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Femtosecond laser irradiation of molecular excitonic films for nanophotonic response control and large-area patterning

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Abstract: Molecular excitonic films such as J-aggregate thin films can show an optically metallic response in the visible region and can be considered as alternative materials for plasmonics. However, there was no direct, top-down method to modify the optical response over a large area. Here, we demonstrate the femtosecond (fs) laser processing of J-aggregate films on the centimeter scale. With proper laser conditions, optically metallic films ($Re[\varepsilon] < 0$) were modified to dielectric ones ($Re[\varepsilon] > 0$) with large changes in optical responses. We performed various optical spectrum measurements to investigate the effect of fs-laser irradiation. Our results demonstrate that the strong modification of the optical response can be induced over a large area by fs-laser processing and this can be useful for novel nanophotonic studies.

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1. introduction

Plasmonic nanostructures can enable extreme light confinement and manipulation down to the nanometer scale [1], and therefore they are important for various nanophotonic devices. Surface polariton modes in such plasmonic structures require material with negative dielectric constants ($Re[\varepsilon] < 0$), and metals have been mainly employed for them. However, there have been many other efforts to find alternative materials for plasmonics [2]. Recently, molecular excitonic films such as J-aggregates have been considered as alternative plasmonic materials too [3–8]. J-aggregates exhibit strong optical responses via exciton generation and coherent transport [9–12]. Owing to the large oscillator strength, J-aggregate films can exhibit a metallic response in the visible region and can support excitonic surface polaritons, which can exhibit field confinement and manipulation in the subwavelength regime, similar to surface plasmon polaritons in metals. These excitonic surface polariton modes have been experimentally verified in the attenuated total reflection (ATR) configuration with a high-index prism [3,4,7]. Moreover, these molecular excitonic materials have a Lorentzian dispersion (not Drude-type dispersion) and possess an epsilon-near-zero (ENZ) crossing point in the visible region [8]. This ENZ response in the visible range could be useful for novel nanophotonic studies such as nonlinear optical enhancement [13]. These organic excitonic films can be spin-coated over a large area and their optical response can be easily adjusted by controlling the dye concentration in the film. Therefore, these molecular excitonic materials hold good promise for various nanophotonic applications, such as strong coupling [14–16], photodetectors [17], perfect absorbers [18], excitonic circuits [19], etc. Giant circular dichroism and molecular chirality in a J-aggregate thin film has been also reported recently,

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and it was ascribed to the large oscillator strength of the excitonic transition and the negative dielectric constants [20]. However, there was no direct, top-down method to modify the optical response over a large area.

Here, we demonstrate the femtosecond (fs) laser processing of molecular excitonic films. This enables the patterning of excitonic films over a whole substrate (on the centimeter scale), thanks to the advances in high repetition rate (~MHz) fs laser amplifiers and high speed laser beam scanners. With proper laser conditions, optically metallic films (Re[ε] < 0) can be modified to dielectric ones (Re[ε] > 0), producing large changes in optical responses. We performed various optical spectrum measurements, such as transmission, reflection, and photoluminescence (PL), to investigate the effect of fs-laser irradiation. Especially, we compare PL from a laser-processed sample to those from a monomer solution and a thermally-degraded film. These PL measurements provide additional information on the fs-laser-induced response change in J-aggregate films. Strong fs-laser fields can induce the structural disorder of molecular stacking in J-aggregates, and this, in turn, results in the strong modification of the excitonic absorption strength and the optical response in molecular excitonic films. Our study suggests that the optical response of molecular excitonic films can be tailored using fs-laser processing in a direct-write manner over a large area and this can be useful for various nanophotonics studies.

