Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information:

A Disk-Aromatic Bowl Cluster B_{30}: Towards Formation of Boron Buckyballs

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The file contains :

- Computational methods;
- Computed results of NICS calculations;
- Shapes of selected molecular orbitals and Cartesian coordinates of isomers **I**, **II** and **III**, and
- Shapes and relative energies of the low-lying isomers of B_{30} that are obtained at the TPSSh/6-311+G(d) level.

Computational Methods. All electronic structure calculations are carried out by using Gaussian09 package .[1] The initial search for all possible lower-lying isomers of B_{30} cluster is performed using a stochastic search algorithm that was implemented by us.[2] Firstly, the possible structures of the B_{30} are generated by a random kick method, and then rapidly optimized at the PBE/3-21G level.[3] In this search procedure, the minimum and maximum distances between atoms are limited to 1.5 and 20 Å, respectively. Geometries of the local minima with relative energies of 0.0 ÷ 5.0 eV and their harmonic vibrational frequencies are further refined using the PW91,[4] PBE,[5] and PBE0,[6] TPSSh[7] functionals, in conjugation with higher 6-311+G(d) basis set.[8] The geometry optimization and calculation of vibrational frequencies of bowl-shaped B_{45} cluster are carried out at PBE/6-311+G(d) level of theory.

Aromaticity of the B_{30} cluster is evaluated by using several methods, including nuclear independent chemical shift (NICS) calculations, and the analysis of canonical MOs and ipsocentric model. [9] HOMO-LUMO gaps of isomers are obtained at the PBE/6-311+G(d) level of theory.

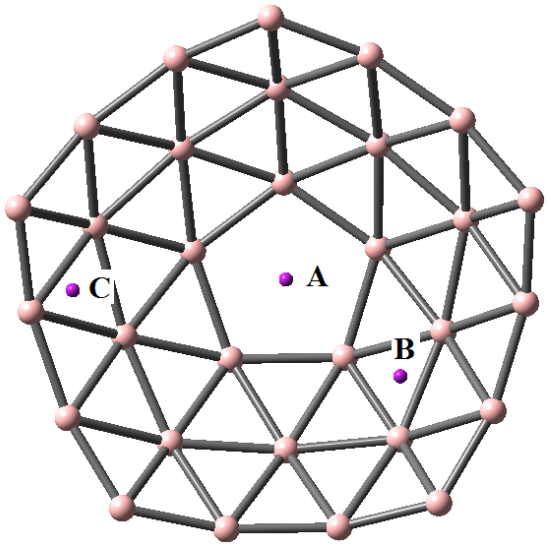
The cohesive energies of the B_{30} and B_{45} clusters are calculated by using expression (1)

$$E_c = (nE_B - E_{Bn})/n \qquad (1)$$

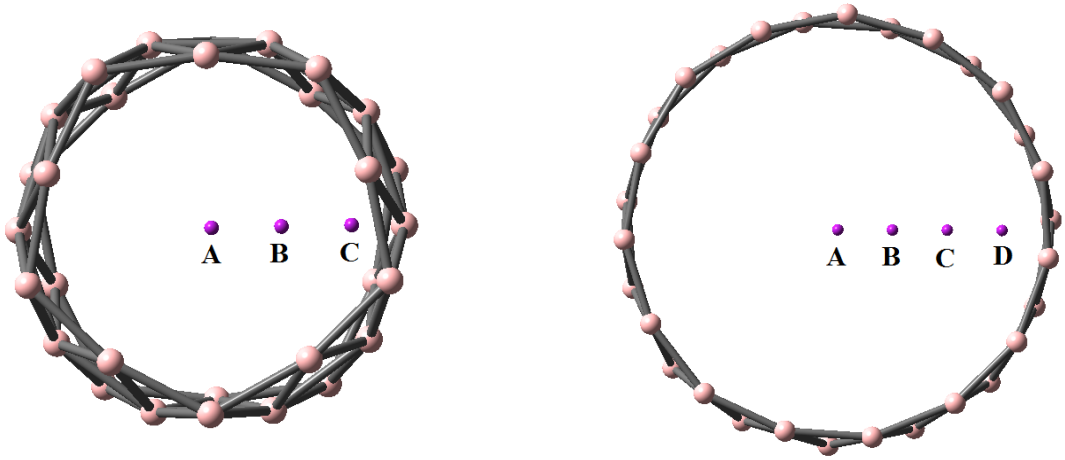
Where E_c is cohesive energy (eV), E_B and E_{Bn} are total energies of B-atom and B_n clusters, respectively. n stands for number of atoms (n = 30 for B_{30} cluster and n = 45 for B_{45} cluster). All energy values are obtained at the PBE/6-311+G(d) level of theory.

