



Development of photoactive supramolecular devices and machines

Organic Photochemistry and Supramolecular Chemistry
in the XXI century

**Prof. Sergey P. Gromov,
A. K. Chibisov, M. V. Alfimov**

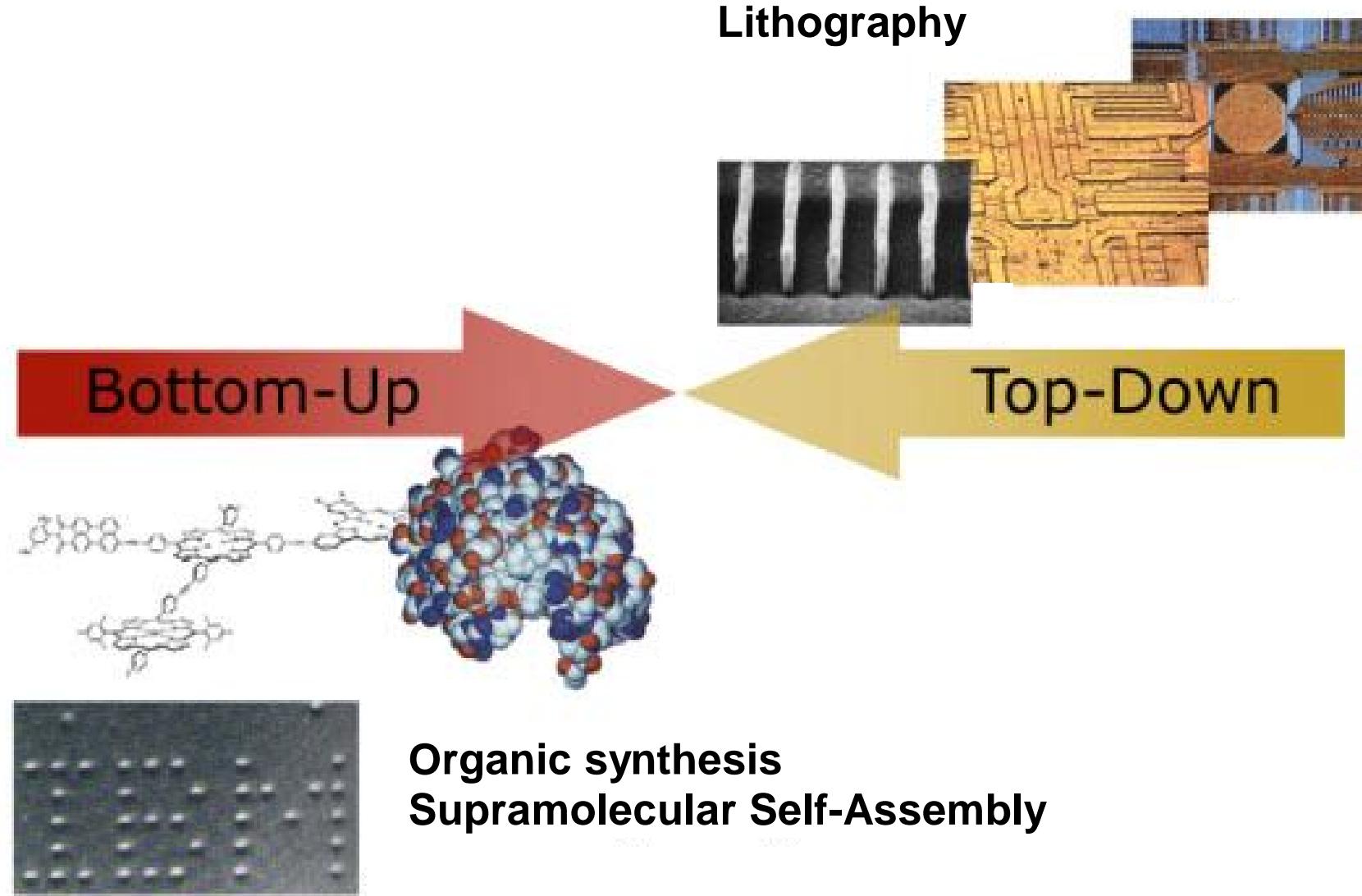
<http://suprachem.photonics.ru>

<http://www.chem.msu.ru/rus/lab/organic/supra-nano.html>

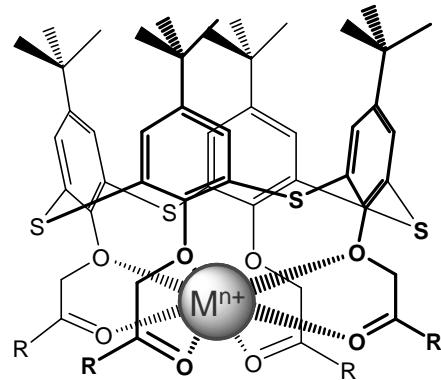


NANOTECHNOLOGY “BOTTOM-UP”

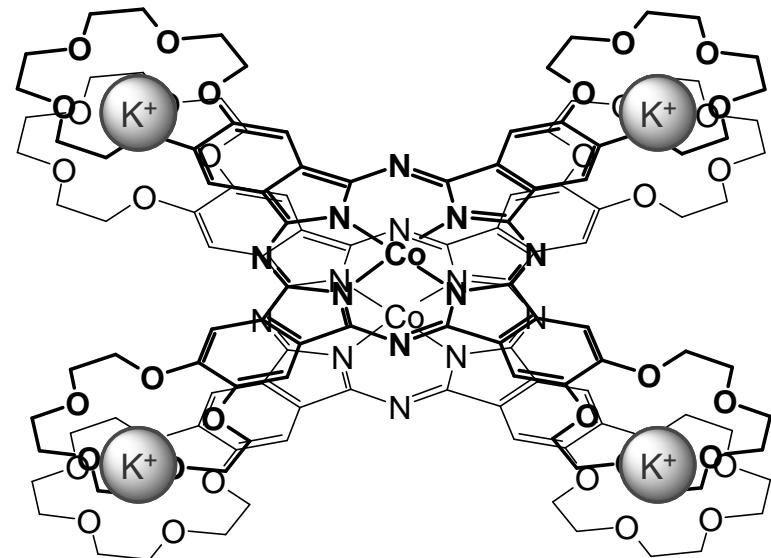
STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES



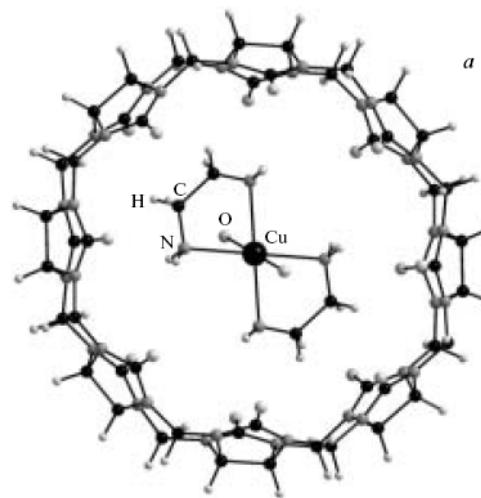
SUPRAMOLECULAR SYSTEMS



Konovalov A. I., Antipin I. S. et al.



Tsivadze A. Yu., Gorbunova Yu. G. et al.



Fedin V. P. et al.

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

Nobel Prize (2016) "for the design and synthesis of molecular machines.".



Jean-Pierre Sauvage



James Fraser Stoddart



Bernard Lucas Feringa

J.-P. Sauvage :

Molecular machines and mechanically linked molecules, including catenans, rotaxanes and nodes.
The first to receive was a trefoil knot and a molecular muscle.

J. F. Stoddart :

Template synthesis, molecular recognition, self-assembly processes and a wide range of questions on the chemistry of mechanically linked molecules.

B. L. Feringa:

Molecular motors.

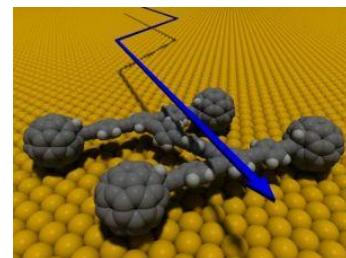
Means for control of supramolecular devices and machines

