

Materials and devices for ultrafast all-optical processing

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ABSTRACT

Molecular photonics, information processing based on strong interactions of photons and molecules, has attracted much attention, since it can fully utilize many superior properties of both photons and molecules. We have been developing materials showing ultrafast absorption changes in the visible to near infrared regions by photoinduced electron transfer and reverse reactions or by excited electronic state formation. Guided wave mode (GWM) geometry composed of a prism, a metal thin film, and a photoresponsive polymer film successfully achieved sensitive, all optical, and very fast control of reflectance by transient or persistent changes of GWM conditions by means of photoinduced complex refractive index changes upon nanosecond to femtosecond laser excitation. All-optical parallel control of reflected probe light by pump (writing) light was demonstrated by photochromic spiropyran or fulgide, and various metallophthalocyanines dispersed in appropriate polymers.

Keywords: Photoinduced changes of electronic states, photochromism, photoinduced electron transfer, guided wave mode, photoinduced complex refractive index changes, all optical and very fast control of reflectance, spiropyran, fulgide, metallophthalocyanines

1. INTRODUCTION

Novel materials, devices and systems are required for much faster data processing, much higher recording density, or much specific and efficient chemical sensing. Ultrafast switching materials which work in less than 1 picosecond (ps) are essential for terahertz (THz) communication. Several attempts have been reported for this purpose, which include optical switching by tunneling bi-quantum well semiconductors or organic nonlinear optical materials¹⁻⁸. Magnetic "hard" disks and heat-mode optical disks such as phase change or magneto-optical memories have rapidly been increasing their recording density owing to the development of new pick-up heads or blue semiconductor lasers. Organic molecules have useful optical and electronic functions which can be easily controlled by the structure, substituent, or external fields. Molecular interactions and organized molecular assemblies also can afford much higher functions than isolated or randomly-distributed molecules. Photons have many superior properties such as wavelength, polarization, phase, ultrashort pulse, or parallel processibility. Through strong interactions of molecules or molecular assemblies with photons, many superior properties of photons can be directly converted to changes in physical properties of materials such as fluorescence, absorption, refractive index, conductivity, or optical nonlinearity. Excited state formation, photochromism, photoinduced electron transfer are some examples among them. Photon-mode recording or switching based on these changes can therefore achieve ultrafast multiple or three-dimensional recording and parallel processibility with ultimate resolution at a molecular level as schematically shown in Figure 1. There will be no doubt that molecular photonics based on interactions of molecules and photons has many advantages as compared with electric or photoelectric switching, heat-mode or magnetic recording.

Rapidly expanding volume of information continuously requires the speed-up of switching and processing in optical telecommunication systems. Since silica-based optical fiber systems show minimum transmission loss at about 1350 - 1650 nm, photoresponsive materials are needed to show ultrafast absorption or refractive index changes in such near infrared (NIR) region. Many types of ultrafast optical processing devices and semiconductors or organic materials have been studied so far¹⁻⁸. Single shot demultiplexing of 1 THz light pulses was proposed on the basis of transient bleaching of organic dye J-aggregate films³⁻⁵. Single-walled carbon nanotubes are also expected for ultrafast optical switching in the NIR region⁶⁻⁸. All of them employ transient bleaching of NIR absorption at the ground state. We proposed all-optical spatial light modulation and parallel switching based on photoinduced complex refractive index changes in guided mode geometry⁹⁻¹⁷. Both transient bleaching and absorption type materials can be used in this system. It will contribute a great deal to achieve THz communication if ultrafast photoresponsive materials that work in less than one picosecond (ps) in the NIR region are developed. We have also been developing ion-pair charge-transfer (IPCT) complexes showing the photoinduced absorption due to photoinduced electron transfer and reverse reactions between redox-active ion-pairs¹⁸⁻²³.

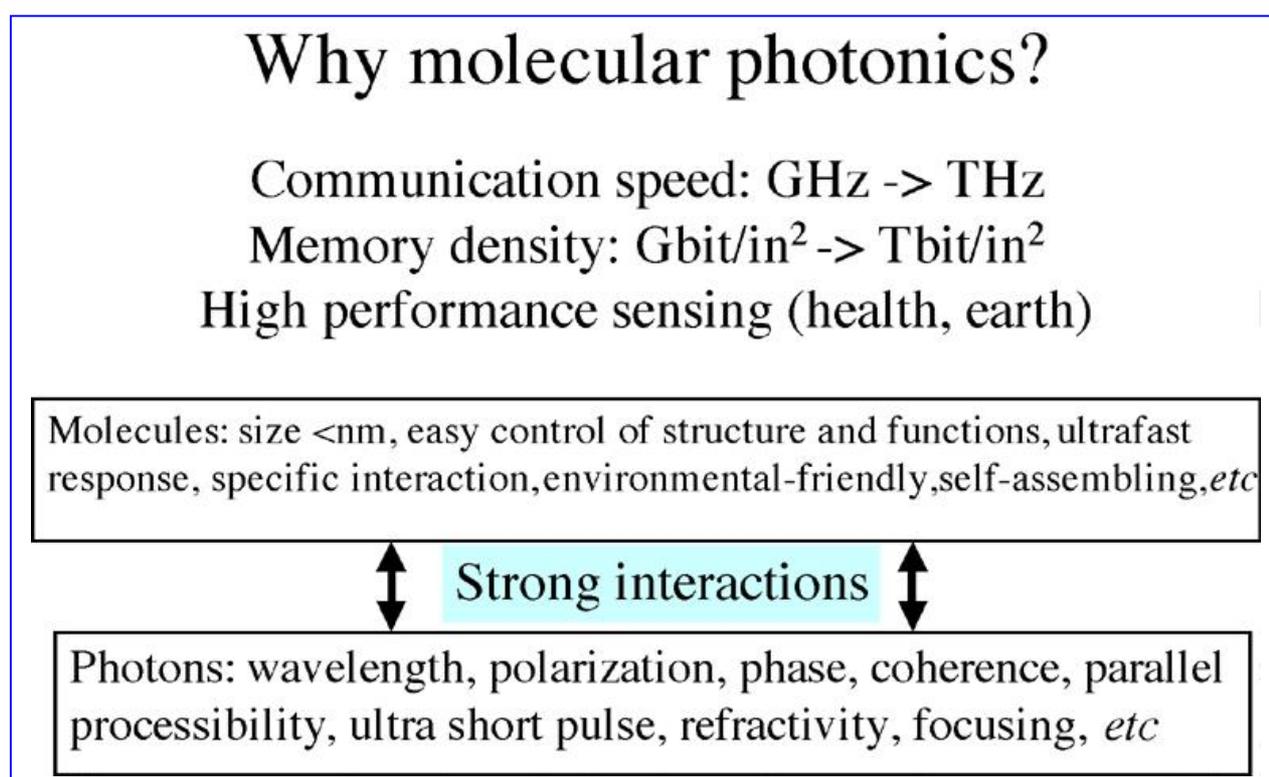


Figure 1: Why can be achieved by molecular photonics?

