3d<sub>z<sup>2</sup></sub>, 3d<sub>xz</sub>, and 3d<sub>yz</sub>) in the radial direction and 2 8c-2e in-plane (d-p) $\sigma$  coordination bonds with the  $\eta^7$ -B<sub>7</sub> ligand around it (two B<sub>7</sub>( $\sigma$ )-Ni(d<sub>8</sub>) bonds).

Such delocalized bonding patterns render spherical aromaticity to metallo-borophenes **1–6** featured in this work, as is evident from their calculated large negative nucleus independent chemical shifts,<sup>50,51</sup> NICS = -35.19, -42.20, -42.29, -43.78, -27.41 and -20.40 ppm, at the geometrical centers, respectively. Their iso-chemical shielding surfaces (ICSSs) based on the calculated NICS-ZZ components of metallo-borospherenes **1–4** are also collectively presented in Fig. 3, in comparison with that of the experimentally known spherically aromatic  $D_{2d} B_{40}$ .<sup>8</sup> As is clearly shown in Fig. 3, the spaces inside the cages and within about 1.0 A above the cage surfaces in the vertical direction belong to chemical shielding regions with negative NICS-ZZ values, while the chemical de-shielding regions with positive NICS values are located in belt-like areas around the cage waists in the horizontal direction, well comparable with the situation observed in  $D_{2d}$  B<sub>40</sub>, providing further evidence that these Ni-decorated metallo-borophenes are spherically aromatic in nature, well supporting the high thermodynamic stabilities of these phNi-decorated metalloborospherenes. The spherical aromaticity of Ni<sub>m</sub>B<sub>n</sub><sup>q</sup> (1–6) mainly originates from the delocalized  $\pi$  bonds over the interwoven BDCs on the B<sub>n</sub><sup>q</sup> ligands, while phNi centers incorporated between in  $\eta^7$ -B<sub>7</sub> heptagons enhance the overall stability of the systems *via* effective 8c–2e (d–p) $\sigma$  coordination bonding.

## One-dimensional phNi-decorated boron double-chain multiple-helix metallo-boronanotubes

The elongated axially chiral Ni<sub>6</sub>  $\in B_{42}^{2+}$  (4), Ni<sub>6</sub>  $\in B_{42}$  (5), and  $Ni_8 \in B_{56}$  (6) can be extended infinitely to form the one-dimensional (1D) phNi-decorated BDC double-helix metallo-boronanotube Ni<sub>4</sub>  $\in$  B<sub>28</sub> (2, 0) (8) (*P*4*m*2), which can be rolled up from the previously predicted two-dimensional (2D) metallo-borophene Ni<sub>2</sub>B<sub>14</sub> ( $P2_1/m$ ) (7) with a = 9.317 Å and b = 4.729 Å <sup>28</sup> in the *a* direction, as shown in Fig. 4. In similar structural motifs, the phNi-decorated 1D triple-helix Ni<sub>6</sub>  $\in$  B<sub>42</sub> (3, 0) ( $P\bar{3}m1$ ) (9) and quadruple-helix  $phNi_8 \in B_{56}(4, 0) (P4mm) (10)$  as cylindrical nanotubes extended in the *a* direction have also been constructed from 2D Ni<sub>2</sub>B<sub>14</sub> (7). These multiple-helix metallo-boronanotubes can be viewed as quasi-multiple-helix DNAs composed of interconnected boron double chains decorated with phNi centers in  $\eta^7$ -B<sub>7</sub> heptagons on the tube surfaces in the atomic ratio of Ni: B = 1:7. As indicated in Fig. 4, the delocalized 3c-2e  $B_3 \sigma$  bonds and 4c-2e  $B_4 \pi$  bonds on  $B_4$  rhombuses and 8c-2e  $B_7(\sigma)$ -Ni( $d_{\delta}$ ) coordination interactions on Ni@B<sub>7</sub> structural units between the interconnected BDCs play major roles in stabilizing the systems. 1D Ni<sub>8</sub>  $\in$  B<sub>56</sub> (0, 4) (P4/m) (11),  $Ni_{10} \in B_{70} (0, 5) (Pm) (12)$ , and  $Ni_{12} \in B_{84} (0, 6) (P2/m) (13)$  as prismatic nanotubes extended in the b direction from 2D  $Ni_2B_{14}$  (7) are also collectively depicted in Fig. S4.<sup>†</sup> The space groups, tube indices (m, n), tube diameters (d), and unit cell heights (h) of the studied phNi-decorated  $Ni_m B_n$  metallo-boronanotubes are comparatively tabulated in Table 1.



**Fig. 3** Calculated iso-chemical shielding surfaces (ICSSs) of (a)  $C_2 \operatorname{Ni}_6 \in B_{39}^{-1}(1)$ , (b)  $D_{2d} \operatorname{Ni}_6 \in B_{40}(2)$ , (c)  $C_1 \operatorname{Ni}_6 \in B_{41}^{+1}(3)$ , and (d)  $C_2 \operatorname{Ni}_6 \in B_{42}^{2+1}(4)$ , compared with that of the spherically aromatic (e)  $D_{2d} B_{40}$ , with the main molecular axes designated as the *z* axis in the vertical direction. Yellow and green regions stand for chemical shielding and chemical deshielding areas.



