

Supporting Information

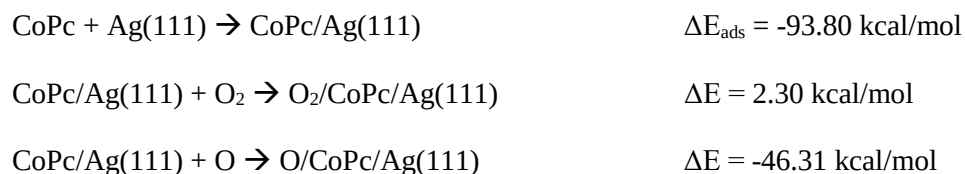
Probing Molecular-Scale Catalytic Interactions between Oxygen and Cobalt Phthalocyanine Using Tip-Enhanced Raman Spectroscopy

Duc Nguyen,[‡] Gyeongwon Kang,[‡] Naihao Chiang,[†] Xu Chen,[†] Tamar Seideman,^{‡,†} Mark C. Hersam,^{‡,†,§} George C. Schatz,[‡] and Richard P. Van Duyne^{‡,†,*}

[‡]Department of Chemistry, [†]Applied Physics Graduate Program, and [§]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

1. Calculation of relative energy for different configurations

Relative energy of each configuration was calculated by comparison to the CoPc/Ag(111) configuration. Energy refers to the sum of electronic energy and entropy due to smearing. Nuclear entropy is not considered in the energy calculation. The chemical equations with balanced stoichiometric ratio used to obtain the relative energy values are shown below.



2. Raman spectrum calculations

Raman scattering cross sections were simulated with time-dependent density functional theory (TDDFT) using NWChem 6.6¹ software package employing available patches. The valence triple-zeta with polarization basis set specially designed for DFT calculations (TZVP-DFT orbital)^{2,3} was used for hydrogen, carbon, and nitrogen atoms. For the cobalt atom, the def2-TZVP basis set⁴ was used. The

Becke88⁵ + Perdew86⁶ (BP86) exchange-correlation functional was used, because it is known to result in moderate accuracy in vibrational frequencies without any corrections.⁷

We used open-shell version of AOResponse module developed by Aquino *et al.*⁸ for calculating polarizability tensors. Due to the expensive computational cost for open-shell Raman simulation, Ag (111) surface was not included in the calculations. In this method, the finite lifetime of the electronic excited states was introduced with the short time approximations⁹⁻¹¹ using the Kramers-Heisenberg-Dirac (KHD) expression of resonance Raman scattering. 632.8 nm excitation wavelength of the perturbation was used. As suggested by Jensen *et al.*,¹² the damping parameter $\Gamma = 0.004$ au was used. Each Raman peak was broadened with a Lorentzian function that has a 10 cm⁻¹ full width at half-maximum.

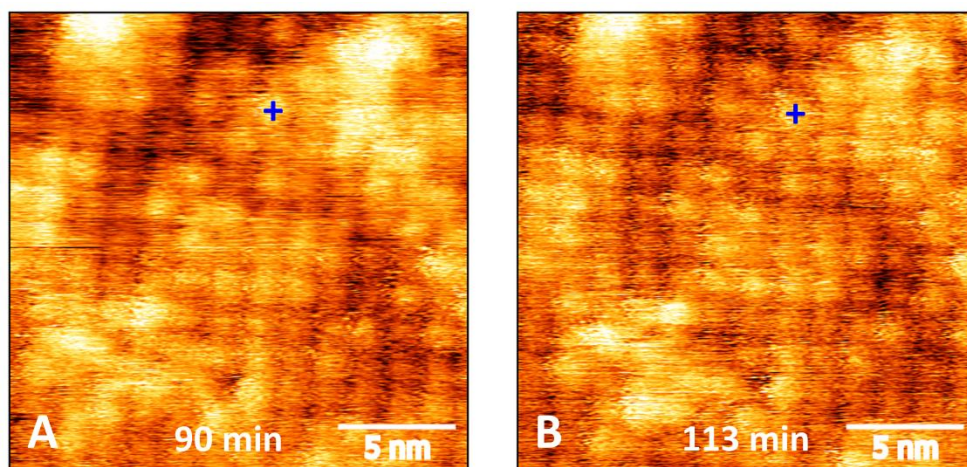


Figure S1. Consecutive STM images of an area containing CoPc/Ag(111), O₂/CoPc/Ag(111) and O/CoPc/Ag(111) after (A) 90 minutes and (B) 113 minutes of equilibration. The blue cross indicates the same molecule. A drift rate is calculated to be ~0.05 nm/min. Scanning conditions: Ag tip, -1.0 V, 500 pA.

