



РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

**XXI Mendeleev Congress
on General and Applied
Chemistry**



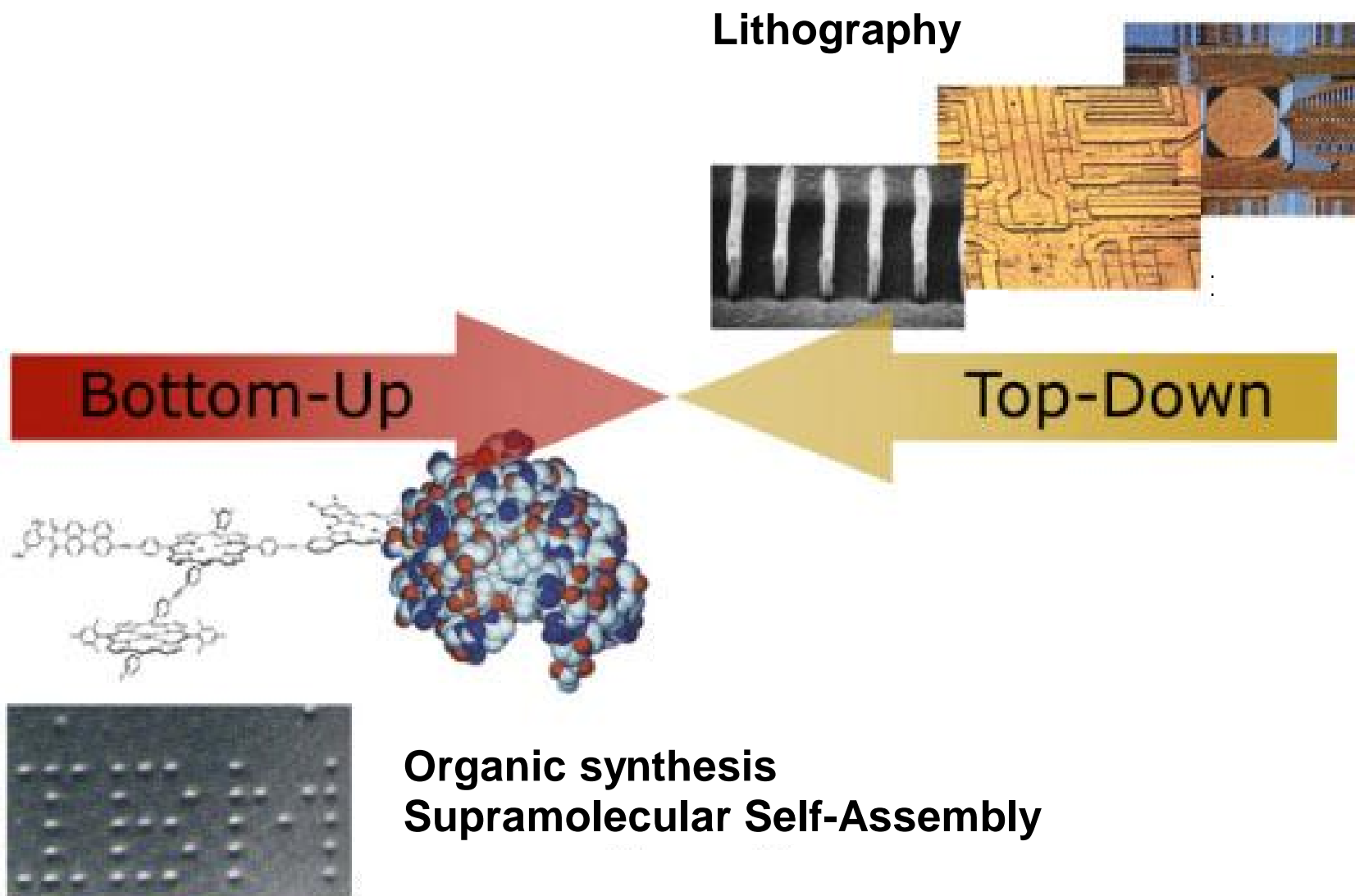
Development of Photoactive Supramolecular Devices and Machines

M. V. Alfimov, S. P. Gromov

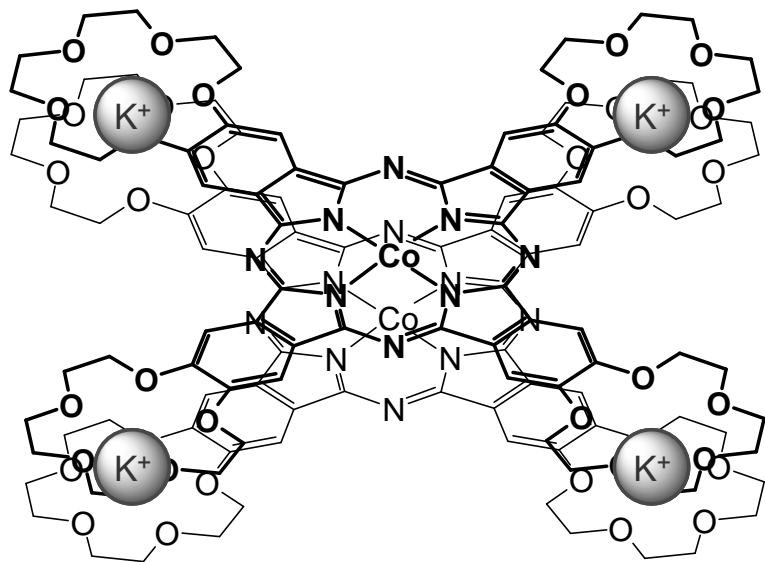
<http://suprachem.photonics.ru;>
[http://www.photonics.ru/.](http://www.photonics.ru/)

NANOTECHNOLOGY “BOTTOM-UP”

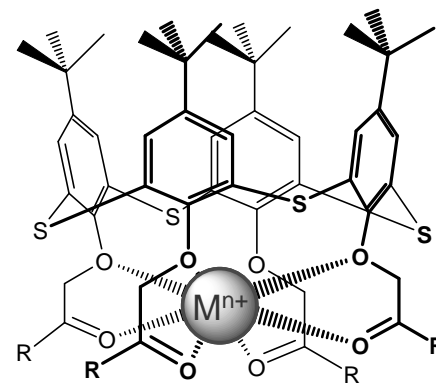
STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES



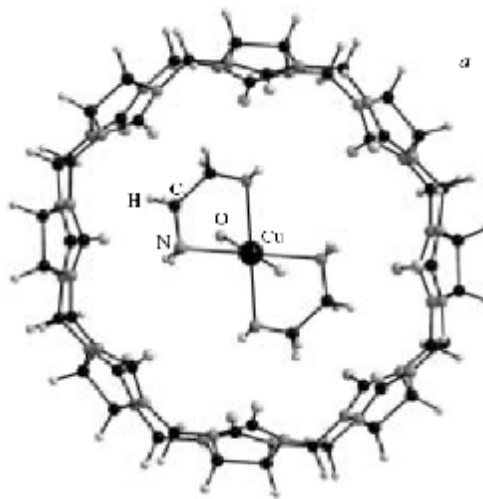
SUPRAMOLECULAR SYSTEMS



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



Konovalov A. I., Antipin I. S. 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.

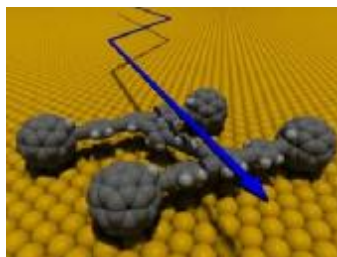
Means for control of supramolecular devices and machines

§ Photoswitching - $h\nu$

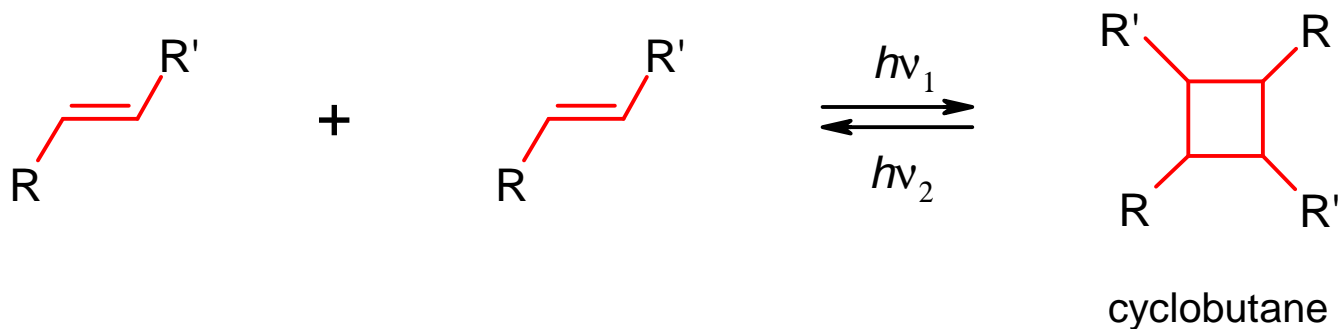
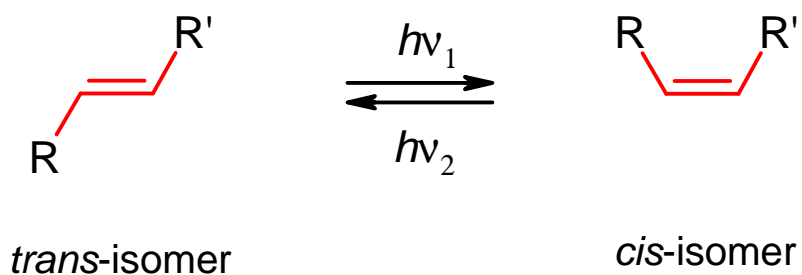
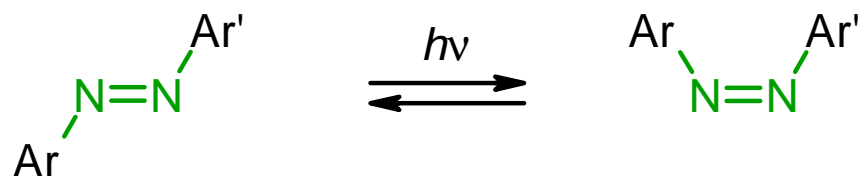
§ Electrochemical switching - e^-

