

Supporting information for

## Facile C≡O Bond Cleavage on Polynuclear Vanadium Nitride Clusters



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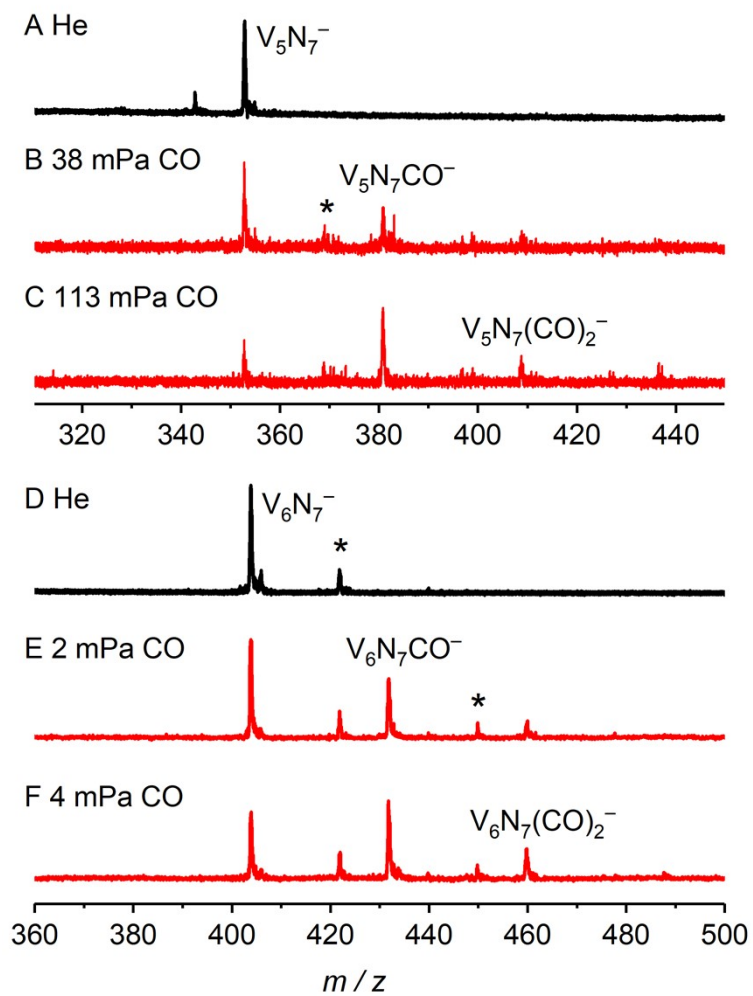
