РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

XX Mendeleev Congress on General and Applied Chemistry

Photoactive Supramolecular Systems Based on Unsaturated and Macrocyclic Compounds

Sergey P. Gromov

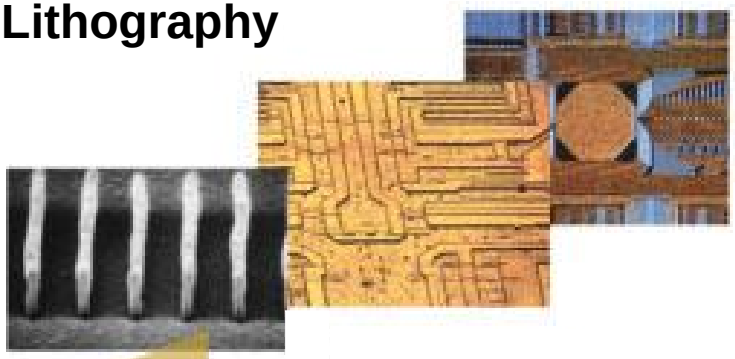
A. I. Vedernikov, E. N. Ushakov, M. V. Alfimov

http://suprachem.photonics.ru;
http://www.photonics.ru

NANOTECHNOLOGY "BOTTOM-UP"

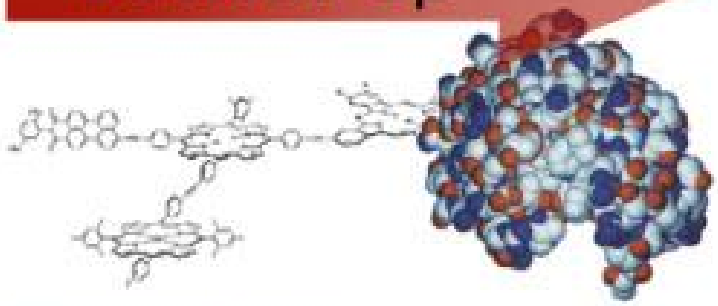
STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES

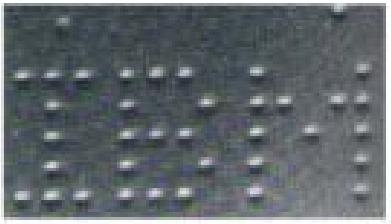
Lithography



Bottom-Up

Top-Down





Organic synthesis
Supramolecular Self-Assembly

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

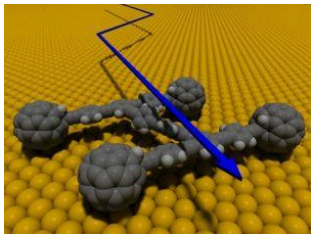
They can be used:

"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.

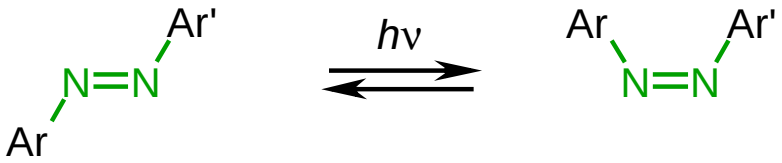
Critical technologies of the RF

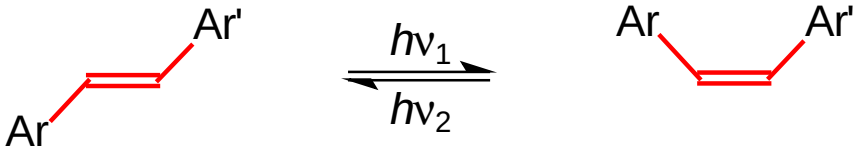
Means for control of supramolecular devices and machines

- **Photoswitching -** $h\nu$
- **Electrochemical switching -** e^-
- **Chemical switching -** H^+, M^{n+}
- **Thermal switching -** Δ



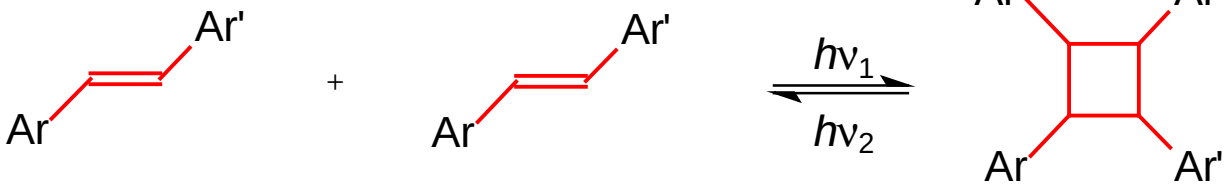
PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS





trans-isomer

cis-isomer



cyclobutane

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).

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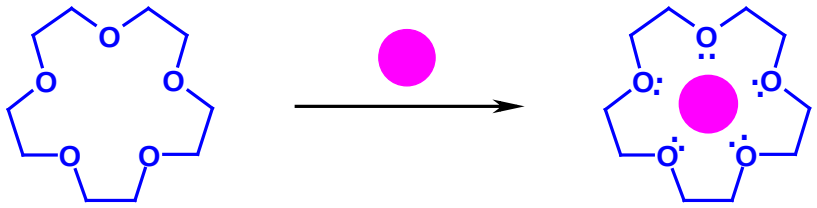
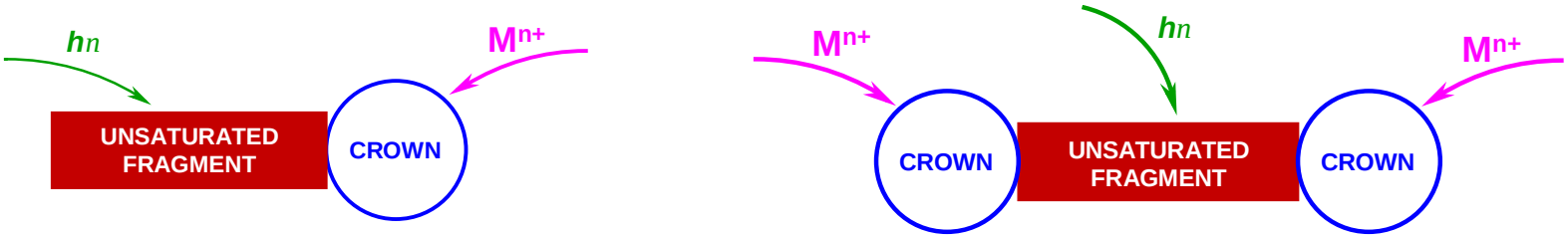
PHOTOCHEMISTRY CENTER

PHOTOSWITCHABLE SUPRAMOLECULAR DEVICES BASED ON UNSATURATED AND CROWN COMPOUNDS



- metal cation



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).

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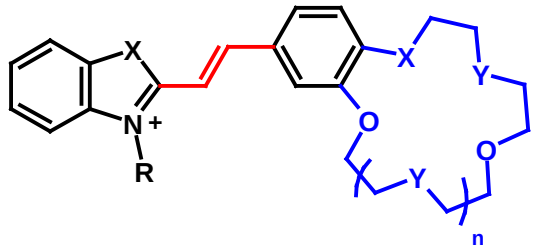
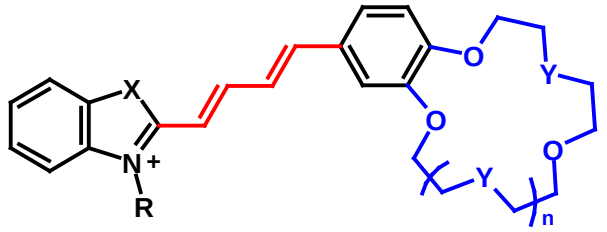
PHOTOCHEMISTRY CENTER

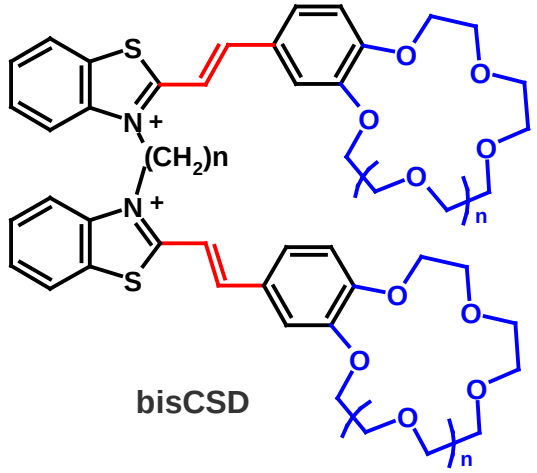
Crown-containing unsaturated compounds



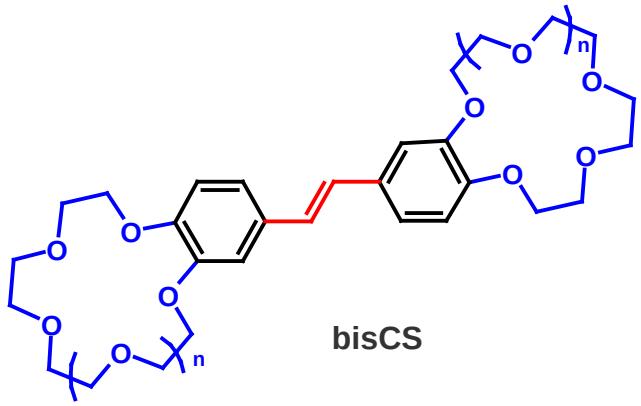
CSD



CBD



bisCSD

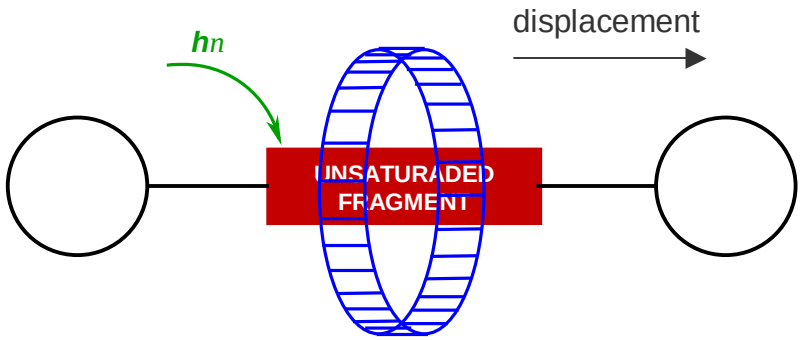


bisCS

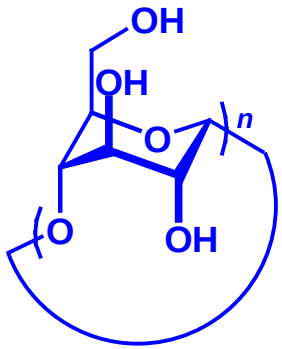
n = 1, 2

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, cyclodextrins and cucurbiturils