§ Chemical switching - H^+ , M^{n+}

§ Thermal switching - Δ



PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS

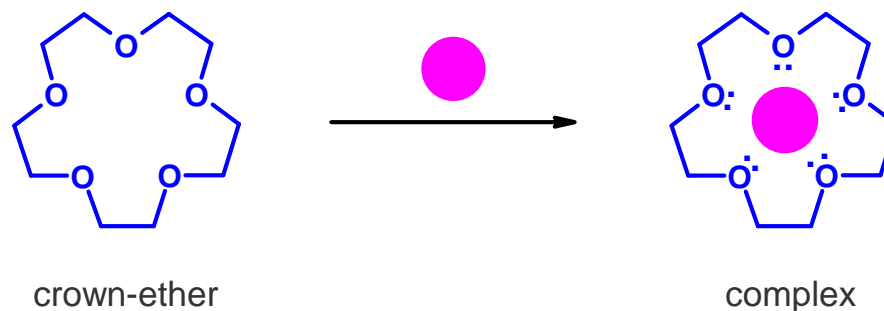


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

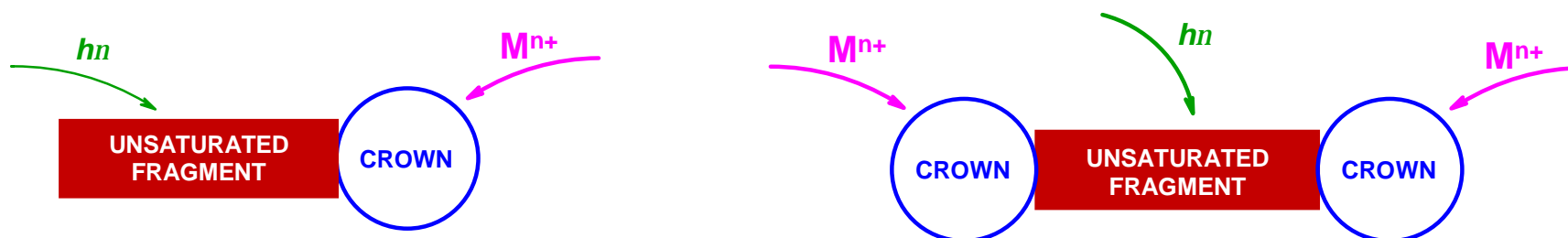
Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review);

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

PHOTOSWITCHABLE SUPRAMOLECULAR DEVICES BASED ON UNSATURATED AND CROWN COMPOUNDS



 - metal cation

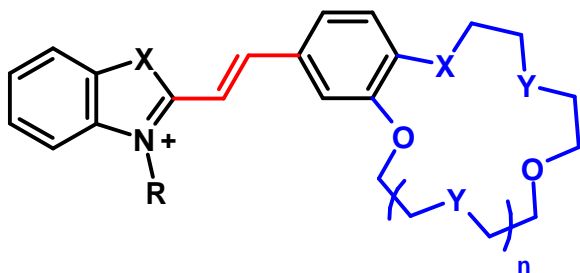


Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

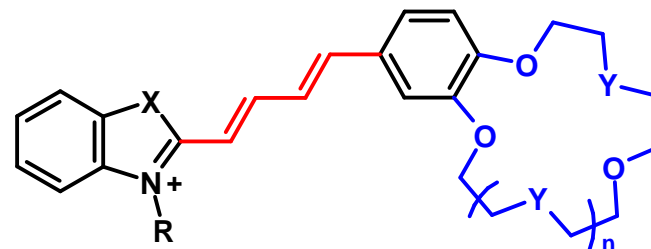
Ushakov E. N., Alfimov M. V., Gromov S. P. *Russ. Chem. Rev.* **2008**, 77, 39 (review);

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

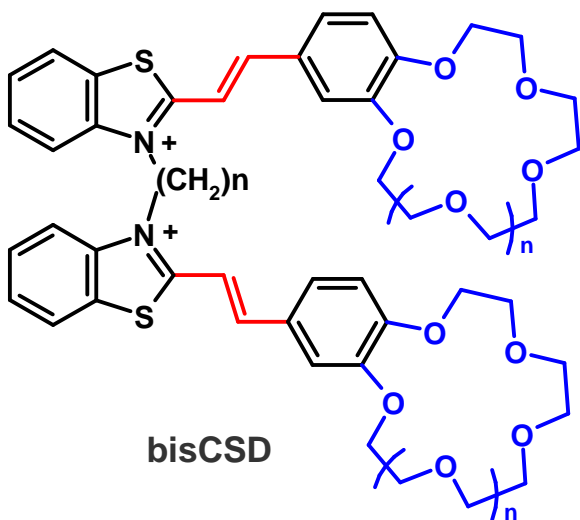
Crown-containing unsaturated compounds



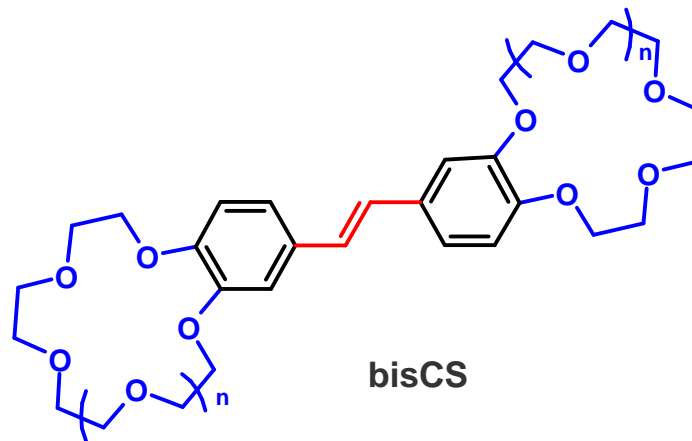
CSD



CBD



bisCSD

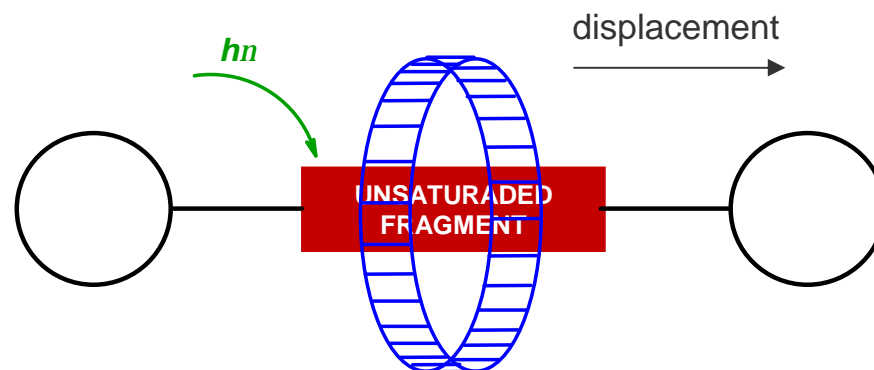


bisCS

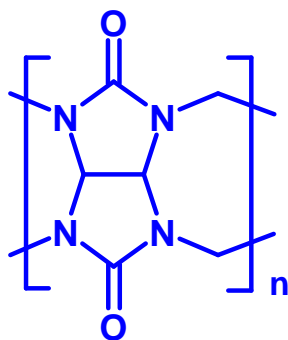
$n = 1, 2$

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

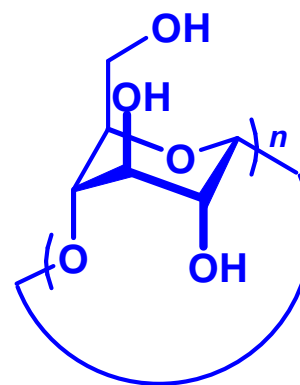


photocontrolled supramolecular machine



cucurbiturils

$n = 6-8$



cyclodextrins

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

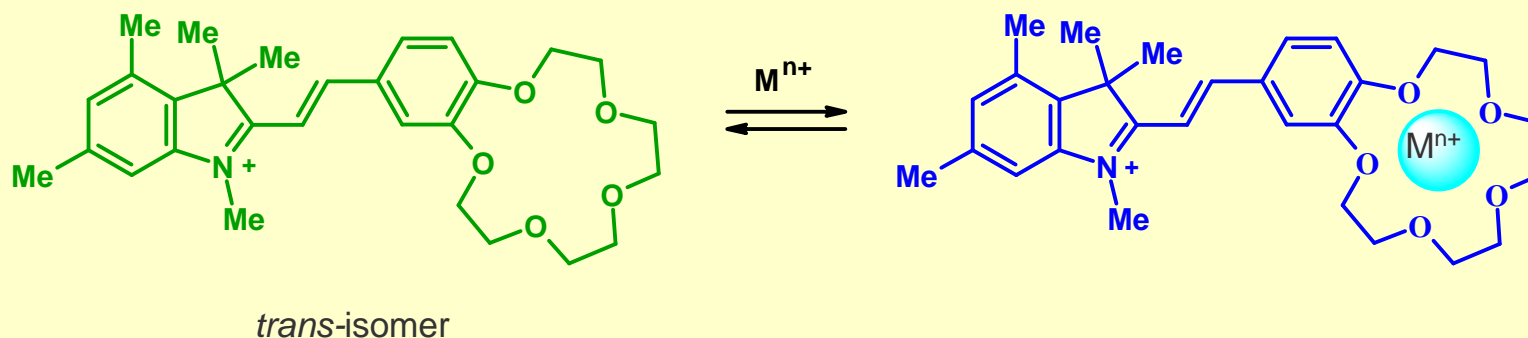
Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review)