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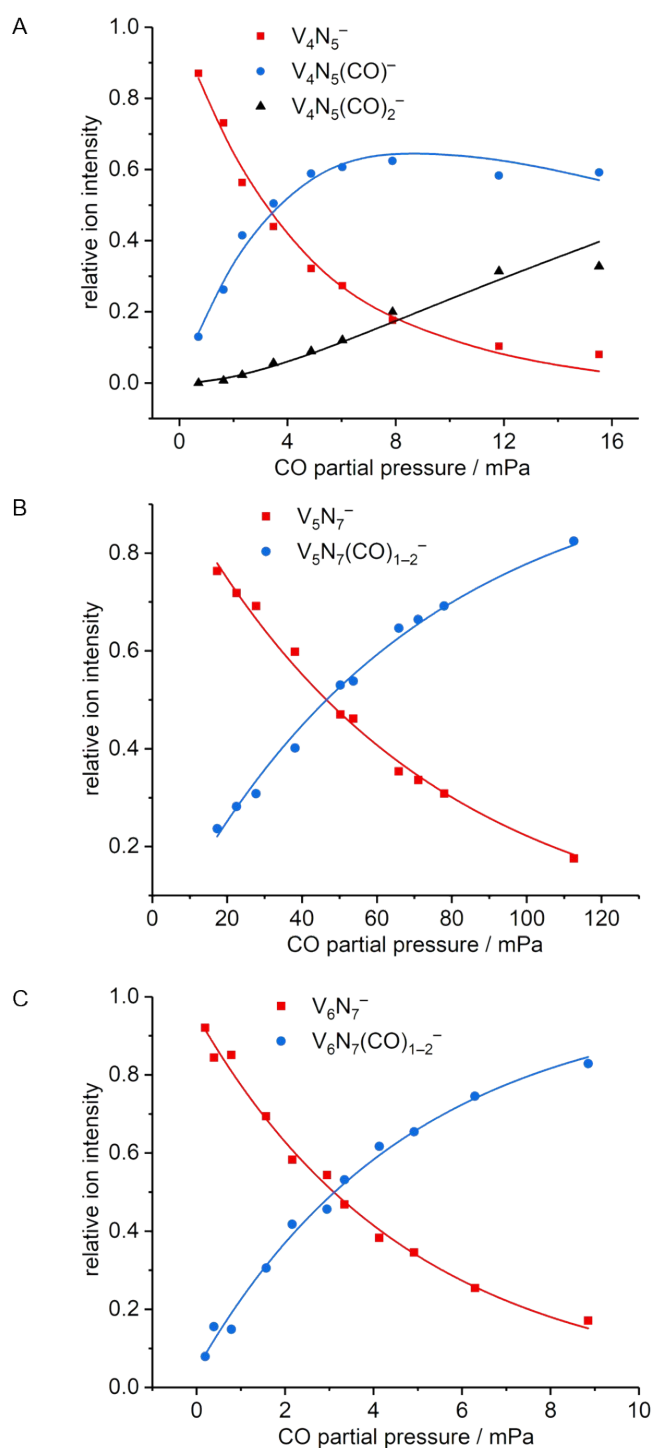
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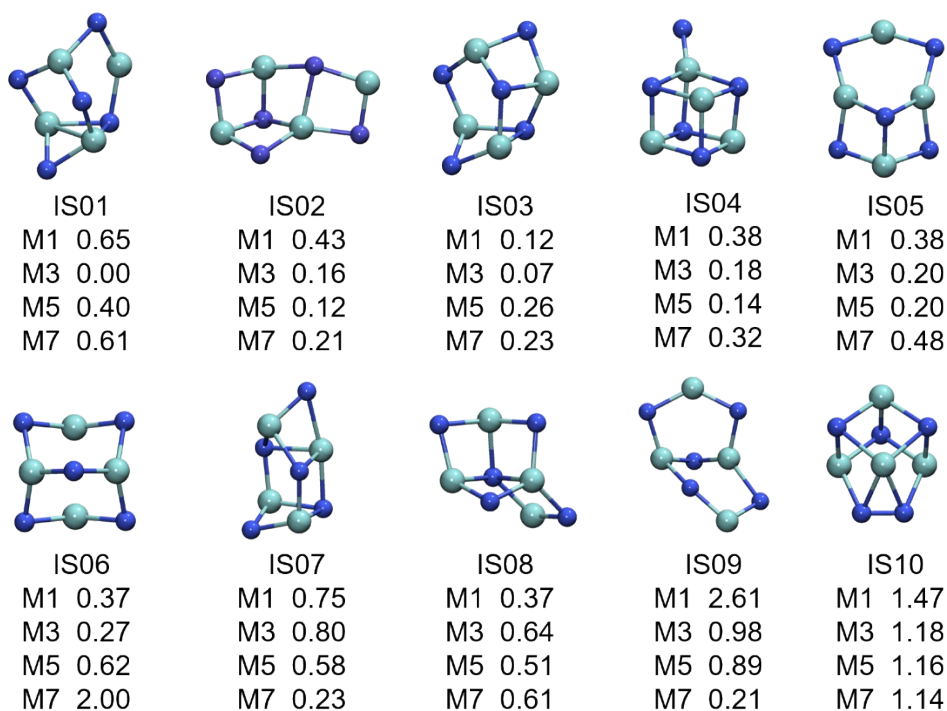