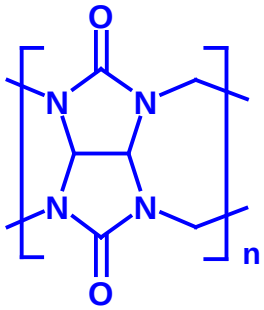


photocontrolled supramolecular machine



cyclodextrins

n = 6-8



cucurbiturils

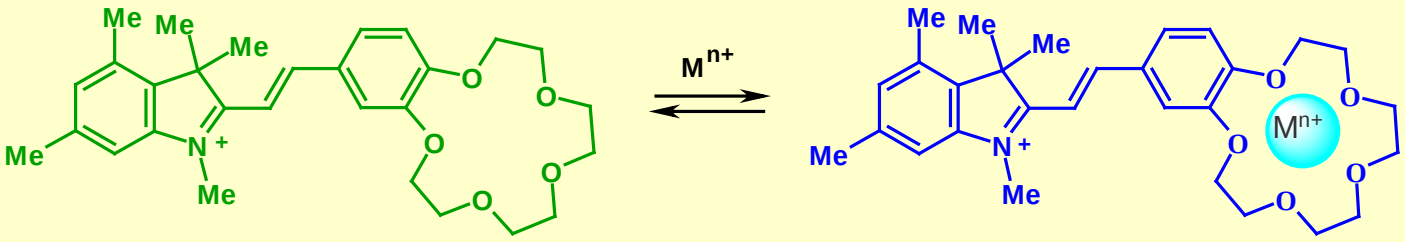
Gromov S. P. *Russ. Chem. Bull*. **2008**, *57*, 1325 (review);
Gromov S. P. *Rev. J. Chem.* **2011**, *1*, 1 (review)
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, *84*, 787 (review).

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

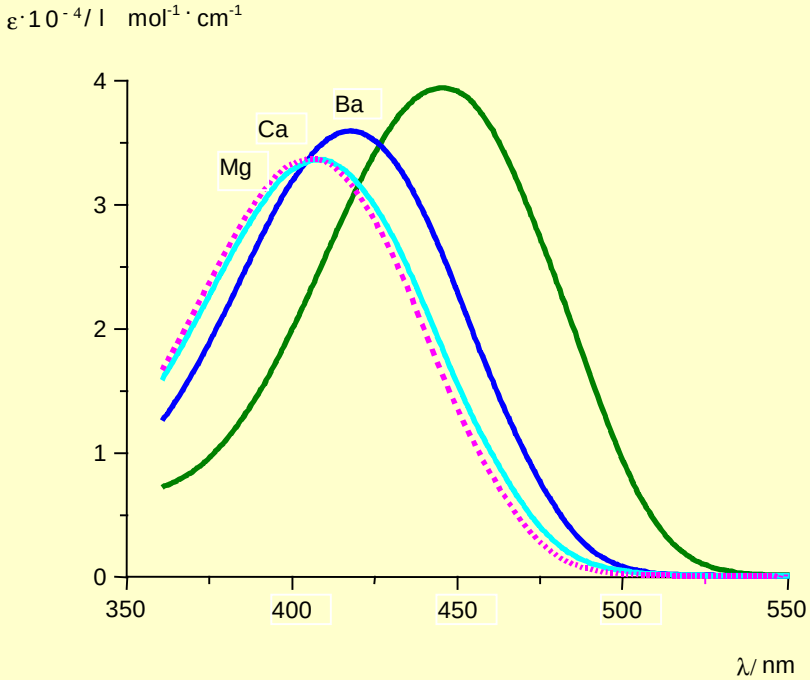
Part I

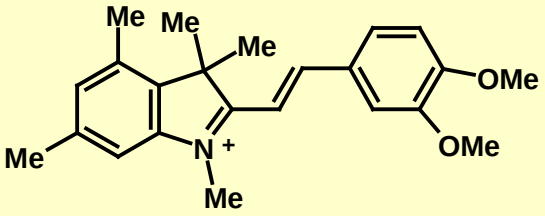
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Complex formation



trans-isomer





Dokl. Chem. **1990**, *314*, 279;
Ushakov E. N., Alfimov M. V., Gromov S. P. *Macroheterocycles.* **2010**, *3*, 189 (review)
J. Org. Chem. **2013**, *78*, 9834.

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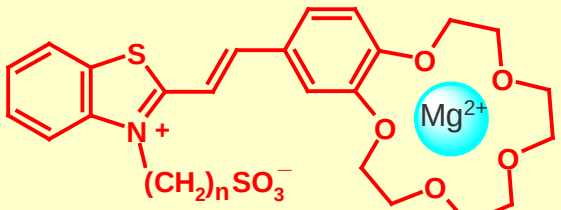
Photoswitchable supramolecular devices

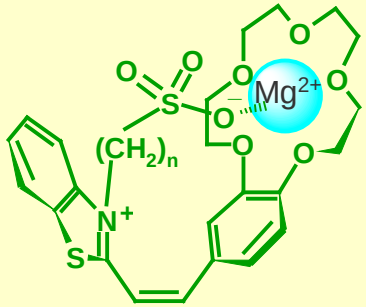


(*trans*-**L**)·Mg^{2+}

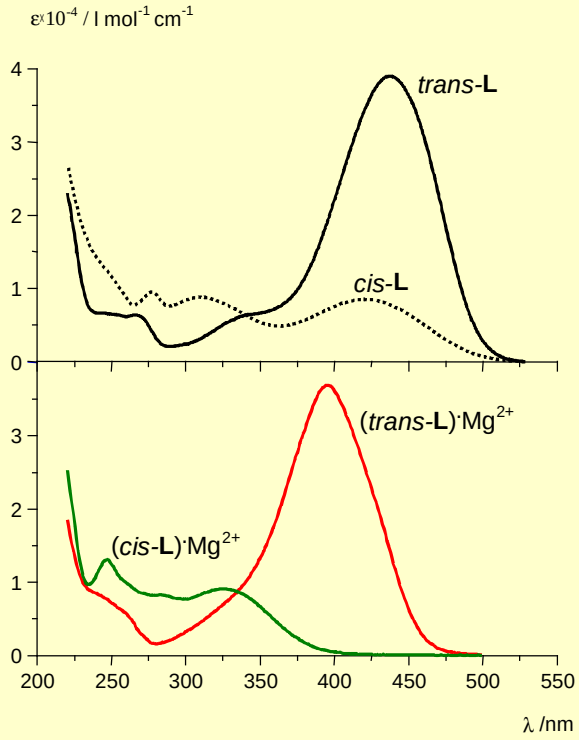
$h\nu_1$ (436 nm)

$h\nu_2$

$j_{tc} \sim 0.5$



anion-“capped”
(*cis*-**L**)·Mg^{2+}



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.

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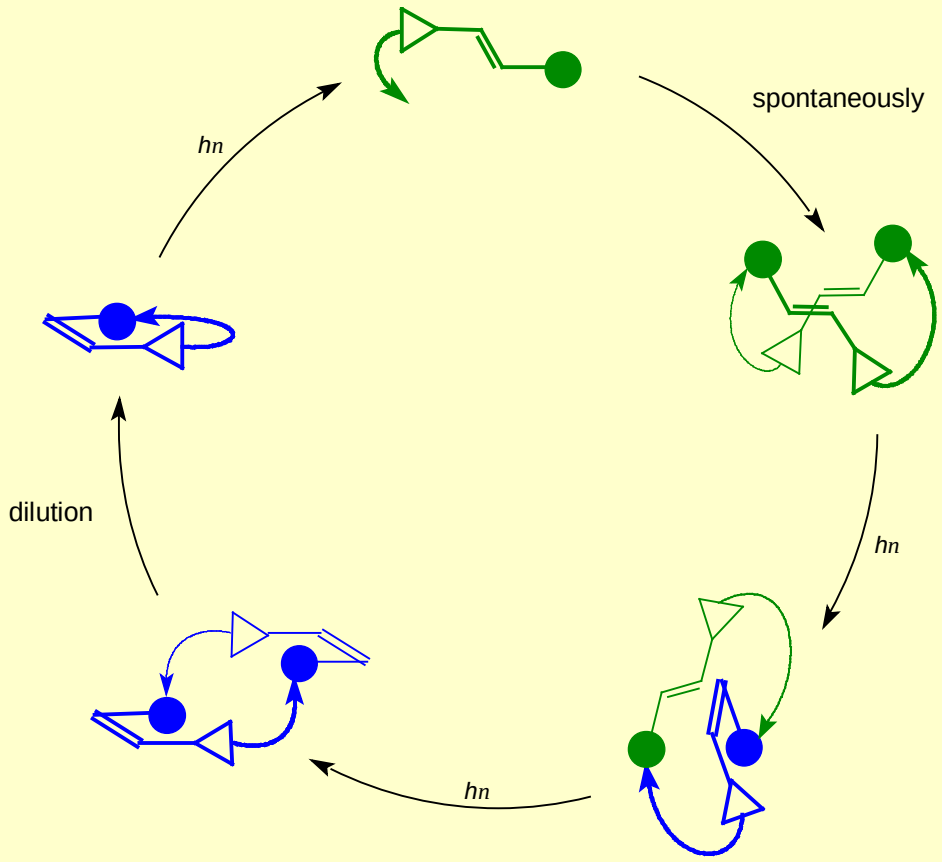
PHOTOCHEMISTRY CENTER

