ELSEVIER

Contents lists available at ScienceDirect

Dyes and Pigments



journal homepage: http://www.elsevier.com/locate/dyepig

Ultrafast excited state dynamics, direct and back [2 + 2]-cross-photocycloaddition of a styryl dye–stilbene charge transfer complex



Valery V. Volchkov^{a,*}, Timofey P. Martyanov^{b,c}, Mikhail N. Khimich^a, Mikhail V. Rusalov^a, Daria A. Neznaeva^d, Fedor E. Gostev^e, Ivan V. Shelaev^e, Victor A. Nadtochenko^e, Mikhail Ya Melnikov^a, Anna A. Moiseeva^a, Evgeny N. Ushakov^{b,c}, Sergey P. Gromov^{a,c,**}

^a Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow, 119991, Russian Federation

^b Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russian Federation

^c Photochemistry Center, FSRC "Crystallography and Photonics", Russian Academy of Sciences, Novatorov Str. 7A-1, Moscow, 119421, Russian Federation

^d Masaryk University, Faculty of Science, Kotlářská 267/2, Brno, 611 37, Czech Republic

e N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygina Str. 4, Moscow, 119991, Russian Federation

ARTICLE INFO

Keywords: Styryl dyes E-Z photoisomerization [2 + 2] photocycloaddition Cyclobutanes Bis-crown ethers Intrasupramolecular photo-driven electron transfer

ABSTRACT

This research is dedicated to the study of bis(ammoniopropyl) derivative of (*E*)-4-(4-mercaptostyryl)pyridine dye (2), forming a highly stable bimolecular complex with a bis(18-crown-6 ether) derivative of (*E*)-stilbene (1) in solution owing to ditopic coordination via hydrogen bonds. The spectral-kinetic parameters of *E* isomer of the dye and its complex were obtained using steady-state absorption, fluorescence, and time-resolved absorption spectroscopy. The stability constant of the complex, quantum yields of cross-PCA and retro-PCA reactions were determined by spectrophotometric titration methods. According to density functional theory calculations, *E–Z* photoisomerization of dye 2 occurs via non-radiative deactivation from intermediate twisted (TICT) state. The detailed study of stereospecific [2 + 2]-cross-photocycloaddition (cross-PCA) of complex (*E*)-1-(*E*)-2 and back reaction of cross-PCA product (*rctt-3*) was carried out. The complexation reaction of cyclobutane *rctt-3* with Ba²⁺ ions has been investigated. A highly efficient direct intrasupramolecular photoelectron transfer and the back electron transfer of a moderate efficiency were found for the complex (*E*)-1-(*E*)-2.

1. Introduction

Organic charge-transfer (CT) complexes became widely known in the fifties. Now they have practical applications in data storage technique using scanning probe microscopy [1], in the development of OLED [2,3] and polymers with adjustable optical parameters [4]. Supramolecular organic complexes, formed by non-covalent D–A interactions, are used in the design of gels, micelles, foldamers, and vesicles [5], organic corrystals for tuning light emission, ferroelectricity and multiferroics, optical waveguides [6,7]. Additionally they serve as a model for the study of inter- and intramolecular electron transfer (ET) dynamics [8]. It is well known that these complexes undergo direct photoinduced electron transfer (ET) upon excitation in the CT absorption band. However, the CT band is often cannot be resolved within the main π - π * band, because of low molar absorptivity. In this case the population of the CT

state can be achieved indirectly using LE \rightarrow CT pathway. Recently the study of such ET process was carried out for supramolecular pseudocyclic complexes of (*E*)-bis(18-crown-6)stilbene **1** with 4,4'-bipyridinium tetraperchlorate bearing two ammonioethyl [9] and ammoniopropyl [10] *N*-substituents, and for the complexes with unsaturated analogues of viologen – ammonioalkyl derivatives of (*E*)-1, 2-di(4-pyridyl)ethylene **DPE** [11].

Also we have found the formation of a single rctt isomer of cyclobutane derivative upon the irradiation of the supramolecular complex of bis-crown stilbene (*E*)-**1** with styryl dye bearing two ammonioalkyl residues (*E*)-**2** [12]. DFT calculations showed that low quantum yield of this photoreaction may result from the fast photoinduced ET.

Obviously, the methods of CT state population are not limited to the excitation in the CT band. It may be populated, for instance, using Förster resonance energy transfer (FRET), electron exchange (EE) [13].

E-mail addresses: volchkov@light.chem.msu.ru, volchkov_vv@mail.ru (V.V. Volchkov), gromov@photonics.ru, spgromov@mail.ru (S.P. Gromov).

https://doi.org/10.1016/j.dyepig.2020.108952

Received 18 September 2020; Received in revised form 20 October 2020; Accepted 20 October 2020 Available online 23 October 2020 0143-7208/© 2020 Published by Elsevier Ltd.

^{*} Corresponding author.

^{**} Corresponding author. Photochemistry Center of RAS, FSRC "Crystallography and Photonics", Russian Academy of Sciences, Novatorov str. 7A-1, Moscow, 119421, Russian Federation.

It is important, that long-wavelength absorption band of styryl dye 2, studied in this work, does not overlap with π - π * absorption band of donor 1 in a region >380 nm. It allows us to observe the ET process occurring by a mechanism of selective excitation of the acceptor residue. The result of this dual HOMO-LUMO, LUMO-CT transfer will be the formation of the excited CT state, where electron density is localized on the acceptor. This CT state is subjected to back electron transfer in a course of deactivation. In contrast to recently studied acceptors, dve 2 is more polarized due to structural asymmetry of aromatic and side residues. Its terminal groups, coordinating to macrocyclic fragments of bis (18-crown-6)stilbene 1, have unequal length. It may result in a deviation from parallel position of donor-acceptor π -systems of the supramolecular complex and affect to the direct and back electron transfer rate constants. It is worth to note that due to ultrafast photoinduced intrasupramolecular ET, all photochemical processes may be suppressed in the complexes between bis-crown stilbene (E)-1 and strong electron acceptors. In particular it is true for the complexes with DPE, where fluorescence is totally quenched. Dye (*E*)-2 has a lower positive charge, than **DPEb**, i. e. lower electron acceptor ability should also result in the diminished ET rate constants.

Nowadays [2 + 2] photocycloaddition reactions (cross-PCA) occurring between two different olefines are actively explored [14–16]. In contrast to [2 + 2] photodimerization, the cross-PCA provides more synthetic possibilities. As shown in Ref. [17–19] the complexation of bis-crown with metal ions induces the cross-PCA or to improve its selectivity. Otherwise, the corresponding retro-PCA reaction has not been studied yet. The detailed investigation of the photochemical and photophysical behavior of the supramolecular complex between bis-crown stilbene (*E*)-1 and styryl dye (*E*)-2 is the main aim of this work. Also it is of interest to reveal the influence of Ba²⁺ ions on the efficiency of retro-PCA. Quantum-chemical calculations should give additional information about spectral-energy parameters of dye 2 and the complex (*E*)-1 ·(*E*)-2, to clarify the mechanism of *E*–*Z* photo-isomerization of the former.

2. Experimental

2.1. Materials

MeCN ("Fisher", HPLC gradient grade, water content 0.0021% and "Cryochrom", special purity grade, water content < 0.03%, v/v) was used to prepare solutions. Bu₄NClO₄ (\geq 99%, for electrochemical analysis) was purchased from Sigma-Aldrich and used as background electrolyte. MeOH and benzene ("chemically pure") were used without additional purification. HClO₄ (70%) was purchased from Sigma-Aldrich. Stilbene (*E*)-1 was prepared by the facile and efficient method reported previously [20]. The synthesis of 1,10-decanediammonium diperchlorate (C10) was described previously in Ref. [21].

