

Functional supramolecular systems using light as an energy source

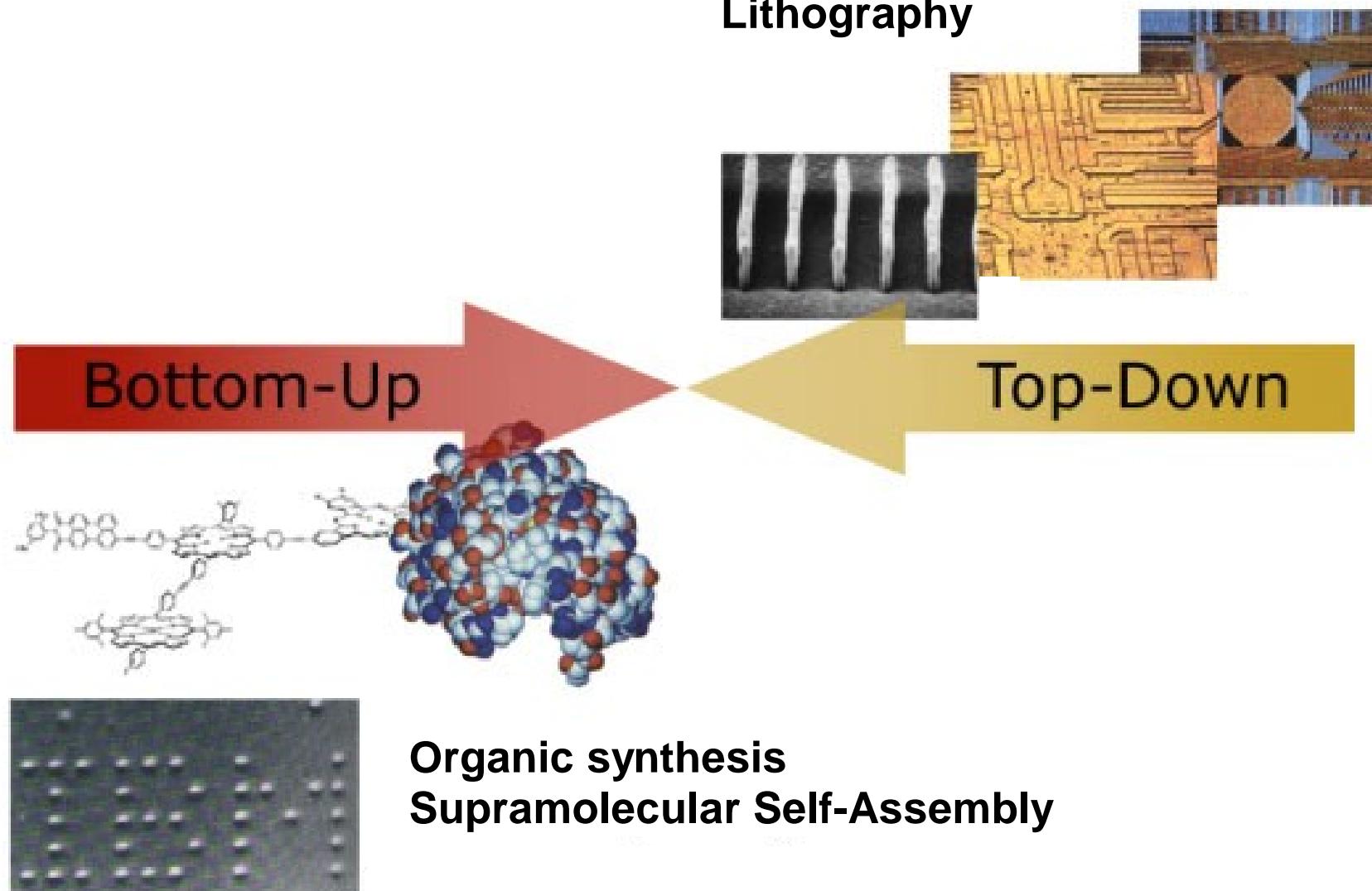
Prof. Sergey P. Gromov

<http://suprachem.photonics.ru>

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

NANOTECHNOLOGY “BOTTOM-UP”

STRATEGIES OF CREATION OF NANOSIZED ARCHITECTURES



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

Supramolecular
ensembles

C.....A

noncovalent bonds
(intermolecular)

TYPES OF INTERMOLECULAR BONDS

Coordination bonds

Ion-ion interactions

Ion-dipole interactions

Hydrogen bonds

Dipole-dipole interactions

Stacking interactions

Hydrophobic interactions

SUPRAMOLECULAR DEVICES AND MACHINES

Supramolecular devices are structurally organized and functionally integrated chemical systems.

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

J.-M. Lehn

They can be used:

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

Critical technologies of the RF

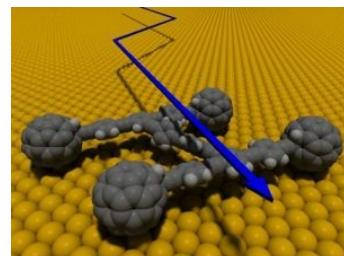
Means for control of supramolecular devices and machines

