Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Lithium doped tubular structure in LiB_{20} and LiB_{20}^-:

A viable global minimum

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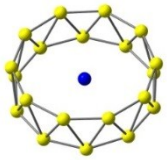
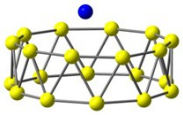


0.0
(0.9)
[0.0]
n01



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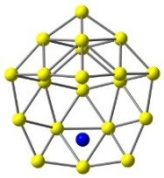

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(14.1)
[19.4]
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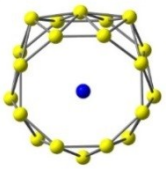

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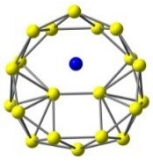
[18.4]
n04



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[14.7]
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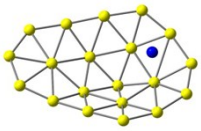

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(17.6)
[17.4]
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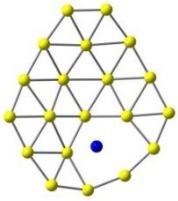
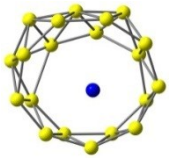


15.7
(17.9)
[17.9]
n07



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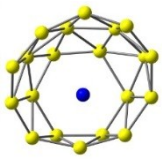

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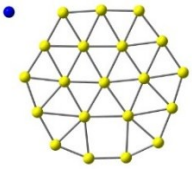

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[18.0]
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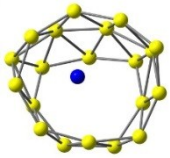

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[23.6]
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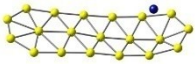

21.5
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[1.7]
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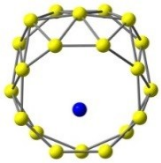

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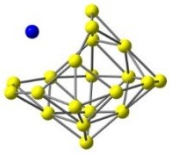

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[24.1]
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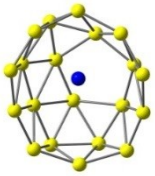

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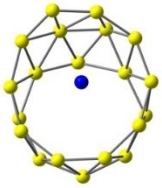

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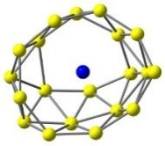

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[27.7]
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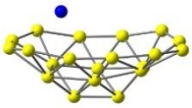

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[26.0]
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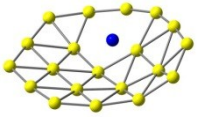

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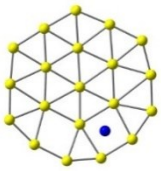
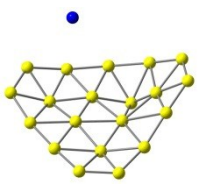


(28.9)
(28.8)
n20



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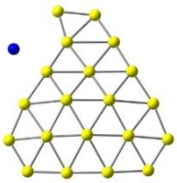

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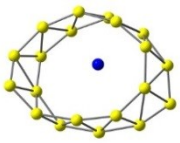

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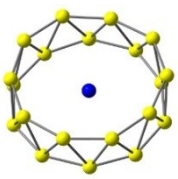
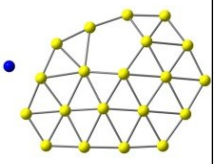
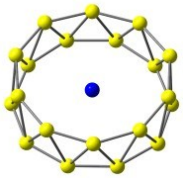


(28.8)
[26.9]
n24 (quartet state)

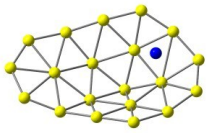


(42.8)
[43.6]
n25 (quartet state)

Figure S1. Structures of the lowest lying isomers of the LiB_{20} system obtained at the TPSSh/6-311+G(d) level. The last two isomers belong to lowest energy ones in the quartet state. Relative energies in kcal/mol were computed at the CCSD(T)/6-311+G(d)//TPSSh/6-311+G(d) level, PBE0/6-311+G(d) (in parenthesis), and TPSSh/6-311+G(d) (in square brackets) levels. All energies are corrected for zero-point energies (ZPE) at their respective levels except for the CCSD(T) single-point calculations, which are ZPE corrected at TPSSh/6-311+G(d).



