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## Ultrafast Transient Spectroscopy of *Trans*-Polyacetylene in the Midinfrared Spectral Range

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*Trans*-polyacetylene [ $t$ -(CH)<sub>x</sub>] possesses twofold ground state degeneracy. Using the Su-Schrieffer-Heeger Hamiltonian, scientists predicted charged solitons to be the primary photoexcitations in  $t$ -(CH)<sub>x</sub>; this prediction, however, has led to sharp debate. To resolve this saga, we use subpicosecond transient photomodulation spectroscopy in the mid-IR spectral range (0.1–1.5 eV) in neat  $t$ -(CH)<sub>x</sub> thin films. We show that odd-parity singlet excitons are the primary photoexcitations in  $t$ -(CH)<sub>x</sub>, similar to many other nondegenerate  $\pi$ -conjugated polymers. The exciton transitions are characterized by two photoinduced absorption (PA) bands at 0.38 and 0.6 eV, and an associated photoluminescence band at  $\sim$ 1.5 eV having similar polarization memory. The primary excitons undergo internal conversion within  $\sim$ 100 fs to an even-parity (dark) singlet exciton with a PA band at  $\sim$ 1.4 eV. We also find ultrafast photogeneration of charge polarons when pumping deep into the polymer continuum band, which are characterized by two other PA bands in the mid-IR and associated photoinduced IR vibrational modes.

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*Trans*-polyacetylene [ $t$ -(CH)<sub>x</sub>] is the simplest but also the most special  $\pi$ -conjugated polymer since it has twofold degenerate ground states—namely, an “A phase” and a “B phase”—as shown in Fig. S1(a) of the Supplemental Material (SM) [1–3]. The synthesis and following studies of this prototype  $\pi$ -conjugated polymer initiated the field of semiconducting polymers [9,10]. The misfit between phase A and phase B in the polymer chain forms a domain wall, a nonlinear shape-preserving excitation that is described by the Su, Schrieffer, and Heeger (SSH) model as a soliton, which may be either neutral,  $S^0$  [Fig. S1(b) of the SM [1]], or charged,  $S^\pm$  [Fig. S1(c) of the SM [3]]. Interestingly a neutral soliton has a single electron and hence is spin 1/2, whereas positively and negatively charge solitons have zero and two electrons, respectively, and hence are spinless. This leads to the so-called reverse spin-charge relationship, in which the charge species is spinless, whereas the neutral species carries spin 1/2. In particular, this model, which includes electron-phonon ( $e$ - $p$ ) interactions but neglects electron-electron ( $e$ - $e$ ) interactions, predicts that upon photon absorption, the photoexcited electron and hole pair is unstable, thereby relaxing within 100 fs to charge a soliton-antisoliton ( $S^+S^-$ ) pair with a state in the middle of the optical gap [11]. Therefore, it is expected that in the subpicosecond (sub-ps) time domain a photoinduced absorption (PA) band will be formed—namely, from either HOMO to  $S^+$  or  $S^-$  to LUMO, as schematized in Fig. S1(d) of the SM [1].

Over the years, the SSH model has attracted substantive attention, where both experimentalists and theoreticians have tried to prove or disprove the photogenerated  $S^+S^-$  prediction. With time, however, other  $\pi$ -conjugated polymers have been synthesized in which the photophysics is dominated by singlet and triplet excitons [12–15], regardless of whether or not their ground state is degenerate. In typical  $\pi$ -conjugated polymers such as polyfluorene, disubstituted polyacetylene, and poly( $p$ -phenylene-vinylene) derivatives, it has been shown that the binding energy of the lowest singlet exciton, the  $1B_u$  is of the order of 0.5 eV [16,17]. The exciton’s primary photoexcitation species in these polymers indicates that the SSH model is not suitable to describe the photophysics of most  $\pi$ -conjugated polymers. Even in  $t$ -(CH)<sub>x</sub>, during the last three decades, the study of photoexcitations has revealed several unexpected phenomena, including photogeneration of a neutral excitation, which were not predicted by the SSH model [18–20]. This indicates that the nature of the primary photoexcitations in  $t$ -(CH)<sub>x</sub> may be very different from the  $S^+S^-$  pair predicted by the SSH model. However, a decisive experiment that elucidates the primary photoexcitations in this polymer has not yet been reported.

