LETTER

Tunneling Electron Induced Fluorescence from Single Porphyrin Molecules Decoupled by Striped-Phase Octanethiol Self-assembled Monolayer

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We investigate tunneling electron induced luminescence from isolated single porphyrin molecules that are decoupled by striped-phase self-assembled monolayer of octanethiol from the underneath Au(111) substrate. Intrinsic single-molecule electroluminescence has been realized by such decoupling at both bias polarities. The photon emission intensity acquired from the molecular lobe is found stronger than that from the molecular center. These results provide useful information on the understanding of electroluminescent behavior and mechanism in molecular tunnel junctions.

Key words: Scanning tunneling microscope induced luminescence, Plasmonics, Porphyrin, Octanethiol, Self-assembled monolayer, Striped-phase

I. INTRODUCTION

Scanning tunneling microscope induced luminescence (STML) can offer insights into the electron-photon conversion at the nanoscale due to highly localized excitation of tunneling electrons [1] and is thus a useful technique for understanding and developing electrically driven nanoscale photon sources [2]. To this end, extensive research has been carried out to explore the electroluminescence from organic molecules in the scanning tunneling microscope (STM) nanocavity [2−11]. It has been found that if molecules are directly absorbed on metallic substrates, the molecular fluorescence will be quenched because of the ultra-fast electron transfer and energy transfer between the emitter and the substrate [12−16]. To generate molecule-specific electroluminescence, the emitter has to be decoupled from the metal substrate, which has been demonstrated by using spacer layers such as oxides [4, 5], halides [6, 7], or molecular multi-layers [8, 9].

On the other hand, self-assembled monolayers (SAMs) of alkanethiols could be an attractive spacer candidate due to their stability, easy preparation, and inertness in ambient conditions [17]. Our previous photoluminescence study has indicated that short-chain alkanethiol SAM can serve as a decoupling layer to produce molecular fluorescence from quasimonolayered porphyrins [18]. However, it remains unknown whether such decoupling is sufficient to generate molecule-specific fluorescence by tunneling electron excitation?

Can we realize single-molecule electroluminescence in this system? In this work, we shall address these issues by investigating STM induced luminescence from single porphyrin molecules decoupled by a striped-phase octanethiol (C_8S) SAM.

II. EXPERIMENTS

The experiments were performed with a custom-designed low-temperature ultra-high vacuum (UHV) STM (Unisoku) at ∼8 K under a base pressure of ∼1×10^{-10} Torr. Electrochemically etched Ag tips were used to perform both STM imaging and STML measurements due to the strong plasmonic field produced by Ag material [19]. The Au(111) substrate was prepared by thermal evaporation of gold (∼200 nm thick) on freshly cleaved mica and cleaned in UHV by cycles of argon ion sputtering and annealing. The C_8S-SAMs on Au(111) were prepared by immersing Au(111) in a solution of 1-octanethiol (3 mmol/L) in ethanol for 24 h at ∼326 K [18]. Then, the sample was taken out of the solution, completely washed with pure ethanol, and finally dried under a stream of nitrogen gas before being transferred into the UHV chamber for STM investigations. The as-prepared sample shows typical close-packed $(\sqrt{3}\times\sqrt{3})R30°$ structure [20]. After annealing at ∼370 K for 20 min in UHV, the close-packed $(\sqrt{3}\times\sqrt{3})R30°$ structure is partially transformed into the striped-phase structure [21−25]. The meso-tetrakis (3,5-di-tertiarybutyl-phenyl) porphyrin (H_2TBPP) with characteristic double-peak Q-band emission was chosen as emitter molecules [8], which were deposited *in situ* onto the top of the SAM surface at ∼8 K. Photons emitted from the tunnel junction

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were collected by a lens inside UHV chamber and then refocused into an optical fiber by another lens placed outside UHV. The collected light was guided into a liquid N_2-cooled charge-coupled-device (CCD) spectrometer (Princeton Instruments) for steady-state spectral measurements [11]. STM images were taken in the constant current mode with the sample biased. STML spectra presented in the work were not corrected for the wavelength-dependent sensitivity of photon collection and detection systems.

