

# Supplementary Information of Can anions possess bound doubly-excited electronic states?

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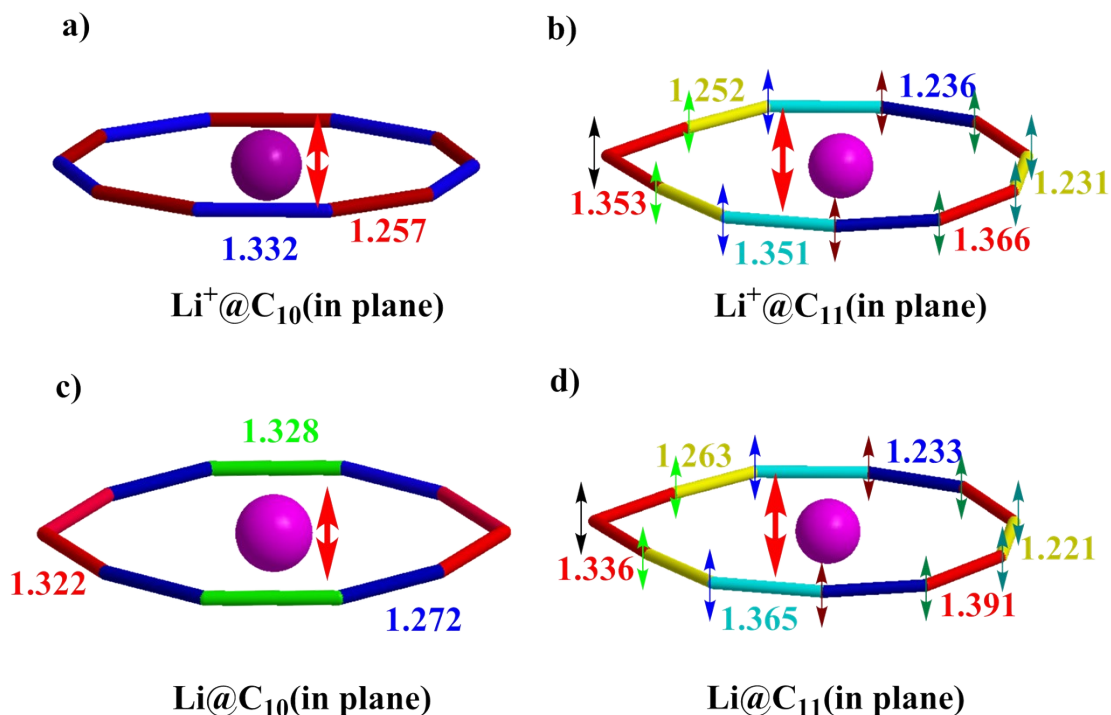
## S1. Smallest endocircular carbon ring system

Monocyclic carbon rings  $C_n$  ( $10 < n < 20$ ) are abundant in ion chromatography experiments. Beyond  $C_{20}$ , monocyclic carbon rings are no longer energy favored. [1-3] Thus, an endocircular system formed by  $C_{10}$  is expected to be the smallest endocircular system.

We have performed all-electron CCSD<sup>[4]</sup> calculations with cc-pVTZ<sup>[5,6]</sup> basis set on the cationic  $Li^+@C_{10}$  and  $Li^+@C_{11}$  as well as EOM-EA-CCSD<sup>[7]</sup> method on the neutral  $Li@C_{10}$  and  $Li@C_{11}$  systems, as implemented in the CFOUR program package.<sup>[8]</sup> In the following we discuss the results for the cationic systems. We shall see that the ring cannot accommodate the Li guest in the plane and one needs a  $C_{12}$  ring to achieve this goal.

The structures and cartesian coordinates of the equilibrium geometries of the ground state of cationic and neutral  $Li@C_{10}$  and  $Li@C_{11}$ , are shown in Figure S1 and Table S1, respectively. To test the stability of these structures, we calculated their vibrational frequencies and the results are shown in Table S2. Planar  $Li^+@C_{10}$  (structure a) and planar  $Li^+@C_{11}$  (structure b) are unstable with imaginary frequencies of the out-of-plane vibrational mode. The vibrational pattern and amplitudes of the  $Li^+$  cation and C atoms are depicted in different colors in Figure S1.

Our calculations on the respective neutrals show that the carbon rings  $C_{10}$  and  $C_{11}$  cannot accommodate the guest atom Li either, i.e., similar to their cationic counterparts, imaginary frequencies for out of plane modes appear. Thus,  $C_{10}$  and  $C_{11}$  cannot form endocircular carbon ring systems with a Li guest atom. As we have already demonstrated before,<sup>[9]</sup> neutral  $Li@C_{12}$  is an endocircular system. It is the smallest endocircular Li system.



**Figure S1.** The geometry and the mode with the imaginary vibrational frequency of the ground state of the cationic  $\text{Li}^+@C_{10}$  and  $\text{Li}^+@C_{11}$  calculated at CCSD/ cc-pVTZ level, and of the neutral  $\text{Li}@C_{10}$  and  $\text{Li}@C_{11}$  calculated at EA-EOM-CCSD/cc-pVTZ level. a) Imaginary vibrational mode of  $\text{Li}^+@C_{10}$ . b) Imaginary vibrational mode of  $\text{Li}^+@C_{11}$ . c) Imaginary vibrational mode of neutral  $\text{Li}@C_{10}$ . d) Imaginary vibrational mode of neutral  $\text{Li}@C_{11}$ . The bold red bidirectional arrows indicate the vibrational pattern of the  $\text{Li}^+$  cation. The bidirectional arrows in different colors indicate the vibrational pattern and amplitudes of the different C atoms. The bond lengths are shown in different colors. The units are Å.

**Table S1. Cartesian coordinates of cationic Li<sup>+</sup>@C<sub>10</sub> and Li<sup>+</sup>@C<sub>11</sub> (optimized at CCSD/cc-pVTZ level) and neutral Li@C<sub>10</sub> and Li@C<sub>11</sub> (optimized at EA-EOM-CCSD level). Unit is Å.**

Structure a	Li	0.0000000	0.0000000	0.0000000
	C	0.0000000	-0.66607055	1.98562805
	C	0.0000000	-1.68261737	1.24706355
	C	0.0000000	-2.09427162	-0.01987793
	C	0.0000000	-1.70598528	-1.21490039
	C	0.0000000	-0.62826049	-1.99791328
	C	0.0000000	0.62826049	-1.99791328
	C	0.0000000	1.70598528	-1.21490039
	C	0.0000000	2.09427162	-0.01987793
	C	0.0000000	1.68261737	1.24706355
	C	0.0000000	0.66607055	1.98562805
	Structure b	Li	0.0000000	0.0000000
C		0.0000000	0.0000000	2.66406007
C		-1.09284487	0.0000000	1.86624842
C		1.09284487	0.0000000	1.86624842
C		-1.99136123	0.0000000	0.99386791
C		1.99136123	0.0000000	0.99386791
C		-2.13224694	0.0000000	-0.34948348
C		2.13224694	0.0000000	-0.34948348
C		-1.75487998	0.0000000	-1.52604827
C		1.75487998	0.0000000	-1.52604827
C		-0.61535059	0.0000000	-2.27891458
C		0.61535059	0.0000000	-2.27891458
Structure c	Li	0.0000000	0.0000000	0.0000000
	C	1.66543862	-1.16613877	0.0000000
	C	-1.66543862	1.16613877	0.0000000
	C	0.66403886	-1.95109931	0.0000000
	C	-0.66403886	1.95109931	0.0000000
	C	-0.66405165	-1.95109252	0.0000000
	C	0.66405165	1.95109252	0.0000000
	C	-1.66544949	-1.16613003	0.0000000
	C	1.66544949	1.16613003	0.0000000
	C	-2.28895199	0.00000811	0.0000000
	C	2.28895199	-0.00000811	0.0000000

**Table S1 (continued)**

Structure d	Li	0.00000000	0.00000000	-0.09523949
	C	0.00000000	0.00000000	2.54838732
	C	-1.12632608	0.00000000	1.83046181
	C	1.12632608	0.00000000	1.83046181
	C	-2.09860997	0.00000000	1.02385803
	C	2.09860997	0.00000000	1.02385803
	C	-2.14841500	0.00000000	-0.33977898
	C	2.14841500	0.00000000	-0.33977898
	C	-1.80463391	0.00000000	-1.52369207
	C	1.80463391	0.00000000	-1.52369207
	C	-0.61069345	0.00000000	-2.23720076
	C	0.61069345	0.00000000	-2.23720076

**Table S2. Vibrational frequencies of equilibrium geometries of planar Li@C<sub>10</sub> and Li@C<sub>11</sub>. All the results are obtained at CCSD/cc-pVTZ level and EOM-EA-CCSD/cc-pVTZ level. Imaginary frequencies are marked in bold. All units are in cm<sup>-1</sup>.**

Structure a		Structure b		Structure c		Structure d	
<b>A2''</b>	<b>241.3214i</b>	<b>B2</b>	<b>120.6297i</b>	<b>Au</b>	<b>211.3005i</b>	<b>B2</b>	<b>35.6451i</b>
E2''	250.1526	A1	144.0747	Bu	201.8806	A1	84.0932
E2''	250.1526	B2	175.7816	Au	222.572	B1	131.6365
E2'	320.5103	B1	197.3691	Ag	233.3317	B1	152.1666
E2'	320.5103	A2	203.2581	Au	254.6078	B2	153.3958
A2'	475.4419	B2	302.2791	Ag	289.3448	A2	172.6346
A1''	476.0806	A1	304.8172	Bu	298.4508	A1	269.5218
E2''	477.1978	B1	312.355	Bg	375.9979	B2	314.0761
E2''	477.1978	A1	368.2226	Ag	409.2198	A1	356.4493
E2'	526.9812	A2	429.4564	Au	437.9675	A2	433.6743
E2'	526.9812	B1	456.7691	Bg	447.2467	B1	444.3491
E1''	560.5355	B2	461.0901	Bu	488.9742	B2	449.1410
E1''	560.5355	A1	490.7184	Bg	503.2058	B1	479.8048
E1'	561.1208	B1	500.2396	Au	542.7519	A2	490.0451
E1'	561.1208	B1	521.1024	Bu	596.9362	B2	501.2349
E1'	628.1991	A2	587.4584	Bu	633.5903	A1	505.8183
E1'	628.1991	B2	591.0721	Ag	655.3521	B1	522.6375
A1'	656.9704	A2	608.8008	Bu	803.9805	A2	531.0911
E1'	1034.8709	A1	611.1624	Ag	808.3602	A1	636.4751
E1'	1034.8709	A1	754.8216	Bu	1028.1439	A1	769.8327
A1'	1124.6304	B1	873.606	Bu	1105.644	B1	879.3564
E2'	1452.5541	A1	935.5626	Ag	1392.5964	A1	921.8256
E2'	1452.5541	B1	1234.7092	Ag	1411.5197	B1	1223.8602

**Table S2. (continued)**

E2'	1977.4017	A1	1294.5207	Bu	1713.5426	A1	1268.3915
E2'	1977.4017	B1	1452.2884	Ag	1930.2422	B1	1381.2019
E1'	2096.9363	B1	1818.3661	Bu	1937.9044	B1	1579.1442
E1'	2096.9363	A1	1872.085	Ag	2075.0804	A1	1937.4052
		A1	2019.9333			A1	2071.0741
		B1	2113.745			B1	2098.0321
		A1	2126.1177			A1	2202.9364



## S2. The optimized geometries of the ground and doubly-excited states

### of Li@C<sub>12</sub><sup>-</sup>

The cartesian coordinates of the optimized geometry of the ground and doubly-excited states of Li@C<sub>12</sub><sup>-</sup> are shown in Table S3. The numbers of occupied orbitals in different irreducible representations are also listed.

