Ultrafast photoresponsive materials and molecular photonics applications by guided wave mode geometry

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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 developed polymeric materials showing ultrafast absorption changes in the visible to near-infrared regions including the telecommunication wavelength by photoinduced electron transfer and reverse reactions between substituted pyridinium and its counter anion. By selecting the counter anion we succeeded in making steady and ultrafast absorption changes. Time-resolved absorption and fluorescence spectroscopy upon femtosecond laser excitation revealed reaction mechanism and ultrafast dynamics. In order to fully utilize such photoresponses in molecular photonics, we proposed guided wave mode (GWM) device composed of a prism, a low refractive index polymer film, and a photoresponsive polymer film. The reflectance in this GWM is controlled by many factors such as thickness values and complex refractive indices of two polymer layers as well as an incident angle and wavelength. We successfully achieved sensitive, all optical, and very fast control of reflectance by means of photoinduced complex refractive index changes upon femtosecond laser excitation.

Keywords: Electronic states of molecules; Molecular photonics; Photoinduced electron transfer; Guided wave mode; Photoinduced complex refractive index changes; All optical and very fast control of reflectance; Femtosecond laser; Molecular photonics; Low refractive index polymer

1. Introduction

Novel materials, devices and systems are required for much faster data processing, much higher density of recording, or much specific and efficient chemical sensing. Ultrafast switching materials which work in less than 1 ps are essential for teraherz (THz) communication. Several attempts have been reported for this purpose, which include optical switching by tunneling bi-quantum well semiconductors or organic materials [1–14]. Organic molecules have many 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 and 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 Fig. 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
Molecular photonics

Molecules: size <nm, easy control of structure and functions, ultrafast response, specific interaction, environmental-friendly

Photons: wavelength, polarization, phase, coherence, parallel processibility, ultra short pulse, refractivity, etc

Strong interactions

All-optical information processing, modulation, photon-mode memory.

Social demands (rapid progress of information society, advanced age society, world-wide environmental problems) for:
Higher communication speed: switching, memory
Fast, accurate identification: recognition and verification
Higher performance chemical sensing: for health, earth

Fig. 1. Schematic representation of molecular photonics.

telecommunication systems. Since silica-based optical fibers which are employed worldwide in such systems show minimum transmission loss at about 1260–1675 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 far [1–14]. Single shot demultiplexing of 1 THz light pulses was proposed on the basis of transient bleaching of organic dye J-aggregate films [3–6]. Single-walled carbon nanotubes and expanded porphyrin derivatives are also expected for ultrafast optical switching in the NIR region [7–10]. All of them employ transient bleaching of NIR absorption at the ground state. We have been developing ion-pair charge-transfer (IPCT) complexes showing transient absorption in the visible to NIR region due to photoinduced electron transfer and reverse reactions between redox-active ion-pairs [11–14]. Very recently we made a preliminary report on synthesis and responses of fluorene-containing redox polymer, which showed new absorption up to 2000 nm by photoinduced electron transfer from a counter anion. As a monomeric model, 2,7-bis(N-octyl-4-pyridiniumyl)-9,9-dioctylfluorene abbreviated as FVX before and after photoinduced electron transfer from a counter anion from 0.24 ps for lifetime due to reverse reaction was controlled by the transfer and reverse reactions between ion pairs. The lifetime due to reverse reaction was controlled by the counter anion from 0.24 ps for X = iodide to infinity for X = TBP− as previously reported [14]. PFVX contains a redox active 2,7-bis(4-pyridiniumyl)fluorene chromophore by 5.2 × 10−4 mol/g (n = 17) as part of the main chain showing absorption changes in the visible to 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 for X = iodide to infinity for X = TBP− as previously reported [14]. PFVX was spin-coated on a glass slide covered with a low refractive index polymer, Cytop (Asahi Glass, Co. Ltd.) 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.

Fig. 2. Structure of photoresponsive polymer PFVX and a monomer model FVX employed, where X represents counter anions.
2.2. Measurements

