Research article

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Tunable nonlinear optical responses of few-layer graphene through lithium intercalation

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Abstract: Intercalation has been demonstrated to be a powerful tool for tuning the physical and chemical properties of two-dimensional (2D) materials, providing the highest possible doping level and an ideal system to study various electronic states. In this work, we demonstrate that the nonlinear absorption effect of few-layer graphene (about 6–8 layers) is changed from saturable absorption (SA) to reverse saturable absorption (RSA) after lithium intercalation. This is attributed to the increase of Fermi energy owing to the charge transfer from Li to graphene layers in intercalated compounds (LiC_6). And the change of nonlinear absorption effect is revisable after deintercalation. In addition, the modulation depth of RSA in lithiated graphene is found to rise with the decrease of incident laser wavelength, different from that of pristine graphene. Besides, the dispersion relationships of degenerate and nondegenerate two-photon absorption are analyzed from the results of nonlinear absorption and transient dynamics of lithiated graphene, indicating the 1.91–2.21 eV upshift of the Fermi surface. Our findings of the intercalation-tunable nonlinear optical absorption effect

pave the way for the construction of nonlinear optical devices based on 2D intercalation compounds.

Keywords: graphene; intercalation; LiC_6 ; nonlinear absorption; two-photon absorption.

1 Introduction

Graphene has attracted extensive interest in fundamental research for its extraordinary physical and chemical properties [1], ever since its discovery by mechanical exfoliation in 2004 [2]. Specifically, graphene exhibits a unique spectral response ranging from terahertz to ultra-violet, with a constant optical absorbance of 2.3% for suspended monolayer [3], due to its special linear and gapless two-dimensional (2D) band structure. Except for their linear optical response, graphene [4–6] and other 2D materials, such as transition metal dichalcogenides [7–9], black phosphorus (BP) [10–12], IV–VI chalcogenide semiconductors [13–15] and topological insulators [16, 17], have exhibited many unique and remarkable nonlinear optical properties compared to traditional bulk materials. Besides, various band structure engineering methods [18], such as layer-number control [19], heterojunction construction [20], doping [21, 22], gate tuning [23–25], and intercalation [18, 26–30], have been studied to improve the performance of graphene- and other 2D materials-based devices in optoelectronics and photonics. Among these methods, intercalation, with charge transferring from intercalant species to host materials, shifts the Fermi level more than any others and therefore has a significant effect on the optical properties [31].

Discovered in 1841, intercalation is the insertion of intercalant species into the void space of a layered host material to form the intercalation compounds, the electronic structure of which yields interesting electronic and optical properties, arousing lots of interest in the 1960s–1970s. In 1965, charge transfer from the intercalant atoms to the bulk graphite was found to result in an optical transmission “window”, where the absorption coefficient is three to five times lower than that of graphite [32]. With extensive

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investigations of bulk layered intercalation compounds and the emergence of graphene and many new 2D materials, the unique properties of 2D intercalation compounds induced by their distinct electronic structure began to inspire curiosity. Owing to Pauli blocking, the interband and intraband transitions in graphene can be actively adjusted as a result of Fermi level change, thus modulating the transmittance of light. Actually, the transmittance of 18-layer graphite is found to be dramatically increased from 74.7 to 90.9% after lithium intercalation [33]. Recently, a controllable tunable nonlinear optical second harmonic generation signal is induced in ultrathin graphite flakes by lithium intercalation [27]. This suggests that the nonlinear optical response of graphene could also be exceptionally strong and promising for optoelectronic applications. However, the studies of nonlinear optical absorption of lithium (Li)-intercalated few-layer graphene are still lacking until now.

Here, we use *in situ* electronic and optical measurements, including Raman spectra, four-probe sheet resistance, transmittance spectra, nonlinear absorption, and transient absorption spectra, to explore the electrical and optical properties changes of few-layer graphene films (about 6–8 layers) after Li intercalation. The disappearance of the Raman peak, the increase of electrical conductivity, and the increase of transitivity after intercalation indicate the charge transfer from Li atoms to graphene layers and the upshift of the Fermi level. A reversible change from saturable absorption (SA) of pristine graphene films to reverse saturable absorption (RSA) of lithiated counterpart was observed, due to the variation of carrier concentration in the conduction band and the shift of the Fermi level. Furthermore, the modulation depth of RSA of graphene intercalated compound – LiC_6 rises with the decrease of incident laser wavelength, reaching about 30% for 400 nm, which is much larger than most 2D materials. Our results open up new prospects for optoelectronic applications based on 2D intercalation compounds in the nonlinear regime and inspire further exploration of the intercalation-correlated optoelectronic phenomena in 2D materials.

