# Coupling of molecular motion and electronic state in the organic molecular dimer Mott insulator $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>

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(Received 16 November 2017; published 19 January 2018)

We have performed <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements to investigate the coupling between molecular dynamics and the electronic state of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>. From the <sup>1</sup>H NMR measurements, we observed a frequency-dependent anomaly in the nuclear spin-lattice relaxation rate <sup>1</sup> $T_1^{-1}$  that originates from the slowing down of the ethylene motion. In the <sup>13</sup>C NMR measurements, we found an anomaly in the linewidth of the NMR spectra at around 150 K, which is attributed to a nuclear spin-spin relaxation rate (<sup>13</sup> $T_2$ ) anomaly. The magnitudes of the anomalies in the linewidth and in <sup>13</sup> $T_2^{-1}$  are related to the hyperfine coupling constant. These results suggest that the ethylene motion modulates the molecular orbital of the BEDT-TTF molecules and gives rise to a difference in the orbital energy between the "staggered" and "eclipsed" conformations. We propose that significant coupling exists between the ethylene motion and the electronic state of the molecular dimer and that the ethylene dynamics can trigger the emergence of charge degrees of freedom inside the dimers and cause the dielectric anomaly in  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>.

DOI: 10.1103/PhysRevB.97.045136

## I. INTRODUCTION

Research concerning electronic ferroelectricity has been making significant progress [1,2]. Among ferroelectric materials, molecular crystals are attracting considerable interest as they show interesting ferroelectric properties owing to charge displacements that are driven by various phase transitions. The large ferroelectric polarization in TTF-CA (where TTF = tetrathiafulvalene and CA = p-chloranil) is induced by a neutral-to-ionic transition [3,4]. Also, the ferroelectricity observed in  $(TMTTF)_2 X$  (where TMTTF = tetramethyltetrathiafulvalene) is caused by charge ordering [5,6]. Interestingly, the ferroelectric nature of dimer Mott insulators, which consist of organic molecules such as BEDT-TTF (where BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene), has also been demonstrated [7-10]. For example, both the quasi-two-dimensional organic molecular crystals  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> and  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> show large anomalies in the temperature dependence of the dielectric constant as well as relaxorlike behavior. This implies the existence of an interacting electric dipole in the dimer [9].

 $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> is a well-known dimer Mott insulator that has an antiferromagnetic transition at  $T_N = 22$  K under ambient pressure [11]. In this salt, a metal-insulator transition of around 6.5 GPa and a superconducting transition at  $T_c =$ 14.2 K and 8.2 GPa have been demonstrated [12]. Figure 1(a) shows the crystal structure of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>. The BEDT-TTF layers and the ICl<sub>2</sub> anion layers are stacked alternately parallel to the  $a^*$  axis (perpendicular to the *bc* plane). Hence, this material is considered to possess a quasi-twodimensional electronic structure. In the  $\beta'$ -type arrangement, two BEDT-TTF molecules form a dimer. If one dimer is regarded as one unit, there is one hole per dimer unit and the electronic system can effectively be regarded as a half-filled system. Strong dimerization in this system is also supported by calculations of the intermolecular transfer integral [13]. When the Coulomb repulsion (U) on a dimer site is much larger than the interdimer transfer integral (t), charge is strongly confined on the dimer, resulting in a dimer Mott insulating state. In addition, <sup>13</sup>C NMR measurement and the Curie constant of the paramagnetic phase at a high temperature shows that the spin per dimer is S = 1/2 [14]. This also supports that the electronic system in this salt can be regarded as a localized spin system. Since there are antiferromagnetic interactions  $(J_{AF})$  among the localized spins, antiferromagnetic ordering occurs below  $T_{\rm N}$ . These magnetic properties also embody that  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> is a typical dimer Mott insulator that has large U/t value.

