Picosecond cyclization reaction dynamics of furan-based diarylethene with thiosemicarbazone side-chain groups

A. A. Khodko\textsuperscript{a}, V. V. Khomenko\textsuperscript{a}, O. D. Mamuta\textsuperscript{a}, Iu. P. Mukha\textsuperscript{b}, D. O. Sysoiev\textsuperscript{c}, T. Huhn\textsuperscript{c}, S. V. Snegir\textsuperscript{b}, and N. M. Kachalova\textsuperscript{a}

\textsuperscript{a}Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine; \textsuperscript{b}Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine; \textsuperscript{c}University of Konstanz, Konstanz, Germany

**ABSTRACT**

Picosecond cyclization reaction dynamics of furan-based photochromic diarylethenes with thiosemicarbazone side-chains were studied by femtosecond transient absorption spectroscopy. The monitored ring-closing reaction in the time range of 0-1100 ps is characterized by two main stages. First stage proceeds during the first 1.1 ps and is associated mainly with redistribution of $\pi-\pi$ molecular orbitals of excited open-ring molecules which consequently leads to the formation of excited closed-ring molecules. During the next 300 ps, a long-term relaxation via vibrational cooling of closed-ring form occurs. The obtained relaxation dynamics curve was fitted by an exponential decay function with 68 ps time constant.

**KEYWORDS**

photochromic molecules; diarylethenes/ difurylethenes; photocyclization reaction; pump-probe spectroscopy; femtosecond laser

**Introduction**

Photochromism is a photoinduced reversible chemical reaction, during which materials change their optical, electrical and conformational properties [1]. Among known photochromic molecules, the diarylethenes (DAEs) can be reversely switched between two well-defined open-ring (OF) and closed-ring (CF) forms by irradiation with ultraviolet/visible light and/or by electrical stimulation. This type of switches attracts much attention for the last few years [2, 3]. Moreover, these molecules can be contacted in two-wire geometry making them applicable as organic elements in optoelectronics [4].

For implementation into real molecular electronics devices such as logic gates [5] and optically switchable transistors [6, 7] both OF and CF of DAEs should possess the key properties [1]: thermal stability, high fatigue resistance, rapid optical response, and minor structural change while switching. Most of these requirements are fulfilled, if appropriate photochromic core and side-chain groups are combined [2, 8]. Among the known photochromic molecules, DAEs display optically-induced reversible switching in solutions in the femtosecond regime [9-18]. Furthermore, while DAEs being attached to metallic electrodes at least ring-closing reaction can be achieved [19, 20]. Unfortunately, the suitable side-chain groups that can be used to link the photochromic core with metal electrodes for further construction of a reversible switchable metal-organic device still were not identified even though numerous
functionalized DAEs were synthesized and discussed in the literature [2, 7]. One of the most successful structures so far is a design by Feringa’s group based on a thiophene switching core, attached via a cross-conjugated meta-phenyl linking group and equipped with gold anchoring groups for molecular grafting onto Au(111) surface [21] and for binding to gold nanoparticles [22]. By replacing the thiophene in the photochromic core with its oxygen homologue furan bearing DAE were accessible. Their conductance on a single-molecule level was investigated recently by break-junction experiments at low temperatures [23]. Moreover, the aromatic linkers were replaced by partly conjugated heteroatom-rich groups efficiently decoupling the molecular switch from the gold electrodes and, thus, avoiding unintended quenching of the exited state [24].

Using this design, a new type of furan-based DAE, the 1,2-bis(2-methyl-5-((E)-(2-thiocarbamoylhydrazono)methyl]-furan-3-yl)-perfluorocyclopentene (CF5-TSC) was synthesized and purified according to [24]. The thiosemicarbazone (TSC) side-chain [25] was used to connect the molecule successfully with gold electrodes [26]. Figure 1a represents
photoinduced ring-closing and ring-opening (a) of CF5-TSC under consecutive UV/vis light irradiation. The formation of the closed form (CF) is characterized in absorption spectra (Figure 1b) by the appearance of a new broad absorption band in the range of 450÷730 nm and a decrease of absorption of the bands in the shorter wavelength range of 250÷450 nm. The reverse ring-opening reaction can be induced by visible light which leads to restoring of initial spectra of OF without absorption band in the visible light region.

