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

Plasma-promoted reactions of the bimetallic anions $CuNb^-$ with dinitrogen and subsequent reactions with carbon dioxide: formation of C−N bonds

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More calculated details:

$$v_1 = \sqrt{\frac{3kT}{m_1}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 298}{185 \times 1.66 \times 10^{-27}}} = 200\ m/s$$

$$v_2 = \sqrt{\frac{\gamma kT}{m_2}} = \sqrt{\frac{1.304 \times 1.38 \times 10^{-23} \times 298}{44 \times 1.66 \times 10^{-27}}} = 271\ m/s$$

$$v = (v_1 + v_2) = (200 + 271) = 471\ m/s$$

$$m_1 = m_{(CuNbN_2^-)}, m_2 = m_{CO_2}$$

k: Boltzmann constant;

γ: Adiabatic Index ($\gamma_{CO_2} = 1.304$);

T = 298 K

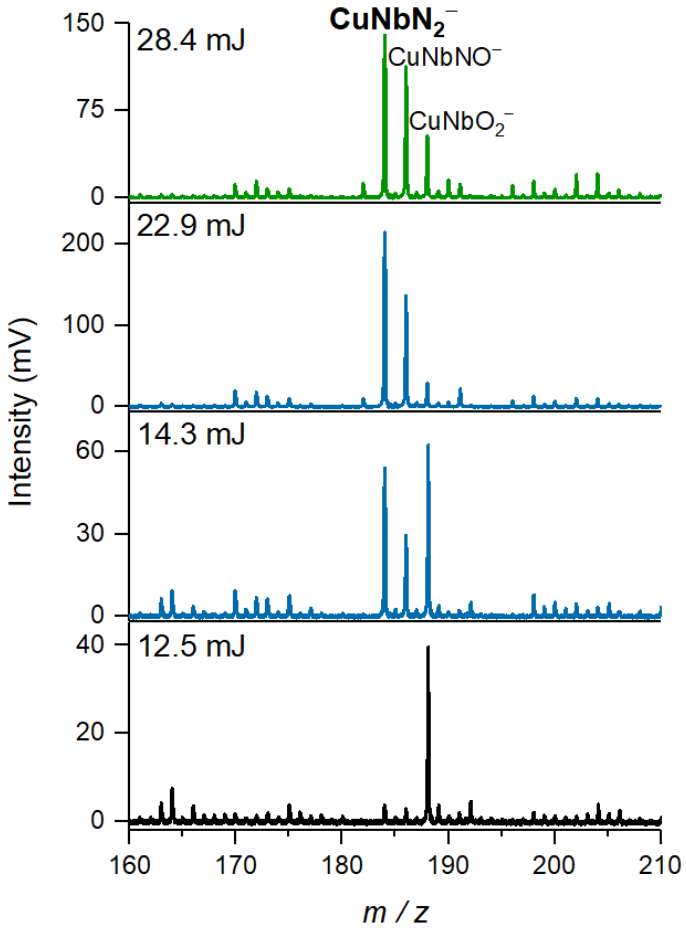

Fig. S1. TOF mass spectra of $CuNb^-$ anions reacting with 20% N_2 under plasma atmosphere provided by different laser power. The laser flash-lamp pulse energy at 12.5, 14.3, 22.9 and 28.4 mJ, respectively.