Photocycle of crown-containing styryl dyes



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

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

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

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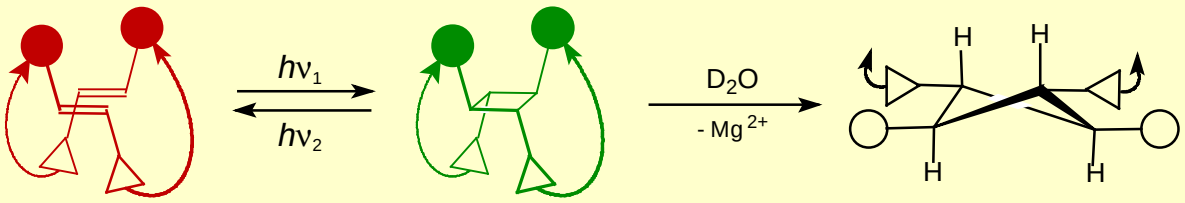
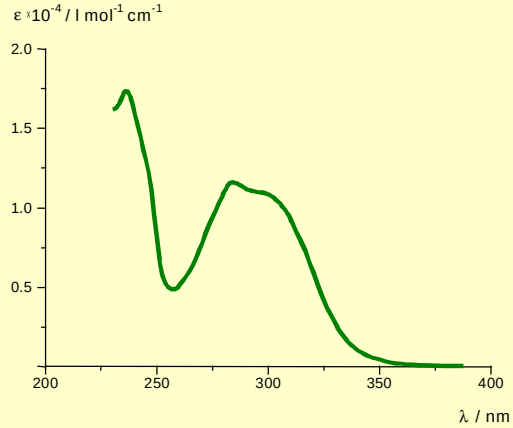
PHOTOCHEMISTRY CENTER

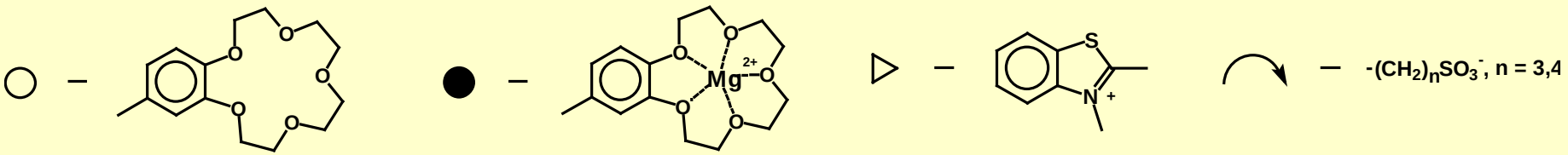
Photoswitchable supramolecular devices



[2+2]- Photocycloaddition of CSD

C_L, /mol · 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;
Изв. АН. Сер. хим. **1993**, *42*, 1449;
J. Chem. Soc., Perkin Trans. 2. **1999**, 601;
J. Org. Chem. **2003**, *68*, 6115.

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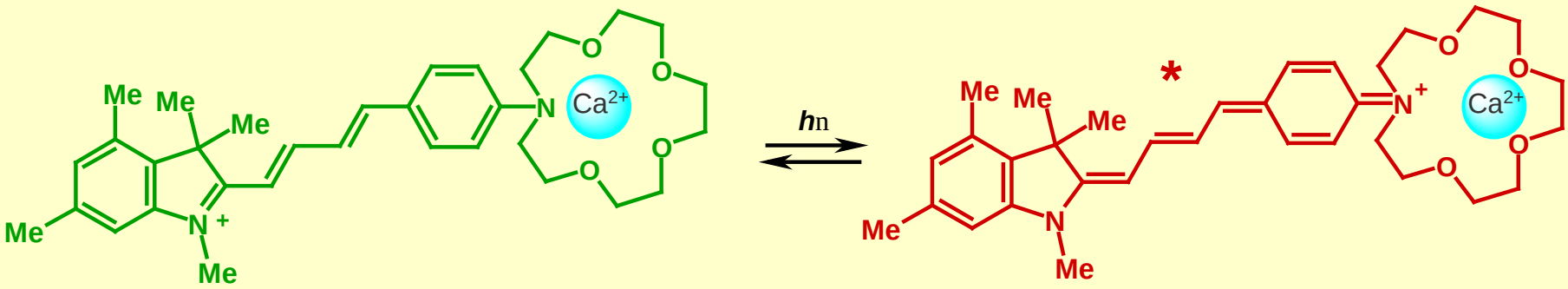
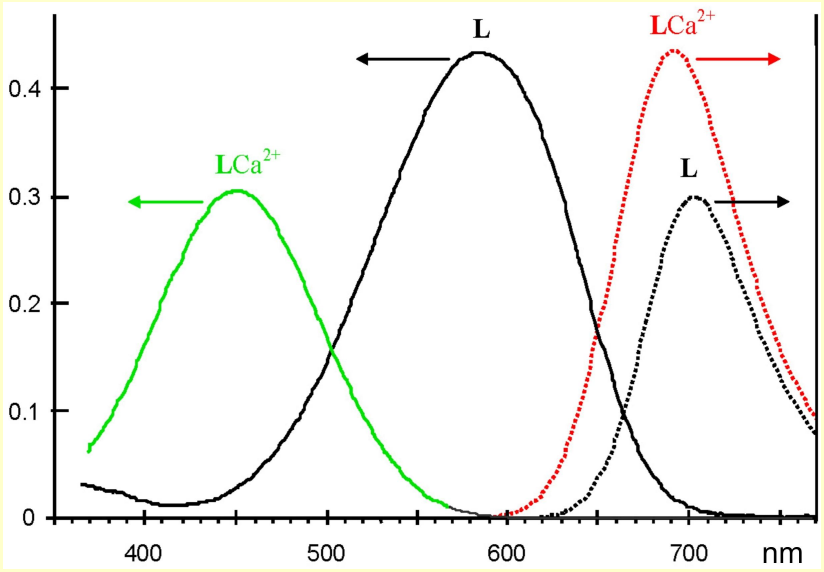
Photoswitchable supramolecular device



Photoinduced recoordination reaction



J. Fluor. **1999**, *9*, 33;
Helv. Chim. Acta **2002**, *85*, 60;
Rusalov M. V., Gromov S. P. et al. *Russ. Chem. Rev.* **2010**, *79*, 1193 (review);
Photochem. Photobio. Sci. **2011**, *10*, 15.

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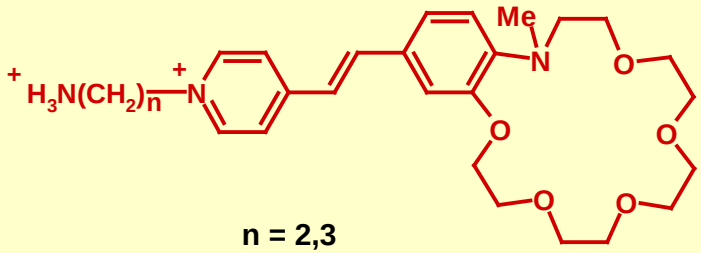
PHOTOCHEMISTRY CENTER

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

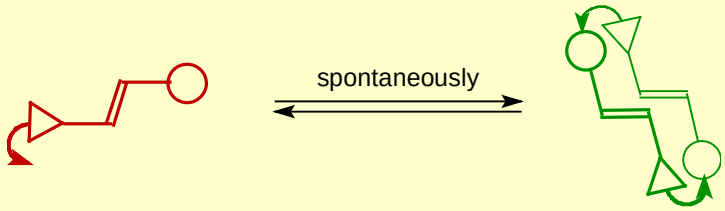
Part II

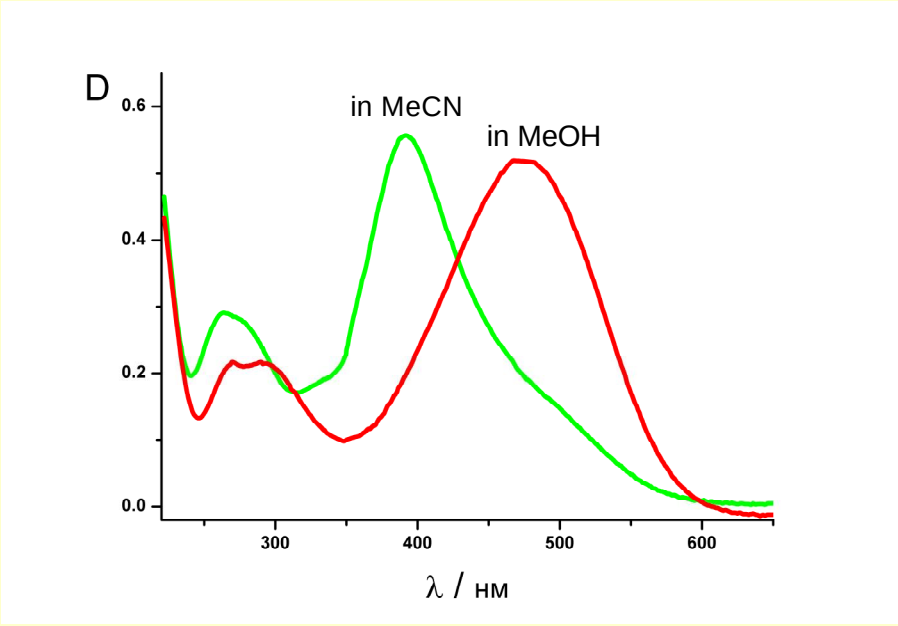
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Dimerization of CSD



n = 2,3





in MeCN in MeOH

RF patent 2278134 **2006**;
J. Org. Chem. **2014**, *79*, 11416;
J. Phys. Chem. A **2015**, *119*, 13025;
New J. Chem. **2016**, *40*, 7542.

