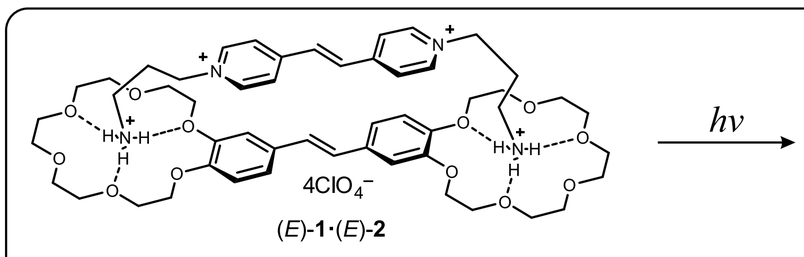
STEREOSPECIFIC [2+2]-CROSS-PHOTOCYCLOADDITION IN A SUPRAMOLECULAR DONOR–ACCEPTOR COMPLEX

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

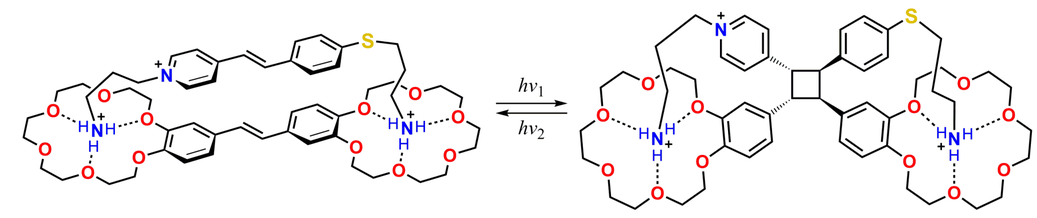
[1]Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia
[2]Photochemistry Center, FSRC "Crystallography and Photonics" RAS, Moscow, Russia

