РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

The Fifth International Scientific Conference:

Advances in Synthesis and Complexing

Molecular meccano of photoactive supramolecular devices and machines based on unsaturated and macrocyclic compounds

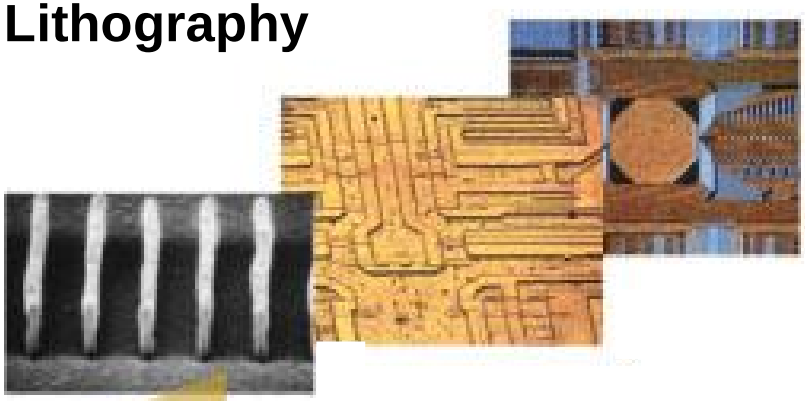
Prof. Sergey P. Gromov

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

NANOTECHNOLOGY “BOTTOM-UP”

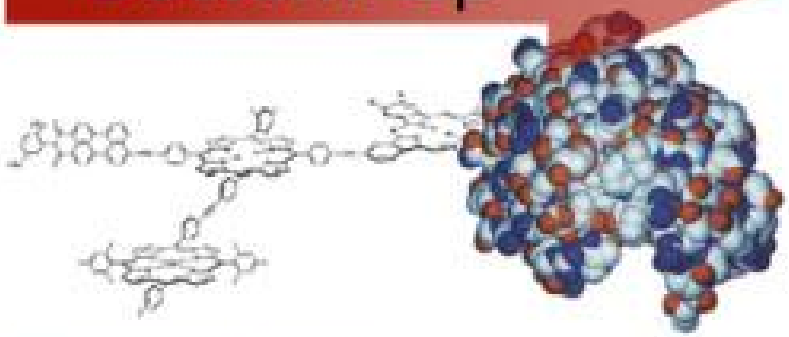
STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES

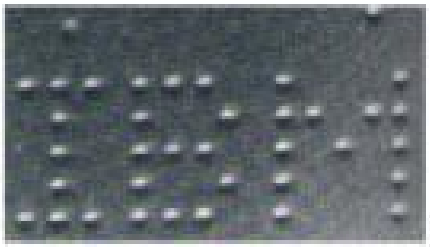
Lithography



Bottom-Up

Top-Down





Organic synthesis
Supramolecular Self-Assembly

HIERARCHY OF STRUCTURAL ORGANIZATION OF MATTER

Atoms a b c

Molecules A (a-a) B (a-b) C (a-c)

covalent bonds

Supramolecular systems A…..A A…..B Supramolecules

A…..B…..C
⋮ ⋮
C…..A

Supramolecular ensembles

noncovalent bonds
(intermolecular)

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TYPES OF INTERMOLECULAR BONDS

Coordination bonds

Ion-ion interactions

Ion-dipole interactions

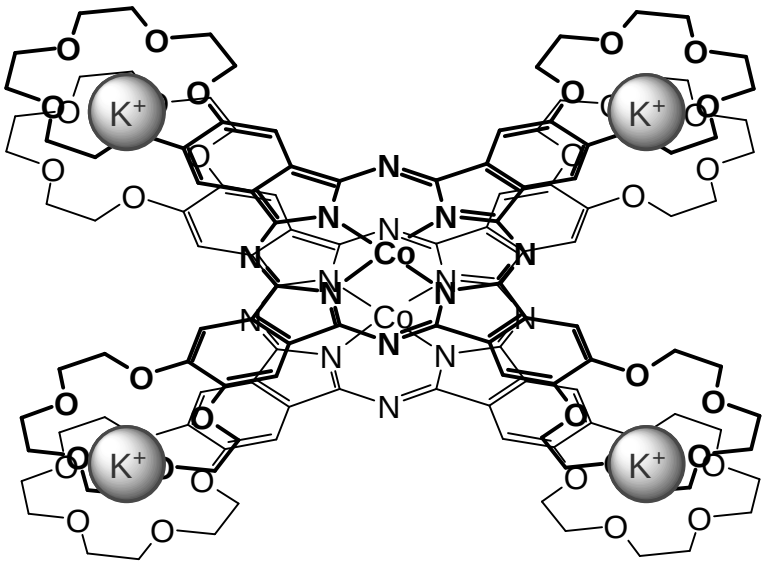
Hydrogen bonds

Dipole-dipole interactions

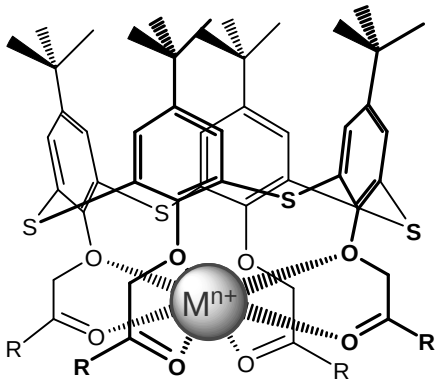
Stacking interactions

Hydrophobic interactions

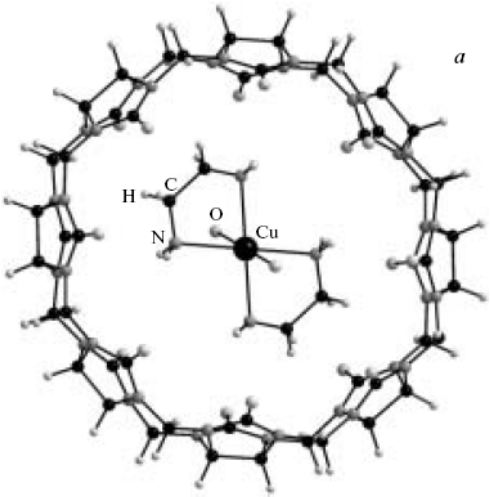
SUPRAMOLECULAR SYSTEMS



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



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



Fedin V. P. et al.

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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

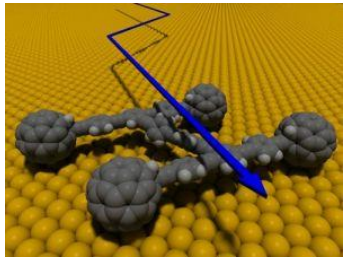
J.-P. Sauvage :
Molecular machines and mechanically linked molecules, including catenans, rotaxanes and nodes. The first to receive was a trefoil knot and a molecular muscle.

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

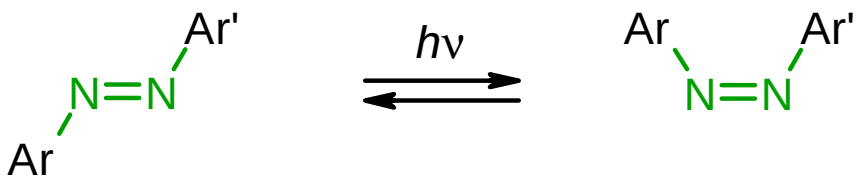
B. L. Feringa:
Molecular motors.

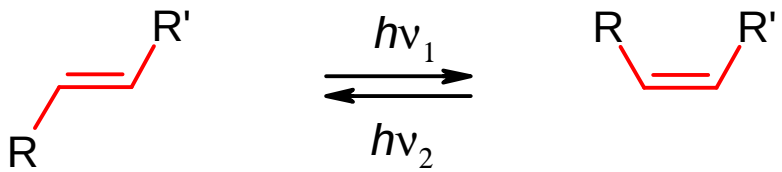
Means for control of supramolecular devices and machines

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

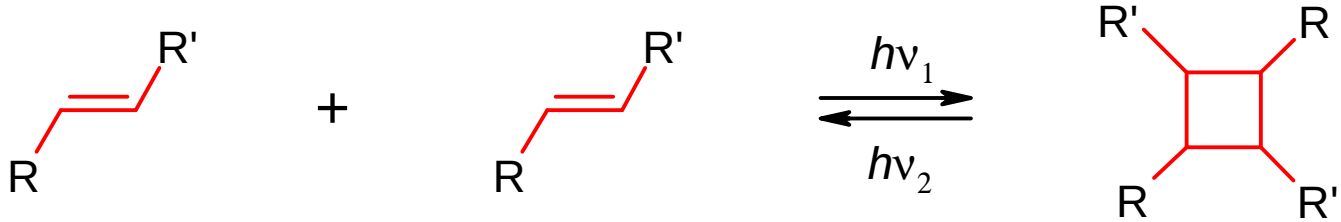


PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS





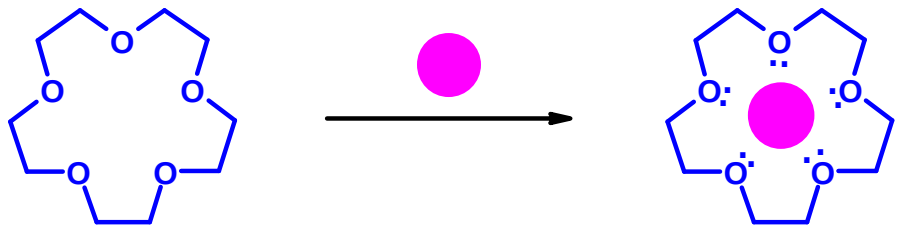
trans-isomer *cis*-isomer



cyclobutane

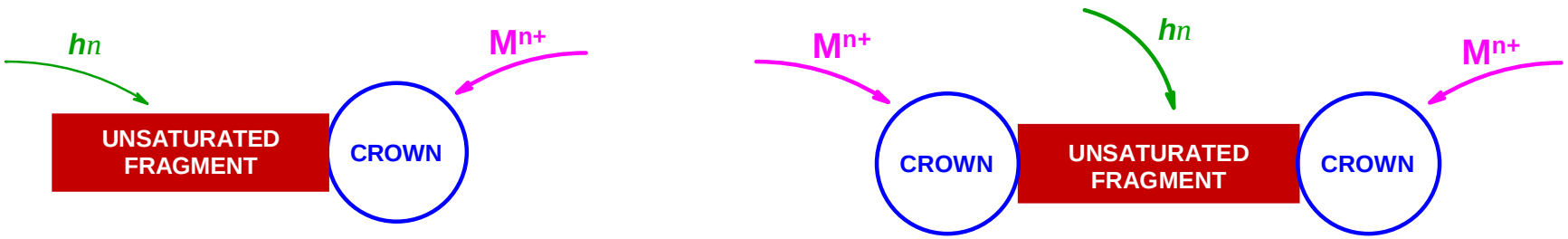
Gromov S. P. *Russ. Chem. Bull*. **2008**, *57*, 1325 (review);
Gromov S. P. *Rev. J. Chem.* **2011**, *1*, 1 (review);
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, *84,* 787 (review).

PHOTOSWITCHABLE SUPRAMOLECULAR DEVICES BASED ON UNSATURATED AND CROWN COMPOUNDS



crown-ether complex

- metal cation



photoswitchable supramolecular device

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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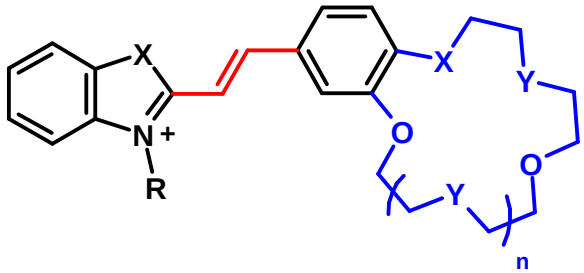
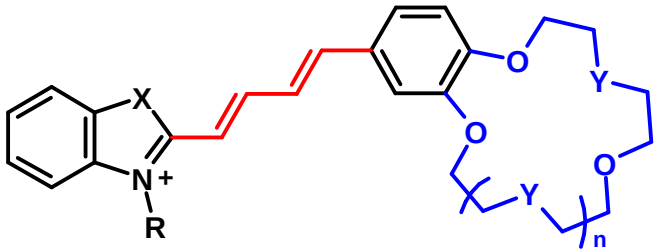
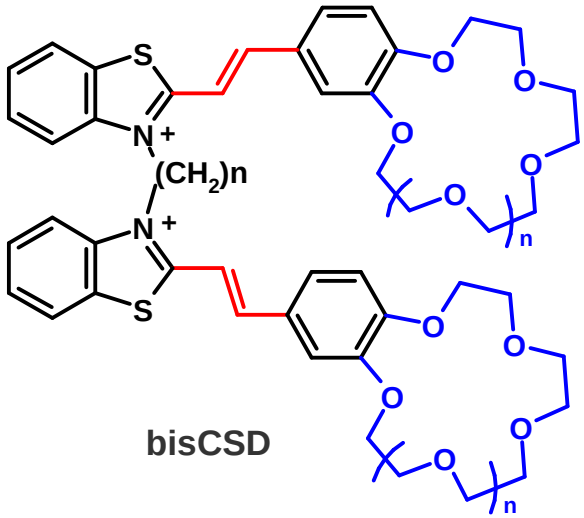
Crown-containing unsaturated compounds



