РОССИЙСКАЯ АКАДЕМИЯ НАУК
ЦЕНТР ФОТОХИМИИ

XXVII International Chugaev Conference on Coordination Chemistry

IV Young Conference School "Physico-Chemical Methods in the Chemistry of Coordination Compounds"

Supramolecular Devices and Machines that Use Light as an Energy Source

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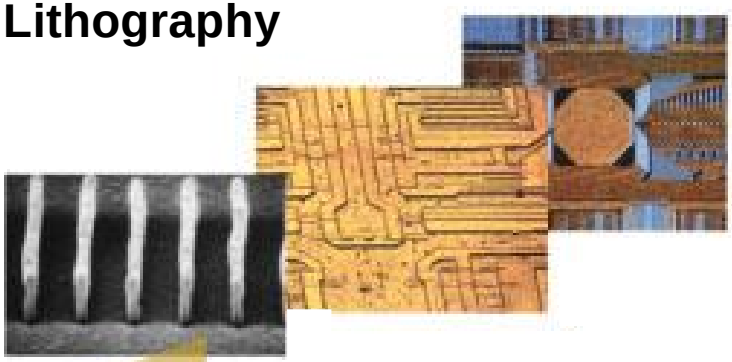
A. K. Chibisov, M. V. Alfimov

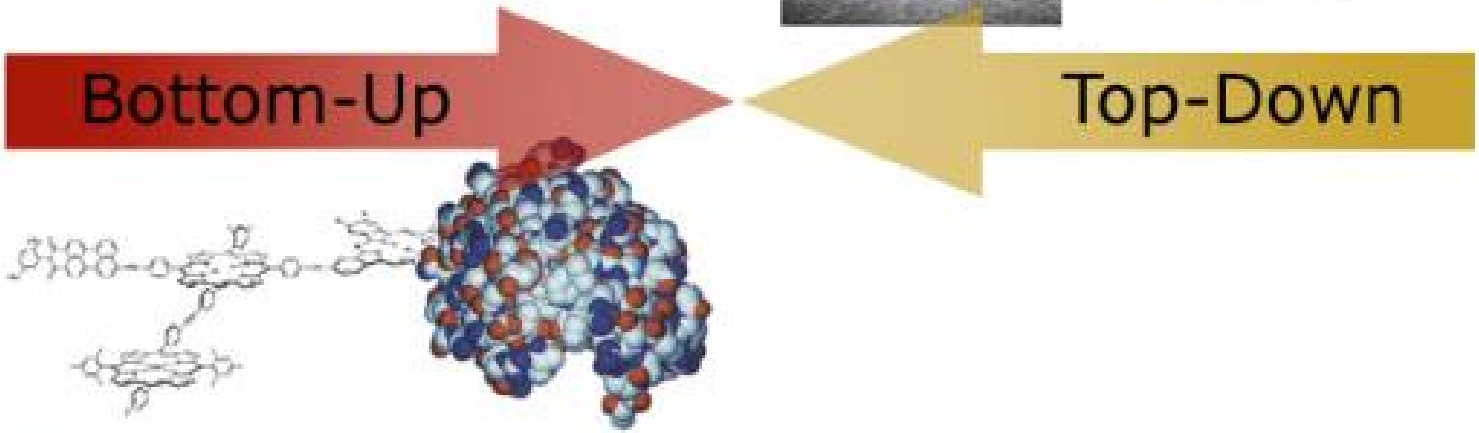
http://suprachem.photonics.ru

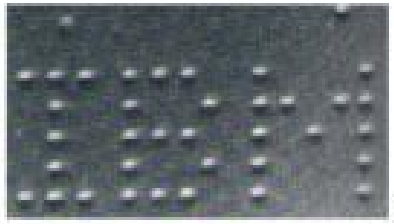
NANOTECHNOLOGY "BOTTOM-UP"

STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES

Lithography







Organic synthesis
Supramolecular Self-Assembly

SUPRAMOLECULAR DEVICES AND MACHINES

Supramolecular devices are structurally organized and functionally integrated chemical systems.

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

J.-M. Lehn

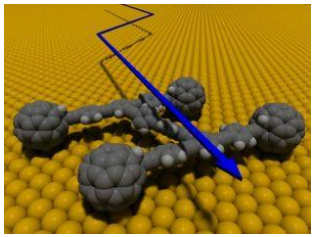
They can be used:

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

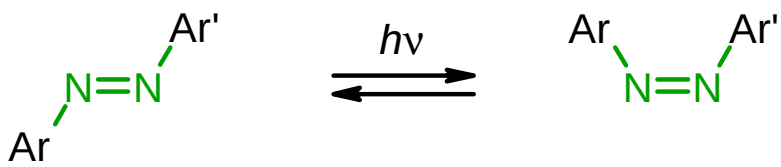
Critical technologies of the RF

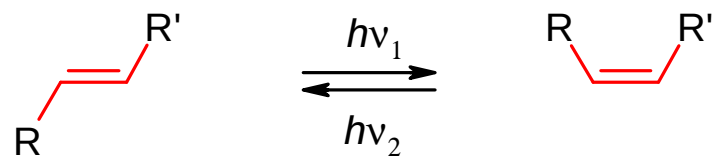
Means for control of supramolecular devices and machines

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

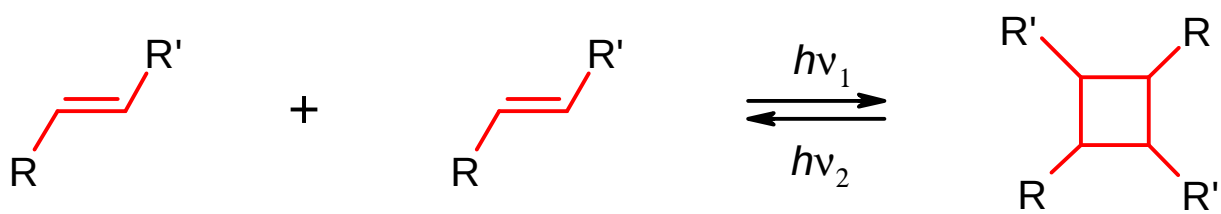


PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS





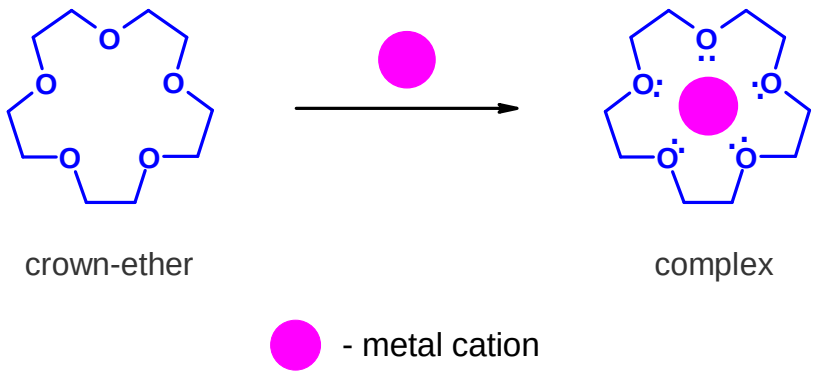
trans-isomer *cis*-isomer

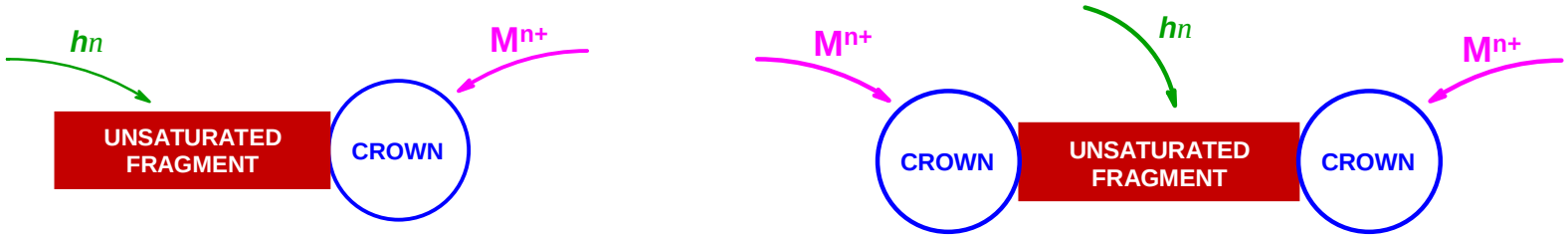


cyclobutane

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





Gromov S. P. *Russ. Chem. Bull*. **2008**, *57*, 1325 (review);
Ushakov E. N., Alfimov M. V., Gromov S. P. *Russ. Chem. Rev.* **2008**, *77*, 39 (review);
Alfimov M. V., Fedorova O. A., Gromov S. P. *J. Photochem. Photobiol., A* **2003**, *158*, 183 (review).

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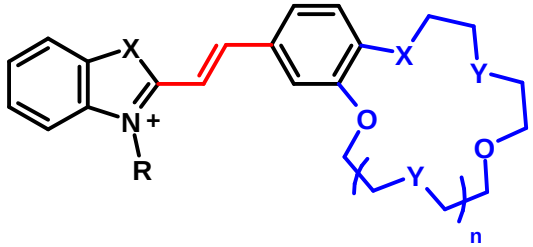
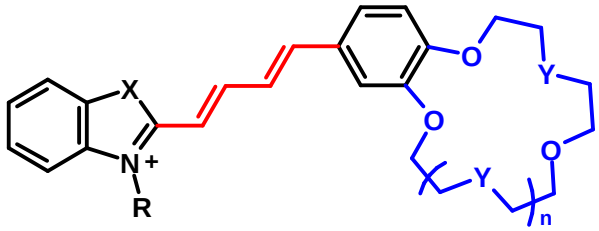
PHOTOCHEMISTRY CENTER

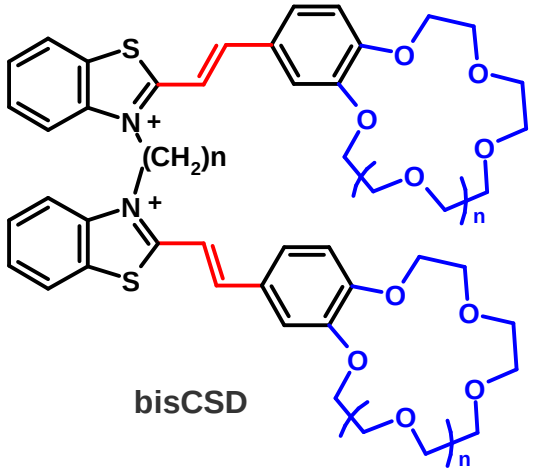
Crown-containing unsaturated compounds



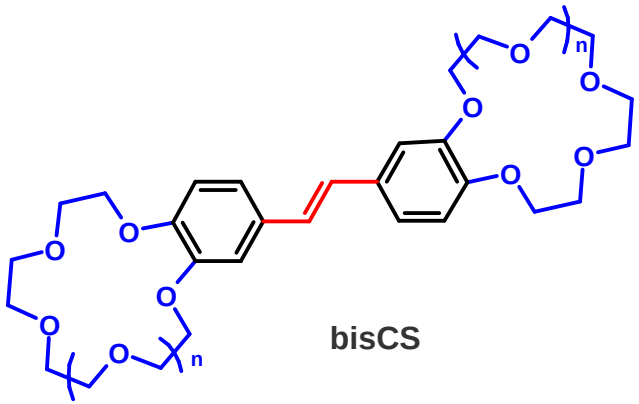
CSD



CBD



bisCSD



bisCS

n = 1, 2

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

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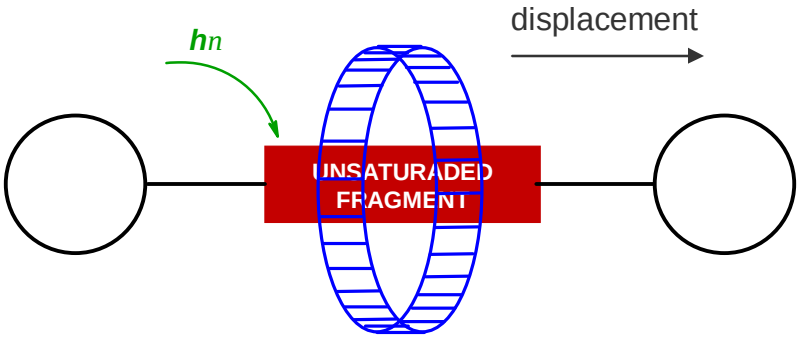
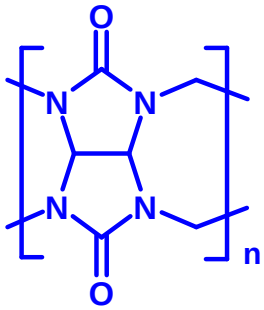
PHOTOCHEMISTRY CENTER

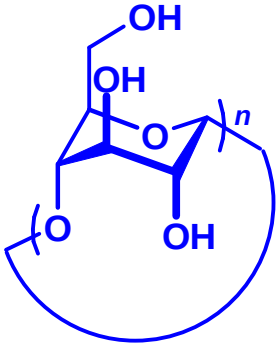
Photocontrolled supramolecular machines based on unsaturated compounds, cucurbiturils and cyclodextrins



photocontrolled supramolecular machine



n = 6-8



cucurbiturils

cyclodextrins

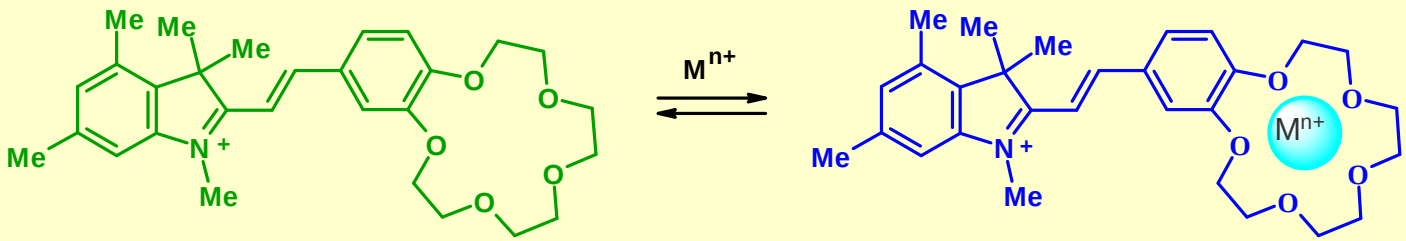
Gromov S. P. *Russ. Chem. Bull*. **2008**, *57*, 1325 (review);
Gromov S. P. *Rev. J. Chem.* **2011**, *1*, 1 (review)
Ushakov E. N., Gromov S. P. *Russ. Chem. Rev.* **2015**, *84*, 787 (review).