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

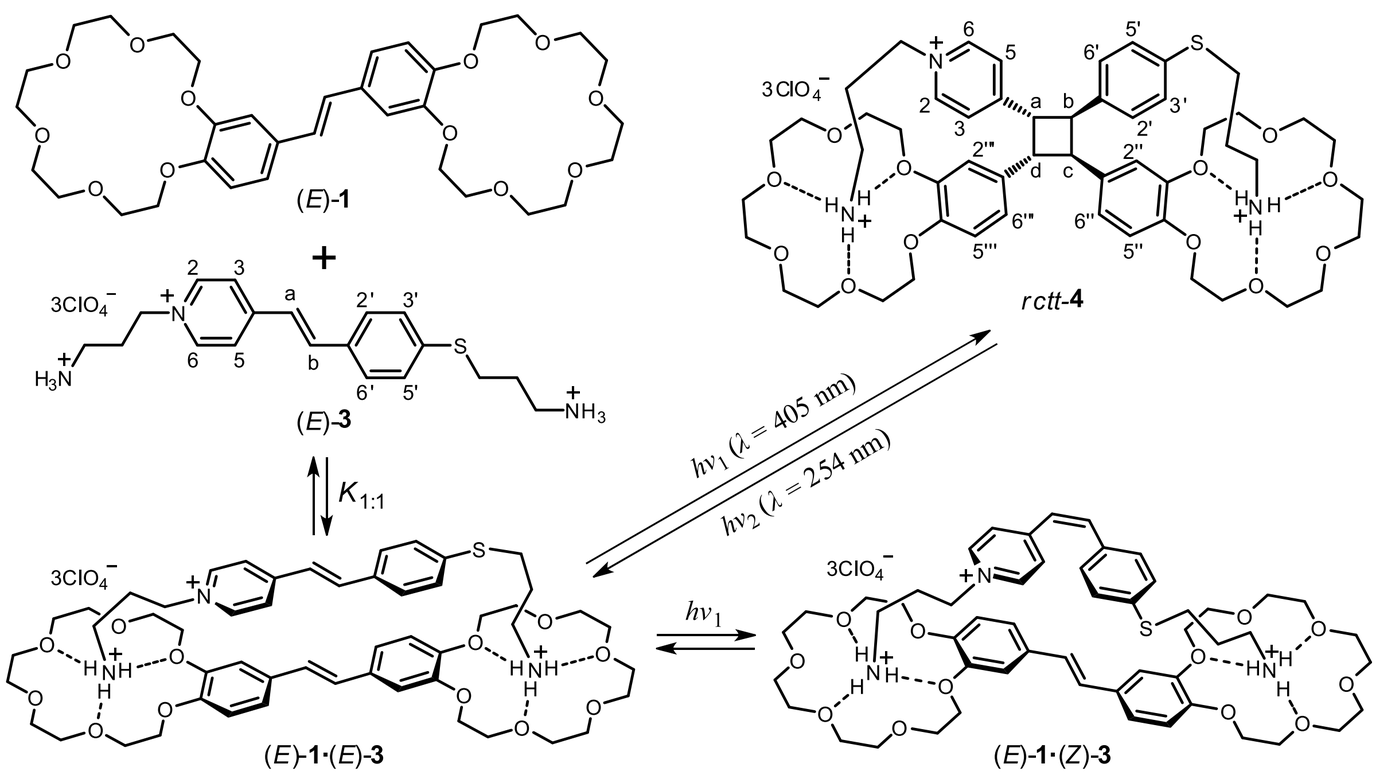


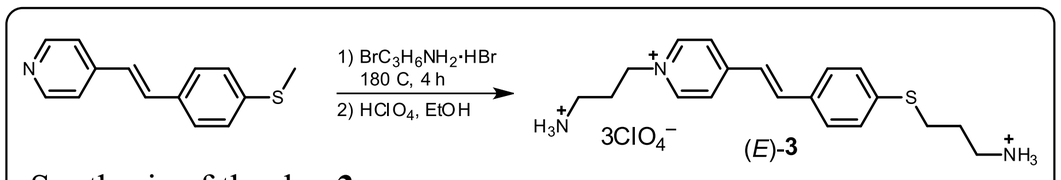
E. N. Ushakov *et al.* // *Chem. Phys.*, 2004, **298**, 251

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



The ditopic coordination of bis(18-crown-6) stilbene (**1**) to a bis(ammoniopropyl) derivative of 4-(4-(methylthio)styryl)pyridine (**3**) in solution leads to a highly stable supramolecular donor–acceptor complex. Upon selective excitation of **3** at > 400 nm, the complexed olefins undergo the [2 + 2]-cross-photocycloaddition leading to the *rctt* cyclobutane isomer with a quantum yield of about $8.0\cdot10^{-4}$. The main reason for the low efficiency of this photoreaction is a fast deactivation of the locally excited state of **3** in the donor–acceptor complex due to the intermolecular electron transfer reaction.





Synthesis of the dye **3**

$$\mathrm{St} + \mathrm{Am} \underset{}{\overset{K_{1:1}}{\rightleftharpoons}} \mathrm{St}\cdot\mathrm{Am}$$

St – stilbene (*E*)-**1**, Am – dye (*E*)-**3**, $K_{1:1}$ – stability constant of the complex (*E*)-**1**·(*E*)-**3**

Table 1. Quantum yields of fluorescence φ_f and reversible *E-Z*-potoisomerization ($\varphi_{E\text{-}Z}$ and $\varphi_{Z\text{-}E}$) for compounds **1** and **3** as free molecules and in the complex.[a]

Compound	φ_f	$\varphi_{E\text{-}Z}$	$\varphi_{Z\text{-}E}$
(*E*)-**1**	0.30	0.24	–
(*E*)-**1**·(*E*)-**3**	0.019	–	–
(*E*)-**3**	0.205	0.34	0.40
(*E*)-**1**·(*E*)-**3**	0.031	0.048	0.64

[a] Photoisomerization quantum yields are measured to within about 20%, fluorescence quantum yields – about 10%.