0.0
(0.0)
[0.0]
a01



4.6
(0.3)
[5.3]
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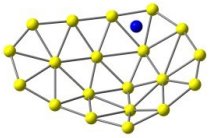
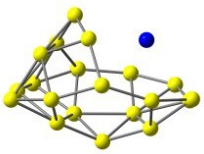
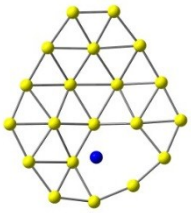


6.6
(2.4)
[7.3]
a03



7.7
(6.3)
[12.4]
a04



9.3
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[9.9]
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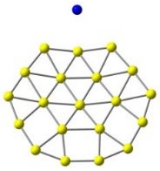

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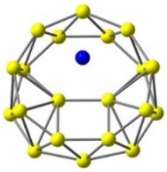

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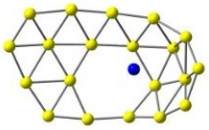

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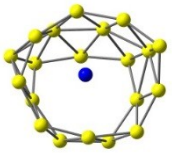

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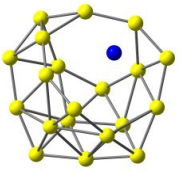

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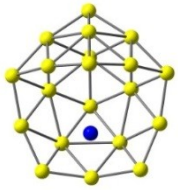

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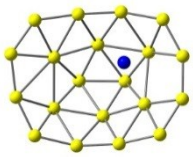
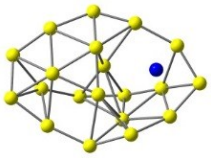


(8.2)
[12.8]
a12

17.1
(8.4)
[11.6]
a13



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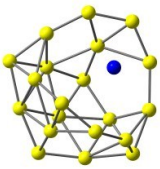

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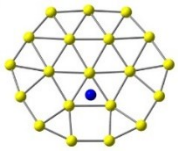

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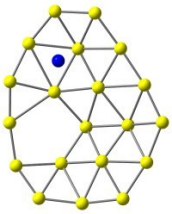

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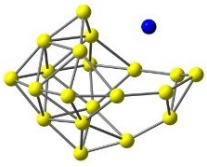

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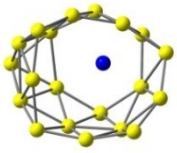

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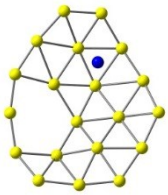

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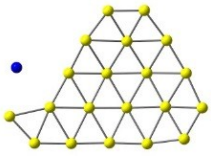

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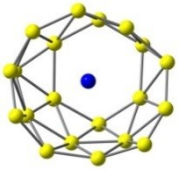

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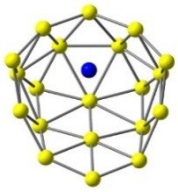
[18.7]