§ **Photoswitching - $h\nu$**

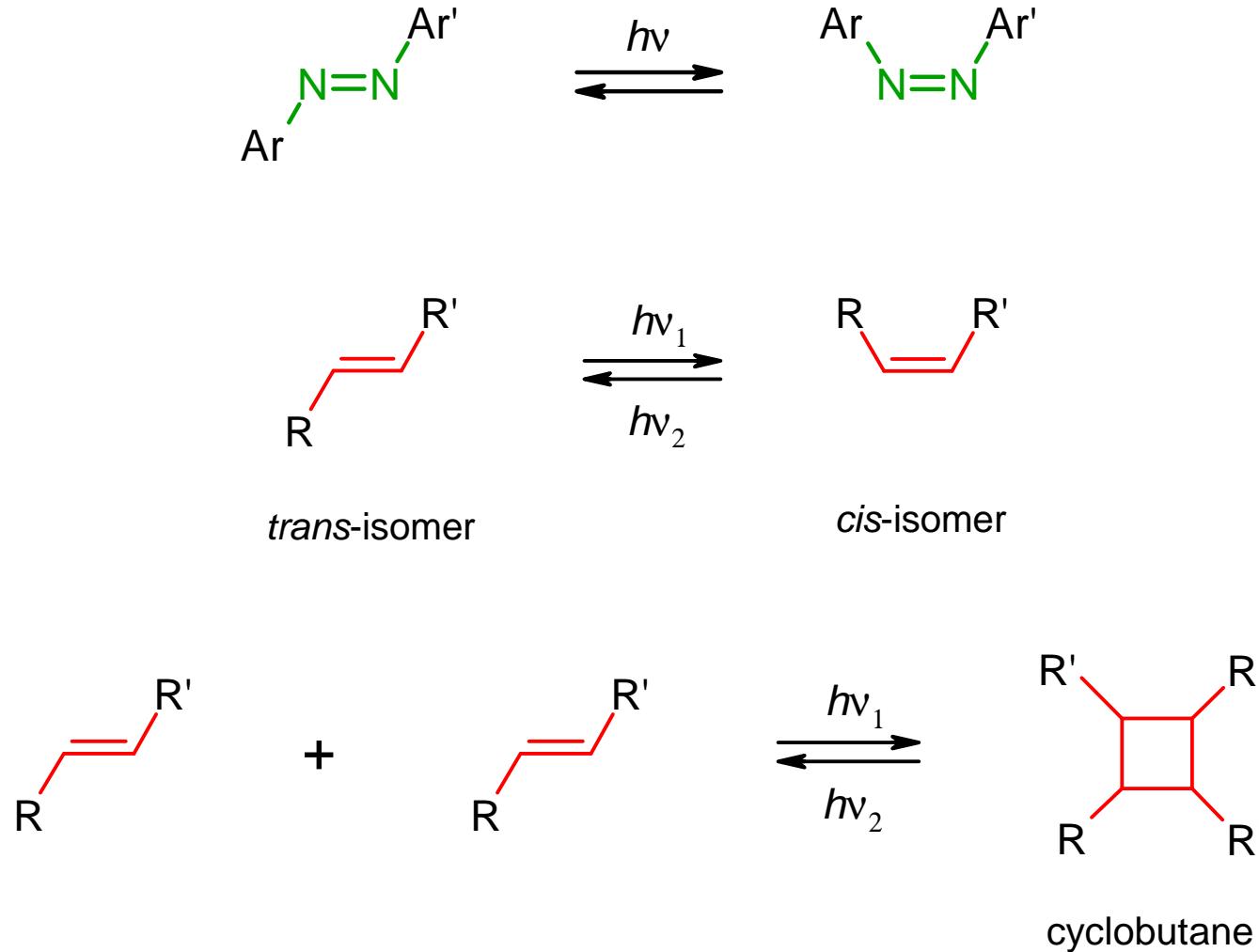
§ **Electrochemical switching - e^-**

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

§ **Thermal switching - D**



PHOTOANTENNAS OF SUPRAMOLECULAR DEVICES AND MACHINES BASED ON UNSATURATED COMPOUNDS



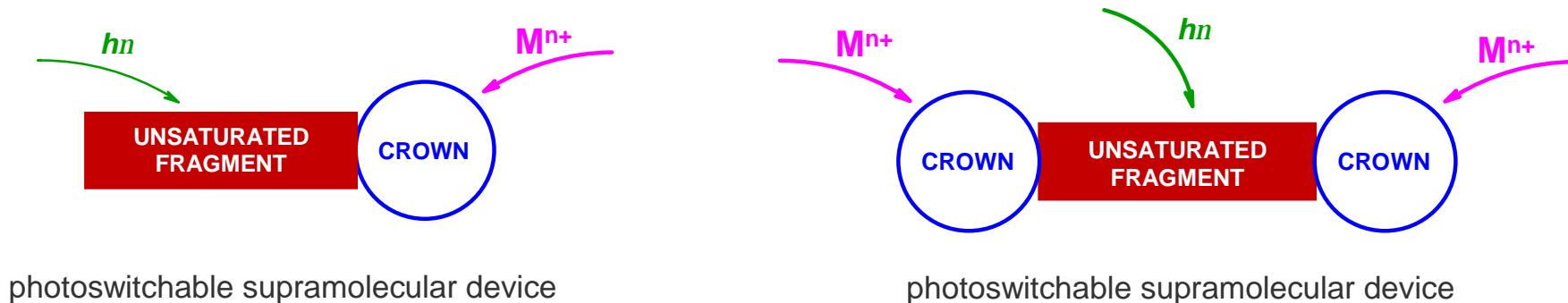
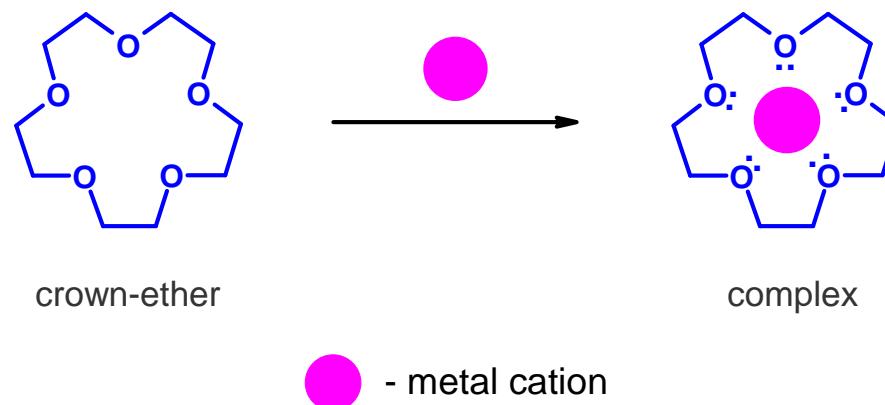
Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

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

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

Alfimov M. V., Gromov S. P., Ushakov E. N. in *Russ. Chem. Rev.* **2021**, 90, 1061 (review).

