NMR captures preformed Cooper pairs persisting far beyond $T_c$ in organic superconductors

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High critical temperature (high-$T_c$) superconductivity in copper oxides emerges when Mott insulators are doped, and various unconventional properties follow. Among them, a focus is the so-called pseudogap behaviour emerging above $T_c$$^{1-3}$, which is discussed in association with competing orders, Fermi-arc and preformed Cooper pairs. Besides doping, there is another way to generate unconventional superconductivity from Mott insulators, that is, by bandwidth control, which involves varying the particle’s kinetic energy instead of particle number. Here, working with layered organic superconductors through NMR experiments, we uncover that in the non-doped case anomalous suppression of spin excitations above $T_c$ arises from the preformed Cooper pairs intertwined with antiferromagnetic spin fluctuations and is not accompanied by complexities of competing orders, unlike what is observed in copper oxides$^{1-8}$. On the verge of the Mott localization of electrons, they preform Cooper pairs that persist up to twice as high as $T_c$.

Lightly doped copper oxides show anomalous electronic and magnetic properties before the superconducting transition$^{1-3}$, a phenomenon called pseudogap that has been discussed in terms of superconducting precursors$^{9,10}$, momentum-dependent quasiparticle coherence (Fermi-arc) and the emergence of competing orders. Although the issue is still under debate, reconstruction of Fermi surfaces$^{11}$ and the emergence of complex competing orders such as charge density wave$^{4-6}$, a time-reversal-symmetry-broken state$^7$ and a nematic state$^8$ in lightly doped systems are among the recent advances related to this issue. The pseudogap has been addressed as an issue of doped Mott insulators, where the density of doped carriers is a controlling parameter. More broadly, however, not only the density of doped carriers but also the strength of interactions among electrons is another key parameter that
dominates the behaviour of correlated electrons; the behaviour should be explored in the parameter plane spanned by doping level and the interaction strength (Fig. 1a). Thus, to look into a situation contrasting to the copper oxides, namely, without doping but with varying strength of the interactions is expected to open a new dimension to this issue.

A layered organic superconductor, $\kappa$-(ET)$_2$X, with a half-filled band is in the desired situation; unconventional d-wave superconductivity$^{12-15}$ emerges from Mott insulators without doping but by varying the bandwidth$^{16,17}$, which controls the relative strength of the interactions to the kinetic energy (Fig. 1a). It is well recognized that the application of physical pressure and/or the substitution of anion X, called chemical pressure, finely tunes the interaction strength, a primary factor that dominates the electronic properties near the Mott transition$^{16-18}$. In particular, $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br with all protons in ET substituted by deuterons (abbreviated to $\kappa$-dBr) is on the verge of the bandwidth-controlled Mott transition (BCMT) (Fig. 1b) from the Mott insulator with an antiferromagnetic (AF) order of a wavevector, $Q = (\pi, \pi)$, (Fig. 1c) to the metal with a cylindrical Fermi surface$^{19,20}$ (Fig. 1d). In the metallic phase, nuclear magnetic resonance (NMR) spin-lattice relaxation rate indicates an anomalous suppression of spin excitations on cooling from above $T_c^{19}$, which is compared to the pseudogap in the cuprates. However, there is no signature of competing phases as observed in cuprates, suggesting that the non-doped case is distinctive from the doped case.

The present work explores the anomalous suppression of spin excitations in $\kappa$-dBr through $^{13}$C NMR under tuning interaction strength by He-gas pressure and systematically suppressing superconductivity by magnetic fields over a 20-fold range. We found that in the non-doped case the anomalous suppression of spin excitations occurs mainly in the channel of AF fluctuations very probably with $Q = (\pi, \pi)$ developing near the BCMT and fades out along with superconductivity under increasing magnetic field, indicating the preformation of Cooper pairs intertwined with AF spin fluctuations, not followed by competing orders unlike what occurs in doped copper oxides.

The $^{13}$C NMR experiments were performed on a single crystal of $\kappa$-dBr, in which the central double-bonded carbon sites of ET molecules had been enriched with $^{13}$C isotopes with nuclear spin I=1/2 and gyromagnetic ratio $\gamma/2\pi=10.705$ MHz/T (Fig. S2). Magnetic fields were applied in the directions of the crystal a axis (in-plane) or b axis (out-of-plane). In both configurations, all of ET molecules in a unit cell are equivalent, thus giving simple NMR spectra (see Fig. 2a for the former case). The metallic phase was clearly separated from the insulating phase in spectrum even when
they coexist on the verge of the Mott transition around ambient pressure (Supplementary Information). The spectra do not show any feature indicative of charge orders as observed in copper oxides. The pressure was finely tuned near the BCMT by using He gas as the pressure medium. The details of the sample preparation, NMR experiments, and pressurizing techniques are available in the Methods and Supplementary Information.