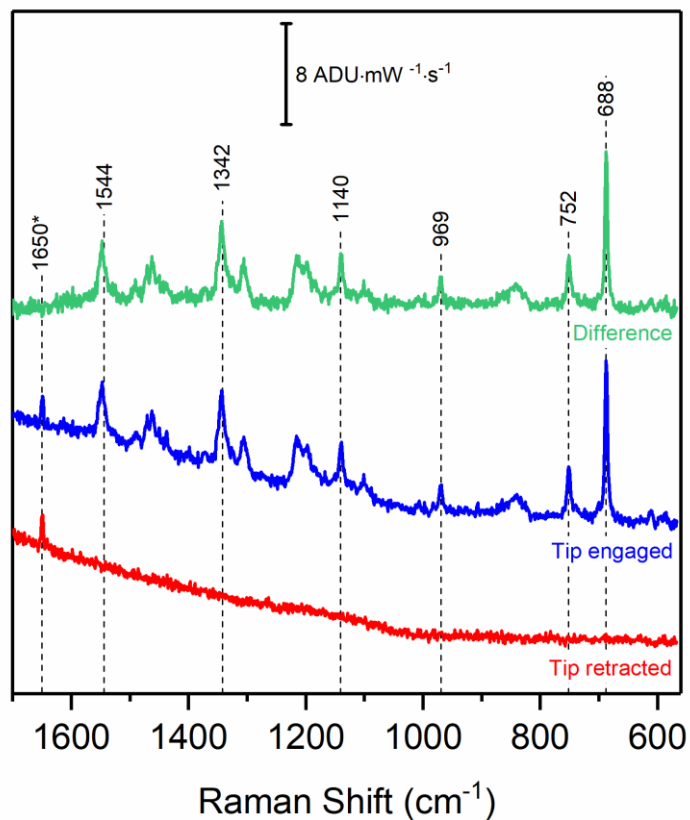


Figure S2. Typical tip-retracted (red spectrum), tip-engaged (blue spectrum) and difference (green spectrum) UHV-TER spectra. The plotted spectrum is for the data before O_2 dosing in Figure 4A, red trace. The band at 1650 cm^{-1} appears in both tip-retracted and tip-engaged spectra with equal intensity; and is also observed in spectra of other molecules excited at 632.8 nm . Thus, it is likely a band resulting from the response of the grating and does not affect the TERS analysis.

