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# Selective triplet exciton formation in a single molecule

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## Summary Paragraph (Abstract):

Exciton formation in organic molecules by charge injection is an essential process in organic light emitting diodes (OLEDs)<sup>1-7</sup>. According to a simple model based on the spin statistics, the injected charges form spin-singlet excitons ( $S_1$ ) and spin-triplet excitons ( $T_1$ ) in a 1:3 ratio<sup>2-4</sup>. After the first report of highly efficient phosphorescence OLED<sup>2</sup>, effective use of  $T_1$  has been the primary strategy for increasing the quantum efficiency of OLEDs. Another key issue to further improve the energy efficiency is reduction of the operating voltage<sup>2-6</sup>. Since  $T_1$  has lower energy than  $S_1$  owing to the exchange interaction, the energy difference, in principle, enables to form only  $T_1$  at low voltage, which would reduce the operating voltage of OLEDs. However, the way to achieve such selective and direct  $T_1$  formation has not been established yet. Here we report a single-molecule investigation of electroluminescence using a scanning tunnelling microscope (STM)<sup>8-20</sup> and demonstrate a simple way for selective  $T_1$  formation which utilizes a charged state of molecule. A 3,4,9,10-perylenetetracarboxylicdianhydride (PTCDA) molecule<sup>21-25</sup> adsorbed on NaCl(3ML)/Ag(111) shows both phosphorescence and fluorescence signals at high applied voltage. In contrast, only phosphorescence occurs at low applied voltage, indicating selective formation of  $T_1$  without creating  $S_1$ . The bias voltage dependence of the phosphorescence in combination with differential conductance measurement reveals that spin-selective electron removal from a negatively charged PTCDA is the dominant  $T_1$  formation mechanism in the system, which is rationalized by the exchange interaction in the charged molecule. Our findings clearly show that the electron transport process accompanying the exciton formation can be controlled by manipulating an electron spin inside a molecule. We anticipate that device designing with consideration of the exchange interaction would realize a novel OLED with a lower operating voltage.

Main text:

An STM combined with an optical detection system provides atomically-precise spectroscopy for investigating both optical and electron transport processes in nanometre scale, which has elucidated fundamental exciton physics in well-defined molecular systems<sup>8–20</sup>. Here we applied this technique to a PTCDA molecule (Fig. 1a) adsorbed on a three monolayer (3ML) thick NaCl(100) film grown on a Ag(111) surface. In an STM image of PTCDA/NaCl(3ML)/Ag(111) (Fig. 1b), the molecules appear as double-lobed structures with a nodal plane along the long axis of the molecule<sup>21–23</sup>. The adsorption angle of PTCDA is tilted 45° with reference to the [100] direction of the NaCl film, which is consistent with the adsorption structure of PTCDA on bulk NaCl(100)<sup>24</sup>.

To examine the electron transport via PTCDA/NaCl(3ML)/Ag(111), we measured a differential conductance ( $dI_t/dV_s$ ) spectrum (Fig. 1c). The  $dI_t/dV_s$  spectrum exhibits two resonant tunnelling peaks at  $V_s = -0.8$  and 1.1 V, and the peak onsets are -0.5 and 0.7 V, respectively. Double-lobed structures are observed in the STM images at both positive and negative sample voltages, and small height image is observed in the gap region of these peaks. The features in the  $dI_t/dV_s$  spectrum are similar to those in the previously reported  $dI_t/dV_s$  spectrum of PTCDA/NaCl(2ML)/Ag(111)<sup>21,22</sup>, indicating that electron transport occurs by the same mechanism on NaCl films of different thicknesses. In the previous report, PTCDA was considered to be negatively charged on NaCl(2ML)/Ag(111) owing to the high electron affinity of the molecule and the low work function of the substrate<sup>21–23</sup>. The authors proposed that LUMO was responsible for the resonant tunnelling channels observed at both positive and negative voltages. This interpretation is also valid for the PTCDA/NaCl(3ML)/Ag(111) system, and is supported by the similar double-lobed structure observed in the STM images at both voltage polarities (Fig. 1d), which are almost identical to the spatial distribution of the LUMO determined from PTCDA/NaCl(3ML)/Au(111) (refer to Extended data Fig. 1, 2 and Method).

