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Synthesis and Photophysical Properties of a Photoelectrochromic Polymer Containing the bis(2-(4-Pyridiniumyl)thiazole) Chromophore

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A new polymer and small molecules containing the chromophore bis(2-(4-pyridiniumyl)thiazole) were synthesized. Their tetraphenylborate salts showed absorption spectral changes in the visible to near-infrared region accompanying a colour change from yellow to green on steady photoirradiation. From electron spin resonance measurements and comparison with Molecular Orbital PACkage (MOPAC) calculations, this was assigned to the formation of bis(2-(4-pyridiniumyl)thiazole) radicals due to a photoinduced electron-transfer reaction from tetraphenylborate and decomposition of its oxidized form. Transient absorption spectra corresponding to those of tetraphenylborate salts were observed for bromide salts on femtosecond laser excitation of the polymer in solid films and solutions. The fastest decay of transient absorption due to back electron transfer was less than 1 picosecond.

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Introduction

Novel materials, devices, and systems are required for much faster data processing, much higher density of recording, or more specific and efficient chemical sensing. Organic molecules have many useful optical and electronic functions that can be easily controlled by 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 useful properties such as wavelength, polarization, phase, ultrashort pulse, or parallel processibility. Through strong interactions of molecules, polymers, or molecular assemblies with photons, many exceptional properties of photons can be directly converted to changes in physical properties of materials, such as fluorescence, absorption, refractive index, conductivity, or optical non-linearity. Excited-state formation, photochromism, and photoinduced electron transfer are some examples of these. 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. Molecular photonics based on interactions of molecules and photons has many advantages compared with electric or photoelectric switching, heat-mode or magnetic recording.

Rapidly expanding volumes of information continuously require the speed-up of switching and processing in optical telecommunication systems. As silica-based optical fibres that are employed worldwide in such systems show minimum transmission loss at $\sim 1260-1675$ nm, photoresponsive materials need to show absorption or refractive index changes in this nearinfrared (NIR) region. As 40 GHz is the maximum speed of electronic signal processing at present, terahertz (THz) pulse trains in optical telecommunications with wavelength domain multiplexing (WDM) need to be spatially converted to more than 25 parallel signals. Ultrafast switching materials that work in less than 25 picoseconds (ps) are thus essential for THz communication or all-optical routing.

Many types of ultrafast optical processing devices and semiconductors or organic materials have been studied so far.^[1-18] 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 to be of use for ultrafast optical switching in the NIR region.^[7–14] All of them employ transient bleaching of NIR absorption at the ground state. We have been developing ion-pair charge-transfer complexes showing transient absorption in the visible to NIR region due to photoinduced electron transfer and reverse reactions between redox-active ion-pairs.^[15–19] Recently, we reported the synthesis and photoresponses of a fluorene-containing redox polymer, which showed new absorption up to 2000 nm by photoinduced electron transfer from the tetraphenylborate anion in addition to extremely fast photoinduced forward and thermal back electron transfer between iodide anion and fluorene-containing redox polymer in the NIR region.^[18,19] We also proposed alloptical spatial light modulation and parallel switching based on photoinduced complex refractive index changes in guided mode geometry.^[20-32] Both transient bleaching and absorption-type materials can be used in this system.

In the present paper, the synthesis and photophysical properties of a new polymer and small molecules containing bis(2-(4-pyridiniumyl)thiazole) are reported to achieve photoinduced electrochromism in broad wavelength and time domains. We



Fig. 1. Absorption and fluorescence spectra of 5 normalized by peak intensity.

demonstrate that instantaneous expansion of the π -conjugated system among four whole aromatic rings connected by carbon– carbon single bonds is possible by the use of a photoinduced electron-transfer reaction. We can also control the 'off' response in the visible and NIR region by back electron transfer in less than 1 ps.

Results and Discussion

Absorption and fluorescence spectra normalized by peak intensity are shown in Fig. 1 for the compound 5 in N.N-dimethylformamide (DMF), acetonitrile (ACN), ethanol (EtOH), tetrahydrofuran (THF), toluene (TOL), and cyclohexane (CHX). Solvents effects on the absorption and fluorescence spectra were not large except for CHX as shown in Fig. 1. The fluorescence quantum yield was relatively low and not sensitive to the solvents, 0.051 in TOL, 0.087 in ACN, and 0.029 in CHX. Compound 4 was soluble almost only in polar solvents. Its fluorescence quantum yield was higher, 0.16 in ACN and EtOH, 0.18 in DMF. The lower fluorescence quantum yield of 5 might be due to the existence of more flexible ether bonds in the alkyl substituents of 4,4'-diethyl-5,5'-di(N-alkyl-4-pyridiniumyl)-2,2'-bithiazole. Easier molecular motion in alkyl substituents will accelerate thermal deactivation of the excited singlet state of 4,4'-diethyl-5,5'-di(N-alkyl-4-pyridiniumyl)-2,2'-bithiazole chromophores. Because the chromophore of 5 has both cationic pyridinium units and neutral thiazole units connected, solvent effects on the stabilization of excited and ground states will work in opposite directions, resulting in very small absorption shifts in solvents with a wide range of polarity.

