The fluorescence of electrofluorochromic molecules depends on their charge state (1, 2) and is responsive to electrical stimuli. The optical properties of oxidized or reduced molecular species are generally addressed by spectroelectrochemistry (3) for large ensembles of molecules within an electrochemical cell. This allows for optical characterization while the oxidation states of a large number of molecules are being switched. Recent progress has shown that single-molecule sensitivity can be reached with this approach (4), but vibronic spectroscopy from molecular fluorescence (5, 6) has not been reported. At the single-molecule limit and in an electrochemical environment, such vibronic signals were only observed in surface-enhanced Raman spectroscopy measurements (7, 8), but at the cost of a direct contact between the molecule and the electrode that may alter the molecular properties. More importantly, it is not possible to obtain direct information regarding the immediate environment of the molecule nor reach submolecular optical resolution with any of these approaches.

Scanning probe microscopies can be used to control the charge state of atoms and molecules (9–14) and excite their vibrationally resolved fluorescence (15–21) with submolecular precision. Here we combine these approaches and report on the scanning tunnel microscopy (STM)−induced fluorescence of a ZnPc molecule in its neutral and (radical) cationic states. The luminescence spectra, obtained for ZnPc molecules decoupled from an Au(111) sample by thin layers of NaCl, reveal the electronic and vibronic signatures of the two oxidation states with a high spectral resolution. These data suggest a fast blinking of the molecule between its neutral and cationic form. Varying the exact number of insulating layers and the plasmonic response of the tip-sample cavity allowed us to manipulate the lifetimes of the charged and excited states. Finally, subnanometric variations of the tip position with respect to the molecule provided additional clues regarding the charging and fluorescence excitation mechanisms of the molecule.

The electronic and electroluminescent (EL) properties of single ZnPc molecules separated from a Au(111) surface by three layers of NaCl are shown in Fig. 1A. The differential conductance dI/dV spectrum, where I is current and V is voltage, acquired on a single molecule (Fig. 1B) revealed an electronic gap of 3.2 eV between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. These orbitals can be readily identified in STM images (Fig. 1B, insets) acquired at the corresponding energies. The same energy gap was reported for ZnPc deposited on salt-covered Ag(111) samples (20, 22), although with a rigid shift of the molecular orbitals to higher energies (+1 eV), reflecting the higher work function of Au(111) (~+0.8 eV) with respect to Ag(111). STM-induced light emission spectra acquired at positive (+2.5 V, Fig. 1C) and negative (~−2.5 V, Fig. 1D) sample voltages revealed a sharp (~20 meV) emission line at 1.89 eV (labeled X−), characteristic of the fluorescence of a single ZnPc molecule in its neutral form (20, 22, 23). The emission is 30 times more intense in the spectrum acquired at V = −2.5 V, where low-energy vibronic features are also observable. Similar light emission features (18, 20, 21, 23–25) were assigned to an excitation of a decoupled molecule by an energy transfer from an inelastic tunneling electron, possibly mediated by localized plasmons (see Fig. 1E).

The spectrum in Fig. 1D also displayed an intense and sharper (~10 meV) emission line at 1.52 eV (labeled X+), which was not reported in previous STM-induced luminescence measurements. This value is in excellent agreement with the fluorescence of ZnPc radical cations (ZnPc+) reported by experimental and theoretical studies (26–28). Figure 1F presents a possible explanation for this observation. For a sufficiently high negative voltage, the Fermi level of the tip becomes resonant with the singly occupied molecular orbital of the ZnPc, allowing for the tunneling of an electron from the molecule to the tip (labeled 1 in Fig. 1F). Because the molecule is decoupled from the metallic substrate by a thin insulating layer, its radical cation may be stabilized long enough for other tunneling events (labeled 2 in Fig. 1F) to occur. The energy lost by one of these electrons may then be transferred to the charged molecule that undergoes an excitation-emission cycle. The radical cation can only be generated at negative voltage, which explains why the X− line is not observed at positive voltage (29). The red-shifted fluorescence of ZnPc+ with respect to ZnPc then follows from the intrinsic changes in the electronic structure upon removal of one electron from the macrocycle (28). The widths of the emission lines are not lifetime limited (30) but rather reflect the dephasing caused by the interactions of the emitter with surface phonons. Indeed, density functional theory (DFT) calculations performed on an extremely close system (14) revealed that charging the molecule led to an important reorganization of the NaCl below the molecule. This hints at a reduction of the dephasing owing to the molecule-salt couplings upon charging. The proposed luminescence mechanism is discussed further in light of the current and voltage dependencies of the X0 and X− contributions in sections S1 and S2 of the supplementary materials.