**Fig. 4** Optimized two-dimensional Ni<sub>2</sub>  $\in$  B<sub>14</sub> (7)<sup>28</sup> and one-dimensional Ni<sub>4</sub>  $\in$  B<sub>28</sub> (8), Ni<sub>6</sub>  $\in$  B<sub>42</sub> (9), and Ni<sub>8</sub>  $\in$  B<sub>56</sub> (10) at the PBE level. Ni: yellow and cyan-blue. B: red, cyan, purple, and green.

**Table 1** Space groups, tube indices, diameters, unit cell heights, and cohesive energies per atom of the phNi-decorated  $Ni_m \in B_n$  (m:n = 1:7) metallo-nanotubes studied in this work

	Space		d	h	F .
	group	Indices	(nm)	(nm)	(eV  per atom)
$\begin{array}{l} \hline \\ \hline Ni_{4} \in B_{28} \left( 8 \right) \\ Ni_{6} \in B_{42} \left( 9 \right) \\ Ni_{8} \in B_{56} \left( 10 \right) \\ Ni_{8} \in B_{56} \left( 11 \right) \\ Ni_{10} \in B_{70} \left( 12 \right) \\ Ni_{12} \in B_{84} \left( 13 \right) \end{array}$	P4m2 P3m1 P4mm P4/m Pm P2/m	$\begin{array}{c} (2, 0) \\ (3, 0) \\ (4, 0) \\ (0, 4) \\ (0, 5) \\ (0, 6) \end{array}$	0.59 0.89 1.19 0.60 0.75 0.90	0.47 0.47 0.47 0.91 0.91 0.92	5.217 5.524 5.541 5.509 5.530 5.540

The relative stabilities of these Ni-B binary naonotubes  $Ni_m B_n$  with m: n = 1:7 can be evaluated quantitatively according to their average cohesive energies per atom  $(E_{\rm coh})$  defined as  $E_{\rm coh} = (mE_{\rm Ni} + nE_{\rm B} - E_{\rm t})/(m + n)$ , where  $E_{\rm t}$ ,  $E_{\rm Ni}$ , and  $E_{\rm B}$  are the total energies of the 1D  $Ni_m B_n$  nanotubes  $Ni_m \in B_n$ , a triplet Ni atom, and a doublet B atom, respectively. As shown in Table 1,  $E_{\rm coh}$  increases almost monotonously with an increase of the tube diameters, with Ni<sub>8</sub>  $\in$  B<sub>56</sub> (4, 0) (10) with a diameter of d = 1.19 nm and a unit cell height of h = 0.47 nm showing the highest  $E_{\rm coh}$  = 5.541 eV per atom in the series. As expected from chemical intuition, these metallo-boronanotubes with diameter-dependent strains appear to be less stable in thermodynamics than their precursor 2D metallo-borophene Ni<sub>2</sub>B<sub>14</sub>  $(P2_1/m)$  (7) with  $E_{\rm coh}$  = 5.939 eV per atom.<sup>28</sup> The calculated band structures and projected density of states (PDOS) of the six 1D  $Ni_m B_n$  metallo-boronanotubes are collectively depicted in Fig. S5.† These nanotubes all appear to be metallic in nature. Both B-2p orbitals and Ni-3d orbitals contribute to the calculated PDOSs near the Fermi level, with the B-2p orbitals making major contributions to the PDOSs near the Fermi level. Single- and multi-walled boron nanotubes have been experimentally realized.52,53 PhNi-decorated metallo-boronanotubes enhanced by effective 8c-2e  $B_7(\sigma)$ -Ni( $d_{\delta}$ ) coordination interactions evenly distributed on the tube surfaces may be targeted in future experiments to further enrich the structural diversity of boron nanomaterials.

## Conclusions

Based on the extensive GM searches augmented with first-principles theory calculations, we have presented in this work a series of phNi-decorated metallo-borospherenes Ni<sub>6</sub>  $\in$  B<sub>39</sub><sup>-</sup> (1), Ni<sub>6</sub>  $\in$  B<sub>41</sub><sup>+</sup> (3), Ni<sub>6</sub>  $\in$  B<sub>42</sub><sup>2+</sup> (4), Ni<sub>6</sub>  $\in$  B<sub>42</sub> (5), and Ni<sub>8</sub>  $\in$  B<sub>56</sub> (6) as global minima of the systems and metallic multiple-helix metallo-boronanotubes Ni<sub>4</sub>  $\in$  B<sub>28</sub> (2, 0) (*P*4*m*2) (8), Ni<sub>6</sub>  $\in$  B<sub>42</sub> (3, 0) (*P*3*m*1) (9), and Ni<sub>8</sub>  $\in$  B<sub>56</sub> (4, 0) (*P*4*mm*) (10) featuring interconnected BDCs on the boron skeletons. These highly stable metallo-borospherenes and metallo-boronanotubes follow the  $\sigma + \pi$  double delocalization bonding pattern on the boron frameworks, with two delocalized 8c–2e (d–p) $\sigma$  coordination bonds formed between each Ni center and its  $\eta^7$ -B<sub>7</sub> ligand, rendering spherical aromaticity and extra stability to the systems.

PhTM-decorated metallo-borospherenes, metallo-borophenes, and metallo-boronanotubes as a new class of boron nanomaterials enhanced by effective  $(d-p)\sigma$  coordination interactions are unique in structural and bonding patterns and may have important applications in materials science, molecular devices, and chemical catalysis.

## Conflicts of interest

There are no conflicts to declare.

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