Electronic Supplementary Material (ESI) for RSC Advances.

Structural Evolution of LiN_n^+ (n=2, 4, 6, 8, and 10) Clusters: Mass Spectrometry and Theoretical Calculations

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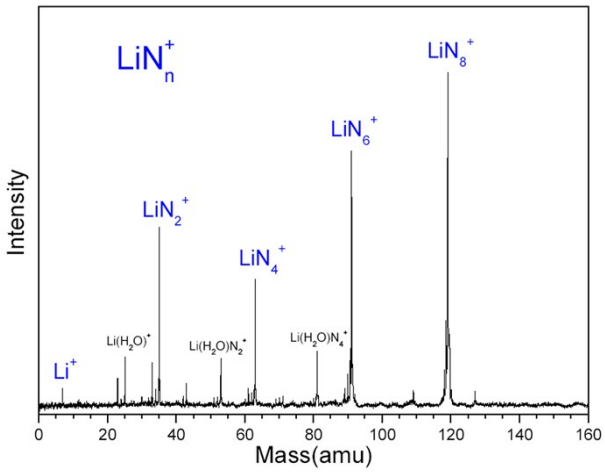

Fig.S1 Typical mass spectrum of Li-N clusters generated by laser ablation of a LiF target with N_2 as carrier gas

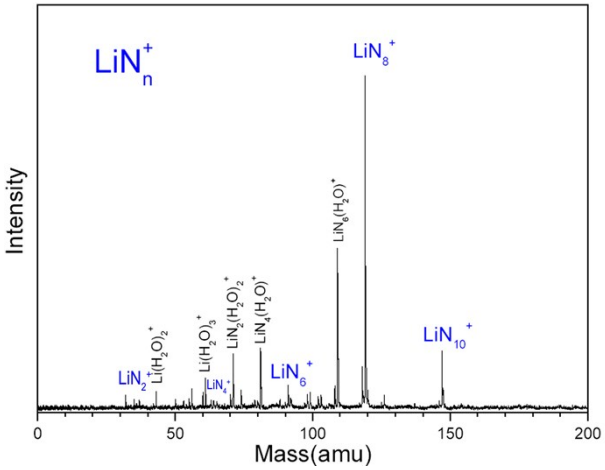

Fig.S2 Typical mass spectrum of Li-N clusters generated by laser ablation of a LiF:ZrN=4:1 mixture target with N_2 as carrier gas

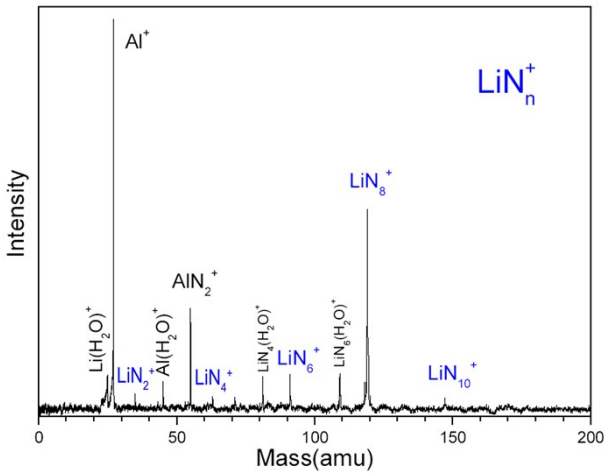

Fig.S3 Typical mass spectrum of Li-N clusters generated by laser ablation of a

LiF:AlN=2:1 mixture target with N_2 as carrier gas

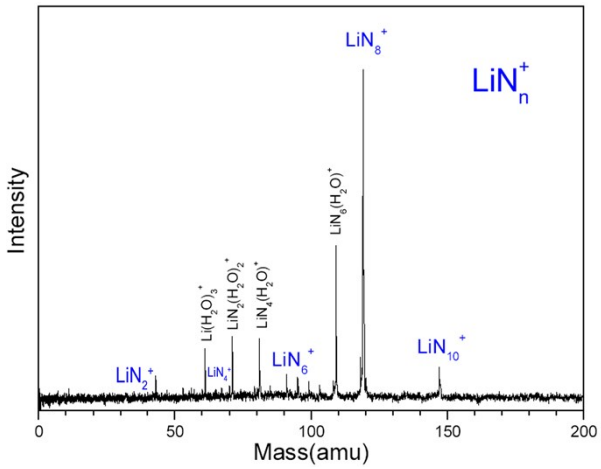

Fig.S4 Typical mass spectrum of Li-N clusters generated by laser ablation of a LiF:BN=2:1 mixture target with N_2 as carrier gas

Table S1 NBO data for LiN_2^+ (LP: lone pair; BD: bonding; BD*: antibonding;E_2: stabilization energy)

