VII INTERNATIONAL CONFERENCE ON PHYSICAL CHEMISTRY OF CROWN COMPOUNDS, PORPHYRINS AND PHTHALOCYANINES

Self-assembly through hydrogen bonding and photochemical properties of supramolecular complexes of bis(18-crown-6)stilbene with alkanediammonium ions

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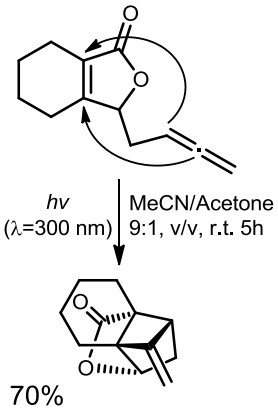
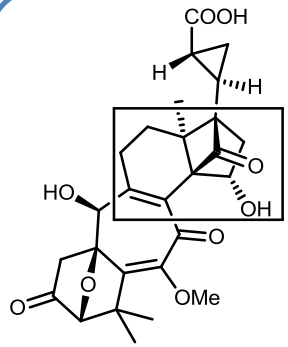
ИПХФ РАН

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

[2+2] Photocycloaddition reaction in organic chemistry

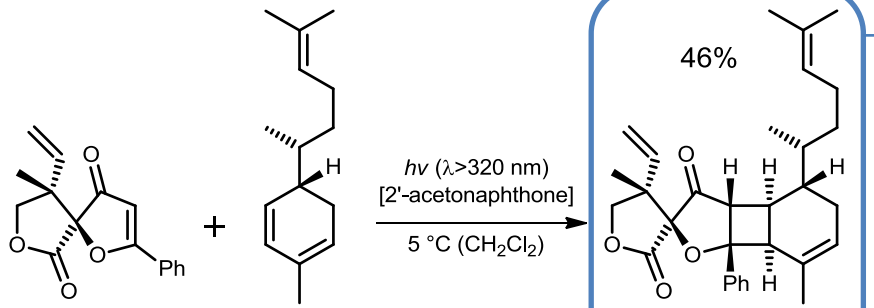




Solanoeclepin A

A natural hatching stimulant of potato cyst nematodes (Globodera rostochiensis and G. pallida), which causes serious damage to food crops over the world.

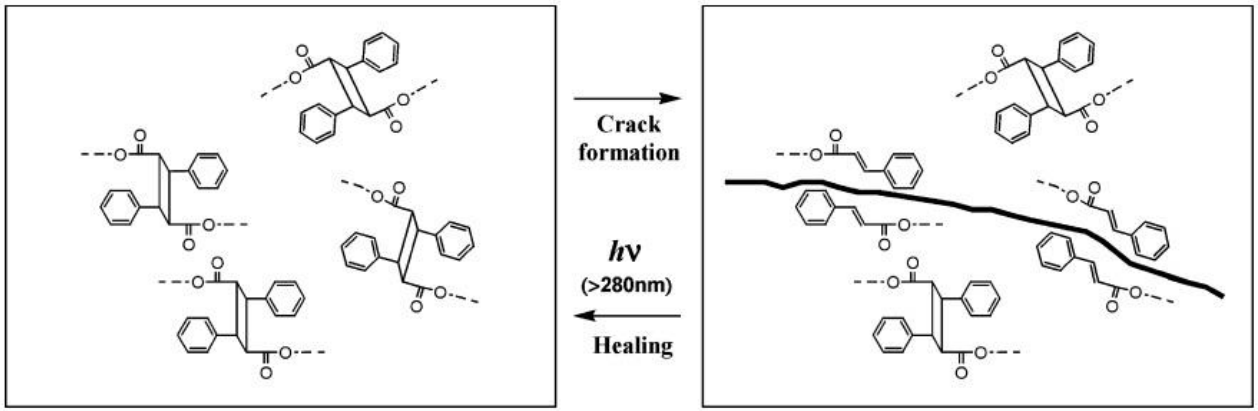
Hue, B. T. B.; Dijkink, J.; Kuiper, S.; Larson, K. K.; Guziec, F. S., Jr.; Goubitz, K.; Fraanje, J.; van Maarseveen, J. H.; Hiemstra, H. // *Org. Biomol. Chem.*, **2003**, *1*, 4364.



(–)-Biyouyanagin A

Biyouyanagin A exhibites significant and selective inhibitory activity against HIV replication in H9 lymphocytes.

K. C. Nicolaou, D. Sarlah, D. M. Shaw // *Angew. Chem. Int. Ed.*, **2007**, *46*, 4708–4711.



1,1,1-tris-(cinnamoyloxymethyl)ethane

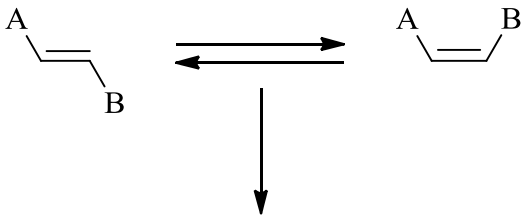
Chung, C.-M.; Roh, Y.-S.; Cho, S.-Y.; Kim, J.-G. Crack healing in polymeric materials via photochemical [2+2] cycloaddition // *Chem. Mater.*, **2004**, *16*, 3982–3984.

Acyclic unsaturated compounds

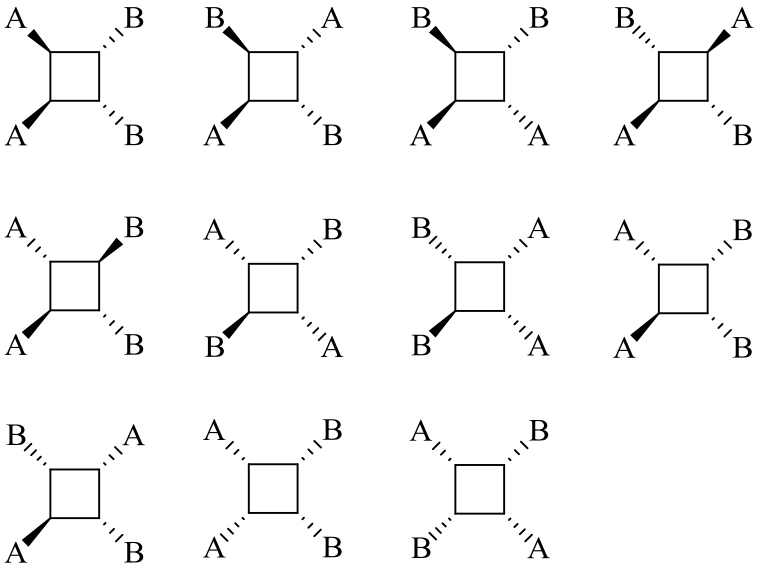
A very low quantum yield because of the short lifetime of the electronically excited state