From its crystallographic symmetry,  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> belongs to the space group  $P\bar{1}$  [13]. There is an inversion center at the center of the dimer site, as shown in Fig. 1(b) by the closed circles, and the two BEDT-TTF molecules that form one dimer are crystallographically equivalent. Hence, it is natural to expect the charge to be equally distributed between the two BEDT-TTF molecules in the dimer, and static charge degrees of freedom are not expected to appear in this salt.

However, Iguchi *et al.* found that the temperature dependence of the dielectric constant of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> shows a ferroelectric relaxorlike frequency dependence at around 80–150 K [7]. When electric fields are applied parallel to the *b* axis (the stacking direction of the dimers), they observed large peaks in the temperature dependence of the dielectric constant at several frequencies. This implies that charge disproportionation (CD) occurs in the dimer. Field-induced CD has also been reported by Hattori *et al.*, who performed Raman-scattering measurements in electric fields with different values [8]. They found a charge transfer  $\Delta \rho = +0.075e$  in the dimer for applied

2469-9950/2018/97(4)/045136(6)

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FIG. 1. (a) The crystal structure of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> seen from the *c* axis. (b) The dimer arrangement viewed along the long axis of the BEDT-TTF molecule. The closed circles represent inversion centers. (c) Two types of conformation of the terminal ethylene groups in the BEDT-TTF molecule. (d) Definition of the "inner" and "outer" <sup>13</sup>C sites in a BEDT-TTF dimer.

electric fields above 5 kV/cm. They also found that the CD state was maintained after they removed the electric field, although the CD state did not appear at low temperatures under zero-field cooling. These results suggest that the inversion symmetry in the dimer is broken and that charge degrees of freedom appear even in the dimer Mott insulating phase in this salt. Although some possible scenarios have been suggested to account for this behavior, the origin of the charge degrees of freedom is still under discussion.

Generally, the terminal ethylene groups of the BEDT-TTF molecule can take two types of conformations, either "staggered" or "eclipsed" as shown in Fig. 1(c) [15–18]. At high temperatures, the ethylene groups fluctuate between these two conformations. This thermal motion of the terminal ethylene groups (ethylene motion) slows down with a decrease in temperature and can affect the physical properties of the material in the temperature range in which the dielectric anomaly is observed in  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>. For example, it has been reported that the slowing dynamics of the ethylene motion scatters conducting electrons and affects the electrical conductivity in  $\kappa$ -type salts, such as  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl[15,16]. This indicates that the ethylene motion is coupled to the conducting electrons in these salts. Although the ground state of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> is not a metal but a dimer Mott insulator, it is possible that the ethylene motion in this material also may be coupled with the localized electrons and affect its dielectric properties.

In this study, we have performed <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements on  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>. We have confirmed that the slowing down of the ethylene motion in the BEDT-TTF molecules occurs in this salt and that it freezes at a temperature that is similar to that at which the dielectric anomaly is observed. We also report the detailed nature of the slowing dynamics of the ethylene groups and discuss the relationship between those dynamics and the electronic state in  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>.



FIG. 2. Temperature dependence of the proton nuclear spinlattice relaxation rate  ${}^{1}T_{1}^{-1}$  at magnetic fields of 0.55 T (green), 1.14 T (red), and 2.00 T (blue). The solid lines represent fitted curves using the BPP model.

#### **II. EXPERIMENT**

We synthesized  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> using an electrochemical method [19]. For the <sup>1</sup>H NMR measurements, we used a polycrystalline sample stuffed into a glass tube, with the edges sealed by a proton-free grease. We performed the <sup>1</sup>H NMR measurements at ambient pressure in magnetic fields of 0.55, 1.14, and 2.00 T. We performed <sup>13</sup>C NMR measurements in a magnetic field of 9.4 T, which we applied parallel to the *a* axis using a platelike single crystal. To prevent the Pakedoublet problem, we enriched one side of the central C=Cbond of the BEDT-TTF molecule with <sup>13</sup>C nuclei, using the cross-coupling method [20,21]. We obtained the NMR spectra using fast Fourier transforms (FFTs) of the echo signal. We determined the nuclear spin-lattice relaxation rate  $(T_1^{-1})$  using the saturation-recovery method and we defined the nuclear spin-spin relaxation rate  $(T_2^{-1})$  as the rate corresponding to Lorentz decay.

