



Multiphoton-gated cycloreversion reaction of a photochromic 1,2-bis(thiazolyl) perfluorocyclopentene diarylethene derivative

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ABSTRACT

Cycloreversion processes of a 1,2-bis(thiazolyl) perfluorocyclopentene photochromic diarylethene **1** with extremely low reaction yield under steady state irradiation in chloroform solution (1.3×10^{-3}) was investigated by means of picosecond and femtosecond laser photolysis methods. The cycloreversion reaction was drastically enhanced by more than two orders of magnitude (*ca.* $\times 400$) by a picosecond 532 nm laser excitation in comparison with a steady state irradiation. From time-resolved transient absorption measurements, double pulse experiments, and excitation intensity dependence of the transient absorbance and the reaction efficiency, this enhancement was attributed to a stepwise two-photon absorption process leading to high excited state.

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1. Introduction

Owing to the massive and worldwide diffusion of information and the growing volume of data generated, boosting our capability to share, transfer and store data is essential. Seeking for high storage capacity and high-speed transfer data storage devices is an important research area, and downscaling the memory bit ("0/1") to the molecular dimension and decreasing the switching time are among current issues. Systems involving the use of photons, so called photonic devices, are promising in this sense.

Molecular photochromic systems are good candidates to fulfill such targets. Indeed, they undergo a photoinduced reversible reaction between two molecular species, which could be assigned to the "0" and "1" states. Due to the fast change of molecular properties via the related chemical bond reconstruction (usually in the picosecond range), such molecules and materials appear to be efficient to provide externally triggered high-throughputs [1–5]. During the past decades, many investigations have been carried out in the synthesis of new families of photochromes [4,6–11]. Among

them, diarylethenes, which undergo a 6π -electrocyclization and cycloreversion on ultrafast timescales [12–21], have known an important development since their discovery about two decades ago [1,22,23].

Among current challenges and issues remaining, the development of molecules capable to undergo photochromism in different states of the matter is a wide topic. In this direction, several diarylethene molecules have proven to be photochromic in pure solid-state bulk materials [24–28], or in nanomaterials [29–33] which are examples of high-density media containing exclusively the active molecule itself. The achievement of non-destructive readout is another challenge. Indeed, probing the absorption of the device to read its state ("0" or "1") is convenient. However, such a probing method requires the use of light at a wavelength, which concomitantly causes switching, and eventually writing/erasing.

To overcome this issue, several approaches are reported in the literature, such as probing by fluorescence [9,34], refractive index [35] or IR measurements [36]. Using two-photon processes is another strategy to reach the same goal. Over the past years, we have reported enhancements of the efficiency of the cycloreversion reaction in diarylethenes in solution [37–39], polymer films [40] and crystalline phases [16,41], when a pulse laser was used instead of a conventional light source. Enhancements over 50-fold were measured on low reaction yield systems (*ca.* 10^{-2}). Indeed, the excitation intensity and pulse duration affect the reaction profile: with pulse laser, higher excited states are attained by multiphoton absorption in the visible region, and more efficient photochromic

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reaction channels opened. These are operational neither with lower power sources in the visible nor by one-photon absorption in the UV [37–39]. This multiphoton-gated reaction may provide an approach to reduce the crosstalk between the reading and the writing/erasing processes, especially for molecules with low one-photon reaction quantum yield. High excited state (S_n) unreachable by one-photon absorption can be populated.

In this article, we report on the study of 1,2-bis(5'-ethoxy-2'-(2''pyridyl)thiazolyl)perfluorocyclopentene (**1**, Scheme 1). The choice of this compound is mainly motivated by its particularly low cycloreversion quantum yield (1.3×10^{-3} in solution), and by its ability to undergo photochromism in solution, in bulk solid-state and in nanoparticles [32]. Moreover, in terms of molecular design, **1** combines two types of heteroaryl groups, pyridine and thiazole, which is rather original. Only few investigations were performed on the influence of nitrogen on high excited state population and multiphoton processes. From this viewpoint, this study represents one of the first attempts to provide information on its possible influence on multiphoton processes. Cycloreversion reaction was followed by ultrafast spectroscopy, and its mechanism was investigated in order to evidence the multiphoton gated photochromism and to evaluate its effect.

2. Materials and methods

2.1. Synthesis, sample preparation and steady-state spectroscopy

1,2-Bis(5'-ethoxy-2'-(2''pyridyl)thiazolyl)perfluorocyclopentene (**1**) was synthesized and purified in its open form (**1(OF)**) as reported in the literature [32]. Chloroform (Wako, infinity pure grade) was used without further purification. Solutions of **1(OF)** were irradiated with a Perfect UV LAX-103 from Asahi Spectra, using adequate filters. In particular, samples for time-resolved spectroscopy measurements, containing more than 99% of **1(CF)**, were obtained by this method. Absorption measurements were performed with a Hitachi U-3500 UV-vis absorption spectrophotometer.

2.2. Time-resolved spectroscopy studies

All time-resolved measurements were performed under O_2 -free conditions. All experiments were carried out at $22 \pm 2^\circ C$.