We have been making efforts to develop new molecular photonics materials and devices by making various organized molecular systems and by optically controlling their electronic states as schematically shown in Fig. 1⁹⁻²³. So far we have achieved photoinduced electrochromism which is color changes due only to the photoinduced electron transfer and reverse reactions, molecular control of the lifetime and wavelength of colored species over extremely wide ranges, amplified fluorescence quenching in LB films, photon-mode super-resolution (PSR) to exceed the diffraction limit of light in optical memory based on transitory photobleaching of phthalocyanine derivatives, ultrafast all-optical two-dimensional control of reflectance and parallel optical self-holding switch based on photoinduced complex refractive index changes. A spatial light modulator (SLM) is a device to two-dimensionally control the intensity or the phase of reading light by another (writing) light, which plays an essential role in a projection TV, wavefront correction and an optical correlator. In the present article, some of our recent achievements will be discussed.

2. EXPERIMENTAL

2.1 Materials

The structures and abbreviations of typical photoresponsive materials employed in the present experiment are shown in Figure 2. Indolyfulgide is a photochromic compound, both forms of which are thermally stable. Another photochromic compound, spiropyran (SP), was also used, in which the colored form is not thermally stable. PFVX is a polymer containing a chromophore showing absorption changes in the visible and optical telecommunication wavelength regions due to photoinduced electron transfer and reverse reactions between ion pairs. The lifetime due to reverse reaction was controlled by the counter anion from 0.24 ps with iodide to infinity with tetraphenylborate (TPB)^{23,24}. Copper phthalocyaninetetrasulfonate (CuPcS) is water-soluble phthalocyanine, the excited triplet state was used for optical modulation. Photoresponsive compounds except PFVX were dispersed with polymers in appropriate solvents, polystyrene (PS), Arton (JSR, Co. Ltd.), or polyvinylalcohol (PVA) with a weight ratio (photoresponsive compound:polymer) of 1:2 - 1:50. These polymers and PFVX were spin-coated on a glass slide covered with a vacuum evaporated silver thin film (50 nm) to form 260-580 nm thick film. Glass slides with thin polymer films were index-matched with a BK7 prism and set on a rotating stage.

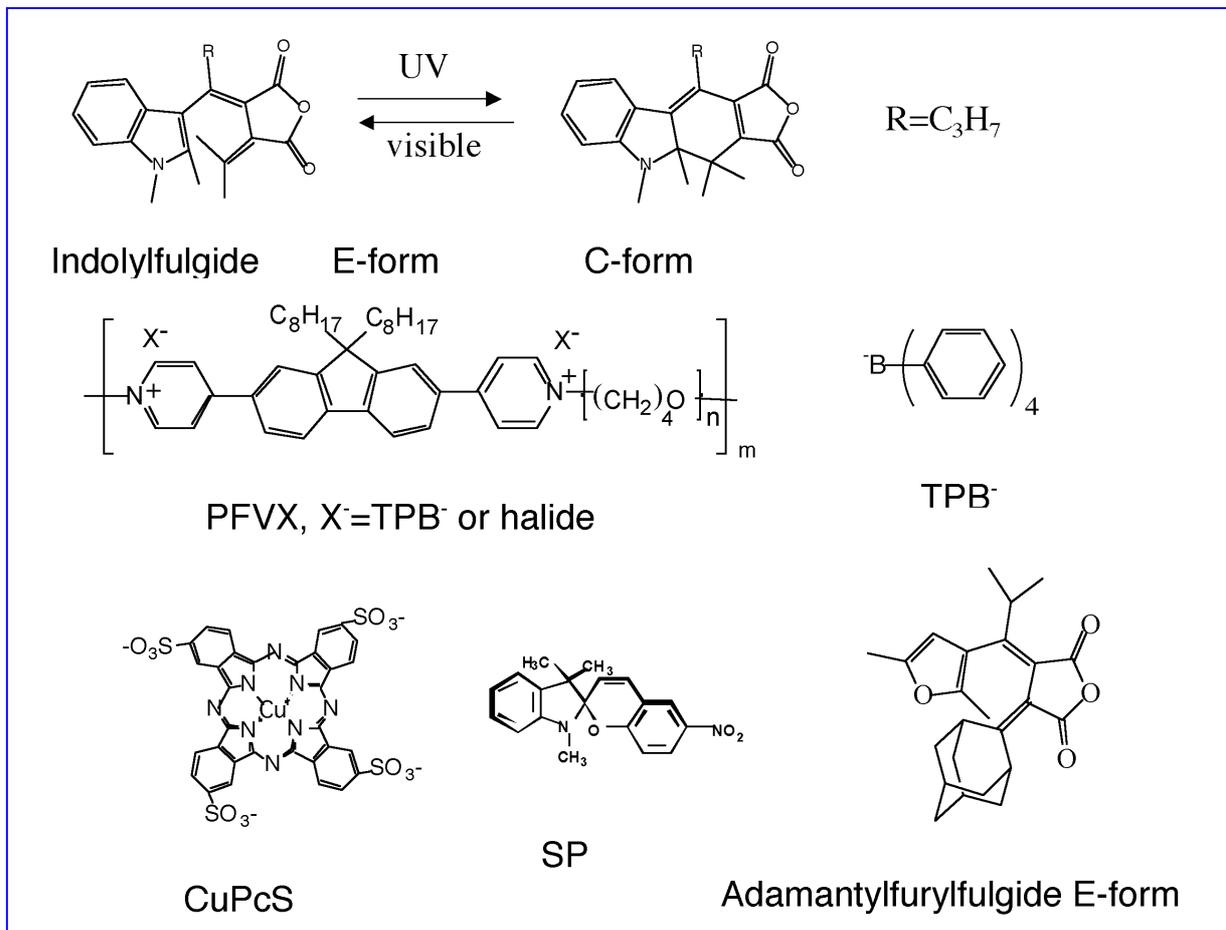


Figure 2 The structures and abbreviations of photoresponsive materials employed in this study.

2.2 Measurements

Reflectance as a function of incident angle was measured at several wavelength using a tunable He-He laser as a probe. Excitation was made by femtosecond (fs) laser at 400 nm and nanosecond (ns) laser at 355 or 670 nm. Femtosecond white light was used as a probe in the system as schematically shown in Figure 3. Transient absorption measurements

were made by a pump-probe method with fs white continuum or NIR light from OPA (optical parametric amplification) as a probe upon excitation at 400 nm²⁵. Amplified Ti-sapphire laser delivered pulses of about 50 fs at the repetition rate of 1 kHz and 1.4 mJ at 800 nm. The probe beam was split by a beam splitter into two beams, which were balanced for two detectors in order to improve the signal-to-noise ratio²⁵.

