



РОССИЙСКАЯ АКАДЕМИЯ НАУК  
ЦЕНТР ФОТОХИМИИ

XIII International Conference  
“Solvation and complex  
formation in solutions”



## **Photoactive supramolecular devices and machines based on macrocyclic and unsaturated compounds**

**Sergey P. Gromov,**

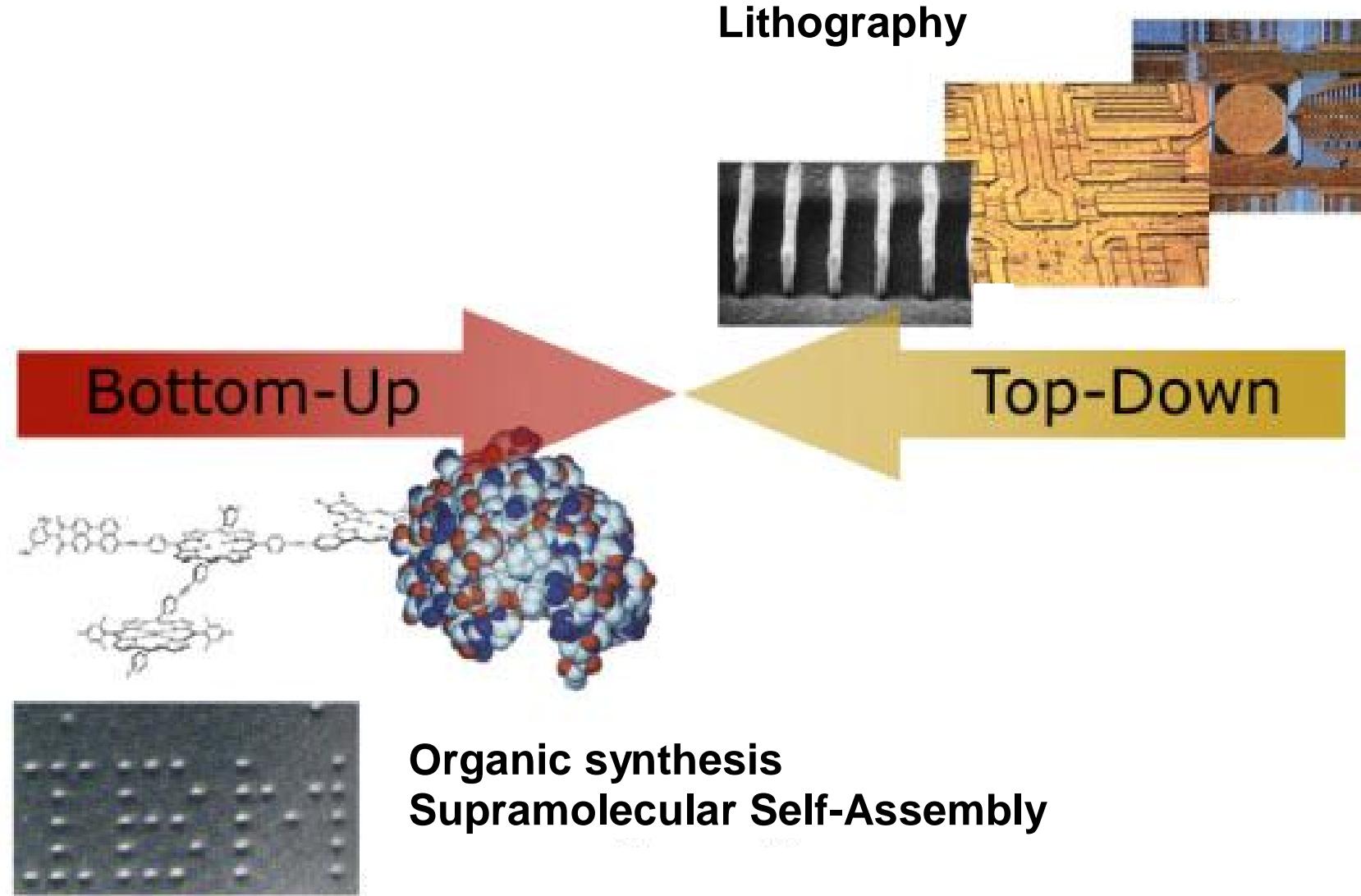
A. I. Vedernikov, E. N. Ushakov, N. Kh. Petrov,

A. K. Chibisov, M. V. Alfimov

<http://suprachem.photonics.ru>

**NANOTECHNOLOGY “BOTTOM-UP”**

# STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES



# SUPRAMOLECULAR DEVICES AND MACHINES

Supramolecular devices are structurally organized and functionally integrated chemical systems.

Systems that function as a result of mechanical motion of components relative to each other are called supramolecular machines.

J.-M. Lehn

*They can be used:*

“to design machines for energy and motion generation, conversion, and transmission at nanolevels, to devise a nanotool for the monitoring and diagnostics of nanoquantities of materials and substances.

Critical technologies of the RF

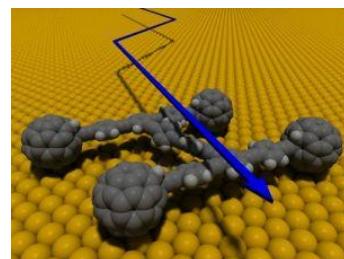
# Means for control of supramolecular devices and machines

§ **Photoswitching** -  $h\nu$

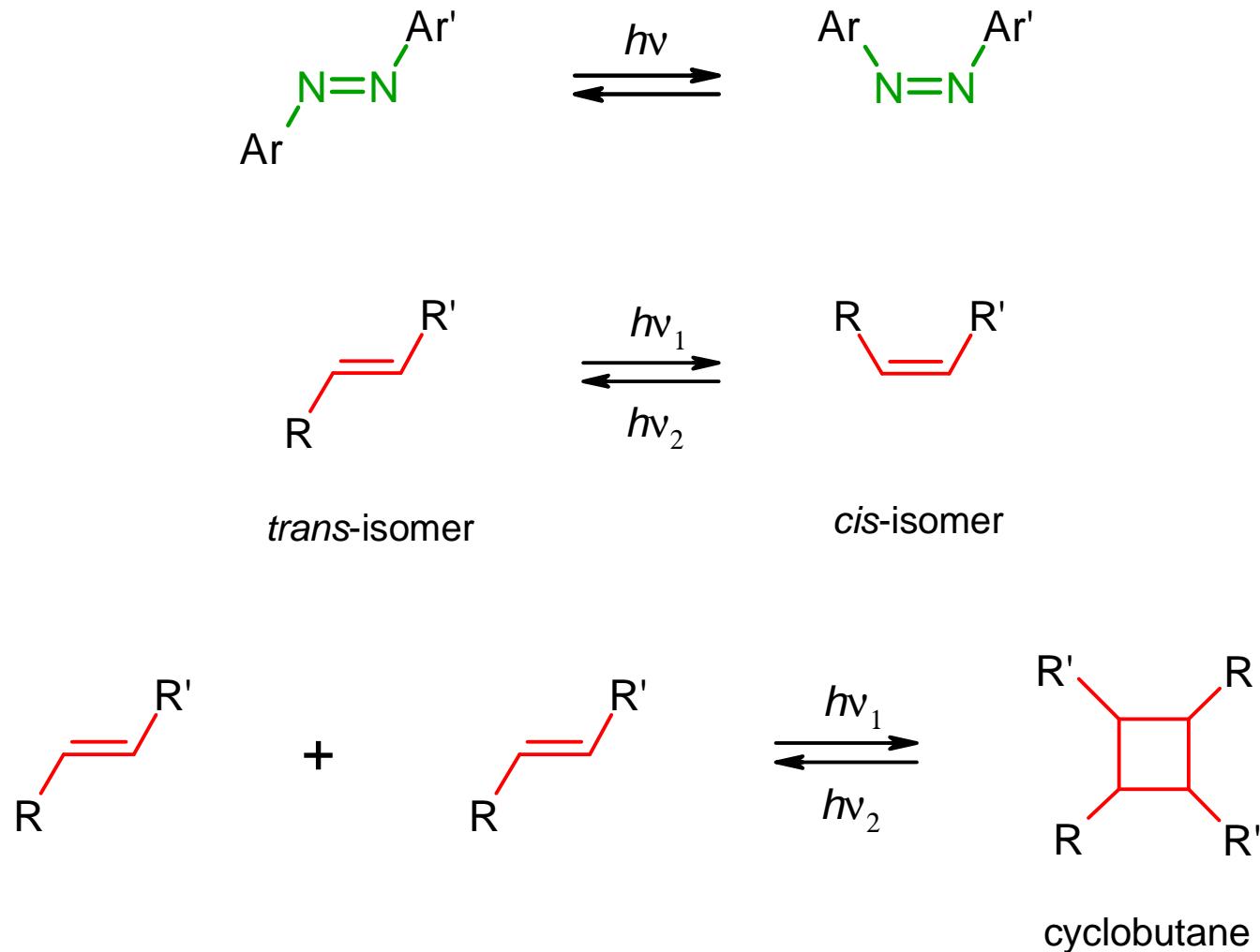
§ **Electrochemical switching** -  $e^-$

§ **Chemical switching** -  $H^+, M^{n+}$

§ **Thermal switching** - D



# PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS

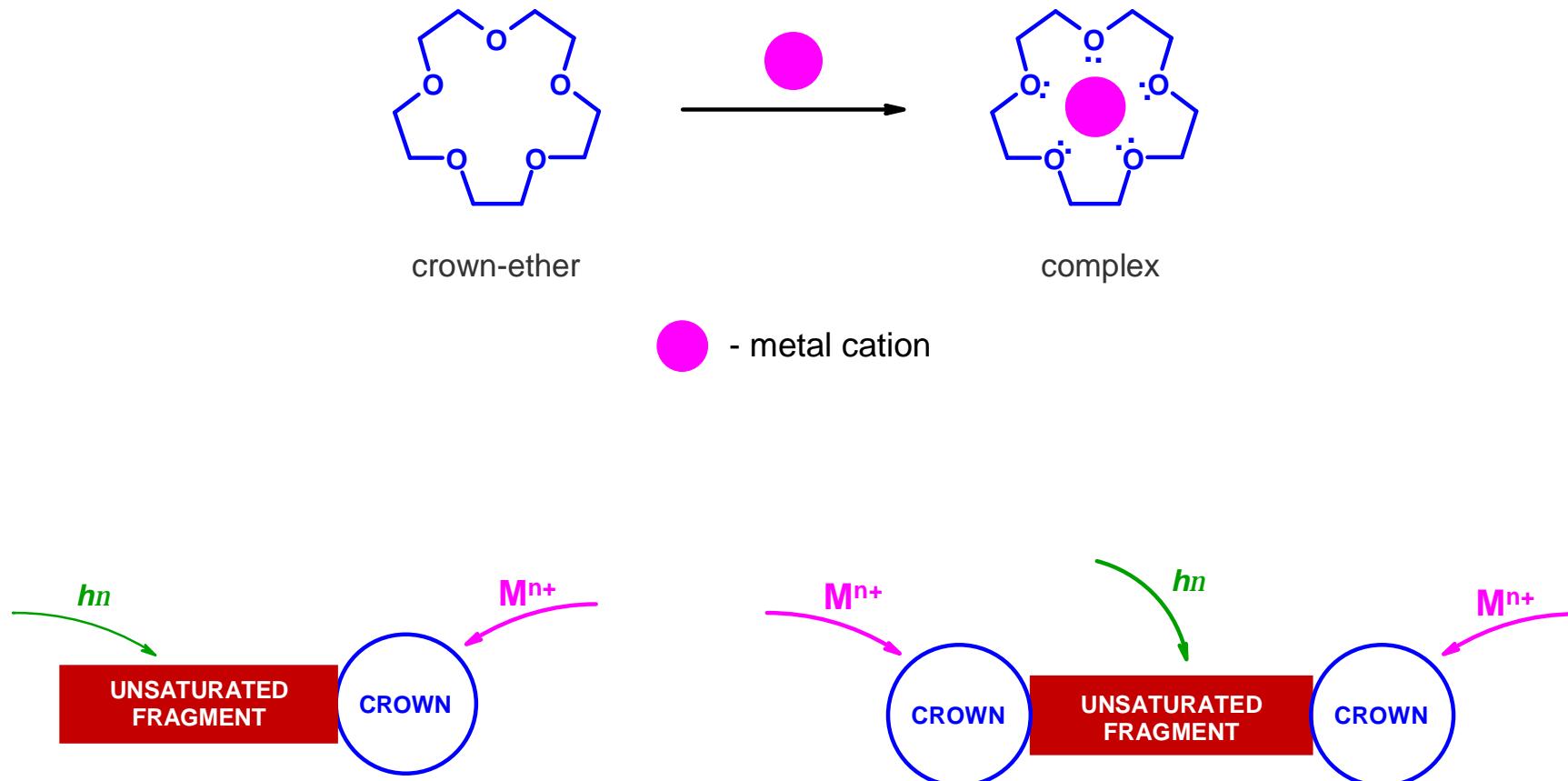


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review);

Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

# PHOTOSWITCHABLE SUPRAMOLECULAR DEVICES BASED ON UNSATURATED AND CROWN COMPOUNDS

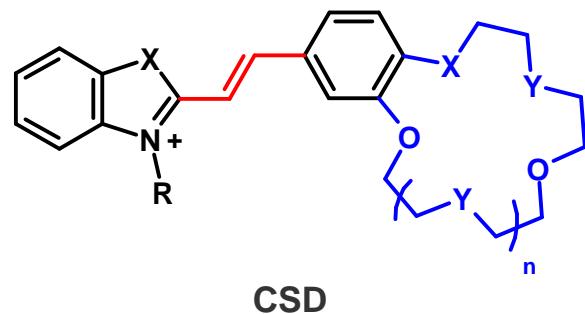


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

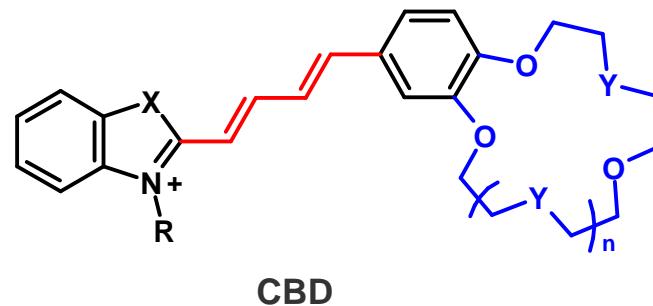
Ushakov E. N., Alfimov M. V., Gromov S. P. *Russ. Chem. Rev.* **2008**, 77, 39 (review);

Alfimov M. V., Fedorova O. A., Gromov S. P. *J. Photochem. Photobiol., A* **2003**, 158, 183 (review).

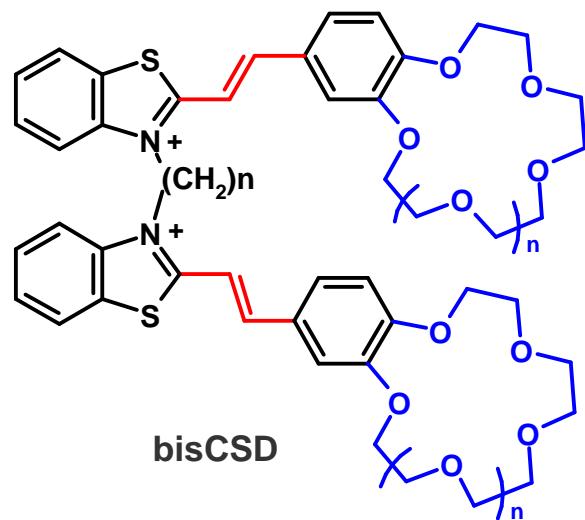
# *Crown-containing unsaturated compounds*



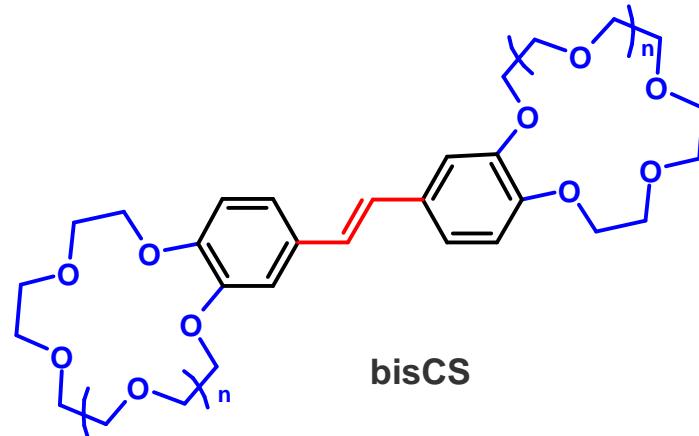
CSD



CBD



bisCSD

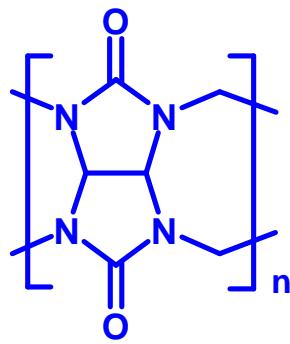
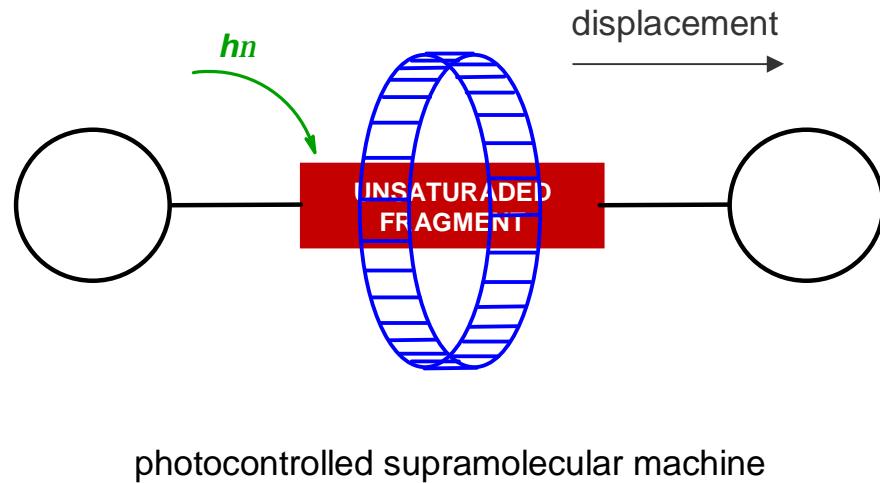


bisCS

$n = 1, 2$

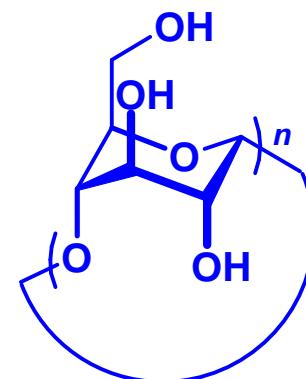
Gromov S. P., Alfimov M. V. *Russ. Chem. Bull.* **1997**, *46*, 611 (review);  
Gromov S. P. *Russ. Chem. Bull.* **2008**, *57*, 1299 (review).