NPA(Natural Population Analysis)		
Atom	Natural Electron Configuration	Natural Charge
Li	$2s^{0.01}2p^{0.01}$	0.976
N2	$2s^{1.57}2p^{3.57}3s^{0.03}3p^{0.01}$	-0.193
N3	$2s^{1.61}2p^{3.13}3s^{0.02}3p^{0.01}3d^{0.02}$	0.217
Main BO(Bond Orbital) analysis		
Bond Orbital	Occupancy(e)	Hybridization
BD(1)N2-N3	1.99988	N2: p 99.86%; N3: p 99.40%
BD(2)N2-N3	1.99988	N2: p 99.86%; N3: p 99.40%
BD(3)N2-N3	1.99876	N2: s 42.85%, p 57.08%; N3: s 37.26%, p 62.27%
LP(1)N2	1.97567	s 58.46%, p 41.53%
LP*(1)Li1	0.02364	s 42.67%, p 57.2%
LP(1)N3	1.98779	s 63.57%, p 36.36%
BD*(3)N2-N3	0.00041	s 42.85%, p 57.08%
Main second order Perturbation analysis		
Donor	Acceptor	E_2(kcal/mol)
LP(1)N2	LP*(1)Li1	8.93

Table S2 NBO data for LiN_4^+ (LP: lone pair; BD: bonding; BD*: antibonding;E_2: stabilization energy)

NPA(Natural Population Analysis)		
Atom	Natural Electron Configuration	Natural Charge
Li	$2s^{0.05}2p^{0.06}$	0.896
N2	$2s^{1.56}2p^{3.56}3s^{0.03}3p^{0.01}$	-0.155
N3	$2s^{1.61}2p^{3.15}3s^{0.02}3p^{0.01}3d^{0.02}$	0.207
Main BO(Bond Orbital) analysis		
Bond Orbital	Occupancy(e)	Hybridization
BD(1)N2-N3	1.99957	N2: p 99.86%; N3: p 99.40%
BD(2)N2-N3	1.99957	N2: p 99.86%; N3: p 99.40%
BD(3)N2-N3	1.99881	N2: s 42.42%, p 57.50%; N3: s 37.39%, p 62.15%
LP(1)N2	1.97567	s 58.92%, p 41.07%
LP(1)N3	1.97567	s 63.36%, p 36.57%
LP*(1)Li	0.05385	p 100.00%
LP*(2)Li	0.04885	s 99.87%
BD*(3)N2-N3	0.00041	s 42.42%, p 57.50%
Main second order Perturbation analysis		
Donor	Acceptor	E_2(kcal/mol)

LP(1)N2	LP*(1)Li1	12.35
LP(1)N2	LP*(2)Li1	10.30
LP(1)N4	LP*(1)Li1	12.35
LP(1)N4	LP*(2)Li1	10.30

Table S3 NBO data for LiN_6^+ (LP: lone pair; BD: bonding; BD*: antibonding; E_2: stabilization energy)

NPA(Natural Population Analysis)		
Atom	Natural Electron Configuration	Natural Charge
Li1	$2s^{0.10}2p^{0.14}$	0.762
N2	$2s^{1.55}2p^{3.52}3s^{0.03}3p^{0.01}$	-0.111
N3	$2s^{1.61}2p^{3.16}3s^{0.01}3p^{0.01}3d^{0.02}$	0.191
Main BO(Bond Orbital) analysis		
Bond Orbital	Occupancy(e)	Hybridization
BD(1)N2-N3	1.99945	N1: s 42.05%, p 57.87%; N2: s 37.62%, p 61.92%
BD(2)N2-N3	1.99900	N1: p 99.85%; N2: p 99.40%
BD(3)N2-N3	1.99889	N1: p 99.85%; N2: p 99.41%
LP*(1)Li1	0.10058	p 99.99%
LP*(2)Li1	0.06760	p 99.96%
LP*(3)Li1	0.06760	p 99.96%
LP*(4)Li1	0.00311	p 100.00%
LP(1)N2	1.92262	s 59.36%, p 40.63%
LP(1)N3	1.98556	s 63.14%, p 36.79%
BD*(1)N2-N3	0.00042	s 42.05%, p 57.87%
BD*(1)N2-N3	0.00020	p 99.85%
Main second order Perturbation analysis		
Donor	Acceptor	E_2(kcal/mol)
LP(1)N2	LP*(1)Li1	16.04
LP(1)N2	LP*(3)Li1	21.33
LP(1)N4	LP*(1)Li1	16.04
LP(1)N4	LP*(2)Li1	15.99
LP(1)N4	LP*(3)Li1	5.33
LP(1)N6	LP*(1)Li1	16.04
LP(1)N6	LP*(2)Li1	15.99
LP(1)N6	LP*(3)Li1	5.33

Table S4 NBO data for LiN_8^+ (LP: lone pair; BD: bonding; BD*: antibonding;E_2: stabilization energy)

NPA(Natural Population Analysis)