§ **Photoswitching** - $h\nu$

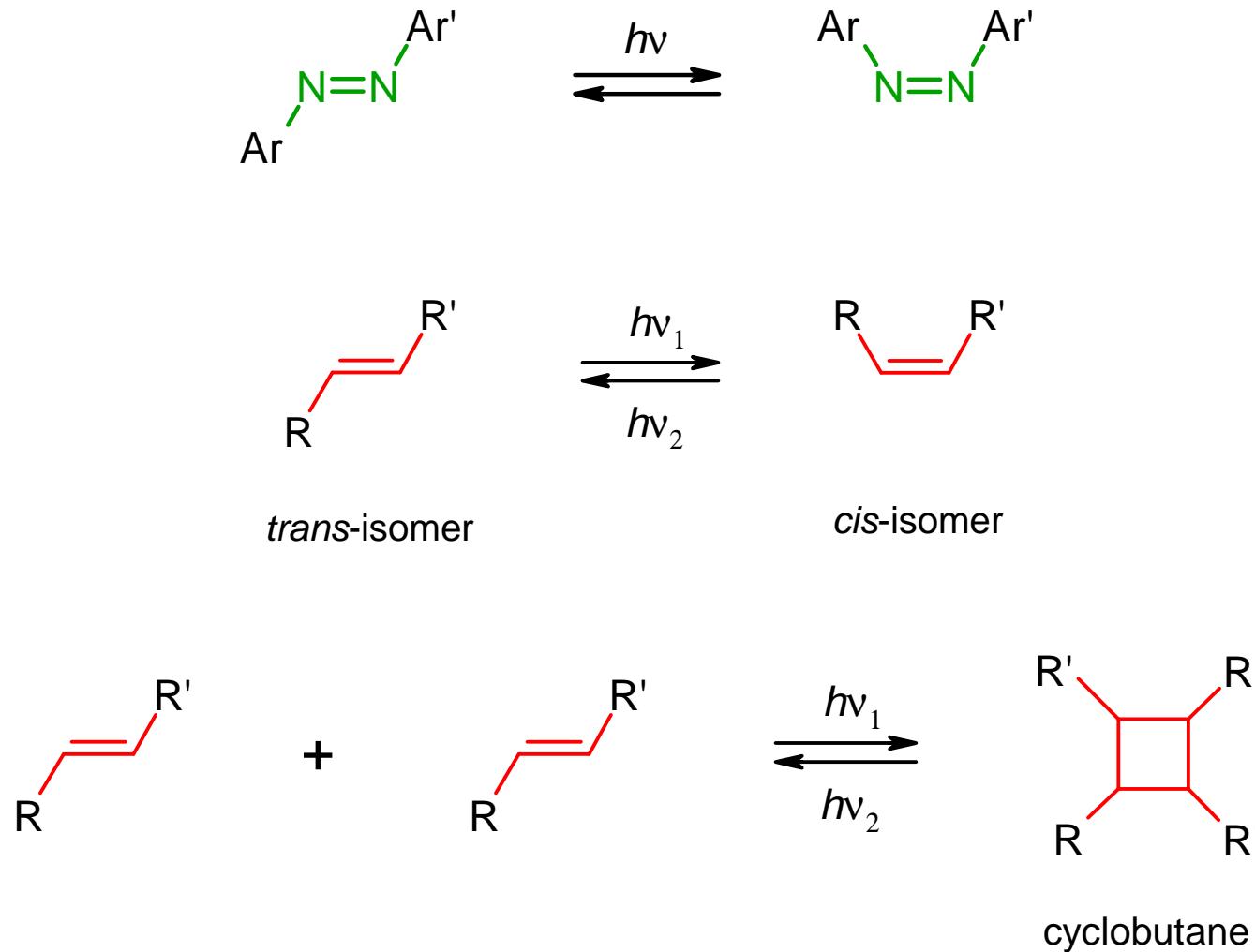
§ **Electrochemical switching** - e^-

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

§ **Thermal switching** - D



PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS

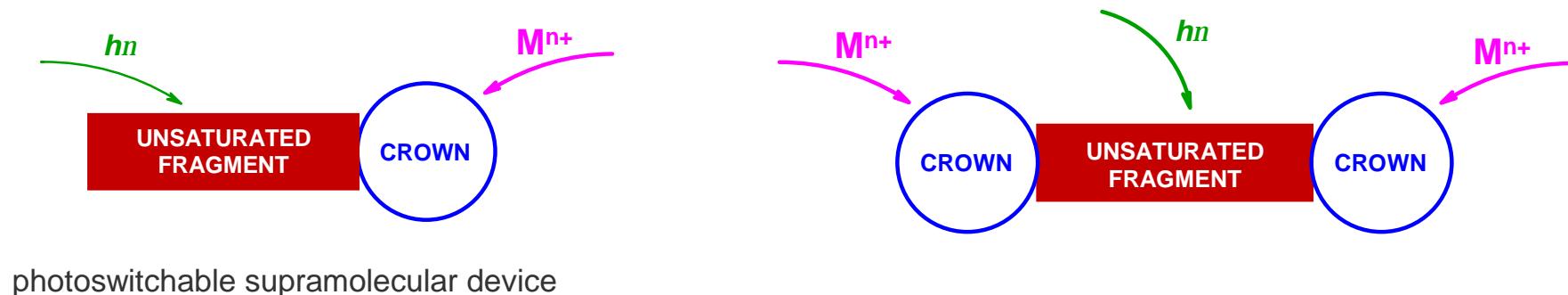
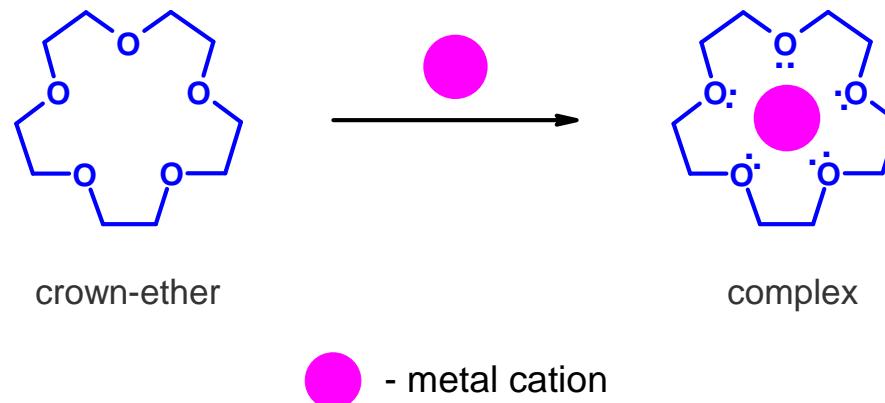


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

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

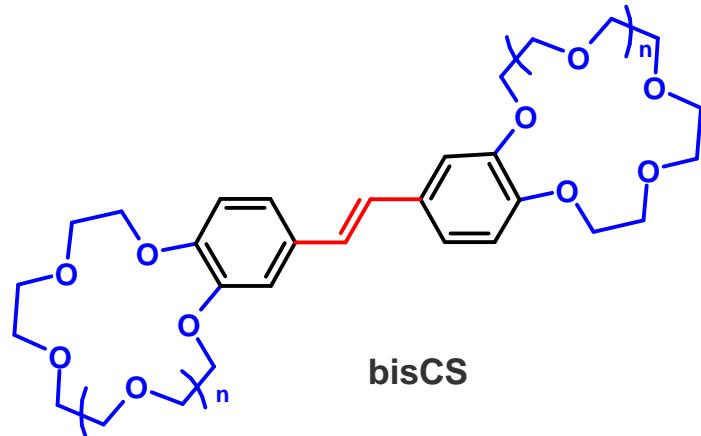
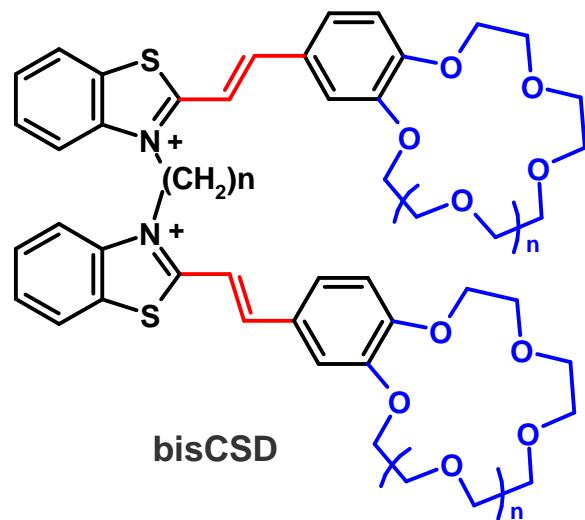
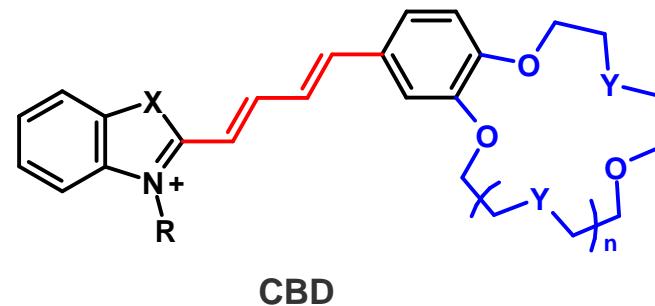
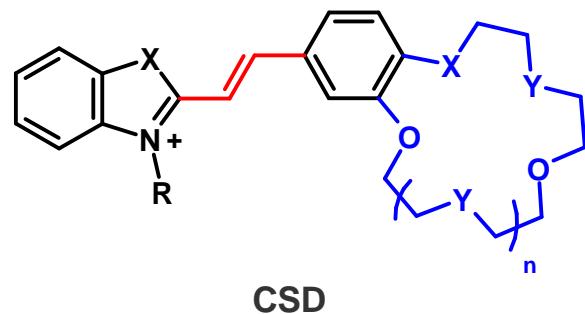


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

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).

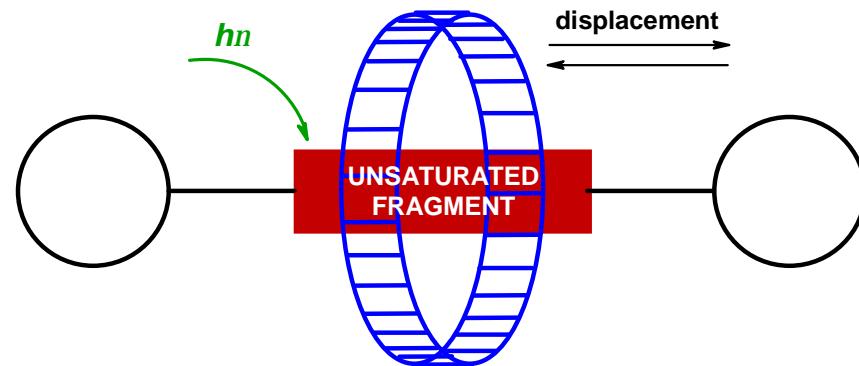
Crown-containing unsaturated compounds



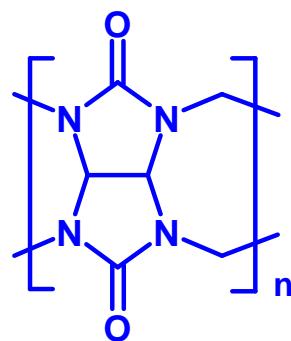
$n = 1, 2$

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

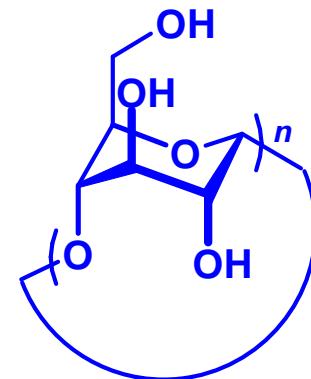


photocontrolled supramolecular machine



cucurbiturils

$n = 6-8$



cyclodextrins

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

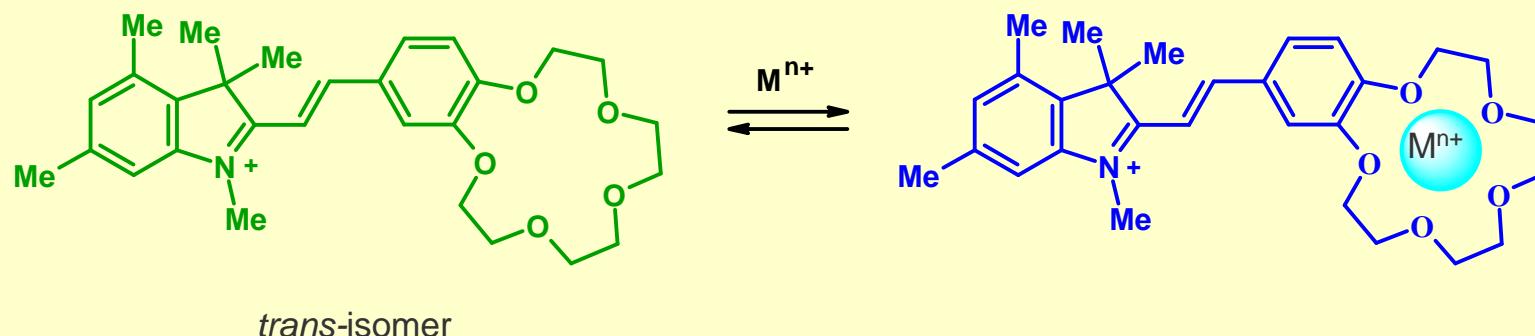
Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review)

