A strained organic field-effect transistor with a gate-tunable superconducting channel

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In state-of-the-art silicon devices, mobility of the carrier is enhanced by the lattice strain from the back substrate. Such an extra control of device performance is significant in realizing high-performance computing and should be valid for electric-field-induced superconducting (SC) devices, too. However, so far, the carrier density is the sole parameter for field-induced SC interfaces. Here we show an active organic SC field-effect transistor whose lattice is modulated by the strain from the substrate. The soft organic lattice allows tuning of the strain by a choice of the back substrate to make an induced SC state accessible at low temperature with a paraelectric solid gate. An active three-terminal Josephson junction device thus realized is useful both in advanced computing and in elucidating a direct connection between filling-controlled and bandwidth-controlled SC phases in correlated materials.
Strained silicon shows enhanced mobility because of the band-structure tuning and is widely used in modern high-speed circuits\(^1\). This technique should be also applicable to the innovation of wider range of electronic devices including a field-induced superconducting (SC) interface\(^2\)–\(^6\). If a strained SC field-effect transistor (FET) is realized, it will contribute in finding new materials for, in figuring out unknown phase diagrams of and in utilizing quantum devices based on, superconductivities. In general, organic materials enjoy soft lattice and therefore the strain effect on its properties should be significant because of the alteration in the non-covalent intermolecular interaction. Indeed, the organic superconductivity is known to be sensitive to the physical and chemical pressure effects, providing a well-investigated platform to check the influence of strain on the SC transition. An organic superconductor that neighbours Mott-insulating (MI) phase has several advantages in realizing SC-FET with a strained interface with following reasons. First, the relationship between the strain and the electron correlation \(U/W\), where \(U\) is the effective Coulomb interaction and \(W\) is the bandwidth, is well established\(^7\)–\(^8\), leading to precise analysis of the obtained result. Second, the relationship between \(U/W\) and SC phase in the phase diagram with half-filled (non-doped) band is already well investigated both experimentally and theoretically\(^9\)–\(^12\). Third, the carrier number required for the induction of SC state is expected to be relatively low because of the large molecular size along with the dimerized crystal structure. For example, the half-filled carrier density for the \(\kappa\)-type BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) material \((ca. 2 \times 10^{14}\text{ cm}^{-2})\)\(^13\) is less than one-third of that for high-T\(_c\) cuprates \((ca. 7 \times 10^{14}\text{ cm}^{-2})\), which will make a field-induced superconductivity within the reach of carrier density modulation with solid paraelectric gate insulator, and thus an active control of the device in a real-time low-temperature experiment is possible. Finally, there should be no dangling bond and associated carrier trap on the surface because molecular crystal is constructed only by weak intermolecular interactions, which is good for transistor operation.

The above four reasons justify a strained organic SC-FET as an ideal test ground for the strain effect in gate-controlled SC devices. At the same time, SC-FET with organic material merits, when it is realized, also in understanding the phase diagram of correlated materials’ superconductivity in simultaneous control of bandwidth and bandfilling, which has been impossible to be studied by other methods. For example, bandwidth-controlled SC phase with half-filled condition has not yet been realized in cuprates because of its hard lattice, although it is important in verifying the superconductivity mechanism to know whether filling-controlled and bandwidth-controlled SC phases are connected to one another or not.

Here we demonstrate an active field-effect control of superconductivity in a strained FET with an organic Mott insulator, \(\kappa\)-(BEDT-TTF)\(_2\)Cu[\(\text{N(CN)}_2\]\)\(_2\)Br (\(\kappa\)-Br), whose ground state is tuned in the vicinity of a strain-induced Mott transition. This device provides a novel three-terminal Josephson junction (JJ) where its transport characteristics reveals a phase diagram of an organic Mott insulator, where a direct connection between filling-controlled and bandwidth-controlled SC phases is suggested.

