Ultrastable actinide endohedral borospherenes†

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Since the discovery of the first all-boron fullerenes B_{40}^{+}/0, metal-doped borospherenes have received extensive attention. So far, in spite of theoretical efforts on metalloborospherenes, the feasibility of actinide analogues remains minimally explored. Here we report a series of actinide borospherenes AnB_{n} (An = U, Th; n = 36, 38, and 40) using DFT-PBE0 calculations. All the AnB_{n} complexes are found to possess endohedral structures (An@B_{n}) as the global minima. In particular, U@B_{36} (C_{2h}, 1A_{g}) and Th@B_{38} (D_{2h}, 1A_{g}) exhibit nearly ideal endohedral borospherene structures. The C_{2h} U@B_{36} and D_{2h} Th@B_{38} complexes are predicted to be highly robust both thermodynamically and dynamically. In addition to the actinide size match to the cage, the covalent character of the metal-cage bonding in U@B_{36} and Th@B_{38} affords further stabilization. Bonding analysis indicates that U@B_{36} and Th@B_{38} can be qualified as 32-electron systems, and Th@B_{38} exhibits 3D aromaticity with σ plus π double delocalization bonding. The results demonstrate that doping with appropriate actinide atoms is promising to stabilize diverse borospherenes, and may provide routes for borospherene modification and functionalization.

Since the recent observation of the first all-boron fullerenes D_{2d} B_{40}^{+}/10 in 2014,1 the chemistry of borospherenes has developed rapidly.2–5 Other subsequently reported borospherenes include B_{39},1,2 B_{38} 2,3 B_{40} 2h,4,5 and B_{36}.6 Metal doping has been used to modify the chemical bonding and to functionalize fullerenes,7 and the slightly smaller diameter of borospherenes (e.g. B_{40}) relative to C_{60} makes them candidates to dope with metal atoms. Recently, Li and co-workers8 explored the first metallaborospherenes, MB_{40} (M = Be, Mg, Ca, and Sr), at the density functional theory (DFT) level. Ca@B_{40} and Sr@B_{40} are predicted to exhibit almost perfect endohedral borospherene geometries, while the Be- and Mg-analogues prefer exohedral borospherene structures. Subsequently, computational reports of other metalloborospherenes have appeared, including Ca@B_{38}3 and Ca@B_{39} 4 with a Ca^{2+} ion at the centers of B_{38} 2h and B_{39} cages. Based on first-principles theory calculations, the Saturn-like Li_{2}B_{36}, Li_{3}B_{36}, and Li_{4}B_{36} 5–7 were identified as viable with a perfect cage-like B_{36} 4h. 8 In addition to alkaline earth and alkali metal atoms, it is predicted that boron cages are stabilized by doping the insides of the cages with transition metal and lanthanide metal atoms.9–12 Jin et al.10 presented a computational investigation of endohedral borospherenes M@B_{40} (M = Sc, Y, and La). Lu et al.11 reported a computational study of endohedral M@B_{38} (M = Sc, Y, and Ti) and exohedral M&B_{38} (M = Nb, Fe, Co, and Ni) fullerenes with a neutral B_{38} cage. It has been predicted that d-block transition metal atoms (M = Ti, Zr, Hf, Cr, Mo, W, Fe, Ru and Os) demonstrate the ability to stabilize the small cage-like boron cluster B_{24} 2h. The possible applications of the metalloborospherenes arouse our interest in more diverse metal-doped borospherenes. Despite the substantial attention devoted to metalloborospherenes, there is so far no evidence for the stabilization of boron cages by actinide metal atoms, except for the recently reported boron cluster U@B_{40}13 which makes fascinating the question of whether other actinide metal-doped borospherenes are viable. Here we assess the feasibility of synthesizing actinide metalloborospherenes AnB_{n} (An = U, Th; n = 36, 38, and 40) using DFT-PBE0 calculations. The results demonstrate that the encapsulated uranium and thorium atoms can stabilize boron cages, and the global minima of U@B_{36} (C_{2h}, 1A_{g}) and Th@B_{38} (D_{2h}, 1A_{g}) exhibit nearly ideal endohedral borospherene structures. Analogous to Ca@B_{40}8 Th@B_{38} has σ plus π double delocalization. This work enriches and expands the metalloborospherene chemistry to the realm of actinoborospherenes, and affords key insights for chemical modification and functionalization of borospherenes.