Absorption spectral changes for tetraphenylborate (TPB⁻) salts of 4 (4.3×10^{-5} M) in THF before and during steady-state photolysis are shown in Fig. 2. TPB⁻ was selected because it is known to work as a sacrificial electron donor owing to decomposition of its oxidized form.^[17] On photoirradiation, original absorption at 405 nm decreased and new peaks at 600, 676, 1210, and 1438 nm increased up to 40 s. After 40 s, absorbance at 600, 676, 1210, and 1438 nm gradually decreased with a concomitant increase of a new peak at 745 nm. When air was introduced after 6 min of irradiation, all peaks disappeared. Electron spin resonance (ESR) spectra having hyperfine structure with at least 27 peaks were observed by steady photoirradiation of TPB⁻



Fig. 2. Absorption spectral changes for tetraphenylborate (TPB⁻) salts of 4 (4.3×10^{-5} M) in THF before and during steady-state.



Fig. 3. Photographs of THF solutions before and after photoirradiation.

salts of 4. These results indicated that radicals were formed and the unpaired electron was distributed among the four aromatic rings of 4. Based on these results, together with comparison with Molecular Orbital PACkage (MOPAC) and Zerner's Intermediate Neglect of Differential Overlap (ZINDO) calculations, new peaks at 600 and 676 nm were assigned to the short-axis transition of photogenerated radicals of 4,4'-diethyl-5,5'-di(N-hexyl-4-pyridiniumyl)-2,2'-bithiazole units. The absorption peaks at 1210 and 1438 nm were assigned to the long-axis transition of the same radicals. Two peaks observed in each band are most likely due to the vibrational structure. The molar extinction coefficient (ε) of radicals at 1438 nm was estimated to be $2.86 \times 10^4 \, \text{M}^{-1} \, \text{cm}^{-1}$ from the decrease of the original absorption at 405 nm with $\varepsilon = 3.90 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The colour of the THF solution changed from yellow to green on photoirradiation as shown in Fig. 3.

To elucidate the origin of the peak at 745 nm that was observed only at longer irradiation time and higher radical concentrations, spectral changes of the sample irradiated for 30 min were

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Fig. 4. Spectral changes of the sample irradiated for 30 min observed during storage at room temperature in the dark.

observed during subsequent storage at room temperature in the dark as shown in Fig. 4. Both visible and NIR absorption peaks due to radicals were found to increase gradually during storage with a concomitant decrease of absorption at 745 nm, as shown in Fig. 4. These results strongly suggest an equilibrium between radical dimers (or aggregates) and monomers depending on the total concentration, which decreased gradually in the dark probably owing to radical coupling or reactions with residual oxygen.

If halide ions such as bromide or iodide were used instead of tetraphenylborate, no colour changes occurred on steady photoirradiation. Meanwhile, transient absorption spectra were observed in the visible to NIR region both in solutions and solid films of polymer 5 on fs laser excitation. Fig. 5 shows transient absorption spectra for solid films in the visible region. A part of the transient absorption spectra decayed faster at \sim 600–800 nm, as shown in Fig. 5, which corresponded well with that observed by steady photoirradiation shown in Fig. 2 and was assigned to the short-axis transition of photogenerated radicals. This thus indicates that there is another transient species, probably the excited singlet state (S_1) of bis(2-(4-pyridiniumyl)thiazole) chromophore, in addition to photogenerated radicals. Analysis of the time profile at 639 nm shown in Fig. 6 gave three components: a fast one (lifetime of a fast decaying component of transient absorption, $\tau_f = 0.83$ ps, 29%), a slow one ($\tau_s = 25$ ps, 17%), and an offset (54%). The offset component is most probably attributable to the S_1 state judging from the fluorescence lifetime mentioned below. The transient absorption spectrum in the NIR region just after fs laser excitation of 5 in solid films is shown in Fig. 7, which corresponds well with that in the NIR region shown in Fig. 2. Schematic representation of photoreactions in 4 or 5 is given in Fig. 8, in which dynamics of the excited state, photoinduced electron transfer, and back electron transfer mainly depend on the distance between cationic chromophores and counter ions.

In addition to transient absorption spectra shown in Fig. 5, bleaching with a negative absorption peak at 500 nm was clearly observed for **5** in THF, which is most probably due to the fluorescence as shown in Fig. 1 at the steady-state. The decay at 639 nm was also not single-exponential in THF with $\tau_f = 4.6$ ps (19%), $\tau_s = 273$ ps (41%), and an offset (40%). The decay due to back electron transfer was much slower (approximately five to 10 times) in solution compared with that in solid films. This result and higher fluorescence intensity was due to increased average



Fig. 5. Time-resolved absorption spectra in the visible region for **5** cast films on fs laser excitation at 400 nm.