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

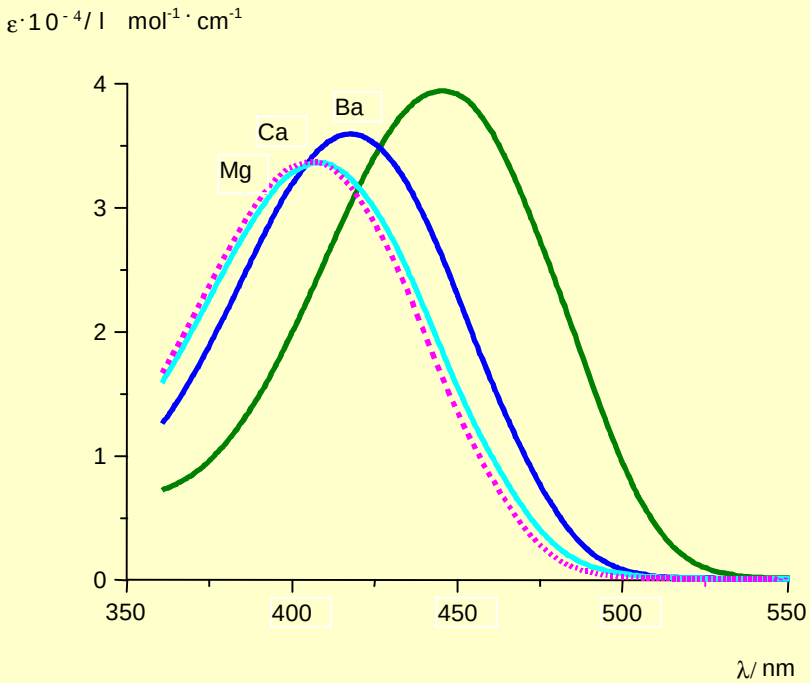
Part I

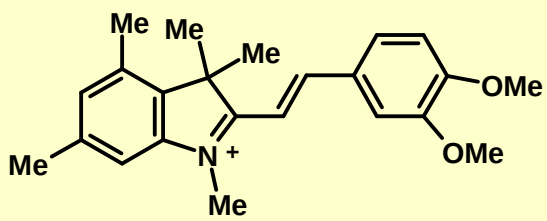
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Complex formation



trans-isomer





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

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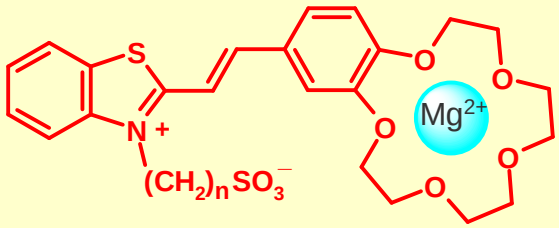
PHOTOCHEMISTRY CENTER

Photoswitchable supramolecular devices

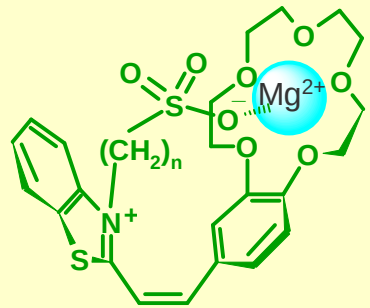


(*trans*-**L**)·Mg^{2+}

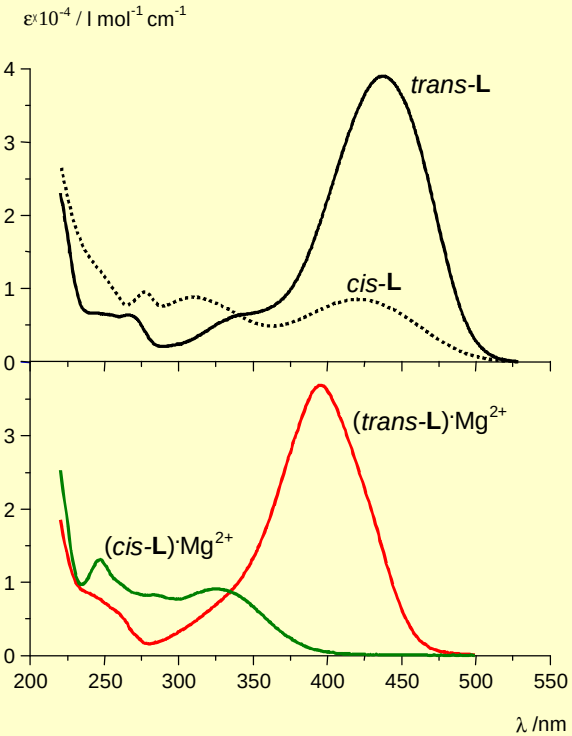
$h\nu_1$ (436 nm)

$h\nu_2$

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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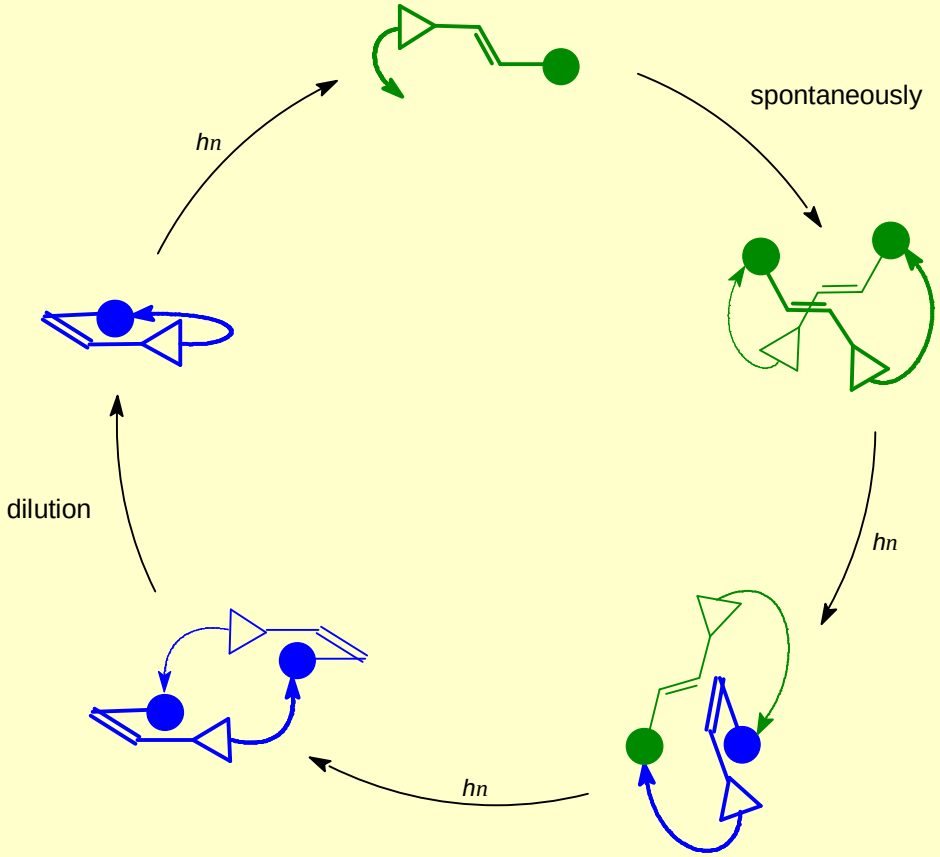
PHOTOCHEMISTRY CENTER

Photocycle of crown-containing styryl dyes



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

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

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

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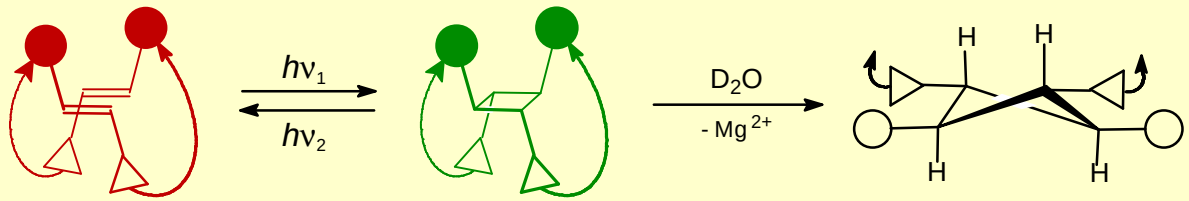
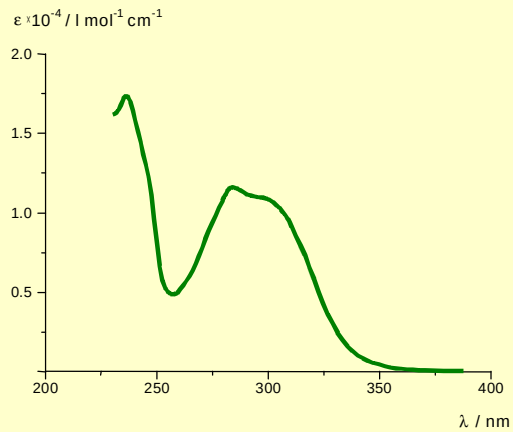
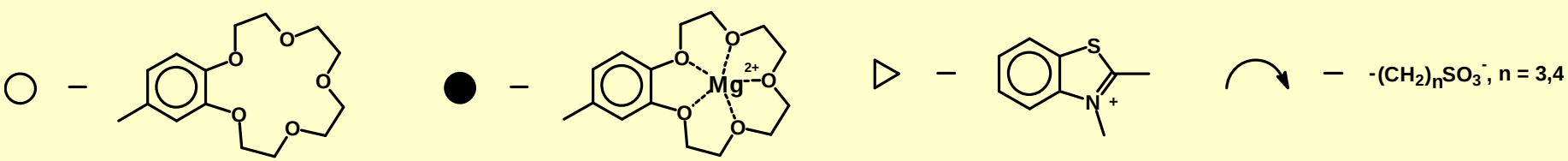
Photoswitchable supramolecular devices



[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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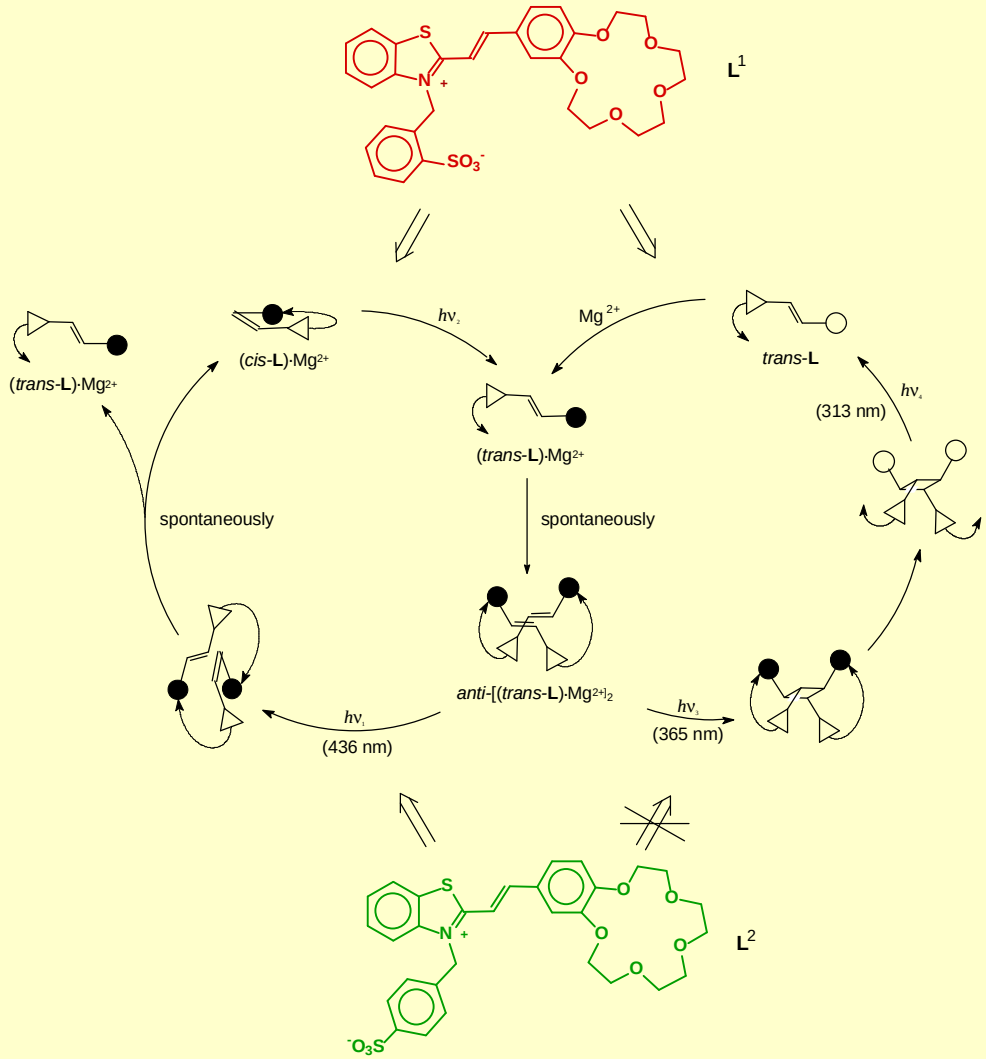
[2+2] PHOTOCYCLOADDITION OF MULTIPHOTOCHROMIC CSD



CSD	R, A°	F	lgK_1
L^1	6.7	0.018	7.3
L^2	9.9	---	10.0

Russ. Chem. Bull. **1998**, *47*, 97; *J. Chem. Soc., Perkin Trans. 2.* **1999**, 601.

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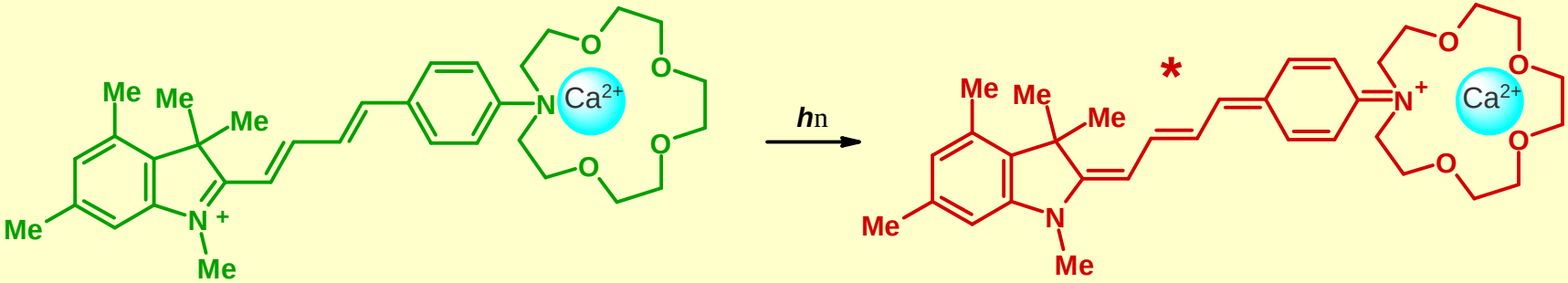
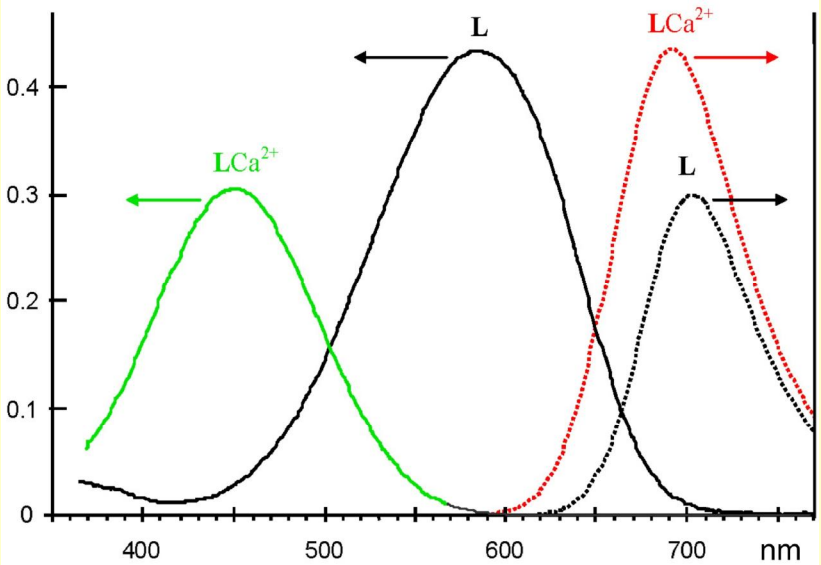
Photoswitchable supramolecular device



Photoinduced recoordination reaction



Russ. Chem. Bull. **1999**, *48*, 525;
J. Fluor. **1999**, *9*, 33;
Rusalov M. V., Gromov S. P. et al. *Russ. Chem. Rev.* **2010**, *79*, 1193 (review).