# Photocontrolled supramolecular machines based on unsaturated compounds, cucurbiturils and cyclodextrins



cucurbiturils

$n = 6-8$



cyclodextrins

Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

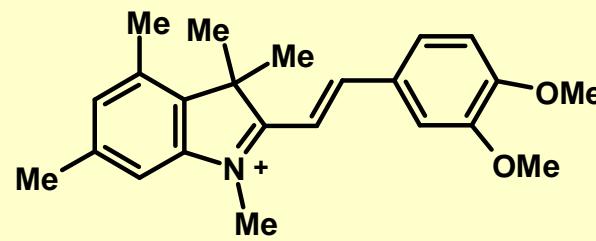
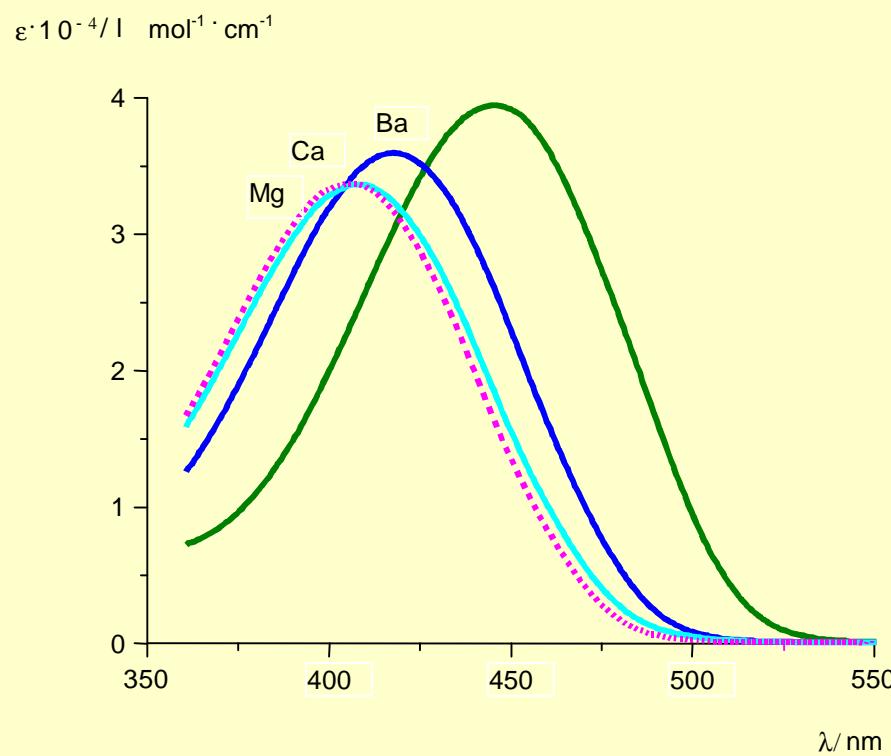
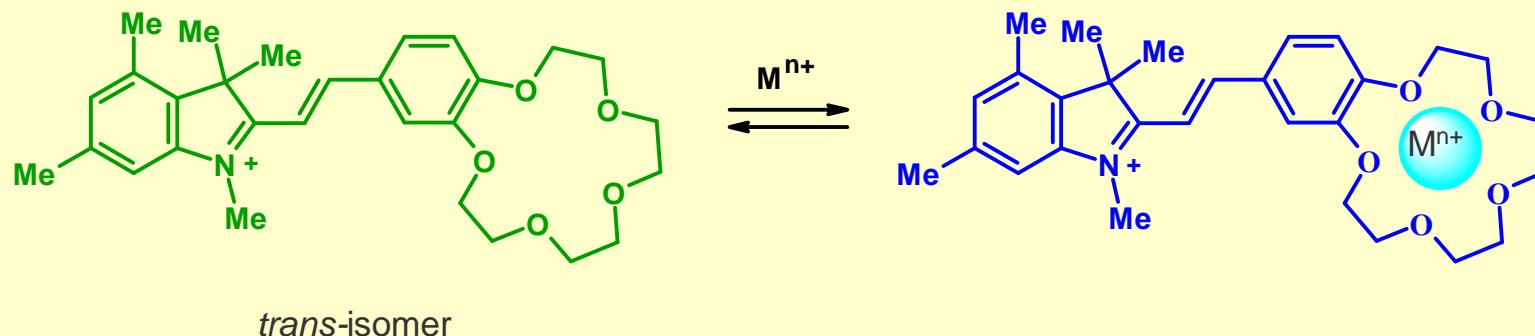
Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review)

Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

**Self-assembly  
of photoswitchable supramolecular devices  
with participation of metal cations**

**Part I**

# Complex formation

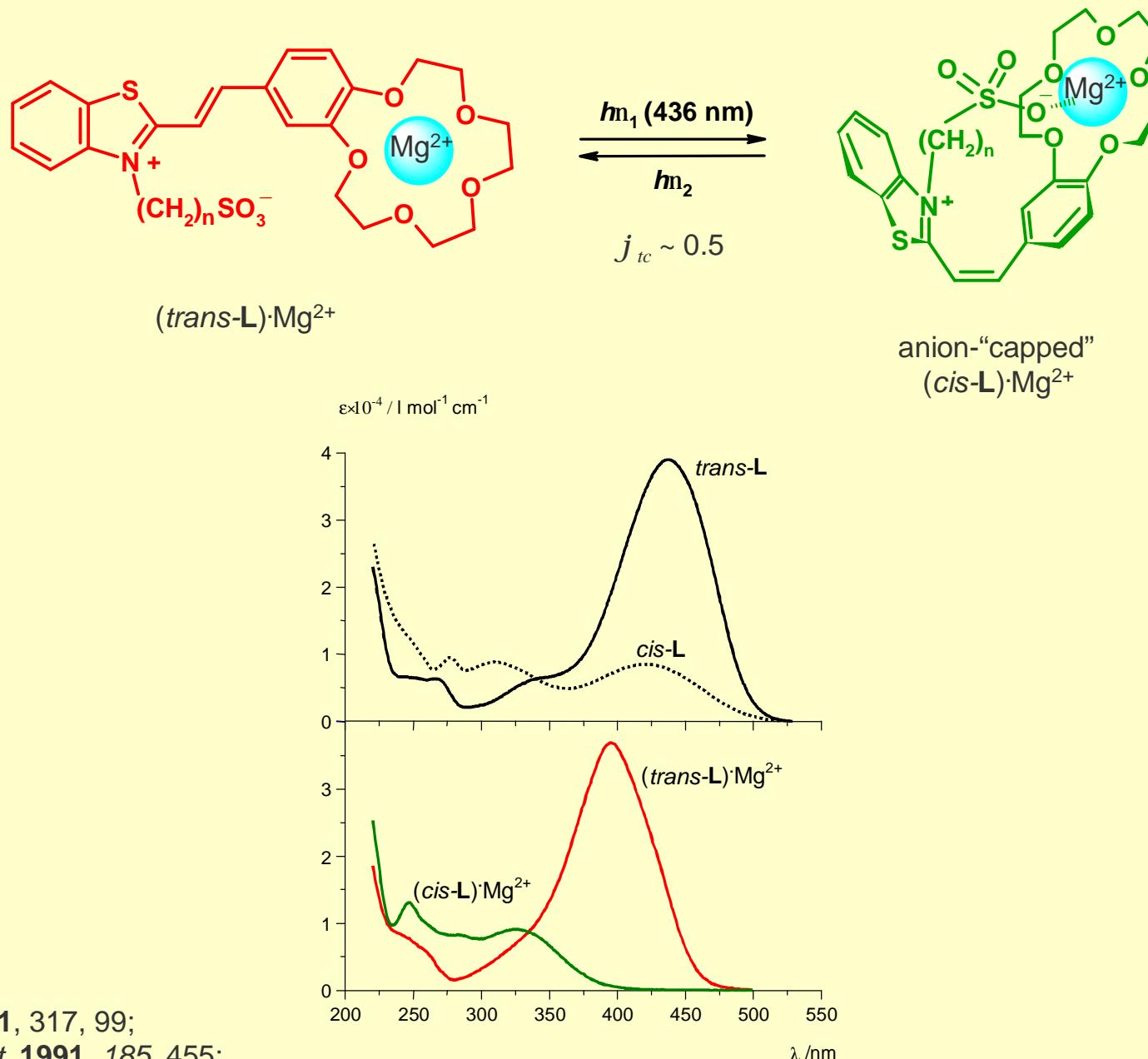


Dokl. Chem. 1990, 314, 279;

Ushakov E. N., Gromov S. P. et al. *Macrocycles*. 2010, 3, 189 (review)

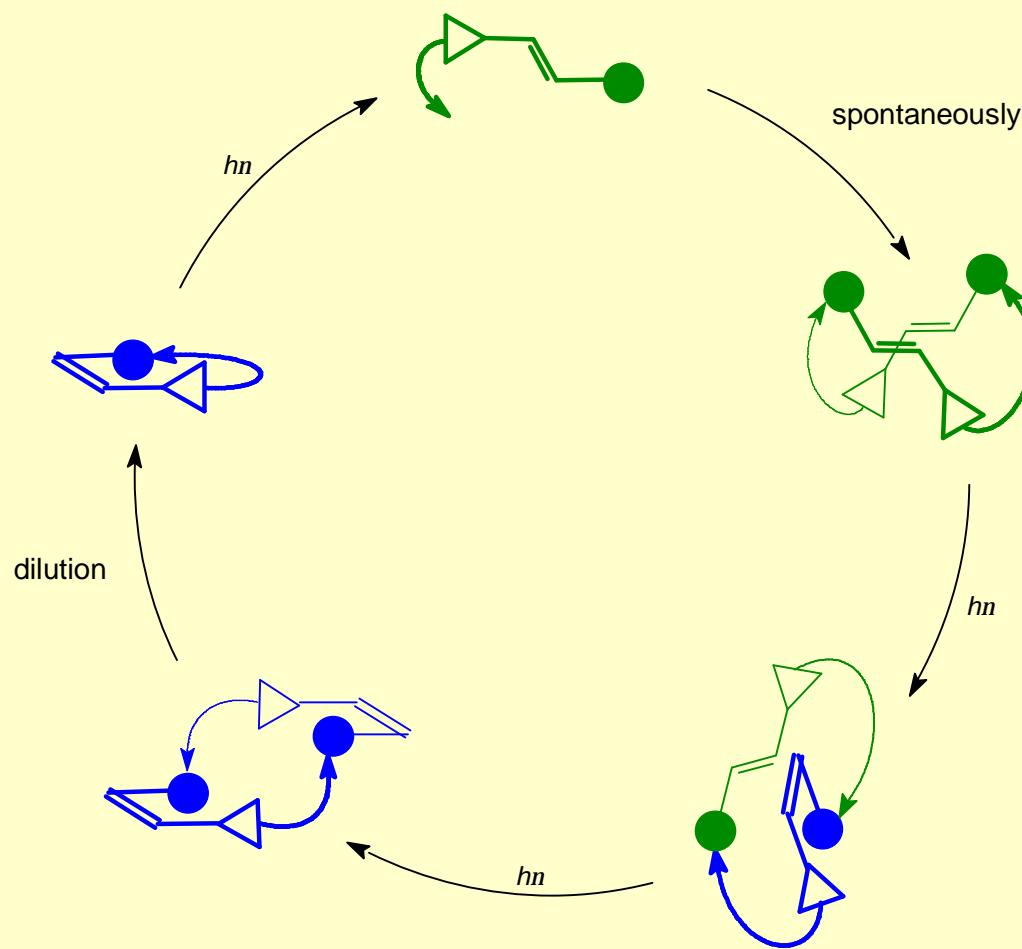
J. Org. Chem. 2013, 78, 9834.

# Photoswitchable supramolecular devices



Dokl. Chem. 1991, 317, 99;  
Chem. Phys. Lett. 1991, 185, 455;  
J. Am. Chem. Soc. 1992, 114, 6381;  
J. Am. Chem. Soc. 1999, 121, 4992.

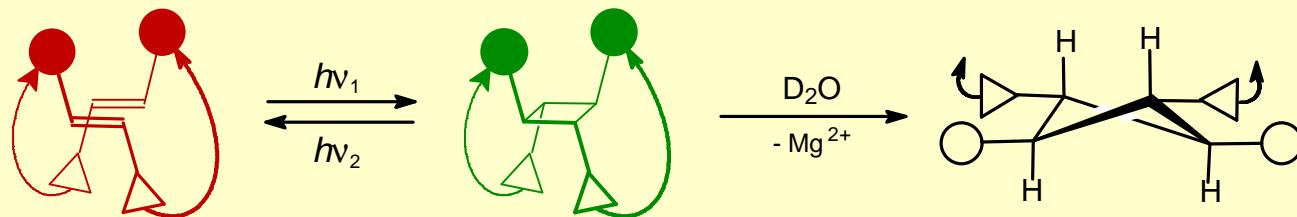
# Photocycle of crown-containing styryl dyes



● - is the benzocrown compounds moiety with  $M^{2+}$  ( $Mg$ ,  $Ca$ ,  $Hg$ ,  $Pb$ );

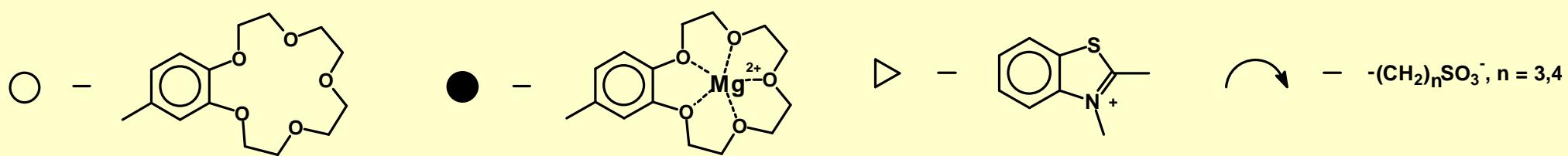
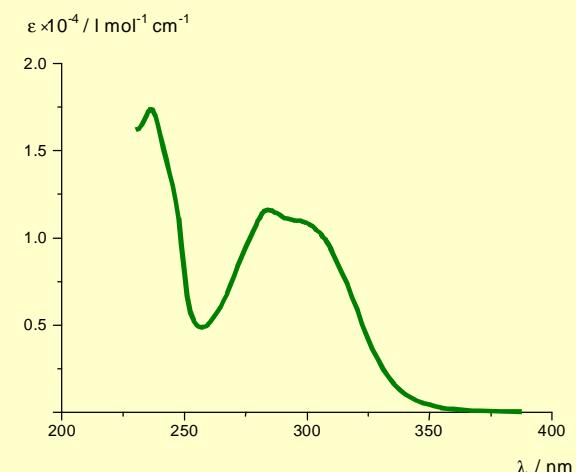
▷ - is the benzothiazolium moiety; ↗ -  $(CH_2)_nSO_3^-$

# Photoswitchable supramolecular devices



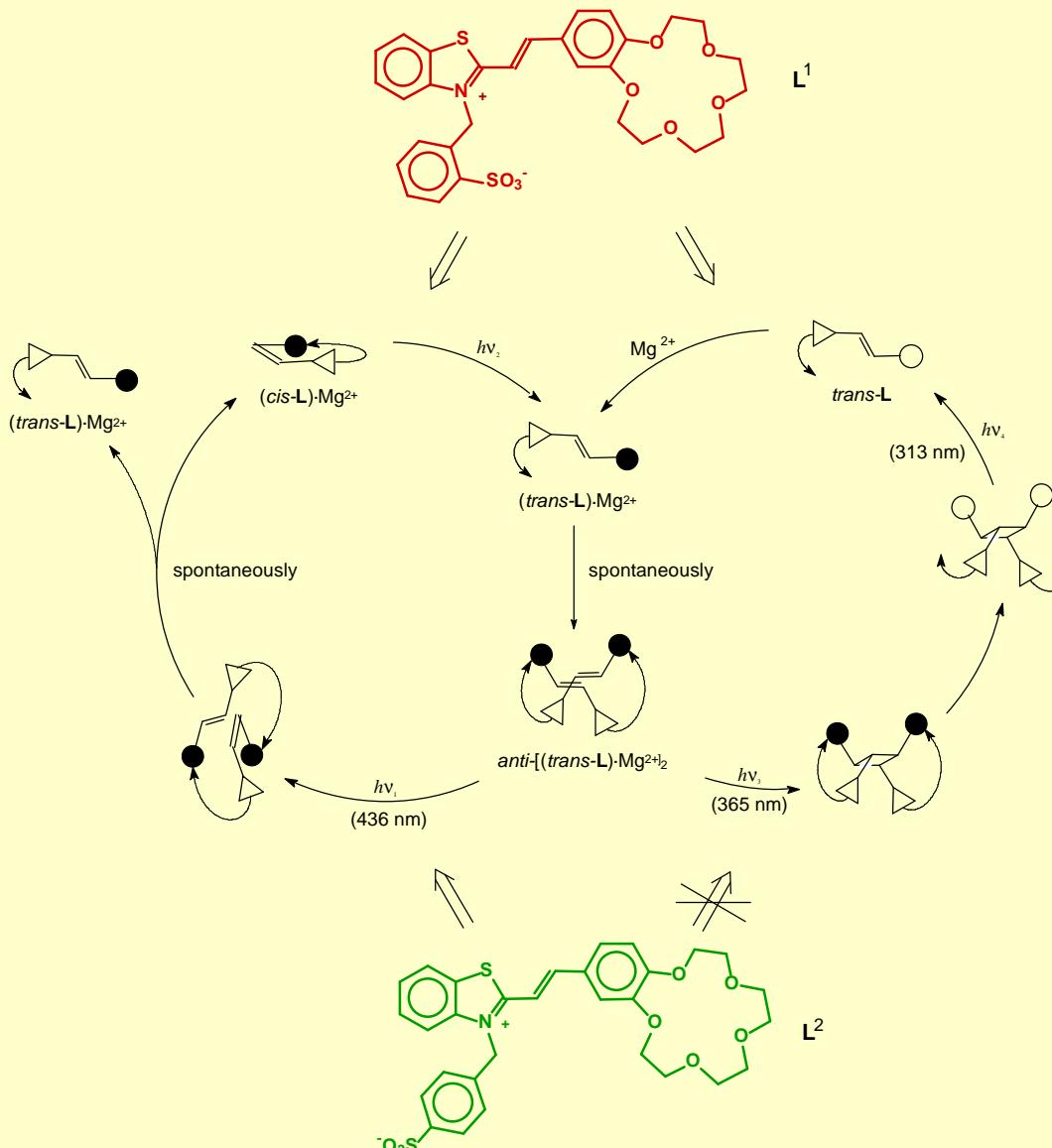
[2+2] Photocycloaddition of CSD

$C_L, / \text{mol} \cdot \text{l}^{-1}$	$5 \cdot 10^{-6}$	$2.4 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$	$2 \cdot 10^{-3}$
$F$	0.0022	0.0043	0.0052	0.0051	0.0055



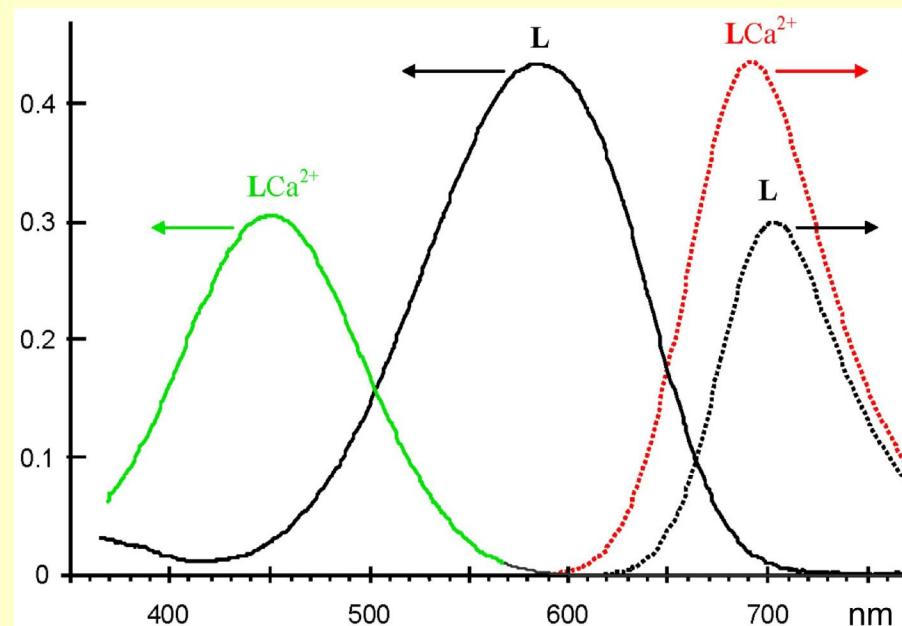
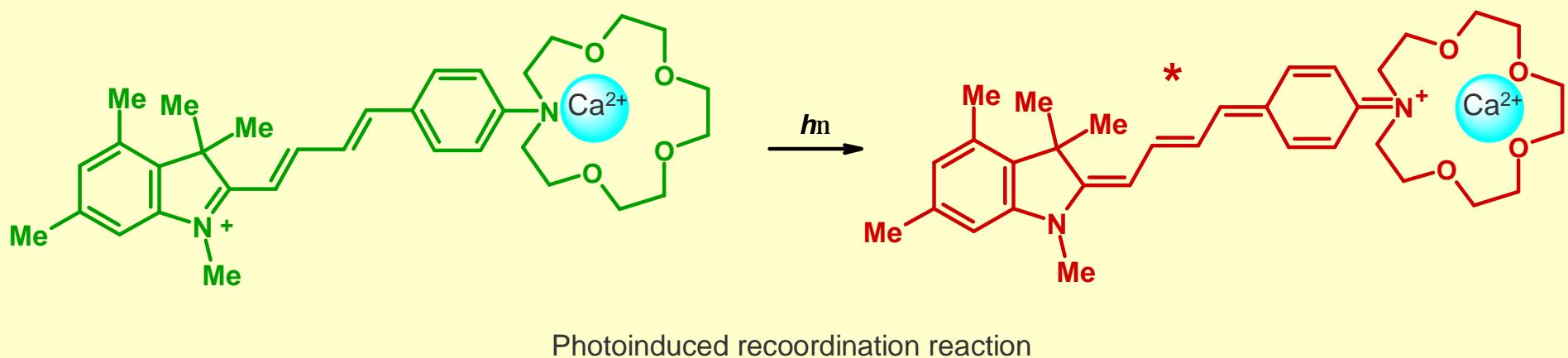
*J. Am. Chem. Soc.* **1992**, *114*, 6381;  
*Russ. Chem. Bull.* **1993**, *42*, 1385;  
*J. Chem. Soc., Perkin Trans. 2* **1999**, 601;  
*J. Org. Chem.* **2003**, *68*, 6115.