2 Experimental section

2.1 Device fabrication and electrochemical intercalation

Chemical vapor deposition (CVD)-grown few-layer graphene films (Nanjing MKNANO, China) were transferred onto the fused silica substrates. And two copper (Cu) electrodes were connected with graphene by conductive silver paste. Then the

device was transferred inside an argon-filled glovebox (Lab2000, Etelux, China), and a small piece of Li was pressed onto the graphene. To prevent oxidation, fused silica (0.5 mm thick) was put on top of the device and sealed by epoxy with a small gap to inject the electrolyte (LiPF_6 in ethylene carbonate/diethyl carbonate, w/w = 1 : 1), which covers the graphene and Li areas. The gap was sealed by epoxy after electrolyte injection, to obtain a galvanic cell. The intercalation process is based on the galvanic cell, where the intercalation reaction occurs at the interface between graphene and lithium metal, when they are in contact with each other. As for the de-intercalation process, the biased current was set as 0.01 A using a Keithley 2636B source meter (Tektronix, USA).

2.2 Optical and electrical characterization

The Raman measurements were conducted using a commercial confocal microscope (LEICA DM 2700 M). Excitation was provided by a linearly polarized continuous-wave laser at a wavelength of 532 nm. The emitted signals were collected and analyzed using a spectrometer (ANDOR SR-500i-B1-R). During measurement, the laser focuses by a 100 $\times$ objective (LEICA, NA = 0.85) on the few-layer graphene films through the top fused silica, and the power is set as 0.1 mW to minimize the heating effect of the laser. The sheet resistance of CVD-grown graphene and Li-intercalated graphene was measured by the van der Pauw (VDP) method, using a Keithley 2636B source meter (Tektronix, USA). An angle-resolved spectrum system (Ideaoptics, China) was chosen to measure the transmittance of the few-layer graphene before and after Li intercalation.

2.3 Nonlinear optical absorption measurements

To study the nonlinear absorption of lithiated graphene, an open-aperture micro-I-scan system was constructed. The high-intensity light, with wavelengths ranging from 400 to 800 nm, was obtained by pumping an optical parametric amplifier with the output of a Ti: sapphire laser (800 nm, 1 kHz). A continuously adjustable neutral density filter (Thorlabs, NDL-10C-4) was adopted to modulate the laser intensity, allowing for the I-scan measurement. Then a chopper was used to modulate the repetition frequency from 1 kHz to 500 Hz and worked together with the dual-channel lock-in amplifier to avoid the influence of scattered light and improve the signal-to-noise ratio (SNR) of the system. Next, the laser is divided into two beams by a 50/50 beam splitter (BS). One of the beams was converged

by the lens into a photoelectric detector (PD) as the reference signal. The other beam entered the real-time video microscope system built by an imaging camera and a confocal microscope (LEICA DM 2700M). The radiation of the femtosecond laser was focused on the sample into a spot with a diameter of 5.7 μm . The transmitted light was collected by the lens and entered a PD as the detection signal. The two signals were input to the dual-channel lock-in amplifier, and finally, the transmittance was obtained.

2.4 Transient absorption measurements

Transient absorption processes were characterized using a homebuilt pump-probe system operating in the transmissive mode. The pump beam (400 nm, 1 kHz) was obtained by pumping a beta barium borate crystal with the output of a Ti: sapphire laser (800 nm, 1 kHz). A small portion of the Ti: sapphire laser was directed into a sapphire crystal to generate supercontinuum white light, then equally divided into two beams by a 50/50 BS, i.e. the probe beam and the reference beam. The reference beam was used as the output power sensor to improve the SNR. The pump and probe beams were aligned to coincide with each other before reaching the objective and the sample. The pump and probe beam waists are of ~ 540 and ~ 100 μm ,

respectively, ensuring the uniform excitation in the probe area. Both probe and reference beams were sent to fiber couple multichannel spectrometer and detected separately by a charge-coupled device (CCD) camera. The time delay between the probe and the pump pulses was controlled by a computer-controlled delay line in the probe path. All the measurements were performed at room temperature.