**Fig. S1** The time-of-flight (TOF) mass spectra for the reactions of mass-selected  $V_5N_7^-$  and  $V_6N_7^-$  clusters with He (A, D) and CO (B, C, E and F) in the ion trap reactor. The reaction time is about 1.8 ms. Peaks marked with asterisks are due to the residual water in the gas-handling system.

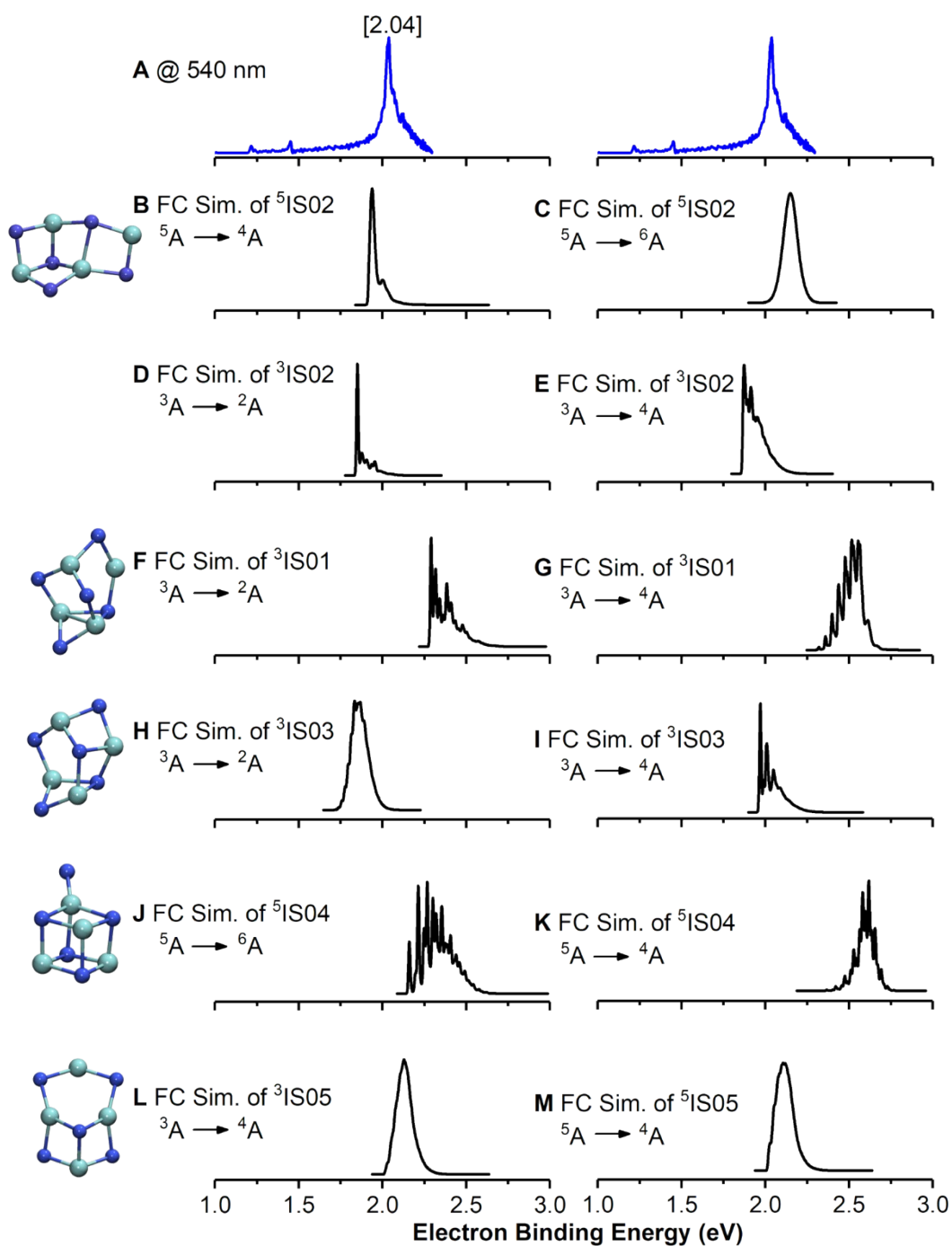


**Fig. S2** Variation of relative ion intensities of reactant and product clusters with respect to the partial pressures of CO for reactions  $V_4N_5^- + CO$  (A),  $V_5N_7^- + CO$  (B), and  $V_6N_7^- + CO$  (C) are shown. The solid lines are fitted to the experimental data points by the least-square procedure.