# [2+2] PHOTOCYCLOADDITION OF MULTIPHOTOCROMIC CSD



CSD	$R, A^\circ$	$F$	$\lg K_1$
$L^1$	6.7	0.018	7.3
$L^2$	9.9	---	10.0

# Photoswitchable supramolecular device

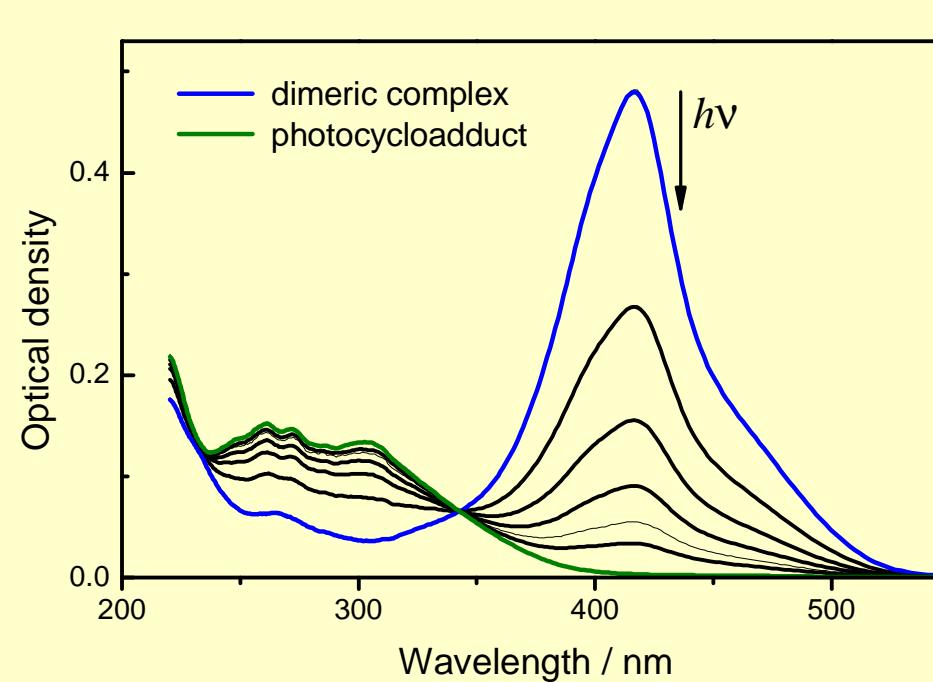
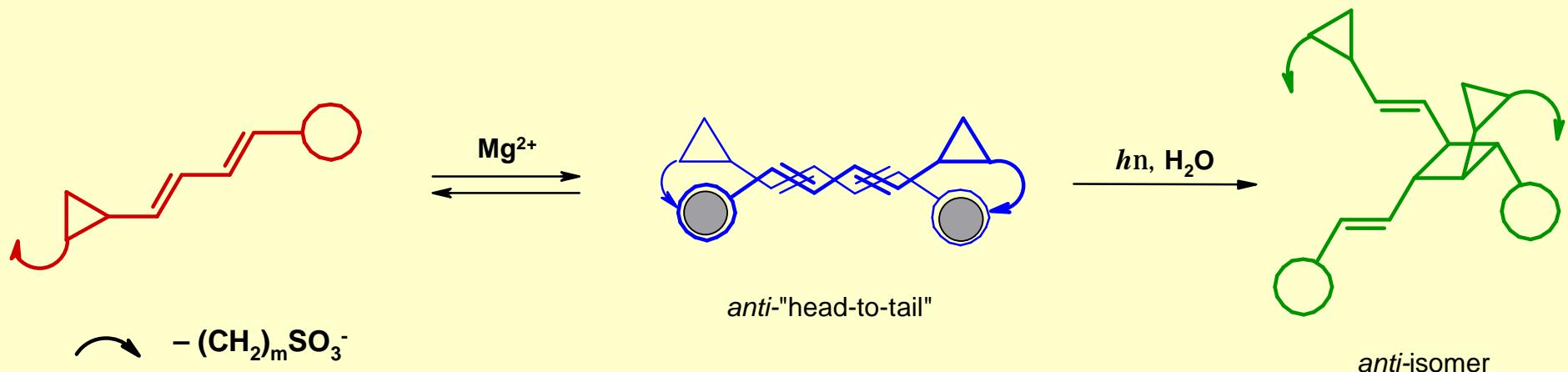


Russ. Chem. Bull. 1999, 48, 525;

J. Fluor. 1999, 9, 33;

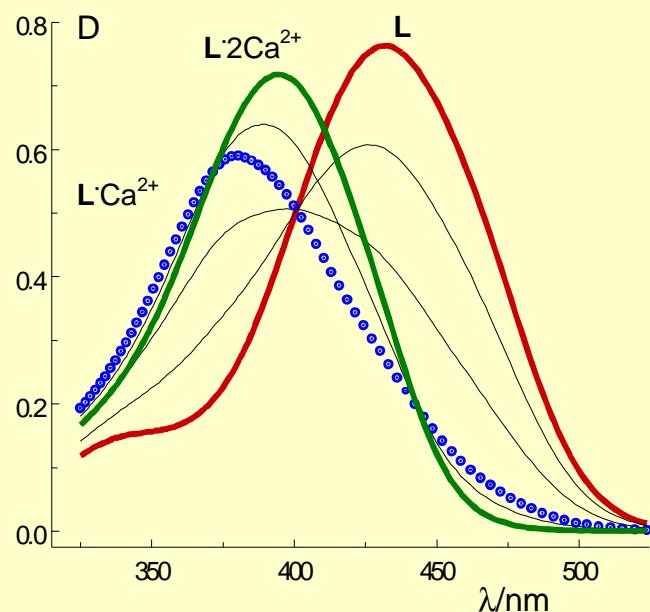
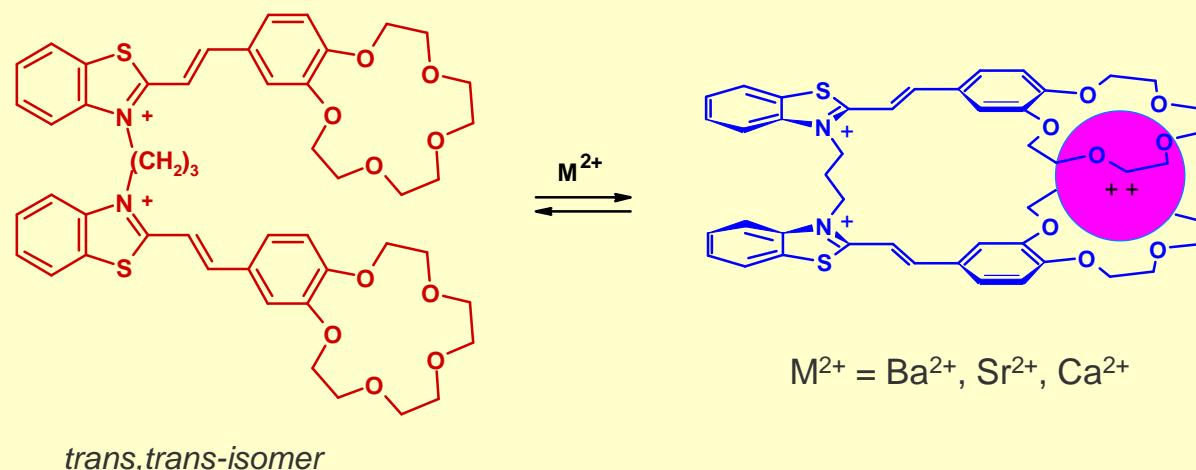
Rusalov M. V., Gromov S. P. et al. Russ. Chem. Rev. 2010, 79, 1193 (review).

## [2+2] PHOTOCYCLOADDITION OF CBD



$F_{\text{PCA}} = 0.35$

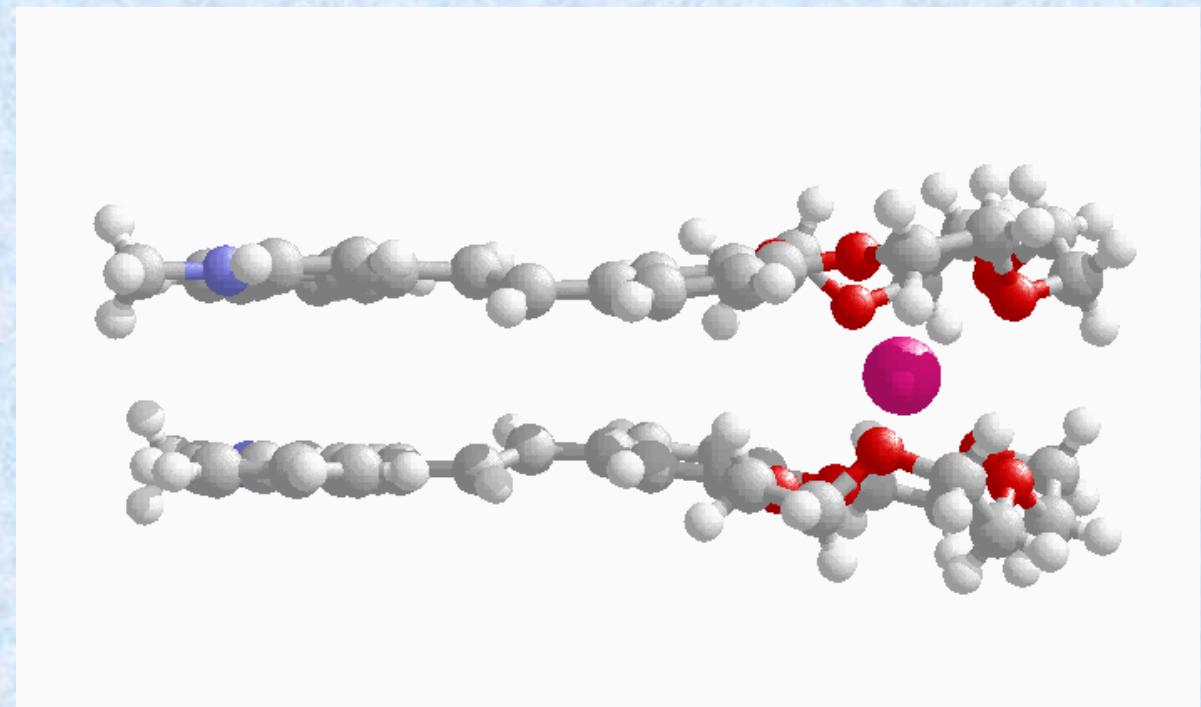
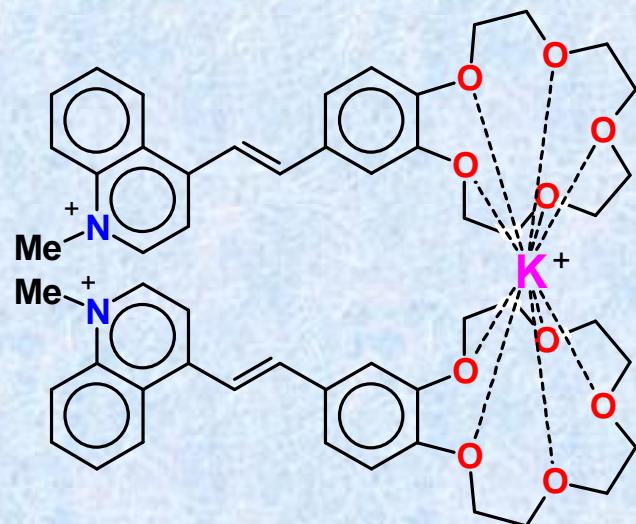
# Self-assembly of sandwich complexes



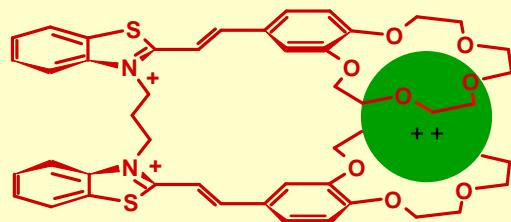
Complex	$\lg K_1$	$\lambda_{LM}$ , nm	$\lambda_L - \lambda_{LM}$ , nm
$L \cdot Ba^{2+}$	8.0	390	42
Monomer · Ba <sup>2+</sup>	4.39	402	28

J. Chem. Soc., Perkin Trans. 2. 1999, 1323;  
 J. Phys. Chem. A. 1999, 103, 11188;  
 RF patent 2389745 2010.

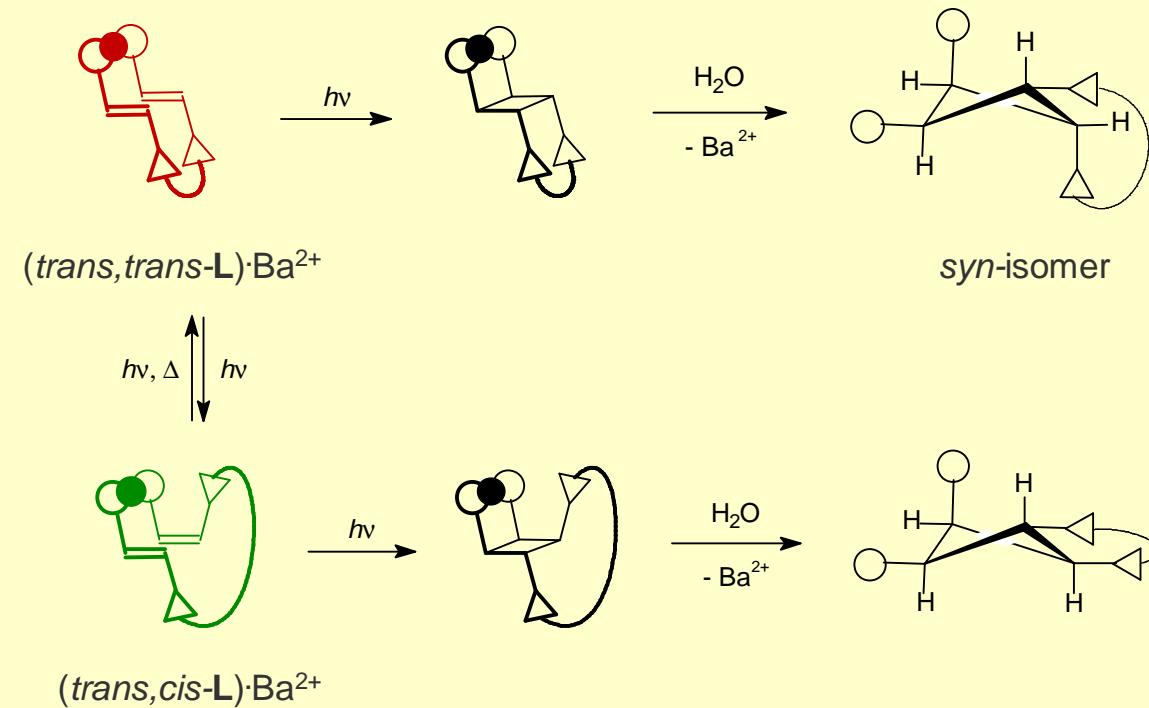
# *X-ray structure determination of sandwich complex*



# Intramolecular [2+2] photocycloaddition of bisCSD

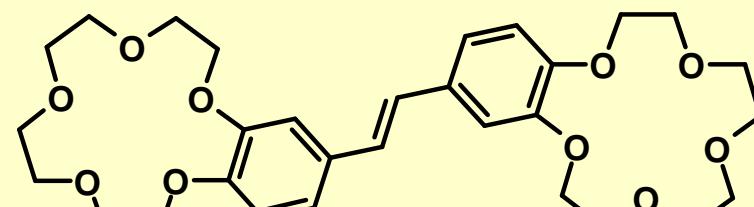


(*trans,trans*-L)·Ba<sup>2+</sup>

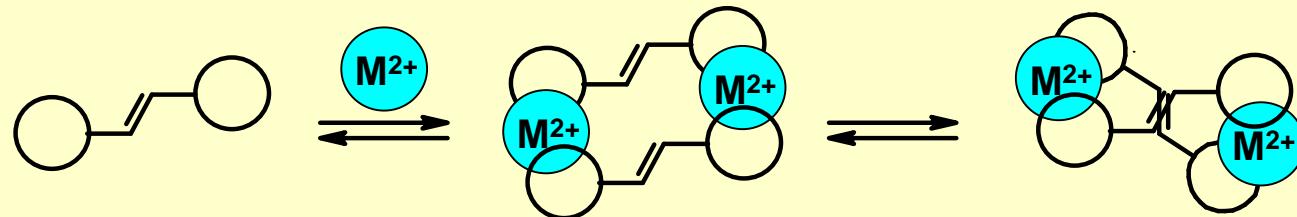
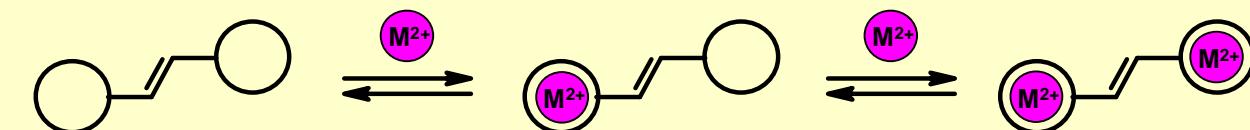
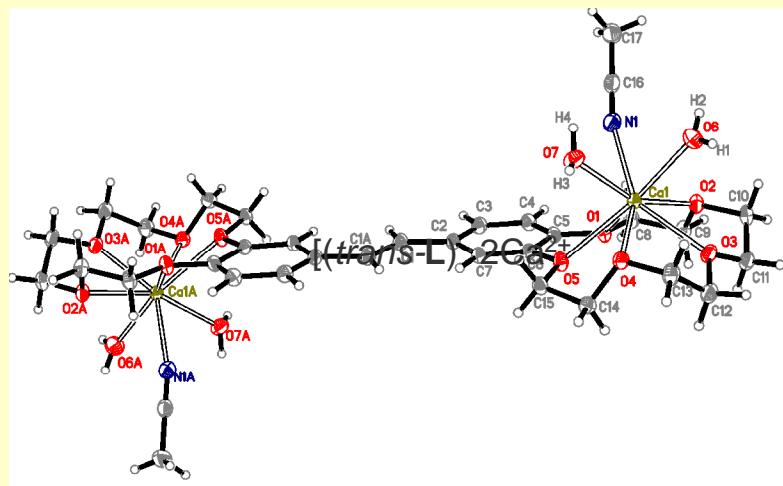