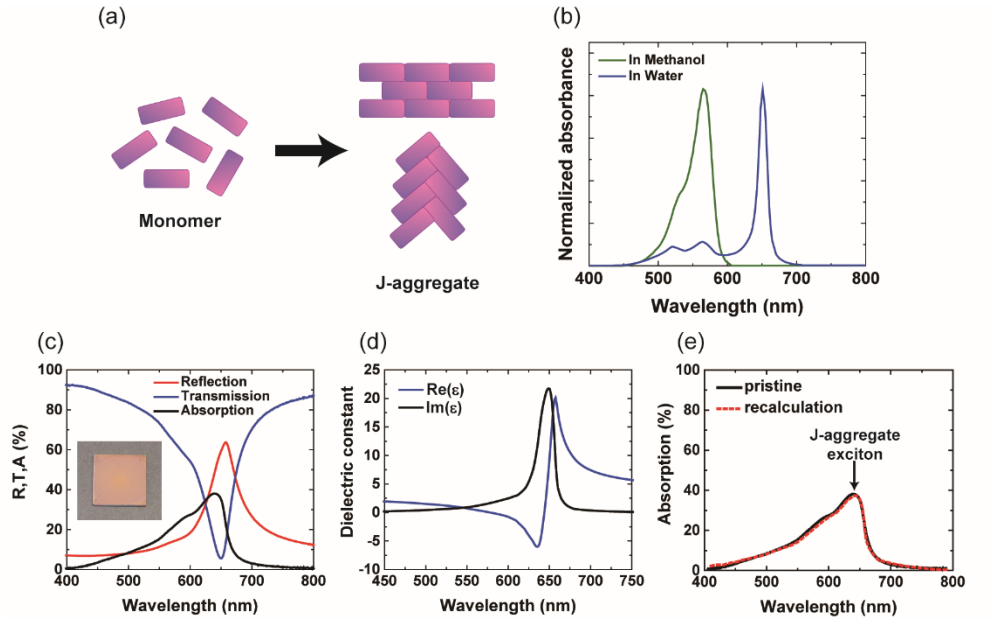

Fig. 1. (a) Schematic of J-aggregate formation. (b) Absorbance spectrum in methanol and water solutions. (c) The reflection, transmission and absorption spectra of a J-aggregate neat film (thickness ~30 nm). Inset: Picture of the spin-coated J-aggregate film. (d) The extracted dielectric constants of the film. It shows optically metallic behavior in the visible region (Re[ε] < 0). (e) Absorption spectrum from experiment (solid line) compared to that recalculated from the extracted dielectric constants (dashed line).

2. Results and discussion

In J-aggregates, monomer dye molecules are aligned parallel to the aggregation direction [see Fig. 1(a)], and this molecular alignment results in a redshifted, very strong excitonic absorption line. Figure 1(b) shows the normalized absorbance in cyanine-dye monomer and J-aggregate solutions (S2275 from Few Chemicals [21], CAS #: 259879-20-4). A cyanine-dye solution in methanol shows a broad monomer absorption band around 500 ~600 nm [green curve in Fig. 1(b)]. However, when dye molecules are dissolved in water, they form J-

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aggregates and a very sharp and strong absorption peak appears in the longer wavelength region [blue curve in Fig. 1(b)].

For the J-aggregate film preparation, cyanine dye molecules were dissolved in water (2.5 wt%) and then were spin-coated on a clean quartz substrate with the spin-speed of 3000 rpm for 60 seconds to obtain a J-aggregate *neat* film (i.e., no polymer matrix was used). The substrate size was 1 cm x 1 cm, and the thickness of the spin-coated film was measured to be ~30 nm using AFM (DI-3100, Veeco). The optical transmission and reflection of an unpatterned, pristine molecular film were measured using a spectrophotometer (Cary 5000, Varian). Figure 1(c) shows the measured transmission and reflection spectra. The measured spectra show a clear metallic response near the excitonic line at 650 nm; reflection is strongly enhanced, while transmission is reduced significantly. The inset in Fig. 1(c) is the picture of the spin-coated film. The film has a clear metallic appearance. The dielectric constants of the film were extracted from reflection/transmission spectra [22–24]. Our molecular excitonic film has a very clear Lorentzian dispersion; Im[ε] has a strong peak that corresponds to J-aggregate excitonic absorption, and the optically metallic region (Re[ε] < 0) appears right below this peak absorption wavelength. Away from the J-aggregate absorption peak, the film exhibits normal dielectric behavior (Re[ε] > 0). This metallic response in the visible region can be understood from the Kramers-Kronig relation; strong absorption at the excitonic line results in a very large peak of the imaginary part of the dielectric constants (Im[ε]). Then, the real part significantly fluctuates around it, resulting in negative dielectric constants (Re[ε] < 0).