In order to confirm the exciton formation by charge injection, we performed scanning tunnelling luminescence (STL) measurements on PTCDA/NaCl(3ML)/Ag(111) (Fig. 2a). The STL spectrum

obtained with the tip located on a PTCDA molecule shows a broad peak ranging from 1.5 to 3.0 eV, and several sharp peaks at approximately 1.3, 2.25, and 2.45 eV (Fig. 2b). The broad peak is attributed to the radiative decay of the plasmon localized near the gap between the STM tip and the substrate<sup>8-20</sup>. For revealing the detailed structure of the sharp peaks, STL spectra were measured at a higher energy resolution in the ranges 2.37-2.52 eV (Fig. 2c) and 1.25-1.40 eV (Fig. 2d). In Fig. 2c, the main peak appears at 2.45 eV (506 nm), and smaller peaks are observed near the main peak. Based on the good agreement with previous photoluminescence (PL) results<sup>25</sup>, the main peak at 2.45 eV is assigned to the 0-0 transition of fluorescence, which represents the transition between the vibrational ground states of  $S_1$  state and ground state ( $S_0$ ). Since the positions of the small peaks near the 0-0 transition peak are almost identical to those in previous PL data (Extended data Fig. 3), they are attributed to the vibrational satellites of the fluorescence. Moreover, the sharp peak at 2.25 eV in Fig. 2b is also attributed to the vibrational satellites.

In the lower energy luminescence spectrum (Fig. 2d), the main peak is at 1.33 eV (932 nm), and vibrational satellites are also observed. The positions of the vibrational satellites are in good agreement with those seen in the fluorescence spectrum (Extended data Fig. 4). Since there has been no report on the low energy luminescence of PTCDA, we performed time dependent density functional theory (TD-DFT) calculations. The energies of  $S_1$  and  $T_1$  were calculated to be 2.49 and 1.18 eV, respectively, which are in reasonable agreement with the observed luminescence peak positions. Thus, the results strongly suggest that the main peak in Fig. 2d originates from the 0-0 transition of phosphorescence.

Next, we analysed the peak widths of the 0-0 transitions, since the peak width is dependent on the lifetime of the excited state (longer lifetimes provide narrower peaks). Figure 2e shows the STL spectra measured at even higher spectral resolution. The 0-0 transition peak of fluorescence (blue dots) and the lower energy luminescence peak (red dots) were fitted using Lorentzian functions (black lines), and the peak widths (full width at half maximum) were determined to be 5.11 and 0.63 meV, respectively. The observed peak width value of 0.63 meV is considerably sharper than in the previously reported STL

fluorescence spectra<sup>15</sup>, suggesting that this peak does not correspond to a fluorescence transition. Since, in general, the lifetime of  $T_1$  is longer than  $S_1$ , the sharpness of the low energy luminescence peak also supports our interpretation that the peak at 1.33 eV originates from phosphorescence. Based on all the observations and discussions presented thus far, we concluded that charge-neutral excitons ( $S_1$  and  $T_1$ ) were formed by charge injection from the STM tip to a negatively charged PTCDA, and that they manifested themselves as fluorescence and phosphorescence in the STL spectra. In our measurement, phosphorescence as well as fluorescence are enhanced by the localized plasmon through exciton-plasmon coupling<sup>26</sup>, therefore significant luminescence signals were observed (Extended data Fig. 5). It should be noted that this is the first observation of phosphorescence from PTCDA, and also the first observation of phosphorescence in a single-molecule STL measurement.

To investigate the exciton formation mechanism, we examined the voltage dependence of the STL spectra. Figure 3a and 3b show a series of phosphorescence and fluorescence spectra measured at different sample voltages. As the sample voltage was decreased, the phosphorescence first appeared at -2.1 V, and the intensity of phosphorescence increased gradually with decreasing sample voltage. In a similar way, the fluorescence appeared at -3.3 V, and its intensity increased as the sample voltage was decreased. The photon intensities of phosphorescence and fluorescence were determined by Lorentzian peak fitting and are plotted as a function of the sample voltage in Fig. 3c, which clearly shows that the threshold voltages for phosphorescence ( $V_{th}^p$ ) and fluorescence ( $V_{th}^f$ ) are at approximately -2.1 and -3.3 V, respectively. Therefore, PTCDA exhibits only phosphorescence between  $V_{th}^p$  and  $V_{th}^f$ , from -2.1 to -3.3 V. The value of  $V_{th}^p$  is smaller than 2.45 V, which corresponds to the energy of  $S_1$  (2.45 eV, determined from the fluorescence peak); this is clear evidence of the direct formation of  $T_1$  without passing through  $S_1$  at low applied voltage. To elucidate the origin of  $V_{th}^p$  at -2.1 V, we conducted a  $dI_V/dV_s$  measurement in negative sample voltage region (Fig. 3d)<sup>12,14</sup>. In addition to the resonant features around the Fermi level (Fig. 1c), the  $dI_V/dV_s$  spectrum shows a new strong resonant peak at -2.5 V with an onset at approximately -2.1 V. The correspondence between the onset voltage of the  $dI_V/dV_s$  peak and

$V_{th}^p$  at -2.1 V indicates that the phosphorescence was triggered by a resonant tunnelling charge injection into a molecular orbital<sup>10-14</sup>. Although another peak is expected around  $V_s = -3.5$  V, we could not measure it because the high tunnelling current in a high applied voltage region often induced molecular movement during the  $dI_t/dV_s$  measurement.