## **III. RESULTS AND DISCUSSION**

#### A. Ethylene motion

Figure 2 shows the temperature dependence of the  ${}^{1}T_{1}^{-1}$ in <sup>1</sup>H NMR at several magnetic fields. Peaks were observed at 273, 287, and 300 K in magnetic fields of 0.55, 1.14, and 2.00 T, respectively. The peaks shift to high temperatures and decrease in magnitude with an increase in magnetic field. Below 200 K the  ${}^{1}T_{1}^{-1}$  converges to the same value, regardless of the applied magnetic field. Similar field-dependent behavior of the peak structure in  ${}^{1}T_{1}^{-1}$  has been observed in other BEDT-TTF salts, such as  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> [22–24]. In these salts, it is well established that the field-dependent behavior can be explained by the Bloembergen-Purcell-Pound (BPP) model and is attributed to the slowing down of the ethylene motion [25]. The BPP model treats the magnetic fluctuations induced



FIG. 3. Temperature dependence of the inverse correlation time of the ethylene motion (time scale of the ethylene motion) determined by  $^{1}$ H NMR measurements.

by molecular motions via a dipole-dipole interaction. Since the terminal ethylene groups are thermally fluctuated, the local fields at proton sites in those groups fluctuate, which can affect the magnetic relaxation of the protons. With a decrease in temperature, the correlation time of the ethylene motion ( $\tau_c$ ) increases. Roughly, a peak is observed in the  ${}^{1}T_{1}^{-1}$  when the time scale of the ethylene motion ( $\tau_{c}^{-1}$ ) becomes the same as the order of the NMR resonance frequency  $\omega$ . According to the BPP model,  $T_{1}^{-1}$  is given by the following equation:

$$\frac{1}{T_1} = C \left( \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right), \tag{1}$$

where *C* is a constant. If we assume an activation energy  $(\Delta E)$  between the staggered and eclipsed conformations, the temperature dependence of  $\tau_c$  can be described by an Arrhenius function as follows:

$$\tau_{\rm c} = \tau_0 \exp\left(\Delta E / k_{\rm B} T\right). \tag{2}$$

Note that not only does the molecular motion contribute to the magnetic relaxation but also the antiferromagnetic fluctuation of the localized electrons contributes. However, the contribution of the antiferromagnetic fluctuation to the  ${}^{1}T_{1}^{-1}$  is very small and is almost constant at high temperatures. Therefore, we add a constant term *a* to Eq. (1), thus obtaining the following equation:

$$\frac{1}{T_1} = C \left( \frac{\tau_{\rm c}}{1 + \omega^2 \tau_{\rm c}^2} + \frac{4\tau_{\rm c}}{1 + 4\omega^2 \tau_{\rm c}^2} \right) + a.$$
(3)

We obtained the solid lines in Fig. 2 by fitting the BPP model to the data using Eqs. (2) and (3). The temperature dependence of  ${}^{1}T_{1}^{-1}$  can be explained by the BPP model using the fitting parameters  $\tau_{0} \sim 1.2 \times 10^{-14}$  s,  $\Delta E/k_{\rm B} \sim 4000$  K,  $C \sim 1.7 \times 10^{8}$  s<sup>-2</sup>, and a = 0.98 s<sup>-1</sup>. Using these parameters and Eq. (2), we can calculate the temperature dependence of  $\tau_{\rm c}^{-1}$ , as shown in Fig. 3.



FIG. 4. Temperature dependence of the linewidths of the <sup>13</sup>C NMR spectra. The inset shows the <sup>13</sup>C NMR spectra between 80 and 250 K.