Figure 1(e) compares the measured absorption spectrum (solid line) with the recalculated spectrum using the extracted dielectric constants (dashed line). The absorption spectrum was obtained from the measured transmission and reflection spectra by taking A = 1 – R – T. The J-aggregate film has a strong excitonic absorption peak together with a broader shoulder in the shorter wavelength region (around 590 nm). This shoulder is not present in J-aggregates in a water solution [Fig. 1(b)], but it is well retrieved from our recalculated absorption spectrum. The extracted dielectric constants in Fig. 1(d) are well represented by a single Lorentzian dispersion, and this dispersion produces a broader shoulder around 590 nm. Thus, we think that this shoulder in the absorption spectrum is related to the optical effect in our thin film rather than monomer or H-aggregate absorption resonance.

The metallic excitonic film was processed using a fs-pulsed laser (τ = ~330 fs) [see the schematic in Fig. 2(a)] [25–27]. An Yb-doped fiber-based fs laser amplifier (λ = 1030 nm, Satsuma HP2, Amplitude systèmes) was used with a galvanometer scanner (IntelliSCAN III, ScanLab). The laser ablation threshold was examined before irradiating a sample. The pulse energy was set to be about 90% of the ablation threshold not to damage the thin film but to maximize the irradiation effect. The pulse energy and frequency were 0.7 μJ and 100 kHz, respectively. The corresponding laser fluence was about ~0.28 J/cm^2, providing the laser intensity of ~0.8 TW/cm^2. The pulse overlap rate was about 98% which means that the cumulative number of pulses per spot was about 50. The high beam scan speed (~30 mm/s) enabled laser patterning over a whole substrate. Figure 2(b) is the optical microscope image of the sample after fs-laser irradiation. Line patterns with a strip width of > 10 μm were drawn over the whole sample (1 cm x 1 cm). The black scale bar is 50 μm. The image shows a clear contrast between lines and the background. After proper laser irradiation, the film thickness change was checked by AFM. Depending on laser fluence, the thicknesses of some films were reduced. However, with proper laser conditions, we find that the film thickness did not change much. Figure 2(c) shows the measured height profile and it does not show a noticeable change in thickness. This means that our fs-laser irradiation with proper conditions does not physically damage the molecular film. See also Appendix for more experimental data and descriptions on fs-laser patterning.

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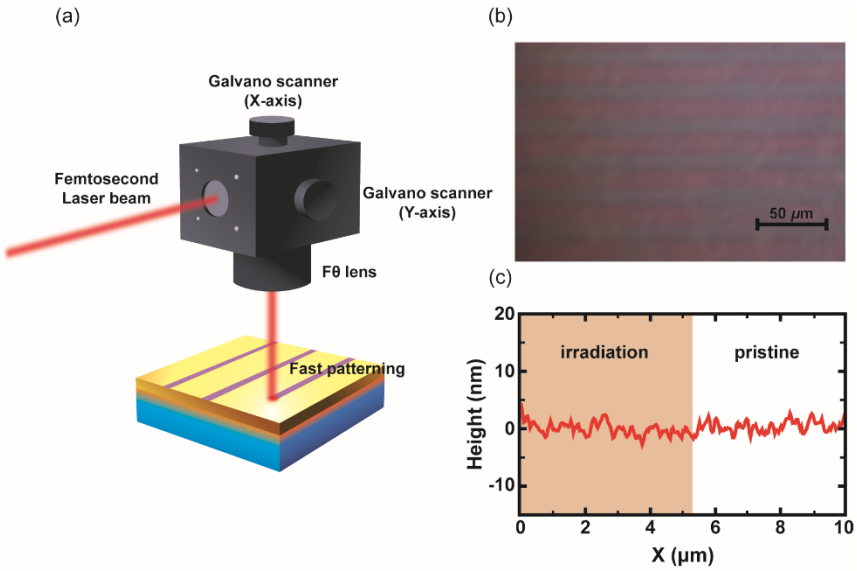

Fig. 2. (a) Schematic of femtosecond (fs) laser patterning on molecular excitonic films. (b) An optical microscope image of the patterned film. (c) The AFM height profile does not show a noticeable change in thickness.