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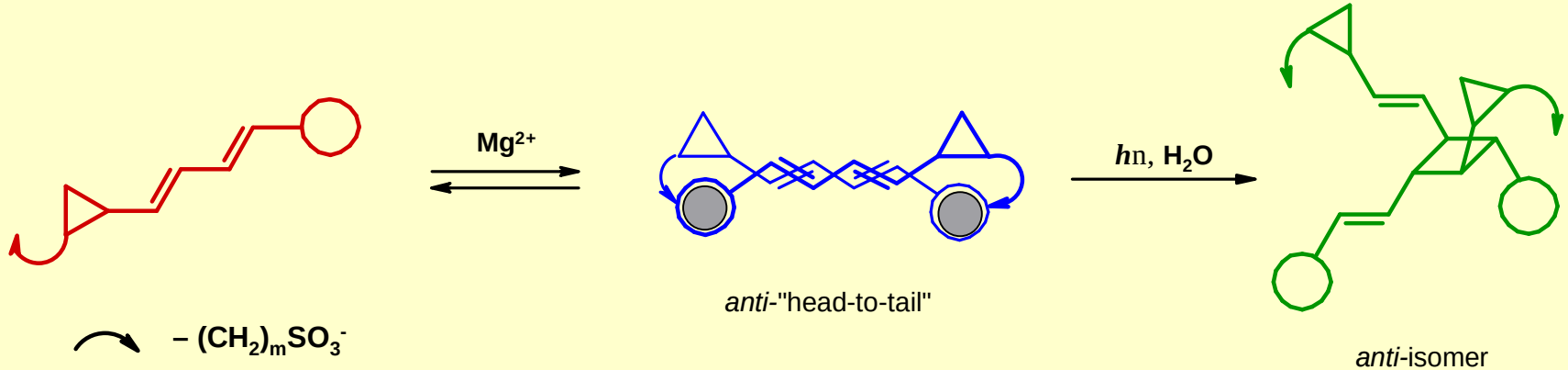
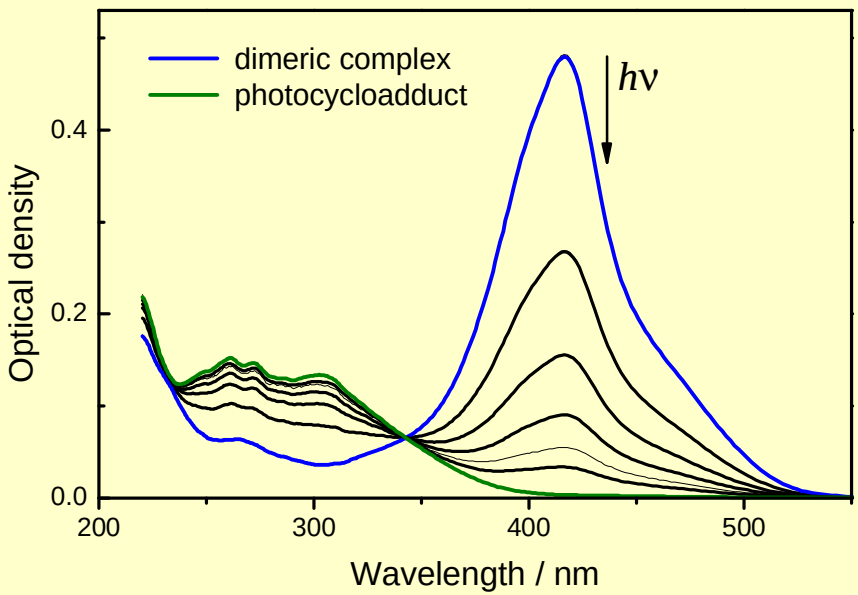
[2+2] PHOTOCYCLOADDITION OF CBD



F_{PCA} = 0.35



Helv. Chim. Acta **2002**, *85*, 60;
Photochem. Photobio. Sci., **2011**, *10*, 15.

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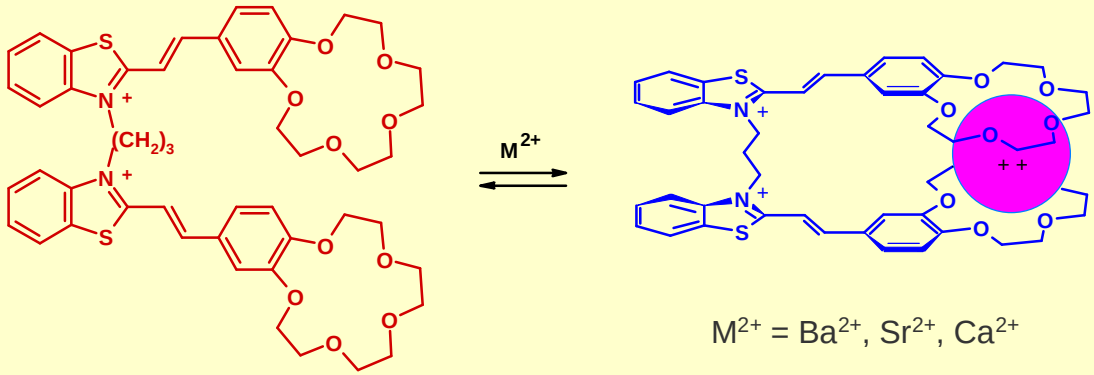
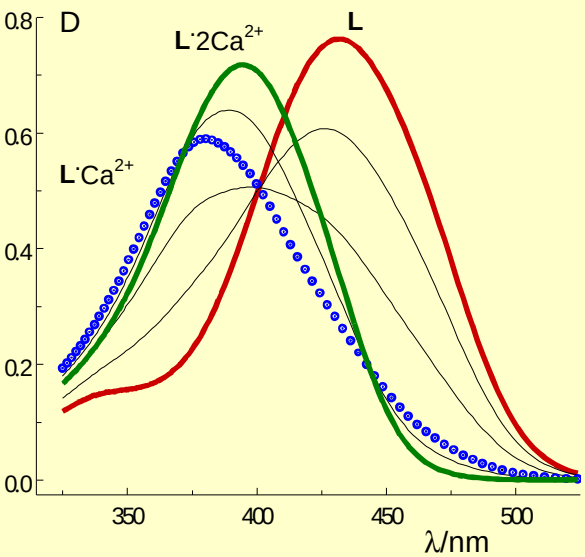
PHOTOCHEMISTRY CENTER

Self-assembly of sandwich complexes



trans,trans-isomer

M^{2+} = Ba^{2+}, Sr^{2+}, Ca^{2+}



Complex	lgK_1	λ_{LM}, nm	λ_L - λ_{LM}, nm
L·Ba^{2+}	8.0	390	42
Monomer · Ba^{2+}	4.39	402	28

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

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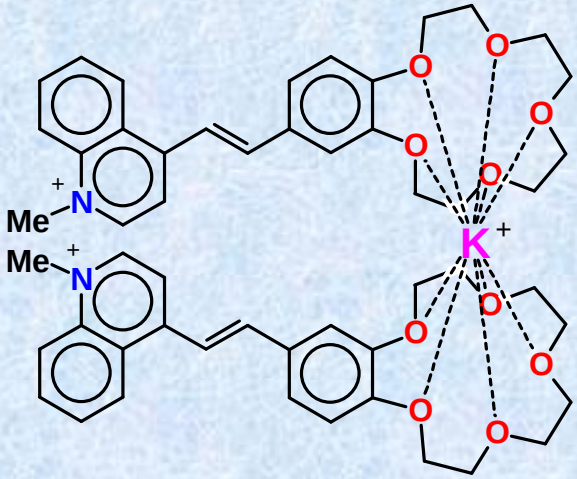
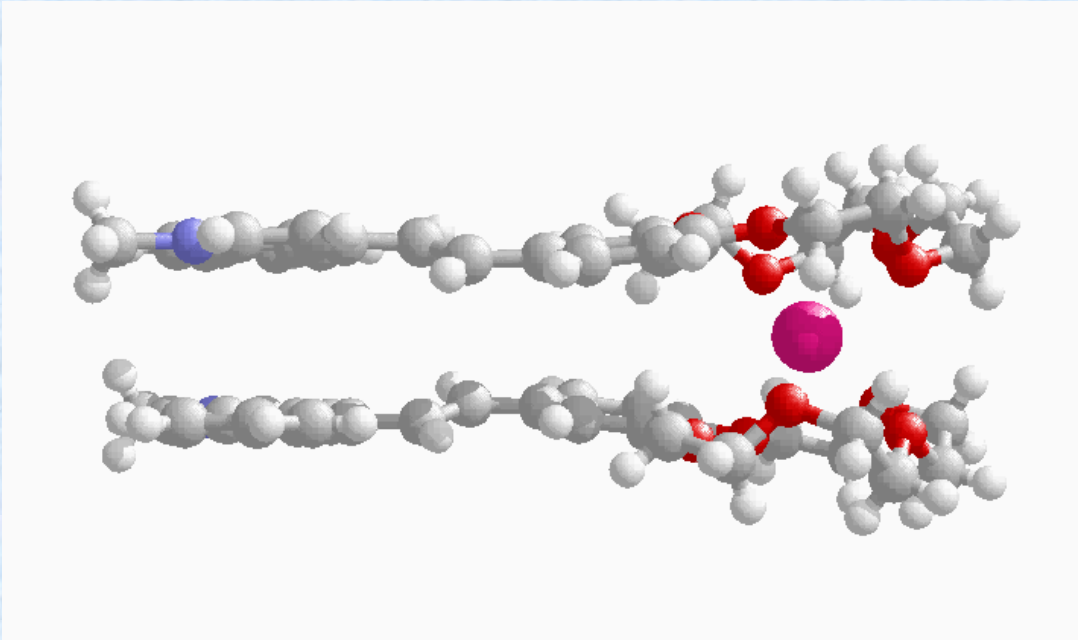
X-ray structure determination of sandwich complex





Crystallography Reports **2003**, *48*, 613.

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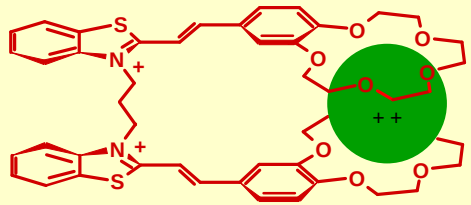
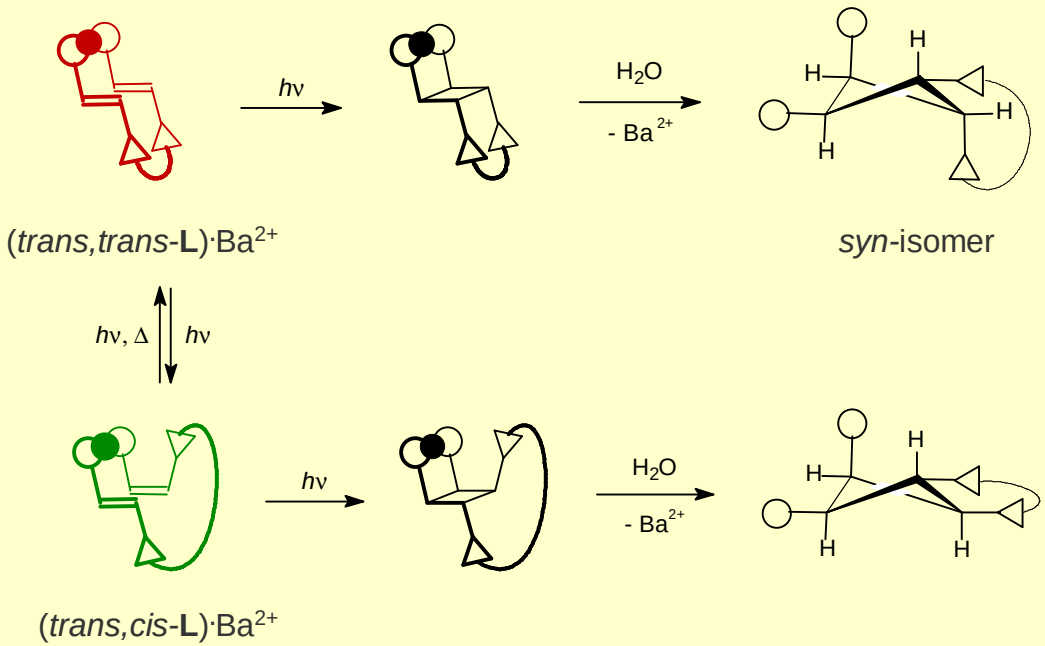
PHOTOCHEMISTRY CENTER

Intramolecular [2+2] photocycloaddition of bisCSD



(*trans,trans*-**L**)·Ba^{2+}



(*trans,trans*-**L**)·Ba^{2+}

syn-isomer

(*trans,cis*-**L**)·Ba^{2+}

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

J. Chem. Soc., Perkin Trans. 2. **1999**, 1323.

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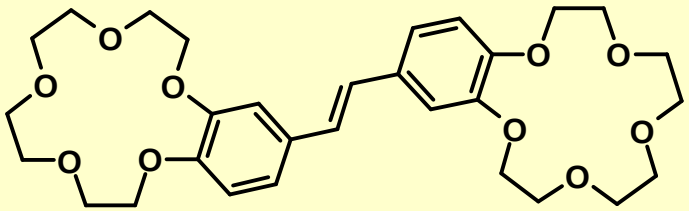
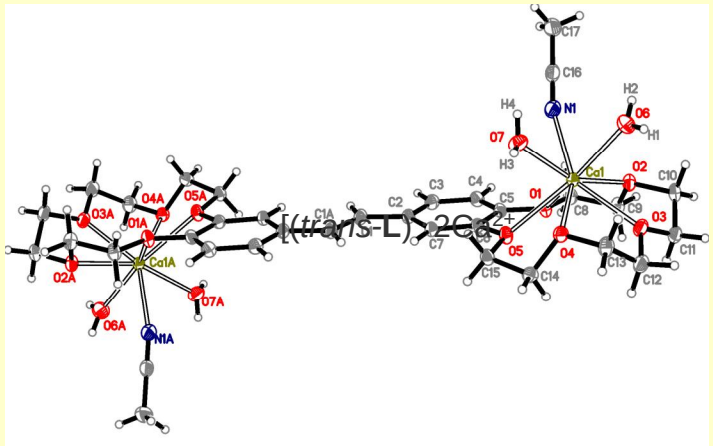
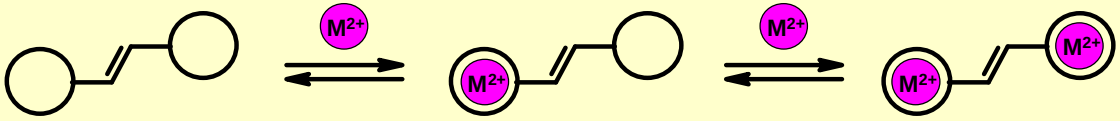
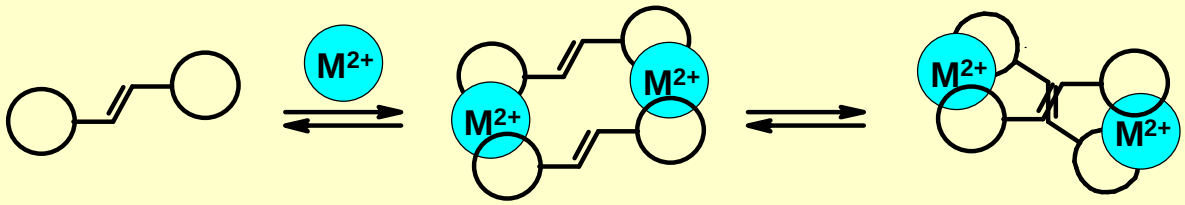
Complex formation of bisCS



trans-**L**







M2+ = Mg^{2+}, Ca^{2+} M2+ = Sr^{2+}, Ba^{2+}

New. J. Chem. **2011**, *35*, 724.

