Pulsed-Laser-Induced Phase Transition of Aqueous Colloidal Gold Nanoparticles at High Pressure: Picosecond Pump-Probe Study.

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[Introduction] Studies on the interaction of gold nanoparticles (AuNPs) with short pulsed-lasers have been a subject of intensive research.\(^1\) Revealing the time evolution of particle temperature initiated by the laser excitation of AuNPs is important because this information is crucial to fully understand the heating-induced phase transformations of the particle and the surrounding medium.\(^2\) For this purpose, transient extinction spectroscopy is appropriate because temperature-induced bleaching has been known to occur for the localized surface plasmon resonance (LSPR), and the bleaching intensity is correlated with the particle temperature. Here we describe the transient spectroscopic study of a laser-induced supercritical layer around AuNPs and related phenomena by excitation with a 15 ps pulse, when the external pressure of 60 MPa is applied. The transient signals are used to figure out the particle temperature evolution and refractive index changes of the surrounding medium.

[Experimental] We used 60-nm diameter AuNPs (BBI EMGC60) that are reshaped into spheres by laser annealing (59 ± 4 nm by TEM). A picosecond pump-probe system with a custom-built mode-locked Nd\(^{3+}\):YAG laser was used to measure the transient spectra at various time delays in the ps-to-ns time regime: third-harmonic light (355 nm) with an FWHM of 15 ps was used as a pump pulse, and the picosecond white light continuum generated by focusing a fundamental pulse into a 10-cm quartz cell containing a 3:1 \(\text{D}_2\text{O}\) and \(\text{H}_2\text{O}\) mixture was used as a probe light. For measurements performed under a pressure of 60 MPa, the cuvette was placed in a hydrostatically pressurized container that enabled solution agitation. Post mortem particle characterization was performed by using transmission electron microscopy (TEM).

[Results and Discussion] Transient extinction spectra evolved instantaneously within the excitation laser pulse and decayed in 20 ns. Given that the picosecond laser excitation contributes solely to the particle heating, the time evolution of spectra was ascribed to heating-

![Figure 1. Time evolution of extinction observed at 630 nm.](image-url)
induced plasmon band broadening and subsequent recovery due to cooling. However, by increasing the excitation laser intensity, something unusual time evolution occurred (Fig.1). The time profile showed the rapid emergence of the positive transient extinction within the response time of the detection system, followed by a decay to a negative value within a few 100 ps. For time delays longer than about 300 ps after excitation, the transient extinction began to increase, reaching a maximum value at about 2 ns, and then decreased until 16 ns. This complicated behavior can be explained by bubble nucleation, expansion and decay when bubble diameter-dependent difference extinction spectra were considered, Fig. 2. Figure 2 shows that for 60-nm diameter AuNP the extinction decreases for small bubbles (see 5 and 30 nm thicknesses) but it increases for bubbles with thicknesses greater than 70 nm (see 80 and 90 nm). The simulation is consistent with the kinetic behavior given in Fig. 1.

At 60 MPa, however, different dynamics were observed. Figure 3 gives two kinetic trances for two wavelengths, (a) 470 nm and (b) 600 nm. Note that bubbles cannot be formed under such a high pressure. What we observed here is supercritical layer formation around the NP. The supercritical water forms at > 22.1 MPa and when the medium temperature exceeds 647 K. Here the supercritical layer forms dynamically: nucleates, grows and decays with time. Figure 3 suggests that max. diameter is reached at 500 ps, decaying out after 2 ns.


Figure 2. Simulated difference extinction spectra dependent on bubble thickness for 60 nm AuNP.

Figure 3. Kinetic traces at 60 MPa at 19.6 mJ cm$^{-2}$ for two wavelengths, (a) 470 nm and (b) 600 nm. Open circle: for 4.5 mJ cm$^{-2}$; closed circle: for 19.6 mJ cm$^{-2}$. 
Relaxation process of the photoexcited state of water-soluble meso-naphthylporphyrins

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[Introduction] Photosensitized singlet oxygen (1O₂) generation by porphyrins is the important mechanism of photodynamic therapy, a promising less invasive treatment of cancer by photochemical reaction. Singlet oxygen is produced through excitation energy transfer from the excited state; in general, triplet excited (T₁) state of porphyrin to oxygen molecules. In the case of DNA photodamage, guanine is the important target of 1O₂. Because the administered photosensitizers necessarily associate with biomacromolecules including DNA, one of the most important target biomacromolecules, the microenvironmental effect of biomacromolecules is important for the activity of photosensitizers. We have previously reported the activity control of the electron-donor-connecting porphyrin photosensitizers using DNA.1,2 In this study, we synthesized novel electron-donor-connecting porphyrins (Figure 1), meso-(1-naphthyl)-tris(N-methyl-p-pyridinio)porphyrin (1-NapTMPyP) and meso-(2-naphthyl)-tris(N-methyl-p-pyridinio)porphyrin (2-NapTMPyP) to examine their photochemical properties under an interaction with DNA.

[Experimental] 1-NapTMPyP and 2-NapTMPyP were synthesized in a method similar to that of previous reports1,2 and characterized with an NMR and a mass spectrometer. To design these photosensitizers, molecular orbital calculations were performed at the Hartree-Fock 6-31G* level. The synthesized 16-mer oligonucleotides (AATT: d(AAAATTTTTAAATTTT)₂ and AGTC: d(AAGCTTTGCAAAGCTT)₂) were used as DNA. Photochemical properties of these porphyrins with DNA were examined by spectroscopic techniques in sodium phosphate buffer (pH 7.6).

[Results and Discussion] Absorption spectral change indicated the association between these porphyrins and DNA. The association constant, which was estimated from the analysis of the absorption spectral change, between 2-NapTMPyP and DNA was slightly larger than that of 1-NapTMPyP. The estimated association constants suggest that almost porphyrins are stably...
binding with DNA through intercalation or groove binding in the presence of 50 μM-base pair (bp) DNA.

The fluorescence quantum yields (Φf) of these porphyrins (10 μM) decreased with an increase of DNA concentration of up to 1~5 μM-bp, possibly due to self-quenching through an aggregation. The Φf increased with an increase in the DNA concentration to more than these concentrations and reached a plateau (Table 1). In the DNA microenvironment, the Φf and the fluorescence lifetime of NapTMPyPs were significantly larger than those without DNA. These results suggest that DNA microenvironment inhibits the quenching of the S1 state of NapTMPyPs through the intramolecular electron transfer and; in addition, stabilizes the S1 state due to suppression of the vibrational deactivation.

To evaluate the ¹O₂ generating activity of NapTMPyPs, we measured the near-infrared emission. The typical near-infrared emission spectrum at around 1,270 nm, which is assigned to the emission of ¹O₂, was clearly observed during the photo-irradiation of 1- and 2-NapTMPyP without DNA. The quantum yield of ¹O₂ generation (ΦΔ) was estimated by the comparing the ¹O₂ emission intensity of NapTMPyPs and that of methylene blue (0.52 in water).³ The apparent values of ΦΔ by NapTMPyPs without DNA were relatively large (Table 1), indicating that the quenching of the photoexcited porphyrins by the naphthyl moiety is not sufficient. Similarly to the Φf values, the ΦΔ decreased by relatively small concentration of DNA. In the presence of sufficient concentrations of DNA (50 μM-bp), the values of ΦΔ were recovered. However, these values were almost the same or rather smaller than those without DNA (Table 1). Because ¹O₂ generation occurs in the microenvironment of DNA, the generated ¹O₂ should interact with DNA strand. AT-only sequences quench ¹O₂ through a mainly physical mechanism, whereas guanine can quench ¹O₂ through chemical process (guanine oxidation). Therefore, the actual values of ΦΔ may be higher than the estimated values. The observed values of ΦΔ suggest that the chemical process plays a major role in the total deactivation process. In addition, the DNA strand may prevent energy transfer from the photoexcited porphyrins to oxygen molecule. Therefore, these results suggest that the limit of the ¹O₂ generating activity of porphyrin photosensitizers under an interaction with DNA.

In conclusion, the S1 states of NapTMPyPs are stabilized in the DNA groove binding or intercalating states. The results of this study suggest the limit of ΦΔ by DNA-binding photosensitizer due to an inhibitory effect of DNA on the energy transfer process and a deactivation of ¹O₂ by DNA strand.

Table 1. Photochemical properties of the photosensitizers with or without DNA

<table>
<thead>
<tr>
<th>Photosensitizer</th>
<th>DNA</th>
<th>Φf</th>
<th>ΦΔ</th>
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<tbody>
<tr>
<td>1-NapTMPyP</td>
<td>without</td>
<td>0.030</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>AATT</td>
<td>0.062</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>AGTC</td>
<td>0.048</td>
<td>0.20</td>
</tr>
<tr>
<td>2-NapTMPyP</td>
<td>without</td>
<td>0.030</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>AATT</td>
<td>0.092</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>AGTC</td>
<td>0.072</td>
<td>0.36</td>
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DNA concentration: 50 μM-bp.

