ABSTRACT: The ability to control the emission from single-molecule quantum emitters is an important step toward their implementation in optoelectronic technology. Phthalocyanine and derived metal complexes on thin insulating layers studied by scanning tunneling microscope-induced luminescence (STML) offer an excellent playground for tuning their excitonic and electronic states by Coulomb interaction and to showcase their high environmental sensitivity. Copper phthalocyanine (CuPc) has an open-shell electronic structure, and its lowest-energy exciton is a doublet, which brings interesting prospects in its application for optospintronic devices. Here, we demonstrate that the excitonic state of a single CuPc molecule can be reproducibly switched by atomic-scale manipulations permitting precise positioning of the molecule on the NaCl ionic crystal lattice. Using a combination of STML, AFM, and ab initio calculations, we show the modulation of electronic and optical bandgaps and the exciton binding energy in CuPc by tens of meV. We explain this effect by spatially dependent Coulomb interaction occurring at the molecule–insulator interface, which tunes the local dielectric environment of the emitter.

KEYWORDS: STML, CuPc, AFM, doublet, exciton, NaCl, switching

When a single-molecule emitter (SME) is placed in a solid or onto a surface, it is subjected to hybridization or screening of its electronic orbital structure with the local environment due to Coulomb interaction. One of the typical consequences is a change in the energies of the molecular electronic excitations, sometimes called spectral diffusion. Photoluminescence and related time-resolved techniques have been widely used to measure exciton environmental effects in SMEs, but achieving high spatial resolution that can resolve individual emitters has remained a challenge. Efforts to study the local environment of excitons in 3D molecular crystals, 2D materials, or 1D carbon nanotubes have been made; however, an atomic spatial resolution is still lacking. Recently, scanning tunneling microscopy induced luminescence (STML) has emerged as a powerful tool to probe optoelectronic properties on the atomic scale, such as exciton charge annihilation, coupled modes on molecular dimers, superradiance in artificially constructed chains, or the charge state. Spectral switching has been investigated by using resonant energy transfer between different excitons in Pc heterodimers and by tautomerization of H,Pc. Nevertheless, the Coulombic effects of the local environment on the excitonic states of SMEs have not been extensively addressed.

For closed-shell single-molecule emitters excited in a tunnel junction, injection is not spin-selective and the formation probability is 75% for dark triplet and only 25% for bright singlet excitons. To obtain higher efficiencies for light-emitting purposes, triplet-to-singlet intersystem crossing and bright triplet states have been proposed to effectively increase the quantum yields. Recently, the discovery of electroluminescence from a doublet, rather than from a singlet or a triplet, has allowed reaching emission quantum yields up to 100%. However, doublet emission has, so far, been only demonstrated for ensembles of radical species easily undergoing chemical degradation, and doublet SMEs have not been reported.

Here, we show using combined STML/AFM measurements and ab initio calculations that the doublet excitonic state of SMEs can be controlled in a deterministic way by atomically precise manipulations. The use of scanning probe technique at cryogenic temperature allows the manipulation of the

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adsorption configuration of individual copper phthalocyanine (CuPc) molecules on ultrathin NaCl films on Ag(111) with sub-Å precision and consequently control their excitonic state. CuPc is an open-shell complex with spin $S = 1/2$ due to an unpaired electron residing in the $d_{x^2-y^2}$ ($b_1^g$) metal orbital.\textsuperscript{21–23} By injection of charge carriers we create electron–hole pairs in the resulting SMEs and detect the photon emission enhanced by the plasmonic picocavity formed by the tunnel junction. We observe a change in the wavelength of the excitonic emission between two configurations. Combination of atomically resolved STM images with AFM frequency shift maps, local tunneling spectroscopy, and \textit{ab initio} calculations allows determining the modification of the electronic structure of the molecules and linking it to the observed shift of its excitonic line.