2.1.1. Purification of dye (E)-2

For recrystallization we took 50 mg of dye (E)-2 obtained by the procedure described previously [12]. The sample was dissolved in a 0.5 mL of a MeCN/MeOH mixture (1/1) with the addition of a 20 μL of 70% HClO₄. Then the solution in a sealed flask was saturated by benzene vapors during 1 week, the residue was filtered off and washed with a 2 mL of EtOH and a 2 mL of MeCN, dried in air for a day. A 27 mg of (E)-2 was obtained as yellow granules, mp 172–174 °C. ¹H NMR (DMSO-d₆, Fig. S1): $\delta = 1.84-1.94$ (m, 2H, SCH₂CH₂), 2.15-2.24 (m, 2H, NCH₂CH₂), 2.82-2.89 (m, 2H, SCH₂CH₂CH₂), 2.90-2.97 (m, 2H, NCH₂CH₂CH₂), 3.14 (t, J = 7.2 Hz, 2H, SCH₂), 4.57 (t, J = 7.0 Hz, 2H, NCH₂), 7.44 (d, J = 8.4 Hz, 2H, 3'-H, 5'-H), 7.52 (d, J = 16.2 Hz, 1H, a-H), 7.64–7.76 (m, 3H, NH₃⁺), 7.71 (d, J = 8.4 Hz, 2H, 2'-H, 6'-H), 7.80 (br. s, 3H, NH_3^+), 8.02 (d, J = 16.2 Hz, 1H, b-H), 8.26 (d, J = 6.8 Hz, 2H, 3-H, 5-H), 8.93 ppm (d, J = 6.8 Hz, 2H, 2-H, 6-H); ¹³C NMR (DMSO- d_6 , Fig. S2): $\delta = 26.45$ (SCH₂CH₂), 27.85 (SCH₂), 28.53 (NCH₂CH₂), 35.76 (SCH₂CH₂CH₂), 37.90 (NCH₂CH₂CH₂), 56.78 (NCH₂), 122.55 (a-C),

123.90 (3-C, 5-C), 127.37 (3'-C, 5'-C), 128.80 (2'-C, 6'-C), 132.22 (1'-C), 139.56 (4'-C), 140.50 (b-C), 144.28 (2-C, 6-C), 153.18 ppm (4-C). Elemental analysis calcd (%) for $C_{19}H_{28}Cl_3N_3O_{12}S$: C 36.29, H 4.49, N 6.68, S 5.10; found: C 36.35, H 4.62, N 6.84, S 4.87. For an equimolar mixture of dye (*E*)-2 and bis-crown stilbene (*E*)-1 (5 × 10⁻⁵ M) in MeCN ESI mass spectrum was obtained, *m*/*z* 488.7531 [1-2–H]²⁺, 326.1704 [1·2]³⁺; calcd. m/z for [1·2–H]²⁺ 488.7530, [1·2]³⁺ 326.1711."

2.1.2. Synthesis of PCA product - rctt-3

A mixture of dye (*E*)-**2** (10.0 mg, 15.9 µmol) and (*E*)-**1** (11.3 mg, 17.5 µmol) was dissolved in MeCN (20 mL) in a glass flask and irradiated with a 4 W LED flashlight ($\lambda = 400$ nm) from a distance of ~30 cm for 30 h. The reaction mixture was evaporated in air to dryness. The precipitate was dissolved in a 10 mL of a H₂O/MeCN mixture (9/1), followed extraction by benzene (3 × 10 mL). The extract contained unreacted (*E*)-**1**. Then water phase was evaporated to dryness in vacuo. The residue was dissolved in a 0.3 mL of MeCN with a 3% H₂O, and then the solution was saturated by MeOH vapor for 1 week. Formed white granules of *rctt*-**3** was purified by decantation of mother liquor and washed by a 0.5 mL of MeOH. The precipitate was dried at ambient temperature for 2 days.

1-(3-Ammoniopropyl)-4-((1S,2S,3S,4S)-2-(4-((3-ammoniopropyl) thio)phenyl)-3,4-bis(2,3,5,6,8,9,11,12,14,15-decahydrobenzo[b] [1,4, 7,10,13,16]hexaoxacyclooctadecin-18-yl)cyclobutyl)pyridin-1-ium triperchlorate (rctt-3) was obtained in 44% yield (9 mg), mp 253-255 °C. ¹H NMR (MeCN-d₃ with 4% D₂O, Fig. S3): δ = 1.34–1.44 (m, 2H, SCH2CH2), 2.08-2.18 (m, 2H, PyCH2CH2), 2.23 (br.s, 2H, PyCH2CH2CH2), 2.61-2.71 (m, 2H, SCH 2), 2.75-2.87 (m, 2H, SCH2CH2CH2), 3.62-3.78 (m, 24H, CH2O), 3.78-3.90 (m, 8H, CH2CH2OAr), 3.91-4.03 (m, 4H, 3"(3")-CH2OAr), 4.05-4.09 (m, 2H, 4"-CH2OAr), 4.12-4.16 (m, 2H, 4"-CH2OAr), 4.48 (br.s, 2H, PyCH2), 4.58-4.66 and 4.70 (m, dd, 2H, d-H, c-H, J = 10.2 and 7.1 Hz), 4.72-4.80 (m, 1H, b-H), 4.84-4.95 (m, 1H, a-H), 6.41 (s, 1H, 2^{1//}-H), 6.47 (s, 1H, 2"-H), 6.82 (d, J = 8.3 Hz, 1H, 5"-H), 6.94 (d, J = 8.4 Hz, 1H, 5^{'''}-H), 6.96–7.02 (m, 1H, 6^{''}-H), 7.06–7.25 (m, 5H, 2',3',5',6',6^{'''}-H), 7.84 (br.s, 2H, 3,5-H), 8.40 ppm (d, J = 6.0 Hz, 2H, 2,6-H). ¹³C NMR (MeCN-d₃ with 4% D₂O, Fig. S6): $\delta = 28.18$ (SCH₂CH₂), 29.85 (PyCH₂CH₂), 31.07 (SCH₂CH₂CH₂), 36.38 (PyCH₂CH₂CH₂), 38.87 (SCH 2), 44.26 and 45.61 (c-CH, d-CH), 47.12 (a-CH), 48.15 (b-CH), 58.98 (PyCH₂), 68.43 (4"-CH₂OAr), 68.53 (3"(3")-CH₂OAr), 68.61 (4^{///}-CH₂OAr), 69.92 (CH₂O), 70.03 (CH₂O), 70.12 (CH₂O), 70.15 (CH₂O), 70.27 (CH₂O), 70.37 (CH₂O), 70.47 (CH₂O), 70.56 (CH₂O), 70.60 (CH₂O), 70.64 (2 CH₂O), 70.98 (CH₂O), 71.14 (CH₂O), 71.16 (CH₂O), 71.23 (2 CH₂O), 111.97 (2¹¹¹,5¹¹¹-C), 112.76 (5¹¹,6¹¹¹-C), 113.46 (2"-C), 129.04 (3,5-C), 130.12 (6"-C), 131.90 (2',3',5',6'-C), 132.55 (1"-C), 133.27 (1"'-C), 133.91 (1'-C), 139.16 (4'-C), 144.02 (2,6-C), 145.87 (4"-C), 146.38 (4"'-C), 146.54 (3"-C), 147.32 (3"'-C), 164.00 ppm (4-C). Elemental analysis calcd (%) for C₅₃H₇₆Cl₃N₃O₂₄S: C 49.83, H 6.00, N 3.29, S 2.51; found: C 50.01, H 6.03, N 3.38, S 2.45.

2.2. Methods

¹H and ¹³C NMR spectra were measured on a Bruker AVANCE III 500 spectrometer. The solvent (MeCN-d₃, $\delta_{\rm H} = 1.940$ ppm, $\delta_{\rm C} = 1.320$ ppm and DMSO-d₆, $\delta_{\rm H} = 2.500$ ppm, $\delta_{\rm C} = 39.52$ ppm) was used as the internal reference [22]. Chemical shifts were determined with 0.01 ppm accuracy and J-coupling constants – with 0.1 Hz accuracy. The elemental analysis was carried out using a Vario MICRO Cube analyzer. Steady state absorption spectra were recorded on a Shimadzu-3100 spectro-photometer or a Specord M40 spectrophotometer in quartz cells with ground-in stoppers. Steady state fluorescence spectra were recorded on a Perkin-Elmer LS-55 and an Elumin-2M spectrofluorometers. Quantitative stationary photolysis was performed using glass-filtered light of a high pressure Hg lamp ($\lambda = 313$, 365 or 405 nm). The light source with $\lambda = 254$ nm was a low pressure Hg lamp with a glass filter. The light intensity was measured by a chemical actinometry. The preparative photolysis was conducted using LED flashlight (4 W) with $\lambda = 400$ nm.

All manipulations, unless otherwise mentioned, with solutions of compound **1**, dye **2**, and cyclobutane **3** were performed in a darkroom under red light (daylight induces *E*–*Z* photoisomerization or retro-PCA). Electrospray ionization (ESI) mass spectra were acquired using an Exactive Orbitrap mass spectrometer (ThermoFisher Scientific, Germany) and a home-made electrospray ion source. The working resolution of the mass spectrometer in reported experiments was 10,000 (FWHM), the accuracy of *m*/*z* values measurement – better than 5 ppm, the mass spectrum registration time – 1 min. The electrospray ion source characteristics were: the quartz capillary inner diameter – 50 µm, the capillary high voltage – +3 kV, the sample solution flow rate – 1.0 µL/min.