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

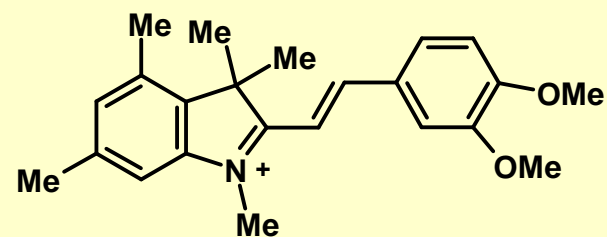
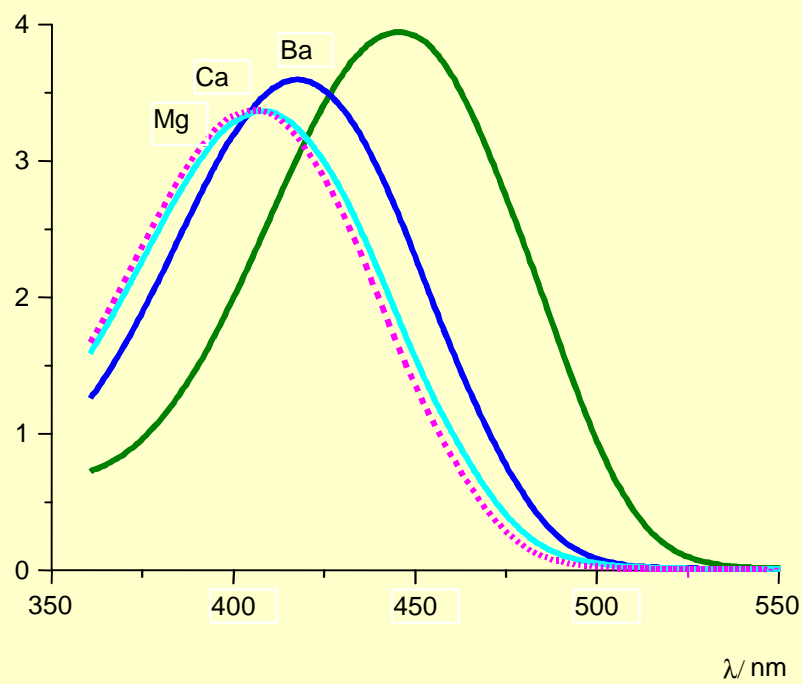
**Self-assembly
of photoswitchable supramolecular devices
with participation of metal cations**

Part I

Complex formation



$\epsilon \cdot 10^{-4} / \text{l mol}^{-1} \cdot \text{cm}^{-1}$

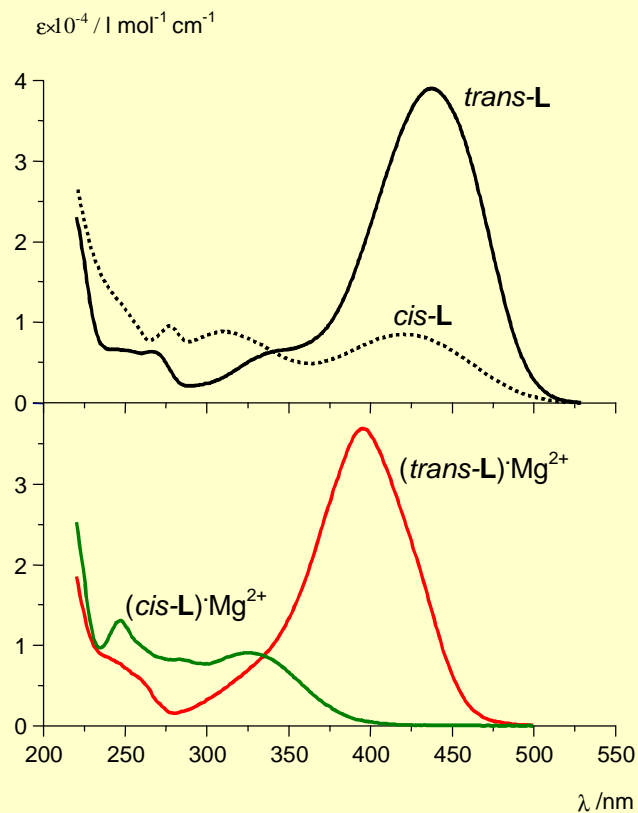
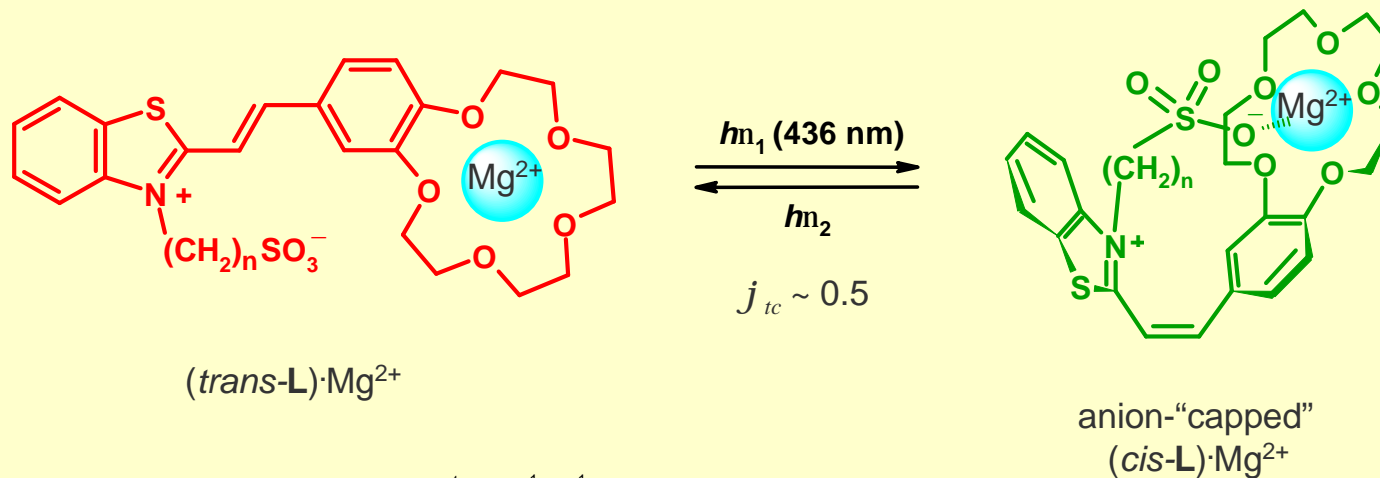


Dokl. Chem. **1990**, 314, 279;

Ushakov E. N., Alfimov M. V., Gromov S. P. *Macroheterocycles.* **2010**, 3, 189 (review)

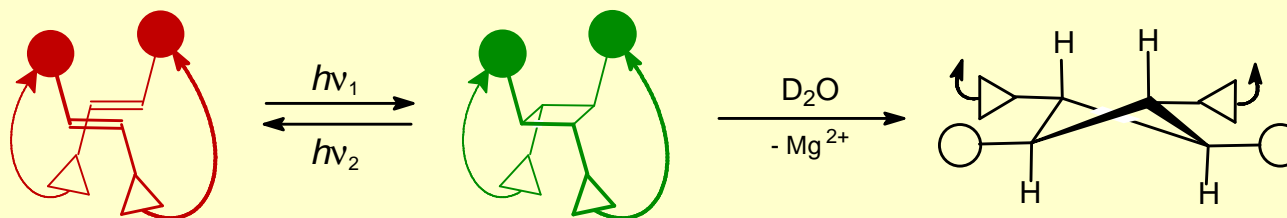
J. Org. Chem. **2013**, 78, 9834.

Photoswitchable supramolecular devices



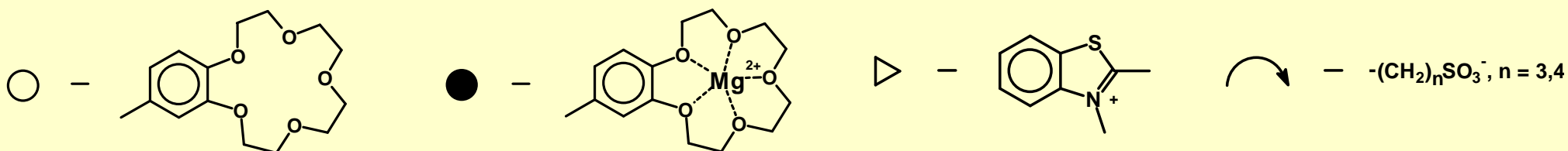
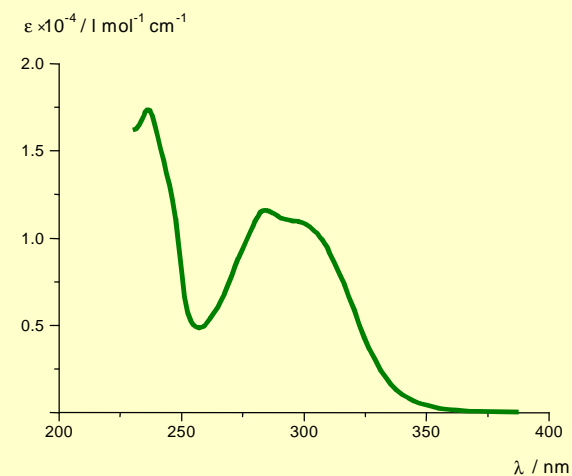
Dokl. Chem. **1991**, 317, 99;
Chem. Phys. Lett. **1991**, 185, 455;
J. Am. Chem. Soc. **1992**, 114, 6381;
J. Am. Chem. Soc. **1999**, 121, 4992.

