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Biexciton in one-dimensional Mott insulators

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Mott insulators sometimes show dramatic changes in their electronic states after photo-irradiation, as indicated by photoinduced Mott-insulator-to-metal transition. In the photoexcited states of Mott insulators, electron wave functions are more delocalized than in the ground state, and long-range Coulomb interactions play important roles in charge dynamics. However, their effects are difficult to discriminate experimentally. Here, we show that in a one-dimensional Mott insulator, bis(ethylenedithio)tetrathiafulvalene-difluorotetracyanoquinodimethane (ET-F₂TCNQ), long-range Coulomb interactions stabilize not only excitons, doublon-holon bound states, but also biexcitons. By measuring terahertz-electric-field-induced reflectivity changes, we demonstrate that odd- and even-parity excitons are split off from a doublon-holon continuum. Further, spectral changes of reflectivity induced by a resonant excitation of the odd-parity exciton reveals that an exciton-biexciton transition appears just below the exciton-transition peak. Theoretical simulations show that long-range Coulomb interactions over four sites are necessary to stabilize the biexciton. Such information is indispensable for understanding the non-equilibrium dynamics of photoexcited Mott insulators.

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The ultrafast dynamics of correlated electron systems after photoexcitation are now attracting considerable attention. This is based upon recent developments in femtosecond laser technology, which enabled us to detect ultrafast electronic responses to a light pulse in solids^{1–4}. Applications of femtosecond pump–probe spectroscopy to correlated electron systems enable us to observe exotic photoinduced phase transitions^{5–18} as represented by a photoinduced Mott-insulator-to-metal transition^{6,12,16–18}, and also to derive detailed information about the interplays between the charge, spin, and lattice degrees of freedom from the transient responses of each degree to a light pulse^{5–11,13–15}. It is difficult to obtain such information from the steady-state transport and magnetic measurements. The growing interest in the ultrafast dynamics of correlated electron systems synchronizes to the development of a new field called “non-equilibrium quantum physics in solids”. In fact, new theoretical approaches have recently been explored to analyze the charge, spin, and lattice dynamics of nonequilibrium states after photoirradiation, as exemplified by the dynamical mean field theory¹⁹ and the time-dependent density-matrix renormalization group method^{20,21}.

In the nonequilibrium quantum physics of correlated electron systems, the charge dynamics of photoexcited Mott insulators is the most fundamental subject to be studied from both the experimental^{6,12,16–18} and theoretical viewpoints^{22–28}. Recent studies have focussed on Mott insulator states realized not only in solids such as transition metal compounds^{6,16–18} and organic molecular materials¹² but also in ultra-cold atoms on an optical lattice^{29–31}. In fact, in the ultra-cold atoms, nonequilibrium dynamics can be investigated by tuning the intersite interaction using a Feshbach resonance²⁹. Among various Mott insulators, a one-dimensional (1D) Mott insulator with large on-site Coulomb repulsion energy U is particularly important since the charge and spin degrees of freedom are decoupled^{32,33}. In the system, we can obtain clear information about the effects of Coulomb interactions on the charge dynamics. When the electronic structure and low-energy excitations in a 1D Mott insulator are theoretically analyzed, the Hubbard model, which includes U and the transfer energy t as the important parameters, is generally used. In the photoexcited states, on the other hand, electron wave functions are more delocalized, and the effects of long-range Coulomb interactions will become important in the charge dynamics. However, it is difficult to evaluate these effects experimentally.

In the present study, we investigated the role of long-range Coulomb interactions in photoexcited states by focusing on the excitons^{34–36} (the bound states of a doublon and a holon) and biexcitons (the bound states of two excitons) in 1D Mott insulators. The studied material is an organic molecular compound, bis(ethylenedithio)tetrathiafulvalene-difluorotetracyanoquinodimethane (ET-F₂TCNQ). To investigate the energy-level structures of the photoexcited states and stabilities of excitons in a 1D Mott insulator of ET-F₂TCNQ, we performed terahertz-pulse-pump optical-reflectivity-probe spectroscopy and measured the electric-field-induced changes in the optical-reflectivity spectrum, which include information not only about one-photon allowed states but also originally one-photon forbidden states. From analyses of the results, we clarified that the odd- and even-parity excitons are split off from the doublon-holon continuum. We next applied pump–probe reflection spectroscopy to ET-F₂TCNQ in the near-infrared region with a resonant excitation to the lowest exciton, and investigated the possible bound state of two excitons, that is, a biexciton. We observed the signature of an exciton–biexciton transition in the optical-reflectivity spectrum, the spectral shape of which was well reproduced by a theoretical simulation taking into account the Coulomb interactions over up to four sites. The results demonstrate the

importance of long-range Coulomb interactions in the dynamics of photoexcited excitons in Mott insulators.