2.2.1. Steady-state fluorescence

Fluorescence quantum yields (ϕ_f) were determined using quinine bisulfate in 1 N H₂SO₄ at 25 °C (ϕ_f = 0.546 [23]) or anthracene in ethanol (ϕ_f = 0.28 [24]) as the reference. The measurements were carried out with freshly prepared aerated solutions. The value of ϕ_f was calculated by the formula:

$$\phi_{\rm f} = (\phi_{\rm f} \, _{\rm r} D_{\rm ex} \, _{\rm r} n^2 S) / (D_{\rm ex} n_{\rm r}^2 S_{\rm r}) \tag{1}$$

where the subscript r refers to the reference parameters, D_{ex} is the optical density at the excitation wavelength, *n* is the refractive index of the solvent, *S* is integrated intensity of the corrected fluorescence spectrum in energy scale. The calculation of the actual fluorescence spectrum of stilbene **1** as part of the complex (*E*)-**1**·(*E*)-**2** was carried out with respect to re-absorption and superposition of stilbene fluorescence with the absorption spectrum of the dye.

2.2.2. Direct and competitive titration

The complexation of (*E*)-**1** with (*E*)-**2** was studied by spectrophotometric and spectrofluorimetric competitive titration in spectral grade anhydrous MeCN. Direct titration of cyclobutane *rctt*-**3** by barium perchlorate was carried out at constant ionic strength of the solution (I = 0.015 M). The equal I for the solutions of ligand and titrant was maintained by the addition of a required quantity of Bu₄NClO₄ to the solution of the ligand.

2.2.3. E-Z photoisomerization quantum yields

The quantum yields for the forward (Φ_{E-Z}) and back $(\Phi_{Z-E}) E-Z$ photoisomerization were determined from the kinetics of absorption spectra observed upon steady-state irradiation of a solution of *E* isomer with 365 nm light. The absorption spectrum of the pure *Z* isomer was calculated using the spectra of the *E*–*Z* photostationary states attained upon irradiation at different wavelengths on the assumption that the Φ_{E-Z}/Φ_{Z-E} ratio is independent of the irradiation wavelength. The absorption spectra were treated using global analysis methods, as described previously [25]. The photoisomerization quantum yields were measured to within ±20%.

2.2.4. Cross-PCA quantum yields

The quantum yield of cross-PCA reaction $(\Phi_{PCA}^{\Phi C})$ was calculated from the absorption spectra of a solution of (E)-1·(E)-2 upon stationary irradiation with 405 nm light. The kinetic equation for irreversible monomolecular photoreaction was used:

$$\frac{dC_{\rm dye}(t)}{dt} = \Phi_{\rm PCA}{}^{405}I_{\rm act}10^3 \frac{\left(1 - 10^{-\varepsilon C_{\rm dye}(t)}\right)}{l}$$
(2)

where I_{act} is the intensity of actinic light (mol·cm⁻²·s⁻¹); ε is the molar absorptivity of the complex at 405 nm, M⁻¹cm⁻¹; C_{dye} is the concentration of the dye as part of the complex; l is the length of the cell, cm.

The back retro-PCA reaction was considered in the calculation of Φ_{PCA}^{313} . The concentrations of reactants $C_{comp}(t)$ and $C_{CB}(t)$ were calculated using numerical solution of the kinetic equation:

$$\frac{dC_{\text{comp}}(t)}{dt} = 10^{3} I_{\text{act}} \left[\Phi_{\text{retro}} \varepsilon_{\text{CB}} C_{\text{CB}}(t) - \Phi_{\text{PCA}}{}^{313} \varepsilon_{\text{comp}} C_{\text{comp}}(t) \right] \frac{\left[1 - 10^{-D(t)} \right]}{D(t)}$$
$$D(t) = \left[\varepsilon_{comp} C_{comp}(t) + \varepsilon_{CB} C_{CB}(t) \right] l \quad C_{\text{CB}}(t) = C_{0} - C_{\text{comp}}(t)$$
(3)

where ε_{CB} and ε_{comp} are the molar absorptivities of cyclobutane **3** and the complex at irradiation wavelength (M⁻¹·cm⁻¹), l is the length of a cell, (cm), C_0 is the concentration of the initial complex (*E*)-1·(*E*)-2 (M).

2.2.5. Retro-PCA quantum yields

Retro-PCA quantum yield of *rctt*-**3** was calculated using eq. (3); the quantum yield of the direct cross-PCA reaction was fixed at 6.7×10^{-4} . Quantum yield of retro-PCA reaction for the complex *rctt*-**3**·(Ba²⁺)₂ was calculated using integral form of equation (2):

$$\Phi_{\text{retro}}^{1:2} = (\Delta CDl) / (10^3 I_{\text{act}} t_{\text{ir}} D_{\text{CB}} (1 - 10^{-D}))$$

$$D = (D_0 - D_{\text{ir}}) / 2 \quad D_{\text{CB}} = (D_0^{\text{CB}} - D_{\text{ir}}^{\text{CB}}) / 2$$

$$(4)$$

where D_0 and D_{ir} are the optical densities of the solution at irradiation wavelength before and after photolysis; D_0^{CB} and D_{ir}^{CB} are the optical densities of the complex *rctt*-3·(Ba²⁺)₂ at irradiation wavelength before and after the photolysis; ΔC is the amount of dye **2** obtained after the photolysis; t_{ir} is the irradiation time with 254 nm light. The ΔC value was measured as follows. After irradiation upon 254 nm during 1000 s, the solution of the complex *rctt*-3·(Ba²⁺)₂ was brought to a photostationary state (PSS) by irradiation upon 405 nm light (Fig. S14). Knowing the PSS spectrum of free dye **2**, the amount of dye obtained after the photolysis was found. The experiment was performed in three repetitions.

2.3. Electrochemical study

The electrochemical experiments were carried out using an IPC-Pro M potentiostat. Cyclic voltammogram of dye (*E*)-**2** was registered in a MeCN/DMF mixture (2/1) using stationary disk glassy carbon electrode with a working surface 3.14 mm². The second voltammogram was obtained similarly using rotating disk glassy carbon electrode (Fig. S15). Potential scan rate was 200 mV s⁻¹. As background electrolyte 0.1 M solution of Bu₄NClO₄ in anhydrous MeCN was used. Concentration of (*E*)-**2** was 1 × 10⁻⁴ M. All measurements were performed in a dry argon atmosphere at 22 °C.

2.3.1. Femtosecond transient absorption

Femtosecond transient absorption spectra were measured at 22 °C on a pump and light supercontinuum probe setup with a 3.33 fs delay step and a 0.5 nm wavelength step. The spectra were subjected to a correction procedure. The details of transient spectra measurements were described in our prior paper [26]. The characteristic times (τ_i) were calculated using the areas under the individual absorption bands in the appropriate time range. Since the experimental flash function convolution (FWHM = 40 fs) with monoexponential decay ($\tau = 50$ –80 fs) changes the τ value by only 1%–3%, the experimental transient absorption kinetics corresponding to faster photo-driven electron transfer were processed without deconvolution. The average measurement error was ~5%.

2.3.2. Quantum chemical calculations

Quantum chemical calculations were performed using the GAMESS (US) [27] program package with the 6-31G(d,p) basis set. The geometry of the compounds in the ground state was optimized by means of DFT; the excited state geometry was optimized by means of TDDFT (CAM-B3LYP functional). The environmental effects were included via the Solvation Model Density continuum model [28]. Absorption and emission spectra were calculated using the Firefly v.8.2 program package [29] by means of state averaged complete active space self-consistent



Scheme 1. Formation of pseudocyclic complex (E)-1·(E)-2 in MeCN.