Lead to a mixture of isomeric cyclobutanes

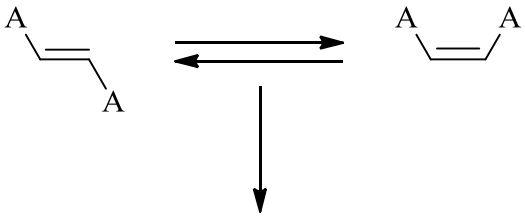
E–*Z* photoisomerization



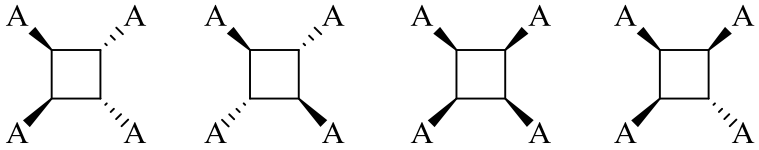
[2+2] photocycloaddition



E–*Z* photoisomerization

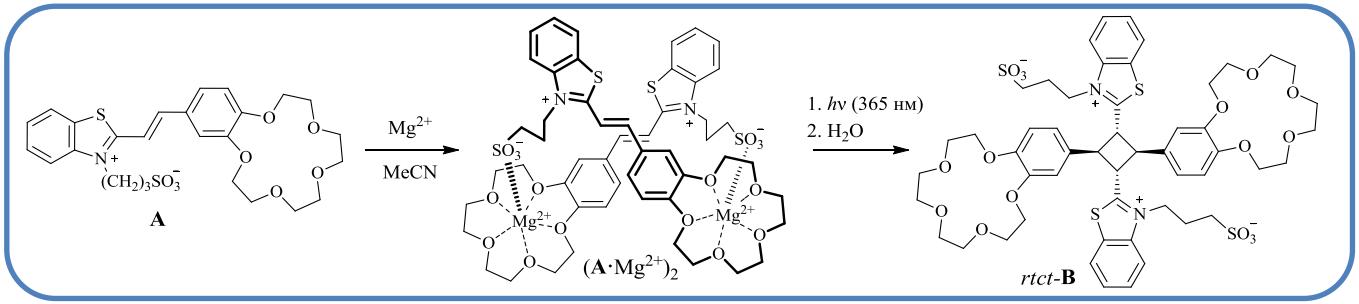


[2+2] photocycloaddition



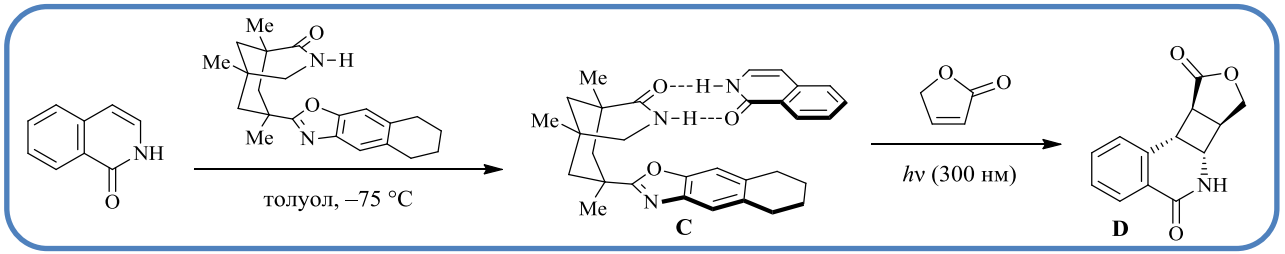
E. N. Ushakov, S. P. Gromov. Supramolecular methods for controlling intermolecular [2+2] photocycloaddition reactions of unsaturated compounds in solutions // *Russ. Chem. Rev.*, **2015**, *84*, 787–802.