Nuclear independent chemical shift (NICS) calculations

Nuclear independent chemical shift ($NICS_{zz}$) arising from the zz component of the shielding tensors [19,20] of isomers **I**, **II** and **III** are calculated at several different positions (**A**, **B**, **C** and **D**) and also at points 1.0 Å and 2 Å above these points (Figure S1).



Isomer **I**



Isomer **II** Isomer **III**

Fig. S1 Shapes of isomers **I**, **II** and **III** with positions (violet points) where the ghost atoms are placed for the $NICS_{zz}$ calculations.

Table S1 The $NICS_{zz}$ values of the B_{30} isomers obtained at B3LYP/6-311+G(d) level of theory

Isomer	position	$NICS_{zz}(0)$	$NICS_{zz}(1)$	$NICS_{zz}(2)$
I	A	+19.0	-57.8	-67.2
	B	-57.9	-79.0	-
	C	-46.1	-72.1	-
II	A	-4.5	-4.1	-8.7
	B	-5.8	-3.8	-11.2
	C	27.6	-29.8	-31.1
III	A	+386.9	+347.7	+262.5
	B	+409.7	+359.6	+259.8
	C	+491.8	+392.1	+240.4
	D	+430.6	+301.8	+172.2

The ipsocentric model: The ipsocentric model is other effective model which was used to evaluate aromaticity of both planar- and tubular-shaped compounds. In framework of this model,

a virtual excitation from an occupied to an unoccupied molecular orbital can result in a contribution to the ring current that is diatropic, paratropic and null. Accordingly, the diatropic current arises if the product of symmetries of occupied and unoccupied orbitals contains the in-plane translational symmetry. Oppositely, the paratropic current arises when the product of symmetries of occupied and unoccupied orbitals contains the in-plane rotational symmetry. This rule is relatively simple for bowled- and tubular-formed structures as our species. If the difference in rotational quantum numbers between the beginning occupied and the final unoccupied orbital is equal to one ($\Delta\Lambda = 1$), it is then diatropic. Otherwise, it is paratropic if this difference is zero ($\Delta\Lambda = 0$).

Shapes of valence and virtual π-MOs of the bowled structure **I** in Figure S2 show that HOMOs of **I** has three vertical nodes ($\Lambda = 3$) and its LUMO+1 pair has four vertical nodes ($\Lambda = 4$). Consequently, virtual excitation from HOMOs to LUMO+1 pair of **I** will results in a diatropic ring current with $\Delta\Lambda = 1$ which makes it aromatic. Similar virtual excitation with increase of rotational quantum number ($\Delta\Lambda = 1$) can be also observed from its HOMO-1 to LUMO+2. This can explain for why the bowled structure **I** is highly aromatic. Similarly, the isomer **II** is aromatic system because virtual excitation from its HOMO to LUMO+3 (and from HOMO-2 to LUMO+1) results in $\Delta\Lambda = 1$. Oppositely, while excitation of tangential stack of isomer **III** results in difference of rotational quantum number ($\Delta\Lambda = 1$), that of its radical stack has $\Delta\Lambda = 0$ (Figure S2). Consequently, the isomer **III** exhibits antiaromatic feature in radical stack similar to those of tubular species B_{2n} with n = 9, 11, 13...