3 Results and discussion

3.1 Preparation and characterization of few-layer graphene before and after Li intercalation

In this work, a sandwich-structured galvanic cell is designed as illustrated in Figure 1(a). The CVD-grown few-layer graphene film contacted with Li flake was immersed in the electrolyte (LiPF_6 in ethylene carbonate/diethyl carbonate, w/w = 1 : 1), which was sealed between the bottom and top transparent fused silica to prevent oxidation. The lithium flake was in direct contact with the graphene, and the galvanic cell was short-circuited, where Li is intercalated into the van der Waals gaps of graphene spontaneously. In addition, it is necessary to prepare a pristine graphene sample immersed in the same electrolyte

Figure 1: (a) Experimental geometry of galvanic cell device; (b) optical images of CVD-grown graphene (left), graphene immersed in the electrolyte (middle), and graphene intercalated compounds (LiC_6) in a galvanic cell. The graphene and Li metal are marked with the blue and red dotted box, respectively; (c) top view (left) and side view (right) of fully lithiated graphene LiC_6 crystal structure; (d) Raman spectra for CVD-grown graphene (red), graphene immersed in an electrolyte (yellow), and fully lithiated graphene LiC_6 (green); (e) I - V curves of few-layer graphene before (yellow) and after (green) intercalation; and (f) linear transmittance spectra of few-layer graphene before (yellow) and after (green) intercalation.

as a reference sample. The optical images of CVD-grown graphene, graphene immersed in the electrolyte, and graphene intercalated compounds (LiC_6) in a galvanic cell are shown in Figure 1(b). Details of the device fabrication are given in the Experimental section.

To study the influence of intercalation on the structure of graphene, we performed *in situ* Raman tests on three different samples as Figure 1(b) shows, and the spectra are depicted in Figure 1(d). It can be seen from the red curve in Figure 1(d) that the pristine graphene shows a typical G peak and 2D peak with Raman shifts of 1582.7 cm^{-1} and 2702.1 cm^{-1} , respectively. When the graphene was immersed in the electrolyte (reference sample), the Raman spectrum is illustrated as the yellow curve in Figure 1(d). The baseline intensity rises; however, the positions and intensities of the G peak and 2D peak remain almost unchanged. For the lithium intercalated graphene, the G peak and 2D peak disappear, as shown in the green line of Figure 1(d), which agrees with previous researches [27, 33, 34].

The disappearance of the G peak and 2D peak in the Raman spectrum of Li-intercalated graphene is attributed to the formation of graphene intercalated compounds LiC_6 . Charge transfer occurs between Li and graphene, shifting up the Fermi level to E_F , which will block the interband optical transition when the energy of the incident photon below $2E_F$. Besides, the disappearance of the Raman peaks indicates that $2E_F$ is larger than the photon energy of 2.33 eV (532 nm) used in the Raman test. In addition, we measured the resistance of graphene before and after Li intercalation by the VDP method that excludes contact resistance. The sheet resistance of the device is reduced from $923.8\text{ }\Omega/\text{sq.}$ (before intercalation) to $69.7\text{ }\Omega/\text{sq.}$ (after intercalation), which further confirms the charge transfer between Li and graphene, as shown by the I - V curves in Figure 1(e).

It can be seen from Figure 1(b) that the lithiated graphene is more transparent compared with the pristine one. The yellow and green curves in Figure 1(f) describe the transmission spectra of graphene before and after Li intercalation, respectively. In the wavelength range of $480\text{--}900\text{ nm}$ (limited by the wavelength range of the test system, the transmission spectrum of $400\text{--}480\text{ nm}$ cannot be measured), the transmittance of graphene increases after Li insertion, with the max increase at 620 nm , from 84.7 to 89.6% . The transmittance increase indicates that the absorption of graphene decreases after Li intercalation. Li, as an active alkali metal, possesses strong electron-donating capacities, the $2s$ electrons of which are easily transferred to the graphene. Hence the Fermi level of lithiated graphene increased, making the transition-allowed electron energy state reduced, and the partial

transition was blocked. The change of sample transparency on the macro-scale allows us to directly perceive the Li intercalation process on the micro-scale.