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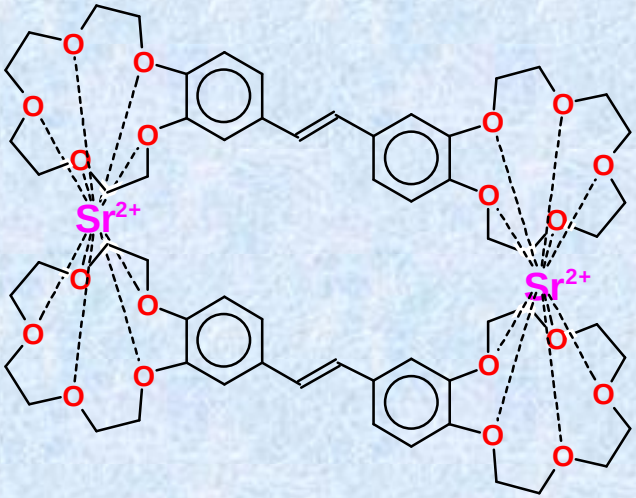
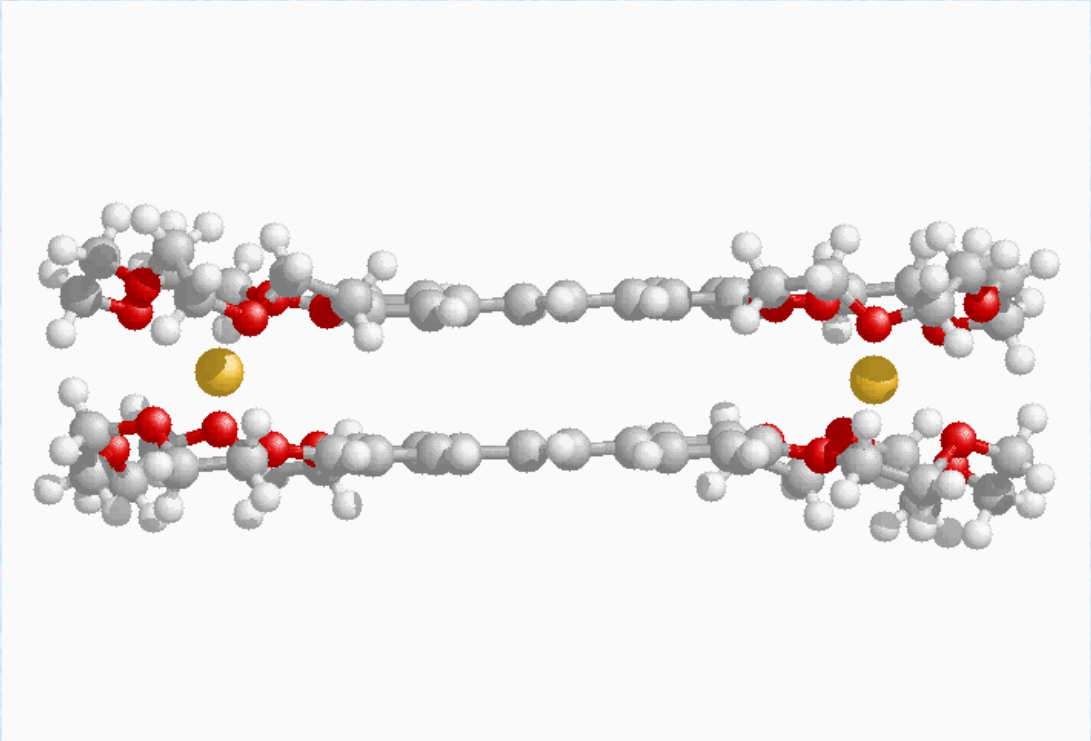
X-ray structure determination of double sandwich complex



2(*trans*-**L**) · $2Sr^{2+}$



New. J. Chem. **2011**, *35*, 724.

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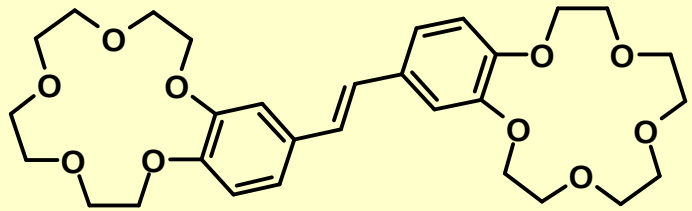
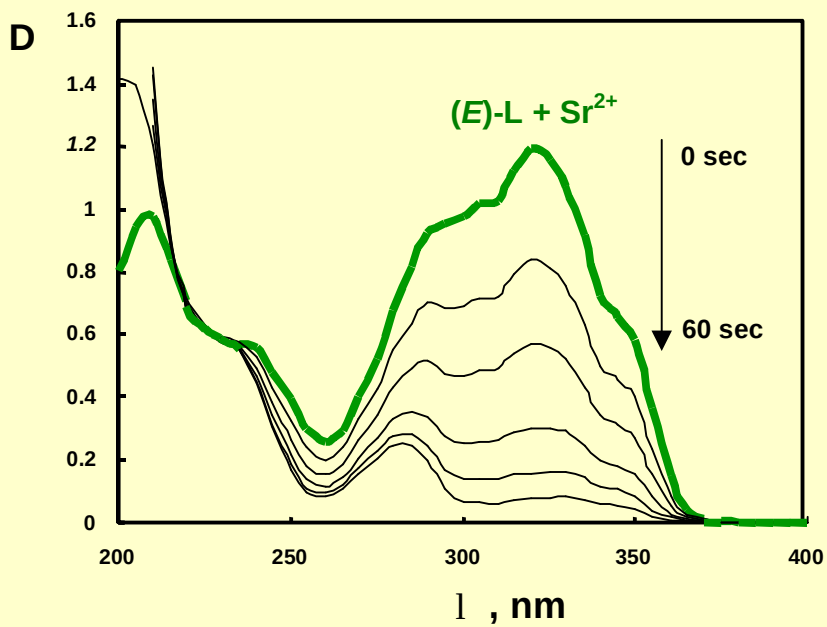
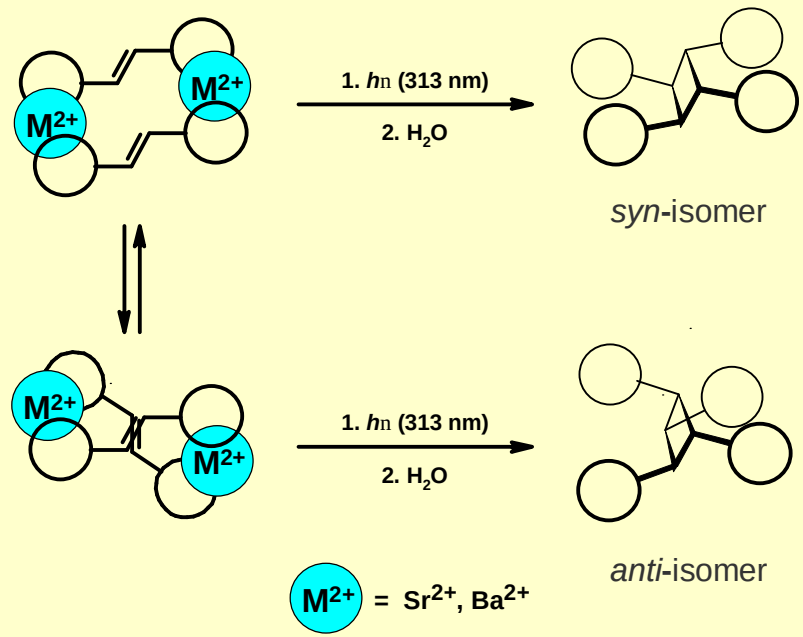
PHOTOCHEMISTRY CENTER

[2+2] Photocycloaddition of bisCS



trans-**L**





New. J. Chem. **2011**, *35*, 724.

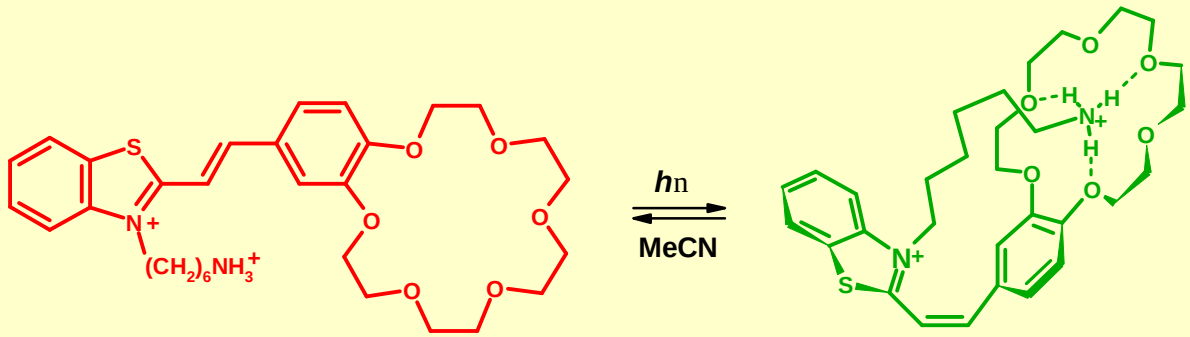
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

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

Part II

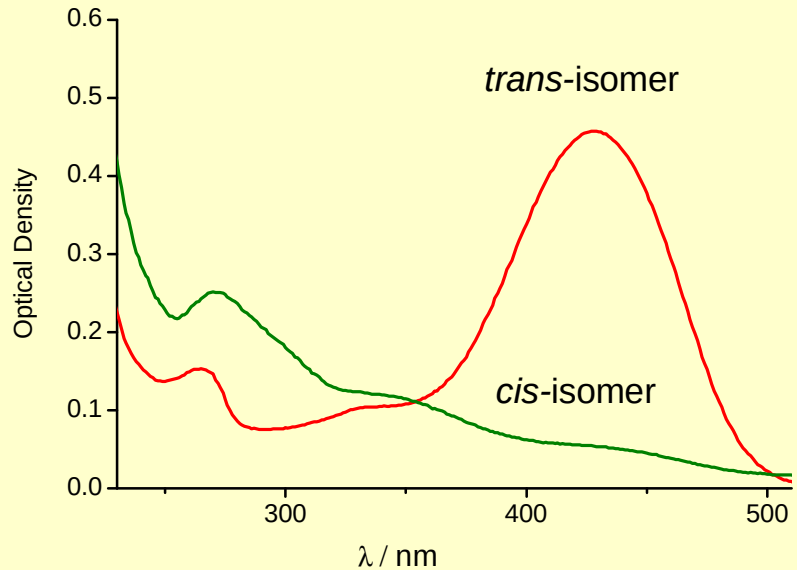
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Intramolecular complexation of *cis*-isomers



trans-isomer

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



Mendeleev Commun. **2007**,*17*, 264;
J. Mol. Structure. **2009**, *935*, 136.

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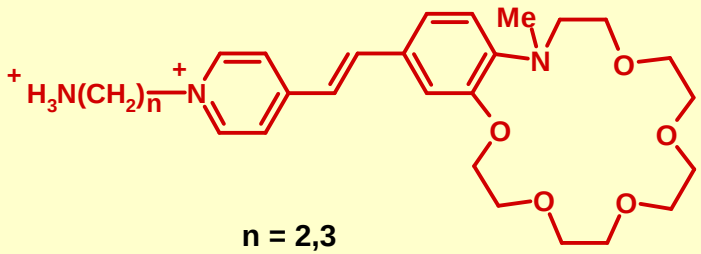
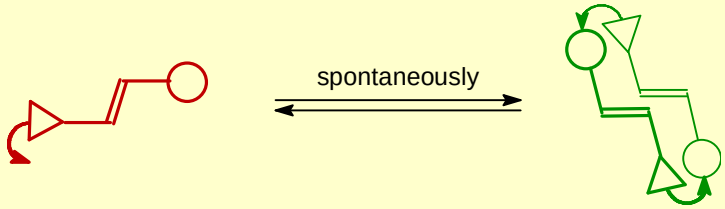
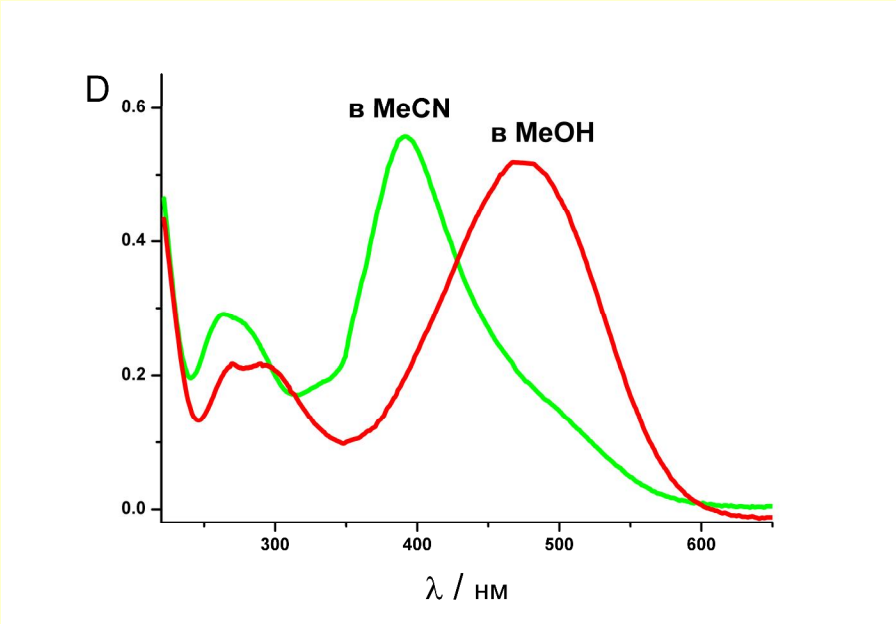
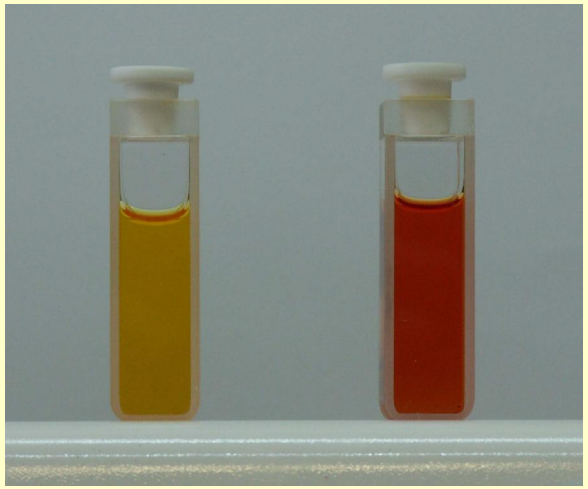
Dimerization of CSD









in MeCN in MeOH

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

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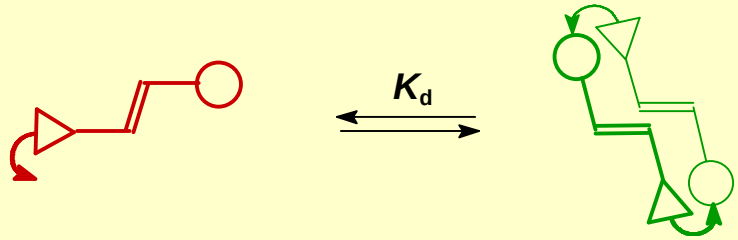
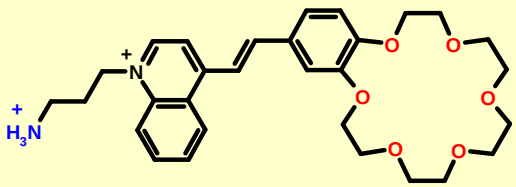
PHOTOCHEMISTRY CENTER