The observation of charged atoms and molecules was reported for several double tunneling junctions (9–14). It is generally associated to a sharp feature in the dI/dV spectra at voltages characteristic of the charging energy. The absence of such a feature in the conductance spectrum (Fig. 1B), together with the simultaneous observation of X0 and X− in the optical spectrum Fig. 1D, suggests a fast blinking between the neutral and the charged states. The frequency of the blinking is >1 kHz, the limit of our setup. Note that the existence of a charged state in our experiment can only be deduced from the optical measurements and would be missed in usual STM and scanning tunneling spectroscopy experiments.

The spectrum in Fig. 1D also revealed several vibronic features on the low-energy side of the X− peak. An enlarged view of this spectrum (Fig. 2A) represents the vibronic lines as a function of their shift in energy with respect to the X− line. A comparison with the vibronic spectrum characteristic of the neutral molecule [Fig. 2B, (31)] revealed that the spectroscopic fingerprint of the ZnPc molecule is strongly affected by its redox state. We found that vibronic lines were
only slightly shifted in energy compared to the neutral case, but their relative intensities were strongly modified. DFT geometry optimizations of ZnPc showed changes of less than 0.01 Å in bond length upon oxidation (see section S3 in the supplementary materials), highlighting the large rigidity of the ZnPc backbone and explaining the absence of shift of the vibronic lines. To understand the changes in peak intensities, we have developed a finite difference method based on time-dependent DFT calculations (see materials and methods for details). We calculated the Frank and Condon factors of A1g vibrational modes as well as the Herzberg-Teller contribution to the transition moment of the first excited states. For the charged molecule, the B2g lines are enhanced and the A1g lines attenuated. In contrast to inelastic electron tunneling spectroscopy, where the selection rules leading to the presence of vibrational features in tunneling spectra are generally poorly defined (32), our fluorescence spectra provide a robust vibronic fingerprint of the probed molecule and its redox state. Similar vibronic information averaged over many charged molecules has previously been obtained from Raman spectroscopy, but here, such a spectroscopic fingerprint is observed in the fluorescence spectrum of an isolated molecule.

We followed the evolution of the EL spectrum recorded at a negative voltage on a single ZnPc molecule as a function of the number of NaCl atomic layers separating the molecule from the Au(111) surface, shown in Fig. 3A. For a molecule adsorbed on a single NaCl layer, the STM-LE spectrum (labeled 1) was similar to the one characteristic of the localized plasmon directly recorded on Au(111) (labeled 0), indicating a quenched molecular emission. The X0 and X+ emission lines appeared in the spectra acquired on molecules separated from the metal by two atomic layers of salt (labeled 2), where the two contributions have similar intensities. By contrast, the emission of the radical cation strongly dominates for three (labeled 3) and four (labeled 4) salt layers. We believe that the relative intensities of the X0 and X+ reflect the time spent by the molecule in the neutral and charged states. Indeed, increasing the molecule-sample distance reduced the neutralization probability of the ZnPc radical cation, whereas the tip-molecule distance that was slightly reduced to compensate for the larger salt barrier increased the charging probability. Thus, the molecule spent more time in its cationic state when the number of salt layers increased (33).

Another notable observation was that, except for the X0 peak that vanished in the 4-monolayer (ML) spectrum, the absolute emission intensity of the two spectral contributions increased as a function of the number of NaCl layers. Overall, this change reflected the progressive reduction of the quenching of the molecular excitons caused by the hybridization with the sample.
Fig. 2. Vibronic fingerprints of neutral and charged ZnPc molecules. (A and B) STM-LE spectra (black lines) revealing the vibronic spectroscopic fingerprint of (A) a single ZnPc radical cation deposited on a trilayer of NaCl on Au(111) 
\((V = −2.5 \text{ V}, I = 300 \text{ pA}, t = 180 \text{ s})\) and (B) a neutral ZnPc [adapted with permission from (20)] belonging to a molecular tetramer deposited on a trilayer of NaCl on Ag(111) 
\(((V = −2.5 \text{ V}, I = 750 \text{ pA}, t = 300 \text{ s})\). The colored bars correspond to theoretical vibronic intensities for the \(A_{1g}\) (black), \(B_{1g}\) (cyan), and \(B_{2g}\) (red) vibrational modes. “×25” and “×50” indicate multiplication factors, and arb. units are arbitrary units.