In this Letter, we study the primary photoexcitations in  $t$ -(CH)<sub>x</sub> thin films using femtosecond (fs) transient and steady state (cw) photomodulation (PM) spectroscopy in order to resolve the controversy in the literature.

Importantly, since the  $t\text{-(CH)}_x$  optical gap is at  $\sim 1.5$  eV, the sub-ps transient PM spectrum was measured in the mid-IR spectral range, where most of the action in this polymer takes place. We found that within 150 fs, the transient PM spectrum is due to *excitons* and *polarons*, in which the photogenerated quantum efficiency ratio depends on the excitation photon energy. This is in contrast to the cw PM spectrum, which shows long-lived charge solitons that are formed at later times, as by-products of the primary photoexcitations.

Semitransparent *trans*-polyacetylene films were synthesized on IR substrates [sapphire, cesium iodide (CsI), and barium fluoride ( $\text{BaF}_2$ )] by exposure of acetylene gas of 99.9999% (or six nine grade) to the Ziegler-Natta catalyst tetra-*n*-butoxytitanium [ $\text{Ti}(\text{O-}n\text{-Bu})_4$ ] and triethylaluminum ( $\text{AlEt}_3$ ) (the detailed sample preparation method is in the Supplemental Material [1]). The sample handling was done in a glovebox under Ar atmosphere. All experiments were done with the sample at room temperature in a dynamic vacuum better than 0.1 Pa. Two femtosecond laser systems based on a Ti:sapphire oscillator were applied to the optical measurements. A low power ( $\sim 0.1$  nJ of energy/pulse) high repetition rate ( $\sim 80$  MHz) laser for the mid-IR spectral range, and a high power (energy/pulse  $\sim 10$   $\mu\text{J}$ ) low repetition rate ( $\sim 1$  kHz) laser for the near-IR–visible spectral range. The pump laser for both laser systems was set at  $\hbar\omega = 3.1$  eV, or at  $\hbar\omega = 1.55$  eV. For the low power laser, we used an optical parametric oscillator (Opal, Spectra-Physics) and a difference frequency generation crystal that forms  $\hbar\omega$  (probe) ranging from 0.14 to 1.05 eV, whereas for the high intensity measurements, a white light supercontinuum was generated for an  $\hbar\omega$  (probe) ranging from 1.15 to 2.7 eV (see the SM [1]). The PM spectrum mainly contains PA bands with  $\Delta T < 0$  due to excited state absorption, where  $\Delta T$  is the change of the film transmission,  $T$ .

In Fig. 1(a), we show the absorption spectrum of  $t\text{-(CH)}_x$  thin film [21]. As was seen, the absorption edge is at 1.55 eV; this calls to mind the dominant allowed exciton transition, the  $1B_u$  at this energy. We also measured a weak polarized photoluminescence (PL) at 1.41 eV having a phonon sideband at 1.37 eV. The  $t\text{-(CH)}_x$  film is not stretch oriented, so the polymer chains are not aligned. That the PL emission is polarized indicates that it occurs on the sub-ps timescale; otherwise the PL polarization memory would be lost. Fast PL has actually been confirmed in the literature [22,23]. We note that PL emission is not predicted in the soliton SSH model, and this, by itself, shows that SSH is not sufficient to describe the photophysics of  $t\text{-(CH)}_x$ . The PL polarization degree is defined as  $P_{\text{PL}} = (\text{PL}_{\parallel} - \text{PL}_{\perp}) / (\text{PL}_{\parallel} + \text{PL}_{\perp})$ , where  $\text{PL}_{\parallel}$  ( $\text{PL}_{\perp}$ ) is the PL component with polarization parallel (perpendicular) to that of the linearly polarized excitation laser beam. We measured  $P_{\text{PL}} \sim 0.25$  at the peak energy of 1.41 eV, and it remains approximately constant throughout the spectrum.