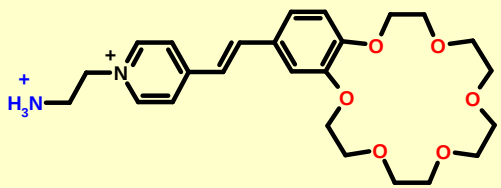
DIMERIZATION



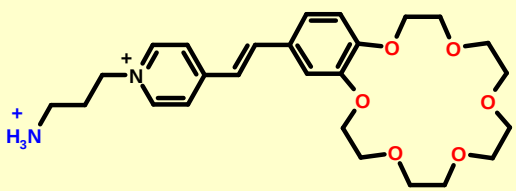
log K_d



8.03

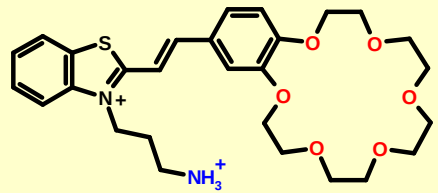


7.90

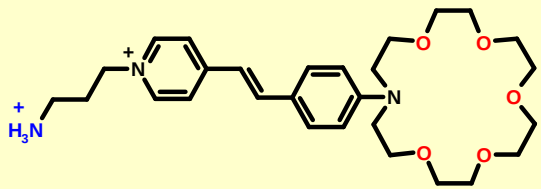


7.12

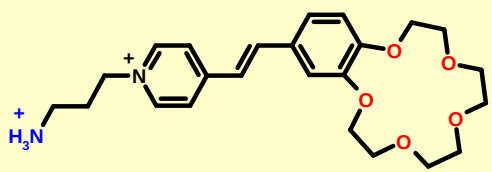
log K_d



5.87



3.61



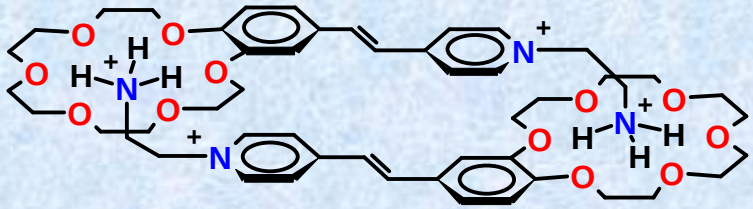
2.44

in CD_3CN

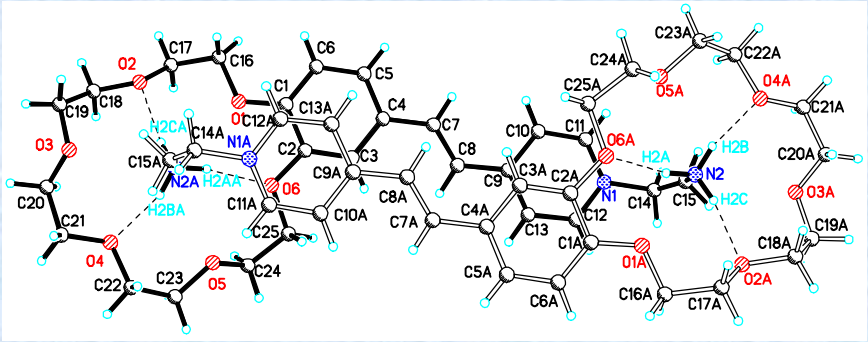
Russ. Chem. Bull. **2009**, *58*, 1211;
J. Org. Chem. **2014**, *79*, 11416;
J. Phys. Chem. A **2015**, *119*, 13025.

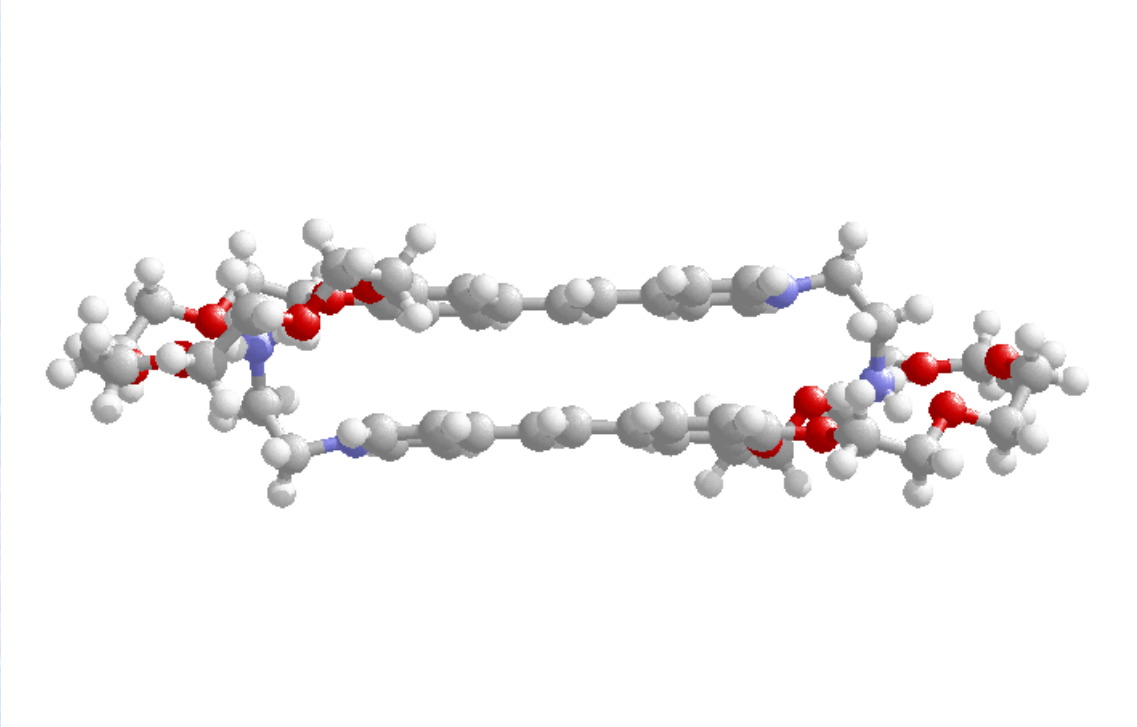
THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

X-ray structure determination of dimeric compex



syn-"head-to-tail" dimeric complex

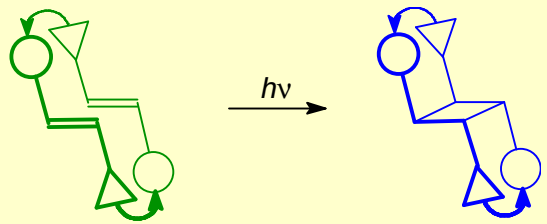




Russ. Chem. Bull. **2009**, *58*, 1211;
J. Org. Chem. **2014**, *79*, 11416.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

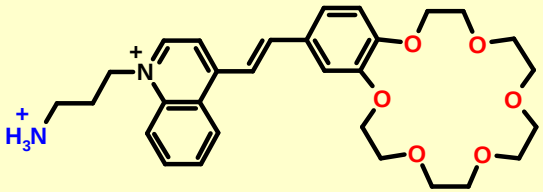
[2+2] Photocycloaddition of CSD



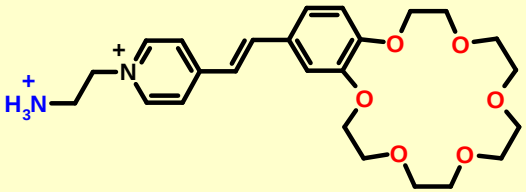
F_{PCA} up to 0.38

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

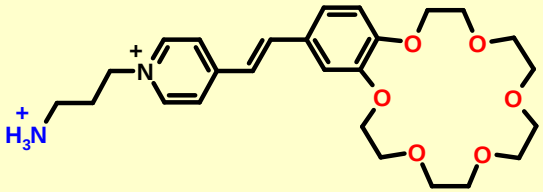
Yield, %



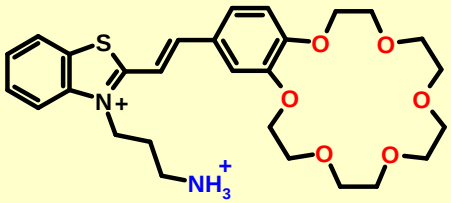
100



33



100



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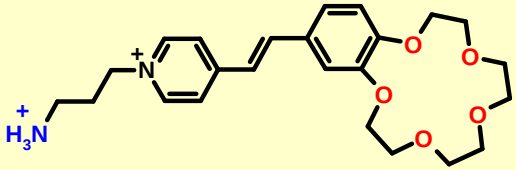
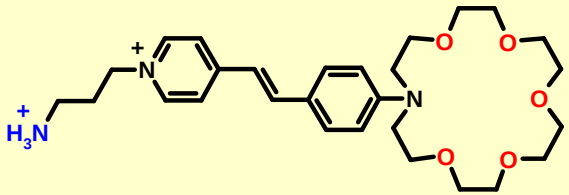


40



0

Yield, %

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
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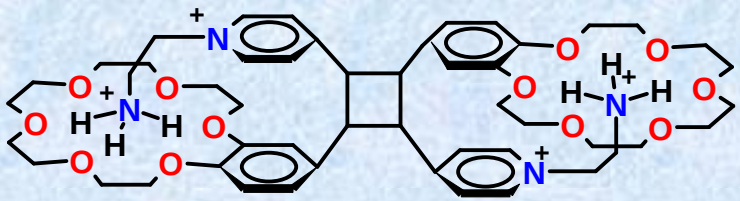
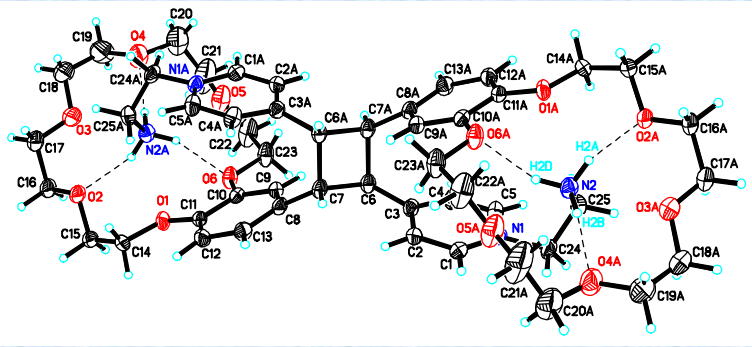
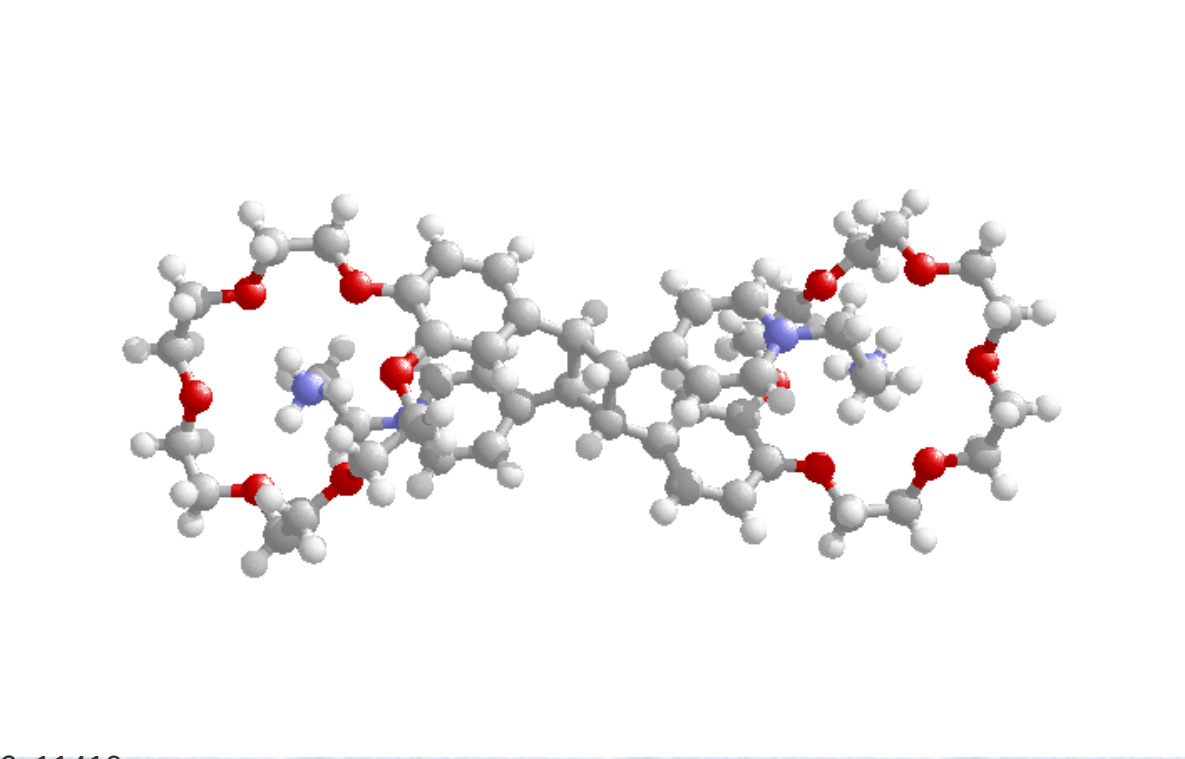
X-ray structure determination of cyclobutane