III. RESULTS AND DISCUSSION

Figure 1(a) illustrates the schematic geometry of a single H_2TBPP molecule inside the STM junction with the striped-phase octanethiol SAM as a decoupling layer on Au(111). The selection of striped-phase C_8S-SAM (Fig.1(b)) rather than the close-packed $(\sqrt{3}\times\sqrt{3})R30°$ phase (inset of Fig.1(b)) is because the H_2TBPP molecules on the nearly isotropic surface of the close-packed phase are highly mobile due to very weak interactions, making the STM imaging and STML experiments highly challenging. Since the striped phase is not only anisotropic in terms of surface structures, but also produces more defect sites on the surface [21−25], the porphyrin molecules can be trapped around the grooves or defects. This is indeed experimentally observed by STM imaging at ∼8 K when H_2TBPP molecules were deposited, as shown in Fig.1(d).

To analyze the structure of the striped phase in Fig.1(b), we investigate the line profiles along the stripe direction (line 1) and perpendicular to the stripes (line 2). As shown in Fig.1(c), the period of the bright dots in line 1 is ∼0.5 nm ($\sqrt{3}\times 0.288$ nm, with 0.288 nm being the lattice constant of the Au(111) surface), which is the same as the period of the $(\sqrt{3}\times\sqrt{3})R30°$ phase; whereas the period of stripes along line 2 is ∼2.26 nm, which is very close to that of 7.5×0.288 nm. Therefore, the striped phase can be viewed as a $(7.5\times\sqrt{3})$ structure, with the octanethiols still in a standing-up geometry but with a different stacking and a smaller tilting angle compared to the close-packed $(\sqrt{3}\times\sqrt{3})R30°$ phase [25−29].

As shown in Fig.1(d), the H_2TBPP molecules deposited onto the striped SAM surface at ∼8 K at low coverage can show up as isolated individual molecules with characteristic four-lobe patterns [30, 31], which allows us to study their STML behavior at the single-molecule scale. Nevertheless, the exact adsorption conformation appears to depend on the local surface environment or defect structures [32], as the four-lobe feature is more or less different from one molecule to the other, which might also affect their luminescent properties [4].

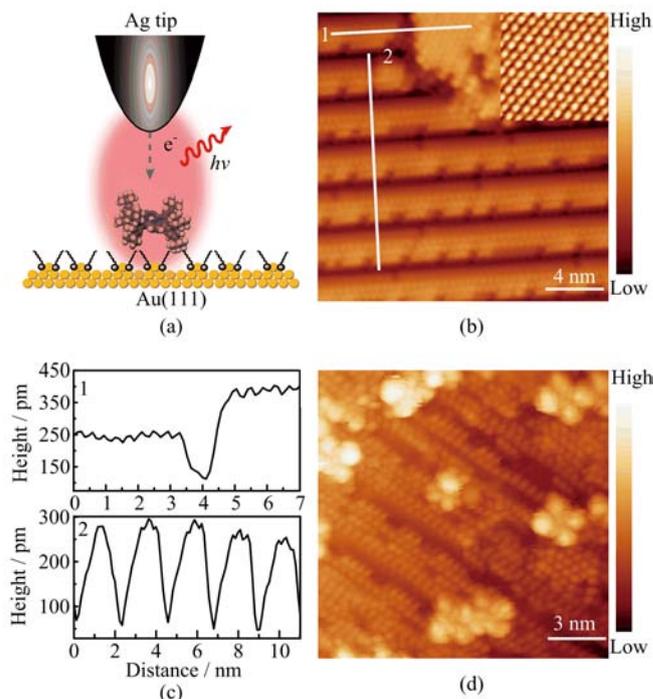The generation of molecule-specific electroluminescence is most authoritative to judge the effectiveness