Table 1

Spectral-luminescent and photochemical parameters of stilbene 1, dye 2 and complex (E)-1·(E)-2 in dry MeCN.^a

Compound	λ ^{max} , nm	$arepsilon^{\max} imes 10^{-4}, \ \mathrm{M}^{-1} \mathrm{cm}^{-1}$	λ_{f}^{max} , nm	$\phi_{ m f}$	Φ_{E-Z}	Φ_{Z-E}	$arphi_{ m PCA} \ imes 10^4$
$(E)-1^{b}$ $(E)-1\cdot(E)-2^{d}$	336 334	3.75 4.82	386 382	0.30 0.0057	0.24 _ ^c	_c	- 7.2
(E)-2 (E)-1·(E)- 2 ^e	392 401	3.65 2.81	559 546	0.18 0.0015	0.34 _ ^c	0.39 _ ^c	- 6.7
<u>=</u> (Z)-2	377	0.99	-	-	0.34	0.39	-

^a λ_a^{\max} is the position of the S₀–S₁ absorption band maximum, ε^{\max} is the molar absorptivity at λ_a^{\max} , λ_f^{\max} is the position of the fluorescence maximum in the corrected spectrum; ϕ_f is the fluorescence quantum yield; Φ_{E-Z} and Φ_{Z-E} are the quantum yields of reversible E–Z photoisomerization (Fig. S12); Φ_{PCA} is the quantum yield of cross-PCA; for (E)-<u>1</u>-(E)-2 the photolysis was done by irradiation at 313 nm, for (E)-1-(E)-2 – by irradiation at 405 nm.

^b Data for (E)-1 are taken from Ref. [34].

^c Reaction does not occur.

^d Parameters were determined for (E)-1 band of the complex.

 $^{\rm e}\,$ Parameters were determined for (E)-2 band of the complex.

field (SACASSCF) improved by second-order quasi-degenerate perturbation theory (XMCQDPT2) [30]. The environmental effects were included via the dielectric polarizable continuum DPCM model [31]. The active space included 12 electrons in ten orbitals. The density matrix was averaged over four lowest singlet and triplet states.

3. Results and discussion

3.1. Synthesis of (E)-2

Styryl dye (E)-2 was synthesized by quaternization of (E)-4-(4-

methylthiostyryl)pyridine with excess 3-bromopropan-1-ammonium bromide, followed by treatment with HClO₄ [12]. Amount of impurities was managed to reduce due to crystallization of MeCN/MeOH solution of the dye by saturation with benzene vapors. Also using extraction with further recrystallization it was managed to obtain spectral pure cyclobutane derivative *rctt*-**3**.

3.2. Complexation

As was shown in Ref. [12] ditopic coordination of bis-crown stilbene (*E*)-1 with dye (*E*)-2 in MeCN leads to the formation of pseudocyclic complex 1:1 (Scheme 1). Energy interval between 0 and 0 transitions of the donor and the acceptor in MeCN, obtained from steady-state spectroscopy data, is equal to -0.836 eV. This value slightly changes upon complexation. Under action of a visual light, the dye (*E*)-2 undergoes efficient *E*–*Z* photoisomerization, resulting in a weak blue and pronounced hypochromic shifts of long-wavelength absorption band (Table 1).

The direct spectrophotometric titration of dye (*E*)-2 by stilbene (*E*)-1 in dry MeCN has shown, that corresponding logK > 7 (Fig. S9). Therefore, for the calculation of the actual stability constant of (*E*)-1·(*E*)-2 we used competitive titration method. 1,10-Decanediammonium diperchlorate (**C10**) was taken as a competitor. The stability constant of the complex (*E*)-1·**C10** was obtained previously (logK_C = 7.58 [32]). Fig. 1 shows the spectrophotometric and spectrofluorometric titration data for a mixture of (*E*)-1 and (*E*)-2 by **C10** salt in MeCN.

The stability constant *K* was calculated using global analysis of spectroscopy data [32]. A complexation model involved two equilibria:

$$S + D \stackrel{\wedge}{\rightleftharpoons} S \cdot D$$
 (5)

$$S + C10 \stackrel{n_c}{\neq} S \cdot C10$$
 (6)

where S is the stilbene (*E*)-1, D is the dye (*E*)-2, S-D is the complex (*E*)-1. (*E*)-2, *K* and *K*_C are the stability constants of the complexes (*E*)-1·(*E*)-2 and (*E*)-1·C10. The spectrophotometric titration data of the complex (*E*)-1·(*E*)-2 gave log*K* = 8.97 (Fig. 1a). A similar value was obtained from spectrofluorimetric titration (log*K* = 8.98, Fig. 1b). In Ref. [33] the stability constants were measured for the complexes of bis(18-crown-6) stilbene 1 with diammonioethyl (log*K* = 9.42) and diammoniopropyl (log*K* = 9.08) derivatives of 4,4'-dipyridylethene (**DPEa,b**). It should be noted that length of the latter is shorter than that of dye 2 by one sulfur atom. Therefore, log*K* of the complex (*E*)-1·(*E*)-2 should be less than 9.08, what is consistent with the value 8.97. The distance between ammonium groups of dye (*E*)-2 slightly exceeds the distance between the centers of crown-ether cavities of stilbene (*E*)-1.

The formation of the complex (E)-1·(E)-2 leads to a weak red and pronounced hypochromic shifts of a long-wavelength π - π * absorption band. Apparently, this is due to stacking interaction between conjugated moieties of the dye and the stilbene. The complex formation also induces strong quenching: the fluorescence quantum yields of the dye and the stilbene decrease by 115 and 52 times, respectively (Fig. S10, S11). Most likely such efficient deactivation is induced by the intrasupramolecular electron transfer. Destruction of the complex (E)-1·(E)-2 was observed during the titration of equimolar mixtures of (E)-1 with (E)-2 by alkaline-earth metal perchlorates. The fluorescent enhancement of free dye (E)-2 and probably stilbene complexes with metal ions were registered (Fig. S13, S14). The highest efficiency of complexation (equilibrium constant) was observed for strontium and barium perchlorates (Fig. S14). Magnesium and strontium ions gave the largest fluorescent enhancement (up to 50 times). The spectral response makes it possible to use the supramolecular complex (E)-1·(E)-2 as a fluorescent sensor for metal ions with a wide spectral range. The main spectral and photochemical parameters of the compounds in free and complexed forms are given in Table 1. The spectral feature of the complex makes it



Fig. 1. *a)* Absorption spectra of equimolar mixture of (*E*)-1 and (*E*)-2 $(1.2 \times 10^{-5} \text{ M})$ in the presence of 1,10-decanediammonium diperchlorate (**C10**) in dry MeCN; C (HClO₄) = 5×10^{-6} M; circles are the experimental spectra, solid curves are approximation using two equilibria (5 and 6), red curve is the calculated spectrum of a mixture of (*E*)-2 and (*E*)-1·C10. *b*) Fluorescence spectra of a mixture of (*E*)-1 $(1.1 \times 10^{-5} \text{ M})$ and (*E*)-2 $(3.2 \times 10^{-5} \text{ M})$ in the presence of different amounts of **C10** (see left panel) in dry MeCN; blue curves are the experimental spectra, red curves are approximations obtained using two equilibria (5 and 6). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Scheme 2. Cross-PCA and retro-PCA reactions.



Fig. 2. Steady-state photolysis of (*E*)-**1**·(*E*)-**2** in MeCN with 405 nm light: 1 cm cell, (*E*)-**1**: 2.84×10^{-5} M, (*E*)-**2**: 2.25×10^{-5} M, HClO₄: 5×10^{-6} M, light intensity: 1.67×10^{-9} mol cm⁻²s⁻¹. Inset: rate of conversion (%) of complexed dye (*E*)-**2** as a function of irradiation time, s. The data were fitted using kinetic equation for irreversible monomolecular photoreaction (2).

prospective as fluorescent sensor on metal cations in a wide spectral range.

3.3. Cross- and retro-PCA reactions

The quantum yields of the cross-PCA reaction (Scheme 2) was obtained for the complex (*E*)- $1 \cdot (E)$ -2 upon irradiation at 405 nm (Fig. 2)



Fig. 3. Steady-state photolysis of rctt-3 in MeCN with 254 nm light, 1 cm cell, rctt-3: 2.27 \times 10⁻⁵ M, HClO₄: 5 \times 10⁻⁶ M, light intensity: 6.02 \times 10⁻¹⁰ mol cm⁻²s⁻¹.

and 313 nm (Fig. S16). Since not only the complex, but also a product – cyclobutane *rctt*-**3** absorbs at 313 nm, back retro-PCA reaction (Eq (3)) was took into account.

As follows from Table 1, the selective excitation of styryl either stilbene chromophore of (*E*)-1·(*E*)-2 weakly effects on cross-PCA quantum yield. A fluctuation of Φ_{PCA}^{405} from Φ_{PCA}^{213} lies within the measurement error. Retro-PCA quantum yield (Φ_{retro}) was obtained from the absorption kinetics upon irradiation of *rctt*-3 at 254 nm. As in a case of Φ_{PCA}^{313} , the calculation involved two photoreactions (Eq (3)).