$$F_{\text{PCA}} = 0.001$$
$$F_{\text{retro-PCA}} = 0.3$$

# Complex formation of bisCS



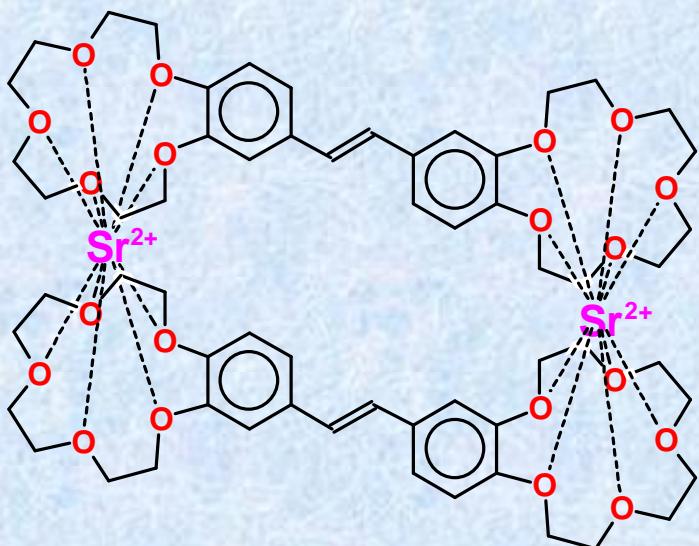
*trans*-L



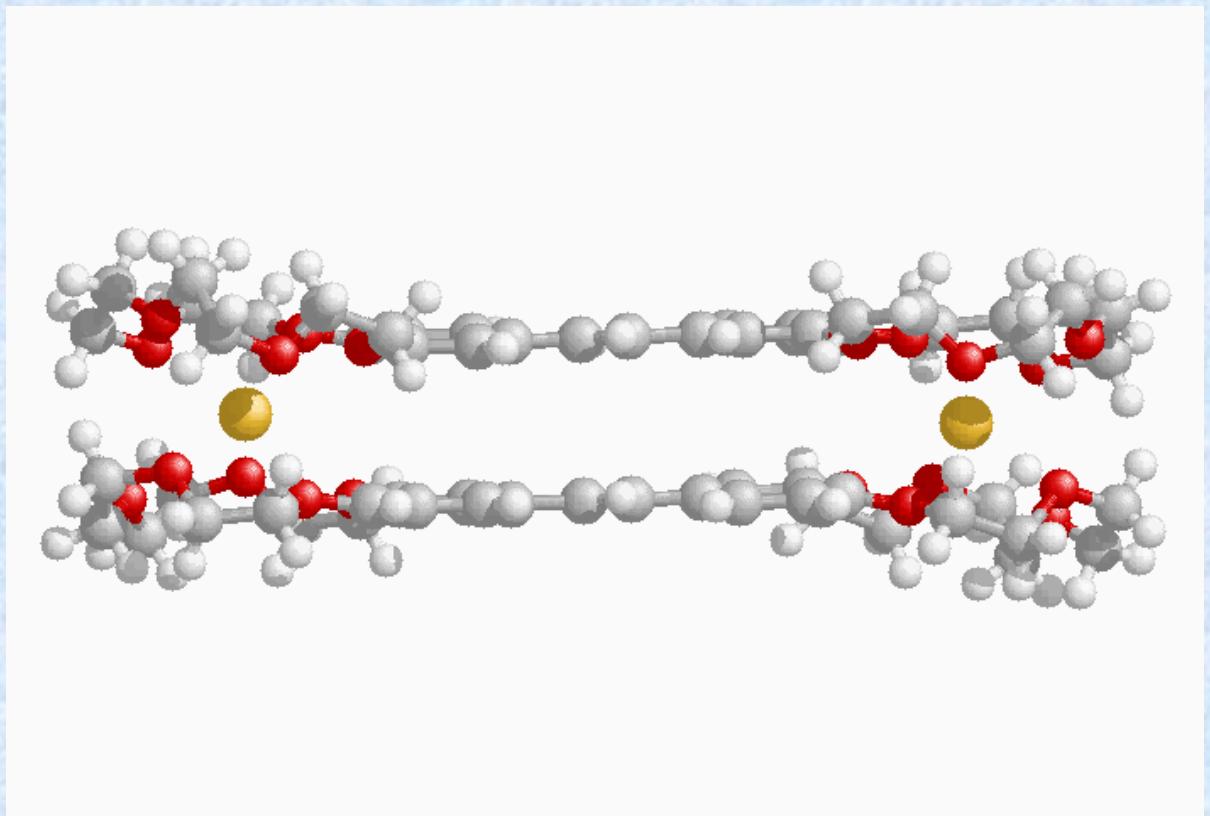
$\text{M}^{2+}$  =  $\text{Mg}^{2+}, \text{Ca}^{2+}$

$\text{M}^{2+}$  =  $\text{Sr}^{2+}, \text{Ba}^{2+}$

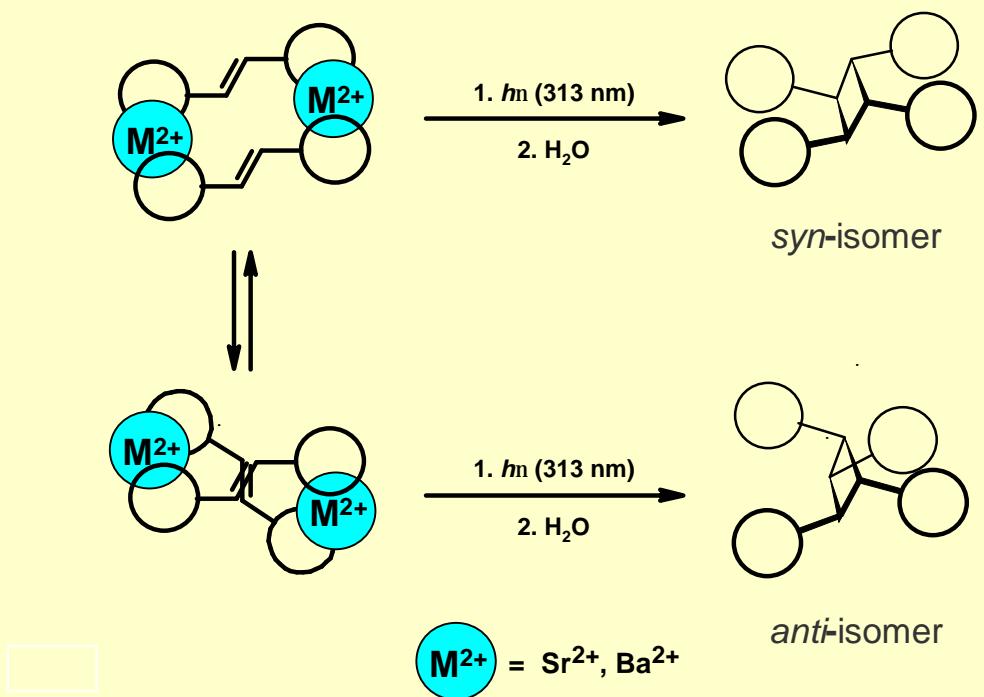
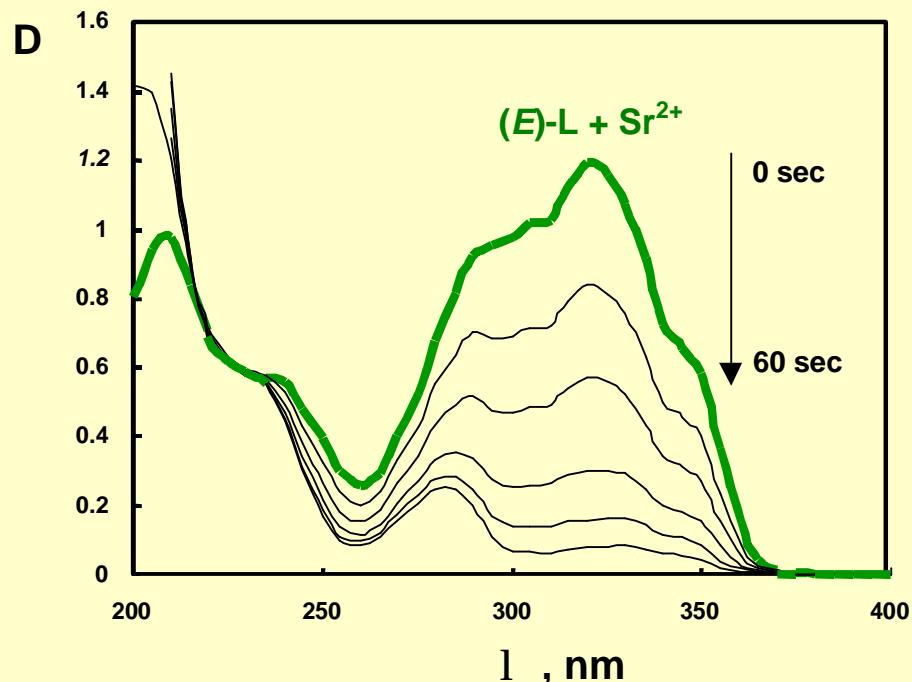
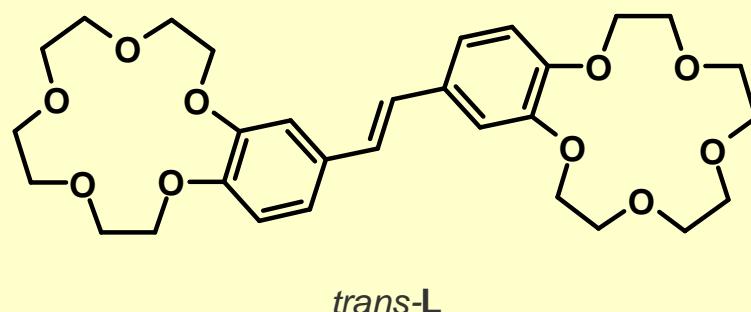
# X-ray structure determination of double sandwich complex



$2(\text{trans-L}) \cdot 2\text{Sr}^{2+}$



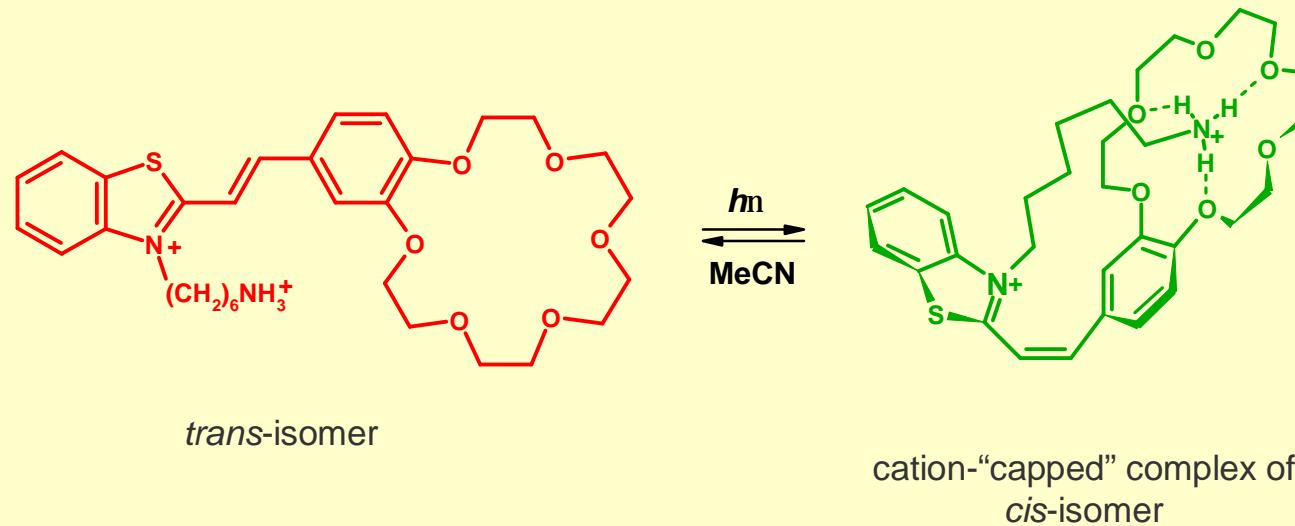
## [2+2] Photocycloaddition of bisCS



**Self-assembly  
of photoswitchable supramolecular devices  
with participation of hydrogen bonds**

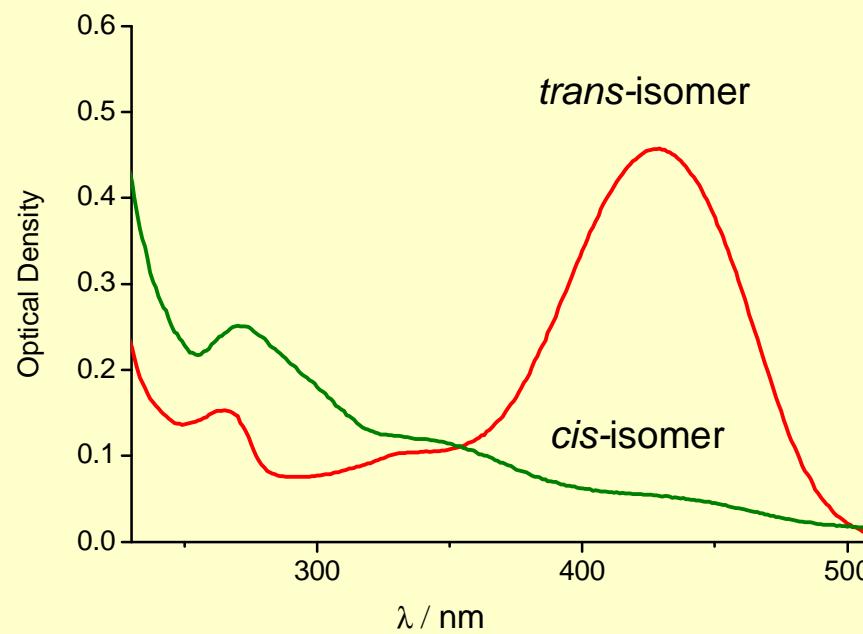
**Part II**

# Intramolecular complexation of *cis*-isomers

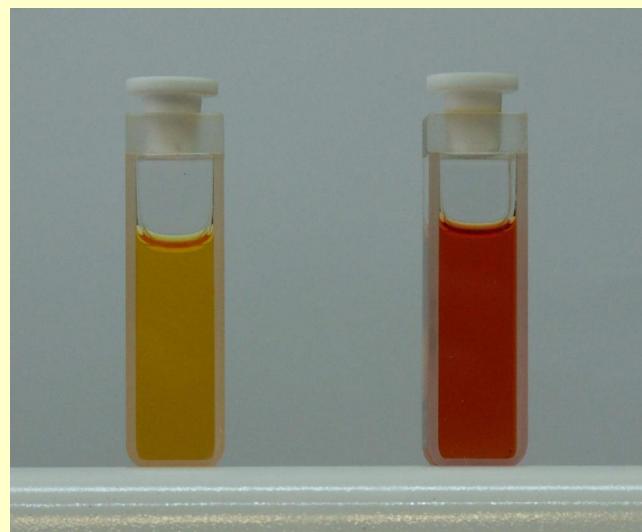
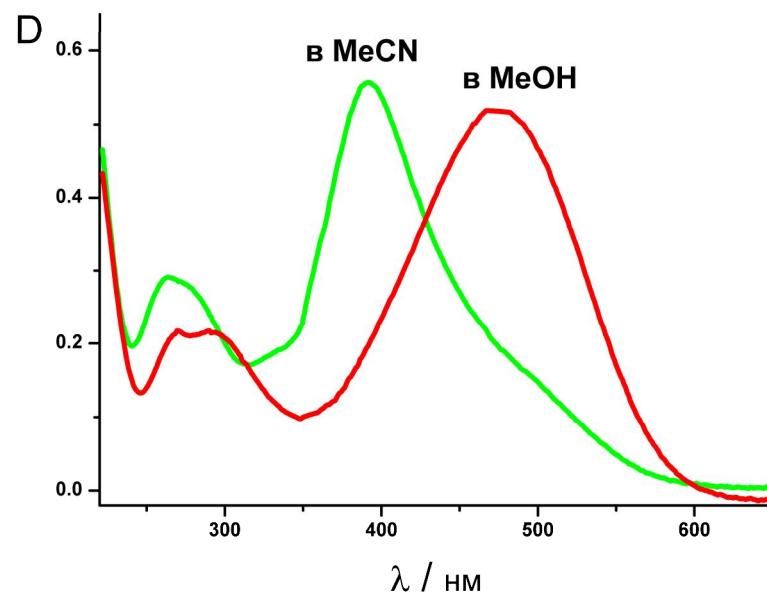
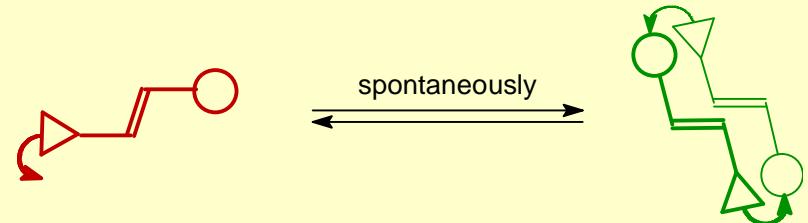
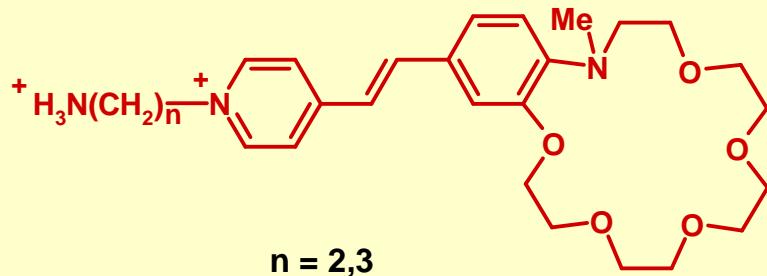


*trans*-isomer

cation-“capped” complex of  
*cis*-isomer



# Dimerization of CSD

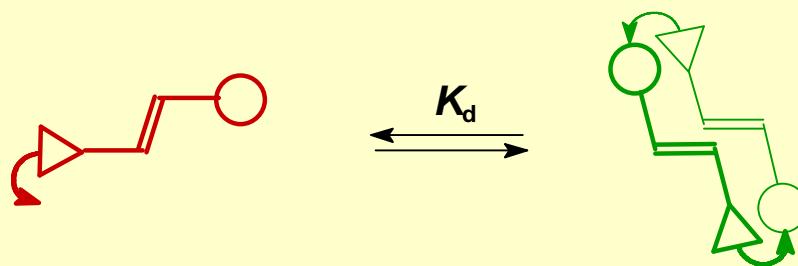


RF patent 2278134 2006;

J. Org. Chem. 2014, 79, 11416;

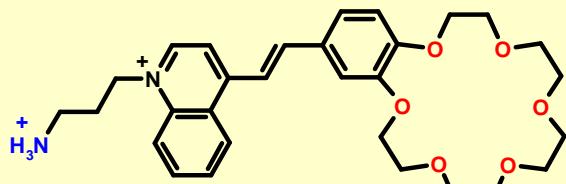
J. Phys. Chem. A 2015, 119, 13025.