The mechanism of the selective  $T_1$  formation in the low applied voltage region is proposed in Fig. 3e. PTCDA has a charge of -1 owing to adsorption on the NaCl(3ML)/Ag(111) surface, and rapidly transits between the -1 charged state and neutral ground state ( $S_0$ ) under the resonant tunnelling condition ( $V_s < -0.5$  V)<sup>21,22</sup>. When a further voltage is applied ( $V_s < -2.1$  V), the electron occupying the highest occupied molecular orbital (HOMO) can be removed from either the  $S_0$  or -1 charged state. Assuming that electron removal occurs from the -1 charged state, the two electrons in the HOMO have different energies owing to the exchange interaction with the electron in the LUMO. If we increase the applied voltage in this situation, it is expected that the electron in the HOMO whose spin is “anti-parallel” to the spin of the electron in the LUMO will be removed first at  $V_{th}^p = -2.1$  V, leading to the exclusive formation of  $T_1$  (Fig. 3e). When further voltage is applied, the removal of the other “parallel-spin” electron in the HOMO becomes possible at  $V_{th}^f = -3.3$  V, then both  $T_1$  and  $S_1$  are formed (Fig. 3e, 3f). The threshold voltage difference between phosphorescence and fluorescence ( $\Delta V_{th} = V_{th}^p - V_{th}^f$ ) is 1.2 V. This  $\Delta V_{th}$  value corresponds to the  $S_1$ - $T_1$  energy difference ( $\Delta E_{ST}$ ) or the exchange interaction energy, 1.12 eV, determined from the STL fluorescence (2.45 eV) and phosphorescence (1.33 eV) peaks. Therefore, the model process given in Fig. 3e can reasonably explain the voltage dependence results. The somewhat larger value of  $\Delta V_{th}$  than  $\Delta E_{ST}$  is probably owing to the potential drop in the NaCl film<sup>27,28</sup>. If we instead assumed that an electron is removed from the HOMO of  $S_0$  and an electron is supplied to the LUMO, both  $T_1$  and  $S_1$  would be formed simultaneously, which is inconsistent with the observed STL voltage dependence. Furthermore, another reported mechanism of exciton formation by energy transfer from a localized plasmon<sup>8,13,15</sup> or from an inelastic tunnelling electron<sup>16,20,29</sup> also cannot fully explain our observations (see Method). Based on the discussions, we conclude that the “anti-

parallel" electron removal from the HOMO of -1 charged state is the primary  $T_1$  formation mechanism in this system. The proposed exciton formation mechanism is substantiated by theoretical simulations of  $dI_t/dV_s$  spectrum and STL voltage dependence based on the many-body description using the Hubbard nonequilibrium Green's function technique<sup>30</sup> (see Supplementary Information).

To reveal the sub-molecular spatial features of the single-molecule phosphorescence, an STL map was obtained at  $V_s = -2.5$  V (Fig. 4a). Phosphorescence spectra were measured at selected pixels on and near the molecule, and the intensity of phosphorescence was determined by Lorentzian fitting at each pixel to create the phosphorescence STL map. There are two bright areas near the edges on the long axis of PTCDA, which is significantly different from the STM topographic image obtained at  $V_s = -2.5$  V (inset image in Fig. 4b).

Based on the  $T_1$  creation mechanism (Fig. 3e), it is expected that the bright spots in the phosphorescence map would correspond to the locations where anti-parallel electron removal occurs efficiently. To verify this,  $dI_t/dV_s$  spectra were measured at four selected points, which are shown in the inset of Fig. 4b. The significant resonant feature at -2.5 V was only observed when the tip was located at position #4, where intense phosphorescence occurs. In contrast, the resonant feature was absent at the positions where the phosphorescence intensity is small (position #2 and #3), supporting our expectation. The peak around -2.5 V can also be observed at the centre of molecule (position #1), despite the very weak phosphorescence intensity at this position. This can be explained by considering the coupling strength between the transition dipole moment (TDM) of PTCDA with the localized plasmon<sup>11,13,14</sup>. In conclusion, the spatial distribution of the resonant tunnelling channel at around -2.5 V by which  $T_1$  is created and the strength of the TDM-plasmon coupling are responsible for the spatial distribution in the phosphorescence STL map.

