

Research paper

An ultrafast pre-organization of the [2 + 2] photocycloaddition of styryl dyes in 1:2 host-guest complexes with cucurbit[8]urils



N.Kh. Petrov^{a,b}, D.A. Ivanov^{a,*}, Yu.A. Shandarov^a, I.V. Kryukov^a, A.D. Svirida^b, V.G. Avakyan^a, M.V. Alfimov^{a,b}, N.A. Lobova^a, S.P. Gromov^{a,b}

^aPhotochemistry Center of the Russian Academy of Sciences, ul. Novatorov 7A, 119421 Moscow, Russia

^bMoscow Institute of Physics and Technology (State University), Institutsky per. 9, 141707 Dolgoprudny, Russia

ARTICLE INFO

Article history:

Received 26 November 2016

In final form 4 February 2017

Available online 7 February 2017

ABSTRACT

The photocycloaddition of styryl dyes **1**, mediated by 1:2 host-guest complexes with cucurbit[8]urils (CB[8]), was studied by fluorescence upconversion techniques. The lifetime of 14.5 ps for photoexcited **1** in aqueous solution and 3.8 ps for that inside the complexes were gained from the fluorescence decay, the rate constant of quenching being obtained within the diffusion control limit. Calculations confirmed that unexcited pairs of **1** inside CB[8] does not fit the topochemical principles. So a translational movement is required to produce a reaction-ready structure that is in agreement with the timeresolved fluorescence anisotropy measured in the range of 5 ps.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The [2+2] photocycloaddition (PCA) is one of the most frequently used photoreaction for producing carbocyclic products. Two olefins, one of which is required to be excited by ultraviolet or visible light, are involved in this process. It could be an alternative approach for obtaining products that cannot be efficiently produced by thermal processes. However, photochemical reactions usually do not proceed as a regio- and/or stereo-specific process that prevents photochemistry from being a common tool in chemical synthesis. Pre-organization of reactants either in the solid state or in supramolecular host-guest assemblies can be used to control and manipulate photoreactions (see for recent review [1]).

Such assemblies can be designed on the basis of cucurbit[*n*]urils (CB[*n*]). These are a relatively new family of barrel-shaped macrocyclic cavitands which are composed of *n* glycoluril units (basically *n* = 5–8) bound by pairs of methylene groups [2]. The PCA can be mediated by host-guest complex with CB[8], the macrocycle which is large enough to accommodate two reacting molecules, as for example in the case of 6-methylcoumarin photodimerization [3].

As another representative example we refer to styryl dyes **1** (see Fig. 1), which form 1:2 host-guest inclusion complexes with CB[8] (the binding constant $\lg K = 11.9$ (L² mol⁻²) [4]). It has been established [5] that cations of dye **1** in the crystal phase form

syn-head-to-tail pairs, which are pre-organized for an efficient PCA to produce a single stereoisomer of the cyclobutane derivative **2** (Fig. 1). Photolysis of aqueous solutions of **1** in the presence of CB[8] results only in **2**, which is one of eleven possible stereoisomers [6], (the quantum yield of **2** is 0.07 in the presence of 0.5 equiv. of CB[8] [4]). It is worth noting that 1:2 host-guest complexes of **1** with CB[8] act as a molecular machine, so called molecular assembler, in which molecules move relatively to one another, mediating the intermolecular photochemical reaction.

The PCA kinetics on the picosecond time scale, in particular in aqueous solutions, has not been studied so thoroughly yet. Hoyer et al. [7] reported on a sub-picosecond time-resolved fluorescence spectroscopic study of different cinnamic acid crystals, model systems for solid-state photodimerization reactions. For α -cyano-4-hydroxycinnamic acid they have found that the dimerization occurs on a timescale of 10 ps and for sinapinic acid, an extremely fast sub-picosecond dimerization. By means of picosecond time-resolved X-ray diffraction, Techert and coworkers [8] have found that in solid state α -styrylpyrylium trifluoromethanesulfonate undergoes an ultrafast photoreaction that leads to the production of dimer state.

There are no doubts that ultrafast dynamics of PCA, occurred in supramolecular assemblies comprising cucurbiturils in aqueous solutions, plays the important role in the general mechanism but it has remained almost unexplored. In this Letter, we report our preliminary results on the ultrafast physical aspects of photodimerization of styryl dyes **1** immobilized in the CB[8] cavity.

