

## Photophysics of hydrogen bonded diarylethene dimers in the liquid phase

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### ARTICLE INFO

#### Article history:

Received 24 September 2012

In final form 7 November 2012

Available online 16 November 2012

### ABSTRACT

Hydrogen bonded diarylethene dimers are formed through a carboxylic acid ligand, as is evident from concentration dependent OH stretching infrared spectra. Dimer formation leads to a red shift, enhancement and broadening of OH stretching absorption characteristic for cyclic carboxylic acid dimers. We compare the electronic spectra and photoinduced ring-opening and -closing kinetics of dimers and monomers. The  $S_0$ - $S_1$  absorption band of the closed form undergoes a slight red-shift when going from the monomer to the singly closed dimer and the doubly closed dimer. The photoreaction kinetics of dimer and monomer are identical. Consequently, the photochrome retains its original photophysical properties in the dimer state.

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### 1. Introduction

Photochromism is the ability of a molecule to undergo a reversible photochemical reaction between optically, chemically or electronically distinct states [1]. Among the broad manifold of photochromes, diarylethenes stand out with excellent thermal stability, unsurpassed fatigue-resistance [2], fast response times and good photoreaction quantum yields. Upon ultraviolet photoexcitation, diarylethenes undergo a transition from an open-ring (o) to a closed-ring (c) isomer which can be fully reversed by irradiation with visible light. This class of molecules has received intense attention and is regarded as a highly promising candidate for future technological applications. Ultrafast all-optical information processing and molecular-level high density data storage are two visionary examples.

A large body of knowledge has been gathered on the basic photochromic process of the diarylethenes by studying highly dilute liquid solutions. However, the realization of devices based on photochromes requires their integration on surfaces and at high densities. Under these circumstances, couplings between neighbouring photochromes become crucially important. Under favourable conditions, the intermolecular coupling can lead to an improved photoreaction yield as has been observed for diarylethene crystals [3] and silyl bridged dimers [4]. It can, however, also become detrimental to the function in through-conjugated diarylethene oligomers where the photoconversion of one molecule renders the neighbouring molecule unswitchable [1,5]. Apart from steric interactions, the intermolecular couplings can broadly be divided into those acting through space and those induced by the chemical bond which is utilized to control the separation between

the pair of photochromes. The chemical bond may lead to an orbital overlap and introduces a level of complexity [6] which makes it hard to single out contributions from different coupling mechanisms. It may even be arguable to what extent the monomer and the oligomer are comparable or whether they represent different chemical species.

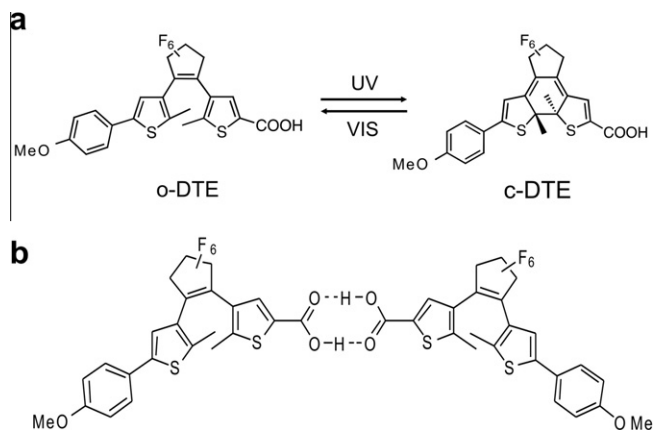
In this Letter, we present new results on hydrogen bonded dimers of diarylethenes formed via a carboxylic acid ligand attached to the chromophore. The occurrence of dimers with a cyclic O-H...O binding geometry is evident from the concentration dependent infrared spectra of the OH stretching vibration. The absence of an orbital overlap between the associated molecules provides access to the through-space contribution of the coupling. Analysis of the electronic spectra, the fluorescence properties and the photoreaction kinetics of the dimers points to a negligible electronic coupling via this route. Likewise, minor changes in the electronic transition energies in the singly and doubly closed dimer do not cause any detectable difference in the photophysical properties of dimer and monomer. Thus, this particular dimer geometry allows for linking chromophores in a well-defined geometry while retaining the photoswitching behavior of the monomers.