First, we show how the AF fluctuations evolve while approaching the Mott transition by applying pressure. Figure 2b shows the temperature dependence of \((T_1 T)^{-1}\) at the pressures indicated in Fig. 1b. A magnetic field of 7.4 T was applied parallel to the \(a\) axis, and the inner line of the metallic phase (Fig. 2a) is investigated to perfectly exclude the possible admixture of the insulating phase in the line investigated (Supplementary Information). Sharp decreases in \((T_1 T)^{-1}\) at approximately 11 K are due to the superconducting transition. It is evident that \((T_1 T)^{-1}\) is sensitive to pressure in the normal state above approximately 11 K. The level of \((T_1 T)^{-1}\) increases while approaching the BCMT as the pressure decreases from 100 MPa to 4 MPa. Concerning the temperature dependence, \((T_1 T)^{-1}\) at 4 MPa, which is very close to the BCMT, anomalously decreases on cooling toward \(T_c\). When the system is driven off the BCMT by pressure, the feature becomes less prominent and, at 100 MPa, \((T_1 T)^{-1}\) is nearly temperature-independent, as expected in conventional paramagnetic metals. The pressure and temperature profiles of \((T_1 T)^{-1}\) show that the anomalous suppression of spin excitations on cooling emerges near the Mott transition, where AF fluctuations develop, as visualized in Fig. 2d.

Compared with the remarkable temperature and pressure dependences of \((T_1 T)^{-1}\), the Knight shift, \(K\), which measures the uniform spin susceptibility \(\chi'(q = 0)\), exhibits only moderate decreases with temperature and less prominent pressure dependence in the normal state, as shown in Fig. 2c. This behaviour of Knight shift indicates that \(\chi'(q = 0)\) is less coupled to the anomalous spin excitations than is the finite-\(q\) spin susceptibility probed by \((T_1 T)^{-1}\). Note that the form factor of the \(^{13}\)C sites in the present system is \(q\)-independent and the so-called Korringa ratio \(\propto (KT_1 T)^{-1}\) estimated from the \((T_1 T)^{-1}\) and \(K\) values yields 8-12, which is much greater than unity, indicating that \((T_1 T)^{-1}\) is dominated by finite-\(q\) spin fluctuations (Supplementary Information). The antiferromagnetic order with \(Q = (\pi, \pi)\) in the adjacent Mott insulating phase and a numerical study showing the enhancement of the \(Q = (\pi, \pi)\) fluctuations on approaching the BCMT\(^{21-23}\) suggest that the spin fluctuations probed by \((T_1 T)^{-1}\) are highly weighted at \(Q = (\pi, \pi)\) near the Mott transition. These features suggest that the suppression of spin
excitations does not emerge on the entire Fermi surface but at particular $k$-regions that affect AF spin fluctuations with $Q = (\pi, \pi)$, which are very likely the crossing points of the Fermi surface and the zone boundary that are connected by $Q = (\pi, \pi)$, as shown in Fig. 1d. This notion is in accordance with the absence of such behaviour as observed here in the nearly triangular-lattice spin-liquid system $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ near Mott localization, which does not show AF ordering in its insulating state.

To characterize the suppression of spin excitations, we assume that it occurs in the AF fluctuations with $Q = (\pi, \pi)$, whose contribution to $(T_1 T)^{-1}$ is evaluated with the difference of $(T_1 T)^{-1}$ from the value at 100 MPa, namely, $\delta(T_1 T)^{-1} = (T_1 T)^{-1} - (T_1 T)^{-1}_{100 MPa}$ because $(T_1 T)^{-1}$ at 100 MPa is nearly temperature-independent and is not expected to include a significant contribution from the anomalous $(\pi, \pi)$ AF fluctuations. Thus, we provides rough estimates of the phenomenological gap, $\Delta$, when $\delta(T_1 T)^{-1}$ is approximated in the form of $\delta(T_1 T)^{-1} \propto \exp(-\Delta / T)$ (see Fig. S10). The $\Delta$ values are plotted against pressure along with $T_c$ in Fig. 3, where $\Delta$ increases more rapidly towards the BCMT than $T_c$ does, suggesting that the suppression of spin excitations are strongly connected with Mott localization.