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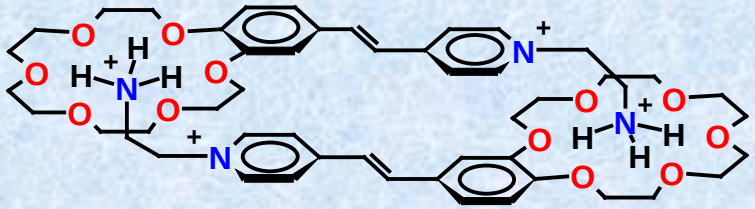
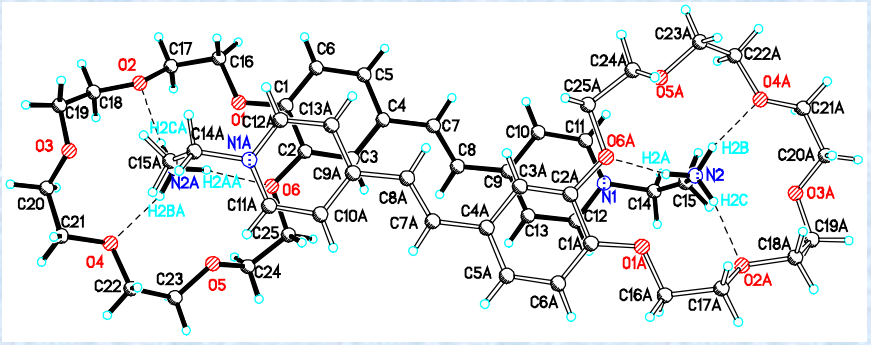
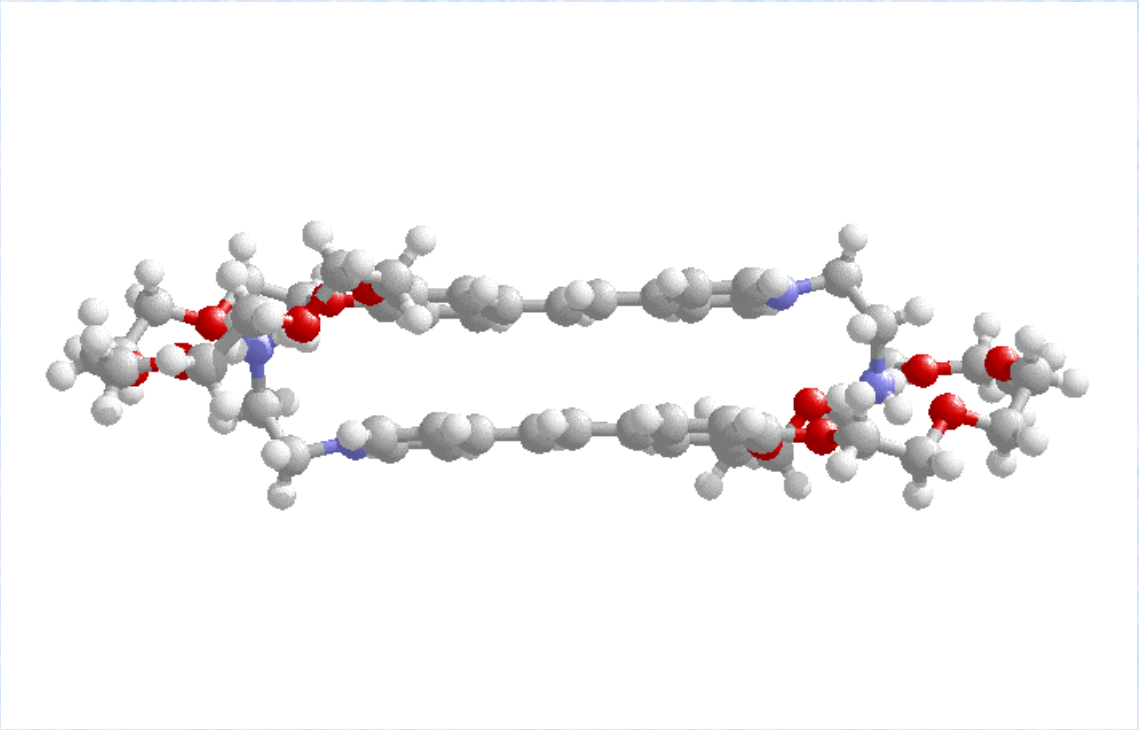
PHOTOCHEMISTRY CENTER

X-ray structure determination of dimeric compex



syn-"head-to-tail" dimeric complex





Russ. Chem. Bull. **2009**, *58*, 1211;
J. Org. Chem. **2014**, *79*, 11416.

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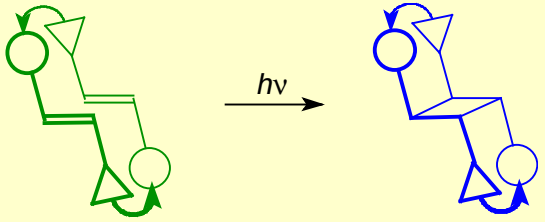
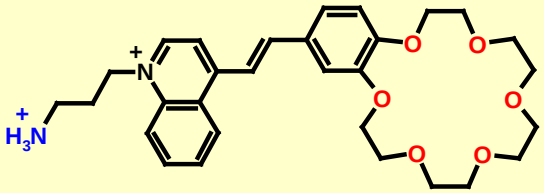
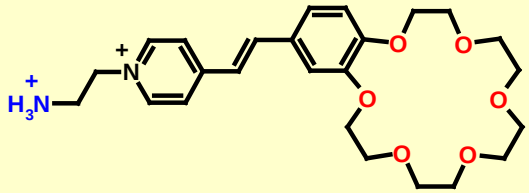
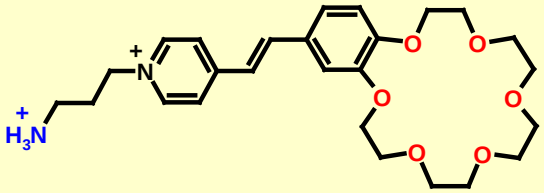
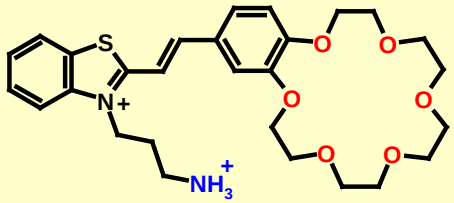
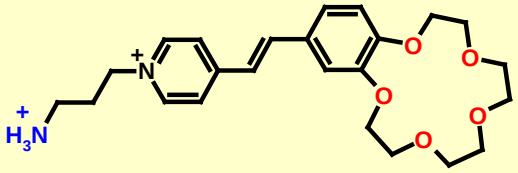
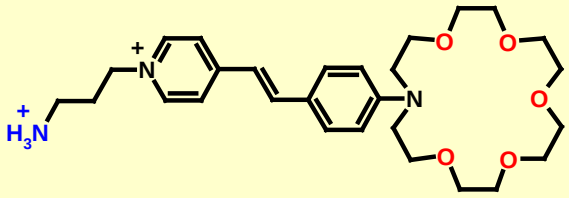
[2+2]-Photocycloaddition of CSD



F_{PCA} up to 0.38

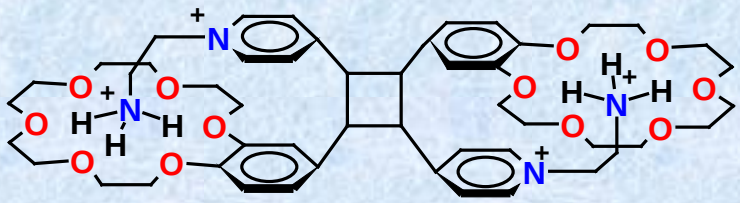
syn-"head-to-tail" *syn*-isomer

	Yield, %		Yield, %
	100		33
	100		0
	40		0

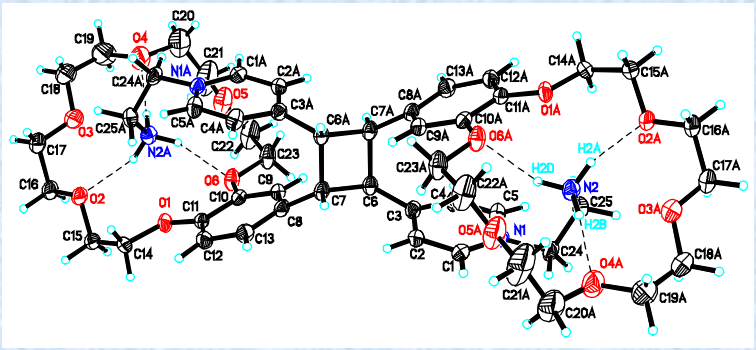
In MeCN, irradiation time, 4 h

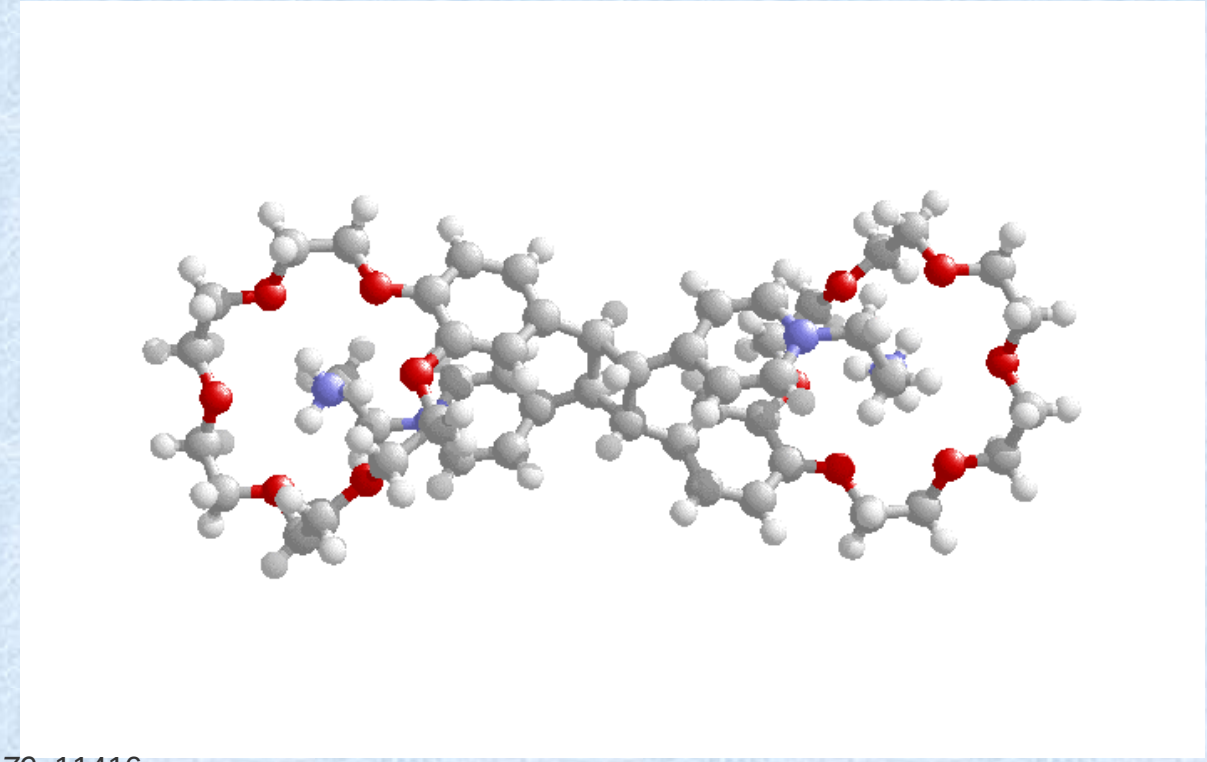
RF patent 2278134 **2006**;
Russ. Chem. Bull. **2009**, *58*, 1211;
J. Org. Chem. **2014**, *79*, 11416;
J. Phys. Chem. A **2015**, *119*, 13025.