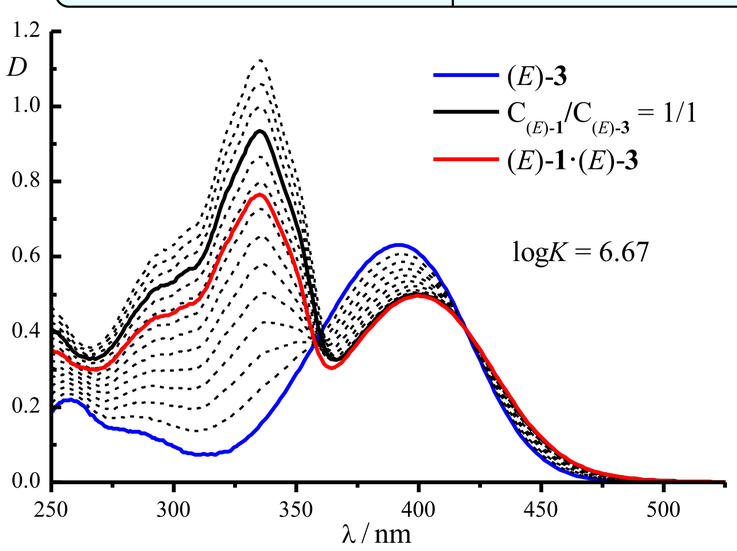


Figure 1. Spectrophotometric titration data for the system (*E*)-**1**·(*E*)-**3** in MeCN ($C_{Am} = 1.9\cdot10^{-5}$ M, $l = 1$ cm) containing 3% H_2O and $2.5\cdot10^{-6}$ M $HClO_4$, the total stilbene concentration C_{st} varies incrementally from 0 to $2.4\cdot10^{-5}$ M. The calculated spectrum of the complex (*E*)-**1**·(*E*)-**3** is shown by red curve.

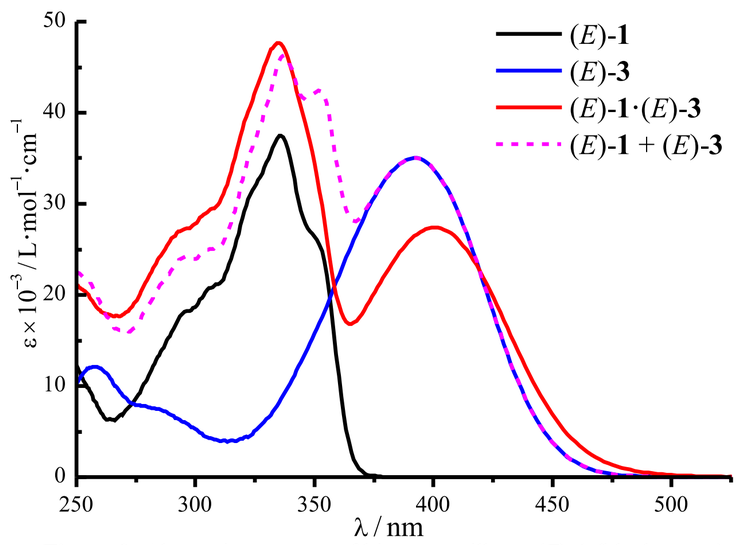


Figure 2. Absorption spectra of biscrownstilbene (*E*)-**1** (black curve), dye (*E*)-**3** (blue curve), their sum (magenta dashed line) and complex (*E*)-**1**·(*E*)-**3** (red curve) in MeCN containing 3% H_2O.

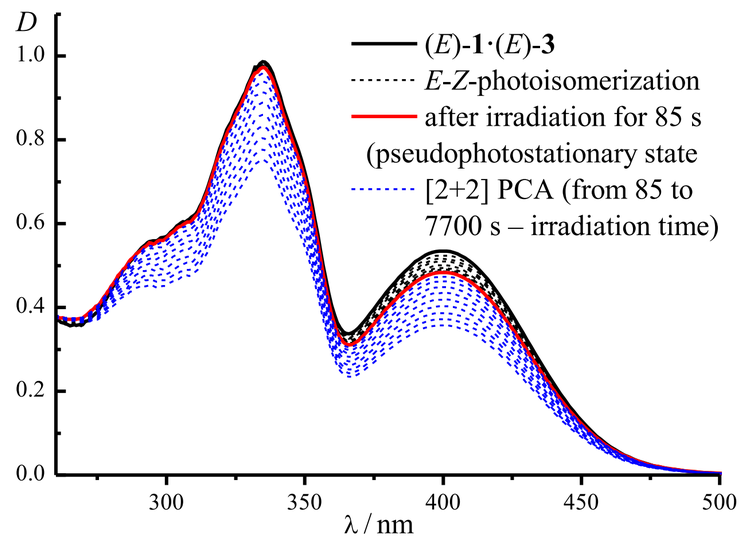


Figure 3. Spectrophotometric data on the steady-state photolysis of complex (*E*)-**1**·(*E*)-**3** in MeCN ($C_{St} = 2.2\cdot10^{-5}$ M, $C_{Am} = 2\cdot10^{-5}$ M, 1 cm cell) with 405 nm, light intensity $2.6\cdot10^{-9}$ mol cm^{-2} s^{-1}.