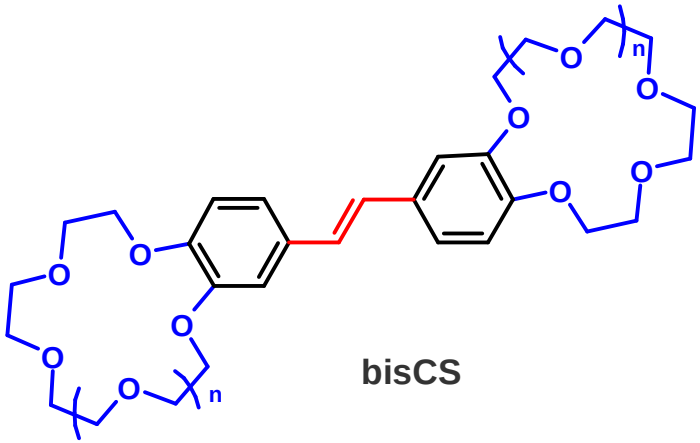
CSD



CBD



bisCSD

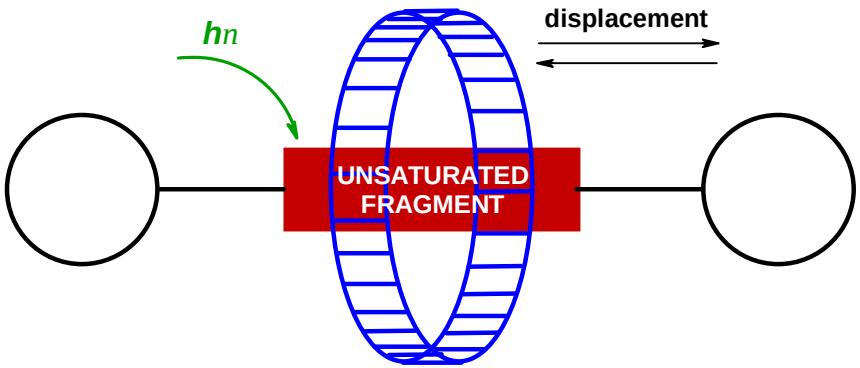


bisCS

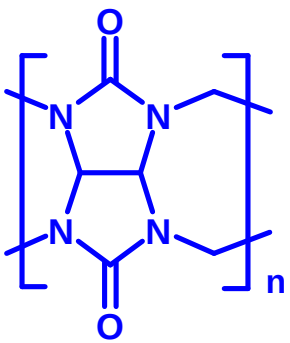
n = 1, 2

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

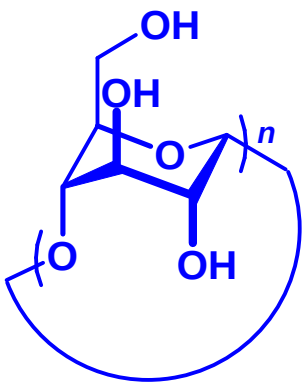
Photocontrolled supramolecular machines based on unsaturated compounds, cucurbiturils and cyclodextrins



photocontrolled supramolecular machine



n = 6-8



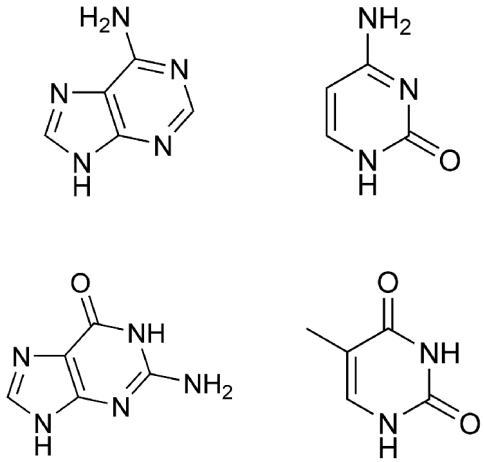
cucurbiturils

cyclodextrins

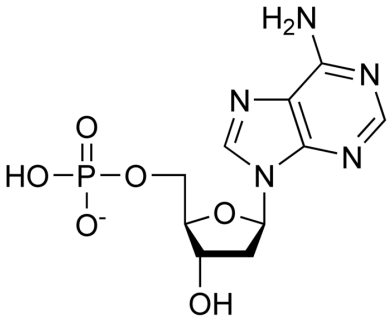
Gromov S. P. *Russ. Chem. Bull*. **2008**, *57*, 1325 (review);
Gromov S. P. *Rev. J. Chem.* **2011**, *1*, 1 (review)
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, *84*, 787 (review).

MOLECULAR MECCANO IN LIVING NATURE

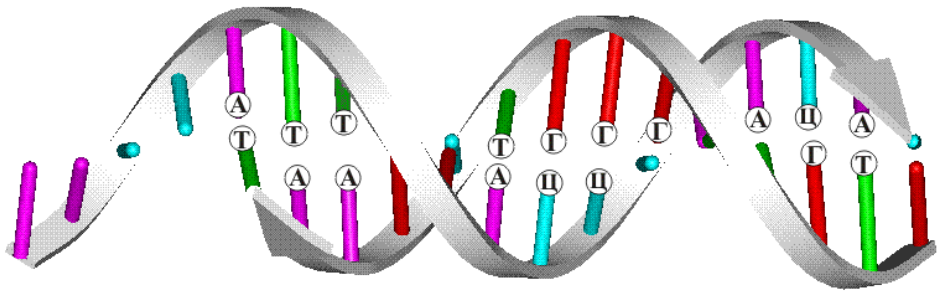
Nucleic acids



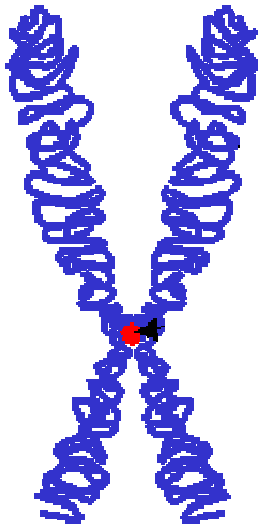
basic nitrogens



nucleotides



nucleic acids



chromosomes

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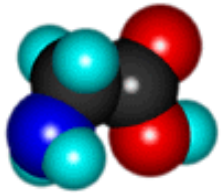
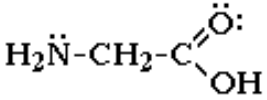
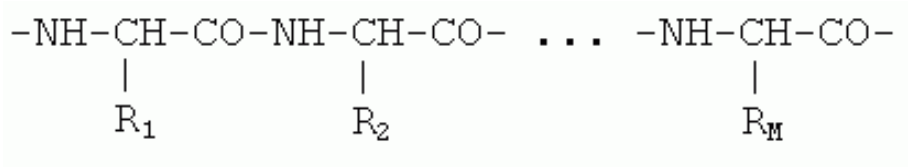
MOLECULAR MECCANO IN LIVING NATURE

Proteins



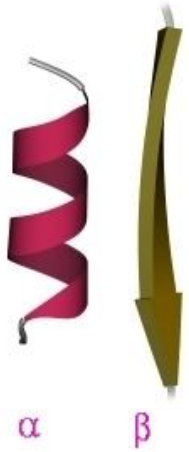


amino acids



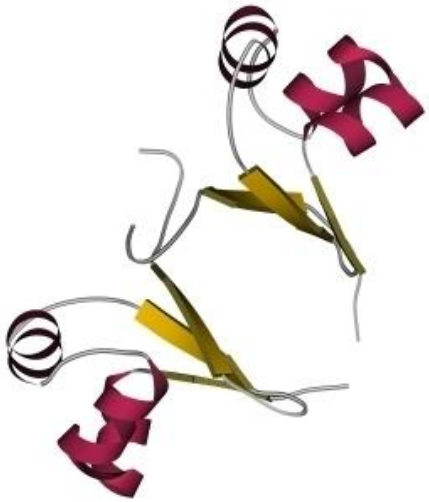
polypeptides

Primary ...–Gly–Val–Tyr–Gln–Ser–Ala–Ile–Asn–Lys–Ala–...



Secondary

Tertiary



Quaternary

proteins

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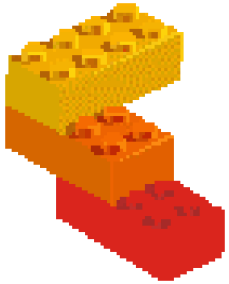
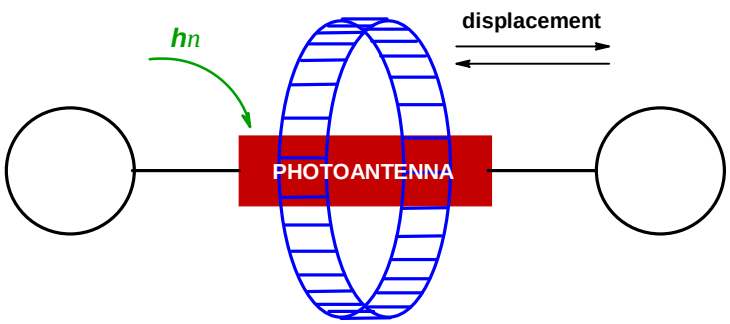
MOLECULAR MECCANO
OF PHOTOACTIVE SUPRAMOLECULAR DEVICES AND MACHINES
IN NANOTECHNOLOGY

photoswitchable supramolecular device





photocontrolled supramolecular machine

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

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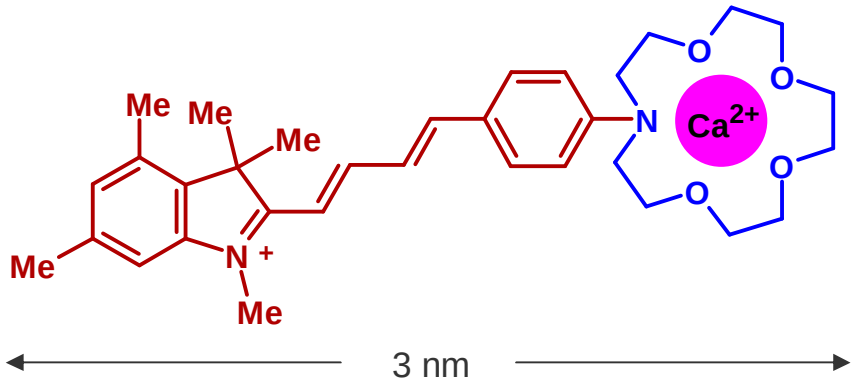
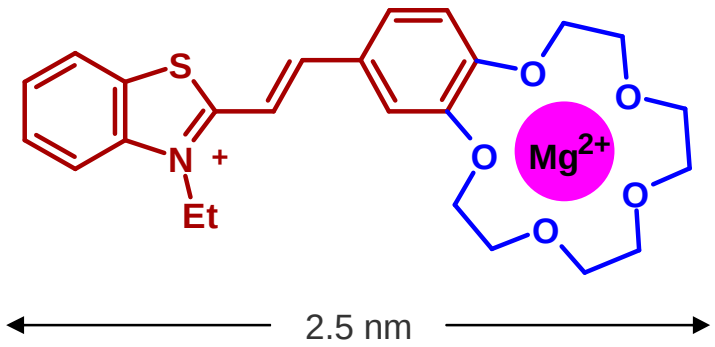
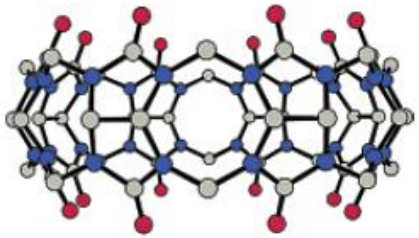
COMPONENT SIZES
IN PHOTOACTIVE SUPRAMOLECULAR DEVICES AND MACHINES



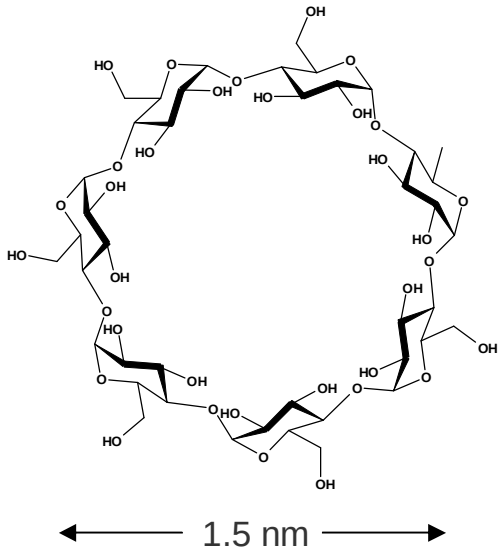
Complex of butadienyl dye



Complex of styryl dye



Cucurbit[8]uril



β-Cyclodextrin

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

Part I

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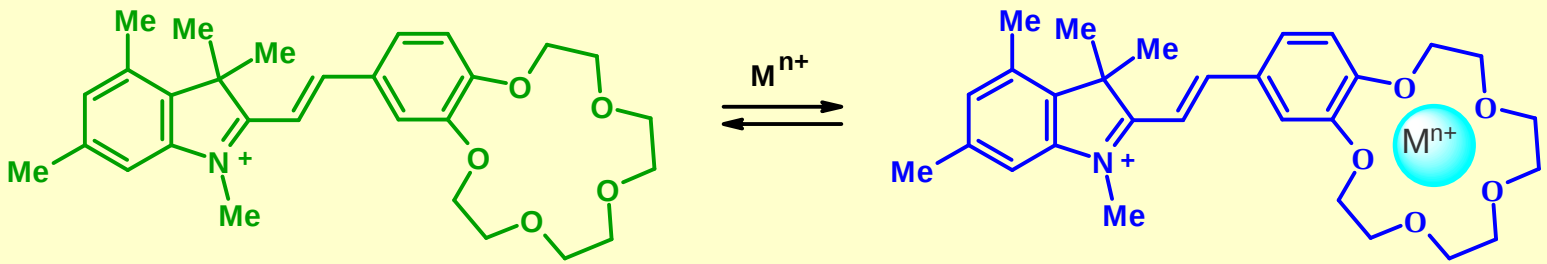
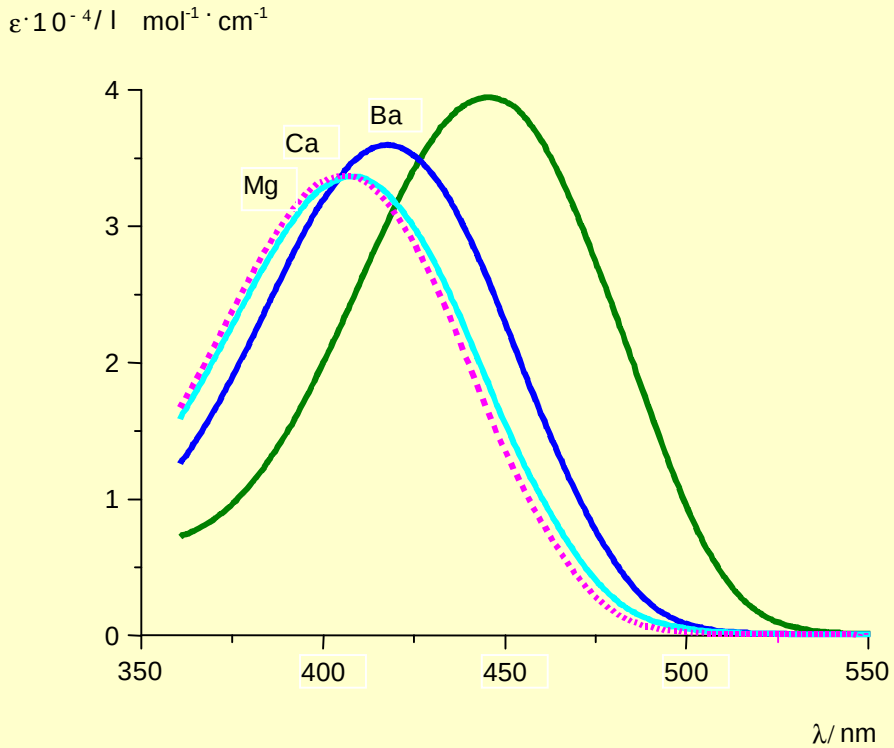
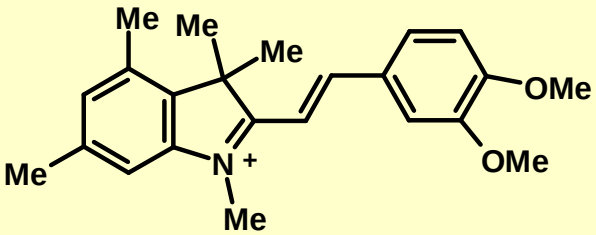
Complex formation



trans-isomer





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

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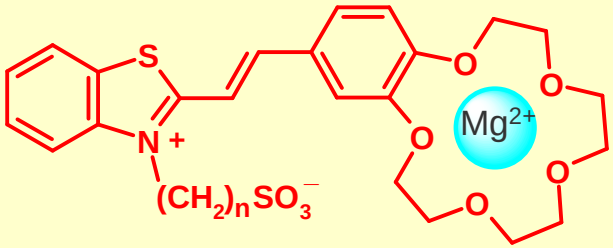
Photoswitchable supramolecular devices