Fig. 4. Absorption spectra of the system *rctt*-**3**–Ba(ClO₄)₂ in MeCN, 1 cm cell, I = 0.015 M, *rctt*-**3**: 2.3×10^{-5} M, concentration of Ba(ClO₄)₂ was varied incrementally from 0 to 1.7×10^{-3} M. The titrant contained HClO₄ (5 mol % relatively to Ba(ClO₄)₂).

Table 2

Stability constants, spectroscopic parameters, and retro-PCA quantum yields for *rctt*-**3** and its complexes with $Ba^{2+,a}$

Compound	logK	λ_a^{max} , nm	$arepsilon_{ m a}^{ m max} imes 10^{-4}$, ${ m M}^{-1}~{ m cm}^{-1}$	$\Phi_{ m retro}$
rctt- 3	-	264	1.83	$\begin{array}{c} 0.067 \ (\varPhi_{\rm retro}) \\ 0.070 \ (\varPhi_{\rm retro}^{1:1}) \\ 0.031 \ (\varPhi_{\rm retro}^{1:2}) \end{array}$
rctt- 3 ·Ba ²⁺	4.14	261	2.13	
rctt- 3 ·(Ba ²⁺) ₂	3.54	260	2.47	

 $^{\rm a}$ Measurement errors of stability constants and quantum yields amounted to $\pm 30\%.$

The Φ_{retro} value was almost 2 orders of magnitude higher, than Φ_{PCA}^{PCA} and Φ_{PCA}^{P13} values, what can be explained by structural asymmetry of *rctt*-**3**. It should be noted that long-wavelength shoulder of a low intensity of *rctt*-**3** (300–370 nm, Fig. 3) actually belongs to photo-adduct, not to an impurity of stilbene **1**. This confirms by the formation of the initial complex (*E*)-**1**·(*E*)-**2** upon irradiation of a solution of cyclobutane *rctt*-**3** with 313 nm or 365 nm light.

3.4. Two-step substitution reaction between rctt-3 and Ba^{2+}

We have studied the effect of complexation between cyclobutane *rctt*-**3** and Ba²⁺ ions on retro-PCA reaction. With the increase of a Ba²⁺ concentration in the solution, a weak blue and pronounced hyperchromic shifts of *rctt*-**3** absorption (Fig. 4, Table 2) appeared. These are typical of donor-acceptor crown-ether chromoionophores [35,36]. The stability constants of the complexes with Ba²⁺ ions were obtained by spectrophotometric titration at constant ionic strength *I*. The complexation involves two substitution reactions (7), (8) shown in Scheme 3.

$$\operatorname{rctt} - \mathbf{3} + \operatorname{Ba}^{2+} \stackrel{\mathrm{A}_{1:1}}{\rightleftharpoons} \operatorname{rctt} - \mathbf{3} \cdot \operatorname{Ba}^{2+}$$
(7)

$$\operatorname{rctt} - \mathbf{3} \cdot \operatorname{Ba}^{2+} + \operatorname{Ba}^{2+} \stackrel{K_{1,2}}{\rightleftharpoons} \operatorname{rctt} - \mathbf{3} \cdot \left(\operatorname{Ba}^{2+}\right)_2$$
(8)

where $K_{1:1}$ and $K_{1:2}$ are the stability constants of barium complexes. Relatively low stability constants of the complexes *rctt*-**3**·Ba²⁺ and *rctt*-**3**·(Ba²⁺)₂ are explained by the need for displacement of ammonioalkyl cations from crown-ether cavities of cyclobutane derivative *rctt*-**3**.

Irradiation with 254 nm light of a solution of *rctt*-3 with excess of Ba $(ClO_4)_2$ leads to the formation of free dye 2 and isomers of the complex $1 \cdot (Ba^{2+})_2$ (Fig. S17). At long-term exposure a new absorption band appears at 254 nm, which probably belongs to photocyclization product of (Z)-1· $(Ba^{2+})_2$. The following procedure was applied for the measuring of



Scheme 3. Two-step complexation of cyclobutane *rctt*-**3** with barium perchlorate in MeCN.

retro-PCA quantum yield of barium complex of *rctt*-**3**. After irradiation, a solution of the product *rctt*-**3**. (Ba²⁺)₂ was brought to the photostationary state (PSS) upon irradiation at 405 nm (Fig. S18). Knowing the PSS spectrum of dye **2**, the amount of dye formed during the photolysis was found. Then retro-PCA quantum yield was calculated for bi-nuclear complex of cyclobutane ($\Phi_{retro}^{1:2}$). Knowing the stability constants of the complexes we have determined at what concentrations of cyclobutane **3** and barium perchlorate in solution the content of the 1:1 complex would be maximum (Fig. S19). Using the obtained concentration ($C(3) = 2.5 \times 10^{-5}$ M, $C(Ba^{2+}) = 1.7 \times 10^{-4}$ M) the corresponding solution with I = 0.015 M was prepared. Its photolysis was carried out (Fig. S20) by analogy with the photolysis of *rctt*-**3**·(Ba²⁺)₂. The estimation of retro-PCA quantum yield for *rctt*-**3**·Ba²⁺ was performed as follows. The total quantum yield (Φ_{total}) was obtained from eq. (4); then $\Phi_{retro}^{1:1}$ was found using eq. (9):

$$\Phi_{\text{retro}}^{1:1} = (\Phi_{\text{total}} D_{\text{CB}} - \Phi_{\text{retro}} D_{\text{L}} - \Phi_{\text{retro}}^{1:2} D_{1:2}) / D_{1:1}$$
(9)

where D_{CB} is the optical density of the initial solution at the excitation wavelength; D_L , $D_{1:1}$, and $D_{1:2}$ are the optical densities of cyclobutane *rctt*-3, the complexes *rctt*-3·Ba²⁺, and *rctt*-3·(Ba²⁺)₂ at the excitation wavelength. The results are shown in Table 2.

The complexation of *rctt*-**3** with only one barium cation does not virtually effect on the efficiency of retro photoreaction (Table 2). The insertion of Ba^{2+} cations into each crown-ether cavity diminishes the efficiency of retro-PCA more than 2-fold. It is probably connected with decreasing electron acceptor ability of both crown-ether residues and, as a consequence, a partial levelling off the electronic effects of the substituents in four aryl residues. Also, we can not exclude the influence of steric hindrances in cyclobutane derivative *rctt*-**3**, which are absent in bi-



Fig. 5. Geometry of complex $[(E)-1\cdot(E)-2]^{3+}$, E and Z isomers of model molecule 2a. Most of hydrogen atoms of $[(E)-1\cdot(E)-2]^{3+}$ are not shown.

rable 3	
Spectral-kinetic parameters of model cation $2a$ and complex $[(E)-1\cdot(E)-2]^{3+}$ in ground and excited singlet states (^a).	

	$E_{\rm S0}$, kJ/mol	$\mu_{\rm S0},{\rm D}$	$\mu_{\rm S1},{\rm D}$	$q_{ m S0}$	$q_{\rm S1}$	n _{S0}	n _{S1}	heta, °	$ heta_{ m Pl},^{\circ}$	$E_{\rm S1}$, eV	$E_{\rm S0 \rightarrow S1}$, eV	$f_{\rm S0 \rightarrow S1}$
(E)- 2a	0	20.1	5.3	0.85	0.52	1.72	1.45	180	11	3.24		1.03
(E)- 2a ^a	22.1	17.0	5.0	0.73	0.43	1.54	1.27	180	0	2.89	2.66	1.33
(Z)-2a	12.2	15.2	1.4	0.89	0.4	1.67	1.44	8	51	3.35	3.23	0.36
(Z)-2a ^a	44.6	14.1	4.3	0.82	0.46	1.53	1.23	20	46	2.94	2.48	0.67
(R)- 2a ^a	203	15.6	3.21	1.02	0.09	1.06	1.07	90	90	2.21	0.11	0.002
$[(E)-1\cdot(E)-2]^{3+}$	_	21.4	12.8	0.87	0.19	1.68, 1.62	1.5, 1.46	179, 177	810	-	2.72	0.07

 E_{S0} and E_{S1} are the energies of the ground and excited states relatively to those for (E)-2a.

 $\mu_{\rm S0}$ and $\mu_{\rm S1}$ are the dipole moments.