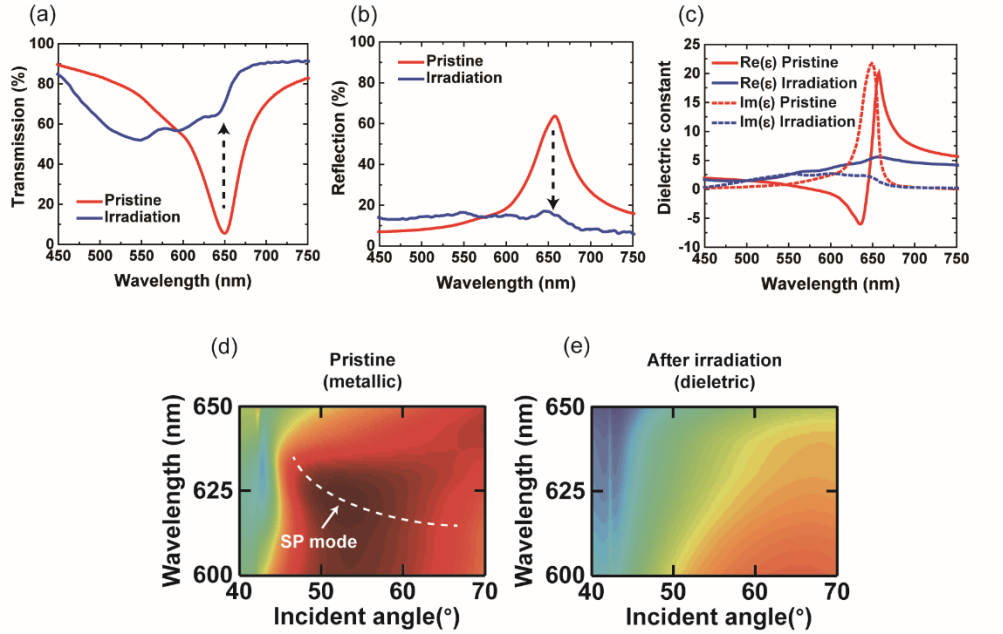

Fig. 3. (a), (b) Transmission and Reflection spectra before and after fs laser irradiation. (c) The extracted dielectric constants before and after laser irradiation. (d), (e) Transfer matrix method calculation of absorption maps with the extracted dielectric constants in (c).

Fs-laser processing induced large changes in optical spectra. Figures 3(a) and 3(b) show the transmission and reflection spectra measured before and after laser irradiation. We used a UV/Visible microspectrometer (20/20/PV, CRAIC) with a white light spot size of ~5.5 μm to collect the optical signal only from the laser-irradiated region (blue curves in Fig. 3). And these spectra were compared to that from an original, pristine film (red curves). In both transmission and reflection spectra, we notice that the metallic response was reduced

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significantly; the strong reflection peak was suppressed and transmission dip was recovered back around the J-aggregate excitonic line (around 650 nm). From the measured transmission/reflection spectra, we calculated the dielectric constants again [Fig. 3(c)] and verified that the film has a strong optical response change: from optically metallic (Re[ε] < 0) to dielectric (Re[ε] > 0) after irradiation. These results imply that fs-laser irradiation can effectively induce the structural disorder of J-aggregate molecules and thus the strong excitonic response disappears after laser irradiation. We recently studied electron-beam-induced response control in molecular aggregate films [28], but the electron-beam-induced processing was limited to a very small area (on the micrometer scale) because of the slow processing speed and high cost. However, the high scan speed of fs-laser beams enables patterning over a whole substrate (on the centimeter scale).

This modulation of optical properties (from metallic to dielectric) can have significant impacts on the nanophotonic response of the film. Figure 3(d) shows the absorption maps as a function of wavelength and incidence angle, obtained from the transfer matrix method (TMM) calculations, for the attenuated total reflection configuration (i.e., [prism/excitonic film/air]). We considered both metallic and dielectric films using the extracted dielectric constants in Fig. 3(c), and compared absorption maps with the dispersion curve of excitonic surface polaritons given by the following equation [29],

$$k_{\parallel} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_{\text{exc}}\varepsilon_{\text{air}}}{\varepsilon_{\text{exc}}+\varepsilon_{\text{air}}}}, \tag{1}$$

where ω and c are the angular frequency and the speed of light. ε_{exc} and ε_{air} are the dielectric constants of the excitonic film and air ($\varepsilon_{\text{air}} = 1$). The in-plane momentum $k_{\parallel}$ is related to the incidence angle θ: $k_{\parallel} = \frac{\omega}{c} n_{\text{glass}} \sin\theta$. The dashed white line is the dispersion of surface polaritons. In the optically metallic film, strong absorption follows the surface polariton branch, while the dielectric one does not. Therefore, our fs-laser processing can significantly modulate the nanophotonics response of molecular excitonic films and this could be useful for novel nanophotonic applications.