* Corresponding author.

E-mail address: ivanovd@photonics.ru (D.A. Ivanov).

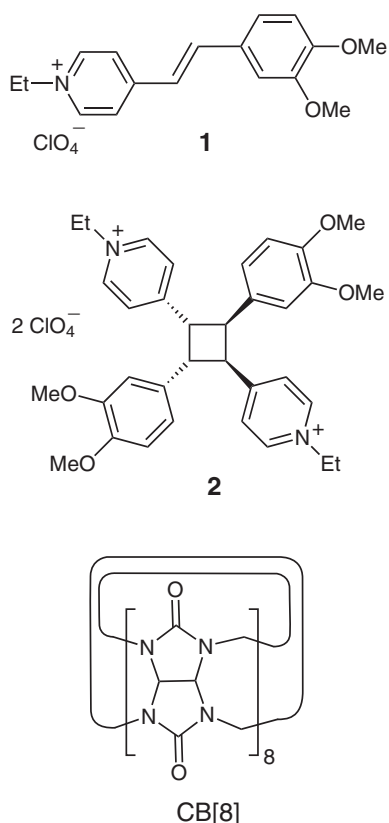


Fig. 1. The structural formula of dye 1, cyclobutane 2, and cucurbit[8]uril (CB[8]).

2. Experimental details

The styryl dye, 4-[(*E*)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate (1) – the chemical structure is shown in Fig. 1 – was obtained according to the procedure described in Ref. [5]. Cucurbit[8]uril, purchased from Aldrich, was used without further purification. To prepare samples, cucurbituril was dissolved in aqueous solutions of the styryl dyes (Millipore water) so that dye concentrations were approximately $1.8 \cdot 10^{-5}$ M in all cases.

Absorption spectra were recorded by a UV-3101PC spectrophotometer (Shimadzu) with an increment of 1 nm in 1-cm quartz cells at room temperature.

A time-resolved fluorescence up-conversion technique (almost the same as was described in Ref. [9]) was used to study a fast relaxation of the dye excited state. Briefly, a Cr:Forsterite laser produces 90 fs pulses centered around 1250 nm at 96 MHz repetition rate with the pulse energy about 7 nJ. A common scheme with a two-step consecutive mixing in nonlinear crystals was used to produce pulses centered around 417 nm (the third harmonic) which then excited dye solutions in 2 mm flow through cell. After the second mixing, the residual part of fundamental pulses with the energy about 2.5 nJ was used as the gating beam after passing through an optical delay line. The fluorescence from the dye solution and the gating beam were collected and focused on an 0.5 mm type I BBO crystal to generate sum-frequency signal. The up-converted beam was selected by a band-pass filter and focused on the entrance slit of a Solar M 266 monochromator. The polarization of the excitation beam can be set either parallel or perpendicular to that of the gating beam so that the up-converted signal carried information on the time resolved fluorescence depolarization of the styryl dye. A spectrally resolved signal was measured by a Hamamatsu photon counter. A personal computer collected the digital output of the photon counter and controlled an optical

delay line. The temporal resolution of the scheme was estimated to be 210 fs and the spectral resolution, about 20 nm. The Fluoft package was used to fit experimental results. The fitting quality was judged by the reduced χ^2 .

Quantum-chemical calculations with full geometry optimization of the structures of 1, its 1:2 host-guest complex with CB[8], cyclobutane, resulted from PCA, and its inclusion complex with CB[8] were carried out by the density functional theory using PBE functional [10] and SVP basis set [11] with Grimme's dispersion correction [12]. The calculations were performed with Orca program package [13]. Dye 1 is a positively charged molecular cation weakly coordinated with ClO₄⁻ anion. So 1 was assumed to be completely dissociated in water and was taken in calculation as a cation; *cyclo-2*, as dication.

3. Results and discussion

Fluorescence decay-curves detected at 560 nm of aqueous solution of 1 excited at 417 nm in the presence of approximately 0.5 equiv. of CB[8] and without it are shown in Fig. 2. The observed decay curves can be fitted by two exponential functions, the results of which are listed in Table 1. Fluorescence is quenched in 1:2 host-guest complexes as compared with that of unbound 1.