Results

Stabilities of excitons and biexcitons. The long-range Coulomb interactions can stabilize not only an exciton but also a biexciton. The schematics of an exciton and biexciton in a half-filled 1D Mott insulator are shown in Fig. 1a. Assuming that the transfer energy t is equal to zero, a simplified understanding of the stabilities of excitons and biexcitons is possible as follows. Here, we consider the intersite Coulomb repulsive energies for the nearest, second-nearest, and third-nearest two sites, which are denoted by V_1 , V_2 , and V_3 , respectively, as shown in Fig. 1a. In this case, the energy of the lowest exciton is $U - V_1$, and the binding energy of the exciton, that is, the Coulomb attractive energy of a doublon (D) and one holon (H) is $-V_1$. The energy of two isolated excitons far distant from each other is $2(U - V_1)$, while that of a neighboring two excitons (DHDH) is $(2U - 3V_1 + 2V_2 - V_3)$, thus giving the stabilization energy or binding energy of the biexciton as $(V_1 - 2V_2 + V_3)$. When we assume that the Coulomb repulsion energies are inversely proportional to the distance between two electrons, $V_2 = V_1/2$ and $V_3 = V_1/3$, the binding energy of the biexciton is $V_1/3$ accordingly, and the biexciton is stable as well as the exciton. Since the binding energy of $V_1/3$ originates from V_3 , an observation of a biexciton can give valuable information about the role of long-range Coulomb interactions in the photoexcited states of 1D Mott insulators. If the long-range Coulomb interaction is important, it will modify the charge dynamics of 1D Mott insulators, e.g., the efficiency of photoinduced Mott-insulator-to-metal transition and the temporal dynamics during the transition.

Studied material and polarized reflectivity measurements. ET-F₂TCNQ is a segregated-stacked charge-transfer (CT) compound consisting of ET (donor) and F₂TCNQ (acceptor) columns, as shown in Fig. 1b³⁷. An electron is transferred from ET to F₂TCNQ. F₂TCNQ[−] molecules are almost isolated, while a finite overlap of wave functions with a transfer energy t of ~ 0.2 eV exists between neighboring ET⁺ molecules along the a -axis (Fig. 1b). Because of the large U on ET, the ET columns are in a 1D Mott insulator state. Figure 1c shows the polarized reflectivity (R) spectra. A sharp peak polarized parallel to the a -axis ($//a$) is observed at 0.7 eV, which corresponds to the Mott gap transition. Such a sharp structure makes us expect an excitonic nature. From the spectral shape, however, we cannot determine whether this peak is attributed to an exciton or an interband transition sharpened owing to the Van-Hove singularity.

Terahertz-pump optical-reflectivity-probe spectroscopy. An effective method to evaluate the energy-level structures of excitons is electroreflectance (ER) spectroscopy^{38–41}, in which reflectivity changes induced by quasistatic electric fields are measured. This enables us to obtain a wide frequency range of the third-order nonlinear susceptibility $\chi^{(3)}$ spectrum without special laser systems. However, the ER spectroscopy cannot be applied to low-resistivity materials, in which an application of high electric fields sometimes gives rise to a dielectric breakdown, destroying the sample owing to excess electric current. In most organic molecular compounds with small gap energies, nonlinear electric transport and current-induced electric-switching phenomena indeed occur. This makes it impossible to adopt the ER method. To overcome this problem, in the present study, we apply terahertz-pump optical-probe spectroscopy to ET-F₂TCNQ (Fig. 2a). Within a terahertz pulse, an electric current hardly flows owing to the short duration of the electric field (~ 1 ps)⁴². In

Fig. 1 Photoexcited states in a one-dimensional (1D) Mott insulator of bis(ethylenedithio)tetrathiafulvalene-difluorotetracyanoquinodimethane (ET-F₂TCNQ). **a** Schematics of a ground state, exciton, and biexciton in a half-filled 1D Mott insulator. The intersite Coulomb repulsive energies for the nearest, second-nearest, and third-nearest two sites are denoted by V_1 , V_2 , and V_3 , respectively. The binding energy of biexciton is $(V_1 - 2V_2 + V_3)$, which is equal to $V_1/3$ in the case that the Coulomb repulsion energies are inversely proportional to the distance between two electrons, $V_2 = V_1/2$ and $V_3 = V_1/3$. **b** Molecular structures and 1D molecular stacks along the a axis of ET-F₂TCNQ. **c** Reflectivity spectra of ET-F₂TCNQ polarized parallel to the a axis ($E//a$) and perpendicular to the a -axis ($E\perp a$)

Fig. 2 Terahertz-pulse-pump optical-reflectivity-probe spectroscopy. **a** A schematic of the experimental setup. **b** A typical electric field waveform E_{THz} of the terahertz pulse. **c**, **d** Time evolutions of the reflectivity change $\Delta R/R$ at **c** 0.72 eV and **d** 0.80 eV (blue open circles). The error bars indicate the standard deviation. The red solid lines show the normalized value of $|E_{THz}|^2$. **e** A reflectivity spectrum (ΔR) polarized along the a axis (solid line) and reflectivity change ($\Delta R/R$) spectrum at 0 ps (open circles). The error bars are smaller than the data points. **f** Imaginary part of the dielectric constant (ϵ_2) spectrum (black solid line), a fitting curve to ϵ_2 spectrum (red solid line), and photoconductivity (PC) spectrum (open circles). The error bars indicate the standard deviation. **g** The change of ϵ_2 ($\Delta\epsilon_2$) or the imaginary part of the third-order nonlinear susceptibility ($\text{Im}\chi^{(3)}$) spectrum (blue solid line) and a fitting curve to the $\text{Im}\chi^{(3)}$ spectrum (red solid line). Open triangles show the energy levels of the excited states. **h** A schematic of the four-level model

addition, the magnitude of the electric field can be increased without sample damages.