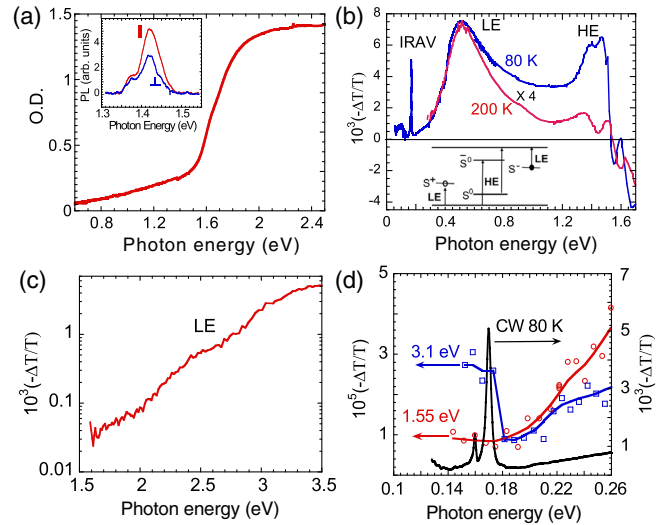


FIG. 1. (a) The absorption spectrum of  $t\text{-(CH)}_x$  thin film. (Inset) The parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) components of the polarized PL emission spectrum with respect to the polarization of the pump excitation. O.D. means optical density. (b) cw photomodulation spectra of  $t\text{-(CH)}_x$  at 80 and 200 K, respectively. The LE PA band was identified as being due to  $S^{\pm}$  [13,19], whereas the HE PA band was ascribed to  $S^0$  [13]. (c) Action spectrum of the LE PA band in the steady state PM spectrum. (d) Transient PM spectra of  $t\text{-(CH)}_x$  film pumped at 3.1 eV (blue squares and line) and 1.55 eV (red circles and line) compared with the steady state PM spectrum (black line) measured at 80 K. The lines through the data points are guides for the eye.

Figure 1(b) presents the quasi-steady state PM spectra of  $t\text{-(CH)}_x$  at 80 and 200 K, respectively, which shows two dominant PA bands at 0.5 eV (low energy, LE) and at 1.4 eV (high energy, HE). Here the value of the PA signal ( $-\Delta T/T$ ) is of the order of  $10^{-3}$ ; thus we have used  $10^3(-\Delta T/T)$ , which represents  $10^3$  times ( $-\Delta T/T$ ), as the units in the y axis throughout the Letter. The LE and HE bands have previously been ascribed to the transitions of photogenerated charged solitons ( $S^{\pm}$ ) and neutral solitons ( $S^0\bar{S}^0$ ), respectively [18], the energy diagram of which is shown in Fig. 1(b) inset. The energy difference of 0.9 eV between the LE and HE transitions, which has been ascribed to the effective electron correlation energy [24], is dramatically different than the zero energy predicted by the SSH model. Therefore, the  $e$ - $e$  interaction cannot be ignored [18,24]. The sharp feature around 0.17 eV is due to photoinduced absorption by infrared-active vibrational (IRAV) modes [25,26], which result from Raman-active vibrational modes that become infrared active by the presence of photogenerated charge carriers on the polymer chains. The excitation spectrum of the LE band ( $S^{\pm}$ ) is shown in Fig. 1(c), in which the PA value increases  $\sim 2$  orders of magnitude for the excitation photon energy in the range of 1.5 to 3.5 eV. This result is consistent with the PM spectrum [27,28] and photoconductivity action spectra measurements [29].

Figure 1(d) compares the steady state PM spectrum of the IRAV modes measured at 80 K to the transient PM spectra at  $t = 0$  pumped by 1.55 and 3.1 eV, respectively, at room temperature. The two transient PM spectra are very different from one another. The PM spectrum excited at 3.1 eV shows strong PA at the same photon energy of the IRAV mode at 0.17 eV [25,30], whereas the PM spectrum excited at 1.55 eV does not show the increase at low energy. We conclude that the excitation dependence of the charged photoexcitations in the picosecond time domain agrees with the steady state PM spectrum shown in Fig. 1(c). From this, we conjecture that charge photoexcitations are photogenerated within the pulse duration when pumped at 3.1 eV. In contrast, when pumped at the band edge (1.55 eV), the primary photoexcitations are *neutral excitons*.