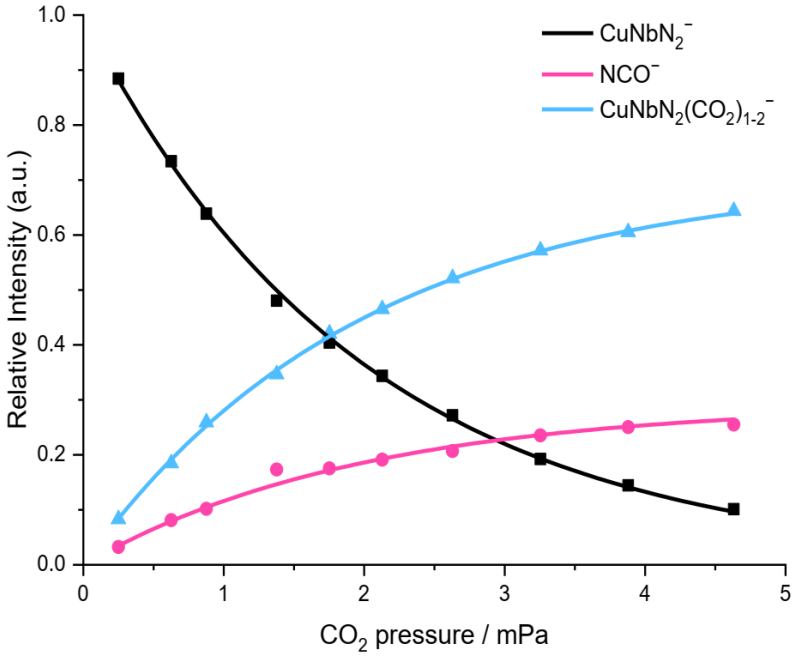

Fig. S2. Variation of relative intensities of the reactant and product ions for the reactions of $CuNbN_2^-$ with CO_2 pressures. The solid lines are fitted to the experimental data points with the approximation of the pseudo-first-order reaction mechanism.

