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SUPPLEMENTARY INFORMATION

Competition between quasi-planar and cage-like structures in the B_{29}^- cluster: photoelectron spectroscopy and *ab initio* calculations†

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Table S1. Comparisons of the experimental vertical detachment energies (VDEs, in eV) of B_{29}^- with the calculated VDEs at the time-dependent PBE0/6-311+G* (TD-PBE0) and ROVGF/6-311+G* levels for isomers **1**–**5**.

Table S2. Cartesian coordinates of isomers **1**–**3** of B_{29}^- at PBE0/6-311+G* level.

Figure S1. Optimized structures for B_{29}^- anion cluster within ~1 eV of the global minimum at PBE0/6-311+G* level. Relative energies are shown in eV, along with those for top five lowest-lying isomers at single-point CCSD(T)/6-311+G*//PBE0/6-311+G* level (in parenthesis). Zero-point energy corrections are done at PBE0/6-311+G*.

Figure S2. Comparison of the experimental photoelectron spectrum of B_{29}^- at 193 nm (6.424 eV) with those simulated for isomers **4** and **5**. The simulations were done by fitting the calculated vertical detachment energies (VDEs) at the time-dependent PBE0/6-311+G* (TD-PBE0) level with unit-area Gaussian functions of 0.05 eV half-width.

Figure S3. Comparisons of the simulated photoelectron spectra for top three lowest-lying isomers (**1**, **2**, and **3**) of B_{29}^- anion cluster at (a) time-dependent PBE0/6-311+G* (TD-PBE0) and (b) OVGF/6-311+G* levels. The two levels of theory are qualitatively consistent with each other, confirming the fact that these three isomers are coexisting in experiment. The overall performance of TD-PBE0 appears to be better than OVGF for the current system.

Figure S4. An alternative version of the adaptive natural density partitioning (AdNDP) schemes at PBE0/6-31G level for (a) C_s B_{29}^- and (b) C_{2v} $C_{18}H_{10}$. This version features the Clar type π bonds, as compared to the Kekule type in Fig. 5. Kekule type π scheme is closer to the truth of bonding for the systems.