Next, we examined the magnetic field dependence of $(T_1 T)^{-1}$. For magnetic fields perpendicular to the layers ($|| b$ axis), the field was varied from 0.9 to 18 T across the upper critical field of $H_{c2}(0 K) \sim 10 T$ (ref. 26). To avoid experimental difficulty in tuning the resonant circuit (parts of which are inside the pressure cell) in frequencies over a 20-fold range, the measurements were performed at ambient pressure without a pressure cell, where the metallic and insulating phases coexist at low temperatures owing to the first-order BCMT; however, the former is clearly separated from the latter in the NMR spectra (Details about the separation of the NMR spectra are explained in Supplementary Information). Apart from the phase mixture, the spectral profile under the field $|| b$ axis largely changes, against field variation over the 20-fold range, from a quartet arising from dipolar mixing of the inner and outer lines at low fields to two well separated doublets at high fields, giving a spurious field-dependence of the absolute value of $(T_1 T)^{-1}$ (Supplementary Information). Thus, $(T_1 T)^{-1}$ is normalized to the values at 50 K, higher than the metal-insulator crossover temperature, where the magnetic field dependence of $(T_1 T)^{-1}$ is expected to be negligible. The normalized $(T_1 T)^{-1}$ is strongly field-dependent at low temperatures (Fig.4a). For a weak perpendicular magnetic field, 0.9 T, a steep decrease in $(T_1 T)^{-1}$ on cooling toward $T_c$, is evident. As the magnetic field is strengthened, however, that becomes less prominent for 11 T and suppressed for 15.5
and 18 T exceeding $H_{c2}$, although there remains a weak $T$-linearity. Thus, the recovery of the suppressed spin excitations proceeds in parallel with the destruction of the superconductivity. In addition, both of the superconductivity and the suppressed spin excitations are hardly affected by a parallel field of 8 T ($\parallel a$ axis) as observed in Fig. 4a. In the parallel magnetic field, the superconductivity is robust against the magnetic field because the orbital depairing does not occur in that magnetic field geometry. The observed common anisotropy in the superconductivity and the anomalous spin excitations indicates their inseparable connection; that is, the latter is the manifestation of superconducting precursor, which persists up to twice as high as $T_c$ (Fig. 4a).

Figure 4b shows $(T_1T)^{-1}$ for non-deuterated $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br ($\kappa$-hBr), which is situated further from the BCMT than is $\kappa$-dBr, at perpendicular magnetic fields of 0.9 T and 11 T, reproducing the essential features in previous reports$^{27,28}$. A decrease in $(T_1T)^{-1}$ on cooling toward $T_c$ is appreciable, but is less prominent than in $\kappa$-dBr. Figure 4c shows $(T_1T)^{-1}$ of $\kappa$-(ET)$_2$Cu(NCS)$_2$ ($\kappa$-NCS, $T_c = 10$ K), located further off the Mott boundary than $\kappa$-hBr, under parallel and perpendicular fields of 9 T. No anomalous behaviour above $T_c$ is evident. These results, in conjunction with the pressure dependence of $(T_1T)^{-1}$ of $\kappa$-dBr described above, indicates that the enhanced precursor to the superconductivity in $\kappa$-dBr originates from the electron correlations that are enhanced near the BCMT. The conventional low-dimensionality-driven fluctuations$^{29}$ comprised of the Aslamasov-Larkin, Maki-Thomson and density-of-states effects is ruled out by the absence of its signature in $\kappa$-NCS, which is the most highly two-dimensional among the three$^{30}$; actually, the former two effects are shown to vanish in $(T_1T)^{-1}$ in d-wave superconductivity$^{31,32}$. Thus, the superconducting precursor is likely to occur as the preformation of phase-incoherent Cooper pairs. It is noted that the Nernst coefficient shows an anomalous increase at temperatures well above $T_c$ in the vicinity of the BCMT, which is discussed in terms of unconventional superconducting fluctuations$^{33}$.

The present observation that the AF correlations and the preformation of Cooper pairs are simultaneously enhanced near the BCMT has a consistent explanation. As the system approaches the Mott metal-insulator transition, double occupancy on a site is gradually prohibited. Consequently, spins take on the localized nature, which leads to the enhancement of the $(\pi, \pi)$ AF correlations. On the other hand, the increasing single-occupancy probability suppresses particle-density fluctuations and enhances the phase fluctuations, making the incoherent Cooper pairs easily preformed (ref. 34). The scattering with $Q = (\pi, \pi)$ has been theoretically suggested to mediate the $d_{\alpha2-y2}$
paring\textsuperscript{35,36}, which, in turn, opens a gap around the regions indicated by the hatched area in Fig. 1d, explaining why the anomalous behaviour is particularly prominent in $(T_1 T)^1$ but is not as prominent in the Knight shift. The anomalous spin excitations that emerge on the verge of the Mott localization of electrons is thus considered to be a closely intertwined manifestation of AF fluctuations and preformed pairs.

The present case is distinct from the widely recognized pseudogap in the copper oxides in that the latter is visible in the Knight shift\textsuperscript{1} and involves a sizable portion of the Fermi surfaces, as revealed by angle-resolved photoemission spectroscopy\textsuperscript{2}, and competing orders\textsuperscript{4-8}. Doped copper oxides are distinguished from the present system with a half-filled band in the following respects. First, copper oxides enter inside the strongly correlated region where double occupancy is strongly prohibited. Second, doping, which introduces vacancies, makes the charge degrees of freedom vital, whereas a half-filled band has no such room; in fact, the NMR spectra of κ-dBr show no signature of charge ordering at every pressure. Thus, the present observation of preformed pairs is addressed as an emergence under limited correlation and prohibited charge redistribution. When both restrictions are relaxed as a result of doping, the pseudogap behaviour as observed in copper oxides might be induced, as summarized in Fig. 1a.
Methods

**Sample preparation.** Single crystals of $\kappa$-(ET)$_2$Cu[N(CN)]$_2$Br ($\kappa$-hBr), its deuterated version ($\kappa$-dBr), and $\kappa$-(ET)$_2$Cu(NCS)$_2$ were grown using the conventional electrochemical method, in which two central carbon atoms in ET and deuterated ET molecules are enriched with $^{13}$C isotope by 99%, as shown in Fig. S2. At the central carbons, the HOMO (highest occupied molecular orbital) has a high population; hence, through the large hyperfine coupling, the $^{13}$C nuclei probe the states of conduction electrons with high sensitivity, for example, compared with the $^1$H nuclei located on the edges of the ET.