**Results**

**Strain effect from the substrate.** We fabricated FETs by laminating thin single crystals of \(\kappa\)-Br on top of metallic Nb-doped SrTiO\(_3\) (STO) substrates covered with 30 nm of Al\(_2\)O\(_3\) dielectric layer grown by atomic layer deposition (Fig. 1a). \(\kappa\)-Br is a highly correlated organic superconductor \((T_c = 11.6\text{ K})\)\(^14\) whose bandwidth-controlled SC phase neighbours an antiferromagnetic MI phase\(^11\) (Fig. 1b). The ground state of \(\kappa\)-Br can be finely tuned by physical and/or chemical pressure. In our previous studies\(^15\), by laminating it onto SiO\(_2\)/Si substrates, we applied tensile strain to thin crystals of \(\kappa\)-Br and guided them into a MI state at low temperature. As thermal expansion coefficients are different between a Si substrate and a \(\kappa\)-Br crystal \((ca. 2 \text{ and } 60 \text{ p.p.m. K}^{-1} \text{ at room temperature}, \text{respectively})\), the \(\kappa\)-Br crystal is ‘expanded’ at low temperature as shown in Fig. 1b, blue arrow. In the present study, STO was chosen as a substrate because of its relatively large thermal expansion coefficient (ca. 10 p.p.m. K\(^{-1}\) at room temperature) to adjust the ground state of \(\kappa\)-Br very close to a partially SC region by a weaker tensile strain. In Fig. 1c, we show normalized temperature dependence of the resistance \((R–T)\) plot for two devices (1 (orange) and 2 (red)) as well as those for \(\kappa\)-Br bulk (black) and \(\kappa\)-Br on a SiO\(_2\)/Si substrate (blue). Because of the weak tensile strain effect from STO substrate, the resistances for these two samples remain in between a complete SC state and a highly resistive MI state, as indicated in Fig. 1b by orange and red arrows. Device 1 showed insulating behaviour at low temperature, whereas device 2 showed a small resistance drop at 12 K, followed by a re-entrant percolation transition around 9 K. This behaviour of device 2 indicates that the system is in the partially SC phase where separation between SC and MI phases occurs and the SC fraction is maximized around 9 K. Such a situation has already been investigated in detail for a bulk material by infrared spectroscopy mapping\(^16\), nuclear magnetic resonance\(^17\), noise measurement\(^18\) and so on. In our devices, magnetization measurement for another sample (device 3) also showed partial superconductivity and maximization of SC fraction at medium temperature range, which will be described later. The above sample dependence between devices 1 and 2 indicates that the conductivity of \(\kappa\)-Br is very sensitive to the small difference in the strain that is produced in the lamination and cooling processes.

**n-type field-effect and superconductivity in device 1.** By applying gate voltage \((V_G)\), the resistance of the device 1 drastically changed with ‘\(n\)-type’ polarity as shown in Fig. 2a. With negative \(V_G\), the resistance increases rapidly, whereas the application of positive \(V_G\) squeezed out the insulating phase into low-temperature region and the device became weakly metallic at \(V_G = 2\) V. By further increasing \(V_G\), it showed superconductivity at \(V_G \approx 8\) V. The current-voltage characteristic in the SC region (Fig. 2a, inset) showed typical bistable switching of a resistance-shunted JJ with a McCumber parameter much larger than unity\(^19\), which implied an inhomogeneous SC transition at the interface. The contour map of the resistance in logarithmic scale is shown in Fig. 2b, suggesting a SC dome very similar to that for cuprate superconductors (white-dashed line). This provides evidences that the cuprates and the \(\kappa\)-type organic system share the common phase diagram in the filling-controlled regime.

**p-type field-effect and superconductivity in device 2.** In Fig. 3a, we show an \(R–T\) plot below 13 K for device 2. The device entered partially SC state at 12 K even at \(V_G = 0\) V, followed by a re-entrant percolation transition around 9 K (OFF”ON transition at 9.2 K and ON”OFF transition at 8.1 K). This re-entrant transition is already known in a \(\kappa\)-type bulk crystal in the vicinity of bandwidth-controlled Mott transition\(^20\), and can be explained by the recurrent decrease of SC volume fraction at low temperature. A schematic image of a percolation transition of a JJ network (JJN) in our device is shown in Fig. 3b. The ‘ON’ switching of JJN designates the minimum of the free energy for the SC state with respect to that for the MI state because the fraction ratio of these two competing phases reflects the relative difference in their free energies. The JJN in device 2 was switchable in situ by changing
either magnetic or electric fields too. When the magnetic field was swept, the device exhibited switching with large hysteresis (ON → OFF at 1.2 T, OFF → ON at 0.8 T; Fig. 3a, inset). As for the gate-electric field, the device exhibited re-entrant JJN switching with ‘p-type’ polarity upon $V_G$ sweeping below 8 K (Fig. 3c). The $V_G$ required for the switching was shifted to larger negative value as the temperature decreased. The whole resistance mapping as a function of $T$ and $V_G$ is shown in Fig. 3d. In a mid-gap $V_G$ area ($-4 \, V < V_G < 11 \, V$), where essentially no mobile carriers were introduced because of mid-gap traps (that is, the essential bandfilling is just 0.5), the JJN was switched to the ON state around 8–9 K (blue area). At $V_G < -4 \, V$, on the other hand, the switching temperature started shifting downwards as the hole injection proceeded. The blue area continued to reach to a fully hole-doped SC state around $(T, V_G) = (3 \, K, -13 \, V)$. As these JJN switchings at around $(T, V_G) = (8.5 \, K, 0 \, V)$ and $(T, V_G) = (3 \, K, -13 \, V)$ reflect the free-energy minima for the bandwidth-controlled and the filling-controlled SC states, respectively, Fig. 3d clearly shows a seamless connection between these two different SC states.