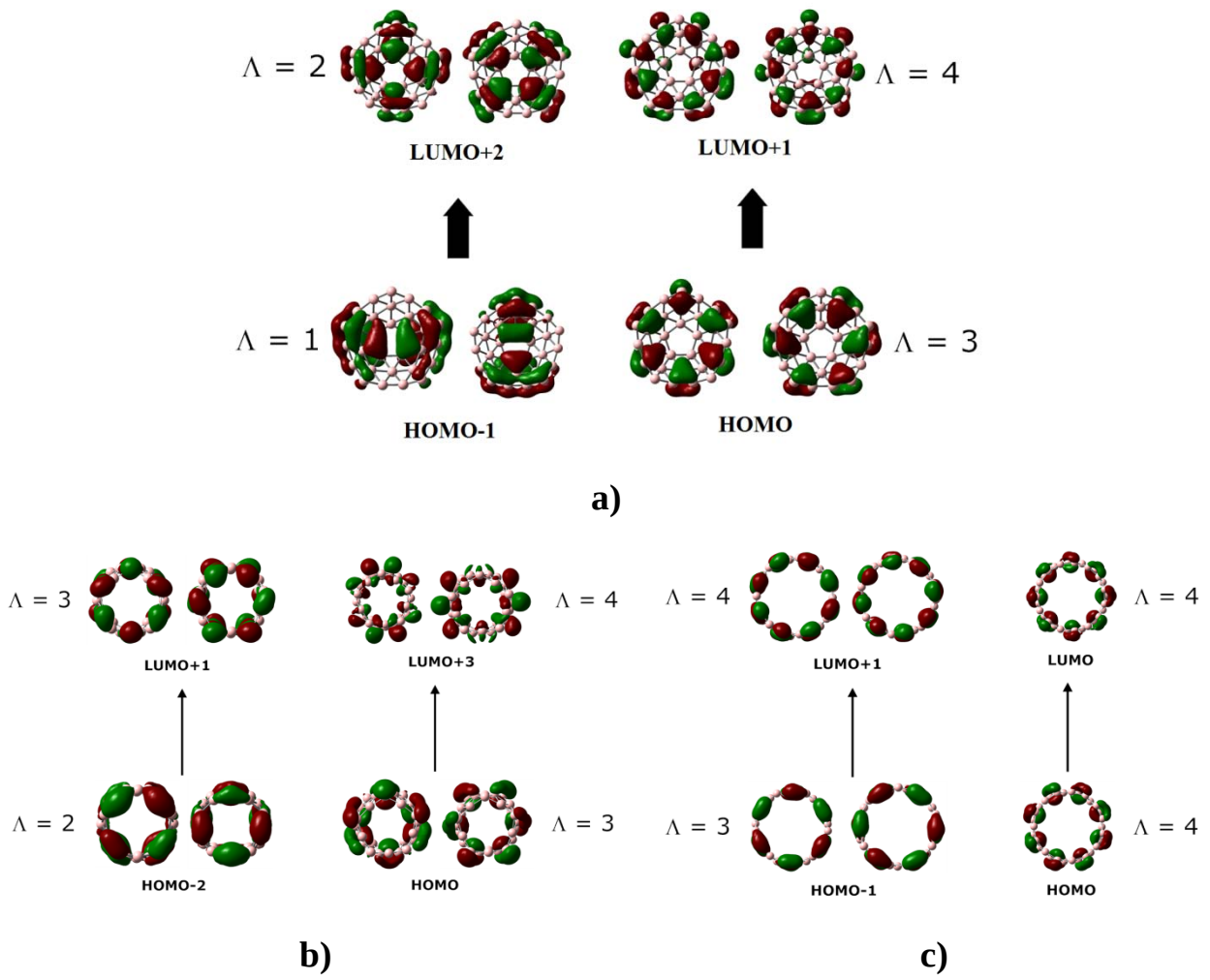


Figure S2. Virtual excitation from the highest occupied molecular orbitals to the lowest unoccupied molecular orbitals of isomer a) **I**, b) **II** and c) **III**

Table S2. The relative energies (kcal/mol) of the lowest-lying isomers **I**, **II** and **III** obtained at several functionals in conjugation with the 6-311+G(d) level of theory

Functional	**Isomer I**	**Isomer II**	**Isomer III**
PW91	0.0	9.4	20.8
PBE	0.0	9.2	26.2
PBE0	0.0	8.1	23.6
TPSSh	0.0	10.4	13.1
CCSD(T)*	0.0	13.3	18.7

*These values are obtained at the CCSD(T)/6-311G(d)//PBE/6-311+G(d) level of theory.