**Table S3. Cartesian coordinates of the ground and doubly-excited states of Li@C<sub>12</sub><sup>-</sup> optimized at CCSD/ cc-pVTZ level. The orbital compositions are in brackets. Unit is Å.**

Li@C <sub>12</sub> <sup>-</sup> (the ground state)  C <sub>2v</sub> symmetry (18 a <sub>1</sub> +4 b <sub>1</sub> +14 b <sub>2</sub> +2 a <sub>2</sub> )	Li	0.00000000	0.00000000	-0.010498728
	C	0.00000000	0.650394151	2.029406450
	C	0.00000000	-0.650394151	2.029406450
	C	0.00000000	1.830109074	1.503931838
	C	0.00000000	-1.830109074	1.503931838
	C	0.00000000	2.935957442	0.791452808
	C	0.00000000	-2.935957442	0.791452808
	C	0.00000000	2.479402796	-0.542350916
	C	0.00000000	-2.479402796	-0.542350916
	C	0.00000000	1.899190222	-1.628731757
	C	0.00000000	-1.899190222	-1.628731757
	C	0.00000000	0.608854335	-2.150639296
	C	0.00000000	-0.608854335	-2.150639296
	cumulenic Li@C <sub>12</sub> <sup>-</sup> (the doubly-excited state)  D <sub>6h</sub> symmetry (10 a <sub>g</sub> +7 b <sub>3u</sub> +8 b <sub>2u</sub> +6 b <sub>1g</sub> +2 b <sub>1u</sub> +2 b <sub>3g</sub> +2 b <sub>2g</sub> +1 a <sub>u</sub> )	Li	0.00000000	0.00000000
C		1.891925904	-1.746199592	0.00000000
C		2.321481710	-0.523433533	0.00000000
C		2.458216158	0.765356099	0.00000000
C		1.614047591	1.748745374	0.00000000
C		0.566290254	2.511555690	0.00000000
C		-0.707434119	2.272178901	0.00000000
C		-1.891925904	1.746199592	0.00000000
C		-2.321481710	0.523433533	0.00000000
C		-2.458216158	-0.765356099	0.00000000
C		-1.614047591	-1.748745374	0.00000000
C		-0.566290254	-2.511555690	0.00000000
C		0.707434119	-2.272178901	0.00000000

### S3. Vibrational frequencies of the ground and doubly-excited state of

#### Li@C<sub>12</sub><sup>-</sup>.

We calculated the vibrational frequencies of the ground and doubly-excited states of Li@C<sub>12</sub><sup>-</sup> at CCSD/cc-pVTZ level. The results are shown in Table S4. All the frequencies are real showing that the found geometries provide minima on the energy surfaces. Due to technical difficulties, the vibrational frequency calculation of the doubly-excited state is carried out using C<sub>6h</sub> symmetry (a subgroup of D<sub>6h</sub>).

**Table S4. Vibrational frequencies of the ground and doubly-excited states of Li@C<sub>12</sub><sup>-</sup>. The frequencies are obtained at CCSD/cc-pVTZ level. All units are in cm<sup>-1</sup>.**

Ground state		Doubly-excited state	
B2	84.7409	E2	46.0467
B1	141.4263	E2	46.0467
A2	153.1312	Au	96.1946
B1	165.2181	Bu	97.2873
A1	184.7483	E2	147.258
B2	219.3191	E2	147.258
A1	249.5153	E1	200.2374
A2	298.8611	E1	200.2374
B1	324.038	E1	249.0257
B2	330.08	E1	249.0257
A1	443.5852	Bg	291.5184
B1	479.8243	Bg	292.5397
B2	488.525	E2	325.1516
A1	497.7203	E2	325.1516

**Table S4 (continued)**

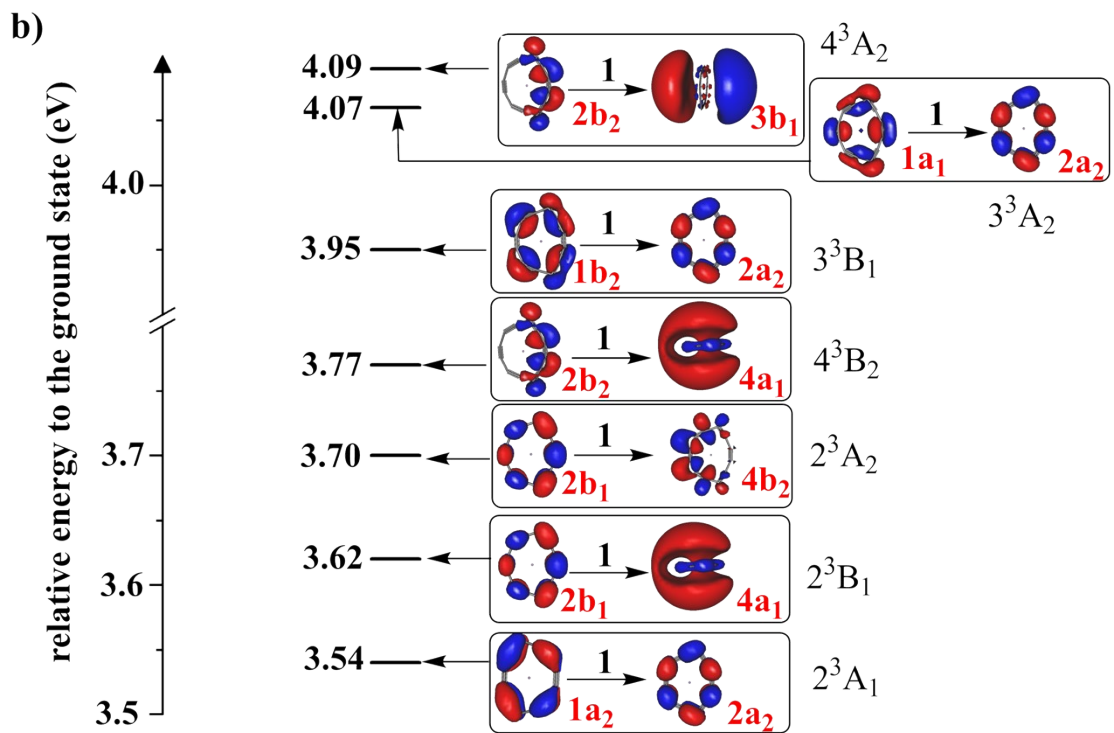
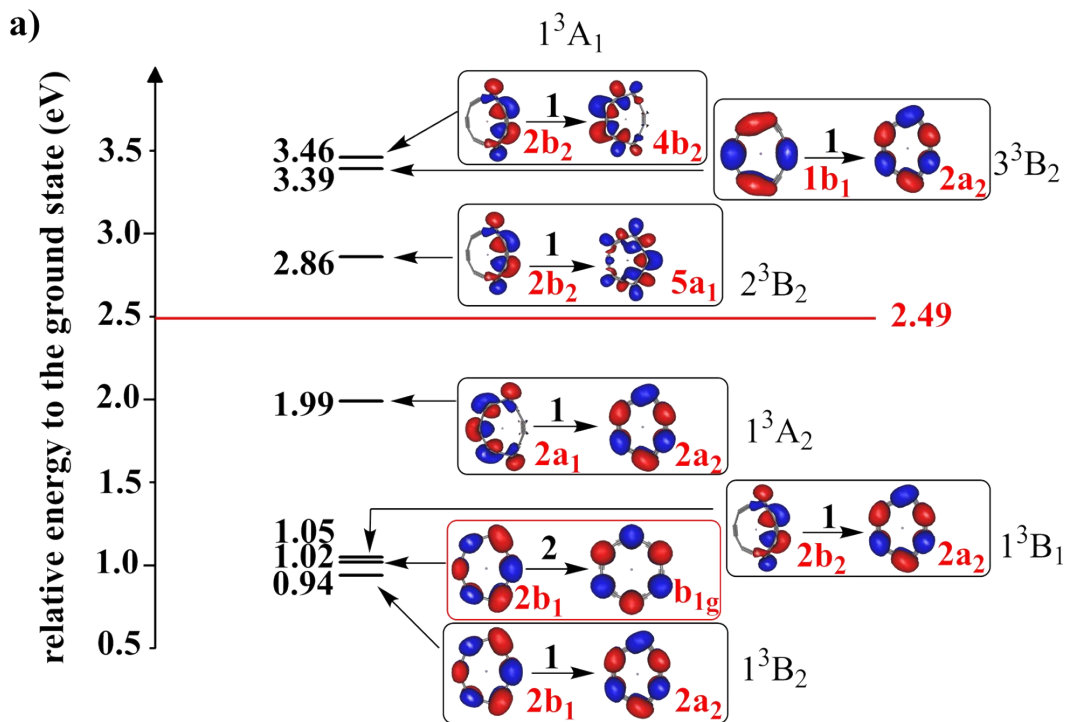
A2	502.755	Au	378.136
B1	515.6978	Bu	486.5221
B2	531.0802	E2	549.4093
A1	572.6854	E2	549.4093
B2	594.4799	E1	572.7357
A2	601.3577	E1	572.7357
A2	655.4695	Ag	608.2976
A1	701.2344	Ag	784.1208
A1	769.8889	Ag	870.3654
B2	872.3695	E1	906.4482
A1	1089.2567	E1	906.4482
B2	1194.2775	E2	1308.9311
B2	1314.0282	E2	1308.9311
A1	1625.2714	Bu	1619.073
B2	1902.1402	Bu	1790.5976
A1	2083.1101	E1	1793.842
A1	2095.8843	E1	1793.842
B2	2098.7795	E2	1982.068
A1	2288.7392	E2	1982.068

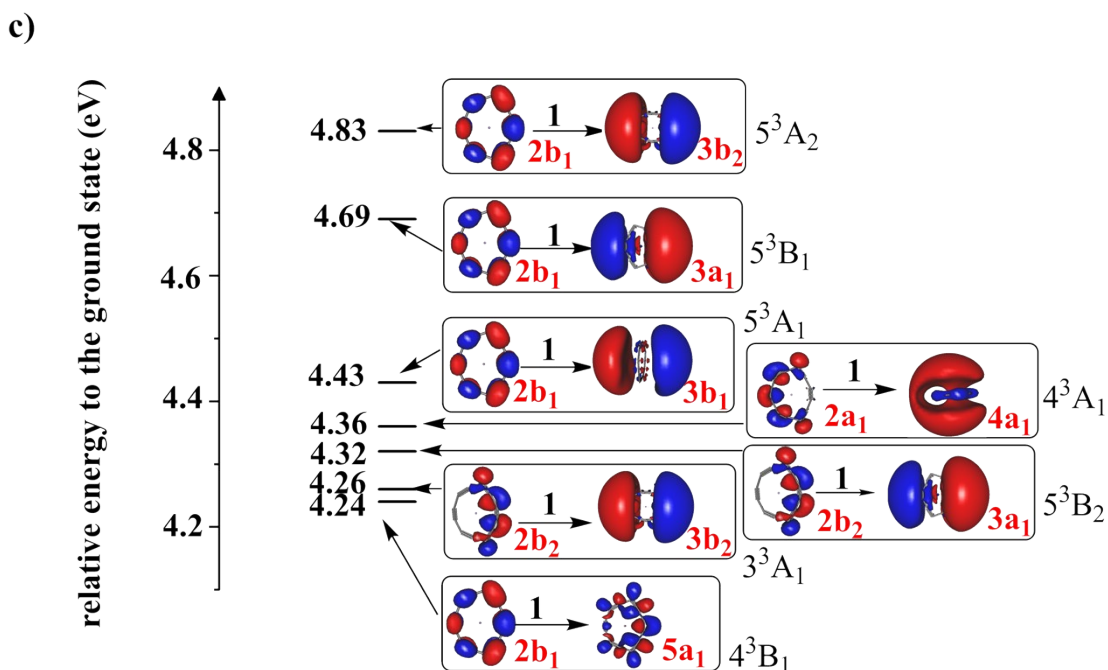
## S4. Full picture of the excited states of $\text{Li@C}_{12}^-$

Due to limitations of text space, only the low-lying excited states which are bound are shown in Figure 2 of the main text. Here, we show in Figure S2 the full picture of all the triplet singly-excited states, which we found at EE-EOM-CCSD/cc-pVTZ level. The corresponding singly-excited singlet states are shown in Figure S3. The energies and irreducible representations of frontier Hartree-Fock (HF) orbitals of the ground state are shown in Table S5. These HF orbitals play the role of initial and final orbitals of singly-excited states. The three low-lying triplet states are formed by exciting one electron from the HOMO, HOMO-1 and HOMO-2 to LUMO, respectively. The fourth singly-excited triplet state is formed by exciting one electron from HOMO-1 to a virtual orbital higher than LUMO.