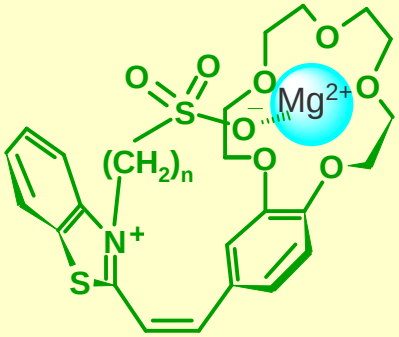


(*trans*-**L**)·Mg^{2+}

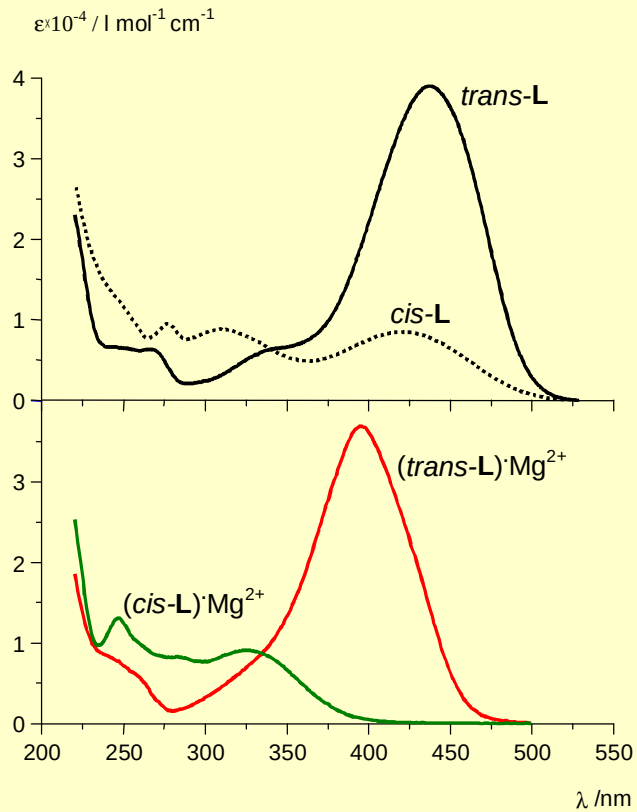
$h\nu_1$ (436 nm) →

← $h\nu_2$

j_{tc} ~ 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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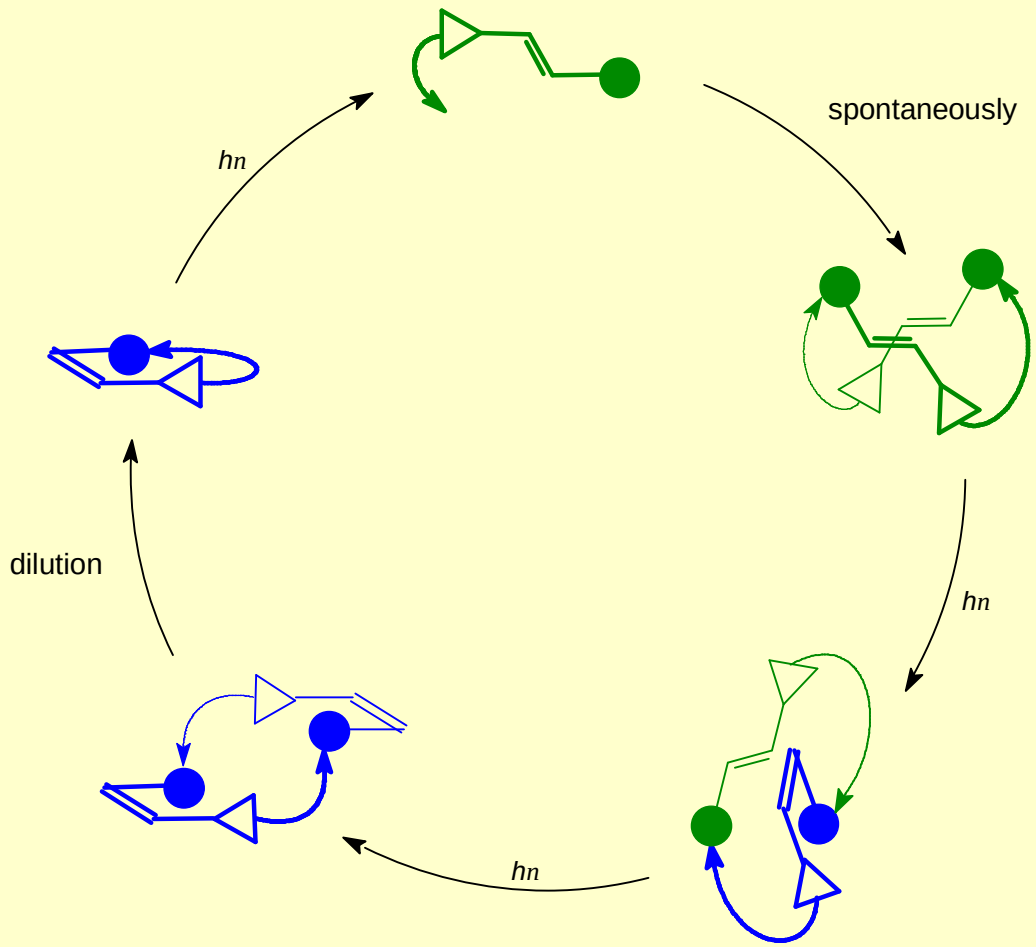
Photocycle of crown-containing styryl dyes



● - 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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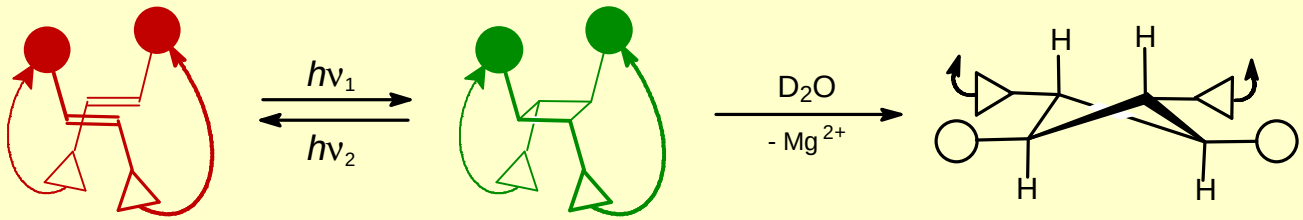
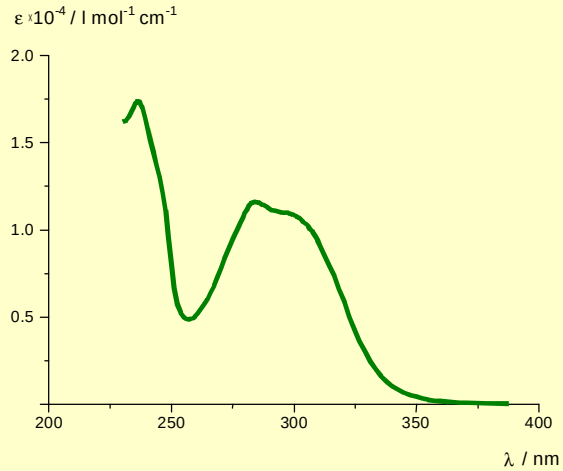
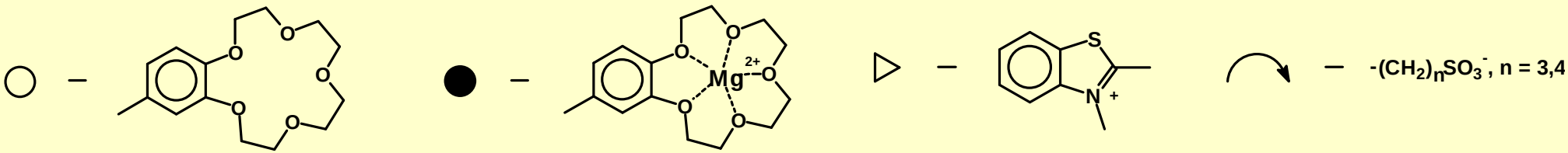
Photoswitchable supramolecular devices



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

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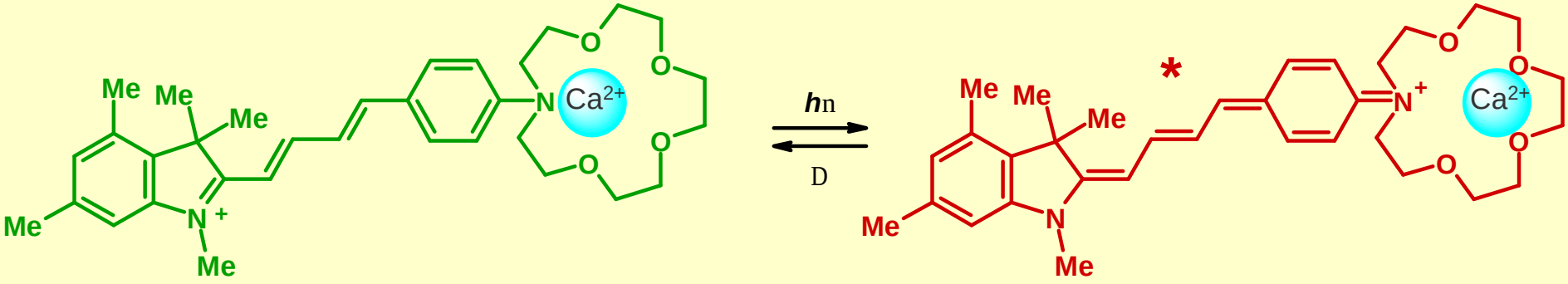
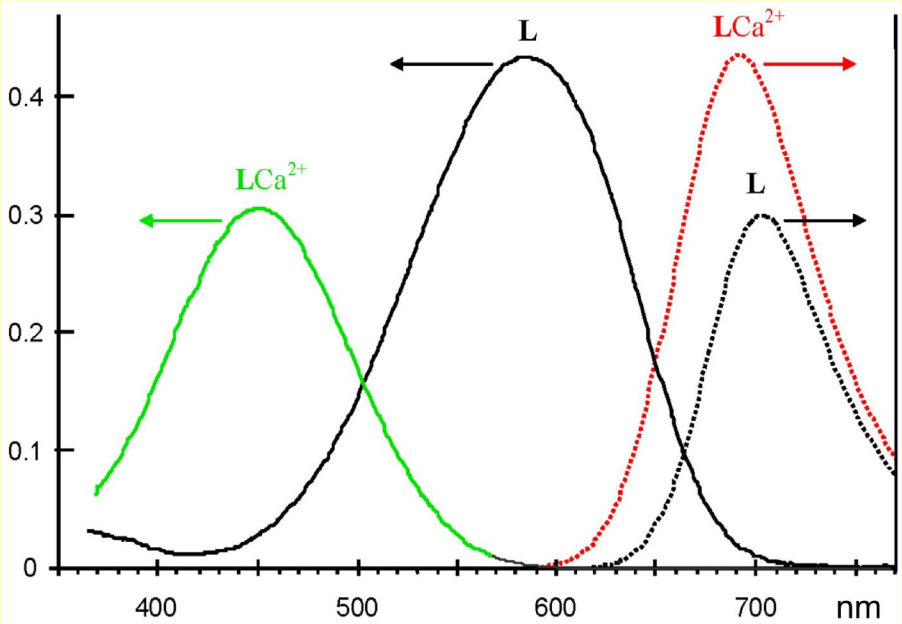
Photoswitchable supramolecular device



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*, 1099 (review).;
Photochem. Photobio. Sci. **2011**, *10*, 15.

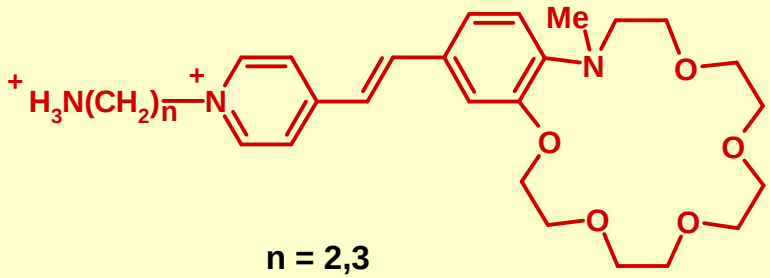
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

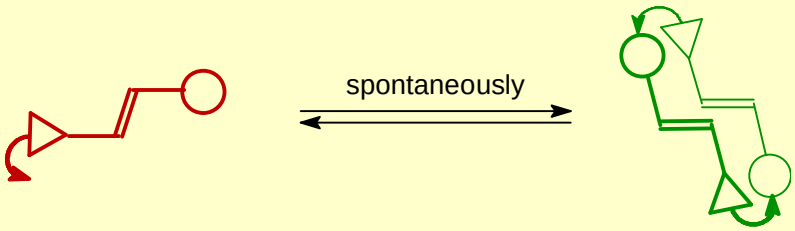
Self-assembly
of photoswitchable supramolecular devices
with participation of hydrogen bonds