FIG. 1 (a) Schematic junction geometry of single molecules adsorbed on striped-phase SAM with localized electrical excitation from a Ag tip. (b) STM image of annealed sample showing dominant striped $(7.5\times\sqrt{3})$ structure coexisting with close-packed $(\sqrt{3}\times\sqrt{3})R30°$ structure (-2.8 V, 2 pA, 20 nm$\times$20 nm). The inset image shows the close-packed structure of the as-prepared sample before annealing (-2.8 V, 2 pA, 5 nm$\times$5 nm). (c) Line scans over different surface structures marked in (b). (d) STM image of H_2TBPP molecules on the striped-phase SAM (-2.8 V, 1 pA, 15 nm$\times$15 nm).

of electronic decoupling effect [8, 9]. Figure 2 shows typical STML spectra acquired on the lobe of a single H_2TBPP molecule (shown in inset) for different bias and polarities. When bias voltage is sufficiently high (*e.g.*, ± 2.5 V), the molecular origin of the fluorescence is evident as the spectra show characteristic double Q-band emission of H_2TBPP at ∼652 and ∼723 nm, which can be assigned to the $Q_x(0,0)$ and $Q_x(0,1)$ transitions respectively [8, 9]. The observed vibrationally resolved molecular fluorescence indicates that the C_8S-SAM with striped $(7.5\times\sqrt{3})$ phase can act as an efficient spacer to block the direct electron transfer and weaken the interaction between the H_2TBPP molecule and the Au substrate, thus suppressing the nonradiative decay from the excited molecules to the metal substrate [8, 18]. In addition, there exists an onset voltage at ∼1.9 V for single-molecule electroluminescence to occur at positive bias (Fig.2(a)). For an excitation bias smaller than the onset voltage, *e.g.*, at 1.8 V, the STML spectra are characteristic of the nanocavity plasmonic emission that is broad and follows the quantum cutoff condition [10]. When the bias is increased
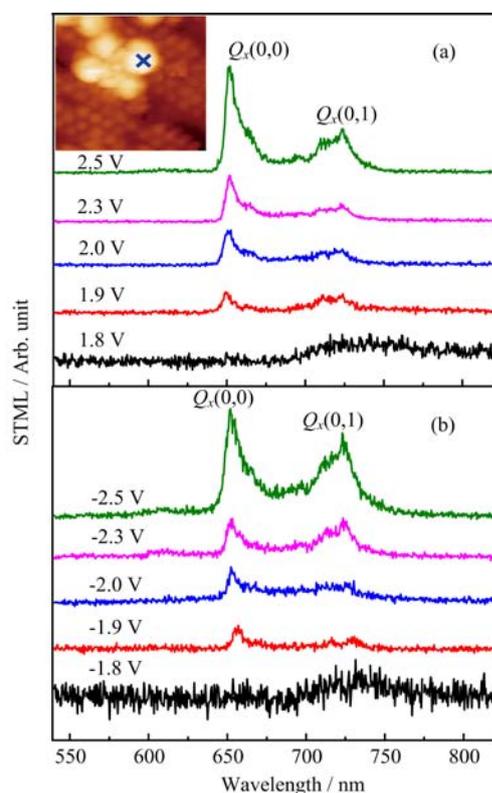
FIG. 2 Bias dependence of STML spectra acquired from single H_2TBPP molecule shown in the inset image (-2.8 V, 1 pA, 5 nm$\times$5 nm). (a) At positive bias. (b) At negative bias. Each STML spectrum was acquired at 30 pA with an exposure time of 60 s. The STML spectra are offset for clarity.