### 2. Experimental

The analyte (1-(2,5-dimethyl-3-thienyl)-2-[2-carboxyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (DTE, Scheme 1a) was synthesized according to a published procedure [7,8]. All solutions of DTE were prepared in degassed carbon tetrachloride (Merck, spectroscopy grade) under a nitrogen atmosphere (<1% oxygen). The open-form isomer (o-DTE) was generated by irradiating the solution with a red power LED source emitting at 625 nm. The absorption spectrum was then inspected (Perkin-El-

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**Scheme 1.** (a) Chemical structure of the open-ring (o-DTE) and the closed-ring (c-DTE) isomer of DTE. Irradiation with UV (VIS) light triggers the ring-closing (ring-opening) reaction. (b) Structure of a hydrogen-bridged dimer formed from two o-DTE molecules.

mer Lambda 2S) in the VIS region in order to preclude the presence of byproducts. The closed-form isomer (c-DTE) was produced by irradiation with a HeCd laser at 325 nm. A CaF<sub>2</sub> cuvette (0.5–10 mm path) was used to measure the vibrational absorption on a Varian 640-IR FTIR spectrometer. Spectra at micro-molar concentrations were measured using a quartz cuvette (Hellma, Suprasil 300, 5 cm path). Fluorescence excited with a 310 nm light emitting diode (LED UVTOP-305-BL, 1 μW) was recorded on a home built micro-spectrometer equipped with a nitrogen cooled CCD sensor in order to avoid spectral distortions due to the photo-transformation of the sample.

The photoreaction kinetics were examined through an actinometric method [9]. In brief, the photoproduct concentration is recorded as a function of time during the irradiation of the sample with a switching beam of known power. Irradiation at the isosbestic point at 325 nm was chosen to facilitate the data analysis [10]. The photoreaction is nearly unidirectional at this wavelength due to the high ratio in the quantum yields between the ring-closing and ring-opening reactions on the order of 125:1 [11]. The buildup of the photoproduct was monitored at 635 nm where only the closed-ring isomer absorbs. At low concentrations the sample solution was homogenized by vigorous stirring. Switching and monitoring beams were arranged at 90°. Due to the high optical density this was not practical for the concentrated solution. Instead, the solution was sealed into a 12 μm thick cuvette and irradiated in a 0° arrangement. Spatially uniform irradiation was accomplished with a microlens array based beam homogenizer.

### 3. Results

The formation of hydrogen bonded dimers (Scheme 1b) was observed through infrared absorption spectroscopy on different concentrations of DTE in carbon tetrachloride. Figure 1a depicts two exemplary spectra for solutions at 8 μM and at 21 mM of the open-ring isomer. At low concentrations (denoted as monomer), the stretching vibration of free OH groups gives rise to the pronounced absorption band with a maximum at 3534 cm<sup>-1</sup> (solid line). The absorption bands between 2840 and 3000 cm<sup>-1</sup> are due to different CH stretching modes of the chromophores and hydrocarbon impurities in the sample (see note in Figure 1a). With increasing DTE concentration, a very broad and intense OH stretching absorption builds up in the frequency range from 2400 to 3200 cm<sup>-1</sup>. At a high DTE concentration of  $c \approx 20$  mM, this broad band with a highly structured spectral envelope (dashed line in