The obtained results can be considered on the basis of a widely accepted model describing the photophysical behavior of styryl dyes (see for example [14] and references therein). The population of the Franck-Condon (FC) state is initially produced by photoexcitation of a planar *trans*-form of styryl dyes, followed by a very fast – on the sub-picosecond time scale – vibrational cooling and intramolecular charge transfer (ICT). It is accompanied by a significant change in the dipole moment of the dye molecule. This change results in a fast reorganization response of the nearest environment (solvation shell) that significantly diminishes the potential energy of the system. The dye molecule, which is supposed to be approximately planar at this stage of relaxation, emits light at wavelengths that become longer upon diminishing the potential energy of the S₁ state. Thus, short time constants τ_1 , values of which are within 1 ps for unbound and embedded 1, should be attributed to intramolecular relaxation processes.

A slower step of relaxation is associated with intramolecular rotations of the styryl dye. It is widely believed that rotations around either single bonds in the C–C=C–C fragment of the dye

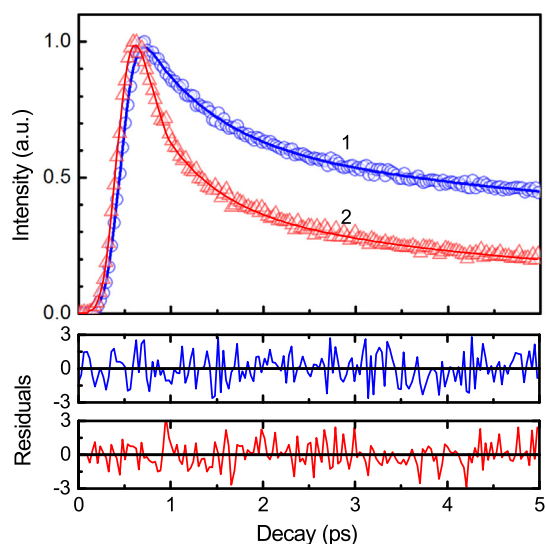


Fig. 2. Normalized fluorescence decay curves of aqueous solutions of dye 1: (1) without CB[8] and (2) in the presence of 0.5 equiv. of CB[8]; corresponding residuals are shown for a two-exponential fit.

Table 1

The best-fit values of the time constants τ_i , their pre-exponential factors A_i ($i = 1, 2$) and the reduced χ^2 for aqueous solutions of dye **1** in the presence of 0.5 equiv. of CB [8] and without it (560 nm fluorescence wavelength).

$A_1, \%$	τ_1, ps	$A_2, \%$	τ_2, ps	χ^2
1				
5	0.83	95	14.5	1.75
1 + CB[8]				
23.5	0.57	76.6	3.76	1.24

lead to a twisted intramolecular charge transfer (TICT) state. The TICT state corresponds to the minimum of potential energy S_1 and is also associated with the conical intersection (CI) region of the dye, which is a very efficient channel of nonradiative transitions to the ground state with a characteristic time of about 100 fs [15]. The vibronically-relaxed ICT state emitting light can get the CI region over a low energy barrier. The confinement of dyes to the cucurbituril cavity increases the barrier between the ICT state and the CI region, making the lifetime of fluorescence longer as compared with unbound fluorophore. This point has been confirmed recently by studying an ultrafast relaxation of excited states of 1:1 complexes of styryl dyes with CB[n] for $n = 6, 7$ [16]. In the framework of this model the life time of electronically-excited state of fluorophore should not be shortened upon the complex production that is not actually observed.

The decrease of the decay time τ_2 from 14.5 ps for unbound **1** to about 3.8 ps for **1** embedded in 1:2 host-guest inclusion complexes with CB[8] should be attributed to quenching electronically excited state of the styryl dye by its neighbor inside the cavity. This bimolecular interaction between electronically excited and unexcited particles results in chemical transformation that can be characterized by absorption. Fig. 3 shows steady-state absorption spectra of $1.8 \cdot 10^{-5}$ M aqueous solutions of **1** in the presence of about 0.5 equiv. of CB[8] before and after laser irradiation in the region of 417 nm during about 30 min. Upon irradiation a peak at 380 nm markedly diminished in the amplitude while a new one appeared in the region of about 230 nm. These spectral changes are associated with the PCA that leads to the major photo-product, cyclobutane **2**, as it has been recently shown in steady-state measurements of the PCA of the styryl dye **1** in 1:2 complex with CB[8] [4].