The motion of entangled polymer chains continues to be an important research topic in polymer science. In particular, the motion of topologically-unique cyclic polymers under the entangled conditions is of great interest as their motion should be distinct from that of the linear counterparts by the absence of the chain ends. However, despite decades of experimental and simulation studies, the motion of entangled cyclic polymers remains controversial because the concept and the role of the entanglement between the cyclic polymers have not been clarified. This is partly due to the lack of a method that can directly characterize the motion of individual polymer chains in an entangled melt and solution under equilibrium conditions. We have recently developed a new single molecule fluorescence imaging technique, cumulative-area (CA) tracking, which allows simultaneous characterization of the diffusion rate, diffusion mode, and conformational relaxation time of individual polymer molecules. As compared with the conventional single-molecule fluorescence imaging technique based on SMLT, CA tracking is especially effective in the analysis of the motion of long polymer chains because the center-of-mass diffusion at the length scale of the chain and conformational relaxation of the molecule under the equilibrium conditions are characterized accurately by analyzing cumulative areas occupied by the moving molecule.

In this study, using the novel CA approach, we investigate the molecular mechanism of the motion of cyclic polymers in an entangled solution at the single molecule level. We used 42 kbp linear and cyclic dsDNA whose contour length is 19 µm as model polymers. We investigate the motion of a cyclic tracer DNA in a concentrated solution of unlabeled cyclic DNA (C-C), and a linear tracer DNA in a concentrated solution of unlabeled linear DNA (L-L) (Fig. 1).

Figure 2 shows time-lapse fluorescence images and the cumulative area images obtained for L-L (Fig. 2a) and C-C (Fig. 2b). The CA tracking analysis of the images suggest that L-L shows one-dimensional (1D) random motion up to the length scale of the square end-to-end distance of the
molecule. In contrast, the motion of C-C cannot be described by either 1D or 2D random diffusion. Figure 3 shows the diffusion coefficients and relaxation times of L-L and C-C determined by the CA tracking analysis. The results obtained in Figure 2 and 3 suggest that the motion and relaxation of L-L can be interpreted by the reptation model (Figure 4a) that is predicted for a long and flexible linear polymers under the entangled conditions. On the other hand, the results obtained for C-C by the CA tracking analysis cannot be interpreted by the reptation model. The results rather suggest that the mutual relaxation of the chains governs the motion and relaxation of the cyclic polymers under the entangled conditions (Figure 4b), underscoring the necessity of developing a new model to correctly describe the cyclic polymer dynamics under entangled conditions by incorporating the effects of mutual relaxation of the chains.5

Figure 2. Time lapse fluorescence images and CA tracking images. (Top) Time lapse fluorescence images of (a) L-L and (b) C-C. (Bottom) The time lapse images of the cumulative area occupied by (a) the moving, fluorescently labeled linear tracer DNA and (b) the moving, fluorescently labeled cyclic tracer DNA. Scale bars = 1 μm.

Figure 3. (top) Mean diffusion coefficients of Dilute L, Dilute C, L-L, and C-C determined by the CA tracking analysis. (bottom) Mean relaxation times of Dilute L, Dilute C, L-L, and C-C determined by the CA tracking analysis.

Figure 4. Schematic illustration of topology-dependent diffusion and relaxation. The motion and conformational relaxation of (a) L-L and (b) C-C (orange lines) occurring within their relaxation times. The cyan dots show obstacles due to the surrounding chains. The crosses show the center-of-mass at each time point.

The Reactive States of Semiconductor Quantum Dots Revealed by Single-molecule Imaging

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[Introduction]  Organic dyes have been extensively exploited as light antennas in the construction of electron and energy donor-acceptor systems for artificial photosynthesis and photodynamic therapy. However, these light antennas generate reactive oxygen species such as singlet oxygen ($^1\text{O}_2$) and subsequently become oxidized, which is ubiquitous and is a major challenge in their prolonged applications. Despite the size-dependent tunable and bright photoluminescence (PL) of semiconductor quantum dots (QDs), like organic dye molecules, these tiny crystals suffer from photo-oxidation and unpredictable PL loss when exposed to high-intensity light for an extended period of time [1,2]. Such PL loss in QDs is classified into digitized blinking, which is reversible, and non-digitized fading, which is irreversible. Blinking is due to ultrafast carrier recombination in ionized QDs [3], whereas non-digitized fading is attributed to oxidation by $^1\text{O}_2$ [2]. Blinking can be resolved to a greater extent by the suppression of non-radiative carrier recombination [3,4]. On the other hand, suppression of PL fading needs protecting shells or $^1\text{O}_2$ scavengers. Nevertheless, a complete solution to the suppression of PL loss is yet to be identified, for which the barrier is unsolved relations among blinking, generation of $^1\text{O}_2$, oxidation, and fluctuation of electronic relaxations. Here, by the detection of $^1\text{O}_2$ generation, and PL blinking and fading of single QDs, we find that oxidation is prevented in the ionized states of QDs, where ultrafast non-radiative carrier recombination processes setback the generation of $^1\text{O}_2$ and oxidation of QDs.

[Experimental]  The generation of $^1\text{O}_2$ by QD was detected using a singlet oxygen sensor green (SOSG) dye or by the measurement of NIR phosphorescence of $^1\text{O}_2$ [5]. The samples for $^1\text{O}_2$ measurements were prepared by mixing 20 nM streptavidin-functionalized CdSe/ZnS QDs (20 nM, PL ca 650 nm) and SOSG (10 mM), and were photoactivated at 532 nm (5 W/cm$^2$) without or after bubbling N$_2$ gas (100 mL/min). Samples for $^1\text{O}_2$ phosphorescence measurements were photoactivated at 532 nm and the phosphorescence decay profiles of $^1\text{O}_2$ were recorded in the 1235-1330 nm range at 5 to 10 nm intervals. Single QD samples were prepared by the covalent tethering of streptavidin-functionalized QDs (5 pM solution in water) to biotinylated cover glass plates. The glass plates were first silanized using 3-aminopropyl triethoxysilane and subsequently biotinylated using biotin 3-sulfo-N-hydroxysuccinimide ester. PL images and intensity trajectories of single QDs immersed in aerated or N$_2$-saturated dimethylsulfoxide (DMSO) or water, with or without $^1\text{O}_2$ scavengers.
and under different excitation power densities (125 to 500 W/cm² @ 532 nm), were obtained in an intervened optical microscope (Olympus IX70) equipped with a 40 x objective lens (Olympus), a fluorescence filter for QDs (Omega), and an EM CCD camera (Andor Technologies).

**[Results and Discussion]** Fluorescence enhancement of SOSG ca 530 nm as a function of time under photoactivation of QD at 532 nm enabled us for the detection of $^1\text{O}_2$ production. Here, $^1\text{O}_2$ uncages the fluorescence of fluorescein in SOSG, which is otherwise caged by intramolecular electron transfer from anthracene to fluorescein. Further, the characteristic phosphorescence band of $^1\text{O}_2$ ca 1270 nm observed in air-, but not N₂-, saturated QD solutions verifies the photosensitized production of $^1\text{O}_2$. Interestingly, single QDs immersed in DMSO and shined with a high-intensity laser beam (532 nm) suffer from PL fading (Figure 1A), which is not observed for QDs present at air/glass interface (Figure 1B), suggesting oxidation of QDs by $^1\text{O}_2$ generated by the energy transfer from QD to dissolved oxygen is responsible for the PL loss. Nonetheless, PL OFF durations of QDs immersed in DMSO were diminished when compared with those at air/glass interface. Despite the monotonous loss of PL of QDs in DMSO, the PL intensity recovers to the original level after laser was turned OFF and ON (Figure 1C), indicating PL loss is solely photoinduced. More importantly, after each intrinsic OFF period due to ionization and neutralization of QDs, the PL intensity recovers to the same level as that before the OFF period (Figure 1D). These observations suggest that ionized QDs in the ground or excited state do not undergo oxidation. In other words, Auger ionization beats oxidation of QDs.

Figure 1. PL intensity trajectories of single QDs tethered on cover glass plates and observed under 500 W/cm² excitation at 532 nm: (A) in DMSO, (B) at air/water interface, (C) in DMSO with 15 min laser ON-OFF intervals, and (D) in DMSO, showing long-living ionized (OFF) states.

Molecular-level study and control of conformation and photophysics in conjugated polymers and oligomers

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Introduction
Molecular-level understanding of photoresponse of conjugated molecular complexes is important both from the point of basic knowledge of molecular photophysics and from the point of applications as optoelectronic or photo-driven nanoscale devices. Molecular complexes with covalently linked chromophores such as conjugated polymers or oligomers represent an important class of organic semiconductors. We study the relationship between the polymer chain shape/conformation and its photophysical properties using single molecule optical detection and spectroscopy [1]. Further, we attempt to actively control the conformational state of the complexes by external stimuli [2]. As examples, we study polyfluorenes where the conformation is strongly influenced by the way the chain is electronically excited, as evidenced by the dramatic differences between single chain photoluminescence and electroluminescence spectra [3]. In another example of poly(phenylene vinylene), the conformation is controlled by the chain topology giving rise to different photophysical properties between cyclic and linear chains.