The PFV(TPB) film was overcoated by a protective layer of poly(vinyl alcohol) to avoid the reaction of oxygen with photogenerated radicals. Steady photolysis was made in films and in deaerated solutions with a 150 W Hg–Xe lamp through a band pass filter at 405 nm. Absorption and fluorescence spectra were measured with Hitachi U-4100 spectrophotometer and F-4500 fluorescence spectrophotometer, respectively. Reflectance as a function of incident angle was measured at several wavelength using a tunable He–Ne laser as a probe. Transient absorption and reflectance measurements were made by a pump-probe method as schematically shown in Fig. 3 with fs white continuum generated by focusing fs 800 nm light into D$_2$O/H$_2$O mixture or carbontetrachloride as a probe and fs 400 nm light as a pump. Amplified Ti–sapphire laser delivered pulses of about 200 fs at the repetition rate of 10 Hz and 3.4 mJ at 800 nm. The probe light was split by a beam splitter into two beams, which were detected with a dual silicon photodiode array in the visible region or with two InGaAs photodiode arrays in the NIR region. Fluorescence lifetime was measured by a streak camera upon 2 ps laser excitation at 400 nm. Electron spin resonance (ESR) spectra was measured with a Bruker ESP300E spectrometer (100 kHz field modulation) at room temperature in 1,2-dimethoxyethane solution after irradiation in vacuo with a 150 W Hg–Xe lamp through a band pass filter at 405 nm.

3. Results and discussion

3.1. Absorption and fluorescence spectra

Fig. 4 shows fluorescence spectra for FV(I) in various solvents excited at 365 nm with the same absorbance. It is clearly indicated that the fluorescence intensity became weaker with decreasing solvent polarity. These results strongly suggest that the fluorescence from bis(4-pyridiniumyl)fluorene units is quenched by counter ions, iodide, in less polar solvents due to decreased distance between ion pairs. Bromide salts showed a similar solvent dependence.

3.2. Steady-state photolysis and ESR spectra

By steady photolysis of TPB$^-$ salts, new absorption peaks in the visible region (500–600 nm) and broad absorption was observed with peaks at 1420 and 1796 nm as reported previously. Similar absorption spectra were observed for PFV(TPB) cast films. 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 that remained in the film or in solutions.

Well-resolved hyperfine structure with at least 19 peaks was observed in the ESR spectrum of FV(TPB) in DME after irradiation at 405 nm as shown in Fig. 5 together with simulated one. It was clearly assigned to 2,7-bis...
(N-octyl-4-pyridiniumyl)-9,9'-dioctyfluorene radical cations from comparison with the simulated spectrum with hyperfine coupling constants corresponding to extensive delocalization of an unpaired electron through whole aromatic rings of a FV'. radical. The best fit hyperfine coupling constants are as follows: 0.259 mT for pyridyl nitrogen, 0.106 for pyridyl protons at ortho positions, 0.083 for pyridyl protons at meta positions, 0.138 for N-methylene protons, 0.021 for fluorene protons at 1- and 3-positions, and 0.010 for fluorene proton at 4-position. From these results absorption spectra were attributed to radical cations (PFV'), which were formed by photoinduced electron transfer from TPB\textsuperscript{-} as a sacrificial donor anion. From comparison of electronic absorption spectrum of these radicals after molecular orbital calculation using MOPAC and ZINDO of the CACHe system, the visible and NIR absorption bands were assigned to the short and long axes transitions of radical cations, respectively [14].

3.3. Transient absorption spectra and dynamics

Effects of counter anions and solution polarity on transient spectra and dynamics of PFVX and FVX in solutions and in solid films were studied with a fs 400 nm excitation laser. Fig. 6 shows time-resolved absorption spectra for 0.1 mM FV(Br) in cyclohexanone as an example. A peak observed at 560 nm just after fs laser excitation decayed accompanying concomitant increase of a new peak at 640 nm which showed no decay in the observed time region up to 1 ns. Similar behavior with slightly red-shifted peaks at 563 and 644 nm was observed for FV(Br) in chloroform. In more polar solvents, however, only a single peak was observed, at 554 nm in methanol and at 555 nm in acetonitrile without a rise or decay as shown in Fig. 7 for the methanol solution as an example. The time constants of decay or rise are summarized in Table 1 for FV(Br) and PFV(Br) in various solutions. It is clearly indicated that the decay of transient absorption at 555–565 nm region became slower with increasing polarity. Its decay constant, $\tau_{1/e} = 1.86$ ns, in acetonitrile corresponded well with the fluorescence lifetime $\tau_{f} = 1.76$ ns in acetonitrile. From these results it is concluded that transient absorption at 555–565 nm region was due to the transition to higher excited singlet states $S_n$ from the lowest excited singlet state $S_1$ of 2,7-bis(N-octyl-4-pyridiniumyl)-9,9'-dioctyfluorene. In other words, photoinduced electron transfer from counter anions is almost prohibited.
in polar solvents by longer inter-ion distance and strong solvation. Transient absorption with a peak at 640 nm observed in less polar solvents is thus most probably attributed to the short-axis transition of photogenerated bis(4-pyridiniumyl)fluorene radicals. Its faster decay is well explained by decreased inter-ion distance with decreasing the polarity.