#### B. Coupling of the ethylene motion to the electronic state

To discuss the relationship between the ethylene motion and the electronic system, we performed <sup>13</sup>C NMR measurements. As shown in Fig. 1(d), there are two crystallographically nonequivalent inner and outer <sup>13</sup>C sites in the  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> [14]. Therefore, two peaks are expected to be observed in the NMR spectra. The inset in Fig. 4 shows the  $^{13}$ C NMR spectra at several temperatures. We observed two distinct peaks that correspond to the inner and the outer  ${}^{13}C$  sites. The temperature dependencies of the linewidths of both the inner and outer <sup>13</sup>C sites are summarized in Fig. 4. We observed anomalous peaks in the linewidths at around 150 K for both the inner and outer sites. The increments of the linewidth for the inner and outer sites at peak temperature are 0.52 and 1.45 kHz, respectively. The increase in the linewidth of the outer site is 2.7 times larger than that of the inner site. Note that the large increase in linewidth that is observed below 50 K is caused by the development of antiferromagnetic fluctuations, which lead to the antiferromagnetic transition at 22 K [14]. In the NMR measurements, the linewidth  $(\Delta f)$  is described as the following equation:

$$\Delta f = \frac{1}{T_2} + \left(\frac{\gamma}{2\pi}\right) \Delta H,\tag{4}$$

where  $\gamma$  is the nuclear gyromagnetic ratio, and  $\Delta H$  is a static inhomogeneity of internal fields. To investigate the origin of the anomalous increase in linewidth, we measured the <sup>13</sup>C nuclear spin-spin relaxation rate ( ${}^{13}T_2^{-1}$ ). Figure 5 shows the temperature dependence of  ${}^{13}T_2^{-1}$  at the inner and outer sites. We observed anomalous peaks at around 150 K for both sites. The increment of the  ${}^{13}T_2^{-1}$  for the inner and outer sites are  $0.41 \times 10^3 \text{ s}^{-1}$  and  $1.66 \times 10^3 \text{ s}^{-1}$ , respectively. The anomalous increments of the  $T_2^{-1}$  for the inner and outer sites are comparable with that of the linewidth at around 150 K. This indicates that the anomalies in the linewidth around 150 K mainly come from the  ${}^{13}T_2^{-1}$  anomaly. In general,



FIG. 5. Temperature dependence of the nuclear spin-spin relaxation rate  $\binom{^{13}T_2^{-1}}{^{13}}$  measured by <sup>13</sup>C NMR.

 $T_2^{-1}$  is sensitive to the slow dynamics for which a typical time scale is of the order of 1–10 kHz. Whereas the  $T_1^{-1}$ detects magnetic fluctuations perpendicular to the external field with resonance frequency, the contributions to the  $T_2^{-1}$ come from magnetic fluctuations parallel to the external field with slow frequencies. One of them is due to the spin-spin coupling between <sup>13</sup>C nuclei which does not show significant temperature dependence and the other is due to the ethylene motion with the correlation time  $\tau_c$ . In the higher temperature region, namely the extreme narrowing condition, the BPP model predicts that the  ${}^{13}T_2^{-1}$  increases proportional to  $\tau_c$ , which increases with a decrease in temperature. As a result, the contribution from the ethylene motion becomes larger than that from the  ${}^{13}\text{C}-{}^{13}\text{C}$  coupling and the  ${}^{13}T_2^{-1}$  increases. However, in the much lower temperature region where the ethylene motion freezes, namely the static condition, the  $T_2$  relaxation originating from the ethylene motion is abruptly suppressed and the  ${}^{13}T_2^{-1}$  should be roughly equal to the hopping rate, resulting in the reduction of the  ${}^{13}T_2^{-1}$ . The peak in the temperature dependence of the  ${}^{13}T_2^{-1}$  was observed around the crossover temperature of the two conditions. In the  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> salts, in which the freezing of the ethylene motion has been observed, similar anomalies have been seen in the linewidths and in the values of  ${}^{13}T_2^{-1}$  [15,16]. In these salts, the slowing down of the ethylene motion causes the development of the anomalous peak in  ${}^{13}T_2^{-1}$ . As confirmed in Fig. 3, the time scale of the ethylene motion at around 150 K is of the order of 1 kHz. Therefore, we conclude that the anomaly in the linewidth is derived from the  ${}^{13}T_2^{-1}$  anomaly at around 150 K and is caused by the dynamics of the ethylene groups of the BEDT-TTF molecules.