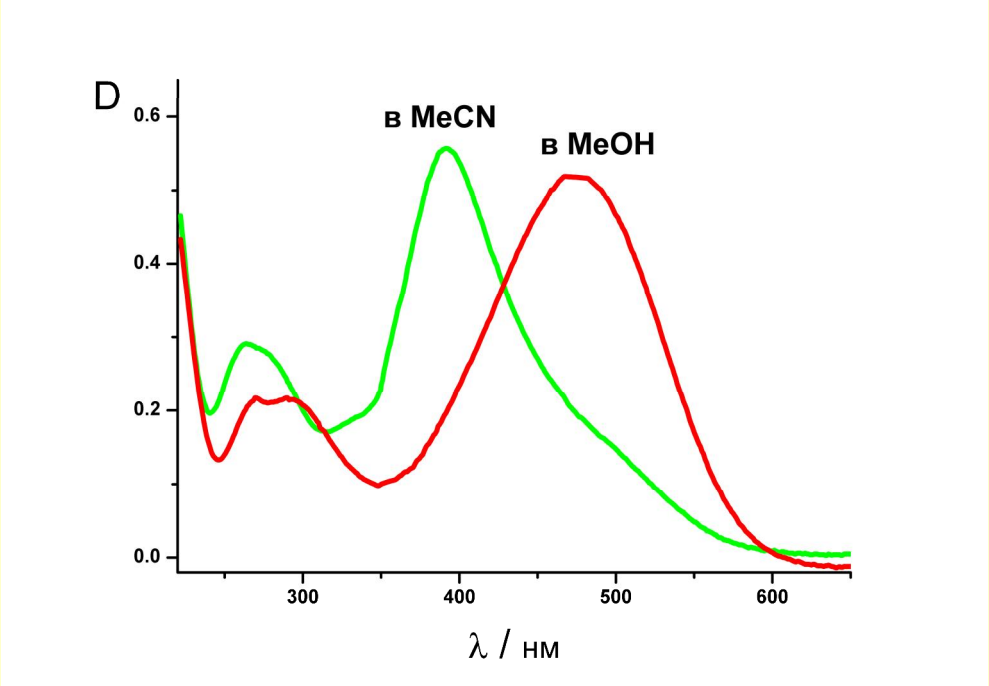
Part II

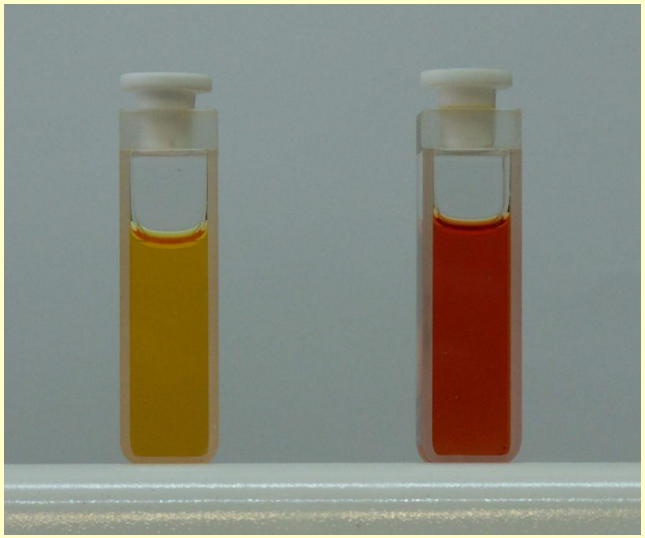
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Dimerization of CSD







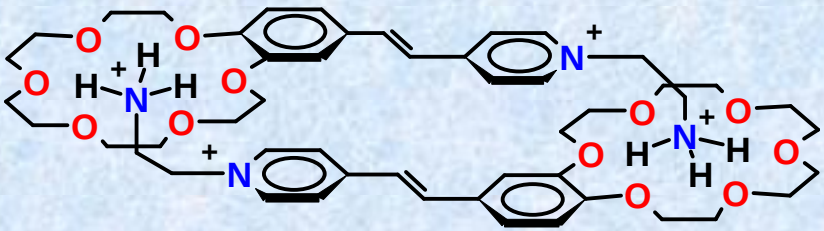


in MeCN in MeOH

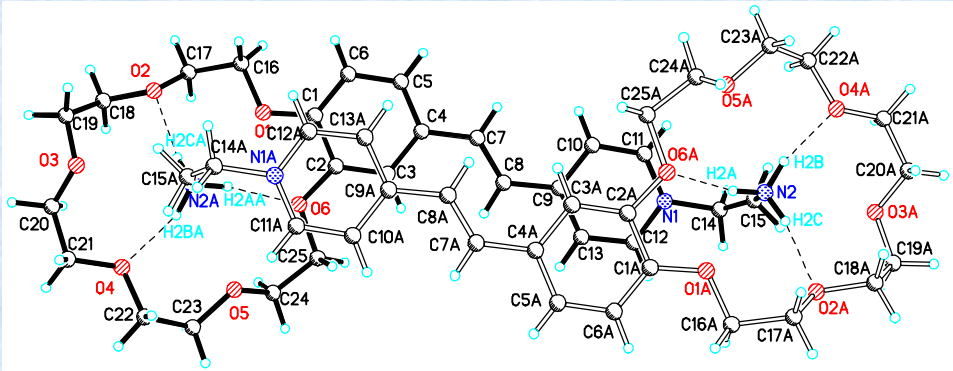
RF patent 2278134 **2006**;
J. Org. Chem. **2014**, *79*, 11416;
J. Phys. Chem. A **2015**, *119*, 13025;
New J. Chem. **2016**, *40*, 7542.

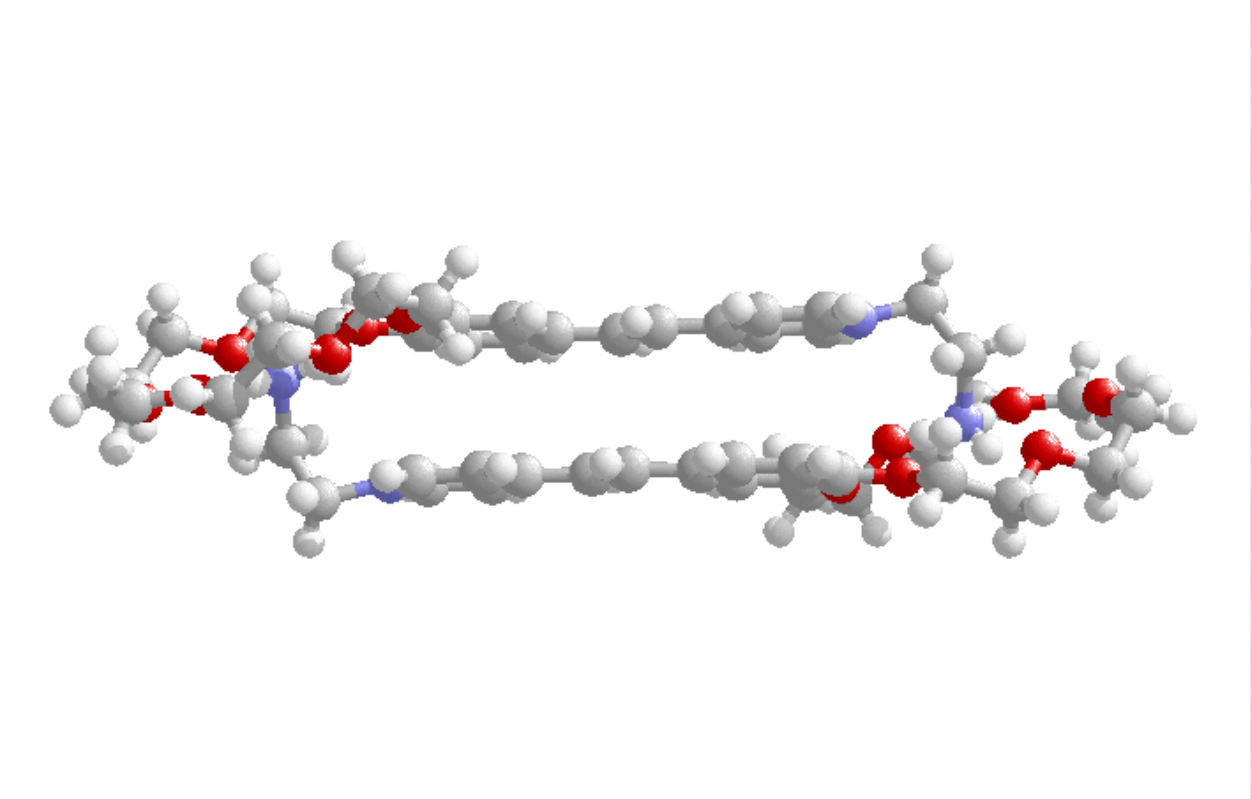
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

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.

THE RUSSIAN ACADEMY OF SCIENCES
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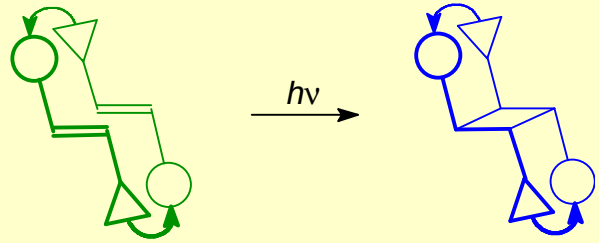
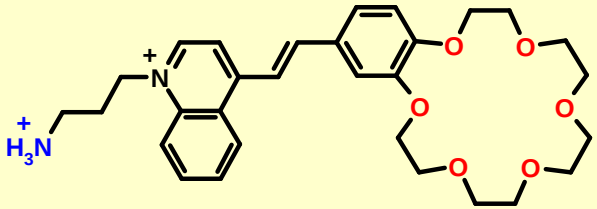
[2+2] Photocycloaddition of CSD



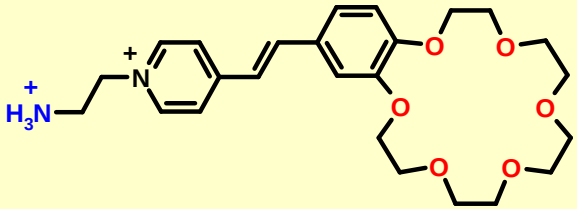
F_{PCA} up to 0.38

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

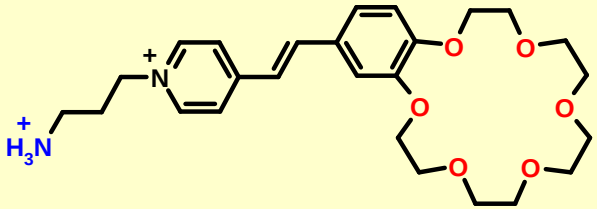
Yield, %



100



33



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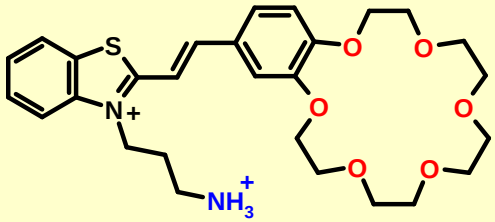

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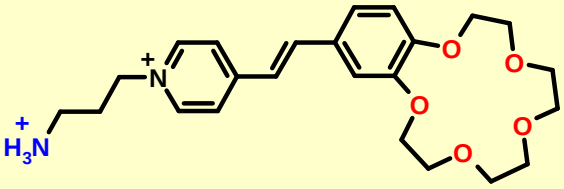
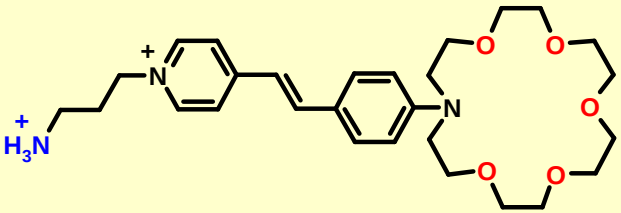


40



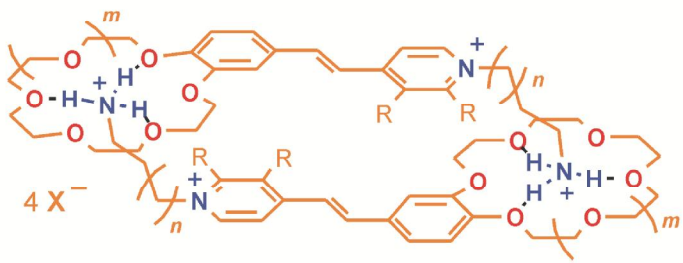
0

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.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