X-ray structure determination of cyclobutane



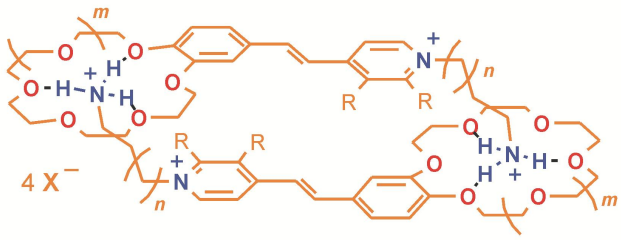
syn-cyclobutane





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

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

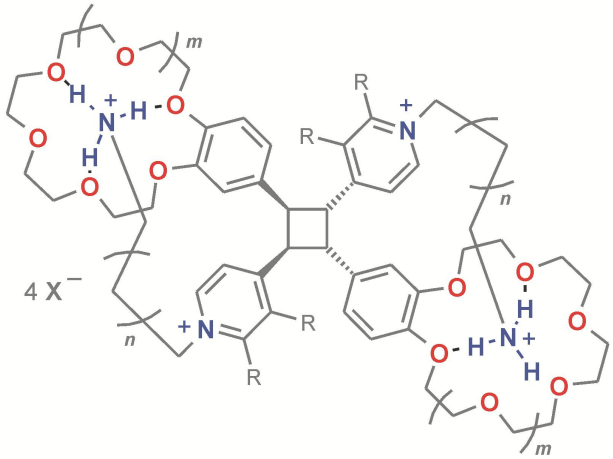


R = H, R + R = benzo; *n, m* = 0, 1

dimeric complexes of styryl dyes

$h\nu_1$ ⇄ $h\nu_2$

solution or solid phase



rctt isomers of cyclobutane derivatives

dye

cyclobutane

(X = ClO_4;
R = H, *n* = *m* = 1

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

J. Org. Chem. **2014**, *79*, 11416;
J. Phys. Chem. A **2015**, *119*, 13025.

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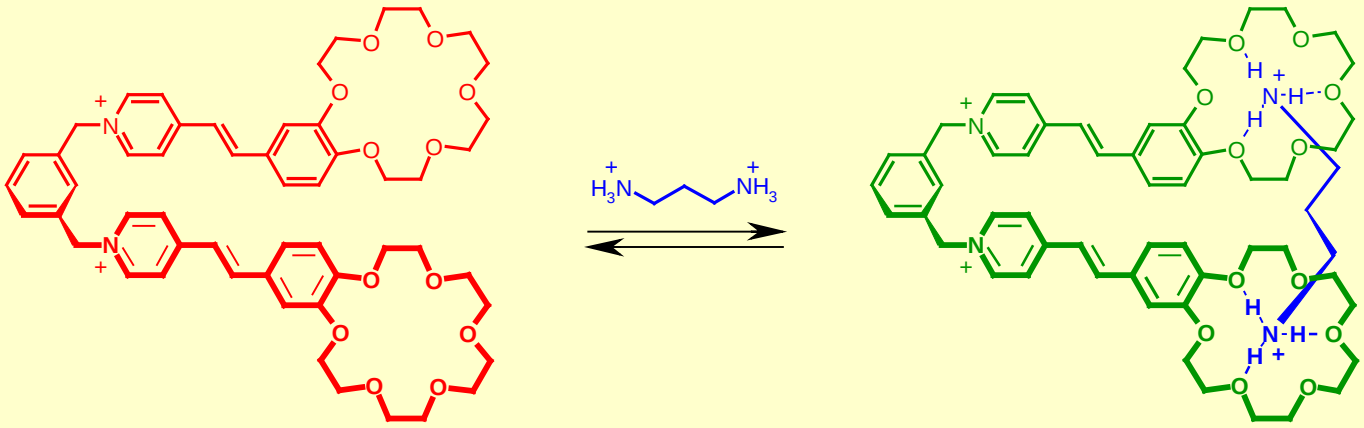
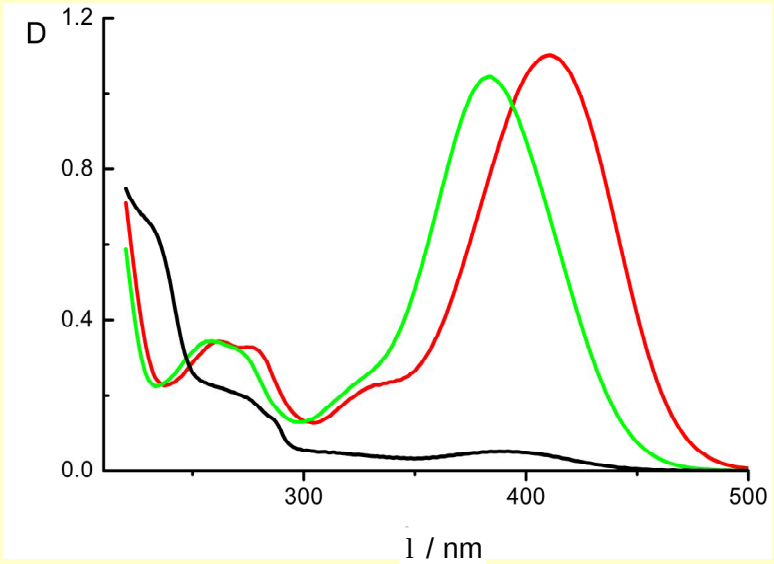
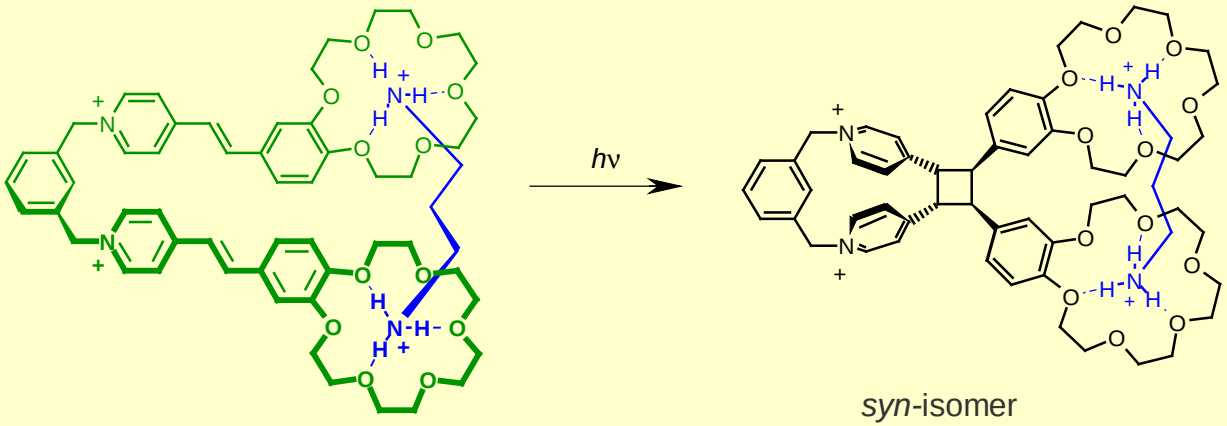
FORMATION OF PSEUDOSANDWICH COMPLEXES



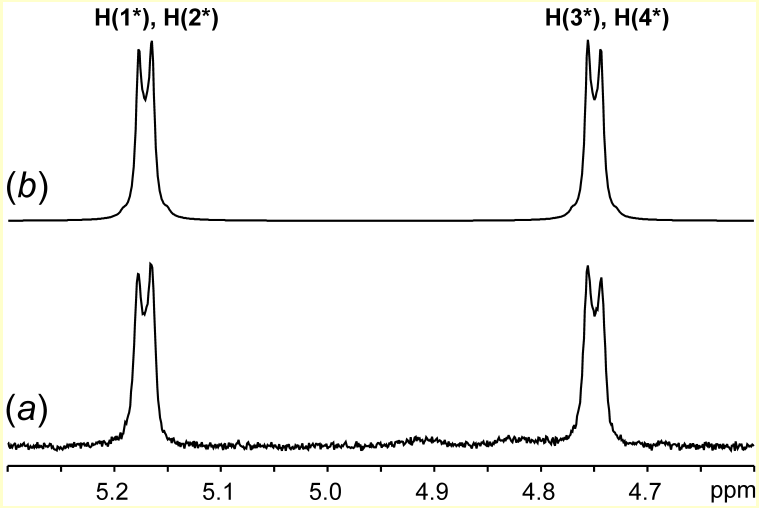


Mendeleev Commun. **2005**, *15*, 173.

Intramolecular [2+2]-photocycloaddition of bisCSD



syn-isomer



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

Mendeleev Commun. **2005**, *15*, 173.