In Fig. 2b, we show a typical electric field waveform $E_{\text{THz}}(t_d)$ of the terahertz pulse as a function of the delay time t_d . The peak magnitude of $E_{\text{THz}}(t_d)$ is $\sim 100 \text{ kV cm}^{-1}$. The electric fields E of both the terahertz pulse and the optical-probe pulse are set to be polarized parallel to the a -axis ($E \parallel a$). Figure 2c, d shows the time evolutions of reflectivity changes $\Delta R(t_d)/R$ at 0.72 and 0.80 eV, respectively (open blue circles). Large $\Delta R(t_d)/R$ signals reaching $\sim -3\%$ at 0.72 eV and $\sim +2\%$ at 0.80 eV are observed. These time evolutions are almost in agreement with $\pm [E_{\text{THz}}(t_d)]^2$ as shown by the red solid lines in Fig. 2c, d. In fact, the $|\Delta R(t_d = 0 \text{ ps})/R|$ values at 0.72 and 0.80 eV are proportional to $[E_{\text{THz}}(t_d = 0 \text{ ps})]^2$ (Supplementary Note 1). These results indicate that $\Delta R/R$ signals are ascribed to the third-order nonlinear-optical response expressed as follows⁴³

$$P^{(3)}(\omega) \propto E_{\text{THz}}(\omega \sim 0)E_{\text{THz}}(\omega \sim 0)E(\omega), \quad (1)$$

where $P^{(3)}(\omega)$ and $E(\omega)$ are the third-order nonlinear polarization and the electric field of the probe light with the frequency of ω , respectively. Such a reflectivity modulation by a terahertz-electric field was previously reported in $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$ (chxn = cyclohexanediamine)⁴².

To obtain detailed information about the energy-level structure, we measured the probe energy dependence of $\Delta R/R$ at $t_d = 0 \text{ ps}$ (open circles in Fig. 2e). By applying the Kramers–Kronig (KK) transformation to the R and $\Delta R(t_d = 0 \text{ ps})/R$ spectra, we obtained the imaginary part of the dielectric constant (ϵ_2) and the change of ϵ_2 ($\Delta\epsilon_2$) spectra, as shown by the solid black line in Fig. 2f and solid blue line in Fig. 2g, respectively. Details of the analyses are reported in Supplementary Note 2. The ϵ_2 spectrum has a sharp peak at 0.7 eV, and the $\Delta\epsilon_2$ spectrum has a plus-minus-plus structure around the sharp peak.

First, we analyze the ϵ_2 spectrum with the following Lorentzian-type dielectric function

$$\epsilon_2(\omega) = \frac{Ne^2}{\hbar} \langle 0|x|1 \rangle^2 \text{Im} \left(\frac{1}{\omega_1 - \omega - i\gamma_1} + \frac{1}{\omega_1 + \omega + i\gamma_1} \right). \quad (2)$$

Here, $|0\rangle$ and $|1\rangle$ show the ground state and the one-photon-allowed odd-parity state, respectively, and $\langle 0|x|1 \rangle$ is the transition dipole moment between them. ω_1 and γ_1 are the energy and damping constants of the odd-parity state, respectively. N denotes the density of the ET molecules, ϵ_0 is the permittivity of the vacuum, e is the elementary charge, and $\hbar$ is the reduced Planck constant. As shown in Fig. 2f, the experimental ϵ_2 spectrum (the solid black line) is almost reproduced by Eq. (2), as shown by the red line. The used parameter values are listed in Table 1.

We next analyzed the $\Delta\epsilon_2$ spectrum showing a plus-minus-plus structure (the solid blue line in Fig. 2g). To analyze this spectrum, we assumed that the frequency of the terahertz-electric field, ω_{THz} , is 0. This assumption is justified under the condition that $\hbar\omega_{\text{THz}}$ ($\sim 4 \text{ meV}$) is sufficiently lower than an energy difference between any of two energy levels of excited states⁴². ET-F₂TCNQ meets this condition, as will be shown later. Using this

assumption, we calculate $\text{Im}\chi^{(3)}$ from $\Delta\epsilon_2$ with the equation

$$\Delta\epsilon_2(\omega) = 3\text{Im}\chi^{(3)}(-\omega; 0, 0, \omega)E_{\text{THz}}(0)^2. \quad (3)$$

The maximum of $|\text{Im}\chi^{(3)}|$ was evaluated to be $1 \times 10^{-7} \text{ esu}$.