**NMR measurements.** The $^{13}$C NMR spectra were obtained by Fourier transformation of the quadrature-detected echo signals. Two types of pulse sequences were employed: the spin-echo pulse sequences of $(\pi/2)_X - (\pi)_X$ and the solid-echo pulse sequences of $(\pi/2)_X - (\pi/2)_Y$, where $X$ and $Y$ denote the axes in the rotational frame. For the pressure-dependence study, a coil wound around a sample was inserted in a pressure cell. Alternatively, for the magnetic-field-dependence study, the measurements were performed at ambient pressure without a pressure cell to avoid the experimental difficulty in tuning the resonant circuit, parts of which are inside the pressure cell, in frequencies over a 20-fold range. The conditions for the NMR measurements are summarized in Table. S1. Details of data analysis are described in Supplementary Information.

**He-gas pressure.** To achieve fine control of the bandwidth of $\kappa$-dBr, we used the He-gas pressure technique. The NMR coil containing the sample was inserted into a pressure cell made of non-magnetic BeCu and compressed hydrostatically in a He pressure medium, which was directly compressed through a capillary tube by a gas-compressing system outside the cryostat. This technique allowed us to perform a continuous pressure-sweep while maintaining a nearly constant temperature, even at low temperatures, unless the He medium solidified.
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**Author Contributions**

All authors designed the experiments. T.F., K.M., and M.M. performed the experiments and analysed the data. All authors interpreted the data. K.M. grew the single crystals for the study. T.F. wrote the manuscript with the assistance of K.M. and K.K. All authors reviewed the manuscript. K.K. headed this project.

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Figure legends

Figure 1 Basic properties of the organic superconductor \( \kappa-(ET)_2X \), where ET represents bis(ethylenedithio)tetrathiafulvalene. a, Comparison of \( \kappa-(ET)_2X \) and copper oxides with distinct anomalous features of the normal states revealed in the present study. \( W \) and \( U \) denote bandwidth and on-site Coulomb energy, respectively. b, Pressure-temperature phase diagram of \( \kappa \)-dBr. The red line represents the first-order BCMT line, which terminates at a critical endpoint. The arrows indicate the temperature scans covered by NMR measurements under pressure. AFM and SC denote antiferromagnet and superconductor, respectively. The pressure medium, helium, solidifies at the broken line, the region below which was inaccessible in the present experiments. c, Crystal structure and magnetic structure of AF long-range ordered \( S = 1/2 \) spins with a \( Q = (\pi, \pi) \) ordering vector in the Mott insulating state of \( \kappa \)-dBr. Each ET dimer, which corresponds to the lattice site of an anisotropic triangular lattice, accommodates one hole. The yellow diamond and the green rectangle correspond to a primitive and an enlarged unit cell of an anisotropic triangular lattice, respectively. d,
Schematic Fermi surfaces of the metallic state of κ-dBr. The yellow diamond and the green rectangle are the first Brillouin zones of the unit cells with the corresponding colours in c. The black arrows indicate a wavevector \( \mathbf{Q} = (Q_x, Q_y) = (\pi, \pi) \), and the hatched area corresponds to the region around which a superconducting gap of \( d_{x^2-y^2} \) symmetry opens.

**Figure 2 Spin excitations in κ-dBr probed by \(^{13}\)C NMR.** a, \(^{13}\)C NMR spectra at 15 K at 2 MPa and 30 MPa. Two peaks originate from two \(^{13}\)C sites (‘inner’ and ‘outer’ sites) in the ET molecule (Supplementary Information). At 2 MPa on the verge of the Mott transition, a broad line coming from the Mott insulating phase appears at higher frequencies, however, it is well separated from the spectrum of the metallic phase. b, The temperature dependences of \((T_1 T)^{-1}\) and c, the Knight shift, \( K \), at several pressures. The data for 50 MPa and 100 MPa at lower temperatures are absent because the area below the He solidification line in Fig. 1b is experimentally inaccessible. The vertical lines indicate the \( T_c \)’s at each pressure, as determined from the kinks in the Knight shift. d, A contour plot of \((T_1 T)^{-1}\) as a function of temperature and pressure.
Figure 3 Evaluation of the energy scale of phenomenological gap at several pressures. The pressure dependence of $\Delta$ and $T_c$, where $T_c$’s are identified by a kink in the Knight shift, $K$, or the midpoint or offset point of resistive transition.

