Two-photon-induced cycloreversion reaction of coumarin photodimers

H-C. Kim [a], S. Kreiling [a], A. Greiner [a,b], N. Hampp [a,b,*]

[a] *Institute of Physical, Nuclear and Macromolecular Chemistry, University of Marburg, Marburg D-35032, Germany*
[b] *Material Science Center, University of Marburg, Marburg D-35032, Germany*

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Abstract

Photochemical reactions induced by two-photon-absorption processes offer several advantages over common one-photon initiated photoreactions, e.g., three-dimensional spatial control. We present the photocleavage reaction of coumarin photodimers via a two-photon process using pulsed frequency-doubled Nd:YAG-laser light. The two-photon-induced cycloreversion reaction leads selectively to the cleavage of the coumarin photodimers resulting in the formation of monomeric coumarin molecules. The two-photon cross section of the coumarin photodimer was determined to be of 1.6×10^{-52} cm^4 s photon^{-1}. The presented reaction is of interest, e.g., for the photo-triggered release of chemicals in areas which cannot be directly optically addressed due to cover layers which have a high absorption at the single-photon-absorption wavelength.
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1. Introduction

Since the first photochemical $[\pi 2s + \pi 2s]$ cyclodimerization of coumarin was reported by Ciamician and Silber [1], the photochemical and photophysical properties of coumarin and its derivates have been intensively investigated. It is well known that direct irradiation ($\lambda > 300$ nm) of coumarin leads exclusively to photochemical dimerization resulting in cyclobutane-type dimers which revert to the starting compound upon irradiation with light of shorter wavelengths [2–6] (Fig. 1). Recently applications of this reaction were explored where coumarin and its derivates have been used as photoreactive materials for applications such as photorecording and photoresists [7–9], and as photolabile protecting groups for biological applications [10]. We introduce here coumarin photodimers as suitable multiphoton-cleavable linkers for photo-triggered release of molecules e.g., from a polymeric backbone in cases where one-photon absorption photochemistry is not desired or not possible.

Since the availability of high power pulsed lasers, intensive studies on multiphoton processes appeared in the areas of two-photon spectroscopy [11–13], opto-electronics [14] and photonics [15,16].

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* Corresponding author. Fax: +49-6421-2825798.
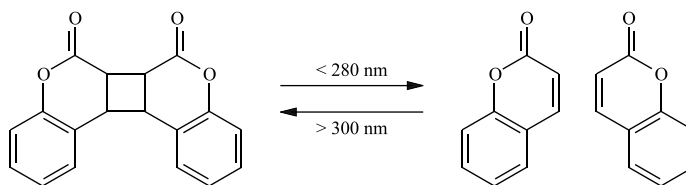*E-mail address:* hampp@mailer.uni-marburg.de (N. Hampp).

Fig. 1. Reversible photodimerization of coumarin under irradiation with UV light.

However, only few contributions were made concerning multi-photon organic photoreactions, e.g., two-photon induced photoisomerization [17,18], photolysis [10] and photodimerization [19]. A quadratic nonlinear dependence of the probability for a two-photon process versus the light intensity results as two-photon processes require the quasi-simultaneous absorption of two photons via a virtual state [20].

The use of light in the VIS region allows the three-dimensional spatially controlled cycloreversion of di-coumarin behind of layers of UV-absorbing materials, a situation which is relevant in several medical applications. This Letter describes for the first time the two-photon-induced cleavage of coumarin dimers in acetonitrile.

2. Experimental

2.1. Preparation of coumarin dimers

Photodimers of coumarin were obtained in isopropanol solution by benzophenone-sensitized photodimerization. The products were recrystallized twice in ethanol prior to further use. The purity of the coumarin dimer was >99% as checked by UV–VIS and HPLC analyses. Single-photon and two-photon-induced photocleavage of coumarin dimers were done in acetonitrile solution using 10 mm path length quartz cuvettes at room temperature.