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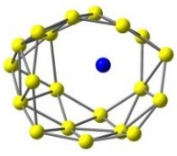
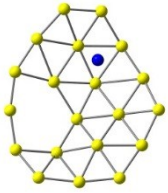
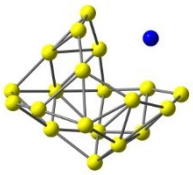
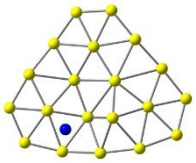
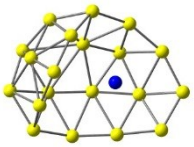
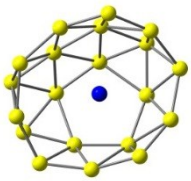
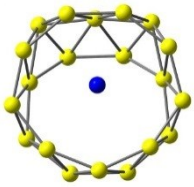
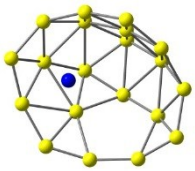
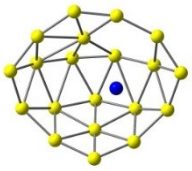
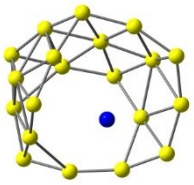
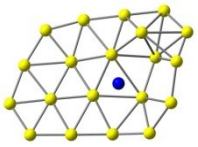
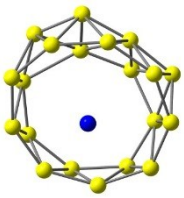
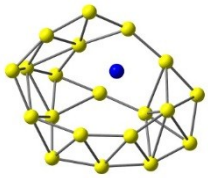
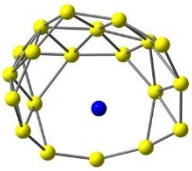
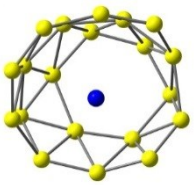
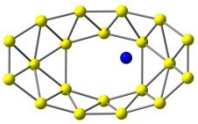
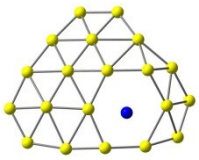
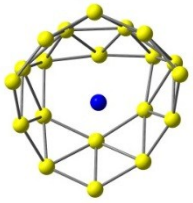
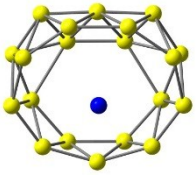
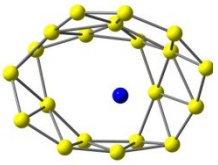
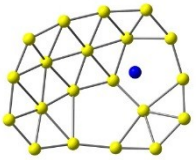
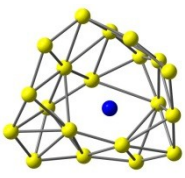
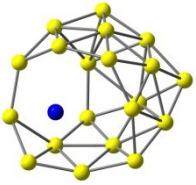
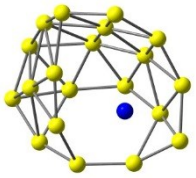
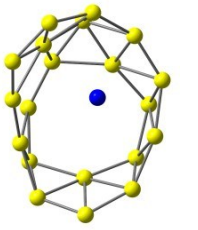
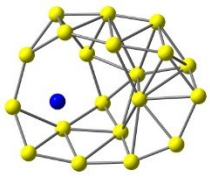
[21.2]

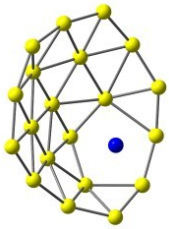


(13.3)
[21.8]

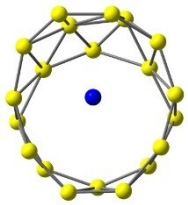


(13.5)
[17.6]

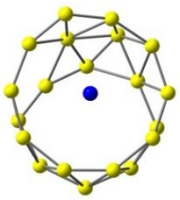
a21	a22	a23	a24	a25
				
(13.6) [20.5]	(13.7) [21.8]	(13.7) [19.5]	(13.8) [20.4]	(14.0) [22.7]
a26	a27	a28	a29	a30
				
(14.0) [21.6]	(14.4) [20.9]	(14.5) [20.9]	(14.6) [20.0]	(14.9) [18.4]
a31	a32	a33	a34	a35
				
(14.9) [22.2]	(14.9) [18.8]	(14.9) [19.1]	(15.1) [23.2]	(15.4) [21.1]
a36	a37	a38	a39	a40
				
(15.8) [21.6]	(15.9) [24.1]	(16.0) [23.3]	(16.9) [22.5]	(17.6) [20.8]
a41	a42	a43	a44	a45
				
(17.7) [23.5]	(18.2) [26.7]	(18.9) [25.5]	(19.0) [24.4]	(19.1) [24.6]
a46	a47	a48	a49	a50