# DIMERIZATION

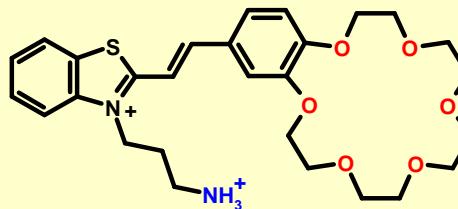


$\log K_d$

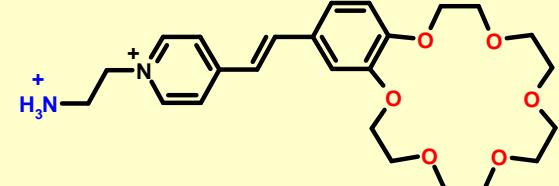
$\log K_d$



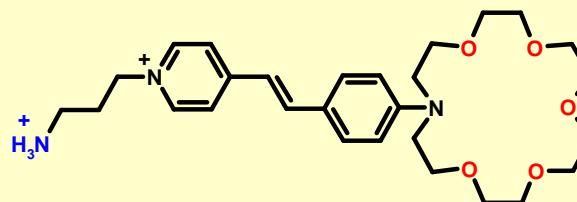
8.03



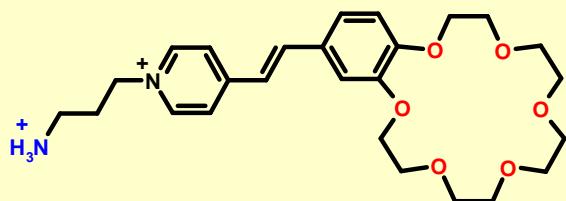
5.87



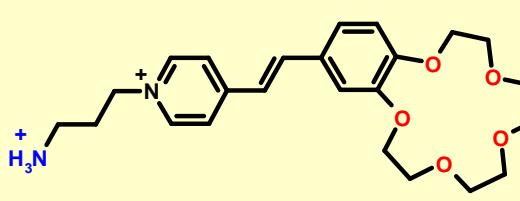
7.90



3.61



7.12

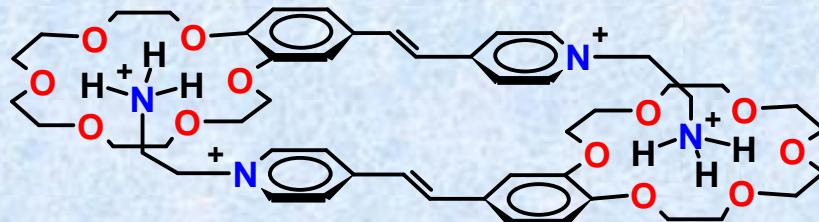


2.44

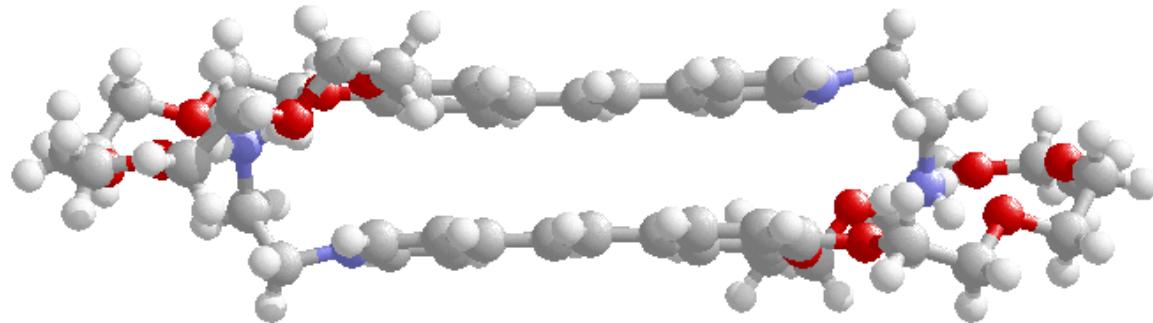
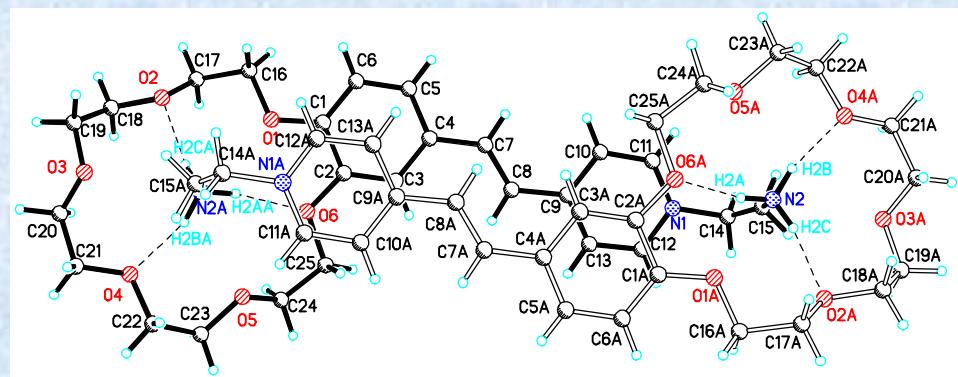
in  $\text{CD}_3\text{CN}$

Russ. Chem. Bull. 2009, 58, 1211;  
J. Org. Chem. 2014, 79, 11416;  
J. Phys. Chem. A 2015, 119, 13025.

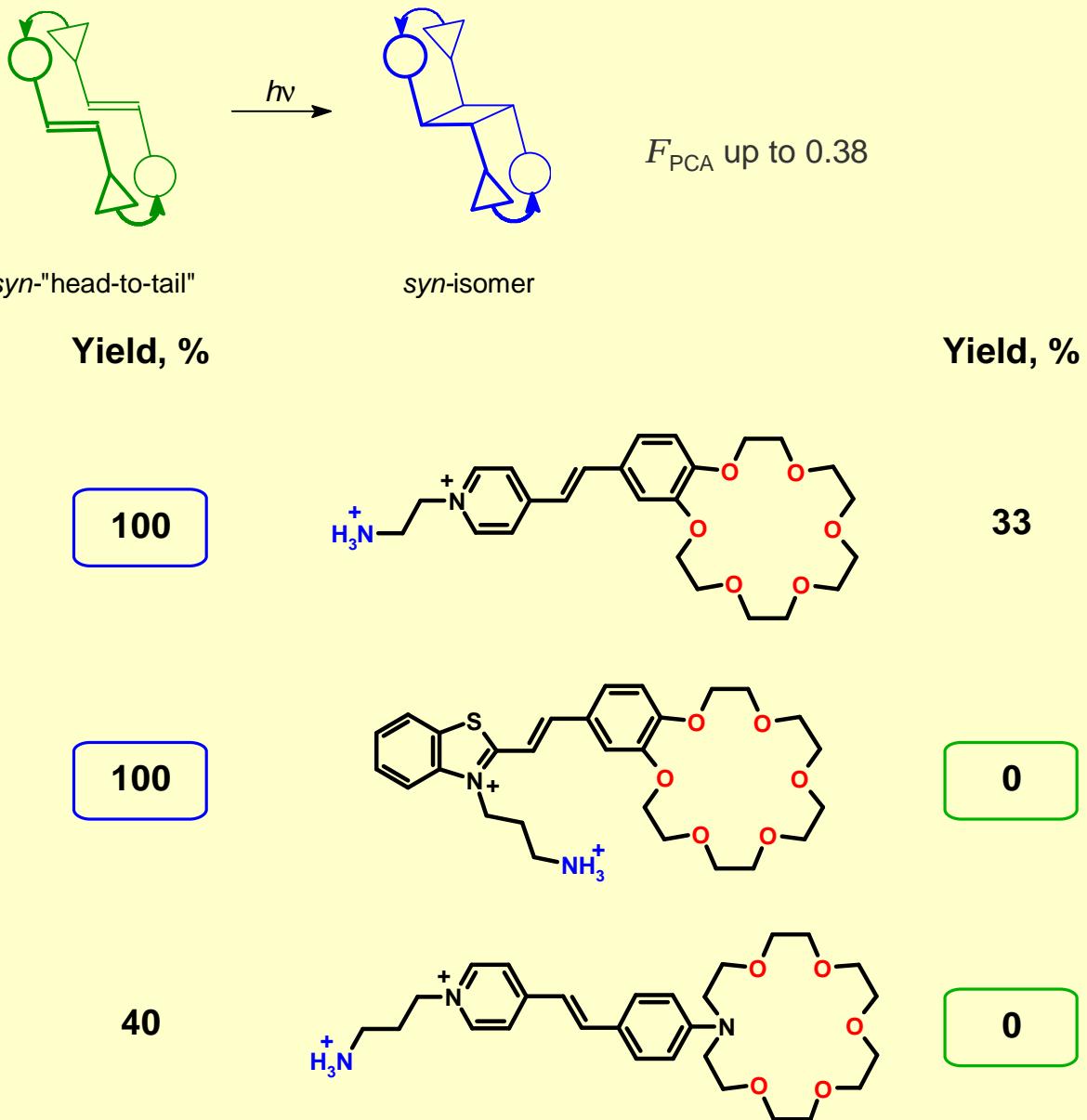
# X-ray structure determination of dimeric complex



syn-'head-to-tail' dimeric complex



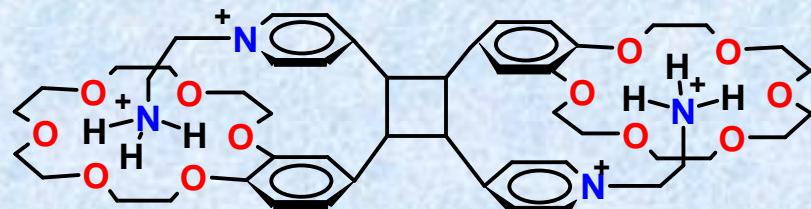
# [2+2] Photocycloaddition of CSD



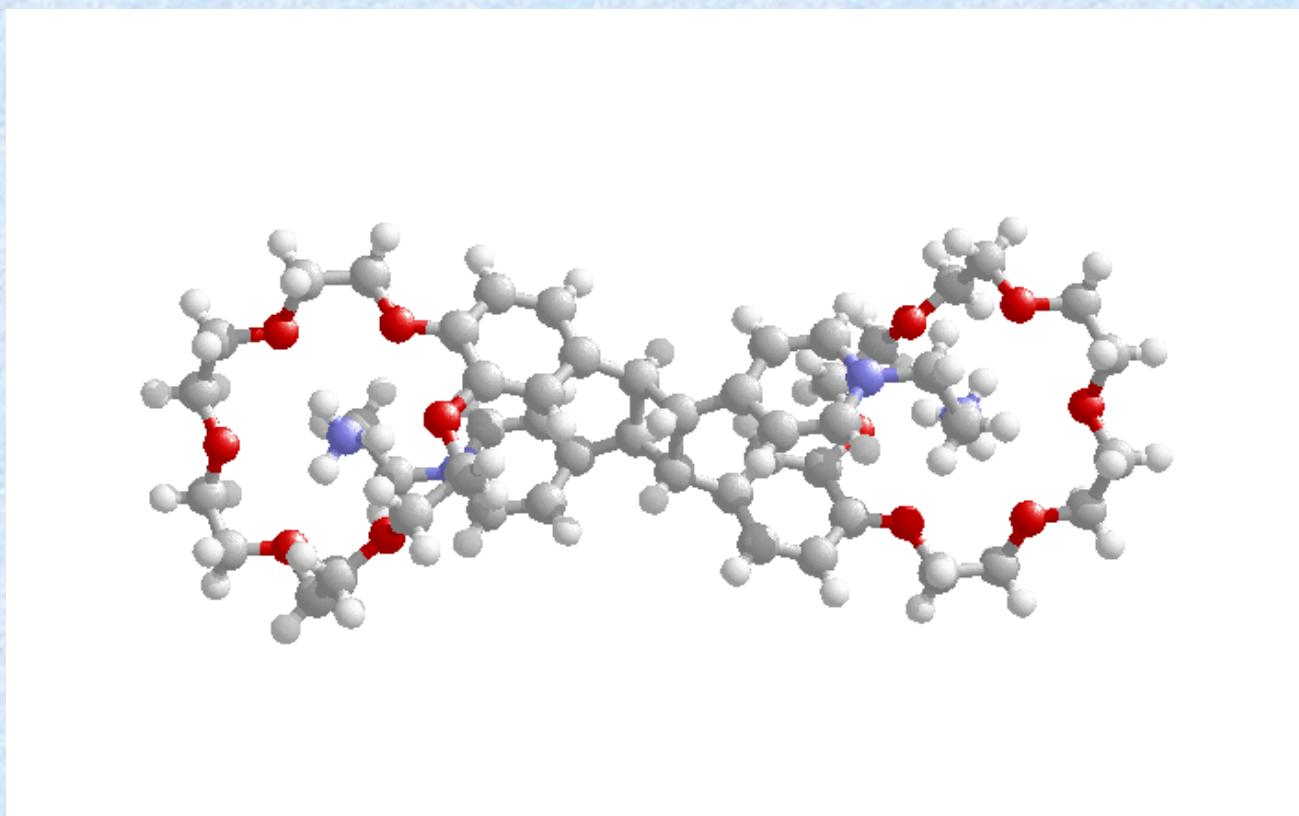
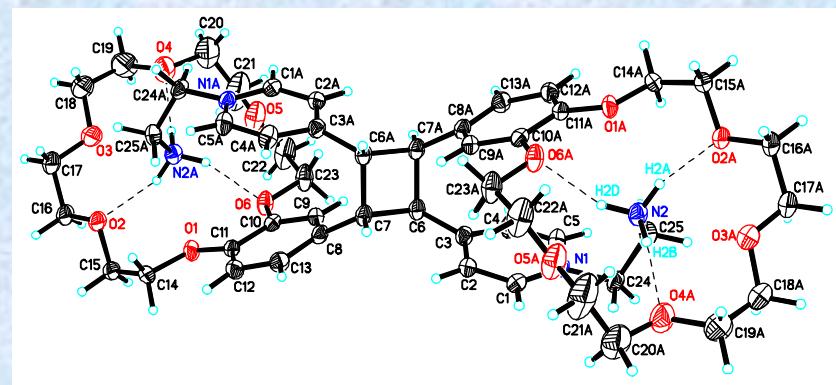
RF patent 2278134 2006;  
Russ. Chem. Bull. 2009, 58, 1211;  
J. Org. Chem. 2014, 79, 11416;  
J. Phys. Chem. A 2015, 119, 13025.

In MeCN, irradiation time, 4 h

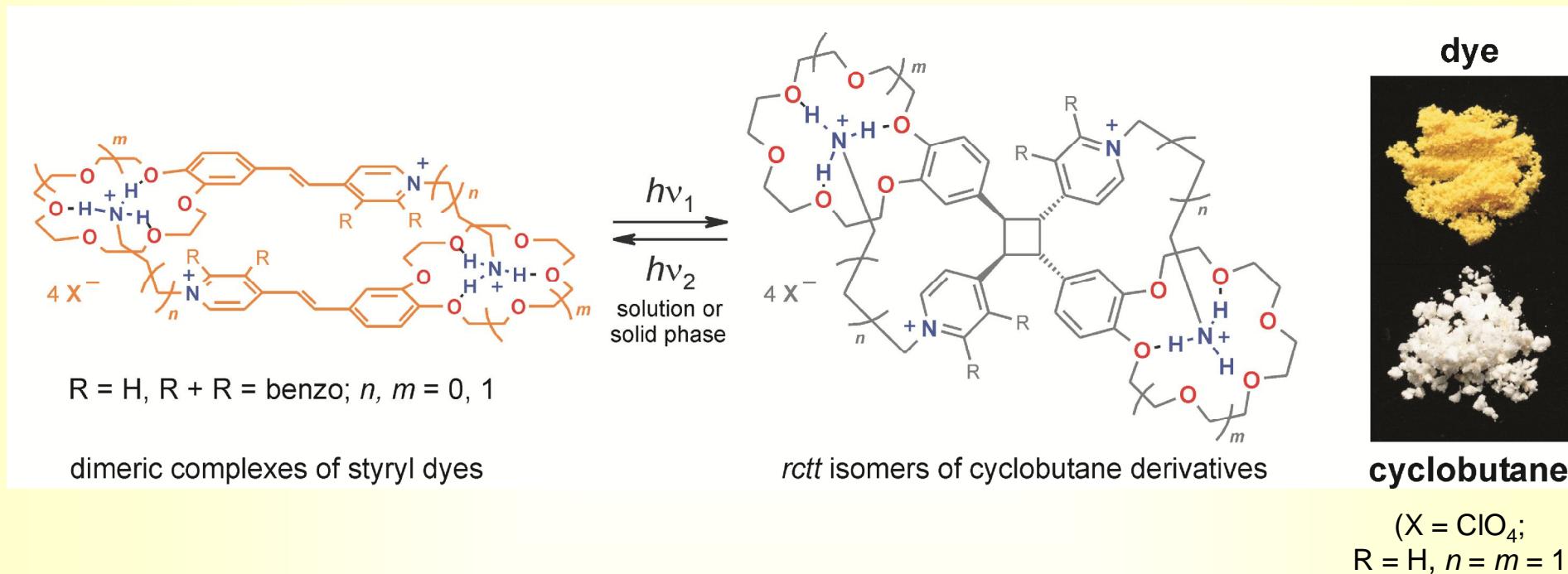
# X-ray structure determination of cyclobutane



syn-cyclobutane

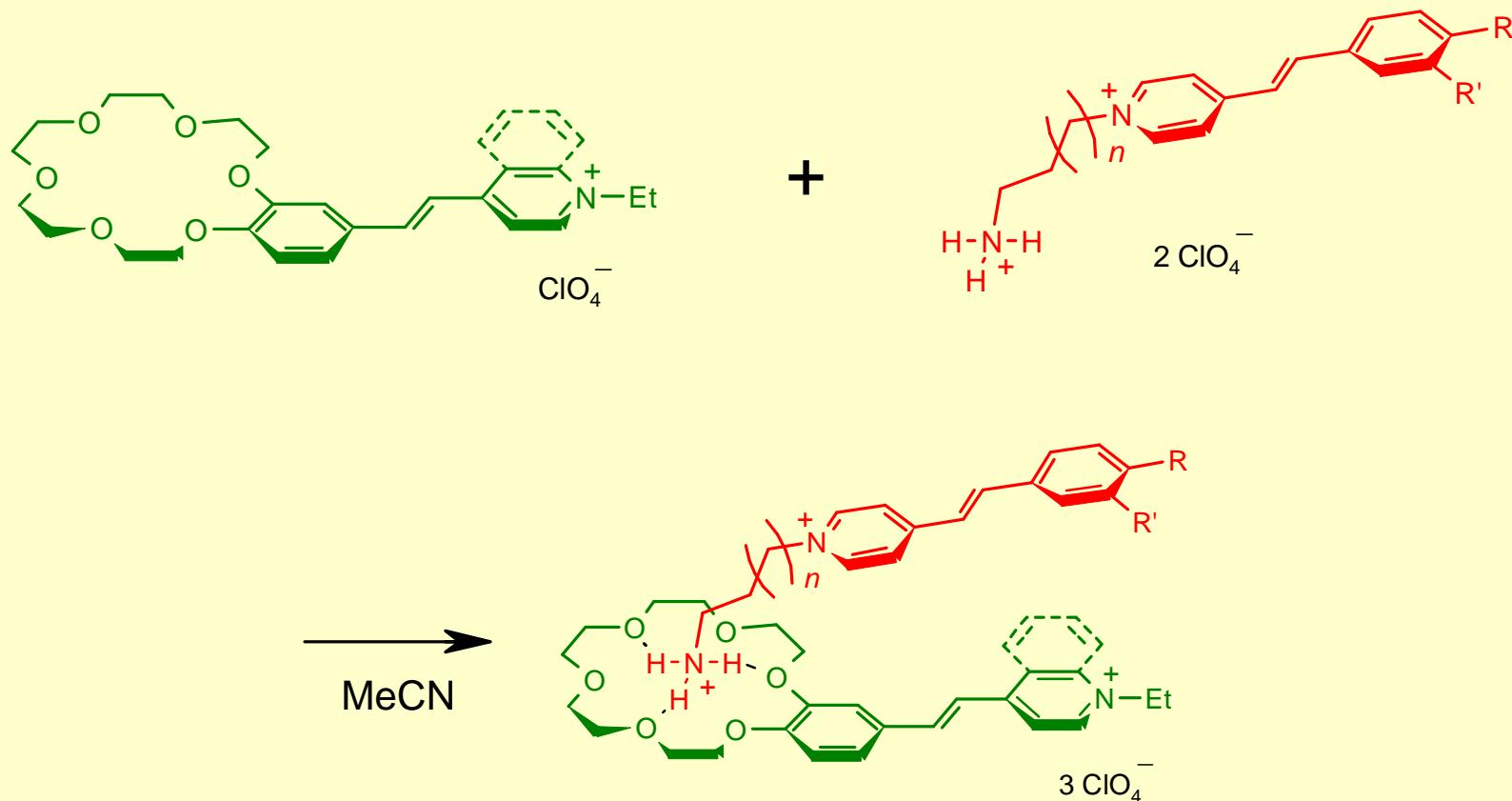


# *Supramolecular photoswitches based on ammonioalkyl derivatives of crown-ether styryl dyes*



Found property provides grounds for believing that the crystals of these photoactive supramolecular systems could be used for data recording and storage.