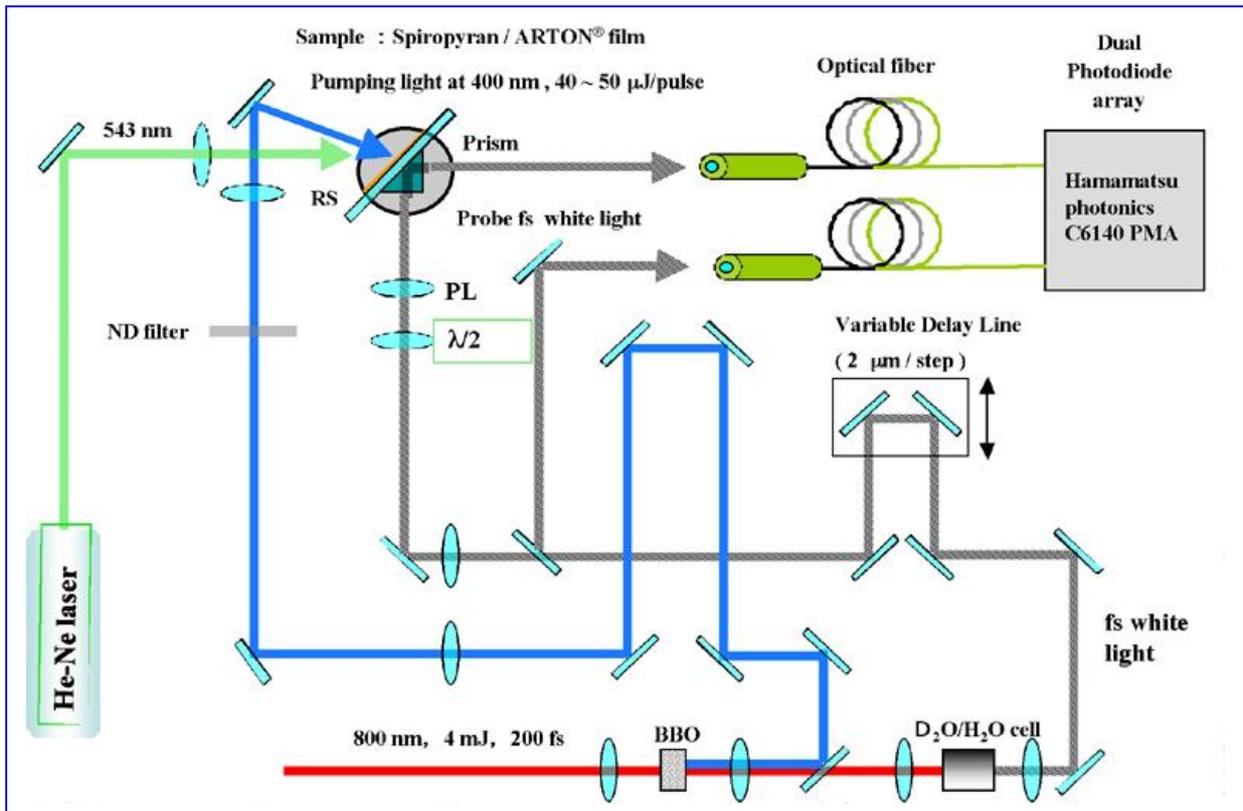


Figure 3 A schematic representation for all-optical recording or modulation by femtosecond laser excitation.

2.3 All-optical reflectance control by guided wave geometry

The principle and a schematic representation of the present GWM device are given in Figure 4. The calculated reflectance is shown in Figure 4A for the guided wave geometry with a polymer film (750 nm) on a silver layer (50 nm), in which the formation of three guided wave modes was found at the incident angle of 72.20, 57.92, and 43.26 degrees, respectively. Examples are also shown in Figure 4B for three values of complex refractive indices calculated by the transfer matrix method. This figure shows that a small imaginary or real part of complex refractive index of a polymer film greatly increases the reflectance at the guided mode resonance angle or shifts the GWM dip angle. It is very easy to cause transient or persistent absorption changes upon photoexcitation by various mechanisms such as excited state formation, photoinduced electron transfer, or photochromism. Since the changes in the imaginary part and the real part of complex refractive index are not independent, or are controlled by the Kramers-Kronig relationship, we can easily achieve real and/or imaginary parts changes depending on the wavelength and materials. These results indicate that very fast light modulation, all-optical recording or switching as schematically shown in Figure 4C is possible at the incident angle corresponding to such guided mode resonance under appropriate combination of a pump (writing) beam, a probe (reading) beam and a dye in the guided wave geometry based on transient or persistent absorption changes due to various mechanisms. The rise time will be fs order, in principle, and the fall time can be controlled over ps to ms depending on the nature of photogenerated transient species.

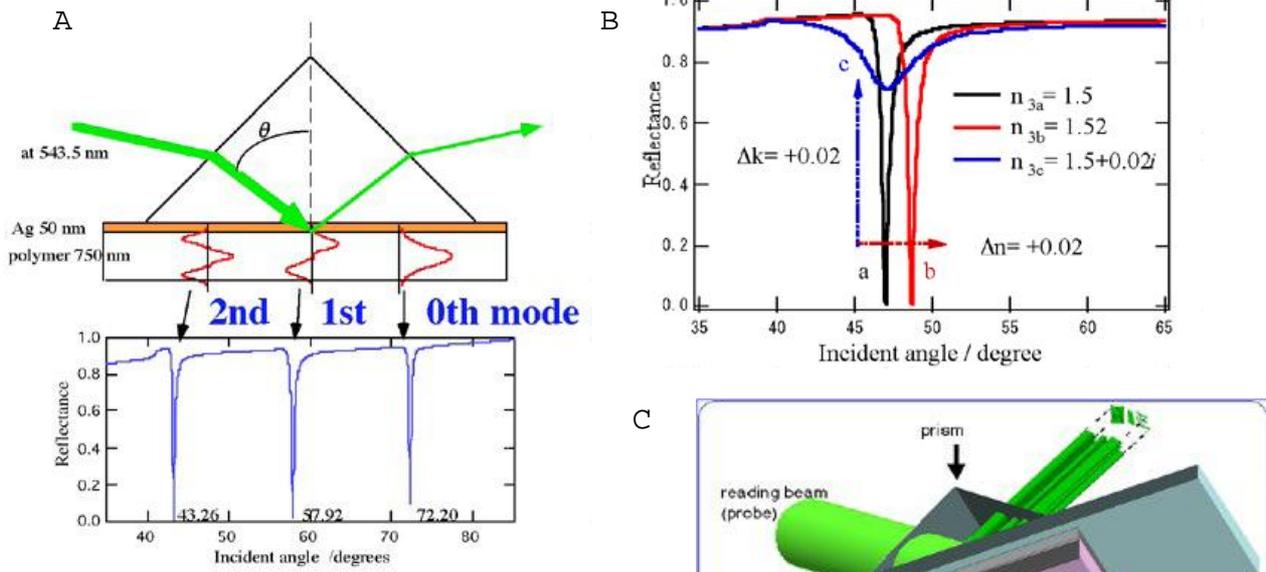


Figure 4 A schematic representation of the present GWM device and its principle. Formation of GWMs for a 750 nm thick polymer film on a 50 nm silver film at 543.5 nm and examples of incident angle dependence of reflectance by complex refractive index changes.

