Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Conversion of Carbon Dioxide to A Novel Molecule $NCNBO^-$ Mediated by $NbBN_2^-$ Anions at Room Temperature

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Table S1. DFT-calculated and experimental bond dissociation energies. The values are in unit of eV.

Method \ EXP.		N–C	Nb–O	Nb–C	O–C	B–O	N–B	σ[1]
		7.76 ±0.03	8.00 ±0.26	5.90 ±0.13	11.16 ±0.004	8.38 ±0.22	3.92 ±0.09	
References		1	2	3	4	2	5	
Hybrid Functionals	B1B95	7.42	7.46	5.07	11.03	8.31	4.51	0.50
	B1LYP	7.25	7.38	4.92	10.70	8.12	4.53	0.61
	B3LYP	7.51	7.63	5.15	10.94	8.33	4.69	0.49
	B3P86	7.74	7.73	5.26	11.20	8.57	4.87	0.49
	B3PW91	7.49	7.45	4.98	10.95	8.38	4.68	0.56
	M05	7.54	7.57	6.22	11.02	8.07	4.36	0.33
	M052X	7.24	7.02	5.01	10.99	8.52	4.41	1.32
	PBE1PBE	7.48	7.37	4.98	10.95	8.36	4.69	0.57
	X3LYP	7.49	7.62	5.14	10.93	8.32	4.69	0.49
	M06	**7.48**	**7.84**	**5.98**	**11.11**	**8.31**	**4.58**	**0.31**
	M062X	7.38	7.49	5.50	11.09	8.58	4.66	1.22
	BH&HLYP	6.55	6.62	4.27	10.21	8.14	4.12	1.71
	BMK	7.40	7.03	4.44	11.24	8.55	4.77	0.81
Pure Functionals	BPW91	8.05	8.02	5.45	11.30	8.71	5.01	0.52
	BLYP	8.04	8.23	5.66	11.23	8.60	5.00	0.48
	BP86	8.25	8.30	5.73	11.48	8.80	5.14	0.59
	BPBE	8.05	8.03	5.46	11.31	8.71	5.01	0.51
	M06L	7.76	7.72	5.85	11.07	8.52	4.85	0.40
	PBE	8.31	8.27	5.74	11.53	8.88	5.18	0.63
	TPSS	7.66	7.85	5.39	10.89	8.29	4.74	0.42
Double Hybrid Functional	DSD-PBEP86	7.11	7.49	5.21	10.76	8.32	3.29	0.43

[1]: $\sigma = \sqrt{\frac{\sum(x_i - x_{exp})^2}{n}}$, x_i is the DFT calculated bond dissociation energy and x_{exp} is the experimental value.

