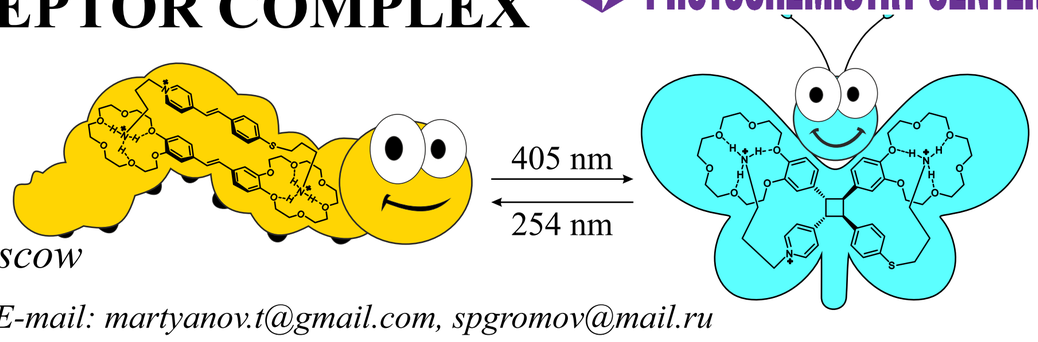
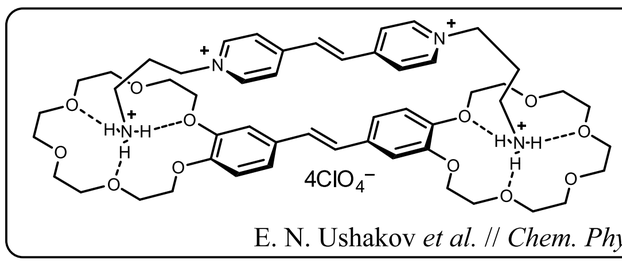
STEREOSPECIFIC [2+2]-CROSS-PHOTOCYCLOADDITION IN A SUPRAMOLECULAR DONOR–ACCEPTOR COMPLEX

Martyanov T.P.[1,2], Ushakov E.N.[1,2], Sazonov S.K.[2], Gromov S.P.[2,3]

[1] *Institute of Problems of Chemical Physics, RAS, Chernogolovka*
[2] *Photochemistry Center of RAS, FSRC "Crystallography and Photonics", RAS, Moscow*
[3] *Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow*

E-mail: martyanov.t@gmail.com, spgromov@mail.ru





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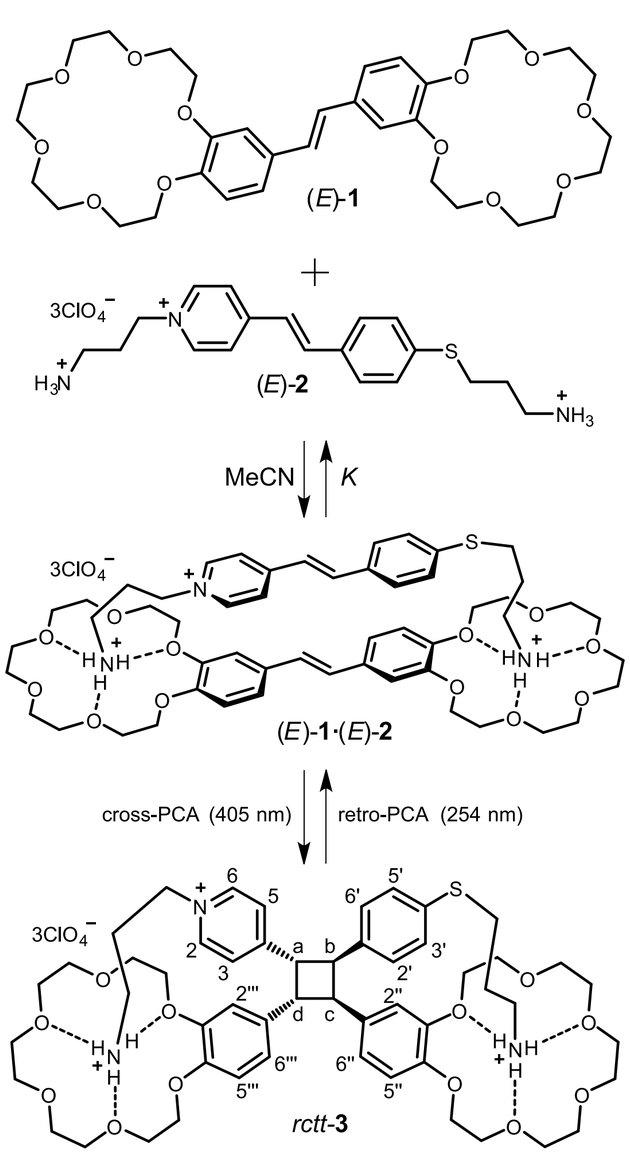
There are no photoreactions and fluorescence due to ultrafast photoinduced electron transfer from the donor (stilbene) to the acceptor (dipyridylethylene).