Atom	Natural Electron Configuration	Natural Charge
Li1	$2s^{0.15}2p^{0.25}$	0.593
N2	$2s^{1.54}2p^{3.49}3s^{0.03}3p^{0.01}$	-0.076
N3	$2s^{1.61}2p^{3.18}3s^{0.01}3p^{0.01}3d^{0.02}$	0.178
Main BO(Bond Orbital) analysis		
Bond Orbital	Occupancy(e)	Hybridization
BD(1)N2-N3	1.99958	N2: s 41.92%, p 58.01%; N3: s 37.72%, p 61.82%
BD(2)N2-N3	1.99847	N2: p 99.85%; N3: p 99.41%
BD(3)N2-N3	1.99847	N2: p 99.85%; N3: p 99.41%
LP*(1)Li1	0.15467	p 100.00%
LP*(2)Li1	0.08403	s 99.85%
LP*(3)Li1	0.08403	s 99.85%
LP*(4)Li1	0.08403	s 99.85%
LP(1)N2	1.90171	s 59.66%, p 40.33%
LP(1)N3	1.98477	s 62.99%, p 36.95%
BD*(1)N2-N3	0.00041	N2: s 41.92%, p 58.01%; N3: s 37.72%, p 61.82%
Main second order Perturbation analysis		
Donor	Acceptor	E_2(kcal/mol)
LP(1)N2	LP*(1)Li1	20.42
LP(1)N2	LP*(2)Li1	10.02
LP(1)N2	LP*(3)Li1	10.02
LP(1)N2	LP*(4)Li1	10.02
LP(1)N4	LP*(1)Li1	20.42
LP(1)N4	LP*(2)Li1	10.02
LP(1)N4	LP*(3)Li1	10.02
LP(1)N4	LP*(4)Li1	10.02
LP(1)N6	LP*(1)Li1	20.42
LP(1)N6	LP*(2)Li1	10.02
LP(1)N6	LP*(3)Li1	10.02
LP(1)N6	LP*(4)Li1	10.02
LP(1)N8	LP*(1)Li1	20.42
LP(1)N8	LP*(2)Li1	10.02
LP(1)N8	LP*(3)Li1	10.02
LP(1)N8	LP*(4)Li1	10.02

Table S5 NBO data for LiN_{10}^{+} (LP: lone pair; BD: bonding; BD*: antibonding;E_2: stabilization energy)

NPA(Natural Population Analysis)		
Atom	Natural Electron Configuration	Natural Charge

Li	$2s^{0.18}2p^{0.35}$	0.474
N2	$2s^{1.54}2p^{3.46}3s^{0.03}3p^{0.01}$	-0.053
N3	$2s^{1.61}2p^{3.20}3s^{0.01}3d^{0.02}$	0.157
N10	$2s^{1.53}2p^{3.47}3s^{0.03}3p^{0.01}$	-0.054
N11	$2s^{1.61}2p^{3.19}3s^{0.01}3d^{0.02}$	0.166

Main BO(Bond Orbital) analysis		
Bond Orbital	Occupancy(e)	Hybridization
BD(1)Li1-N2	1.97065	Li1: s 20.60%, p 54.38%, d 25.02%; N2: s 60.89%, p 39.10%
BD(1)Li1-N10	1.99036	Li1: s 17.60%, p 82.30%, d 0.09%; N10: s 61.23%, p 38.76%
BD(1)N2-N3	1.99933	N2: s 40.83%, p 59.10%; N3: s 37.95%, p 61.58 %
BD(2) N2-N3	1.99840	N2: p 99.84%; N3: p 99.41%
BD(3) N2-N3	1.99834	N2: p 99.83%; N3: p 99.40%
BD(1)N10-N11	1.99950	N10: s 40.39%, p 59.54%; N11: s 37.88%, p 61.66 %
BD(2)N10-N11	1.99805	N10: p 99.84%; N11: p 99.41%
BD(3)N10-N11	1.99805	N10: p 99.84%; N11: p 99.41%
BD*(1)Li1-N2	0.03100	Li1: s 20.60%, p 54.38%, d 25.02%; N2: s 60.89%, p 39.10%
BD*(1)Li1-N10	0.01458	Li1: s 17.60%, p 82.30%, d 0.09%; N2: s 61.23%, p 38.76%
BD*(1)N2-N3	0.00050	N2: s 40.83%, p 59.10%; N3: s 37.95%, p 61.58 %, d 0.47%
BD*(2)N2-N3	0.00154	N2: p 99.84%; N3: p 99.41%

Main second order Perturbation analysis		
Donor	Acceptor	E_2(kcal/mol)
BD(1)Li1-N2	BD*(1)Li1-N4	13.44
BD(1)Li1-N2	BD*(1)Li1-N6	12.27
BD(1)Li1-N2	BD*(1)Li1-N8	13.44
BD(1)Li1-N4	BD*(1)Li1-N2	13.44
BD(1)Li1-N4	BD*(1)Li1-N6	13.44
BD(1)Li1-N4	BD*(1)Li1-N8	12.27
BD(1)Li1-N6	BD*(1)Li1-N2	12.27
BD(1)Li1-N6	BD*(1)Li1-N4	13.44
BD(1)Li1-N6	BD*(1)Li1-N8	13.44
BD(1)Li1-N8	BD*(1)Li1-N2	13.44
BD(1)Li1-N8	BD*(1)Li1-N4	12.27
BD(1)Li1-N8	BD*(1)Li1-N6	13.44