The concept of topology has been widely applied in condensed matter physics, leading to the identification of peculiar electronic states on three-dimensional (3D) surfaces or 2D lines separating topologically distinctive regions. In the systems explored so far, the topological boundaries are built-in walls; thus, their motional degrees of freedom, which potentially bring about new paradigms, have been experimentally inaccessible. Here, working with a quasi-1D organic material with a charge-transfer instability, we show that mobile neutral-ionic (dielectric-ferroelectric) domain boundaries with topological charges carry strongly 1D-confined and anomalously large electrical conduction with an energy gap much smaller than the one-particle excitation gap. This consequence is further supported by nuclear magnetic resonance detection of spin solitons, which are required for steady current of topological charges. The present observation of topological charge transport may open a new channel for broad charge transport–related phenomena such as thermoelectric effects.

RESULTS AND DISCUSSION
Enhancement and 1D confinement of electrical conduction at the NI crossover
First, we present a pressure-temperature phase diagram up to 35 kbar (Fig. 1A) constructed on the basis of the intrachain (a-axis) resistivity (Fig. 1B) and previous nuclear quadrupole resonance (NQR) studies (7, 11, 12). The temperature profile of the resistivity is different below and above approximately 9 kbar. Below 9 kbar, the resistivity is characterized by a kink between strongly insulating behavior at low temperatures and a moderate temperature dependence at high temperatures (section S1). The low-temperature behavior indicating a
large charge gap is robust against pressure, whereas the resistivity above the kink temperature is rapidly reduced down to the range of 0.1 to 1 ohm-cm, and the kink structure becomes less sharp with increasing pressure. As seen in Fig. 1A, the temperatures associated with the resistivity kinks (orange circles) correspond well to those of the long-range dimerization order detected by NQR (open squares) (7, 11, 12, 15). For pressures above 9 kbar, the resistivity monotonously increases below room temperature without a clearly identifiable kink. The resistivity at high temperatures, above 250 K, increases with pressure, contrary to the behavior below 9 kbar. A contour plot of the absolute values of the conductivity (Fig. 1A) illustrates that a highly conducting state emerges in the crossover region. Figure 2 shows the pressure dependences of the a axis conductivity (Fig. 2A) and the anisotropy of conductivity (Fig. 2B) at room temperature. The geometries of electrodes against the crystal axis are depicted in Fig. 2C, D. We find that the a axis conductivity reaches a maximum value of 7 S/cm at 8.8 kbar (Fig. 2A), which is comparable to the room temperature conductivities of organic conductors. It is most remarkable that such a high conductivity appears between the two types of insulators.

The anisotropies of the conductivity, (σa/σc) and (σa/σb), shown in Fig. 2B, become highly 1D at approximately 9 kbar, where the a-axis conductivity is maximum (Fig. 2A), indicating that the charge transport is confined in the chains in the crossover region. The NIDW, which separates the neutral and ionic segments, carries a topological charge of \( \rho_{\text{NIDW}} = \pm e (\rho_1 - \rho_2)/2 \) (22) and is mobile only within the 1D chain, where \( \rho_1 \) and \( \rho_2 \) are the molecular valences in the I and N phases, respectively, and \( e \) is the elementary charge. In general, the neutral and ionic segments are 3D-locked by long-range Coulomb interactions. As predicted theoretically, however, the interchain Coulomb coupling cancels out in TTF-CA because of the particular molecular arrangement in the b-c plane (29), allowing the NIDWs to travel freely. Optical measurements indicate that the neutral and ionic states dynamically coexist at approximately 9 kbar (8), consistent with mobile NIDWs.

**Charge excitation gap**

To further examine possible NIDW conduction, we measured the temperature dependence of the resistivity at 0.1-kbar intervals around the NI crossover pressure. Figure 3A shows the conductivity landscape, the magnitude of which is projected onto the P-T plane with a range of colors; the orange circles and gray line indicate the positions of the kinks and maxima in the P and T dependences of the conductivity, respectively. The kink positions coincide with the transition points of the long-range dimer order identified by the NQR measurements, whereas the gray line runs along the NI crossover line, where sharp charge transfer is detected by NQR and optical probes (3, 5, 8–10, 12). We note that the infrared spectroscopy under
pressure at room temperature \( \langle 6, 9 \rangle \) detected a steep increase in the molecular vibrational \( a_g \) mode, which is sensitive to the local dimer formation, at a pressure close to the gray line. Since the intensity of the \( a_g \) mode absorption measures the density of local dimers, that indicates a sharp increase in the dimer density at the pressure of the conductivity maxima; thus, the gray line denoted hereafter by \( P_c \) is regarded as the Widom line between a dimer gas and a dimer liquid as well as between the N phase and the I phase.