Figure 4 Magnetic fields suppress the superconductivity and the anomalous spin excitations simultaneously. The temperature dependence of $(T/T)_1^{-1}$ with different magnitudes and directions [$\parallel b$ (out-of-plane) or $\parallel a$ (in-plane)] of the magnetic field in a, $\kappa$-dBr, b, $\kappa$-hBr, c, $\kappa$-NCS. The values of $(T/T)_1^{-1}$ are normalized to the values at 50 K (Supplementary Information).
Supplementary Information

A. Characterization of superconductivity in κ-dBr at ambient pressure

In the present study, the field dependence of $^{13}$C NMR measurements was performed at ambient pressure, where superconducting and Mott-insulating phases are coexistent due to the first-order Mott transition. From the NMR spectral profile, the volume fraction of the superconducting phase is approximately 15%. To examine the homogeneity of $T_c$ in the superconducting domains, we measured AC susceptibility of the κ-dBr crystal used in the NMR measurements. Figure S1 shows the AC susceptibility measured with the AC filed of 17 Hz in frequency and 0.005 gauss in amplitude applied perpendicular to the conducting plane. The demagnetizing effect is corrected with the demagnetization factor of 0.58, which was determined by the measurements of Sn shaped into the same geometry as the κ-dBr crystal. A sharp transition at 11 K is evident and there is no feature indicative of distribution of $T_c$. The diamagnetic susceptibility is nominally 85% in shielding diamagnetism, which largely overestimates the superconducting volume fraction as expected.

B. NMR spectra:

1. General features of $^{13}$C NMR spectra

When an external magnetic field is applied to κ-dBr or κ-hBr with an arbitrary orientation to the crystal axes, the $^{13}$C NMR spectra generally consist of 16 (2 x 2 x 4 as explained below) resonance lines, which have three different origins of the line splitting: (i) the shifted face-to-face dimerization of ET molecules makes the two central carbon sites in ET inequivalent (called “inner” and “outer” sites, as depicted in Fig. S2b), giving two lines with different shifts; (ii) each line further splits into two, owing to the nuclear dipolar fields from the adjacent $^{13}$C nuclei, which is called the “Pake doublet”; (iii) the unit cell contains four dimers (two in a layer), which are all inequivalent with respect to the magnetic field direction except for high-symmetry magnetic field orientations ($\mu_0 H \parallel a$, $\parallel b$, or $\parallel c$) (see Fig. S3).

In the present study, magnetic fields, $\mu_0 H$, were applied parallel to the $a$ axis (in-plane) or the $b$ axis (out-of-plane). In these situations, all of the dimers are equivalent, so the splitting of the origin (iii) does not occur; thus, the number of NMR lines is reduced to four. In particular, in the case $\mu_0 H \parallel a$, the splitting from the origin (ii) is negligible because the angle between the $^{13}$C-13C bonding direction and the magnetic field direction is close to the special angle called the magic angle, at which the
dipolar splitting vanishes. Thus, only two lines are observed, and these correspond to the inner- and outer-site spectra, owing to splitting origin (i).

(2) NMR spectra under pressure variation

In NMR experiments under pressure, a magnetic field of 7.4 T was applied parallel to the \( a \) axis (in-plane); hence, two lines were observed, as shown in Fig. S4, which indicates the pressure evolution of the NMR spectra at 15.5 K and 23 K under pressure. The two lines at 15 K arise from a metallic phase; the line at the lower frequency of approximately 79.227 MHz is from the inner site and the other one of approximately 79.235 MHz is from the outer site (see also Fig. S2b). At 2 MPa, a broad line appearing at a higher frequency of approximately 79.280 MHz in the inset of Fig. S4a arises from an antiferromagnetic Mott insulating phase, because the metallic and insulating phases coexist around the critical pressure of the Mott transition owing to its first-order nature; however, they are clearly separated in the NMR spectra. The pressure evolution of the volume fraction of the metallic phase, which is evaluated from the intensity of the inner-site line (approximately 79.227 MHz) of the metallic phase, is shown in Fig. S5. The data around ambient pressure are lacking because the experiments with the He-gas-pressure apparatus were performed under finite pressures applied. A separate ambient-pressure measurement without the He-gas apparatus showed that the metallic-phase fraction is 15 \%, which is reasonable if Fig. S5 is compared with the corresponding results of \( \kappa \)-(ET)\(_2\)Cu[N(CN)\(_2\)]Cl (Ref. S1)). Above approximately 5 MPa, the whole volume of the sample is the metallic phase. Even at the lower pressures, the metallic phase is well separated from the coexisting insulating phase in spectra. However, as temperature is increased, the line of the Mott insulating phase is gradually shifted toward lower frequencies and overlaps with the outer-site line of the metallic phase. At 23 K (Fig. S4b), while the low-frequency line at approximately 79.227 MHz rapidly develops in intensity with the growth of the metallic-phase volume by pressure, the high-frequency line at approximately 79.235 MHz appears unchanged (although its shape is slightly changed). This is because an increase in the intensity of the outer-site line in the metallic phase is compensated by the decrease in that of the inner-site line in the Mott-insulating phase. To avoid the contamination by the Mott insulating phase in analysis, the Knight shift and the relaxation rate in the metallic phase were defined for the inner-site spectra in the pressure-dependent measurements.