Results and Discussion
1. Polyfluorene
Conformational changes of a conjugated polymer polyfluorene with polyethylene oxide (PEO) sidechains (BDOH-PF) are studied on single-chain level upon excitation by linear absorption of light and by charge recombination. For the charge recombination mechanism individual BDOH-PF chains have been confined in vertical cylinders of a phase-separated block copolymer film and the hybrid film has been used as an active layer in a light-emitting device. Both excitation mechanisms lead to dramatically different photophysical properties that reflect different intramolecular aggregation processes. The explanation of the differences has been based on density functional theory (DFT) calculations which show that fluorene molecules form ground-state dimers and that the dimers are further stabilized by the presence of a charge on one of the monomers. In photoluminescence of BDOH-PF in PEO matrix the emission spectra are dominated by either singlet excitons or excimers formed via neutral ground-state aggregates. In electroluminescence the singlet exciton emission is absent and the spectra are either due to formation of charged ground-state aggregates or excimers. In both photoluminescence and electroluminescence thermally induced conformational dynamics of the polyfluorene chains leads to strong spectral dynamics on timescales of seconds (Figure 1). The role of the intramolecular interchain interactions and of the conformation dynamics in the observed spectral dynamics is further confirmed by studying photoluminescence of single
BDOH-PF chains dispersed in polymer matrices of different glass transition temperature. Unlike in the PEO matrix which is in a rubbery state at the experimental temperature, BDOH-PF molecules do not undergo significant spectral changes in Zeonex which is in glassy state and in which the lack of the matrix chain Brownian motion prevents conformational changes of the BDOH-PF guest molecules.

Figure 1. Photoluminescence (left) and electroluminescence (right) spectra of single polyfluorene chains

2. Poly(phenylene vinylene)

Ensemble and single-molecule characterization of cyclic poly(phenylene vinylene) (C-PPV) together with its linear counterpart (L-PPV) of the same molecular weight has been carried out. We characterize conformation of single PPV chains by measuring absorption (excitation) anisotropy and by comparing the measured values with a simulated distribution assuming the absorption of all conjugated segments on the chain. The results are complemented by measuring and simulating single chain emission anisotropy including the effect of energy transfer which causes emission from a limited number of conjugated segments. The size of the segments and amount of intrachain structural disorder are estimated by measuring the single chain fluorescence spectra (Figure 2). The origin of the disorder is reconstructed from spectral characterization of both PPV species doped into a bulk polymer film at different degrees of film stretching.

Figure 2. Single molecule spectral characterization of linear (left) and cyclic (right) poly(phenylene vinylene) chains

Design and synthesis of new two-photon-absorption (TPA) chromophore with EGTA unit

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[Introduction] Encapsulation of biologically active substrate (i.e. caging) by using organic synthesis and release (i.e. uncaging) the active substrate under the photolysis conditions is the key technique for understanding the mechanism of biologically active compounds in living organism. Calcium ions (Ca$^{2+}$) are essential in cell physiology, wide variety of cells and cellular functions is controlled by the change of the concentration of Ca$^{2+}$. The development of new calcium chelators i.e. calcium caged compounds using organic synthesis is a significant task for chemists. In this study we newly achieved the synthesis of a new two-photon absorption (TPA) chromophore with an EGTA unit that is a calcium chelator.

[Experimental Result and discussion] The synthesis of a new TPA chromophore with an EGTA unit that is a calcium chelator was accomplished by using 11 steps synthesis from commercially available starting material. One photon (OP) bond-cleavage reaction of EGTA (10 mM in C$_6$D$_6$, $\lambda_{\text{max}} = 362$ nm with $\varepsilon 18771$) was conducted at 360 ± 10 nm using Xenon lamp (Figure 1). The two-photon-induced bond cleavage reaction was confirmed under the 740 nm irradiation (Figure 2) conditions. The photo-induced bond cleavage reaction was monitored by $^1$H NMR (400 MHz) spectroscopic analysis (Figure 3). The structural dissociation of EGTA unit was observed after 10 h irradiation. The quantum yield of EGTA ($\varepsilon_{360} 18771$) was determined to be 0.3 at 360 nm irradiation using Xenon lamp. The photon counting was conducted using ferric oxalate as a chemical actionometer. The $\varepsilon_{360} \Phi$ value was 5631 M$^{-1}$ cm$^{-1}$.

Figure 1: One photon uncaging followed by HPLC analysis at 360 nm.
Figure 2: Two-photon uncaging followed by HPLC analysis at 740 nm.

Figure 3: (A) $^1$H NMR (400 MHz) of EGTA unit in C$_6$D$_6$. (B) $^1$H NMR spectrum (2.6-5.5 ppm) after 4 hr irradiation by using Xenon lamp (360 nm) in C$_6$D$_6$. (C) $^1$H NMR spectrum after 8 hr irradiation of in C$_6$D$_6$.


Excited state dynamics of silicon-containing rhodamine and its aggregates

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[Introduction] Self-assembly formation has been paid considerable attention for the development of nanodevice as well as artificial natural system. Furthermore, they are also intriguing phenomena for the design of fluorescence probes based on properties such as aggregation-induced emission and colorimetric changes. Compared to porphyrin, perylene diimide, and cyanine derivatives that many rational molecular designs have been introduced to induce various aggregation, however, there have been limited reports to control self-assembly of fluorophores in solution without a help of external templates.

We have recently reported 9-phenylanthracenyl rhodamine derivatives that form J-aggregate of rhodamine moieties in the aqueous solution. In the case of silicon-containing rhodamine (Si-TMR) and 9-phenylanthracene dyad (SiR-An, Fig. 1a), it undergoes a transition from H- to J-aggregate as [NaCl] increases (Fig. 1b). From X-ray crystallographic analysis, this unprecedented J-aggregation originates from (1) the cooperative stacking between rhodamine and anthracene moieties and (2) π–π interaction of the C-N bond at both ends of the rhodamine moieties that stabilizes slipped–stacked rhodamine–rhodamine arrays. Herein, we investigate dynamics of Si-TMR monomer and its aggregate prepared by 9-phenylanthracenyl substitutions using various time-resolved spectroscopic methods.

![Figure 1.](image)

Figure 1. (a) Chemical structures of SiR-An and Si-Me. (b) Absorption spectral changes of 5 μM SiR-An in ultrapure water as [NaCl] increases.

[Experimental] All measurements of various Si-TMR species in the excited state were carried out using a reference compound, Si-Me (Fig. 1a), dissolved in methanol or aqueous solution by means of femtosecond laser flash photolysis and pulse radiolysis. Next, H- and J-aggregates of Si-TMR were prepared by dissolving 100 μM SiR-An in the aqueous solution without and with 20 mM NaCl, respectively. Since approximately 100-nm red-shift occurs during H-to-J transition of SiR-An (Fig.
1b), pulsed laser with the wavelength at 650 and 740 nm was used for the selective excitation of H- and J-aggregates, respectively.

[Results and Discussion] First, Si-TMR in the excited state exhibits similar spectral shapes apart from approximate 20-80 nm red-shift, as compared to the previous report on tetramethylrhodamine (Fig. 2a).\textsuperscript{23} When Si-TMR is directly connected to dimethylanthracene (DMA), we previously reported that photoinduced electron transfer (PET) occurs from DMA to Si-TMR in the excited state.\textsuperscript{3} However, Si-TMR of SiR-An in the singlet excited state is not deactivated via PET, but relaxes through fluorescence and internal conversion upon the selective excitation of Si-TMR ($\lambda_{ex} = 650$ nm). Prohibition of PET in SiR-An is due to the intermolecular distance of a phenyl group between Si-TMR and anthracene moieties.

In the case of SiR-An H-aggregate ($\lambda_{ex} = 650$ nm), three transient species ($\tau = 0.6, 16.8, >200$ ps) were monitored, assigned to the internal conversion between two exciton bands, relaxation to the intermediate state, and relaxation to the ground state, respectively. For SiR-An J-aggregate, characteristic transient absorption spectra of exciton in J-aggregates were monitored ($\lambda_{ex} = 740$ nm, Fig. 2b). Interestingly, a decay profile and spectral shapes of the positive transient absorption possess a strong dependency on the intensity power, implying the presence of two-exciton state. In addition, the exciton-exciton annihilation process was also observed (Fig. 2b, inset). The obtained results in this study suggest the potential of SiR-An J-aggregate as a novel optical material for near-IR absorption and energy transport.

![Figure 2](attachment:image.png)

**Figure 2.** (a) Absorption spectra of Si-Me in the singlet excited state (black), Si-Me radical anion (blue), and Si-Me radical cation (green). (b) Transient absorption spectra of SiR-An J-aggregate in the aqueous solution with 20 mM NaCl ($\lambda_{ex} = 740$ nm and app. 40 nJ pulse\textsuperscript{-1}). (Inset) Time profile of SiR-An exciton population observed at 730 nm.

Highly photostable luminescent organic radicals

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[Introduction] Luminescent molecules have been studied extensively as promising candidates for organic light-emitting diodes and chemical sensors. While almost all the luminescent molecules are of closed-shell nature in the ground state, the luminescence of open-shell organic molecules such as monoradicals has attracted much interest recently owing to the characteristic photofunctions.[1] The radicals show fluorescence from the lowest excited doublet state ($D_1$) to the ground doublet state ($D_0$). The emission processes do not suffer from annihilation through the triplet state generally observed in the processes of closed-shell molecules; therefore, a high luminescence efficiency in electroluminescent devices would be expected. However, several problems have hindered investigation of the photofunctions of luminescent organic radicals, including: (1) there are relatively few examples of luminescent organic radicals, and (2) the molecules degrade upon photoexcitation.