 $q_{\rm S0}$ and $q_{\rm S1}$ – the positive charge localized on the pyridinium residue.

 $n_{\rm S0}$ and $n_{\rm S1}$ are the central bond orders in the molecule.

 θ is the dihedral angle between C₁–C₂–C₃–C₄ atoms (between two aromatic residues, Fig. 5.

see bonds marked in red).

 θ_{Pl} is the dihedral angle between aromatic planes of the A₁A₂ residues of the acceptor and the D₁D₂ residues of the donor.

 $E_{S0 \rightarrow S1}$ and $f_{S0 \rightarrow S1}$ are the energy of 0-0 transfer and the oscillator strength of the S₀-S₁ absorption band.

(R)-2a is the twisted conformer of 2a.

^a Structure is optimized for S_1 at a fixed θ angle.

nuclear complex *rctt*- $3 \cdot (Ba^{2+})_2$.

3.5. Electrochemical study

Using a mixture of MeCN/DMF (2:1) allowed us to improve the solubility of dye (*E*)-**2**. Increasing the content of a polar solvent act beneficially on the resolution of the obtained voltammogram. The numbers of peaks on cyclic voltammograms (CVA-curves) correspond to a number of stepwise redox transitions (SCH 2). Trication (*E*)-**2** can accept three electrons: the first one into the electron-deficient π -system of pyridinium and other two for the reduction of ammonium groups accompanied by hydrogen evolution. The appearance of only two peaks (A, B) in the cathodic region indicates that the reduction of both ammonium groups takes place simultaneously. Anodic processes are localized on the system consisting of a central double bond conjugated with two aromatic rings. The first oxidation potential (peak C) of (*E*)-**2** (0.81 V) is close to that (0.84 V) of the related acceptor **DPEb**.

3.6. Quantum chemical calculations

For quantum chemical modelling, a cation of dye (E)-**2a** (Fig. 5) was taken as an analogue of (E)-**2**. It was found that cation **2a** exists in MeCN as a mixture of E and Z isomers. The isomer (E)-**2a** is more stable, more planar, and polarized (Table 3). In addition, due to a mutual repulsion of



HOMO

Fig. 6. Molecular orbitals calculated for model cation (E)-2a.



Fig. 7. Conformational curves of S_0 and S_1 states of model cation of (*E*)-**2a** in MeCN; θ is dihedral angle between pyridinium and phenyl residues (xMCQDPT2+PCM).

aromatic hydrogens, isomer (*Z*)-2a is more twisted. Its energy is on 10–15 kJ/mol higher than that of isomer (*E*)-2a.

Up to 90% of positive charge of cation 2a in the ground state is localized on pyridinium residue. Calculated energies of $S_0 \rightarrow S_1$ transfer for (*E*)-2a and (*Z*)-2a are close to the experimental values. The oscillator strength of (*Z*)-2a is much lower than that of (*E*)-2a (Tables 1 and 3). The main transfer here is from HOMO, localized on thioanisole moiety to LUMO, localized on pyridinium residue (Fig. 6). The positive charge in S_1 is almost equally distributed between two aromatic moieties of the cation, the dipole moment is lower (Table 3).

From Fig. 6 is seen, that HOMO is bonding, but LUMO is antibonding orbital, with respect to both central carbon atoms. The following decrease of the central bond order promotes twisting the aromatic rings upon excitation. According to the calculations, the ground state barrier (1.88 eV) for *E–Z* isomerization transforms to the minimum in S₁ (Fig. 7). These data totally agree with the observation of *E–Z* isomerization upon irradiation of a solution of (*E*)-2 in MeCN (Fig. S12). Small gap between conformational curves at $\theta = 90^{\circ}$ facilitates nonradiative deactivation, that is the reason of low fluorescence quantum yield of the twisted conformer (*R*)-2 (Table 3). It should be noted, that gradual accumulation of isomer (*Z*)-2 up to photostationary state (PSS), observed upon irradiation of (*E*)-2, occurs due to its higher molar absorptivity.

The optimized geometry and the parameters of model complex [(E)- $1 \cdot (E) \cdot 2$ ³⁺ are shown in Fig. 5 and Table 3. A distance between the center of mass of the donor and the acceptor equals to 3.53 Å; their structures are close to planar. The angles between four aromatic planes of the donor and the acceptor $(D_1A_1, D_2A_2, A_1A_2, and D_1D_2)$ do not exceed 10°. The charge distribution in GS of the complex is close to that of free components (E)-1, (E)-2a. The positive charge is localized on the acceptor (0.98), mostly on its pyridinium residue (0.87). The calculated energy and the oscillator strength $S_0 \rightarrow S_1$ of the complex are significantly lower than those of free components (Table 3). The main transfer here is from HOMO of the donor to LUMO of the acceptor. The positive charge in S_1 is localized mostly on the donor residue (0.97); thioanisole moiety has a small negative charge (-0.17). Thus, the S₁ state has a chargetransfer (CT) character. The corresponding long-wavelength (CT) absorption band of the complex (E)-1·(E)-2 is not observed due to its overlap with the intense $S_0 \rightarrow S_2$ band. The parameters of the latter (E =3.11 eV, f = 0.67) are close to those of $S_0 \rightarrow S_1$ band of free acceptor. The main transfer here is also from HOMO of the donor to LUMO of the acceptor. The electron density distribution of the complex in S2 is similar

Table 4

Spectral-kinetic	parameters of	of TA	spectra	of o	dye and	l complex.
------------------	---------------	-------	---------	------	---------	------------

Compound	λ_a^{\max} , nm	τ_1 , fs	τ_2 , ps
(E)-1	561	69 ± 3	~ 1100 [25]
(E)-2	445, 508	27 \pm 4	860 \pm 30
(E)-1 ⋅(E)-2	447	11.5 \pm 1	21 \pm 1



Fig. 8. Differential absorption of (*E*)-**2** (spline) within 6.6–135 fs (*a*) and (*E*)-**1**. (*E*)-**2** (spline) within 1 ps–315 ps (*b*) after excitation in MeCN with a 40-fs pulse at 400 nm. Insets: time plot of the areas under the transient absorption spectra of (*E*)-**2** (*a*) and (*E*)-**1**.(*E*)-**2** (*b*). The smooth curves are from fitting to a monoexponential: $y = 2721 \times exp(-t/0.027) - 19.6$ (*a*), $y = 0.468 \times exp(-t/21) + 0.004$ (*b*).

to S_1 state of (*E*)-**2a**: the positive charge is localized mostly on the acceptor (0.75), the charges of pyridinium and thioanisole moieties are equal to 0.32 and 0.43, respectively. Thus, it can be concluded, that $S_2(LE) \rightarrow S_1(CT)$ relaxation of the acceptor involves the pronounced transfer of electron density from unexcited donor moiety of the complex.

3.7. Transient absorption study

All measurements were performed in a darkroom under red light to prevent E–Z isomerization. The transient absorption kinetics of donor (E)-1 in MeCN was recently studied in Refs. [25] (Table 4). Upon excitation by 40 fs pulse at 400 nm the TA spectra of dye (E)-2 in MeCN demonstrates the following evolution. During the first 130 fs the enhancement of a narrow band at ~510 nm was observed (Fig. 8a). Then we observed a rise of less intense band at 450 nm along with stimulated emission (SE) at 560 nm (Fig. S21a). Within 230 to 250 fs we observed



Fig. 9. Differential absorption of (*E*)- $1 \cdot (E)$ -2 within 80–110 fs after excitation in MeCN with a 40-fs pulse at 400 nm. Inset: differential absorption of (*E*)- $1 \cdot (E)$ -2 within 110–220 fs.

gradual quenching of the former band due to overlap with rising SE band of negative absorption. Further, up to 10 ps, the intensities of the initial and SE bands rose equally, showing, respectively, a blue and red shifts by 485 and 570 nm, Then up to 500 ps, the intensities of both bands decreased by 2.8 and 3.4 times (Fig. S21b). The corresponding kinetics was satisfactorily fitted by a monoexponential with a small constant background signal (Table 4). Appearing the second band in TA spectrum of dye (*E*)-2, unlike single-band spectrum of unsaturated analogue of viologen **DPEb** ($\lambda^{max} \sim 515$ nm [25]) within 400–700 nm, may be explained by molecular asymmetry of (*E*)-2. Reducing the olefin bond order upon excitation diminishes conjugation of the aromatic residues (Table 3). As a result, pyridinium and phenyl chromophores of the dye manifest as weakly-coupled π -systems. The molar absorptivity of phenyl chromophore is lower. The relatively short lifetime of (*E*)-2 is explained by the *E*–*Z* photoisomerization.