3. RESULTS AND DISCUSSION

3.1 Parallel optical recording

Indolyfulgide and adamantylfurylfulgide were used as thermally stable photon-mode recording and erasing materials in the GWM geometry. Absorption spectra are shown in Figure 5 for the E- and C-forms of indolyfulgide. The extinction coefficient change estimated from the absorption spectrum change observed in Figure 4 and the film thickness is shown in Figure 6 together with the refractive index change estimated from Δk by the Kramers-Kronig relationship.

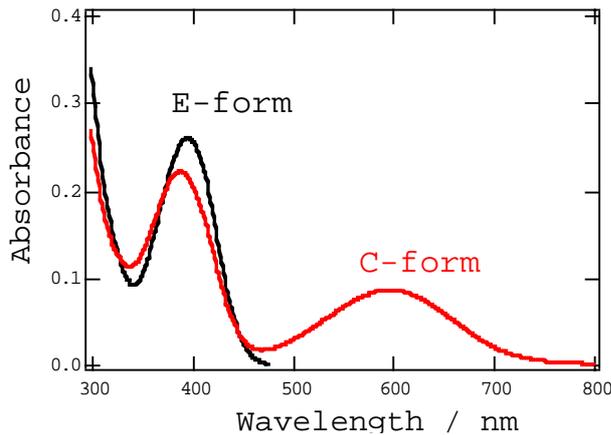


Figure 5 Absorption spectra of both forms of indolyfulgide

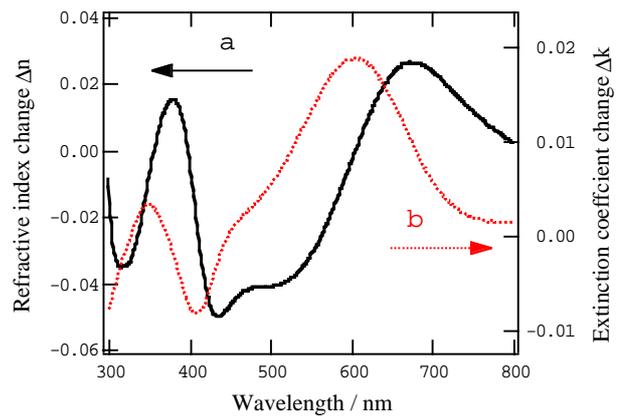


Figure 6 Wavelength dependence of Δk and Δn for indolyfulgide upon photochromism

It is shown in Figure 6 that a broad spectral range can be used for all-optical recording or switching in the present GWM geometry. The observed incident angle dependences of reflectance at 543-633 nm of He-Ne laser and at 690 nm of diode laser are shown in Figure 7. Very sharp dips due to the GWM were observed, which shifted to a smaller incident

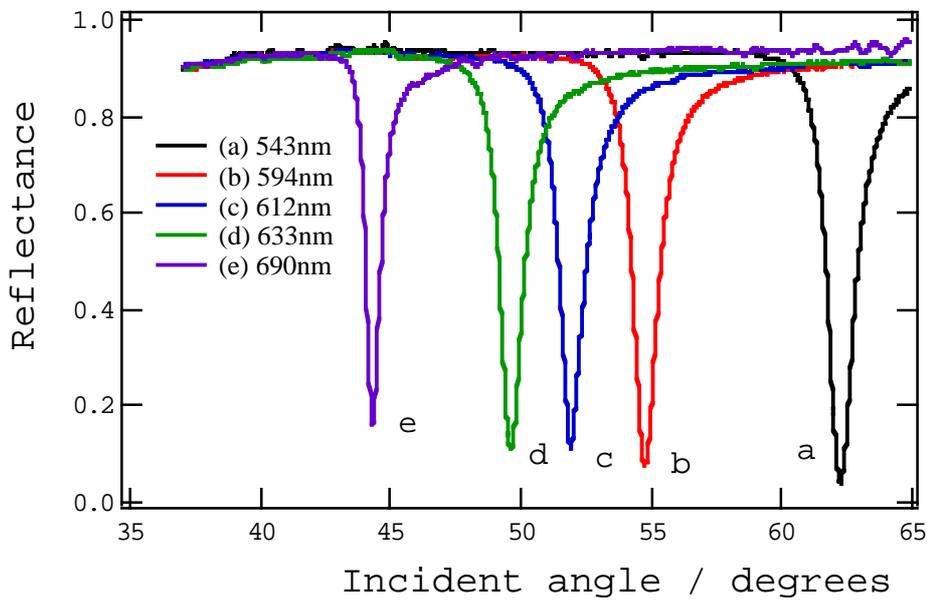


Figure 7 Incident angle dependences of reflectance at various wavelength for 582 nm thick Arton film containing indolylfulgide (33 wt%) spin-coated on a silver film (50 nm).

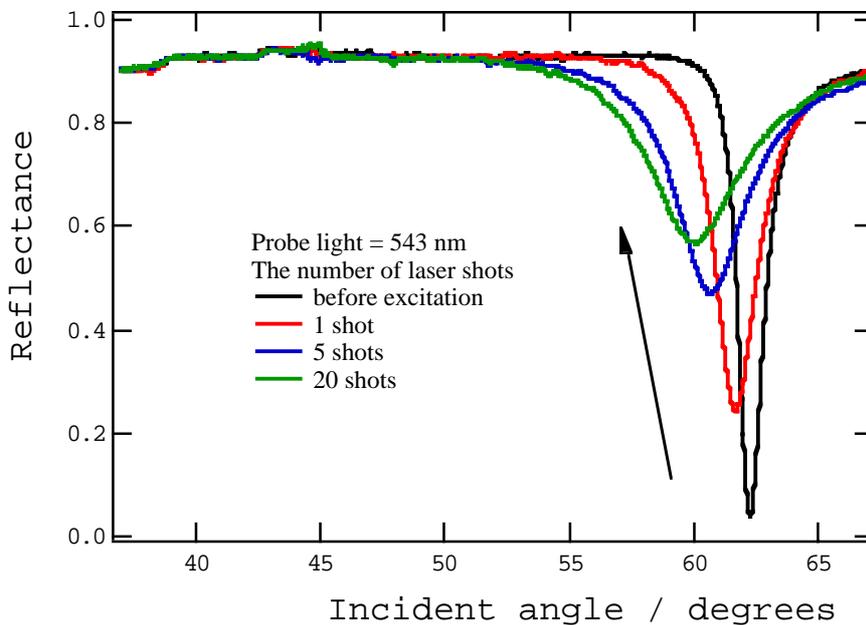


Figure 8 Incident angle dependences of reflectance at 543 nm for GWM geometry in Fig. 7 before and after ns laser excitation at 355 nm.