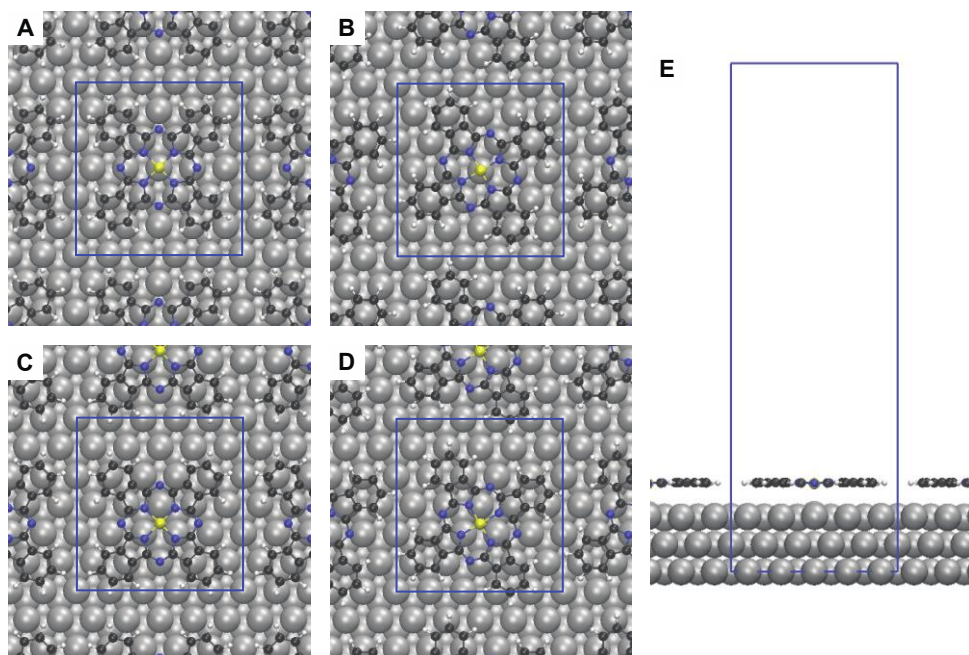


Figure S3. (A-D) Top view of different CoPc adsorption configurations on Ag(111) slab. O_2 and O binding energies are within 1 kcal/mol on different configurations. (E) Side view of adsorption configuration shown in (A). Periodic boundary boxes are shown in blue.

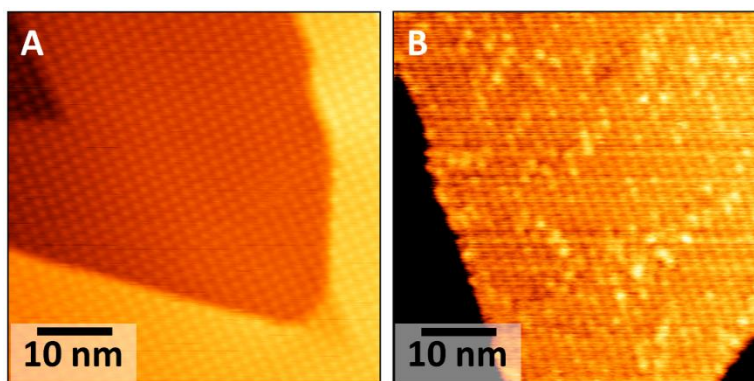


Figure S4. Large scale STM images of CoPc/Ag(111) before and after O_2 dosing. (A) Before dosing. Scanning conditions: W tip, -1.0 V, 500 pA. (B) After O_2 dosing showing an area with O_2 /CoPc/Ag(111) and O/CoPc/Ag(111) adsorption configurations. Scanning conditions: Ag tip, -1.0 V, 500 pA. Pairs of O/CoPc/Ag(111) molecules (dimmer bright spots) are frequently observed in (B).

