Supporting Information

Probing Single-Molecule Dissociations from a Bimolecular Complex NO-Co-Porphyrin

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Chemical potential of NO gas.

The chemical potential of NO gas $\mu_{NO}(T,P)$ can be decomposed into the zero-temperature, finite-temperature and pressure contributions. Zero-temperature contributions include the total energy and zero-point energy of NO gas, which are already considered in ΔE and ΔZPE of Eq. (1) in main text, and pressure contribution is the logarithmic term of Eq. (1) in main text. Temperature dependent (or finite-temperature contributed) chemical potential of NO gas $\mu^0_{NO}(T)$ can be deduced from the relation $G = H - TS$, as represented,

$$\mu^0_{NO}(T) = H^0(T) - H^0(0) - TS^0(T), \tag{1}$$

where G is Gibbs free energy, H is enthalpy, T is temperature and S is entropy. H^0 and S^0 are the enthalpy and entropy of NO gas, which were taken from the thermodynamic table, at standard pressure $p^0 = 0.1$ MPa (or 1 bar), respectively. The $\mu^0_{NO}(T)$ values obtained from thermodynamic table are listed in Table S1. By using the polynomial fitting $\mu^0_{NO}(T) = \sum C_i T^i$ ($i = 0, \dots, 6$), we can estimate the μ^0_{NO} of -0.12 eV at 80 K, as shown in Fig. S1.

NO vibration modes calculation.

We first calculated minimum-energy configurations of NO adsorbed on CoTPP/Au(111) with the vdW correction, obtaining adsorption energy of 1.50 eV. For accurate calculations of vibrational spectra, we first tightly optimized the atomic forces less than 10^{-2} eV/Å, and then calculated dynamic matrices separately for an adsorbed NO. [1] Table S2 and Fig. S2

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summarizes six characteristic vibrational normal modes. To calculate ZPE of NO adsorbed CoTPP/Au(111), we only consider the dynamical matrices of Co-N_4 framework and NO molecule for simplicity of calculation. The ZPE of a free NO molecule is calculated to be 119 meV with the N-O stretching mode of 238 meV, irrespective of the vdW correction.

Table S1. Chemical potential of NO gas at standard pressure $p^0 = 0.1$ MPa.

T (K)	μ^0_{NO} (eV)	T (K)	μ^0_{NO} (eV)
100	-0.15	450	-0.90
200	-0.35	500	-1.02
250	-0.45	600	-1.25
298.15	-0.56	700	-1.50
300	-0.56	800	-1.74
350	-0.67	900	-2.00
400	-0.78	1000	-2.25