(3) NMR spectra under field variation

In the magnetic-field-dependent \(^{13}\)C NMR measurements, magnetic fields ranging from 0.9 T to 18 T were applied parallel to the \( b \) axis (out-of-plane). In this case, four
lines emerge owing to the splitting mechanisms of (i) and (ii). The splitting of (i) is proportional to the magnetic field, whereas the splitting of (ii) is independent of the magnetic field; so, the spectral profile is largely influenced by the magnetic field. In weak magnetic fields, splitting mechanism (ii) is dominant, and splitting mechanism (i) is secondary; accordingly, the Pake doublet formed by (ii) is modified into a quartet with two inner lines of small intensities (Ref. 28, S2). This modification is the case for the spectrum at 0.9 T, although two inner lines have merged into a central line in this particular magnetic field (Fig. S6a). In this case, each line has an indistinguishable relaxation rate owing to the admixture of the inner-site and outer-site relaxation rates, which are several-fold different. As a magnetic field is increased, the splitting of (i) becomes comparable to or larger than that of (ii); thus, the quartet comes to consist of an inner-site doublet and an outer-site doublet. At much stronger magnetic fields (11, 15.5, and 18 T), each of the inner- and outer-site doublets loses the two-peak structure because the linewidth increases in proportion to the magnetic field (in other words, the splitting of the doublet decreases in ppm in inverse proportion to magnetic field), resulting in two lines with different relaxation rates $T_1^{-1}$'s (see Fig. S6b for the spectrum at 11 T). From the spectral profiles, the difference between the inner- and outer-site shifts (splitting (i)) is estimated to be 200–300 ppm, and the splitting of the Pake doublet (splitting (ii)) is approximately 3 kHz.

(4) Spectral separation of metallic and insulating components coexistent at ambient pressure

As with the case of the pressure-dependence study, the phase separation in κ-dBr was observed in the field-dependence measurements over 0.9–18 T at ambient pressure. The degree of phase separation depends on temperature; the volume fraction of the metallic phase in the sample used was larger than 90 % above approximately 20 K and decreases to 5–15 % at 5 K, as determined from the spectral intensities. Figure S7 shows the temperature dependence of $^{13}$C NMR spectra of κ-dBr at a perpendicular field of 11 T at ambient pressure. The sharp double-peaked spectra of the metallic phase staying around 117.78 MHz and the broad double lines of the insulating phase that move toward higher frequencies on cooling are well separated without any continuous distribution. The scale of the metallic and insulating domains are macroscopic (of the order of 100 μm) according to the characterization using the scanning micro-region infrared spectroscopy by Sasaki et al.$^{S3}$ As indicated by the AC susceptibility measurements (Fig.S1), the superconductivity in the domains is homogeneous. (Ref. S1). The spectra of κ-hBr at 0.9 and 11 T were similar to those of κ-dBr but did not exhibit any phase separation.
C. The Knight shift

The Knight shifts in Fig. 2c correspond to the peak frequencies of the inner-site spectra at each temperature. The metallic phase of κ-dBr shows singlet superconductivity at low temperatures, where the Knight shift is expected to vanish at absolute zero without a residual shift owing to the negligible spin-orbit interaction in the present materials; accordingly, the origin of the Knight shift was determined by extrapolating the peak frequencies at 4 MPa to absolute zero.

D. The NMR spin-lattice relaxation rate, $T_1^{-1}$

The nuclear spin-lattice relaxation rate, $T_1^{-1}$, was determined from the recovery curves of nuclear magnetization following the saturation comb pulses: i.e., $1 - I(t)/I(\infty) = A \exp(-t/T_1)$, where $t$ is the recovery time, $A$ is the fitting constant, and $I(t)$ is the integrated intensity of NMR spectra at time $t$.

(1) Extracting $T_1^{-1}$ of the metallic phase free from the coexisting insulating phase on the verge of the Mott transition

As mentioned above, at ambient or low pressures, κ-dBr is on the verge of the Mott-transition boundary and contains both metallic and insulating phases. These phases are well separated in the NMR spectra at low temperatures, but the inner-site line of the insulating phase tends to approach the outer-site line of the metallic phase at high temperatures. In addition, in strong magnetic fields of 15.5 and 18 T, the whole spectra from the metallic phase were extended, respectively, over 150 and 200 kHz, the whole range of which was not covered by the present NMR pulses. For these two reasons, we used the inner-site lines for the evaluation of $T_1^{-1}$. The relaxation curves for the inner lines of metallic signals were single-exponential functions of time even at low pressure, confirming the single-phase (metallic-phase) nature of the line investigated; for example, the data of 4 MPa are shown in Fig. S8. The admixture of the insulating phase, the $T_1^{-1}$ of which differs considerably from that of the metallic phase, would have resulted in the bending the relaxation curve.