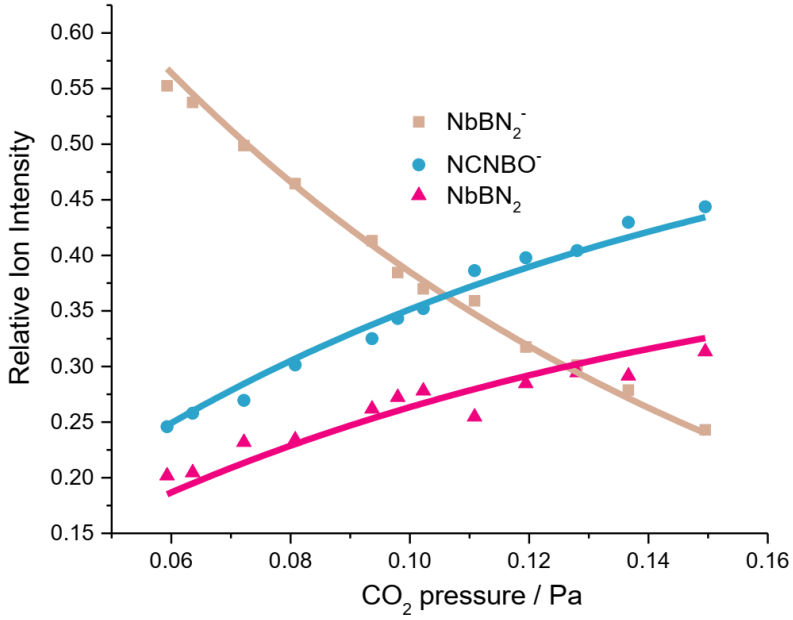

Fig. S1 Variations of the relative intensities of the reactant and product cations in the reaction of $NbBN_2^-$ and CO_2 with respect to the CO_2 pressures for 0.9 ms. The solid lines are fitted to the experimental data points by using the equations derived with the approximation of the pseudo-first-order reaction mechanism.

The pseudo-first-order rate constants (k_1) for the reactions between cluster ions and reactant molecules can be estimated by this equation.

$$ln\frac{I_R}{I_T} = -k_1\frac{P_{\text{effective}}}{kT}t_R$$

in which I_R is the intensity of the reactant cluster ions after the reaction, I_T is the total ion intensity including product ion contribution, $P_{\text{effective}}$ is the effective pressure, t_R is the reaction time, *k is* the Boltzmann constant, and T is the temperature (≈*298 K*). The R value for Fig. S1 is 0.98.

The fitted pseudo-first-order rate constant (k_1) of Reactions 1a and b were estimated to be (3.7±0.7) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The errors of t_R (±5%), T (±2%), and P (±20%) were taken into account to estimate the error for rate constant.

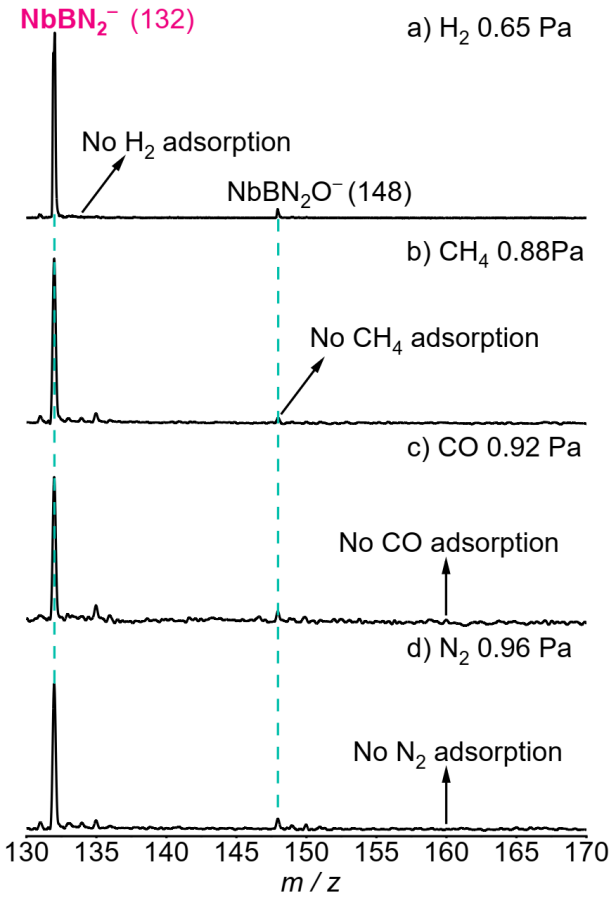

Fig. S2 Time-of-flight (TOF) mass spectra for the reactions of the mass-selected $NbBN_2^-$ with (a) H_2, (b) CH_4, (c) CO and (d) N_2. The effective reactant gas pressures are shown.