The non-charge-separated excited states are not low-lying and they are all higher in energy than the neutral  $\text{Li@C}_{12}$ . The non-charge-separated state with lowest energy in Figure S2(b) is  $2^3B_1$  (3.62 eV higher than the ground state). The next two non-charge-separated states, i.e.,  $4^3A_2$  and  $4^3A_1$ , also possess relative high energies (3.77 eV and 4.09 eV). It is noteworthy that the non-charged-electron states of neutral of  $\text{Li@C}_n$  are low-lying states.<sup>[9]</sup>

As shown in Figure S3, all the singly-excited singlet states are higher in energy than their triplet counterparts (in Figure S2) and the doubly-excited state (in its equilibrium geometry). The three lowest singlet singly-excited states are the counterparts of the three lowest triplet states. There is a moderately large energy gap between valence singly-excited singlet states and their triplet counterparts, e.g.,  $\sim 1$  eV ( $1^3B_1$  and  $1^1B_1$ ). In contrast, the gaps between non-charge-separated singlet and triplet states are much smaller, e.g.,  $\sim 0.1$  eV ( $2^3B_1$  and  $2^1B_1$ ).

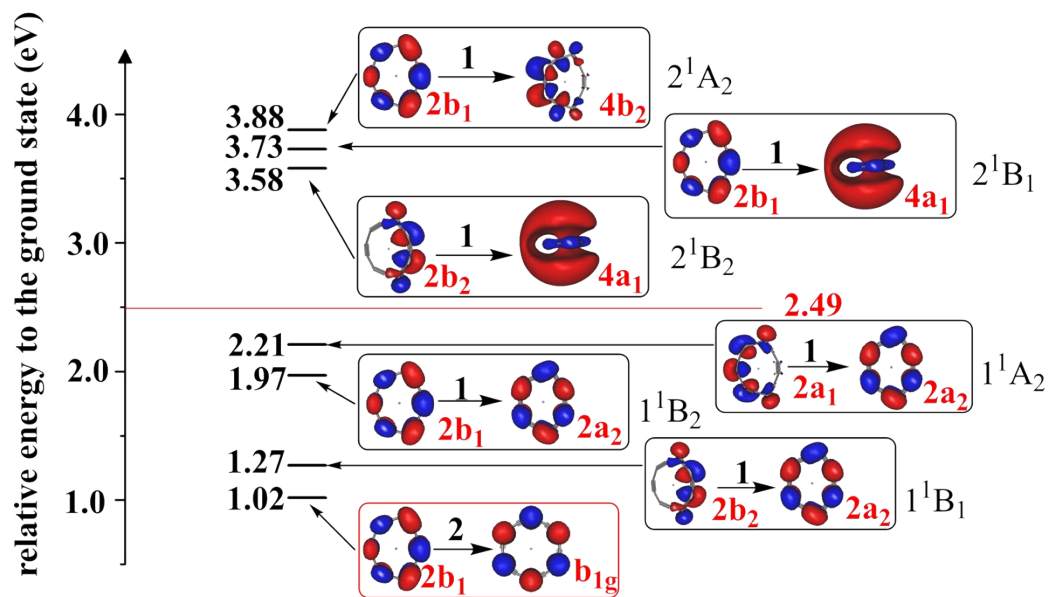




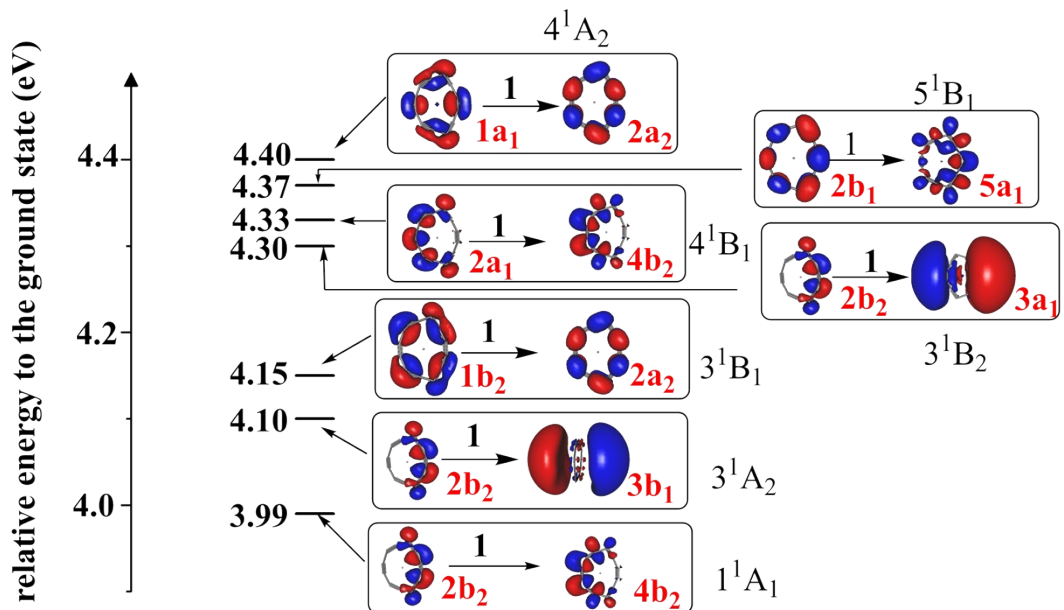
**Figure S2.** The energies of the singly-excited triplet states of  $\text{Li@C}_{12}^-$  relative to that of its global ground state. The states in black and red blocks are singly-excited triplet and doubly-excited singlet states, respectively. The doubly-occupied HOMO of the doubly-excited state and the singly-occupied orbitals of the singly-excited states are shown.

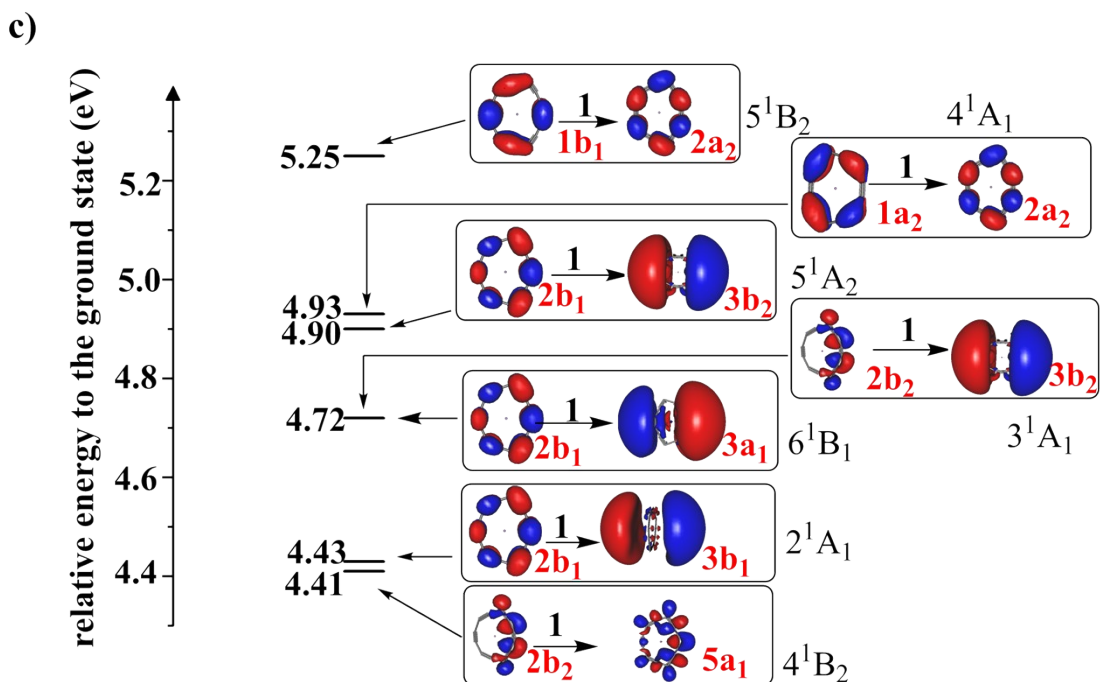
a) The excited states with a relative energy to the ground state between 0.5 and 3.5 eV. b) The excited states with relative energy to ground state between 3.5 and 4.1 eV. c) The excited states with a relative energy to the ground state between 4.1 and 4.9 eV. The energies of the singly-excited states are vertical excitation energies based on the equilibrium geometry of the anion in its ground state. The energy of the doubly-excited is obtained at its own optimized equilibrium geometry.

a)



b)





**Figure S3.** The relative energies of the singly-excited singlet states of  $\text{Li@C}_{12}^-$  relative to that of its global ground state. The states in black and red blocks are singly-excited singlet state and doubly-excited singlet state, respectively. The doubly-occupied HOMO of the doubly-excited state and the singly-occupied orbitals of the singly-excited states are shown. a) The excited states with a relative energy to the ground state between 1.0 and 4.0 eV. b) The excited states with a relative energy to the ground state between 4.0 and 4.4 eV. c) The excited states with a relative energy to the ground state between 4.4 and 5.3 eV. The energies of the singly-excited states are vertical excitation energies based on the equilibrium geometry of the anion in its ground state. The energy of the doubly-excited is obtained at its own optimized equilibrium geometry.



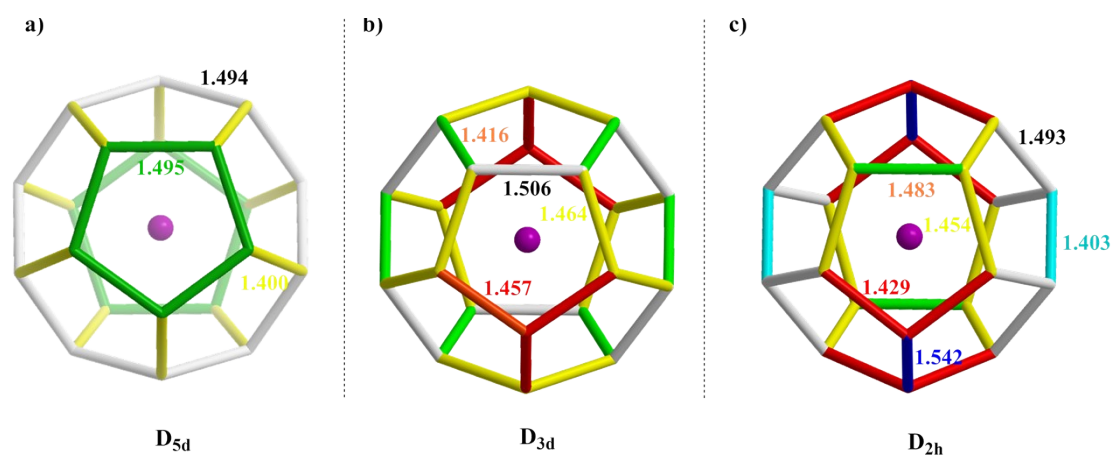
**Table S5. The frontier HF orbitals of the ground state of Li@C<sub>12</sub><sup>-</sup> at HF/cc-pVTZ level.**

<b>Occupied orbitals</b>				
<b>Orbital number</b>	<b>HF Orbital eigenvalue (a.u.)</b>	<b>HF Orbital eigenvalue (eV)</b>	<b>Irreducible representation</b>	<b>symbols in Figure S2/S3</b>
32	-0.282059	-7.675213	A1	1a <sub>1</sub>
33	-0.266895	-7.262578	B2	1b <sub>2</sub>
34	-0.260971	-7.101376	B1	1b <sub>1</sub>
35	-0.256898	-6.990550	A2	1a <sub>2</sub>
36	-0.171314	-4.661692	A1	2a <sub>1</sub>
37	-0.139003	-3.782472	B2	2b <sub>2</sub>
38	-0.125571	-3.416970	B1	2b <sub>1</sub>
<b>Virtual orbitals</b>				
<b>Orbital number</b>	<b>HF Orbital eigenvalue (a.u.)</b>	<b>HF Orbital eigenvalue (eV)</b>	<b>Irreducible representation</b>	<b>symbols in Figure S2/S3</b>
39	0.139472	3.795226	A2	2a <sub>2</sub>
40	0.151360	4.118718	B1	3b <sub>1</sub>
41	0.156967	4.271297	A1	3a <sub>1</sub>
42	0.165662	4.507903	B2	3b <sub>2</sub>
43	0.174822	4.757139	A1	4a <sub>1</sub>
44	0.234374	6.377652	B2	4b <sub>2</sub>
45	0.249653	6.793408	A1	5a <sub>1</sub>

## **S5. The optimization of the geometries of the ground and doubly-excited states of the endohedral fullerene $\text{Li@C}_{20}^-$ anion**

We optimized the geometries of the ground state and the doubly-excited state of the endohedral fullerene anion  $\text{Li@C}_{20}^-$  in different symmetries (see in the main text). The geometries and relative energies in different symmetries are shown in Figure S4 and Table S6. The cartesian coordinates of the optimized geometries of the ground and doubly-excited states of  $\text{Li@C}_{20}^-$  are shown in Table S7. One can see that the ground state of  $\text{Li@C}_{20}^-$  in  $D_{5d}$  symmetry is the energy favored structure.