We discuss in detail the origin of the coupling between the ethylene motion and the local field at the <sup>13</sup>C nuclei. We found that the values of the linewidth and of <sup>13</sup> $T_2^{-1}$  at the anomaly depend upon the hyperfine coupling constant. There are two possible mechanisms for coupling between the ethylene motion and the local field at the <sup>13</sup>C nuclei. One is direct coupling and the other is indirect coupling [16]. The direct coupling originates from the dipole fields of the <sup>1</sup>H nuclei. In this mechanism, the linewidth and the  $T_2$  anomaly show no site dependence because the distance between the <sup>1</sup>H and both the outer and inner <sup>13</sup>C sites are almost the same. On the other hand, the indirect coupling originates from the modulation of the molecular orbital caused by the ethylene motion. In this case, the modulated molecular orbitals generate magnetic fluctuations at the <sup>13</sup>C sites through the hyperfine coupling constant, resulting in significant site dependence. If the anomaly in the linewidth is caused by indirect coupling, the spectrum should be broadened in proportion to the hyperfine coupling constant, and the magnitude of the  ${}^{13}T_2^{-1}$  anomaly should be proportional to the square of the hyperfine coupling constant [16,26]. Previously, Eto et al. determined the hyperfine coupling tensor for both the outer and inner <sup>13</sup>C sites and found that the ratio of its magnitude at the outer site to that at the inner site is  $\sim 3$  [14]. The ratios of both the linewidth and  ${}^{13}T_2^{-1}$  at the outer site to their values at the inner site, as evaluated in this study, are  $\sim$ 2.7 and  $\sim$ 4.3, respectively. These results suggest that the anomalies in linewidth and  ${}^{13}T_{2}^{-1}$  are related to the hyperfine coupling constant and that the slowing down of the ethylene motion is coupled with the electronic system of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> through the indirect coupling. These results indicate that the ethylene motion modulates the electronic state of the BEDT-TTF molecule in  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> significantly.

## C. The possible origin of the electric dipole in a dimer

As discussed above, the ethylene groups can possess either a staggered or an eclipsed conformation and the ethylene motion modulates the electronic state. Depending on the conformation, the molecular orbital of the BEDT-TTF molecule can be modulated, thus producing a significant energy gap  $\Delta \epsilon$ in the highest occupied molecular orbital (HOMO). From theoretical calculations,  $\Delta \epsilon$  is estimated to be of the order of  $10^1$  meV [15,18,27]. The modulation of  $\Delta \epsilon$  triggers the indirect coupling between the ethylene motion and the local field [15]. In addition, from band-structure calculations and infrared (IR) absorption measurements, the intradimer transfer integral ( $t_d$ ) is estimated to be 250 meV [28,29]. Thus,  $\Delta \epsilon$  is large enough to affect the electronic state in a dimer. Therefore, we consider the possible emergence of charge degrees of freedom due to the ethylene motion. The electronic state in a dimer  $(\Psi_{\text{dimer}})$  can be described as a linear combination of the wave functions of the two BEDT-TTF molecules in the dimer,  $\psi_1$  and  $\psi_2$ . It can be represented by the following equation:

$$\Psi_{\text{dimer}} = c_1 \psi_1 + c_2 \psi_2. \tag{5}$$

As shown in Figs. 6(a) and 6(b), if the ethylene group of both BEDT-TTF molecules in the dimer possesses the same conformation either staggered or eclipsed, the coefficients  $c_1$ and  $c_2$  are equal owing to inversion symmetry at the center of the dimer. In this case, a CD state does not occur. However, if one BEDT-TTF molecule is in a staggered conformation, while the other is in an eclipsed conformation, then  $c_1$  and  $c_2$ are no longer equal, and a CD state can develop in the dimer,