E. N. Ushakov *et al.* // *Chem. Phys.*, 2004, **298**, 251

Bis(18-crown-6)stilbene **1** and the bis(ammoniopropyl) derivative of 4-(4-mercaptostyryl)pyridine **2** form a highly stable supramolecular donor–acceptor complex in solution due to ditopic coordination via hydrogen bonds. Photoirradiation of the complex induced the reaction of [2+2]-cross-photocycloaddition, which afforded cyclobutane derivative **3** as a single *rctt* isomer; the reaction quantum yield was measured to be as low as 7×10^{-4}. The main reason for the low efficiency of this photoreaction is a fast deactivation of the excited state of the complex due to electron transfer from the donor (stilbene derivative) to the acceptor (styrylpyridinium dye).



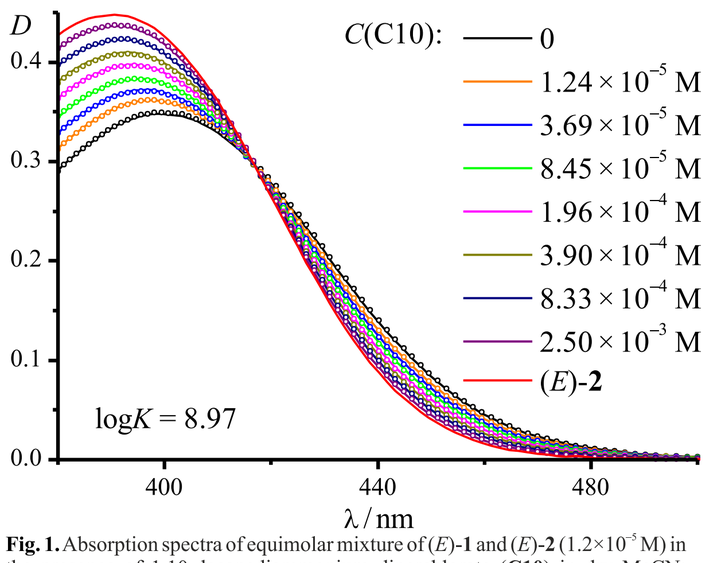


Fig. 1. Absorption spectra of equimolar mixture of (*E*)-**1** and (*E*)-**2** (1.2×10^{-5} M) in the presence of 1,10-decanediammonium diperchlorate (**C10**) in dry MeCN; $C(HClO_4) = 5\times10^{-6}$ M; circles are the experimental spectra, solid curves are approximation using two equilibria, red curve is the calculated spectrum of a mixture of (*E*)-**2** and (*E*)-**1**·**C10**.