In this work, we demonstrated selective  $T_1$  formation by spin-selective electron transport through a single molecule which has an unpaired electron. Here, we prepared a negatively charged molecule by tuning the energy level alignment between the LUMO of the molecule and the Fermi level of the



substrate, indicating the spin-selective electron transport occurs in various combinations of molecules and electrodes. In addition to the charged molecules, radical molecules, which also have an unpaired electron, could be available for implementing the selective  $T_1$  formation to OLEDs<sup>7</sup>. The selective  $T_1$  formation mechanism based on exchange interaction would be valid for explaining low-voltage operation of OLEDs reported recently<sup>5,6</sup>. This study also proved the capability of our method to monitor the transition among spin states with spin angular momentum of  $s = 0$  ( $S_0, S_1$ ),  $1/2$  (charged state), and  $1$  ( $T_1$ ). This combination of the versatile functions of STM provides a unique and powerful experimental platform for quantum spintronics and excitonics at the single atomic and molecular level.

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## Author Contributions

K.K. and H.I. designed the experiments. K.K., M.I.-I., and S.K. performed the experiment. K.K. and H.I. analysed the data. K.M. and M.G. developed the calculation method. K.M. conducted the theoretical calculations. Y.K., M.K., and J.T. directed the project. All authors discussed the results and wrote the manuscript.

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## Competing interests

The authors declare no competing interests.

## Main figure legends

Figure 1| **STM measurement of the PTCDA/NaCl(3 ML)/Ag(111) system.** **a**, Molecular structure of PTCDA (brown, C; red, O; beige, H). **b**, A constant current STM image showing three PTCDA molecules on the NaCl(3ML) surface ( $25 \times 25 \text{ nm}^2$ ,  $V_s = 1.0 \text{ V}$ ,  $I_t = 10 \text{ pA}$ ). The directions of the long axes of the PTCDA molecules are identified by the black arrows. **c**, The  $dI_t/dV_s$  spectrum of the PTCDA/NaCl(3ML)/Ag(111) system. **d**, STM images of PTCDA measured at the sample voltages indicated by the black arrows in **c** ( $4 \times 4 \text{ nm}^2$ ,  $I_t = 5 \text{ pA}$ ).

Figure 2| **STL measurement of PTCDA/NaCl(3ML)/Ag(111).** **a**, Schematic of STL measurement. **b**, STL spectrum of a PTCDA ( $V_s = -3.5 \text{ V}$ ,  $I_t = 50 \text{ pA}$ , exposure time  $t = 60 \text{ s}$ ). **c-d**, STL spectra with middle energy-resolution ( $V_s = -3.5 \text{ V}$ ,  $I_t = 50 \text{ pA}$ ,  $t = 180 \text{ s}$ ). **c**: 2.37–2.52 eV (blue region in **b**), and **d**: 1.25–1.40 eV (red region). **e**, Peak widths of the 0-0 transitions ( $I_t = 50 \text{ pA}$ ,  $t = 600 \text{ s}$ ) of fluorescence (blue,  $V_s = -3.5 \text{ V}$ ) and phosphorescence (red,  $V_s = -2.5 \text{ V}$ ). Black lines show the Lorentzian fitting results.

Figure 3| **The voltage dependence of the STL spectra of the PTCDA/NaCl(3ML)/Ag(111) system.** **a-b**, Series of STL spectra ( $I_t = 30 \text{ pA}$ ,  $t = 180 \text{ s}$ ). **a**: Phosphorescence ( $V_s = -2.0 \text{ V} - -2.4 \text{ V}$ ) and **b**: fluorescence ( $V_s = -3.1 \text{ V} - -3.5 \text{ V}$ ). **c**, Sample voltage dependences of the intensities of fluorescence (blue circle) and phosphorescence (red square). **d**, The  $dI_t/dV_s$  spectrum of the PTCDA/NaCl(3ML)/Ag(111) system. **e-f**, Schematic images of the exciton formation mechanism. The blue arrows represent electrons. **e**:  $V_s < -2.1 \text{ V}$ , and **f**:  $V_s < -3.3 \text{ V}$ .

Figure 4| **Phosphorescence STL map of the PTCDA/NaCl(3ML)/Ag(111) system.** **a**, Phosphorescence STL spectra were measured at selected pixels in a  $3.3 \times 3.3 \text{ nm}^2$  area with  $V_s = -2.5 \text{ V}$ ,

$I_t = 30$  pA,  $t = 30$  s/pixel. The intensities of 0-0 peak of phosphorescence are measured by Lorentzian fitting and plotted. **b**,  $dI_t/dV_s$  spectra obtained at four selected points in PTCDA. Tip positions are shown as coloured dots and numbered in the inset STM image ( $V_s = -2.5$  V,  $I_t = 10$  pA). The  $dI_t/dV_s$  spectrum at #4 is identical to the spectrum in Fig. 3d.