Here we prepared a novel luminescent stable radical, PyBTM, exhibiting superior photostability.[2] We report on the molecular and electronic structures, luminescent properties, and stability upon photolysis. The properties of PyBTM could be tuned using chemical stimuli, such as $H^+$ and $Au$.[3]

[Experimental] The molecular structure was analyzed by single-crystal X-ray diffraction. The electronic structure was calculated using density functional theory (DFT) methods. The photostability was examined using a HITACHI F-4500 spectrometer by monitoring the intensity of fluorescence at $\lambda_{em} = 570$ nm under continuous photoirradiation at $\lambda_{ex} = 370$ nm.

[Results and Discussion] The molecular structure of PyBTM in the crystalline state is shown in Figure 1b. The central methyl carbon atom (shown in red in Figure 1b), on which appreciable spin density is located, is shielded sterically by six chlorine atoms.

As shown in Figure 2, PyBTM in CH$_2$Cl$_2$ displayed a strong near-UV absorption band at 370 nm ($\varepsilon = 2.54 \times 10^4$ M$^{-1}$cm$^{-1}$) and a weak visible absorption band at 541 nm ($\varepsilon = 1.01 \times 10^3$ M$^{-1}$cm$^{-1}$). DFT and TDDFT calculations suggested that the latter band is attributed to a transition from $128\beta$ ($\pi$ orbital centered on the pyridyl moiety) to $129\beta$ (lowest unoccupied spin orbital) to form the D$1$ state, from which the fluorescence of PyBTM arises. Fluorescence spectrum
under excitation at 370 nm showed an emission maximum at 585 nm and shoulders in the longer wavelength region. The fluorescence lifetime (τ) was 6.4 ± 0.2 ns with single exponential decay, similar to those of the chlorinated triphenylmethyl radical TTM (τ = 7 ns), a previously reported luminescent radical, supporting its fluorescent character. The absolute photoluminescence quantum yield (ϕem) was typically 0.01-0.03 in the solution state, which increased to 0.26 when the PyBTM molecules were dispersed into PMMA matrix at 298 K. The excellent ϕem value of 0.81 was obtained in EPA (diethyl ether : isopentane : ethanol = 5:5:2) at 77 K. The improved ϕem values result from the suppression of the molecular vibrations that promote non-radiative decay to decrease the fluorescence.

The photostability of PyBTM was compared with that of TTM. The decay of the fluorescence intensity of PyBTM (1/τPyBTM) in acetone was 115 times smaller than that of TTM (1/τTTM). PyBTM was more stable than TTM in other solvents, showing the superior photostability of PyBTM. We expect that the introduction of the pyridyl group into the TTM skeleton lowers the energies of the molecular orbitals involved in the luminescent process, affording the greater photostability.

The pyridine moiety of PyBTM acts as a stimuli responsive site, thereby allowing for control of the electronic and optical properties of the radical by external stimuli such as proton. We revealed that the photophysical and photochemical properties were positively modulated upon coordination to Au(I); the ϕ value, fluorescence wavelength, and the photostability all increased.

Figure 2. Absorption and emission spectra of PyBTM in CH₂Cl₂ at 298 K.

Figure 3. Decays of fluorescence of PyBTM and TTM in acetone under continuous 370 nm excitation. Ratios of half-lives (τ₁/₂) in various solvents are shown.

“The excited state C–C bond cleavage–luminescence” phenomenon of methylenecyclopropanes induced by intermolecular energy transfer

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[Introduction] An adiabatic photochemical reaction is one that proceeds on the sole potential surface. One of the most famous examples is the excited state intramolecular proton-transfer reaction of benzothiazolylphenol derivatives, which exhibit characteristic fluorescence with a large Stokes shift. In the course of study of benzophenone (BP)-sensitized energy transfer (ET) reactions of biphenyl-substituted methylenecyclopropanes (1a–b, Fig. 1), we unexpectedly found out an adiabatic reaction of 31* affording the corresponding excited trimethylenemethane biradical 32••* (Path B) and its unique fluorescence associated with T1–T0 transition. Thus, we named this system “the excited state C–C bond cleavage–luminescence” and examined ET reaction of 1 by using the single and double laser flash photolysis (S- and D-LFP).1,2

[Experimental] LFP studies were carried out using 355- and 532-nm Nd:YAG lasers and a Xe arc lamp (150 W) as a monitoring light with a suitable cutoff filter. The sample solutions were degassed with freeze (77 K)–pump (0.1 mmHg)–thaw (ambient temperature) cycles.

[Results and Discussion] Analysis of the energy diagram for BP-sensitized ET reaction of 1a–b (Fig. 1) was carried out. The triplet energy levels of 31a–b* (2.82 eV) were determined using their phosphorescence wavelengths (440 nm), suggesting that ET reaction from 3BP* (2.98 eV) to 1a–b proceeds exergonically. The energy levels of 32a–b••* were also found to be 0.47 eV by using DFT calculations ((U)B3LYP/cc-pVDZ). Furthermore, the energy levels of 32a••* (2.44 eV) and 32b••* (2.55 eV) were determined as the sum of their excitation energies and relative energy levels of 32•• relative to 1. These analyses revealed that adiabatic formations of 32a–b••* from 31a–b* are thermodynamically-allowed.

Rate constants for quenching of 3BP* (k0) by 1a–b were evaluated by analysis of time-dependent changes of the absorption band of 3BP* at 530 nm at various concentrations of 1.
The \( k_0 \) value for \( 1a \) (2.0 \( \times \) 10\(^9\) M\(^{-1}\) s\(^{-1}\)) is determined to be twice as large as that of \( 1b \) (1.0 \( \times \) 10\(^9\) M\(^{-1}\) s\(^{-1}\)) because the number of biphenyl moieties in \( 1a \) is twice than that in \( 1b \).

The S-LFP of a benzene solution containing \( 1a \) and BP afforded at first (a delay time of 100 ns) a transient absorption of \( ^3\)BP\(^*\) at 530 nm (Fig. 2a). This band readily decayed with the progress of ET reaction affording \( ^3\)1a\(^*\) (Fig. 2b). Then, an intense transient absorption of \( ^3\)2a\(^*\), generated by ring-opening reaction of \( ^3\)1a\(^*\) (Fig. 1, Path A), appeared at 380 nm (Fig. 2a, black). The D-LFP excitation of \( ^3\)2a\(^*\) and \( ^3\)2b\(^*\) gave their fluorescence at 630 and 600 nm (Fig. 2c), respectively. Note that fluorescence quantum yield (\( \Phi_{FL} \)) and lifetime (\( \tau_{FL} \)) of \( ^3\)2a\(^*\) were successfully determined to be 0.031 and 144 ns.

Interestingly, the emission of \( ^3\)2a\(^*\) at 630 nm (Fig. 3a) was also observed only S-LFP. When the concentration of \( 1a \) is 1 mM, emission intensity (\( E \)) is fitted by quadratic function of laser excitation intensity (\( L \)) (Fig. 3b, dotted). Thus, contribution of path A is not negligible. On the other hand, when the concentration of \( 1a \) is decreased ([1a] = 0.1 mM), \( E \) linearly correlates with \( L \) (Fig. 3b, solid). These results suggest that the adiabatic reaction (Path B), that we call “the excited state C–C bond cleavage–luminescence”, takes place to generate \( ^3\)2a\(^*\) exclusively. In the presentation, we also discuss the results of \( 1b \).

**Fig. 2.** (a) Transient absorption spectra observed at 1 \( \mu \)s after LFP (355 nm) of a benzene solution containing BP (dashed line), \( 1a \) or \( 1b \) and BP (solid line). (b) Time-dependent changes of \( \Delta OD \) at 380 nm and 530 nm. (c) A transient fluorescence spectra from \( ^3\)2a\(^*\) and \( ^3\)2b\(^*\) on double LFP (355 and 532 nm, respectively).

**Fig. 3.** (a) Transient emission spectra observed upon LFP (355 nm) of a benzene solution containing \( 1a \) or \( 1b \) and BP. (b) Relationship between \( L \) (355 nm) and \( E \) (630 nm).

References:
Molecular Water Oxidation Catalysis on Aluminum Porphyrins
(Tokyo Metropolitan Univ.) KUTTASSERY, Fazalurahman; MATHEW, Siby; SAGAWA, Shogo; YAMAMOTO, Daisuke; ONUKI, Satomi; NABETANI, Yu; TACHIBANA, Hiroshi; INOUE, Haruo.

[Introduction]  An artificial photosynthetic device based on earth abundant elements is a key point of research all over the globe. Visible light induced production of oxygen via four-electron process from water is the real bottle-neck in the field of artificial photosynthesis\(^1\). Mechanistic aspect of Ru-Porphyrins based two-electron photo-oxygenation pathway induced by one-photon was well established by our group\(^1\). Recently we synthesized and characterized different metalloporphyrins by incorporating the most abundant metal in the earth crust, aluminum, gave much interest for the development of cost-effective water oxidation terminal\(^2\)-\(^3\). The electrochemical studies shows that one-electron oxidized radical cation of aluminum porphyrins exhibit catalytic current in water, which leads our interest to develop efficient total water splitting pathway with water oxidation catalyzed by aluminum porphyrins as the key-step. The water oxidation process and mechanistic aspects will be discussed in detail.

