Electronic Supplementary Information:

Observation of d-p hybridized aromaticity in lanthanum-doped boron clusters

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Figure S1. The calculated lowest-energy structures and low-lying states of anionic and neutral LaB\textsubscript{2} clusters determined at the B3LYP/SDDTZ level of theory. Bond lengths are given in angstroms (Å) and spin multiplicities are denoted as a superscript. The relative energies \( \Delta E \) to the ground state are shown in eV.

Figure S2. The calculated lowest-energy structures and low-lying states of anionic and neutral LaB\textsubscript{3} clusters determined at the B3LYP/SDDTZ level of theory. Bond lengths are given in angstroms (Å) and spin multiplicities are denoted as a superscript. The relative energies \( \Delta E \) to the ground state are shown in eV.

Figure S3. The calculated lowest-energy structures and low-lying states of anionic and neutral LaB\textsubscript{4} clusters determined at the B3LYP/SDDTZ level of theory. Bond lengths are given in angstroms (Å) and spin multiplicities are denoted as a superscript. The relative energies \( \Delta E \) to the ground state are shown in eV.

Figure S4. Size dependence of the NICS values (in ppm) in neutral and anionic LaB\textsubscript{x} (x = 2-4): (a) NICS values calculated at the ring center in the molecular plane, (b) NICS values calculated at 0.5 Å above the plane, and (c) NICS values calculated at 1.0 Å above the plane, respectively.

Figure S5. Occupied valence molecular orbitals of the LaB\textsubscript{3}\textsuperscript{−}, LaB\textsubscript{4}\textsuperscript{−}, LaB\textsubscript{2}, and LaB\textsubscript{4} clusters. The isosurface value of the MOs is 0.04 au.
Figure S1. The calculated lowest-energy structures and low-lying states of anionic and neutral LaB$_2$ clusters determined at the B3LYP/SDDTZ level of theory. Bond lengths are given in angstroms (Å) and spin multiplicities are denoted as a superscript. The relative energies $\Delta E$ to the ground state are shown in eV.
Figure S2. The calculated lowest-energy structures and low-lying states of anionic and neutral LaB$_3$ clusters determined at the B3LYP/SDDTZ level of theory. Bond lengths are given in angstroms (Å) and spin multiplicities are denoted as a superscript. The relative energies $\Delta E$ to the ground state are shown in eV.
Figure S3. The calculated lowest-energy structures and low-lying states of anionic and neutral LaB$_4$ clusters determined at the B3LYP/SDDTZ level of theory. Bond lengths are given in angstroms (Å) and spin multiplicities are denoted as a superscript. The relative energies $\Delta E$ to the ground state are shown in eV.
Figure S4. Size dependence of the NICS values (in ppm) in neutral and anionic LaB\textsubscript{x} (x = 2-4): (a) NICS values calculated at the ring center in the molecular plane, (b) NICS values calculated at 0.5 Å above the plane, and (c) NICS values calculated at 1.0 Å above the plane, respectively.
Figure S5. Occupied valence molecular orbitals of the LaB$_3^-$, LaB$_4^-$, LaB$_2$, and LaB$_4$ clusters. The isosurface value of the MOs is 0.04 au.