Transient absorption and its dynamics were then studied by replacing counter anions with iodide. Transient absorption for FV(I) in acetonitrile showed a single peak at 554 nm with a lifetime of 1.66 ns, which corresponded well with a fluorescence lifetime of 1.75 ns. In cyclohexanone, FV(I) showed faster decay of the S1-state at 564 nm and formation of a very small peak at 635 nm due to photogenerated radicals. These results strongly suggested that iodide accelerated both photoinduced forward and thermal reverse electron transfer reactions. It is most probably attributed to the smaller oxidation potential of iodide, +0.54 V vs. NHE as compared with that of bromide, +1.07 V vs. NHE. The energy diagram for FV(Br) and FV(I) is shown in Fig. 8 using the first reduction potential of FV measured in acetonitrile, 0.47 V vs. NHE and the S1 energy level of 2.79 eV estimated from fluorescence peak at 445 nm. The total reorganization energy \( \lambda \) in the classical Marcus theory was reported as 0.90 eV for nitrostyrylpyridinium salts [13] and 0.63 eV for bipyridinium metal dithiolene salts [27]. According to the Marcus theory, the rate of electron transfer becomes maximum if the free energy change, \( -\Delta G \), equals \( \lambda \). Estimated values of \( -\Delta G \) for the reverse reactions are 1.01 and 1.54 eV for FV(I) and FV(Br), respectively. It is thus clearly shown the iodide salts will give the fastest reverse electron transfer, whereas that in bromide salts will be slower, since the \( -\Delta G \) value lies in the inverted region.

Transient absorption measurements were also made in solid PFVX films spin coated from tetrahydrofuran or chloroform solutions which are essential for device applications. Broad absorption spectra were observed in the NIR between 1050–1550 nm due to the long-axis transition of photogenerated 2,7-bis(4-pyridiniumyl)-9,9'-dioctylfluorene cation radical as reported previously[14] in addition to the transient absorption in the visible region as shown in Fig. 9 for the spin-coated film from chloroform. Multi-exponential decay was observed with lifetimes of 0.24 ps (25.6%), 1.82 ps (44.0%) and an offset (30.4%) for PFV(I), and 0.88 ps (25.2%), 11.0 ps (44.4%) and an offset (30.4%) for PFV(Br) at 1380 nm. No accumulation was observed during repeated fs laser excitation at 1 kHz [14]. The decay of transient absorption in the NIR region for methanol solutions was single exponential with \( \tau = 57 \) ps [14]. It is thus strongly suggested that the inter-ion distance

![Fig. 7. Time-resolved absorption spectra for 0.1 mM FV(Br) in methanol upon fs laser excitation at 400 nm.](image)

![Fig. 8. The energy diagram for FV(Br) and FV(I).](image)

| Compounds | Solvents | \( \lambda_{\text{peak}} \) (nm) | \( \tau_{\text{fast}} \) (ps) (%) | \( \tau_{\text{slow}} \) (ps) (%) | \( \text{Abs}_{\text{offset}} \) (%) |
|-----------|---------|----------------|----------------|----------------|----------------|
| FV\(^{2+}\) (Br\(^{-}\))\(_2\) | Acetonitrile (\( \varepsilon = 37.5 \)) | 555 | 1860 (100%) | — | 0 (0%) |
| | Cyclohexanone (\( \varepsilon = 18.3 \)) | 560 | 6.09 (28.4%) | 83.5 (28.3%) | 0.171 (43.3%) |
| | | 640 | 1.21 (24.0%) | 16.4 (22.5%) | — (53.5%) |
| PFV\(^{2+}\) (Br\(^{-}\))\(_2\) | Chloroform (\( \varepsilon = 4.81 \)) | 555 | (Rise) (69.7%) | (30.3%) | — |
| | DME (\( \varepsilon = 6.57 \)) | 565 | 9.55 (12.3%) | 345 (51.2%) | 0.112 (36.5%) |

DME—1,2-dimethoxyethane.
in solid films is much smaller than that in methanol and has a distribution. Effects of counter anions were more clearly observed in solid films than that in solutions. 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 [14]. 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.