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



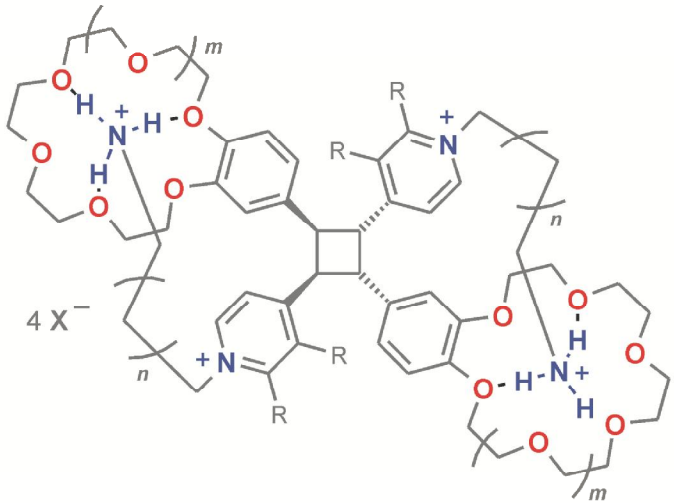
R = H, R + R = benzo; *n, m* = 0, 1

dimeric complexes of styryl dyes

$h\nu_1$ ⇀

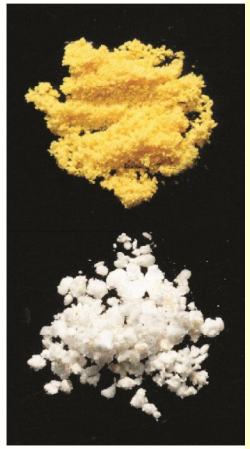
↽ $h\nu_2$

solution or solid phase



rctt isomers of cyclobutane derivatives

dye



cyclobutane

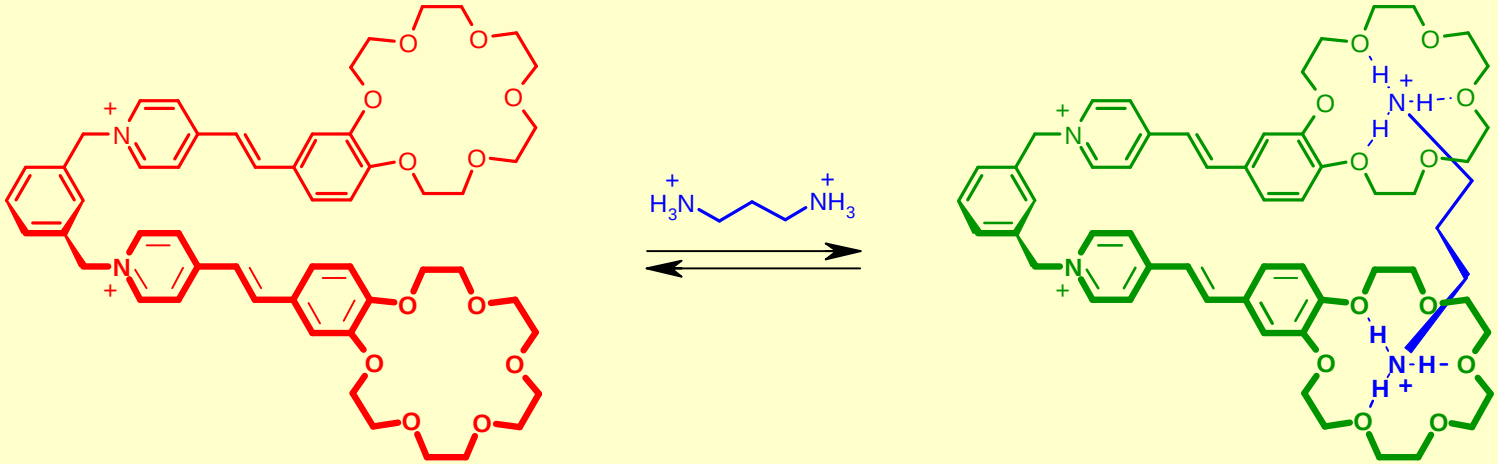
(X = ClO_4;
R = H, *n* = *m* = 1

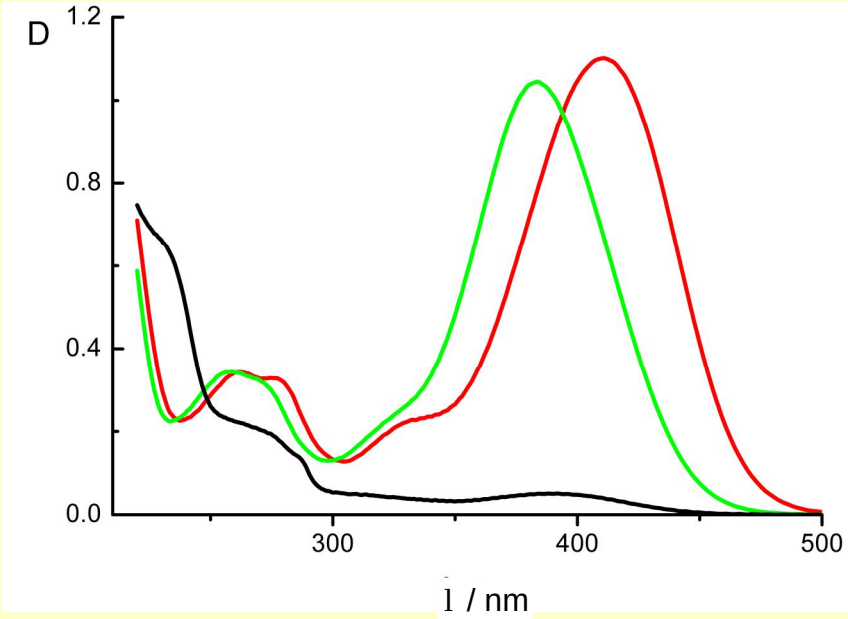
Found property provides grounds for believing that the crystals of these photoactive supramolecular systems could be used for data recording and storage.

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

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

FORMATION OF PSEUDOSANDWICH COMPLEXES

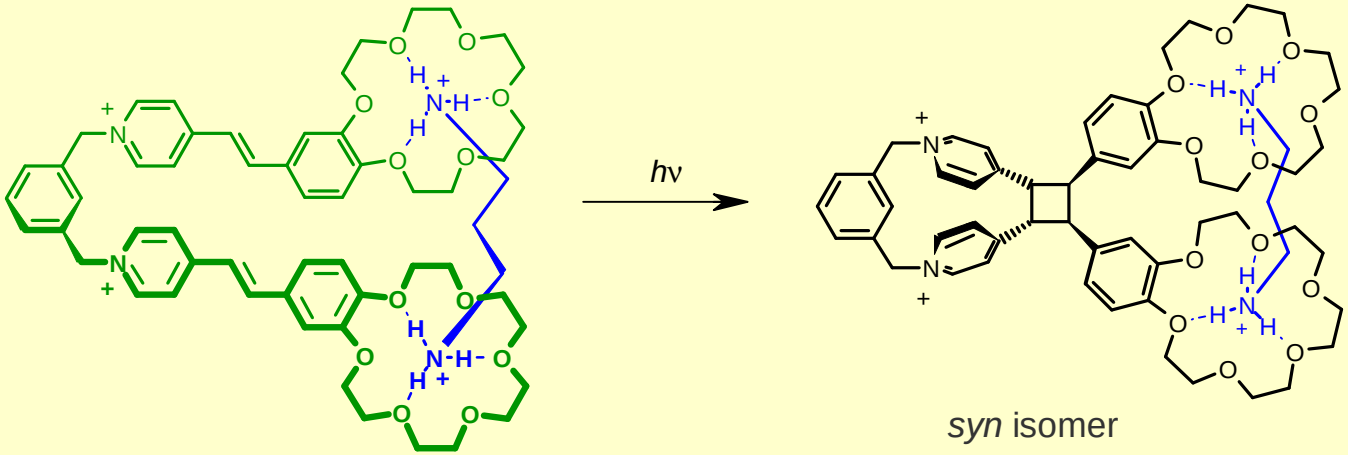


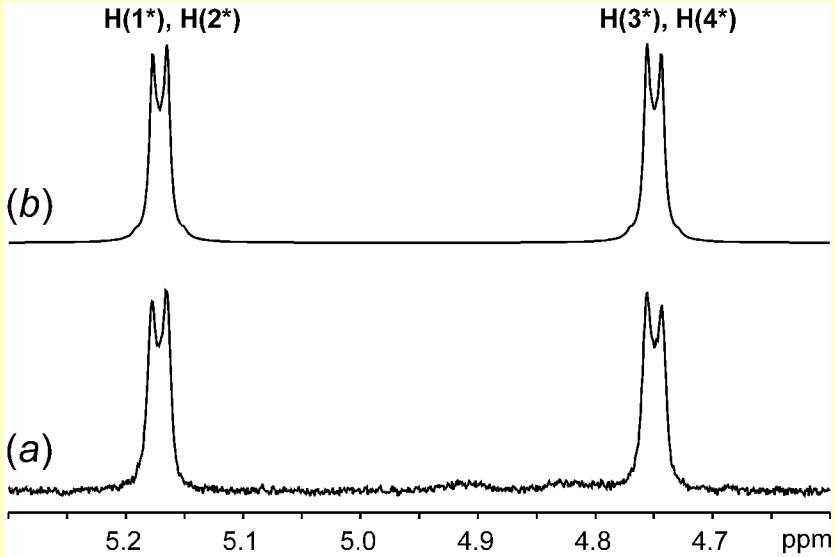


Mendeleev Commun. **2005**, *15*, 173.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Intramolecular [2+2] photocycloaddition of bisCSD





(*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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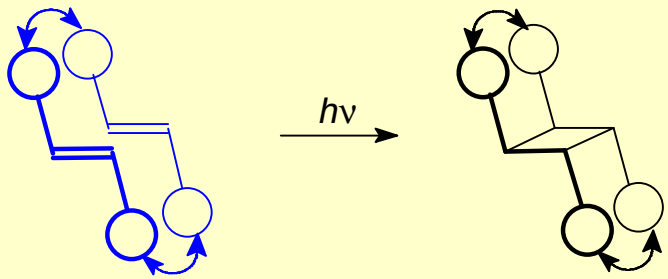
PHOTOCHEMISTRY CENTER

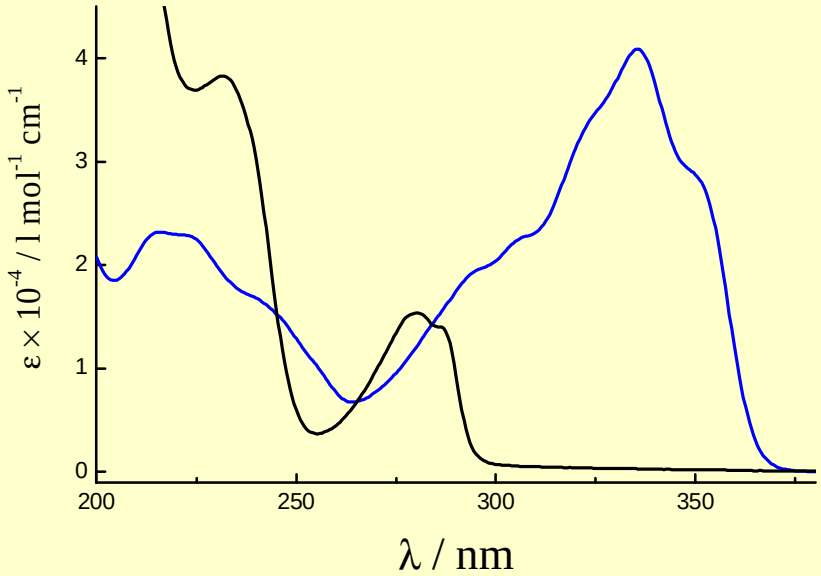
Formation of bispseudosandwich complexes and [2+2] Photocycloaddition

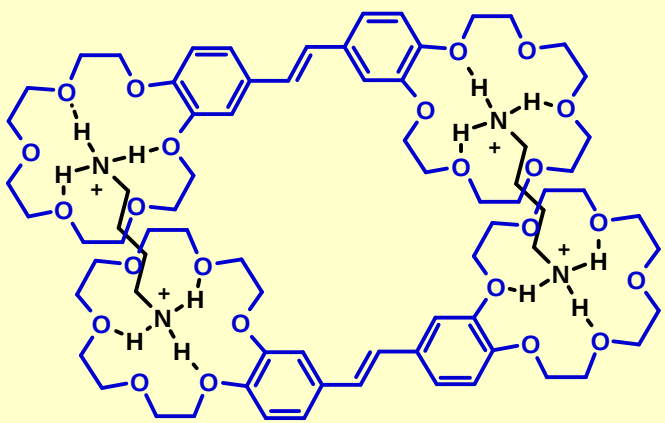


syn-complex *syn-isomer*

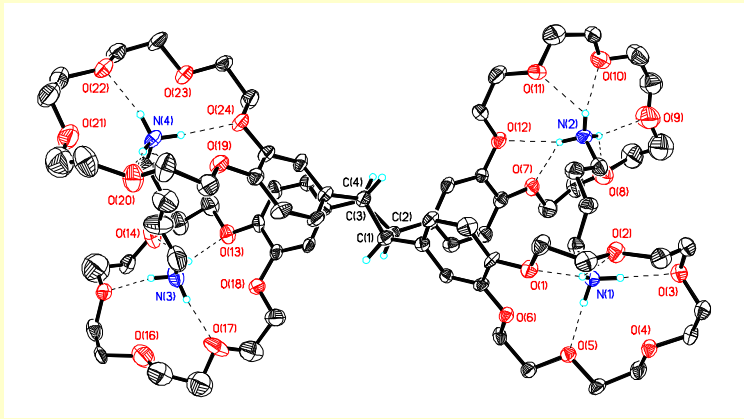
F_{PCA} up to 0.27

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





hν

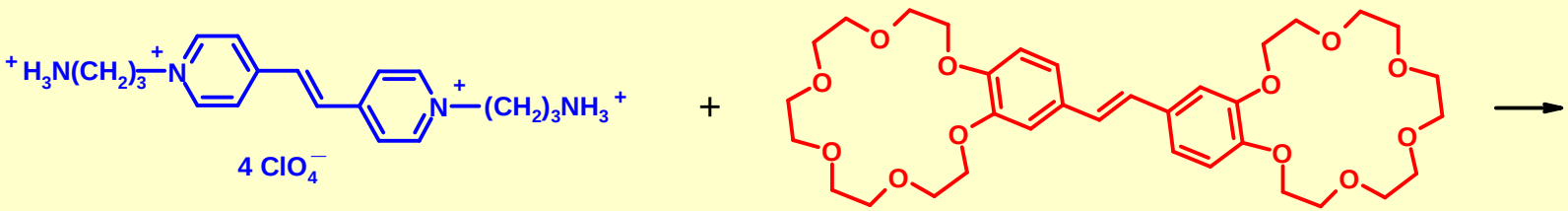


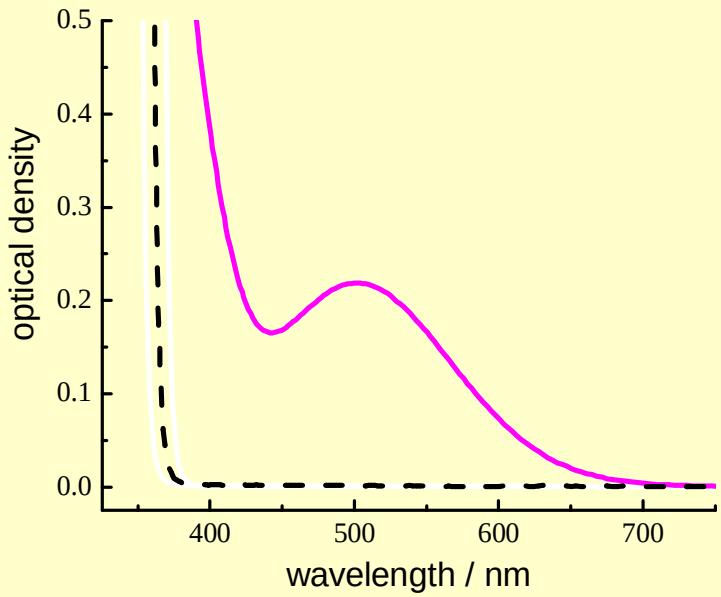
syn-isomer

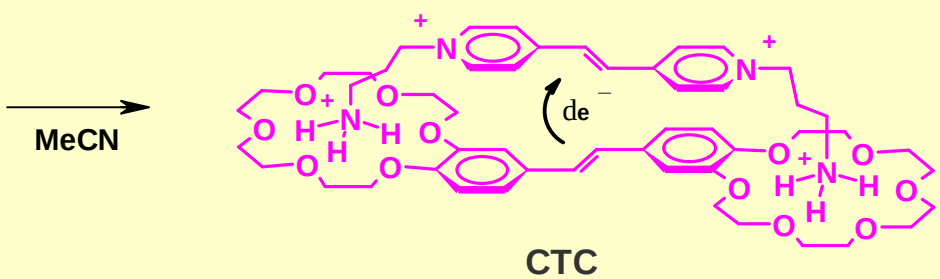
Russ. Chem. Bull. **2009**, *58*, 108;
New. J. Chem. **2011**, *35*, 724;
J. Photochem. Photobiol. A. **2017**, *340*, 80;

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Formation of Charge Transfer Complex of bisCS







log K = 9.08

Org. Lett. **1999**, *1*, 1697 ;
New. J. Chem. **2005**, *29*, 881;
J. Org. Chem. **2011**, *76*, 6768;
J. Photochem. Photobio. A. **2019**, *372*, 89.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