$$\frac{\mathrm{d}C_L(t)}{\mathrm{d}t} = \varphi_{[2+2]} I N_A^{-1} 10^3 \frac{(1-10^{-\varepsilon C_L(t) l})}{l}$$

I – light intensity, cm^{-2}s^{-1}; N_A – Avogadro constant, mol^{-1}; ε – molar absorptivity of complex at irradiation wavelength (405 nm), M^{-1}cm^{-1}; l – path length of the light, cm.

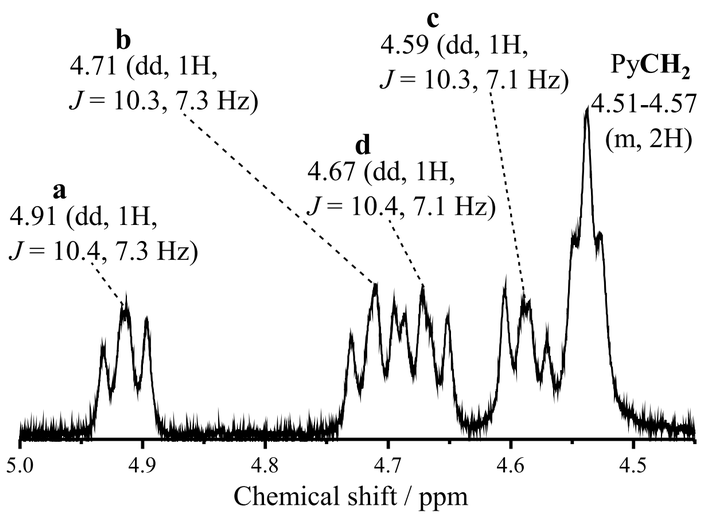
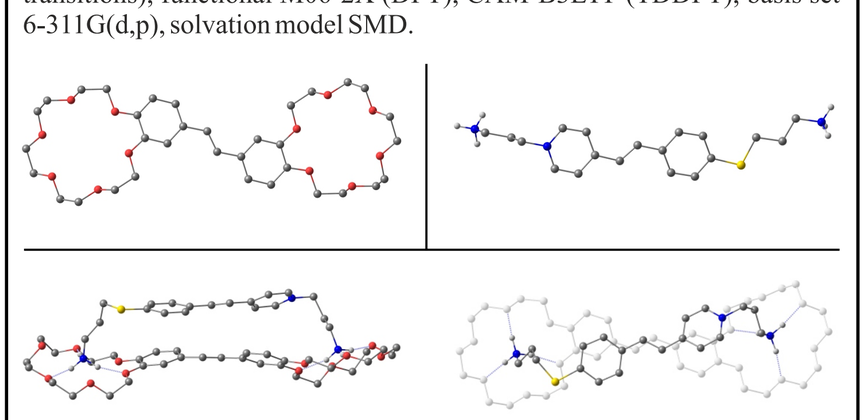


Figure 5. ^{1}H NMR spectrum of *rctt*-**4** in DMSO-d_6 (region of cyclobutane protons).