Figure 2(a) shows transient PM spectra of  $t$ -(CH) $_x$  film pumped at 1.55 eV, at  $t = 0$  and  $t = 1$  ps, respectively. The PA spectrum is composed of two prominent PA bands in the midinfrared—namely, PA $_1$  at 0.37 eV and PA $_2$  at

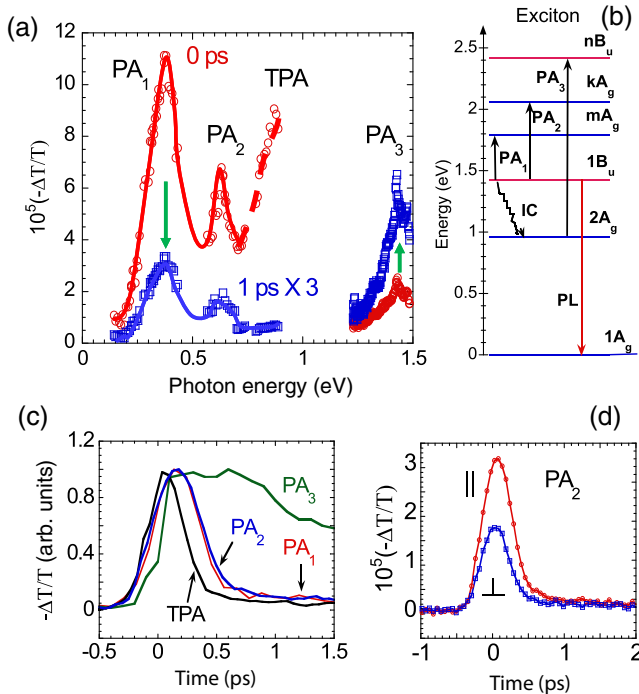


FIG. 2. Transient PM spectra and decay dynamics of  $t$ -(CH) $_x$  film in the mid-IR spectral range excited at 1.55 eV. (a) The transient PM spectra at  $t = 0$  (red circles) and  $t = 1$  ps (blue squares). The lines through the data points are for guides for the eye. Various bands are assigned (defined in the text). TPA is pump-probe two-photon absorption. (b) Schematic of the energy levels and optical transitions of singlet excitons.  $1B_u$ ,  $nB_u$ ,  $1A_g$ ,  $2A_g$ ,  $mA_g$ , and  $kA_g$  are odd- and even-parity exciton states in the neutral manifold. IC is the internal conversion from the  $1B_u$  state to the  $2A_g$  state. (c) The transient rise and decay dynamics of the main PA bands assigned in (a). (d) Transient polarized response of PA $_2$ ; both the  $\Delta T_{\parallel}$  and  $\Delta T_{\perp}$  components are shown.

0.64 eV—as well as two PA features in the near infrared, PA $_3$  at 1.4 eV and two-photon absorption (TPA) with an onset at  $\sim 0.9$  eV. Here the TPA is defined as a nonlinear optical process of one photon from the pump beam and one photon from the probe beam. The transient dynamics of the various PA features are shown in Fig. 2(c). The flat transient response at 0.17 eV indicates that charge photoexcitations are not generated when pumped at the band edge (Fig. S3 of the SM [1]). We found that the dynamics of PA $_1$  and PA $_2$  are the same, with both showing instantaneously photogeneration followed by a fast decay component of  $\sim 110$  fs (Fig. S4 of the SM [1]). However, the transient response of PA $_3$  consists of  $\sim 100$  fs *buildup*, followed by a much slower decay (Fig. S5 of the SM [1]). The similarity between the decay rate of the PA $_1$  (or PA $_2$ ) band and the buildup rate of the PA $_3$  band suggests that the two features associated with these bands are connected via internal conversion. In contrast, the TPA feature shows an instantaneous response and fast decay dynamics which follows the cross-correlation trace of the pump and probe beams. This justifies the TPA feature to be ascribed to two-photon absorption of pump and probe beams (see Fig. S6 and the discussion in the SM [1]).