The observed quenching may be described by the classical Stern-Volmer equation [17] slightly adapted to this case:

$$\frac{1}{\tau_2^e} = \frac{1}{\tau_2^0} + k_q[Q]. \quad (1)$$

Here τ_2^e and τ_2^0 refer to the lifetime values of excited **1** in the presence and absence of quencher, respectively; k_q is the rate constant

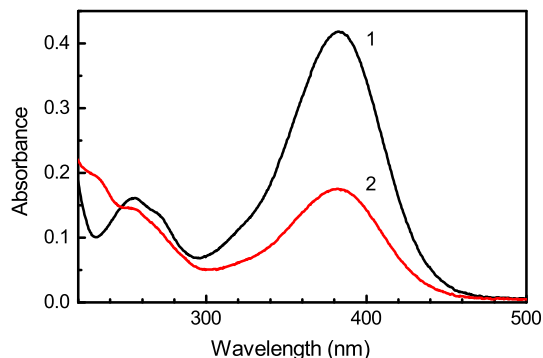


Fig. 3. Absorption spectra of aqueous solution of dye **1** in the presence of 0.5 equiv. of CB[8]: (1) before and (2) after laser irradiation (about 30 min at 417 nm).

of quenching and $[Q]$ is the local concentration of **1** inside the cavity. Taking into account that the volume of the cavity is about 500 \AA^3 [2] and it comprises two molecule of **1**, one obtains $[Q] \approx 7 \text{ M}$. So it follows from Eq. (1) that $k_q \approx 3 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The obtained value of quenching rate-constant is within the diffusion control limit for bimolecular reactions in nonviscous organic solvents and seems to reflect a low energy barrier of cycloaddition. It is worth noting that on the basis of the characteristic time $1/k_q[Q]$ (in this case it is about 5 ps) one can formulate a necessary condition for the PCA to be occur: the lifetime of excited states of reactants involved in the photoreaction should be longer than $1/k_q[Q]$.

Fig. 4 shows the calculated energy-minimized structure of 1:2 host-guest inclusion complexes of dye **1** with CB[8] in the ground state and the structure of 1:1 complex between CB[8] and cyclobutane, the product of photodimerization. In equilibrium two planar dye particles are located on parallel planes, which are separated by approximately 3.6 Å. Distances between C atoms of the participating double bonds are in the range from 4.1 to 4.2 Å. This structure fulfills almost all topochemical postulates except the reactive double bonds being located one on top of the other. In order to fit it, the excited cationic **1**, which is still almost planar, should be shifted by about 2.2 Å with respect to another styryl dye along the line parallel to the CB[8] axis. In addition, upon cycloaddition two new C—C bonds of 1.585 Å length each are formed. They are significantly shorter than 3.6 Å, a distance separated the dye particles before photoexcitation. So the dye particles come by about 2 Å closer to each other after excitation.

Thus in the course of the PCA, the geometry of the 1:2 host-guest complexes undergoes a significant structural change, namely, a marked displacement of excited reactants to fit the topochemical principles. The driving force of such a movement inside the cavity may be sophisticated coulombic interactions involving negatively charged portals of CB[8] and positive charges of the cationic dye particles, one of which shifts from the pyridinium moiety to the styryl group upon ICT. Note that the initial charge distribution in cationic **1** is calculated to be more negative at the dimethoxyphenyl group and more positive at the pyridinium moiety. Such distribution facilitates the dyes to form an anti-parallel pairs inside the CB[8] cavity owing to electrostatic and π -stacking interactions with each other and electrostatic one with the cucurbituril portals.