[Experimental]  Different aluminum porphyrins being synthesized and multi-protolytic equilibria of axially coordinated water molecules were well studied by different analytical techniques\(^2\)-\(^3\). Electrochemical studies was performed on Hokuto Denko HA1010mA Potentiostat with glassy carbon electrode and Boron doped diamond electrode was used. The specially designed cell with BDD holder was used to perform controlled potential electrolysis with salt-bridge connected with reduction terminal. Pt coil was used as the counter electrode and Ag/Ag\(^+\) was used as the reference electrodes. Catalytic turn over frequency was estimated using modified Randles-Sevick equation. The controlled potential electrolysis was performed in separated electrolysis cell under different buffered and non-buffered conditions. The oxygen and hydrogen were detected using Gas chromatography techniques and the isotope labelled experiments was carried out to confirm the source of electron and oxygen with water containing

Fig1: Scheme of total water splitting pathway using aluminum porphyrin as homogeneous electrocatalyst for water oxidation.
10% isotope labelled water (H\textsubscript{2}O\textsuperscript{18}). The analysis of partial oxidation product hydrogen peroxide was performed by spectrophotometric method using TiTPyP solution.

**Results and Discussion** The cationic aluminum porphyrin AlTMPyP shows excellent catalytic TOFs up to 382 S\textsuperscript{-1} under NaOH-NaOAc condition at pH 12.6. The water oxidation process was investigated under different conditions. The oxygen and hydrogen evolution was observed with ~ 45-80% faradaic yield (F.Y.). The decrease of the F.Y. of oxygen evolution upon prolonged electrolysis was observed due to the generation of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) as the partial oxidation product. The source of oxygen in oxygen and H\textsubscript{2}O\textsubscript{2} was confirmed by isotope labelled experiments using O-18 labeled water. The peroxy aluminum complex as a key reaction intermediate was confirmed using different photo physical and electrochemical methods. The laser Raman studies shows characteristic Raman scattering corresponds to O-O bond. Based on detailed experimental results and DFT calculations we propose the reaction mechanism for water oxidation on aluminum porphyrins induced by one-electron oxidation of aluminum porphyrins. The water oxidation on most abundant metal in earth crust with the low overpotential is highly promising to develop practical artificial photosynthetic devices.

**References**


Revealing transient species of fast photochromic molecules by time-resolved infrared absorption spectroscopy

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[Introduction] Fast photoswitch compounds have received much attentions because of their potentials not only for novel applications to dynamic holography and security devices but also for developing fundamental photochemistry. Recent developments of fast photoswitches enable to simplify these syntheses1 and functionalize more complex properties2 on them. In the meanwhile, the short lifetime of transient species usually makes the characterization more difficult than the case of stable intermediates because the standard methods such as NMR and X-ray crystallographic analyses cannot be applied to these short-lived transient species. In this study, we apply time-resolved infrared absorption spectroscopy to reveal the structural information of transient species. As a demonstration, the photochromic property of a novel photoswitch compound (Py-RPIC) shown in Scheme 1 is discussed.

[Results and Discussion] Figure 1a shows the transient absorption spectra of Py-RPIC excited at 355 nm of ns laser pulses (5.7×10−5 M in benzene at 297 K). Two transient absorption bands were observed at 520 and 810 nm at tens of ns after the excitation. This spectrum was gradually converted to the other spectrum with the isosbestic points in several hundreds of ns. It indicates that the first transient species was sequentially converted to the other species. Transient absorption dynamics at 400 and 560 nm shows corresponding rise and decay with the time constant of 290 ns (Figure 1b). The sequentially formed species goes back to the initial form in several ms and these reactions can be repeated many times. This result shows that Py-RPIC shows a characteristic and complex photochromism.

Figure 1. (a) Transient absorption spectra and (b) dynamics of Py-RPIC.
differently from standard photochromic compounds.

While transient absorption spectra in the visible region contain a lot of information about the electronic states, it is difficult to obtain the structural information of the transient species such as radicals because the transient absorption spectra of radicals are usually broad. To obtain the structural information of the transient species of Py-RPIC, we conducted the time-resolved IR measurements. Figure 2a shows the time-resolved IR spectra of Py-RPIC excited at 355 nm of ns laser pulses (~0.29 M in CD$_2$Cl$_2$ at 297 K). Strong peaks at 1360 and 1582 cm$^{-1}$ and several small peaks and bleaches were observed at 100 ns after the excitation. The peaks at 1360 and 1582 cm$^{-1}$ gradually decreased, and alternatively, a peak at 1630 cm$^{-1}$ gradually increased in several hundreds of ns. The time profiles of the IR signals at 1360 and 1630 cm$^{-1}$ are very similar to the decay and rise kinetics observed at the transient absorption spectra at the visible region (Figure 2b). The time-resolved IR measurements of the bridged-imidazole dimer systems and the quantum chemical calculations suggest that the peak at 1360 cm$^{-1}$ is originated from the C–N bond of the imidazolyl radical. A previous report suggests that the C=O stretching mode of the phenoxyl radical gives the IR peak at 1582 cm$^{-1}$. The alternative increase at 1630 cm$^{-1}$ indicates that the C=O bond becomes stiffer. In addition, the time profile of the bleach signal at 1670 cm$^{-1}$ revealed that the thermal back reaction from the biradical to the initial form is the rate-controlling step and takes several ms.

These experimental results indicate the following reaction scheme. 1) The photoexcitation of Py-RPIC leads to form the imidazolyl radical and phenoxyl radical, 2) this biradical is converted to the quinoid species with the time constant of 290 ns and two species are equilibrated, and 3) the thermal back reaction from the biradical species to the initial form takes several ms.

[Introduction] Molecules with multi-photon induced optical properties have captured the interest of researchers for the underlying scientific principles and their potential in industrial applications such as two photon microscopy. While the two-photon absorption through a virtual state can be induced only by a pulse laser due to their high power thresholds (~MW/cm²), the two-photon absorption through long-lived transient species such as triplet states and electronic states of rare-earth compounds can be induced even by using incoherent continuous wave (CW) light. The stepwise two-photon processes have great potential and are not only interesting photochemical phenomenon but also can be useful as efficient light harvesters.

Recently, we have designed [2.2]paracyclophane-bridged bis(imidazole dimer)¹ and bis(phenoxyl-imidazolyl radical complex) (bisPIC), that are composed of two photochromic units and absorbs two photons in the stepwise manner. The absorption of the first photon leads to the formation of a short-lived biradical species, while the absorption of the additional photon by the biradical species triggers a subsequent photochromic reaction to afford the long-lived quinoid species. The short-lived biradical species and the long-lived quinoid species display significantly different absorption spectra and rates of the thermal back reaction. The stepwise two-photon excitation process in this photochromic system can be initiated even by the incoherent continuous wave light irradiation, indicating that this two-photon reaction is highly efficient. In this study, we designed and synthesized m-bisPIC in which the imidazole rings are substituted at the 1,3-positions of the central phenyl ring, and investigated the stepwise photochromic properties in detail.

Scheme 1 Stepwise photochemical reaction of m-bisPIC1 and m-bisPIC2.

[Results and Discussion] Fig. 1 shows the absorption spectra of bisPIC and m-bisPIC. The absorption maximum of m-bisPIC is blue-shifted, compared with that of bisPIC, because the two imidazole rings of bisPIC are substituted at the 1,4-positions of the central phenyl ring.
while the imidazole rings of \textit{m-bisPIC} are substituted at the 1,3-positions. Fig. 2 and 3 show the transient absorption spectra and the decay profiles of the photogenerated transient species of \textit{m-bisPIC1} in benzene. The excitation and probed wavelengths are 355 and 550 nm, respectively. Because the excitation with 355 nm induces the sequential photocleavage reactions of the two C–N bonds, the mixture of the biradical and quinoid species are generated by the excitation with 355 nm. The absorption spectrum of the quinoid species is similar with that of \textit{PHOX-Im}, in which the imidazolyl radical and phenoxyl radical are substituted at the 1,4 positions of a benzene ring, indicating the efficient interaction between the imidazolyl radical and phenoxyl radical after the sequential reaction of \textit{m-bisPIC1}. The fast and slow decay components are observed in the decay profiles of the transient absorption dynamics. The amounts of the slow component and the absorption band of the quinoid species increase with the increase in the excitation energy (Fig. 3 and 4). Thus, the stepwise two-photon process is plausible mechanism summarizing the photochromic reactions of \textit{m-bisPIC1}. On the other hand, the weak interaction between the imidazolyl radical and the phenoxyl radical for \textit{m-bisPIC2} is observed due to the large dihedral angle between the imidazolyl and phenoxyl radical caused by the steric repulsion of the \textit{tert}-butyl groups.