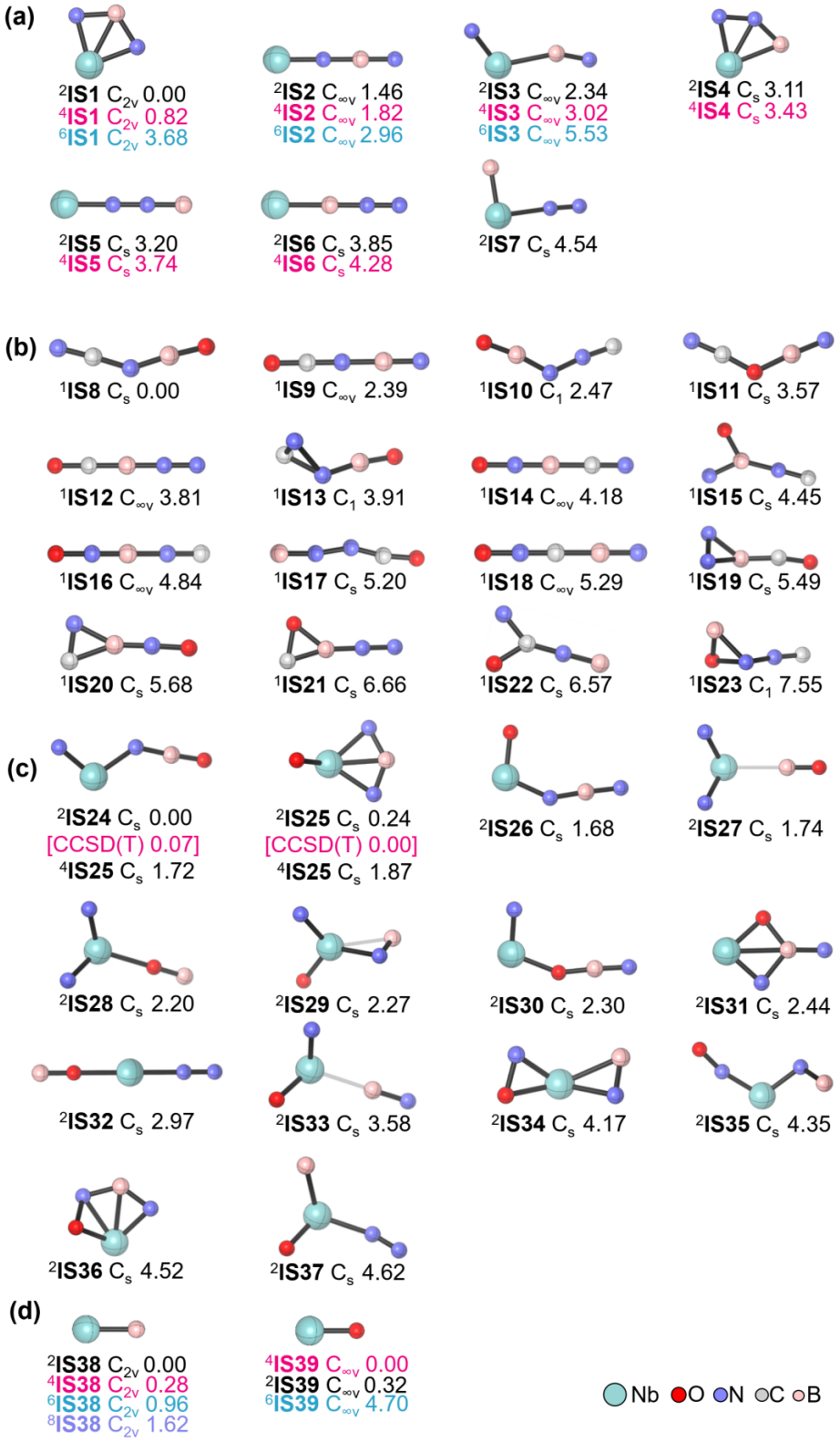

Fig. S3 DFT-calculated structures and relative energies of (a) $NbBN_2^-$, (b) $NCNBO^-$, (c) $NbBN_2O^-$ and (d) NbB^-, NbO^-. In panel c, CCSD(T)-calculated structures and relative energies of (c) ^{2}**IS24** and ^{2}**IS25** are given parentheses. The point group is given under each structure and the superscripts indicate the spin multiplicities. The zero-point vibration corrected energies (ΔH_{0K} in eV) of each structure are given.