Methods for controlling intermolecular [2+2] photocycloaddition reaction



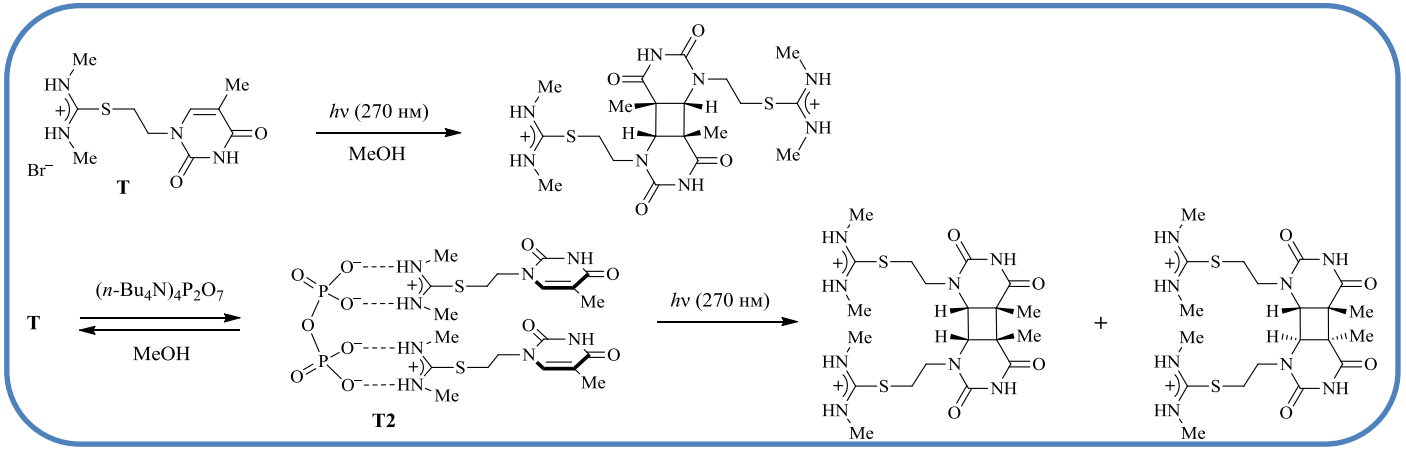
Cation-induced self-assembly

Russ. Chem. Bull., **1993**, *42*, 1385



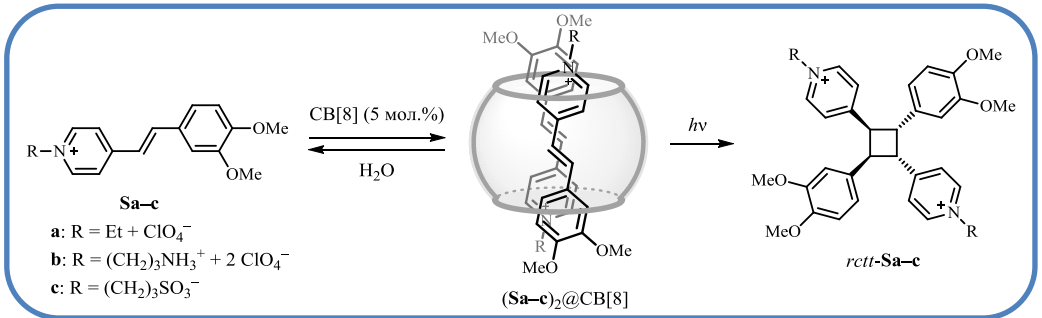
Control by hydrogen bonding

J. Am. Chem. Soc., **2013**, *135*, 14948



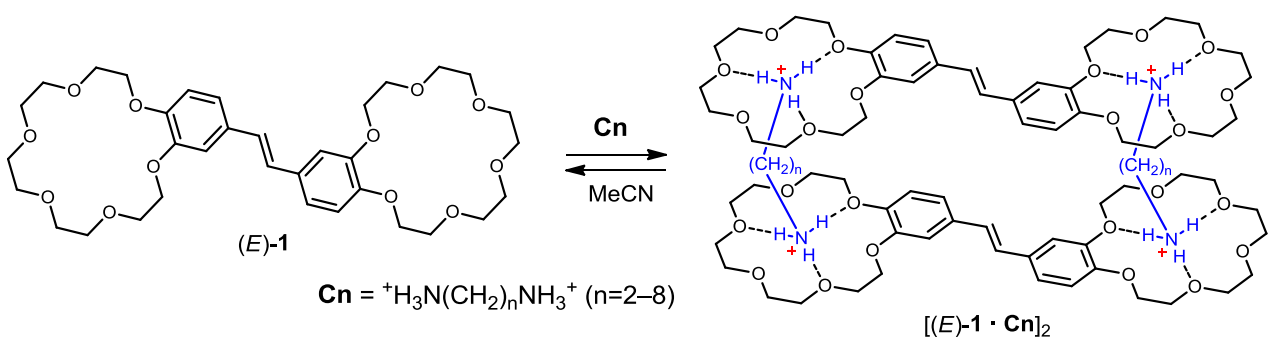
Anion-templated self-assembly

Org. Lett., **2002**, *4*, 4407



Confinement in supramolecular containers

Eur. J. Org. Chem., **2010**, 2587



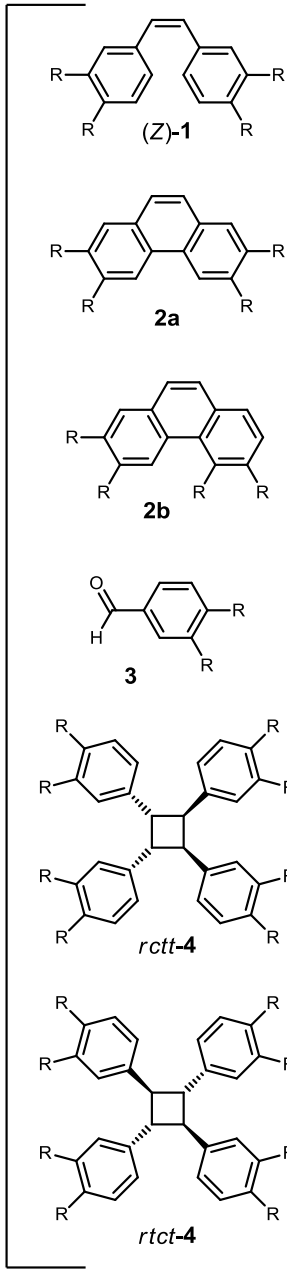


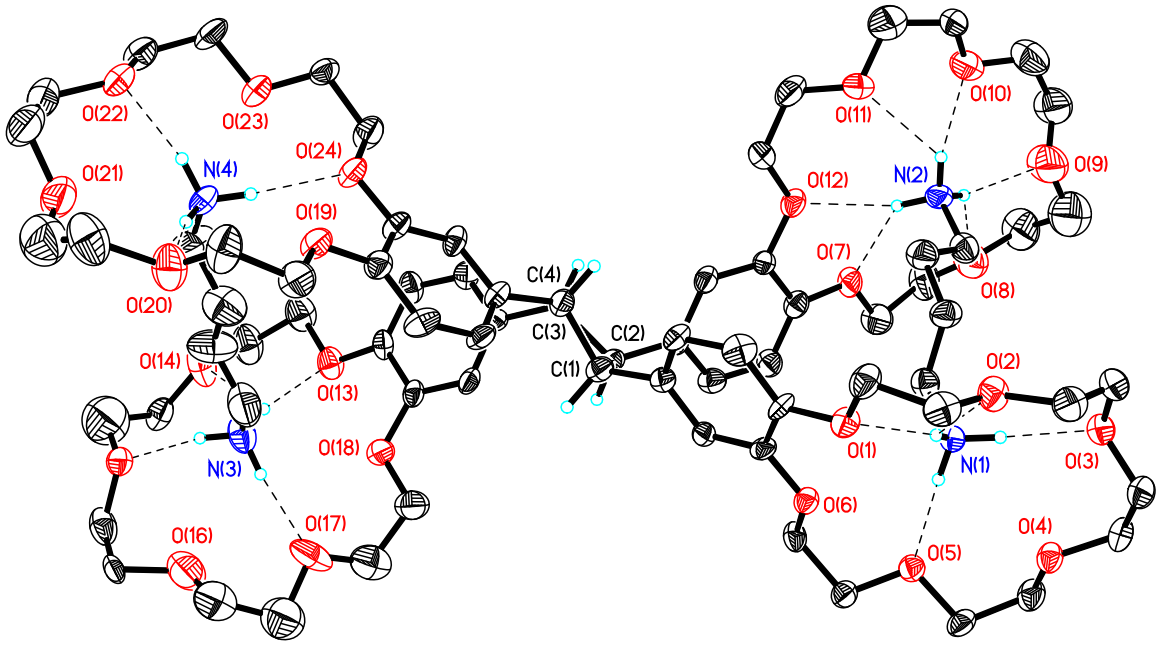
Table. Composition and the ratio of the photolysis products of stilbene (*E*)–**1** solutions in the absence and presence of ethylammonium and alkanediammonium perchlorates.[a]

Salt	Photolyzate composition (mol. %) [b]						
	(*E*)-**1**	(*Z*)-**1**	**2a**	**2b**	**3**	*rctt*-**4**	*rtct*-**4**
–	12	55	18	8	5	2	0
$EtNH_3^+ClO_4^-$	13	76	7	2	2	0	0
C2	0	24	0	0	0	70	6
C3	0	13	0	0	0	83	4
C4	0	19	0	0	1	73	7
C5	1	57	0	0	6	33	3
C6	3	62	0	1	3	28	3
C7	4	72	2	3	6	11	2
C8	3	78	1	3	4	7	4
C9	5	66	20	5	4	0	0
C10	8	53	31	6	2	0	0
C12	29	40	24	3	4	0	0

[a] MeCN, $C_1 = 1 \cdot 10^{-3}$ mol L^{-1}, 1.1 equivalents of salt **Cn** or 2.2 equivalents of $EtNH_3^+ClO_4^-$.
[b] According to the ^1H NMR spectral data.