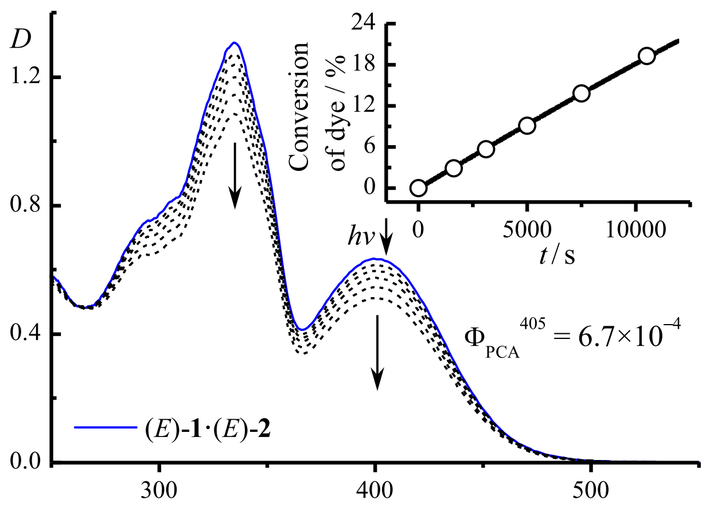
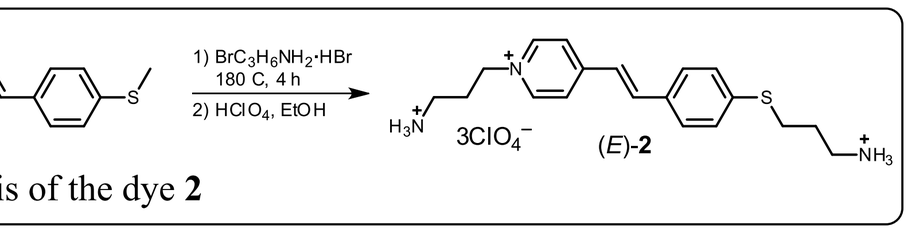


Fig. 2. Steady-state photolysis of (*E*)-**1**·(*E*)-**2** in MeCN with 405 nm light: 1 cm cell, (*E*)-**1**: 2.84×10^{-5} M, (*E*)-**2**: 2.25×10^{-5} M, $HClO_4$: 5×10^{-6} M, light intensity: 1.67×10^{-9} mol·cm^{-2}s^{-1}. Inset: rate of conversion (%) of complexed dye (*E*)-**2** as a function of irradiation time, s. The data were fitted using kinetic equation for irreversible monomolecular photoreaction.



Synthesis of the dye **2**

$$\frac{dC_{comp}(t)}{dt} = 10^3 I_{act}[\Phi_{retro}\varepsilon_{CB}C_{CB}(t) - \Phi_{PCA}{}^{405}\varepsilon_{comp}C_{comp}(t)]\frac{[1-10^{-D(t)}]}{D(t)}$$

$$D(t) = [\varepsilon_{comp}C_{comp}(t) + \varepsilon_{CB}C_{CB}(t)]l \qquad C_{CB}(t) = C_0 - C_{comp}(t)$$