PHOTOSWITCHABLE SUPRAMOLECULAR DEVICES BASED ON UNSATURATED AND CROWN COMPOUNDS



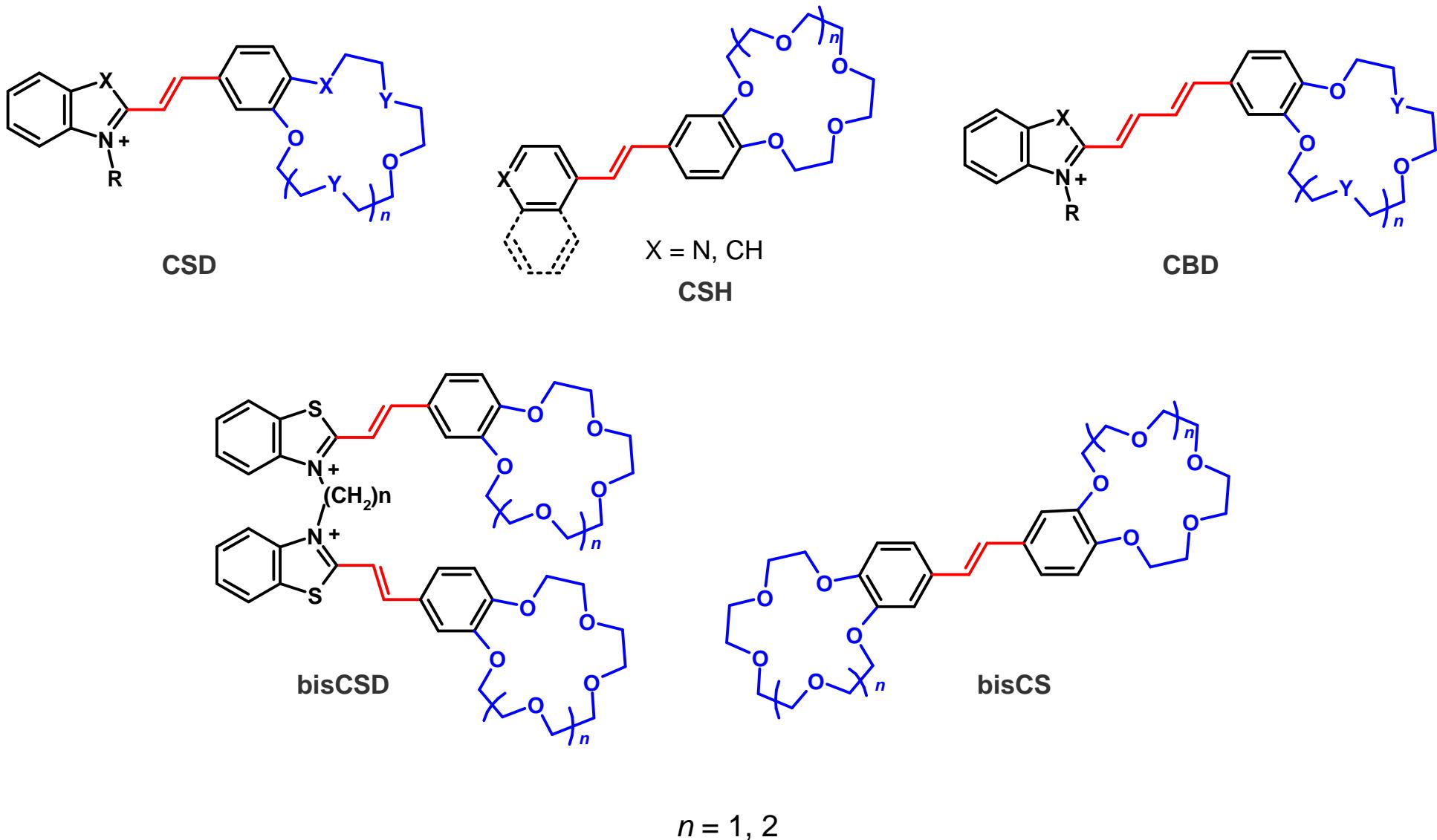
Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1325 (review);

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);

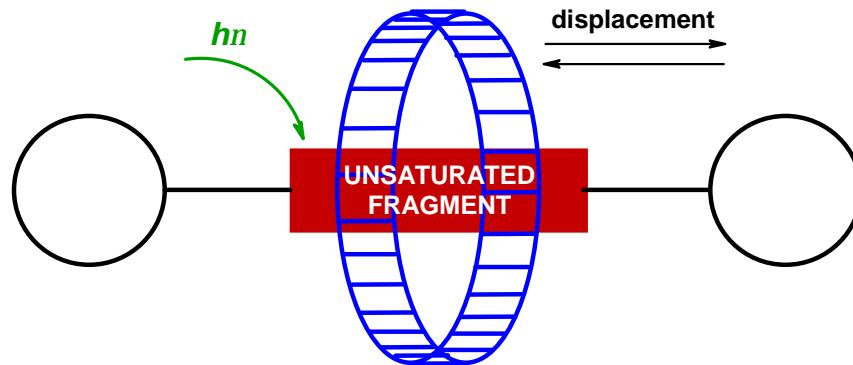
Alfimov M. V., Gromov S. P., Ushakov E. N. in *Russ. Chem. Rev.* **2021**, 90, 1061 (review).

Crown-containing unsaturated compounds

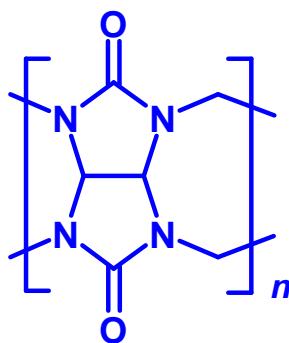


Gromov S. P., Alfimov M. V. *Russ. Chem. Bull.* **1997**, 46, 611 (review);
Gromov S. P. *Russ. Chem. Bull.* **2008**, 57, 1299 (review).