RESULTS AND DISCUSSION

Figure 1 shows a sequence of STM images, an AFM image, and electroluminescence spectra obtained during a manipulation experiment of SMEs. In Figure 1a–c the same two CuPc molecules are resolved in the two possible adsorption positions, namely, dynamic and steady states (see below), on top of a two-monolayer (ML) of NaCl on Ag(111) (for details of sample preparation see the Methods section). In Figure 1a both CuPc molecules manifest a 16-lobe pattern characteristic of molecules in a dynamic configuration arising from a bistable adsorption geometry. The distinctive STM appearance can be rationalized by the overlapping electronic structures of two chirally rotated adsorption configurations oscillating at a frequency well beyond the STM bandwidth.\textsuperscript{24} STML spectrum 1 in Figure 1e, typical for dynamic CuPc, taken at $-2.5$ V above a lobe consists of a sharp line at $1.9$ eV on a plasmonic background (Spectrum 6). Spectrum 2 taken on the dynamic molecule on the right-hand side of the panel in Figure 1a however reveals a different spectral fingerprint. It shows the sharp line at $1.9$ eV accompanied by an intense shoulder at lower energies, which is an indication of a sudden modification of the molecular exciton state. Indeed, a subsequent image (Figure 1b) confirms the molecule changed its appearance to an eight-lobe shape typical for a steady stabilized molecule. STML spectrum 3 remeasured on the now steady molecule shows a broad peak at the shoulder position at $1.86$ eV and disappearance of the $1.9$ eV feature. Spectra 4 and 5 reproduce the same behavior on the second molecule upon switching from dynamic to the steady configuration, visualized by the STM in Figure 1b,c. Therefore, spectrum 2 can be rationalized as a linear combination of the spectra from the dynamic and steady states.

In our investigation of the dynamic to steady state conversion of molecules on 2 and 3 MLs of NaCl on Ag(111) we found that molecular switching from the dynamic to the steady state occurs reproducibly after applying 100 pA and $-2.3$ V or at biases over $2.0$ V, similarly as described by Zhang \textit{et al} for manipulation of ZnPc molecules.\textsuperscript{11} The conversion from steady to a dynamic state process can be achieved at biases of $-2.5$ V and below, by applying lateral forces with the CO-passivated tip to prevent picking up the molecule, however with a significantly lower efficiency, strongly indicating that the steady state is energetically favored over the dynamic state (for details see the Supporting Information). Switching CuPc to steady state produces a systematic red-shift and broadening of the STML lines of the spectrum. We have measured red-shifts of $20.6 \pm 3.4$ meV for molecules at 3 ML and $34.0 \pm 3.5$ meV at 2 ML, plus broadenings of $63 \pm 13\%$ and $103 \pm 29\%$ (Figure 2b, Figure S2, and Table S1), respectively. Both effects are more pronounced on 2 ML of NaCl than on 3 ML. The environmentally induced exciton modification presented here has not been observed in photoluminescence nor in electroluminescence of CuPc single crystals\textsuperscript{26,27} or thin films.\textsuperscript{28,29} The exciton switching of the CuPc must therefore originate from the interaction of the electronic structure of the molecule with its nearest local environment.

An atom-scale characterization of the steady and dynamic adsorption configurations of CuPc on NaCl provides the link between their adsorption configuration and the spectral switching. A high-resolution STM image obtained with a CO-functionalized tip in Figure 2a shows two molecules, each in one of the configurations, together with the underlying NaCl lattice. It has been shown that STM topographs of NaCl typically image Cl$^-$ ions as protrusions.\textsuperscript{25,27} Accordingly it can
Figure 2. Analysis of the adsorption geometry in relation to the STML fingerprint. (a) STM constant-current image of CuPc molecules in the steady and dynamic configurations and their registration with the NaCl lattice obtained with a CO-functionalized tip. Parameters: 7.5 × 3.2 nm², −2.3 V, 1 pA. (b) Representative STML fingerprints of the dynamic (green) and steady (violet) configuration on 3 ML NaCl. (c–f) Computationally optimized theoretical models of the steady (c, e) and dynamic geometries (d, f). (g) AFM constant-height frequency shift map with two different tip heights enabling submolecular resolution on the CuPc and atomic resolution on the NaCl substrate for registration. Parameters: 1.7 × 2.8 nm², 25 mV. The spheres in the models in panels (c)−(f) representing the atoms have sizes corresponding to their atomic radii.