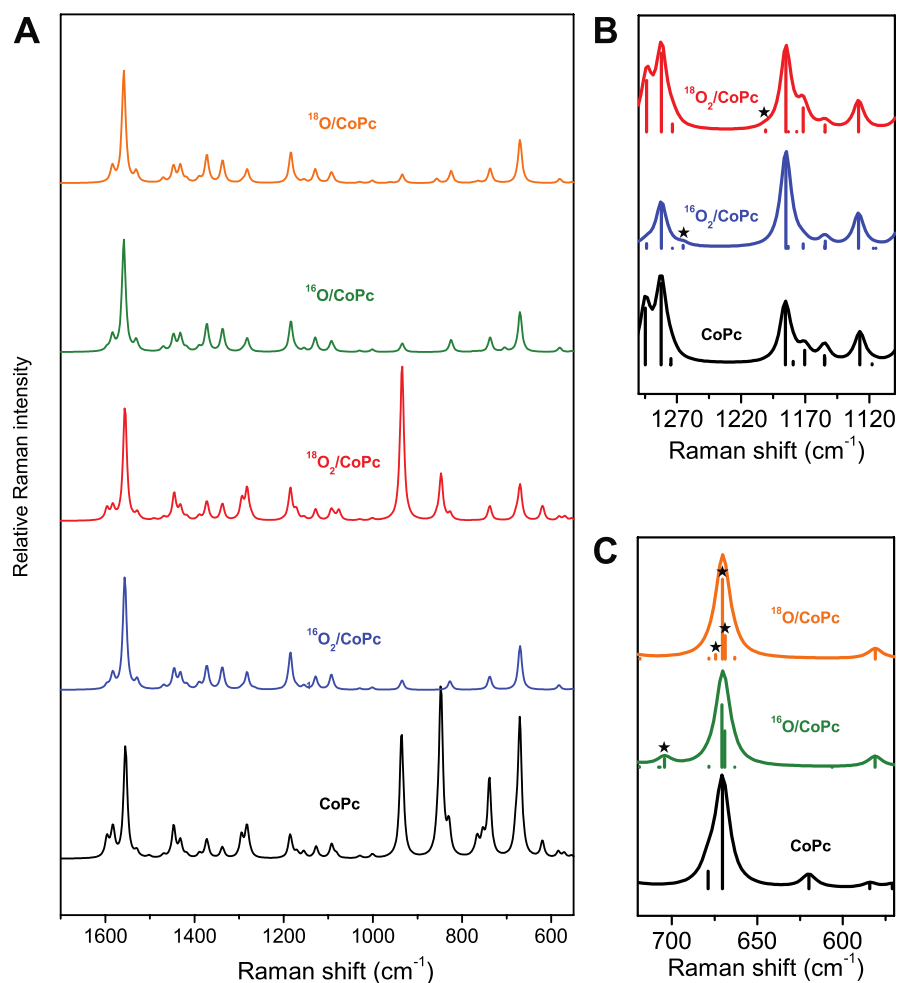


Figure S5. (A) TDDFT calculated Raman spectra of CoPc (black spectrum), $^{16}\text{O}_2/\text{CoPc}$ (blue spectrum), $^{18}\text{O}_2/\text{CoPc}$ (red spectrum), $^{16}\text{O}/\text{CoPc}$ (green spectrum), and $^{18}\text{O}/\text{CoPc}$ (orange spectrum) without Ag(111) surface. (B) Zoomed-in calculated Raman spectra of CoPc (black stick and spectrum), $^{16}\text{O}_2/\text{CoPc}$ (blue stick and spectrum), and $^{18}\text{O}_2/\text{CoPc}$ (red stick and spectrum). (C) Zoomed-in calculated Raman spectra of CoPc (black stick and spectrum), $^{16}\text{O}/\text{CoPc}$ (green stick and spectrum), and $^{18}\text{O}/\text{CoPc}$ (orange stick and spectrum). Oxygen related modes are marked with black stars in (B) and (C). Overall, the CoPc modes are not altered (in terms of frequency and relative intensity) upon oxygen adsorption. However, due to the lack of the Ag(111) surface, the calculated O-O and Co-O vibrational frequencies in the Raman spectra are blue shifted compared to the corresponding frequencies from normal mode calculations with Ag(111) surface (Table 2). Vibrational mode coupling is also observed when the energy of the O-O or Co-O vibrations are close to the Pc vibrations (Panel C, $^{18}\text{O}/\text{CoPc}$ orange spectrum).

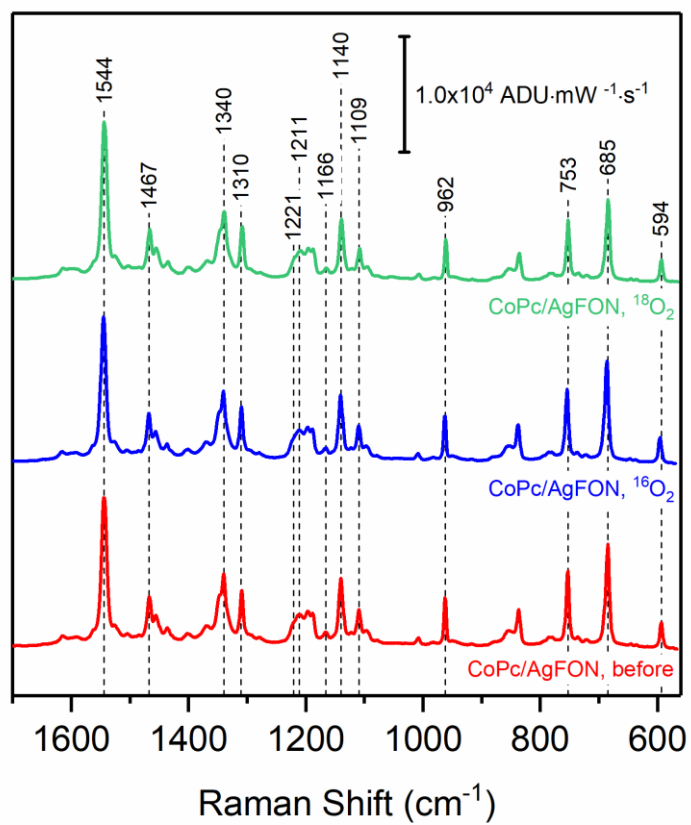


Figure S6. Wide range UHV-SER spectra of CoPc/AgFON before (red spectrum) and after $^{16}\text{O}_2$ (blue spectrum) and $^{18}\text{O}_2$ (green spectrum) dosing.