FIG. 6. Schematic diagram of the electronic state in a dimer when both BEDT-TTF molecules are (a) eclipsed or (b) staggered. The electronic state when one BEDT-TTF is staggered and the other is eclipsed is shown in (c). Blue circles and squares represent a dimer and individual BEDT-TTF molecule, respectively. Yellow ellipses represent the charge distribution in a dimer. The shaded portion of the ellipse corresponds to the existence probability. In case (c), CD occurs in the dimer and an electric dipole is generated.

as shown in Fig. 6(c). Let us define the wave function of a molecular orbital of BEDT-TTF in a staggered or an eclipsed conformation as  $\psi_{is}$  or  $\psi_{ie}$  (i = 1,2), respectively. The extent of charge transfer in the dimer can be determined by using the parameters  $\Delta \epsilon$  and  $t_{d}$ . If the Hamiltonian ( $\mathcal{H}$ ) includes the intradimer interaction, we obtain the following secular equation:

$$\begin{bmatrix} \langle \psi_{1e} | \mathcal{H} | \psi_{2e} \rangle & \langle \psi_{1e} | \mathcal{H} | \psi_{2s} \rangle \\ \langle \psi_{1s} | \mathcal{H} | \psi_{2e} \rangle & \langle \psi_{1s} | \mathcal{H} | \psi_{2s} \rangle \end{bmatrix} \Psi_{\text{dimer}} = E \Psi_{\text{dimer}}, \quad (6)$$

where  $\Psi_{\text{dimer}} = c_1 \psi_{1\alpha} + c_2 \psi_{2\beta}$  ( $\alpha, \beta = e \text{ or } s$ ). The offdiagonal elements  $\langle \psi_{1e} | \mathcal{H} | \psi_{2s} \rangle$  and  $\langle \psi_{1s} | \mathcal{H} | \psi_{2e} \rangle$  correspond to the intradimer transfer integral ( $t_d$ ). If we define the orbital energy level  $\langle \psi_{1e} | \mathcal{H} | \psi_{2e} \rangle$  as 0, then the difference between the orbital energies is  $\Delta \epsilon$ . We can calculate the coefficients and intrinsic energy in the case of Fig. 6(c) as follows:

$$|c_1|^2 = \frac{1}{2} \left( 1 + \frac{\Delta \epsilon}{\sqrt{(\Delta \epsilon)^2 + 4(t_d)^2}} \right),\tag{7}$$

$$|c_2|^2 = \frac{1}{2} \left( 1 - \frac{\Delta \epsilon}{\sqrt{(\Delta \epsilon)^2 + 4(t_d)^2}} \right),\tag{8}$$

$$E_{\pm} = \frac{\Delta \epsilon \pm \sqrt{(\Delta \epsilon)^2 + 4(t_d)^2}}{2}.$$
 (9)

The extent of the charge transfer is given by  $\Delta \rho = ||c_1|^2 - |c_2|^2|e$ . Where *e* is the elemental charge. If we assume  $\Delta \epsilon = 40$  meV [15], we obtain the charge transfer  $\Delta \rho = +0.08e$ , which is almost the same as the value of the charge transfer found by Hattori *et al.* [8]. Referring to their results, the extent of the charge transfer is independent of the magnitude of the applied electric field. This is also consistent with our model because the expected extent of charge transfer depends