Photocontrolled supramolecular machines based on unsaturated compounds, cucurbiturils and cyclodextrins

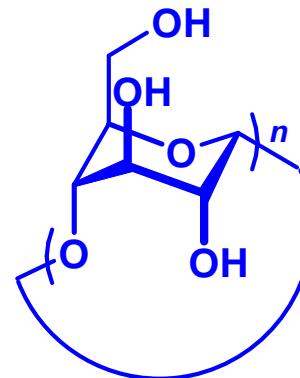


photocontrolled supramolecular machine



cucurbiturils

$n = 6-8$



cyclodextrins

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

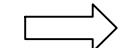
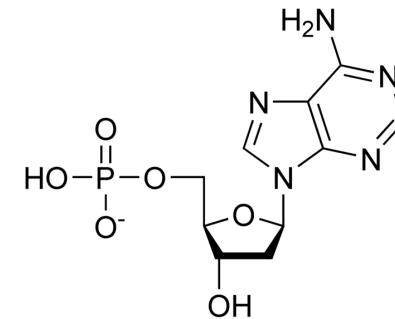
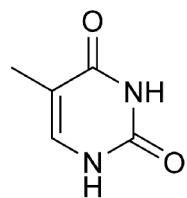
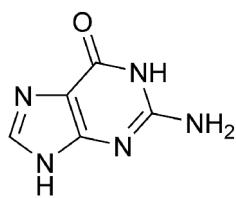
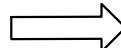
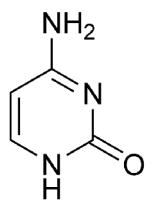
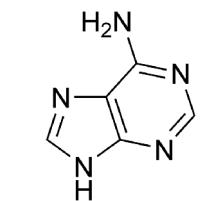
Gromov S. P. *Rev. J. Chem.* **2011**, 1, 1 (review)

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

Alfimov M. V., Gromov S. P., Ushakov E. N. in *Russ. Chem. Rev.* **2021**, 90, 1061 (review).

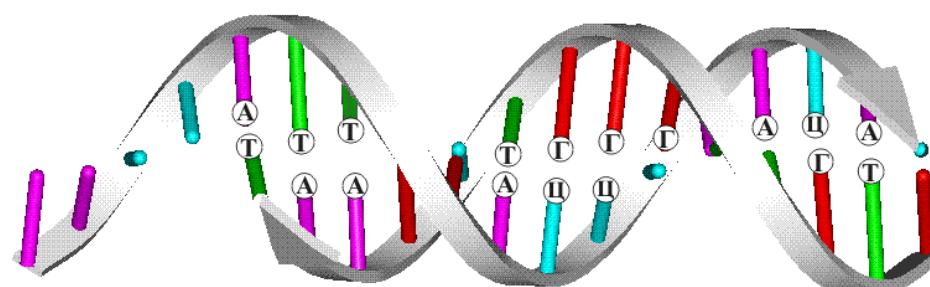
MOLECULAR MECCANO IN LIVING NATURE

Nucleic acids

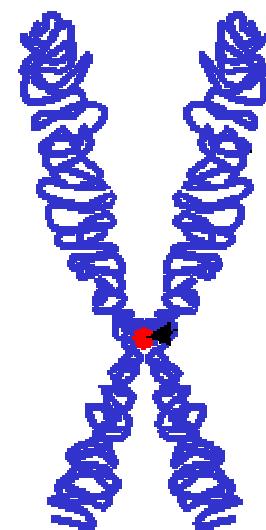
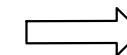


basic nitrogens

nucleotides



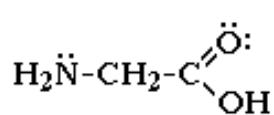
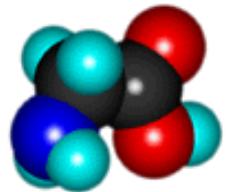
nucleic acids



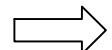
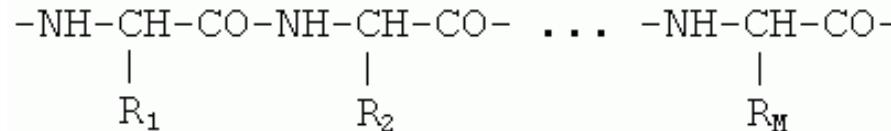
chromosomes

