

Supporting Information for

**Charge carrier injection electroluminescence with CO functionalized tips on single molecular emitters.**

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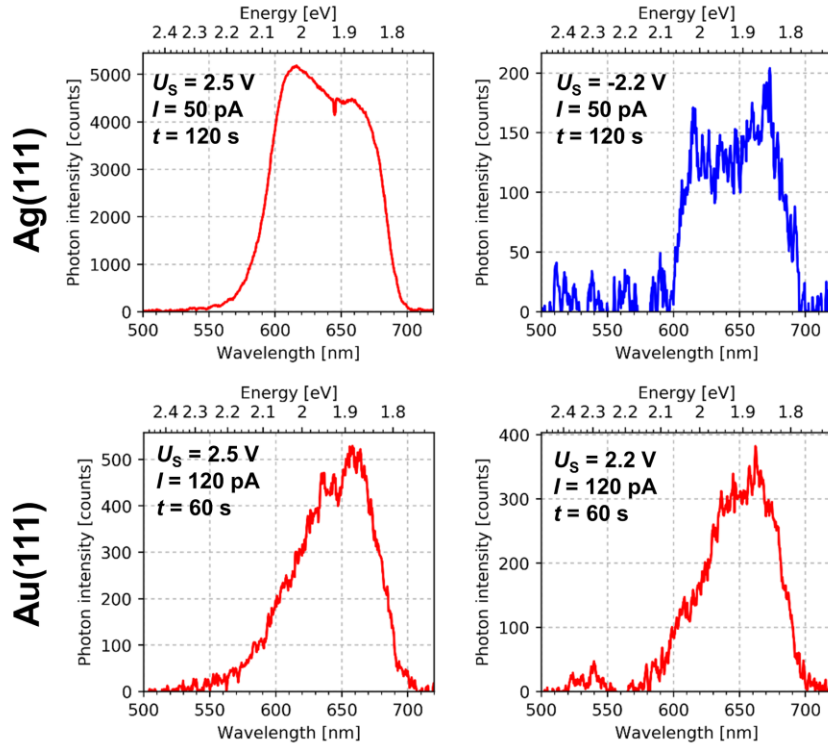
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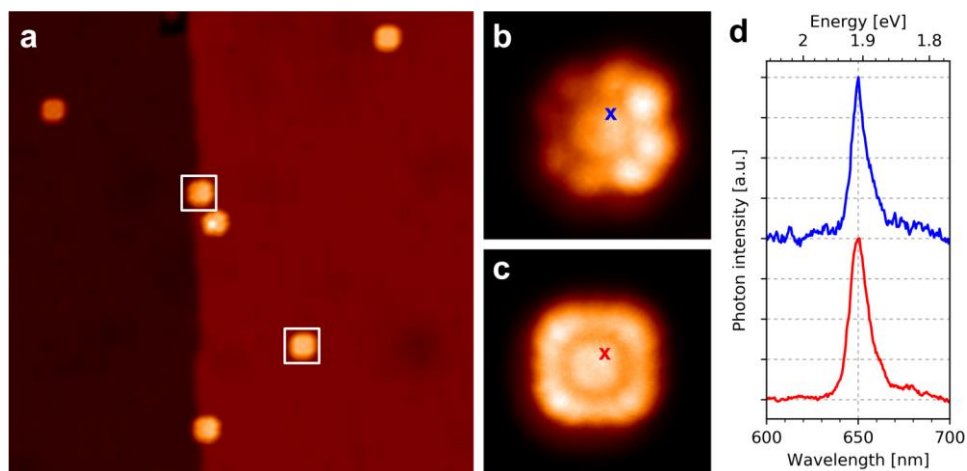
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## **Experimental details:**