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

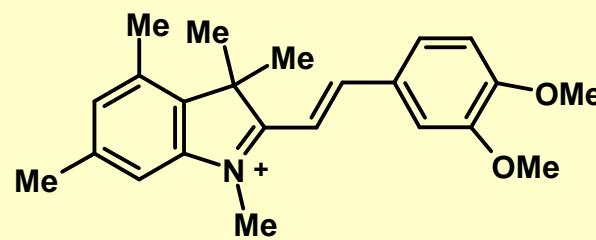
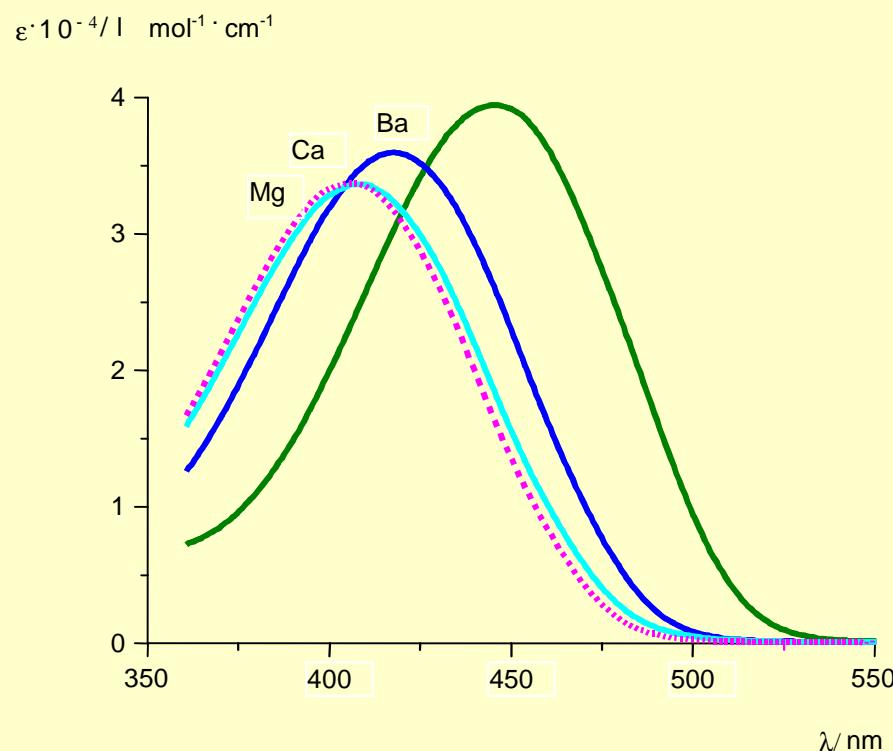
**Self-assembly
of photoswitchable supramolecular devices
with participation of metal cations**

Part I

Complex formation



trans-isomer

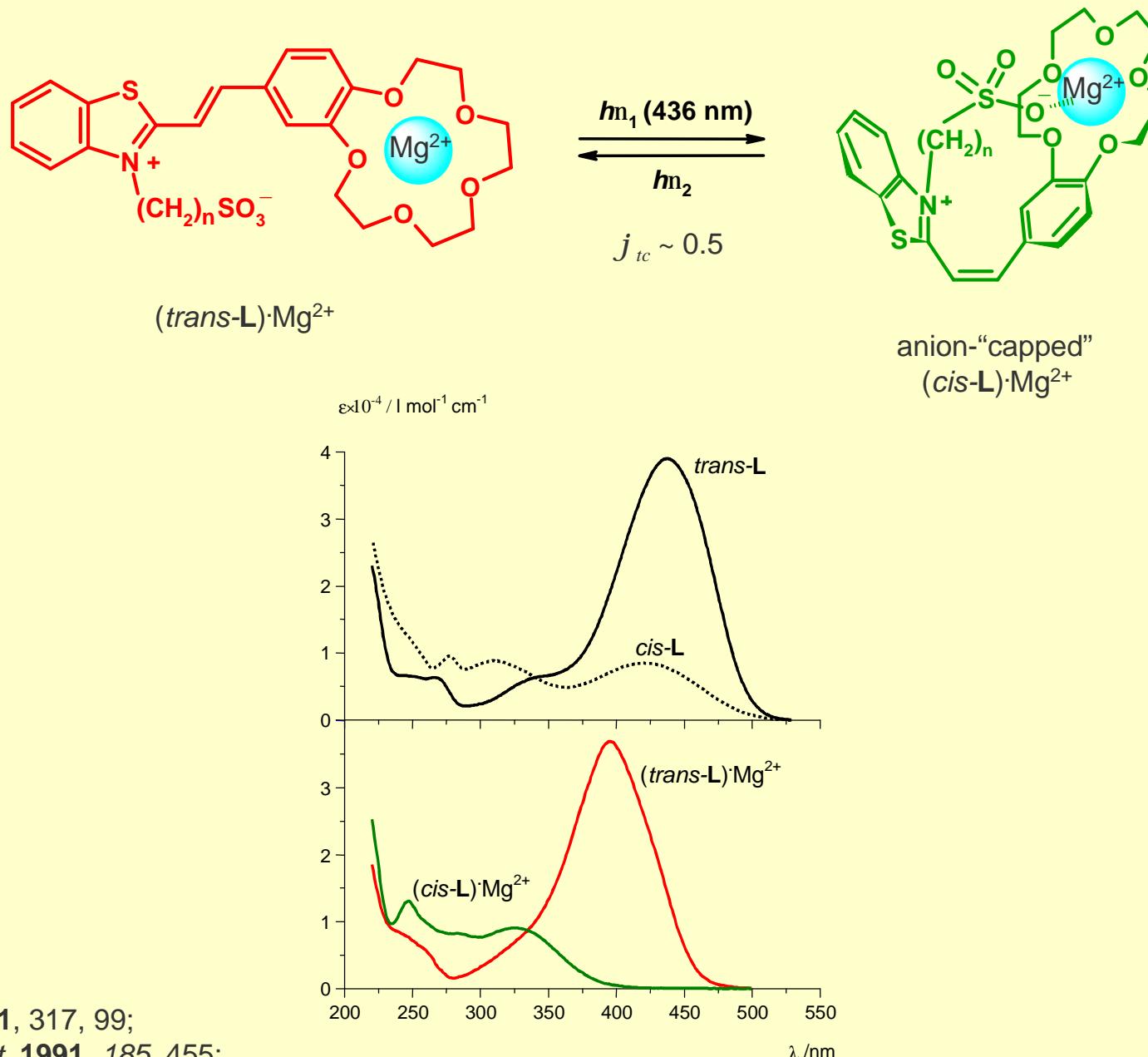


Dokl. Chem. 1990, 314, 279;

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

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

Photoswitchable supramolecular devices



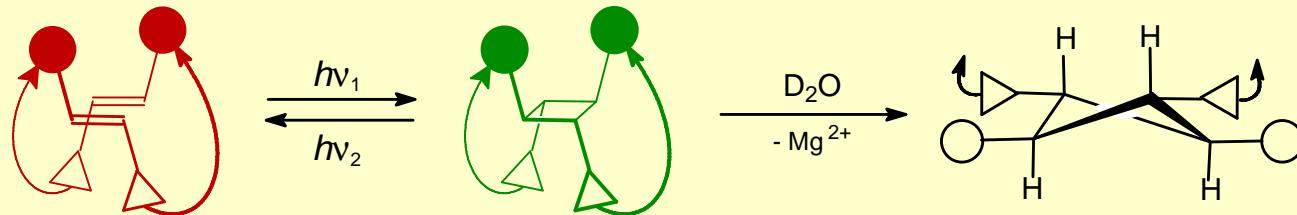
Dokl. Chem. 1991, 317, 99;

Chem. Phys. Lett. 1991, 185, 455;

J. Am. Chem. Soc. 1992, 114, 6381;

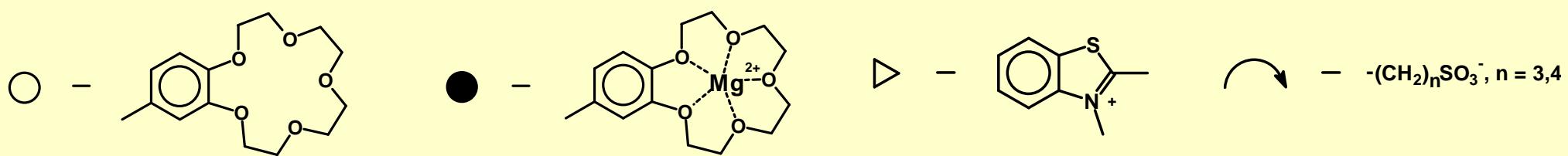
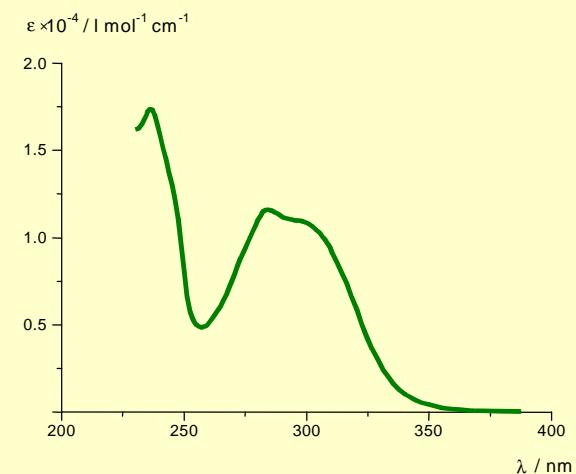
J. Am. Chem. Soc. 1999, 121, 4992.

Photoswitchable supramolecular devices



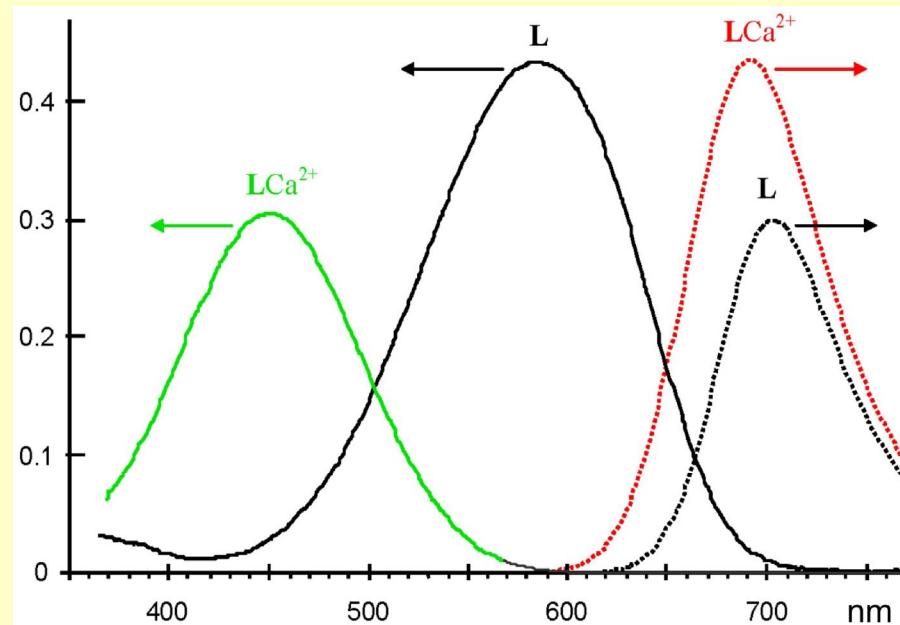
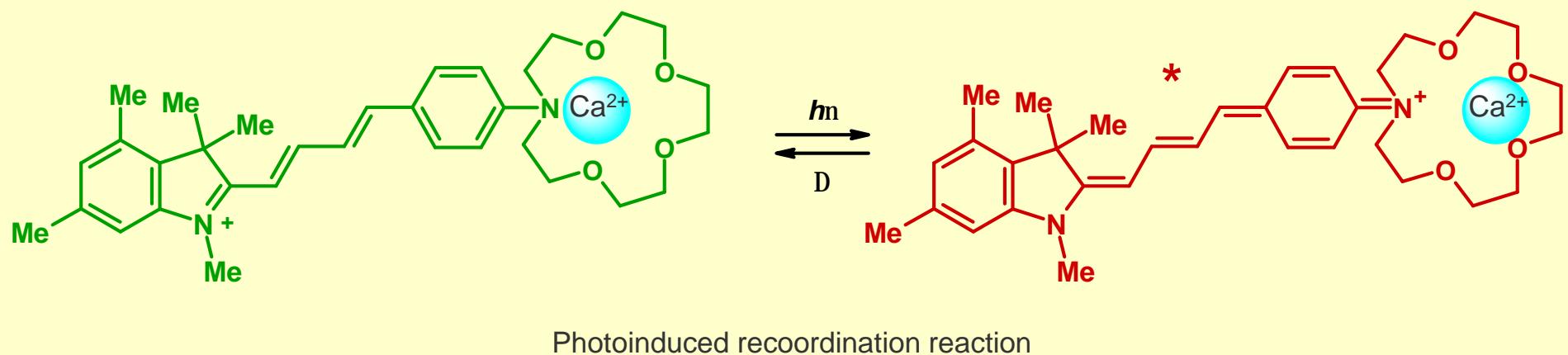
[2+2] Photocycloaddition of CSD

$C_L, /mol \cdot l^{-1}$	$5 \cdot 10^{-6}$	$2.4 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$	$2 \cdot 10^{-3}$
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.