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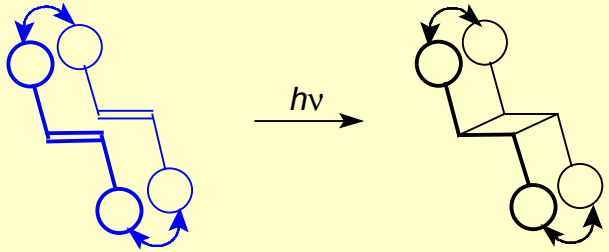
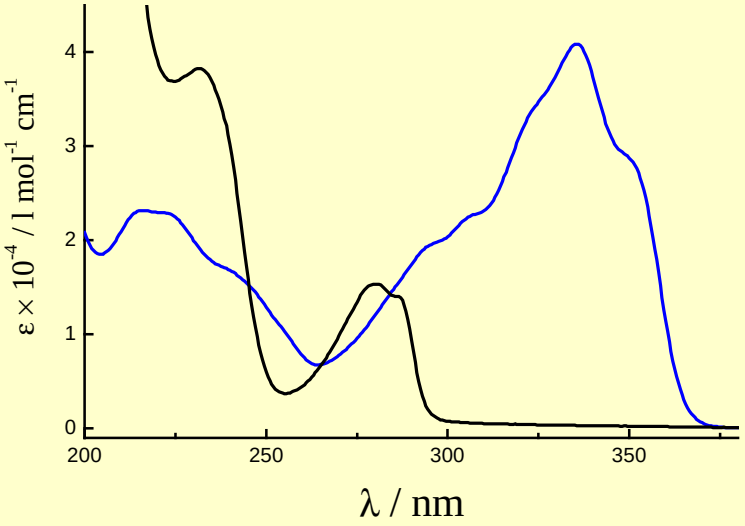
Formation of bispseudosandwich complexes and [2+2]-Photocycloaddition

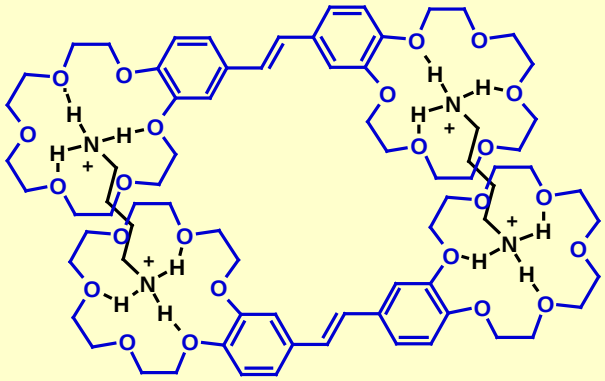


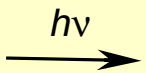
syn-complex *syn-isomer*

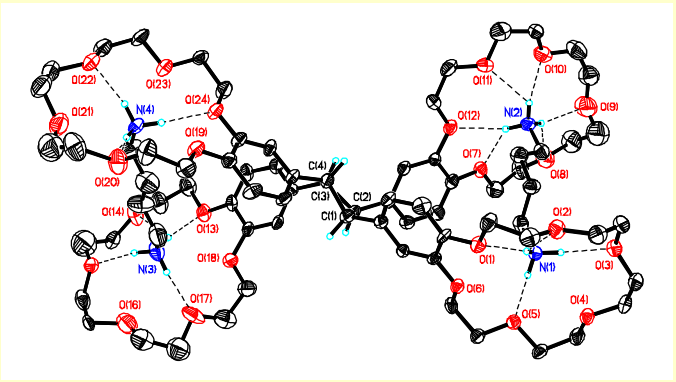
F_{PCA} up to 0.27

– $H_3N^+(CH_2)_nNH_3^+$ 2 ClO_4^-, *n* = 2-10, 12









syn-isomer

Russ. Chem. Bull. **2009**, *58*, 108;
New. J. Chem. **2011**, *35*, 724.

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PHOTOCHEMISTRY CENTER

Self-assembly

of photocontrolled supramolecular machines

Part III

THE RUSSIAN ACADEMY OF SCIENCES
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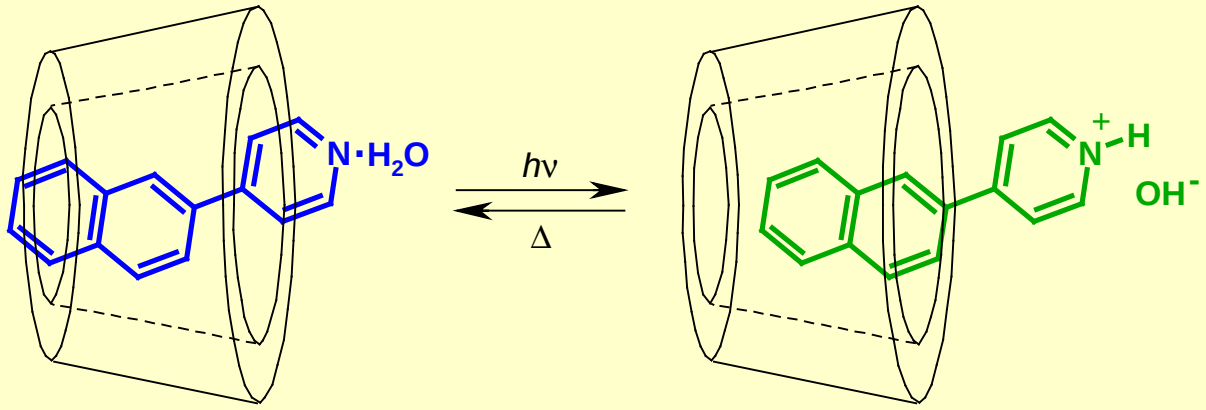
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



1·H_2O@HP-β-CD

lg*K* = 1.9

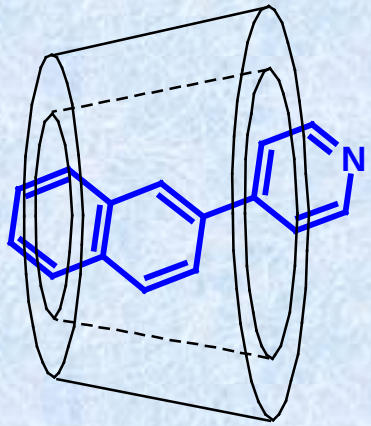
1H^+OH^-@HP-β-CD

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

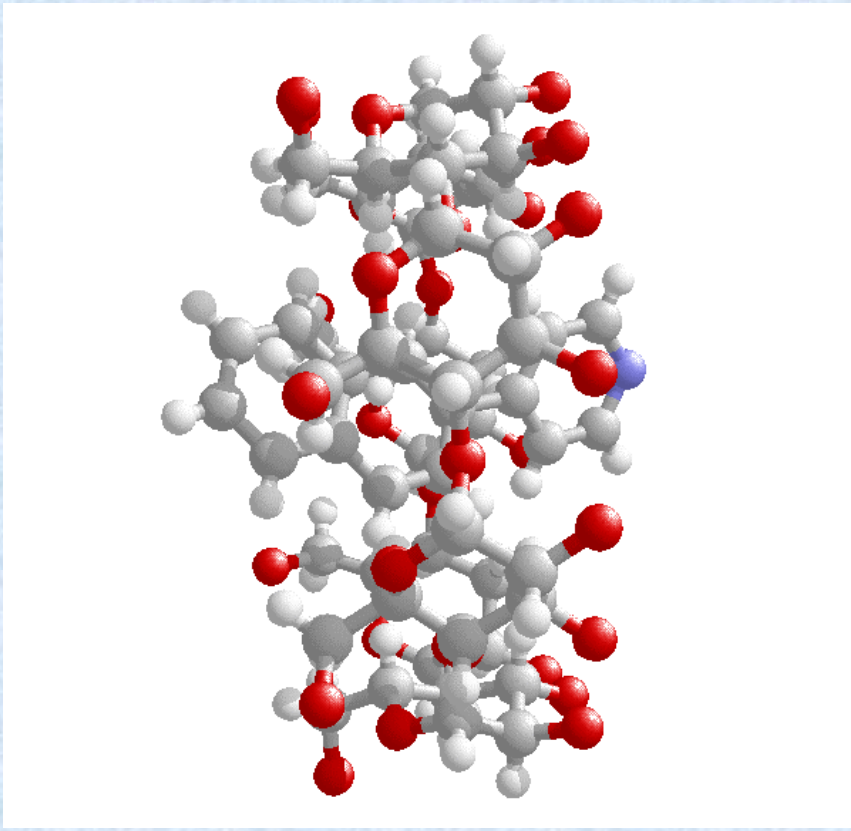
Russ. Chem. Bull. **2004**, *53*, 2525;
J. Photochem. Photobiol. **2011**, *217*, 87;
Russ. Chem. Bull. **2013**, *62*, 2150.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

X-ray structure determination of photocontrolled supramolecular machine

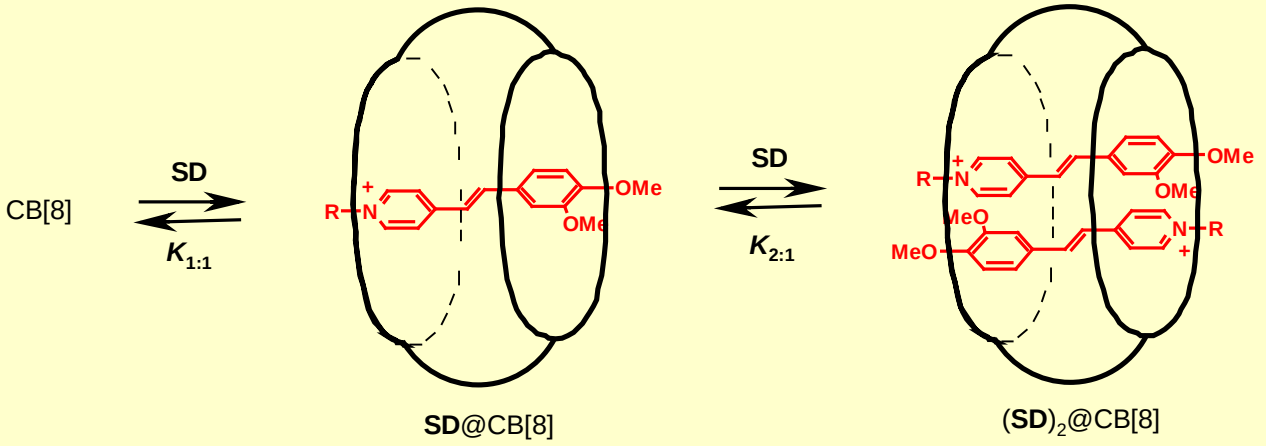


1@β-CD



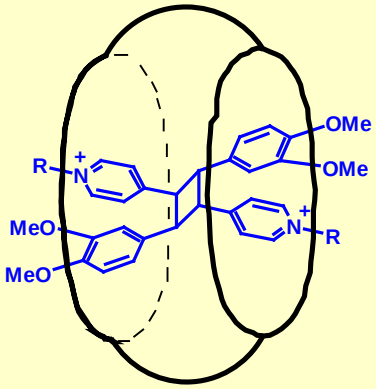
Russ. Chem. Bull. **2004**, *53*, 2525;
J. Photochem. Photobiol. **2011**, *217*, 87;
Russ. Chem. Bull. **2013**, *62*, 2150.