Both CF and OF are thermally stable, reversibly switchable and have appropriate optical properties (photoconversion quantum yields: cyclization – 0.28, cycloreversion – 4.9·10^{-3}) [25]. This makes molecules attractive candidates for further applications in the molecular-scaled flexible devices with optically modulated properties [4]. However, to use them in a construction of devices with a rapid optical response the dynamics of ring-closing and opening reactions have to be studied. This will allow not only to define the time ranges, during which these reactions occur, but clarify possible operation time limits of the devices as well.

Consequently, we continue study of the optical properties of CF5-TSC and particularly will pay attention to the ring-closing reaction, using femtosecond pump-probe spectroscopy. We expect that cyclization reaction of CF5-TSC will be a complicated combination of sequential processes on ultrafast timescale: from hundreds of femtoseconds up to tens of picoseconds as for DAEs with similar thiophene-based photochromic core [10]. If monitored ring-closing reaction of the CF5-TSC will occur similarly to the thiophene-based DAES it will mean that oxygen substituting in the photochromic core has no influence on the ring-closing time range compared to thiophene-based DAES [9–16].

Experimental

The photoinduced dynamics were explored by femtosecond transient absorption spectroscopy at the Center for collective use “Femtosecond Laser Complex” at the Institute of Physics (Kyiv, Ukraine) [27, 28]. The amplified femtosecond pulses (E = 0.5 mJ, τ = 150 fs, λ = 800 nm, υ = 1 kHz) from Ti:Sapphire laser (Coherent, USA) were split into two channels: “pump” initiated cyclization reaction, while probe tracked the ultrafast changes in absorption, which have occurred in the sample. Since cyclization occurs under UV illumination (Figure 1b), we used the third harmonic generation (E = 0.4 μJ, t = 150 fs, λ = 266 nm, υ = 250 Hz), obtained via the femtokit for third harmonic generation (Eksma Optics). As probe pulse white light supercontinuum generation (SC) – λ = 540÷600 nm, obtained in Al2O3 crystal by femtosecond pulses at λ = 800 nm was used. The spectral range of probing was chosen in accordance to the CF absorption band under stationary UV/vis illumination (Figure 1b). The probe beam was split into signal and idler beams before crossing the sample, then both beams were recorded by multichannel spectrograph (Imaging Spectrograph SP-2500i, Acton, USA). To correct SC fluctuations, the transient absorbance spectra were obtained by comparing signal and idler spectra for different time delays, and then, the group-velocity dispersion was corrected at all obtained transient traces [29].

Ethanolic solution of CF5-TSC with optimal concentration C = 5·10^{-5} mol·L^{-1} was used. The CF5-TSC solution was pumped through a quartz flow cell with 2 mm optical path using a peristaltic pump with flow rate, Q = 2 ml/s. To avoid accumulation of CF, we irradiated the solution in the buffer volume by broad visible radiation (Schott KL 1500 LCD, P = 150 W), which caused the reversible ring-opening reaction. All studies were performed at room temperature T = 22 ± 0.2°C. All solutions of CF5-TSC were stored in the dark to avoid
uncontrolled photochromic reactions which may occur under the action of natural or/and artificial light.

**Results and discussion**

The photoinduced changes in optical density of photochromic molecules with TSC side chains were studied by pump-probe measurements using femtosecond UV pump pulses ($\lambda = 266$ nm) and SC probe pulses ($\lambda = 540\text{--}600$ nm) at a variable temporal delay. We monitored the transition from OF to CF in two separate time ranges. The first stage is associated mainly with ring-closing reaction (Figure 1a). This stage was studied in a time range from $0\text{--}3$ ps (Figure 3). The further long-term relaxation (Figure 2) [10] of exited CF after the process of C-C bond formation was monitored in the range of $0\text{--}1100$ ps (Figure 4).

At the beginning of the first stage each pump pulse initiates the cyclization reaction: OF molecules absorb UV light and move to a higher excited state $S_n$ (Figure 2). After a fast electronic state mixing, an electron density is redistributed. In consequence, the excited OF is passing through the conical intersection [11] to the transitional state (TR) between the OF and CF ground states. The further formation of C-C bond occurs following by $\pi - \pi$ orbital coupling in the photochromic core at TR (i.e., appearance of CF molecules).

These consistent processes are tracked by a probe pulse, since the growth of optical density of OF starts at 0 ps and finishes near 1.6 ps (Figure 3).