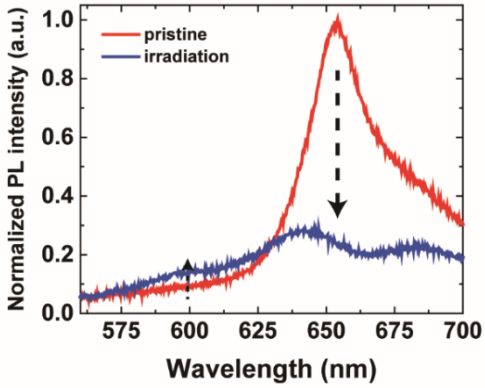

Fig. 4. Photoluminescence (PL) spectra in pristine and irradiated positions. The strong J-aggregate PL peak was significantly suppressed, while the PL in the monomer region rather increased.

To further clarify the effect of fs-laser processing, we conducted the PL measurements of the laser-irradiated film in a custom-built, micro-PL setup. Cyanine-dye J-aggregates have strong PL with a very small Stokes shift from the excitonic line (see the red curve in Fig. 4) [30]. PL peak positions are directly related to the energy levels, and thus a PL spectrum can provide important information on the molecular structure of excitonic films. A diode laser at

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532 nm was used as an excitation source (laser power ~6 μW) and was focused on a film to a small spot using a 50X microscope objective lens (NA: 0.42). The small laser spot size was ensured to collect PL only from the laser-irradiated line. The spectrum was obtained using a monochromator and a silicon CCD camera with the integration time of 1 second and 10-times accumulation. The blue curve in Fig. 4 shows the PL spectrum of the excitonic film after fs-laser irradiation. The strong PL peak around 654 nm was suppressed significantly and this again confirms that fs-laser irradiation effectively reduces the excitonic response of molecular films.

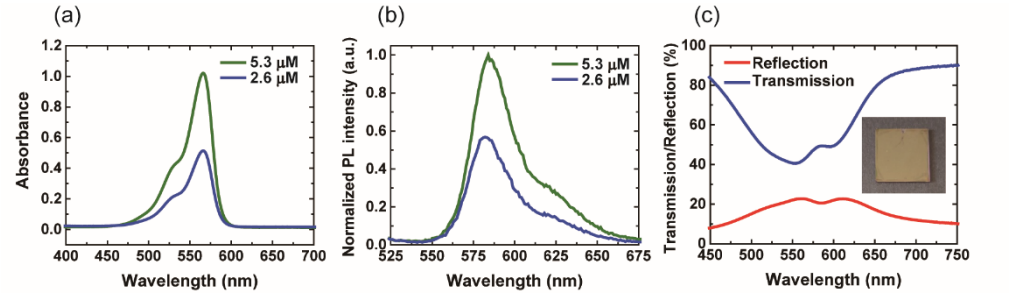

Fig. 5. (a) Absorbance spectra of monomers in a methanol solution. (b) PL spectra of monomers in a methanol solution. The PL spectrum shows a broad monomer emission band without a J-aggregate PL peak around 650 nm. (c) Measured transmission/reflection spectra of a spin-coated film from 1 wt% methanol solution (film thickness ~42 nm). The inset shows the picture of the film.

We also notice that the PL in the shorter wavelength region (575 ~625 nm) increased at the same time. To understand this behavior more clearly, we compare this PL spectrum to that from a monomer solution. We prepared two cyanine-dye solutions in methanol (2.6 μM and 5.3 μM) in which molecules do not form J-aggregates. The absorbance of cyanine-dye solutions in methanol was first measured using a spectrophotometer [Fig. 5(a)], which shows a broad monomer absorption band in the wavelength region of 500 ~600 nm. No J-aggregate absorption peak is present at 650 nm, as expected for monomers. Note that this absorbance is obtained from transmission values by Abs = $-\log_{10}(T) = -\log_{10}(I/I_0)$, where I_0 and I are incident and transmitted light intensities, respectively. We also measured PL from two cyanine-dye solutions. The PL from the methanol solutions showed a broad peak around 550 ~650 nm [Fig. 5(b)] without a J-aggregate PL peak. This suggests that, after our fs-laser irradiation, J-aggregate molecules can be dissociated into a random mixture of monomers, dimers, etc., together with J-aggregate residues, and thus monomer-region PL can slightly increase, as shown in Fig. 4, while the J-aggregate PL peak was significantly reduced.