The previous ER spectroscopy of 1D Mott insulators of transition metal compounds revealed that a plus-minus-plus structure in $\text{Im}\chi^{(3)}$ spectra can be interpreted by a three-level model in which the one-photon forbidden state with even parity ($|2\rangle$) is assumed in addition to the ground state $|0\rangle$ and the odd-parity state $|1\rangle$ ^{38–41}. In ET-F₂TCNQ, small negative signals appear above $\sim 0.85 \text{ eV}$, as shown in Fig. 2g, in addition to the plus-minus-plus structure. Such a negative signal can be explained by considering the second-lowest odd-parity state ($|3\rangle$)⁴¹. In a four-level model consisting of $|0\rangle$ – $|3\rangle$, the $\chi^{(3)}$ spectrum is represented by the equation⁴³

$$\begin{aligned} \chi^{(3)}(-\omega_\sigma; \omega_i, \omega_j, \omega_k) &= \frac{Ne^4}{6\epsilon_0\hbar^3} \wp \sum_{abc} \left[\frac{\langle 0|x|a \rangle \langle a|x|b \rangle \langle b|x|c \rangle \langle c|x|0 \rangle}{(\omega_a - \omega_\sigma - i\gamma_a)(\omega_b - \omega_j - \omega_k - i\gamma_b)(\omega_c - \omega_k - i\gamma_c)} \right. \\ &+ \frac{\langle 0|x|a \rangle \langle a|x|b \rangle \langle b|x|c \rangle \langle c|x|0 \rangle}{(\omega_a + \omega_i + i\gamma_a)(\omega_b - \omega_j - \omega_k - i\gamma_b)(\omega_c - \omega_k - i\gamma_c)} \\ &+ \frac{\langle 0|x|a \rangle \langle a|x|b \rangle \langle b|x|c \rangle \langle c|x|0 \rangle}{(\omega_a + \omega_i + i\gamma_a)(\omega_b + \omega_i + \omega_j + i\gamma_b)(\omega_c - \omega_k - i\gamma_c)} \\ &\left. + \frac{\langle 0|x|a \rangle \langle a|x|b \rangle \langle b|x|c \rangle \langle c|x|0 \rangle}{(\omega_a + \omega_i + i\gamma_a)(\omega_b + \omega_i + \omega_j + i\gamma_b)(\omega_c + \omega_\sigma + i\gamma_c)} \right] \quad (4) \end{aligned}$$

$\langle l|x|m \rangle$ shows the transition dipole moment between states $|l\rangle$ and $|m\rangle$. ω_l and γ_l are the frequency and the damping constant for the state $|l\rangle$, respectively. $\wp$ is the permutation of $(\omega_i, \omega_j, \omega_k)$. $|a\rangle$ and $|c\rangle$ show odd-parity states, and $|b\rangle$ shows an even-parity state. A schematic of the four-level model is shown in Fig. 2h. Among the combinations of (a, b, c) , the terms with $b = 0$ are much smaller than the others. Thus, they can be excluded, and $(a, b, c) = (1, 2, 1), (1, 2, 3), (3, 2, 1), (3, 2, 3)$ should be considered. Using Eqs. (3) and (4), the $\text{Im}\chi^{(3)}$ spectrum is almost reproduced, as shown by the red line in Fig. 2g. The energies of three excited states ($\hbar\omega_1 = 0.694 \text{ eV}$, $\hbar\omega_2 = 0.720 \text{ eV}$, and $\hbar\omega_3 = 0.850 \text{ eV}$) are indicated by triangles in the same figure. The obtained parameters are also listed in Table 1.

The splitting between $|1\rangle$ and $|2\rangle$, $\hbar(\omega_2 - \omega_1)$, was small (26 meV), indicating that the two states are nearly degenerate. In addition, $\langle 1|x|2 \rangle$, which is the most important parameter dominating the magnitude of $\chi^{(3)}$, was very large at $\sim 18 \text{ Å}$. In ET-F₂TCNQ, the ratio $\langle 1|x|2 \rangle / \langle 0|x|1 \rangle$ is equal to 13. The enhancement of $\langle 1|x|2 \rangle$ is attributable to the fact that the wave functions of the odd- and even-parity states are similar to each other except for their phases, as schematically shown in Fig. 2h, and the spatial overlap of these wave functions becomes very large. These features are characteristic of 1D Mott insulators^{38,39}. The observation of a higher odd-parity state $|3\rangle$ demonstrates that the lower two states $|1\rangle$ and $|2\rangle$ are excitonic states.