**Magnetic measurement for n-type device 3.** We also confirmed by magnetic susceptibility measurement (for device 3, Fig. 4) that the devices exhibited diamagnetic shielding effect whose volume fraction could be modulated by applying $V_G$. Although there was strong sample dependence, device 3 exhibited the largest Meissner and shielding effect among several samples we have measured, with the magnetic field applied parallel to the BEDT-TTF layers. At $V_G = 0 \, V$, the OFF-state shielding effect was observed below 7 K, whereas the shielding effect was enhanced by applying a positive $V_G$, implying the device switching to the ON state with the $n$-type characteristics. This enhancement was reproducible at $V_G$ sweep. With an assumption that the shielding effect is proportional to the volume fraction of the superconductivity and that the volume fraction of the (unstrained) bulk crystal is 100%, one
can estimate the SC fraction of both OFF and ON states of the device by comparing the diamagnetic values of device 3 with that of bulk $\kappa$-Br. As a result, the temperature dependency of the volume fraction of superconductivity in device 3 at various $V_G$ is estimated as shown in Fig. 4b. Taking into account that the thickness of the charge accumulation layer is one or two layers.
and the thickness of κ-Br crystal on the device 3 (550 nm) corresponds not only to take place in the charge-injected layers but also to propagate into the neighbouring layers in the thickness direction because ca. 5% of the change of the volume fraction between OFF (\( V_G = 0 \) V) and ON (\( V_G = 10 \) V) states well exceeds the expected value for monolayer transition (ca. 0.3%). Such a bulk phase transition seems to originate from an interlayer dielectric screening of the Coulomb interaction \( U \). The maximization of the SC fraction (or recurrent decrease of SC fraction) around 5 K of device 3 also designates a characteristic feature of κ-Br system in this percolative region, which is commonly seen in the re-entrant percolation transition of device 2.

Discussion

So far, the hole- or electron-doped cuprates’ superconductivity and κ-type organic superconductivity have been separately discussed as in Fig. 5a, although scientists have pointed out many common physical properties\(^{22}\). These similarities are a consequence of a Mott transition, where doping controls the bandfilling of cuprates while a pressure/strain controls bandwidth of organic Mott insulators. However, the simultaneous control of the strain (bandwidth) and the carrier density (bandfilling) in a single Mott device is necessary for a deeper discussion of SC–MI phase competition in the unified diagram. For example, the order parameter symmetry is pointed out to be \( d_{x^2-y^2} \) for cuprate and \( d_{x^2} \) for κ-BEDT-TTF\(^{23,24}\). To discuss the origin of this discrepancy, it is important to realize both filling-controlled and bandwidth-controlled superconductivity in the same material and map out the connection between these two phases, which has been impossible to be checked with cuprates that exhibits a hard lattice. In the present experiments, it turned out that these SC phases are directly connected to one another as drawn in Fig. 5b. Inside the yellow SC arc, the \( U/W \) is too high to evoke superconductivity, whereas it is too weak outside the arc. The present organic FET devices having controllable bandwidth and bandfilling therefore provide an indispensable opportunity for exploring a phase diagram of a channel material in a wider parameter space.

Judging from the \( R-T \) plots for devices 1 and 2, the difference in the strain for these devices corresponds to ca. 10 MPa difference in hydrostatic pressure for bulk material\(^{20}\). From crystallographic experiment, the lattice of κ-type BEDT-TTF material is known to shrink at a rate of about 0.025% per 10 MPa, and the transfer integrals between molecules increases at a rate of about 0.02% per 10 MPa (ref. 25). This means that the difference in \( U/W \) for devices 1 and 2 (in Fig. 5b) is only 0.2% with respect to the absolute value of \( U/W \) (an order of unity), when one takes into account the fact that \( W \) is proportional to the transfer integral \( W \) (because \( U \approx 2|t_{\text{dimer}}| - 4t_{\text{dimer}}^2/U_{\text{bare}} \) where \( t_{\text{dimer}} \) is intra-dimer transfer integral whose value is about 0.25 eV and \( U_{\text{bare}} \) is on-site Coulomb repulsion for a single BEDT-TTF molecule whose value is about 1.0 eV, small changes in \( t_{\text{dimer}} \) cancels out). As such a small strain of 0.025% in the lattice evokes a drastic change in the conductivity behaviour and associated FET characteristics, the present results have proved that the control of the strain is a significant tool for the quest for organic SC-FETs.