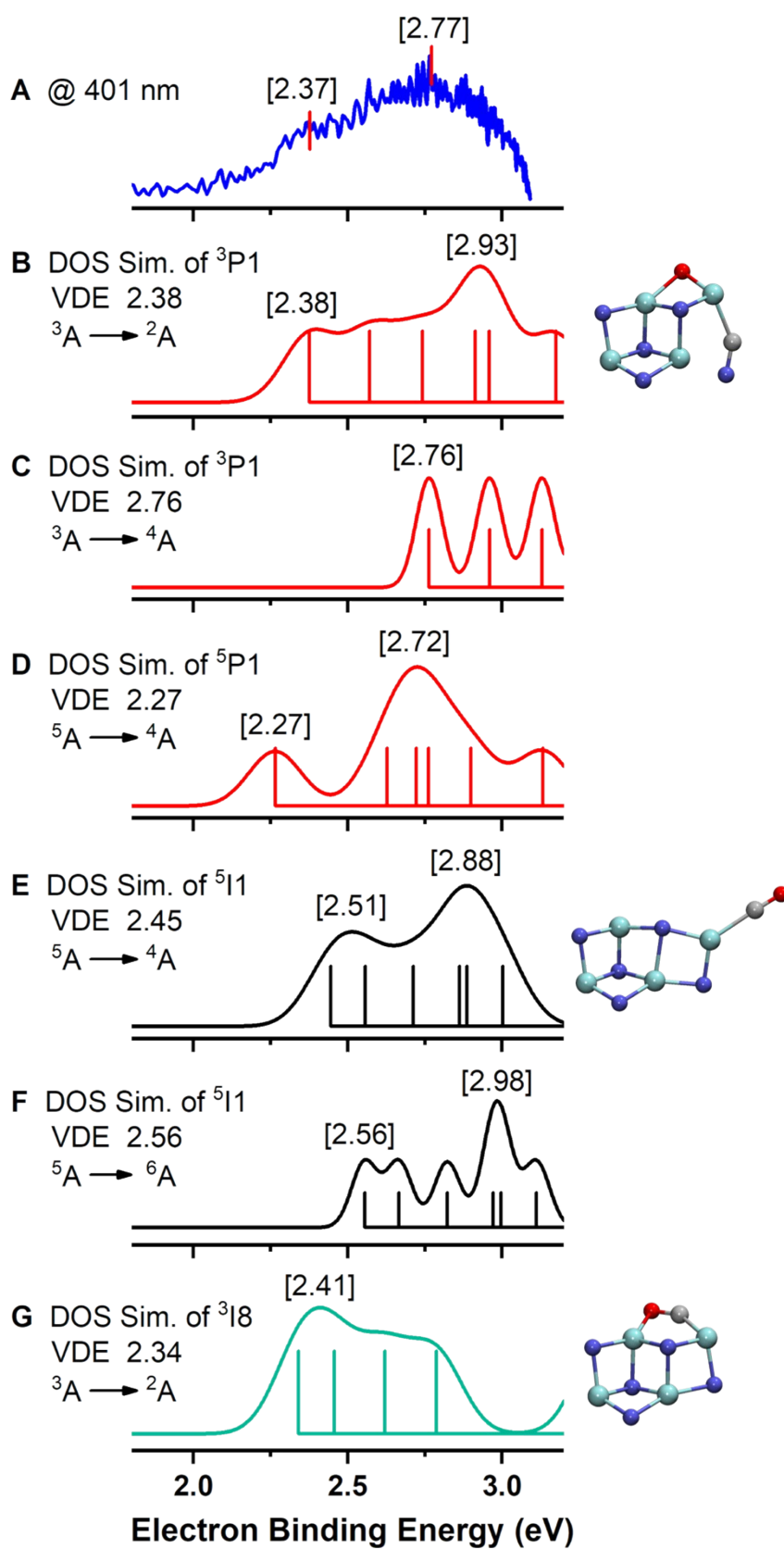
The fitted rate constants in unit of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  are  $k(V_4N_5^- + CO \rightarrow V_4N_5CO^-) = 5.8 \pm 0.24$ ,  $k(V_5N_7^- + CO \rightarrow V_5N_7CO^-) = 0.35 \pm 0.004$ , and  $k(V_6N_7^- + CO \rightarrow V_6N_7CO^-) = 4.9 \pm 0.09$ . The uncertainties ( $\pm \delta$ ) given are one standard error in the least-square fitting. The reaction time and reactant gas pressure have systematic errors. The uncertainties of the absolute and relative rate constants are within  $\pm 40\%$  and  $\pm 20\%$ , respectively.