To obtain evidence of the excitonic effect from the transport property, we measured the excitation profile of photoconductivity

Table 1 Parameters evaluated from the fitting analysis

$\langle 0 x 1 \rangle$	$\langle 1 x 2 \rangle$	$\langle 2 x 3 \rangle / \langle 3 x 0 \rangle$	$\hbar\omega_1$	$\hbar\omega_2$	$\hbar\omega_3$	$\hbar\gamma_1$	$\hbar\gamma_2$	$\hbar\gamma_3$
1.4 Å	18 Å	-7.1 Å^2	0.694 eV	0.720 eV	0.850 eV	0.050 eV	0.146 eV	0.081 eV

(PC), which is shown by open circles in Fig. 2f. The PC signals are very low at $\hbar\omega_1$ and $\hbar\omega_2$, suggesting that $|1\rangle$ and $|2\rangle$ are excitonic states. With an increase in the photon energy, the PC increases and saturates at around $\hbar\omega_3 = 0.850$ eV. In the energy region of the doublon-holon continuum, a number of both odd and even states exist continuously. Thus, field-induced reflectivity changes $\Delta R/R$ originating from their mixings cancel each other, and $\Delta R/R$ signals appear only at the lower edge of the continuum state⁴¹. Therefore, it is reasonable to consider that the continuum state starts at around $\hbar\omega_3 = 0.850$ eV, and that $\hbar(\omega_3 - \omega_1) = 0.156$ eV and $\hbar(\omega_3 - \omega_2) = 0.130$ eV are crude measures of the binding energies of the lowest $|1\rangle$ and second-lowest excitonic states $|2\rangle$, respectively.

Optical-pump optical-reflectivity-probe spectroscopy. To observe a biexciton, we next performed optical-pump optical-reflectivity-probe spectroscopy (Fig. 3a) by resonant excitation of the lowest odd-parity exciton ($\hbar\omega_1 = 0.694$ eV). Electric fields of the pump pulses were polarized parallel to the a -axis as well as the probe pulses with $E//a$.

Figure 3b shows the time evolutions of $\Delta R/R$ for three typical probe energies: 0.58, 0.694, and 0.96 eV. We set the excitation fluence I_{ex} to be $5.1 \mu\text{J cm}^{-2}$, which corresponds to the excitation photon density x_{ph} of 0.0015 photons per ET molecule. This excitation photon density is low enough to detect the transition of an isolated exciton to a biexciton state. Excitation photon density dependence of exciton-biexciton transition is detailed in Supplementary Note 3. The reflectivity at 0.694 eV corresponding to the exciton peak decreases just after the photoirradiation, and

most of the change recovers within 0.15 ps. Such an ultrafast change and recovery of $\Delta R/R$ is not observed by the higher-energy excitation at 1.55 eV as previously reported⁴⁴ (see Supplementary Note 4). Therefore, this response is attributable to the coherent response, which is observed in the resonant excitation to an exciton in semiconductors⁴⁵. That can be interpreted as a kind of third-order nonlinear responses such as an optical Stark effect and a stimulated emission⁴⁵. These responses may become important when a probe pulse is incident to a sample within a phase coherence time of an electronic polarization induced by a pump pulse. Besides the ultrafast component due to the coherent response, $\Delta R/R$ at 0.694 eV should also include the bleaching signal owing to the real excitations of excitons as a component with a finite decay time. $\Delta R/R$ at 0.96 eV, which is higher than the exciton peak, also seems to partly include the ultrafast coherent response as well as the bleaching signal. By contrast, $\Delta R/R$ at 0.58 eV below the exciton peak increases after the photoirradiation and is accompanied by an oscillatory component, which will be discussed in detail later.

The probe energy dependences of ΔR at $t_d = 0.3, 1.0$, and 5.0 ps are shown in Fig. 3c, together with the original R spectrum. For these delay times, the coherent responses mentioned above almost disappear, and the ΔR spectra can reflect the effects of real exciton excitations. ΔR is negative around the original exciton peak (~ 0.7 eV) owing to the bleaching of the exciton transition. In the lower energy region below ~ 0.64 eV, ΔR becomes positive, as seen in the time evolution of $\Delta R/R$ at 0.58 eV in Fig. 3b. To obtain the information about photoexcited states, we calculated the photoinduced change of ϵ_2 ($\Delta\epsilon_2$) by the

Fig. 3 Optical-pump optical-reflectivity-probe spectroscopy. **a** A schematic of the experimental setup. **b** Time evolutions of the reflectivity changes at 0.58 eV (red solid line), 0.694 eV (green solid line) and 0.96 eV (blue solid line). **c** Reflectivity change (ΔR) spectra at 0.3 ps (black open circles), 1.0 ps (orange open circles), and 5.0 ps (blue open circles). The black solid line shows a reflectivity spectrum (R) polarized along the a -axis. The error bars are smaller than the data points. **d** Imaginary part of the dielectric constant (ϵ_2) spectrum (black solid line) and the change of ϵ_2 ($\Delta\epsilon_2$) spectrum (blue solid line) from the experimental results. **e** A schematic of the excitations of exciton, biexciton and two excitons. **f** ϵ_2 spectrum (black solid line) and $\Delta\epsilon_2$ spectrum (blue solid line) obtained by the theoretical calculations

KK transformation of the $\Delta R/R$ spectrum at $t_d = 0.3$ ps. The details of the analyses are reported in Supplementary Note 2. The obtained $\Delta\epsilon_2$ spectrum is shown in Fig. 3d together with the original ϵ_2 spectrum. In addition to a negative $\Delta\epsilon_2$ around the lowest exciton peak, a positive $\Delta\epsilon_2$ peak is clearly observed at 0.630 eV. Such a photoinduced absorption is not observed in the case of higher-energy excitation at 1.55 eV¹². This indicates that the observed photoinduced absorption is characteristic of the lowest-energy exciton. A possible origin of this peak is the transition of the lowest-energy exciton to a biexciton.