3.4. Transient reflection spectra by GWM device

Recently we reported a composite guided mode geometry composed of a low-refractive-index polymer and a photoresponsive polymer without using a metal thin film as schematically shown in Fig. 10 [25]. We used a soluble perfluoroalkyl polymer, Cytop® (Asahi Glass Co., Ltd., Japan), as a low-refractive-index material with very low dispersion \( (n = 1.3395 \text{ at } 632.8 \text{ and } 1.3335 \text{ at } 1550 \text{ nm}) \), respectively. The calculated incident angle dependence by the optical transfer matrix technique [28] is shown in Figs. 11 and 12 at 632.8 nm for a photoresponsive polymer of 400 nm thick with complex refractive-index, \( n^* = 1.51 + ki \), on Cytop film of 380 nm thick. The incident angle mentioned in this paper is the angle of incidence at the active interface. The \( k \) value was increased from zero to 0.02 as shown in Figs. 11 and 12. Very high reflectance due to total reflection expected at the GWM dip was found to depend on the wavelength of probe light and the thickness of two polymer layers. Such dependence was experimentally confirmed by using appropriate dyes dispersed in polymer films as reported previously [26]. Incident angle dependence of reflectance shifts to a lower angle if the real part \( n \) of complex refractive index \( n^* \) decreases, and vice versa. Okamoto et al. reported somewhat similar but more complex geometry composed of cladding, waveguide, and sample layers on a BK7 prism for a totally different purpose [29,30]. They used such three-layer geometry as an optical waveguide sensor, in which a poly(methylmethacrylate) layer was sandwiched by a low-refractive-index Teflon polymer and an aqueous solution containing dyes. They reported similar dependence of dip absorbance on the extinction coefficient of the dye in aqueous solution for their three-layer geometry, when the \( k_e \) value at 979 nm thick Teflon cladding layer was 0.0001 [30].

Upon excitation at 400 nm by fs laser, transient reflectance spectral changes were observed in the wavelength region from about 400–800 nm region as shown in Fig. 13 for 220 nm PFVI and 300 nm Cytop films at three incident angles, 65°, 70°, and 75°. Observed transient absorption of the 220 nm thick film is also shown in Fig. 13 for comparison. The \( Y \)-axis values were calculated from the
probe light (either reflected or transmitted) intensity $I_0$ before and $I$ after excitation at specific wavelength, respectively. The increase of extinction coefficients due to transient absorption is concluded to have caused the observed decrease of reflection as predicted in Figs. 11 and 12. There are several clear differences between reflectance and absorption spectra. Firstly, transient reflectance spectra showed much larger changes compared with transient absorption spectrum. Secondly, the peak wavelength of reflection spectra sensitively depended on the incident angle and shifted to shorter wavelength with increasing incident angle; 679, 593, and 477 nm at 65°, 70°, and 75°, respectively. No such dependence was observed for transient absorption spectrum with a peak at 612 nm which is the same as that observed in the thick film as shown in Fig. 9. The time profile of reflectance was similar to those of transient absorption. Calculated incident angle and wavelength dependences of reflectance based on absorption spectrum of PFVI in the NIR region upon photoinduced electron transfer as reported previously [14] is for 900 nm Cytop and 800 nm PFVI layers shown in Fig. 14 and Fig. 15, respectively. Sharp GWM dips predicted in these

![Fig. 12. Expanded incident angle dependence of calculated reflectance as a function of extinction coefficients of the photoresponsive layer from 0 to 0.02 at 632.8 nm. Parameters are the same as those in Fig. 10.](image)

![Fig. 13. Transient reflectance spectra observed for a spin-coated PFVI film (220 nm) on Cytop® film (300 nm) at 65°, 70°, and 75° together with conventional transient absorption spectrum upon excitation at 400 nm by fs laser.](image)

![Fig. 14. Calculated incident angle dependence of reflectance for 800 nm PFVI film on 900 nm Cytop layer in the NIR region from 1200 to 1600 nm.](image)

![Fig. 15. Calculated wavelength dependence of reflectance for 800 nm PFVI film on 900 nm Cytop layer in the NIR region from 1100 to 1600 nm at various incident angles.](image)
figures depending on the incident angle or wavelength will be observed for PFVI on Cytop layers upon fs laser excitation due to photoinduced electron transfer and back electron transfer reactions. Transient ultrafast reflectance changes in the NIR region are being studied in detail and will be reported elsewhere. From these results the present GWM geometry is expected to be useful as an all-optical parallel-processing device in a broad spectral region.

4. Conclusion

New photoelectrochromic polymer was developed which showed strong absorption changes in the visible to optical telecommunication wavelength region due to photoinduced electron transfer from counter anion to 2,7-bis(4-pyridiniumyl)fluorene units in the main chain. The lifetime of photogenerated radicals was controlled over a very broad range; from infinity for tetraphenylborate salts to 240 fs for iodide salts. From time-resolved absorption and fluorescence spectroscopy upon femtosecond laser excitation, reactions mechanism and ultrafast dynamics were elucidated in solutions and in spin-coated films. This photoresponsive polymer was applied to ultrafast all-optical modulation based on novel composite polymer guided wave mode geometry. Appropriate combination of materials and devices is essential for molecular photonics, which can fully utilize superior properties of both molecules and photons for information processing with ultimate time and/or spatial resolution. The present results will contribute a great deal for such purposes.

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