Photoswitchable supramolecular device



J. Fluor. **1999**, *9*, 33;

Helv. Chim. Acta **2002**, *85*, 60;

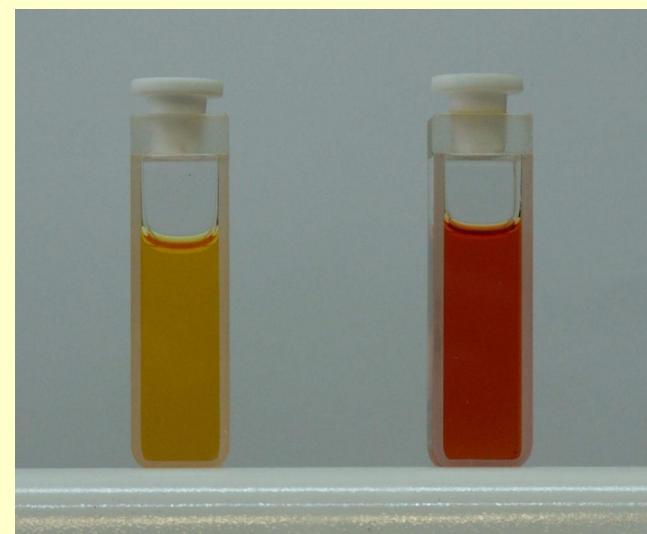
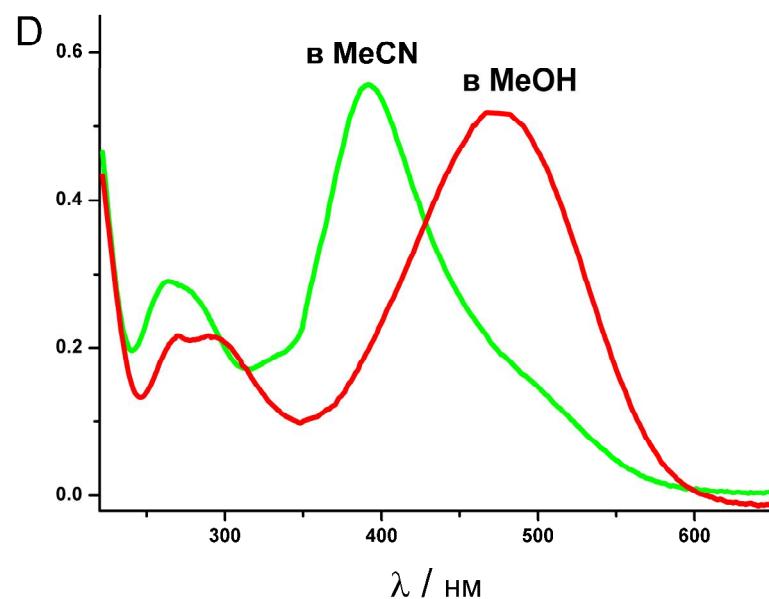
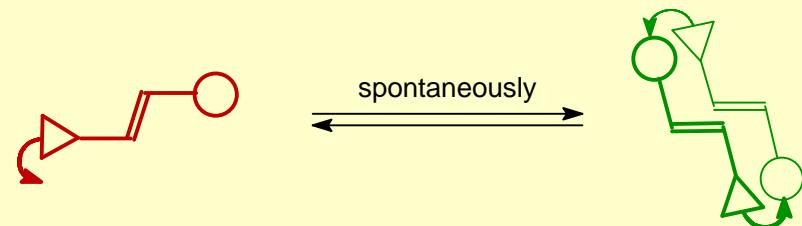
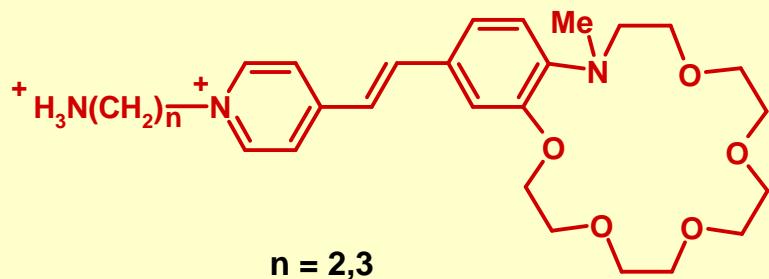
Rusalov M. V., Gromov S. P. et al. *Russ. Chem. Rev.* **2010**, *79*, 1099 (review);

Photochem. Photobio. Sci. **2011**, *10*, 15.

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

Part II

Dimerization of CSD

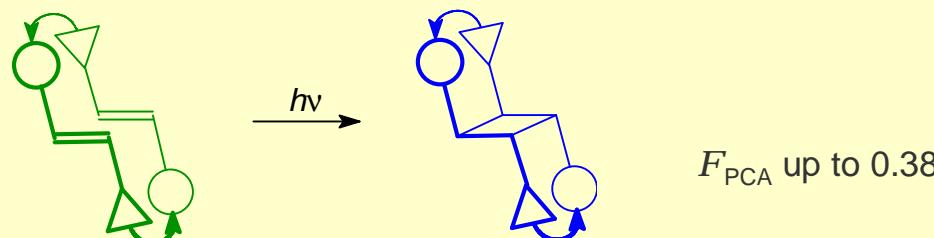


in MeCN

in MeOH

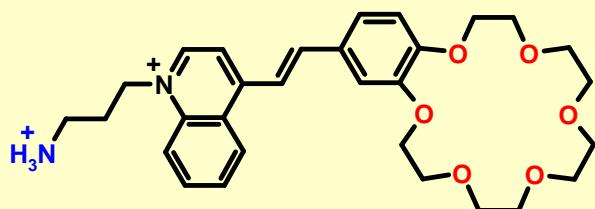
RF patent 2278134 2006;
J. Org. Chem. 2014, 79, 11416;
J. Phys. Chem. A 2015, 119, 13025;
New J. Chem. 2016, 40, 7542.

[2+2] Photocycloaddition of CSD

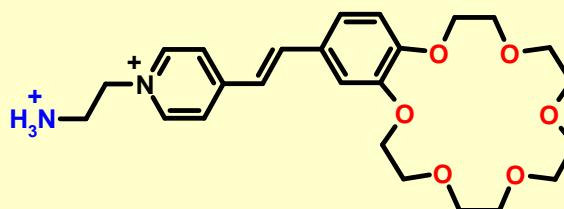


Yield, %

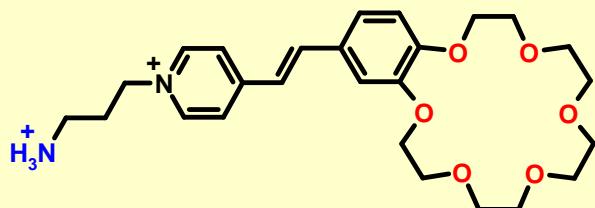
Yield, %



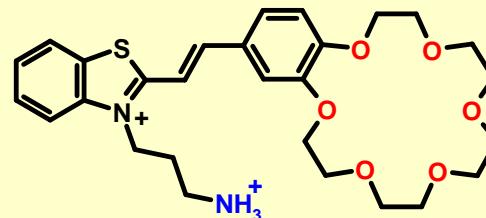
100



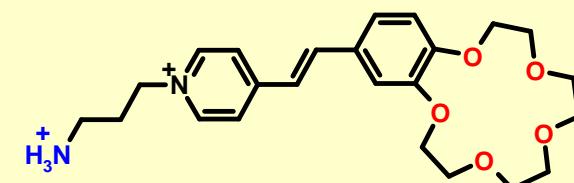
33



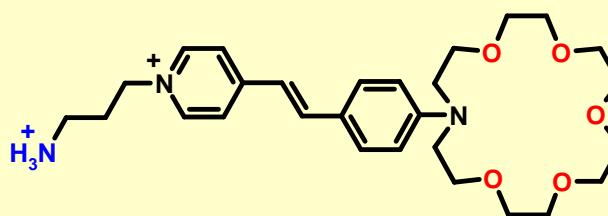
100



0



40

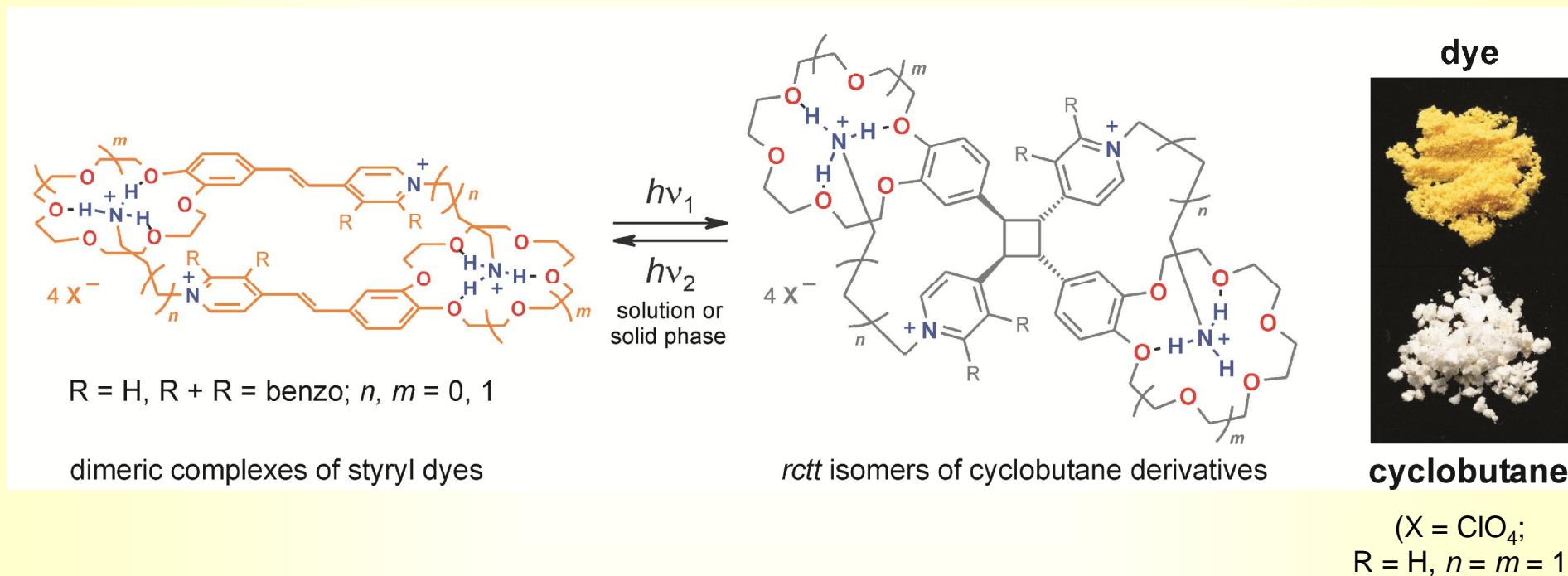


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RF patent 2278134 2006;
Russ. Chem. Bull. 2009, 58, 1211;
J. Org. Chem. 2014, 79, 11416;
J. Phys. Chem. A 2015, 119, 13025.