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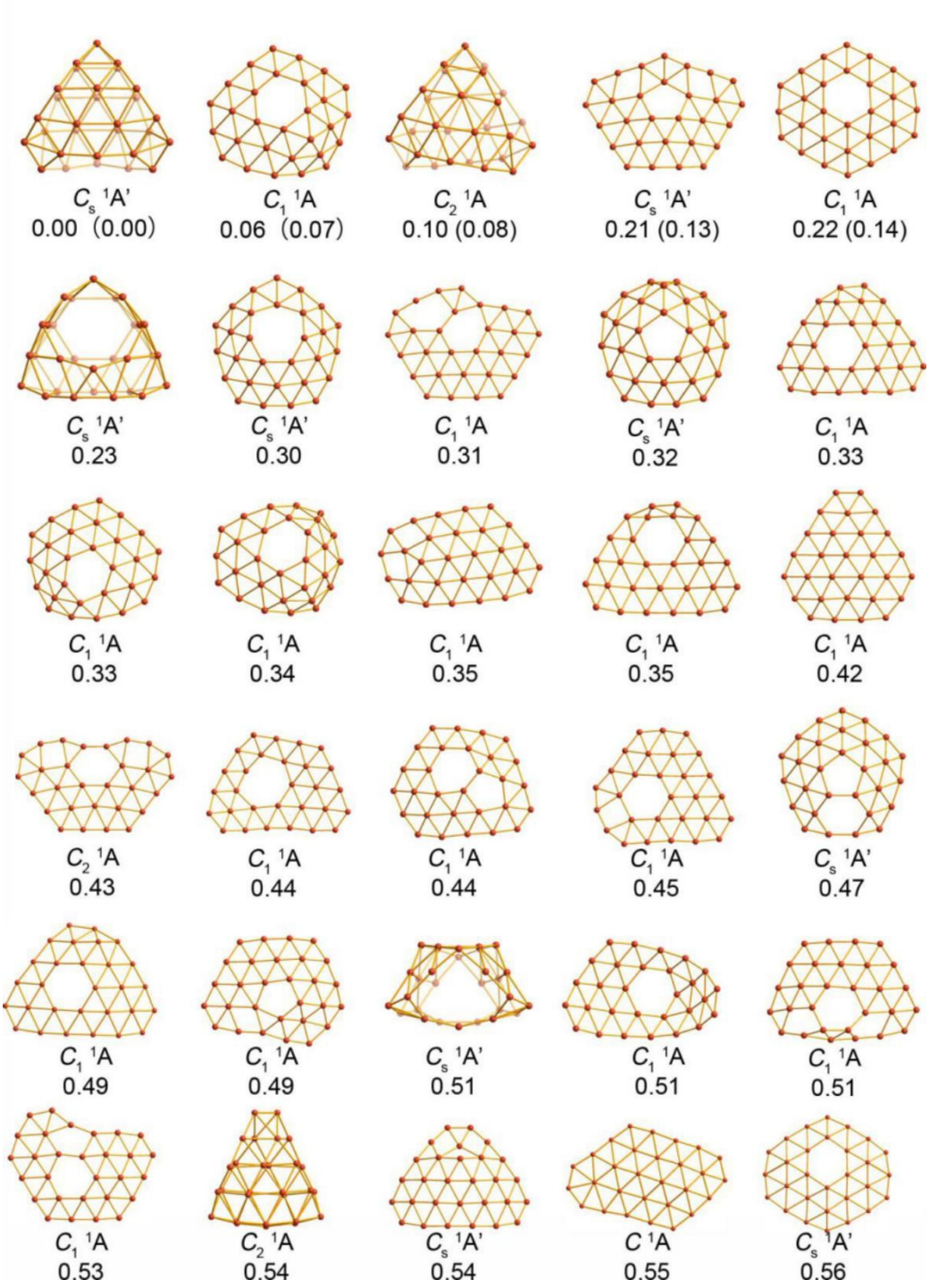
Feature	VDE (exptl.)	Final state and electronic configuration	VDE(theo.)	
			TD-PBE0[a]	ROVGF[b]
		Isomer **1** (C_s, ^{1}A')		
X	4.37 ± 0.03	^{2}A"{···20a'^{2} 17a"^{2} 21a'^{2} 22a'^{2} 18a"^{2} 23a'^{2} 19a"^{2} 24a'^{2} 20a"^{1}}	4.17	4.14
A	4.84	^{2}A'{···20a'^{2} 17a"^{2} 21a'^{2} 22a'^{2} 18a"^{2} 23a'^{2} 19a"^{2} 24a'^{1} 20a"^{2}}	4.74	4.83
B	4.97	^{2}A"{···20a'^{2} 17a"^{2} 21a'^{2} 22a'^{2} 18a"^{2} 23a'^{2} 19a"^{1} 24a'^{2} 20a"^{2}}	4.83	4.57
		^{2}A'{···20a'^{2} 17a"^{2} 21a'^{2} 22a'^{2} 18a"^{2} 23a'^{1} 19a"^{2} 24a'^{2} 20a"^{2}}	4.88	4.65
C	5.44	^{2}A"{···20a'^{2} 17a"^{2} 21a'^{2} 22a'^{2} 18a"^{1} 23a'^{2} 19a"^{2} 24a'^{2} 20a"^{2}}	5.58	5.46
D	5.70	^{2}A'{···20a'^{2} 17a"^{2} 21a'^{2} 22a'^{1} 18a"^{2} 23a'^{2} 19a"^{2} 24a'^{2} 20a"^{2}}	5.69	5.69
		^{2}A'{···20a'^{2} 17a"^{2} 21a'^{1} 22a'^{2} 18a"^{2} 23a'^{2} 19a"^{2} 24a'^{2} 20a"^{2}}	5.87	5.86
E	6.04	^{2}A"{···20a'^{2} 17a"^{1} 21a'^{2} 22a'^{2} 18a"^{2} 23a'^{2} 19a"^{2} 24a'^{2} 20a"^{2}}	6.17	6.27
		^{2}A'{···20a'^{1} 17a"^{2} 21a'^{2} 22a'^{2} 18a"^{2} 23a'^{2} 19a"^{2} 24a'^{2} 20a"^{2}}	6.19	6.33
		Isomer **2** (C_s, ^{1}A')		
X'	~3.4	^{2}A'{···22a"^{2} 15a'^{2} 23a'^{2} 16a"^{2} 24a'^{2} 17a"^{2} 25a"^{2} 18a'^{2} 26a'^{1}}	3.54	3.36
		^{2}A'{···22a"^{2} 15a'^{2} 23a'^{2} 16a"^{2} 24a'^{2} 17a"^{2} 25a"^{2} 18a'^{1} 26a'^{2}}	4.14	3.90
		^{2}A"{···22a"^{2} 15a'^{2} 23a'^{2} 16a"^{2} 24a'^{2} 17a"^{2} 25a"^{1} 18a'^{2} 26a'^{2}}	4.16	3.85
		^{2}A"{···22a"^{2} 15a'^{2} 23a'^{2} 16a"^{2} 24a'^{2} 17a"^{1} 25a"^{2} 18a'^{2} 26a'^{2}}	4.73	4.48
		^{2}A'{···22a"^{2} 15a'^{2} 23a'^{2} 16a"^{2} 24a'^{1} 17a"^{2} 25a"^{2} 18a'^{2} 26a'^{2}}	4.95	4.87
		^{2}A"{···22a"^{2} 15a'^{2} 23a'^{2} 16a"^{1} 24a'^{2} 17a"^{2} 25a"^{2} 18a'^{2} 26a'^{2}}	5.19	5.00
		^{2}A'{···22a"^{2} 15a'^{2} 23a'^{1} 16a"^{2} 24a'^{2} 17a"^{2} 25a"^{2} 18a'^{2} 26a'^{2}}	5.25	5.08
		^{2}A'{···22a"^{2} 15a'^{1} 23a'^{2} 16a"^{2} 24a'^{2} 17a"^{2} 25a"^{2} 18a'^{2} 26a'^{2}}	5.61	5.64
		^{2}A"{···22a"^{1} 15a'^{2} 23a'^{2} 16a"^{2} 24a'^{2} 17a"^{2} 25a"^{2} 18a'^{2} 26a'^{2}}	5.69	5.58
		Isomer **3** (C_1, ^{1}A)		
X"	~3.9	^{2}A{···37a^2 38a^2 39a^2 40a^2 41a^2 42a^2 43a^2 44a^1}	3.89	3.92
		^{2}A{···37a^2 38a^2 39a^2 40a^2 41a^2 42a^2 43a^1 44a^2}	4.34	4.34
		^{2}A{···37a^2 38a^2 39a^2 40a^2 41a^2 42a^1 43a^2 44a^2}	4.64	4.30