S. P. Gromov, A. I. Vedernikov, L. G. Kuz'mina, N. A. Lobova, S. S. Basok, Yu. A. Strelenko, M. V. Alfimov // *Russ. Chem. Bull.*, **2009**, *58*, 108–114.

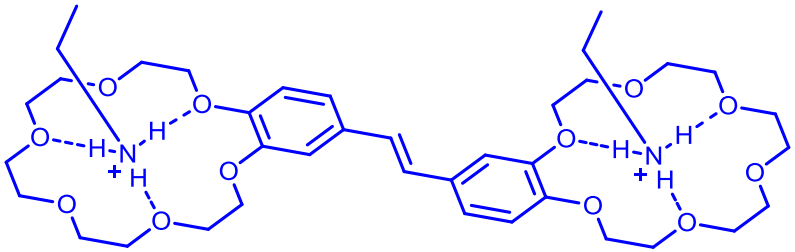
X-ray crystallography



Structure of the main components of complex [*rctt*-**4**•(**C4**)$_2$] shown in thermal ellipsoids with the 20% probability. The most part of the hydrogen atoms and disordering of the fragments of the macrocycles are omitted. Hydrogen bonds are shown by dashed lines.

S. P. Gromov, A. I. Vedernikov, L. G. Kuz'mina, N. A. Lobova, S. S. Basok, Yu. A. Strelenko, M. V. Alfimov // *Russ. Chem. Bull.*, **2009**, *58*, 108–114.

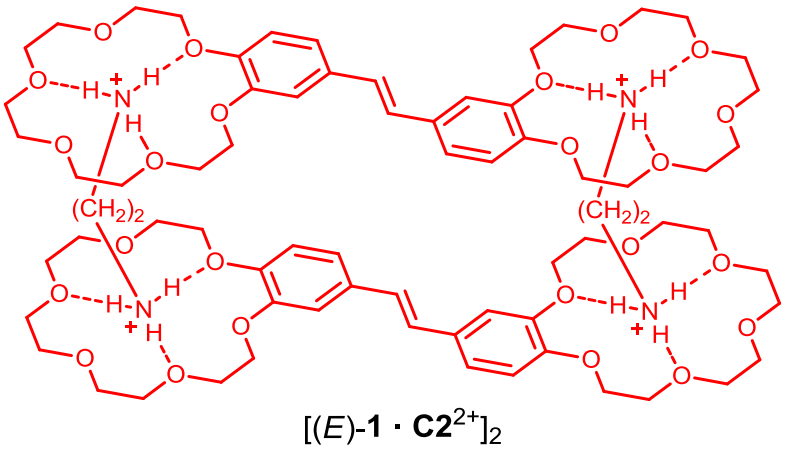
Spectrophotometric study



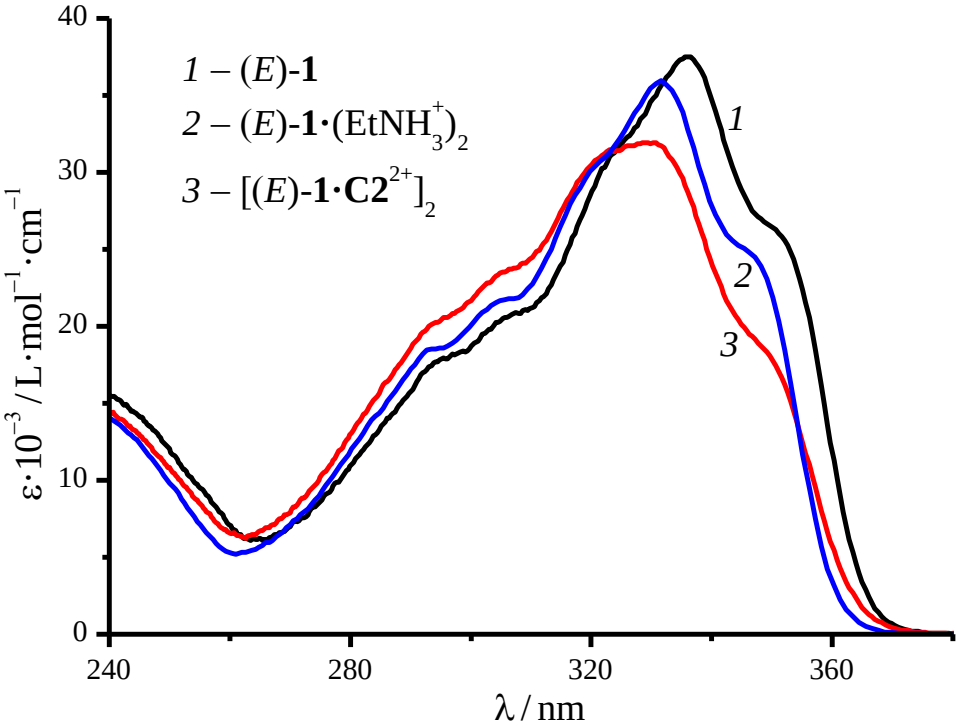
(*E*)-**1**·[$EtNH_3^+$]$_2$

$$(E)\text{-}\mathbf{1} + \mathbf{Cn}^{2+} \overset{K_{1:1}}{\rightleftharpoons} (E)\text{-}\mathbf{1}\cdot\mathbf{Cn}^{2+}$$

$$(E)\text{-}\mathbf{1}\cdot\mathbf{Cn}^{2+} + (E)\text{-}\mathbf{1}\cdot\mathbf{Cn}^{2+} \overset{K_{2:2}}{\rightleftharpoons} [(E)\text{-}\mathbf{1}\cdot\mathbf{Cn}^{2+}]_2$$



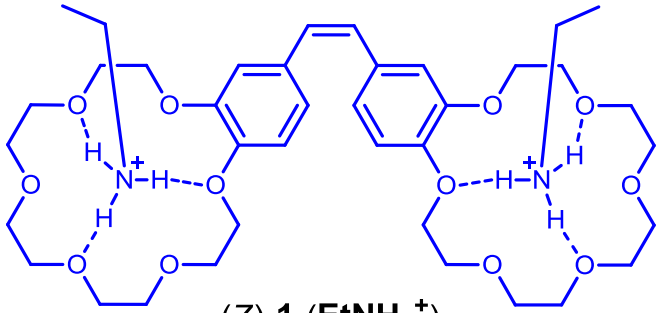
[(*E*)-**1** · **C2**$^{2+}$]$_2$



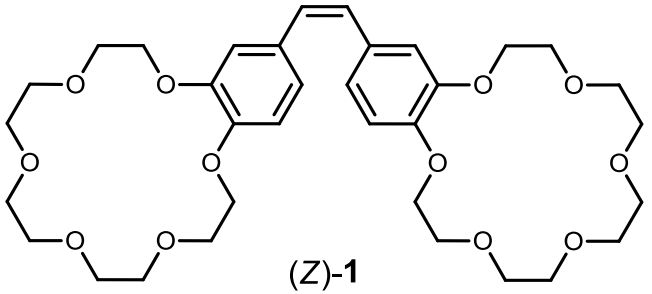
Absorption spectra of (*E*)-**1** (*1*), (*E*)-**1**·($EtNH_3^+$)$_2$ (*2*), [(*E*)-**1**·**C2**$^{2+}$]$_2$ (*3*) in MeCN.