PHOTOCONTROLLED SUPRAMOLECULAR MACHINES



SD@CB[8]

(**SD**)$_2$@CB[8]



cyclobutane@CB[8]

SD	**CB[8]**		
R	**lg $K_{1:1}$**	**lg $K_{2:1}$**	**lg K_{cyclo}**
Et	4.9	4.1	4.3
$(CH_2)_3NH_3^+$	5.0	4.4	4.8
$(CH_2)_3SO_3^-$	4.0	**2.6**	**3.2**

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

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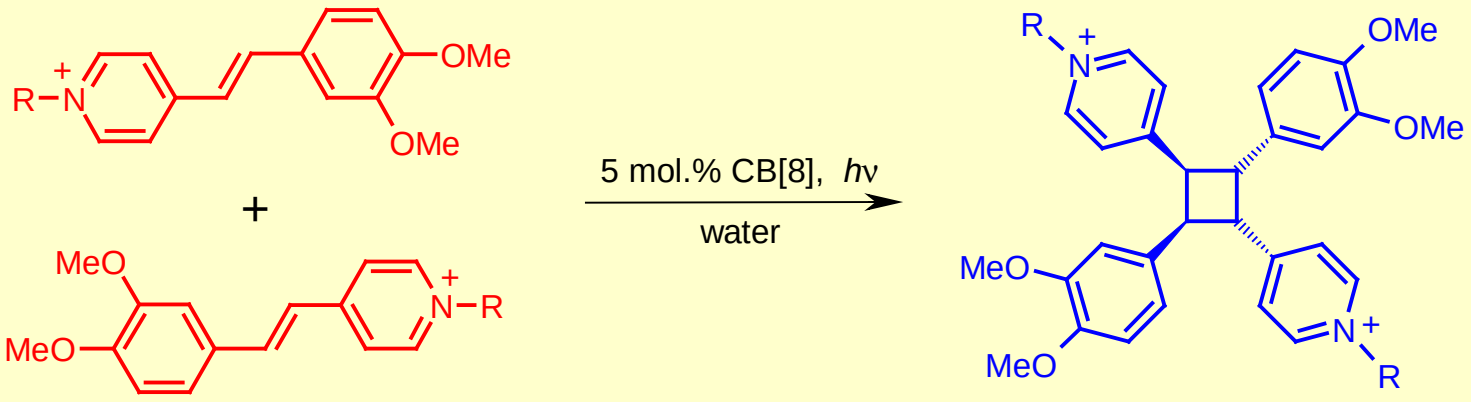
PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL

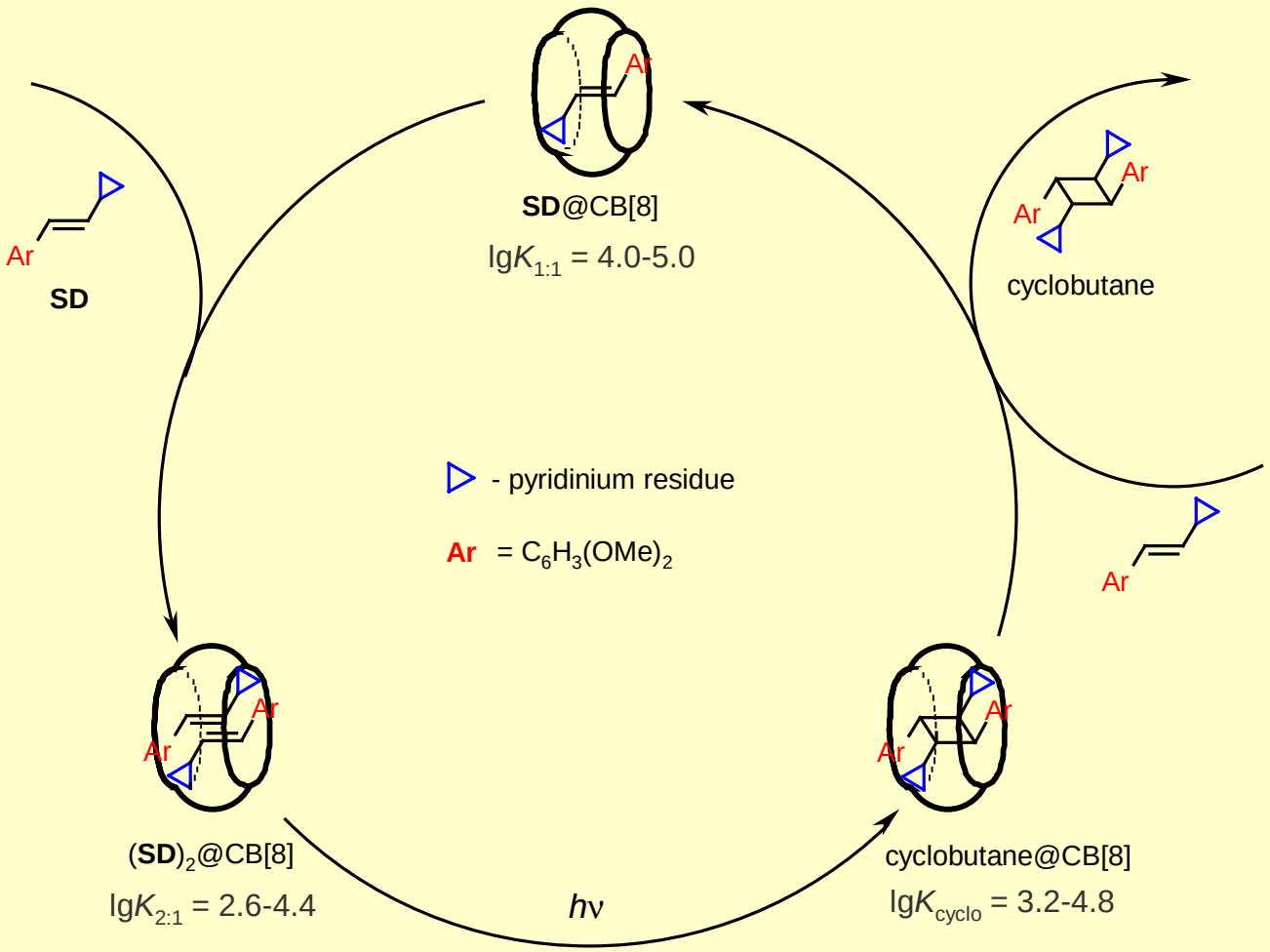


styryl dye (**SD**)

rctt-isomer of cyclobutane

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

PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL



Eur. J. Org. Chem., **2010**, 2587;
J. Phys. Chem. A., **2011**, *115*, 4505;
J. Photochem. Photobiol. A, **2013**, *253*, 52;
High Energy Chem., **2014**, *48*, 253.

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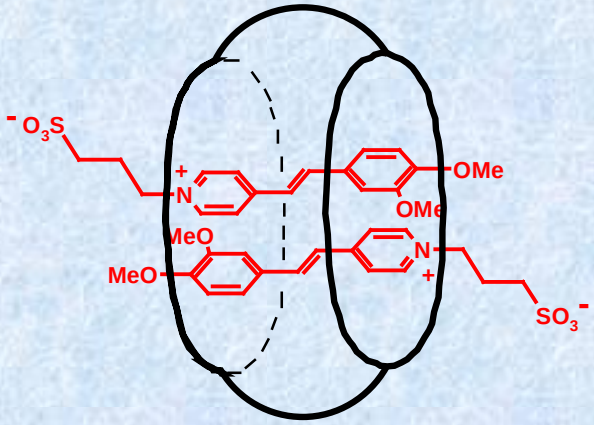
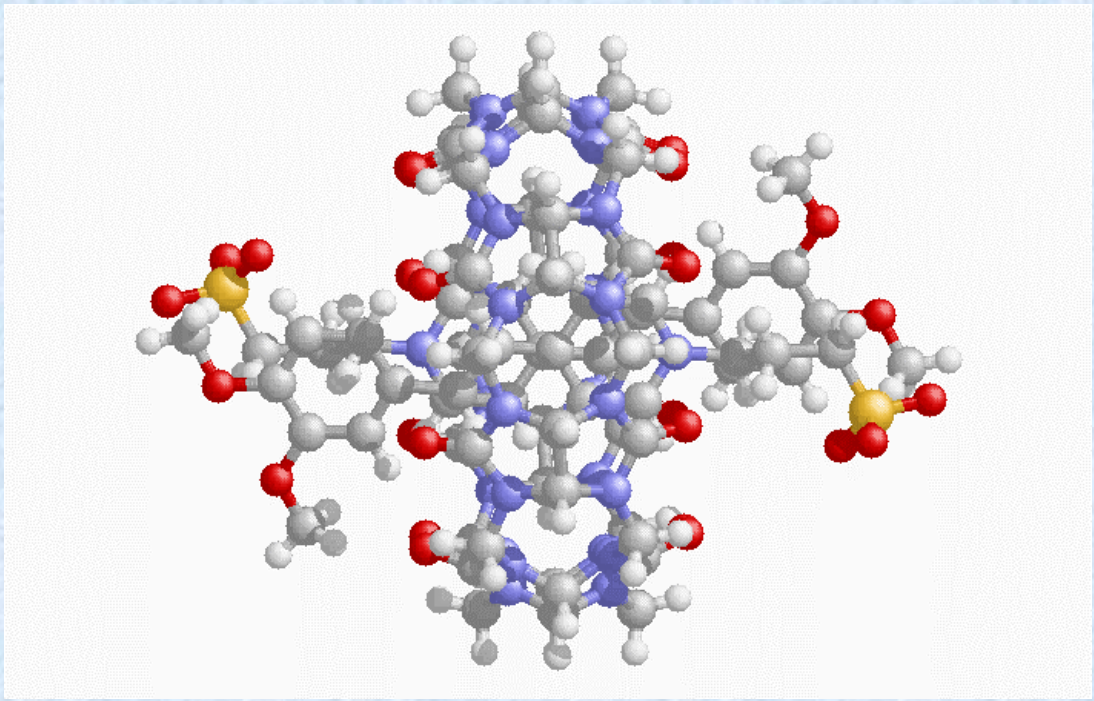
X-ray structure determination of photocontrolled supramolecular assembler