In order to avoid excitation of free dye at 400 nm, the TA spectra of the complex (E)-1·(E)-2 were registered using a solution with a 12-fold excess of donor (E)-1. The presence of a small amount of unstable complexes (*E*)- $1 \cdot (E) \cdot 2 \cdot (E) \cdot 1$ can be neglected. In spite of a full overlap between absorption of the acceptor and fluorescence of the donor, Förster resonance energy transfer (FRET) is absent here, because the donor component of the complex virtually does not absorb at 400 nm. The evolution of TA spectra of the complex (E)-1·(E)-2 at the excitation in long-wavelength absorption band of the dve (E)-2 is the following. Initially, during the first 70 fs the enhancement of a single band at \sim 510 nm is observed (LE* state). The position of this band coincides with that of free acceptor at the same delay time. Then within 70-130 fs we observe quenching of this band and appearance (after 80 fs) a weak negative band of a stimulated emission (SE) ($\lambda_a^{\text{max}} = 580 \text{ nm}$, Fig. 9). The position of the SE band is similar to that of a free acceptor ($\lambda_a^{max} = 560$ nm). Apparently it originates from the LE° state of the complex, formed due to internal conversion from higher vibrational levels ($LE^* \rightarrow LE^\circ$). Then the SE band gradually decreases and a new intense absorption band, showing monoexponential growth, appears at 445 nm. It should be noted that this band is close to the intense CT band of the complex (λ_a^{\max} = 450 nm, f = 0.75) obtained from quantum-chemical

calculations. After saturation, within 1–315 ps this band demonstrates monoexponential quenching to a background signal (Fig. 8b). The electron transfer processes occurring at the excitation of the acceptor moiety of the complex (*E*)-1·(*E*)-2 is depicted on Scheme 4. The calculated decay times are shown in Table 4.

Apparently the 11.5 fs day time represents the inverse sum of the rate constants of direct electron transfer and vibrational relaxation ($\text{LE}^* \rightarrow \text{LE}^\circ$). The 21 ps day time applies to the back electron transfer. Due to more negative reduction potential of the dye (*E*)-**2** (Fig. S15) the back electron transfer goes much slower in comparison with related complexes of bis-crown stilbene with viologen-like compounds [25,37].

4. Conclusions

The absorption and fluorescence spectra, molar absorptivities, and fluorescence quantum yields of *E*- and *Z*-isomers of dye **2** are varied, what is supported by quantum chemical| x-MCQDPT2 and TDDFT calculations. According to the calculations of model cation **2a**, the *E*–*Z* photoisomerization of (*E*)-**2** occurs at nonradiative deactivation from twisted intramolecular charge-transfer (TICT) state. A double-band character of TA spectra of dye (*E*)-**2** within 130–250 fs indicates a weak conjugation between pyridinium and phenyl residues in S₁. The supramolecular donor-acceptor 1:1 complex (*E*)-**1**·(*E*)-**2** formed between *E*-isomers of dye **2** and bis(18-crown-6) stilbene **1** is highly stable. Its spectral-luminescent parameters indicate the intrasupramolecular photo-electron transfer, which is confirmed by transient absorption spectroscopy. The direct electron transfer from unexcited donor to the S₁(CT) state of the acceptor moiety is highly efficient, the back electron transfer occurs much slower.

The formation of pseudocyclic complex (*E*)-**1**·(*E*)-**2** makes it possible to carry out [2 + 2] cross-photocycloaddition. It was shown that selective excitation of styryl or stilbene chromophore of the complex (*E*)-**1**· (*E*)-**2** weakly effects on cross-PCA quantum yield. The product of cross-PCA – cyclobutane derivative *rctt*-**3** undergoes to the back (retro) reaction upon excitation at 254 nm. Values of Φ_{retro} are almost 2 orders of magnitude higher than Φ_{PCA}^{405} and Φ_{PCA}^{313} , what can be explained by asymmetric structure of *rctt*-**3**. The interaction of cyclobutane *rctt*-**3** with Ba²⁺ cations is accompanied by a displacement of ammoniopropyl cation from bis-crown cavities. It is shown that a value of Φ_{retro} for binuclear complex *rctt*-**3**·(Ba²⁺)₂ is almost 2 times lower than that of free cyclobutane *rctt*-**3**.

The results of this research can be used for the targeted design of photoactive supramolecular assemblies with the specified values of electron transfer rate constants and in the development of new methods for the synthesis of cyclobutane derivatives using [2 + 2]-cross-photocycloaddition.

CRediT authorship contribution statement

Valery V. Volchkov: Writing - review & editing, steady state measurements, writing, editing, measurements of time-resolved spectra. Timofey P. Martyanov: Writing - review & editing, steady state measurements, writing, editing, purification and synthesis. Mikhail N. Khimich: quantum chemistry calculations. Mikhail V. Rusalov: Writing - review & editing, Formal analysis, global analysis, editing. Daria A. Neznaeva: steady state measurements. Fedor E. Gostev: measurements of time-resolved spectra. Ivan V. Shelaev: measurements of time-resolved spectra. Victor A. Nadtochenko: measurements of time-resolved spectra. Mikhail Ya Melnikov: Writing - review &

$$A^{3+} \cdots D \xrightarrow{hv} (A^{3+})^* \cdots D \xrightarrow{ET} (A^{\bullet 2+} \cdots D^{\bullet +})^* \xrightarrow{back ET} A^{3+} \cdots D$$

Scheme 4. The intrasupramolecular electron transfer in the complex (*E*)- $1 \cdot (E)$ -2 at 400 nm excitation. A³⁺ – trication of the dye (*E*)-2 (acceptor), D – bis(crown) stilbene (donor).

editing, editing, helpful discussions. Anna A. Moiseeva: electrochemical measurements. Evgeny N. Ushakov: Writing - review & editing, editing, helpful discussions. Sergey P. Gromov: Writing - review & editing, editing, helpful discussions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Russian Science Foundation (in respect of organic synthesis, photochemical and NMR studies, project no. 19-13-00020), and by Ministry of Science and Higher Education of the Russian Federation (in respect of the femtosecond pump and probe setup, Government Assignment 0082-2019-0001, registration no. AAAA-A19-119012890064-7 and in respect of the metal complexes formation, Government Assignment 0089-2019-0003, registration no. AAAA-A19-119090900055-9). Quantum chemical calculations were carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University.

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108952.

References

- [[1]] Peng H, Liu ZF. Organic charge-transfer complexes for STM-based thermochemical-hole-burning memory. Coord. Chem Rev 2010;254:1151–68. https://doi.org/10.1016/j.ccr.2010.02.016.
- [2] Lee HL, Jang HJ, Lee JY. Single molecule white emission by intra- and intermolecular charge transfer. J Mater Chem C 2020;8:10302–8. https://doi.org/ 10.1039/d0tc02205e.
- [3] Sze P-W, Huang Ch-J, Lin F-Y, Lan W-H. Enhancement performances in white organic light-emitting diode (WOLED) by formation of charge-transfer (CT) complex. J Nanosci Nanotechnol 2015;15:9178–83. https://doi.org/10.1166/ jnn.2015.11413.
- [4] Narasimha K. Macromolecular effect stabilized color-tunable and room temperature charge-transfer complexes based on donor– acceptor assemblies. ACS Appl. Polym. Mater. 2020;2:1145–59. https://doi.org/10.1021/acsapm.9b00917.
- [5] Das A, Ghosh S. Supramolecular assemblies by charge-transfer interactions between donor and acceptor chromophores. Angew Chem Int Ed 2014;53:2038–54. https://doi.org/10.1002/anie.201307756.
- [6] Zhang Q, Huang Y, Wang Z, Chen Z. Towards emerging properties and applications of organic cocrystals beyond electrical conductivities and field-effect transistors (FETs). Angew Chem 2019;58(29):9696–711. https://doi.org/10.1002/ anie.201900501.
- [7] Wang Z, Zhang Q. Organic donor acceptor cocrystals for multiferroic applications. Asian J. Org.Chem. 2020;9(9):1252–61. https://doi.org/10.1002/ajoc.202000024.
 [8] Foster R. Organic charge-transfer complexes. New York: Academic Press; 1969.
- [9] Rusalov MV, Volchkov VV, Ivanov VL, Melnikov M Ya, Shelaev IV, Gostev FE, et al. Ultrafast excited state dynamics of a stilbene-viologen charge transfer complex and its interaction with alkanediammonium salts. J Photochem Photobiol Chem 2019; 372:89–98. https://doi.org/10.1016/j.jphotochem.2018.12.007.
- [10] Volchkov VV, Khimich MN, Rusalov MV, Gostev FE, Shelaev IV, Nadtochenko VA, et al. Melnikov. Formation of supramolecular charge-transfer complex. Ultrafast excited state dynamics and quantum-chemical calculations. Photochem Photobiol Sci 2019;18:232–41. https://doi.org/10.1039/c8pp00328a.
- [11] Rusalov MV, Volchkov VV, Ivanov VL, Mel'nikov M Ya, Shelaev IV, Gostev FE, et al. Femtosecond excited state dynamics of a stilbene–viologen charge transfer complex assembled via host–guest interaction. Photochem Photobiol Sci 2017;16 (12):1801–11. https://doi.org/10.1039/c7pp00170c.
- [12] Ushakov EN, Martyanov TP, Vedernikov AI, Sazonov SK, Strelnikov IG, Klimenko LS, et al. Stereospecific [2+2]-cross-photocycloaddition in a supramolecular donor-acceptor complex. Tetrahedron Lett 2019;60:150–3. https://doi.org/10.1016/j.tetlet.2018.11.077.
- [13] Mako TL, Racicot JM, Levine M. Supramolecular luminescent sensors. Chem Rev 2019;119:322–477. https://doi.org/10.1021/acs.chemrev.8b00260.
- [14] Volodin AD, Korlyukov AA, Zorina-Tikhonova EN, Chistyakov AS, Sidorov AA, Eremenko IL, et al. Diastereoselective solid-state crossed photocycloaddition of olefins in a 3D Zn(II) coordination polymer. Chem Commun 2018;54:13861–4. https://doi.org/10.1039/c8cc07734g.