Photoswitchable supramolecular devices



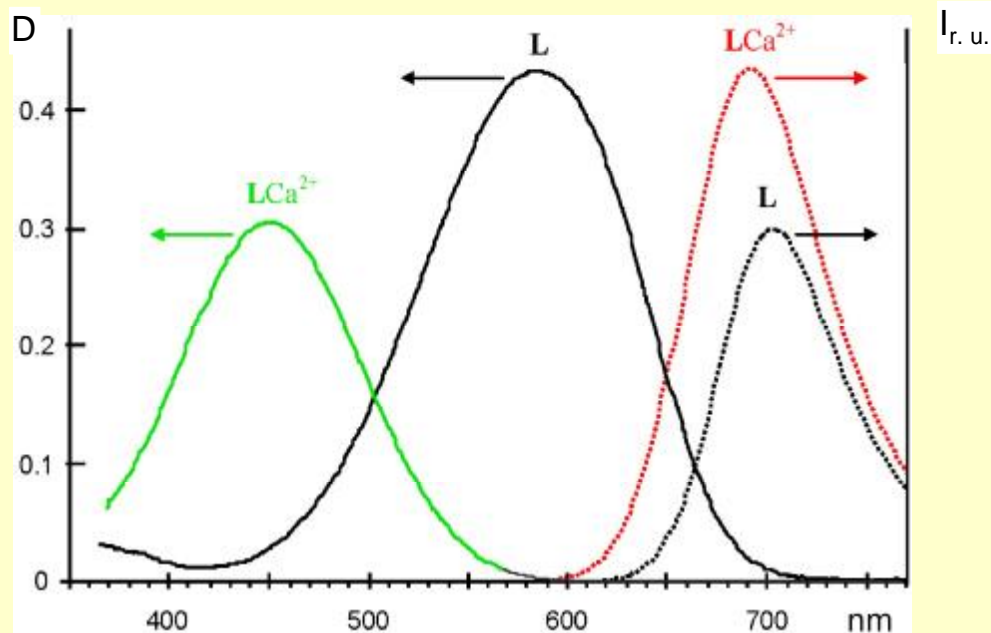
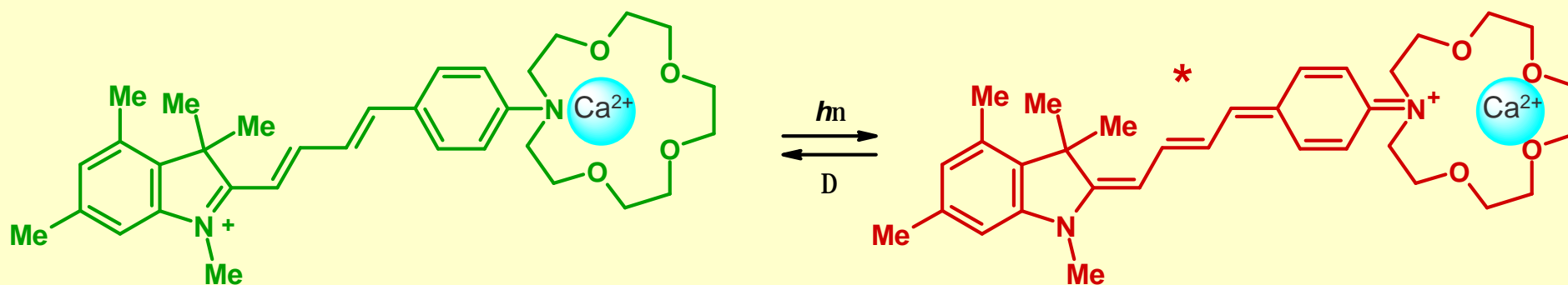
[2+2] Photocycloaddition of CSD

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

Photoswitchable supramolecular device



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

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

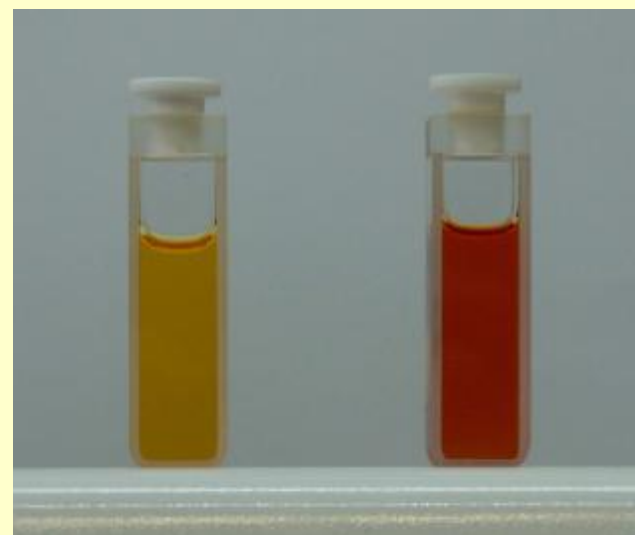
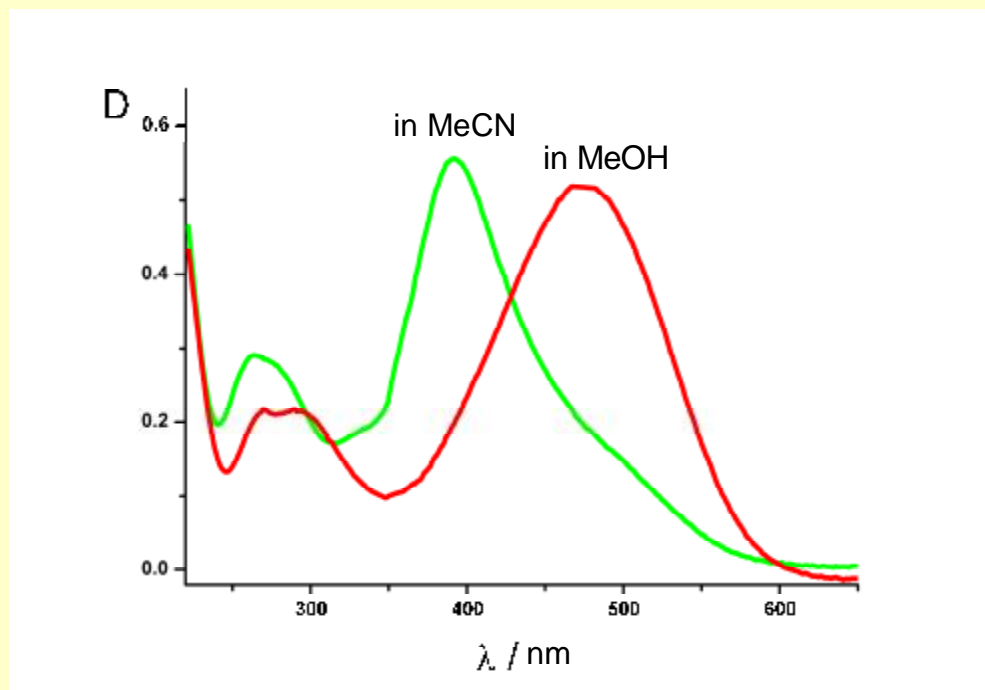
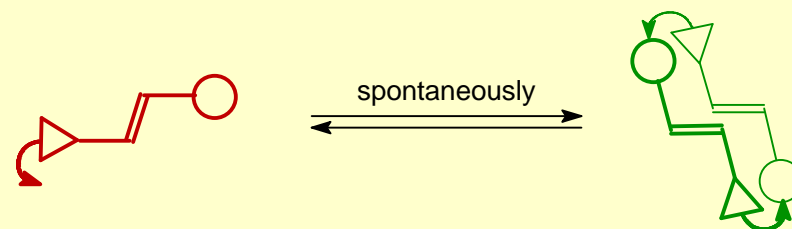
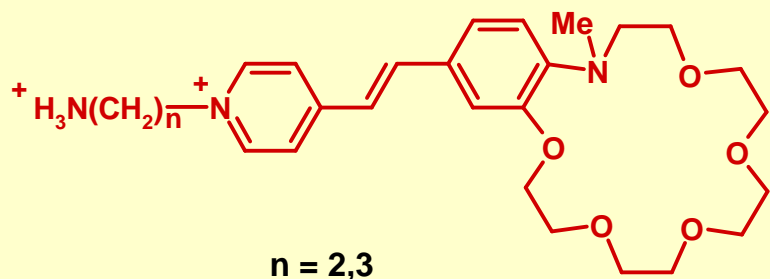
Rusalov M. V., Alfimov M. V., Gromov S. P. et al. *Russ. Chem. Rev.* **2010**, 79, 1099 (review).;

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

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

Part II

Dimerization of CSD

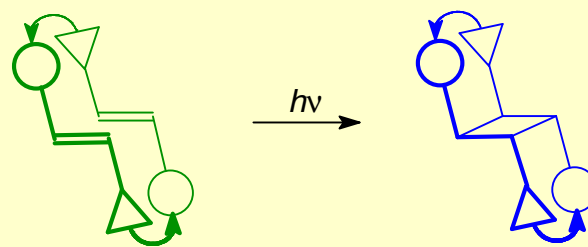


in MeCN

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



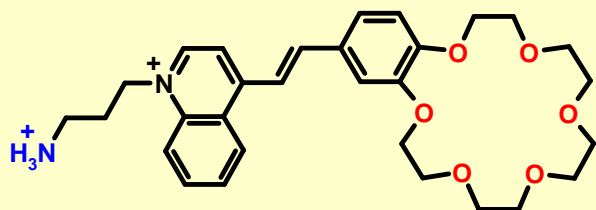
F_{PCA} up to 0.38

syn-"head-to-tail"