E.N. Ushakov, T.P. Martyanov, A.I. Vedernikov, O.V. Pikalov, A.A. Efremova, L.G. Kuz'mina, J.A.K. Howard, M.V. Alfimov, S.P. Gromov // *J. Photochem. Photobiol. A: Chem.*, **2017**, *340*, 80–87.

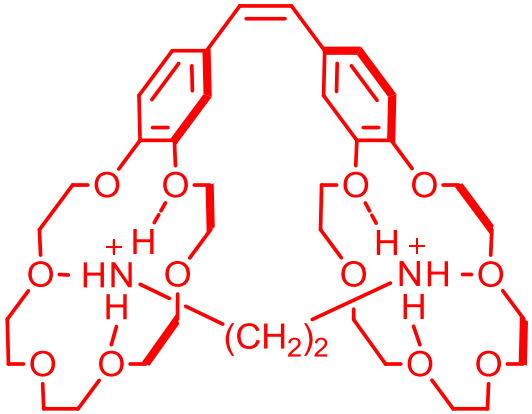
Spectrophotometric study



(*Z*)-**1**·(**EtNH$_3^+$**)$_2$

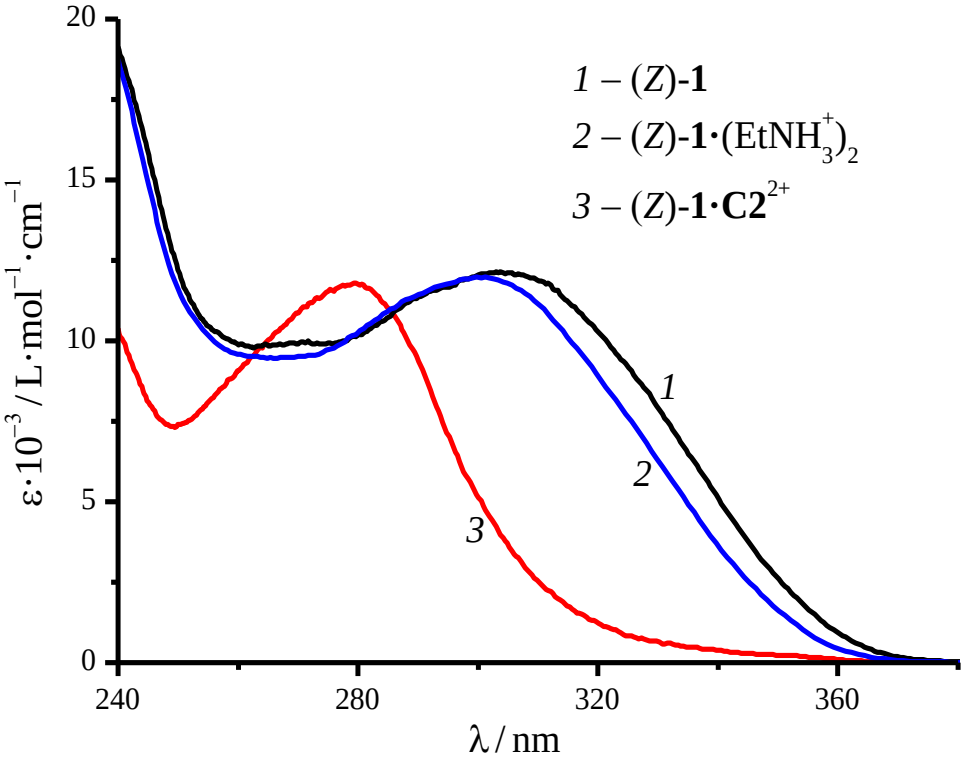


(*Z*)-**1**



(*Z*)-**1**·**C2**$^{2+}$

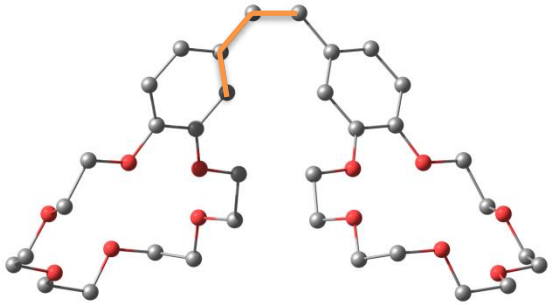
log*K* > 7



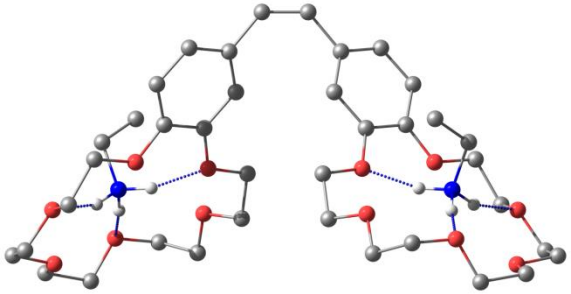
Absorption spectra of (*Z*)-**1** (*1*), (*Z*)-**1**·(EtNH$_3^+$)$_2$ (*2*), (*Z*)-**1**·**C2**$^{2+}$ (*3*) in MeCN.

E.N. Ushakov, T.P. Martyanov, A.I. Vedernikov, O.V. Pikalov, A.A. Efremova, L.G. Kuz'mina, J.A.K. Howard, M.V. Alfimov, S.P. Gromov // *J. Photochem. Photobiol. A: Chem.*, **2017**, *340*, 80–87.

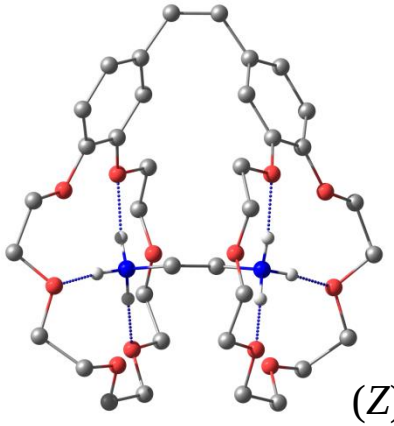
Quantum chemical calculations



(*Z*)-**1**



(*Z*)-**1**·$(EtNH_3^+)_2$



(*Z*)-**1**·**C2**$^{2+}$

Torsion angle	34.0°	34.3°	46.6°

Most probable conformations of stilbene (*Z*)-**1**, complex (*Z*)-**1**·$(EtNH_3^+)_2$, and complex (*Z*)-**1**·**C2**$^{2+}$ in MeCN, as calculated by the M06-2X/6-31G(d)/SMD method; hydrogen atoms are not shown, except those of the ammonium groups.