Figure 3. Theoretical analyses of the excited and ground states and the impact of the adsorption geometry. (a) Scheme of the simulated orbital energy level reordering upon transfer of an electron (marked by red color) from HOMO to LUMO within an isolated CuPc molecule, showing the occupied and virtual levels of the frontier orbitals. The ground doublet state is denoted as D₀; the excited doublet state as D₁. Corresponding orbital geometries are depicted in the same order, parallel to the scheme for clarity. (b–g) Calculated charge redistribution isosurface plots and profiles, showing the accumulation (blue) and depletion (red) (at ±0.003 e⁻/Å³, respectively) of electrons in the CuPc/2 ML-NaCl systems in the dynamic (b, c) and steady (e, f) configuration. (d, g) Corresponding profiles of the electron density, obtained by integration in the directions parallel to the NaCl surface. Plots are superimposed onto the atomistic model for orientation. The spheres in the models in panels (b)−(g) representing the atoms have sizes corresponding to their atomic radii.
be determined that the dynamic molecule is adsorbed with its metal core located on top of a Cl\textsuperscript{−} site (darker color, higher Z-value), while the steady state latches on top of a Na\textsuperscript{+} site (brighter color, lower Z-value). This is further confirmed by the frequency shift channel, measured on the steady configuration in Figure 2g. The image is composed of two sections measured in constant tip—sample height at different offsets facilitating atomic resolution on both the molecule and the substrate. It permits a straightforward identification of the molecular backbone (in the upper section of the panel) and enables a very precise registration with the substrate (lower section). As the image is taken in a regime where repulsive forces dominate, the lower frequency shift regions can be unambiguously attributed to Na\textsuperscript{+} atoms.\textsuperscript{30} By extrapolation of the substrate lattice it is then easily demonstrated that the steady CuPc is centered above a Na\textsuperscript{+} site (see AFM simulations in Figure S1).

These findings agree with first-principles simulations, in which a model CuPc molecule was positioned with different angles of in-plane rotation with respect to the 2 ML-NaCl lattice, over Na\textsuperscript{+} or Cl\textsuperscript{−} ions. After a self-consistent minimization of the total energy of the system, the most stable configuration is found to be a 45°-rotated molecule above the Na\textsuperscript{+} site, and the second most stable at an ±9° angle sitting on the Cl\textsuperscript{−} site (see Figure 2c,e and Figure 2d,f, respectively). These two configurations perfectly match the experimentally observed steady and dynamic configurations, respectively. The calculated total energy difference between them is 90 meV in favor of the steady geometry. The simulated relaxations of the molecular backbone and the separation from the NaCl surface in both configurations are comparable and only marginally different, as in both cases the peripheral parts are slightly bent toward the substrate.\textsuperscript{31}

The modification of the exciton energy described above can be reproduced by excited-state DFT calculations performed for isolated CuPc and the dynamic and steady configurations on the NaCl substrate, placed on either the Na\textsuperscript{+} or Cl\textsuperscript{−} sites. NaCl is modeled by point charges, and the equilibrium geometries are derived from the previous DFT simulations. The excitation is represented by a transfer of a spin-up or spin-down electron from the highest occupied molecular orbital (HOMO) of CuPc in its ground state D\textsubscript{0} into the lowest unoccupied molecular orbital (LUMO), producing an excited state D\textsubscript{1}. In the ground state of the isolated molecule, the singly occupied orbital (SOMO) is energetically below the doubly occupied HOMO and HOMO−1 orbitals (Figure 3a). The corresponding unoccupied orbital (SOMO) is above the degenerate LUMO orbitals. Upon the HOMO to LUMO electron transfer, the HOMO orbital is destabilized and the degeneracy in LUMO orbitals is removed. The orbital ordering below the HOMO is also a subject of rearrangement, mainly reversing the relative energy ordering of the HOMO−1 and SOMO levels. Despite being able to obtain the emission energy solely for the isolated molecule, the scenarios simulating the adsorbed molecules produce consistent values for the absorption in both spin branches and manifest the same orbital energy reordering upon excitation (see Table S3). Only subtle energy changes ensue as a result of the electrostatic field action, particular for each adsorption configuration on NaCl and due to spin asymmetry. Therefore, we estimate by extrapolation that the optical gap of the steady state is 22 meV lower than of the dynamic state, in good agreement with the experiment.