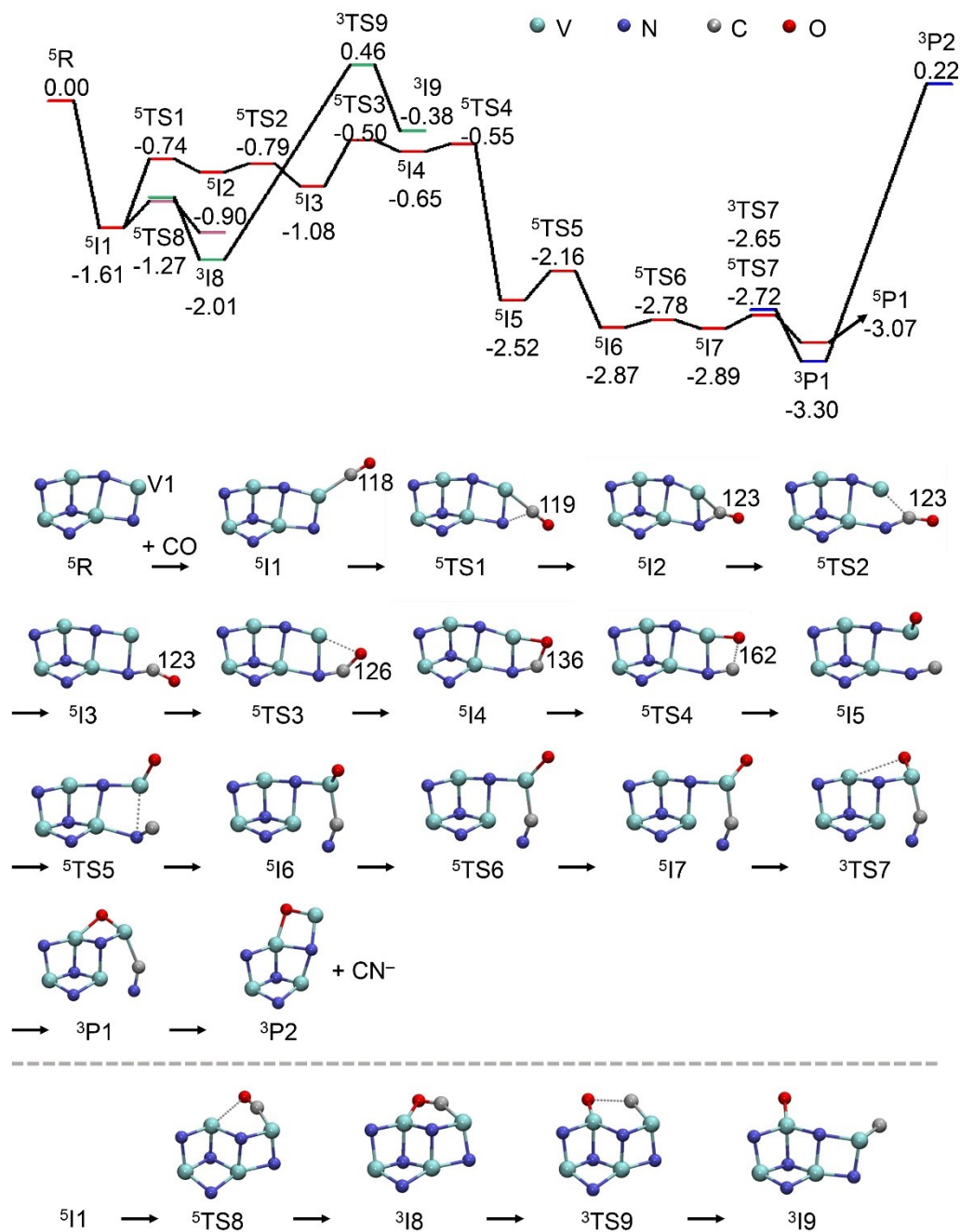
**Fig. S3** The density functional theory (DFT) calculated low-lying isomers of  $\text{V}_4\text{N}_5^-$  at the bp86 level. The relative energies with respect to the lowest-lying isomer are given in eV.  $M_x$  ( $x = 1, 3, 5,$  and  $7$ ) below each isomer represents different spin multiplicities and bond lengths (pm) are given. Note that the electronic energy of IS09 (M1) is given.