- [15] Duncan AJE, Dudovitz RL, Dudovitz SJ, Stojaković J, Mariappan SVS, MacGillivray LR. Quantitative and regiocontrolled crossphotocycloaddition of the anticancer drug 5-fluorouracil achieved in a cocrystal. Chem Commun 2016;52: 13109–11. https://doi.org/10.1039/c6cc06570h.
- [16] Martyanov TP, Vedernikov AI, Ushakov EN, Sazonov SK, Aleksandrova NA, Lobova NA, et al. Pseudodimeric complexes of 4-styrylpyridine derivatives: structure-property relationships and a stereospecific [2+2]-crossphotocycloaddition in solution. Dyes Pigments 2020;172:107825. https://doi.org/ 10.1016/j.dyepig.2019.107825.
- [17] Marquis D, Desvergne J-P, Bouas-Laurent H. Photoresponsive supramolecular systems: synthesis and photophysical and photochemical study of bis-(9,10anthracenediyl)coronands AAO_nO_n. J Org Chem 1995;60:7984–96. https://doi. org/10.1021/jo00129a045.
- [18] Ke Ch, Yang Ch, Mori T, Wada T, Liu Y, Inoue Y. Catalytic enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylic acid mediated by a nonsensitizing chiral metallosupramolecular host. Angew Chem Int Ed 2009;48: 6675–7. https://doi.org/10.1002/anie.200902911.
- Salomon RG. Homogeneous metal-catalysis in organic photochemistry. Tetrahedron 1983;39:485–575. https://doi.org/10.1016/S0040-4020(01)91830-7.
- [20] Vedernikov AI, Basok SS, Gromov SP, Kuz'mina LG, Avakyan VG, Lobova NA, et al. Synthesis and structure of bis-crown-containing stilbenes. Russ J Org Chem 2005; 41:843–54. https://link.springer.com/article/10.1007/s11178-005-0255-2.
- [21] Vedernikov AI, Kuz'mina LG, Botsmanova AA, Strelenko Yu A, Howard JAK, Alfimov MV, et al. Stacking structures of complexes between bis(crown) azobenzene and a dipyridylethylene derivative in a crystal and in solution. Mendeleev Commun 2007;17:148–50. https://doi.org/10.1016/j. mencom.2007.05.005.
- [22] Gottlieb HE, Kotlyar V, Nudelman A. NMR chemical shifts of common laboratory solvents as trace impurities. J Org Chem 1997;62(21):7512–5. https://doi.org/ 10.1021/jo971176v.
- [23] Melhuish WH. Quantum efficiencies of fluorescence of organic substances: effect of solvent and concentration of the fluorescent solute. J Phys Chem 1961;65:229–35. https://doi.org/10.1021/j100820a009.
- [24] Suzuki K, Kobayashi A, Kaneko S, Takehira K, Yoshihara T, Ishida Y, et al. Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector. Phys Chem Chem Phys 2009;11:9850–60. https://doi.org/10.1039/B912178A.
- [25] Ushakov EN, Nadtochenko VA, Gromov SP, Vedernikov AI, Lobova NA, Alfimov MV, et al. Ultrafast excited state dynamics of the bi- and termolecular stilbene-viologen charge-transfer complexes assembled via host–guest interactions. Chem Phys 2004;298:251–61. https://doi.org/10.1016/j.chemphys.2003.12.002.
- [26] Volchkov VV, Gostev FE, Shelaev IV, Nadtochenko VA, Dmitrieva SN, Gromov SP, et al. Melnikov. Complexation of donor-acceptor substituted aza-crowns and alkali and alkaline earth metal cations. Charge transfer and recoordination in excited state. J Fluoresc 2016;26:585–92. https://doi.org/10.1007/s10895-015-1744-5.
- [27] Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, et al. General atomic and molecular electronic structure system. J Comput Chem 1993; 14:1347–63. https://doi.org/10.1007/10.1001/jcc.540141112.
- [28] Marenich AV, Cramer CJ, Truhlar DG. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. J Phys Chem B 2009;113:6378–96. https://doi.org/10.1021/jp810292n.
 [29] Granovsky AA. Firefly 8.2, build 10203. https://classic.chem.msu.su/gran/Fi
- [29] Granovsky AA. Firefly 8.2, build 10203. https://classic.chem.msu.su/gran/Firefly/index.html; 2017.
- [30] Granovsky AA. Extended multi-configuration quasi-degenerate perturbation theory: the new approach to multi-state multi-reference perturbation theory. J Chem Phys 2011;134:214113–26. https://doi.org/10.1063/1.3596699.
- [31] Miertus S, Scrocco E, Tomasi J. Electrostatic interaction of a solute with a continuum. A direct utilization of AB initio molecular potentials for the prevision of solvent effects. Chem Phys 1981;55:117–29. https://doi.org/10.1016/0301-01048185090-2.
- [32] Ushakov EN, Gromov SP, Vedernikov AI, Malysheva EV, Botsmanova AA, Alfimov MV, et al. Self-organization of highly stable electron donor-acceptor complexes via host-guest interactions. J Phys Chem A 2002;106:2020–3. https:// doi.org/10.1021/jp012082z.
- [33] Gromov SP, Vedernikov AI, Ushakov EN, Alfimov MV. Unusual supramolecular donor-acceptor complexes of bis(crown)stilbenes and bis(crown)azobenzene with viologen analogs. Russ Chem Bull 2008;57(4):793–801. https://doi.org/10.1007/ s11172-008-0118-4.
- [34] Gromov SP, Vedernikov AI, Ushakov EN, Lobova NA, Botsmanova AA, Kuz'mina LG, et al. Novel supramolecular charge-transfer systems based on bis(18crown-6)stilbene and viologen analogues bearing two ammonioalkyl groups. New J Chem 2005;29:881–94. https://doi.org/10.1039/B500667H.
- [35] Ushakov EN, Alfimov MV, Gromov SP. Design principles for optical molecular sensors and photocontrolled receptors based on crown ethers. Russ Chem Rev 2008;77(1):39–58. https://doi.org/10.1070/RC2008v077n01ABEH003757.
- [36] Minkin VI, Dubonosov AD, Bren VA, Tsukanov AV. Chemosensors with crown ether-based receptors. ARKIVOC 2008;(4):90–102. https://doi.org/10.3998/ ark.5550190.0009.410.
- [37] Butin KP, Moiseeva AA, Gromov SP, Vedernikov AI, Botsmanova AA, Ushakov EN, et al. Prospects of electroanalytical investigations of supramolecular complexes of a bis-crown stilbene with viologen-like compounds bearing two ammonioalkyl groups. J Electroanal Chem 2003;547:93–102. https://doi.org/10.1016/S0022-0728(03)00142-6.