Knowing that the distinct spectral fingerprints are linked to their respective adsorption geometries, we now focus on a detailed electronic structure characterization of CuPc on 3 ML NaCl using differential conductance tunnelling spectroscopy (dI/dV). Figure 4a shows the dI/dV spectra in a bias range encompassing the peaks originating from LUMO and HOMO of the steady and dynamic molecules, measured before and after a controlled stabilization of the CuPc at their lobes, for various Z set points. Using normalization we determine that the gap of the steady CuPc is about 100 mV narrower than of the dynamic CuPc (Figure 4bc). The apparent LUMO and HOMO positions of the stabilized molecule are shifted toward the Fermi level by 70 and 30 meV, respectively. Additional local contact potential differences measured with various tips over both configurations using Kelvin probe parabolas show a small shift up to 45 meV (see Figure S5), consistent with a decrease of the overall electrostatic potential on the steady molecules with respect to the dynamic ones.\textsuperscript{32}

One can anticipate that a lower HOMO−LUMO gap will be reflected in a lower exciton energy upon D\textsubscript{0} → D\textsubscript{1} transition, following an orbital level renormalization. However, the 100 meV value measured by the dI/dV exceeds by far the difference of the corresponding exciton energies obtained from the optical spectroscopy (21 meV). The apparent HOMO−LUMO energy difference measured from dI/dV represents the transport gap of the system, which may generally differ from the real HOMO−LUMO gap due to transient renormalization of the frontier orbital energies upon
The electronic gap of solid CuPc thin films on Au(111) has been reported to be 3.1 eV by direct and inverse photoemission. These results compare well with the 3.0 and 2.9 eV gaps measured here by dV/dI for dynamic and steady molecules, respectively, and imply that neither the high electric fields of the tunnel junction nor the presence of the tip and insulating substrate alters the measured electronic bandgap of the molecules significantly.

The difference between the HOMO–LUMO gap derived from dV/dI and the optical gap measured from STML is a strong indication of a modification of the exciton binding energy (ΔE_{BE}). The difference (ΔE_{BE}) between its values on the Na⁺ and Cl⁻ sites (E_{BE}^{Na}, E_{BE}^{Cl}) can be estimated using all the measured transport and optical gaps. In particular, taking the measured transport (E_{GAP}^{Na}, E_{GAP}^{Cl}) and optical gaps (E_{OPT}^{Na}, E_{OPT}^{Cl}) for the dynamic and steady CuPc molecules, ΔE_{BE} follows:

\[
\Delta E_{BE} = (E_{GAP}^{Cl} - E_{OPT}^{Cl}) - (E_{GAP}^{Na} - E_{OPT}^{Na}) = (E_{GAP}^{Cl} - E_{GAP}^{Na}) - (E_{OPT}^{Cl} - E_{OPT}^{Na}) = (100 \text{ meV}) - (21 \text{ meV}) = 79 \text{ meV}
\]

meaning that the exciton of the steady molecule is less stable than that of the dynamic molecule. We note that this derivation provides the relative differences among the configurations rather than absolute values of the exciton binding energies in CuPc (reported to be 0.6 eV). Since our measurements of the dV/dI gap and STML have been performed for the two very similar systems and with identical tip, most uncertainties are removed, which allows us to conclude that the 79 meV can only be related to the change of the CuPc doublet exciton binding energy.