angle side as expected by increasing the wavelength of the probe light. A little shallower dip at 690 nm is due to less quality of the laser diode beam as compared with the He-Ne laser. Figure 8 shows the incident angle dependences of reflectance at 543 nm for GWM geometry in Fig. 7 before and after ns laser excitation at 355 nm. The dip reflectance increased and the dip angle shifted to a lower side by photochromism from E-form to C-form upon excitation at 355 nm. Incident angle dependences of reflectance at 612 nm for GWM geometry in Fig. 7 before and after ns laser excitation at 355 nm are shown in Figure 9, which indicates the reflectance value increased with no changes of the dip angle. Figure

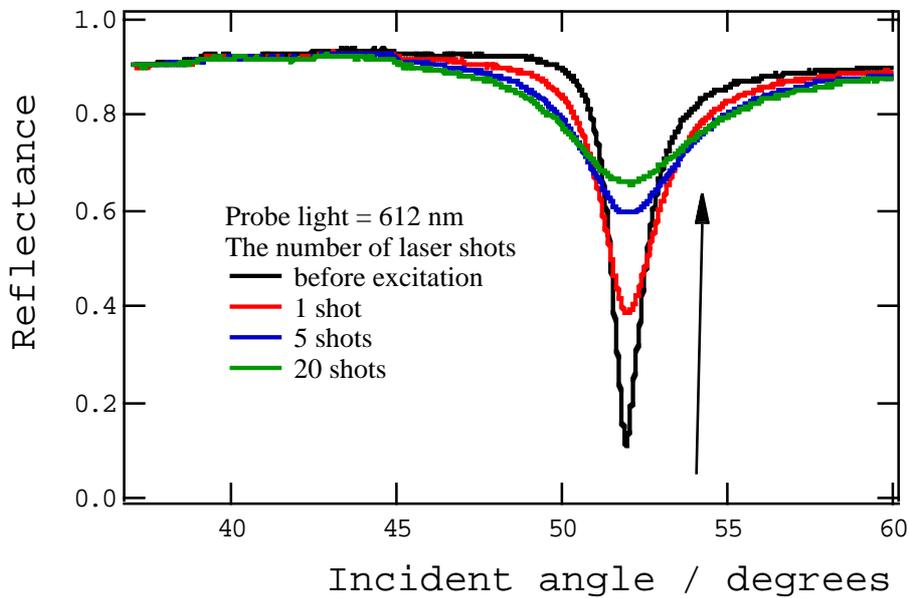


Figure 9 Incident angle dependences of reflectance at 612 nm for GWM geometry in Fig. 7 before and after ns laser excitation at 355 nm.

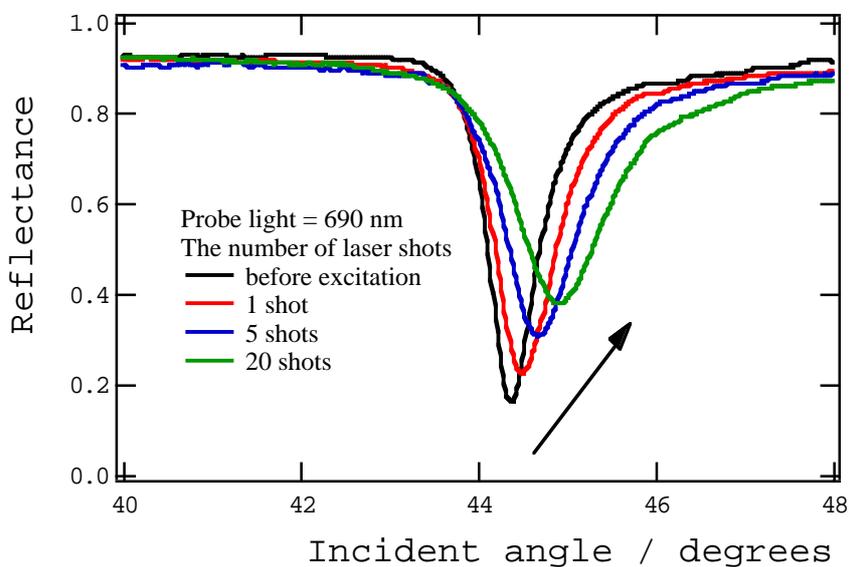


Figure 10 Incident angle dependences of reflectance at 690 nm for GWM geometry in Fig. 7 before and after ns laser excitation at 355 nm.

10 shows the incident angle dependences of reflectance at 690 nm for GWM geometry in Figure 7 before and after ns laser excitation at 355 nm. At this wavelength the dip shifted to higher angle side and the reflectance at the dip angle increased with increasing the number of laser shots at 400 nm. These very different behavior simply reflected the sign and the magnitude of Δn and Δk of the photoresponsive layer containing indolyfulgide, which actually well corresponded with the results shown in Figure 6; $\Delta n < 0$, $\Delta k > 0$ at 543 nm, $\Delta n = 0$, $\Delta k > 0$ at 543 nm, $\Delta n > 0$, $\Delta k > 0$ at 543 nm, respectively. We can select the wavelength where only refractive index Δn changes.

Similar reversible changes of reflectance were achieved by adamantylfurylfulgide dispersed in Arton in GWM geometry upon ns laser excitation at 355 nm and 532 nm. Figure 11 shows the incident angle dependence of reflectance by a single shot of laser at 355 nm (ON) and 532 nm (OFF). Repeated reflectance changes upon ns laser excitation at 355 nm and 532 nm at the incident angle of 50.4 degrees at 612 nm are shown in Figure 12, which indicated the present system can be used as a single shot image memory for both recording and erasing. Superior properties of fulgides such as repeated durability, thermal stability, absorption at the second and the third harmonics of YAG laser are can fully utilized in the present GWM geometry.

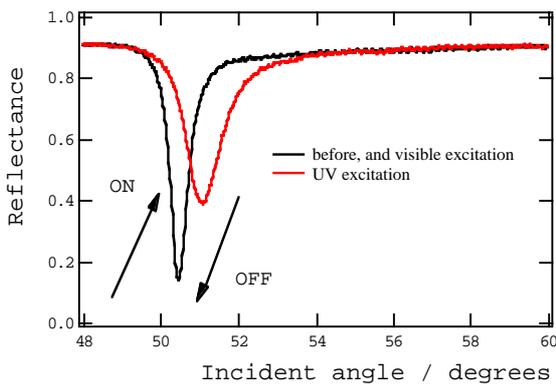


Figure 11 Incident angle dependence of reflectance by a single shot of laser at 355 nm (ON) and 532 nm (OFF).