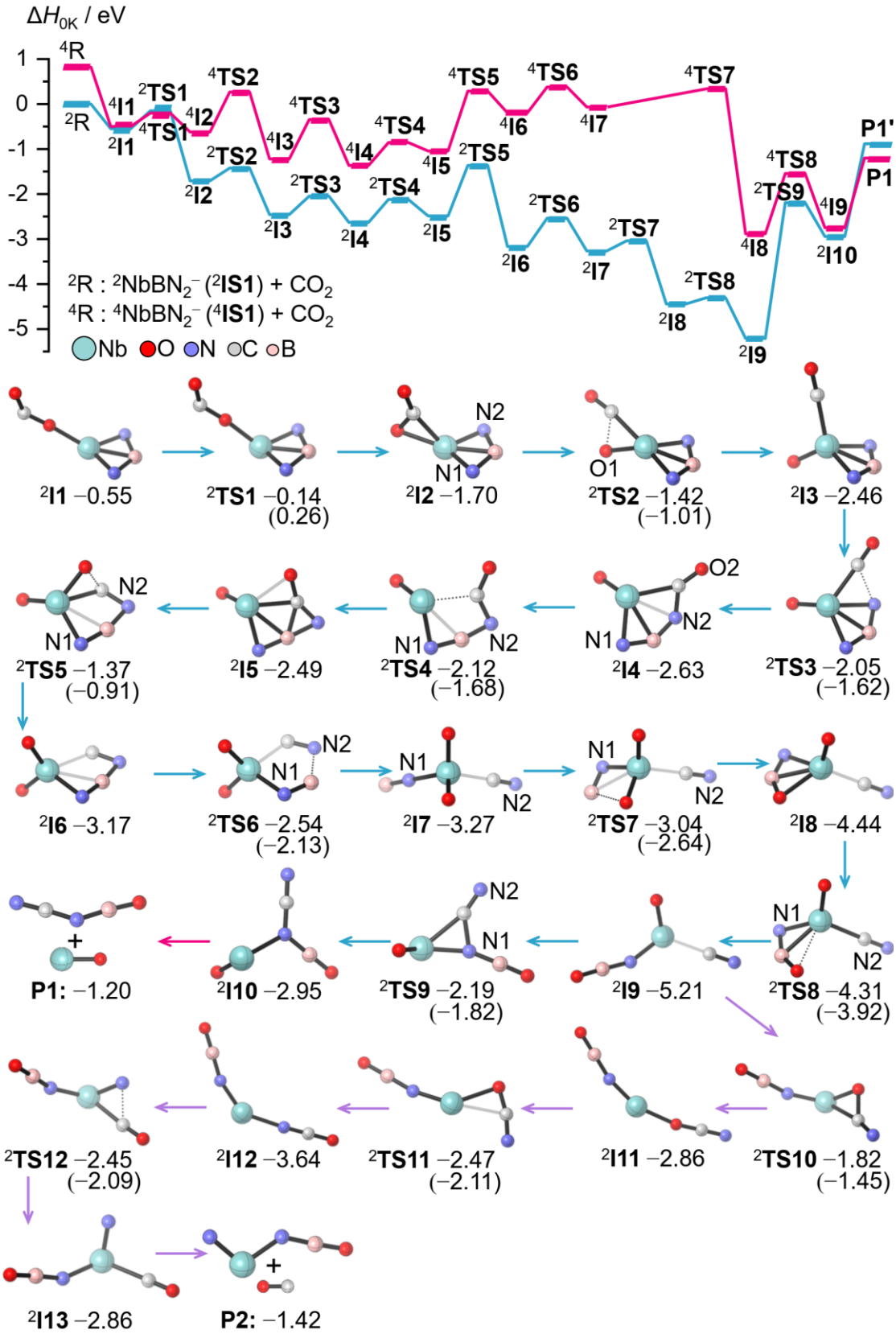

Fig. S4 M06-calculated potential energy surfaces for the reactions of $NbBN_2^-$ with CO_2. The zero-point vibration-corrected energies (ΔH_{0K} in eV) and the Gibbs free energies ($\Delta G_{298.15K}$ in eV) in parentheses of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin multiplicities.