		^{2}A{···37a^{2} 38a^{2} 39a^{2} 40a^{2} 41a^{1} 42a^{2} 43a^{2} 44a^{2}}	4.75	4.53
		^{2}A{···37a^{2} 38a^{2} 39a^{2} 40a^{1} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	4.89	4.76
		^{2}A{···37a^{2} 38a^{2} 39a^{1} 40a^{2} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	5.40	5.40
		^{2}A{···37a^{2} 38a^{1} 39a^{2} 40a^{2} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	6.18	6.09
		^{2}A{···37a^{1} 38a^{2} 39a^{2} 40a^{2} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	6.37	6.58
		Isomer **4** (C_1, ^{1}A)		
		^{2}A{···37a^{2} 38a^{2} 39a^{2} 40a^{2} 41a^{2} 42a^{2} 43a^{2} 44a^{1}}	3.71	3.75
		^{2}A{···37a^{2} 38a^{2} 39a^{2} 40a^{2} 41a^{2} 42a^{2} 43a^{1} 44a^{2}}	4.07	3.98
		^{2}A{···37a^{2} 38a^{2} 39a^{2} 40a^{2} 41a^{2} 42a^{1} 43a^{2} 44a^{2}}	4.74	4.42
		^{2}A{···37a^{2} 38a^{2} 39a^{2} 40a^{2} 41a^{1} 42a^{2} 43a^{2} 44a^{2}}	5.00	4.67
		^{2}A{···37a^{2} 38a^{2} 39a^{2} 40a^{1} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	5.20	5.26
		^{2}A{···37a^{2} 38a^{2} 39a^{1} 40a^{2} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	5.62	5.72
		^{2}A{···37a^{2} 38a^{1} 39a^{2} 40a^{2} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	5.91	6.05
		^{2}A{···37a^{1} 38a^{2} 39a^{2} 40a^{2} 41a^{2} 42a^{2} 43a^{2} 44a^{2}}	6.13	6.60
		Isomer **5** (C_2, ^{1}A)		
		^{2}B{···18b^{2} 18a^{2} 19a^{2} 19b^{2} 20b^{2} 20a^{2} 21b^{2} 21a^{2} 22a^{2} 22b^{1}}	3.46	3.29
		^{2}A{···18b^{2} 18a^{2} 19a^{2} 19b^{2} 20b^{2} 20a^{2} 21b^{2} 21a^{2} 22a^{1} 22b^{2}}	3.88	3.68
		^{2}A{···18b^{2} 18a^{2} 19a^{2} 19b^{2} 20b^{2} 20a^{2} 21b^{2} 21a^{1} 22a^{2} 22b^{2}}	4.35	4.18
		^{2}B{···18b^{2} 18a^{2} 19a^{2} 19b^{2} 20b^{2} 20a^{2} 21b^{1} 21a^{2} 22a^{2} 22b^{2}}	4.44	4.19
		^{2}A{···18b^{2} 18a^{2} 19a^{2} 19b^{2} 20b^{2} 20a^{1} 21b^{2} 21a^{2} 22a^{2} 22b^{2}}	4.84	4.66
		^{2}B{···18b^{2} 18a^{2} 19a^{2} 19b^{2} 20b^{1} 20a^{2} 21b^{2} 21a^{2} 22a^{2} 22b^{2}}	4.98	4.92
		^{2}B{···18b^{2} 18a^{2} 19a^{2} 19b^{1} 20b^{2} 20a^{2} 21b^{2} 21a^{2} 22a^{2} 22b^{2}}	5.24	5.15
		^{2}A{···18b^{2} 18a^{2} 19a^{1} 19b^{2} 20b^{2} 20a^{2} 21b^{2} 21a^{2} 22a^{2} 22b^{2}}	5.41	5.27
		^{2}A{···18b^{2} 18a^{1} 19a^{2} 19b^{2} 20b^{2} 20a^{2} 21b^{2} 21a^{2} 22a^{2} 22b^{2}}	5.60	5.53
		^{2}B{···18b^{1} 18a^{2} 19a^{2} 19b^{2} 20b^{2} 20a^{2} 21b^{2} 21a^{2} 22a^{2} 22b^{2}}	6.34	6.55

[a] VDEs were calculated at the TD-PBE0/6-311+G* level.

[b] VDEs were calculated at the ROVGF/6-311+G* level.

Figure S1. Optimized structures for B_{29}^- anion cluster within ~1 eV of the global minimum at PBE0/6-311+G* level. Relative energies are shown in eV, along with those for top five lowest-lying isomers at single-point CCSD(T)/6-311+G*//PBE0/6-311+G* level (in parenthesis). Zero-point energy corrections are done at PBE0/6-311+G*.