Table. Experimental and TDDFT calculated parameters of the S_0–S_1 electronic transition of stilbene (*Z*)-**1** and its complexes with cations.[a]

Compound	λ_{max}	$\Delta\lambda_{max}$	ε_{max}	λ_{calc}[b]	$\Delta\lambda_{calc}$	f_{calc}
(*Z*)-**1**	304		12600	304		0.70
(*Z*)-**1**·$(EtNH_3^+)_2$	301	3	12400	300.5	3.5	0.69
(*Z*)-**1**·$(Ba^{2+})_2$	300	4	12500			
(*Z*)-**1**·**C2**$^{2+}$	280	24	12200	274.5	29.5	0.44

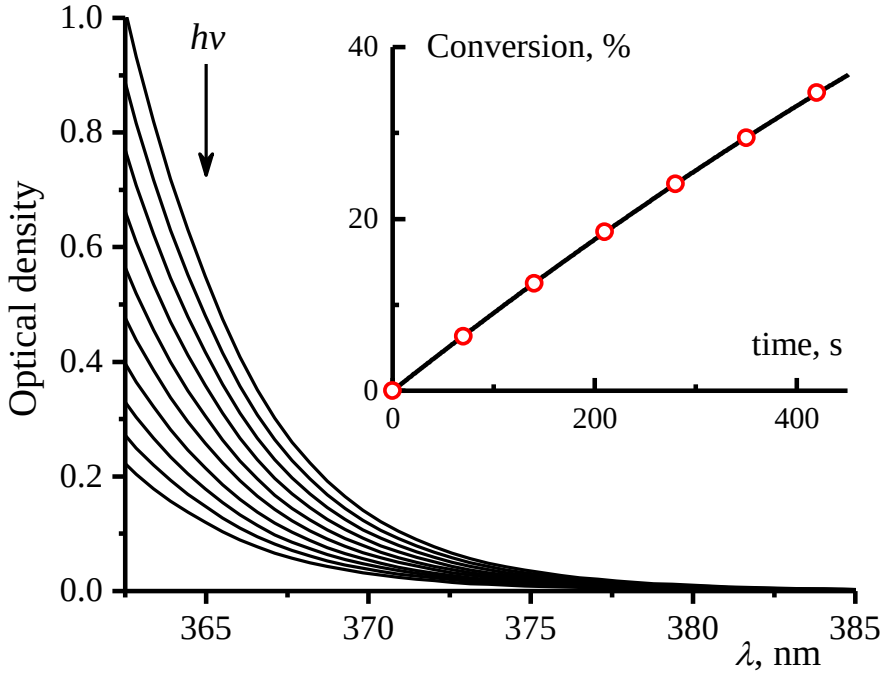
[a] In MeCN, λ_{max} (nm) is the position of the absorption maximum, ε_{max} (M^{-1} cm^{-1}) is the molar absorptivity at λ_{max}, $\Delta\lambda_{max}$ = λ_{max}(ligand) – λ_{max}(complex), λ_{calc} (nm) is the calculated wavelength of the S_0–S_1 transition, f_{calc} is the oscillator strength, $\Delta\lambda_{cal}$ = λ_{cal}(ligand) – λ_{cal}(complex).

[b] The calculated S_0–S_1 transition energies were corrected by a factor of 0.978.

Photochemical properties

1) The total quantum yield for the conversion of (*E*)-**1** (φ_{tot})

$$\varphi_{tot} = \varphi_{PCA} + \varphi_{E\text{-}Z}$$



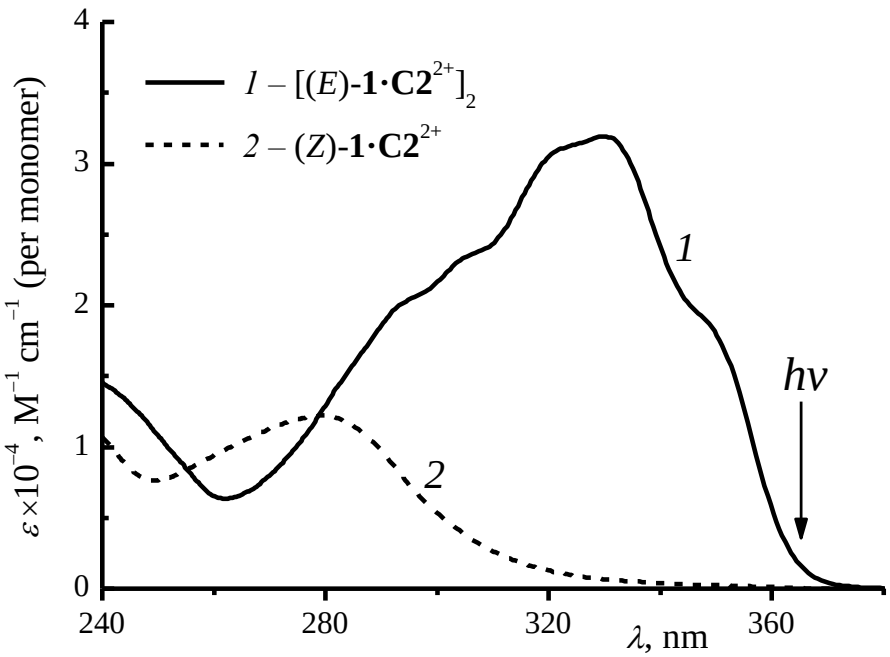
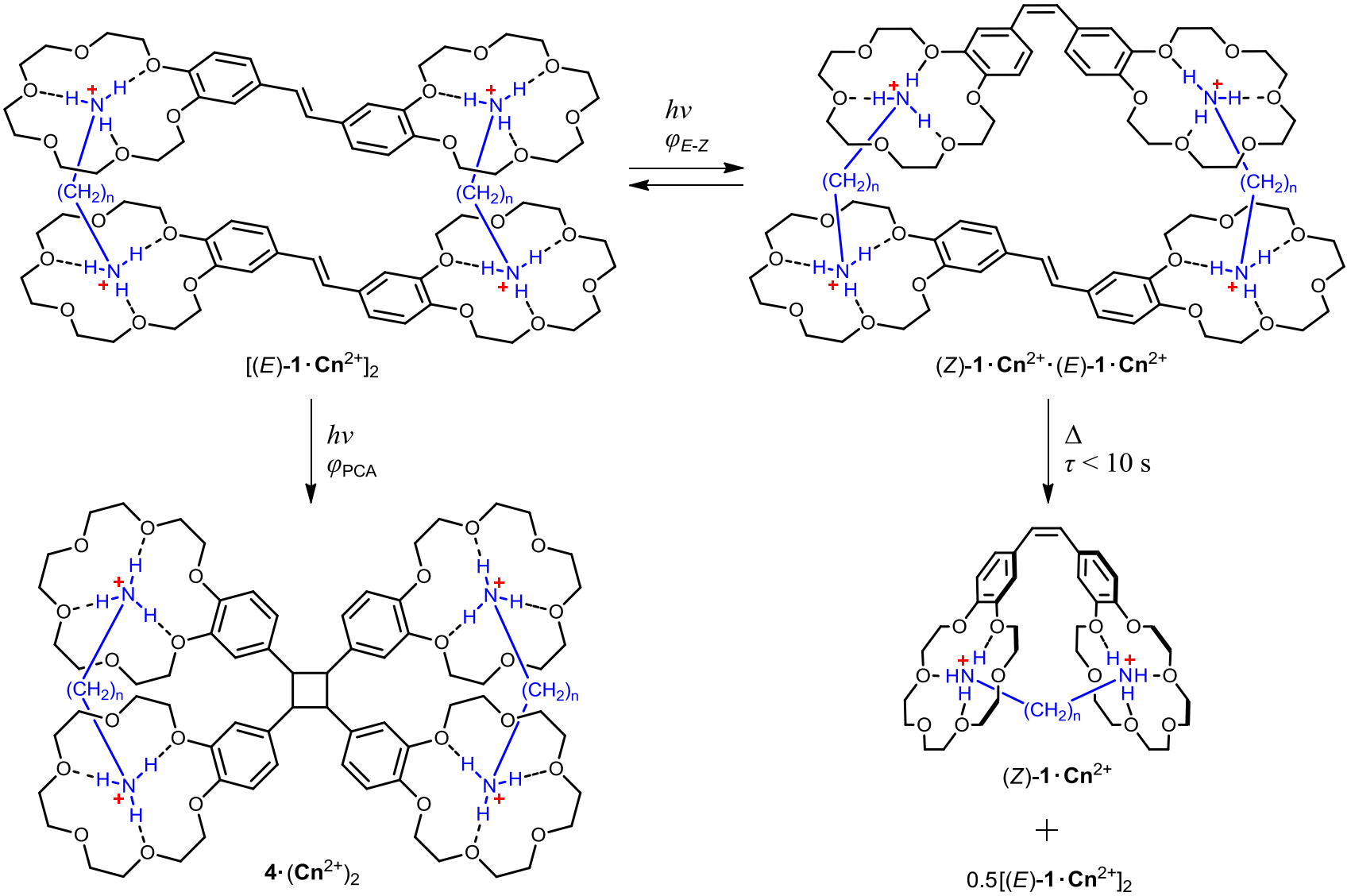