In order to shed light on the displacement of guest particles inside of CB[8], we have measured time-resolved fluorescence anisotropy of the supramolecular assembly

$$r(t) = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}, \quad (2)$$

where I_{\parallel}, I_{\perp} are the fluorescence intensities, detected through parallel and crossed positions of analyzer with respect to linear polarized excitation pulse respectively. For molecules close in shape to a prolate ellipsoid, as is the case with **1**, the temporal dependence of fluorescence anisotropy is as follows [18]:

$$r(t) = r_0 \exp\left(-\frac{t}{\varphi}\right), \quad (3)$$

where φ is the time of rotational relaxation, which is of the order of 10^2 ps for styryl dyes in host-guest complexes with cucurbiturils at room temperature [19]. The initial value of fluorescence anisotropy r_0 is determined by the angle between the absorption and emission transition dipoles of fluorophores and related to their average angular displacements that occur between adsorption and subsequent emission acts

$$r_0 = \frac{2}{5} \left(\frac{3 \cos^2 \beta - 1}{2} \right). \quad (4)$$

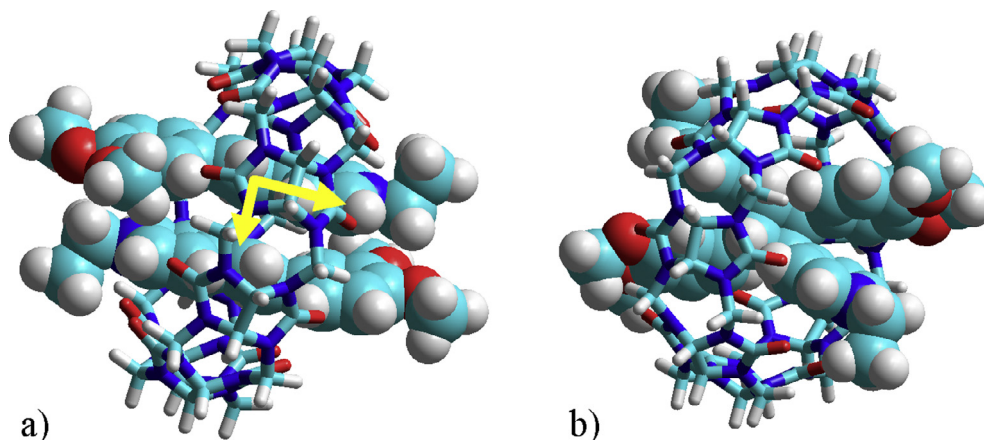


Fig. 4. The structures of 1:2 host-guest complex of **1** with CB[8] cavity (a), and 1:1 host-guest complex of cyclo-butane with CB[8]. Here, carbon is blue, oxygen is red, nitrogen is deep blue, and hydrogen is grey. Arrays show the direction of displacement of the double bond moiety after irradiation in order to form a four-membered cycle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

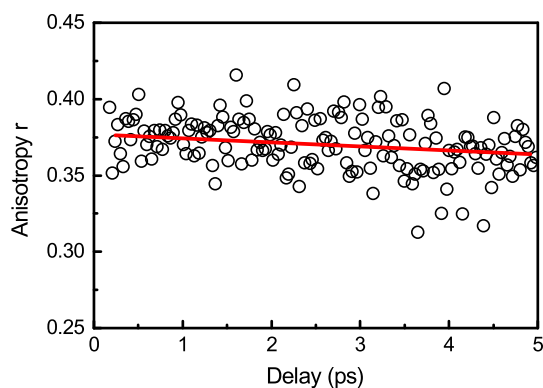


Fig. 5. The temporal dependence of fluorescence anisotropy of aqueous solution of **1** in the presence of 0.5 equiv. of CB[8]: (a) Etotol, -6532.14216 Hartree, (b) Etotol, -6532.10287 Hartree.

Here β is the angle between absorption and emission transition dipoles of the styryl dye. It follows from formulas (4) that if they are parallel then $r_0 = 0.4$ as maximum. The measurements of $r(t)$ on the sup-picosecond scale can reflect the character of fast motions of an electronically-excited guest molecule with respect to the cavity. Fig. 5 shows that the fluorescence anisotropy is about 0.38 that is close to the maximum value of fluorescence anisotropy and almost independent of time within the error of experiment over the range from 1 to 5 ps. A slight tendency for decrease of fluorescence anisotropy upon increasing delay time in principle may be associated with rotation of the complex as a whole. Unfortunately, we cannot extend the range of measurements for longer delay times in order to improve this point because of weak fluorescence intensity. Nevertheless, this experimental result shows that the motion of excited **1** to the reaction-ready position probably occurs along a direction almost parallel to cucurbituril's axis in agreement with the results of quantum-chemical calculations.