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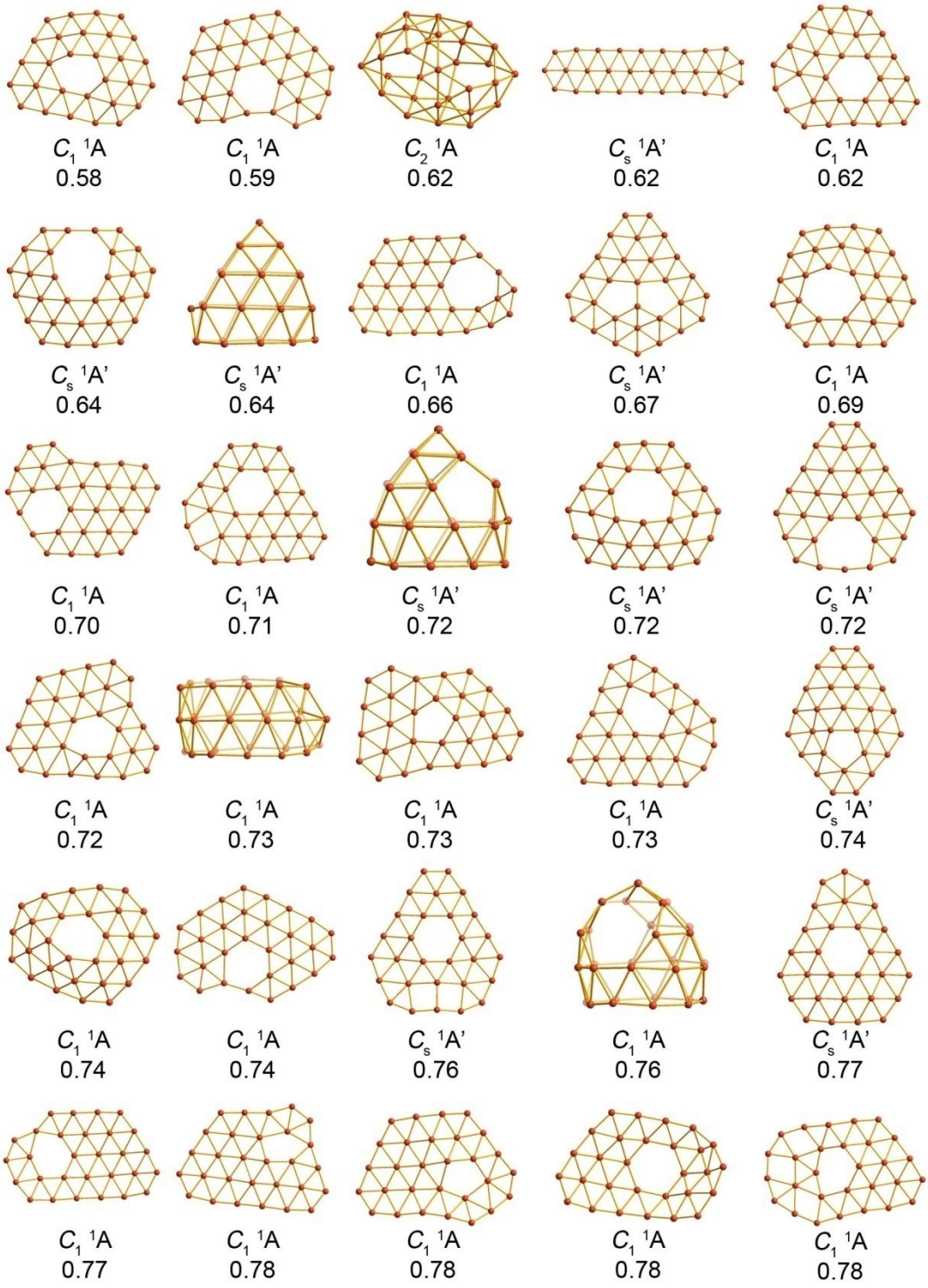
C_1 ^{1}A
0.58
C_1 ^{1}A
0.59
C_2 ^{1}A
0.62
C_s ^{1}A'
0.62
C_1 ^{1}A
0.62
C_s ^{1}A'
0.64
C_s ^{1}A'
0.64
C_1 ^{1}A
0.66
C_s ^{1}A'
0.67
C_1 ^{1}A
0.69
C_1 ^{1}A
0.70
C_1 ^{1}A
0.71
C_s ^{1}A'
0.72
C_s ^{1}A'
0.72
C_s ^{1}A'