# **Formation of pseudodimeric complexes**



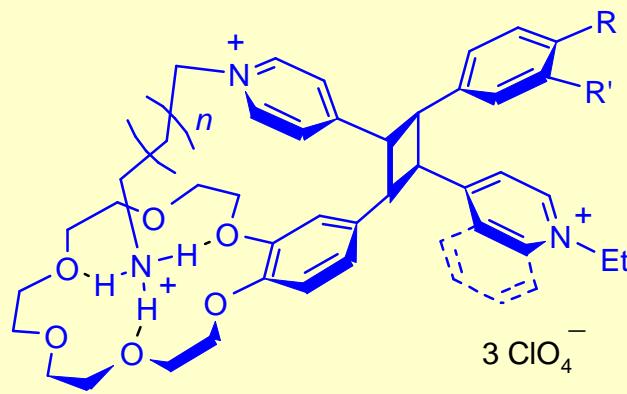
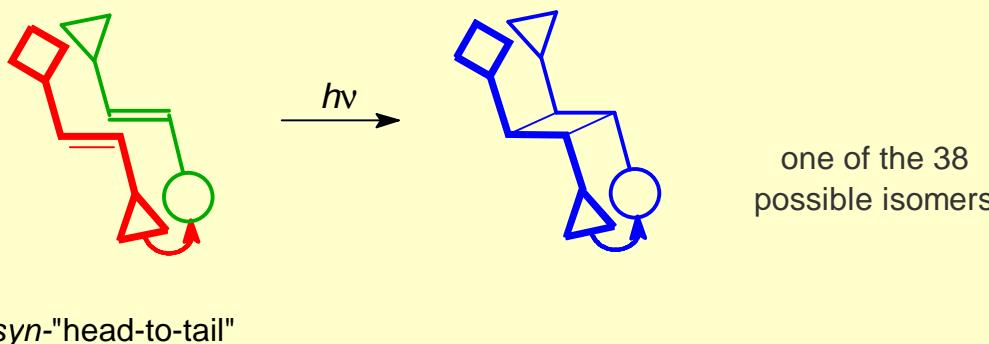
R, R' = H, OMe, SMe, NMe<sub>2</sub>, NO<sub>2</sub>, Cl

n = 0, 1, 3

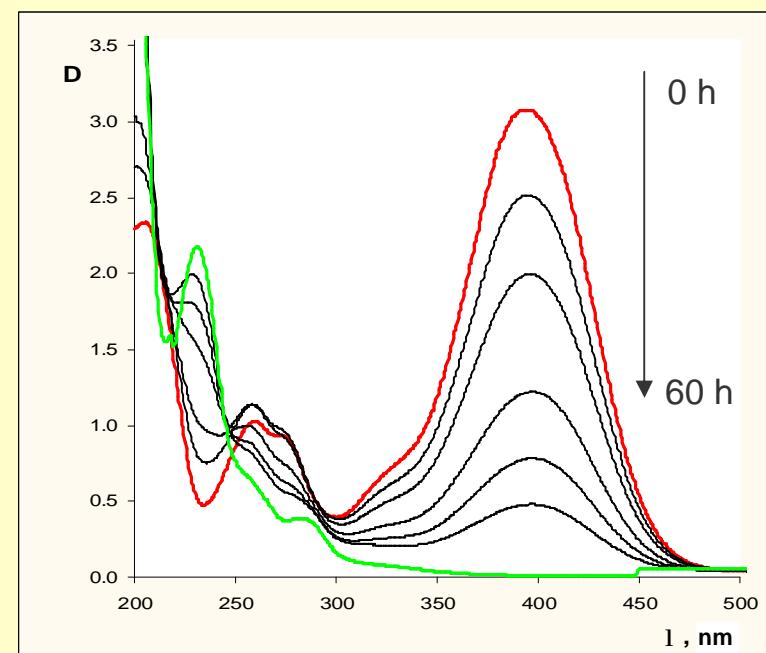
log K = 3.1 - 3.7

Mendeleev Commun., 2007, 17, 29;  
Russ. Chem. Bull. 2009, 58, 1955;  
New. J. Chem. 2016, 40, 7542.

# Cross [2+2] Photocycloaddition

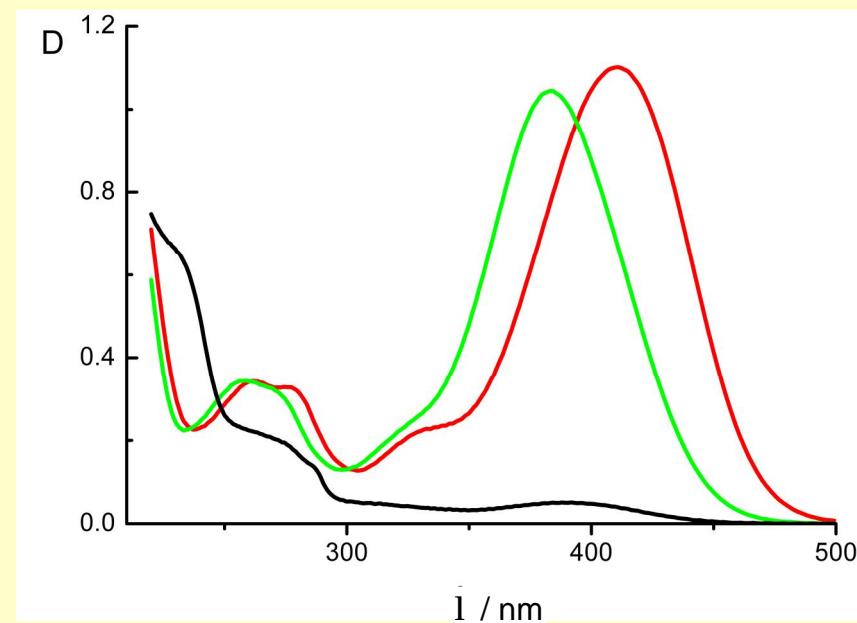
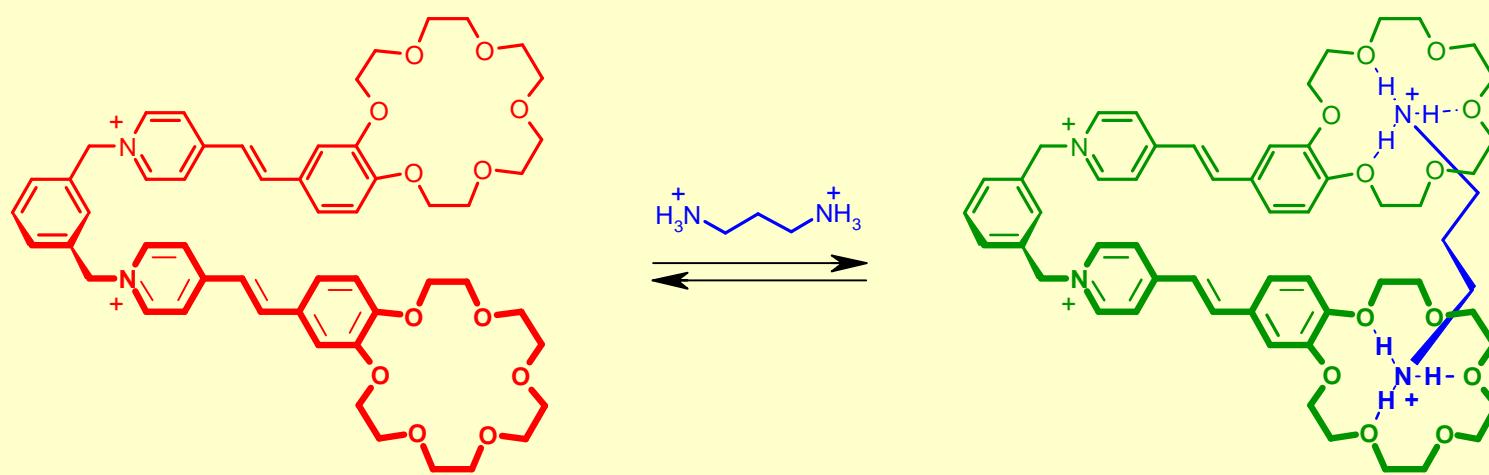


rctt isomers

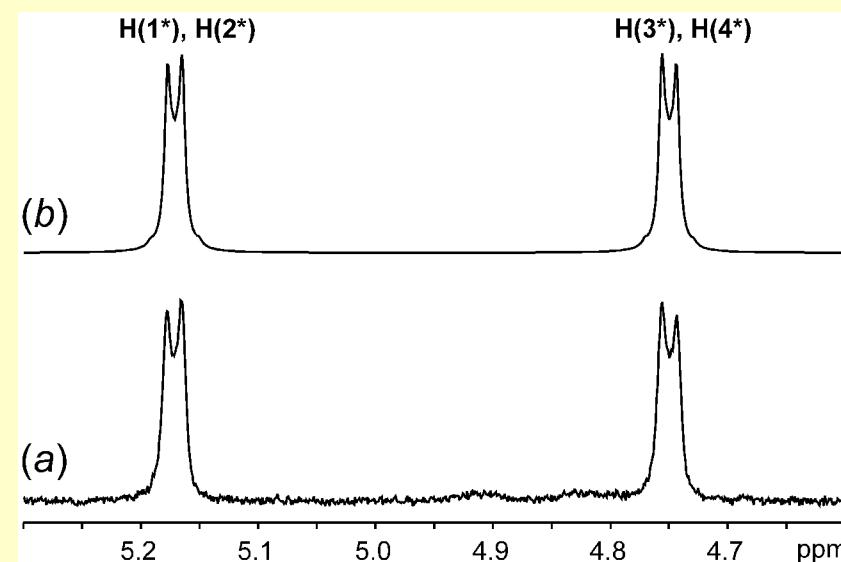
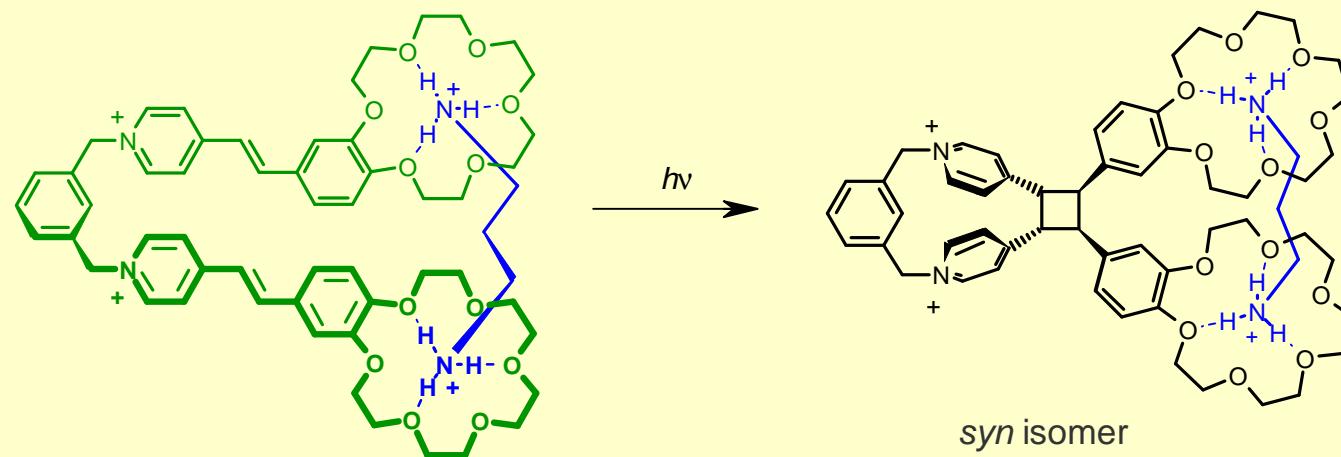


Mendeleev Commun., 2007, 17, 29;  
Russ. Chem. Bull. 2009, 58, 1955;  
RF patent 2383571 2010;  
New. J. Chem. 2016, 40, 7542.

# FORMATION OF PSEUDOSANDWICH COMPLEXES

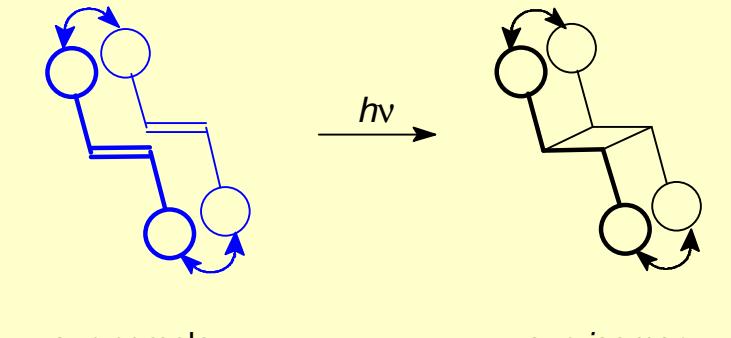


# Intramolecular [2+2] photocycloaddition of bisCSD

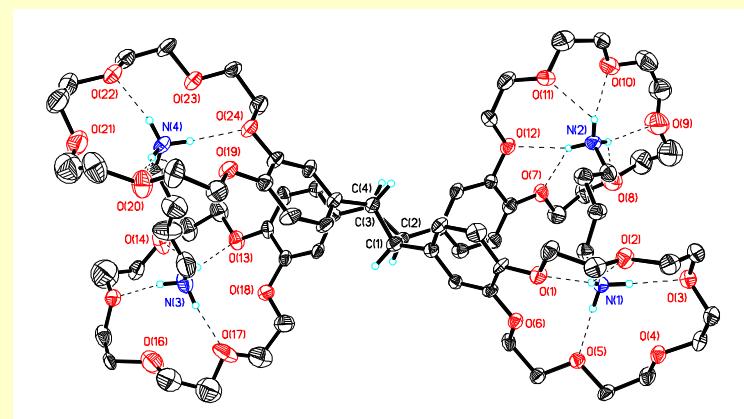
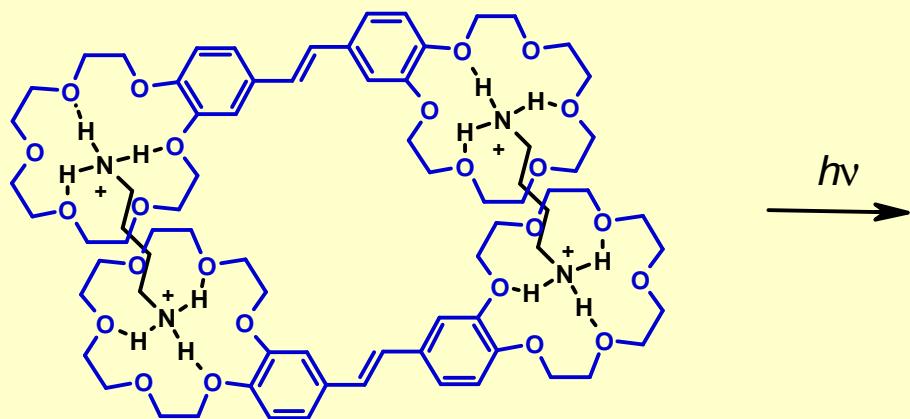
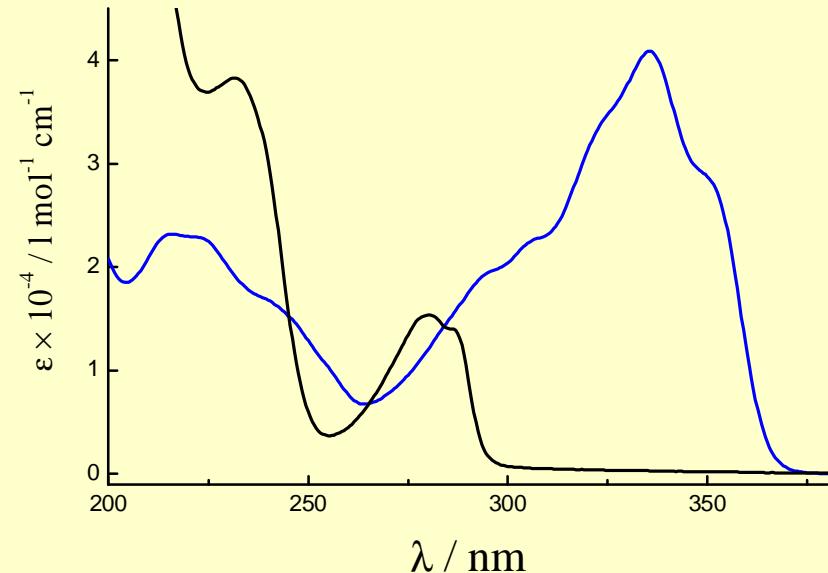
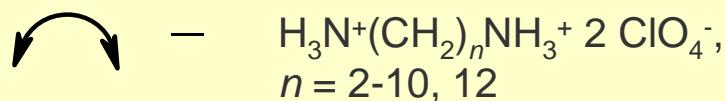


(a)  $^1\text{H}$  NMR spectrum of the cyclobutane protons and (b) its best fit to an AA'BB' spin system.