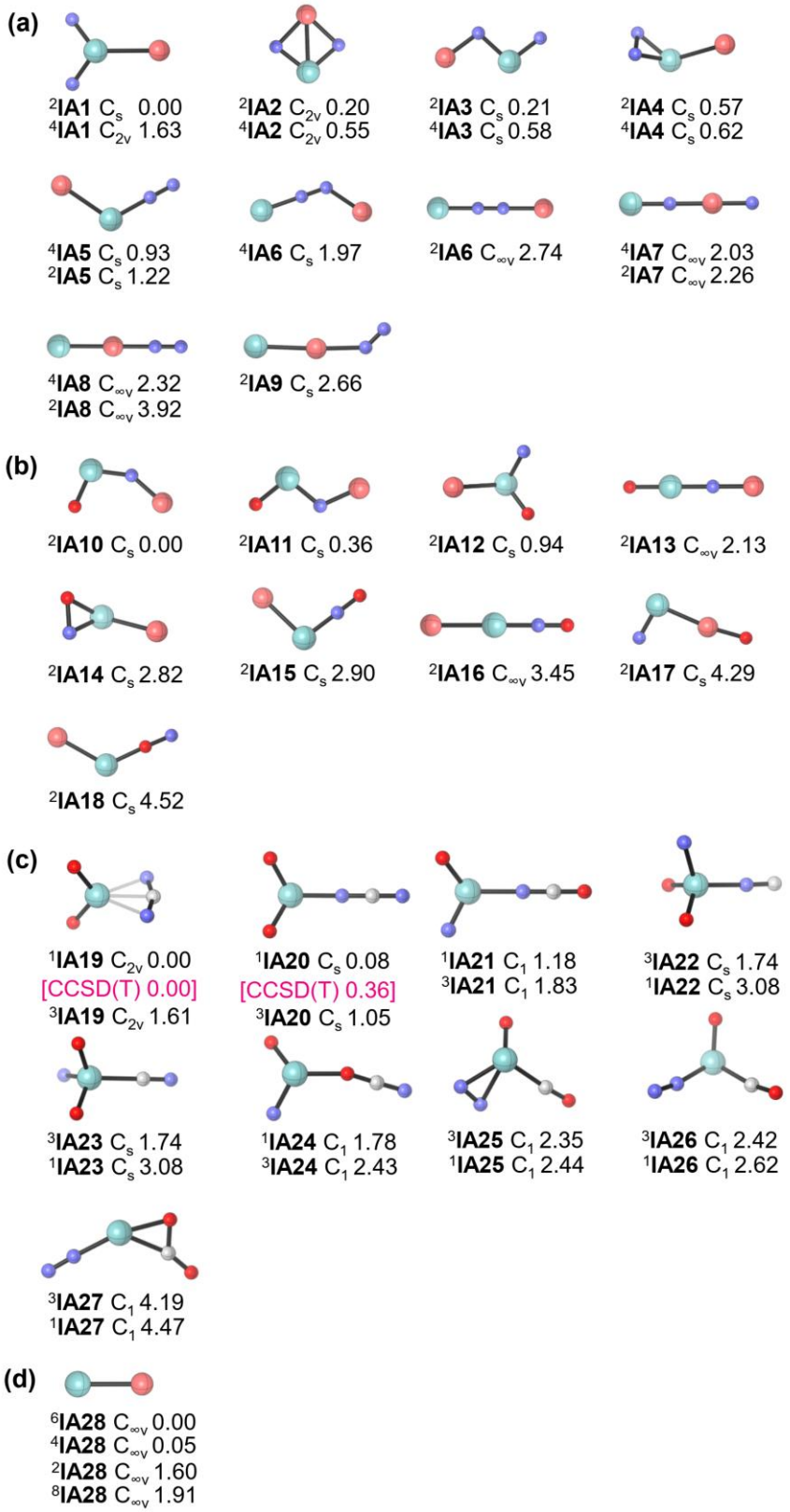

Fig. S3. DFT-calculated structures and relative energies of (a) $CuNbN_2^-$, (b) $CuNbNO^-$, (c) $NbN_2CO_2^-$, and (d) $CuNb^-$ at the B3LYP/6-311+G*, aug-cc-pVTZ-pp and def2-TZVPD level of theory. In panel c, CCSD(T)-calculated structures and relative energies of (c) ^{1}**IA19** and ^{1}**IA20** are given parenthes. The point group is given under each structure. The superscripts indicate the spin states. The zero-point vibration corrected energies (ΔH_{0K} in eV) of each structure are given.

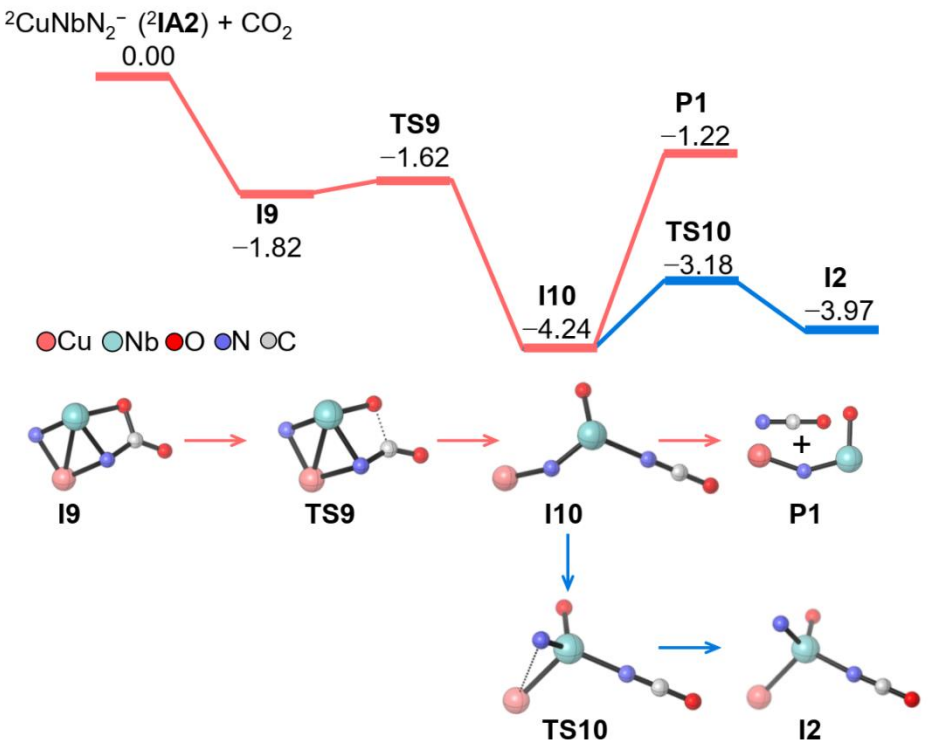

Fig. S4. B3LYP-D3-calculated PESs for the reaction of $CuNbN_2^-$ (^{2}**IA2**) with CO_2. Zero-point vibration-corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin states.