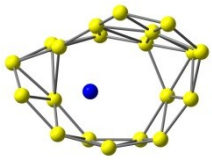
(19.2)
[24.5]
a51



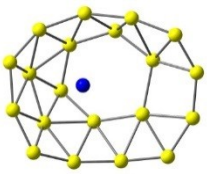
(19.7)
[25.4]
a52



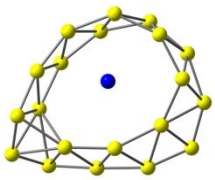
(20.0)
[25.3]
a53



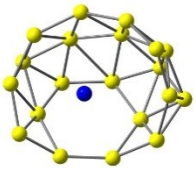
(20.2)
[25.0]
a54



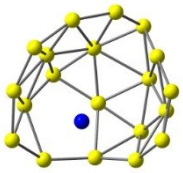
(20.6)
[24.3]
a55



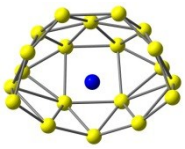
(21.1)
[25.8]
a56



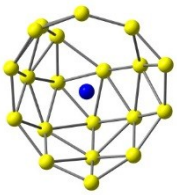
(21.1)
[28.0]
a57



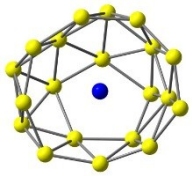
(21.1)
[28.6]
a58



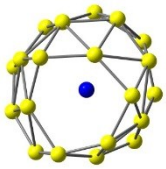
(21.3)
[27.0]
a59



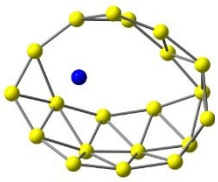
(21.3)
[28.6]
a60



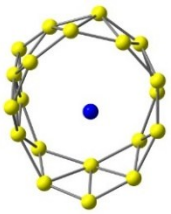
(21.5)
[31.3]
a61



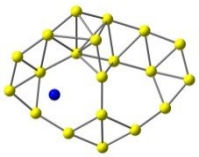
(21.8)
[30.8]
a62



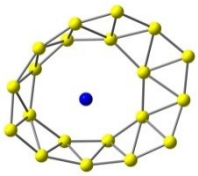
(22.7)
[28.8]
a63



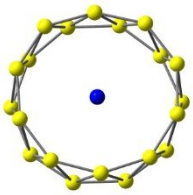
(28.8)
[34.2]
a64



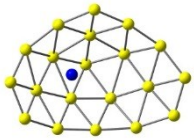
(29.0)
[30.6]
a65



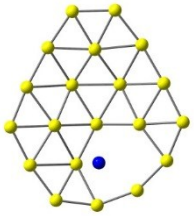
(29.0)
[33.0]
a66



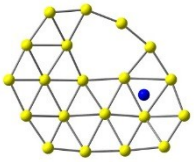
10.7
(0.9)
[5.0]
a67 (triplet)



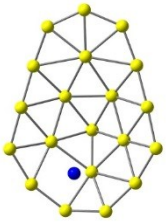
(9.7)
[18.0]
a68 (triplet)



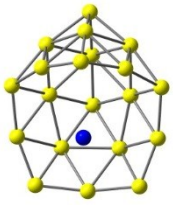
(11.7)
[16.5]
a69 (triplet)



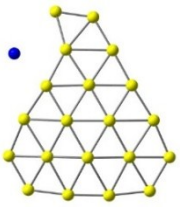
(14.6)
[19.4]
a70 (triplet)



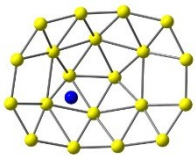
(15.0)
[19.2]



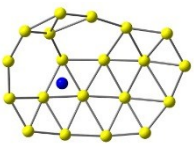
(16.4)
[25.1]



(16.9)
[23.6]