syn-cyclobutane

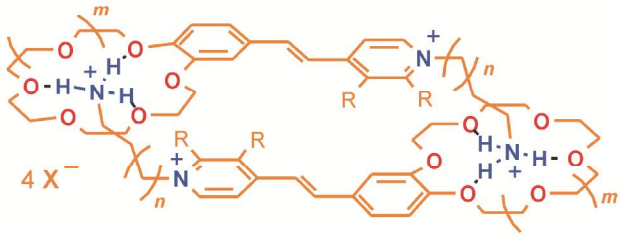




J. Org. Chem. **2014**, *79*, 11416.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

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



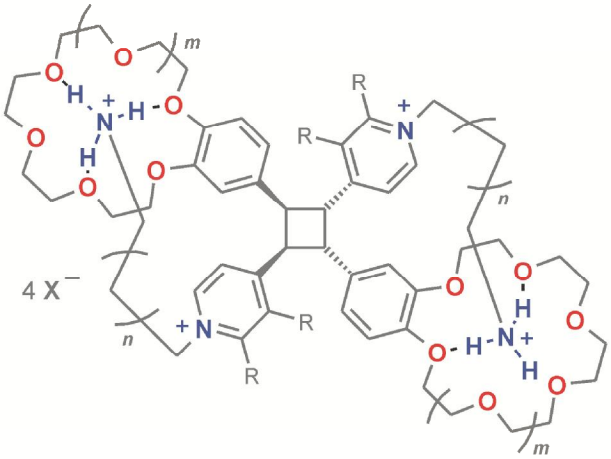
R = H, R + R = benzo; *n, m* = 0, 1

dimeric complexes of styryl dyes

$h\nu_1$

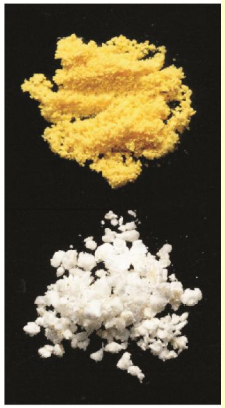
$h\nu_2$

solution or solid phase



rctt isomers of cyclobutane derivatives

dye



cyclobutane

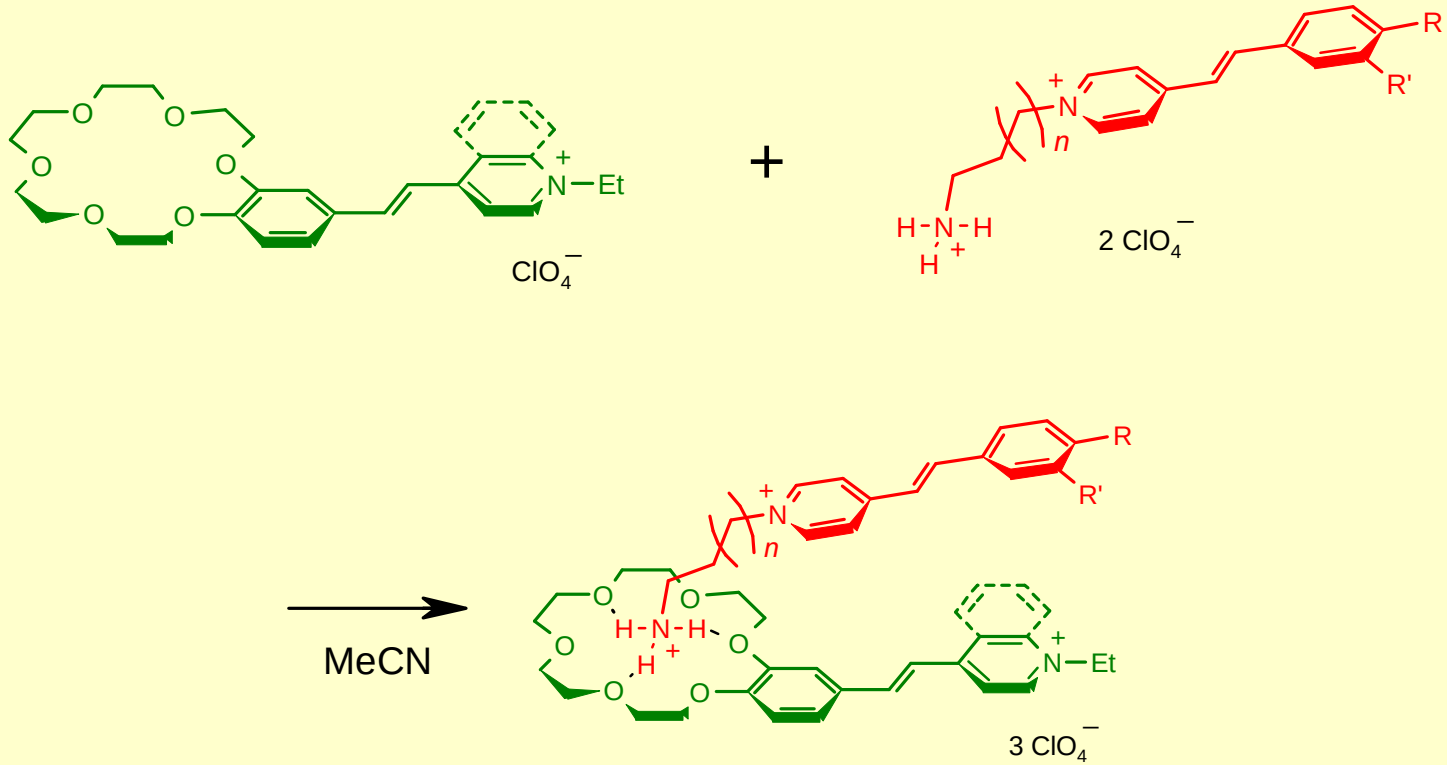
(X = ClO_4;
R = H, *n* = *m* = 1

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 pseudodimeric complexes



R, R' = H, OMe, SMe, NMe_2, NO_2, Cl

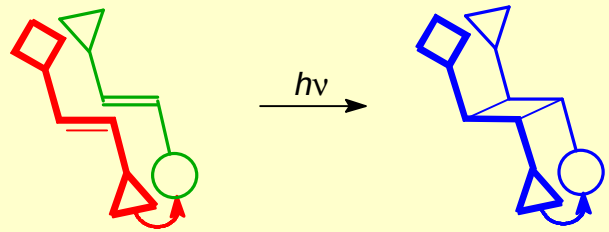
n = 0, 1, 3

log *K* = 3.1 - 3.7

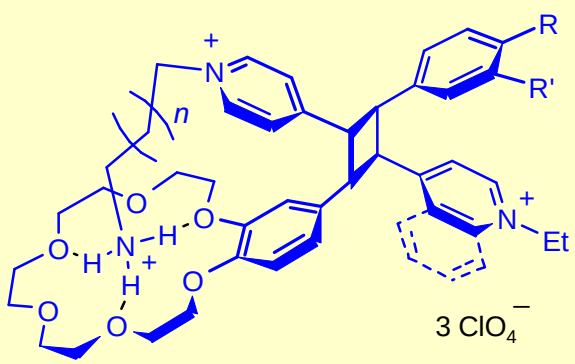
Mendeleev Commun., **2007**, *17*, 29;
Russ. Chem. Bull. **2009**, *58*, 1955;
New. J. Chem. **2016**, *40*, 7542.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

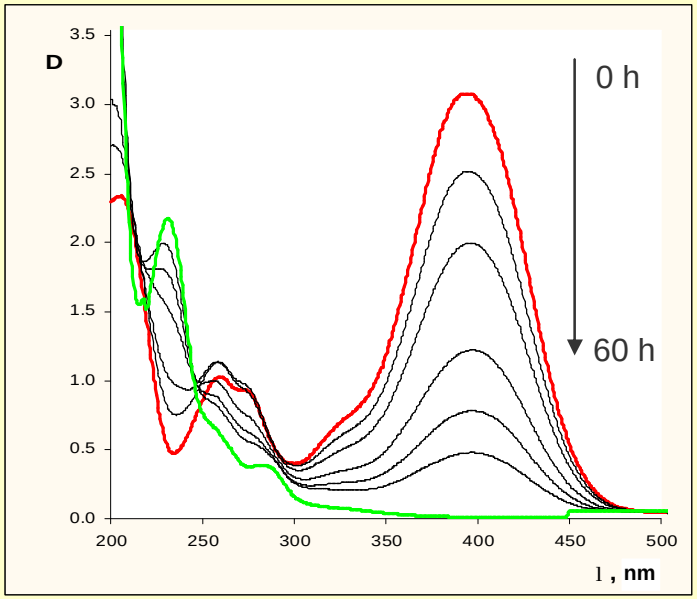
Cross [2+2] Photocycloaddition



syn-"head-to-tail"



rctt isomers



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

THE RUSSIAN ACADEMY OF SCIENCES
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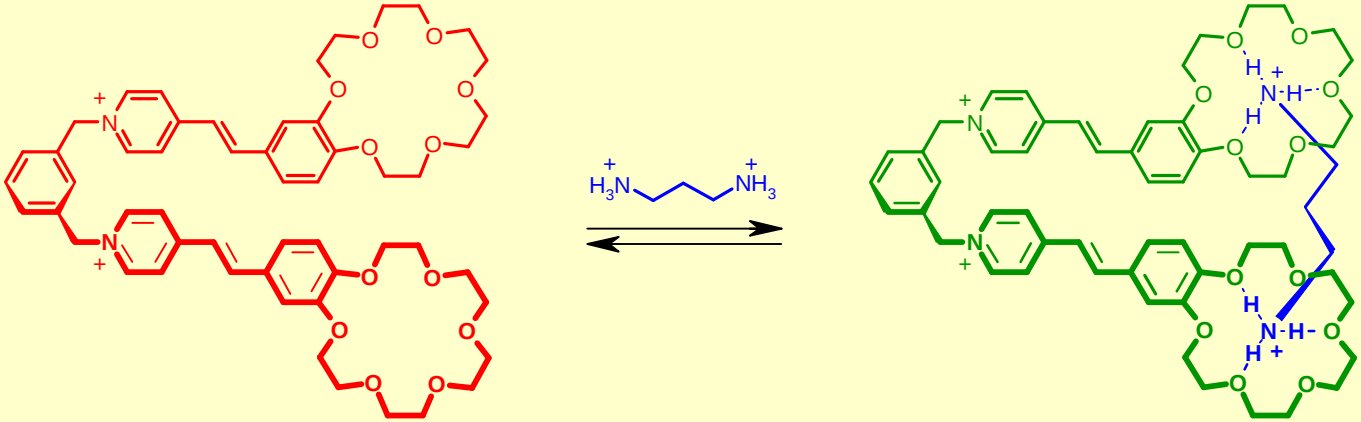
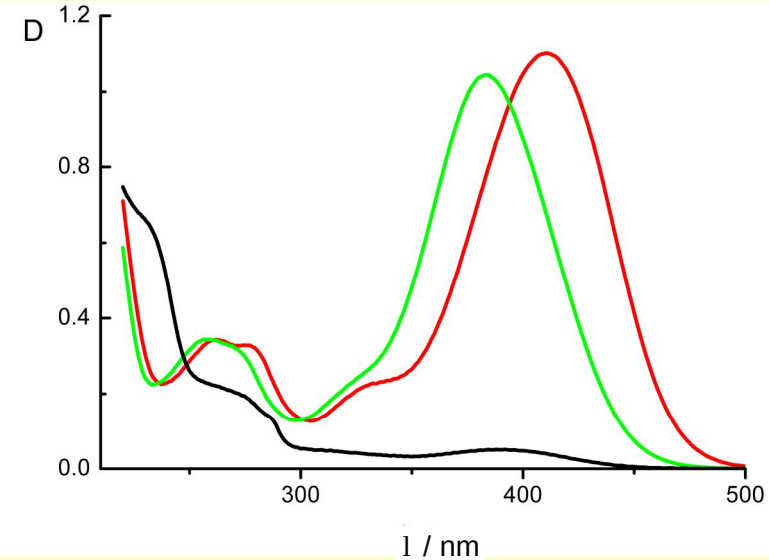
FORMATION OF PSEUDOSANDWICH COMPLEXES

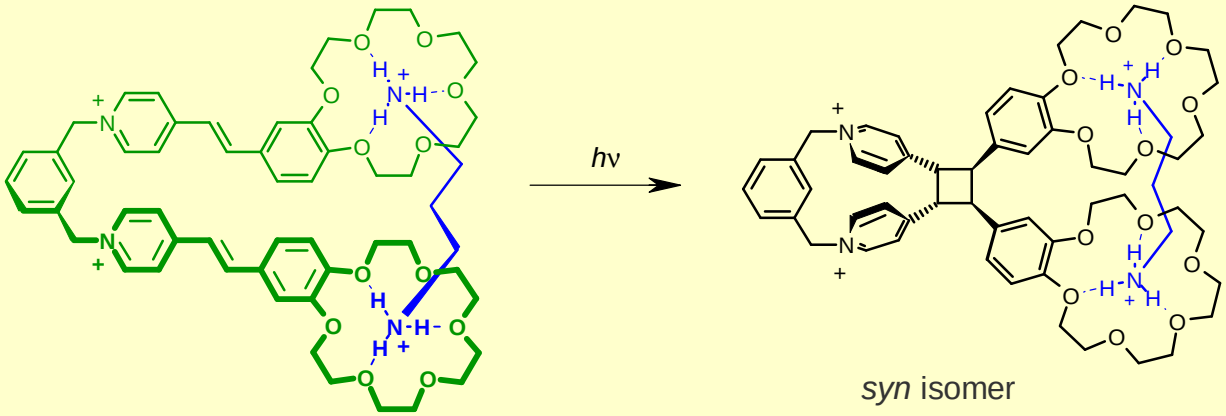


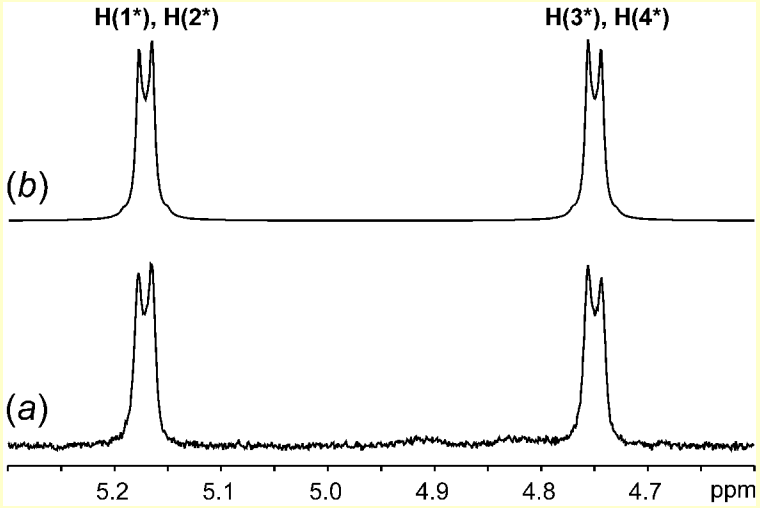


Mendeleev Commun. **2005**, *15*, 173.

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

Intramolecular [2+2] photocycloaddition of bisCSD



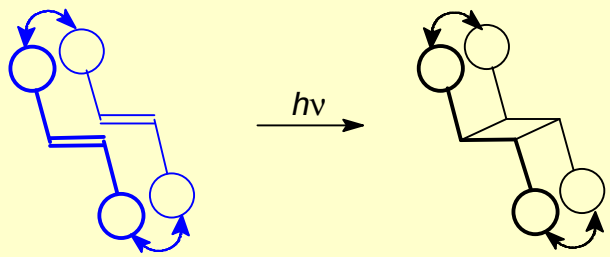


(*a*) ^{1}H NMR spectrum of the cyclobutane protons and (*b*) its best fit to an AA'BB' spin system.