(2) Spurious field dependence of $T_1^{-1}$

As explained in detail in Section B.(3), the NMR spectrum under the field perpendicular to the layers ($\| b$ axis) is comprised of a quartet that comes from the nuclear-dipole coupling of two adjacent $^{13}$C sites (‘inner’ and ‘outer’ sites) with different Knight shifts in the ET molecule. At high fields (11, 15.5, 18 T), the dipolar coupling is secondary compared with the difference of the Knight shift so that the ‘inner’ doublet and ‘outer’ doublet are well separated; thus, the relaxation rate of the inner site is investigated as in the parallel-field case (see also B.(1)). At low fields (0.9 T),
however, the two doublets are mixed up and the relaxation rates for the inner and outer sites get inseparable; therefore, the relaxation rate measured at low fields yields an average of the rates for the two sites. This situation gives a spurious field-dependence of the \((T_1T)^{-1}\) values.

Figure S9a shows the temperature dependence of \((T_1T)^{-1}\) for various magnetic fields. Except at low temperatures (below 20 K), where the system exhibits superconductivity and anomalous spin excitations, the \((T_1T)^{-1}\) values at 11, 15.5 and 18 T are nearly coincident with each other in magnitude, because they correspond to the values for the inner-site. At 0.9 T, the magnitude of \((T_1T)^{-1}\) becomes greater because of the averaging of the inner- and outer-site values, as described above.

To remove this spurious magnetic field dependence, the values of \((T_1T)^{-1}\) are normalized to the values at 50 K, where \(\kappa\)-dBr is in a paramagnetic Mott insulating phase and the magnetic field dependence of \((T_1T)^{-1}\) is expected to be negligible. As shown in Fig. S9b, the temperature dependences of the normalized values for different magnetic fields nearly coincide above 20 K. The steep decreases at approximately 30 K reflect a sharp crossover from the high-temperature Mott insulating phase to the low-temperature metallic phase, confirming that the metallic phase at low temperatures is properly captured by the present measurements and analyses.

We also note that by using the so-called solid-echo pulse sequence, which is effective (ineffective) for refocusing the dipole-split (spin-shifted) lines, the quartet coming from the metallic phase with small spin shift is selectively picked up at low magnetic fields (see Table S1).

**E. Evaluation of NMR relaxation-rate enhancement factor (the Korringa ratio)**

NMR relaxation rate measures the wave vector \((q)\)-summation of spin fluctuations weighted with the squared form factor \(|A(q)|^2\) over the 1\(^{st}\) Brillouin zone, as expressed by \((T_1T)^{-1} \propto \Sigma_q |A(q)|^2 \chi''(q, \omega_{\text{NMR}})/\omega_{\text{NMR}}\), where \(\chi''(q, \omega)\) is the imaginary part of the dynamic spin susceptibility and \(\omega_{\text{NMR}}\) is the resonance frequency of NMR measurement. In the present case, the form factor \(A(q)\) of the \(^{13}\text{C}\) site located at the midst of the molecular orbital in the ET molecule is \(q\)-independent and thus \((T_1T)^{-1} \propto \Sigma_q \chi''(q, \omega_{\text{NMR}})^{-1}\) and Knight shift \(K_s\) provides information on the \(q\) profile of \(\chi''(q, \omega)\). In case of the isotropic hyperfine coupling, it is well known that \(K_s\) is given by

\[
K_s = \frac{(\hbar / 4\pi k_B)(\gamma_e / \gamma_n)^2(1/T_1T)K_i^{-2}}{1/4},
\]

where \(\hbar\) is Plank’s constant, \(k_B\) Boltzmann’s constant, and \(\gamma_n\) and \(\gamma_e\) are the gyromagnetic ratios of nuclear spin and electron spin,
respectively. In the present case, however, the hyperfine coupling is anisotropic and expressed by a tensor; the principal values of the hyperfine coupling tensor of the inner $^{13}$C are $a_{xx} = -1.4$ kOe/$\mu_B$, $a_{yy} = -3.3$ kOe/$\mu_B$ and $a_{zz} = 10$ kOe/$\mu_B$ with $x$, $y$ and $z$ axes indicated in Fig. S2 according to Ref. S4, 20), where $\mu_B$ is the Bohr magneton. In this case, the Korringa ratio is expressed by $K_{\alpha} = \beta(\zeta, \eta)(h/4\pi k_B)(\gamma_e/\gamma_n)^2 (1/T_1 T) K_{\alpha}^{-2}$.

where $\beta(\zeta, \eta)$ is given by

$$\beta(\zeta, \eta) = \frac{2}{(a_{xx}/a_{zz})^2} \left[ (a_{xx}/a_{zz})^2 \sin^2 \zeta \cos^2 \eta + (a_{yy}/a_{zz})^2 \sin^2 \zeta \cos^2 \eta + (a_{zz}/a_{zz})^2 \cos^2 \zeta \sin^2 \eta + \sin^2 \zeta \right] .$$

$\zeta$ is the angle between the external field and the $z$-principal axis and $\eta$ is the polar angle measured from the $x$-principal axis in the $xy$ plane of Fig. S2.