## Methods

### STM/STS observations

All experiments were conducted using a low-temperature STM (Omicron) operating at 4.7 K under ultrahigh vacuum (UHV). Differential conductance ( $dI_t/dV_s$ ) spectra were measured using a standard lock-in technique with a bias modulation of 20 mV at 625.5 Hz.

### Preparation of sample and tip

Clean Ag(111) and Au(111) surfaces were prepared by repeated cycles of Ar<sup>+</sup> ion sputtering and annealing. The deposition of NaCl onto Ag(111) or Au(111) was performed using a home-made evaporator heated to 850 K. PTCDA was deposited onto the NaCl/Ag(111) or NaCl/Au(111) surface, which was cooled to 4.7 K–10 K in the STM head, using another home-made evaporator heated to 620 K. The STM tip was prepared by electrochemical etching of a Ag wire in HClO<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH electrolyte and conditioned by controlled-indentation and voltage pulse on the Ag(111) or Au(111) surfaces.

### STL measurement

An optical lens (solid angle of ~0.5 sr) was equipped in the STM stage. The emitted light was collimated using the lens and directed out of the UHV chamber, where it was refocused onto a grating spectrometer (Acton, SpectraPro 2300i) with a charge-coupled-device photon detector (Princeton, Spec 10) cooled with liquid nitrogen. Gratings with either 50 grooves/mm (Fig. 2b, Extended data Fig.5), 300 grooves/mm (Fig. 2c-d, 3a-b, and Extended data Fig.3-4), or 1200 grooves/mm (Fig. 2e) were used for the optical measurements.

In our sample, NaCl(3ML) films as well as NaCl(2ML) films were grown on the metal surface. As reported in the previous report<sup>31</sup>, the luminescence intensity is strongly dependent on the thickness of NaCl film. In the case of PTCDA/NaCl(3ML)/Ag(111) system, phosphorescence intensity is 10 times

stronger than that of PTCDA/NaCl(2ML)/Ag(111). Strong luminescence signals enable to clearly determine the threshold voltage for luminescence and to obtain STL mapping. Owing to this technical reason, we focused on a PTCDA adsorbed on NaCl(3ML) film in this letter. **The typical tip position is shown as a red dot in the inset STM image of Fig. 2b.**

### **DFT and TD-DFT calculation**

First principles calculations based on the density functional theory (DFT) were performed using the triple-zeta valence basis augmented with diffuse functions and double polarization functions, 6-311++G(2d, 2p) basis, implemented in the software package Gaussian 16<sup>32</sup>. Following the previous report<sup>33</sup>, the hybrid functional B3LYP was utilized. In order to obtain the structural information, the geometry of ground electronic state of PTCDA molecule was optimized, and the vibrational frequencies of the obtained geometry were computed to ensure that all positive frequencies were obtained. Furthermore, in order to investigate the luminescence spectra of PTCDA molecule, the geometry optimization and vibrational analysis for excited electronic states ( $S_1$  and  $T_1$ ) were performed using time-dependent density functional theory (TD-DFT) with the Tamm-Dancoff approximation at B3LYP/6-311++G(2d, 2p) level. The obtained information for the vibrational frequencies of the ground and excited electronic states were utilized to calculate the vibrational overlap integrals accompanying electronic transitions. The calculated energy for the transition between the ground vibrational states of  $S_1$  and  $S_0$  ( $T_1$  and  $S_0$ ) was 2.49 eV (1.18 eV). In the previous report, the vertical excitation energy from  $S_0$  to  $S_1$  was calculated as 2.39 eV by TD-DFT calculation at the B3LYP/6-311++G(d, p) level, which is almost identical to our result<sup>33</sup>.

### **Theoretical analysis of the single molecule electroluminescence using the molecular many-body states description.**

Theoretical analysis for electroluminescence from an isolated PTCDA molecule adsorbed on NaCl(3ML)/Ag(111) is conducted within the basis of the many-body state representation of the



molecule. The Hubbard nonequilibrium Green's function (NEGF) method, which was recently introduced by us<sup>29</sup>, was applied to simulate tunnelling current and electroluminescence in the system composed of the single molecule positioned between two metal electrodes. The details are given in the Supplementary Information.