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

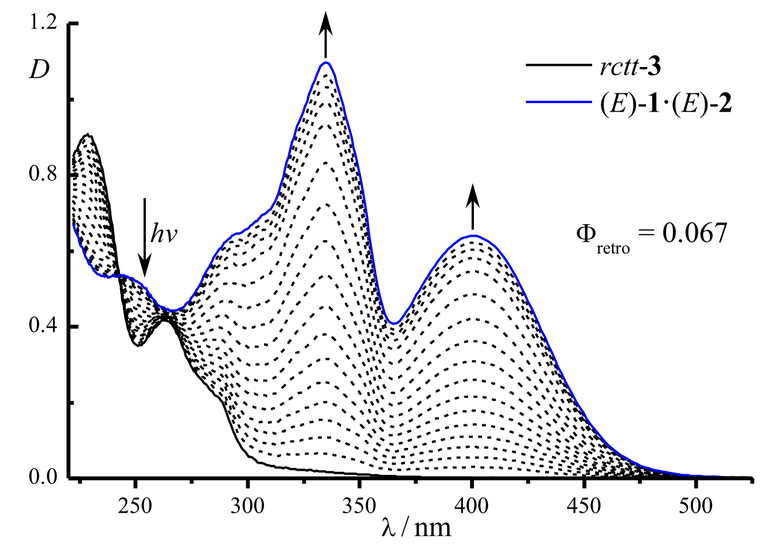


Fig. 3. Steady-state photolysis of *rctt*-**3** in MeCN with 254 nm light, 1 cm cell, *rctt*-**3**: 2.27×10^{-5} M, $HClO_4$: 5×10^{-6} M, light intensity: 6.02×10^{-10} mol·cm^{-2}s^{-1}.

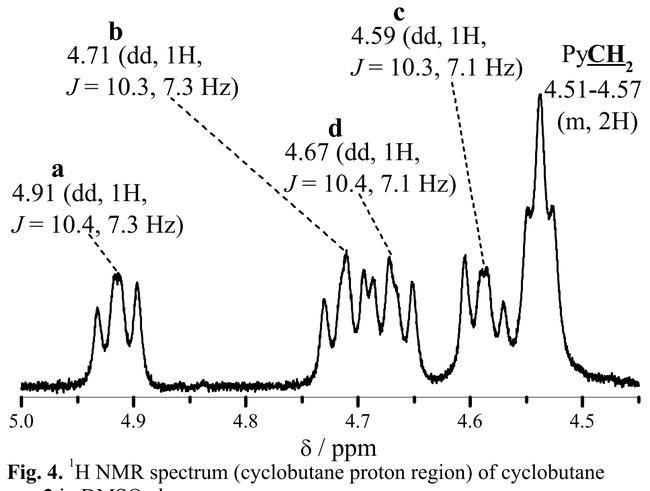


Fig. 4. ^{1}H NMR spectrum (cyclobutane proton region) of cyclobutane *rctt*-**3** in DMSO-d_6.

Table 1. Spectral-luminescent and photochemical parameters of free stilbene **1**, dye **2** and complex (*E*)-**1**·(*E*)-**2** in dry MeCN.[a]

Compoud	λ_{max}^{abs}, nm	$\varepsilon_{max}\times10^{-4}$, M^{-1} cm^{-1}	λ_{max}^{fl}, nm	φ_{fl}	φ_{E-Z}	φ_{Z-E}	$\Phi_{PCA}\times10^4$
(*E*)-**1**[b]	336	3.75	386	0.30	0.24	–	–
(*E*)-**1**·(*E*)-**2**	334	4.82	382	0.0057	–[c]	–[c]	7.2
(*E*)-**2**	392	3.65	559	0.18	0.34	0.39	–
(*E*)-**1**·(*E*)-**2**	401	2.81	546	0.0015	–[c]	–[c]	6.7

[a] In MeCN, λ_{max}^{abs} is the position of maximum of long-wavelength absorption band, ε_{max} is the molar absorptivity at λ_{max}^{abs}, λ_{max}^{fl} is the position of the fluorescence maximum in the corrected spectrum, in case of (*E*)-**1**·(*E*)-**2** λ_{max}^{abs} and λ_{max}^{fl} was determined for stilbene band in complexed form, φ_{fl} is the fluorescence quantum yield, φ_{E-Z} and φ_{Z-E} are the quantum yields of the reversible *E*–*Z* photoisomerization, Φ_{PCA} is the quantum yield of cross-PCA, for (*E*)-**1**·(*E*)-**2** photolysis was done with 313 nm light, for (*E*)-**1**·(*E*)-**2** – with 405 nm light.
[b] Data for **1** are taken from [E. N. Ushakov *et al*, Chem. Phys. 2004, v. 298, p. 251–261].
[c] Reaction does not occur.

Quantum-chemical calculations: DFT (structure), TDDFT (electronic transitions), functional M06-2X (DFT), CAM-B3LYP (TDDFT), basis set 6-311G(d,p), solvation model SMD.