The substitution of the experimental data in Figs. 2b and 2c, and the experimental angles, $\zeta = 55^\circ$ and $\eta = 43^\circ$ to the form of $K_{\alpha}$ yields $K_{\alpha} \approx 8 - 12$ (e.g. $K_{\alpha} = 8.1$ for $P = 100$ MPa and $T = 15$ K), which greatly exceeds unity. It means that $(T_{1} T)^{-1} \propto \Sigma_{q} \chi''(q, \omega_{NMR})$ is overwhelmingly contributed by components with $q \neq 0$, namely antiferromagnetic fluctuations. A numerical study predicts that $Q = (\pi, \pi)$ fluctuations is dominant and progressively grows on approaching the Mott transition$^{21-23}$.

| Pressure-dependence study | Sample | Pressure [MPa] | Magnitude of field [T] | Field orientation | Pulse sequence | Integral interval |
|---------------------------|--------|----------------|------------------------|-------------------|----------------|------------------|
| \(\kappa\)-dBr (sample #1) | 4      | 7.4            | \(\mu_0 H \parallel a\) (parallel to the conducting plane) | spin echo         | inner-site spectra |
|                           | 20     |                |                        |                   |                |                  |
|                           | 50     |                |                        |                   |                |                  |
|                           | 100    |                |                        |                   |                |                  |
| Magnetic-field- | sample #2 | | | | | |
| dependence study | | | | | | |
| \(\kappa\)-dBr           | Ambient pressure | 0.9   | \(\mu_0 H \parallel b\) (perpendicular to the conducting plane) | solid echo        | whole spectra   |
|                           |             | 11    |                        | spin echo         | inner-site spectra |
|                           |             | 15.5  |                        |                   |                |                  |
|                           |             | 18    |                        |                   |                |                  |
| \(\kappa\)-hBr           | Ambient pressure | 0.9   | \(\mu_0 H \parallel b\) (perpendicular to the conducting plane) | solid echo        | whole spectra   |
|                           |             | 11    |                        | spin echo         | inner-site spectra |
| \(\kappa\)-NCS           | Ambient pressure | 9     | \(\mu_0 H \parallel\) conducting layer | spin echo         | whole spectra   |
|                           |             | 9     |                        |                   |                |                  |

**Table S1** Conditions for the NMR measurements
**Fig. S1** Temperature dependence of the AC susceptibility of \( \kappa \)-dBr at ambient pressure. Demagnetizing field was corrected.

**Fig. S2** Schematic of ET molecules enriched with \(^{13}\)C isotopes. \( \textbf{a} \), ET and deuterated ET molecules labelled with \(^{13}\)C isotopes at the two central carbons. \( \textbf{b} \), \(^{13}\)C nuclei at the inner and outer sites with different hyperfine fields in a dimer of ET molecules.

**Fig. S3** Layered structure (\( \textbf{a} \)) and in-plane arrangement of ET molecules in the layer A and layer B in \( \kappa \)-dBr (\( \textbf{b,c} \))
Fig. S4 $^{13}$C NMR spectra of $\kappa$-dBr under pressures at (a) 15.5 K and (b) 23 K. A magnetic field of 7.4 T is applied parallel to the conducting layers.

Fig. S5 Pressure dependence of the volume fraction of the metallic phase at 15.5 K and 23 K in $\kappa$-dBr.
Fig. S6 $^{13}$C NMR spectra of $\kappa$-dBr under perpendicular magnetic fields of (a) 0.9 T (24 K) and (b) 11 T (26 K) at ambient pressure.
Fig. S7 Temperature dependence of the NMR spectra of κ-dBr at ambient pressure under a magnetic field of 11 T applied perpendicular to the conducting layer: (left) a narrow frequency region, in which the metallic-phase spectra reside, and (right) a wide frequency range, which covers the insulating-phase spectra as well as the metallic-phase one.
Fig. S8 $^{13}$C NMR relaxation curves of κ-dBr at a pressure of 4 MPa under a magnetic field of 7.4 T applied parallel to the layers. The recovery of nuclear magnetization $I(t)$ is plotted in the form of $\log \left[ 1 - \frac{I(t)}{I(\infty)} \right]$ vs $t$ for several temperatures, where $t$ is the time of recovery and $I(\infty)$ is the saturated value of $I(t)$. All of the data are well fitted by straight lines: $1 - \frac{I(t)}{I(\infty)} \propto \exp(-t/T_1)$ with $T_1$ nuclear spin-lattice relaxation time.
Fig. S9 Temperature dependence of $(T_1 T)^{-1}$ for various magnetic fields. (a). Raw values of $(T_1 T)^{-1}$. (b). $(T_1 T)^{-1}$ normalized to the values at 50 K.

Fig. S10 The Arrhenius plot of $\delta(T_1 T)^{-1}$ for various pressures. $\delta(T_1 T)^{-1} = (T_1 T)^{-1} - (T_1 T)^{-1}_{100 \text{ MPa}}$. $\delta(T_1 T)^{-1}$ is approximated in the form of $\delta(T_1 T)^{-1} \propto \exp(-\Delta T)$. 
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