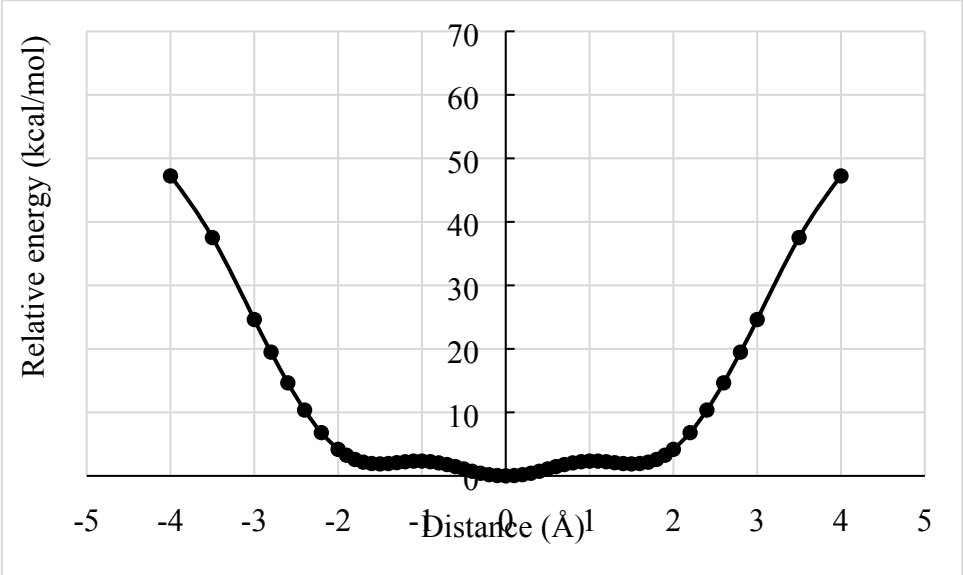
(18.1)
[23.5]



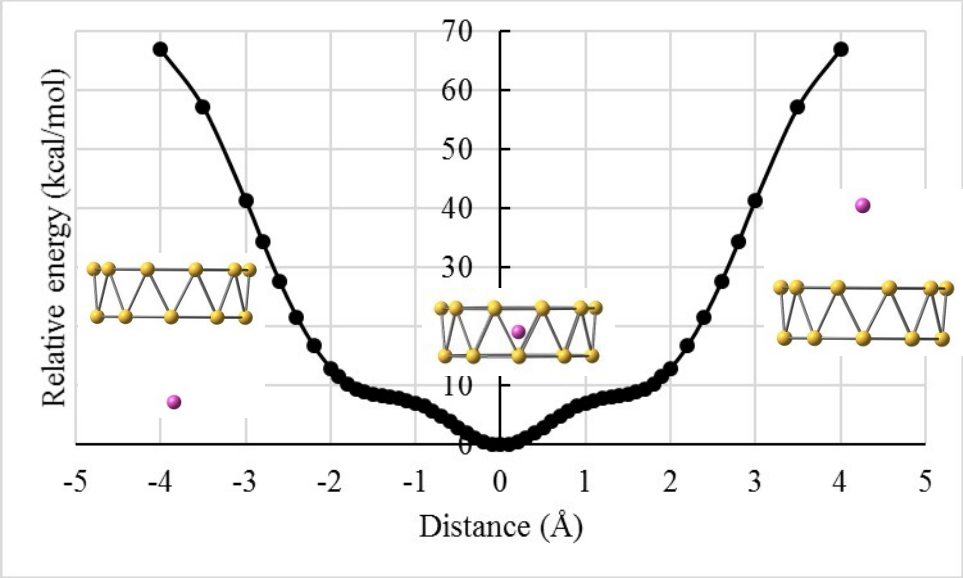
(28.2)
[32.3]

a71 (triplet)	a72 (triplet)	a73 (triplet)	a74 (triplet)	a75 (triplet)

Figure S2. Structures of the lowest lying isomers of the LiB_{20}^- system at the TPSSh/6-311+G(d) level. The last nine isomers belong to lowest energy ones in the triplet state. Relative energies in kcal/mol were computed at the CCSD(T)/6-311+G(d)//TPSSh/6-311+G(d) level, PBE0/6-311+G(d) (in parenthesis), and TPSSh/6-311+G(d) (in square brackets) levels. All energies are corrected for zero-point energies (ZPE) at their respective levels except for the CCSD(T) single-point calculations, which are ZPE corrected at TPSSh/6-311+G(d).