A detailed analysis of the ab initio calculations of the ground states in Figure 3b–g allows us to evaluate the total electron density redistribution on the adsorption configurations and points out the origin of the exciton energy difference between the two states. Data show the density difference (Δρ) of the fully perturbed CuPc and NaCl substrate relative to their unperturbed states. Isosurfaces plots (at Δρ = ±0.003 e/A³) in Figure 3b,c,e,f corresponding to the electron density increase (blue) and depletion (red) reveal the characteristic interaction of individual atoms within the molecule with the Na⁺ and Cl⁻ sites in their vicinity. A systematic electron increase is visible under the atoms atop the Na⁺ in the interface region; conversely for atoms residing above the Cl⁻ ions an electron density depletion occurs. The most striking difference is on the metal core, where the charge redistribution is of opposite sign for the two configurations centered above Na⁺ and Cl⁻. It also leads to the distinct spatial redistributions at the ligand. This can be understood in terms of the simple electrostatic action of the substrate on the electron envelope of the molecule (see the Hartree potential in Figure S6).

The net effect of the surface potential on the molecule is an electron accumulation in the interface region and depletion at the molecule, visible in the plots of Δρ integrated across the axes parallel to the surface, plotted as a function of Z (Figure 3d,g). The electron density difference in the interface region is slightly larger in the case of the dynamic configuration, hinting at a higher overall positive field acting on the molecule. Indeed, the total numbers of Na⁺ and Cl⁻ ions directly acting on the molecule vary between 9 Na⁺, 12 Cl⁻ on the steady and 12 Na⁺, 13 Cl⁻ at the dynamic configurations, respectively.

The altered charge redistribution demonstrates the extent to which the exact NaCl lattice orientation and registry with the molecular backbone affect charges within the system. The differences in the Coulomb interaction will impose an inevitable correction on the electron–hole bound state (exciton) and the transport gap. Apparently, as seen from the experiment, the stabilization of the molecule leads to lowering of the electronic gap, exciton and binding energies, and widening of the main spectral line. While the exciton and gap energetics can be explained using the interaction with the substrate potential and screening by the substrate, the spectral line width, which is notoriously difficult to split into individual contributions due to a number of both radiative and nonradiative recombination processes, remains an open question. We can merely state, based on the experiments, that the excitons on the steady CuPc appear to have a higher probability of nonradiative decay into the bulk (by, for example, coupling to the phonon bath), causing the spectral line broadening.

**CONCLUSIONS**

In conclusion, we have demonstrated mechanooptical switching of a single CuPc molecule on NaCl on Ag(111). A change in energetics of its doublet excitonic state could be triggered through atomic-scale manipulations that allow precisely defining the adsorption configuration, with the CuPc molecule centered above either a Na⁺ or Cl⁻ ion. From the measured values of the optical transitions and changes in the system transport gaps, we estimate a difference of the exciton binding energies: the exciton on the dynamic molecule is 79 meV more stable than on the steady one. Theoretical calculations confirm the experimentally determined geometries as the most favored, reproduce the changes in the exciton energy, and provide details on the Coulomb-mediated charge redistribution within these systems. This allows linking the local effect of the NaCl lattice potential on the CuPc orbital levels with modifications in the exciton energy and electronic gaps. Our results represent a step toward a detailed understanding of the effect of the local environment in the many-body excitations in single-molecule emitters.

**METHODS/EXPERIMENTAL**

**Preparation of Sample and Tip.** The experiments were performed in a ultra-high-vacuum (UHV) system with a base pressure of 5 × 10⁻¹¹ mbar. NaCl was evaporated on Ag(111) kept at 400 K to produce 2 and 3 ML NaCl islands. The CuPc molecules were evaporated onto the sample kept at T < 10 K from a tantalum crucible. CO dosing has been achieved by exposure of the cold sample to a CO partial pressure of 10⁻⁷ mbar for 1 min.