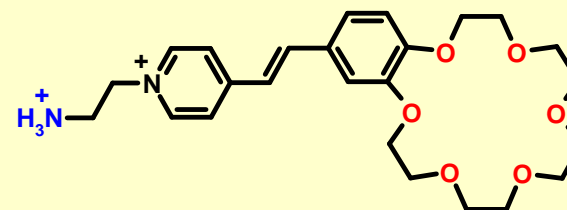
syn-isomer

Yield, %

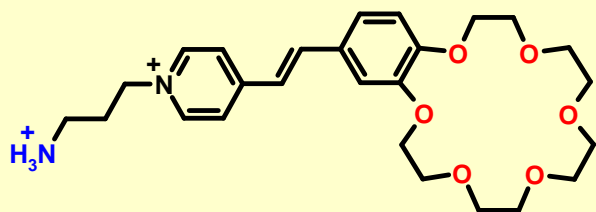
Yield, %



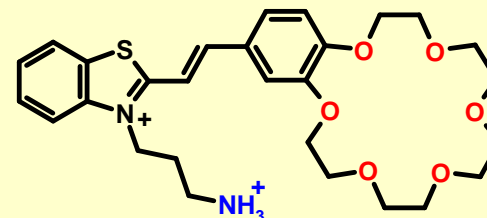
100



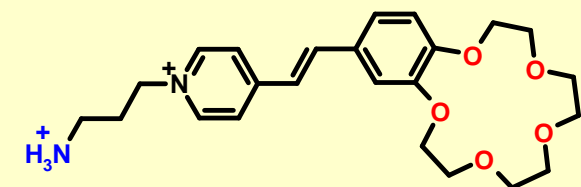
33



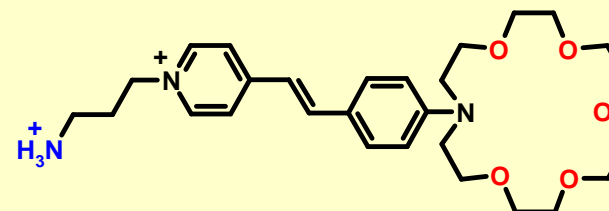
100



0



40

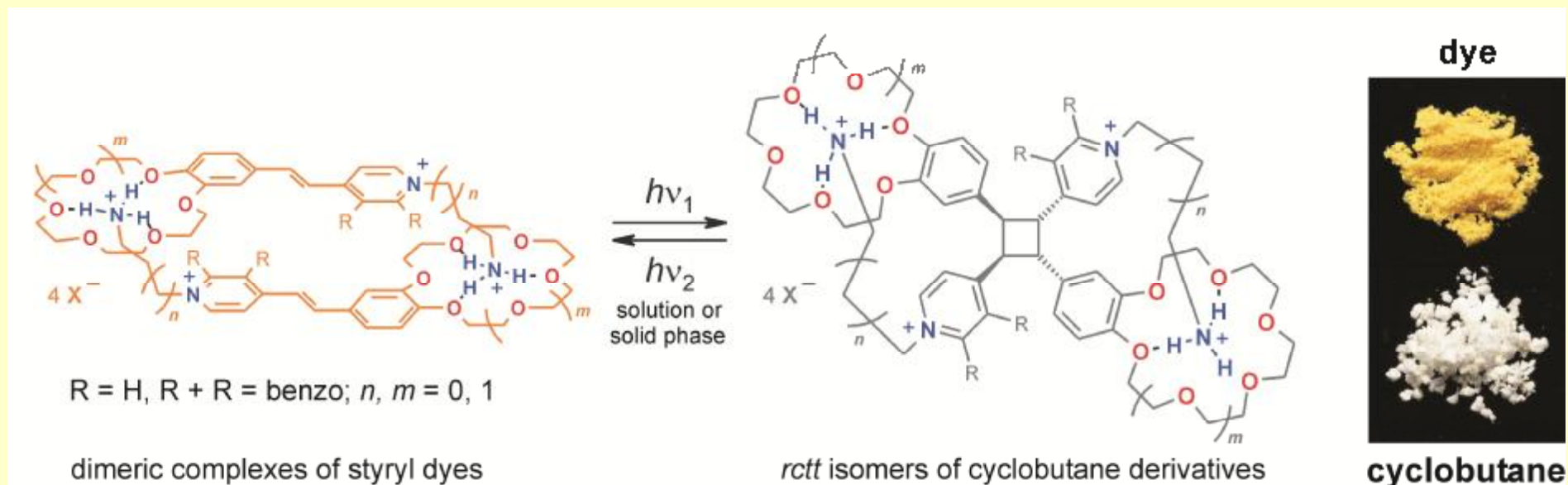


0

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

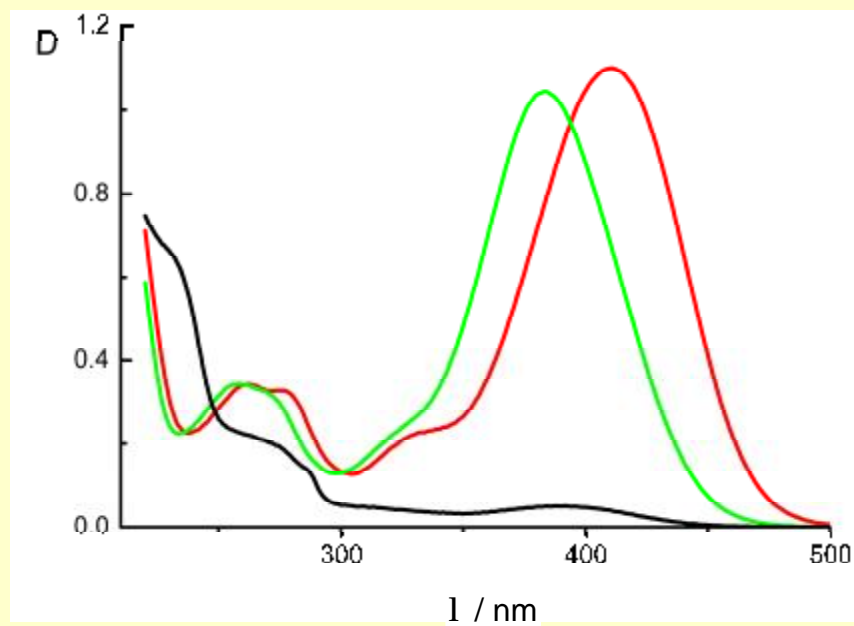
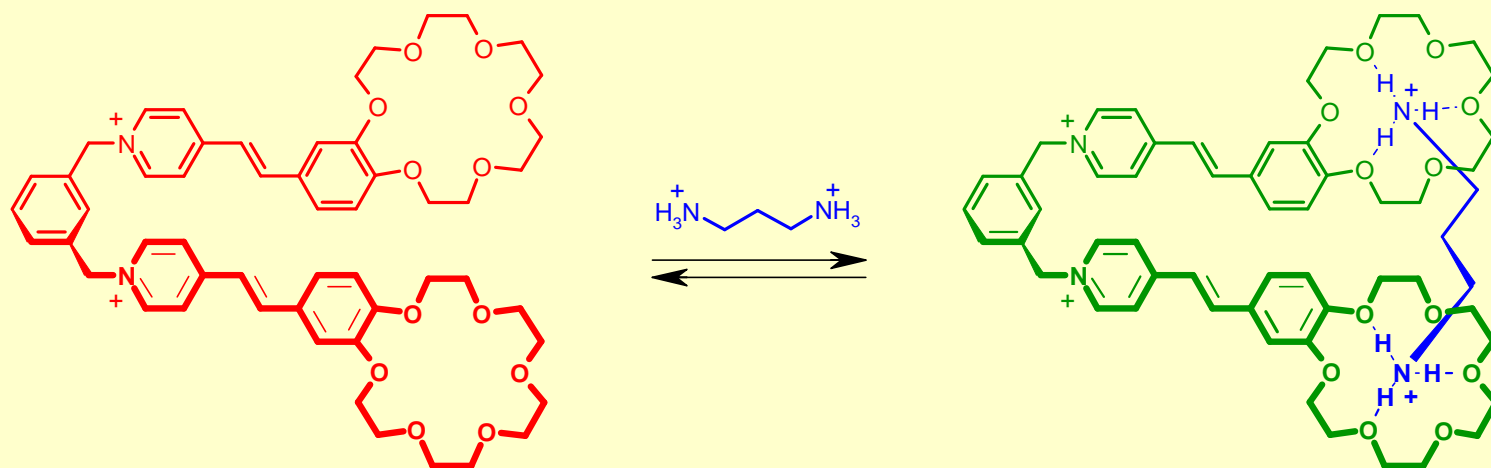
Supramolecular photoswitches based on ammonioalkyl derivatives of crown-ether styryl dyes



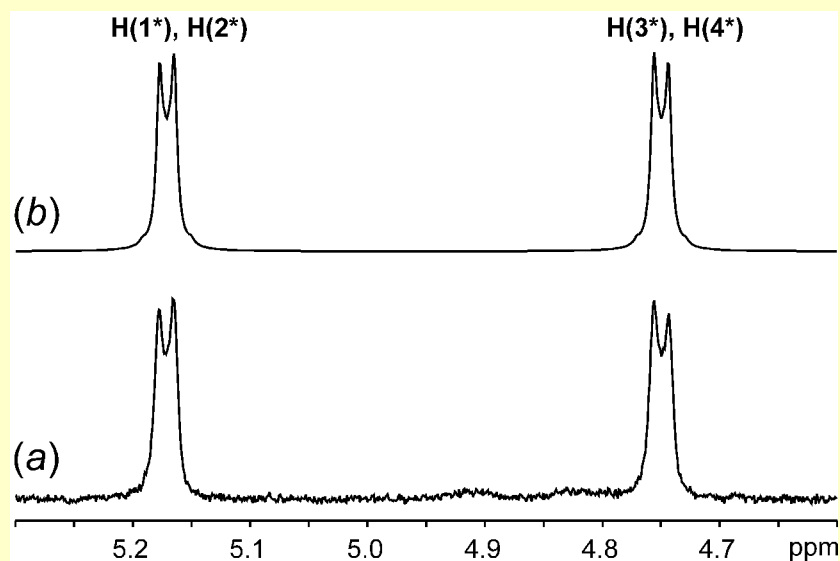
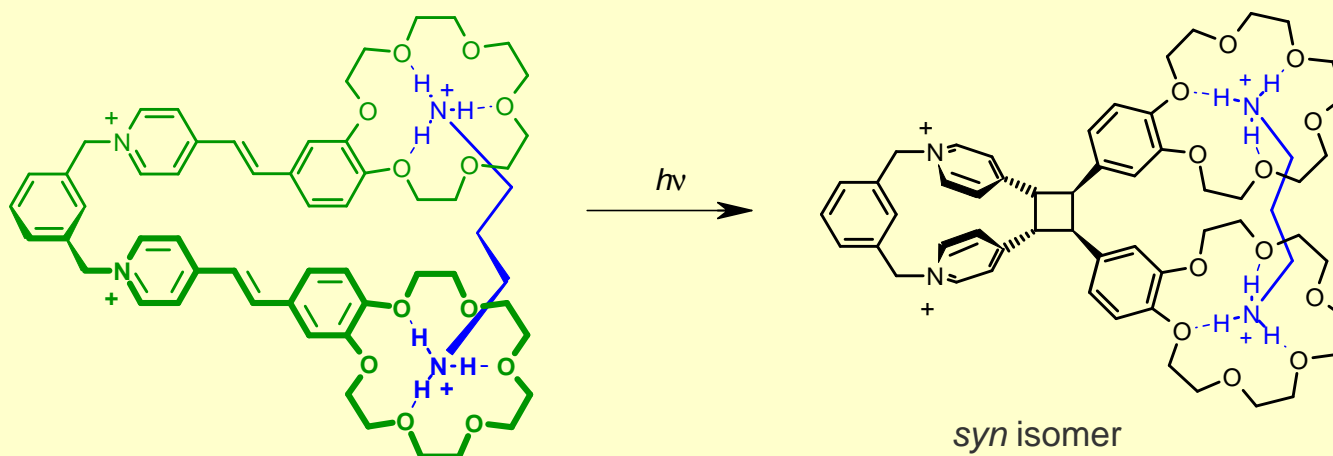
($X = \text{ClO}_4^-$;
 $R = H, n = m = 1$)