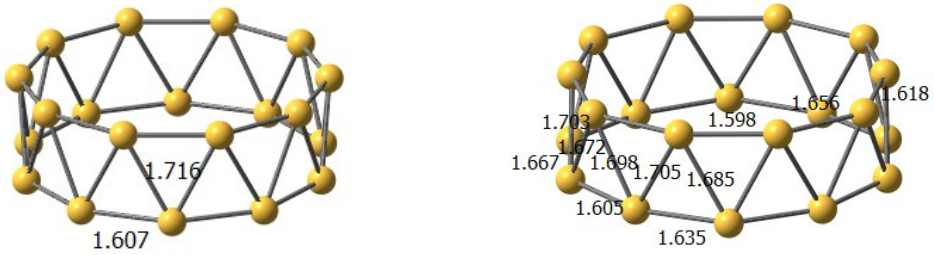


(a)



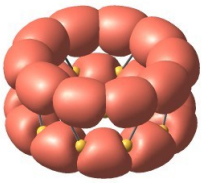
(b)

Figure S3. Potential energy surfaces of LiB_{20} (a) and LiB_{20}^- (b) species for the out-of-center of Li atom along the axis of tubular structure computed at the TPSSh/6-311+G(d) level.

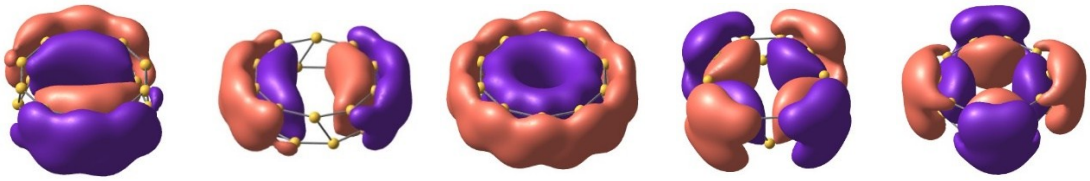


B_{20} B_{20}^{2-}

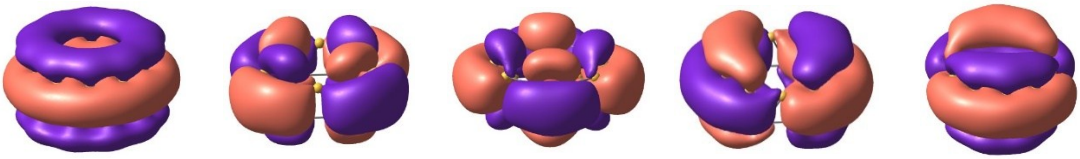
Figure S4. Structural properties of B_{20} and B_{20}^{2-} clusters.



Twenty 2c-2e σ bonds ON=1.80 |e|



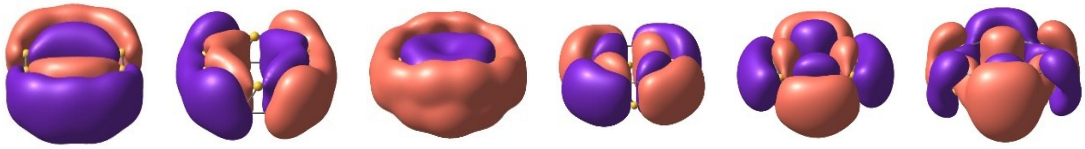
Five 21c-2e σ+σ bonds ON=2.00 |e|



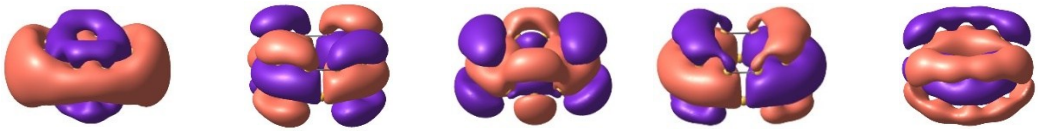
Five 21c-2e π+π bonds ON=2.00 |e|

Figure S5. AdNDP analysis for B_{20} computed at the PBE0/6-31G(d) level, and ON stands for occupation number.

Twenty 2c-2e σ bonds ON=1.78~1.80 |e|



Six 21c-2e σ+σ bonds ON=2.00 |e|



Five 21c-2e π+π bonds ON=2.00 |e|

Figure S6. AdNDP analysis for B_{20}^{2-} computed at the PBE0/6-31G(d) level, and ON stands for occupation number.