3.2 Nonlinear optical properties of pristine and Li-intercalated graphene

Pristine graphene displays broadband SA characteristics [35], that is, the absorbance decreases and finally reduces to zero (transmittance increases and finally stays constant) when the excitation intensity is large enough and continues to rise. As the I -scan results in Figure 2(a) depicted, unintercalated graphene immersed in the electrolyte exhibits SA in a wide range of wavelengths from 400 to 800 nm . In addition, the modulation depth Δ ($\Delta = |T(I_{\max}) - T(I_{\min})|$) of SA at different wavelengths ranging from 1.3% (400 nm) to 2.1% (800 nm), the difference among which is relatively small.

However, it can be seen from Figure 2(b) that the lithiated graphene exhibits RSA, which refers to the absorbance increases (transmittance decreases) when the excitation intensity is large enough and continue to rise. And the modulation depth of RSA sharply increases from 0.02% at 800 nm to 30.01% at 400 nm . As demonstrated in Section 3.1, charge transfer happens between Li and graphene. Thus, the nonlinear absorption properties are affected, showing a transition from SA to RSA. Since electrons are fermions limited by the Pauli Exclusion Principle, no two electrons can fill the same energy state. The $2s$ electrons donated by Li fill the conduction band of graphene from a low energy state to high, increasing the Fermi level to E_F . Therefore, the optical transition where the photon energy $\hbar\omega < 2E_F = E_{\text{eg}}$ (E_{eg} denotes equivalent energy gap) is blocked, resulting in the transparency to the corresponding laser. As the excitation intensity goes up, the electrons in the valence band of lithiated graphene tend to absorb two photons simultaneously to achieve the interband transition, i.e. two-photon absorption (TPA); and ones in the conduction band tend to absorb one photon to achieve the intraband transition, i.e. free carrier absorption (FCA). These two absorbing mechanisms give rise to RSA consequently. Additionally, the initial and final states of the optical transition vary with the photon energy $\hbar\omega$, so does the transition probability, leading to the big difference in the modulation depth of RSA. Considering the TPA and FCA at the same time, the absorption rate can be expressed by Eq. (1),

$$\alpha(I) = \sigma_{\text{abs}}N + \beta I \quad (1)$$

where σ_{abs} , N , β , and I denote FCA cross-section, the number density of free carriers, TPA coefficient, and laser

Figure 2: (a) *I*-scan results of SA for pristine graphene; (b) *I*-scan results of RSA for lithiated graphene (LiC₆); (c) electron transition schematic of TPA (top) and FCA (bottom); (d) dispersion curves of TPA coefficient; and (e) nonlinear absorption results during deintercalation.

intensity, respectively. Resulting from TPA-generation and interband relaxation, the number density of free carriers varies with time, which satisfies Eq. (2),

$$\frac{dN}{dt} = \frac{\beta I^2}{2\hbar\omega} - \frac{N}{\tau} \quad (2)$$

where τ is the carrier lifetime. However, because the pulse width of the laser used in the experiment is about 35 fs, which is much shorter than the carrier lifetime, interband relaxation can be neglected, thus the carrier density can be represented as Eq. (3),

$$N = N_0 + \frac{\beta I^2 \tau_p}{2\hbar\omega} \quad (3)$$

where τ_p is the pulse width, and N_0 is the free carrier density due to the charge transfer between Li and graphene, which is about 10^{19} cm^{-3} to 10^{22} cm^{-3} [31]. Taking $\beta = 10^3 \text{ cm}^3 \text{ GW}^{-1}$, $\tau_p = 35 \text{ fs}$, $\hbar\omega = 3 \text{ eV}$, $I = 300 \text{ GW cm}^{-2}$, the free carrier density generated by TPA given by $\beta I^2 \tau_p / 2\hbar\omega$ can be estimated to be about $7 \times 10^{16} \text{ cm}^{-3}$. It is much smaller than N_0 so that can be neglected. Therefore, $N \approx N_0$ and $\sigma_{\text{abs}} N$ does not change with time. So

experimental data (circles) in Figure 2(b) can be fitted using Eq. (4),

$$T = \exp\left(-\left(\sigma_{\text{abs}} N + \frac{\beta_0 I}{(1 + I/I_s)^2}\right)L\right) \quad (4)$$

where L denotes the thickness of lithiated graphene. Considering the saturation of TPA, $\beta = \beta_0 / (1 + I/I_s)^2$ is introduced and I_s denotes saturation intensity. Table 1 shows the fitting parameters of RSA, from which it can be seen that β_0 decreases with the increase of the incident laser wavelength from 400 to 800 nm.