The energy difference ΔE (~ 60 meV) between the original exciton peak in ϵ_2 (0.694 eV) and the photoinduced absorption peak in $\Delta\epsilon_2$ (0.630 eV) corresponds to the binding energy of the biexciton, as shown in Fig. 3e. As mentioned above, a simplified model with $t = 0$ shows that the stabilization energy of the biexciton is one-third of the intersite Coulomb interaction V_1 , $-V_1/3$. The binding energy of the lowest odd-parity exciton (~ 160 meV) is expected to be almost equal to V_1 . Thus, the biexciton binding energy is estimated to be $V_1/3 \sim 53$ meV, which is in accord with $\Delta E \sim 60$ meV. This supports the validity of our interpretation that the photoinduced absorption is attributed to the biexciton.

Simulation of exciton–biexciton transition. To investigate the biexciton formation more strictly, we theoretically calculate ϵ_2 in the ground state and in the presence of the lowest exciton using an extended Hubbard model, as follows:

$$H = -t \sum_{i,\sigma} \left(e^{iA(t_d)} C_{i,\sigma}^\dagger C_{i+1,\sigma} + \text{H.c.} \right) + U \sum_i \left(n_{i,\uparrow} - \frac{1}{2} \right) \left(n_{i,\downarrow} - \frac{1}{2} \right) \\ + V_1 \sum_i (n_i - 1)(n_{i+1} - 1) + V_2 \sum_i (n_i - 1)(n_{i+2} - 1) \\ + V_3 \sum_i (n_i - 1)(n_{i+3} - 1) \quad (5)$$

where $C_{i,\sigma}^\dagger$ ($C_{i,\sigma}$) is the creation (annihilation) operator of an electron with spin σ at i site, $n_{i,\sigma} = C_{i,\sigma}^\dagger C_{i,\sigma}$, $n_i = n_{i,\uparrow} + n_{i,\downarrow}$. V_j is the Coulomb interaction between two electrons distant for j sites, as mentioned above. We assume again that V_j is inversely proportional to a doublon–holon distance as $V_1 : V_2 : V_3 = 1 : \frac{1}{2} : \frac{1}{3}$. In Fig. 3f, we show the ϵ_2 spectrum in the ground state, which was calculated by the Lanczos method with a system size (site number) of $L = 14$. The parameter values in the system are set to be $t = 0.14$ eV, $U = 1.4$ eV, and $V_1 = 0.6$ eV to reproduce the peak energy of the ϵ_2 spectrum for the odd-parity exciton.

Next, we calculated the ϵ_2 spectrum after the resonant excitation to the odd-parity exciton⁴⁶. The temporal shape of the pump pulse is assumed to be Gaussian, as follows:

$$A_{\text{pump}}(t_d) = A_0 e^{-t_d^2/2\tau^2} \cos(\omega_0 t_d) \quad (6)$$

ω_0 , A_0 , and τ are the frequency, amplitude, and temporal width of the pump pulse, respectively. We calculated $\Delta\epsilon_2$ with the parameter values of $\omega_0 = 0.694$ eV and $\tau = 78$ fs, which correspond to a full-width half-maximum of 130 fs. The result for $t_d = 0.3$ ns is shown by the solid blue line in Fig. 3f, which reproduces the important feature of the experimental $\Delta\epsilon_2$ spectrum, that is, the presence of the induced absorption just below the original absorption peak at 0.630 eV attributable to the exciton–biexciton transition. The exciton–biexciton transition owing to long-range Coulomb interactions was also theoretically predicted in 2D Mott insulators⁴⁷. From an increase in the energy in the system, we evaluated the photocarrier density δ to be 0.003, which ensures a weak excitation condition. These theoretical

calculations ascertain that the biexciton as well as the exciton are stable in 1D Mott insulators.

Exciton relaxation observed as coherent oscillations. In this subsection, we discuss the results of the time evolutions and the probe energy dependence of the oscillatory component $\Delta R_{\text{OSC}}/R$ observed in the photoinduced reflectivity changes $\Delta R/R$. In Fig. 4a, we show a typical time characteristic of $\Delta R_{\text{OSC}}/R$ by open circles, which is extracted from the time evolution of $\Delta R/R$ at 0.58 eV (see Supplementary Note 5). In this experiment, the excitation photon density x_{ph} is set at 0.01 photon per ET molecule. This oscillation is almost reproduced by the convolution of a damped oscillator expressed below and the Gaussian profile corresponding to the time resolution (150 fs) as shown by the solid red line in Fig. 4a.

$$\frac{\Delta R_{\text{OSC}}}{R} = A_{\text{OSC}} \exp\left(-\frac{t_d}{\tau}\right) \cos(\omega_{\text{OSC}} t_d + \phi) \quad (7)$$

The oscillation frequency ω_{OSC} is 82 cm^{-1} , and the relaxation time τ is 2.0 ps. The value of the phase $\phi (= 14^\circ)$ is small, suggesting that the generation mechanism of the oscillation is the dispersive excitation of the coherent phonon⁴⁸. The Fourier power spectrum of the experimental time characteristic of $\Delta R_{\text{OSC}}/R$ and the fitting curve are shown in Fig. 4b by open circles and the solid red line, respectively, which agree with each other.