0.72
C_1 ^{1}A
0.72
C_1 ^{1}A
0.73
C_1 ^{1}A
0.73
C_1 ^{1}A
0.73
C_s ^{1}A'
0.74
C_1 ^{1}A
0.74
C_1 ^{1}A
0.74
C_s ^{1}A'
0.76
C_1 ^{1}A
0.76
C_s ^{1}A'
0.77
C_1 ^{1}A
0.77
C_1 ^{1}A
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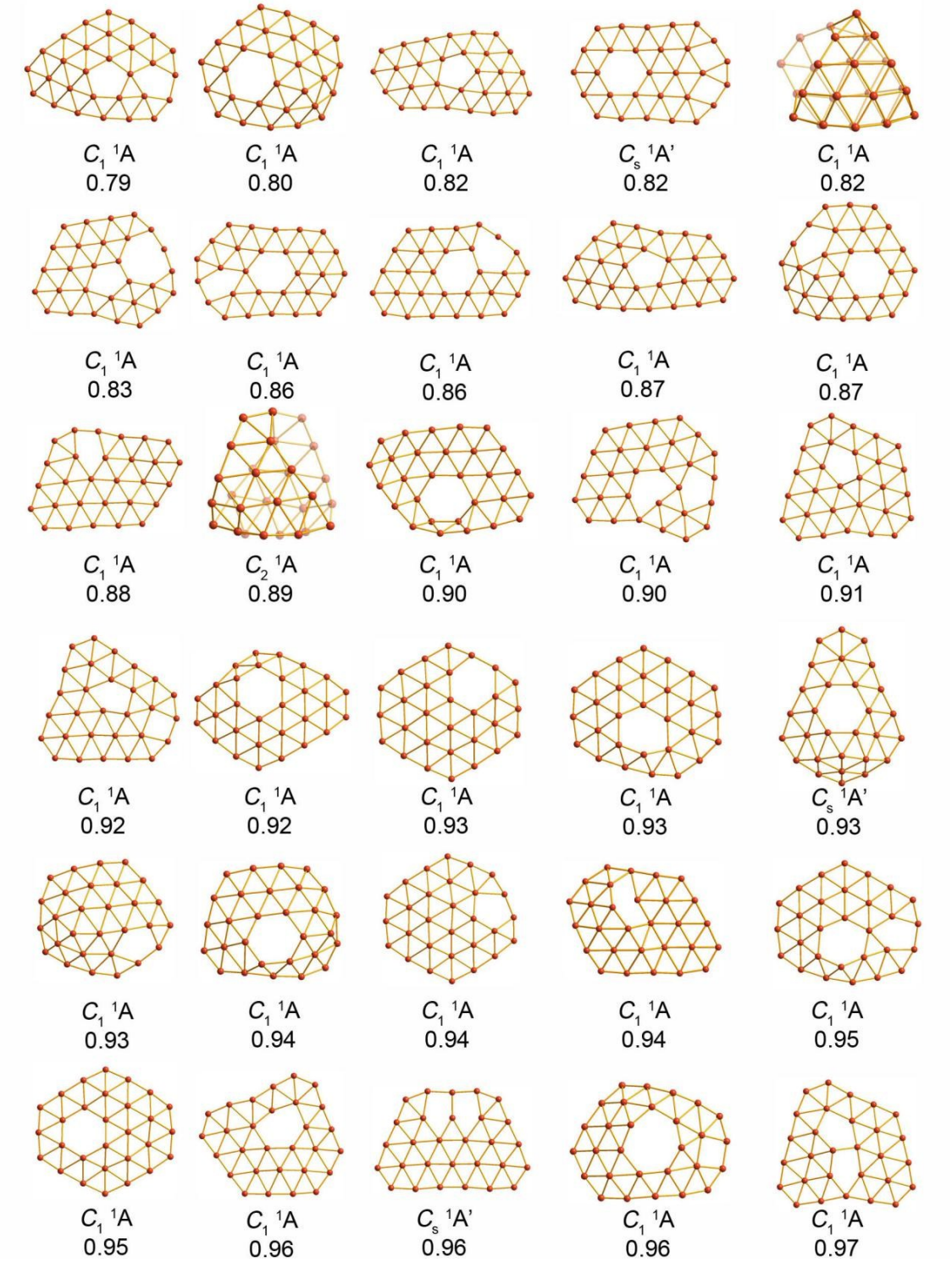
C_1 ^{1}A
0.78
C_1 ^{1}A
0.78
C_1 ^{1}A
0.78