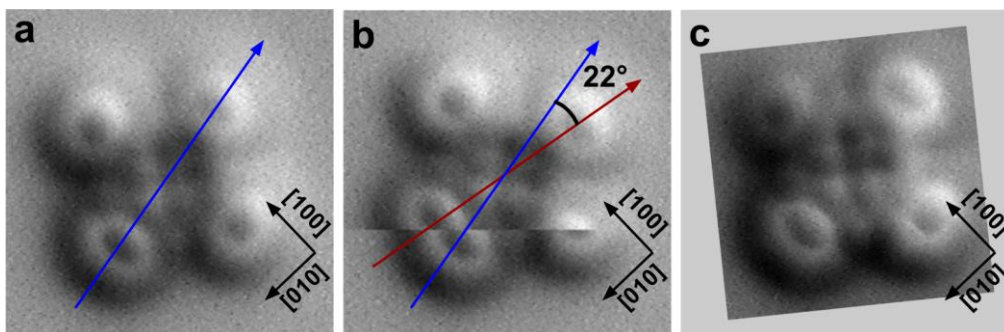
We performed the experiments in an ultrahigh vacuum system (UHV) equipment with a base pressure of  $5 \times 10^{-11}$  mbar consisting on a preparation chamber and an analysis chamber. The SPM scanner and ncAFM sensor (Createc GmbH) are placed inside a cryogenic bath at 4 K. The q-plus sensor consists of a 30 kHz mechanical oscillator with an Au tip, sharpened by focused Xe ion beam (Tescan FERA3). The resulting quality factor of the sensor at 6 K was over 22000. The oscillation amplitude setpoint to record the frequency shift images was set to 50 pm. The optical path consists of two lenses, first fixed to the coarse scanner and second on the air side, coupling the photons into a fiber of a spectrograph. The spectrograph is a Shamrock with Andor iStar 720 CCD. The overall spectral resolution was 3.5 nm FWHM, the spectral range was 400 - 700 nm. All spectra and maps were collected in a photon-counting regime. Photon maps were measured in a constant height mode, by taking a spectrum in every point, with accumulation period per pixel typically 7 s. In the presented maps, each pixel represents part of a corresponding spectrum, integrated in the given range of wavelengths. Photon maps are recorded in constant-height mode. The constant-height mapping mode is a rational choice for taking the photon-maps, since the constant-current mapping may introduce ambiguity due to the variable Z-height, e.g. by modulating the nanocavity optical density, that is likely to produce unphysical features in the photon maps. The ZnPc molecules were thermally evaporated onto clean Ag(111) and Au(111) substrates kept at 400 K with bi- and trilayer islands of NaCl. CO has been deposited onto the sample by increasing the partial pressure of CO to  $10^{-7}$  mbar in the cryostat chamber and opening an evaporation port for 1 min.



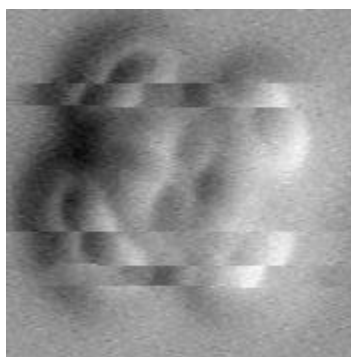
**Figure S1: Plasmonic spectra of the tips used in the experiments.** Typical STML spectra recorded prior to taking the STML photon maps on 3ML-NaCl/substrate on both 3ML-NaCl/Au(111), showing the plasmonic electroluminescence of the tips used in the measurements, presented in the main text. In all cases it was ensured that this plasmonic emission spectrally overlaps with the excitonic line of the ZnPc, for an efficient near-to-far-field coupling, such that they reach maximum around the excitonic line of the neutral ZnPc. The tunneling conditions and integration times are specified in the respective panels. The data are presented as they are, i.e. without any smoothing or filtering.



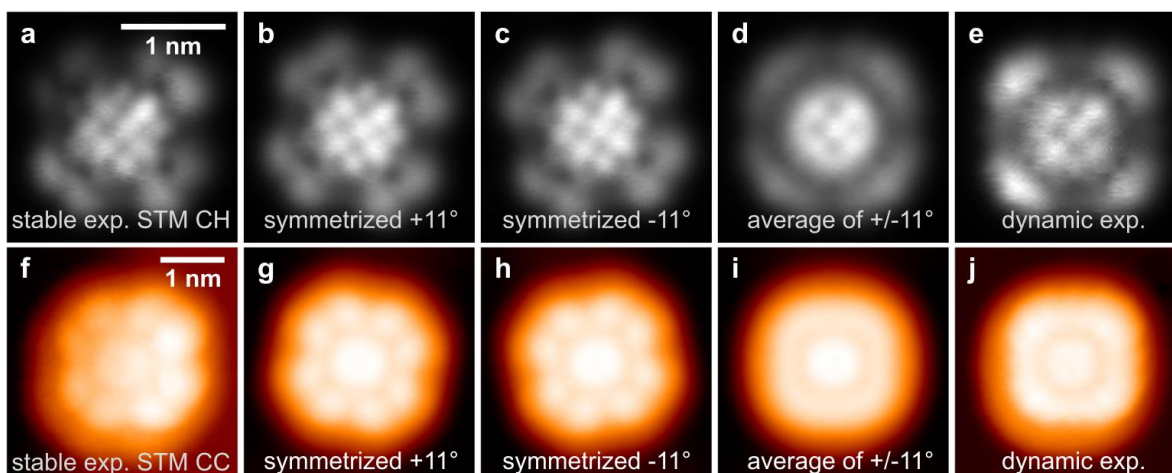
**Figure S2: Overview of the area showing the locations of measured molecules and their STML spectra.** a) STM constant-current overview of the area with the stable and dynamic ZnPc/3ML-NaCl/Au(111) molecules used for electroluminescence mapping (marked by white squares). Size 50x50 nm<sup>2</sup> setpoint 2.2 V, 3 pA. b,c) STM constant-current details of the stable and dynamic molecule, size 3.6 x 3.6 nm<sup>2</sup>, setpoint 2.2 V, 1 pA. d) Electroluminescence spectra for the stable (blue) and dynamic (red) ZnPc, taken at positions marked in b) and c), at setpoint 2.2 V.