The NI crossover line (gray line) is tilted with respect to the \( P \) and \( T \) axes and interrupted by the appearance of the \( I_{\text{terro}} \) phase, indicating that the long-range dimerization ordersuppresses anomalous conduction in the crossover (Fig. 3A). If the NIDW excitations are responsible for electrical conduction, then the conductivity should depend on the pressure deviation from the Widom line, \( P - P_c \). Thus, we “corrected” the inclined boundary line \( P_c(T) \) by taking \( \Delta P = P(T) - P_c(T) \) as the pressure axis instead of \( P \); the conductivity versus \( P \) at each \( T \) (Fig. 3B) is converted to conductivity versus \( \Delta P \) (Fig. 3C). Figure 3D shows an Arrhenius plot of the conductivity along the NI boundary of \( \Delta P = 0 \) (the gray line in Fig. 3C), which yields an activation energy, \( E_a \), of 0.055 eV. The values of \( E_a \) determined similarly for other pressures vary with \( \Delta P \), exhibiting a minimum at the NI boundary (Fig. 3E), reminiscent of the \( V \)-shaped profile of the charge-transfer (CT) excitations expected around the NI transition \( \langle 2 \rangle \). However, the minimum value, 0.055 eV, is one order of magnitude smaller than the CT excitation energy, 0.6 to 0.7 eV \( \langle 2, 30 \rangle \), contradicting the one-particle charge excitations, thus invoking emergent excitations. Quantum Monte Carlo simulations predict NIDW excitation energies comparable to the present values with a \( V \)-shaped variation against the intersite Coulomb interaction \( \langle 19 \rangle \), which is varied by pressure experimentally. The rounding of the \( V \) shape (Fig. 3E) is an effect of finite temperature; note that the simulation assumes a temperature of absolute zero. We note that band structure calculations for TTF-CA predict a bandgap of 0.52 eV \( \langle 2, 30, 32 \rangle \), which is also much larger than the observed value.

**Evaluation of the density of NIDWs**

We estimate the density of thermally excited NIDWs by mapping the NI transition system to a 1D quantum XXZ antiferromagnetic spin model \( \langle 33 \rangle \), which is further reduced to the Ising model, particularly for \( V > 2t \), as in the present case, where \( t \) is the transfer integral between the donor and acceptor molecules (section S2). The NIDW corresponds to a spinon in the Ising spin system; thus, the correlation length in the Ising model, \( \xi \sim 1/\ln(\coth(E_{DW}/2k_B T)) \), measures the mean distance between the NIDWs; namely, the NIDW density is given by \( n \sim 1/2\xi \sim \ln(\coth(E_{DW}/2k_B T)) \). This form is approximately of the Arrhenius type for \( E_{DW} > k_B T \) and rationalizes the activation-type temperature dependence of the conductivity, which is assumed to be proportional to the number of NIDWs. At room temperature, \( n \) yields one NIDW per approximately five donor-acceptor pairs, which explains the high conductivity in the NI crossover at room temperature. A more rigorous evaluation of \( n \) based on free energy consideration gives approximately the same value of \( n \) (section S2).