MOLECULAR MECCANO IN LIVING NATURE

Proteins

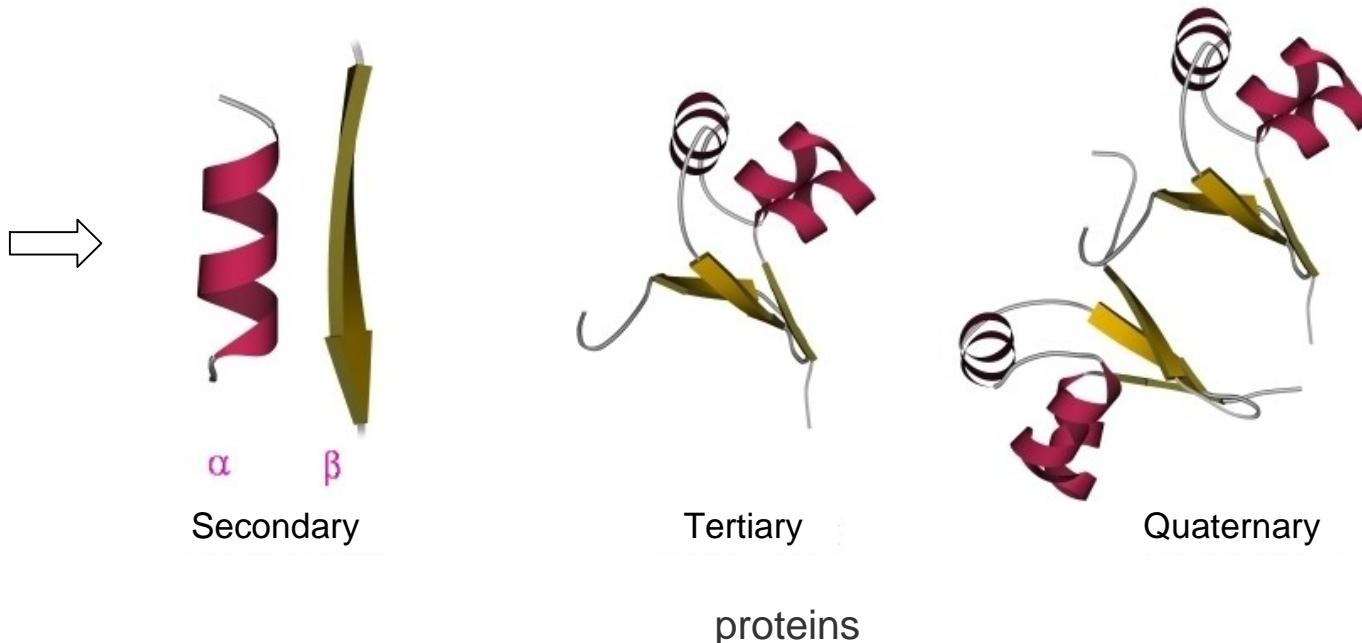


amino acids

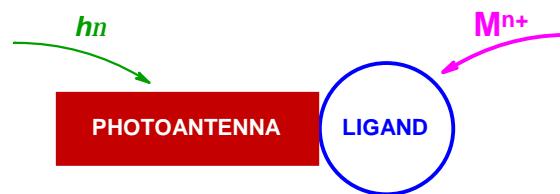


polypeptides

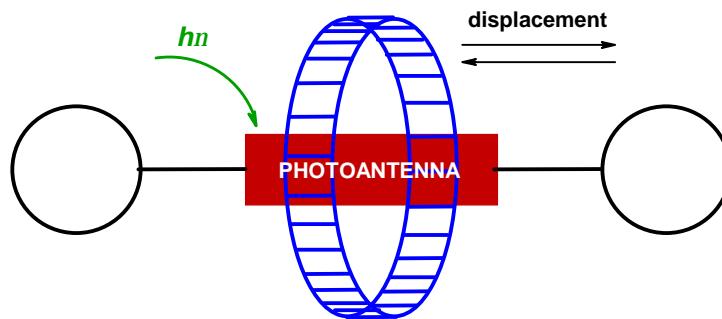
Primary ... - *Gly-Val-Tyr-Gln-Ser-Ala-Ile-Asn-Lys-Ala-* ...