Fig. 3. Tuning the luminescence intensities. (A) STM-LE spectra acquired, with the same STM tip, on the bare Au(111) surface (labeled 0, \(V = −2.5 \text{ V}, I = 300 \text{ pA}, t = 60 \text{ s}\)) and on single ZnPc molecules 
\((V = −2.5 \text{ V}, I = 300 \text{ pA})\) separated from the Au(111) surface by an increasing number of NaCl layers [1 ML (\(t = 300 \text{ s}\)), 2 ML (\(t = 180 \text{ s}\)), 3 ML (\(t = 120 \text{ s}\)), and 4 ML (\(t = 10 \text{ s}\)) labeled 1 to 4, respectively; see sketch]. The spectra labeled 0 to 4 have been vertically shifted for clarity. “×2” and “×15” indicate multiplication factors. (B) Two STM-LE spectra [black lines, \(V = −2.5 \text{ V}, I = 300 \text{ pA}, t = 300 \text{ s}\) (top panel) or \(t = 60 \text{ s}\) (middle panel)] acquired on single ZnPc on 3 ML of NaCl on Au(111) with two different STM tips, whose plasmonic response is deduced from STM-LE spectra acquired in front of the NaCl-Au(111) surface (red lines, \(V = −2.5 \text{ V}, I = 300 \text{ pA}, t = 120 \text{ s}\); green lines, \(V = −2.5 \text{ V}, I = 300 \text{ pA}, t = 60 \text{ s}\)). The bottom panel displays the molecular emission spectra normalized by the respective plasmonic responses of the junction.

We have shown that STM-LE is an extremely valuable tool for fluorescence measurements of charged species with molecular- and even submolecular-scale precision. In our experiments, we could control the lifetime of the charged molecule and the radiative decay probabilities of the molecule by adjusting, respectively, the thickness of the insulator separating the molecule from the surface and the plasmonic response of the tip-sample cavity. The ability to address the interplay between the redox and excited states of organic structures with atomic-scale spatial accuracy will be highly valuable for characterizing states as the number of NaCl layers increased and the large field enhancement (34) that is expected for plasmonic gaps of ≈1 nm. The disappearance of the \(X^0\) peak in the 4-ML spectrum suggests that, for this large molecule-sample distance, the molecule spent most of the time in its cationic form. We could also tune the relative intensity of the \(X^+\) and the \(X^-\) lines by changing the spectral response of the plasmons localized at the tip-sample junction (Fig. 3B). As expected (15, 18), the presence of a plasmon resonance at the energy of the molecular emission lines amplifies their emission, a phenomenon explained by a stronger Purcell effect. Normalizing the molecular spectra by those of the plasmons (Fig. 3B, bottom panel) revealed a linear dependence of the emission line intensities with plasmon intensity, confirming the above interpretation.