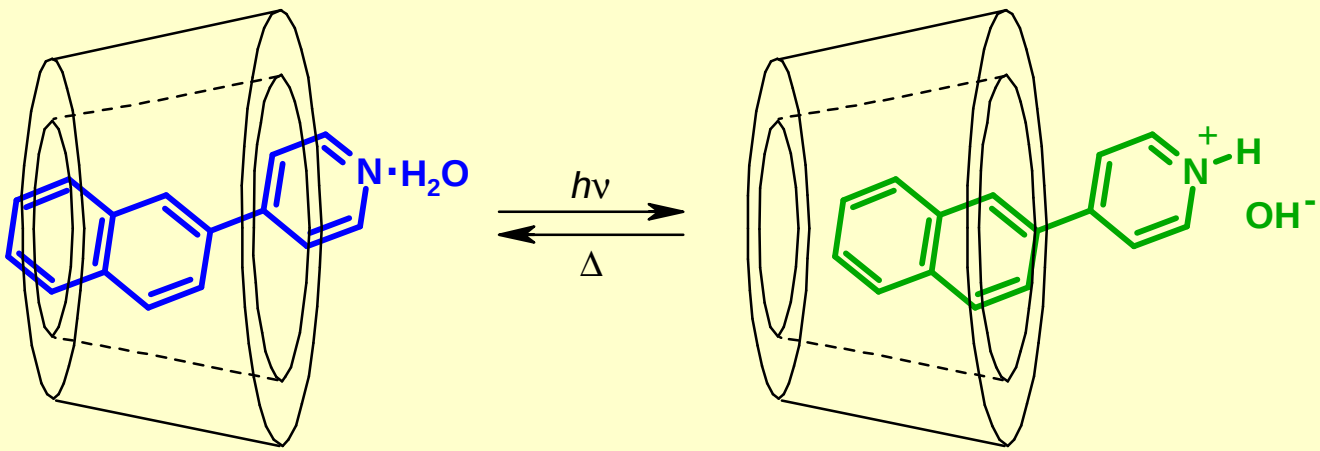
Self-assembly

of photocontrolled supramolecular machines

Part III

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



1·H_2O@HP-β-CD

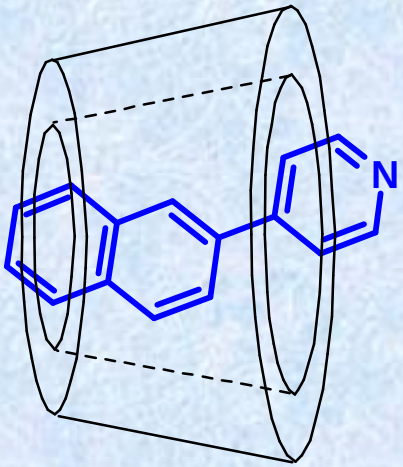
log*K* = 1.9

1H^+OH^-@HP-β-CD

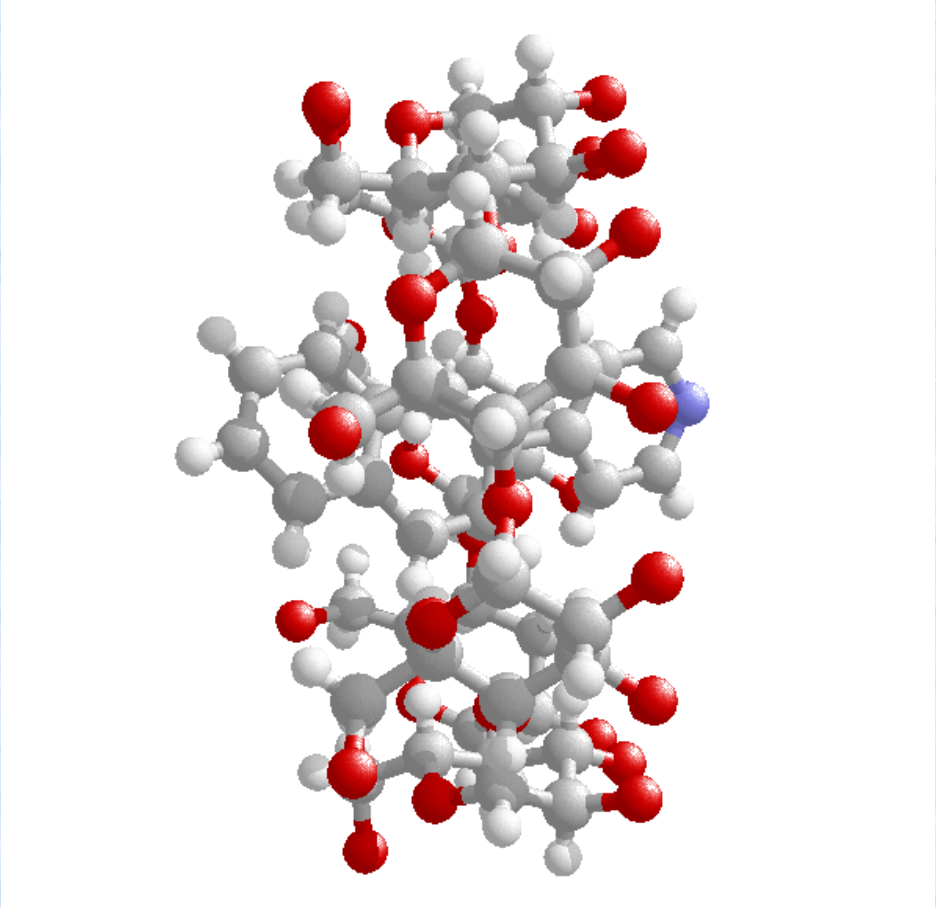
Discovery of the reversible photoinduced mechanical displacement of naphthylpyridine in the β-cyclodextrin cavity allowed us to develop a new type of photocontrolled molecular machines.

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

X-ray structure determination of photocontrolled supramolecular machine



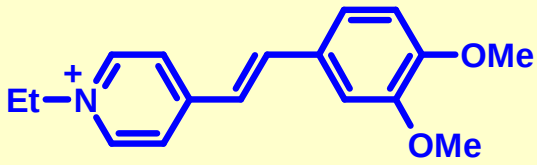
1@β-CD



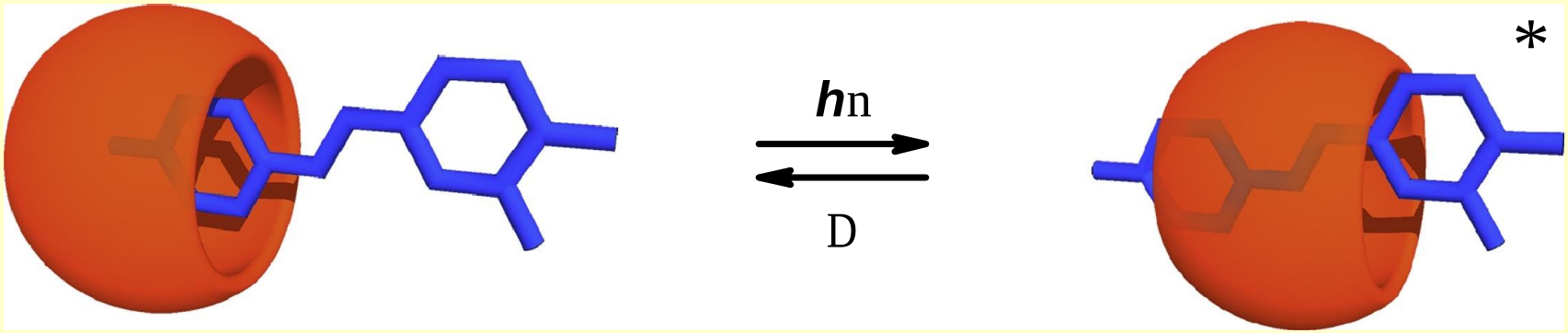
Russ. Chem. Bull. **2004**, *53*, 2525;
J. Photochem. Photobiol. A **2011**, *217*, 87;
Russ. Chem. Bull. **2013**, *62*, 2150.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



SD



SD@CB[7]

SD@CB[7] *

Chem. Phys. Lett. **2016**, *647*, 157.

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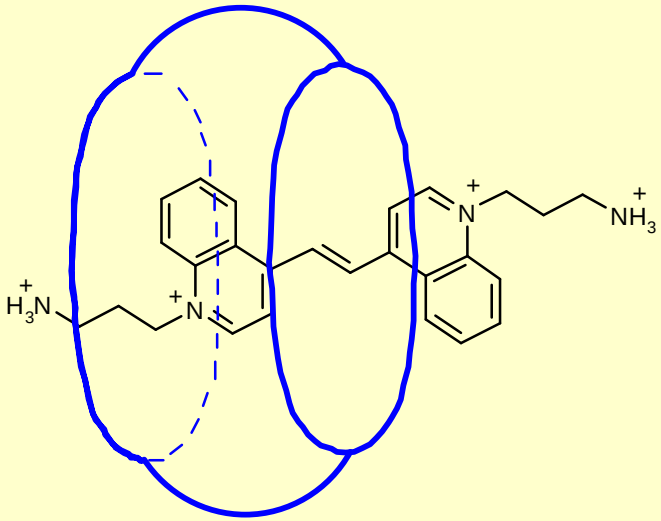
PHOTOCHEMISTRY CENTER

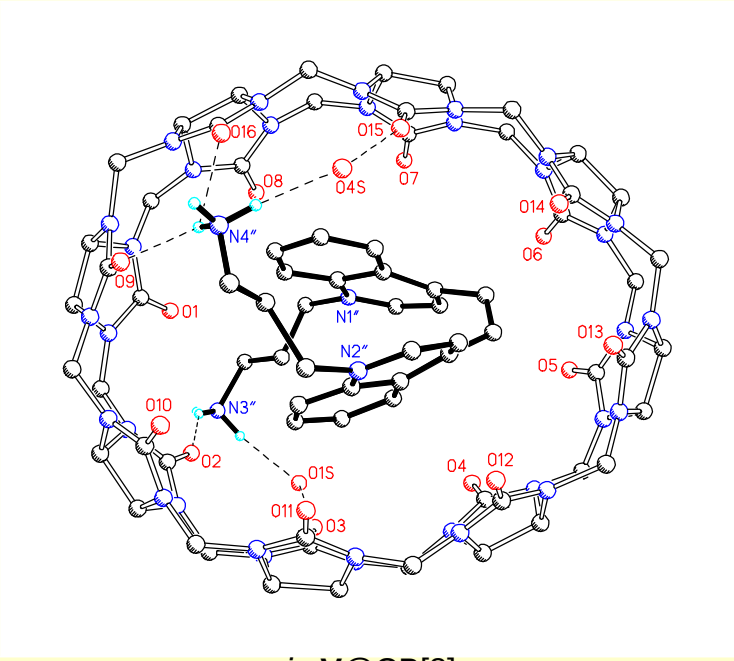
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



trans-**V**@CB[8]

log *K* = 4.6

$h\nu$



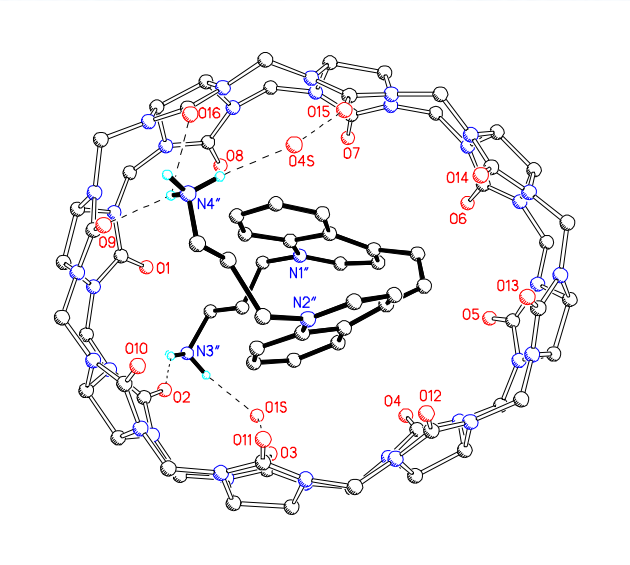
cis-**V**@CB[8]

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

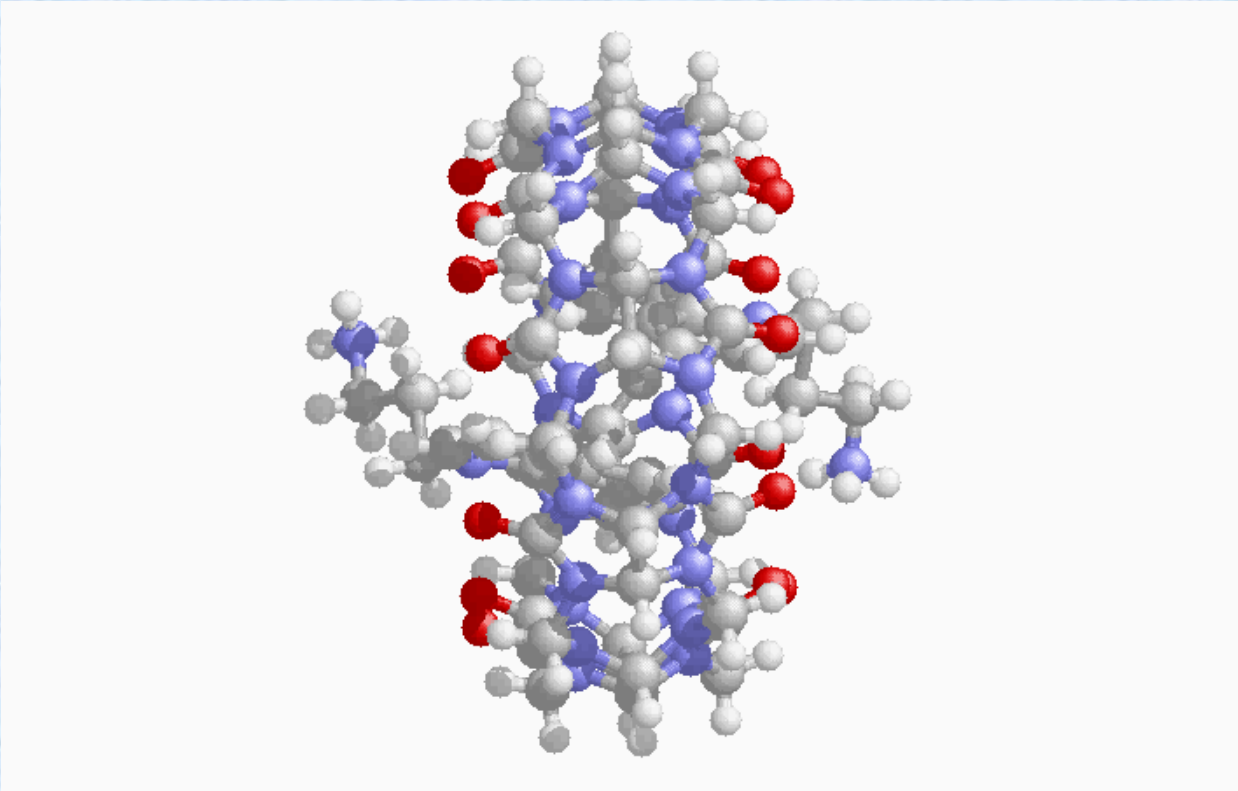
New. J. Chem. **2006**, *30*, 458.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

X-ray structure determination of photocontrolled supramolecular machine



cis-**V**@CB[8]



New. J. Chem. **2006**, *30*, 458.