Figure 5(c) shows the measured transmission/reflection spectra of a spin-coated film from methanol solution. The inset shows the picture of this film. Compared to the spin-coated film from water solution [Fig. 1(c)], we clearly see that there is no J-aggregate peak at 650 nm in the monomer film. We also find that the spectra look very similar to those from the laser-irradiated film [see blue curves in Figs. 3(a) and 3(b)], except that the laser irradiated J-aggregate film shows an additional peak (or dip) around 650 nm. This could be originated from residual J-aggregates after fs-laser processing. This spectral similarity between monomer and laser-irradiated films again confirms that our fs-laser processing induces the disorder of molecular stacking in J-aggregates.

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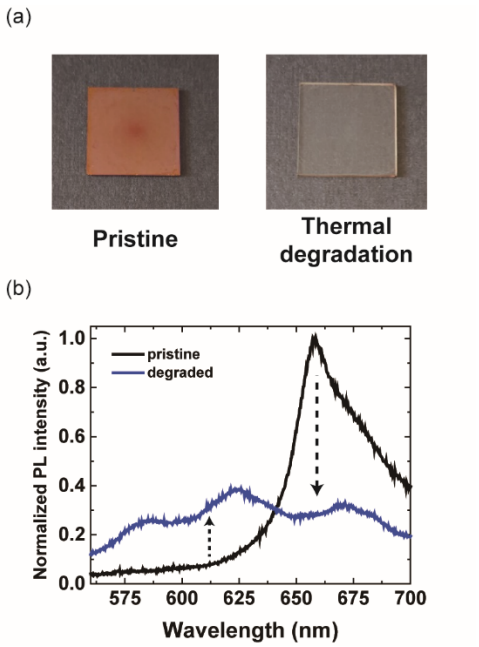

Fig. 6. (a) When a spin-coated, neat J-aggregate film is heated at 300 °C for one hour in the ambient condition, the whole film lost its metallic appearance and became transparent. (b) PL spectra before and after thermal degradation. The PL spectrum change is similar to that from fs laser patterning in Fig. 4.

Finally, we also checked PL in a thermally degraded film. In J-aggregates, monomer dye molecules are aligned parallel to the aggregation direction. It is well known that this molecular alignment is rather weak and can be agitated with heat treatment at high temperature. The spin-coated, neat J-aggregate film was heated at 300 °C for one hour in the ambient condition. Figure 6(a) compares the pictures of the original, pristine film and the degraded film. It is clearly visible that the whole film lost its metallic appearance completely and became *transparent* after thermal degradation. We measured PL before and after this thermal degradation [Fig. 6(b)], and obtained PL spectra similar to those from fs-laser processing. After thermal degradation, the J-aggregate PL peak was suppressed, while PL in the shorter wavelength region (550 ~640 nm) increased at the same time. From AFM measurements, we also found that the film thickness decreased from ~75 nm to ~56 nm. During the thermal treatment, a large part of J-aggregate molecular stacking can be dissociated into a mixture of monomer, dimer, etc. Therefore, the PL spectrum loses a sharp J-aggregate PL peak. The decreased film thickness could be also related to this change in molecular packing. This spectral change agrees well with PL from our laser-processed film and indicates that our fs-laser irradiation effectively induces changes in the molecular structure of organic excitonic films. Our studies suggest that fs-laser processing is a very effective method to modify the optical response of molecular excitonic films.

In general, fs-laser processing is known to be a 'cold' process without local heating within the material of interest, as the pulse duration under 1 ps is shorter than the heat diffusion time of most materials. In our case, all the laser writing was done at the pulse repetition of 100 kHz, which corresponds to the pulse interval to be 10 μs. We expect that this pulse interval is too long to induce any heat accumulation in the film. Moreover, in our work, the J-aggregate film has no intrinsic absorption in the near-infrared laser wavelength (1030 nm). However, we suppose that the high intensity of fs-laser pulses on the order of a few hundreds of GW/cm^2 can still induce multi-photon nonlinear absorption in the film [31–33] and this can locally induce the disorder of J-aggregate molecular stacking, resulting in a large change of

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optical response. Because the strength of J-aggregate excitonic absorption is very sensitive to the molecular alignment, relatively small changes of the molecular orientation can result in a sharp decrease of the J-aggregate absorption peak. In fact, our film has some linear absorption in the ultra-violet region (300 ~350 nm) and we also performed similar fs-laser irradiation experiments using third-harmonic pulses at 343 nm. The optical microscope image, AFM height profile, and the results of optical measurements (transmission/reflection, PL spectra) are given in Fig. 7. We find them very similar to those from the infrared irradiation results given in the main text; the strong reflection peak was suppressed and transmission dip was recovered back after irradiation. The strong J-aggregate PL peak was significantly suppressed too.