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

FORMATION OF PSEUDOSANDWICH COMPLEXES

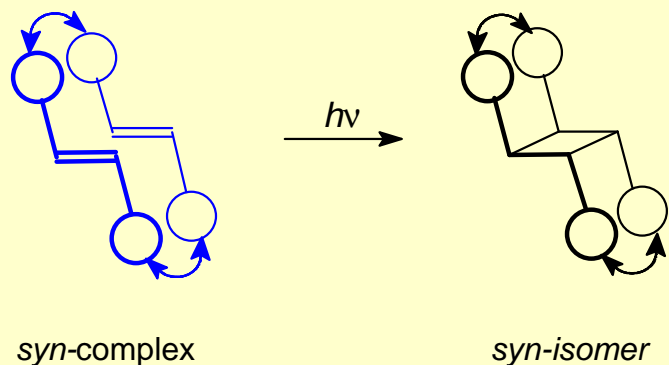


Intramolecular [2+2] photocycloaddition of bisCSD

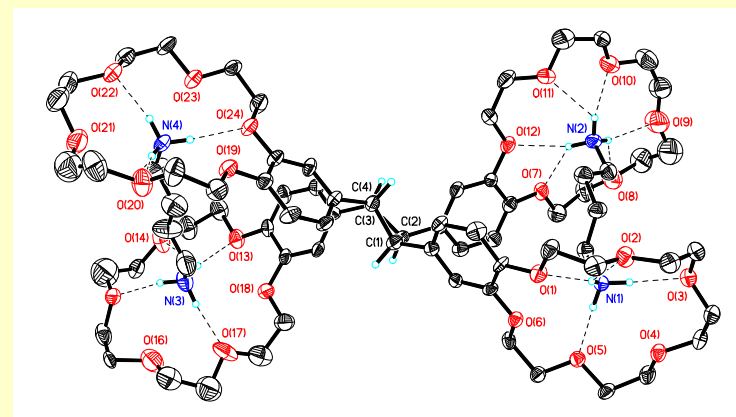
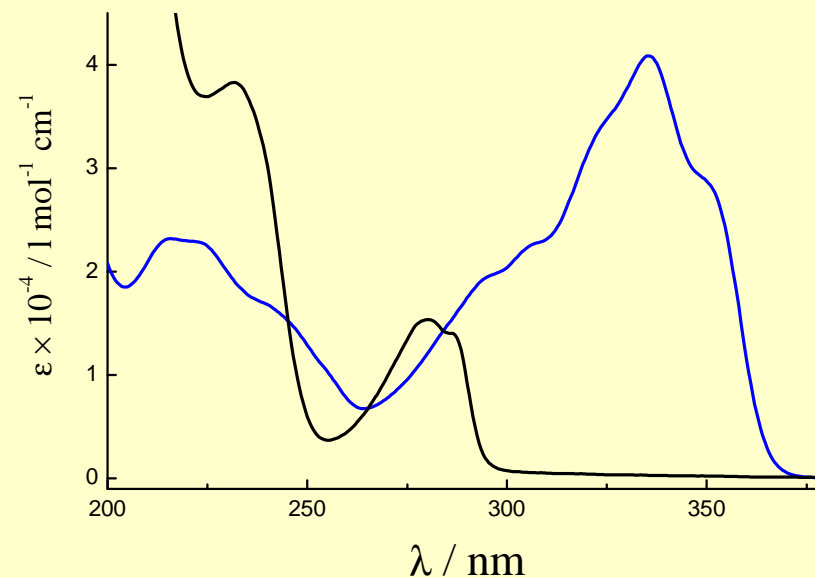
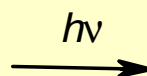
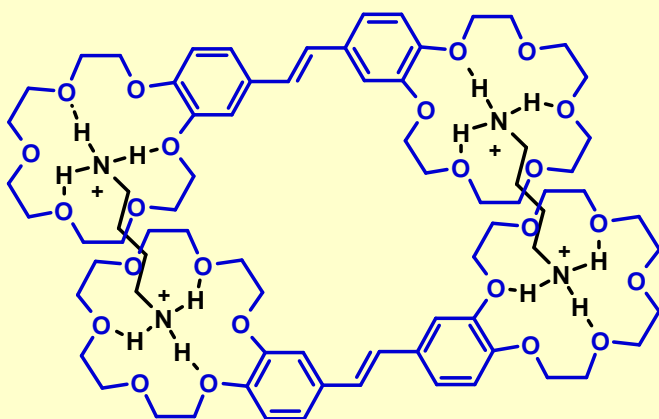
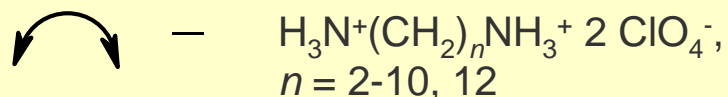


(a) ^1H NMR spectrum of the cyclobutane protons and (b) its best fit to an AA'BB' spin system.

Formation of bispseudosandwich complexes and [2+2] Photocycloaddition



F_{PCA} up to 0.27



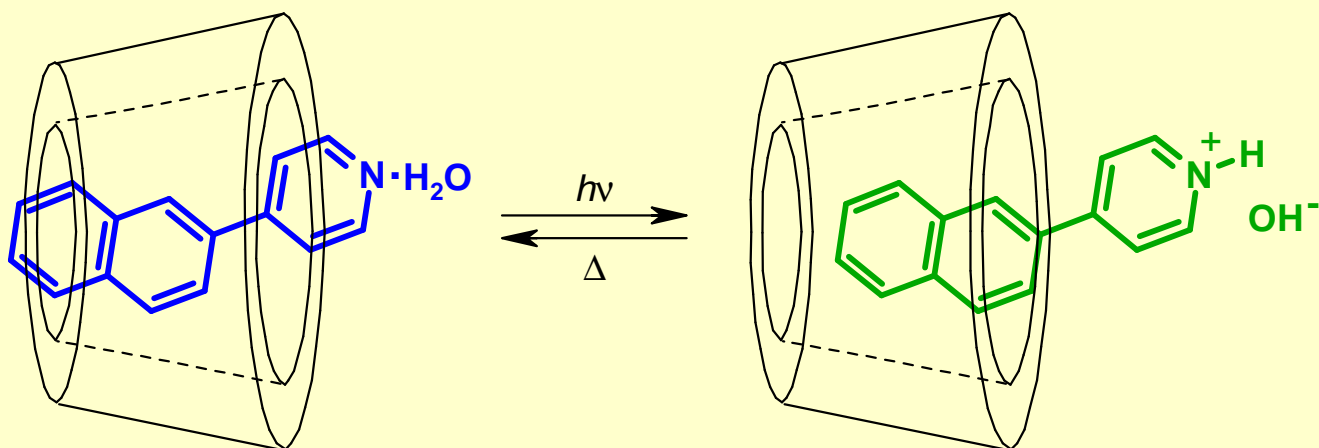
syn-isomer

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



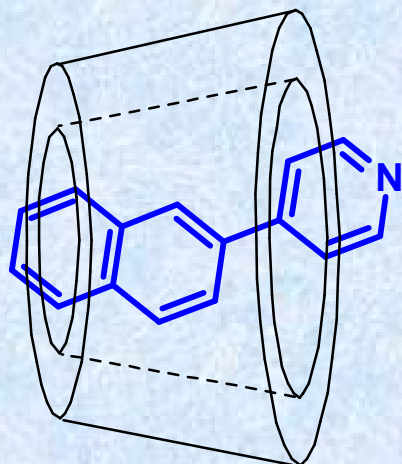
$1 \cdot \text{H}_2\text{O} @ \text{HP-}\beta\text{-CD}$

$\log K = 1.9$

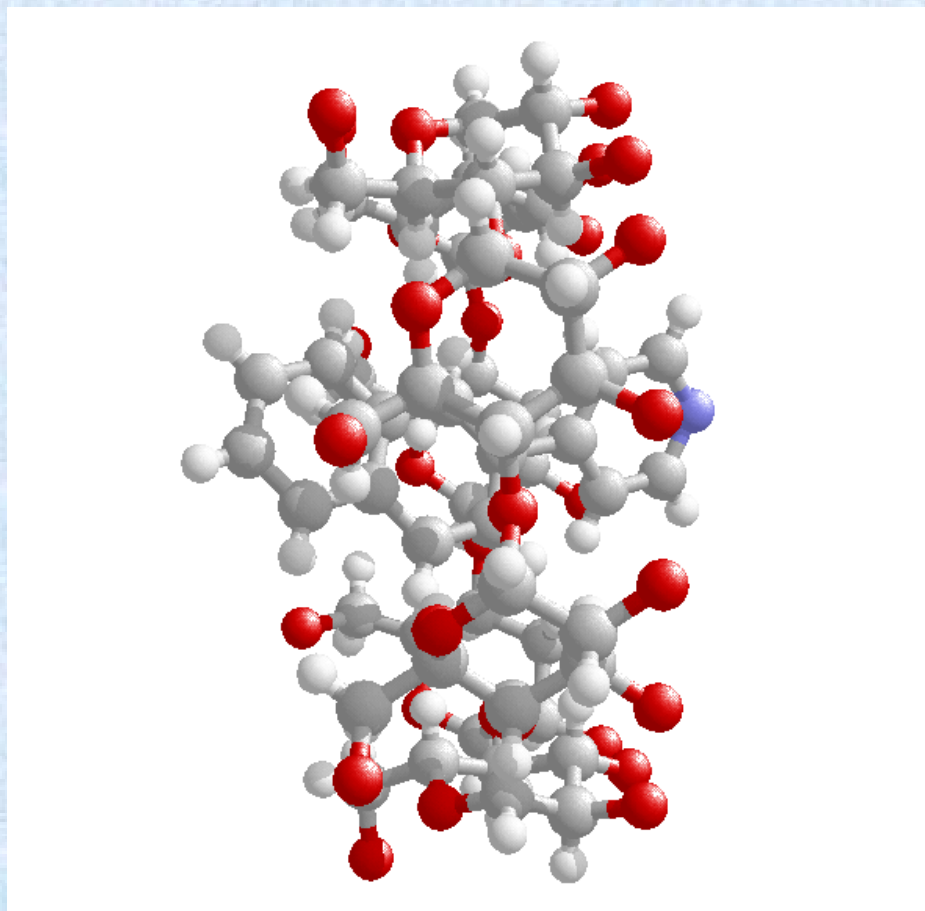
$1\text{H}^+\text{OH}^- @ \text{HP-}\beta\text{-CD}$

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.

