Supporting Information

Structural evolution and electronic properties of anionic carbon nitrogen clusters

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Table S1. The bond lengths Re (in Å) for N-N in N_2 and C-N in HCN and the dissociation energies De (in eV) for N_2 and CN were calculated at the M06-2X/6-311+G(d) level and compared with experimental values.

	N_2		HC-N		CN	
	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.
Re	1.090	1.097[a]	1.144	1.157[b]		
De	9.602	9.756[c]			7.524	7.66±0.05[d]

[a]See Ref.1. [b]See Ref.2. [c]See Ref.3. [d]See Ref.4.

Table S2. The electron affinity potential energies EA (in eV) of C, N_3, and CN were calculated at the M06-2X/6-311+G(d) level and compared with experimental values.

	C		N_3		CN	
EA	theory	exptl	theory	exptl	theory	exptl
	1.248	1.262[e]	2.749	2.7 ± 0.1[e]	4.080	3.862[e]

[e]See Ref.5.

Table S3. The calculated total energies and lowest frequencies of all ground states and metastable isomers of optimized CN_n^- clusters (n =4-16).

n	Ground state (na)/eV	Frequency (na)/cm^{-1}	Isomer (nb) /eV	Frequency (nb)/cm^{-1}	Isomer (nc) /eV	Frequency (nc)/cm^{-1}
4	-6993.284	177.40	-6992.219	63.18	-6991.982	94.30
5	-8482.639	85.35	-8481.699	283.38	-8481.625	166.86
6	-9974.864	119.30	-9971.240	99.15	-9969.954	92.63
7	-11461.691	50.04	-11461.130	111.02	-11459.832	92.47
8	-12950.872	51.91	-12949.806	48.37	-12948.751	86.31
9	-14440.029	122.48	-14438.855	62.12	-14437.665	96.08
10	-15930.689	35.49	-15930.217	37.33	-15926.453	26.95
11	-17418.337	-76.00	-17416.124	40.80	-17412.455	117.83
12	-18908.925	39.57	-18907.784	24.09	-18903.297	49.59
13	-20394.279	22.44	-20393.196	67.91	-20393.091	44.99
14	-21884.246	80.83	-21882.142	21.44	-21880.058	54.14
15	-23370.076	50.91	-23368.677	27.19	-23367.789	40.00
16	-24860.863	19.57	-24859.940	63.10	-24858.015	43.06

Table S4. The calculated the detachment energy of a single N atom ($\Delta_N E$) and a single N_2 molecule (ΔE_{N_2}) for the ground state structures of anionic CN_n^- (n = 4-16) clusters as a function of N atoms.

n	$\Delta_N E$ (eV)	ΔE_{N_2} (eV)
4		
5	3.888	
6	6.758	1.045
7	1.361	-1.482
8	3.715	-4.526
9	3.691	-2.197
10	5.194	-0.717
11	2.181	-2.227
12	5.123	-2.298
13	-0.113	-4.592
14	4.501	-5.214
15	0.364	-4.737
16	5.321	-3.916

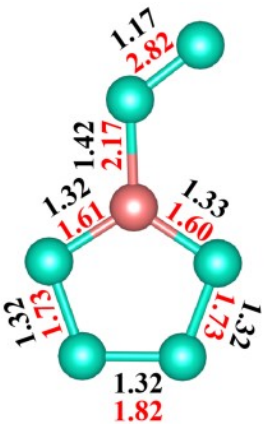

Fig. S1 Calculated bond lengths (R, Å) and different bond orders (WBIs) {MBO} [WBI on the basis of orthogonalization] of CN_6^- clusters at the M06-2X/6-311+G(d) level, shown in black and red, respectively.

Formula for the detachment energy of a single N atom：

$$\Delta E_N(CN_n^-) = E(CN_{n-1}^-) + E(N) - E(CN_n^-)$$

where E is the total energy of the clusters or atoms shown in parentheses.

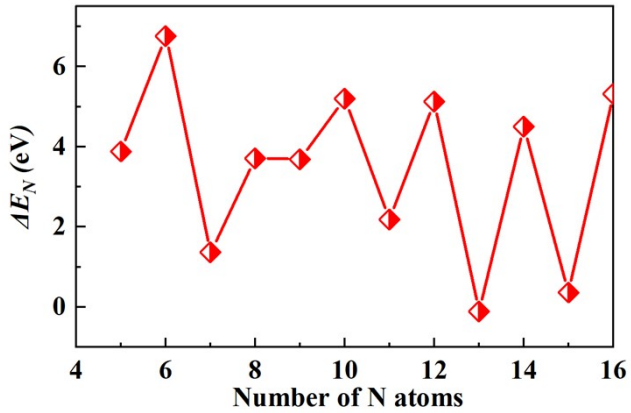

Fig. S2 Detachment energy of a single N atom for the ground state structures of anionic CN_n^- (n = 4-16) clusters as a function of N atoms.

Formula for the detachment energy of a single N_2 molecule：

$$\Delta E_{N_2}(CN_n^-) = E(CN_{n-2}^-) + E(N_2) - E(CN_n^-)$$

where E is the total energy of the clusters or atoms shown in parentheses.

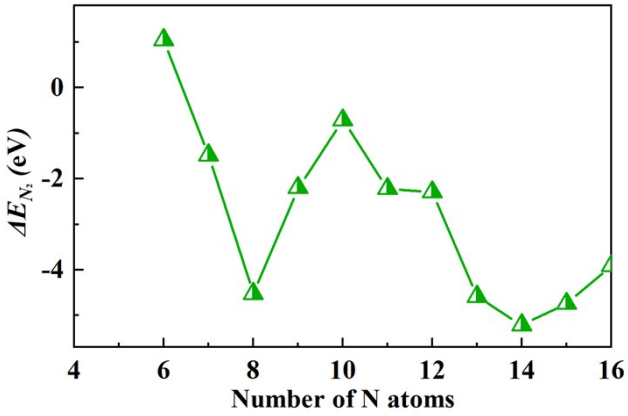

Fig. S3 Detachment energy of a single N_2 molecule for the ground state structures of anionic CN_n^- (n = 4-16) clusters as a function of N atoms.

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