A picosecond laser photolysis system [42,43] with a repetitive mode locked Nd^{3+} :YAG laser was used for transient absorption spectral measurements in the picosecond–nanosecond time region. The second harmonic (532 nm) with a pulse duration of 16 ps (FWHM) was focused in the sample with a spot size of ca. 1.5 mm diameter. A picosecond white light continuum generated by focusing the fundamental pulse into a 10 cm quartz cell containing D_2O and H_2O (3:1) was employed as a monitoring light. A sample cell with a 2 mm optical length was used. The transient spectrum was obtained only with one-shot laser exposure. For the measurement of the excitation intensity dependence appropriate filters were used to tune the laser excitation intensity. The energy of the picosecond laser light was measured by a laser power meter (Gentec, ED-200).

To investigate the dynamic behavior under femtosecond laser light excitation, a dual NOPA/OPA laser system was used for transient absorption spectroscopy [16,37–41,44–48]. Briefly, the output of a femtosecond Ti:Sapphire laser (Tsunami, Spectra-Physics) pumped by the SHG of a cw Nd^{3+} :YVO₄ Laser (Millennia V, Spectra-Physics) was regeneratively amplified with 1 kHz repetition rate (Spitfire, Spectra-Physics). The amplified pulse (1 mJ pulse⁻¹ energy, 85 fs FWHM, 1 kHz) was divided into two pulses with the same energy (50%). One of the two pulses at

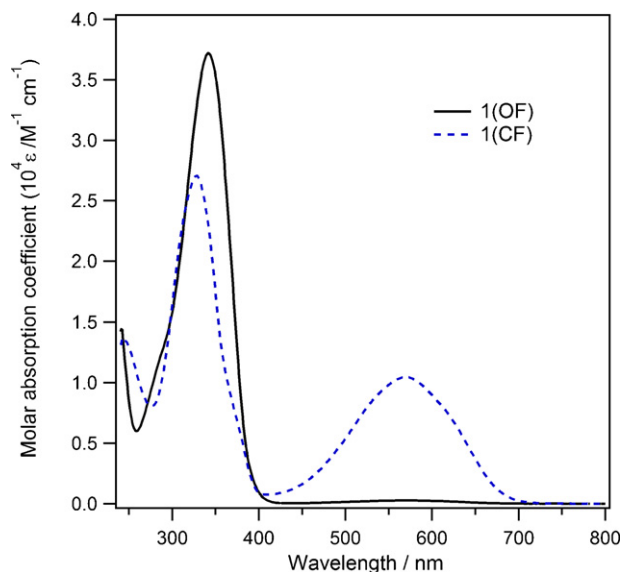


Fig. 1. Steady state absorption spectra of **1** in the open-ring isomer, **1(OF)** (full line) and in the closed-form **1(CF)** (dashed line) in chloroform solution.

802 nm was guided into a non-collinear optical parametric amplifier (NOPA) system (TOPAS-white, Light-Conversion) which covers the wavelength region between 500 and 780 nm with 1–40 mW output energy with ca. 20–40 fs FWHM. The wavelength of the NOPA was tuned at 580 nm in the present study. Pulse duration at the sample position was estimated to be ca. 30 fs FWHM by FROG signals.

The other pulse at 802 nm was guided into an OPA system (OPA-800, Spectra-Physics) and converted to 1200 nm pulse (1–10 mW output energy with ca. 120 fs FWHM), which was focused into 3 mm CaF_2 plate to generate a white-light continuum covering the wavelength region from 350 nm to 1000 nm. This white light was used as a probe pulse. Polarization angle between the pump and probe pulses was set at the magic angle for all the measurements. The probe pulse was divided into signal and reference pulses and detected with multichannel photodiode array systems (PMA-10, Hamamatsu) and sent to a personal computer for further analysis. The chirping of the monitoring white light continuum was corrected for transient absorption spectra. The FWHM of the cross correlation between the pump and probe pulses was ca. 80 fs at the sample position. A rotating sample cell with an optical length of 2 mm was utilized and the absorbance of the sample at the excitation wavelength was set to ~ 1.0 .

3. Results and discussion

3.1. Steady-state absorption spectra

Fig. 1 shows steady-state absorption spectra of diarylethene **1** in solution. The open-form of **1**, **1(OF)** only absorbs light in the UV region whereas the closed-form of **1**, **1(CF)** has absorption bands both in the UV and visible regions. Maximum absorption wavelengths are respectively located at 328 nm and 570 nm in chloroform solution. Quantum yields for the cyclization reaction (OF to CF) and cycloreversion reaction (CF to OF) are respectively 0.32 and 1.3×10^{-3} [32]. Irradiation of **1(OF)** in the UV region leads to an almost quantitative transformation ($>99\%$) to the closed form.

3.2. Femtosecond laser photolysis

We measured the transient absorption spectra (ΔAbs spectra) of **1(CF)** in chloroform solution (Fig. 2), excited with a femtosecond

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