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Published in:
Ultrafast Phenomena XIV

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Hania, R., Pugžlys, A., Kudernac, T., Jonkman, H., & Duppen, K. (2005). Ultrafast quenching of ring closure in molecular switches, self-assembled on gold nanoparticles. In S. DeSilvestri, T. Kobayashi, T. Kobayashi, K. A. Nelson, & T. Okada (Eds.), *Ultrafast Phenomena XIV* (Vol. 79, pp. 679-681). University of Groningen, The Zernike Institute for Advanced Materials.

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Ultrafast quenching of ring closure in molecular switches, self-assembled on gold nanoparticles

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Abstract. We report the ultrafast quenching of the ring-closure reaction in BTE-based photochromic switches self-assembled on gold nanoparticles. The photoinduced population dynamics of the switches reveals that the electronic states of the switch molecules are strongly mixed with the states of the gold particles.

1. Introduction

In recent years, there has been increasing interest in the synthesis, investigation and application of organic photochromic materials as a possible basis for opto-electronic and photo-optical devices [1, 2 and references therein]. Bisthiénylene (BTE) based compounds in particular attracted much attention because of their low fatigue, high thermal stability, remarkable switching sensitivity and rapid response [3]. Implementation of such photochromic switches into electronic elements is expected to open new perspectives in the creation of novel opto-electronic devices with unique functionalities. Therefore, determination of the pathways of excitation relaxation in photochromic switches assembled on metal contacts, such as occur in devices, is an important issue from both fundamental and practical point of view.

Ring opening and ring closure reactions in free BTE-based photochromic switches were extensively studied in the past decade. It was demonstrated that the ring closure reaction in the switch molecule proceeds via ultrafast equilibration of the initially excited state with an electronic state of different symmetry, from which a transition to the ground state of the closed form occurs in a few picoseconds [2,3]. The reaction quantum yield (QY) was shown to be close to 0.5. Very recently, it was demonstrated that in a BTE-based molecular switch attached to gold contacts, the ring closure reaction is fully quenched and switching occurs only in one direction, namely from the closed to the open form [4]. It was suggested that the absence of the ring closure is caused by the quenching of the precursor state of the open form by gold.

Here, we discuss the dynamics of the ring closure of a thiophene substituted bisthiénylcyclopentene photochromic switch (T-DTCP) in solution and compare this to the dynamics of the same switch attached to gold nano-particles. The studies are performed by means of femtosecond, polarization selective, frequency resolved pump-probe experiments.

2. Experimental Methods

The isolated T-DTCP molecules, the same molecules self-assembled on gold nano-particles and reference dodecanethiol-coated gold nanoparticles were all dissolved in toluene. In order to avoid photodecomposition, the solution was flowed through a 100 μm cell by a peristaltic pump.

Pump-probe experiments were performed in the standard geometry [2]. All samples were excited with 100 nJ, 350 nm pulses, while the photoinduced population dynamics was probed in the 490-620 nm spectral region. Gaussian fits of two-color two-photon absorption in a 100 μm glass plate indicated a time resolution of the experiments of 63 fs at wavelengths larger than 520 nm and up to 90 fs at 490 nm.

3. Results and discussion

Characterization of the T-DTCP photochromic switch. In Fig. (1a) the chemical structure of the T-DTCP switch molecule in the open and the closed form is shown. Switch molecules in the open-ring form absorb only in the near-UV spectral region (solid line in Fig. 1b). Ground-state interconversion between the open-ring and closed-ring isomers does not occur, but upon UV-irradiation the open-ring isomer converts to the closed-ring one. As a consequence of the near-coplanar geometry of the thiophene moieties in the closed-ring form, π -conjugation spreads throughout the molecule resulting in the appearance of a new red shifted absorption band (dashed line in Fig. 1b). Upon visible irradiation the ring opens, which breaks this conjugation. Our estimate of the QY of the ring closure reaction in toluene solution is 0.4 ± 0.1 . This is mainly determined by the co-existence in a close to 1:1 ratio of switchable and non-switchable conformers (for details see ref. 2).

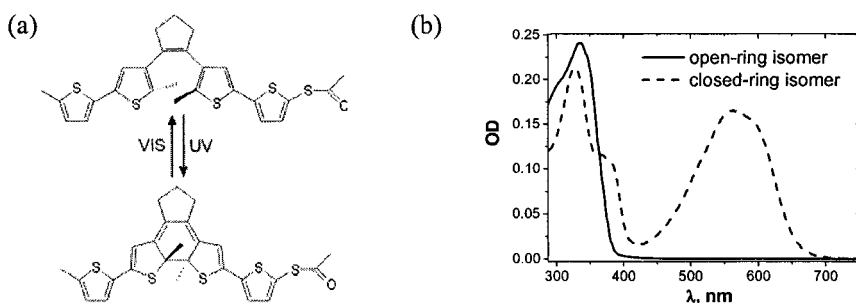


Fig. 1. Panel (a): chemical structure of the thiophene substituted BTE molecule in the open-ring (top) and closed-ring (bottom) forms. Panel (b): steady state absorption spectra of the molecules depicted in panel (a).

Dynamics of the ring closure reaction in the isolated T-DTCP switch. The dynamics of T-DTCP, measured at different probe wavelengths, reveal that the initially excited state, similar to the case of the benzene substituted bithienyl-

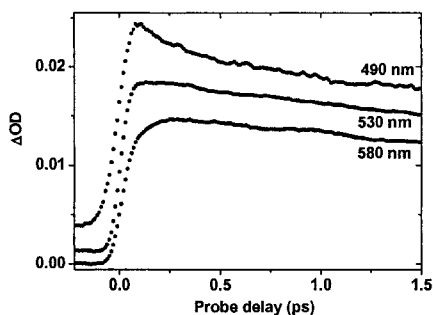


Fig.2. Pump probe transients of T-DTCP in solution at different probe wavelengths.

cyclopentene molecular switch (B-DTCP) [2], decays via mixing with an intermediate state. From this latter state a transition occurs to the ground state of the closed form.

The time constants of the dynamics are obtained by fitting pump-probe transients measured at probe wavelengths of 490 nm and 580 nm (see Fig. 2) at which, respectively, the initially excited and intermediate states are probed.

This reveals an evident precursor-successor relation with a transition time of 95 fs. This resembles the reported scheme of the ring closure reaction of B-DTCP [2]. The ring closure itself is observed by monitoring the formation of the ground state of the closed form. The time constant, thus obtained, is 3.7 ± 0.3 ps, which is typical for ring closure of perhydro-BTE derivatives [3].

Dynamics in T-DTCP self-assembled on gold nanoparticles. In the case of T-DTCP molecules attached to gold nano-particles with sub 5-nm diameter, the dynamics change dramatically. The pump-probe transients measured at different probe wavelengths are, after normalization, identical within noise level. The signals are formed instantaneously, which is followed by bi-exponential decay with time constants of 300 ± 30 fs and 3.1 ± 0.2 ps.

The observed instantaneous formation of the signal reveals that the energy transfer from the intermediate state to the gold manifold, suggested in [4], is oversimplified. The observed decay times are close to the time constants that were observed for the reference gold particles (0.3 ± 0.1 ps and 3.3 ± 0.3 fs). These times are characteristic for the surface-plasmon dynamics of gold, due to electron-electron and electron-phonon scattering, respectively [5]. This indicates that strong mixing of electronic states takes place after the covalent self-attachment of the switch molecule to the gold surface. An independent treatment of the switch molecule and the gold surface is then impossible.

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