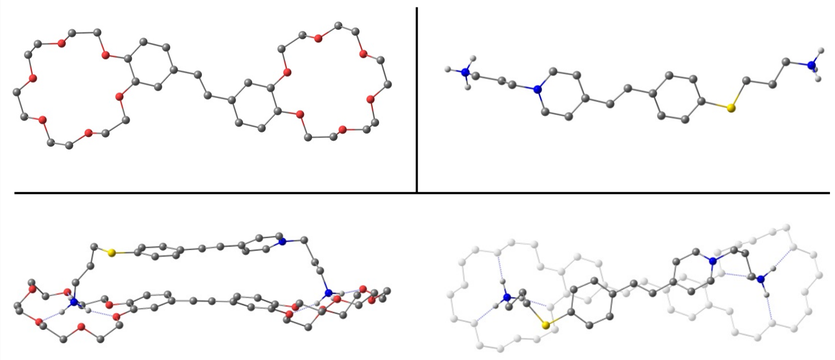


Fig. 5. Parameters of low-energy electronic transitions in the most stable conformers of stilbene (*E*)-**1**, dye (*E*)-**3** and complex (*E*)-**1**·(*E*)-**3**.

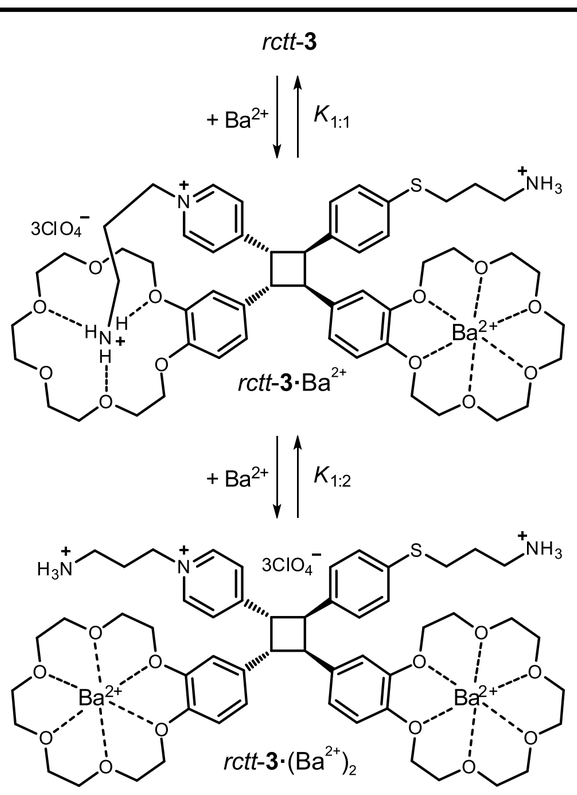


Table 2. Stability constants, spectroscopic parameters, and retro-PCA quantum yields for *rctt*-**3** and its complexes with Ba^{2+}.[a]

Compound	log*K*	λ_{max}^{abs}, nm	$\varepsilon_{max}\times10^{-4}$, M^{-1} cm^{-1}	Φ_{retro}
rctt-**3**	–	264	1.83	0.067 (Φ_{retro})
rctt-**3**·Ba^{2+}	4.14	261	2.13	0.070 ($\Phi_{retro}^{1:1}$)
rctt-**3**·$(Ba^{2+})_2$	3.54	260	2.47	0.031 ($\Phi_{retro}^{1:2}$)

[a] Measurement errors of stability constants and quantum yields amounted to ±30%.