**Mechanism of the topological charge transport**

As was theoretically shown \( \langle 21, 22, 28 \rangle \), stationary current necessitates spin solitons in ionic domains (Fig. 4, A and B, and section S3) \( \langle 26 \rangle \). Solitonic spin excitations in TTF-CA were evidenced by NMR \( \langle 27 \rangle \); the analyses of the NMR shift and relaxation rate, \( T_1^{-1} \), found one spin soliton excited per 10 to 25 donor-acceptor pairs around the NI crossover. Since one NIDW per five donor-acceptor pairs means one ionic domain per 10 donor-acceptor pairs, it turns out that spin solitons and NIDWs are excited with comparable densities around \( P_c \). To determine the spin soliton density in a wide pressure range across \( P_c \), we measured \( ^{13}C \)-NMR \( T_1^{-1} \), which probes local field fluctuations produced by electron spins, in more detail than previously performed \( \langle 27 \rangle \). A single spectral species observed in the NMR spectrum represents motional narrowing due to the diffusive
motion of spin solitons (section S4). Considering that sparsely excited spin solitons should behave as free spins with negligible exchange interactions, the intensity of the local field fluctuations at a nuclear site, probed by $T_1^{-1}$, is proportional to the soliton density. As the pressure is increased, $T_1^{-1}$ exhibits an exponential increase that parallels the conductivity for $P < P_c$ and then levels off in contrast to the decreasing conductivity for $P > P_c$ (Fig. 4B).

As the pressure decreases or increases from $P_c$, the minor phase domains (ionic for $P < P_c$ and neutral for $P > P_c$) become more sparsely excited, shrinking toward the solitons sandwiched by the NIDWs (Fig. 4B). For $P < P_c$, the excitations are NIDW-sandwiched spin solitons (or equivalently polarons) (Fig. 4B). Their dominant role in electrical conductivity is evidenced by the parallel increases in $T_1^{-1}$ and conductivity for $P < P_c$ (Fig. 4B) [a donor-acceptor pair containing no spin soliton does not carry charges (section S3)]. For $P > P_c$, $T_1^{-1}$ retains large values, which is indicative of a high spin soliton density. The decrease in conductivity that does not scale with the behavior of $T_1^{-1}$ reflects a decrease in the excitations of the minor phase species, namely, charge solitons sandwiched by the NIDWs. Consistent with this expectation, the excitation energy of the charge solitons is theoretically indicated to increase as the system gets deeper into the ionic region far from the NI crossover (21) or transition (22). Thus, at pressures away from $P_c$, the conductivity is governed by spin solitons ($P < P_c$) or charge solitons ($P > P_c$). We note that, for $P > P_c$, resistivity shows no clear anomalies at the $P_{para}$-to-$P_{ferro}$ transition upon cooling (Fig. 1B). This may be an indication that charge solitons survive in the form of polarons, which do not break the long-range dimer order, in the $P_{ferro}$ phase.

**Concluding remarks**

A spin (charge) soliton can hop into a charge (spin) soliton site in an adjacent chain by transferring an electron, resulting in their exchange
Fig. 4. Topological excitations carrying electrical currents and the pressure profile of the electrical conductivity and spin excitations. (A) Three types of topological excitations in the Ni transition systems: NIDWs (I), spin solitons (II), and charge solitons (III). Donor and acceptor molecules are represented as D and A, respectively. The NIDW has an effective charge of ±(1 − ρD)/(2 − ρD), where ρD and ρA are the degrees of charge transfer in the ionic and neutral states, respectively, and are 0.7 to 0.8 and 0.3 to 0.4 around the Ni crossover (8, 9). The spin and charge solitons have effective charges of ±e(1 − ρD) and ±eρD, respectively, corresponding to excessive and deficient charges from the dimerized-ionic background, as depicted. These charges are called topological charges, as their fractional nature has the topological origin in the charge degrees of freedom; however, they take noninvariant values and thus are distinguished from the topological charge characterized by quantum numbers. (B) Pressure dependence of the conductivity (black circles) and 13C-NMR T1 (open squares) at room temperature. The mechanism of electrical conduction is divided into three regimes: In the N phase at low pressures (blue-colored region), spin solitons sandwiched by NIDWs (called polarons), which carry both charges and spins, are sparsely excited in the neutral background and lead to electrical conduction. In the Ni crossover region at middle pressures (red-colored region), the NIDWs and spin solitons are excited with comparable densities and carry electrical currents (section S3). In the I phase at high pressures (orange-colored region), the charge solitons are sparsely excited in the ionic background and, in conjunction with more densely excited spin solitons, carry electrical currents.