X-ray structure determination of photocontrolled supramolecular machine

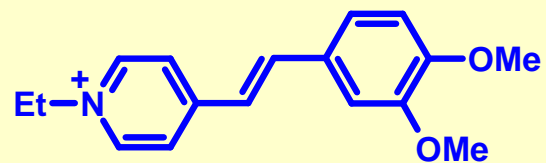


1@ β -CD

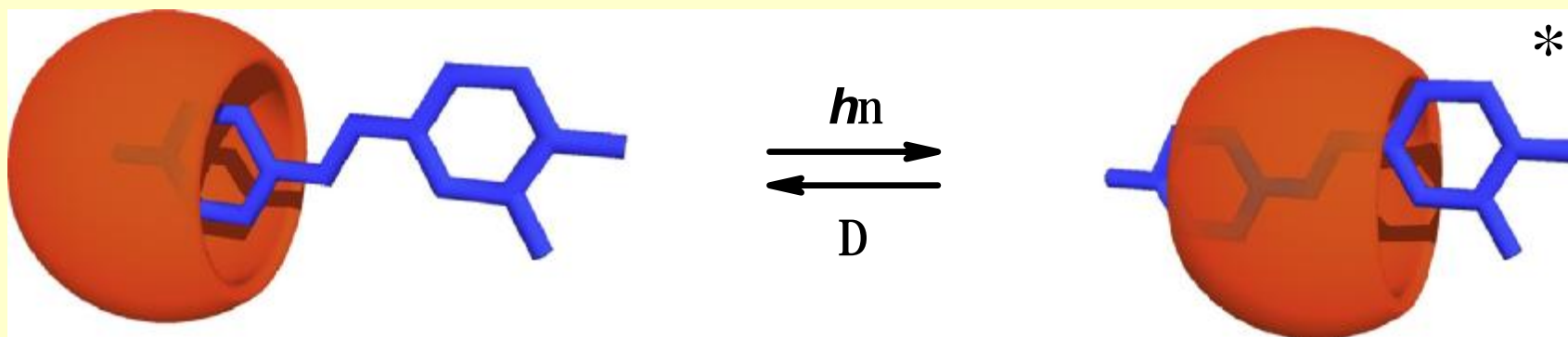


Russ. Chem. Bull. **2004**, 53, 2525;
J. Photochem. Photobiol. A **2011**, 217, 87;
Russ. Chem. Bull. **2013**, 62, 2150.

PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



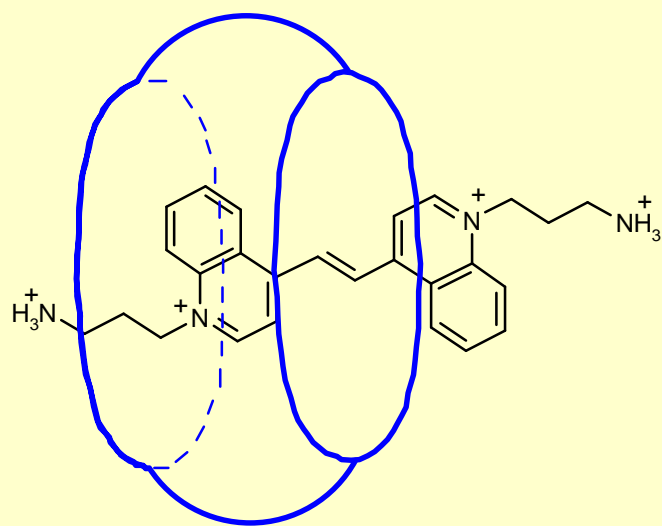
SD



SD@CB[7]

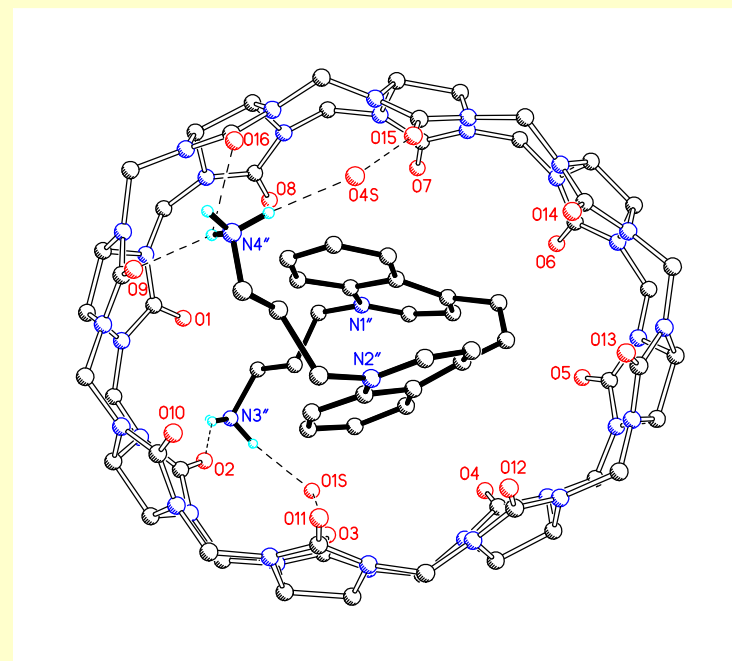
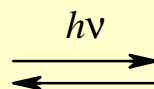
SD@CB[7]*

PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



trans-V@CB[8]

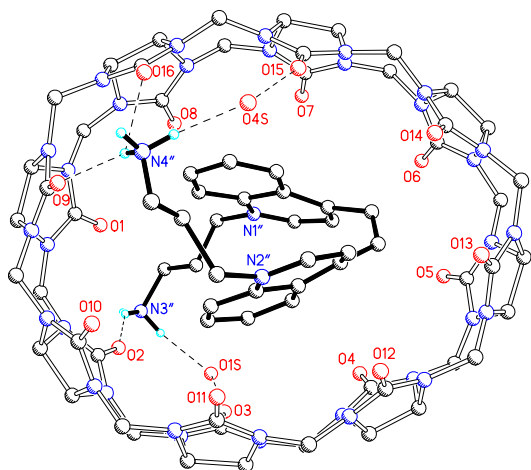
$\log K = 4.6$



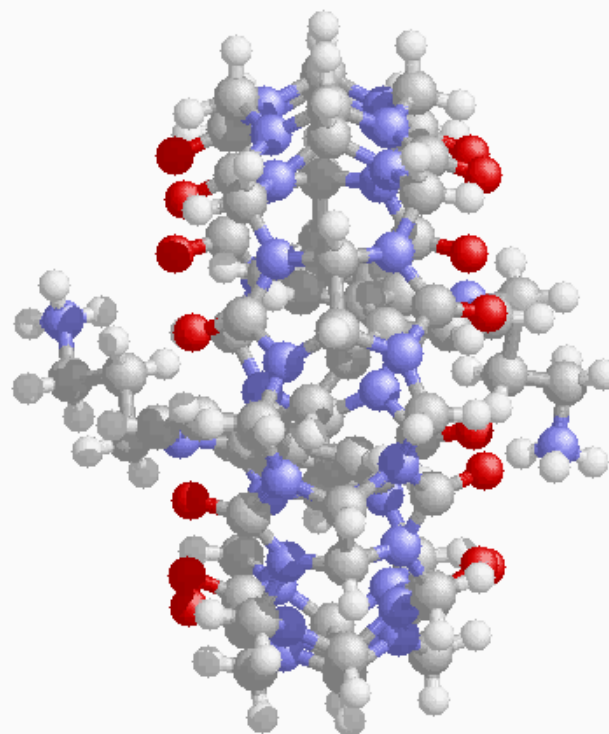
cis-V@CB[8]

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

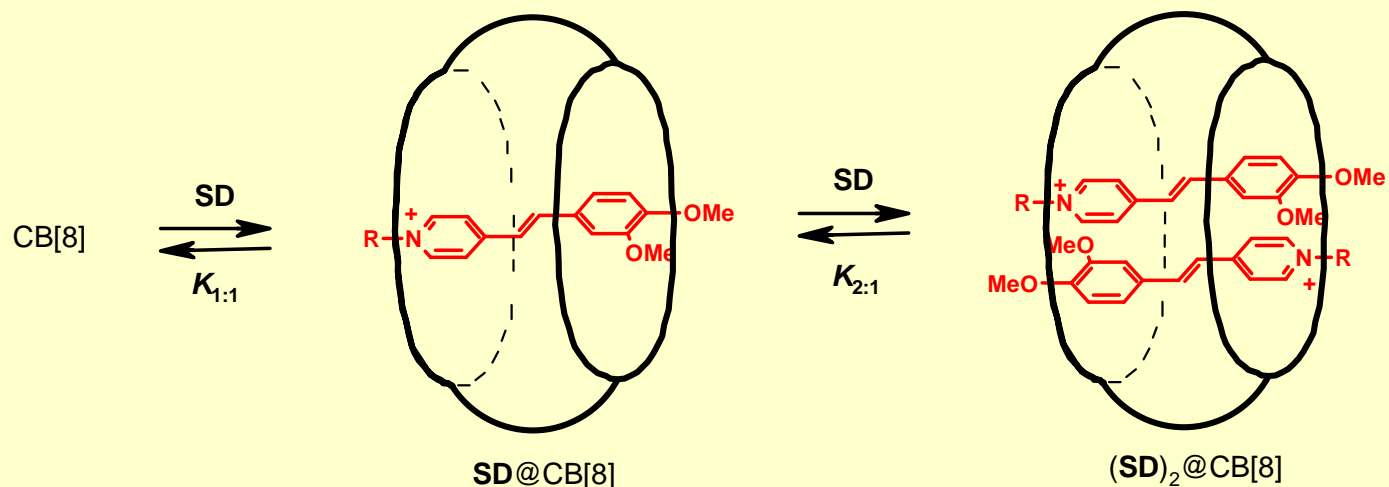
X-ray structure determination of photocontrolled supramolecular machine



cis-V@CB[8]