2.2. Single-photon-absorption (SPA) induced photocleavage

2 mM solutions of coumarin dimer in acetonitrile were irradiated at 266 nm using a Shimadzu

spectrofluorimeter model RF-1502. The incident light intensity at 266 nm was 1.086×10^{14} photons s^{-1} cm^{-2} as determined by azobenzene as a chemical actinometer [21]. The exposure area was 2 cm^2.

2.3. Two-photon-absorption (TPA) induced photocleavage

5 mM solutions of coumarin dimer in acetonitrile were irradiated with 532 nm pulses of 3 ns duration from an Infinity 40–100 (Coherent) mode-locked Nd:YAG laser operating at 20 Hz. The beam diameter was 3 mm.

2.4. Analysis of the photoconversions

The photocleavage of coumarin dimers was monitored using UV/VIS absorption spectroscopy and HPLC analysis. UV/VIS absorption spectra were recorded on an UVIKON 922 (Kontron) spectrophotometer. HPLC analyses were performed on a Hewlett–Packard Model 1050 system equipped with a diode array detector. A RP-18 column (250 mm × 3 mm i.d., Bischoff) was used with a linear water–acetonitrile gradient eluant.

3. Results and discussion

3.1. SPA-induced photocleavage of coumarin dimer

The absorption spectra of coumarin and coumarin dimer are given in Fig. 2. Coumarin dimers show only one absorption band at about 270 nm, but monomeric coumarin has two strong absorption bands at 270 and 310 nm which are assigned to π–π*- and n–π*-transitions [22]. Photocleavage
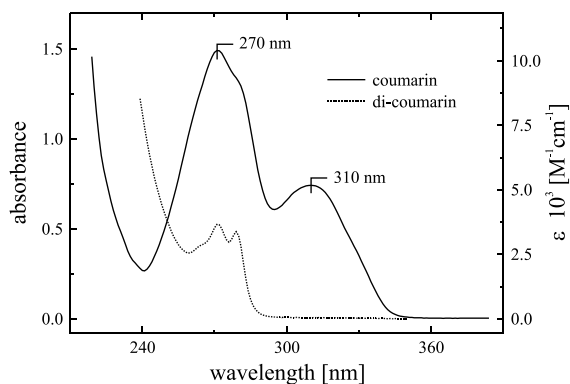
Fig. 2. UV spectra of coumarin and coumarin dimer. Both compounds were measured in a 10 mm pathlength cell at a concentration of 0.14 mM in acetonitrile.
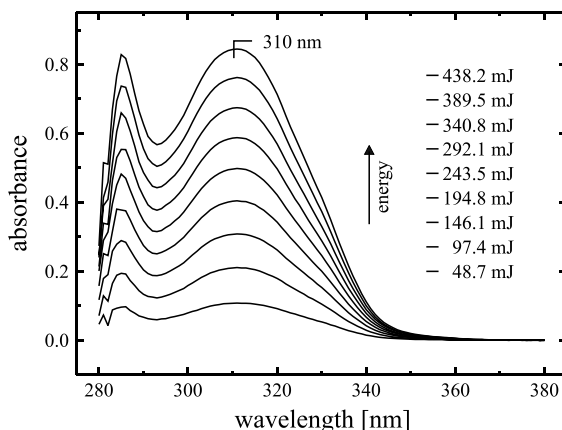

Fig. 3. Single-photon-induced cycloreversion reaction of coumarin dimer (2 mM in acetonitrile). Energy-dependent UV difference spectra of coumarin dimer during the course of irradiation with 266 nm light (1.086×10^{14} photons s^{-1} cm^{-2}).

of the coumarin dimers was analyzed by measuring the increase of absorbance at $\lambda_{max} = 310$ nm employing a molar extinction coefficient of ε_{310}(coumarin) = 5170 M^{-1} cm^{-1}.