Figure S1. The $\mu^0_{NO}(T)$ curve fitted with polynomials $\sum C_i T^i$ ($i = 0, \ldots, 6$). The black solid line and black circular dot represent the fitting curve and experimental data, respectively. From this curve, we can estimate μ^0_{NO} of -0.12 eV at 80 K.
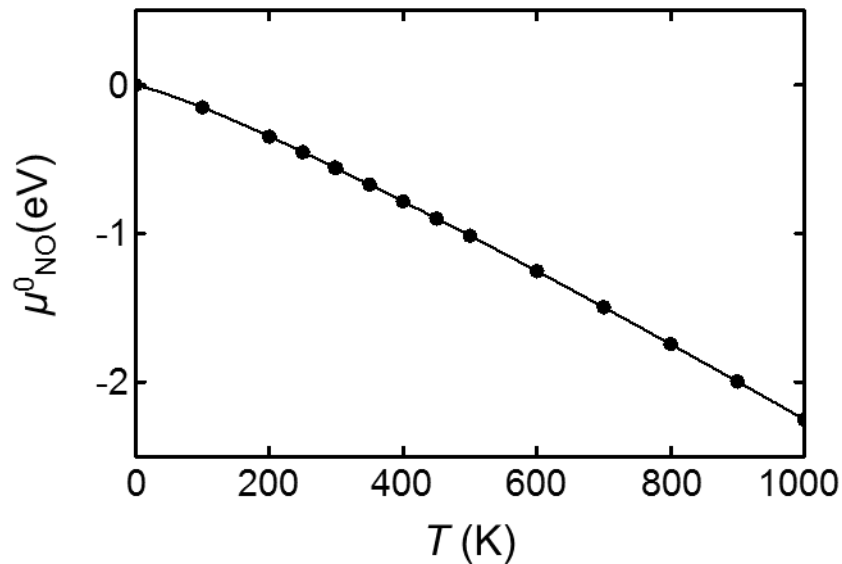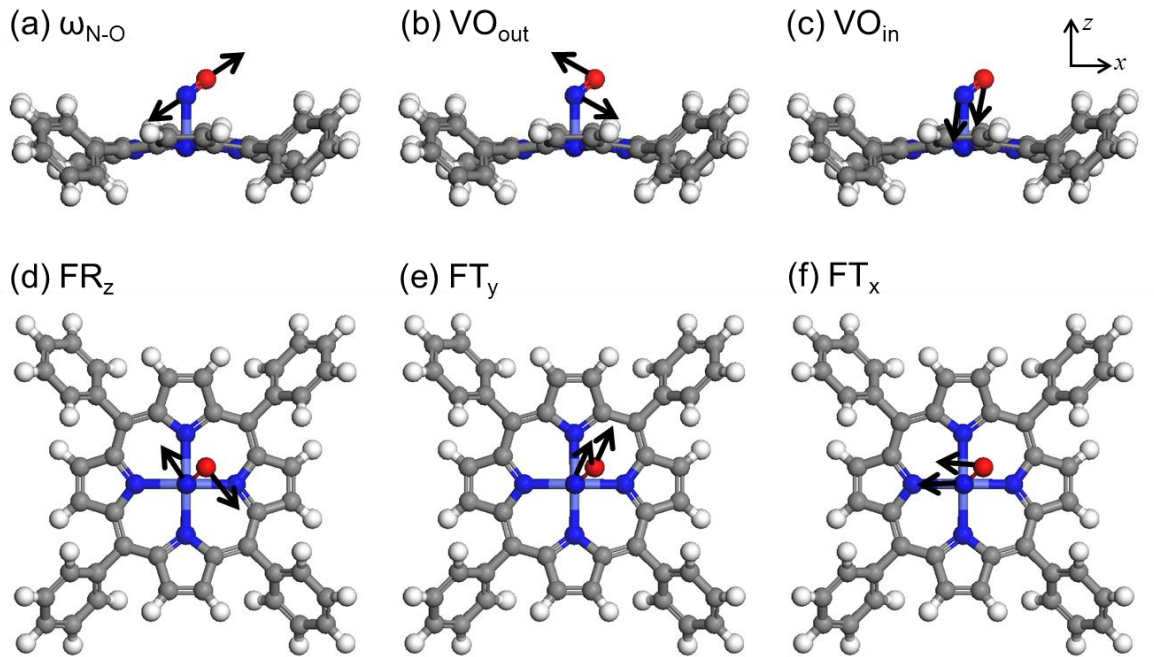
Table S2. Vibration energy (in the unit of meV) of NO-related normal modes on CoTPP/Au(111). The normal modes consist of N-O stretching motion (ω_{N-O}), frustrated rotations (VO$_{out}$ and FR$_z$) and frustrated translations (VO$_{in}$, FT$_x$ and FT$_y$), as shown in Fig. S2.
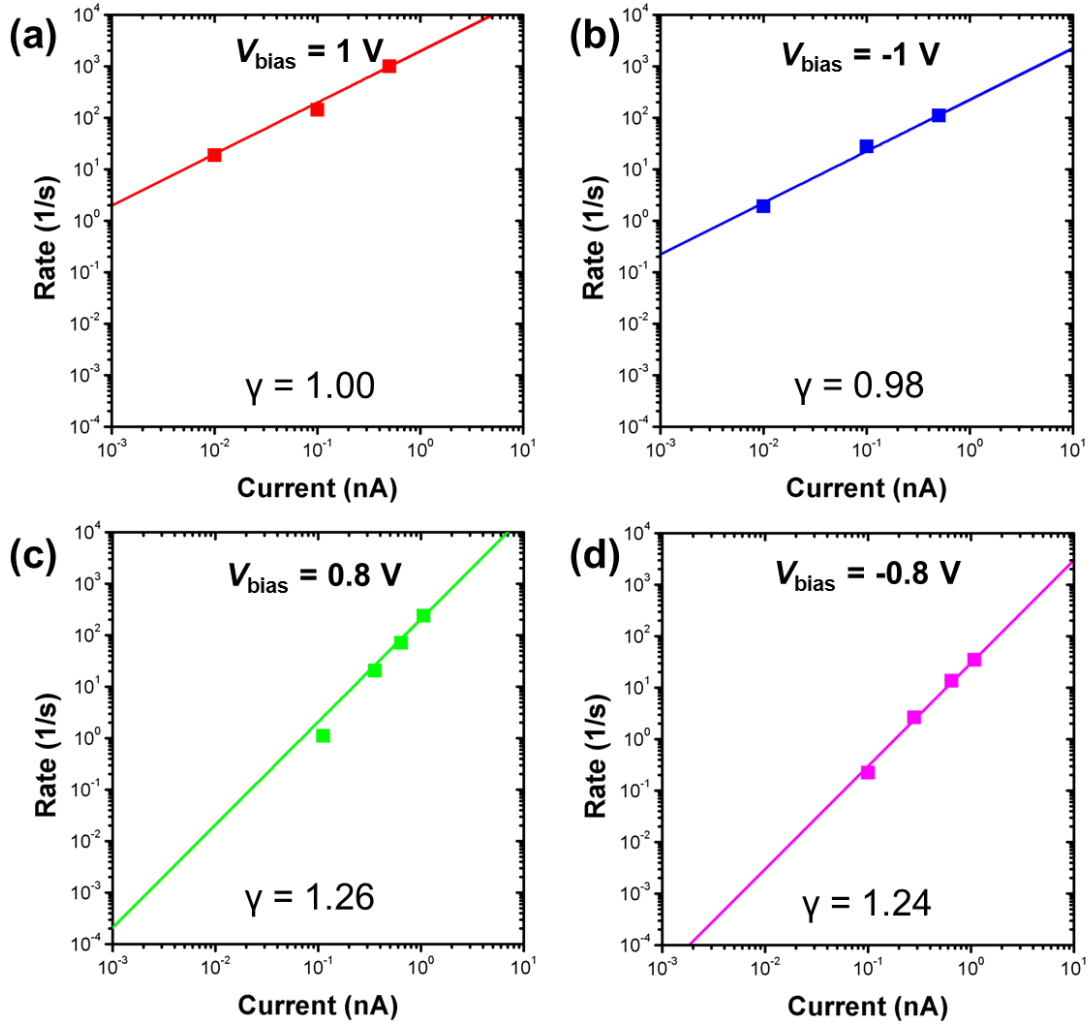
ω_{N-O}	VO$_{out}$	VO$_{in}$	FR$_z$	FT$_x$	FT$_y$
213.39	67.06	37.86	23.93	13.95	11.82