SUPRAMOLECULAR MECCANO OF PHOTOACTIVE SUPRAMOLECULAR DEVICES AND MACHINES IN NANOTECHNOLOGY

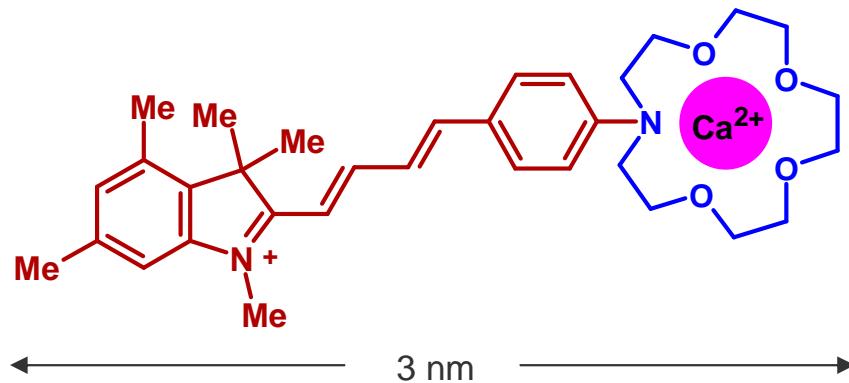


photoswitchable supramolecular device

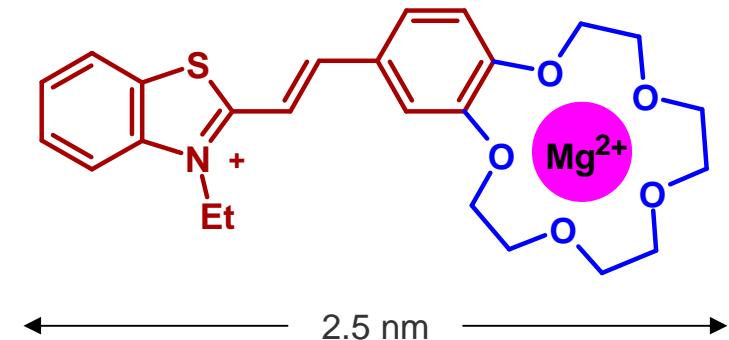


photocontrolled supramolecular machine

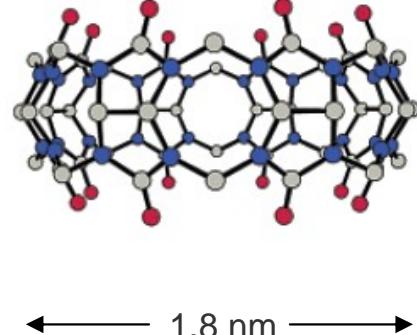
COMPONENT SIZES IN PHOTOACTIVE SUPRAMOLECULAR DEVICES AND MACHINES



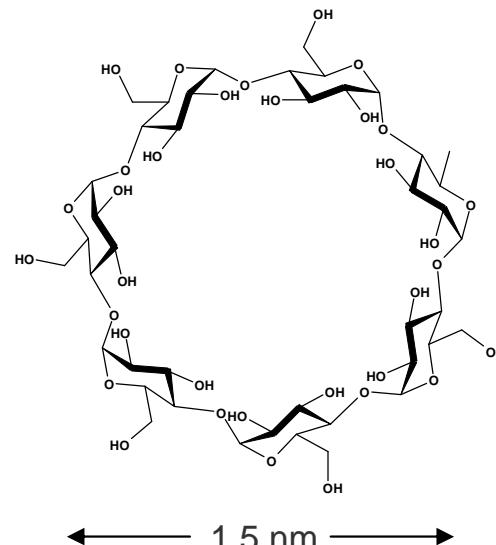
Complex of butadienyl dye



Complex of styryl dye



Cucurbit[8]uril

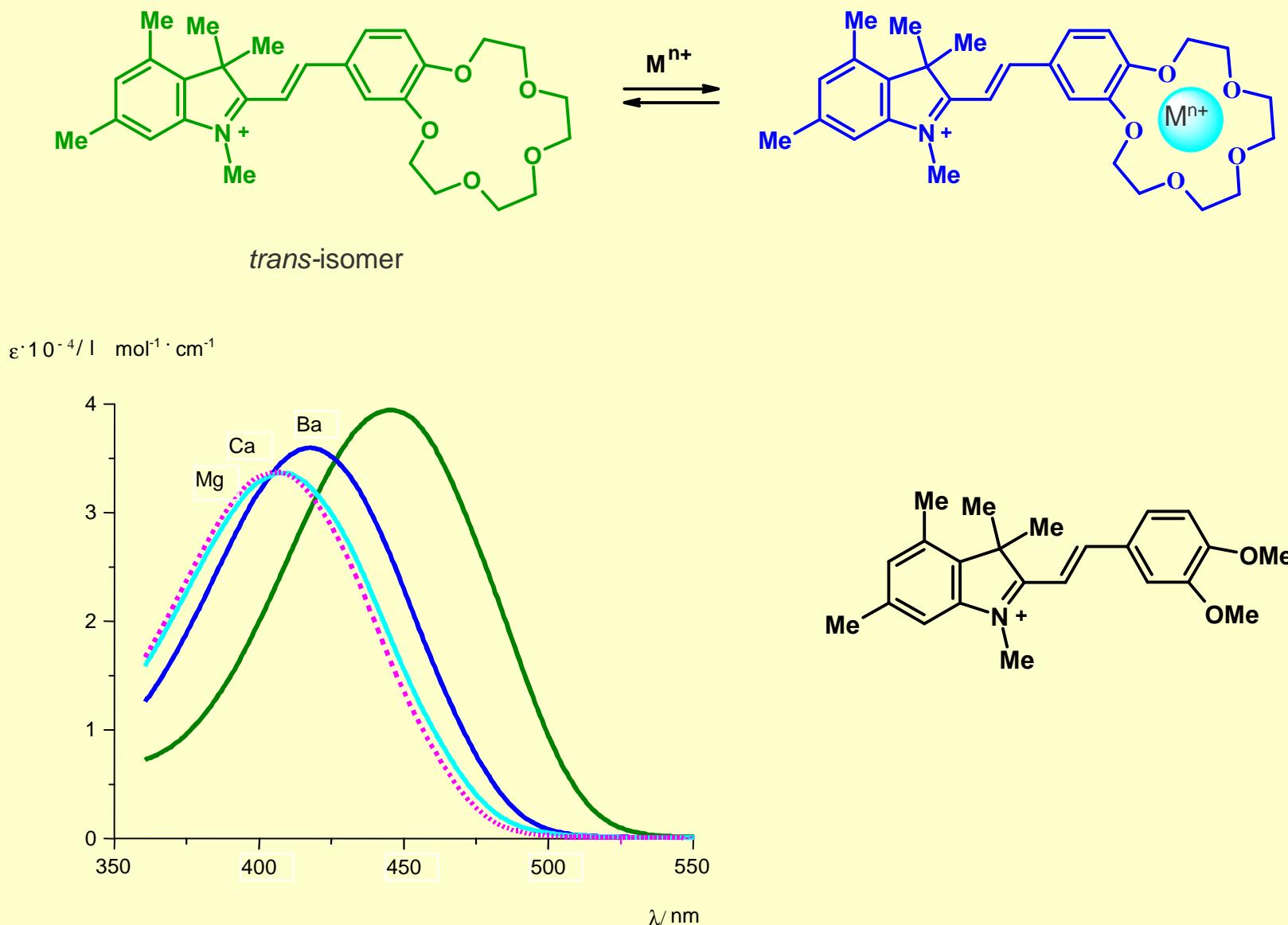


β -Cyclodextrin

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