Figure. Spectrophotometric data on the stationary photolysis of complex [(*E*)-**1**·**C2**$^{2+}$]$_2$ in MeCN with 365 nm light: (*E*)-**1** 3.4×10^{-4} M, **C2**$^{2+}$2ClO_4^- 5.4×10^{-4} M, ionic strength 0.01 M ($Bu_4N^+ClO_4^-$), 1 cm cell, light intensity 1.3×10^{-9} mol cm^{-2} s^{-1}, irradiation time varied from 0 to 20 min. Inset: percentage of conversion of (*E*)-**1** as a function of the irradiation time; the solid curve is from global fitting to a kinetic equation for irreversible unimolecular photoreactions.

Photochemical and thermal processes occurring during stationary irradiation of complexes $[(E)\text{-}\mathbf{1}\cdot\mathbf{Cn}^{2+}]_2$, n = 2–6, in MeCN with 365 nm light.



2) The concentration ratio of the two photoproducts for different percentages of conversion of (*E*)-**1**

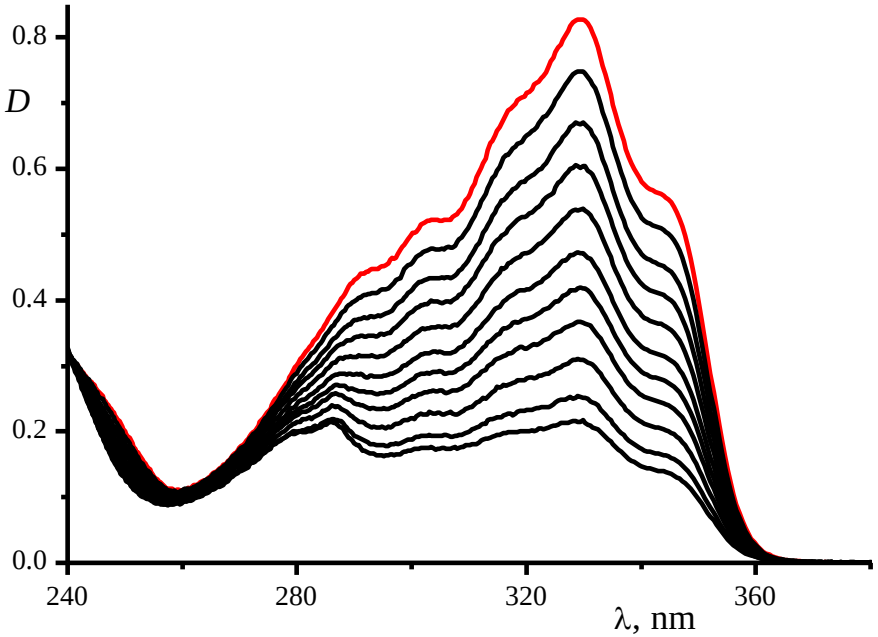


Figure. *Black curves:* Absorption spectra of the photolysate samples (aliquots) taken after stationary irradiation of complex $[(E)\text{-}\mathbf{1}\cdot\mathbf{C3}^{2+}]_2$ (3.6×10^{-4} M, ionic strength 0.01 M) in MeCN with 365 nm light and then diluted by a MeCN solution of $Ba(ClO_4)_2$ (1×10^{-3} M); the irradiation intervals are 120–140 s; the resulting solutions contain three light-absorbing components, *viz.*, complexes $(E)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$, $(Z)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$, and $\mathbf{4}\cdot(Ba^{2+})_4$. *Red curve:* Absorption spectrum of $(E)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$.