Consistent with literature data [2–6], a cycloreversion reaction of coumarin dimers in solution upon irradiation with 266 nm light is observed. HPLC analyses confirmed that the SPA photocleavage reaction leads selectively to the formation of monomeric coumarin molecules. Absorption spectra of di-coumarin solutions in dependence on the light energy are shown in Fig. 3. The overall efficiency of the SPA induced photocleavage is characterized by the quantum yield Φ_{SPA} which is defined as the ratio of the number N_{dimer} of molecules transformed to the number Q of photons absorbed [23].

$$\Phi_{SPA} = \frac{N_{dimer}}{Q}. \tag{1}$$

For low degrees of photoconversion of coumarin dimers Eq. (1) can be expressed in terms of the initial rate of photoconversion $v_0^{monomer}$ in molecules s^{-1}, and the actinic power I_0 of the light in photons s^{-1} cm^{-2} multiplied by the area A which is irradiated, here 2 cm^2.

$$\Phi_{SPA} \approx \frac{(1/2) \cdot v_0^{monomer}}{I_0 \cdot A}. \tag{2}$$

Eq. (2) holds for high initial optical densities at the wavelength of the actinic light because it is assumed that all the incident light is initially absorbed by the dimer. In the experiments described here the optical density at 266 nm was ≈ 2, so only about 1% of the actinic light is not absorbed. A value of $v_0 = 9.1 \times 10^{13}$ molecules s^{-1} was measured and the quantum yield of the SPA-induced photocleavage of coumarin dimers was determined to be $\Phi_{SPA} \approx 0.21$.

3.2. TPA-induced photocleavage of coumarin dimer

Upon irradiation of coumarin dimer solutions with intense 532 nm pulses the photocleavage of the cyclobutane ring is observed. Fig. 4 shows the change in the absorption spectrum of the reaction mixture during the course of irradiation. The increase in absorbance at $\lambda_{max} = 310$ nm in the UV spectrum is characteristic for the formation of monomeric coumarin. HPLC analyses confirmed that coumarin is the only product. Of course, due to the different mechanism and the intrinsically lower absorption probability the photocleavage rate is much smaller compared to that of the one-photon-reaction.

In order to verify that a two-photon reaction is observed the expected quadratic dependence of the rate of coumarin formation on the irradiation power [20] was analyzed. We performed cycloreversion experiments in dependence on the intensity
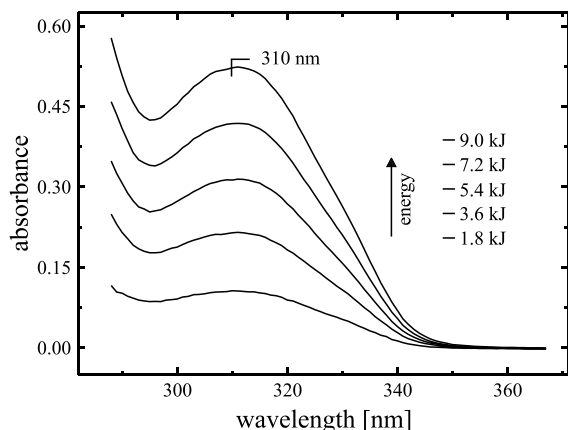
Fig. 4. Two-photon-induced cycloreversion reaction of coumarin dimer (5 mM in acetonitrile). UV difference spectra under irradiation with 3 ns pulses at 20 Hz having a diameter of 3 mm. The light intensity at 532 nm was 50 mJ pulse^{-1}.

of the laser pulses in the range from 10 to 80 mJ pulse^{-1} (Fig. 5a). Considering the quadratic dependence on the irradiation power and employing again the measurement of the initial rates [24], the following equation describes the relation between the square of the photon density F and the initial rate of coumarin monomer formation v_0, which increases at twice the speed the dimer decreases:

$$v_0^{monomer} = 2 \cdot C_0^{dimer} \cdot \Phi_{TPA} \cdot \sigma_{TPA} \cdot F^2, \quad (3)$$

where c_0^{dimer} is the initial concentration of coumarin dimer and Φ_{TPA} is the quantum yield of the TPA-induced photocleavage and σ_{TPA} is the TPA cross-section of coumarin dimer. From Eq. (3) follows that in a plot of the logarithm of the initial rate of coumarin formation $\ln v_0$ versus the logarithm of the photon density $\ln F$ a linear dependence with a slope of 2 is expected. As shown in Fig. 5b an experimental value of 1.8 is measured. This confirms that we observe a two-photon induced cycloreversion of coumarin dimers. The deviation from the theoretical value of 2 is presumably due to the occurrence of additional absorption processes via excited states which cannot be excluded completely.