In fact, cyanine-dye J-aggregates had been considered for optical recording, and the optical response change of J-aggregate films using a *diode* laser was studied before [34,35]. However, the metallic response (Re[ε] < 0) of J-aggregate films, which is important for subwavelength field confinement and manipulation, was not considered before. Moreover, our results demonstrate that fs-laser processing can induce a significant change in the optical response, from metallic to dielectric, over a large area efficiently. Especially, our PL studies in several different samples demonstrate the effectiveness of fs-laser processing in molecular excitonic films.

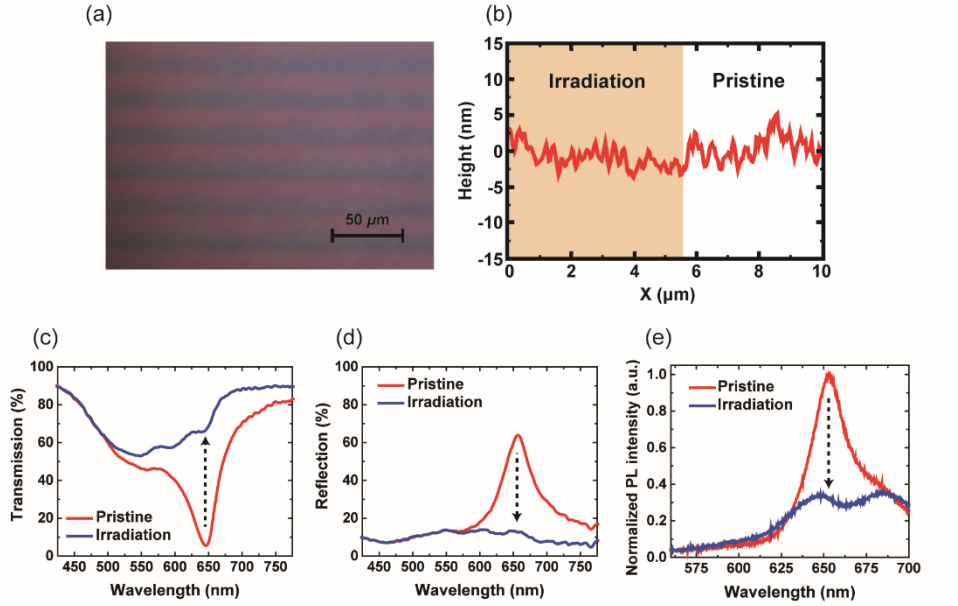

Fig. 7. Fs-laser irradiation with third harmonic pulses (343 nm): (a) The optical microscope image of a patterned film, (b) AFM height profile across a line pattern, (c) Reflection spectrum, (d) Transmission spectrum, (e) Photoluminescence spectrum.

3. Conclusions

We have demonstrated the fs-laser processing and patterning of molecular excitonic films on the centimeter scale. With proper laser irradiation conditions, J-aggregate thin films were not physically damaged but their optical response was significantly modified from metallic to dielectric. The high scan speed of fs-laser beams enabled patterning over a whole substrate. We performed various optical spectrum measurements and found that strong fs-laser fields can effectively induce the structural disorder of molecular aggregates. This disorder induces the strong modification of the excitonic absorption strength and the optical response in molecular excitonic films. Especially, we compared the PL from a laser-processed sample to that from other reference samples. Our study suggests that the optical response of molecular

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excitonic films can be significantly modified over a large area using fs-laser irradiation and this could be useful for novel nanophotonics studies.

4. Appendix

We first performed single-shot dot patterning with different pulse energies (Fig. 8). We could see the dot size increasing with larger pulse energy. Then, we conducted line patterning based on this. Figures 9(a) and 9(b) show more line patterns with different widths for 1030 nm fs-pulses; 9(a) has a line width of ~ 20 μm, while 9(b) has a line width of ~ 40 μm. Figure 9(c) shows a line pattern obtained from third harmonic (343 nm) pulses. In all line patterns, the optical spectrum change was very similar; like Figs. 3(a) and (b), a reflection peak was strongly suppressed, while transmission dip was recovered back after irradiation. Therefore, the metallic response was reduced significantly after irradiation in all patterns.