# Formation of bispseudosandwich complexes and [2+2] Photocycloaddition

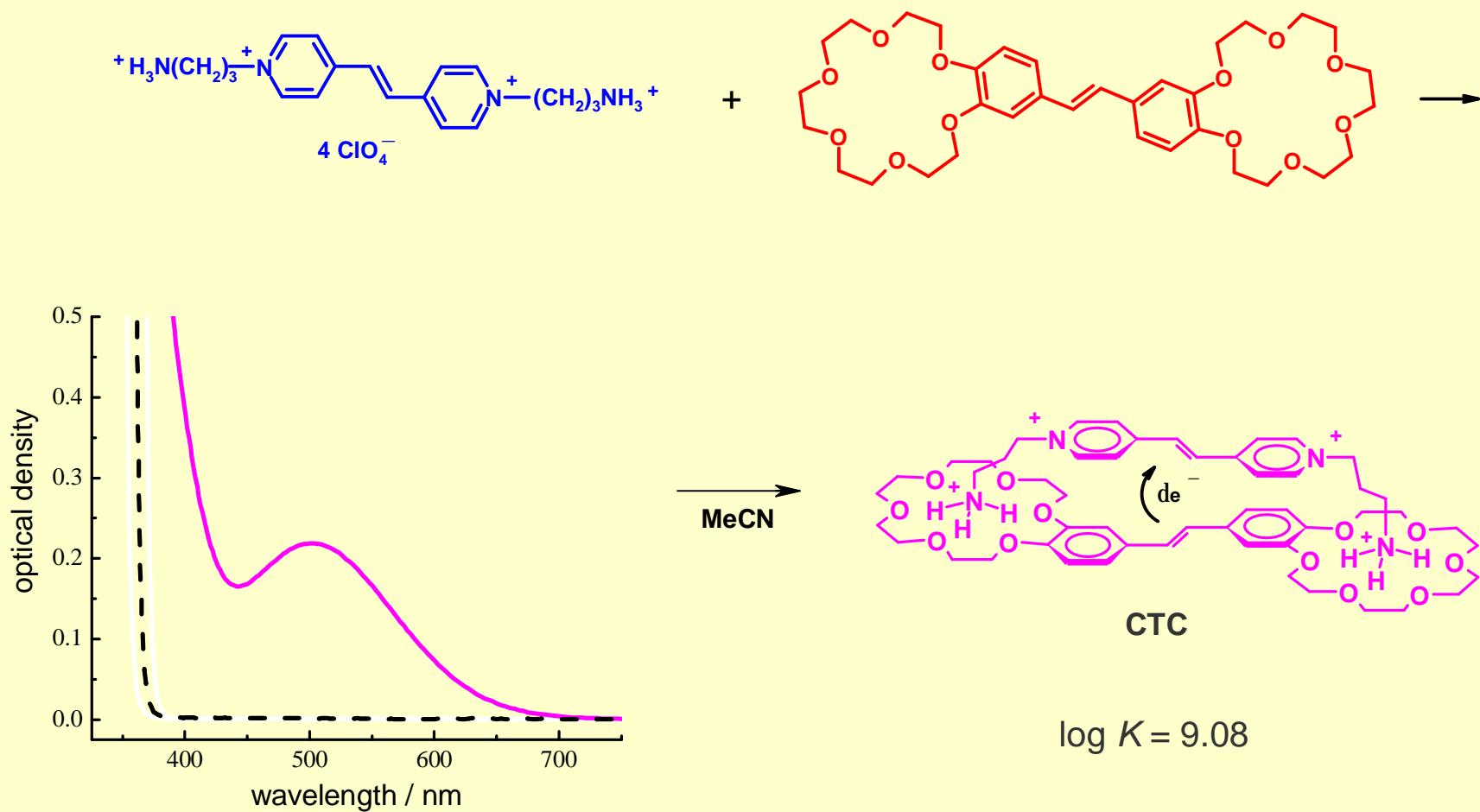


$F_{\text{PCA}}$  up to 0.27



Russ. Chem. Bull. 2009, 58, 108;  
 New. J. Chem. 2011, 35, 724;  
 J. Photochem. Photobiol. A. 2017, 340, 80;

# Formation of Charge Transfer Complex of bisCS

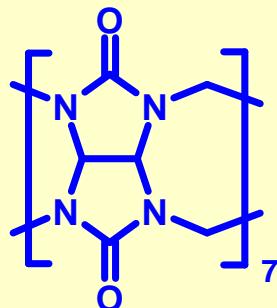


Org. Lett. **1999**, *1*, 1697 ;  
New. J. Chem. **2005**, *29*, 881;  
J. Org. Chem. **2011**, *76*, 6768;  
Photochem. Photobiol. Sci. **2017**, *16*, 1801.

# **Self-assembly of photocontrolled supramolecular machines**

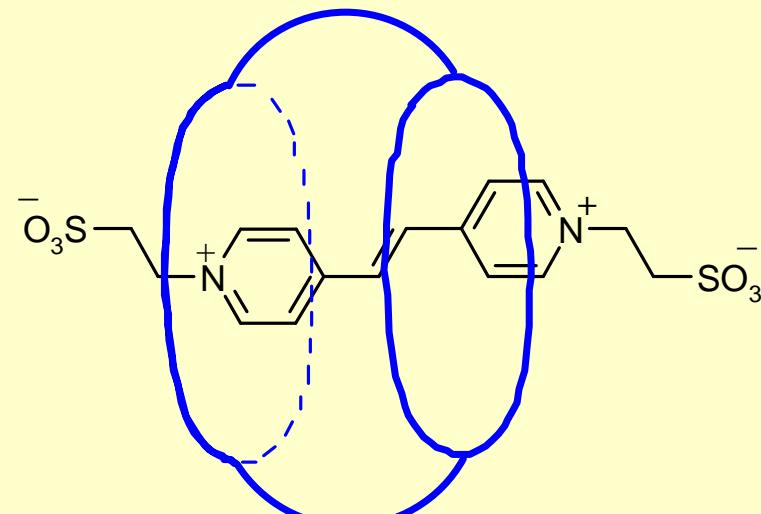
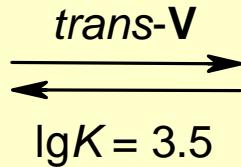
**Part III**

# PSEUDOROTAXANE COMPLEXES OF CUCURBITURILS



CB[7]

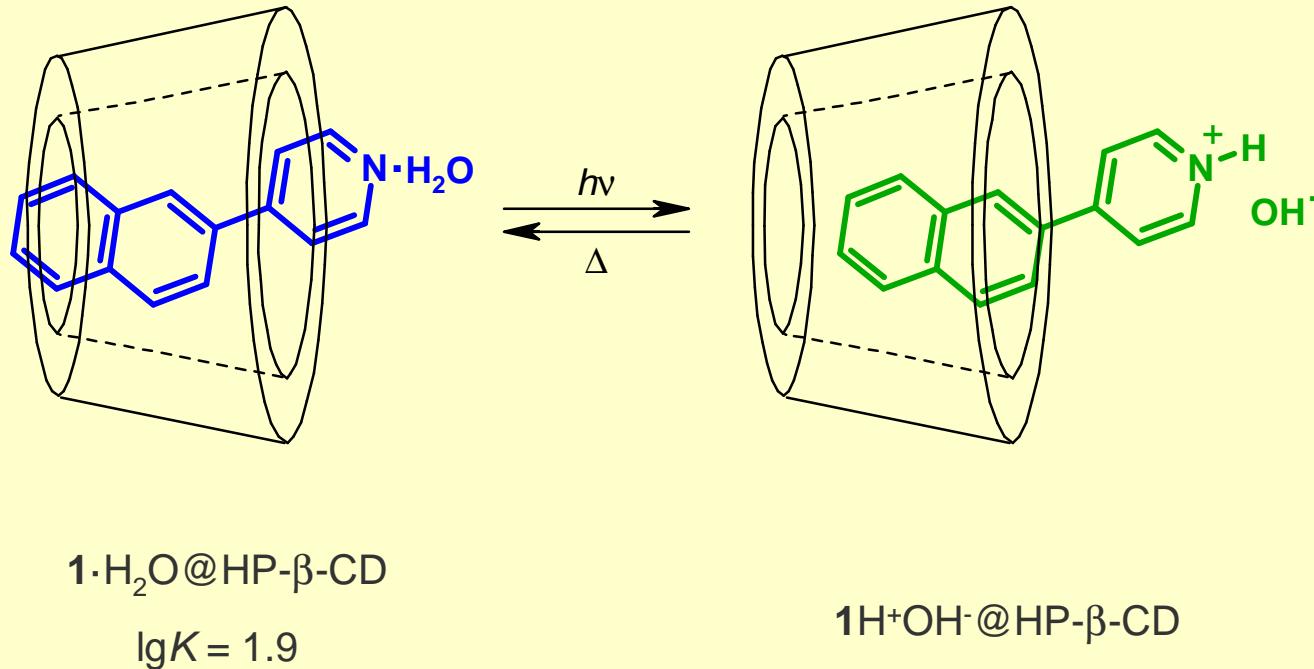
cucurbit[n]urils



*trans*-V@CB[7]

Russian Nanotechnologies **2007**, 2, 56;  
J. Mol. Struct. **2011**, 989, 114;  
Chem. Phys. Lett. **2014**, 610-611, 91;  
J. Photochem. Photobio. A. **2018**, 353, 34.

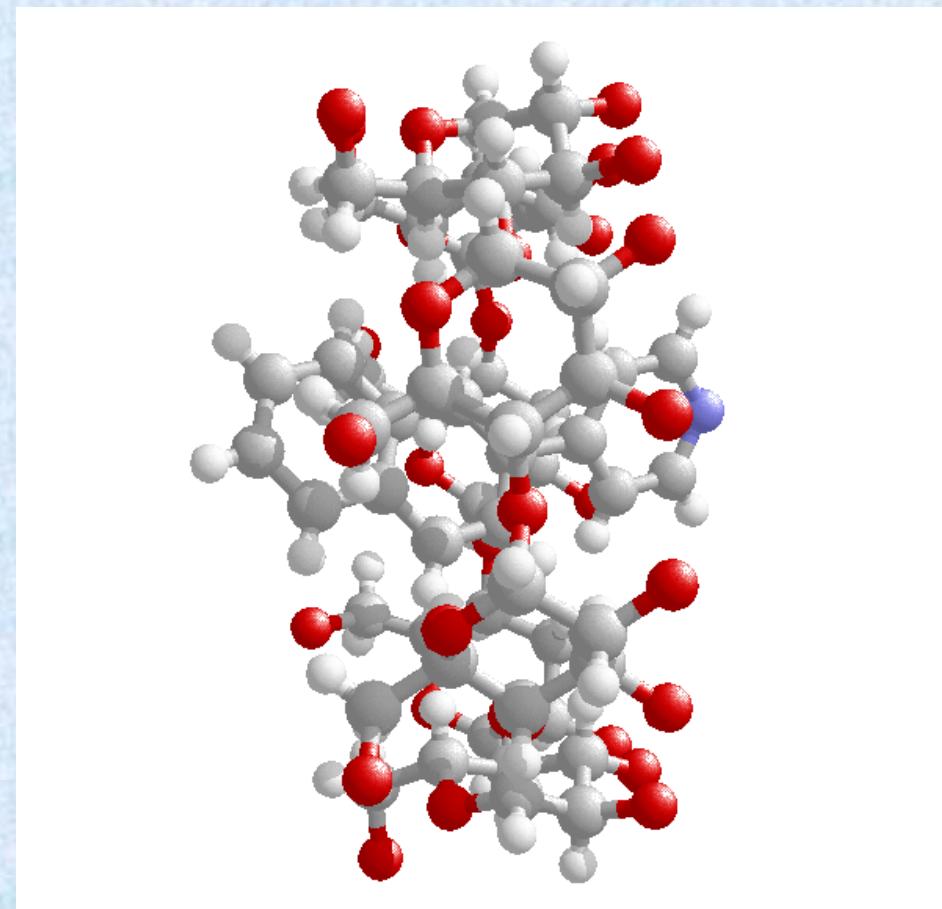
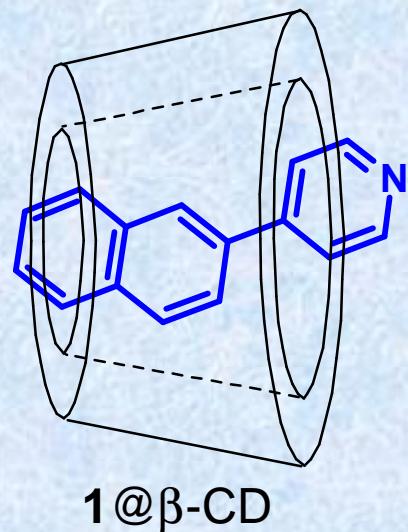
# PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



Discovery of the reversible photoinduced mechanical displacement of naphthylpyridine in the  $\beta$ -cyclodextrin cavity allowed us to develop a new type of photocontrolled molecular machines.

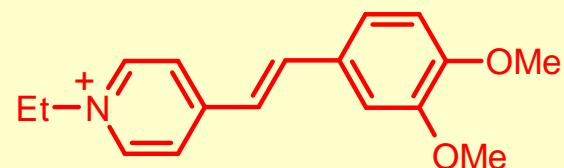
*Russ. Chem. Bull.* **2004**, 53, 2525;  
*J. Photochem. Photobiol.* **2011**, 217, 87;  
*Russ. Chem. Bull.* **2013**, 62, 2150.

# *X-ray structure determination of photocontrolled supramolecular machine*

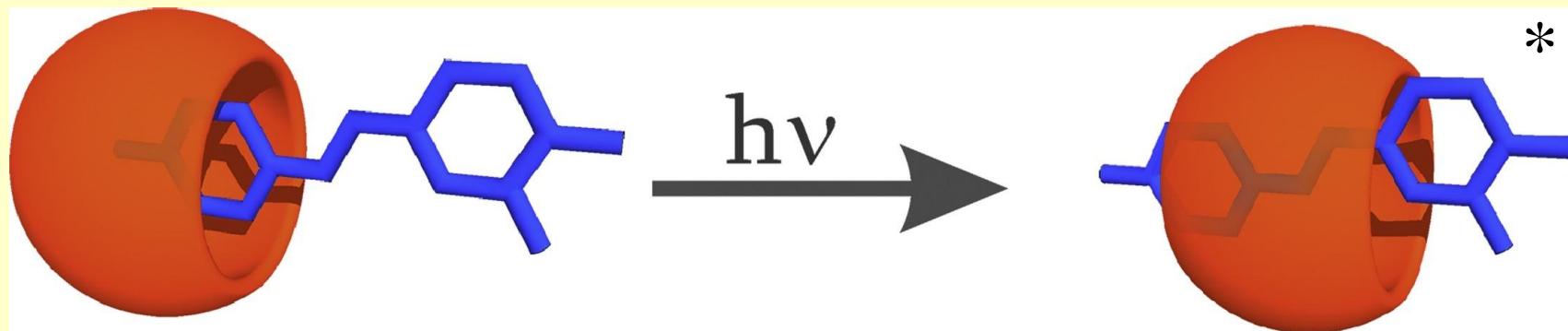


*Russ. Chem. Bull.* **2004**, 53, 2525;  
*J. Photochem. Photobiol.* **2011**, 217, 87;  
*Russ. Chem. Bull.* **2013**, 62, 2150.

# PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



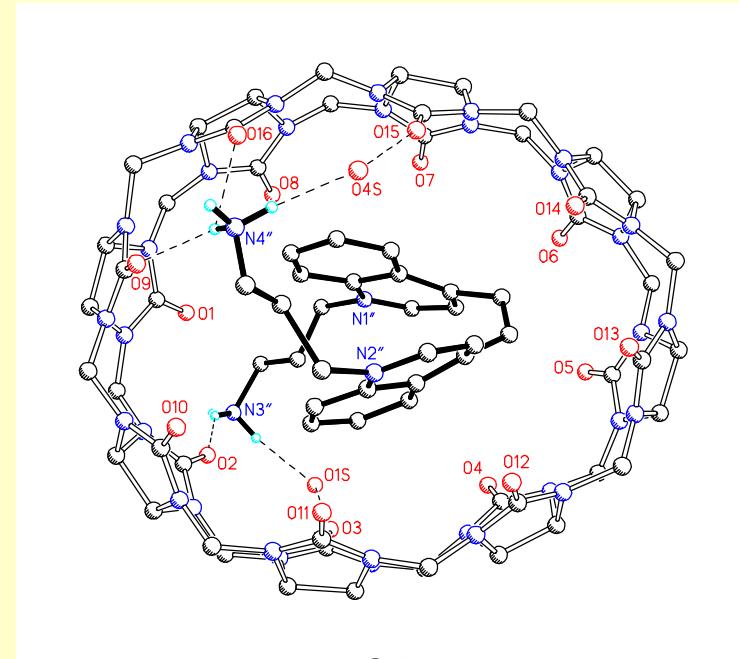
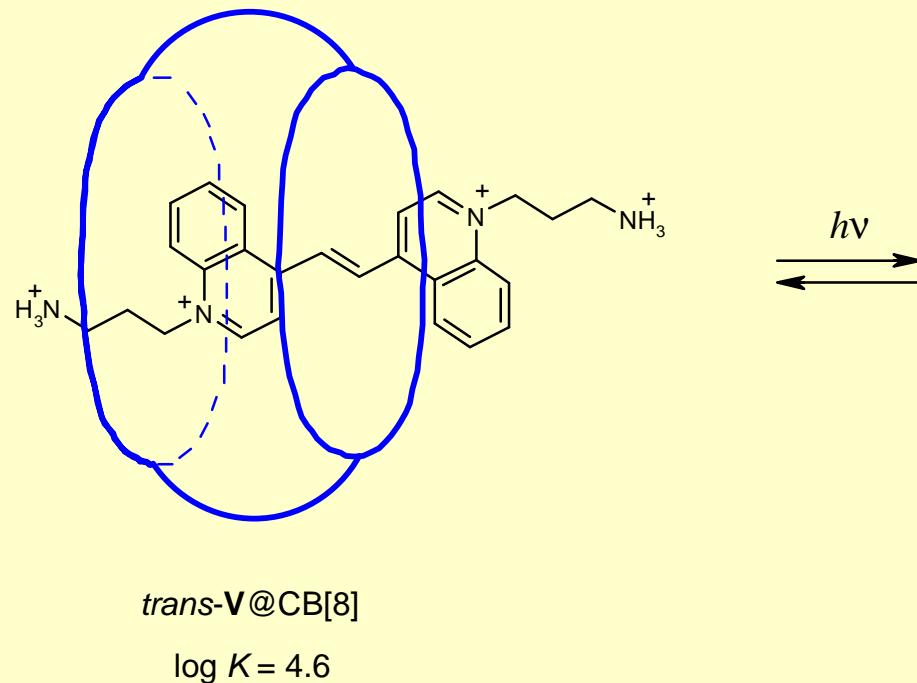
SD



SD@CB[7]

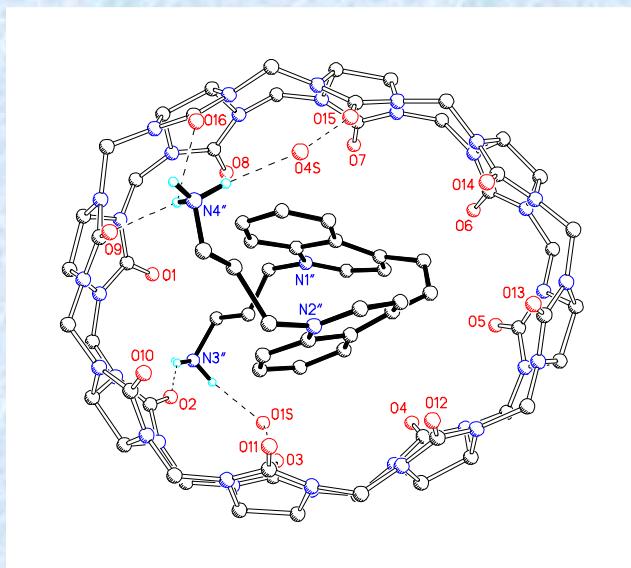
SD@CB[7] \*

# PHOTOCONTROLLED SUPRAMOLECULAR MACHINE

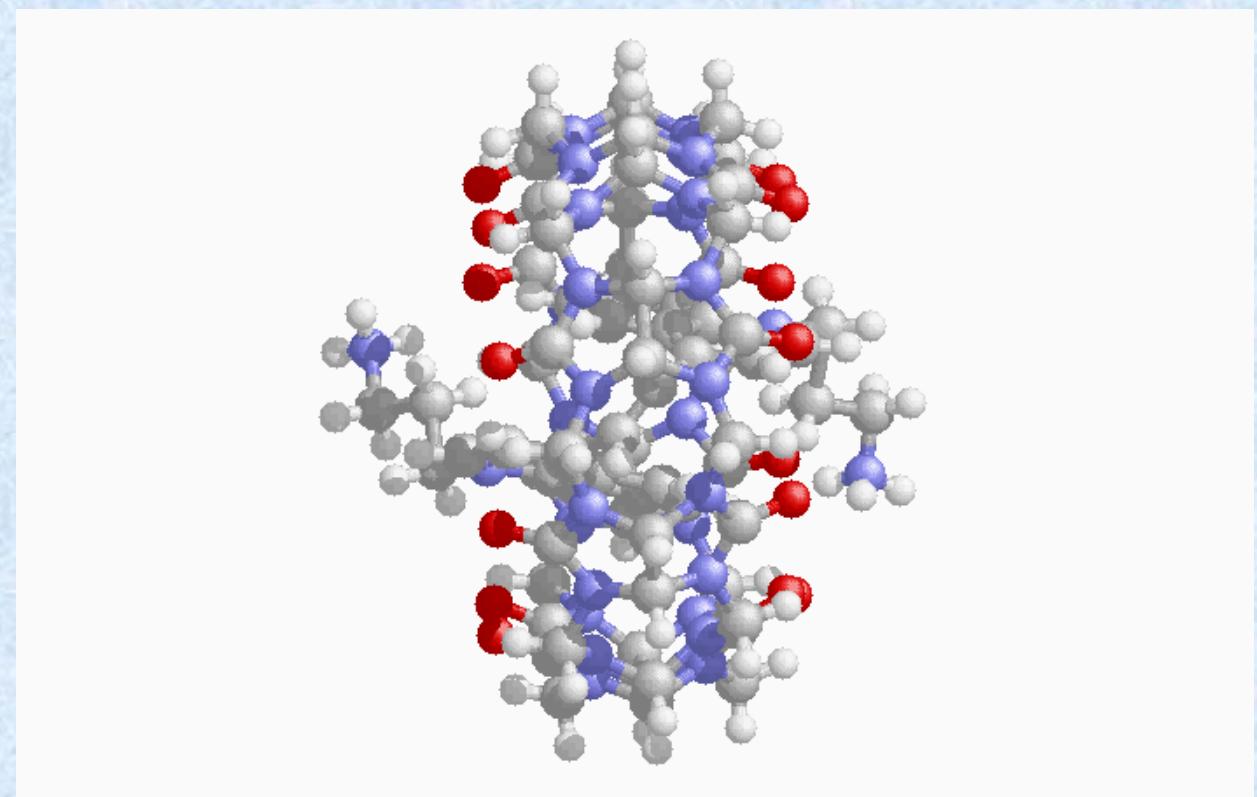


Pseudorotaxane complexes of cucurbiturils and unsaturated viologen analogues as the design of new-type photocontrolled supramolecular machines