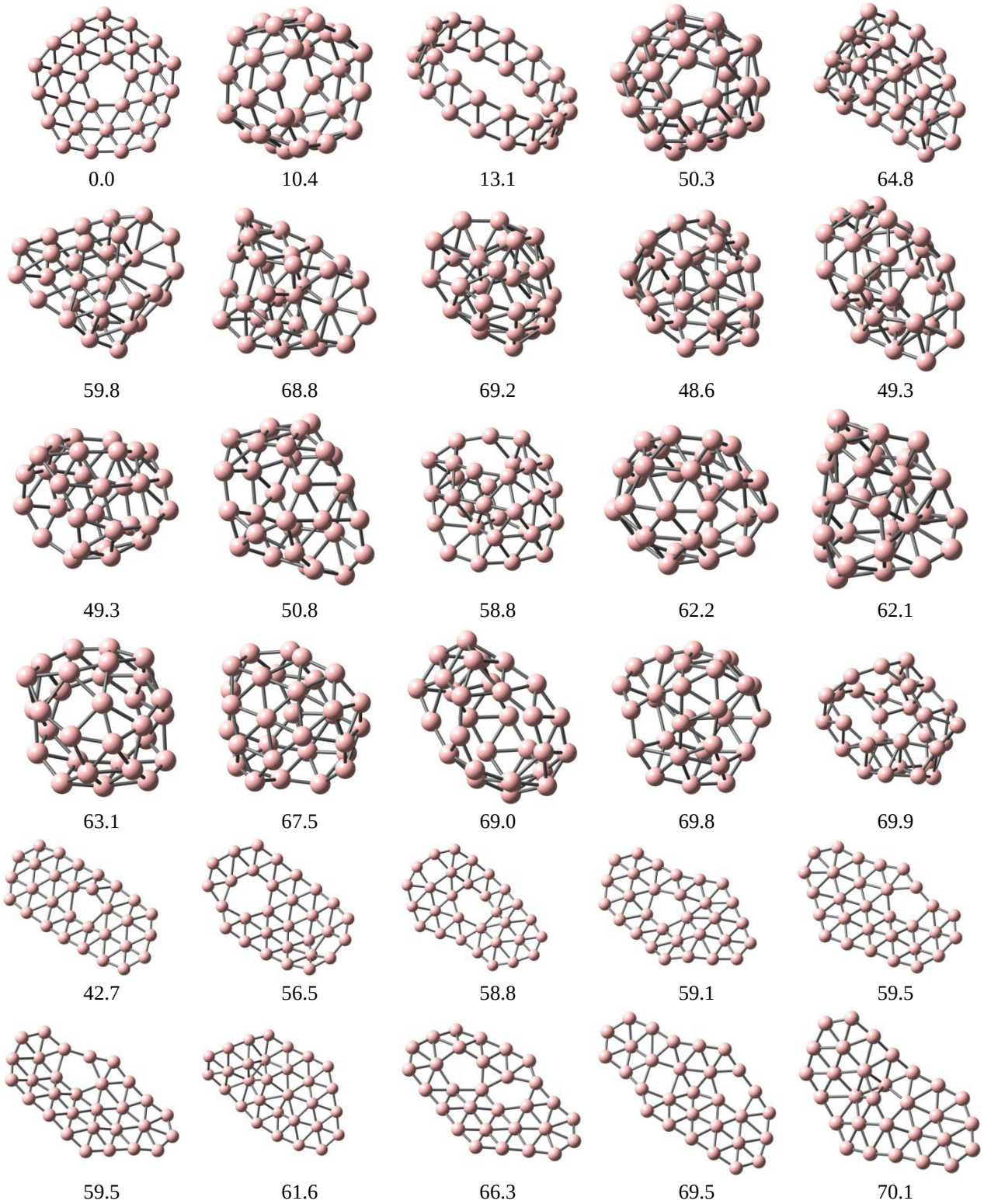


Figure S3. Shapes and relative energies (kcal/mol) of some low-lying isomers B_{30} obtained at TPSSh/6-311+G(d) level of theory.

Table S3. Coordinates of the lowest-lying isomers **I**, **II** and **III** obtained at the PBE/6-311+G(d) level of theory.