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

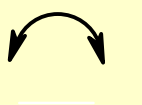
THE RUSSIAN ACADEMY OF SCIENCES PHOTOCHEMISTRY CENTER

Formation of bispseudosandwich complexes and [2+2] Photocycloaddition

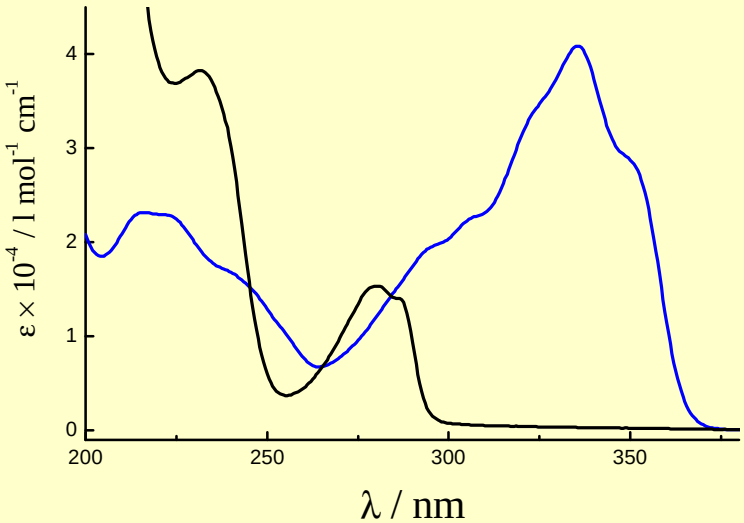


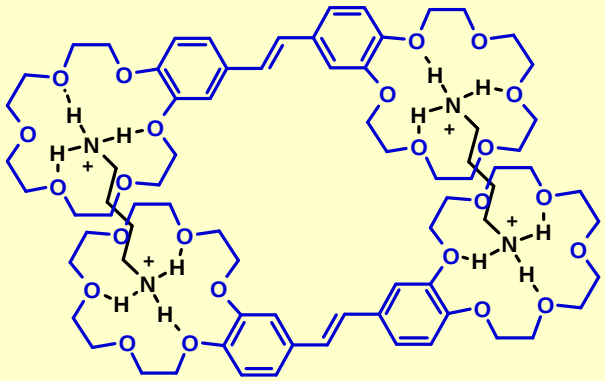
syn-complex *syn-isomer*

F_{PCA} up to 0.27

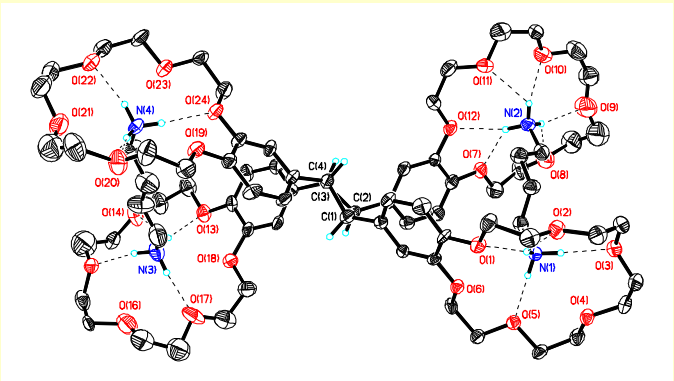


– $H_3N^+(CH_2)_nNH_3^+$ 2 ClO_4^-, n = 2-10, 12





hν



syn-isomer

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

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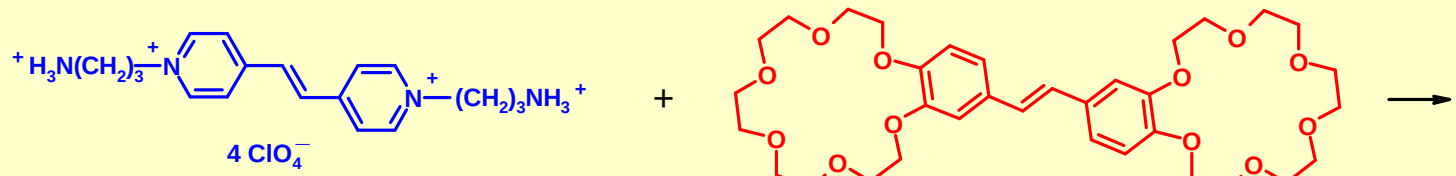
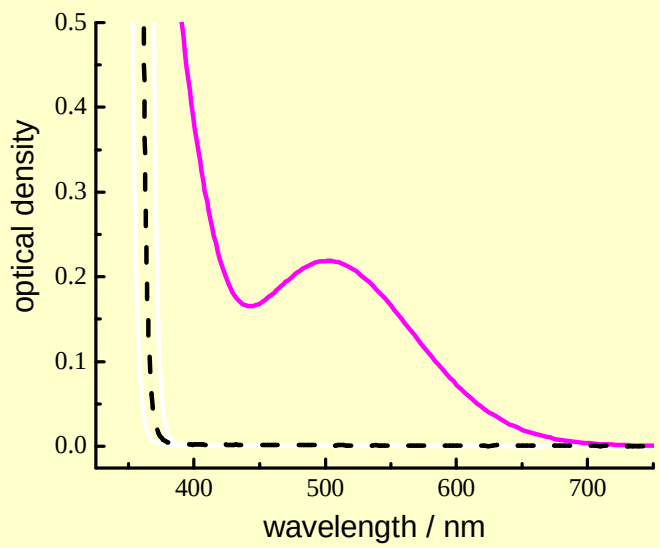
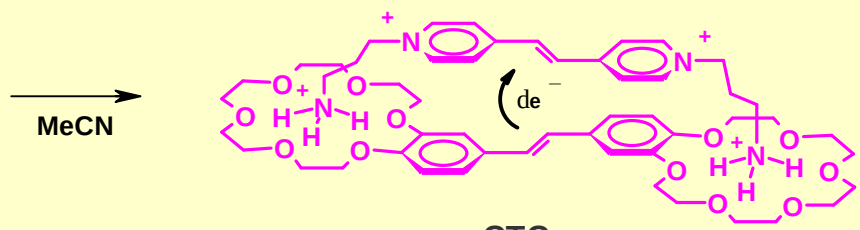
PHOTOCHEMISTRY CENTER

Formation of Charge Transfer Complex of bisCS







CTC

log *K* = 9.08

Org. Lett. **1999**, *1*, 1697 ;
New. J. Chem. **2005**, *29*, 881;
J. Org. Chem. **2011**, *76*, 6768.

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PHOTOCHEMISTRY CENTER

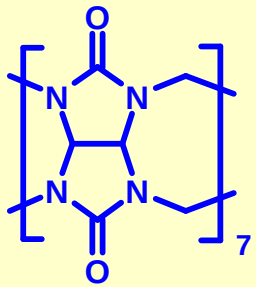
Self-assembly

of photocontrolled supramolecular machines

Part III

THE RUSSIAN ACADEMY OF SCIENCES
PHOTOCHEMISTRY CENTER

PSEUDOROTAXANE COMPLEXES OF CUCURBITURILS

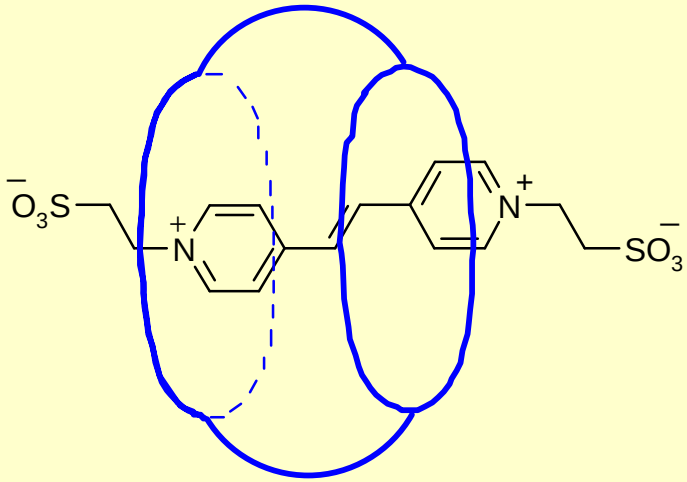


CB[7]

cucurbit[n]urils

trans-**V**

lg*K* = 3.5



trans-**V**@CB[7]

Russian Nanotechnologies **2007**, *2*, 56;
J. Mol. Struct. **2011**, *989*, 114;
Chem. Phys. Lett. **2014**, *610-611*, 91.

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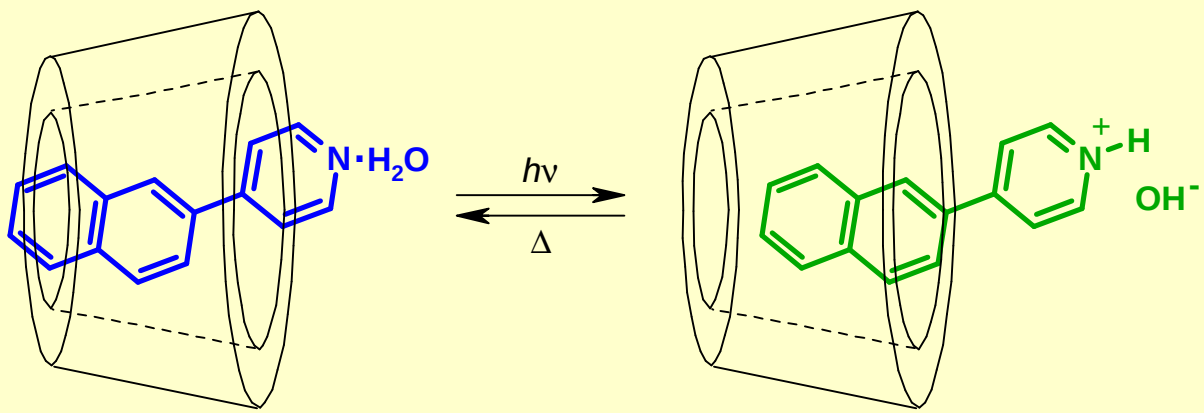
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



1·H_2O@HP-β-CD

lg*K* = 1.9

1H^+OH^-@HP-β-CD

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

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

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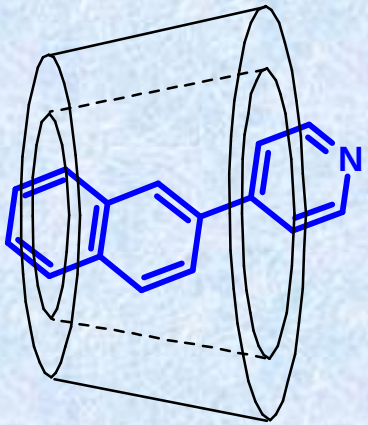
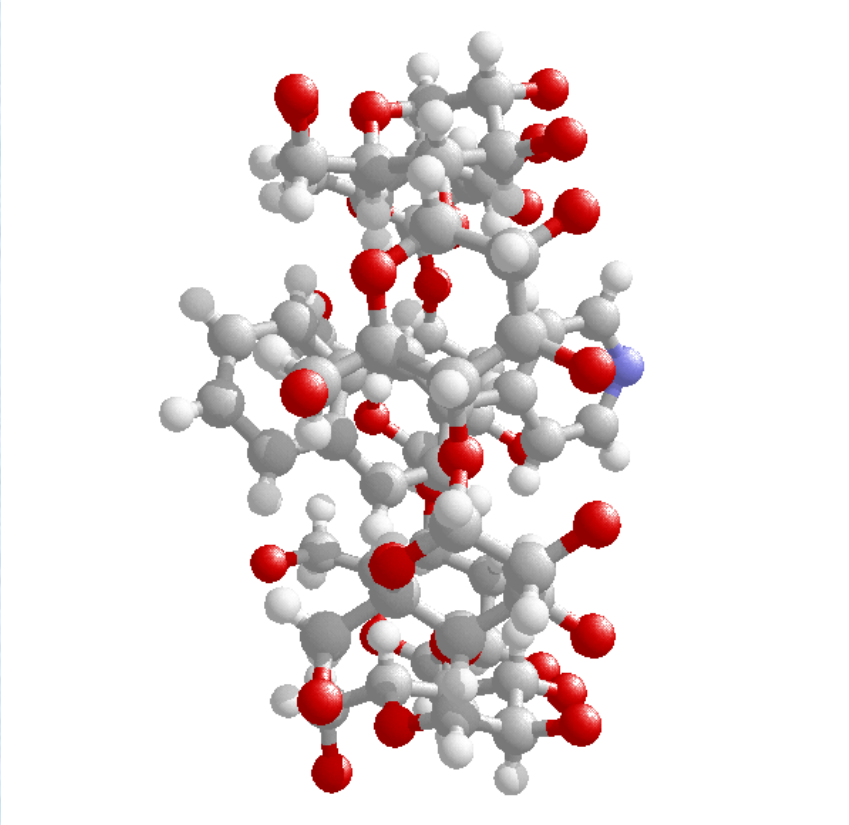
X-ray structure determination of photocontrolled supramolecular machine



1@β-CD



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

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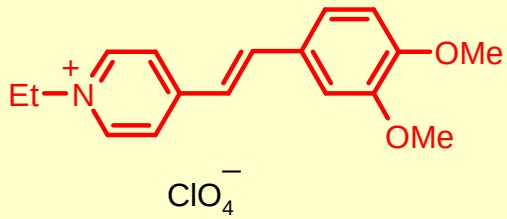
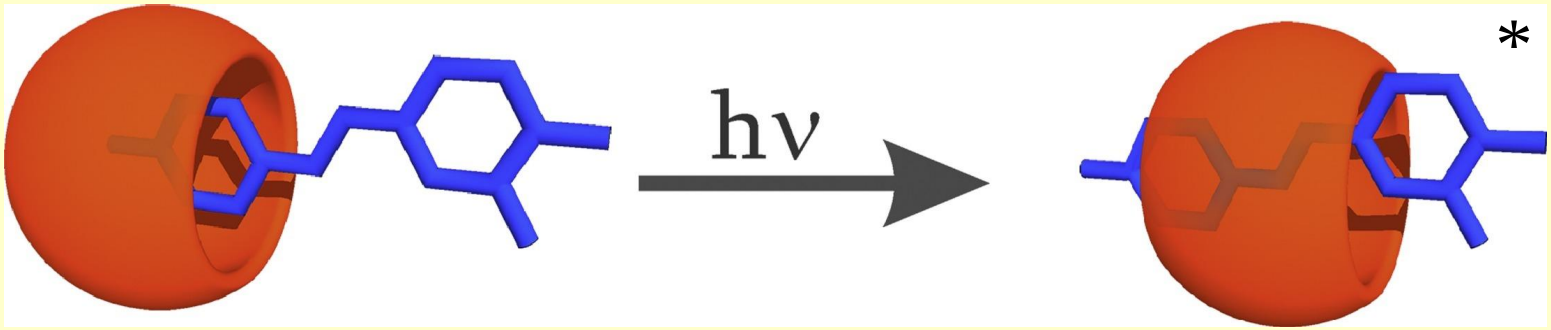
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE





SD@CB[7]

SD@CB[7] *

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

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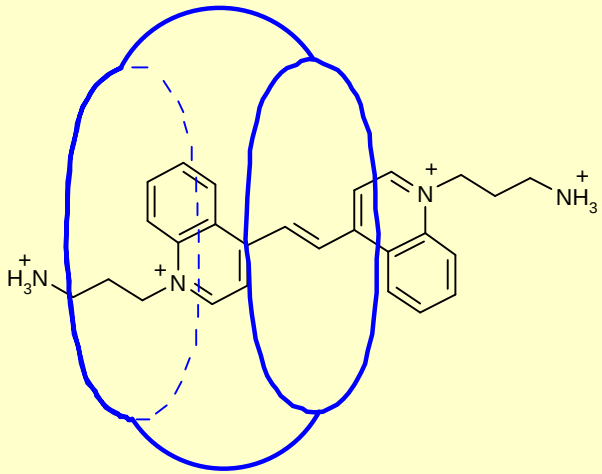
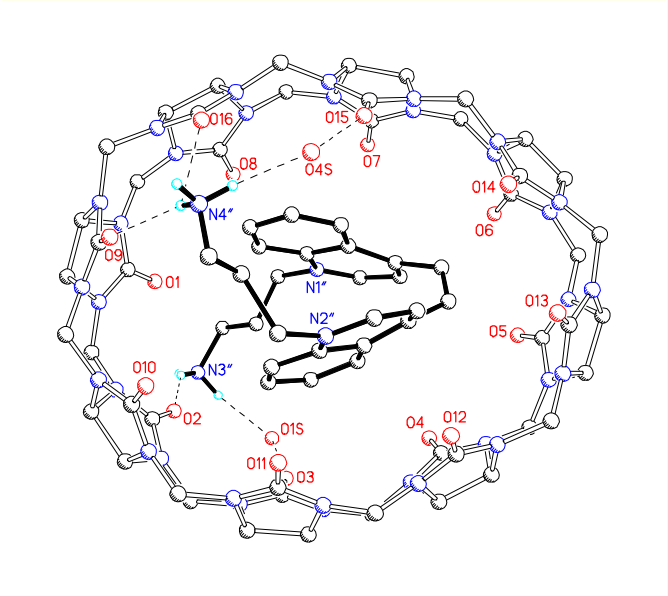
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



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.