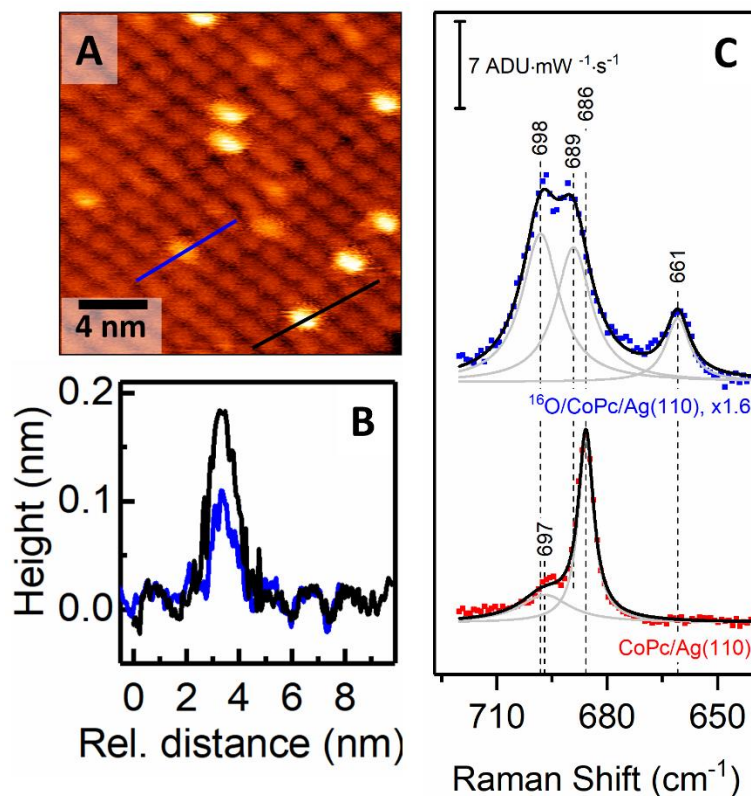


Figure S7. (A) A STM image of ~ 1 ML of $\text{CoPc}/\text{Ag}(110)$ after dosing with ~ 1800 L of $^{16}\text{O}_2$ with selected line profiles shown in (B). Two adsorption configurations are observed: $\text{O}_2/\text{CoPc}/\text{Ag}(110)$ (brighter spots, black line profile) and $\text{O}/\text{CoPc}/\text{Ag}(110)$ (dimmer bright spots, blue line profile). (C) TERS before (red spectrum) and after $^{16}\text{O}_2$ dosing (blue spectrum) measured on an $\text{O}/\text{CoPc}/\text{Ag}(110)$ rich area, with Lorentzian peak fitting showing changes at the ~ 680 cm^{-1} spectral region. Similar to $\text{O}/\text{CoPc}/\text{Ag}(111)$, a new band appears at 661 cm^{-1} after O_2 dosing. The CoPc band at 697 cm^{-1} grows in intensity and the band at 686 cm^{-1} is slightly shifted to 689 cm^{-1} . This explains the origin of the shifting and broadening of the 688 cm^{-1} band in $\text{O}/\text{CoPc}/\text{Ag}(111)$ after O_2 dosing. In the case of $\text{O}/\text{CoPc}/\text{Ag}(111)$, the weak ~ 697 cm^{-1} band is not observed before dosing. In addition, the bands at 688 cm^{-1} and ~ 699 cm^{-1} are not well resolved making them appear as a single blue-shifted and broader band. The relative intensity of the 688 cm^{-1} and 699 cm^{-1} bands determines the peak frequency of the unresolved combined band.

Movie S1. Movie for the vibrational normal modes in Figure 3.

Movie S2. Movie for the vibrational normal modes in Figure 5.

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