(continued)


C_1 ^{1}A
0.79
C_1 ^{1}A
0.80
C_1 ^{1}A
0.82
C_s ^{1}A'
0.82
C_1 ^{1}A
0.82
C_1 ^{1}A
0.83
C_1 ^{1}A
0.86
C_1 ^{1}A
0.86
C_1 ^{1}A
0.87
C_1 ^{1}A
0.87
C_1 ^{1}A
0.88
C_2 ^{1}A
0.89
C_1 ^{1}A
0.90
C_1 ^{1}A
0.90
C_1 ^{1}A
0.91
C_1 ^{1}A
0.92
C_1 ^{1}A
0.92
C_1 ^{1}A
0.93
C_1 ^{1}A
0.93
C_s ^{1}A'
0.93
C_1 ^{1}A
0.93
C_1 ^{1}A
0.94
C_1 ^{1}A
0.94
C_1 ^{1}A
0.94
C_1 ^{1}A
0.95
C_1 ^{1}A
0.95
C_1 ^{1}A
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C_s ^{1}A'
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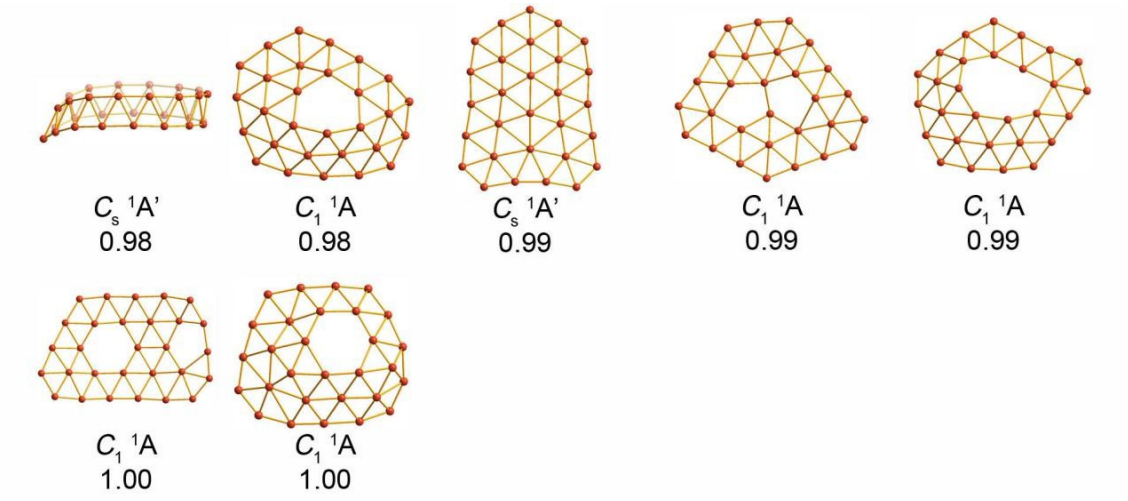
0.96
C_1 ^{1}A
0.97

(continued)



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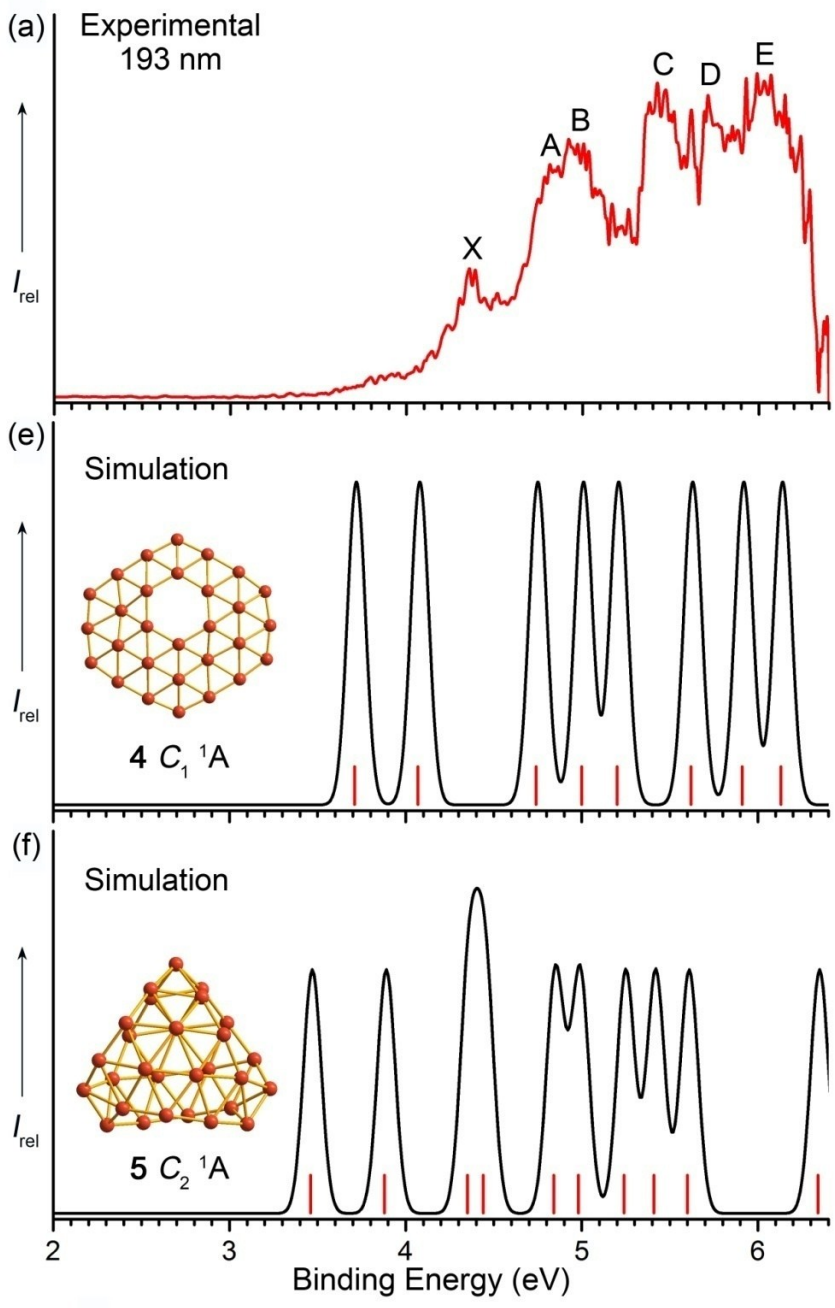