Isomer I			
5	-1.355237000	0.440343000	1.231782000
5	-0.837583000	-1.152834000	1.231782000
5	0.837583000	-1.152834000	1.231782000
5	0.000000000	1.424981000	1.231782000
5	1.355237000	0.440343000	1.231782000
5	0.000000000	2.857614000	0.313759000
5	2.717753000	0.883051000	0.313759000
5	1.679664000	-2.311859000	0.313759000
5	-1.679664000	-2.311859000	0.313759000
5	-2.717753000	0.883051000	0.313759000
5	1.444741000	1.988516000	0.545596000
5	2.337640000	-0.759545000	0.545596000
5	0.000000000	-2.457941000	0.545596000
5	-2.337640000	-0.759545000	0.545596000
5	-1.444741000	1.988516000	0.545596000
5	0.000000000	3.945065000	-0.948550000
5	3.751980000	1.219092000	-0.948550000
5	2.318851000	-3.191625000	-0.948550000
5	-3.751980000	1.219092000	-0.948550000
5	-2.318851000	-3.191625000	-0.948550000
5	-1.414867000	3.349896000	-0.571293000
5	2.748723000	2.380793000	-0.571293000
5	-2.748723000	2.380793000	-0.571293000
5	1.414867000	3.349896000	-0.571293000
5	3.623158000	-0.310443000	-0.571293000
5	3.113671000	-1.878485000	-0.571293000
5	0.824368000	-3.541761000	-0.571293000
5	-0.824368000	-3.541761000	-0.571293000
5	-3.113671000	-1.878485000	-0.571293000
5	-3.623158000	-0.310443000	-0.571293000
Isomer II			
5	1.431109000	1.938094000	-1.510275000
5	0.019306000	2.713149000	-1.471641000
5	2.591062000	0.820571000	-1.470966000
5	-1.403380000	1.958270000	-1.510226000
5	-2.579139000	0.857415000	-1.470896000
5	-2.300874000	-0.729271000	-1.509958000
5	-1.612387000	-2.185790000	-1.470502000
5	-0.017208000	-2.409331000	-1.509161000
5	1.580969000	-2.208482000	-1.470559000
5	2.290114000	-0.761953000	-1.509958000
5	2.300897000	0.729283000	1.509953000
5	1.612414000	2.185795000	1.470495000
5	2.579150000	-0.857399000	1.470883000

5	0.017238000	2.409307000	1.509174000
5	-1.580945000	2.208453000	1.470571000
5	-2.290125000	0.761920000	1.509942000
5	-2.591125000	-0.820592000	1.470947000
5	-1.431142000	-1.938077000	1.510274000
5	-0.019326000	-2.713102000	1.471657000
5	1.403391000	-1.958259000	1.510253000
5	2.243007000	1.604389000	-0.000291000
5	0.870229000	2.612876000	-0.000657000
5	2.757298000	-0.019652000	-0.000052000
5	-0.832848000	2.624901000	-0.000608000
5	-2.219925000	1.636164000	-0.000227000
5	-2.757326000	0.019643000	0.000031000
5	-2.243029000	-1.604390000	0.000266000
5	-0.870208000	-2.612836000	0.000659000
5	0.832858000	-2.624903000	0.000634000
5	2.219946000	-1.636193000	0.000241000

Isomer III

5	2.152088000	-3.220240000	0.752282000
5	0.643033000	-3.844065000	0.742530000
5	-0.951348000	-3.739658000	0.757363000
5	-2.427686000	-3.055966000	0.739948000
5	-3.408069000	-1.787326000	0.761012000
5	3.278354000	-2.090993000	0.746607000
5	3.847483000	-0.558005000	0.746930000
5	3.734242000	1.032738000	0.751905000
5	2.997864000	2.490517000	0.742738000
5	1.723232000	3.453470000	0.757099000
5	0.158041000	3.899257000	0.740100000
5	-1.412656000	3.579888000	0.760788000
5	-2.791203000	2.730124000	0.738865000
5	-3.603525000	1.339779000	0.762349000
5	-3.896998000	-0.244129000	0.738846000
5	1.412656000	-3.579888000	-0.760788000
5	-0.158041000	-3.899257000	-0.740100000
5	-1.723232000	-3.453470000	-0.757099000
5	-2.997864000	-2.490517000	-0.742738000
5	-3.734242000	-1.032738000	-0.751905000
5	2.791203000	-2.730124000	-0.738865000
5	3.603525000	-1.339779000	-0.762349000
5	3.896998000	0.244129000	-0.738846000
5	3.408069000	1.787326000	-0.761012000
5	2.427686000	3.055966000	-0.739948000
5	0.951348000	3.739658000	-0.757363000
5	-0.643033000	3.844065000	-0.742530000
5	-2.152088000	3.220240000	-0.752282000
5	-3.278354000	2.090993000	-0.746607000
5	-3.847483000	0.558005000	-0.746930000

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