Intermolecular interactions and photochromism of a diarylethene possessing phenanthroline groups

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1. Introduction
A diarylethene 1 possessing two phenanthroline groups at both ends of a bisthienylethene skeleton was synthesized. Phenanthroline is known to work as a ligand for Lewis acidic metal cations as well as an organic base. In this presentation, we will show the synthetic pathways of this compound, complexation of 1 with different metal cations and their effect on the photochromism, the acid-base reaction of 1 with mono- and dibasic organic acids and its effect on the photochromism and solubility, and the non-contact control of the absorption wavelength of 1c by the photochemically generated acids combined with the photochromism of 1 itself.

2.3. Experiments, results and discussion
1. Synthesis of 1o
The synthesis of 1o was first carried out by the addition of lithiated thiophene to phenanthroline followed by oxidation in 21% yield, with subsequent improvement by Suzuki coupling of thiopheneboronic acid to chlorophenanthroline to afford 1o of 55% yield.

2. Cu(I) complexation of 1 [1]
Photochromism of 1o was performed in various solvents such as acetonitrile, chloroform, or dichloromethane with good results. Figure 1 shows the change in the absorption spectra during 366-nm light irradiation of the 1o acetonitrile solution. The quantum yields of ring closure and opening were measured and are summarized in Table 1. The effects of metal ions on the

Fig. 1. Absorption spectra of 3.52 x 10^{-5} M 1o in acetonitrile under different irradiation time by 366-nm light. Light intensity: 0.23 mW cm^{-2}, 0 – 240 sec.
photochromism of 1 were examined. Among the metal salts, Cu(I)PF₆ showed the most remarkable effects. The absorption maximum of 1c in acetonitrile shifted to longer wavelength by 13 nm and the ring-closing quantum yield became 1/30. Spectroscopic data and quantum yields of the photoreactions are shown in Table 1. Job’s plot of 1c and Cu(I) proved the complex ratio to be 1:1.

Table 1. Spectroscopic data of the colored forms, the quantum yields of photoreactions, and conversion ratio of 1o and [1o-Cu(I)]⁺ PF₆⁻ to 1c and [1c-Cu(I)]⁺ PF₆⁻, respectively, in acetonitrile.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>λ_max/nm (ε_max/mmol⁻¹ dm³ cm⁻¹)</th>
<th>Quantum yields</th>
<th>1c/1o at PSS (366 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>630 (15,800)</td>
<td>Φ_OC 0.75</td>
<td>99.5/0.5</td>
</tr>
<tr>
<td>[1-Cu(I)]⁺ PF₆⁻</td>
<td>643 (11,500)</td>
<td>Φ_CO 0.0066</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Φ_PO 0.0035</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Φ_CO 0.0011</td>
<td></td>
</tr>
</tbody>
</table>

3. Salt formation of 1 and oxalic acid – Solubility control of the salt by photochromism [2]
Upon addition of an equivalent amount of oxalic acid dissolved in acetone to chloroform solution of 1o (2.1 x 10⁻³ mol dm⁻³), a white precipitate suddenly appeared. Job’s plot with a total component concentration of 3.50 x 10⁻⁴ mol dm⁻³ proved the ratio of 1o and oxalic acid to be 1:1. The properties of the precipitate were examined by SEM, low-coherence DLS and PXRD to confirm its crystalline-like structure, and the particle size was around 2 μm.
When the salt suspension was irradiated with 366-nm light, its color changed to blue and the precipitate gradually dissolved. Irradiation of visible light then induced reversible precipitate formation. The transparency at around 900 nm could thus be controlled by light irradiation.

4. Absorption wavelength control of 1c by the combination of another photochromic species
Spiropyran 2 changes the acidity of the proton upon photochromic reaction. When 2 was irradiated with 450-nm light with the absorbance of both 1o and 1c at almost zero, 2mc changed to 2sp. The protons released from the hydroxy group combine with the phenanthroline moieties of 1c which are the strongest base in the system. Accordingly, the absorption band shifted to longer wavelengths by 30 nm. When 2sp reverted back to 2mc by heat, the absorption band returned to its original state. Since photochromic transformations between 1o and 1c are possible, four different states can be generated on demand by photoirradiation and thermal treatment.

References
Aggregation-induced enhancement in photochirogenesis. Circularly polarized UV-visible photons swap sign of luminescent helical polymers

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[Introduction] Understanding an efficient generation and reversibility of optically active substances in the absence of chiral chemical influence has long been challenging among chemists and scientists. This approach is called absolute asymmetric synthesis (AAS) that is beneficial to shorten multiple-step synthesis requiring specific chiral chemical sources with high ee. AAS using circularly polarized (CP) light source was first predicted by Le Bel and van’t Hoff independently. This idea stimulated W. Kuhn and E. Brown to the first experimental verification of the AAS hypothesis. These pioneering works led to many AAS researchers over 150 years because of no need of expensive chemicals. However, researchers had believed that left-handed CP light source preferentially generates left- (or right-) handed molecule or vice versa, because the molecular chirality is solely determined by the CP light hand [1,2].

Previously, in a series of CP-light pumping experiments using six different photon wavelengths to fluorene-azobenzene copolymer (F8AZO) aggregates, we pointed out that the resulting CD sign depends on pumping wavelength of the same r-CP-light source, which (i) a negative-sign CD pumped at shorter wavelengths, conversely, (ii) a positive-sign CD pumped at longer wavelengths [3].

To verify generality of the CP-light wavelength dependent circular polarization and to demonstrate a versatility of photonic spin controlled circular polarization, depolarization and inversion in the ground and photoexcited states, we chose highly photoluminescent fluorene-bithiophene alternating copolymer, poly[(di-n-octyl-fluorenyl-2,7-diyl)-alt-bithiophene] (PF8T2). Non-photochromic PF8T2 aggregates were dispersed in a mixed chloroform-methanol cosolvent [4]. The aggregate sizes are ≈0.6 µm in diameter and enabled us to efficiently confine photonic spins in an optofluidic medium to tailor refractive index of cosolvent [5].

[Experimental] PF8T2 \( (M_w=4.13\times10^4, M_n=2.45\times10^4, M_w/M_n=1.68) \) was purchased from Luminescent Technology and purified by fractional precipitation. Spectroscopic grade chloroform (CHCl₃) and methanol (MeOH) were used as received. The CD and UV-vis spectra of the solutions were recorded on JASCO J-725 spectropolarimeters (Tokyo, Japan) equipped with Peltier-controlled housing using synthetic quartz grade cuvette with 10 mm path length at 25 °C. The CPL spectrum was recorded on a JASCO CPL-200 spectrofluoropolarimeter with a path length of 10 mm at room temperature. The photoluminescence (PL) spectrum was recorded on a JASCO FP-6500 spectrofluorometer with a path length of 10 mm at room temperature.
**[Results and Discussion]** From Fig. 1, when the PF8T2 was irradiated by right-handed \((r)\)-CP-photon at 546 nm (and 577 nm, not shown here), a positive CD band at 536 nm and negative CD band at 386 nm appeared, while, by left-handed \((l)\)-CP-photon at these wavelengths, these signs were inverted (not shown here). Conversely, when the PF8T2 was irradiated by \(r\)-CP-photon at 365 nm (and 313 nm, not shown here), a negative CD band at \(\approx\) 535 nm and positive CD band at \(\approx\) 390 nm appeared, while, these signs by \(l\)-CP-photon were inverted (not shown here).

Fig. 1. Changes in CD and UV-vis spectra of PF8T2 aggregates in CHCl3/Methanol (2.1/0.9 (v/v)) induced by \(l\)-CP-photon at 365 nm.

From Fig. 2, the \(g_{CD}\) values of PF8T2 aggregates were resonantly magnified at \(n_D = 1.412\) from a plot of the \(g_{CD}\) as a function of \(n_D\) values of the cosolvents. Regardless of CP-photon induced and (\(R\))-limonene-induced chiroptical polarization [4], however, the absolute CD magnitudes resonantly maximized at \(n_D \approx\) 1.40±0.05 [4,5]. The CD amplitude decreases above and below this specific \(n_D\) value. This feature might be an evidence of an optofluidic effect due to confinement of CP-photon into the aggregates by surrounding cosolvent medium. Similar effects are already reported in several limonene-induced optically active \(\pi\) - and \(\sigma\)-conjugated polymer aggregates including F8AZO by our group. This specific refractive index value of the surrounding solvents relative to the higher refractive index value of PF8T2 and F8AZO and should satisfy an attenuated resonant condition of imperfect cavity like a whispering gallery mode of an ideal spherical microresonator.

Light intensity and particle size-dependent photocatalytic activity in heterogeneous photocatalysis

(Hokkaido University) OHTANI, Bunsho; TAKEUCHI, Shugo; HORI, Haruna; TAKASE, Mai

Introduction For heterogeneous photocatalysis, it is well known that photocatalytic oxidation of water into oxygen (O₂) is induced by particulate photocatalysts in the presence of electron acceptors. This reaction has been presumed to proceed through a four-electron (hole) process, and therefore it is expected that reaction rate depends on light intensity and particle size of photocatalyst, which influence the number of photons absorbed by one photocatalyst particle. However such light-intensity dependences have rarely been reported and discussed so far. In this study, we report light-intensity and particle-size dependences of rate of oxygen (O₂) evolution and acetic acid decomposition by particulate titania and bismuth tungstate (Bi₂WO₆: BTO) photocatalysts, respectively.