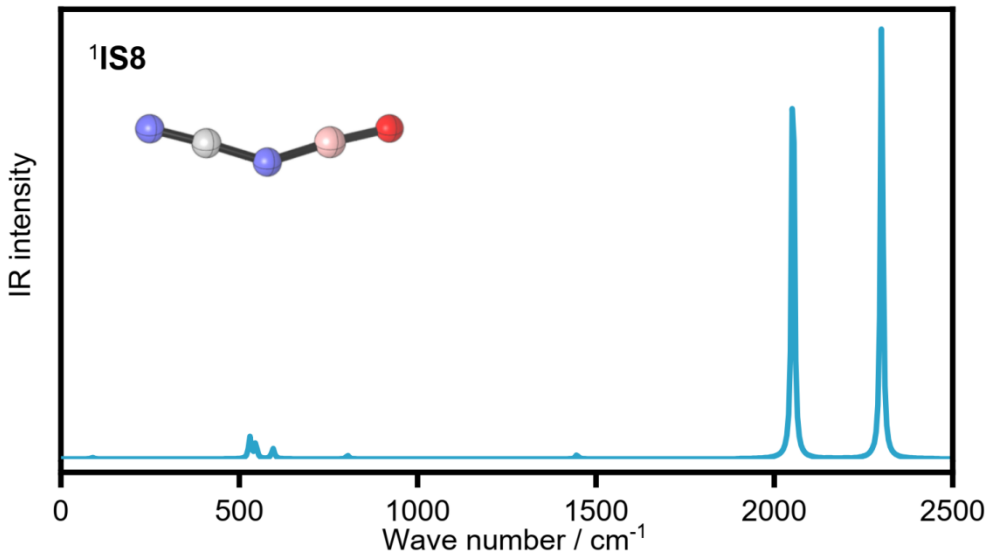

Fig. S5 The calculated infrared spectrum of NCNBO$^-$ (^{1}**IS8**).

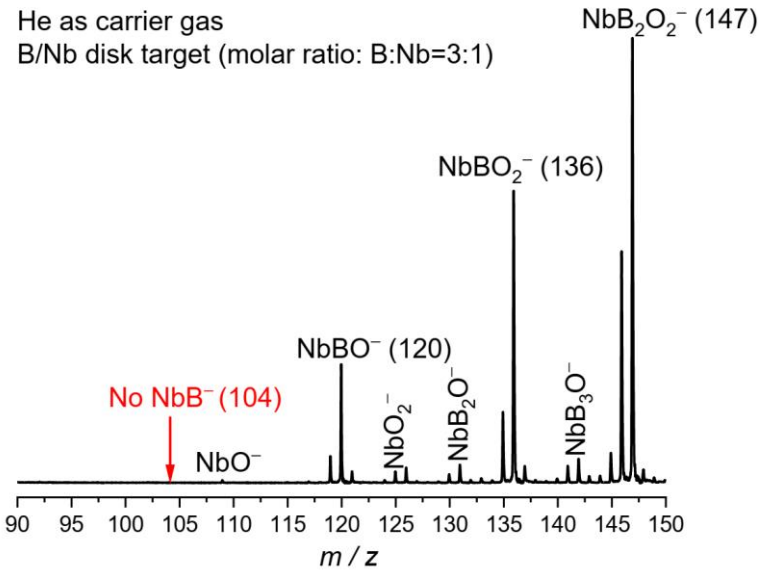

Fig. S6 The full generation spectrum of $NbB_xO_y^-$. No NbB^- anions were generated.