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



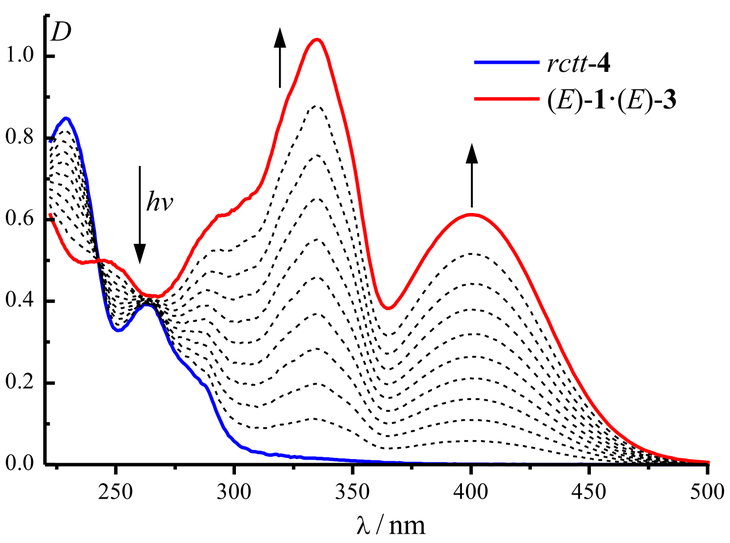


Figure 6. Spectrophotometric data on the steady-state photolysis of cyclobutane *rctt*-**4** with 254 nm in MeCN.

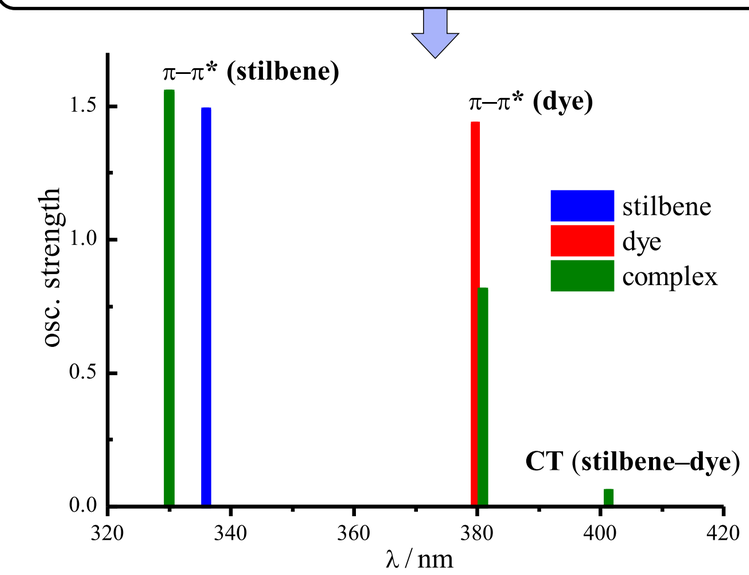


Figure 7. Parameters of low-energy electronic transitions in the most stable conformers of stilbene (*E*)-**1**, dye (*E*)-**3** and complex (*E*)-**1**·(*E*)-**3**.

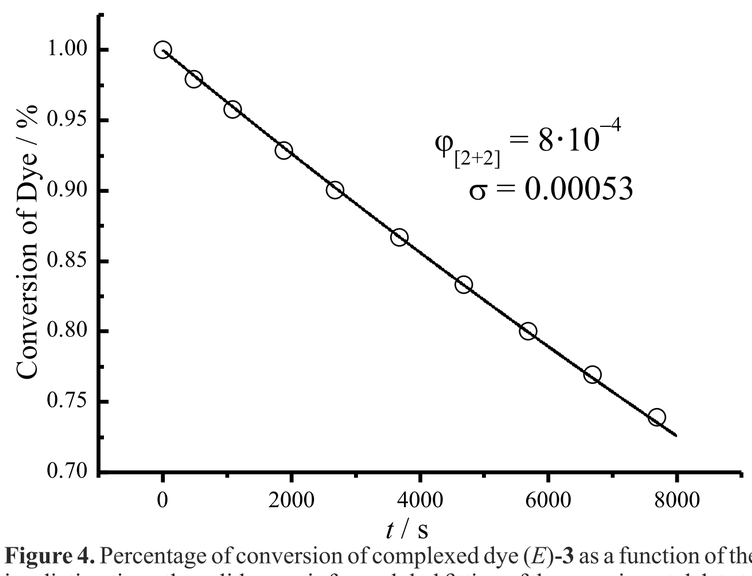


Figure 4. Percentage of conversion of complexed dye (*E*)-**3** as a function of the irradiation time: the solid curve is from global fitting of the experimental data to a kinetic equation for irreversible unimolecular photoreactions.

This work was supported by the Russian Science Foundation (project no. 19-13-00020).

Ushakov E. N., Martyanov T. P., Vedernikov A. I., Sazonov S. K., Strelnikov I. G., Klimenko L. S., Alfimov M. V., Gromov S. P. // *Tetrahedron Letters*, 2019, V. 60, p. 150-153.