Part I

Complex formation

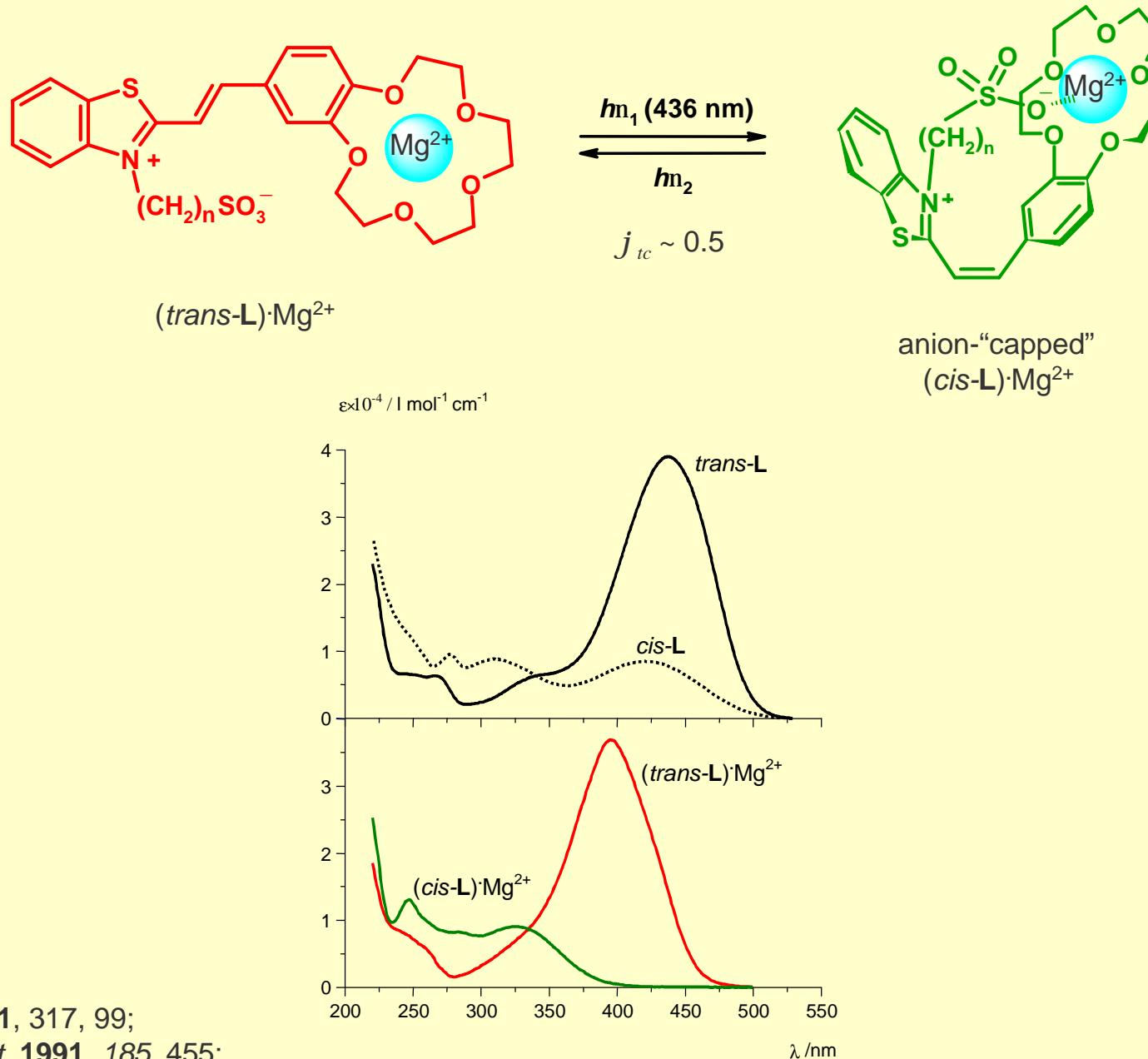


Dokl. Chem. 1990, 314, 279;

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

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

Photoswitchable supramolecular devices



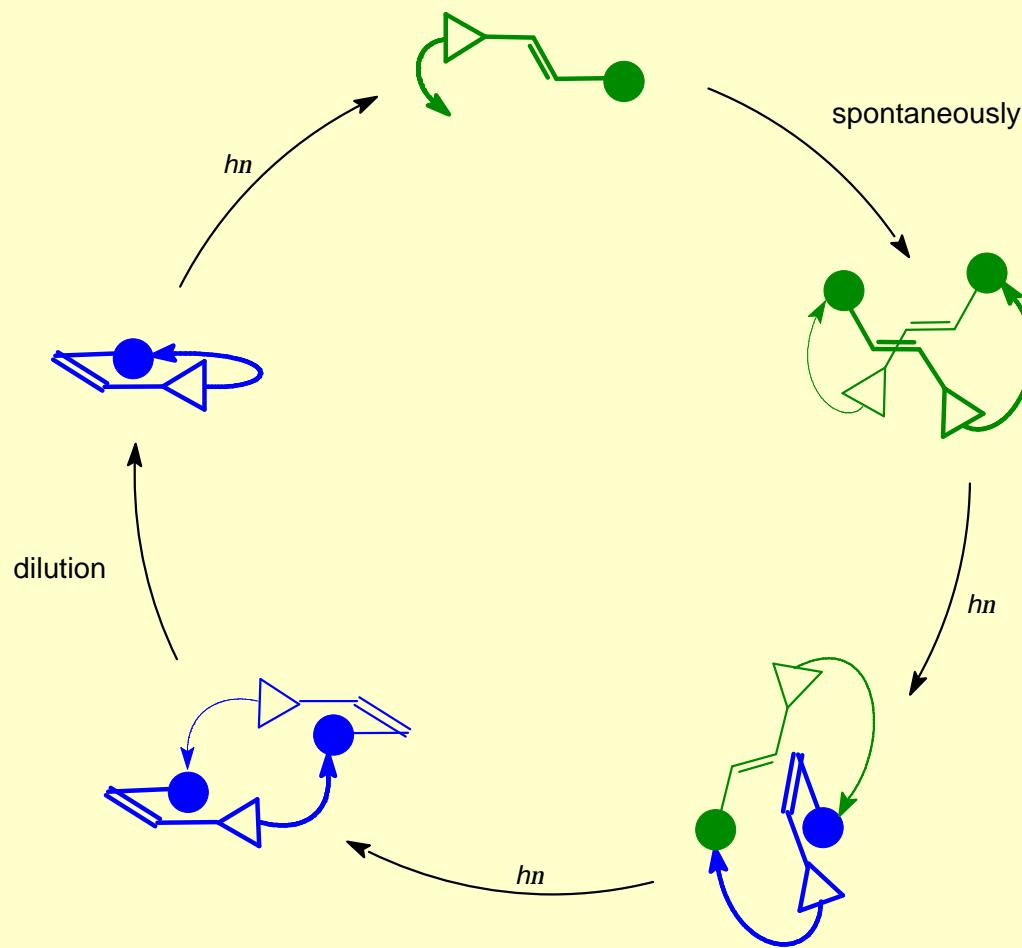
Dokl. Chem. 1991, 317, 99;

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

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

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

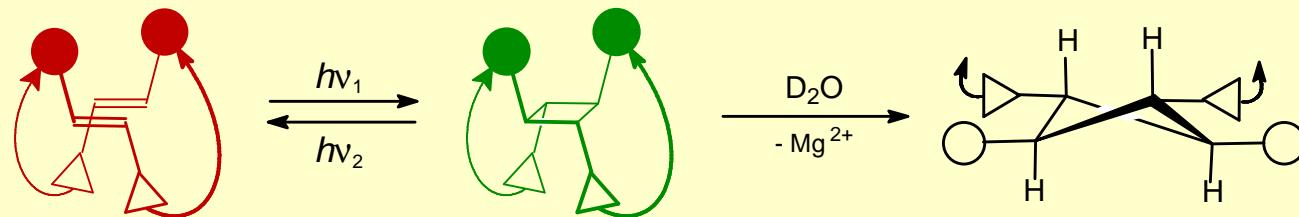
Photocycle of crown-containing styryl dyes