(e.g., between II and III in Fig. 4A), which is expected to give conventional electron current in the transverse direction. In contrast, unbound NIDWs resulting from the fractionalization of solitons around P\textsubscript{c} have no way to hop into adjacent chains, resulting in highly 1D transport confined in the chain around P\textsubscript{c}, as observed here. The charge transport by the topological excitations distinct from the conventional quasiparticles is possible particularly in 1D where the topological boundaries are in the form of points, which are mobile. The exotic nature and pressure controllability of such transport are expected to open a new door to a wide range of charge transport–related issues; for example, the thermoelectric effect by topological charge excitations may give a new channel in developing thermoelectric materials with high performance. A large thermoelectric effect by a topological spin texture is reported (35).

**MATERIALS AND METHODS**

**Sample preparation**

Single crystals of TTF-CA were prepared by a cosublimation method for both 13C-enriched and non-enriched samples; ampules containing the purified compounds were set in a vacuum-sealed glass tube, which were heated with a three-zone temperature-controlled furnace. In the 13C-enriched sample, the central double-bonded carbon atoms in TTF were substituted by 13C isotopes with a 99% concentration (27).

**Electrical resistivity measurements under pressure**

Resistivity measurements of TTF-CA were performed for single crystals with the four-terminal method. Hydrostatic pressure was applied to the sample using a BeCu/ NiCrAl dual-structured clamp-type cell with Daphne 7373 (P < 20 kbar) and Daphne 7474 (20 kbar < P < 35 kbar) oils as the pressure media. The solidification pressures of the Daphne 7373 and Daphne 7474 oils are approximately 22 and 37 kbar at room temperature, respectively (36). In the measurements in the wide range of pressures displayed in Figs. 1 and 2, we monitored the external pressure during the pressurization at room temperature and converted it to internal pressure using a pressure efficiency of 0.9, which was separately determined by the resistance of a Manganin wire mounted in the pressure cell. In the measurements under the finely tuned pressures displayed in Fig. 3, we monitored the internal pressure through the resistance of a Manganin wire mounted with the sample in the same cell. The pressure values indicated in the main text are the internal pressures determined at room temperature.

**13C-NMR measurements under pressure**

We conducted 13C-NMR measurements for a TTF-CA single crystal, in which the central double-bonded carbon sites in TTF molecules were enriched by 13C isotopes. A magnetic field of 8 T was applied in a direction approximately 35° tilted from the a axis to the c axis. We used the so-called solid-echo pulse sequence of [(π/2)/2]−τ−(π/2)z.
to acquire the $^{13}$C-NMR signals, where $(\pi/2)$, means a $\pi/2$ pulse of a radio frequency wave applied along the $i$ axis in the rotational frame and $\tau$ is the time interval between the two $\pi/2$ pulses. The nuclear spin-lattice relaxation rate $T_1^{-1}$ was measured by the standard saturation recovery method. The relaxation curve of nuclear magnetization was well fitted by a single exponential function for every pressure studied (section S4). We used a clamp-type pressure cell made of nonmagnetic BeCu to apply hydrostatic pressure to the sample. The pressure medium used was Daphne 7373 oil. The pressure values quoted in the main text are the room temperature values.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/11/eaax8720/DC1

Section S1. Temperature dependence of the resistivity

Section S2. Analysis of the conductivity in the NI transition region in terms of the Ising model

Section S3. Electrical current by the NIDW and spin soliton excitations

Section S4. $^{13}$C-NMR spectra and relaxation curves of nuclear magnetization

Fig. S1. Temperature dependence of the resistivity in the NI crossover region.

Fig. S2. Correspondence between molecular states and virtual spins.

Fig. S3. Fitting of the temperature dependence of the conductivity by the 1D ferromagnetic

Fig. S4. Correspondence between molecular states and virtual spins.

Fig. S5. Schematic of the transport of NIDWs and spin solitons that contribute to the electrical conductivity.

Fig. S6. $^{13}$C-enriched TTF molecule, $^{13}$C-NMR spectrum, and relaxation curve.

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measurements, and K.S. and K.M. carried out the NMR measurements. R.K. synthesized the
\(^{13}\text{C}\)-enriched TTF molecules. T.M., H.O., and S.H. prepared the TTF-CA single crystals. R.T.
wrote the manuscript with the assistance of K.S., K.M., and K.K. R.T., K.M., and K.K. designed
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