Fig. 8. Single-shot dot patterning with different pulse energies

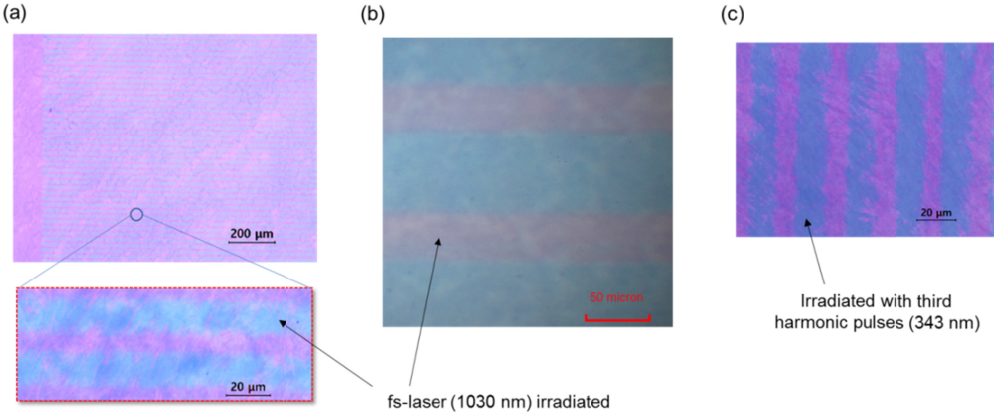

Fig. 9. Line patterns with different widths

Regarding the proper laser conditions, we tried not to involve any material removal from the film surface. Thus, the ablation threshold of the film was experimentally determined before laser exposure. Then the proper laser power was examined under 90% of the ablation threshold power. The final pulse energy and frequency we used for line patterning was 0.7 μJ

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and 100 kHz, respectively, at the beam scan speed of ~ 30 mm/s, as described in the main text. In fact, fs-laser irradiation can still induce a slight film thickness change at this condition, depending on laser focusing. For example, in Fig. 10, we used the same laser condition as Fig. 2. But, laser focusing was better than Fig. 2 and we could obtain sharper line edges [see Fig. 10(a)]. In this case, we find that the film thickness was decreased by ~ 5 nm [Fig. 10(b)]. However, the spectrum changes after irradiation [Fig. 10(c),(d)] were still very similar to Fig. 3(a) and (b). In both cases, we obtained strong optical response changes, from metallic (Re[ε] < 0) to dielectric (Re[ε] > 0).

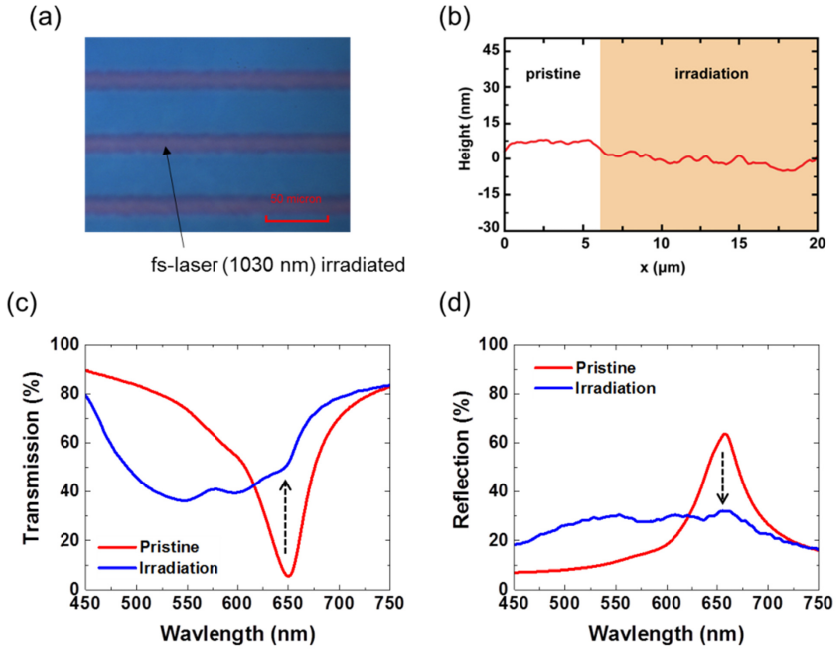

Fig. 10. Line patterning with sharper edges

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