Fig. 6. Time profile of transient absorption at 639 nm for **5** cast films on fs laser excitation at 400 nm.



Fig. 7. Transient absorption spectrum in the near infrared region for **5** cast films just after fs laser excitation at 400 nm.

distance between ion pairs in solution as reported previously for a similar polymer containing 4,4'-bipyridinium units.

Fluorescence decay curves were measured in order to get more information on the excited state. The results are shown



Fig. 8. Schematic representation of photoreactions for the present system. The four groups in the chromophore are schematically represented by ellipses.

in Fig. 9 for 4 in DMF and chloroform, which were singleexponential with $\tau_{\rm f} = 1.16$ ns in DMF and double-exponential with $\tau_f = 0.32$ ns (87%) and 1.29 ns (13%) in chloroform. Contribution of excited singlet-singlet (S-S) annihilation to the shorter lifetime component is excluded in dilute solutions. As average distance is expected to be smaller in less polar solvents such as chloroform than in polar solvents like DMF, the shorter fluorescence lifetime component observed in chloroform is attributed to electron-transfer quenching by counter ions. Meanwhile, the decay for polymer 5 was double-exponential even in DMF, with $\tau_f = 0.62$ ns (64%) and 2.46 ns (36%). The solvent polarity ranging from toluene, THF to DMF hardly affected the fluorescence decay of polymer 5. From these results, the microenvironment around 4,4'-diethyl-5,5'-di(Nalkyl-4-pyridiniumyl)-2,2'-bithiazole in the main chain and its counter anions (bromide) is not directly affected by solvents, but is most probably determined by the microenvironment of poly(tetramethyleneoxide), in which ether oxygen will interact with cationic units of chromophores in a similar manner as coordination. The fluorescence decay of 5 became faster in cast films, with $\tau_f = 0.26$ ns (60%) and 1.57 ns (40%). This result also strongly suggests decrease of the average distance between ion pairs in solid films. Although local concentration of chromophores can be higher in solid films, contribution of S-S annihilation seems to be very small because of the above-mentioned microenvironmental effects on ion pairs of 5,5'-di(N-hexyl-4-pyridiniumyl)-2,2'-bithiazole in the polymer 5.

Conclusions

A new photoelectrochromic polymer was developed that showed strong absorption changes in the visible to NIR wavelength region due to photoinduced electron transfer from counter anion to 5,5'-bis(4-pyridiniumyl)-2,2'-bithiazole groups in the main chain. The lifetime of photogenerated radicals was controlled over a very broad range: from infinity for tetraphenylborate salts to 830 fs for bromide salts in solid films. From time-resolved absorption and fluorescence spectroscopy, reaction mechanisms and ultrafast dynamics were elucidated in solutions and in solid films. This photoelectrochromic polymer can be applied to ultrafast all-optical modulation in the guided wave mode geometry we have been studying with various photoresponsive materials. The present results will contribute a great deal to molecular



Fig. 9. Fluorescence decay curves for 4 $(1 \times 10^{-6} \text{ M})$ in DMF and chloroform excited at 400 nm.

photonics, which can fully utilize the superior properties of both molecules and photons for information processing with ultimate time or spatial resolution.

Experimental

Synthetic procedures for small molecules employed in the present study are summarized in Scheme 1.

4,4'-Diethyl-2,2'-bithiazole 1

1-Bromo-2-butanone (2.1 mL, 25 mmol) was added to solution of dithiooxamide (1.53 g, 12.7 mmol) in dehydrated ethanol under a nitrogen atmosphere according to the literature.^[33] The mixture was refluxed for 7 h. After cooling to room temperature and keeping overnight in a refrigerator, red-brown crystals were obtained. Recrystallization from methanol afforded 1 (1.48 g, 59%). $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 6.94 (s, 2H, thiazole ring proton (Tz)), 2.85 (4H, m, -CH₂-), 1.32 (6H, t, -CH₃).

5,5'-Dibromo-4,4'-diethyl-2,2'-bithiazole 2

Bromine (0.30 mL, 5.80 mmol) in chloroform (20 mL) was added dropwise to **1** (0.51 g, 2.28 mmol) in chloroform (50 mL). The mixture was refluxed for 4 h under a nitrogen atmosphere and cooled to room temperature. The reaction mixture was



Scheme 1. Structures of and synthetic procedures for compounds employed in the present study. TPB, tetraphenylborate.