Figure S2. Six vibrational normal modes (marked by arrows) of a NO molecule adsorbed onto CoTPP/Au(111), to simplify the atomic structure we ignore Au atoms: (a) bond stretching mode (ω_{N-O}), (b) vertical out-of-phase oscillation (VO$_{out}$), (c) vertical in-phase oscillations (VO$_{in}$), (d) frustrated rotation along the z axis (FR$_z$), (e) frustrated translation in the y direction (FT$_y$), and (f) frustrated translation in the x direction (FT$_x$).

NO dissociation rate by *n*-electrons scattering. Using Arrhenius equation as represented Eq. (2) in main text, we fitted the experiment data as shown in Fig. S3.

Figure S3. Fitting curves of NO dissociation rate to Eq. (2) in main text for each bias voltage; (a) 1 V, (b) -1 V, (c) 0.8 V, and (d) -0.8 V. (a) and (b) represent one-electron-vibrational mode scattering and (c) and (d) represent two-electron-vibrational mode scattering. We fitted the experiment data to $R(1) = 1/(\tau_1)\exp[-(\Delta G - \gamma e|V_{bias}|)/k_BT]$ and $R(2) = 1/(2\tau_1)(\tau_0/\tau_1)\exp[-(\Delta G - \gamma e|V_{bias}|)/k_BT]$ for one- and two-electron-vibrational mode scattering, respectively.

References

[1] Woo, S.-J.; Lee, E.-S.; Yoon, M.; Kim, Y.-H., Finite-Temperature Hydrogen Adsorption and Desorption Thermodynamics Driven by Soft Vibration Modes. *Phys. Rev. Lett.* **2013,** *111*, 066102.