on only  $\Delta \epsilon$  and  $t_d$ . We can thus explain the field-induced CD state both quantitatively and qualitatively in terms of the conformation changes of the BEDT-TTF molecules in the dimer. This mechanism is also consistent with the fact that this material shows no static electric dipole at low temperatures in the absence of an electric field. At low temperatures, the ethylene motion slows down, and almost all the BEDT-TTF molecules are likely to freeze into either the staggered or the eclipsed conformation [18,30]. As a result, the CD state cannot occur in the absence of an electric field at low temperatures. However, if an electric field larger than E = 5 kV/cm is applied, an electric dipole moment p can be generated in the dimer accompanied by a conformation change of the ethylene group since the CD state is then realized. Once the conformation of BEDT-TTF changes, it is unlikely to return to the original conformation rapidly. Hence, the CD state can be maintained even if the applied electric field is removed.

Finally, we discuss the possibility that the conformation change of BEDT-TTF molecules triggers the relaxorlike behavior in the dielectric constant of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> salt [7]. As mentioned above, an electric dipole can be induced in a dimer if two BEDT-TTF molecules take different ethylene conformation from each other. In the higher temperature region, the ethylene groups are thermally fluctuated very rapidly compared to the time scale of the permittivity measurement as shown in Fig. 3. Thus, the conformation changes are averaged over and the dipoles would not be produced in the dimers. Therefore, no anomaly would be observed in the dielectric constant at higher temperature region. On the other hand, the permittivity measurement frequencies are much larger than the time scale of the ethylene motion around 100 K. In such case, the induced dipoles can be regarded as static ones and these electric dipoles would produce a large-scale charge inhomogeneity and domains on the BEDT-TTF layers. They can respond to the applied electric fields and would result in the ferroelectric relaxorlike behavior. The formation of such ferroelectric domains is confirmed by Raman and polarization measurements [8]. In contrast, almost all the ethylene groups may freeze with a thermally stable conformation either staggered or eclipsed in the lowtemperature region as mentioned above [18,30]. In this situation, there would also be no electric dipoles in the BEDT-TTF dimers and no anomaly in the dielectric constant would be appeared.

## **IV. CONCLUSION**

In conclusion, we have performed <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements for the dimer Mott insulator  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>. Our <sup>1</sup>H NMR measurements confirm the slowing down of the ethylene motion in  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>. We have also confirmed the existence of significant coupling between the ethylene motion and the electronic system of  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> by <sup>13</sup>C NMR measurements. The ethylene motion modulates the molecular orbital of the BEDT-TTF molecules and affects the electronic state in the dimer. In addition, we have discussed a possible scenario for the emergence of an electric dipole in a dimer in terms of conformation changes of the BEDT-TTF molecules. Our model can explain

the nature of both the field-induced CD state and the relaxorlike ferroelectric anomaly in the dielectric constant. Therefore, we propose that the slowing down of the ethylene motion can trigger the emergence of charge degrees of freedom and the dielectric anomaly in  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>.

## ACKNOWLEDGMENTS

The authors are grateful to Y. Eto for his valuable information and experimental data. This work was supported by the Japan Society for the Promotion of Science KAKENHI Grant No. JP16K0542706.