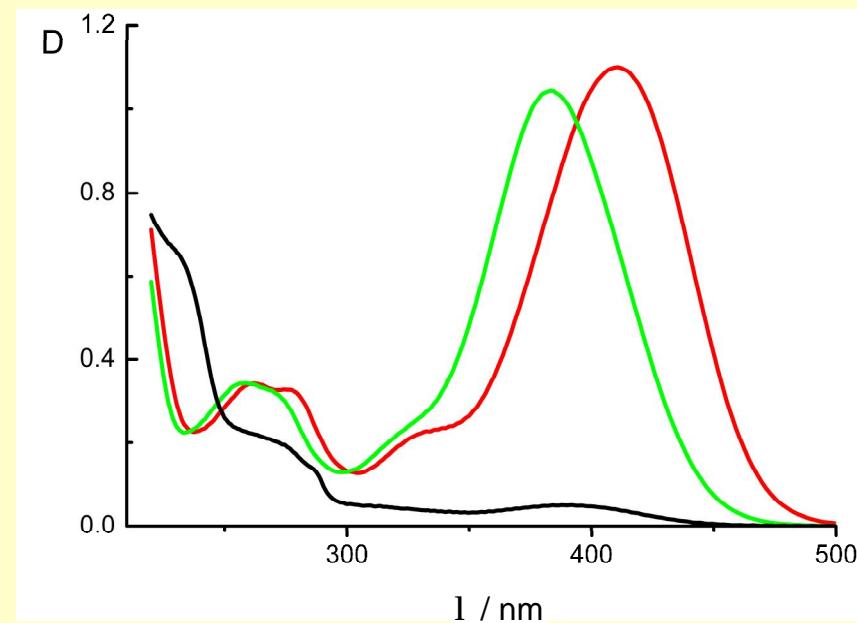
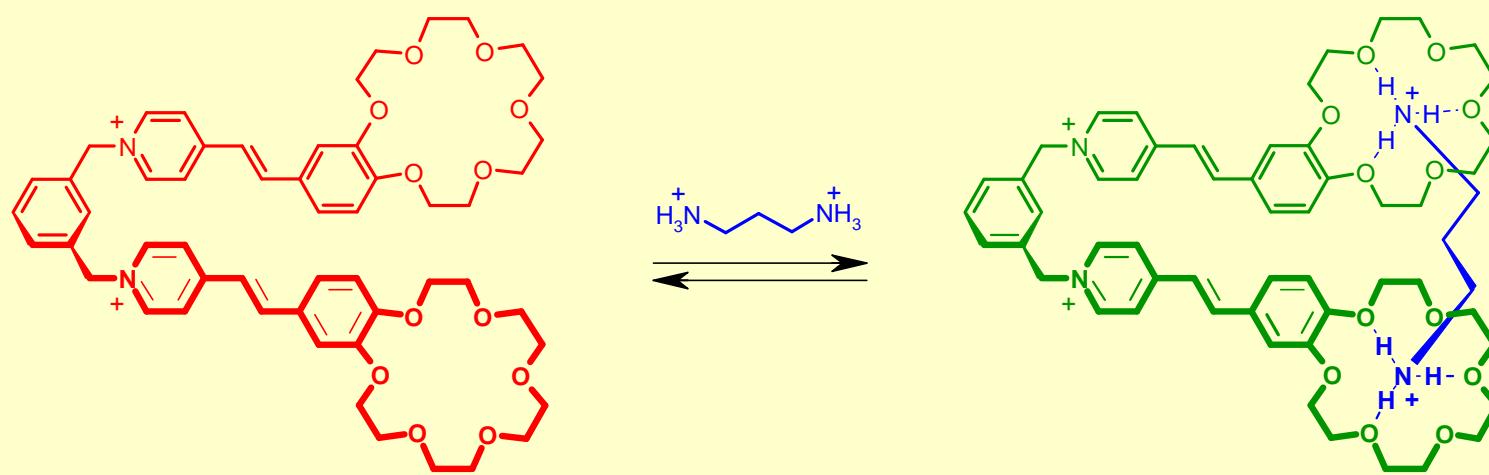
In MeCN, irradiation time, 4 h

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

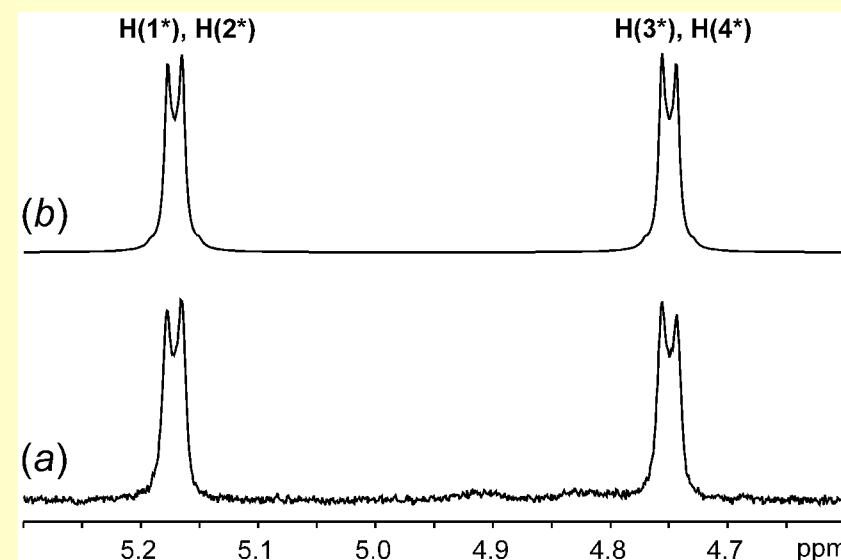
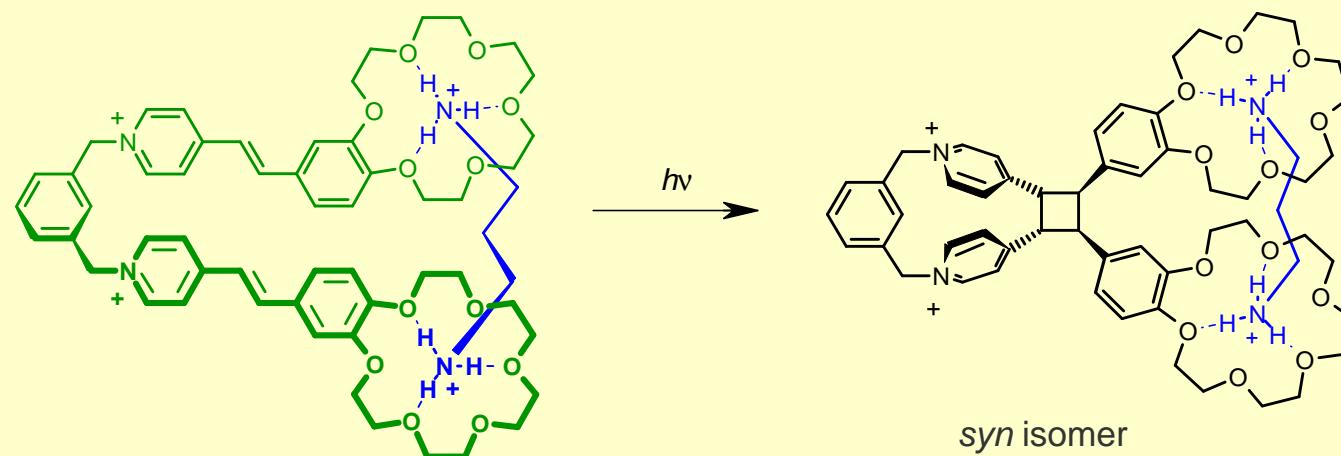


Found property provides grounds for believing that the crystals of these photoactive supramolecular systems could be used for data recording and storage.