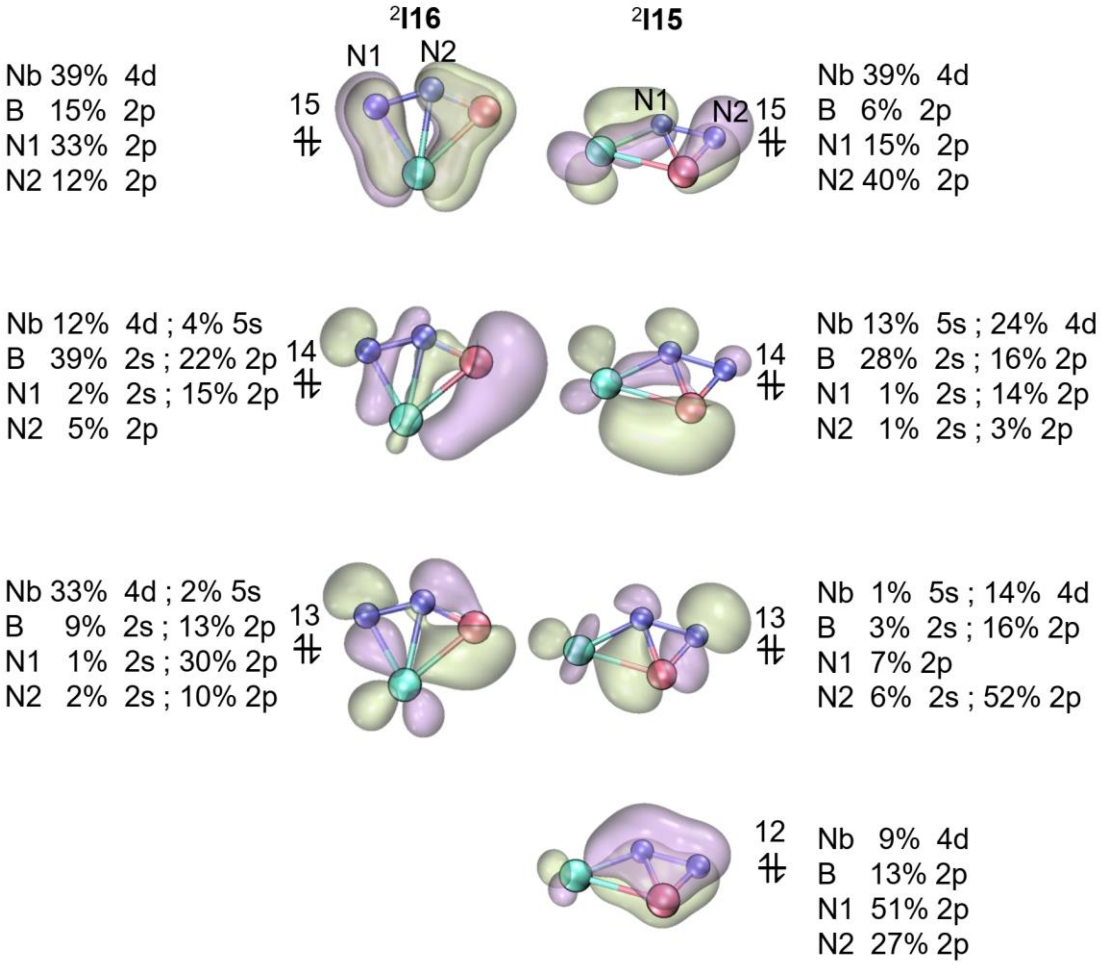

Fig. S7 Schematic molecular orbital diagrams for (a) ^{2}**I16** and (b) ^{2}**I15**. The compositions of some key molecular orbitals are given. Natural orbital partial occupation numbers are given.

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