THE RUSSIAN ACADEMY OF SCIENCES
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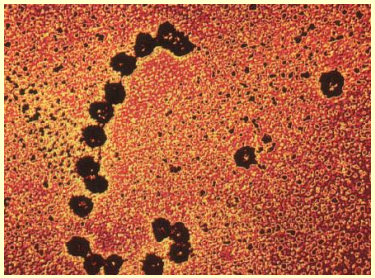
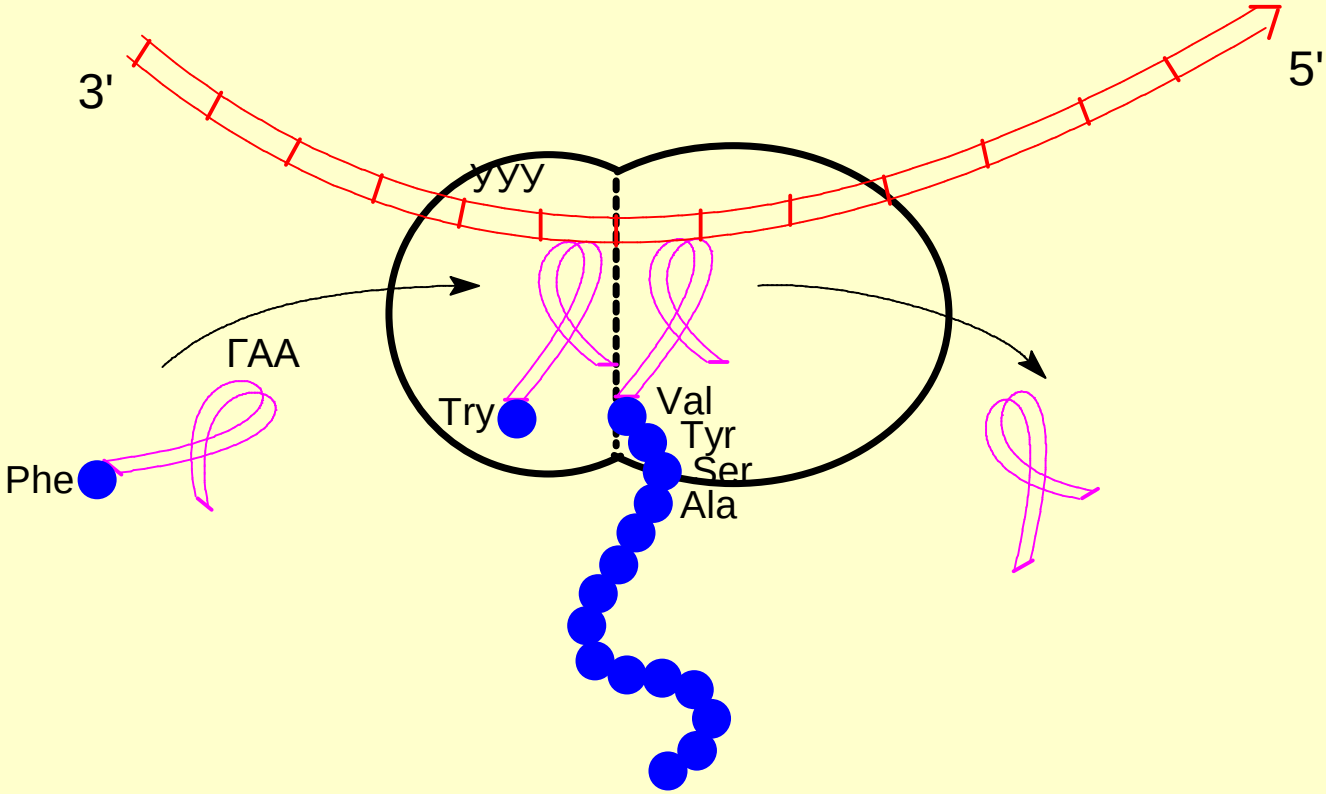
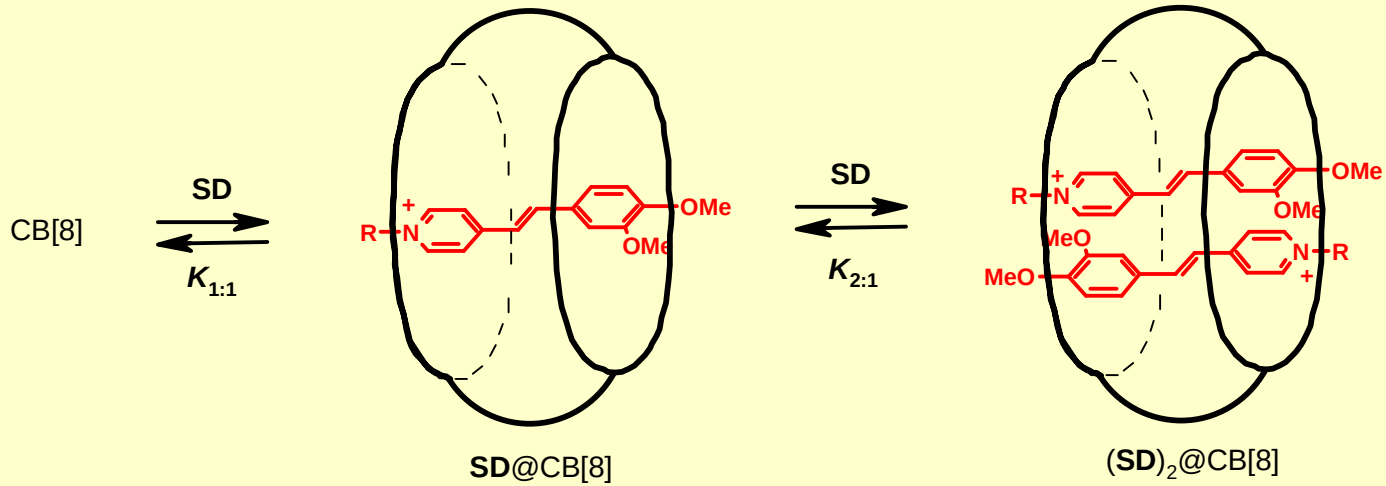
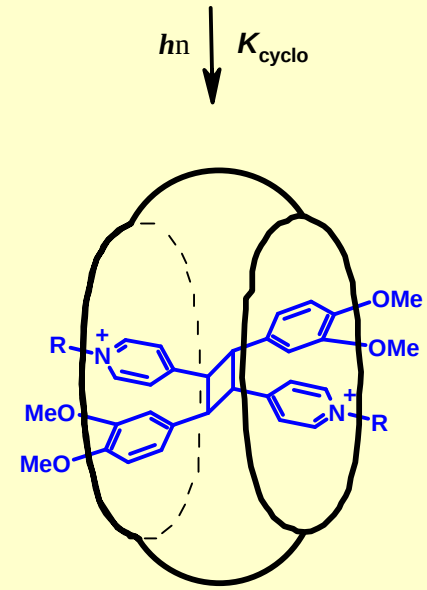
Ribosome - natural molecular assembler





PHOTOCONTROLLED SUPRAMOLECULAR MACHINES

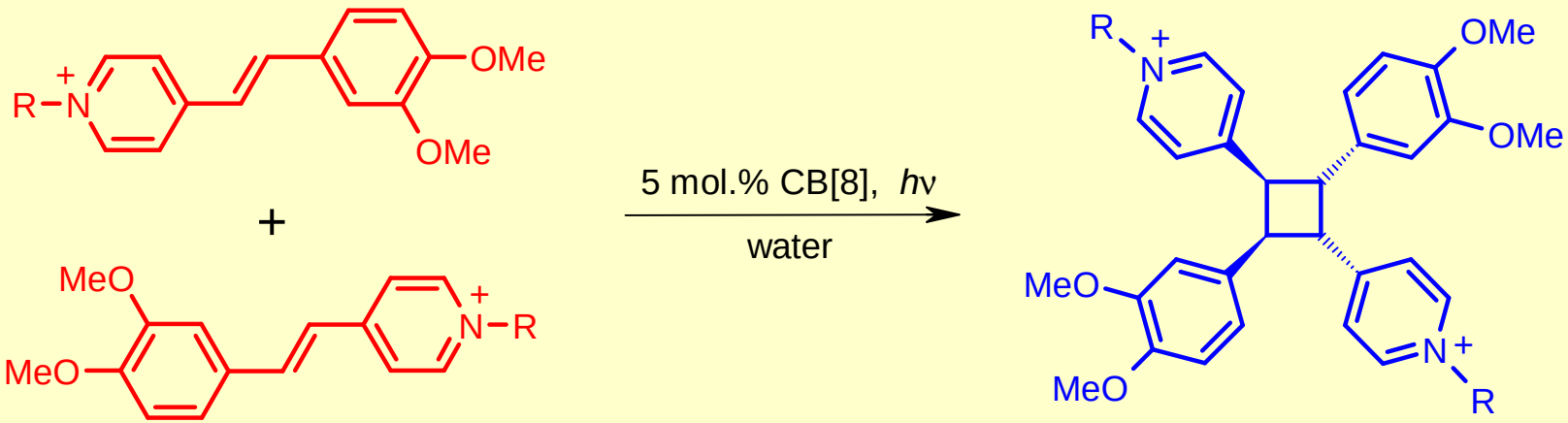




SD	CB[8]		
R	log $K_{1:1}$	log $K_{2:1}$	log K_{cyclo}
Et	4.9	4.1	4.3
$(CH_2)_3NH_3^+$	5.0	4.4	4.8
$(CH_2)_3SO_3^-$	4.0	**2.6**	**3.2**

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

PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL



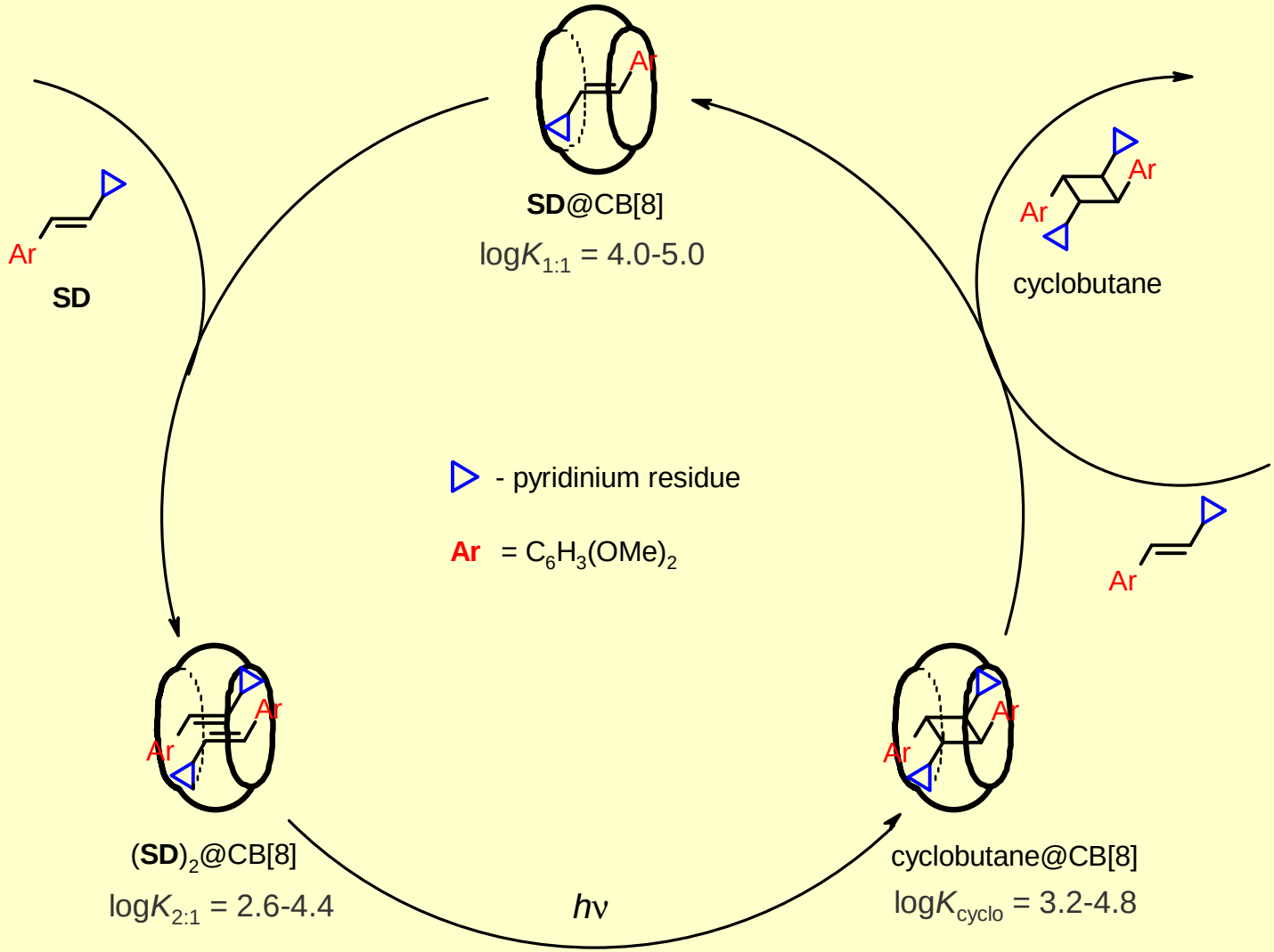
styryl dyes (**SD**)

rctt isomers of cyclobutanes

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

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

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.