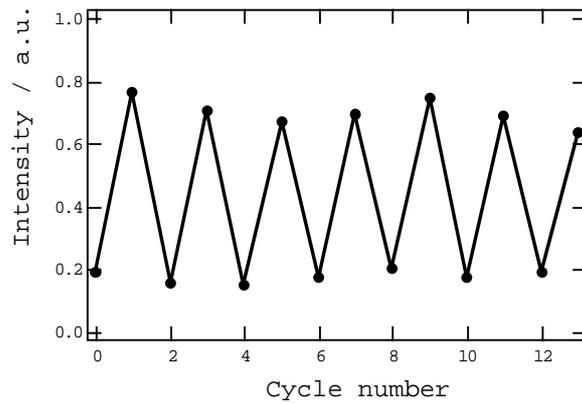


Figure 12 Repeated reflectance changes upon alternative ns laser excitation at 355 nm and 532 nm at the incident angle of 50.4 degrees at 612 nm.

The spatial resolution of the present GWM device is better than about 3 μm as shown in Figure 13 by the image written through a USAF Test Target as a mask upon a single shot of ns 355 nm laser (1 mJ/pulse) for a spiropyran-doped PS film deposited on a silver film. The reflectance changes are compared in Figure 14 for the GWM geometry and the ATR geometry for the same spiropyran-doped PS film with and without a silver film. The sensitivity is clearly shown to be much higher in the present geometry. With a single shot of ns 355 nm laser, the reflectance increased by 16.4 times in the GWM geometry, whereas it decreased by 0.67 times in the ATR geometry through twice transmission. The relative sensitivity in this case was concluded to be more than 20 times higher in the present GWM geometry.

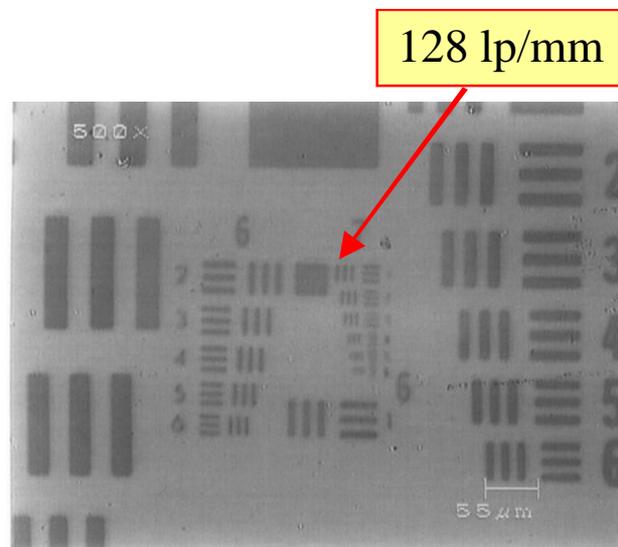


Figure 13 A microscopic picture of an image written through a USAF Test Target as a mask upon a single shot of ns 355 nm laser for a spiropyran-doped PS film deposited on a silver film.

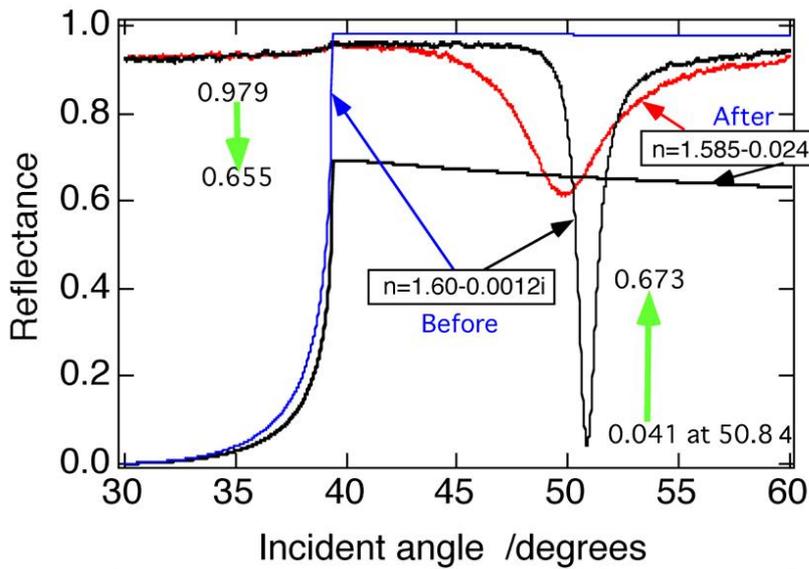
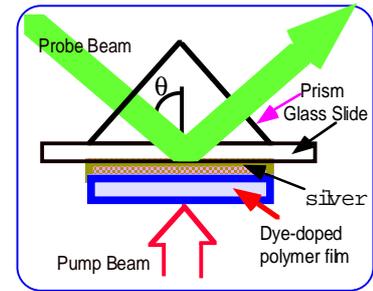
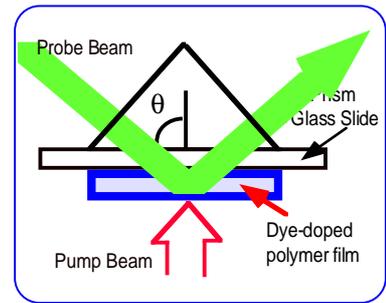


Figure 14 Comparison of reflectance changes in the GWM and ATR geometry for spiropyran in polystyrene film with and without a silver layer upon a single shot ns laser excitation at 355 nm.



Guided wave mode



ATR method

GWM formation and its optical control were then studied by fs white light upon fs laser excitation at 400 nm for writing (ON) and He-Ne laser excitation for erasing (OFF) in the pump-probe arrangement as schematically shown in Figure 3. The GWM dip was actually observed in the fs white as shown in Figure 15, for example, at 626 nm in the same GWM geometry as studied by ns laser excitation. The dip angle shifted to longer wavelength side with increasing the incident angle as shown in Figure 15 – Figure 18, which clearly indicated the observed dip is due to the formation of the GWM. Upon fs laser excitation at 400 nm, the dip angle and/or dip reflectance changed depending on the incident angle and returned to the almost original value upon He-Ne laser excitation at 594 nm for reverse photochromism from the C-form to the E-form. At the incident angle of 48.9 degrees, almost “vertical” changes were observed for the dip at 626 nm as shown in Figure 16, which corresponded to the results shown in Figure 9. The dip observed at 528 nm at the incident