In most cases reported in the literatures, the quantum yield of the two-photon excited fluorescence has been assumed to be the same as that
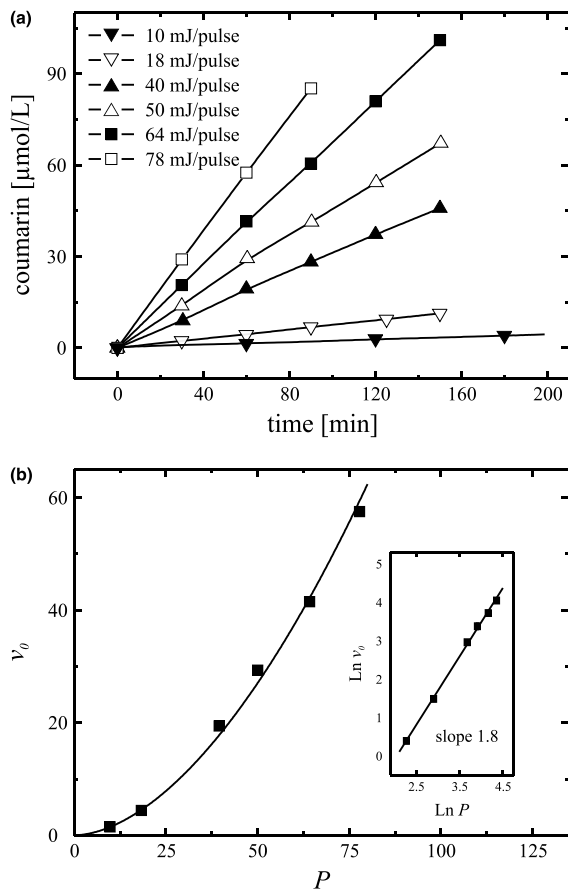

Fig. 5. Two-photon induced photocleavage of coumarin dimers in acetonitrile. (a) Coumarin formation measured as the increase of absorption at 310 nm in dependence on the incident laser power. (b) The TPA-induced nature of the photocleavage of coumarin dimer corresponds with the slope of 1.8 when $\ln v_0$ is plotted against $\ln F$.

for the fluorescence excited by one-photon absorption [25]. In order to derive the TPA cross-section of coumarin dimer σ_{TPA} we assume that the quantum yield of the TPA-induced photocleavage of coumarin dimer is the same as that for the corresponding SPA-induced process, i.e., $\Phi_{SPA} = \Phi_{TPA}$. With this assumption the two-photon cross-section can be derived from Eq. (3). The photocleavage rate v_0 was measured by UV- and HPLC-methods. Using the data shown in Fig. 5a the two-photon cross-section of coumarin dimer is determined to be $\sigma_{TPA} = 1.6(\pm0.27) \times 10^{-52}$ cm^4 s photon^{-1}.

4. Conclusions

The experiments reported analyze the single-photon- and two-photon-induced photocleavage of coumarin dimers in acetonitrile solutions. The single-photon and two-photon cycloreversion of coumarin dimers leads exclusively to the formation of monomeric coumarin. The quantum yield of the SPA-induced photocleavage of coumarin dimer was determined to be $\Phi = 0.21$ and the TPA cross-section of coumarin dimer was found to be 1.6×10^{-52} cm^4 s photon^{-1} at 532 nm. The TPA photo-triggered cleavage of the coumarin dimers characterizes them as suitable candidates for linker-systems which allow the release of an immobilized compound behind an absorption barrier which prevents SPA-photorelease.

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