(**SD**)$_2$@CB[8]



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

Self-assembly
to photoactive LB-monolayers
and crystal engineering

Часть IV

THE RUSSIAN ACADEMY OF SCIENCES
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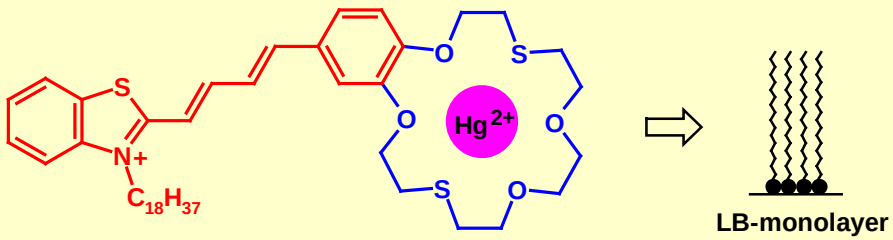
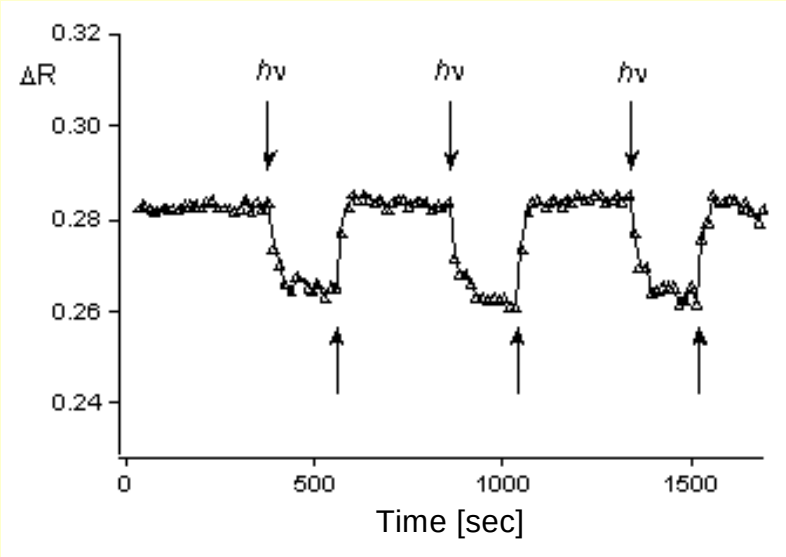
MONOLAYERS OF IONSELECTIVE BUTADIENYL DYE





The dye monolayer upon photoactivation
on the 1 mM solutions of $Hg(ClO_4)_2$

New. J. Chem. **2002**, *26*, 543;
Langmuir **2006**, *22*, 1571.

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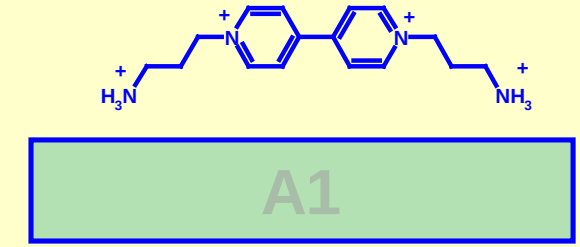
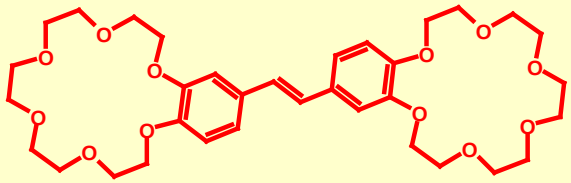
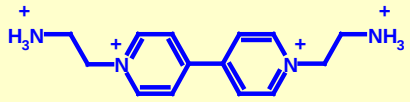
CRYSTAL ENGINEERING



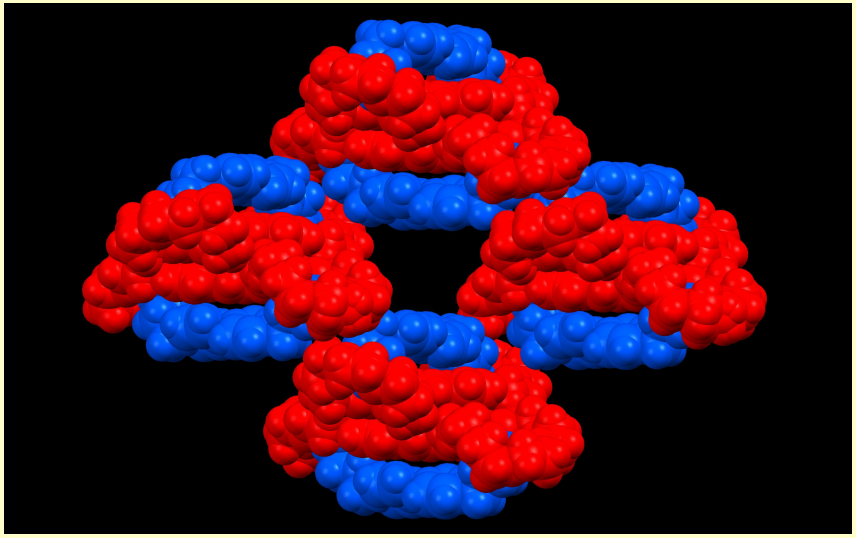
A1

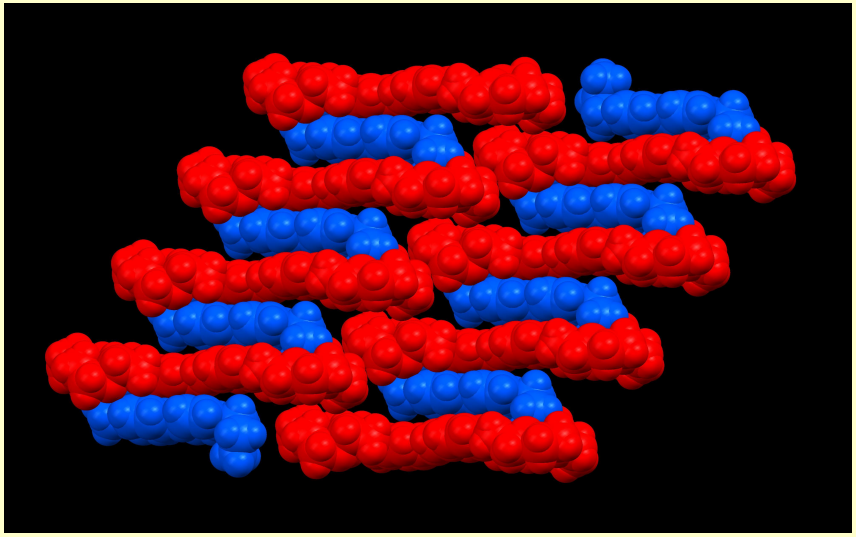


D



A2





New. J. Chem. **2007**, *31*, 980;
CrystEngComm. **2015**, *17*, 4584.

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It is possible to implement all main types of photoprocesses:

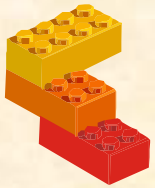
- Fluorescence, excimer formation
- Photodissociation
- Photoisomerization
- Photocycloaddition
- photoelectrocyclization
- charge-transfer complex formation, electron transfer
- excitation transfer
- TICT state

Gromov S. P. *Russ. Chem. Bull*. **2008**, *57*, 1325 (review);
Ushakov E. N., Alfimov M. V., Gromov S. P. *Russ. Chem. Rev.* **2008**, *77*, 39 (review);
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, *84,* 787 (review).

Molecular meccano

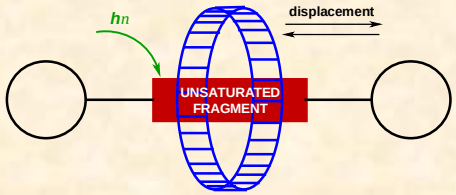
of photoactive supramolecular systems

Gromov S. P., Alexander Butlerov prize of RAS



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).

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Applied potential:

new strategy for the design of materials for nanophotonics

Demonstrated by an example of design:

- **Optical chemosensor materials**
- **Data optical recording and storage systems**
- **Supramolecular switches**
- **Photoswitchable supramolecular devices**
- **Photocontrolled supramolecular machines**
- **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).

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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
- North Carolina State University, U.S.A.
- The Florida State University, U.S.A.
- Universita' Degli Studi Di Bologna, Italy

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- RFBR (1994-2016)
- Russian Academy of Sciences (2003-2016)
- The Ministry for Science and Technology of Russia (1999-2014)
- Moscow Government (2003-2005)
- INTAS (1993-2005)
- CRDF (1996-2004)
- DFG (1996-2004)
- ISF (1993-1994)

Thank You!

XX Mendeleev Congress
on General and Applied Chemistry