FORMATION OF PSEUDOSANDWICH COMPLEXES

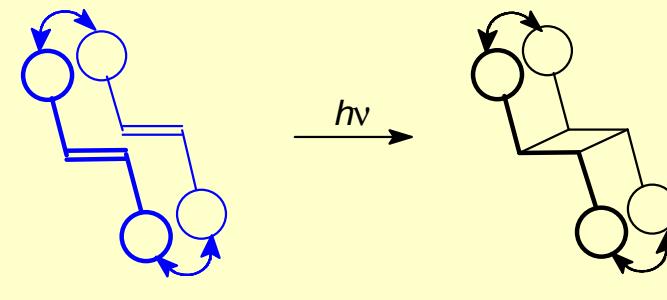


Intramolecular [2+2] photocycloaddition of bisCSD



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

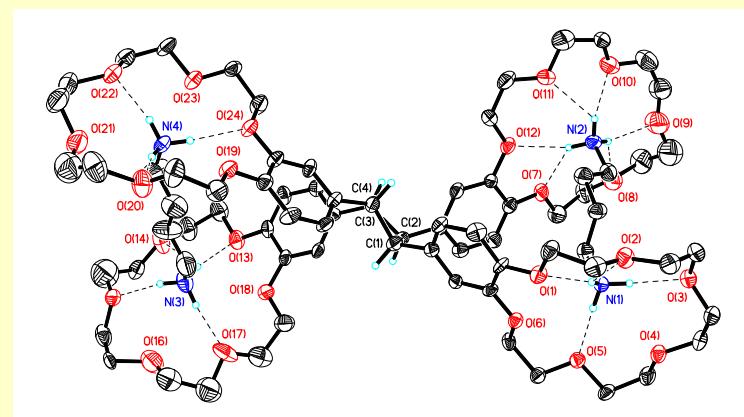
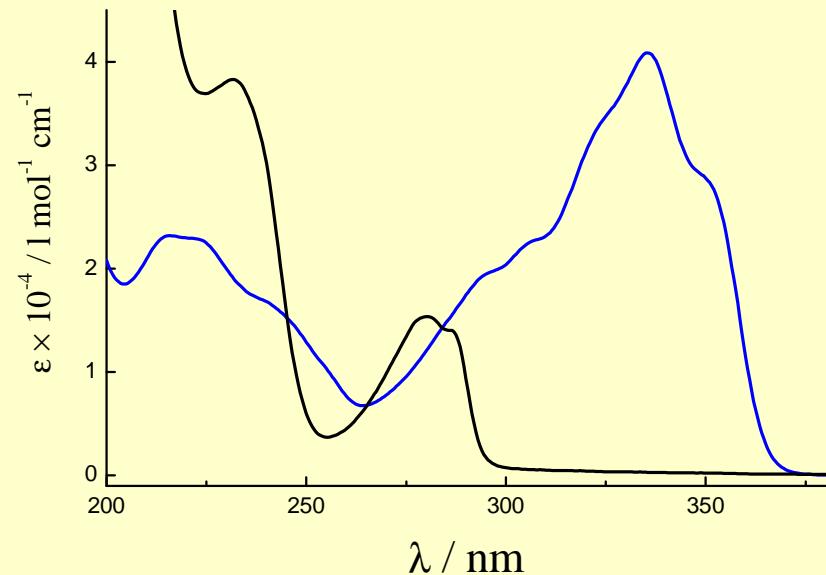
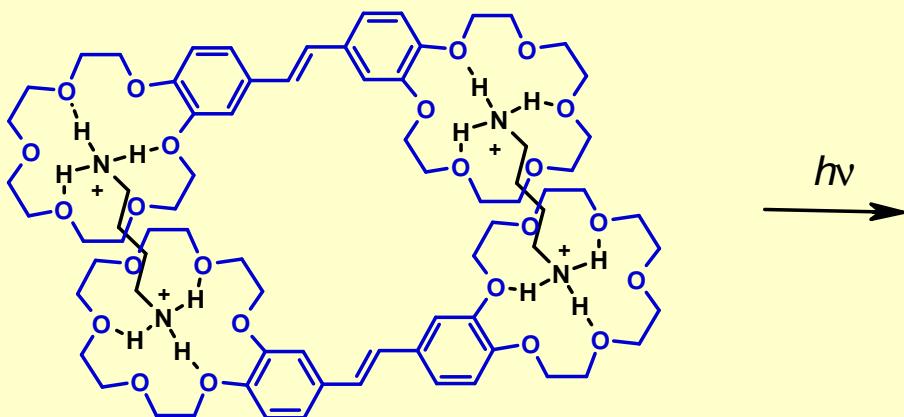
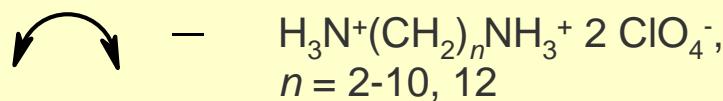
Formation of bispseudosandwich complexes and [2+2] Photocycloaddition



syn-complex

syn-isomer

F_{PCA} up to 0.27



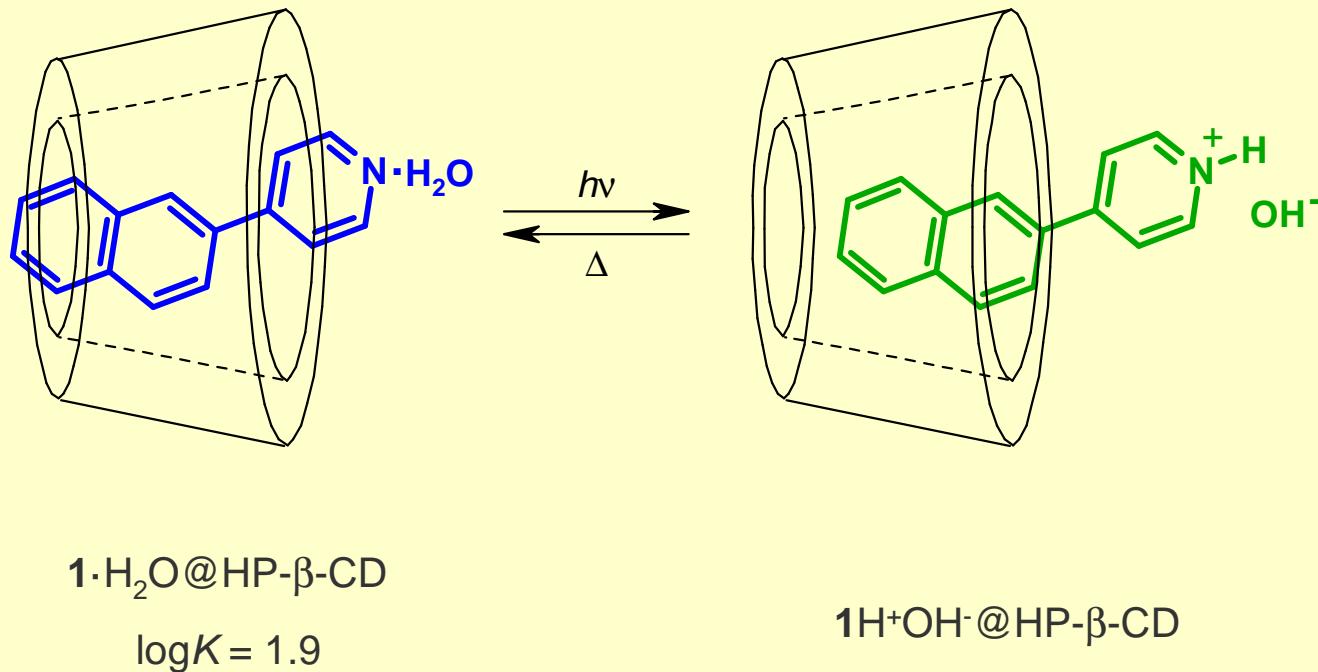
syn-isomer

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

Self-assembly of photocontrolled supramolecular machines

Part III

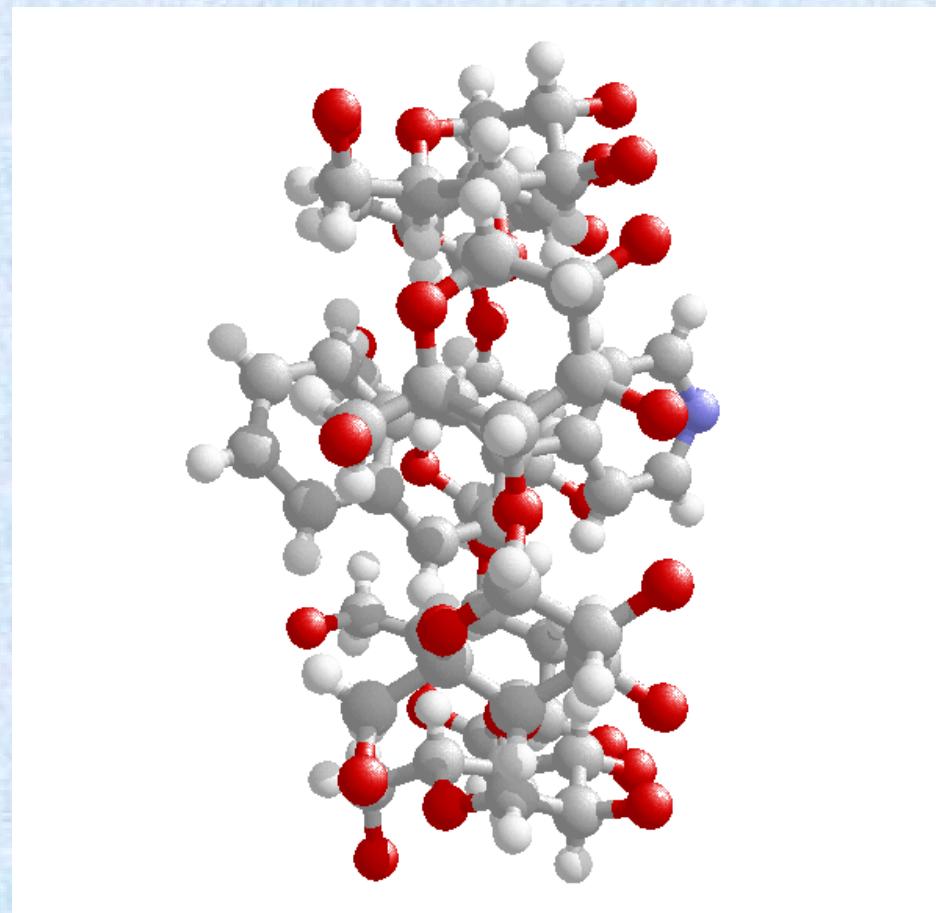
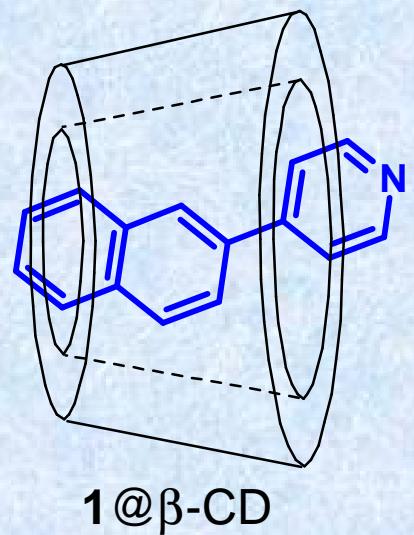
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



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.

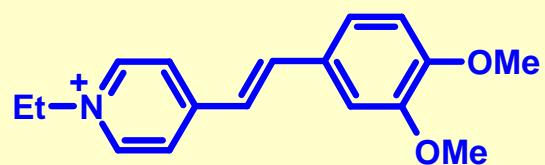
Russ. Chem. Bull. 2004, 53, 2525;
J. Photochem. Photobiol. A 2011, 217, 87;
Russ. Chem. Bull. 2013, 62, 2150.

X-ray structure determination of photocontrolled supramolecular machine

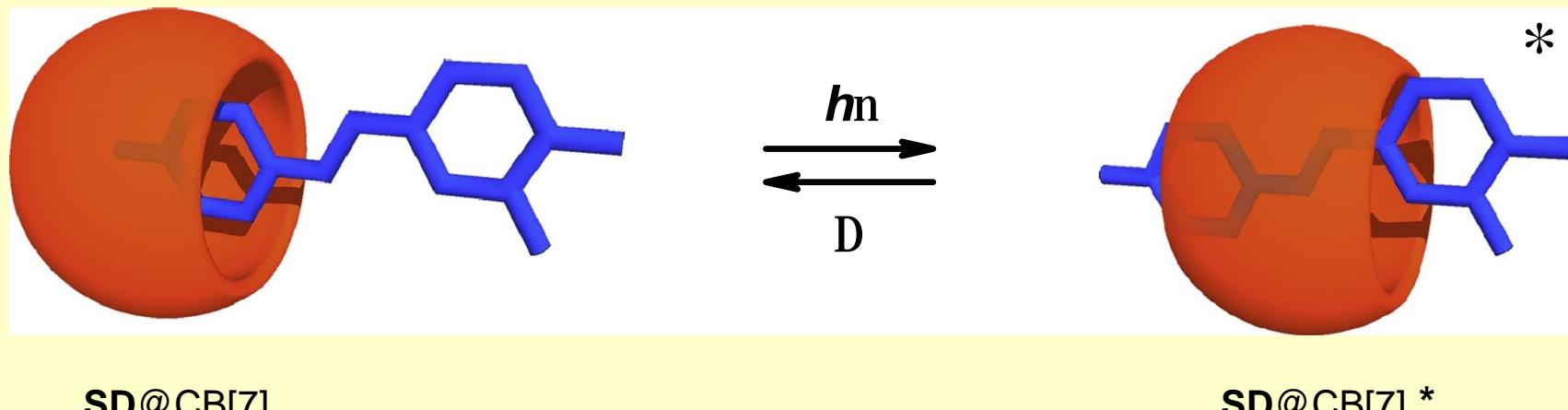


Russ. Chem. Bull. 2004, 53, 2525;
J. Photochem. Photobiol. A 2011, 217, 87;
Russ. Chem. Bull. 2013, 62, 2150.