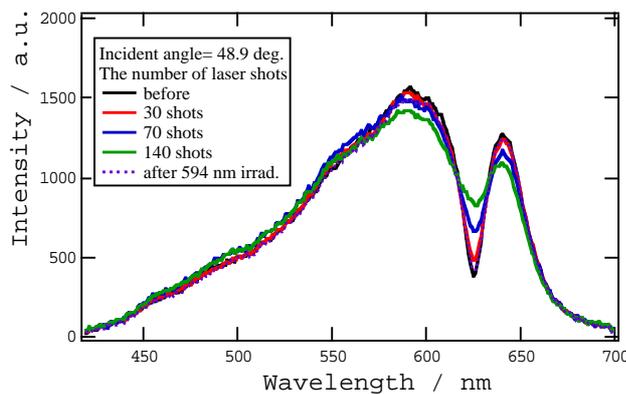


Figure 15 Femtosecond white light spectra reflected from GWM Arton film containing indolyfulgide spin-coated on a silver film before and after fs laser excitation at 400 nm for writing (ON) and He-Ne laser excitation for erasing (OFF) at the incident angle of 48.9 degrees

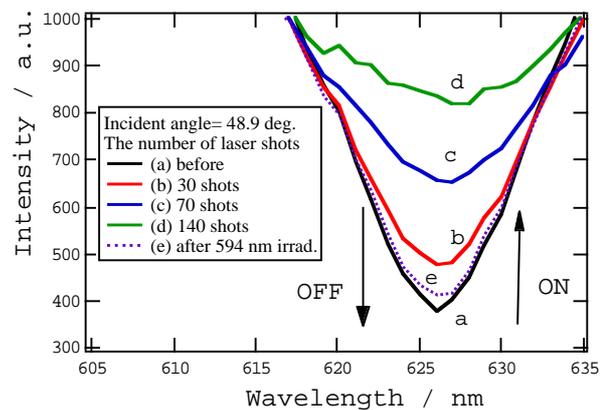


Figure 16 Expanded representation of the reflected fs white light spectra shown in Figure 15 at the incident angle of 48.9 degrees.

angle of 61.9 degrees shifted to a shorter wavelength side accompanying the reflectance increase during photochromism from the E-form to the C-form, while at 43.76 degrees the dip observed at 710 nm shifted to a longer wavelength side. All these changes well corresponded to complex refractive index changes by photochromism of indolyfulgide as shown in Figure 6. The present results strongly suggested a proper combination of ultrafast photoresponsive materials with the present GWM geometry can achieve all-optical, highly sensitive, ultrafast, and parallel recording or switching.

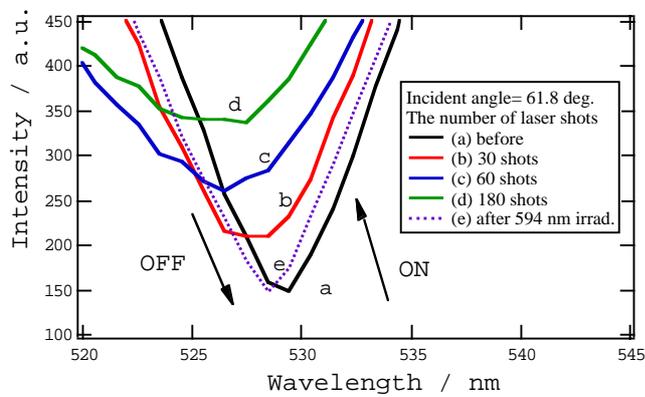


Figure 17 Part of the reflected fs white light spectra for GWM Arton film containing indolyfulgide spin-coated on a silver film before and after fs laser excitation at 400 nm for writing (ON) and He-Ne laser excitation for erasing (OFF) at the incident angle of 61.8 degrees.

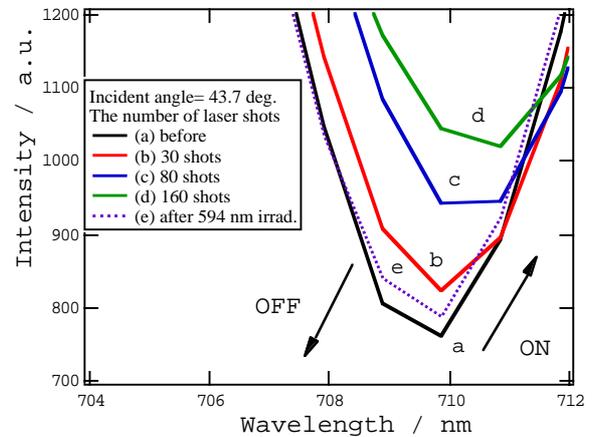


Figure 18 Part of the reflected fs white light spectra for GWM Arton film containing indolyfulgide spin-coated on a silver film before and after fs laser excitation at 400 nm for writing (ON) and He-Ne laser excitation for erasing (OFF) at the incident angle of 43.76 degrees.

3.2 Ultrafast photoresponsive polymer in the optical telecommunication wavelength region

As one of the promising candidates to achieve ultrafast photoresponses in the optical telecommunication wavelength region, we newly designed compounds by making transitory expansion of a π -electronic system with photoinduced electron transfer and reverse reactions between redox-active ion-pairs as schematically shown in Figure 19. Upon photoinduced electron transfer from a counter anion, strong absorption in the NIR region can be observed if a π -molecular orbital for an unpaired electron is considerably extended in photogenerated radical cations. Due to thermodynamic driving force, very fast reverse electron transfer reaction will occur to an oxidized counter anion to form an original less delocalized π -electronic system. It is thus possible to control ultrafast photoresponse without changes of chemical bond or conformation and also to achieve high stability against repeated laser excitation. We have synthesized monomeric and polymeric 2,7-bis(4-pyridiniumyl)fluorene (abbreviated as FV²⁺ and PFV²⁺) salts. 2,7-Bis(4-pyridinyl)fluorene was synthesized by a cross-coupling reaction between 2,7-dibromofluorene and (4-pyridyl)trimethyltin²⁶. A polymer containing 2,7-bis(4-pyridiniumyl)fluorene ion as a part of the main chain shown in Figure 2 was prepared from tetrahydrofuran (THF) in a similar manner as reported previously for a polymer containing 4,4'-bipyridinium unit²⁵. The content of 2,7-bis(4-pyridiniumyl)fluorene units in this polymer was determined to be 5.2×10^{-4} mol/g ($n = 17$) from its absorption spectrum.