Over 500 isomers of each actinide metal-doped borospherene were found by global structural searches. The predicted ten low-lying isomers along with the low-lying exohedral structures of...
six studied AnB\textsubscript{n} at the hybrid DFT-PBE0 level are displayed in Fig. S1–S6, ESI.\textsuperscript{1} Notably, all the global minimum isomers have endohedral metallaborospherene structures (An@B\textsubscript{n}), while the exohedral structures (An\&B\textsubscript{n}) are much higher in energy. For each species, the lowest energy structures are well defined with alternative structures being \sim 0.3 eV higher in energy at the PBE0 level. The global minimum structures of U@B\textsubscript{36} and Th@B\textsubscript{38} are particularly intriguing, having triplet and singlet configurations adopting relatively high symmetry (\textit{Dh}) in comparison with Sr. It is thus reasonable to consider that U\&B\textsubscript{36} and Th\&B\textsubscript{38} are predicted to be 210 and 223 kcal mol\textsuperscript{-1}, respectively, which are much more negative than those reported for endohedral M@B\textsubscript{36} (M = Ca and Sr)\textsuperscript{8} and M@B\textsubscript{38} (M = Sc, Y, and Ti).\textsuperscript{11} These extremely high energies indicate the exceptional stabilities of U@B\textsubscript{36} and Th@B\textsubscript{38}, and the substantial interactions between the actinides and the borospheranes. Molecular dynamics (MD) simulations were carried out to evaluate the dynamic stabilities of C\textsubscript{2h} U@B\textsubscript{36} and D\textsubscript{2h} Th@B\textsubscript{38}. As shown in Fig. S9 and S10 (ESI\textsuperscript{1}), U@B\textsubscript{36} and Th@B\textsubscript{38} are dynamically stable at 300 and 500 K for the 30 ps duration, with the root-mean-square-deviations (RMSD) of 0.10, 0.25 and 0.10, 0.12 Å (on average), respectively. These results show that U@B\textsubscript{36} and Th@B\textsubscript{38} are highly robust at least up to 500 K.

The exceptional stability of U@B\textsubscript{36} and Th@B\textsubscript{38} further spurs interest in the nature of the metal–boron cage, particularly given the relatively long U–B and Th–B distances. At the PBE0/RECP/6-311+G* level of theory, QTAIM analysis\textsuperscript{20–22} was performed on C\textsubscript{2h} U@B\textsubscript{36} as the representative complex to explore the metal–boron bonding properties (Fig. S11 and Table S1, ESI\textsuperscript{1}). As shown in Fig. S11 (ESI\textsuperscript{1}), the clearly observed twelve U–B BCPs indicate the existence of U–B interactions in U@B\textsubscript{36}. The ring critical points (RCPs) and cage critical points (CCPs) can be also found. In the U–B BCPs, the small electron density ($\rho$) and positive Laplacian of electron density ($\nabla^2 \rho$) values as well as the small electron localization function (ELF)\textsuperscript{23–25} and localized orbital locator (LOL)\textsuperscript{26} values suggest the strongly polar bonds of the U–B bonding. Nonetheless, the $H(r)$ values are all negative even with small absolute quantities, indicating slightly covalent interaction of the U–B bonds. These results are consistent with the MO and AdNDP analyses discussed below.

To further elucidate the electronic properties of the metal–boron bonding, MO analyses of C\textsubscript{2h} U@B\textsubscript{36} and D\textsubscript{2h} Th@B\textsubscript{38} were carried out at the PBE0/RECP/6-311+G* level of theory. The Kohn–Sham frontier MOs are displayed in Fig. 2, and the compositions of the MOs of U@B\textsubscript{36} and Th@B\textsubscript{38} are listed in Tables S2 and S3 (ESI\textsuperscript{1}). As shown in Fig. 2, the MO plots give a
pictorial description of the metal–ligand bonding, suggesting covalent character of the metal–boron cage bonds. Specifically, for each species, there are seven frontier occupied MOs primarily attributed to the interactions of 5f orbitals of the actinides and 2p orbitals of the boron atoms. In contrast, the lowest unoccupied molecular orbitals LUMO and LUMO+1 represent metal–ligand antibonding. For C_{2h} U@B_{36}, SOMO(a_u), SOMO–1(b_u), and MOs ranging from HOMO(b_u) up to HOMO–4(a_u) have mixed U 5f and B 2p orbitals. The MOs immediately below, i.e. HOMO–5(a_u), are essentially due to interactions of B 2p orbitals. Moreover, five MOs with strong participation of U 6d orbitals were also found in U@B_{36} (Fig. S12 and S13, ESI†). The D_{2h} Th@B_{38} complex shows similar MOs to those of C_{2h} U@B_{36} though the Th 6d orbital contributions are relatively larger than most of the 5f orbitals. In addition to these MOs, three and one MOs individually attributed to the interactions of 7s and 7p orbitals of An and B 2p orbitals can be also observed in U@B_{36} and Th@B_{38}. Consequently, for each species, the 16 MOs involve the An 7s, 7p, 6d and 5f orbitals hybridized with the boron cages, and these actinode borospherenes seem to correspond to 32-electron systems, which are similar to the reported actinide centered clusters.13,19,27–32