Figure 1a) is orders of magnitude stronger than the residual absorption of free OH groups at 3534 cm<sup>-1</sup>. The red shift, broadening and enhancement of the OH stretching absorption are caused by the formation of hydrogen bonded dimers of DTE molecules for which the cyclic O–H···O binding geometry shown in Scheme 1b represents the preferred geometry. The change of OH stretching absorption found here is characteristic for dimer formation in a wider class of carboxylic acids as will be discussed below. As a reference, we plot the OH stretching absorption of cyclic dimers of acetic acid dissolved in carbon tetrachloride (dashed line in Figure 1b). Consistent with the OH absorption, a gradual modification of the C=O stretch vibration of the carboxylic acid is also observed (not shown). The two bands at 1680 and 1730 cm<sup>-1</sup> associated with the dimer and the monomer, respectively [12], exhibit a characteristic redistribution of intensity as the concentration is decreased.

The rise of the broad absorption band is accompanied by a reduction in magnitude of the free OH stretching absorption relative to the DTE concentration. In Figure 2, we plot the free OH stretching absorption spectrally integrated from 3450 to 3600 cm<sup>-1</sup> as a function of DTE concentration (symbols). It is apparent that the free OH vibration is super-linearly suppressed as the concentration of the solution increases. The data points are well described by a bi-molecular reaction scheme of the form  $2 \text{DTE}_{\text{mon}} \leftrightarrow \text{DTE}_{\text{dim}}$ . A corresponding function (solid line) is displayed along with the data in Figure 2. The dashed line in the inset of Figure 2 represents the linear rise of monomer OH stretching absorption expected in the absence of dimer formation. The measured absorption deviates from this linear dependence at concentrations around 100 μM already, due to dimer formation. While monomeric DTE strongly prevails at a low concentration of 9 μM, the fraction of monomers is less than 5% at 21 mM.

Figure 3 shows the electronic absorption spectra of DTE at high (40 mM) and low (26 μM) concentrations (solid and dashed lines). To compare the spectral shape, the graphs were scaled at the isosbestic point at 325 nm which is independent of the concentration. The spectra of the open form (o-DTE, solid lines) agree closely both in peak position and shape. The curves of the closed-ring isomer (c-DTE, dashed lines), however, show deviations. The S<sub>0</sub>–S<sub>1</sub> absorption with maximum around 602 nm displays a small red-shift on the order of 5 nm when going from the closed monomer (grey curve) to the doubly closed dimer (black curve). Concomitantly, there is a slight increase in spectral width and absorption strength. The higher lying bands around 360–380 nm exhibit a smaller red-shift on the order of 2 nm, most apparent at the falling slope around 390 nm. A comparison of the normalized spectra (not displayed) shows that no additional absorption bands appear at high concentrations.

A small red-shift of the closed-ring S<sub>0</sub>–S<sub>1</sub> absorption also occurs as the doubly closed dimer forms with increasing PSS (inset of Figure 3). In contrast, it remains at the same position for the monomer solution (26 μM). The fractional content of c-DTE (abscissa scale of the inset) was estimated according to  $\text{PSS} = \varepsilon_{\text{mon}}(600 \text{ nm}) / \varepsilon_{\text{mon}}(323 \text{ nm}) \times A(323 \text{ nm}) / A(600 \text{ nm})$ , where PSS stands for the photostationary state,  $\varepsilon_{\text{mon}}$  is the molar extinction coefficient of the monomer and A is the absorbance. Since the precise extinction coefficients of the dimer are not known, we estimate the accuracy of such figures to ~5%.

The photophysics of the open-ring isomer was scrutinized by fluorescence spectroscopy. The emission spectrum of the dimer (solid circles) for excitation at 310 nm agrees both in position and shape with that of the monomer (open circles). The fluorescence quantum yields (QY) were determined by comparing with coumarin 151 (QY = 0.53 [13]) and have values of  $\text{QY}_{\text{mon}} = 3.3 \times 10^{-4}$  for the monomer and  $\text{QY}_{\text{dim}} = 3.0 \times 10^{-4}$  for the dimer which are identical within the experimental accuracy. The partial

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