THE RUSSIAN ACADEMY OF SCIENCES
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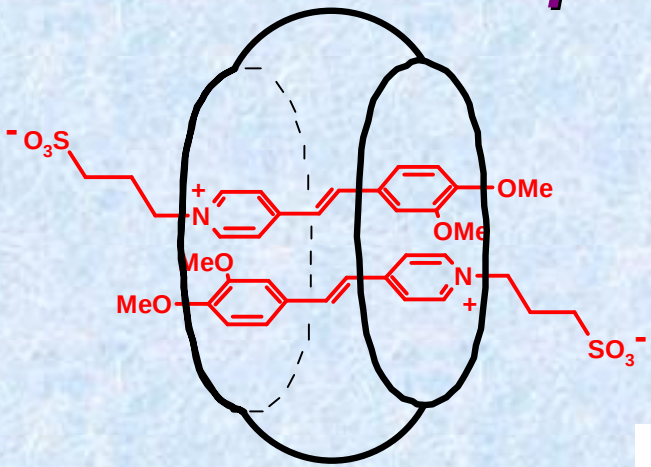
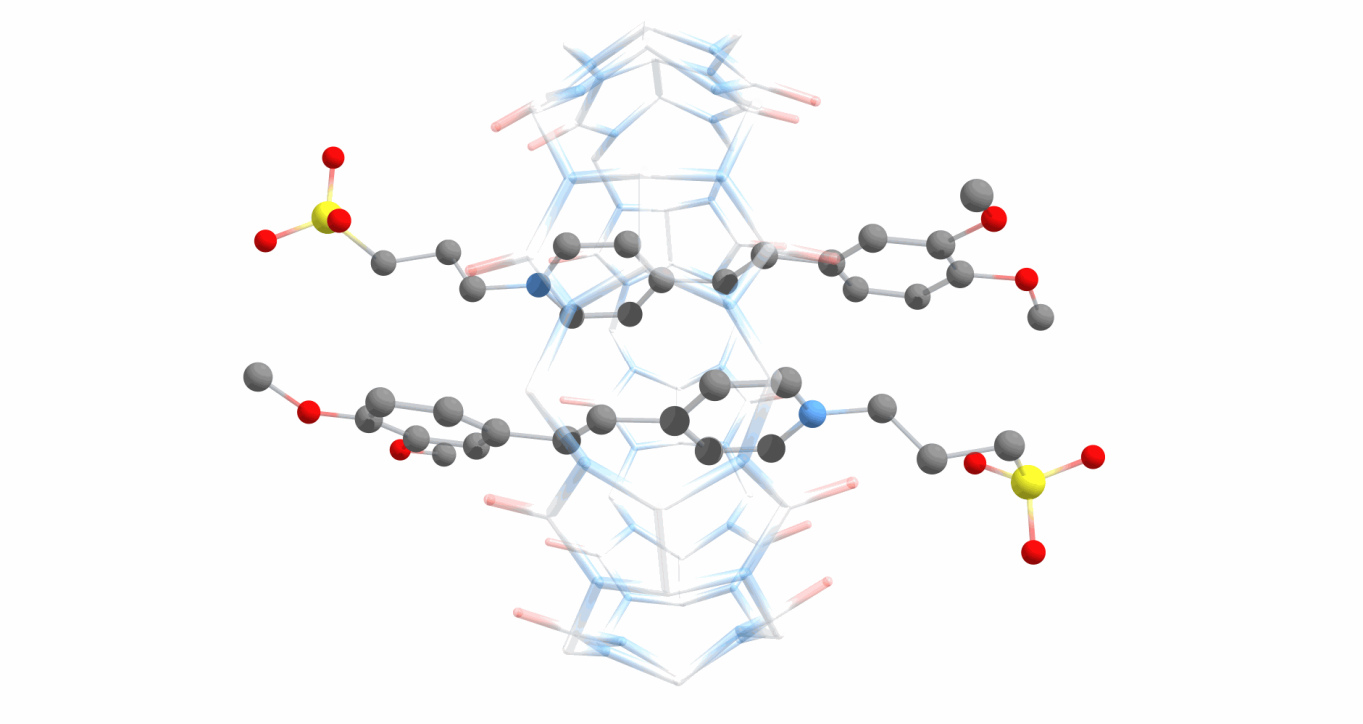
X-ray structure determination of photocontrolled supramolecular assembler



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

Time of pre-organization ~ 4 ps



Eur. J. Org. Chem., **2010**, 2587;
Chem. Phys. Lett. **2017**, *673*, 99.

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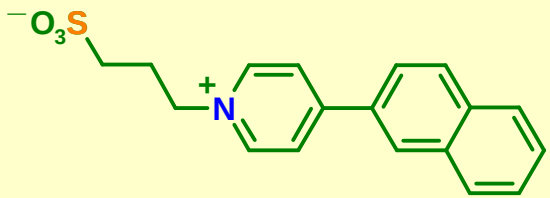
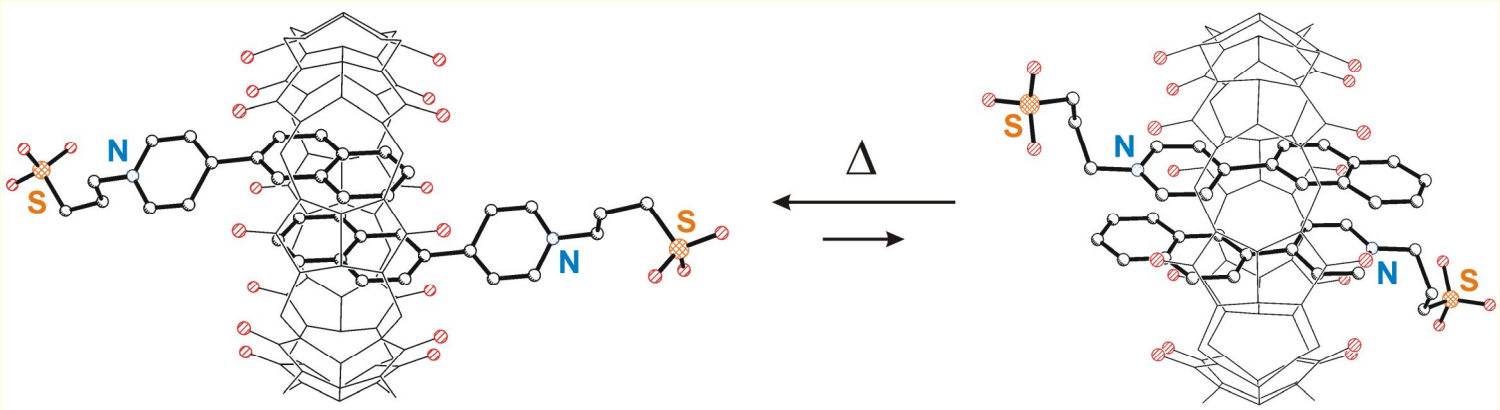
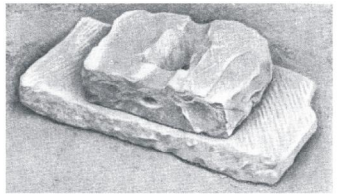
SUPRAMOLECULAR MILLSTONES BASED ON CUCURBIT[8]URIL





exo-complex
(guest)$_2$@CB[8]

endo-complex
(guest)$_2$@CB[8]



ancient
millstone

Naphthalene derivatives and cucurbiturils form inclusion complexes of various structures and stoichiometries; guests are capable of translocation in cucurbit[7,8]uril cavities.

New J. Chem. **2019**, *30*, 458.

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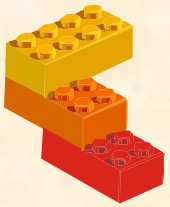
It is possible to implement all main types of photoprocesses:

- Fluorescence, excimer formation
- Photodissociation
- Photoisomerization
- Photocycloaddition
- photoelectrocyclization
- charge-transfer complex formation, electron transfer
- proton 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).

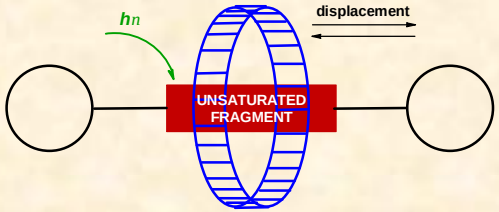
Molecular meccano

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

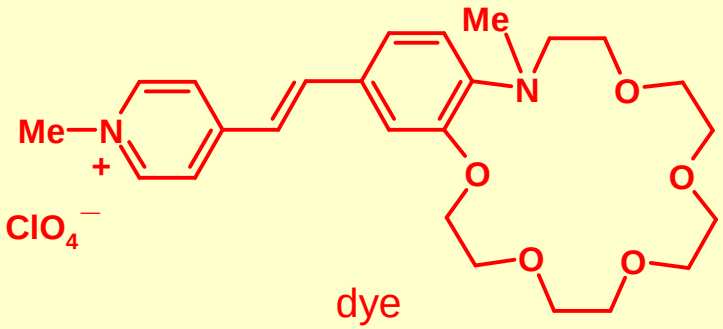
18 patents

Demonstrated by an example of design:

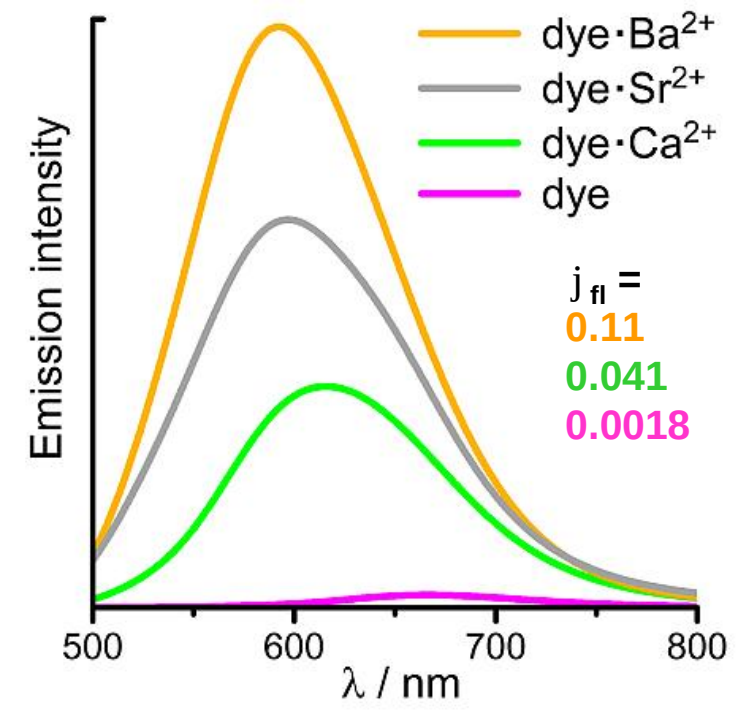
- § **Photoswitchable supramolecular devices**
- § **Photocontrolled supramolecular machines**
- § **Optical chemosensor materials**
- § **Supramolecular photoswitches**
- § **Data optical recording and storage systems**
- § **Photochromic ionophores and photocontrolled membrane transport**
- § **Photoswitchable 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).

Fluorescent supramolecular sensor based on CSD



The fluorescence enhancement upon complexation with Ba^{2+}



Fluorescence spectra in MeCN.

RF patent 2398800 **2010**;
J. Org. Chem. **2013**, *78*, 9834.

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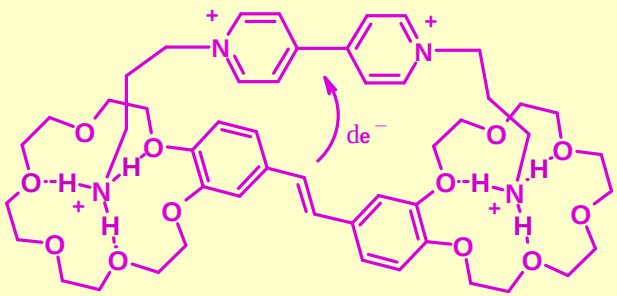
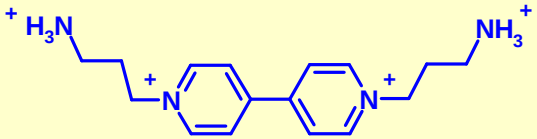
Fluorescent supramolecular sensors based on charge transfer complexes (CTC)



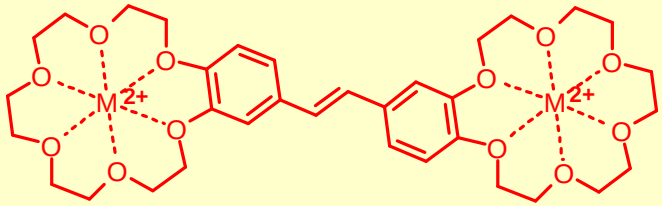
CTC
does not fluoresce

M^{2+}
M = Ba, Ca

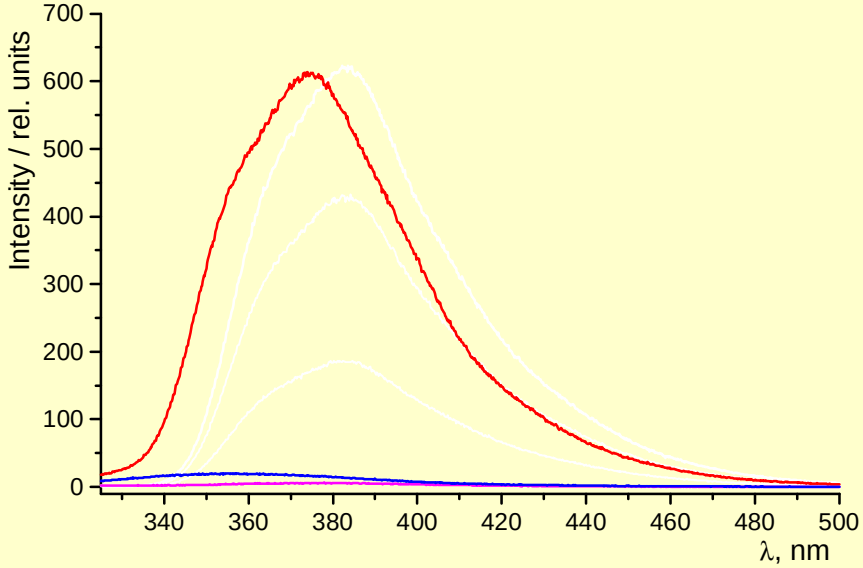


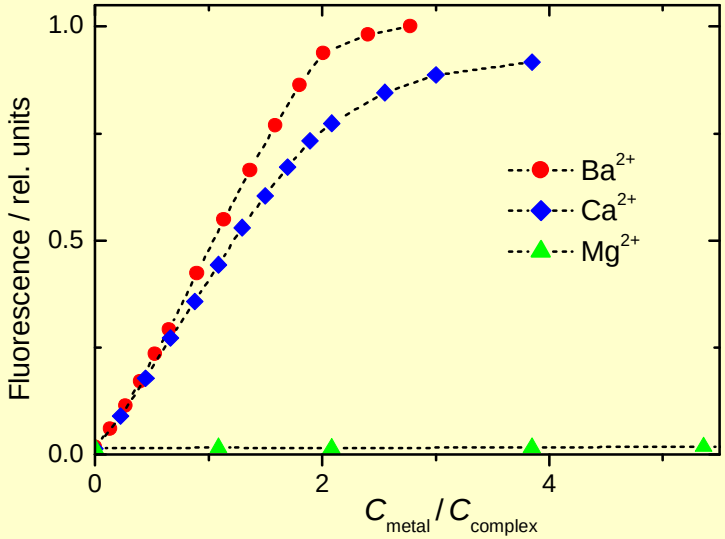
weakly fluoresces, j = 0.015

+



fluoresces, j = 0.30





Org. Lett. **1999**, *1*, 1697;
J. Org. Chem. **2011**, *76*, 6768;
J. Photochem. Photobio. A. **2019**, *372*, 89.

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

Acknowledgment

This work was supported by the following organizations:

- Russian Science Foundation (2014 - 2019)
- RFBR (1994 - 2019)
- Russian Academy of Sciences (2003 - 2018)
- The Ministry for Science and Technology of Russia (1999 - 2019)
- Moscow Government (2003 - 2005)
- The Royal Society (1997 - 2017)
- INTAS (1993 - 2005)
- CRDF (1996 - 2004)
- DFG (1996 - 2004)
- ISF (1993 - 1994)

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)

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

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Thank You

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

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