The main transient features shown in Fig. 2 can be fully explained by the exciton picture that has been used to describe the photophysics in most of homopolymer  $\pi$ -conjugated polymers. In this picture, the exciton eigenstates are classified as even parity,  $A_g$ , and odd parity,  $B_u$ , states [Fig. 2(b)] [31–33]. We thus conclude that the  $1B_u$  exciton is instantaneously photogenerated in  $t$ -(CH) $_x$  upon photon absorption with energy close to the optical gap ( $E_g$ ). Above the  $1B_u$  exciton, there are a number of  $B_u$  and  $A_g$  states; however, the strongest coupling between the  $1B_u$  and these states is to an even state, so-called  $mA_g$ . Thus the PA $_1$  band in Fig. 2(a) is the transition from  $1B_u$  to  $mA_g$ . In this picture, the PA $_2$  band may be a transition from the  $1B_u$  to another, higher two-photon state, so-called  $kA_g$  [31–33]. Although the exciton in  $t$ -(CH) $_x$  has characteristic PA bands similar to many other polymers in the  $\pi$ -conjugated polymer family, it is still unique because the photogenerated  $1B_u$  exciton decays within  $\sim 100$  fs to a “dark,” lower lying exciton (the so-called  $2A_g$  state) that is non-radiative [34–39]. The transient PM spectra and decay dynamics clearly show that the generation of a  $2A_g$  exciton is at the expense of a  $1B_u$  exciton. Importantly, the  $2A_g$ , which is the lowest two-photon state, occurs below the  $1B_u$  in most nonluminescent polymers [34–40], whereas it lies above the  $1B_u$  in luminescent polymers [41,42]. The relative ordering of the  $2A_g$  and  $1B_u$  states is a consequence of the relative strength of the  $e$ - $e$  interactions [13,36]. In this model, the PA $_3$  band is due to a transition from  $2A_g$  to a higher  $B_u$  state—namely,  $kB_u$ —with slower decay [Figs. S5(a) and S7 of the SM [1]], or, alternatively, is due to a breather mode in the polymer chain [43].

We also measured the transient polarized PM with 1.55 eV pump excitation, as shown in Fig. 2(d). The polarization memory degree  $P$  is defined as  $P = [(\Delta T/T)_{\parallel} - (\Delta T/T)_{\perp}] / [(\Delta T/T)_{\parallel} + (\Delta T/T)_{\perp}]$ , where  $\parallel$  and  $\perp$  denote the polarization of pump-probe beams either parallel or perpendicular to each other. As seen in Fig. 2(d),  $P = 0.25$  during the  $PA_1$  lifetime ( $\sim 0.11$  ps). This supports the assignment of  $PA_1$  as being due to excitons since it agrees with the PL polarization degree of 0.25 shown in the Fig. 1(a) inset.

Figure 3(a) presents the transient PM spectra of the same  $t-(CH)_x$  film at  $t = 0$  and  $t = 10$  ps, respectively, excited at 3.1 eV. The PM spectrum contains two PA bands, peaked at  $\sim 0.45$  eV ( $P_1$ ) and 0.9 eV ( $P_2$ ), which are different from the bands  $PA_1$  and  $PA_2$  as well as the LE PA band (0.5 eV) in the steady state PM shown in Fig. 1(b). Furthermore,  $P_1$ ,  $P_2$ , and IRAV share the same dynamics [Fig. 3(c)], which suggests that they belong to the same photoexcitation species. Since the photoexcitations here are charged but do not agree with charge solitons ( $S^{\pm}$ ), we identify the primary photoexcitations as polarons. The energy diagram model of charge polaron in the gap, and related optical transitions are well known in the literature, as shown in Fig. 3(b) [13,15,18,24,34]. Following this model, the

energy difference between the polymer HOMO and LUMO may be estimated from the relation  $E_g = 2P_1 + P_2$ . Consequently we get  $E_g = 1.81$  eV. This energy differs from the absorption edge  $\sim 1.55$  eV and the PL peak  $\sim 1.41$  eV. From these results, it is possible to estimate the exciton binding energy,  $E_B$  in  $t-(CH)_x$ , as  $1.81 - (1.55 + 1.41)/2 = \sim 0.33 \pm 0.04$  eV (Fig. S8 of the SM [1]). The obtained  $E_B$  is smaller than that in other  $\pi$ -conjugated polymers [13] but is larger than  $k_B T$  at room temperature; therefore, the excitons in  $t-(CH)_x$  are stable at ambient temperature.