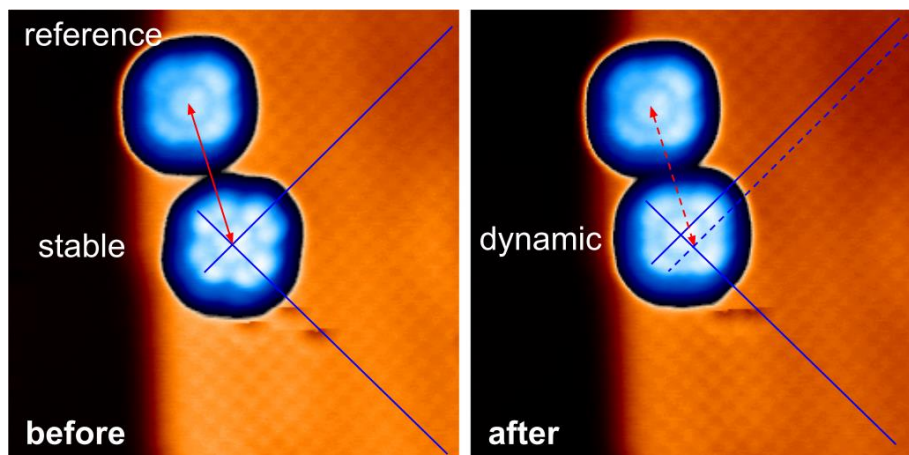
**Figure S3: Analysis of rotational angles of ZnPc molecule from frequency shift maps taken at constant height.** a) first and b) second metastable position of the molecule in its rotational state. c) image of a molecule stabilized at a step edge. The blue and red arrows denote orientations of the molecules for comparison. Black arrows mark the directions of principal axes of the NaCl(001) substrate, transferred from STM images. All images are presented at the same scale  $2.2 \times 2.2 \text{ nm}^2$ , including the padding in c).



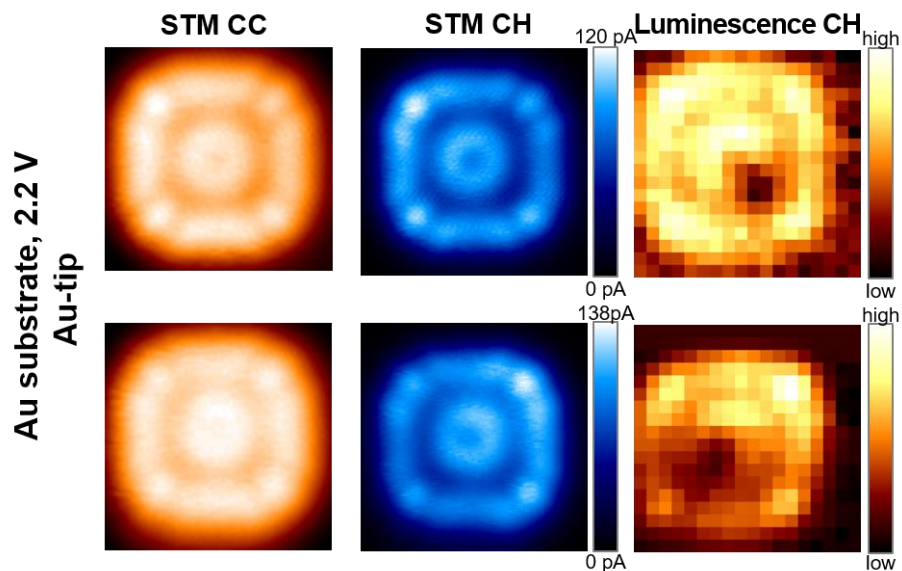
**Figure S4: AFM constant-height image of a dynamically switching molecule.** The peripheral benzene rings maintain the same distance from the center of the molecule after rotation, which demonstrates that the molecule does not move laterally while switching. Size of the image is  $2.2 \times 2.2 \text{ nm}^2$ , bias 25 mV.



**Figure S5: Test of correspondence between STM contrasts of a dynamic molecule, and a composed image derived from averaging data of a stable molecule rotated computationally.** a) The original constant height current map of a stable molecule. b) ideal image of a stable molecule, symmetrized by averaging vertically and horizontally flipped original images in a) and rotated  $+11^\circ$ . c) symmetrized image b) rotated  $-11^\circ$ . d) average of b) and c). e) the original constant height current map of a dynamic molecule. Physical size of images a)-e) are  $2.2 \times 2.2 \text{ nm}^2$ . f) The original constant current image of a stable molecule. g) ideal image of a stable molecule, symmetrized by averaging vertically and horizontally flipped original images in f) and rotated  $+11^\circ$ . h) symmetrized image g) rotated  $-11^\circ$ . i) average of g) and h). j) the original constant current image of a dynamic molecule. Physical size of images f)-j) are  $3.6 \times 3.6 \text{ nm}^2$ . All the 2D transformations and averaging have been performed in the GNU Data Language program.