To find out whether the ground and doubly-excited states are bound or not, we also optimized the geometries of neutral  $\text{Li@C}_{20}$  in different symmetries. We found that the energy favored geometry is in  $D_{3d}$  symmetry. The electron affinity of neutral  $\text{Li@C}_{20}$  is found to be around 2.59 eV. The cartesian coordinates of the equilibrium geometry of the ground state of neutral  $\text{Li@C}_{20}$  in  $D_{3d}$  symmetry are shown in Table S8.



**Figure S4.** The equilibrium geometries of the ground state of  $\text{Li@C}_{20}^-$  in different symmetries optimized at CCSD/cc-pVTZ level. a)  $\text{Li@C}_{20}^-$  in  $D_{5d}$  symmetry. b)  $\text{Li@C}_{20}^-$  in  $D_{3d}$  symmetry. c)  $\text{Li@C}_{20}^-$  in  $D_{2h}$  symmetry. The units are Å.

**Table S6.** Energies of the ground state and doubly-excited state of  $\text{Li@C}_{20}^-$  in different symmetries at CCSD/ cc-pVTZ level. The orbital compositions of the ground and doubly-excited states are in brackets.

$\text{Li@C}_{20}^-$	Total energy (a.u.)	Relative energy(eV)
$D_{5d}$ (ground state) (20 $a_g$ +13 $a_u$ +17 $b_u$ +12 $b_g$ )	-767.700336	0.00
$D_{3d}$ (ground state) (20 $a_g$ +13 $a_u$ +17 $b_u$ +12 $b_g$ )	-767.672992	0.74
$D_{2h}$ (ground state) (14 $a_g$ +9 $b_{2u}$ +9 $b_{3u}$ +6 $b_{1g}$ +8 $b_{1u}$ +6 $b_{3g}$ +6 $b_{2g}$ +4 $a_u$ )	-767.688547	0.32
$D_{5d}$ (doubly-excited state) (20 $a_g$ +14 $a_u$ +16 $b_u$ +12 $b_g$ )	-767.649670	1.38

**Table S7. Cartesian coordinates of Li@C<sub>20</sub><sup>-</sup> in different symmetries optimized at CCSD/ cc-pVTZ level. The orbital compositions of the ground and doubly-excited states are in brackets. Unit is Å.**

<p style="text-align: center;">Li@C<sub>20</sub><sup>-</sup> (ground state) D<sub>5d</sub> symmetry (20 a<sub>g</sub>+13 a<sub>u</sub>+17 b<sub>u</sub>+12 b<sub>g</sub>)</p>	Li	0.000000000	0.000000000	0.000000000	
	C	-1.028614541	1.558147894	-0.747332210	
	C	-1.028614541	1.558147894	0.747332210	
	C	0.392895793	1.558147894	1.209208914	
	C	1.271437497	1.558147894	0.000000000	
	C	0.392895793	1.558147894	-1.209208914	
	C	1.028614541	-1.558147894	0.747332210	
	C	-0.392895793	-1.558147894	1.209208914	
	C	-1.271437497	-1.558147894	0.000000000	
	C	-0.392895793	-1.558147894	-1.209208914	
	C	1.028614541	-1.558147894	-0.747332210	
	C	-1.659592623	0.395586796	-1.205764621	
	C	-1.659592623	0.395586796	1.205764621	
	C	0.633907972	0.395586796	1.950968142	
	C	2.051369301	0.395586796	0.000000000	
	C	0.633907972	0.395586796	-1.950968142	
	C	1.659592623	-0.395586796	1.205764621	
	C	-0.633907972	-0.395586796	1.950968142	
	<p style="text-align: center;">Li@C<sub>20</sub><sup>-</sup> D<sub>3d</sub> symmetry (20 a<sub>g</sub>+13 a<sub>u</sub>+17 b<sub>u</sub>+12 b<sub>g</sub>)</p>	Li	0.000000000	0.000000000	0.000000000
		C	0.000000000	1.960202930	0.000000000
C		-0.692297755	1.505079206	1.199094892	
C		1.384595516	1.505079206	0.000000000	
C		-0.692297755	1.505079206	-1.199094892	
C		0.249850509	0.662632126	1.938812353	
C		1.554135498	0.662632126	-1.185783062	
C		-1.803986007	0.662632126	-0.753029290	
C		-1.803986007	0.662632126	0.753029290	
C		1.554135498	0.662632126	1.185783062	
C		0.249850509	0.662632126	-1.938812353	
C		0.000000000	-1.960202930	0.000000000	
C		-1.384595516	-1.505079206	0.000000000	
C		0.692297755	-1.505079206	-1.199094892	
C		0.692297755	-1.505079206	1.199094892	
C		-1.554135498	-0.662632126	-1.185783062	
C		1.803986007	-0.662632126	-0.753029290	

**Table S7 (continued)**

	C	-0.249850509	-0.662632126	1.938812353
	C	-1.554135498	-0.662632126	1.185783062
	C	-0.249850509	-0.662632126	-1.938812353
	C	1.803986007	-0.662632126	0.753029290
<p style="text-align: center;">Li@C<sub>20</sub><sup>-</sup> D<sub>2h</sub> symmetry (14 a<sub>g</sub>+9 b<sub>2u</sub>+9 b<sub>3u</sub>+6 b<sub>1g</sub>+ 8 b<sub>1u</sub>+6 b<sub>3g</sub>+6 b<sub>2g</sub>+4 a<sub>u</sub>)</p>	Li	0.000000000	0.000000000	0.000000000
	C	1.917497686	0.000000000	0.701285016
	C	1.917497686	0.000000000	-0.701285016
	C	-1.917497686	0.000000000	0.701285016
	C	-1.917497686	0.000000000	-0.701285016
	C	0.000000000	-0.771088279	1.893030456
	C	0.000000000	0.771088279	1.893030456
	C	0.000000000	-0.771088279	-1.893030456
	C	0.000000000	0.771088279	-1.893030456
	C	0.741585134	-2.009020526	0.000000000
	C	-0.741585134	-2.009020526	0.000000000
	C	0.741585134	2.009020526	0.000000000
	C	-0.741585134	2.009020526	0.000000000
	C	-1.136347869	1.195109579	1.137969099
	C	-1.136347869	-1.195109579	1.137969099
	C	-1.136347869	-1.195109579	-1.137969099
	C	-1.136347869	1.195109579	-1.137969099
	C	1.136347869	1.195109579	1.137969099
C	1.136347869	-1.195109579	1.137969099	
C	1.136347869	-1.195109579	-1.137969099	
C	1.136347869	1.195109579	-1.137969099	
<p style="text-align: center;">Li@C<sub>20</sub><sup>-</sup> (doubly-excited state) D<sub>5d</sub> symmetry (20 a<sub>g</sub>+14 a<sub>u</sub>+16 b<sub>u</sub>+12 b<sub>g</sub>)</p>	Li	0.000000000	0.000000000	0.000000000
	C	-1.004325003	1.625059505	-0.729684826
	C	-1.004325003	1.625059505	0.729684826
	C	0.383618014	1.625059505	1.180654853
	C	1.241413980	1.625059505	0.000000000
	C	0.383618014	1.625059505	-1.180654853
	C	1.004325003	-1.625059505	0.729684826
	C	-0.383618014	-1.625059505	1.180654853
	C	-1.241413980	-1.625059505	0.000000000
	C	-0.383618014	-1.625059505	-1.180654853
	C	1.004325003	-1.625059505	-0.729684826
	C	-1.627951739	0.383404194	-1.182776172
	C	-1.627951739	0.383404194	1.182776172
	C	0.621822231	0.383404194	1.913772045
	C	2.012259012	0.383404194	0.000000000
	C	0.621822231	0.383404194	-1.913772045
	C	1.627951739	-0.383404194	1.182776172

**Table S7 (continued)**

	C	-0.621822231	-0.383404194	1.913772045
	C	-2.012259012	-0.383404194	0.000000000
	C	-0.621822231	-0.383404194	-1.913772045
	C	1.627951739	-0.383404194	-1.182776172

**Table S8. Cartesian coordinates of the equilibrium geometry of the ground state of neutral Li@C<sub>20</sub> in D<sub>3d</sub> symmetry calculated at EOM-EA-CCSD/cc-pVTZ level. The orbital compositions of the closed-shell Li<sup>+</sup>@C<sub>20</sub> reference in different irreducible representations are listed. Unit is Å.**

Neutral Li@C <sub>20</sub> D <sub>3d</sub> symmetry (20 a <sub>g</sub> +13 a <sub>u</sub> +16 b <sub>u</sub> +12 b <sub>g</sub> )	Li	0.000000000	0.000000000	0.000000000
	C	0.000000000	1.959354368	0.000000000
	C	-0.686171518	1.483501474	1.188483936
	C	1.372343041	1.483501474	0.000000000
	C	-0.686171518	1.483501474	-1.188483936
	C	0.250181964	0.657627290	1.944998445
	C	1.559327081	0.657627290	-1.189163156
	C	-1.809509046	0.657627290	-0.755835284
	C	-1.809509046	0.657627290	0.755835284
	C	1.559327081	0.657627290	1.189163156
	C	0.250181964	0.657627290	-1.944998445
	C	0.000000000	-1.959354368	0.000000000
	C	-1.372343041	-1.483501474	0.000000000
	C	0.686171518	-1.483501474	-1.188483936
	C	0.686171518	-1.483501474	1.188483936
	C	-1.559327081	-0.657627290	-1.189163156
	C	1.809509046	-0.657627290	-0.755835284
	C	-0.250181964	-0.657627290	1.944998445
	C	-1.559327081	-0.657627290	1.189163156
	C	-0.250181964	-0.657627290	-1.944998445
C	1.809509046	-0.657627290	0.755835284	

## S6. Vibrational frequency calculation for the ground state of Li@C<sub>20</sub><sup>-</sup>.

To ensure that the found structure of the ground state of Li@C<sub>20</sub><sup>-</sup> within D<sub>5d</sub> symmetry provides a minimum on the energy surface, we calculate the vibrational frequencies and the results are shown in Table S9. All frequencies are found to be real proving that it is indeed a minimum.

**Table S9. Vibrational frequencies of the ground state of Li@C<sub>20</sub><sup>-</sup>. The frequencies are obtained at CCSD/cc-pVTZ level. All units are in cm<sup>-1</sup>.**

Ground state							
E1g	403.8985	E1g	641.6806	E2g	976.3586	E1u	1301.3981
E1g	403.8985	E1u	645.8426	E1g	1032.7195	A2u	1348.7908
E2g	428.6872	E1u	645.8426	E1g	1032.7195	E1g	1361.7835
E2g	428.6872	A2u	648.0605	A1g	1040.3395	E1g	1361.7835
A1g	522.5631	A1u	685.5082	E2u	1107.9418	E2u	1382.8369
E1u	525.1411	E2g	750.8833	E2u	1107.9418	E2u	1382.8369
E1u	525.1411	E2g	750.8833	E1u	1139.4284	E2g	1393.648
E2u	607.5067	E2u	764.031	E1u	1139.4284	E2g	1393.648
E2u	607.5067	E2u	764.031	E2u	1182.368	A1g	1446.876
E2u	616.6023	A2u	807.123	E2u	1182.368		
E2u	616.6023	A2g	816.0372	E2g	1205.8876		
E1u	623.1821	A1g	822.4694	E2g	1205.8876		
E1u	623.1821	A2u	906.5265	E1g	1232.8247		
E2g	623.773	E1u	916.892	E1g	1232.8247		

E2g	623.773	E1u	916.892	A1u	1277.8321	
E1g	641.6806	E2g	976.3586	E1u	1301.3981	

### S7. The full picture of the excited states of Li@C<sub>20</sub><sup>-</sup>

The singly-excited triplet and singly-excited singlet states of Li@C<sub>20</sub><sup>-</sup>, obtained at EOM-EE-CCSD/cc-pVTZ level, are shown in Figure S5 and S6, respectively. For the degenerate states, only one component is shown. The orbital energies and irreducible representations of frontier HF orbitals are shown in Table S10. The low-lying triplet states are formed by exciting one electron from HOMO, HOMO-1 and HOMO-2 to LUMO and LUMO+1. All low-lying states are valence states.