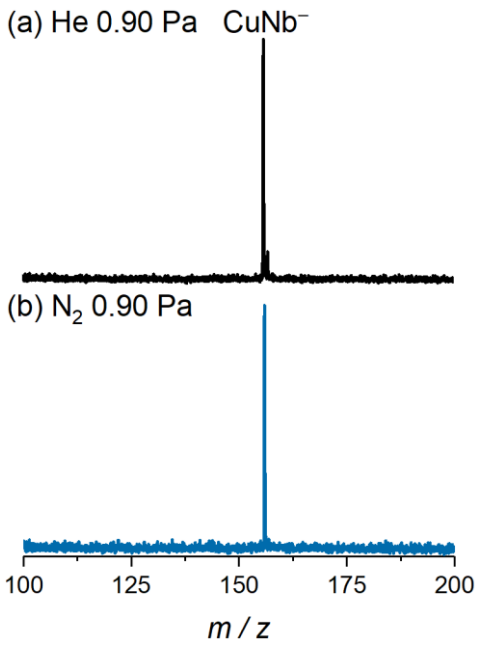

Fig. S5. Time-of-flight mass spectra for the reactions of mass-selected $CuNb^-$ cluster with (a) He, and (b) N_2. The reaction time is about 14 ms, and the effective reactant gas pressures are shown.

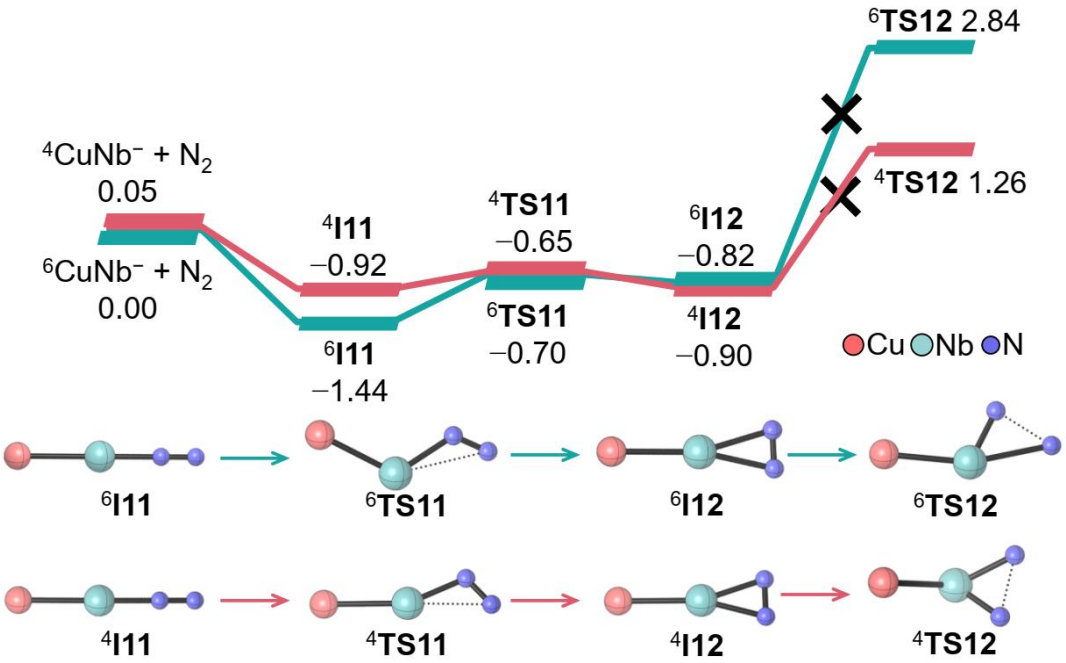

Fig. S6. B3LYP-D3-calculated PESs for the reaction of $CuNb^{-}$ with N_2. Zero-point vibration-corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin states.