From the previous work on two-photon transition [36–38], the TPA coefficient can be expressed as Eq. (5),

$$\begin{aligned} \beta_0(\omega_1; \omega_2) &= \sum_{n=0}^2 \beta_0^{(n)}(\omega_1; \omega_2) \\ \beta_0^{(n)}(\omega_1; \omega_2) &= \frac{f_n K \sqrt{E_p}}{n_1 n_2 E_g^3} F_2^{(n)}\left(\frac{\hbar\omega_1}{E_g}; \frac{\hbar\omega_2}{E_g}\right) \\ F_2^{(n)}(x_1; x_2) &= \frac{(x_1 + x_2 - 1)^{n+1/2}}{2^7 x_1 x_2^2} \left(\frac{1}{x_1} + \frac{1}{x_2}\right)^2 \end{aligned} \quad (5)$$

Table 1: Fitting parameters of RSA.

λ nm	$\sigma_{\text{abs}}N$ $\times 10^5 \text{ cm}^{-1}$	β_0 cm GW^{-1}	I_s GW cm^{-2}
400	2.346	19844.01	304
480	2.958	2021.29	2255
500	3.432	1663.21	483
550	3.089	1075.19	1164
600	3.202	1053.63	359
650	3.121	437.84	338
700	2.919	268.00	7956
750	2.994	179.37	1112
800	2.946	82.62	2787

where $n = 0, 1$ and 2 denote to allowed-allowed (a-a), allowed-forbidden (a-f), and forbidden-forbidden (f-f) transitions; f_n is a numerical factor that depends on the angular averages of the interband matrix elements; the fundamental constants K and E_p are almost the same for any semiconductor. These expressions are the general situation for TPA describing the absorption of the ω_1 beam

owing to the presence of the ω_2 beam. However, degenerate TPA took place in the I -scan test, that is, the electrons absorb two identical photons for transition, leaving $\omega_1 = \omega_2 = \omega$. Therefore, for practical fitting to get the equivalent energy gap E_{eg} of lithiated graphene, $\beta_0(\omega; \omega) = \sum_{n=0}^2 C_n E_{\text{eg}}^{-3} F_2^{(n)}(\hbar\omega/E_{\text{eg}}; \hbar\omega/E_{\text{eg}})$ can be used, and the fitting curves are displayed in Figure 2(d). To ensure data reliability, four Li-intercalated graphene devices were prepared and tested, the E_{eg} of which are 4.34 eV, 4.41 eV, 3.88 eV, and 3.81 eV, respectively.

From $2E_F = E_{\text{eg}}$, the uplift of the graphene Fermi surface by Li-intercalation can be estimated as about 1.91–2.21 eV, which is higher than 1.6 eV [31]. However, it is worth noticing that the relationship between β_0 and $\hbar\omega$ described in Eq. (5) is derived based on semiconductors, but the Li-intercalated graphene behaves more like metal due to the charge transfer from Li to graphene. Consequently, the relationship is not completely consistent with the equations. At the same time, the conduction band of LiC_6 is also filled with photogenerated carriers injected by TPA, which will further lift the Fermi surface.

Figure 3: Transient absorption for few-layer graphene after intercalation: (a) transient absorption spectra; (b) dispersion curve of absorbance difference at zero delays; (c) measured differential transmittance transients; and (d) fast (black) and slow (red) carrier relaxation times.

The intercalation is reversible. When a reverse bias current was added to both ends of the lithiated graphene, the Li inserted between the graphene layers deintercalated due to the loss of electrons, and the reaction $\text{LiC}_6\text{H}_{14} = 6\text{C} + \text{Li}$ took place. The Fermi energy of graphene begins to decrease, so it can be inferred that the influence of Li intercalation on the nonlinear absorption of graphene will also be restored. The results of nonlinear absorption at 400 nm laser incidence during deintercalation are shown in Figure 2(e). As the current-appliance time increases from zero to 16 min (intercalated $\rightarrow$ deintercalation 4 min $\rightarrow$ deintercalation 16 min), first the device exhibits RSA with the modulation depth decreasing gradually and then changes to SA. After 16 min, the modulation depth of SA is 17%, which is greater than 1.3% of pristine graphene under 400 nm laser excitation, indicating deintercalation-induced defects.