Comparing singly-excited singlet states to triplet states, one can easily see that there is a moderate energy gap between the singlet states and their triplet counterparts, i.e., ~0.50 eV (<sup>1</sup>E<sub>1g</sub> and <sup>1</sup>E<sub>1g</sub>, or <sup>1</sup>E<sub>2g</sub> and <sup>1</sup>E<sub>2g</sub>). All other singlet states are higher in energy than the neutral Li@C<sub>20</sub> except of the singly-excited singlet states <sup>1</sup>E<sub>1g</sub> and <sup>1</sup>E<sub>2g</sub>.



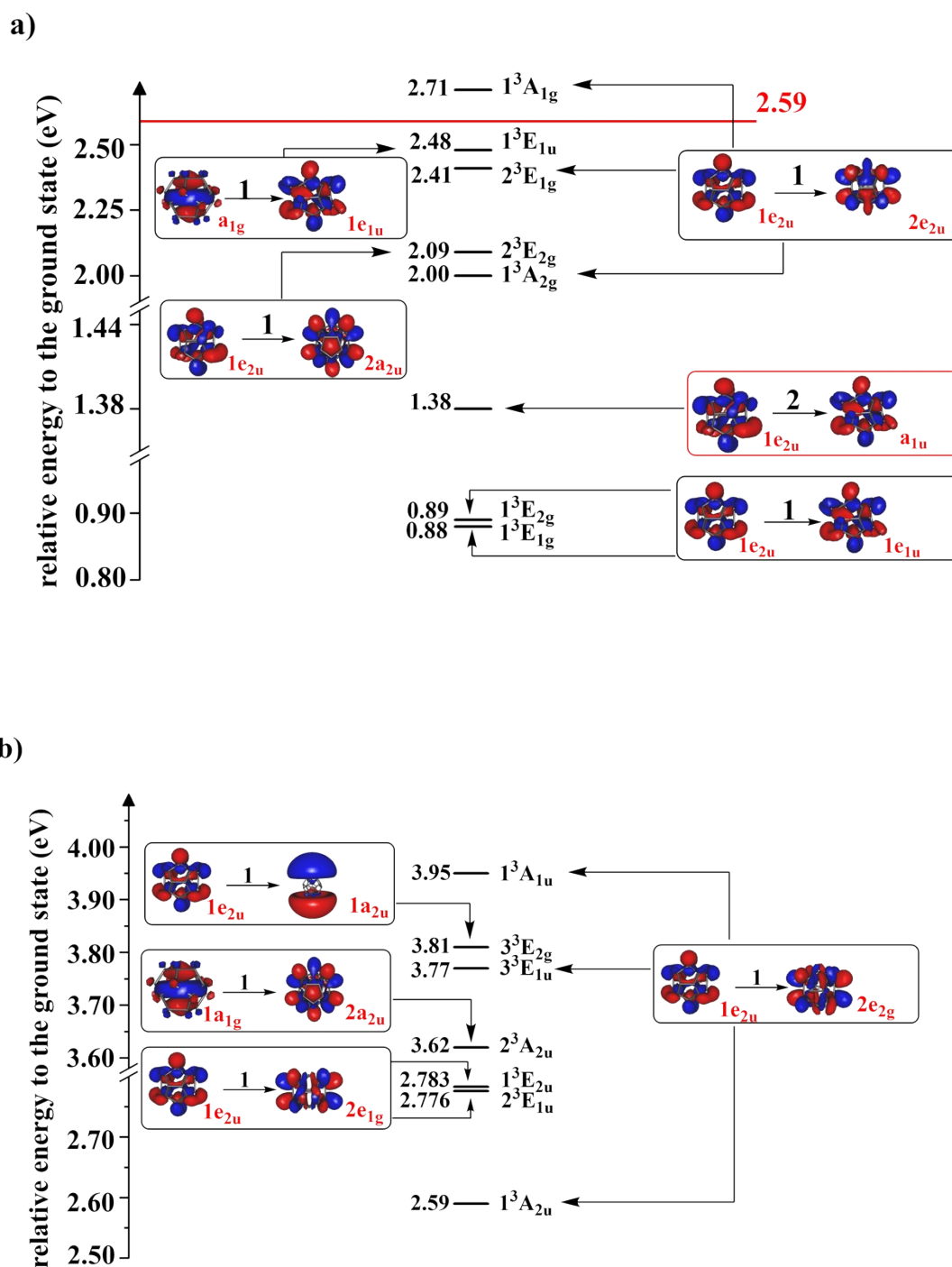


Figure S5. The relative energies of the singly-excited triplet states of  $Li@C_{20}^-$  relative to that of its global ground state. The states in black blocks are singly-excited triplet states and the doubly-excited singlet state is shown for comparison in a red block. The doubly-occupied

**HOMO of the doubly-excited state and the singly-occupied orbitals of the singly-excited states are shown. a) The excited states with a relative energy to the ground state between 0.5 and 2.5 eV. b) The excited states with a relative energy to the ground state between 2.5 and 4.0 eV. The irreducible representations of the orbitals and the states are also shown. The energies of the singly-excited states are vertical excitation energies based on the equilibrium geometry of the anion in its ground state. The energy of the doubly-excited state is obtained at its  $D_{5d}$  equilibrium geometry.**

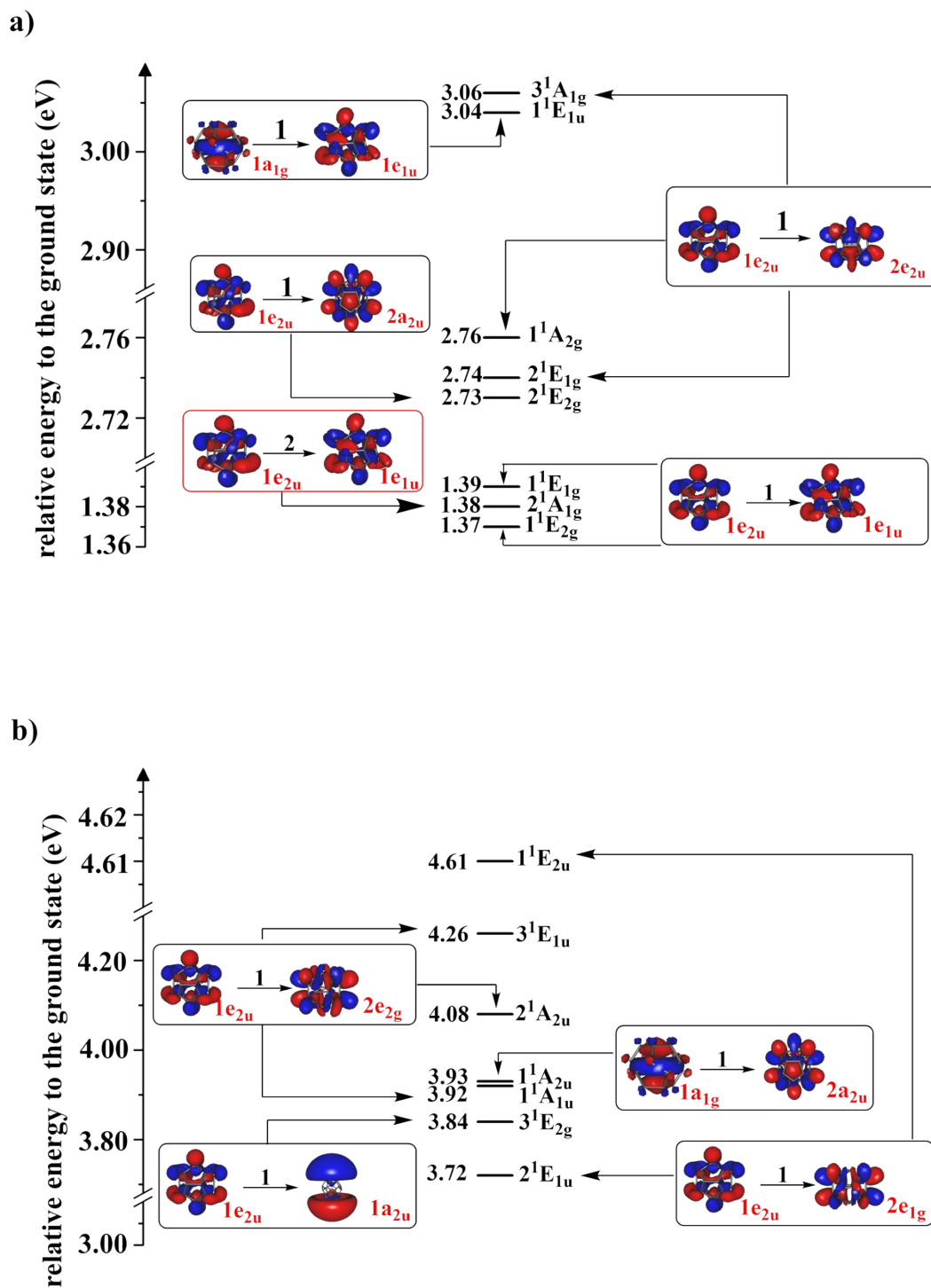


Figure S6. The energies of the excited singlet states of  $\text{Li}@C_{20}^-$  relative to that of its global ground state. The states in black and red blocks

are singly-excited singlet and doubly-excited singlet states, respectively. a) The excited states with a relative energy to the ground state between 1.0 and 3.0 eV. b) The excited states with a relative energy to the ground state between 3.0 and 4.2 eV. The irreducible representation of the orbitals and the states are also shown. For simplicity the orbitals of the ground state are shown in all boxes. The energies of the singly-excited states are vertical excitation energies based on the equilibrium geometry of the anion in its ground state. The energy of the doubly-excited state is obtained at its  $D_{5d}$  equilibrium geometry.

**Table S10. The frontier HF orbitals of the ground state of Li@C<sub>20</sub><sup>-</sup> at HF/cc-pVTZ level.**

<b>Occupied orbitals</b>				
<b>Orbital number</b>	<b>HF Orbital eigenvalue (a.u.)</b>	<b>HF Orbital eigenvalue (eV)</b>	<b>Irreducible representation</b>	<b>symbols in Figure S5/S6</b>
56+57	-0.238712	-6.495675	E2g	1e <sub>2g</sub>
58+59	-0.223383	-6.078550	E1g	1e <sub>1g</sub>
60	-0.145743	-3.965870	A1g	1a <sub>1g</sub>
61+62	-0.099573	-2.709521	E2u	1e <sub>2u</sub>
<b>Virtual orbitals</b>				
<b>Orbital number</b>	<b>HF Orbital eigenvalue (a.u.)</b>	<b>HF Orbital eigenvalue (eV)</b>	<b>Irreducible representation</b>	<b>symbols in Figure S5/S6</b>
63+64	0.142043	3.865188	E1u	1e <sub>1u</sub>
65	0.153227	4.169509	A2u	1a <sub>2u</sub>
66+67	0.157881	4.296157	E1u	2e <sub>1u</sub>
68	0.196743	5.353640	A1g	2a <sub>1g</sub>
69	0.206359	5.615314	A2u	2a <sub>2u</sub>
70+71	0.224254	6.102267	E2u	2e <sub>2u</sub>
72+73	0.260323	7.083745	E1g	2e <sub>1g</sub>
74+75	0.279731	7.611855	E2g	2e <sub>2g</sub>

## S8. Potential energy surface scan of low-lying closed-shell states of Li@C<sub>12</sub><sup>-</sup>

As mentioned in the main text, we scanned the potential energy surface of the low-lying closed-shell states of Li@C<sub>12</sub><sup>-</sup> anion. We scanned them along two minimum energy pathways,  $q_1$  and  $q_2$ . The polyynic D<sub>6h</sub> structure is obtained by geometry optimization keeping the contributed orbitals (18a<sub>1</sub>+3b<sub>1</sub>+14b<sub>2</sub>+3a<sub>2</sub>). The internal coordinate parameters used in Figure 3 of the main text are obtained using the following equation:

$$P_{final} = P_{polyynic} + (P_{C_{2v}} - P_{polyynic}) * q_1 \quad (\text{eq1})$$

where  $P_{final}$  are the parameters of the points used in Figure 3.  $P_{C_{2v}}$  and  $P_{polyynic}$ , which are shown in the Table S11, are the parameters of the C<sub>2v</sub> and polyynic D<sub>6h</sub> structures, respectively. Along  $q_1$ , we keep the working group as C<sub>2v</sub>.