### **STM and $dI_t/dV_s$ measurements of PTCDA on NaCl(3ML)/Ag(111) and NaCl(3ML)/Au(111).**

A PTCDA molecule is considered to be negatively charged on the NaCl(3ML)/Ag(111) surface owing to the high electron affinity of the molecule and low work function of the substrates<sup>21–23</sup>. The electron transport properties are affected by the charge state of the molecule. Therefore, we prepared a neutral PTCDA and compared the results of neutral and charged molecules to understand the electron transport mechanism in the PTCDA/NaCl(3ML)/Ag(111) system.

We deposited PTCDA onto a NaCl(3 ML)/Au(111) surface, which has a larger work function than that of NaCl(3ML)/Ag(111)<sup>34–38</sup>. The  $dI_t/dV_s$  spectrum of the PTCDA/NaCl(3ML)/Au(111) system exhibits two resonant tunnelling peaks with onsets at  $V_s = -2.8$  V and 0.9 V (Extended data Fig. 1a), which shows different features from the  $dI_t/dV_s$  spectrum of the PTCDA/NaCl(3ML)/Ag(111) system (Fig. 1c). STM images were obtained at the sample voltages indicated by the black arrows in Extended data Fig. 1a. In order to prevent the STM tip from picking up the molecule, we conducted constant height mode scanning at -3.0 V and suppressed the magnitude of the tunnel current (Extended data Fig. 1b). STM images at 0.6 V and 1.0 V were obtained with constant current mode (Extended data Fig. 1c, d). An eight-lobed structure is observed in the STM image at the negative sample voltage, and a double-lobed structure is observed at the positive sample voltage. In contrast to the PTCDA/NaCl(3ML)/Ag(111) system shown in Fig. 1d, different spatial distributions are obtained at both voltage polarities in the case of the PTCDA/NaCl(3ML)/Au(111) systems. Based on the good agreements with the spatial distribution of molecular orbitals calculated by DFT (Extended data Fig. 1e), the eight-lobed structure is attributed to the spatial distribution of the HOMO, and the double-lobed structure is attributed to the spatial

distribution of the LUMO. From these results, it is concluded that PTCDA is neutral on the NaCl(3ML)/Au(111) surface and the peaks at  $V_s = -2.8$  V and 0.9 V in the  $dI_t/dV_s$  spectrum originate from the resonant tunnelling through the HOMO and LUMO, respectively.

The spatial distribution of the LUMO in the PTCDA/NaCl(3ML)/Au(111) system (Extended data Fig. 1d) is almost identical to the double-lobed structures observed in the PTCDA/NaCl(3ML)/Ag(111) system (Fig. 1d). Therefore, it is suggested that the LUMO is responsible for both the resonant tunnelling channels with onsets at -0.5 V and 0.7 V observed in the  $dI_t/dV_s$  spectrum of the PTCDA/NaCl(3ML)/Ag(111) system (Fig. 1c and Extended data Fig. 2a). Considering that PTCDA is negatively charged on the NaCl(3ML)/Ag(111) surface<sup>21-23</sup>, the following model can be proposed for the electron tunnelling. At negative sample voltage ( $V_s < -0.5$  V), the pre-existing electron in the LUMO first moves to the tip, and the neutral state ( $S_0$ ) is formed. The neutral state returns to the initial state (-1 charged state) by an electron supply from the substrate to the LUMO (Extended data Fig. 2b). Similarly, at positive voltage ( $V_s > 0.7$  V), the -2 charged state is formed by the injection of a second electron into the singly occupied LUMO, and the molecule returns to the initial state by passing an electron to the substrate (Extended data Fig. 2c).

The similar mechanism was proposed in the previous reports dealing with the PTCDA/NaCl(2ML)/Ag(111) system<sup>21,22</sup>. In the previous reports, the authors speculated that the resonant tunnelling channel at negative sample voltage through the LUMO was overlapped with another tunnelling channel through the HOMO. However, here we propose that only the LUMO is responsible for the resonant tunnelling channel in  $-2.1$  V  $< V_s < -0.5$  V according to the exciton formation mechanism (Fig. 3e) based on the STL voltage dependence in combination with the  $dI_t/dV_s$  measurement results. The HOMO starts to contribute to the tunnelling at  $V_s < -2.1$  V in our model.

### **Notation of molecular orbitals**

An electron occupies the LUMO of a PTCDA owing to the adsorption onto NaCl(3ML)/Ag(111) surface<sup>21,22</sup>, which can be described in another way that the LUMO becomes singly occupied molecular orbital (SOMO). The SOMO is widely used to describe the electron transport character in this type of junction<sup>39,40</sup>. However, in this letter, we would like to use the names of intrinsic molecular orbitals (HOMO or LUMO) for labelling, and describe “SOMO” as “LUMO with an unpaired electron”, because this description is useful for explaining the optical transitions.