**STM, STS, AFM, and Kelvin Probe.** The combined STM and ncAFM sensors attached to a scanner of a 4K UHV SPM instrument (Createc GmbH) were based on a tuning-fork sensor operating at 30 kHz, equipped with a Ag or Pt/Ir tip, sharpened by a focused Xe-ion beam (Tescan FERA3). The resulting quality factor of the sensor at 7 K was >22 000. The set point amplitude of oscillation for the frequency modulation mode was set to 50 pm.

**STML.** 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 connected to a spectograph. The spectograph is a Shamrock 163i with an iDus 401 BV or Newton 920 BEX2-DD CCD camera. The overall spectral resolution was 3.5 nm fwhm, and the spectral range was 400–840 nm. All spectra were collected in an accumulating regime.

**Density Functional Theory Calculations of the Geometries and Charge Redistribution.** The calculations were carried out using the Vienna Ab initio Simulation Package (VASP) for the ground-state electronic structure of CuPc in its ground state.
using the FHI-aims code\textsuperscript{37} to describe the electronic structure of the CuPc molecule on the bilayer NaCl(100) surface. The calculations were performed using the GGA-PBE approximation of the exchange–correlation potential including the Tkatchenko–Scheffler approach of the van der Waals interactions.\textsuperscript{38,39} The relativistic effects were taken into account by applying the scaled zeroth-order regular approximation.\textsuperscript{39} The NaCl(100) surface was modeled by a $7 \times 7$ supercell made of two layers on which a single CuPc molecule was placed in on-top position at the Na$^+$ or Cl$^-$ ion, respectively. The molecule was rotated by $15^\circ$, $30^\circ$, and $45^\circ$ with respect to the high-symmetry axes. Structural relaxations of the slab were performed for all the atoms, except the bottom NaCl layer. The calculations were considered converged when the remaining atomic forces and the total energy were found below $10^{-3}$ eV/Å and $10^{-6}$ eV, respectively. A single gamma point was used for the integration in the Brillouin zone. The total energy calculations were conducted to find the best adsorption site. Furthermore, the total density and the Hartree potential were used to determine the electronic interactions between the surface and the molecule.

**Excited-State DFT Calculations.** Self-consistent solutions of the electron wave functions and geometrical optimization were obtained using the wB97XD\textsuperscript{40} and LC-wPBE\textsuperscript{41-45} functionals in the spin-unrestricted mode, employing the SVP basis set.\textsuperscript{44,45} Visible absorption and emission spectra were derived using the comparison of the total energies of the D$_0 \rightarrow$ D$_1$ transiently excited systems with their corresponding ground states, independently for both spin branches. The electrostatic field of the NaCl substrate was simulated by a fixed bilayer of charges placed beneath the CuPc, calculated using the B3LYP\textsuperscript{46-48} functional, geometrically equivalent to the Na$^+$ and Cl$^-$ ion coordinates in the steady and dynamic configurations of the system (for more details see the Supporting Information). The Gaussian program package (Gaussian 16, revision C.01, M. J. Frisch al.\textsuperscript{,} Gaussian, Inc., Wallingford CT, 2016) was used for the calculations.

**ASSOCIATED CONTENT**

\* Supporting Information \* The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c03730. AFM simulations of NaCl and adsorbed CuPc molecules; AFM images of the steady and dynamic configurations; statistical analysis of the exciton switching on 2 and 3 ML of NaCl; switching steady and dynamic state; Kelvin probe measurement on steady and dynamic states; theoretical stability of steady and dynamic states; 2D representation of the Hartree potential for the dynamic and steady states; exciton energy calculations (PDF)

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**Author Contributions**

P.M. and M.S. conceived the experiments. J.D. and M.S. performed experiments and analyzed the experimental data. P.Mu., D.N., and P.J. performed theoretical simulations. P.M. and M.S. wrote the manuscript. All authors discussed the results thoroughly and provided comments on the manuscript.

**Notes**

The authors declare no competing financial interest.

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