Based on the calculated nucleus-independent chemical shifts (NICS),33 D_{2h} Th@B_{38} possesses three-dimensional (3D) aromaticity with an NICS value of −330 ppm at the center of the B_{38} cage, while U@B_{36} seems to be antiaromatic (NICS: 5404 ppm). These properties can be further demonstrated by chemical bonding analysis using the adaptive natural density partitioning (AdNDP) method. As depicted in Fig. 3, for the 59 pairs of valence electrons in Th@B_{38} there are 48 delocalized σ bonds: 28 3c–2e σ bonds on the 28 B_{3} triangles, 16 4c–2e σ bonds on the 16 B_{3} triangles along with the central Th atom, and 4 5c–2e σ bonds on the quasi-planar B_{4} quadrangles on the B_{38} cage surface with Th participation. The remaining 22 valence electrons constructed the π framework, involving four 7c–2e π bonds at the top and bottom of the cage, and four 5c–2e π bonds around the waist, as well as three 38c–2e π bonds completely delocalized over the entire B_{38} cage surface. Consequently, all 118 valence electrons in Th@B_{38} take part in either delocalized σ or π covalent bonds, conforming to the general bonding pattern of σ + π double delocalization of the borospherene family. Apart from 4c–2e and partial 5c–2e σ bonds with small participation of the central Th atom, the four 7c–2e and three 38c–2e π bonds also have minor involvement of Th. This bonding picture is in contrast to the alkali-metal-doped borospherenes, such as Ca@B_{40} and Ca@B_{38},3 in which the Ca atoms are not involved in the σ + π double delocalization bonding, based on AdNDP analysis. In the case of U@B_{36} although it has 57 pairs of valence electrons, only 54 delocalized bonds have been observed (Fig. S14, ESI†). Consequently, U@B_{36} appears to be antiaromatic according to the AdNDP analysis, which is consistent with the NICS analysis. Besides, different from Th@B_{38} with three 38c–2e π bonds, there are no 36c–2e π bonds in U@B_{36}. Therefore, the different bonding patterns of U@B_{36} and Th@B_{38} are probably responsible for the distinct aromaticity properties of these complexes.

To aid future experimental characterization of the C_{2h} U@B_{36} and D_{2h} Th@B_{38} endohedral borospherenes, the photoelectron spectroscopy (PES) spectra of the monoanions C_{2h} U@B_{36} and D_{2h} Th@B_{38} were simulated using time-dependent DFT (TD-DFT). As displayed in Fig. 4, the predicted first vertical detachment energies (VDE) and adiabatic detachment energies (ADE) are respectively 2.57 and 2.15 eV for U@B_{36}, and 1.09 and 1.87 eV for Th@B_{38}, which are weak predicted PES bands that arise from the detachment of the electron from the SOMOs/HOMOs. There are relatively sizable energy gaps of 1.36 and 1.05 eV between the first and the second bands for U@B_{36} and Th@B_{38}, respectively, reflecting the high electronic stabilities of the neutral species. The predicted vertical ionization potentials of U@B_{36} and Th@B_{38} are relatively high (6.10 and 5.89 eV), which are comparable to that of Ca@B_{38} (7.35 eV)3 and further indicate high thermodynamic stability of these actinide borospherenes. The C_{2h} U@B_{36} and D_{2h} Th@B_{38} were simulated at the PBE0/RECP/6-311+G* level of theory.

![Fig. 2](image_url) The frontier molecular orbitals of U@B_{36} and Th@B_{38}.

![Fig. 3](image_url) Bonding pattern of the global minimum D_{2h} Th@B_{38} from AdNDP analysis with the occupation numbers (ONs) indicated.

![Fig. 4](image_url) Simulated photoelectron spectrum of (a) C_{2h} U@B_{36} and (b) D_{2h} Th@B_{38} at the PBEO/RECP/6-311+G* level of theory.
dianions seem to be less thermodynamically stable compared to $C_{2h} U@B_{36}^{-2}$ and $D_{2h} Th@B_{38}^{-}$, with calculated ADEs for both of about $-1.0$ eV at the PBE0 level (Fig. S15 and S16, ESI†). The main infrared (IR) absorption spectrum features of the $C_{2h} B_{36}$ and $D_{2h} B_{36}$ cages in $C_{2h} U@B_{36}^{-2}$ and $D_{2h} Th@B_{38}^{-}$ (Fig. S17, ESI†) could also promote and assist future experimental explorations of actinide endohedral borospherenes.

In summary, our calculations validated the viability of actinide borospherenes. The actinide size (atomic radii) appears to be crucial in forming stable actinide endohedral borospherenes. The $B_{40}$ borospherenes can be stabilized by larger actinide metal atoms, such as Ac (atomic radii: 1.88 Å). In contrast to alkaline earth metalloborospherenes, for example, the covalent character in bonding between actinides and the boron cages is an essential factor for the stability of actinoborospherenes. The current results demonstrate the possibility of chemical modification and functionalization of boron fullerenes by doping with actinide metal atoms, thereby enhancing their stabilities and modifying surface reactivity. In view of the diversity of the borospherenes, we will further investigate the stabilization of various borospherenes by doping with Th, U and other actinides.

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Conflicts of interest
There are no conflicts to declare.

Notes and references