We found that the polaron transient  $PA(t)$  decays as a power law  $(t/t_0)^{-\alpha}$ , with  $\alpha \sim 0.5$  for  $t < 10$  ps, followed by  $\alpha \sim 0.13$  for  $t > 10$  ps [see Fig. 3(c) and Fig. S9 of the SM [1]]. In general, a power law decay of the form  $(t/t_0)^{-\alpha}$  may originate from a distribution of the lifetime,  $g(\tau)$ , with the form of  $\tau^{-(1+\alpha)}$  [44], or dispersive diffusion toward recombination centers [4]. We adopt the former explanation since the polymer film is disordered. In addition we found that the transient response of the photogenerated polarons also has polarization memory (Fig. S10 of the SM [1]), where  $\Delta T_{\parallel} > \Delta T_{\perp}$ . Since the photoinduced anisotropy decays relatively slowly, we believe that the photogenerated polarons are still subjected to a quasi-one-dimensional environment, even at 3.1 eV pump excitation. The polarons may be photogenerated directly by the high energy photons because the 3.1 eV is much larger than the continuum band in  $t-(CH)_x$  [45,46]. Alternatively, the photogenerated polarons may be a by-product of hot exciton dissociation since the exciton binding energy is  $\sim 0.33$  eV, whereas the photon energy is 1.5 eV higher than the optical gap [47]. It is worth noting that no PA related to charge soliton pairs [characterized schematically in Fig. S1(d) of the SM [1]] has been observed in the transient PM spectra, irrespective of the pump photon energy [48]. We thus conclude that the SSH model is *unable* to describe the intrinsic photophysics of  $t-(CH)_x$ .

In conclusion, depending on the excitation photon energy, both singlet excitons (binding energy of about  $\sim 0.33$  eV) and polarons are instantaneously photogenerated in  $t-(CH)_x$ . Importantly, no soliton-antisoliton pairs are photogenerated directly upon photon absorption. With these findings, the saga of photoexcitations in  $t-(CH)_x$  has been solved. The photophysics of  $t-(CH)_x$  in the ps time domain is governed by a dark exciton that lies below the allowed exciton state but otherwise is in agreement with other homopolymers  $\pi$ -conjugated polymers.

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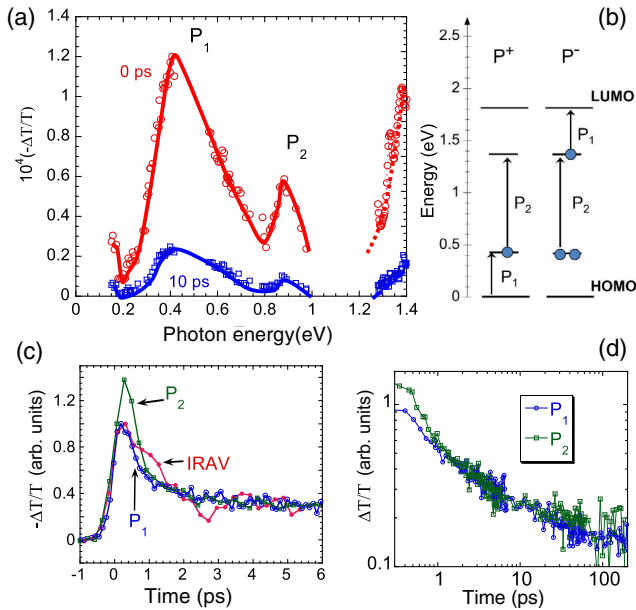


FIG. 3. Transient PM spectra and decay dynamics of  $t-(CH)_x$  film in the mid-IR spectral range excited at 3.1 eV. (a) The transient PM spectra at  $t = 0$  (red circles) and  $t = 10$  ps (blue squares); the lines through the data points are guides for the eye. Various PA bands are assigned. (b) Schematic of the energy levels and optical transitions of charge polaron excitation. HOMO (LUMO) is the highest (lowest) occupied (unoccupied) molecular orbital in the charge manifold. (c) The transient decay dynamics of the main PA bands assigned in (a). (d) Transient decay dynamics of the  $P_1$  and  $P_2$  bands plotted in log-log scale.

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- [1] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.124.017401>, which includes Figs. S1–S10 and Refs. [2–8], for elaboration on the following issues: Sec. S1, an introduction to photoexcitations in *trans*-polyacetylene described by SSH model; Sec. S2, experimental methods; and Sec. S3, supporting experimental results and energy diagram.
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*Correction:* An affiliation has been added for the second author, necessitating renumbering of affiliations for the second and fifth authors.