### **How to discern two exciton formation mechanisms in single-molecule electroluminescence from the experiment**

Two exciton formation mechanisms have been reported in single-molecule electroluminescence measurements using an STM<sup>7</sup>. One is an exciton formation by charge injection to the molecular orbitals<sup>10–14,31</sup>, and the other is by energy transfer from a localized plasmon or from an inelastic tunnelling electron<sup>12,13,15,16,41</sup>.

In the former mechanism, exciton is created by resonant tunnelling to a molecular orbital<sup>10–14,31</sup>. Therefore, a clear peak originated from resonant tunnelling is expected in the  $dI_V/dV_s$  spectrum. As clearly shown in previous reports<sup>12,14</sup>, the position of the peak onset in the  $dI_V/dV_s$  spectrum corresponds to the threshold voltage for the luminescence ( $V_{th}$ ) in this mechanism. In contrast, in the latter mechanism, electronic transition owing to the energy transfer from a localized plasmon or from an inelastic tunnelling electron is responsible for the exciton formation<sup>8</sup>, thus the  $V_{th}$  corresponds to the excitation or absorption energy of the molecule. In particular, when the Stokes shift (energy difference between absorption and emission) of the molecule is quite small, the  $V_{th}$  corresponds to the emission energy of the molecule as observed in previous reports<sup>12,15,41</sup>. In this energy transfer mechanism, the molecule is excited by the inelastic tunnelling electron itself<sup>17</sup> or the localized plasmon generated by inelastic tunnelling<sup>8,15,41</sup>. Therefore, no apparent peak is expected in the  $dI_V/dV_s$  spectrum around the  $V_{th}$ <sup>12,14</sup>, because this process is based on inelastic tunnelling which has a much smaller tunnelling

probability than resonant (elastic) tunnelling. According to the discussion here, the comparison between the  $V_{th}$  and the onset voltage of a  $dI_t/dV_s$  peak enables to determine the exciton formation mechanism in the single-molecule electroluminescence.

### **The exciton creation mechanism in the PTCDA/NaCl(3ML)/Ag(111) system**

For PTCDA in isolated form, a small Stokes shift ( $< 1$  meV) was confirmed by PL measurements<sup>25</sup>. Therefore, it is expected that  $V_{th}$  corresponds to the emission energy if a PTCDA is excited dominantly by the energy transfer mechanism. However, the  $|V_{th}^p|$  value of 2.1 V is significantly larger than 1.33 V (determined from the energy of phosphorescence, 1.33 eV) and the  $|V_{th}^f|$  value of 3.3 V is also larger than 2.45 V (determined from the energy of fluorescence, 2.45 eV), indicating the energy transfer mechanism has a negligible effect in this system.

In our experiment, the threshold voltage for phosphorescence was measured as  $V_{th}^p = -2.1$  V (Fig. 3c), and the  $dI_t/dV_s$  spectrum exhibited a resonant tunnelling peak at -2.5 V with an onset at -2.1 V (Fig. 3d). The correspondence between the peak onset voltage in the  $dI_t/dV_s$  spectrum and  $V_{th}^p$  at -2.1 V suggests that the phosphorescence from PTCDA was triggered by resonant tunnelling. Based on the all results and discussions, it is concluded that the primary exciton formation mechanism in the PTCDA/NaCl(3ML)/Ag(111) system is resonant tunnelling of the “antiparallel-spin” electron from -1 charged PTCDA molecule, by which  $T_1$  is selectively created.

## Method references

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## Data and code availability

The data that support the findings of this study and associated codes are available from the corresponding authors (Y.K., M.G., and H.I.) on reasonable request.

## Extended data figure legends

Extended Data Figure 1| **STM measurement of the PTCDA/NaCl(3 ML)/Au(111) system.** **a**, The  $dI_t/dV_s$  spectrum of the PTCDA/NaCl(3ML)/Au(111) system. PTCDA is neutral on the NaCl(3ML)/Au(111) surface, because NaCl(3ML)/Au(111) surface has a larger work function than NaCl(3ML)/Ag(111) surface. The resonant tunnelling peaks at  $V_s = -2.8$  V and 0.9 V in the  $dI_t/dV_s$  spectrum originate from the HOMO and LUMO, respectively. **b**, A constant height STM image of PTCDA ( $4 \times 4$  nm<sup>2</sup>,  $V_s = -3.0$  V), where the tunnelling current was measured as a function of the tip position. **c-d**, Constant current STM images of PTCDA ( $4 \times 4$  nm<sup>2</sup>,  $I_t = 5$  pA). **c**:  $V_s = 0.6$  V, **d**:  $V_s = 1.0$  V. A small eight-lobed structure is observed in the STM image at -3.0 V, and a double-lobed structure is observed at 1.0 V. In contrast to the PTCDA/NaCl(3ML)/Ag(111) system, different spatial distributions are obtained at negative and positive voltages in the case of the PTCDA/NaCl(3ML)/Au(111) systems. **e**, DFT calculation of the spatial distribution of the HOMO (left, yellow spatial distribution) and LUMO (right, blue spatial distribution). Based on the good agreements between the STM images and the spatial distribution of molecular orbitals, the small eight-lobed structure in **b** is attributed to the spatial distribution of the HOMO, and the double-lobed structure in **d** is attributed to the spatial distribution of the LUMO.