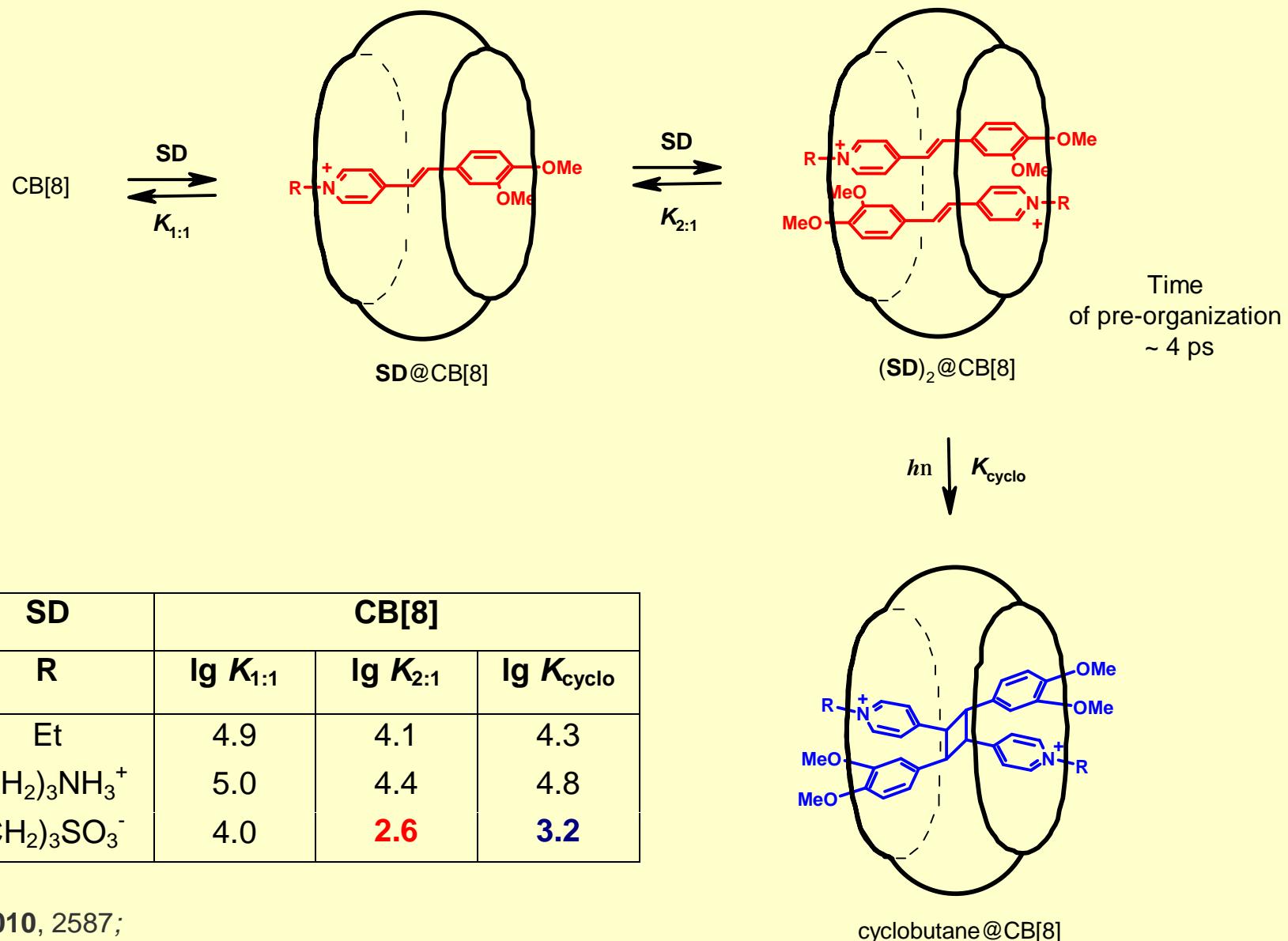
# *X-ray structure determination of photocontrolled supramolecular machine*



*cis*-V@CB[8]

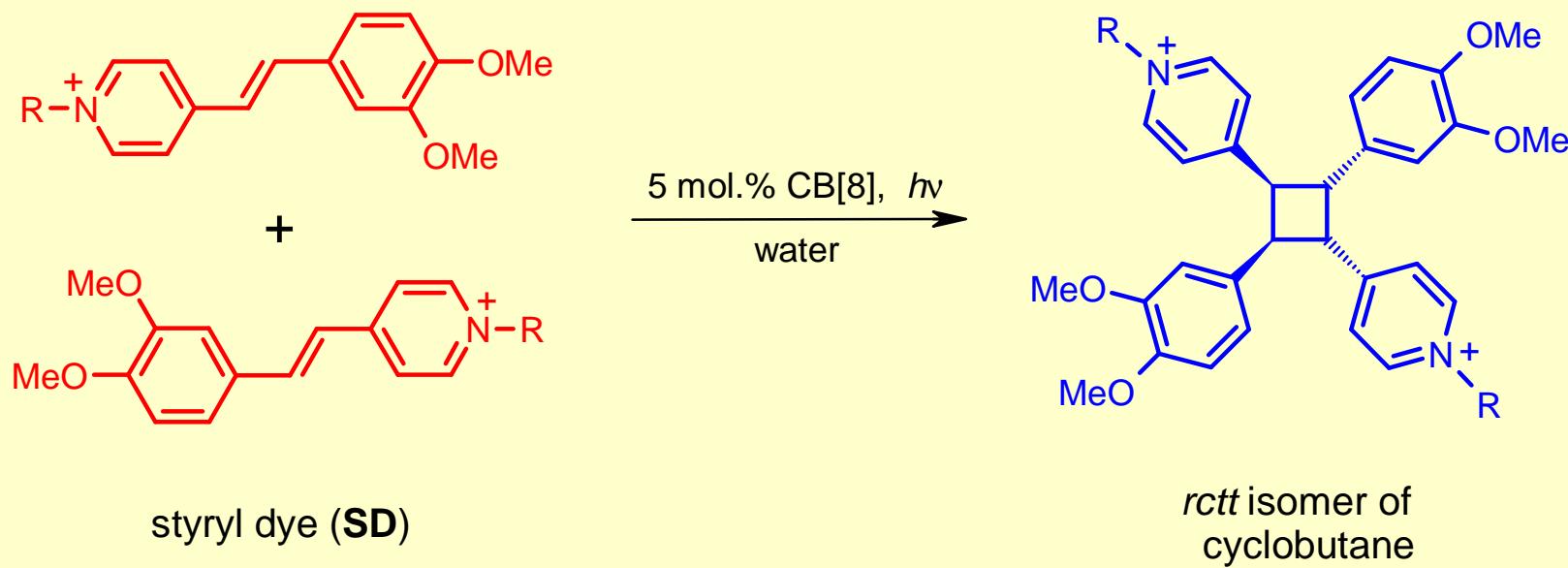


# PHOTOCONTROLLED SUPRAMOLECULAR MACHINES

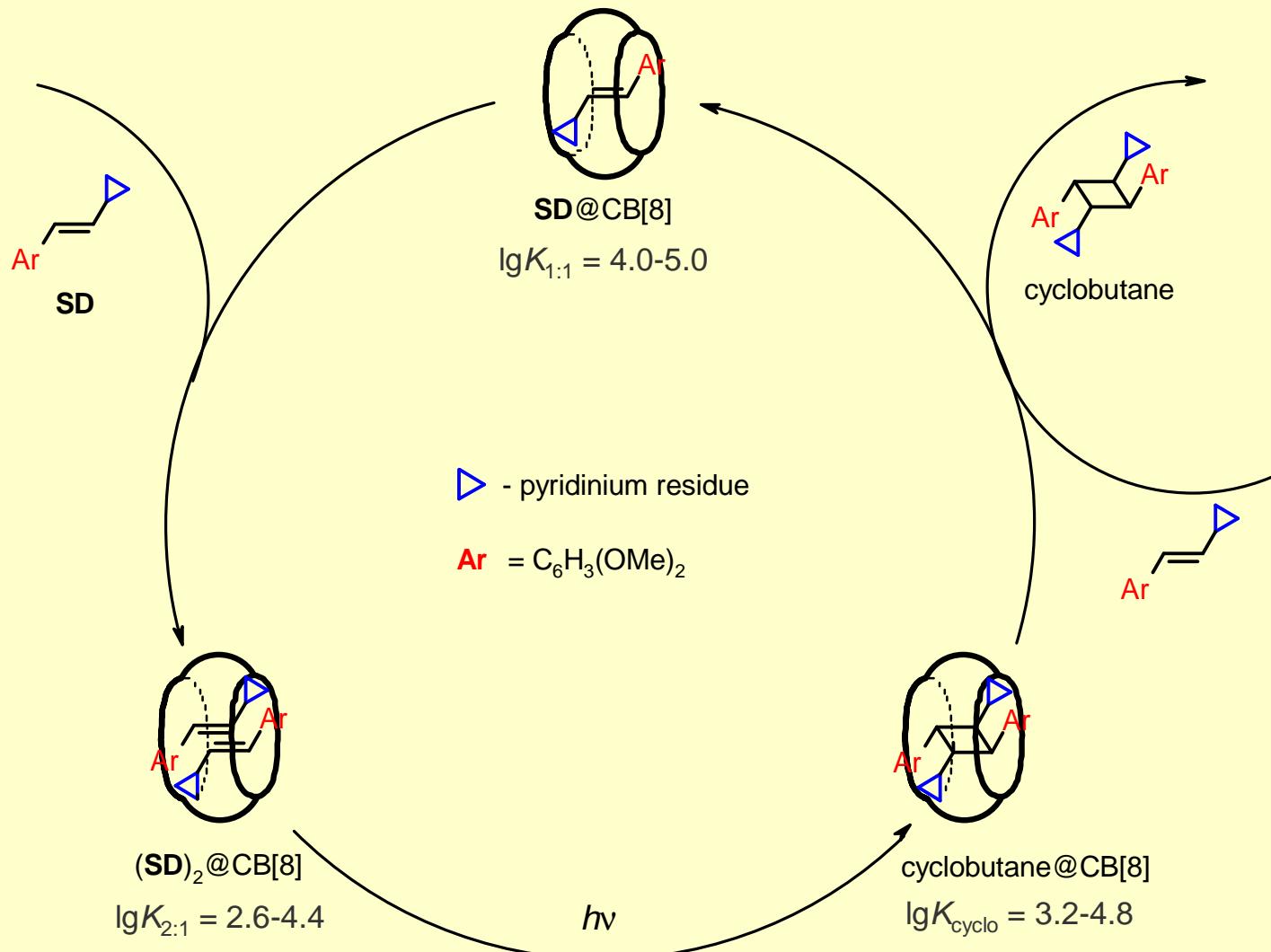


Eur. J. Org. Chem. 2010, 2587;  
 J. Phys. Chem. A. 2011, 115, 4505;  
 J. Photochem. Photobio. A. 2013, 253, 52;  
 Chem. Phys. Lett. 2016, 647, 157.

# PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL

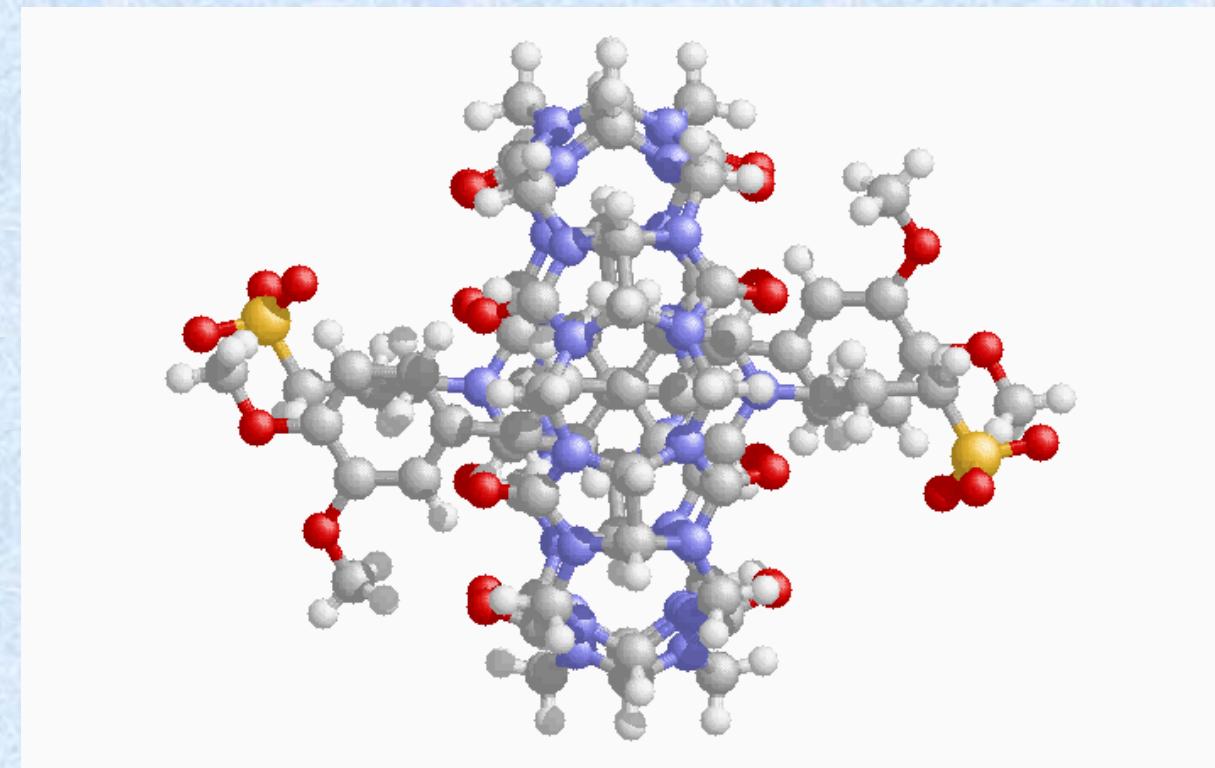
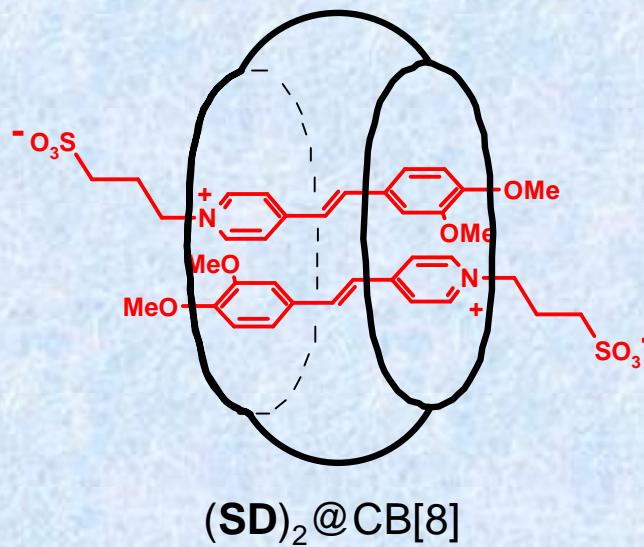


# PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL



Eur. J. Org. Chem., 2010, 2587;  
J. Phys. Chem. A., 2011, 115, 4505;  
High Energy Chem., 2014, 48, 253;  
Chem. Phys. Lett. 2017, 673, 99.

# *X-ray structure determination of photocontrolled supramolecular assembler*



# **It is possible to implement all main types of photoprocesses:**

- § **Fluorescence, excimer formation**
- § **Photodissociation**
- § **Photoisomerization**
- § **Photocycloaddition**
- § **photoelectrocyclization**
- § **charge-transfer complex formation,  
electron transfer**
- § **excitation transfer**
- § **TICT state**

Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

Ushakov E. N., Gromov S. P. et al. *Russ. Chem. Rev.* **2008**, 77, 39 (review);

Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

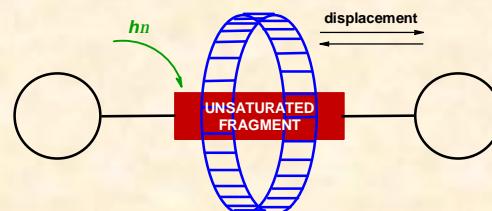
# Supramolecular meccano of photoactive supramolecular systems



A. Butlerov prize of RAS,  
State Prize of the Russian Federation

**Unique set of characteristics needed:**

- § Accessibility through organic synthesis.
- § Tendency for spontaneous organization into various supramolecular architectures.
- § The ability to undergo different types of photochemical transformations depending on the structure.
- § The feature of high-efficiency molecular photoswitching.



Gromov S. P. Russ. Chem. Bull. 2008, 57, 1325 (review);  
Gromov S. P. Rev. J. Chem. 2011, 1, 1 (review).

# Applied potential: new strategy for the design of materials for nanophotonics

Demonstrated by an example of design:

- § Photoswitchable supramolecular devices
- § Photocontrolled supramolecular machines
- § Supramolecular photoswitches
- § Optical chemosensor materials
- § Data optical recording and storage systems
- § Photochromic ionophores and photocontrolled membrane transport
- § Photoswitchable polymeric and LB films
- § Laser dyes

Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

Ushakov E. N., Gromov S. P. et al. *Russ. Chem. Rev.* **2008**, 77, 39 (review);

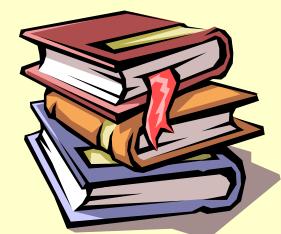
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

## ***Publications :***

**More than 320 publications in scientific journals and patents**

## ***Collaboration***

- Institute of Problems of Chemical Physics of RAS
- Kurnakov Institute of General and Inorganic Chemistry of RAS
- Lomonosov Moscow State University, Chemical Department
- Institute of Bioorganic Chemistry of RAS
- Lomonosov Moscow State Academy of Fine Chemical Technology
- Zelinsky Institute of Organic Chemistry of RAS
- University of Durham, Great Britain
- Max-Planck-Institut fur Biophysikalische Chemie, Germany
- am Engler-Bunte Institut der Universitat Karlsruhe, Germany
- University of Umea, Sweden
- Bogatsky Physicochemical Institute of NAS, Ukraine
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- The Florida State University, U.S.A.
- Universita' Degli Studi Di Bologna, Italy



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- Moscow Government (2003 - 2005)
- INTAS (1993 - 2005)
- CRDF (1996 - 2004)
- DFG (1996 - 2004)
- ISF (1993 - 1994)



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научный  
фонд





# Thank You

XIII International Conference “Solvation and  
complex formation in solutions”