We performed similar analyses of the coherent oscillations in $\Delta R/R$ signals at various probe energies and plotted the magnitude of the fitting functions (A_{OSC}) in Fig. 4c (red circles) together with the original R spectrum (black line). The data show a clear peak at 0.64 eV, which corresponds well to the peak (0.630 eV) of $\Delta\epsilon_2$ assigned to the exciton-to-biexciton transition shown in Fig. 3d. This suggests that the energy and/or the intensity of the exciton-to-biexciton transition is modulated at a frequency of 82 cm^{-1} , which is observed as the oscillatory structure of the reflectivity changes. The origin of this oscillation is discussed in the next section.

Discussion

First, we comment on the stabilization mechanism of the biexciton in 1D Mott insulators. In the simulation with an extended Hubbard model, we investigated several parameter sets. When we consider only the intersite Coulomb interactions V_1 and V_2 , no peak is observed just below the lowest exciton transition in $\Delta\epsilon_2$, even if their magnitudes are enhanced. This demonstrates that the long-range Coulomb attractive interaction characterized by V_3 plays a significant role in the stabilization of the biexciton. This is consistent with the simplified picture of the energy gain of biexciton formation in Fig. 1a.

Next, we discuss the origin of the coherent oscillation. As seen in the spectrum of the magnitude of the oscillatory components in Fig. 4c, the oscillation is observed around the exciton–biexciton transition at 0.630 eV (Fig. 3d). In addition, the frequency of the oscillation, 82 cm^{-1} , is a typical frequency of a lattice mode in organic molecular compounds. It is, therefore, reasonable to consider that the oscillation is ascribed to molecular displacements in the lattice relaxation process of the lowest-energy exciton generated by the resonant excitation at 0.694 eV. A possible origin is the molecular displacement associated with the molecular dimerization stabilizing the exciton as illustrated in Fig. 4d, which corresponds to the phonon mode with the wave-number $k = \pi/a_0$. Here, a_0 is the lattice constant along the a axis. Such dimeric molecular displacements and the subsequent coherent oscillation are considered to be produced over several sites around the exciton and change the intersite Coulomb

Fig. 4 Coherent oscillations after photoexcitation. **a, b** Open circles show a time evolution of the oscillatory component of the reflectivity change $\Delta R/R$ at 0.58 eV (**a**) and its Fourier transformation (**b**). The red solid lines show fitting curves. The error bars indicate the standard deviation. **c** Magnitude of the fitting functions (A_{osc}) (open circles) together with the original reflectivity spectrum polarized along the a axis (the black line). The error bars indicate the standard deviation of the least squares fit. Red solid line is guided for eyes. **d** A schematic of the coherent oscillations after photoexcitation

attractive interactions V_1 and V_3 that stabilizes the biexciton. Note that in a region at a distance from the sites where excitons are produced by the pump pulse, no oscillations are generated, so that coherent oscillations are hardly detected around the peak energy (0.7 eV) of the original exciton transition. Thus, the oscillation modulates the energy and intensity of the exciton–biexciton transition, which results in an oscillatory signal $\Delta R_{\text{osc}}/R$ on $\Delta R/R$ only around the exciton–biexciton transition.

The time evolution of the induced absorption due to the exciton–biexciton transition (the positive $\Delta R/R$ signal at 0.58 eV in Fig. 3b) and that of the bleaching signal due to the real excitations of excitons (the negative $\Delta R/R$ signals at 0.694 and 0.96 eV in Fig. 3b) should reflect the decay dynamics of excitons. To evaluate the exciton decay dynamics, we performed the fitting analyses on the time evolutions of $\Delta R/R$ at 0.58, 0.694, and 0.96 eV. The details of the analyses are reported in the Supplementary Note 6.

The results showed that the time evolutions of $\Delta R/R$ at 0.694 and 0.96 eV consist of the fast component with the decay time τ_{fast} of 0.39 ps and the slow component with the decay time τ_{slow} of 8.6 ps. The value of τ_{fast} is consistent with those reported in the previous experimental studies^{44,49} and in the theoretical calculations⁵⁰. This ultrafast decay of excitons may be attributed to the emission of intramolecular vibrations. Their frequencies range from 500 to 1500 cm^{-1} , so that an exciton with the energy of ~ 0.7 eV (~ 5600 cm^{-1}) can decay via the emission of several high-frequency phonons. The slow decay component with the decay time τ_{slow} of 8.6 ps can be related to the lattice relaxation of excitons. When the exciton is relaxed by the dimeric molecular displacements, the exciton is better stabilized and the decay time becomes longer possibly up to several picoseconds. This decay time is still very short compared to a decay time of excitons in inorganic semiconductors, which is on the order of nanoseconds. The analysis also revealed that the time evolution of $\Delta R/R$ at 0.58

eV also includes the slow decay component with the decay time τ_{slow} of 8.3 ps. The fast decay component with the decay time τ_{fast} of 0.39 ps might also be included in the $\Delta R/R$ signal at 0.58 eV, however, it cannot be discriminated owing to the presence of the large negative signal coming from the coherent response. We note that the relaxation of excitons due to dimeric molecular displacements strengthens the intensity and decreases the energy of the exciton–biexciton transition via an increase in the intersite Coulomb attractive interactions V_1 and V_3 by the decrease in the distance between the nearest and third-nearest two molecules, respectively.