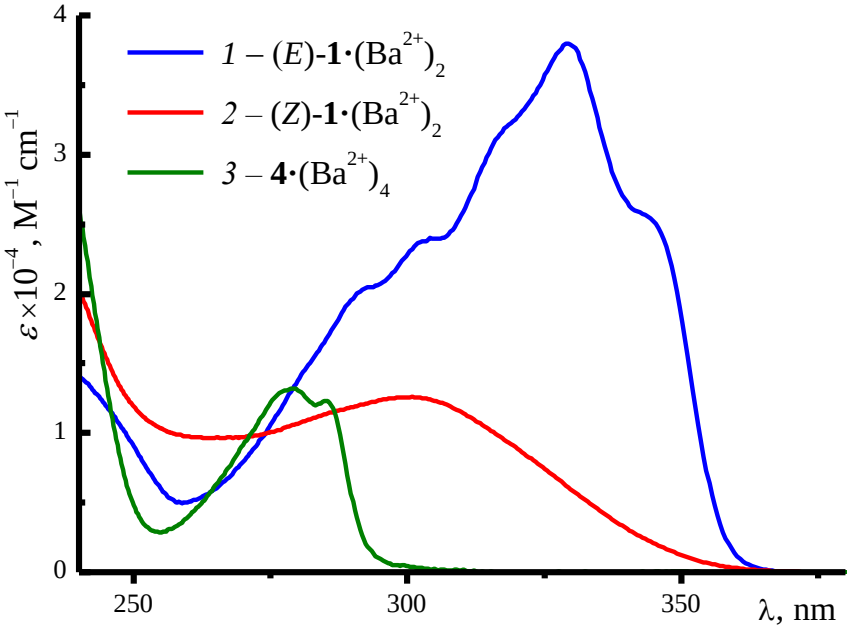


Figure. Absorption spectra of complexes $(E)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$ (*1*), $(Z)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$ (*2*), and $\mathbf{4}\cdot(Ba^{2+})_4$ (*3*) in MeCN.

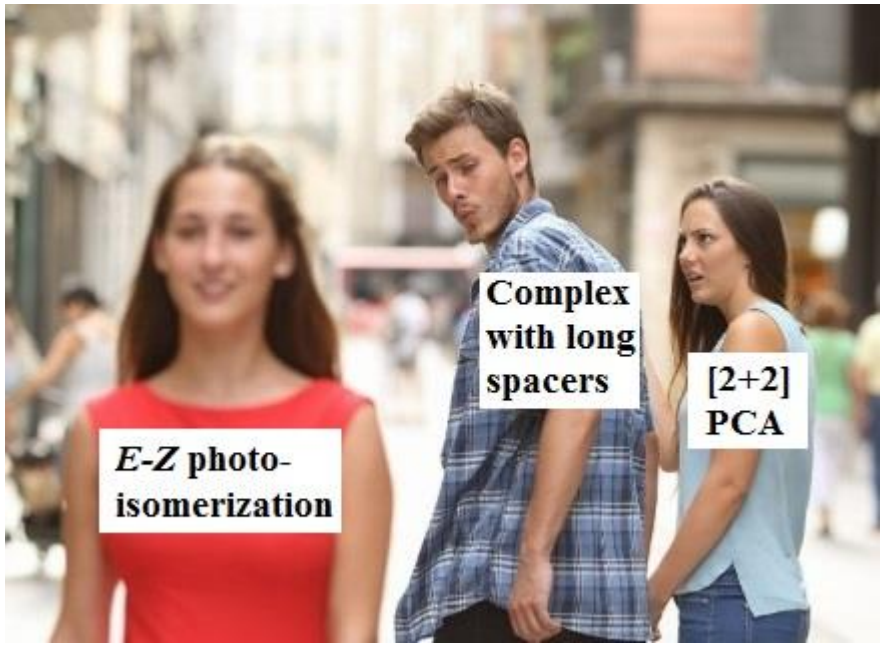
$$R_C = [\mathbf{4}]/[(Z)\text{-}\mathbf{1}] = \varphi_{PCA}/\varphi_{E\text{-}Z}$$

$$D(\lambda) = \varepsilon_E(\lambda)[E]l + \{\varepsilon_Z(\lambda) + R_C\varepsilon_{cb}(\lambda)\}[Z]l$$

where $\varepsilon_E(\lambda)$, $\varepsilon_Z(\lambda)$, and $\varepsilon_{cb}(\lambda)$ are the known molar absorptivities of complexes $(E)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$, $(Z)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$, and $\mathbf{4}\cdot(Ba^{2+})_4$, respectively; $[E]$ and $[Z]$ are the concentrations of $(E)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$ and $(Z)\text{-}\mathbf{1}\cdot(Ba^{2+})_2$;

Table. Quantum yields of the PCA and *E–Z* photoisomerization reactions in complexes $[(E)\text{-}\mathbf{1}\cdot\mathbf{Cn}^{2+}]_2$.[a]

Compound	φ_{tot}	φ_{PCA}	φ_{E-Z}
(*E*)-**1**			0.24
$[(E)\text{-}\mathbf{1}\cdot\mathbf{C2}^{2+}]_2$	0.33	0.27	0.06
$[(E)\text{-}\mathbf{1}\cdot\mathbf{C3}^{2+}]_2$	0.28	0.21	0.07
$[(E)\text{-}\mathbf{1}\cdot\mathbf{C4}^{2+}]_2$	0.23	0.13	0.10
$[(E)\text{-}\mathbf{1}\cdot\mathbf{C5}^{2+}]_2$	0.12	0.02	0.10
$[(E)\text{-}\mathbf{1}\cdot\mathbf{C6}^{2+}]_2$	0.14	0.02	0.12
(*E*)-**1**$\cdot(EtNH_3^+)_2$			0.26



[a] MeCN solution, irradiation with 365 nm light, the quantum yields are measured to within about ±20%.

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Conclusions

1) Generally, the efficiency of photocycloaddition in pseudocyclic structures in solution is dependent not only on the spacing and orientation of the reacting bonds but also on other factors, such as steric strain in the pseudocycle. In the case of 2:2 complexes of (*E*)-bis(18-crown-6)stilbene, the spacing of the two olefinic bonds is likely to be the main factor affecting the photocycloaddition efficiency.

2) It was shown for the first time that the *Z* isomer of bis(18-crown-6)stilbene is able to form pseudocyclic 1:1 complexes even with very short alkanediammonium ions, such as 1,2-ethanediammonium ion. The peculiar spectral properties of these complexes arise from large torsion angles around the ethylene–benzocrown single bonds.

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O
Oxygen
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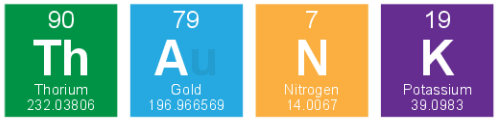
86
Rn
Radon
[222]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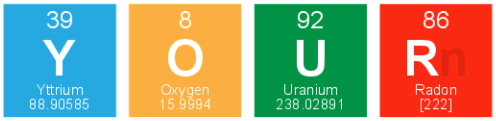
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U
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Rn
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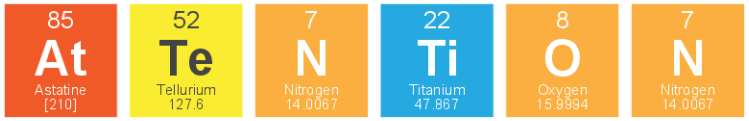
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