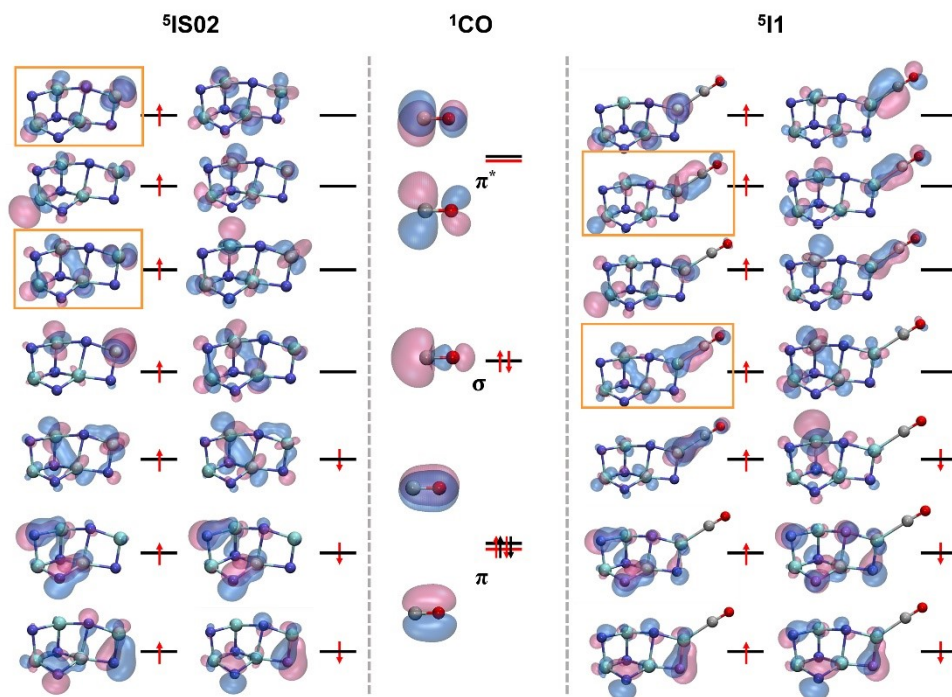
**Fig. S4** The experimental photoelectron spectrum of  $V_4N_5^-$  was taken at the laser wavelength of 540 nm (A). The Franck-Condon (FC) simulated spectra for the low-lying isomers of  $V_4N_5^-$  (Figure S3) are shown in panels B-M.



**Fig. S5** The experimental photoelectron spectrum of  $V_4N_5CO^-$  was taken at the laser wavelength of 401 nm (A). The simulated density of states (DOS) spectra are shown in panels B-G.