FIG. 3 Site-dependent STML spectra acquired at different positions over a H_2TBPP molecule, with positions marked in the inset (-2.8 V, 1 pA, 5 nm$\times$5 nm). The nanocavity plasmon emission aquired from the striped-phase SAM is also shown for comparison (bottom curve). Each STML spectrum was acquired at 2.5 V and 30 pA with an exposure time of 120 s. The STML spectra are offset for clarity.

from 1.9 V to 2.5 V, the molecular emission bands at 652 and 723 nm remain essentially constant because the radiative decay of the excited molecule is associated with given energy gaps. The gradual increase of emission intensity with increased voltages is related to both the growing number of energetically allowed channels that could contribute to molecular fluorescence and the enhanced electromagnetic field underneath the tip [4, 8].

A similar trend is observed for molecular electroluminescence at negative bias polarities with an onset voltage of about -1.9 V (Fig.2(b)). The two onset bias voltages of ± 1.9 V match with the optical band gap of the H_2TBPP molecule. The occurrence of single-molecule electroluminescence at both bias polarities suggests a double-barrier junction structure [6, 8]. The junction between the tip and molecule is a vacuum barrier while the SAM spacer sandwiched between the emitter and the metal substrate serves as another barrier. Once the porphyrin molecule is excited by tunneling electrons, the excited molecule decays radiatively back to the ground state via Franck-Condon $\pi^* \rightarrow \pi$ transitions [8, 9, 33].

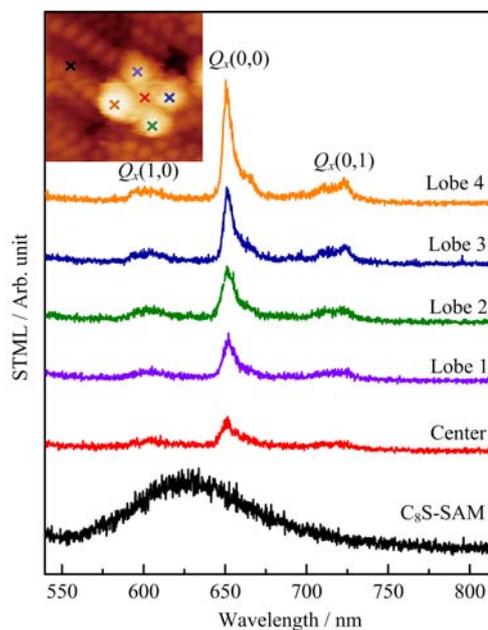Figure 3 shows five STML spectra acquired on repre-

sentative sites of a single H_2TBPP molecule on molecular center and lobes, respectively. The spectrum taken on the nearby C_8S-SAM surface is also shown for reference, highlighting the resonance mode of the nanocavity plasmon depending on the geometry of the tip used. The inset STM image marks the positions at which the STML spectra were measured. The H_2TBPP molecule appears slightly tilted as it shows different lobe brightness. The overall spectral profiles for different molecular sites appear very similar in terms of the number of emission peaks and peak positions. However, the intensities of each emission peak vary from site to site. In general, those on the lobe appear stronger than that at the center, which might pertain to the site-specific difference in total dipole symmetry when molecular transition dipole is coupled with the nanocavity plasmon [5]. A stronger emission acquired from lobe 4 can be correlated with a larger dipole moment component along the tip axial direction. In addition to the conventional double Q-band emission peaks of $Q_x(0,0)$ (at $\sim$651 nm) and $Q_x(0,1)$ (at $\sim$722 nm), we also observe a higher-energy emission band at $\sim$602 nm, which could be attributed to the hot luminescence $Q_x(1,0)$. The generation of hot electroluminescence here is owing to strongly resonant emission enhancement of the $Q_x(1,0)$ radiative channels by the frequency-matched nanocavity plasmon peaked around 625 nm [9].

IV. CONCLUSION

We have realized single-molecule electroluminescence from a neutral H_2TBPP molecule using striped-phase octanethoil SAM as a decoupling layer on Au(111). The molecular electroluminescence is found to occur at both bias polarities and with site-dependent emission intensities over the molecule. These results provide useful information for the development of SAM-based electrically driven nano emitters.

V. ACKNOWLEDGMENTS

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