Similarly, we obtained the internal coordinate parameters along  $q_2$  using the following equation:

$$P_{final} = P_{polyynic} + (P_{cumulenic} - P_{polyynic}) * q_2 \quad (\text{eq2})$$

where  $P_{final}$  are the parameters of the points used in Figure 3.  $P_{cumulenic}$  and  $P_{polyynic}$ , which are shown in the Table S12, are the parameters of cumulenic and polyynic D<sub>6h</sub> structures, respectively. Along the  $q_2$ , the working point group is C<sub>2h</sub> symmetry.

By changing the occupation numbers, one can obtain the ground and doubly-excited states. For example, in the  $q_1$  region of Figure 3, the  $1^1A_1$  ( $18 a_1+4 b_1+14 b_2+2 a_2$ ),  $2^1A_1$  ( $17 a_1+4 b_1+14 b_2+3 a_2$ ), and  $3^1A_1$  ( $18 a_1+3 b_1+14 b_2+3 a_2$ ) states possess different occupations. We also listed the HOMO, HOMO-1, and HOMO-2 orbitals of these three states at HF/cc-pVTZ level in Tables S13, S14, and S15, respectively. It is noteworthy that the three orbitals are different in different states and the same state would possess the same three highest occupied molecular orbitals along  $q_1$ . This finding shows the validation of our delta-SCF method.

In the  $q_2$  region of Figure 3, the state corresponding to  $2^1A_1$  and  $3^1A_1$  possess different occupations. Their three highest occupied orbitals at HF/cc-pVTZ level are shown in Table S16 and S17. However, the state  $1^1A_1$  possesses the same occupation numbers as  $3^1A_1$ . Due to the limitation of delta-SCF, we cannot obtain the energy of  $1^1A_1$  in the  $q_2$  region. Thus, there are only two curves in the  $q_2$  region. The change in geometry along  $q_2$ , i.e., from  $D_{6h}$  polyynic to  $D_{6h}$  cumulenic, is rather small, so that one can expect the variation of the energy of  $1^1A_1$  to be also rather moderate in the  $q_2$  region.

**Table S11. The internal coordinates of Li@C<sub>12</sub><sup>-</sup> anion in C<sub>2v</sub> symmetry. The parameters changed along the q<sub>1</sub> are marked bold.**

**Unit is Å.**

Li@C <sub>12</sub> <sup>-</sup>  C <sub>2v</sub> symmetry	Li	
	X 1 RX	
	C 1 RC1 2 A90	
	C 1 RC1 3 A1 2 D90	
	C 3 RC2 1 A2 4 D180	
	C 4 RC2 1 A2 5 D180	
	C 5 RC3 1 A3 3 D180	
	C 6 RC3 1 A3 4 D180	
	C 7 RC4 1 A4 5 D180	
	C 8 RC4 1 A4 6 D180	
	C 9 RC5 1 A5 7 D180	
	C 10 RC5 1 A5 8 D180	
	C 11 RC6 1 A6 9 D180	
	C 12 RC6 1 A6 10 D180	
	RX =	1.0000000000000000
	<b>RC1 =</b>	<b>2.141080330955184</b>
	A90 =	90.0000000000000000
	<b>A1 =</b>	<b>35.368253826291742</b>
	D90 =	90.0000000000000000
	<b>RC2 =</b>	<b>1.291452908929988</b>
<b>A2 =</b>	<b>83.674736736275321</b>	
D180 =	180.0000000000000000	
<b>RC3 =</b>	<b>1.315494851727502</b>	
<b>A3 =</b>	<b>107.598973791597459</b>	
<b>RC4 =</b>	<b>1.409778076064243</b>	
<b>A4 =</b>	<b>55.826604748063758</b>	
<b>RC5 =</b>	<b>1.231612652067053</b>	
<b>A5 =</b>	<b>74.001230172832805</b>	
<b>RC6 =</b>	<b>1.391888603532719</b>	
<b>A6 =</b>	<b>62.455206786282538</b>	



**Table S11. (continued)**

<p style="text-align: center;"><math>\text{Li@C}_{12}^-</math></p> <p style="text-align: center;">Polyynic <math>D_{6h}</math> (working group <math>C_{2v}</math> symmetry)</p>	<p>Li X 1 RX C 1 RC1 2 A90 C 1 RC1 3 A1 2 D90 C 3 RC2 1 A2 4 D180 C 4 RC2 1 A2 5 D180 C 5 RC3 1 A3 3 D180 C 6 RC3 1 A3 4 D180 C 7 RC4 1 A4 5 D180 C 8 RC4 1 A4 6 D180 C 9 RC5 1 A5 7 D180 C 10 RC5 1 A5 8 D180 C 11 RC6 1 A6 9 D180 C 12 RC6 1 A6 10 D180</p> <p>RX = 1.00000 A90 = 90.00000 D90 = 90.0000 D180 = 180.00000 <b>RC1 = 2.502600906</b> <b>A1 = 30.95454072</b> <b>RC2 = 1.25512426</b> <b>A2 = 75.47723373</b> <b>RC3 = 1.335668295</b> <b>A3 = 74.52273885</b> <b>RC4 = 1.255124308</b> <b>A4 = 75.47731372</b> <b>RC5 = 1.335668326</b> <b>A5 = 74.52267479</b> <b>RC6 = 1.255124142</b> <b>A6 = 75.4772469</b></p>
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**Table S12. The internal coordinates of  $\text{Li@C}_{12}^-$  anion in  $C_{2v}$  symmetry. The parameters changed along the  $q_1$  are marked bold.**

**Unit is Å.**

<p style="text-align: center;"><math>\text{Li@C}_{12}^-</math> cumulenic <math>D_{6h}</math></p>	<p>Li X 1 R12 C 1 R13 2 A90 C 1 R14 3 A314 2 D90 C 1 R13 3 A315 2 D90 C 1 R14 5 A314 2 D90 C 1 R13 5 A315 2 D90 C 1 R14 7 A314 2 D90 C 1 R13 7 A315 2 D90 C 1 R14 9 A314 2 D90 C 1 R13 9 A315 2 D90 C 1 R14 11 A314 2 D90 C 1 R13 11 A315 2 D90 C 1 R14 13 A314 2 D90</p> <p>R12 = 1.00000000 <b>R13 = 2.5746053907</b> <b>R14 = 2.3797598225</b> <b>A314 = 30.0000000000</b> A315 = 60.000 D90 = 90.00 A90 = 90.00</p>
<p style="text-align: center;"><math>\text{Li@C}_{12}^-</math> Polyynic <math>D_{6h}</math></p>	<p>Li X 1 R12 C 1 R13 2 A90 C 3 R34 1 A134 2 D90 C 1 R13 3 A315 2 ND90 C 5 R34 1 A134 2 D90 C 1 R13 5 A315 2 ND90 C 7 R34 1 A134 2 D90 C 1 R13 7 A315 2 ND90 C 9 R34 1 A134 2 D90 C 1 R13 9 A315 2 ND90 C 11 R34 1 A134 2 D90 C 1 R13 11 A315 2 ND90 C 13 R34 1 A134 2 D90</p> <p>R12 = 1.0000000000000000</p>

	A90 = 90.0000000000000000
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**Table S12. (continued)**

<p>Li@C<sub>12</sub><sup>-</sup></p> <p>Polyynic D<sub>6h</sub></p>	<b>R13 = 2.5026013</b>
	<b>R34 = 1.3356689</b>
	<b>A134 = 74.5227274</b>
	D90 = 90.0000000000000000
	A315 = 60.0000000000000000
	ND90 = -90.0000000000000000

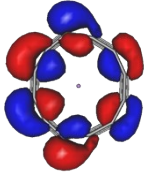
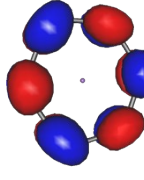
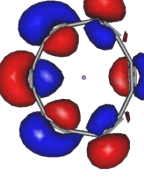
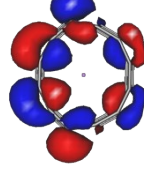
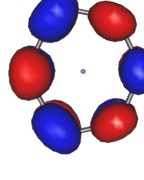
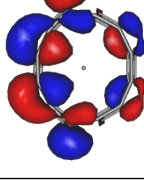
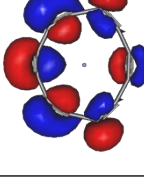
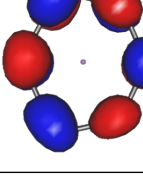
**Table S13. The HOMO, HOMO-1, HOMO-2 of the state  $1^1A_1$  of  $Li@C_{12}^-$  changes along  $q_1$  mode in  $C_{2v}$  symmetry ( $18a_1+4b_1+14b_2+2a_2$ ) at HF/cc-pVTZ level.**

$q_1$	Relative energy (eV)	Orbital	Orbital energy (a.u.)	Orbital energies (eV)	Symbol	Orbital images
0.0	3.44	HOMO	-0.050263	-1.37	$a_1$	
		HOMO-1	-0.074678	-2.03	$b_1$	
		HOMO-2	-0.116109	-3.16	$b_2$	
0.1	2.96	HOMO	-0.060423	-1.64	$a_1$	
		HOMO-1	-0.080833	-2.20	$b_1$	
		HOMO-2	-0.113173	-3.08	$b_2$	

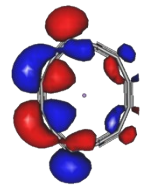
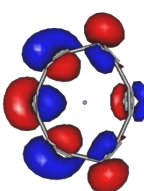
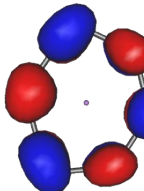
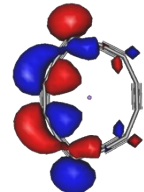
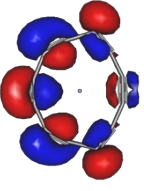
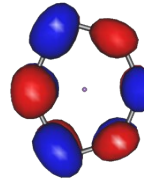
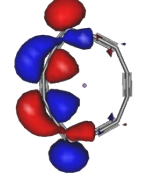
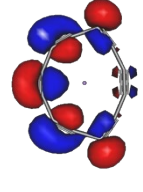
**Table S13. (continued)**

0.2	2.49	HOMO	-0.073562	-2.00	a <sub>1</sub>	
		HOMO-1	-0.086726	-2.36	b <sub>1</sub>	
		HOMO-2	-0.112940	-3.07	a <sub>2</sub>	
0.3	2.04	HOMO	-0.087203	-2.37	a <sub>1</sub>	
		HOMO-1	-0.092292	-2.51	b <sub>1</sub>	
		HOMO-2	-0.113881	-3.10	b <sub>2</sub>	
0.4	1.61	HOMO	-0.097575	-2.66	b <sub>1</sub>	
		HOMO-1	-0.100834	-2.74	a <sub>1</sub>	

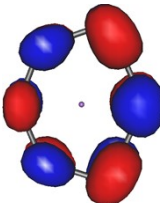
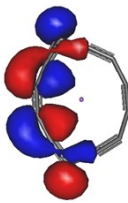
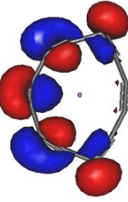
**Table S13. (continued)**

0.4	1.61	HOMO-2	-0.115813	-3.15	b <sub>2</sub>	
0.5	1.21	HOMO	-0.102615	-2.79	b <sub>1</sub>	
		HOMO-1	-0.114164	-3.11	a <sub>1</sub>	
		HOMO-2	-0.118633	-3.23	b <sub>2</sub>	
0.6	0.83	HOMO	-0.107455	-2.92	b <sub>1</sub>	
		HOMO-1	-0.122191	-3.32	b <sub>2</sub>	
		HOMO-2	-0.126978	-3.46	a <sub>1</sub>	
0.7	0.50	HOMO	-0.112138	-3.05	b <sub>1</sub>	

**Table S13. (continued)**

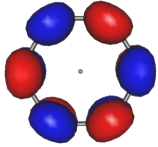
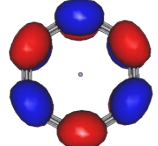
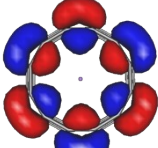
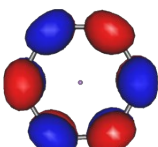
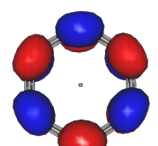
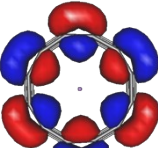
0.7	0.50	HOMO-1	-0.126285	-3.44	b <sub>2</sub>	
		HOMO-2	-0.139139	-3.79	a <sub>1</sub>	
0.8	0.24	HOMO	-0.116703	-3.18	b <sub>1</sub>	
		HOMO-1	-0.130660	-3.56	b <sub>2</sub>	
		HOMO-2	-0.150582	-4.10	a <sub>1</sub>	
0.9	0.07	HOMO	-0.121176	-3.30	b <sub>1</sub>	
		HOMO-1	-0.135016	-3.67	b <sub>2</sub>	
		HOMO-2	-0.161300	-4.39	a <sub>1</sub>	