Figure 20 shows the absorption spectra for a cast film of its tetraphenylborate (TPB⁻) salt before and after steady photoirradiation with a Xe-Hg lamp for 15 min through a band pass filter ($\lambda_{ex} = 405$ nm) at room temperature. The PFV²⁺(TPB⁻)₂ film was overcoated by a protective layer of poly(vinyl alcohol) to avoid the reaction of oxygen with photogenerated radicals. TPB⁻ is well known to be decomposed after one-electron oxidation and works as a sacrificial donor in photoreactions. In addition to new absorption in the visible region, fairly strong and broad absorption was observed with peaks at 1400 and 1830 nm as shown in Figure 20. The absorption spectrum gradually decayed and entirely disappeared in several hours after stopping photoirradiation most probably due to coupling reaction of radicals or the electron transfer reactions from radical cations to a small amount of oxygen remained in the film or in solutions. FV²⁺(TPB⁻)₂ in 1,2-dimethoxyethane (DME, 0.4 mM) also showed similar spectral changes as those of PFV²⁺(TPB⁻)₂ in

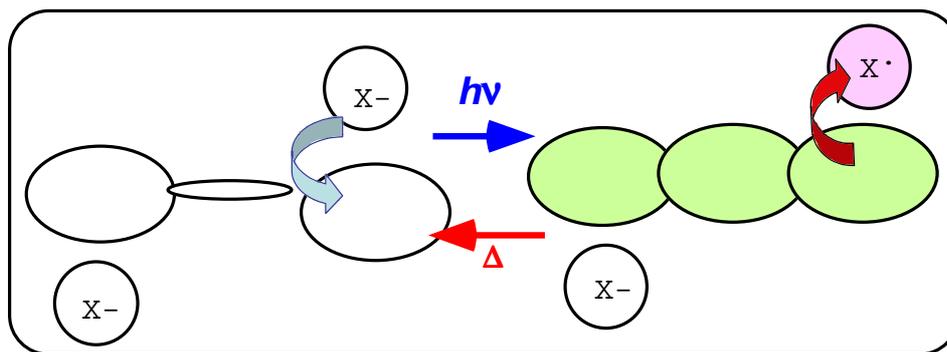


Figure 19 Schematic representation for transient absorption in the near infrared region by photoinduced electron transfer and reverse reactions due to transitory expansion of a π -electronic system.

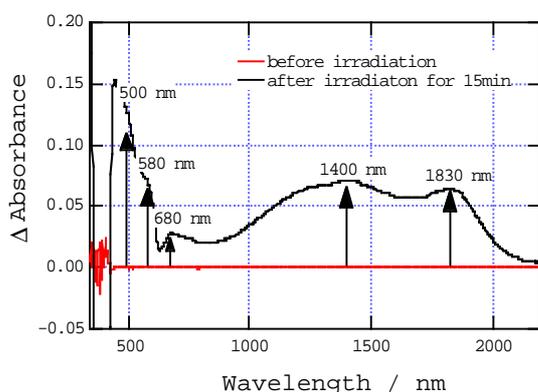


Figure 20 Absorption spectra of a $PFV^{2+}(TPB)_2$ cast film before and after photoexcitation by a Xe-Hg lamp at 405 nm in degassed conditions.

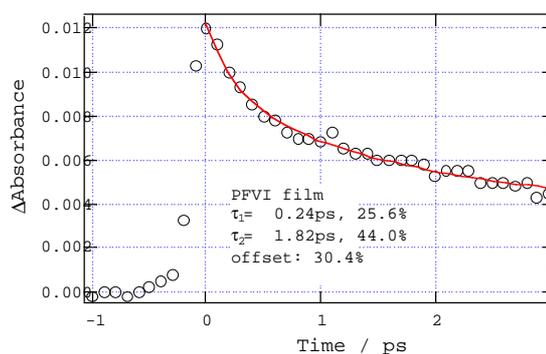


Figure 21 Time dependence of transient absorption at 1380 nm for a spin-coated film of $PFV^{2+}(I)_2$ upon excitation with 50 fs laser at 400 nm.

degassed condition. Well-resolved hyperfine structure with at least 19 peaks was observed in the Electron Spin Resonance spectrum of $FV^{2+}(TPB)_2$ in DME after irradiation at 405 nm. It was clearly assigned to 2,7-bis(N-octyl-4-pyridiniumyl)-9,9'-dioctylfluorene radical cations from comparison with the simulated spectrum by the use of hyperfine coupling constants corresponding to extensive delocalization of an unpaired electron through whole aromatic rings of a FV^+ radical. Newly observed absorption spectra in Figure 20 were thus concluded to be attributed to radical cations (PFV^+), which were formed by photoinduced electron transfer from TPB^- as a sacrificial donor anion. From comparison of electronic absorption spectrum of these radicals after molecular orbital calculation, the visible and NIR absorption bands were assigned to the short and long axes transitions, respectively.

Figure 21 shows the time dependence at 1380 nm for a spin-coated film of iodide salts showing no absorption changes upon steady irradiation, $PFV^{2+}(I)_2$. Transient absorption showing a peak around 1400 nm reached a maximum within 100 fs after laser excitation. It was assigned to 2,7-bis(4-pyridiniumyl)fluorene radical cations formed by the photoinduced electron transfer from counter anions, I^- . Reverse electron transfer gave very fast decay of transient absorption which was fitted double-exponentially in a 10 ps time range to yield a fast component (0.24 ps, 25.6%), a slow component (1.82 ps, 44.0%) and an offset. No accumulation of absorption was observed during repeated fs excitation at 1 kHz. The decay was single-exponential with a lifetime of 57 ps in methanol solution. Observed multi-component decay will thus reflect the distribution of distance and/or orientation of ion pairs in solid films. Efforts are being made to decrease components with longer lifetime by using less polar solvents and annealing. Almost the same decay profile was observed in the second pump-probe measurement which was made after about 400,000 laser shots during the first decay experiments. This polymer film was thus demonstrated to be very stable against repeated fs laser

excitation due to fast dissipation of an excited state by electron transfer between ion-pairs. Similar ultrafast responses were observed at whole NIR wave region studied, 1050-1550 nm. We previously reported the polymeric 4,4'-bipyridinium iodides salts showed color changes in the visible region with $\tau = 1.2$ ps for cast films of IPCT complexes¹⁹. The present result clearly demonstrated ultrafast dynamics in the optical telecommunication wavelength region by single electron transfer in IPCT complexes. Thus, polymeric 2,7-bis(4-pyridiniumyl)fluorene salts with redox-active anions showed remarkably strong and ultrafast absorption changes in the 1000-2000 nm region due to photoinduced electron transfer reaction. The thermal reverse reaction was controlled over an extremely broad range by counter anions from fs order for I⁻ to infinity for TPB⁻. The fastest OFF response time of 0.24 ps was achieved by I⁻-salts of PFV²⁺ in spin-coated films as shown in Figure 21.

4. CONCLUSION

Materials and devices were proposed for ultrafast all-optical data processing, molecular photonics. Single shot all-optical memory and ultrafast all-optical switching can be achieved by the present GWM device by appropriate combination with various photoresponsive materials.

5. ACKNOWLEDGEMENTS

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