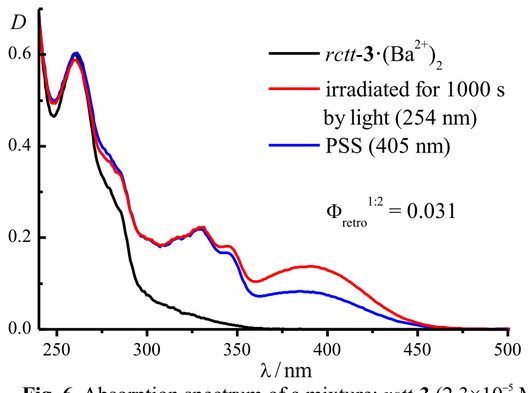


Fig. 6. Absorption spectrum of a mixture: *rctt*-**3** (2.3×10^{-5} M), $Ba(ClO_4)_2$ (1.7×10^{-3} M), and $HClO_4$ (8.3×10^{-5} M) in MeCN, I = 0.015 M (black curve); red curve depicts the spectrum obtained after irradiation of this solution at 254 nm during 1000 s (I_{act} = 2.74×10^{-10} mol·cm^{-2}·s^{-1}); blue curve depicts the spectrum of the PSS state, obtained upon irradiation at 405 nm.

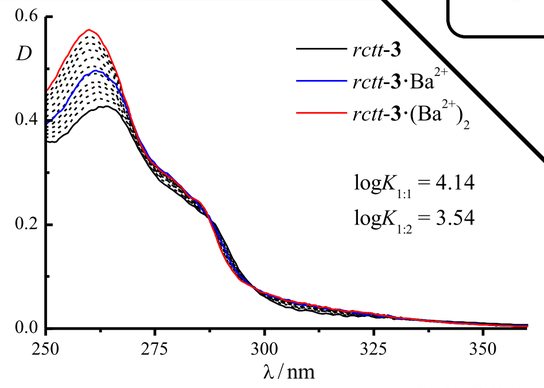


Fig. 7. Absorption spectra of the system *rctt*-**3**–$Ba(ClO_4)_2$ in MeCN, 1 cm cell, I = 0.015 M, *rctt*-**3**: 2.3×10^{-5} M, concentration of $Ba(ClO_4)_2$ was varied incrementally from 0 to 1.7×10^{-3} M. The titrant contained $HClO_4$ (5 mol % relatively to $Ba(ClO_4)_2$).

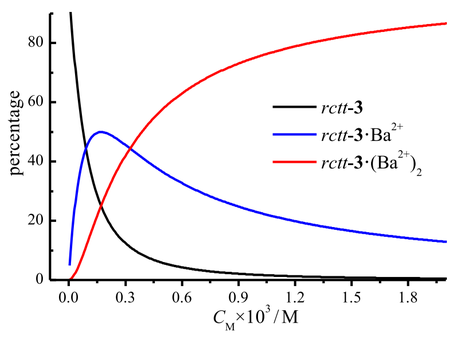


Fig. 8. Concentrational curves for the system *rctt*-**3**–$Ba(ClO_4)_2$ in MeCN, C(**3**) = 2.5×10^{-5} M.

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

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

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**·$(Ba^{2+})_2$ at irradiation wavelength before and after the photolysis; ΔC is the amount of dye **2** formed after photolysis; t_{ir} is the irradiation time with 254 nm light. The ΔC value was measured as follows. After irradiation with 254 nm light for 1000 s, the solution was brought to a photostationary state (PSS) by irradiation with 405 nm light (Fig. 6). Knowing the PSS spectrum of free dye **2**, the amount of dye formed after the photolysis was found. The experiment was performed in three repetitions.

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

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 free cyclobutane *rctt*-**3**, the complexes *rctt*-**3**·Ba^{2+}, and *rctt*-**3**·$(Ba^{2+})_2$ at the excitation wavelength.

E. N. Ushakov, T. P. Martyanov, A. I. Vedernikov, S. K. Sazonov, I. G. Strelnikov, L. S. Klimenko, M. V. Alfimov, S. P. Gromov, Stereospecific [2+2]-cross-photocycloaddition in a supramolecular donor–acceptor complex, *Tetrahedron Lett.*, 2019 , v 60, p. 150–153.

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