We recorded the evolution of the optical spectrum as a function of subnanometric variations in the lateral distance separating the STM tip from a ZnPc molecule (Fig. 4, A and B). At negative voltage (Fig. 4C), a Fano-like feature was observed at the energy of the \(X^+\) contribution even when the tip was located on top of the NaCl layer at ≈0.5 nm from the molecule’s edge. This response, first reported on in (25) and later in (27, 23), reflects the coupling between the localized plasmons and the molecular exciton. Except for a subtle modification of the peak shape, this contribution did not change when the tip was moved on top of the molecule, suggesting that the fluorescence mechanism remained the same in this case. The response was rather different for the \(X^-\) line, which only appeared when the tip was located on top of the molecule (Fig. 4B). Indeed, whereas the plasmon-exciton coupling may have a measurable impact on the spectrum even when the tip is not located directly on top of the molecule, the oxidation reaction can only take place when an electron tunnels from the molecule to the tip, which requires a direct overlap between the tip and molecular orbitals. Finally, we performed the same experiment at positive voltage (Fig. 4D). In this case, surprisingly, the \(X^-\) contribution was only observed when the tip and molecular orbitals overlapped, in contrast with the results observed at negative voltage. The voltage dependency of this contribution revealed a multiple-electron excitation process (see section S4 in the supplementary materials), an observation that hints at an excitation of the molecule by charge rather than by energy transfer at positive voltage.
Fig. 4. Distance-dependent measurements of the luminescence contributions. (A) Sketch of the experiment, in which the light emission from the junction is monitored as a function of the lateral position of the tip with respect to a ZnPc molecule. The black wave-line illustrates the coupling between the localized plasmon and the molecular exciton. (B) STM image (with magnification on right) acquired at I = 30 pA and V = −2.5 V. (C and D) STM-LE spectra acquired for subnanometric variations of the lateral position of the STM tip with respect to a single ZnPc molecule [sketched in (A)] for (C) negative voltage (V = −2.5 V, I = 180 pA, t = 180 s) and (D) positive voltage (V = 2 V, I = 60 pA, t = 180 s). The position of the tip for each spectrum is marked by a colored dot in the STM image in (B).

internal charge transfer and exciton separation at covalently linked donor-acceptor molecular dimers and low-band gap copolymers. No less than three different luminescence mechanisms have been evidenced for this single system, illustrating the complexity of STM-LE measurements on single molecules.

REFERENCES AND NOTES

29. The voltage drops essentially on the vacuum separating the tip and the molecule.
30. The excited lifetime of ZnPc on NaCl is in the nanosecond range (35, corresponding to a linewidth <1 µeV).
31. The vibronic features in the spectra of ZnPc molecules, Fig. 1C, are too broad for a detailed comparison. The spectrum shown in Fig. 2B was acquired on a ZnPc tetramer separated from a Ag(111) by 2 ML of NaCl. There, the coherent coupling between the molecular dipoles leads to a sharpening of the emission lines (22). This does not affect the energy positions or the relative intensities of the vibronic peaks (20).
33. A similar behavior has been reported for single Au atoms on NaCl multilayers (36).

ACKNOWLEDGMENTS

The authors thank V. Speesser, M. Romeo, J.-G. Faulkunel, and O. Cregut for technical support. Funding: The Agence National de la Recherche (project SMALL LED no. ANR-14-CE26-0016-01), the Labex NIE (contract no. ANR-11-LABX-0058_NIE), and the International Center for Frontier Research in Chemistry (FRC) are acknowledged for financial support. Author contributions: All authors contributed jointly to all aspects of this work. Competing interests: The authors declare no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in this paper and the supplementary materials.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/361/6399/251/suppl/DC1

Materials and Methods

Supplementary Text

Figs. S1 to S4

References

30 January 2018; accepted 17 May 2018

10.1126/science.aat1603

Doppagne et al., Science 361, 251–255 (2018) 20 July 2018

4 of 4

Downloaded from http://science.sciencemag.org/ on July 8, 2021
Electrofluorochromism at the single-molecule level
Benjamin Doppagne, Michael C. Chong, Hervé Bulou, Alex Boeglin, Fabrice Scheurer and Guillaume Schull

Science 361 (6399), 251-255.
DOI: 10.1126/science.aat1603

Changing emission with charge states
The fluorescence of electrochromic molecules changes with their charge state. Doppagne et al. studied the optical emission of single zinc-phthalocyanine molecules excited by electron injection from a scanning tunneling microscope tip. The molecules were adsorbed on salt layers grown on a gold surface, so that the cationic and neutral molecules could both be observed. The primary emission shifted to lower energy for the cation, and, in addition, vibrational side bands were observed.

Science, this issue p. 251

ARTICLE TOOLS http://science.sciencemag.org/content/361/6399/251
SUPPLEMENTARY MATERIALS http://science.sciencemag.org/content/suppl/2018/07/18/361.6399.251.DC1
REFERENCES This article cites 31 articles, 3 of which you can access for free http://science.sciencemag.org/content/361/6399/251#BIBL
PERMISSIONS http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service