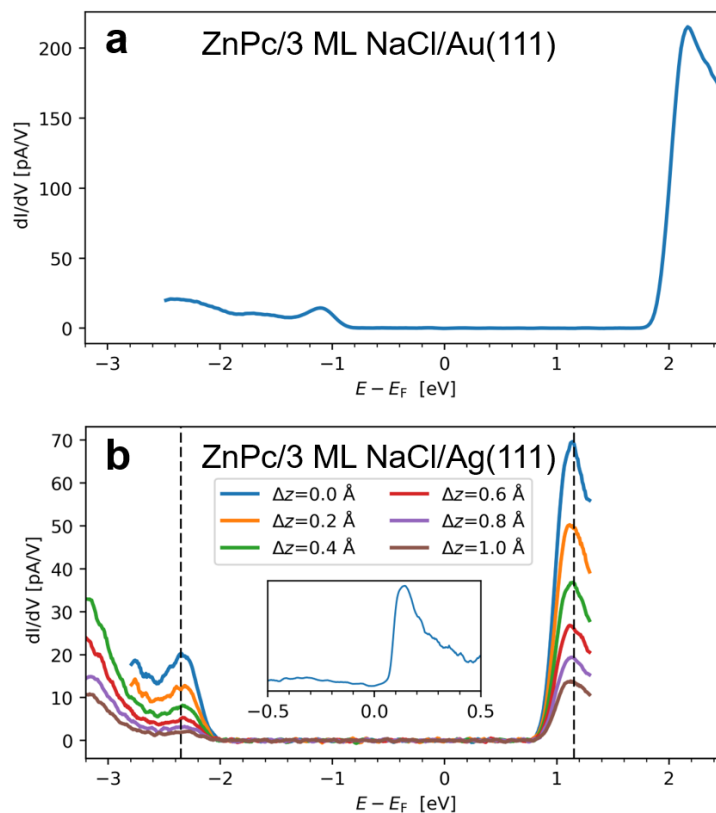


**Figure S6:** Example of unpinning of a stable ZnPc/3ML-NaCl/Au(111), starting in one of the rotational orientations. Blue solid lines denote the registry of the molecule center above the Cl sites and red arrow marks the relative position with respect to a reference dynamic ZnPc. Blue dashed line and dashed arrow show the registry and relative position as it was before the manipulation. The lateral movement of the molecule corresponds to one unit vector of NaCl(001). Dark streaks in the lower part of the image are CO molecules, moved by the tip in the process of scanning. A composite color scale is used to enhance the contrast of the substrate.



**Figure S7: Tip state and position of the intensity minimum in the photon maps.** ZnPc/3ML-NaCl/Au(111) STM CC, STM CC and luminescence CH maps with two different Au tips, measured at 2.2 V. The luminescence maps show pronounced dips in two distinct positions near the center of the molecule. The position of the intensity dip in the photon maps is tip-dependent. The measurements have been taken in two separate sessions, each after a new tip preparation by nanoindentation. A very likely explanation for the variation of the dip position is a strong dependence of the plasmonic coupling of the tip to the molecular emitter on the mesoscopic shape of the tip as implied by other works [Ref. S1, S2].





**Figure S8: Differential conductance spectra for ZnPc on the two substrates.** a)  $dI/dV$  spectrum of ZnPc/3ML-NaCl/Au(111) measured at the molecule lobe. The setpoint was -2.5 V and 200 pA. b)  $dI/dV$  spectrum of ZnPc/3ML-NaCl/Ag(111) measured at the molecule lobe as a function of  $\Delta Z$  setpoint change, demonstrating a negligible voltage drop effect across the 3ML-NaCl on the HOMO/LUMO energy. The reference  $\Delta Z=0$  was set at 1.3 V, 25 pA. The inset shows a detail  $dI/dV$  of the interface state near to the fermi level, detectable at the  $z=-2 \text{ \AA}$  (interface state is not changed on the molecule). Dashed lines in mark the positions of HOMO and LUMO.

## Supporting Information references

[S1] Chen, C., Chu, P., Bobisch, C. A., Mills, D. L. & Ho, W., Phys. Rev. Lett. 105, 217402 (2010).

[S2] Neuman, T., Esteban, R., Casanova, D., García-Vidal, F. J. & Aizpurua, Nano Letters 18, 2358–2364 (2018).