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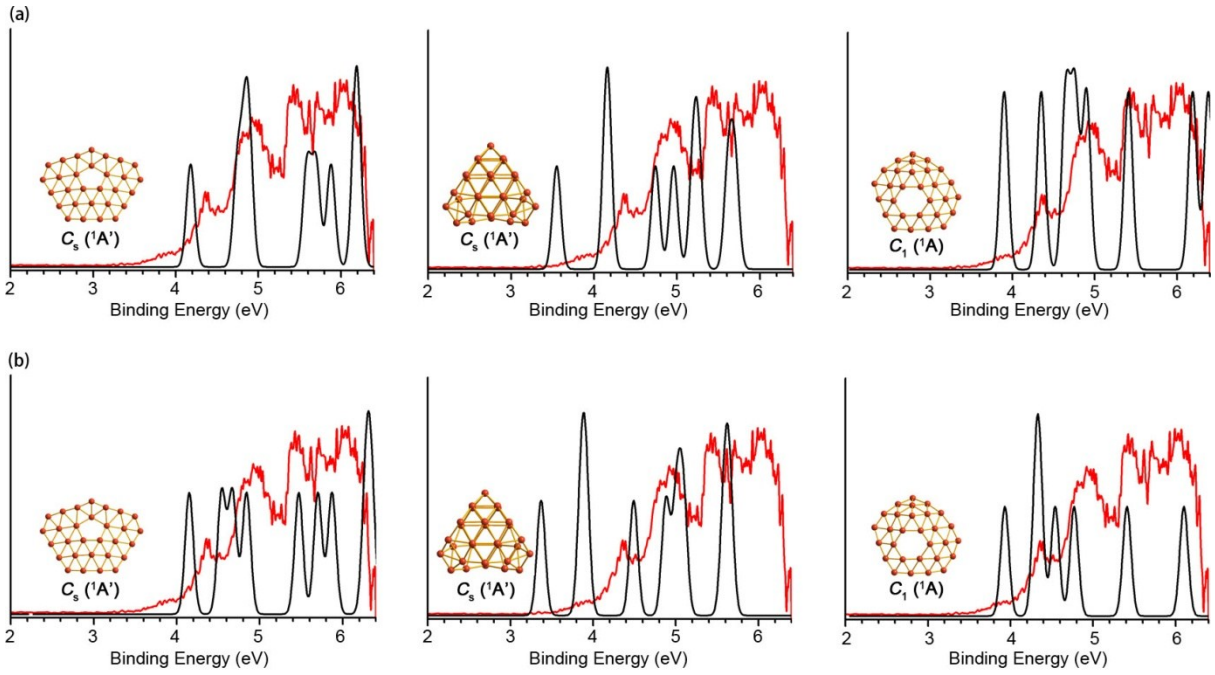

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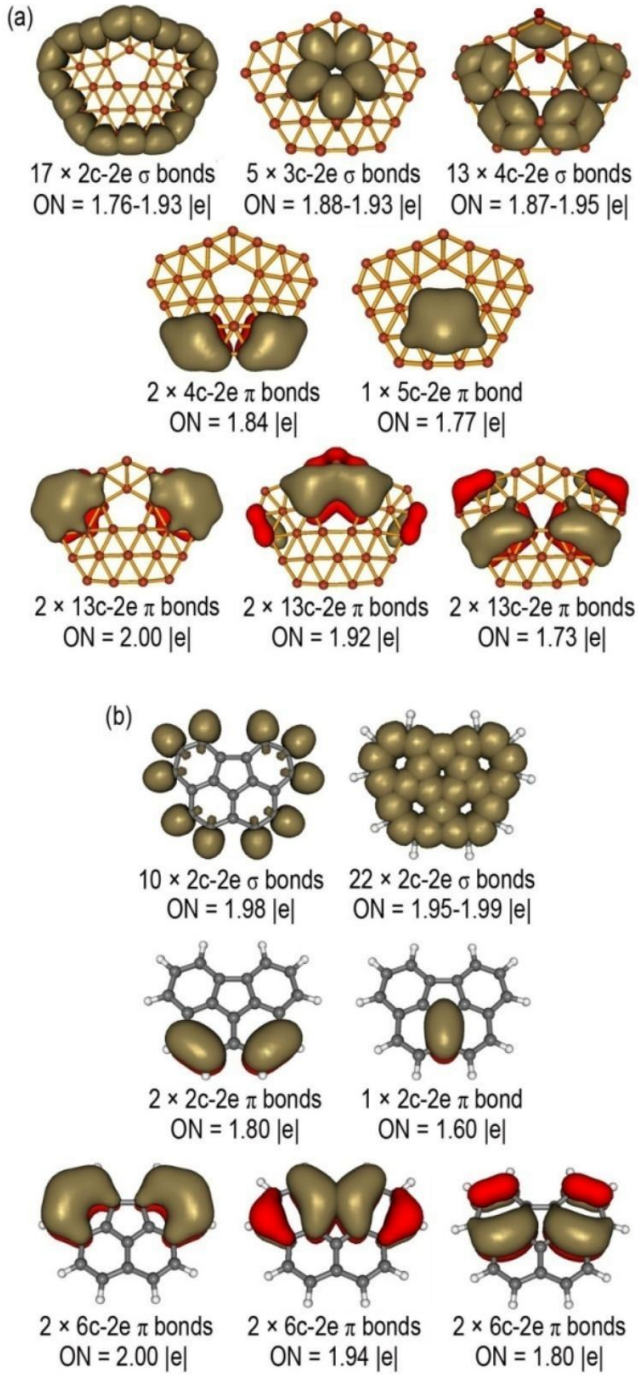

Table S2. Cartesian coordinates of isomers **1–3** of B_{29}^- at PBE0/6-311+G* level.