As the gate insulator in the present device is made of a paraelectric solid, an active switching of JJ has become possible. Such an electrostatically switchable three-terminal JJ device may find applications in SC computation methods such as rapid single-flux quantum\(^{26}\) and quantum computers\(^{27}\) because these ‘beyond Complementary Metal-Oxide Semiconductor’ methods utilize SC quantum interference device. In addition, an in situ gate-sweep measurement at low temperature allows a detection of first-order (hysteretic) transitions in the bandfilling-controlled regime. One example of such a transition is already visible in Fig. 3c, where the resistance showed a bistable behaviour depending on the sweep direction just inside the SC region. This first-order phase transition is presumably relevant to the discrepancy in one-particle excitation spectrum of a Mott insulator that is dependent on the sweep direction of the correlation strength as anticipated by theories\(^{28–30}\).

In summary, we have realized a strained organic FET with gate-tunable SC channel. The phase diagram obtained by the device operation shows a direct connection between bandwidth-controlled and filling-controlled SC phases around a MI phase, which has been impossible to realize in inorganic cuprates. The gate-tunable JJ may be useful in ‘beyond Complementary Metal-Oxide Semiconductor’ quantum devices and detecting a hidden first-order phase transition in a filling-controlled regime.
**Methods**

**Substrate preparation.** A 30-nm-thick amorphous Al₂O₃ gate insulator was grown at 150 °C on a 0.05 wt% Nb-doped SrTiO₃ (001) single-crystal substrate (Shinkosha Co., Ltd.), which was used as a bottom gate. A thickness of Al₂O₃ was evaluated by low-angle X-ray reflection measurement. A surface roughness was <0.2 nm, which is comparable to that of a substrate. Typical electrical properties of a Al₂O₃ dielectric layer were characterized by current-voltage and capacitance-voltage characteristics of a capacitor made of Au/Ti/Al₂O₃/Nb/SrTiO₃, showing large breakdown field (~6–7 MV cm⁻¹) and high dielectric constant (~9–10).

**Crystal growth and lamination process.** All the chemical compounds were purchased from commercial sources and used without further purification unless noted. 1,1,2-trichloroethane was purified by a basic aluminum column. TTP[N(CN)₂][Cl] (TTP, tetraphenylphosphonium) was precipitated from an equimolar mixture of Na[N(CN)₂] and TTP-Br aqueous solutions and recrystallized from ethanol-ethyl acetate. A thin (100–300 nm) single crystal of χ-Br was grown electrochemically by oxidizing BEDT-TTF (50 mg) dissolved in 100 ml of TTP-Br was immersed in the same ethanol and the crystal was guided on top of the substrate using the tip of a strand of hair. The substrate was then removed from the alcohol to be dried.

**Transport measurements.** The χ-Br crystal was cut by laser (V-technology; VL-C30-GP) to form terminals. Gold wires (15 μm) were attached to these terminals with silver and/or carbon paste. Standard four-probe measurement was done under He atmosphere in an automatic cryochamber (Niki-glass) equipped with silver and/or carbon paste. Standard four-probe measurement was done with silver and/or carbon paste. Standard four-probe measurement was done under He atmosphere in an automatic cryochamber (Niki-glass) equipped with a SC magnet.

**Magnetic measurements.** The magnetization of the device was measured using SC quantum interference device (Quantum Design, MPMS) equipped with reciprocating sample option. The weight of the thin χ-Br crystal on device 3 was calculated by using its thickness, area and specific gravity. Two phosphorous bronze wires were attached on the χ-Br and the gate substrate to modulate the Vₓ during the magnetic measurement. For field-cooled measurement, the device was cooled down from 20 to 2 K, during which time a magnetic field of 8 T was applied, before the measurement. The magnetization was measured at a magnetic field of 100 Oe that is parallel to the BEDT-TTF layers in all the measurements.

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Author contributions
H.M.Y., M.N. and Y.I. designed the project. M.N. provided the substrates to H.M.Y. who grew the crystal, made the devices and measured the transport properties. M.S. measured the magnetic susceptibility. All authors discussed the results and commented on the manuscript.

Additional information
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