3.3 Nonlinear optical properties of pristine and Li-intercalated graphene

For further investigation of the nonlinear absorption properties, a transient absorption test of lithiated graphene was conducted using a pump-probe technique with a transmission geometry. Specifically, the carrier dynamics of Li-intercalated graphene were explored and analyzed at a 400 nm laser pump and supercontinuum white light (500–730 nm) probe. The de-chirped transient differential transmittance spectra are depicted in Figure 3(a). And the details in the spectra are extracted in Figure 3(b) and (c).

Figure 3(b) shows the difference between probe absorbance with and without pump (ΔA) of our sample at 0 fs time-delay, in which the peaks of pump and probe arrive at the sample simultaneously and lead to the largest ΔA . With high-intensity pump laser incidence, nondegenerate TPA of the pump and probe light took place, and so did FCA of pump light, the former increased the probe absorbance while the latter decreased it. Therefore, the relationship between ΔA and wavelength contains two parts, i.e. the contribution of both nondegenerate TPA and FCA of pump light. From Section 3.3, we find the wavelength dependence of TPA is much bigger than that of FCA in the nonlinear absorption test. Accordingly, the contribution of FCA is disregarded. The data (circles) in Figure 3(b) are simply fitted by Eq. (5) with $\omega_2 = 2\pi/400$ nm (curve), and the E_{eg} is solved to be 3.75 eV, which is in good agreement with the nonlinear absorption fitting results. However, the fitting curve deviates from the data when the wavelength is smaller than 510 nm because the nondegenerate TPA is reduced so that the wavelength dependence of FCA cannot be neglected. From Figure 3(a), we can also find that the differential transmittance $\Delta T/T$ at delay > 0 is greater

than that at delay < 0 only with the pump wavelength smaller than 510 nm, which is of the same reason as the deviation. The dynamics of lithiated graphene are surveyed in Figure 3(c). The relaxation signal under high pump excitation is divided into two parts, that is, the signal has a sharp dip (~ 65 fs) representing the thermalization process of light-excited carriers after TPA, followed by a slow rise (greater than 1.67 ps) representing the fast (electron–phonon coupling) and slow (electron–hole recombination) relaxation process. And $\Delta T/T_{t>0} > 0$ only happens at an excitation wavelength smaller than 510 nm where the nondegenerate TPA is reduced and the influence of FCA becomes more obvious. As one can see, the signal decay can be well fitted with a biexponential function, $\Delta T/T(t) = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, and the two-time constants τ_1 and τ_2 are solved and plotted in Figure 3(d). Compared to the pristine graphene [39–42], the carrier recombination time τ_2 increases, as the result of charge transfer from Li to graphene.

4 Conclusions

In summary, we have successfully developed the Li-intercalated graphene device using an electrochemical galvanic cell, accomplishing the reversible change of nonlinear absorption from SA to RSA. Moreover, we have carried out an in-depth investigation on the dispersion relationship of degenerate and nondegenerate TPA from the results of nonlinear absorption and transient dynamics of lithiated graphene. Our experimental results indicate that the total upshift of the Fermi surface is about 1.91–2.21 eV, which has been verified to correspond to the charge transfer from Li to graphene and the carrier injection induced by TPA. Our work not only provides a fundamental understanding of the nonlinear absorption process of Li-intercalated graphene devices but also shows excellent potential for the implementation of adjustable nonlinear absorption devices.

Author contribution: Tian Jiang and Renyan Zhang designed the research. Chenxi Zhang did the nonlinear absorption experiments, processed all the data, drafted the manuscript, and revised the paper. Ganying Zeng contributed to the sample fabrication and experiments of Raman spectra, VDP resistance test, and linear absorption spectra. Yuxiang Tang and Qirui Liu conducted the transient absorption experiments. Tian Jiang helped organize the manuscript. Renyan Zhang helped revise the paper. All authors have given approval to the final version of the manuscript.

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