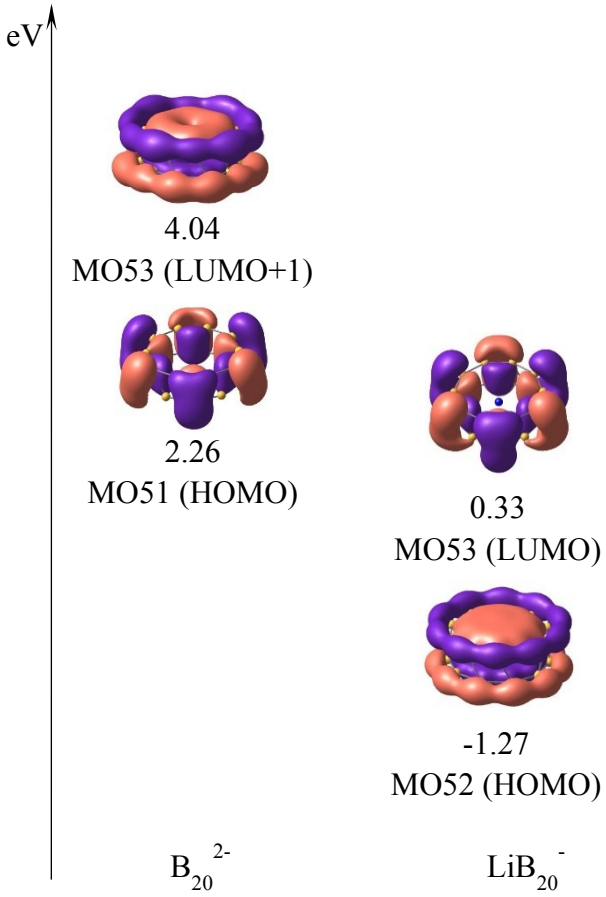


Figure S7. The orbital energy in eV of the delocalized σ-σ molecular orbitals in the tubular B_{20}^{2-} and LiB_{20}^{-} clusters.

Table S1. Smallest frequencies (V_{min}, cm^{-1}), NPA charge on Li and B (Q_{Li} and Q_B, |e|), Bond properties (Wiberg bond indices in parenthesis and bond length (Å)), HOMO–LUMO gap (gap, eV). All values have been computed at the B3LYP/6-311+G(d) level based on TPSSh/6-311+G(d) geometries.

System	V_{min}	B_{Li-B}	B_{B-B}	Q_{Li}	Q_B	Gap
LiB_{20}	76.7	2.702 (0.01)	1.600 (1.02) 1.744 (0.60)	0.85	-0.04	1.3
LiB_{20}^-	126.7	2.695 (0.02)	1.593 (1.09) 1.770 (0.55)	0.84	-0.09	1.4

Table S2. The calculated vertical detachment energies (VDE) from the lowest isomer of LiB_{20}^-. All energies are in eV.

Feature	Final state and electronic configuration	VDE TD-TPSSh
X	$^2B_2$; $2E_6^4\,5A_1^2\,4E_1^4\,3E_2^4\,4E_2^4\,3B_2^1$	2.56
A	$^2E_2$; $2E_6^4\,5A_1^2\,4E_1^4\,3E_2^4\,4E_2^3\,3B_2^1$	3.71
B	$^2E_2$; $2E_6^4\,5A_1^2\,4E_1^4\,3E_2^3\,4E_2^4\,3B_2^1$	4.62
C	$^2E_1$; $2E_6^4\,5A_1^2\,4E_1^3\,3E_2^4\,4E_2^4\,3B_2^1$	5.80

The first VDE was calculated as the difference in energy between the anionic ground state and the neutral ground state at the anion geometry at the TPSSh/6-311+G(2df)//TPSSh/6-311+G* level. Higher VDEs were computed using TD-TPSSh level on the neutral species and then adding the first VDE.

Table S3. The calculated vertical detachment energies (VDE) from the second lowest isomer of LiB_{20}^-. All energies are in eV.