Scheme 2. Structure of and synthetic procedure for photoelectrochromic polymer 5.

washed with saturated sodium bisulfite, H₂O, and brine. The reaction mixture was dried with MgSO₄ and concentrated under reduced pressure to give orange solid **2** (0.54 g, 62.3%). $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 2.78 (4H, m, -CH₂-), 1.28 (6H, t, -CH₃).

4,4'-Diethyl-5,5'-di(4-pyridyl)-2,2'-bithiazole 3

Trimethyl(4-pyridyl)tin (0.50 g, 2.07 mmol) and tetrakis (triphenylphosphine)palladium(0) (0.20 g, 0.17 mmol) as a catalyst were added to a solution of **2** (0.30 g, 0.79 mmol) in toluene (30 mL). The reaction mixture was refluxed for 6.5 h under a nitrogen atmosphere. Ammonium solution (1 M) was added to the mixture after cooling to room temperature. The solution was extracted with chloroform. The extracts were washed with brine and dried with MgSO₄, and concentrated under reduced pressure. Recrystallization with ethanol afforded yellow solid **3** (0.19 g, 60.4%). $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 8.70 (4H, d, *o*-Py), 7.40 (4H, d, *m*-Py), 2.92 (4H, m, -CH₂-), 1.39 (6H, t, -CH₃).

4,4'-Diethyl-5,5'-di(N-hexyl-4-pyridiniumyl)-*2,2'-bithiazole Dibromide* **4**

3 (39.0 mg, 0.10 mmol) in 1-bromohexane was refluxed for 14 h under a nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure and washed with hexane to give orange solid **4** (62.5 mg, 89.8%). $\delta_{\rm H}$ ([D₄]methanol, 400 MHz, TMS) 9.01 (4H, d, *o*-Py⁺), 8.26 (4H, d, *m*-Py⁺), 4.64 (4H, m, Py⁺-CH₂-), 3.10 (4H, m, Tz-CH₂-), 2.06 (4H, m, Py⁺CH₂-CH₂-), 1.39–1.47 (18H, m, TzCH₂-CH₃ and Py⁺C₂H₄-(CH₂)₃-), 0.94 (6H, t, -CH₃).

Poly[4,4'-diethyl-5,5'-di(N-tetramethyleneoxide-4-pyridiniumyl)-2,2'-bithiazole]dibromide **5**

Photoelectrochromic polymer 5 was prepared according to Scheme 2. Tetrahydrofuran (7 mL, 86.3 mmol) was polymerized by the living-cation method at 0°C using trifluoromethanesulfonic anhydride $(115 \,\mu\text{L})$ as an initiator for 35 min under an argon atmosphere. After confirming the viscosity was high enough, a solution of 3 (13.0 mg, 0.034 mmol) in THF (3 mL) was dropped into the reaction mixture at -70° C and was stirred for 3 h, and for another 2 h at 0°C. The rubbery product was dissolved in chloroform and its ions exchanged with an aqueous solution of sodium bromide to get 5 (2.36 g). The number-average molecular weight (M_n) was evaluated by gel permeation chromatography (GPC) on the basis of polystyrene calibration. Two peaks were observed in GPC at $M_1 = 17400$ and $M_2 = 34900$. As a large excess of two living cations of poly(tetramethylene oxide) will attack 3 at two pyridine nitrogen atoms, two kinds of polymers will be formed: reacted and non-reacted. M_2 and M_1 most probably correspond to polymers with quarternized chromophore 3 in the central part of the main chain and poly(tetramethyleneoxide) homopolymers without chromophore, respectively.

Measurements

Absorption and fluorescence spectra were measured with a Hitachi U-4100 spectrophotometer and F-4500 fluorescence spectrophotometer, respectively. Transient absorption measurements were made by a pump-probe method with fs white-continuum generated by focussing fs 800-nm light into a D_2O/H_2O mixture or carbon tetrachloride as a probe and fs 400-nm light as a pump.^[16] An amplified Ti-sapphire laser delivered pulses of ~200 fs at a 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.^[16] Fluorescence lifetime was determined by a single-photon counting system with a streak camera (Hamamatsu Photonics, C4334-01) on 1.5-ps laser excitation at 400 nm. Fluorescence quantum yield was determined in several solvents using quinine sulfate as a standard (fluorescence quantum yield of a standard quinine sulphate, $\phi_{ST} = 0.546$ at $\lambda_{ex} = 365$ nm). Samples for steady-state photolysis were deaerated by the freeze-pump-thaw method. Steady photolysis was made in films and in de-aerated solutions with a 150-W Hg-Xe lamp through a band pass filter at 405 nm. ESR spectra were measured with a Bruker EMX-plus spectrometer (100 kHz field modulation) at room temperature in tetrahydrofuran solution after irradiation under vacuum with a 150-W Hg-Xe lamp through UV and IR cut-off filters (UV-33 and IRA; Asahi Techno Glass Co., Ltd).

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