**Table S13. (continued)**

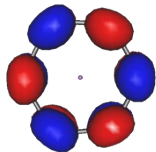
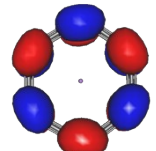
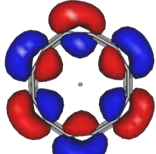
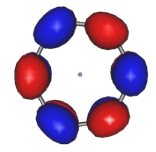
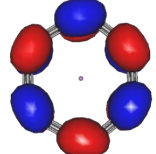
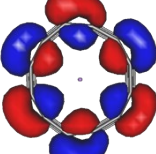
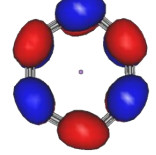
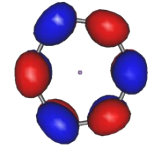
1.0	0.00	HOMO	-0.125571	-3.42	$b_1$	
		HOMO-1	-0.139003	-3.78	$b_2$	
		HOMO-2	-0.171314	-4.66	$a_1$	



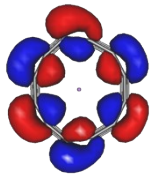
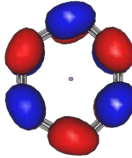
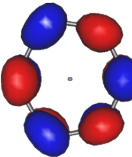
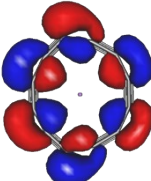
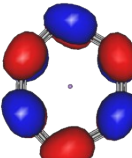
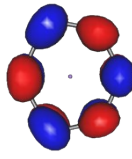
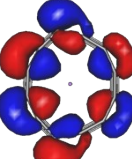
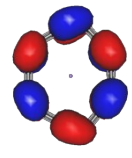
**Table S14. The HOMO, HOMO-1, HOMO-2 of the state  $2^1A_1$  of  $\text{Li}@C_{12}^-$  changes along  $q_1$  mode in  $C_{2v}$  symmetry ( $17a_1+4b_1+14b_2+3a_2$ ) at HF/cc-pVTZ level.**

$q_1$	Relative energy (eV)	Orbital	Orbital energy (a.u.)	Orbital energies (eV)	Symbol	Orbital images
0.0	1.09	HOMO	-0.058182	-1.58	$b_1$	
		HOMO-1	-0.104108	-2.83	$a_2$	
		HOMO-2	-0.115066	-3.13	$b_2$	
0.1	1.13	HOMO	-0.065161	-1.77	$b_1$	
		HOMO-1	-0.098874	-2.69	$a_2$	
		HOMO-2	-0.110453	-3.01	$b_2$	

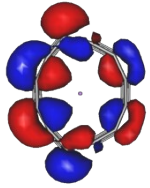
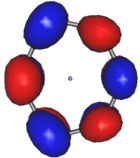
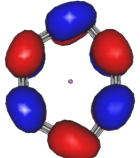
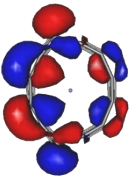
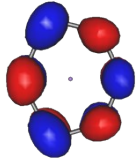
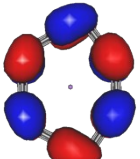
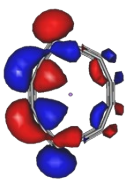
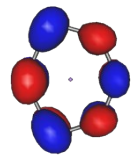
**Table S14. (continued)**

0.2	1.26	HOMO	-0.072160	-1.96	$b_1$	
		HOMO-1	-0.093989	-2.56	$a_2$	
		HOMO-2	-0.106568	-2.90	$b_2$	
0.3	1.46	HOMO	-0.078999	-2.15	$b_1$	
		HOMO-1	-0.089339	-2.43	$a_2$	
		HOMO-2	-0.103511	-2.82	$b_2$	
0.4	1.72	HOMO	-0.084815	-2.31	$b_2$	
		HOMO-1	-0.085507	-2.33	$b_1$	

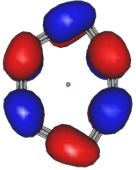
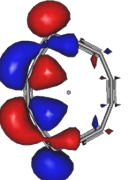
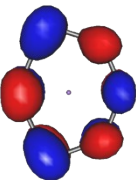
**Table S14. (continued)**

0.4	1.72	HOMO-2	-0.101375	-2.76	$a_2$	
0.5	2.04	HOMO	-0.080324	-2.73	$a_2$	
		HOMO-1	-0.091561	-2.49	$b_1$	
		HOMO-2	-0.080324	-2.19	$b_2$	
0.6	2.41	HOMO	-0.075776	-2.72	$a_2$	
		HOMO-1	-0.097121	-2.64	$b_1$	
		HOMO-2	-0.100040	-2.06	$b_2$	
0.7	2.85	HOMO	-0.071069	-1.93	$a_2$	

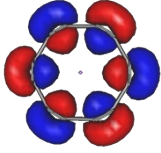
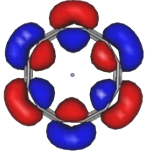
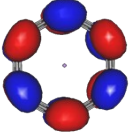
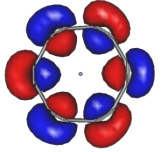
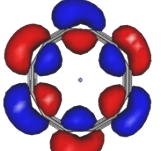
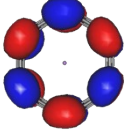
**Table S14. (continued)**

0.7	2.85	HOMO-1	-0.100716	-2.74	$b_2$	
		HOMO-2	-0.102246	-2.78	$b_1$	
0.8	3.35	HOMO	-0.107065	-1.80	$a_2$	
		HOMO-1	-0.102002	-2.78	$b_2$	
		HOMO-2	-0.066099	-2.91	$b_1$	
0.9	3.93	HOMO	-0.060773	-1.65	$a_2$	
		HOMO-1	-0.103538	-2.82	$b_2$	
		HOMO-2	-0.111733	-3.04	$b_1$	

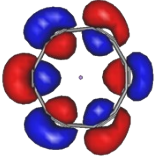
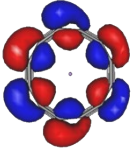
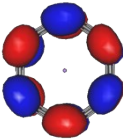
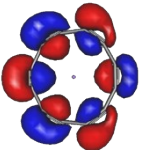
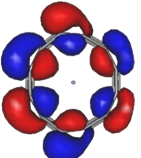
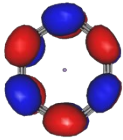
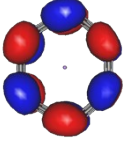
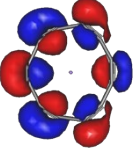
**Table S14. (continued)**

1.0	4.61	HOMO	-0.055037	-1.50	$a_2$	
		HOMO-1	-0.104879	-2.85	$b_2$	
		HOMO-2	-0.116402	-3.17	$b_1$	

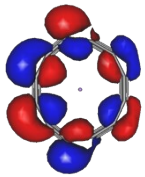
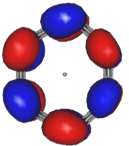
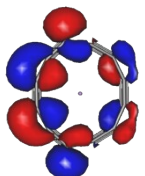
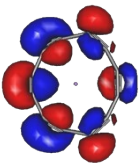
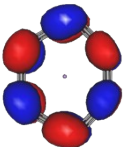
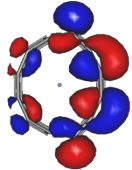
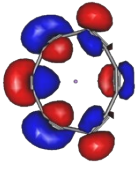
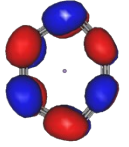
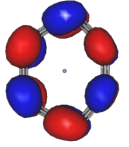
**Table S15. The HOMO, HOMO-1, HOMO-2 of the state  $3^1A_1$  of  $Li@C_{12}^-$  changes along  $q_1$  mode in  $C_{2v}$  symmetry ( $18a_1+3b_1+14b_2+3a_2$ ) at HF/cc-pVTZ level.**

$q_1$	Relative energy (eV)	Orbital	Orbital energy (a.u.)	Orbital energies (eV)	Symbol	Orbital images
0	1.19	HOMO	-0.057425	-1.56	$a_1$	
		HOMO-1	-0.102411	-2.79	$b_2$	
		HOMO-2	-0.126551	-3.44	$a_2$	
0.1	1.20	HOMO	-0.067066	-1.82	$a_1$	
		HOMO-1	-0.099954	-2.72	$b_2$	
		HOMO-2	-0.121271	-3.30	$a_2$	

**Table S15. (continued)**

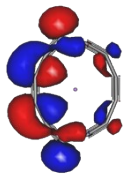
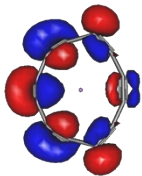
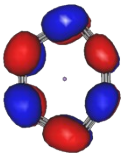
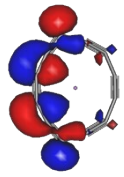
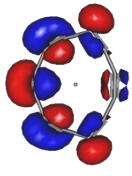
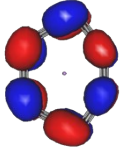
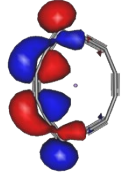
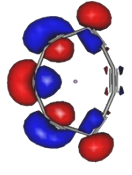
0.2	1.22	HOMO	-0.080215	-2.18	a <sub>1</sub>	
		HOMO-1	-0.101581	-2.76	b <sub>2</sub>	
		HOMO-2	-0.116189	-3.16	a <sub>2</sub>	
0.3	1.24	HOMO	-0.094234	-2.56	a <sub>1</sub>	
		HOMO-1	-0.105163	-2.86	b <sub>2</sub>	
		HOMO-2	-0.111225	-3.03	a <sub>2</sub>	
0.4	1.27	HOMO	-0.106166	-2.89	a <sub>2</sub>	
		HOMO-1	-0.108092	-2.94	a <sub>1</sub>	

**Table S15. (continued)**

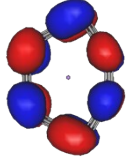
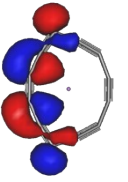
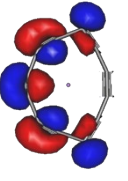
0.4	1.27	HOMO-2	-0.109895	-2.99	$b_2$	
0.5	1.33	HOMO	-0.100845	-2.74	$a_2$	
		HOMO-1	-0.115384	-3.14	$b_2$	
		HOMO-2	-0.121402	-3.30	$a_1$	
		HOMO	-0.095159	-2.59	$a_2$	
0.6	1.42	HOMO-1	-0.121315	-3.30	$b_2$	
		HOMO-2	-0.134034	-3.65	$a_1$	
		HOMO	-0.089052	-2.42	$a_2$	
0.7	1.57	HOMO	-0.089052	-2.42	$a_2$	



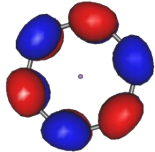
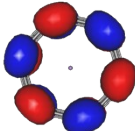
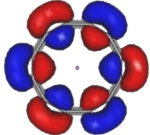
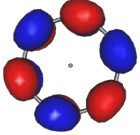
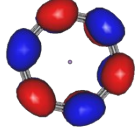
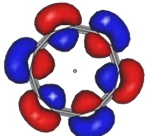
**Table S15. (continued)**

0.7	1.57	HOMO-1	-0.127370	-3.47	b <sub>2</sub>	
		HOMO-2	-0.145988	-3.97	a <sub>1</sub>	
0.8	1.78	HOMO	-0.082501	-2.24	a <sub>2</sub>	
		HOMO-1	-0.133221	-3.63	b <sub>2</sub>	
		HOMO-2	-0.157323	-4.28	a <sub>1</sub>	
0.9	2.09	HOMO	-0.075495	-2.05	a <sub>2</sub>	
		HOMO-1	-0.138517	-3.77	b <sub>2</sub>	
		HOMO-2	-0.168118	-4.57	a <sub>1</sub>	

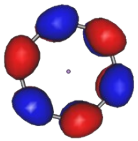
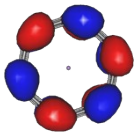
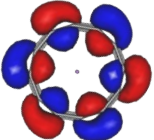
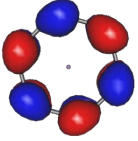
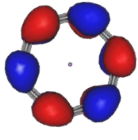
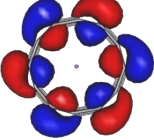
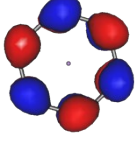
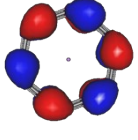
**Table S15. (continued)**