Feature	Final state and electronic configuration	VDE TD-TPSSh
X	^{2}A', 14A'^{2}10A"^{2}15A'^{2}16A'^{2}11A"^{2}12A"^{2}17A'^{2}18A'^{2}19A'^{1}	3.22
A	^{2}A', 14A'^{2}10A"^{2}15A'^{2}16A'^{2}11A"^{2}12A"^{2}17A'^{2}18A'^{1}19A'^{2}	4.05
B	^{2}A', 14A'^{2}10A"^{2}15A'^{2}16A'^{2}11A"^{2}12A"^{2}17A'^{1}18A'^{2}19A'^{2}	4.38
C	^{2}A", 14A'^{2}10A"^{2}15A'^{2}16A'^{2}11A"^{2}12A"^{1}17A'^{2}18A'^{2}19A'^{2}	4.51
D	^{2}A", 14A'^{2}10A"^{2}15A'^{2}16A'^{2}11A"^{1}12A"^{2}17A'^{2}18A'^{2}19A'^{2}	5.03
E	^{2}A', 14A'^{2}10A"^{2}15A'^{2}16A'^{1}11A"^{2}12A"^{2}17A'^{2}18A'^{2}19A'^{2}	5.14
F	^{2}A', 14A'^{2}10A"^{2}15A'^{1}16A'^{2}11A"^{2}12A"^{2}17A'^{2}18A'^{2}19A'^{2}	5.80
G	^{2}A", 14A'^{2}10A"^{1}15A'^{2}16A'^{2}11A"^{2}12A"^{2}17A'^{2}18A'^{2}19A'^{2}	6.20

The first VDE was calculated as the difference in energy between the anionic ground state and the neutral ground state at the anion geometry at the TPSSh/6-311+G(2df)//TPSSh/6-311+G* level. Higher VDEs were computed using TD-TPSSh level on the neutral species and then adding the first VDE.

Table S4. Coordinates

LiB_{20}

B	-0.405099000	2.557494000	0.772047000
B	1.175525000	2.307168000	0.772047000
B	2.557504000	-0.405037000	0.772047000
B	1.830990000	-1.830945000	0.772047000
B	0.405099000	-2.557494000	0.772047000
B	-1.175525000	-2.307168000	0.772047000
B	-2.307139000	-1.175581000	0.772047000
B	-2.557504000	0.405037000	0.772047000
B	-1.830990000	1.830945000	0.772047000
Li	0.000000000	0.000000000	0.000000000
B	-1.175525000	2.307168000	-0.772047000
B	0.405099000	2.557494000	-0.772047000
B	2.557504000	0.405037000	-0.772047000
B	2.307139000	-1.175581000	-0.772047000
B	1.175525000	-2.307168000	-0.772047000
B	-0.405099000	-2.557494000	-0.772047000
B	-1.830990000	-1.830945000	-0.772047000
B	-2.557504000	-0.405037000	-0.772047000
B	-2.307139000	1.175581000	-0.772047000
B	1.830990000	1.830945000	-0.772047000
B	2.307139000	1.175581000	0.772047000

LiB_{20}^-

Li	0.000000000	0.000000000	0.000000000
B	2.577399000	0.000000000	-0.787592000
B	2.085159000	-1.514957000	-0.787592000
B	0.796460000	-2.451252000	-0.787592000
B	-0.796460000	-2.451252000	-0.787592000
B	-2.085159000	-1.514957000	-0.787592000
B	-2.577399000	0.000000000	-0.787592000
B	-2.085159000	1.514957000	-0.787592000
B	-0.796460000	2.451252000	-0.787592000
B	0.796460000	2.451252000	-0.787592000
B	2.085159000	1.514957000	-0.787592000
B	2.451252000	0.796460000	0.787592000
B	1.514957000	2.085159000	0.787592000
B	0.000000000	2.577399000	0.787592000
B	-1.514957000	2.085159000	0.787592000
B	-2.451252000	0.796460000	0.787592000
B	-2.451252000	-0.796460000	0.787592000
B	-1.514957000	-2.085159000	0.787592000
B	0.000000000	-2.577399000	0.787592000

B	1.514957000	-2.085159000	0.787592000
B	2.451252000	-0.796460000	0.787592000