Extended Data Figure 2| **Proposed model for electron tunnelling in the PTCDA/NaCl(3ML)/Ag(111) system.** **a**, The  $dI_t/dV_s$  spectrum of the PTCDA/NaCl(3ML)/Ag(111) system. (identical to the spectrum in Fig. 1c). **b** and **c**, Schematic energy diagrams of resonant tunneling. Blue dots represent electrons. **b**:  $V_s < -0.5$  V, **c**:  $V_s > 0.7$  V. At negative sample voltage ( $V_s < -0.5$  V), the pre-existing electron in the LUMO first moves to the tip, and the neutral state is formed. The neutral state returns to the initial state via the supply of an electron to the LUMO from the substrate. Similarly, at positive voltage ( $V_s > 0.7$  V),

the -2 charged state is formed by the injection of a second electron into the singly occupied LUMO, and the molecule returns to the initial state by supplying an electron to the substrate. This mechanism was also proposed in the previous reports dealing with the PTCDA/NaCl(2ML)/Ag(111) system<sup>21,22</sup>.

Extended Data Figure 3| **Comparison of the positions of the vibrational satellites in the fluorescence spectra.** **a**, Comparison of the fluorescence STL spectrum and the PL spectrum<sup>25</sup>. The blue spectrum shows fluorescence from PTCDA ( $V_s = -3.5$  V,  $I_t = 30$  pA,  $t = 180$  s). The vertical dashed lines show the peak positions of the vibrational satellites with respect to the 0-0 peak position in the PL spectrum of PTCDA on a thick KCl film (~10ML film) grown on a Ag(100) surface<sup>25</sup>. The long dashed lines show the position of the vibrational satellites in the PL spectrum which were also observed in the STL spectrum. **b**, Table of the positions of the vibrational satellites in the PL and STL spectra. These comparison shows that the positions of the small peaks near the 0-0 transition peak are almost identical to those in the previous PL data.

Extended Data Figure 4| **Comparison of the positions of the vibrational satellites.** **a**, Comparison of the STL and calculated spectra of fluorescence and phosphorescence. The blue and red spectra show the fluorescence and phosphorescence from PTCDA, respectively. The solid lines show experimental STL spectra (blue;  $V_s = -3.5$  V,  $I_t = 30$  pA,  $t = 180$  s. red;  $V_s = -2.5$  V,  $I_t = 30$  pA,  $t = 300$  s) The dashed lines show the calculation results by TD-DFT. The positions of the 0-0 transition peak are fixed to the origin. The positions of the small peaks (2, 5, 6, and 7) in the STL phosphorescence spectrum ( $T_1 \rightarrow S_0$ ) agreed with those of the fluorescence peaks ( $S_1 \rightarrow S_0$ ). In both the fluorescence and phosphorescence spectra, a small peak was observed at 30 meV higher energy than the 0-0 transition peak. The luminescence peak was attributed to hot luminescence<sup>42</sup>, which is defined as transition from the vibrational excited states of

$S_1$  (or  $T_1$ ) to the vibrational ground states of  $S_0$ . **b**, Table summarizing the positions of the vibrational satellites in the experimental PL<sup>25</sup> and STL spectra and calculation results.

Extended Data Figure 5| **An STL spectrum of PTCDA/NaCl(3ML)/Ag(111) using a tip with a different plasmon resonance.** We intentionally changed the condition of the tip to modify the plasmon resonance<sup>13</sup>, and an STL spectrum was measured ( $V_s = -3.5$  V,  $I_t = 50$  pA,  $t = 60$  s). In the STL spectrum, both phosphorescence signal at 1.33 eV and fluorescence signal at 2.45 eV are observed. However, the relative intensity between them is significantly different from the STL spectrum in Fig. 2b, despite the same tunnelling conditions. Compared to the spectrum in Fig. 2b, the plasmon resonance at high energy region is weak in this spectrum. This result clearly indicates that the presence of plasmon resonance at the energy of the molecular luminescence amplifies its photon intensity, and the relative intensity between phosphorescence and fluorescence is varied depending on the plasmon resonance of tip.