The gradual changes of optical density in the current experiment was monitored in the range of $\lambda = 540\text{--}600$ nm (Figure 3a) according to the position of CF maximum (Figure 1b), that appears during photoinduced cyclization reaction. This is expected since freshly formed CF molecules absorb light in this range (Figure 1b). From the obtained data we plotted time profile of the optical spectra changes at 580 nm (Figure 3b). This plot has nonlinear behavior reflecting the dynamics of ring-closing reactions. To characterize the gradual growth of the optical density, we determine the rise time as the time where absorbance changes from 10% to 90% of the final value of optical density. We found the upper boundary of the rise time is close to 1.1 ps (Figure 3b). Another approach to characterize this process is fitting of the experimental data with convolution of exponential function and instrument response function (Figure 3b). For the minimal expected instrument response function (FWHM = 212 fs), we obtained...
Figure 3. Photoinduced changing of optical density during transition of OF to excited closed-ring molecules (CF<sub>ex</sub>), initiated by femtosecond pump pulses at $\lambda = 266$ nm and probed at $\lambda = 540-600$ nm: (a) Time-resolved spectra in the time range 0–3 ps; (b) Normalized time profile of ring-closing reaction obtained by the monitoring of optical density growth at 580 nm was fitted by sigmoidal and exponential functions [30].

an upper boundary of the time constant of 0.49 ps. Further measurements with shorter laser pulses are required for a more precise determination of the ring-closing time constant. We do not exclude that in solvents with different polarity CF<sub>5-TSC</sub> might display different time of cyclization reaction [15, 35].

The next stage was associated with further long-term relaxation processes of CF<sub>ex</sub> of the newly formed molecules (Figure 2). They are characterized by vibrational cooling of a hot CF species to the thermal equilibrium (Figure 4). After 3 ps delay a noticeable decrease of the optical density was detected that corresponds to the further relaxation of CF<sub>ex</sub>.

After 300 ps, the optical density level is stabilized, which means that the relaxation process is finished. The relaxation time profile was fitted by exponential decay function with time constant, $t_{relax} = 68 \pm 15$ ps, in line with the proposed reaction model [10] with similar dynamics compared to other DAEs [11, 12]. Thus, we found that the upper boundary of the rise time is 1.1 ps for photoinduced cyclization reaction of CF<sub>5-TSC</sub>. The determined time is slightly larger than the one for some others similar thiophene-based DAEs [10–13], but is lower compared to equivalent DAEs with various modifications of side-chains groups [14–16]. Therefore, we suspect that exactly the side-chain groups of the molecules play the key role in processes of ring-closing reaction [31, 32]. This might be explained by the difference in the nature of these groups, since some can withdraw electron density from the photochromic core, while others can donate electron density [33, 34]. Therefore, the cyclization reaction
dynamics, which involves the process of $\pi-\pi$ molecular orbitals (MO) redistribution within the photochromic core, may have quite different time scale. Moreover, such reaction may be sensitive to the pump wavelength [18] and solvent polarity [15, 35].

The other quite important finding of our work is the study of the substituent effect of oxygen atoms within a structure of CF5 photochromic core. Taking into account that the determined cyclization time of CF5-TSC is close to all CF5-based DAEs studied by pump-probe spectroscopy [10, 12, 16] and the relaxation profile has a similar shape [9, 11, 13], we conclude that the exchange of thiophene against furan apparently has no impact on the ring-closing dynamics of the resulting DAE. Hence, for an application of CF5-based DAE in a combination with gold electrodes, the use of furan-based DAE will be a technical benefit, since oxygen atoms are chemically inert towards gold when compared with sulfur [25].

**Conclusions**

The picosecond cyclization and further relaxation dynamics of a new sulfur-free furan-based DAE with functional TSC side chains were studied by femtosecond transient absorption spectroscopy in detail. We found that the upper boundary of the rise time is 1.1 ps for the cyclization of CF5-TSC, in which the sulfur atoms in the photochromic core were replaced by oxygen. This is equivalent value to the cyclization time range of similar thiophene-based molecules. After $\pi-\pi$ orbital coupling, the long-term relaxation to thermal equilibrium of CF was detected for CF5-TSC molecules. Therefore, the femtosecond pump-probe technique is a suitable tool to systematically study the correlation of structural modifications of DAEs and their optical properties on the ultrafast time scale aiming to develop further functionalization strategies.

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## References