Experimental Commercial titania samples with or without calcination in air were used as a titania photocatalyst for O₂ evolution from suspensions of commercial titania samples using iodate (IO₃⁻) and iron(III) (Fe³⁺) ions as an electron acceptor under intense UV-LED irradiation (365 nm; < 300 mW). BTO was prepared from bismuth(III) chloride and sodium tungstate under hydrothermal conditions [1]. The as-prepared flake ball-shaped (FB), ball-milled samples (L and H) and their 773 K-calcin samples (500FB, 500L and 500H) were used for decomposition of acetic acid in aerated aqueous suspensions under monochromatic photoirradiation by a diffraction grating type illuminator (Jasco CRM-FD) equipped with a 300-W xenon lamp or by the UV-LED.

Results and Discussion Figure 1 shows the light-intensity dependence of rate of O₂ evolution from a suspension of rutile (Tayca MT-150A; 13.2 nm) with Fe³⁺. A higher-order non-linear dependence was observed in the relatively lower (< 190 mW = threshold intensity, \(I_\text{thr}\)) intensity range, while the rate was almost proportional to the intensity (with slope, \(a\)) in the higher intensity range, and those dependences could be reproduced by second and first-order equations, respectively. Similar bimodal dependences were also observed when the other titania samples were used in the presence of IO₃⁻ or Fe³⁺ with different \(a\) and \(I_\text{thr}\). Assuming a kinetic model (Scheme 1) in which second-photon...
absorption by a one photon-absorbing particle \((\text{TiO}_2(\text{h}^+))\) within its lifetime leads to oxygen evolution, a rate equation (eq. 1) was derived using parameters of lifetime of \(\text{TiO}_2(\text{h}^+)\), secondary photon-absorption efficiency and rate constant of oxygen evolution by a two-photon absorbing particle(\(\text{TiO}_2^*\)), and further derivation for lower and higher intensity limits to eqs. 2 and 3, respectively, reproduced the bimodal light-intensity dependences. Threshold intensity \((I_{\text{thr}})\) at which order of light-intensity dependence formally changes from second to first is defined as intensity for the equal rates of eq. 1 and 2 are equal. Differences in \(I_{\text{thr}}\) and \(a\) depending on the kind of electron acceptors, crystalline structure (anatase or rutile) and particle size are discussed. When small anatase particles (Ishihara Sangyo ST-01) were used, intensity dependence at higher intensity region (> 250 mW) could be simulated with fourth order kinetics, suggesting four-electron transfer happens in this photocatalytic reaction system.

Figure 2 shows light-intensity dependence of the reaction of acetic acid decomposition under aerated conditions by BTO samples. Except for the samples L and H, BTO showed almost first-order light-intensity dependences at wavelengths between 320 and 410 nm. In the intensity-dependence measurement using the UV-LED, similar dependences were observed for FB, L and H. As has been reported previously, photocatalytic acetic acid decomposition proceeds through radical-chain mechanism with peroxy radicals as a chain carrier when titania was used as a photocatalyst, and the dependence of rate on light intensity was square root, i.e., 0.5th \([2]\). The above-mentioned first-order dependence for most of the BTO samples could be interpreted by a product of 0.5th and second-order dependences, the latter of which is attributable to possible two-electron \(\text{O}_2\) reduction by photoexcited electrons in BTO, since the conduction bottom position seems to be lower than the potential for hydrogen evolution (0 V vs NHE at pH=0) which must be lower than the potential for one-electron reduction of \(\text{O}_2\) into \(\text{HO}_2^-\) (−0.13 V).

Table 1 Order of light-intensity dependence of photocatalytic acetic acid decomposition by various BTO samples.

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Luminescence behavior and magnetic properties of cobalt complexes with a dioxolene ligand containing an anthracene-BODIPY unit

(Osaka City Univ.) KATAYAMA, Koichi; HIROTSU, Masakazu; KINOSHITA, Isamu; NAKAJIMA, Hiroshi; TEKI, Yoshio

[Introduction] Control of spin states by external stimuli is applicable to molecular switches and molecular-based memory devices.\(^1\) We have investigated the spin dynamics of \(\pi\)-radical spin system in the photo-excited spin states intending to spin manipulation.\(^2\) The spin systems, which consist of stable radicals, an aromatic hydrocarbon such as anthracene, and a functional moiety, are ideal ones to study the spin alignment on the photo-excited states. When BODIPY (boron dipyrromethene) derivatives known as energy acceptor of anthracene\(^3\) is chosen as the functional moiety, the spin system shows a unique spin dynamics, which is the competition of the mechanisms via not only spin-orbit intersystem crossing but also a quantum-mixed charge separated ion-pair state.\(^2\) On the other hand, some metal complexes show molecular bistability.\(^4\) Valence tautomerism shows a reversible change between electronic isomers formed by the combination of two redox-active centers. Cobalt complexes with a tetradentate ligand and a dioxolene ligand are known to show the change of spin states between diamagnetic (\(\text{Co}^{III}\) (low-spin)-Catecholate, \(\text{Co}^{III}\)-Cat) and paramagnetic (\(\text{Co}^{II}\) (high-spin)-Semiquinonate, \(\text{Co}^{II}\)-SQ) species.

Here, we report a new spin system, composed of anthracene, BODIPY or H, and cobalt complexes (Figure 1). In this system, both luminescence behavior and magnetic properties can be controlled by the valence tautomerism of Co center, because of the spin dynamics on the photo-excited states being affected by the tautomerism. In addition, we expect that the luminescence induced by energy transfer from anthracene to BODIPY (Figure 2) is suppressed by competition of spin-orbit intersystem crossing in the \(\text{Co}^{II}\)-SQ form.

\[\text{Co}^{III}\text{-Catecholate form} \quad \text{Co}^{II}\text{-Semiquinonate form}\]

\[R^1, R^2 = \text{H or Me} \quad R^4 = \text{H (L\(^1\)) or BODIPY (L\(^2\))}\]

**Figure 1.** Molecular structures of cobalt complexes

\[\Delta, h\nu \quad \pi\text{-radical spin system}\]

**Figure 2.** The switching of \(\pi\)-radical spin system by valence tautomerism (R = BODIPY moiety)
[Experimental] [Co(TPA)(L^n)]PF$_6$ (1, $n = 1$; 1B, $n = 2$), [Co(Me$_2$TPA)(L^n)]PF$_6$ (2, $n = 1$; 2B, $n = 2$), and [Co(Me$_3$TPA)(L^n)]PF$_6$ (3, $n = 1$; 3B, $n = 2$) were synthesized by using the combination of TPA or Me$_2$TPA ($n = 2, 3$) ligands, and anthracene-dioxolene ligand L$^1$, or a BODIPY-anthracene-dioxolene ligand L$^2$.

[Results and Discussion] We previously reported the properties of cobalt complexes 1–3.$^5$ In the solid state and the solution state, the spectroscopic data at room temperature indicate that complex 1 is Co$^{III}$-Cat species, 3 is the Co$^{II}$-SQ species, and 2 is the mixture of Co$^{III}$-Cat and Co$^{II}$-SQ species. Complex 2 shows valence tautomerism in the range of 300–400 K and light-induced valence tautomerism at 5 K in the solid state.

Compared with complexes 1–3 in CH$_3$CN, absorption spectra of BODIPY-containing complexes 1B–3B show the strong $S_0$-$S_1$ transition band of BODIPY at 497 nm along with a shoulder band at 480 nm, and nearly double $\varepsilon$ of the $\pi\pi^*$ absorption bands of anthracene moiety around 375 nm (Figure 3). In complex 1-B, the absorption bands at 600–900 nm is assigned to LMCT bands, Co$^{III}$-Cat species (Figure 3, inset), because the $^1$H NMR signals of 1-B in CD$_3$CN were observed in the range of normal chemical sifts. Complex 3-B shows the broad absorption bands at 550-900 nm along with a MLCT band at 570 nm, and no $^1$H NMR signals. These spectral features are consistent with those of Co$^{II}$-SQ species. The absorption and $^1$H NMR spectra of complex 2-B show a mixture of Co$^{III}$-Cat and Co$^{II}$-SQ species. The solution behaviors of complexes 1-B–3-B are similar to those of 1–3, respectively. The IR spectral features of complexes 1-B–3-B in the solid state are also in accordance with those of complexes 1–3, respectively. These findings indicate that the magnetic properties of cobalt complexes are controlled by the number of methyl groups on the pyridine. In complexes 1B–3B, the luminescence of BODIPY was observed by using excitation wavelength at 470 nm, which is the edge of absorption bands of BODIPY moiety.

![Figure 3. Absorption spectra of complexes 1-B (--), 2-B(— —), and 3-B (-----) at room temperature in CH$_3$CN. Inset: enlarged view of absorbance in the range of 500–900 nm.](image)

Effects of microchannel size and flow rate on photocatalytic decomposition of 4-chlorophenol in porous glass waveguide

(Shinshu Univ.) USAMI, Hisanao; OKUMURA, Kai; DOI, Takumi; OHTA, Kazuhide

[Introduction]
Reaction rate of photocatalytic system is controlled by photon flux onto each photocatalyst and the adsorption equilibria of substrate and product (s) in addition to intrinsic characteristics of the photocatalysts. Recently photocatalyst has been applied to synthesis of organic materials or decomposition of water to produce hydrogen. These application will require extreme scaling-up for practical use instead of dispersion system of photocatalyst powder, microchannel reactor in glass plate or Teflon tubing reactors. However, no reaction systems with sufficient photon flux waveguide and pathway to deliver substrate and product between each photocatalyst and the bulk phase\(^1\). We have developed a model reactor with porous glass monolith to deliver the excitation light, substrate and products. In this paper, effect of channel size on photocatalytic reactivity controlled by the diameter of component beads will be reported from viewpoints of expansion of internal surface area of the reactor and control of channel size to introduce substrate to the each photocatalysts.