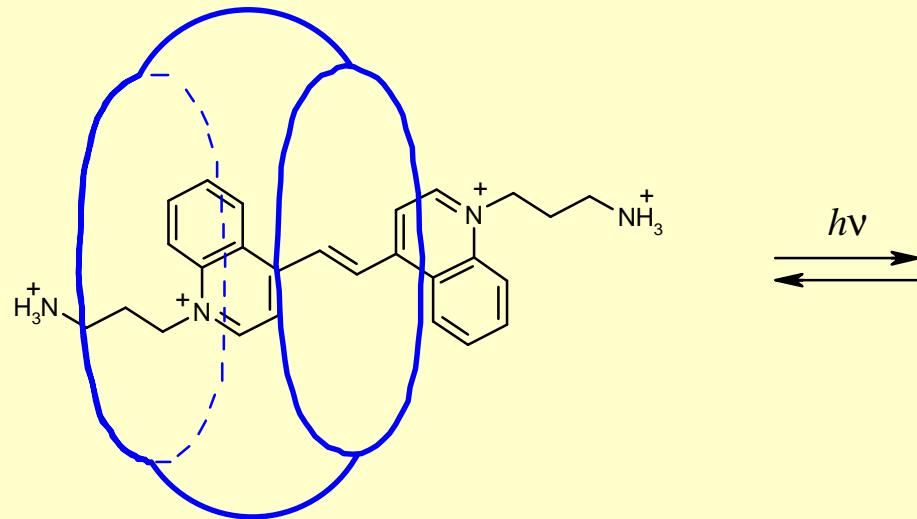
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



SD

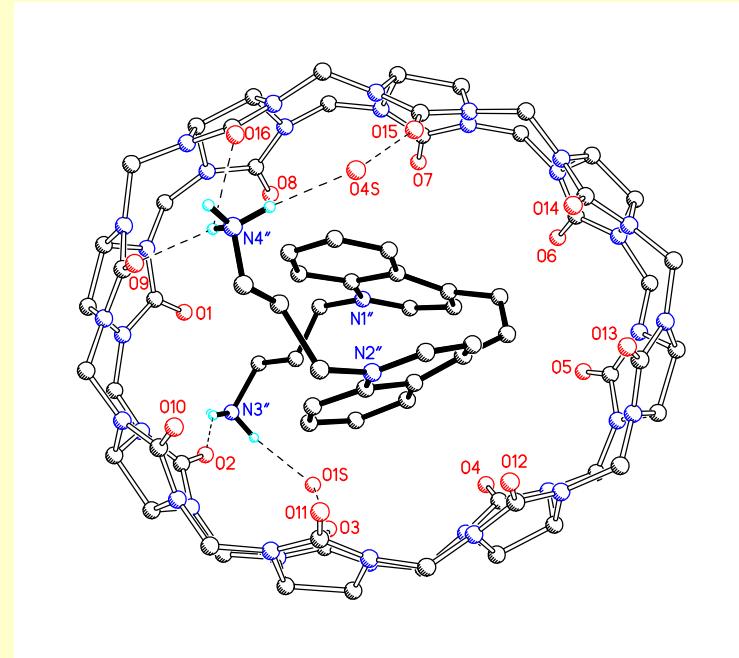


PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



trans-V@CB[8]

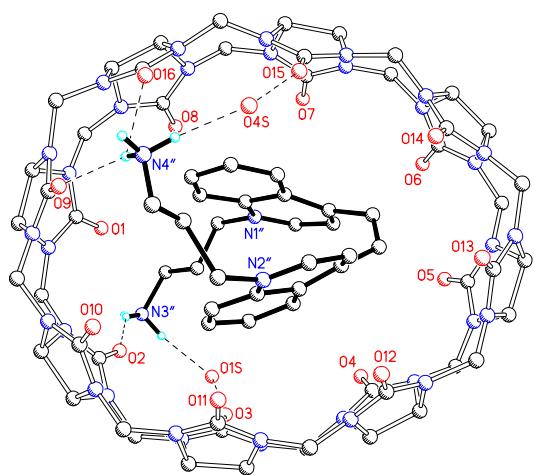
$$\log K = 4.6$$



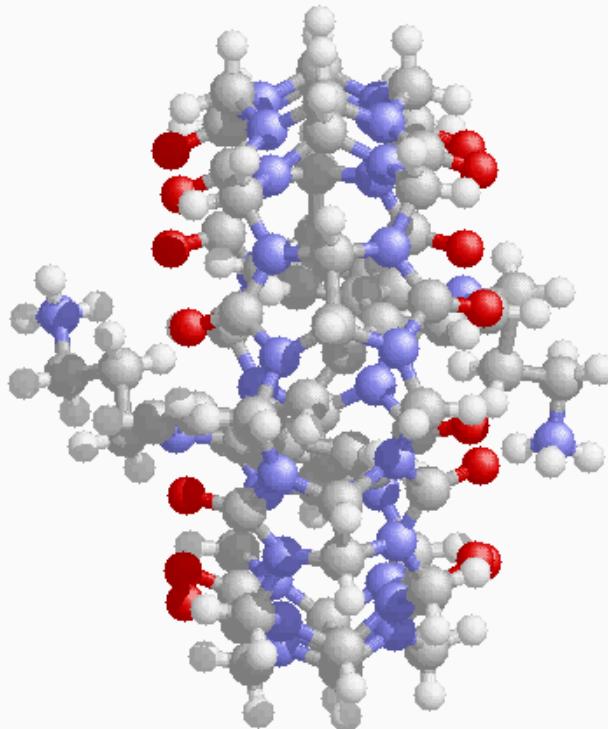
cis-V@CB[8]

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

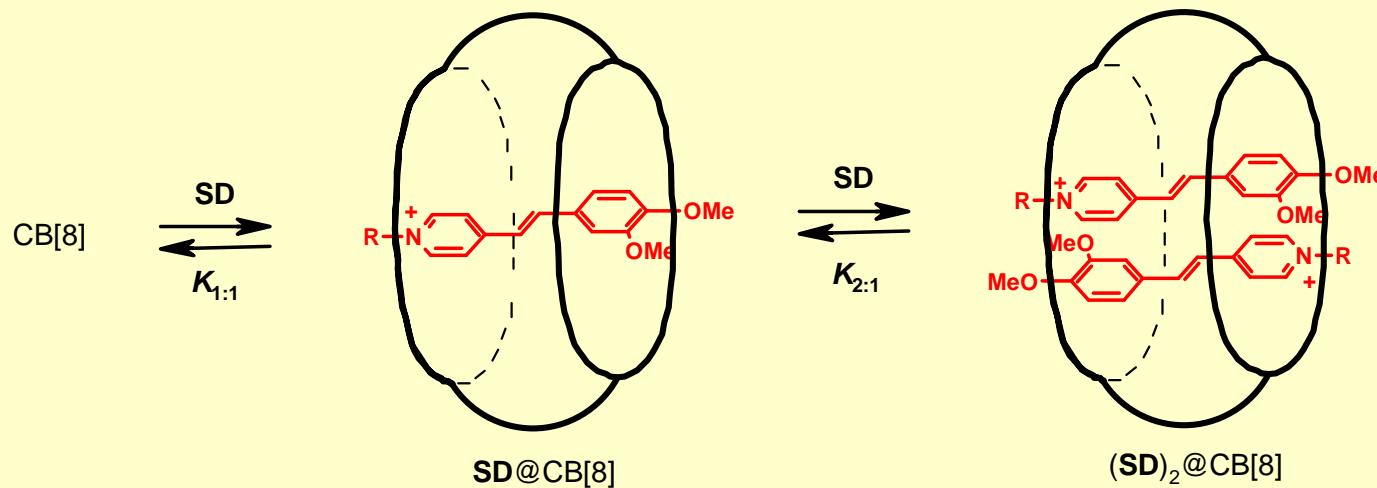
X-ray structure determination of photocontrolled supramolecular machine



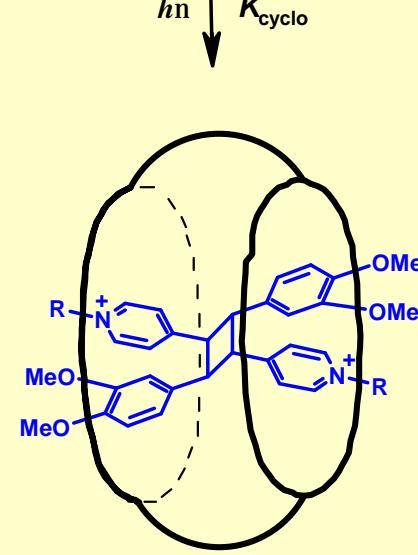
cis-V@CB[8]