Isomer 1, C_s (^{1}A')

B	0.91809900	-0.38999200	3.21186900
B	-0.61760600	-0.51902000	4.00762900
B	2.58574400	-0.02824700	2.85093500
B	2.88841400	0.55219100	1.40099000
B	-0.43525600	-0.03898500	2.34113200
B	-0.42559800	0.58523300	-0.82425800
B	3.43209300	0.94305100	0.00000000
B	-0.42559800	0.58523300	0.82425800
B	-2.01899100	-0.28218100	3.20863800
B	0.91809900	-0.38999200	-3.21186900
B	-2.01899100	-0.28218100	-3.20863800
B	1.11327400	0.09333700	-1.50209900
B	-1.90734500	0.66486100	0.00000000
B	-1.91747300	0.33998000	-1.62051900
B	-3.32756200	-0.08391900	-2.35408500
B	-0.61760600	-0.51902000	-4.00762900
B	-3.43255100	0.24737200	-0.82957300
B	-3.32756200	-0.08391900	2.35408500
B	-3.43255100	0.24737200	0.82957300
B	1.11327400	0.09333700	1.50209900
B	-0.43525600	-0.03898500	-2.34113200
B	-1.91747300	0.33998000	1.62051900
B	0.73734700	-0.75693600	-4.81711100
B	2.16493400	-0.51314700	-4.28430300
B	2.88841400	0.55219100	-1.40099000
B	2.58574400	-0.02824700	-2.85093500
B	0.73734700	-0.75693600	4.81711100
B	2.16493400	-0.51314700	4.28430300
B	2.00970600	-0.01928100	0.00000000

Isomer 2, C_s (^{1}A')

B	0.77403500	2.41573200	0.00000000
B	1.08894700	1.00622700	2.50969400
B	1.70553400	-0.45598100	-1.53674900
B	-0.71918800	2.50956800	0.86579800
B	-1.90893600	-0.43506200	0.00000000
B	0.70050500	2.31822800	1.66771300
B	0.92438400	-0.47206600	3.06729700
B	-0.44285200	-1.07477500	-2.20895800
B	-2.09538800	2.41650800	0.00000000
B	-0.64752300	-3.04790500	0.00000000
B	1.59712400	1.13650900	0.85647500
B	-0.44285200	-1.07477500	2.20895800
B	-1.32523500	-1.75284800	0.89574300
B	0.70050500	2.31822800	-1.66771300
B	-1.32523500	-1.75284800	-0.89574300
B	-1.80233800	-0.35509100	-1.66287500
B	-2.08103300	1.05184400	-0.87703600
B	-2.08103300	1.05184400	0.87703600
B	-1.80233800	-0.35509100	1.66287500
B	1.07646700	-1.86215300	-2.35185100
B	0.14045600	-2.63267400	-1.32249600
B	1.08894700	1.00622700	-2.50969400
B	1.59712400	1.13650900	-0.85647500
B	0.14045600	-2.63267400	1.32249600
B	-0.71918800	2.50956800	-0.86579800
B	1.07646700	-1.86215300	2.35185100
B	0.92438400	-0.47206600	-3.06729700
B	1.70553400	-0.45598100	1.53674900
B	2.15226800	-0.18284800	0.00000000

Isomer 3, C_1 (^{1}A)

B	−2.56827100	−1.26174900	0.26629900
B	0.93404000	3.46115500	−0.26990600
B	0.52848900	−2.26932100	0.87106600
B	3.69199500	0.20277200	−0.71616300
B	−0.36553600	2.54842000	0.35580400
B	−1.45699300	−0.18619300	0.94531600
B	−3.96382800	−0.74050800	−0.66876600
B	1.05644200	−3.13796700	−0.70479800
B	−3.43558800	−2.22272400	−0.75360600
B	2.12975600	−2.06037900	0.19060100
B	2.71774300	−0.46405100	0.53318900
B	−3.09925700	1.97136900	−0.33521700
B	1.58601100	−1.18603800	1.54261000
B	0.05251700	−0.61557700	1.31337500
B	1.21924900	2.01541400	0.74702700
B	−0.92281600	−1.66263300	0.31732500
B	−1.60116800	1.49524100	0.38866700
B	2.46811900	−2.71969800	−1.25615300
B	3.21574000	−1.36634600	−0.96255400
B	1.40954000	0.45860700	1.24199500
B	3.58194200	1.76792700	−0.90454000
B	−1.82568100	3.07385300	−0.26784000
B	−4.10599600	0.84952800	−0.72135000
B	2.33392900	1.04719500	−0.07056000
B	2.35396600	2.69255500	−0.44450500
B	−0.47025000	−3.22527500	−0.09827800
B	−0.55877400	3.96948200	−0.47642000
B	−2.86905200	0.42744800	0.32196100
B	−2.03627000	−2.86250600	−0.38457700