- [1] S. Ishihara, J. Phys. Soc. Jpn. 79, 011010 (2010).
- [2] M. Naka and S. Ishihara, J. Phys. Soc. Jpn. 79, 063707 (2010).
- [3] K. Kobayashi, S. Horiuchi, R. Kumai, F. Kagawa, Y. Murakami, and Y. Tokura, Phys. Rev. Lett. 108, 237601 (2012).
- [4] J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, Phys. Rev. Lett. 46, 253 (1981).
- [5] F. Nad, P. Monceau, C. Carcel, and J. M. Fabre, Phys. Rev. B 62, 1753 (2000).
- [6] P. Monceau, F. Y. Nad, and S. Brazovskii, Phys. Rev. Lett. 86, 4080 (2001).
- [7] S. Iguchi, S. Sasaki, N. Yoneyama, H. Taniguchi, T. Nishizaki, and T. Sasaki, Phys. Rev. B 87, 075107 (2013).
- [8] Y. Hattori, S. Iguchi, T. Sasaki, S. Iwai, H. Taniguchi, and H. Kishida, Phys. Rev. B 95, 085149 (2017).
- [9] M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, Phys. Rev. B 82, 125119 (2010).
- [10] M. Abdel-Jawad, N. Tajima, R. Kato, and I. Terasaki, Phys. Rev. B 88, 075139 (2013).
- [11] N. Yoneyama, A. Miyazaki, T. Enoki, and G. Saito, Bull. Chem. Soc. Jpn. 72, 639 (1999).
- [12] H. Taniguchi, M. Miyashita, K. Uchiyama, K. Satoh, N. Mori, H. Okamoto, K. Miyagawa, K. Kanoda, M. Hedo, and Y. Uwatoko, J. Phys. Soc. Jpn. 72, 468 (2003).
- [13] H. Kobayashi, R. Kato, A. Kobayashi, G. Saito, M. Tokumoto, H. Anzai, and T. Ishiguro, Chem. Lett. 15, 89 (1986).
- [14] Y. Eto and A. Kawamoto, Phys. Rev. B 81, 020512 (2010).
- [15] Y. Kuwata, M. Itaya, and A. Kawamoto, Phys. Rev. B 83, 144505 (2011).
- [16] M. Matsumoto, Y. Saito, and A. Kawamoto, Phys. Rev. B 90, 115126 (2014).

- [17] U. Geiser, A. J. Schults, H. H. Wang, D. M. Watkins, D. L. Stupka, J. M. Williams, J. E. Schirber, D. L. Overmyer, D. Jung, J. J. Novoa, and M. H. Whangbo, Physica C 174, 475 (1991).
- [18] D. Guterding, R. Valenti, and H. O. Jeschke, Phys. Rev. B 92, 081109 (2015).
- [19] H. Taniguchi, R. Sato, K. Satoh, A. Kawamoto, H. Okamoto, T. Kobayasi, and K. Mizuno, J. Low Temp. Phys. 142, 437 (2006).
- [20] M. Yamashita, A. Kawamoto, and K. Kumagai, Synth. Met. 133-134, 125 (2003).
- [21] S. Hirose, M. Misawa, and A. Kawamoto, Crystals 2, 1034 (2012).
- [22] Y. Maniwa, T. Takahashi, and G. Saito, J. Phys. Soc. Jpn. 55, 47 (1986).
- [23] T. Takahashi, T. Tokiwa, K. Kanoda, H. Urayama, H. Yamochi, and G. Saito, Synth. Met. 27, A319 (1988).
- [24] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. 75, 1174 (1995).
- [25] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).
- [26] C. P. Slichter, *Principles of Magnetic Reasonance* (Springer-Verlag, Berlin, 1990).
- [27] E. Scriven and B. J. Powell, J. Chem. Phys. 130, 104508 (2009).
- [28] T. Koretsune and C. Hotta, Phys. Rev. B 89, 045102 (2014).
- [29] K. Hashimoto, R. Kobayashi, H. Okamura, H. Taniguchi, Y. Ikemoto, T. Moriwaki, S. Iguchi, M. Naka, S. Ishihara, and T. Sasaki, Phys. Rev. B 92, 085149 (2015).
- [30] H. H. Wang, K. D. Carlson, U. Geiser, A. M. Kini, A. J. Schultz, J. M. Williams, L. K. Montgomery, W. K. Kwok, U. Welp, K. G. Vandervoort, S. J. Boryschuk, A. V. Strieby Crouch, J. M. Kommers, D. M. Watkins, J. E. Schriber, D. L. Overmyer, D. Jung, J. J. Novoa, and M. H. Whangbo, Synth. Met. 42, 1983 (1991).