In summary, the fluorescence upconversion technique is a useful tool for studying ultrafast dynamic aspects of the PCA of styryl dyes mediated by cucurbit[8]uril. It has been shown that equilibrium state of reactants inside of the cavity does not coincide with a reaction-ready geometry. Being in translational motion during its

lifetime (about 4 ps), an excited styryl dye inside host-guest complex gets the position that corresponds to the topochemical postulates. The driving force of such a movement is the intramolecular charge transfer caused by photoexcitation of the styryl dye.

Acknowledgement

The work was supported by the Russian Scientific Foundation (project no. 14-13-00751).

References

- [1] (a) V. Ramamurthy, J. Sivaguru, *Chem. Rev.* 116 (2016) 9914–9993; (b) E.N. Ushakov, S.P. Gromov, *Russ. Chem. Rev.* 84 (8) (2015) 787–802.
- [2] J.W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, *Acc. Chem. Res.* 36 (2003) 621.
- [3] B.C. Pemberton, R.K. Singh, A.C. Johnson, S. Jockusch, J.P. Da Silva, A. Ugrinov, N. J. Turro, D.K. Srivastava, J. Sivaguru, *Chem. Commun.* 47 (2011) 6323–6325.
- [4] D.A. Ivanov, N.Kh. Petrov, M.V. Alfimov, A.I. Vedernikov, S.P. Gromov, *High Energy Chem.* 48 (4) (2014) 253–259.
- [5] A.I. Vedernikov, L.G. Kuz'mina, S.K. Sazonov, N.A. Lobova, P.S. Loginov, A.V. Churakov, Yu.A. Strelenko, J.A.K. Howard, M.V. Alfimov, S.P. Gromov, *Russ. Chem. Bull. Int. Ed.* 56 (9) (2007) 1860–1883.
- [6] S.P. Gromov, A.I. Vedernikov, L.G. Kuz'mina, D.V. Kondratuk, S.K. Sazonov, Y.A. Strelenko, M.V. Alfimov, J.A.K. Howard, *Eur. J. Org. Chem.* (2010) 2587–2599.
- [7] T. Hoyer, W. Tuszynski, Ch. Lienau, *Chem. Phys. Lett.* 443 (2007) 107–112.
- [8] J. Hallmann, W. Morgenroth, C. Paulmann, J. Davaasambuu, Q. Kong, M. Wulff, S. Techert, *J. Am. Chem. Soc.* 131 (2009) 15018–15025.
- [9] N.Kh. Petrov, D.A. Ivanov, Yu.A. Shandarov, I.V. Kryukov, V.G. Avakyan, M.V. Alfimova, S.K. Sazonov, S.P. Gromov, *Nanotechnol. Russ.* 11 (3–4) (2016) 221–226.
- [10] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [11] A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* 97 (1992) 2571–2577.
- [12] (a) S. Grimme, *J. Comput. Chem.* 25 (2004) 1463–1473; (b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* 32 (2011) 1456–1465; (c) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 132 (2010) 154104.
- [13] F. Neese, *The ORCA program system*, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2 (2012) 73–78.
- [14] D.A. Ivanov, N.Kh. Petrov, A.A. Ivanov, M.V. Alfimov, A.I. Vedernikov, S.P. Gromov, *Chem. Phys. Lett.* 610–611 (2014) 91–94.
- [15] B.G. Levine, T.J. Martinez, *Annu. Rev. Phys. Chem.* 58 (2007) 613–634.
- [16] A.D. Svirida, D.A. Ivanov, N.Kh. Petrov, A.V. Vedernikov, S.P. Gromov, M.V. Alfimov, *High Energy Chem.* 50 (1) (2016) 21–26.
- [17] N.J. Turro, V. Ramamurthy, J.C. Scaiano, *Modern Molecular Photochemistry of Organic Molecules*, University Science Books, Sausalito, California, 2010, Par. 8.17.
- [18] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, 1983.
- [19] D.A. Ivanov, N.Kh. Petrov, E.A. Nikitina, M.V. Basilevsky, A.I. Vedernikov, S.P. Gromov, M.V. Alfimov, *J. Phys. Chem. A* 115 (2011) 4505.