In summary, we successfully measured the spectra of the ultrafast reflectivity changes by a terahertz-electric field and by the resonant excitation of the lowest exciton in a 1D Mott insulator of an organic molecular compound, ET-F₂TCNQ. By analyzing the spectra of reflectivity changes induced by the terahertz-electric field, we revealed the energy-level structures of the exciton and continuum states, and evaluated the binding energy of the lowest-energy exciton to be about 160 meV. In addition, from the spectrum of reflectivity changes by the resonant optical excitation to excitons, we demonstrated that the biexciton is stable owing to long-range Coulomb interactions and that its binding energy is about 60 meV, which is almost equal to one third of the exciton binding energy as predicted in a case with a strong electron correlation limit. Such information about biexcitons as well as excitons is significantly important for the understanding of nonequilibrium dynamics in photoexcited 1D Mott insulators.

Methods

Sample preparation. Single crystals of ET-F₂TCNQ were grown by the recrystallization method³⁷.

Pump-probe reflectivity measurements. In the terahertz-pulse-pump optical-reflectivity-probe experiments, the output of Ti:Al₂O₃ regenerative amplifier (pulse width: 130 fs, photon energy: 1.58 eV, repetition frequency: 1 kHz) were divided into two beams. One was used for the generation of terahertz-pump pulses through the optical rectification in a LiNbO₃ crystal by the pulse-front-tilting method^{51,52}. The other was introduced to an optical parametric amplifier (OPA) to obtain probe lights from 0.48 to 1.08 eV. A temporal waveform of terahertz-electric field [$E_{\text{THz}}(t_d)$] was measured by the electro-optical sampling with a 1 mm-thick (110) oriented ZnTe crystal⁴². Magnitude of the terahertz-electric field was changed by two wire-grid polarizers and a Si plate inserted in the terahertz-pulse path. The time origin for the terahertz-pump experiments is set at the maximum of the terahertz-electric field amplitude. Time difference between pump and probe pulses t_d was controlled by a changing the path length of the probe pulse. Polarizations of all pulses are parallel to the 1D stacking-axis a .

In the optical-pump experiments, the output of Ti:Al₂O₃ regenerative amplifier (pulse width: 110 fs, photon energy: 1.55 eV, repetition frequency: 1 kHz) was also divided to two beams. These two beams were respectively introduced to two OPAs, and the pump and probe pulses were generated. The excitation photon density x_{ph} was evaluated from the average within the penetration depth of the pump pulse (l_{ex}) using the equation $x_{\text{ph}} = (1 - R_{\text{ex}})(1 - 1/e)I_{\text{ex}}/I_{\text{ex}}$, where R_{ex} and I_{ex} are the reflectivity and intensity per unit area of the pump pulse, respectively. Time difference between pump and probe pulses t_d was controlled by changing the path length of the pump pulse. Polarizations of all pulses are also parallel to the 1D stacking-axis a .

All the experiments were performed at 294 K.

Polarized reflectivity measurements. The polarized reflectivity (R) spectra were measured using a Fourier transform infrared spectrometer and a spectrometer with a 25-cm-grating monochromator, which were equipped with an optical microscope.

PC measurements. The PC was measured using a spectrometer with a 150-W tungsten-halogen lamp and a 10-cm-grating monochromator⁴⁰. The incident light was polarized along the a -axis. The PC measurement was performed at 92 K to avoid thermal excitations of carriers. We ascertained that the photocurrents are proportional to the intensity of the excitation light. The excitation spectrum of PC was obtained by using the formula, $I_{\text{PC}} \propto A_{\text{PC}}/[I_{\text{p}}(1 - R_{\text{p}})]$. Here, A_{PC} , I_{p} , and R_{p} are the photo-current signal, the photon density of the excitation light per unit area, and the reflection loss.

Data availability

The data that support the findings of this study are available from the corresponding author on request.

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Author contributions

T. Miyamoto, T. Terashige, D.H., H. Yamakawa, T. Morimoto, N.T., and H. Yada constructed the terahertz-pump optical-reflectivity-probe systems. T. Miyamoto,

T. Terashige and N.T. performed terahertz-pump optical-reflectivity-probe measurements. T. Miyamoto, T.K. and H.M. carried out optical-pump optical-reflectivity-probe measurements. Y.T. and T.H. provided single crystals of ET-F₂TCNQ. T. Tohyama performed theoretical calculations. H.O. coordinated the study. All of the authors discussed the results and contributed to writing the paper.

Competing interests

The authors declare no competing interests.

Additional information

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