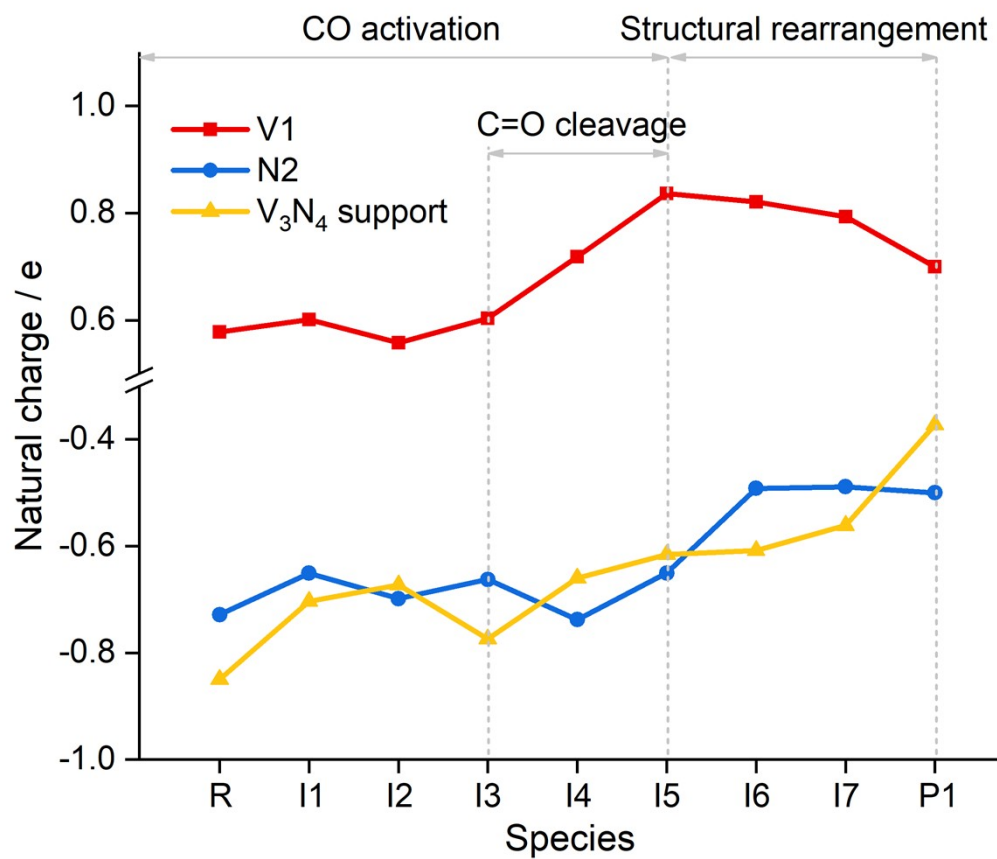


**Fig. S6** The DFT-calculated potential energy profile for reaction  $V_4N_5^- + CO$ . The zero-point vibrational corrected energies ( $\Delta H_0$ , in eV) of intermediates (Is), transition states (TSs), and products (Ps) with respect to the separated reactants are given. Bond lengths are given in pm.

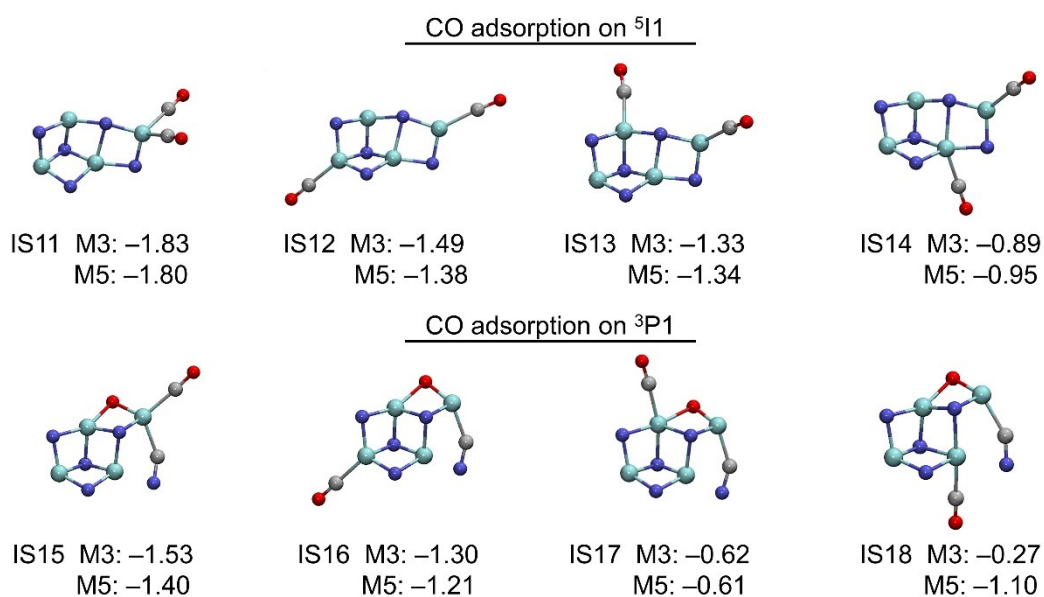


**Fig. S7** Molecular orbital presentation of  $\text{V}_4\text{N}_5^-$  ( ${}^5\text{IS02}$ , Fig. 2A),  $\text{CO}$ , and  $\text{V}_4\text{N}_5\text{CO}^-$  ( ${}^5\text{I1}$ ). The up and down arrows denote  $\alpha$  and  $\beta$  electrons, respectively.





**Fig. S8** The DFT-calculated natural charges (e) on V1 atom, N2 atom, and the V<sub>3</sub>N<sub>4</sub> support during the pathway of CO dissociation on the V<sub>4</sub>N<sub>5</sub><sup>-</sup> cluster (Fig. 3).



**Fig. S9.** The DFT calculated isomers for the adsorption of the second CO molecule on  $^5\text{I1}$  and  $^3\text{P1}$  (Fig. 3). The relative energies of IS11–IS14 with respect to  $^5\text{I1} + \text{CO}$  and IS15–IS18 with respect to  $^3\text{P1} + \text{CO}$  are given in eV.  $\text{M}_x$  ( $x = 3$  and  $5$ ) below each isomer represents different spin multiplicities.