PHOTOCONTROLLED SUPRAMOLECULAR MACHINES



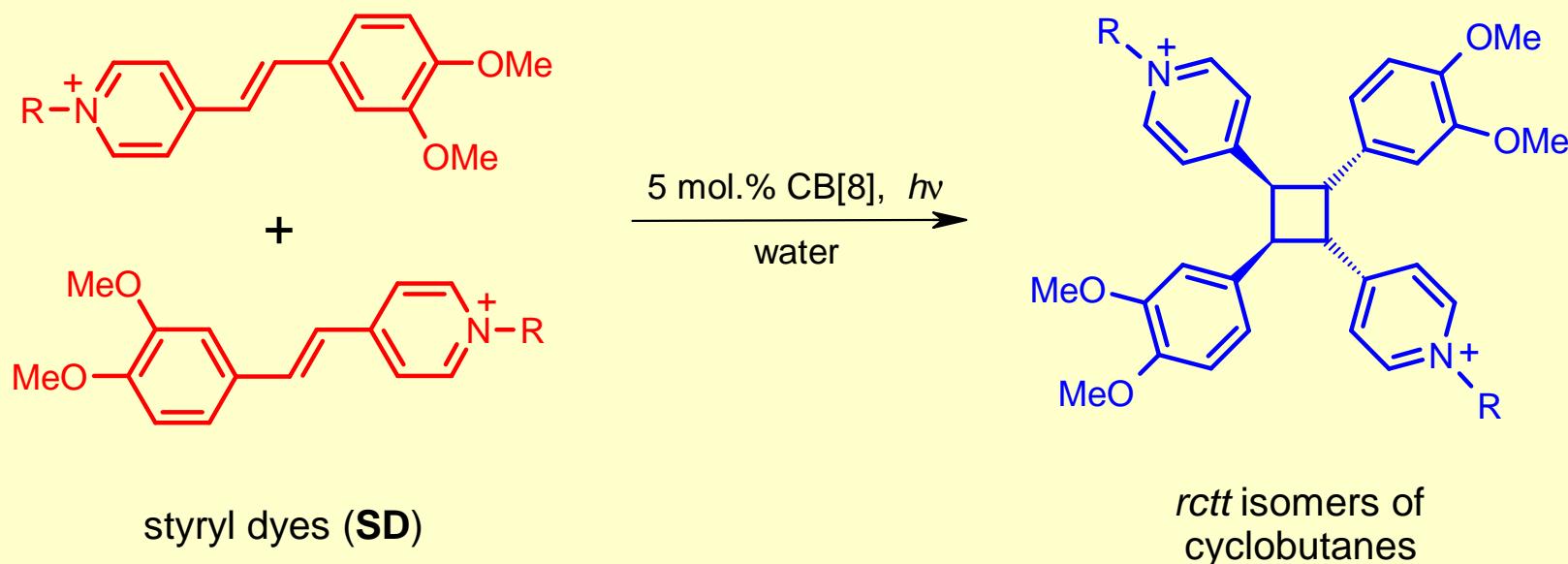
SD	CB[8]			
	R	$\log K_{1:1}$	$\log K_{2:1}$	$\log K_{\text{cyclo}}$
Et	4.9	4.1	4.3	
$(\text{CH}_2)_3\text{NH}_3^+$	5.0	4.4	4.8	
$(\text{CH}_2)_3\text{SO}_3^-$	4.0	2.6	3.2	



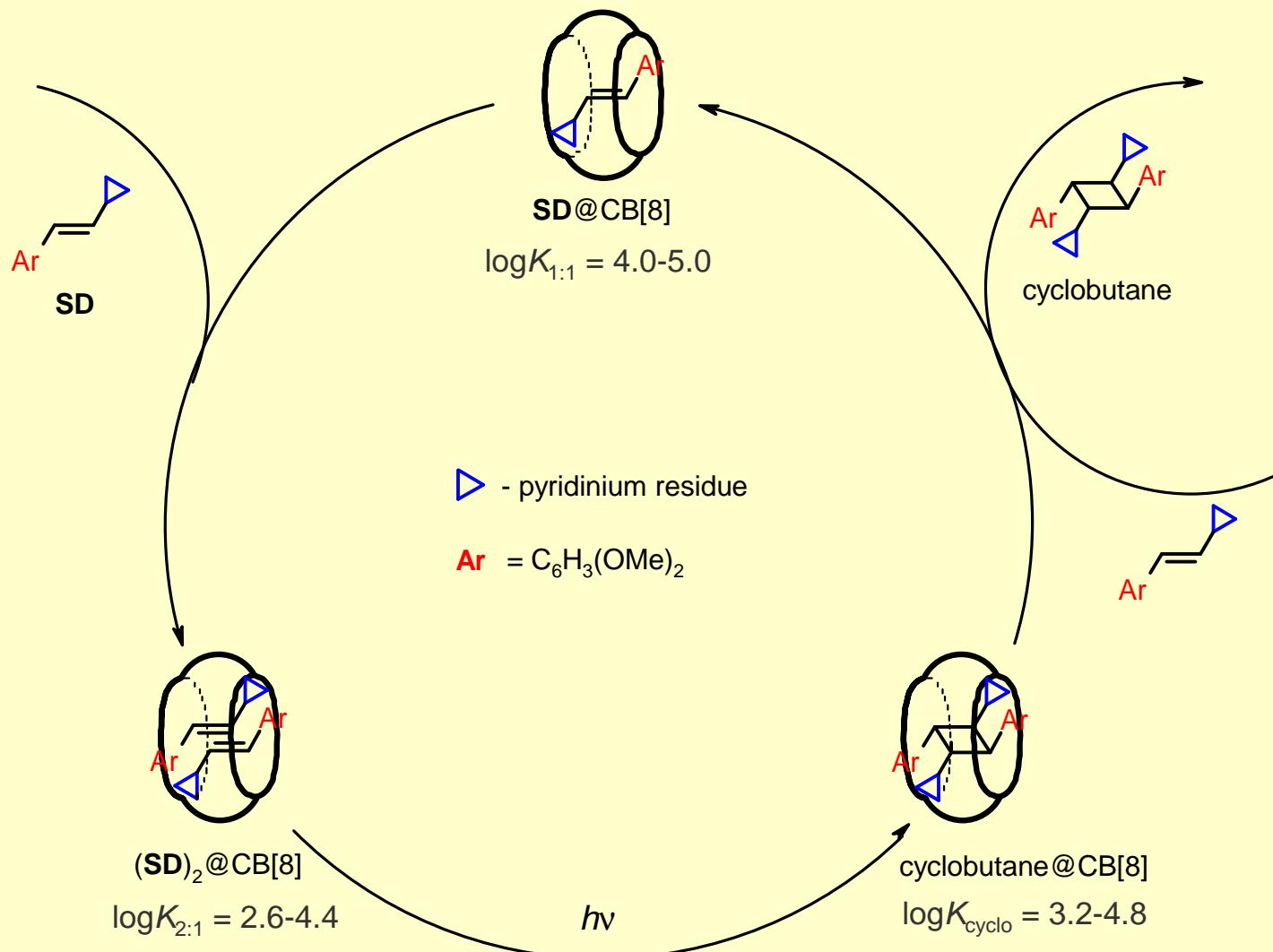
cyclobutane@CB[8]

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

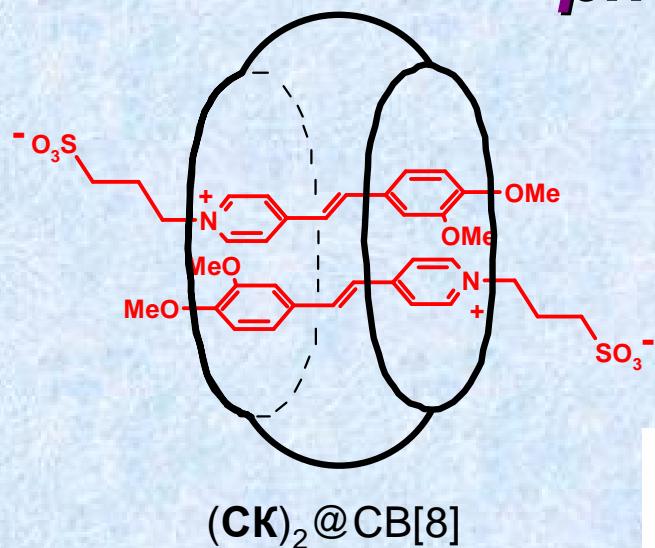


PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL

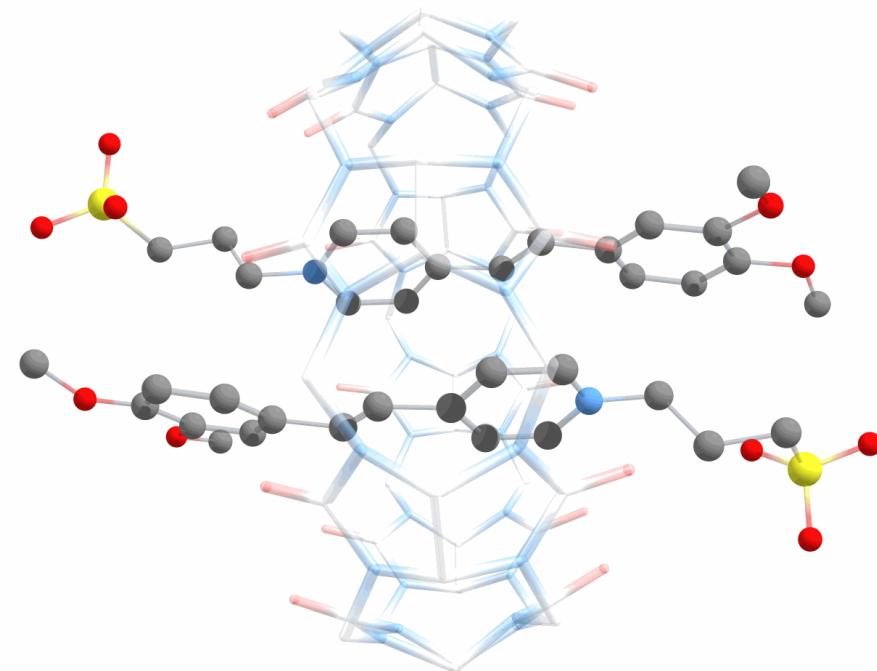


Eur. J. Org. Chem., 2010, 2587;
J. Phys. Chem. A., 2011, 115, 4505;
High Energy Chem., 2014, 48, 253.

X-ray structure determination of photocontrolled supramolecular assembler



Time of pre-organization ~ 4 ps



It is possible to implement all main types of photoprocesses:

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

Chibisov A. K., Shvedov S. V., Goerner H. J. *Photochem. Photobiol. A.* **2001**, *141*, 39;

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);

Chibisov A. K., Zakharova G. V. *Photochem. Photobiol. Sci.* **2012**, *11*, 893;

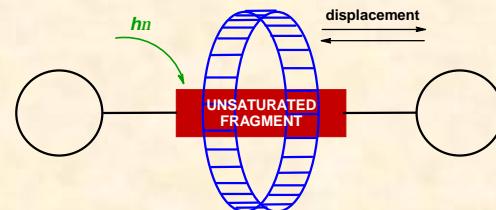
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, *84*, 787 (review).

Molecular meccano of photoactive supramolecular systems



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

19 patents

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);

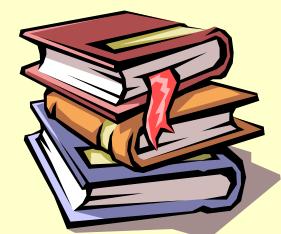
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

Publications :

More than 320 publications in scientific journals and books

Collaboration

- Institute of Problems of Chemical Physics of RAS
- Kurnakov Institute of General and Inorganic Chemistry of RAS
- Lomonosov Moscow State University, Chemical Department
- Zelinsky Institute of Organic Chemistry of RAS
- Institute of Bioorganic Chemistry of RAS
- Lomonosov Moscow State Academy of Fine Chemical Technology
- 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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- INTAS (1993 - 2005)
- CRDF (1996 - 2004)
- DFG (1996 - 2004)
- ISF (1993 - 1994)



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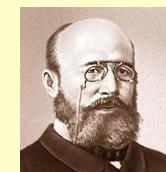
Acknowledgment

Awards and Prizes:

State Prize of the Russian Federation (2018)



A. Butlerov prize of Russian Academy of Sciences (2006)



Scientific discovery of the USSR (1980)





Thank You



<http://suprachem.photonics.ru>;
<http://www.chem.msu.ru/rus/lab/organic/supra-nano.html>