1	2.51	HOMO	-0.068038	-1.85	a <sub>2</sub>	
		HOMO-1	-0.142878	-3.89	b <sub>2</sub>	
		HOMO-2	-0.178451	-4.86	a <sub>1</sub>	

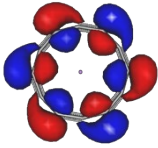
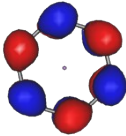
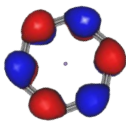
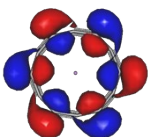
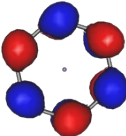
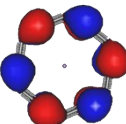
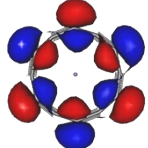
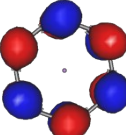
**Table S16. The HOMO, HOMO-1, HOMO-2 of the doubly-excited state (green curve in Figure 3 of the main text) changes along  $q_2$  mode in  $C_{2h}$  symmetry ( $16a_g+3a_u+15b_u+4b_g$ ) at HF/cc-pVTZ level.**

$q_2$	Relative energy (eV)	Orbital	Orbital energy (a.u.)	Orbital energies (eV)	Symbol	Orbital images
0	1.09	HOMO	-0.058182	-1.58	$b_g$	
		HOMO-1	-0.104108	-2.83	$b_g$	
		HOMO-2	-0.115066	-3.13	$b_u$	
0.1	1.09	HOMO	-0.060666	-1.65	$b_g$	
		HOMO-1	-0.101947	-2.77	$b_g$	
		HOMO-2	-0.112917	-3.07	$b_u$	

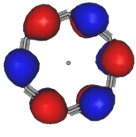
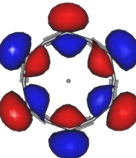
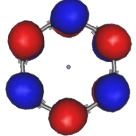
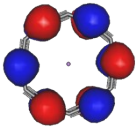
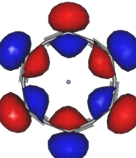
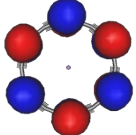
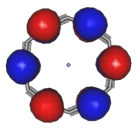
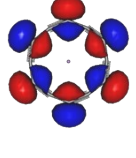
**Table S16. (continued)**

0.2	1.10	HOMO	-0.062198	-1.69	$b_g$	
		HOMO-1	-0.101427	-2.76	$b_g$	
		HOMO-2	-0.111867	-3.04	$b_u$	
0.3	1.12	HOMO	-0.062780	-1.71	$b_g$	
		HOMO-1	-0.102436	-2.79	$b_g$	
		HOMO-2	-0.112083	-3.05	$b_u$	
0.4	1.13	HOMO	-0.063085	-1.72	$b_g$	
		HOMO-1	-0.103983	-2.83	$b_g$	

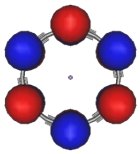
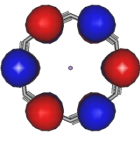
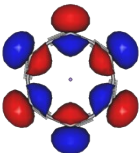
**Table S16. (continued)**

0.4	1.13	HOMO-2	-0.113608	-3.09	$b_u$	
0.5	1.14	HOMO	-0.063718	-1.73	$b_g$	
		HOMO-1	-0.105118	-2.86	$b_g$	
		HOMO-2	-0.116304	-3.16	$b_u$	
0.6	1.13	HOMO	-0.064795	-1.76	$b_g$	
		HOMO-1	-0.105545	-2.87	$b_g$	
		HOMO-2	-0.119900	-3.26	$b_u$	
0.7	1.10	HOMO	-0.066144	-1.80	$b_g$	

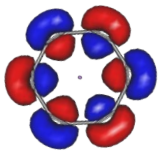
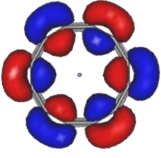
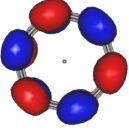
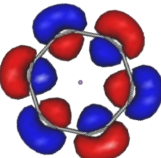
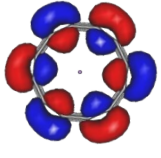
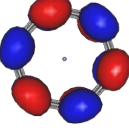
**Table S16. (continued)**

0.7	1.10	HOMO-1	-0.105413	-2.87	$b_g$	
		HOMO-2	-0.124108	-3.38	$b_u$	
0.8	1.06	HOMO	-0.067548	-1.84	$b_g$	
		HOMO-1	-0.104985	-2.86	$b_g$	
		HOMO-2	-0.128699	-3.50	$b_u$	
0.9	1.03	HOMO	-0.068826	-1.87	$b_g$	
		HOMO-1	-0.104490	-2.84	$b_g$	
		HOMO-2	-0.133516	-3.63	$b_u$	

**Table S16. (continued)**

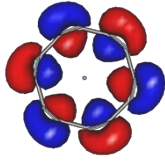
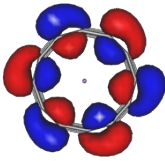
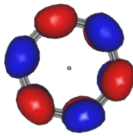
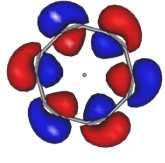
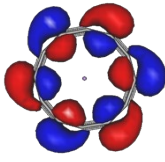
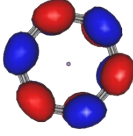
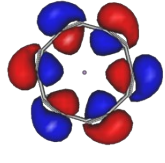
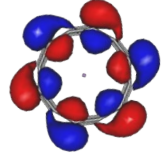
1	1.02	HOMO	-0.069839	-1.90	$b_g$	
		HOMO-1	-0.104105	-2.83	$b_g$	
		HOMO-2	-0.138452	-3.77	$b_u$	

**Table S17. The HOMO, HOMO-1, HOMO-2 of the doubly-excited state (blue curve in Figure 3 of the main text) of  $\text{Li}@\text{C}_{12}^-$  changes along  $q_2$  mode in  $\text{C}_{2h}$  symmetry ( $16a_g+3a_u+16b_u+3b_g$ ) at HF/cc-pVTZ level.**

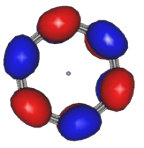
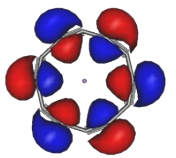
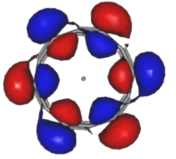
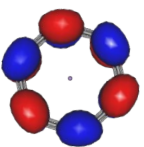
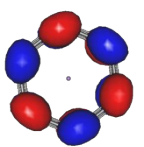
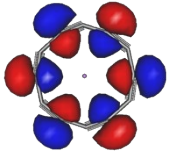
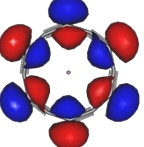
$q_2$	Relative energy (eV)	Orbital	Orbital energy (a.u.)	Orbital energies (eV)	Symbol	Orbital images
0.0	1.19	HOMO	-0.057425	-1.56	$b_u$	
		HOMO-1	-0.102411	-2.79	$b_u$	
		HOMO-2	-0.126551	-3.44	$b_g$	
0.1	1.21	HOMO	-0.059706	-1.62	$b_u$	
		HOMO-1	-0.100126	-2.72	$b_u$	
		HOMO-2	-0.123866	-3.37	$b_g$	

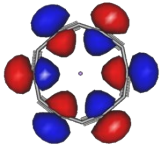


**Table 17. (continued)**

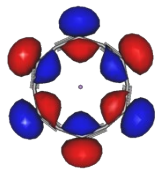
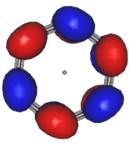
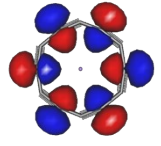
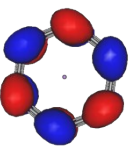
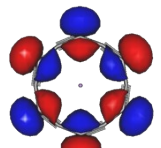
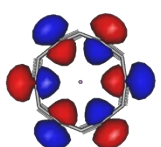
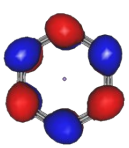
0.2	1.25	HOMO	-0.060946	-1.66	$b_u$	
		HOMO-1	-0.099046	-2.70	$b_u$	
		HOMO-2	-0.121170	-3.30	$b_g$	
0.3	1.32	HOMO	-0.061014	-1.66	$b_u$	
		HOMO-1	-0.099302	-2.70	$b_u$	
		HOMO-2	-0.118468	-3.22	$b_g$	
0.4	1.42	HOMO	-0.060071	-1.63	$b_u$	
		HOMO-1	-0.100730	-2.74	$b_u$	

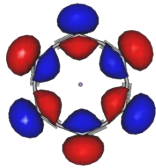
**Table S17. (continued)**

0.4	1.42	HOMO-2	-0.115765	-3.15	$b_g$	
0.5	1.54	HOMO	-0.058528	-1.59	$b_u$	
		HOMO-1	-0.102926	-2.80	$b_u$	
		HOMO-2	-0.113069	-3.08	$b_g$	
0.6	1.69	HOMO	-0.056908	-1.55	$b_u$	
		HOMO-1	-0.105373	-2.87	$b_u$	
		HOMO-2	-0.110394	-3.00	$b_g$	

0.7	1.87	HOMO	-0.055831	-1.52	$b_u$	
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**Table S17. (continued)**

0.7	1.87	HOMO-1	-0.107476	-2.92	$b_u$	
		HOMO-2	-0.107762	-2.93	$b_g$	
0.8	2.07	HOMO	-0.056098	-1.53	$b_u$	
		HOMO-1	-0.105231	-2.86	$b_g$	
		HOMO-2	-0.108472	-2.95	$b_u$	
0.9	2.29	HOMO	-0.058271	1.59	$b_u$	
		HOMO-1	-0.103023	-2.80	$b_g$	

		HOMO-2	-0.107828	-2.93	$b_u$	
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### S9. CASSCF calculations on the ground and excited states of $\text{Li}@C_{12}^-$ in $C_{2v}$ symmetry

In the main text, our calculations are based on the single-reference CCSD and EOM-CCSD methods. To better understand the situation, it is relevant to check the amount of the multi-configurational character of the electronic states involved. We employed the state-averaged complete active space self-consistent field (CASSCF) method using the MOLPRO software package,<sup>[10]</sup> which is a good tool to study multi-configurational effects.

We ran the CASSCF (6e, 8o) with eight active orbitals (orbital 36-43 in Table S5) and six active electrons, and calculated 20 states at the equilibrium geometry of the ground state of  $\text{Li}@C_{12}^-$  in  $C_{2v}$  symmetry. The results are shown in Table S18. The ground and doubly-excited states  $1^1A_1$ ,  $2^1A_1$  and  $3^1A_1$  were found among these 10 states. All three states are found to be mainly dominated by a single reference as indicated by the leading coefficient 0.959 ( $1^1A_1$ ), 0.820 ( $2^1A_1$ ), 0.916 ( $3^1A_1$ ). The

single-reference character justifies the use of the CCSD and EOM-CCSD methods employed in this work.

**Table S18. Coefficient of the CI vector of the  $1^1A_1$ ,  $2^1A_1$ , and  $3^1A_1$  states calculated by CAS (6,8). The leading coefficients of states  $1^1A_1$ ,  $2^1A_1$ , and  $3^1A_1$  are marked in Bold.**

	Coefficient						
<b><math>1^1A_1</math></b>	<b>0.959</b>	-0.017	0.009	0.158	-0.010	0.012	0.035
	-0.016	-0.002	-0.003	0.004	-0.078	0.015	0.001
	0.049	0.001	-0.018	-0.001	0.002	-0.008	
<b><math>2^1A_1</math></b>	-0.006	-0.274	-0.007	-0.126	-0.004	0.007	-0.006
	-0.004	0.003	-0.004	-0.027	-0.012	<b>0.820</b>	0.029
	0.089	-0.001	-0.005	0.047	-0.002	-0.145	
<b><math>3^1A_1</math></b>	-0.031	<b>0.916</b>	0.015	0.244	0.016	-0.016	0.015
	0.012	0.001	0.002	-0.009	-0.002	0.247	0.005
	0.032	-0.001	-0.004	0.009	-0.001	-0.013	

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