[Experimental]
Borosilicate glass beads (d = 1 mm and 5 mm, Ohashi Steel Ball) were filled in borosilicate glass column (30 mm in O.D., 500 mm in length), then fused with each other and inner surface of the column. Anatase titanium nanoparticle paste (PST-18NR, JGC Catalysts and Materials) was deposited on the inner surface of the porous column reactor. Incident light delivered via the glass network in the columnar reactor was measured for a glass made cylindrical cup (d = 50 mm) filled with fused glass beads (d’ = 5 mm) located at the center of a ring-shaped black lamp (Hitachi, 30 W) using an Ocean Optics USB-2000 fiber optical spectrometer. Photon flux was measured by chemical actinometry using ferrioxalate actinometer. Product analysis was carried out using a Jasco 800 series HPLC system and absorption spectra were measured by a Shimadzu UV-2400PC spectrometer.
[Results and Discussion]

Distribution of photon flux was measured for a cylindrical model of columnar reactor, for which spectrum of the delivered light at each bead was monitored. The spectrum at each beads was the same as that of the lamp, suggesting no diffraction was occurred at each bead. The intensity of delivered light at 365 nm showed no dependence of location, but it seemed to depend on the number of contacting points with the adjacent beads. Filling ratio of the beads was ca. 60 % for the columnar reactor of 1 mm and 5 mm beads and inner surface area for these reactors were calculated as shown in Table 1.

Photocatalytic reactivity of the porous glass reactor coated with anatase photocatalyst was estimated by photocatalytic decomposition of 4-chloro phenol (4CP). It is notable that the reactivity is proportional to the internal surface area of the reactor. Considering the homogeneous distribution of incident light throughout the reactor, mass transport process between the bulk solution and the surface of photocatalyst could be assigned to the rate limiting step. According to Langmuir-Hinshelwood model, the plot of inverse of the reaction rate against the reciprocal initial concentration of D showed almost linear relationship as shown in Fig. 2, resulting that the adsorption equilibrium constant, $K_D$, was estimated as $5.3 \times 10^4$ and $3.3 \times 10^4$ M$^{-1}$ for 1 mm and 5 mm beads reactor, respectively. The equilibrium constants comparable with the value for suspension system$^2$ suggests an efficient mass transfer is achieved in this porous glass reactor system.

![Fig. 2. Plot of 1/R against bulk concentration of substrate D for Langmuir-Hinshelwood analysis for the porous glass reactor with 1 mm beads.](image)

### Table 1. Characteristics of glass beads reactor

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>diameter of bead</th>
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<tbody>
<tr>
<td></td>
<td>5 mm</td>
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<tr>
<td>Number of beads/ 10$^3$</td>
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<tr>
<td>Surface area/ m$^2$</td>
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<tr>
<td>Reactor volume/ 10$^{-4}$ m$^3$</td>
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<tr>
<td>S/V ratio*/ m$^2$m$^{-3}$</td>
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<tr>
<td>Reaction rate/ nmol s$^{-1}$</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Surface area vs. reactor volume ratio

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Single-particle absorption spectroscopy of plasmonic nanostructures

(Rice University) LINK, Stephan

[Introduction] Applications of plasmonic nanostructures take advantage of their large absorption and scattering cross sections that depend sensitively on the nanoparticle size, shape, and local environment. Effects due to distributions in these parameters can be understood using single particle spectroscopy techniques, especially when combined with structural imaging and electromagnetic simulations. Single particle spectroscopy methods have, however, been mostly developed to investigate the scattering or extinction of plasmonic nanostructures. The latter equals the absorption, but only if the nanoparticles of interest are small and do not scatter significantly. Photothermal imaging is capable of measuring the absorption only of nanostructures, and is based on the heating of the local environment following absorption and nonradiative decay. Photothermal imaging is typically limited to a single wavelength though as it requires a coherent light source for excitation.

[Experimental] Single-particle absorption spectroscopy on strongly scattering plasmonic nanoparticles is investigated by photothermal microscopy with a supercontinuum laser. With the use of a white light supercontinuum source we are able to record absorption spectra of plasmonic nanoparticles of different sizes/shapes. The absorption spectra are compared to scattering spectra of the same individual gold nanoparticles and correlated with electron microscopy images that characterize the size and shape of the nanostructures [1]. Furthermore, time-resolved transient absorption spectroscopy is employed to follow in real time the nonradiative decay of the initially absorbed photon energy [2].

[Results and Discussion] The figure below shows absorption spectra of individual gold nanorods correlated with scattering, morphology and simulations. a, b, and c are measured (●) absorption spectra, correlated with measured scattering (▬) spectra on the same nanorods. The experiments are repeated for nanorods with different scattering (absorption) plasmon resonances of 610.6 nm (606.8 nm), 652.0 nm (649.6 nm) and 687.8 nm (687.7 nm) for a, b, and c, respectively. The correlated SEM images of the nanorods are shown in the insets of a, b, and c (the size of each image is 250 nm). Using the SEM images, the lengths and widths of the nanorods are determined as 61.5 nm × 40 nm, 63.5 nm × 34 nm, and 71.5 nm × 34 nm for the nanorods in a, b, and c, respectively. These sizes are used to perform simulations with the results given shown in d, e, and f. The calculated scattering (absorption) plasmon resonances
in d, e, and f are 613.4 nm (608.9 nm), 650.6 nm (649.0 nm), and 685.8 nm (684.7 nm). The measured (calculated) peak shift between absorption and scattering for the longitudinal plasmon resonance is 3.8 nm (4.5 nm), 2.4 nm (1.6 nm), and 0.1 nm (1.1 nm).


Active control of the plasmon response

(Rice University, Houston, TX USA) LANDES, Christy

Novel chemical and physical processes occur at nanoparticle surfaces, both aided and reported by the broad tunability of their plasmonic properties. Active control is one way to relate plasmon resonance shifts to underlying changes in morphology, composition, and surface chemistry. We approach this challenge with electrochemical redox tuning of bimetallic nanoparticles and assembled structures. Our method allows us to deposit silver and/or its salts on the surface of gold nanostructures and selectively grow silver metal on the surface of these structures. We demonstrate repeatable spectro-electrochemical tuning of single nanoparticles and dimers. Potential applications include novel heterogeneous catalysis routes, experimental tests of charge transfer plasmonics, and nanoscopic plasmonic switches.
Fluorescent switches at the molecular level had attracted considerable interest during recent years because they afford promising electronic devices and controllable fluorescent labeling of biomolecules [1]. The photochemical transformations associated with photochromic compounds can be exploited to switch the emission of complementary fluorophores under the influence of optical stimulations [2]. In current work we studied both photochromic and fluorescent properties of several diarylethenes and chromenes (figure 1) as well as their non-fluorescent analogues. It was found previously that colored forms of these compounds are not fluorescent because of the efficient intramolecular energy transfer.

In the course of the preliminary experiments we found that fluorescence efficiency and position of emission band depends on the solvent polarity. The more polar is solvent the higher is the fluorescence quantum yield and the more red-shifted is fluorescence band. It is well known that such behavior indicates formation of so-called twisted internal charge transfer (TICT) state [3]. This state is stabilized in polar solvents such as acetonitrile. Moreover, the dependence of photochromic reaction efficiency on polarity of the solvent was observed. In non-polar solvents (e.g. in heptane) quantum yield of photocoloration is much higher than in polar ones.

**Figure 1.** Two types of compounds studied. 1 – chromene, 2 diarylethene

Compounds were studied by means of two ultrafast time-resolved methods: femtosecond transient absorption for UV/Vis/NIR broadband coverage and femtosecond fluorescence spectroscopy by broadband upconversion. Experiments were carried out in two different solvents: non-polar heptane and polar acetonitrile.
Kinetic curves of excited states decays were measured. Lifetimes of transient states were calculated from the data obtained. Figures 1 and 2 show typical kinetics of both an excited states formation and a decay of compounds studied (on the example of compound 1) measured in the course of experiments. Comparative analysis of kinetics measured in acetonitrile and heptane reveals differences in relaxation dynamics after the laser pulse. Two decay processes are present in acetonitrile, while only one heptane. This fact supports an assumption made on the basis of steady-state preliminary experiments that in polar solvents occurs stabilization of TICT state.

**Figure 2.** Kinetics of transient absorption measured by femtosecond pump-probe method at different wavelengths. Left - in acetonitrile, right - heptane.

![Figure 2](image)

**Figure 3.** Kinetics of transient absorption measured by femtosecond fluorescence upconversion method at 500 nm. Left - in acetonitrile, right - heptane. Black squares - experimental data, red line - calculated process.

![Figure 3](image)