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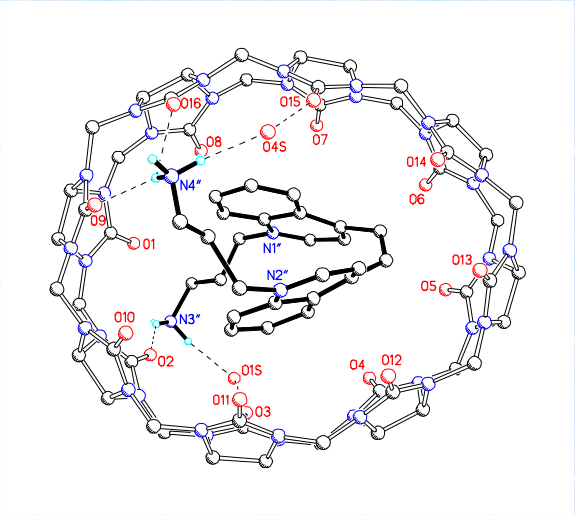
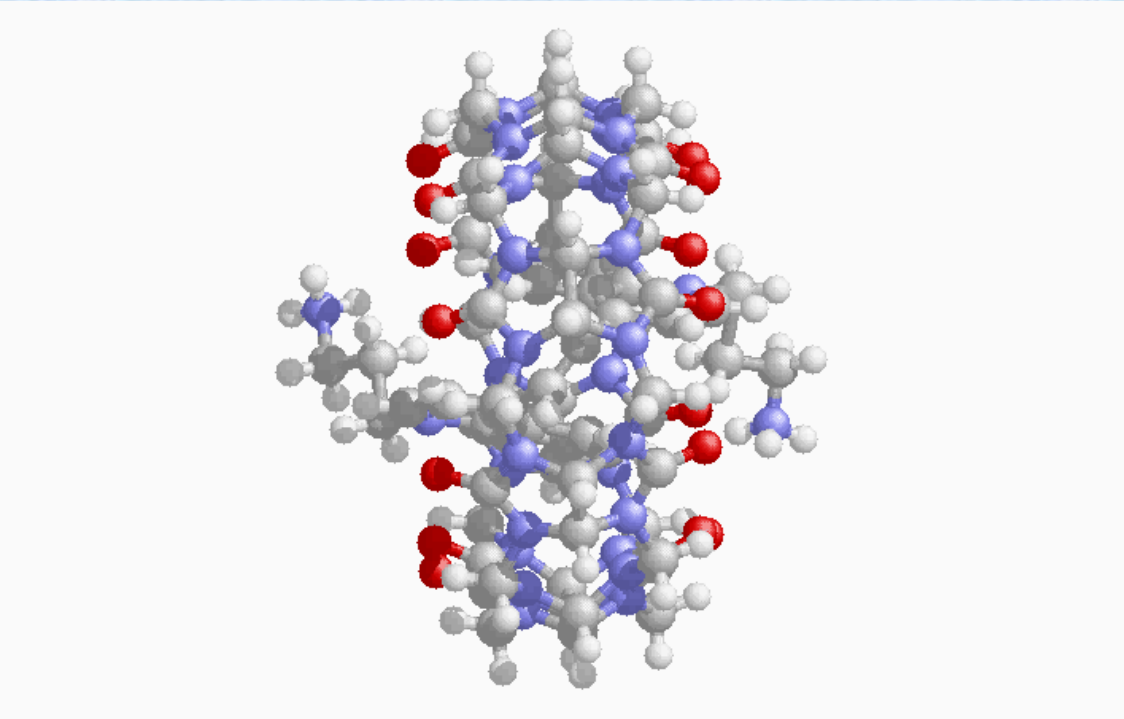
X-ray structure determination of photocontrolled supramolecular machine



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



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

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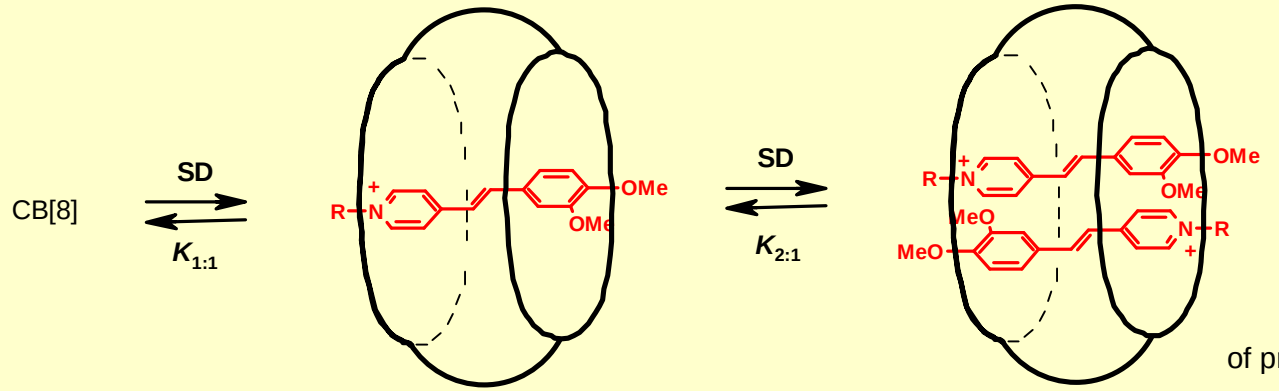
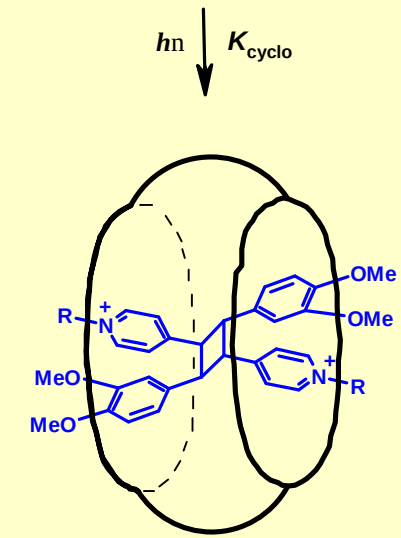
PHOTOCONTROLLED SUPRAMOLECULAR MACHINES



SD@CB[8]

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

Time
of pre-organization
~ 4 ps



cyclobutane@CB[8]

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

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

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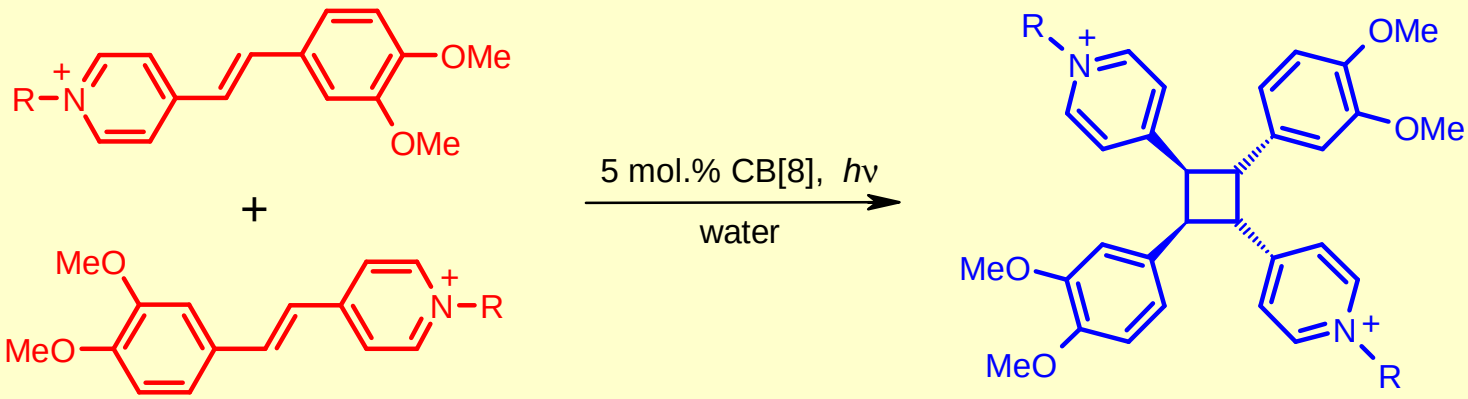
PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL



styryl dye (**SD**)

rctt isomer of cyclobutane

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

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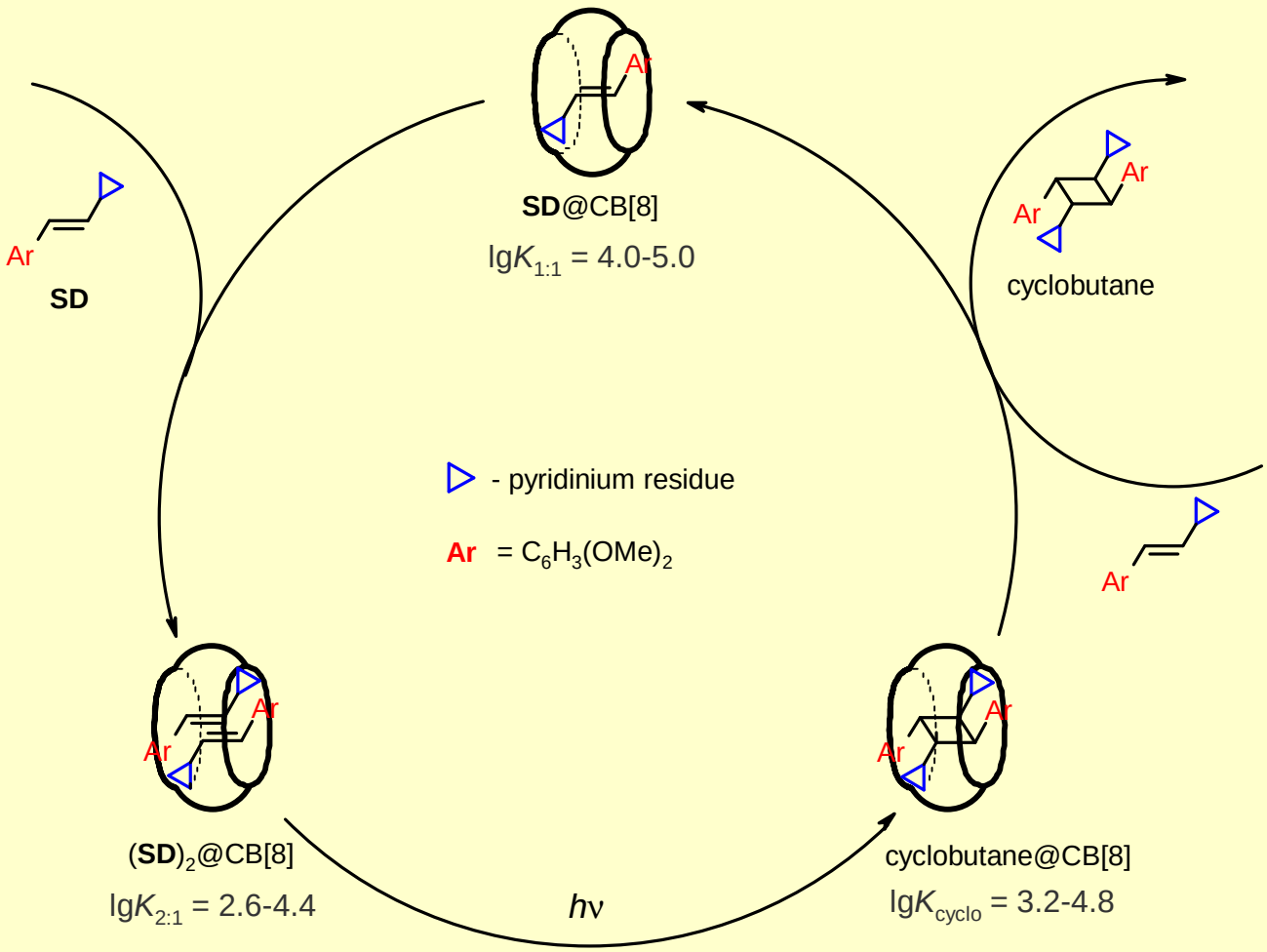
PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL



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

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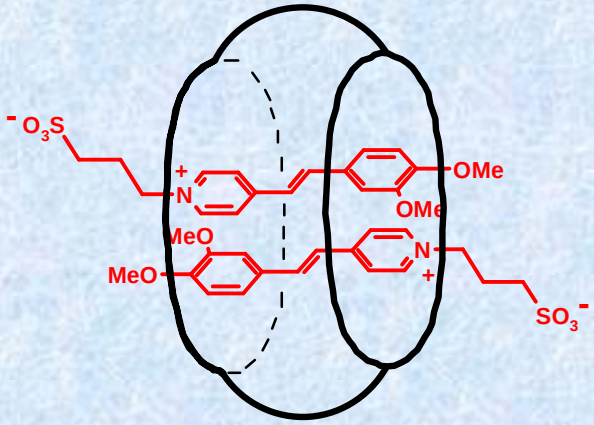
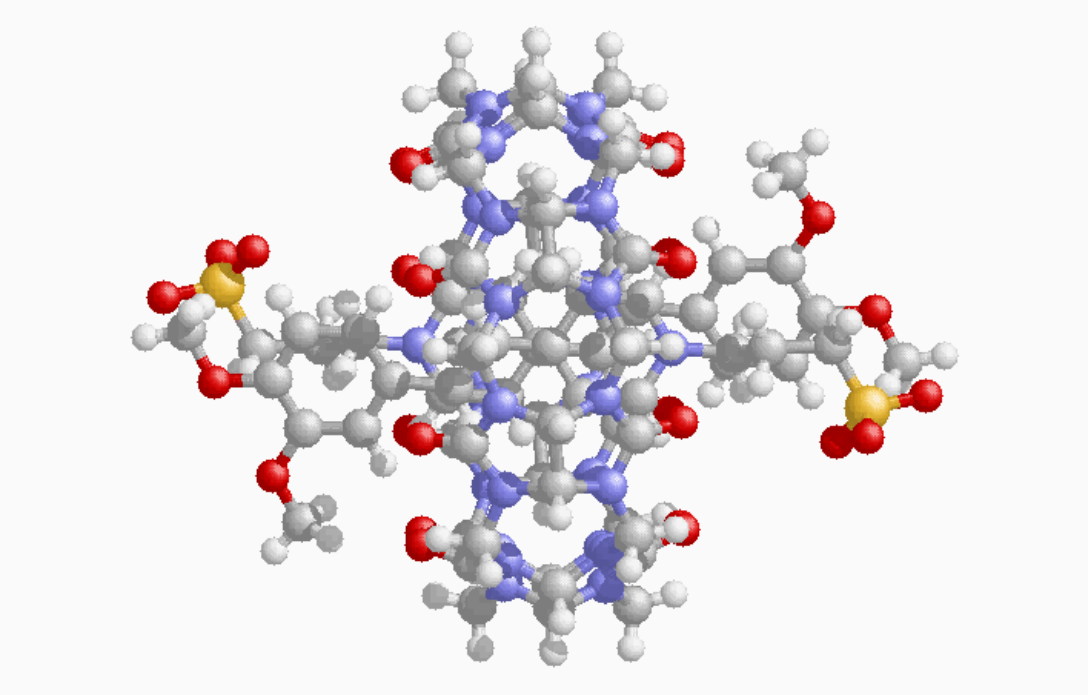
X-ray structure determination of photocontrolled supramolecular assembler



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



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

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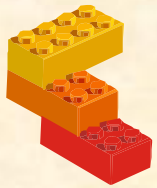
It is possible to implement all main types of photoprocesses:

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

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

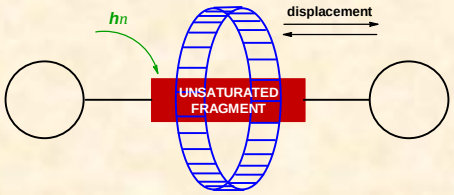
Molecular meccano
of photoactive supramolecular systems

Gromov S. P., Alexander Butlerov prize of RAS



Unique set of characteristics needed:

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



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

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Applied potential:

new strategy for the design of materials for nanophotonics

Demonstrated by an example of design:

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

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

Publications :

More than 320 publications in scientific journals and patents

Collaboration

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

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

Thank You

XXVII International Chugaev Conference on Coordination Chemistry

IV Young Conference School “Physico-Chemical Methods in the Chemistry of Coordination Compounds”

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

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