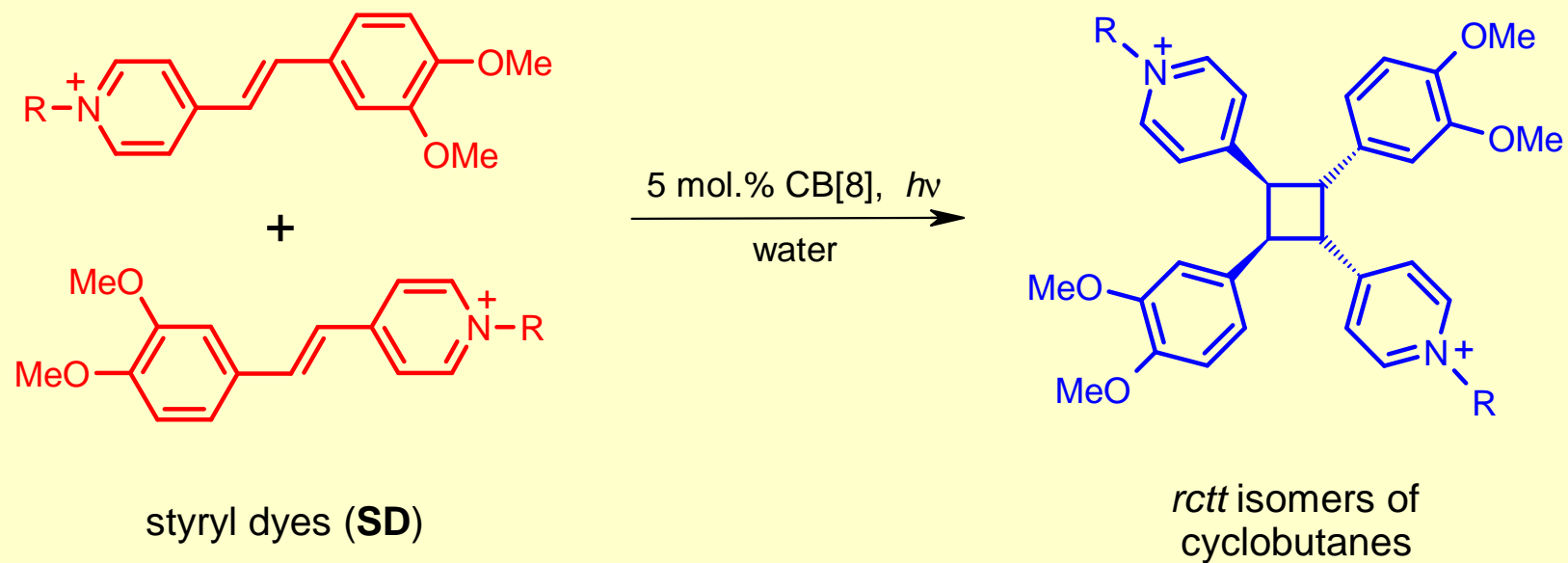
PHOTOCONTROLLED SUPRAMOLECULAR MACHINES



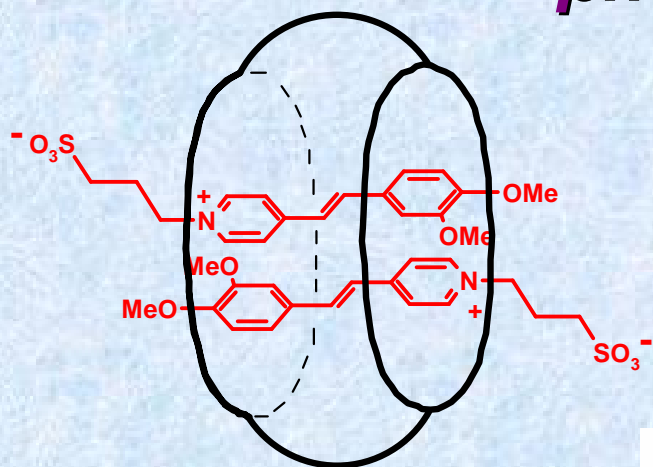
SD	CB[8]		
R	log $K_{1:1}$	log $K_{2:1}$	log K_{cyclo}
Et	4.9	4.1	4.3
$(\text{CH}_2)_3\text{NH}_3^+$	5.0	4.4	4.8
$(\text{CH}_2)_3\text{SO}_3^-$	4.0	2.6	3.2

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

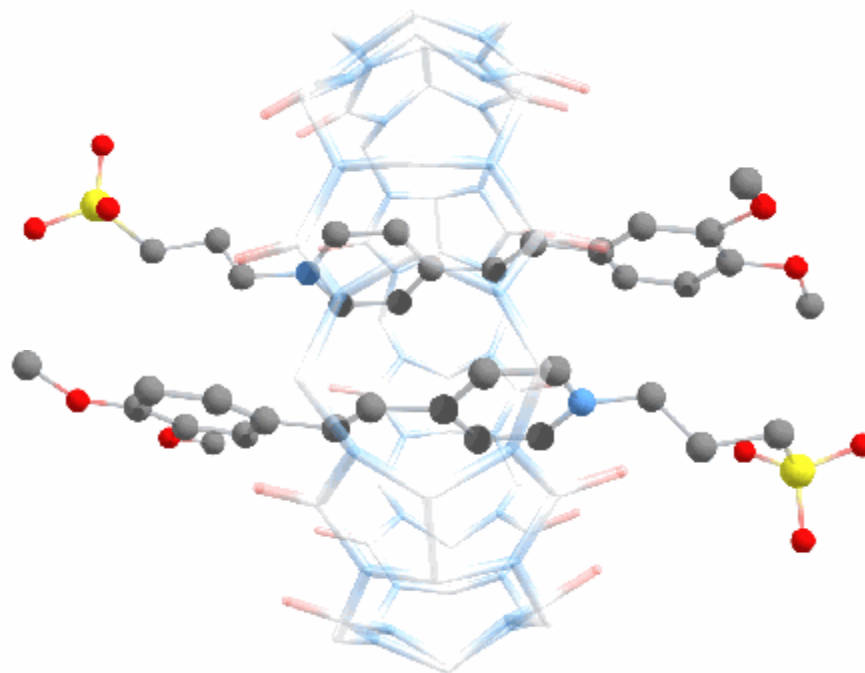


X-ray structure determination of photocontrolled supramolecular assembler



(CK)₂@CB[8]

Time of pre-organization ~ 4 ps



It is possible to implement all main types of photoprocesses:

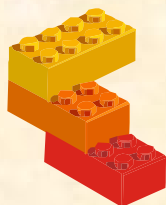
- § Fluorescence, excimer formation
- § Photodissociation
- § Photoisomerization
- § Photocycloaddition
- § photoelectrocyclization
- § charge-transfer complex formation,
electron transfer
- § proton transfer
- § excitation transfer
- § TICT state

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);

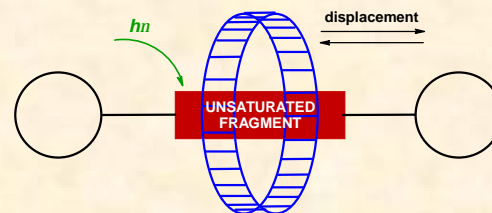
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, 84, 787 (review).

Molecular meccano of photoactive supramolecular systems

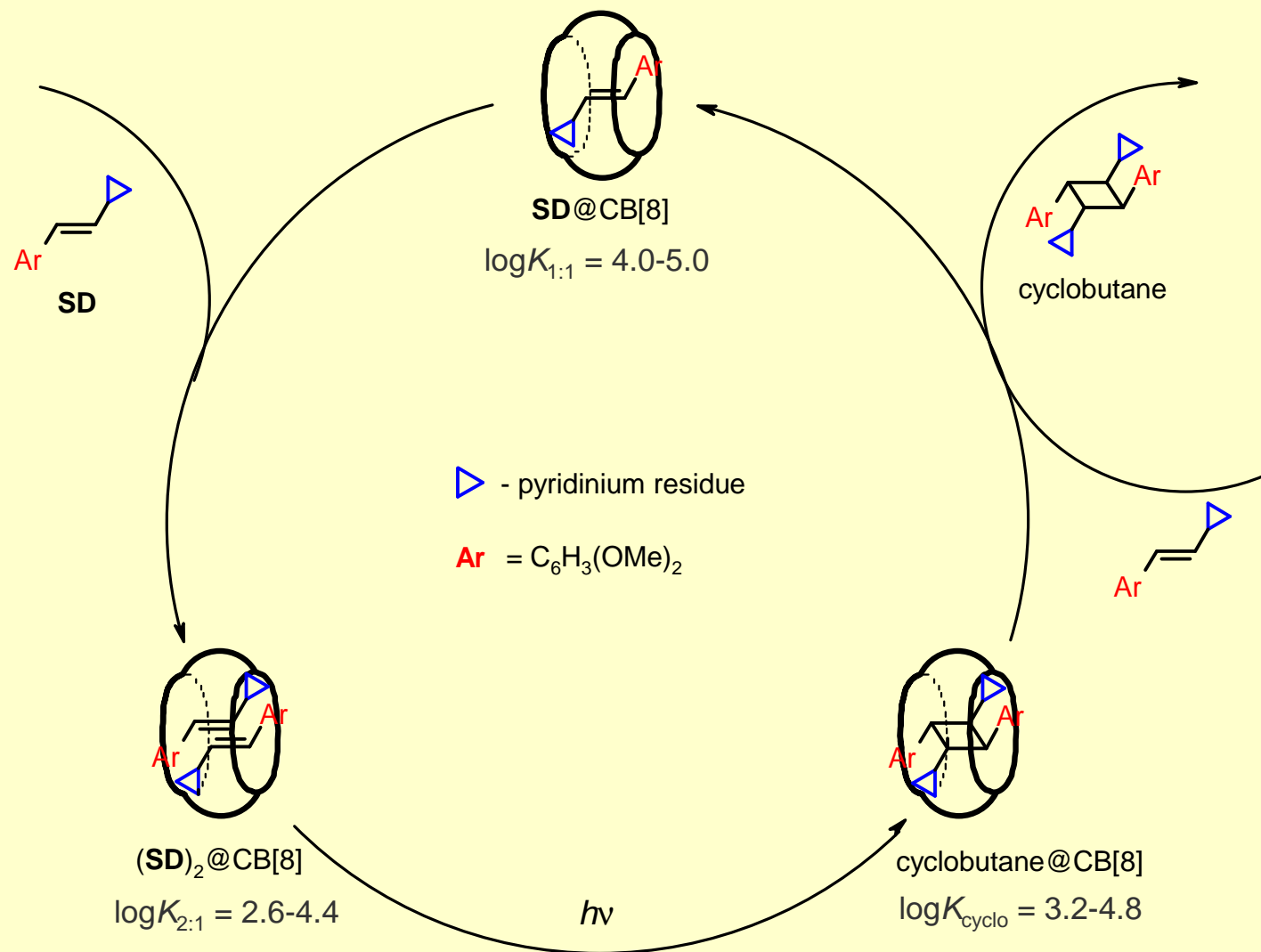


Unique set of characteristics needed:

- § 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.



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.

Thank You!

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