● - is the benzocrown compounds moiety with M²⁺ (Mg, Ca, Hg, Pb);

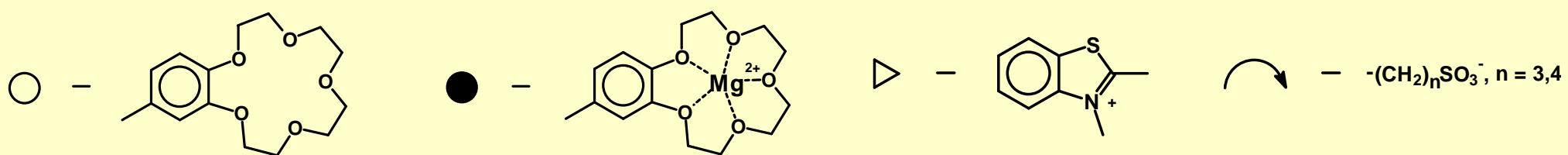
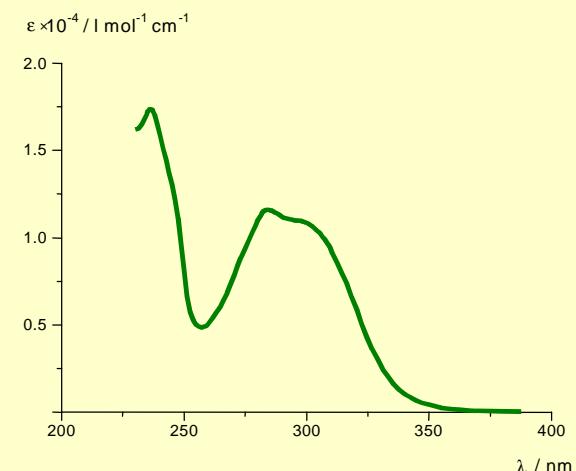
▷ - is the benzothiazolium moiety; ↗ - $(CH_2)_nSO_3^-$

Photoswitchable supramolecular devices



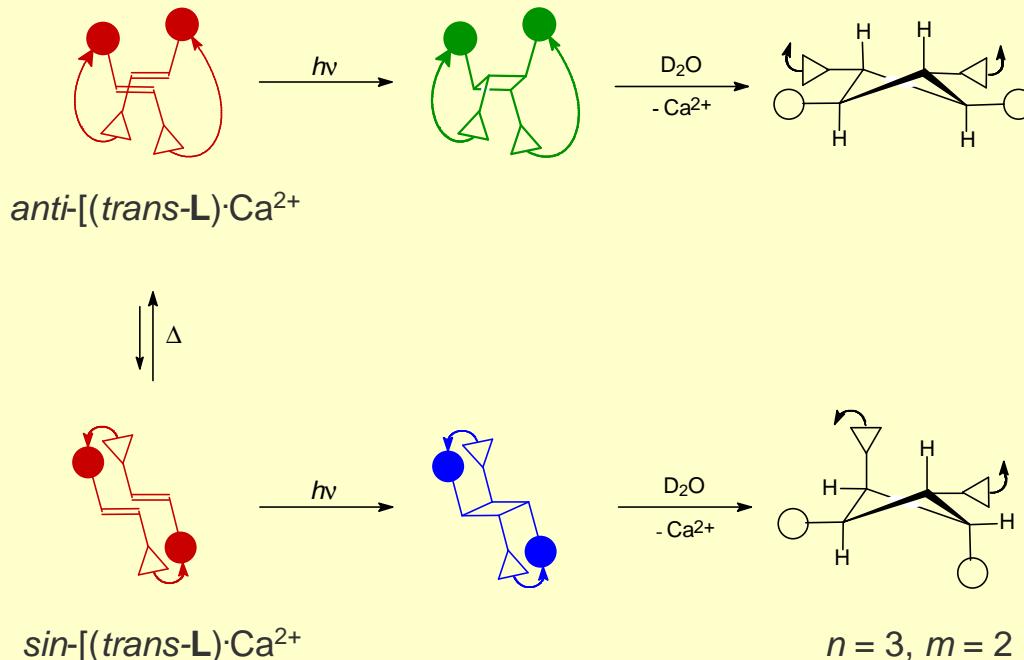
[2 + 2] Photocycloaddition of CSD

$C_L, / \text{mol} \cdot \text{l}^{-1}$	$5 \cdot 10^{-6}$	$2.4 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-4}$	$2 \cdot 10^{-3}$
F	0.0022	0.0043	0.0052	0.0051	0.0055

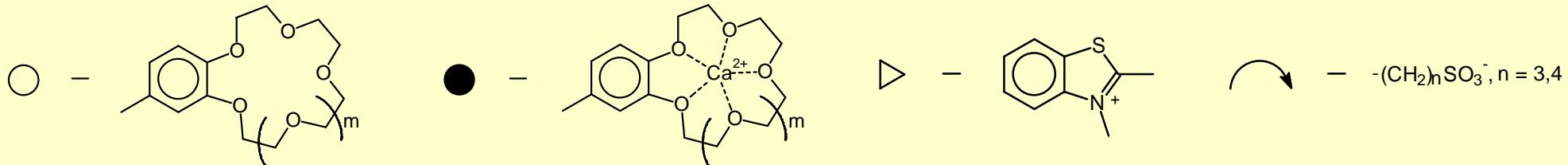


- J. Am. Chem. Soc.* **1992**, *114*, 6381;
Russ. Chem. Bull. **1993**, *42*, 1385;
J. Chem. Soc., Perkin Trans. 2 **1999**, 601;
J. Org. Chem. **2003**, *68*, 6115.

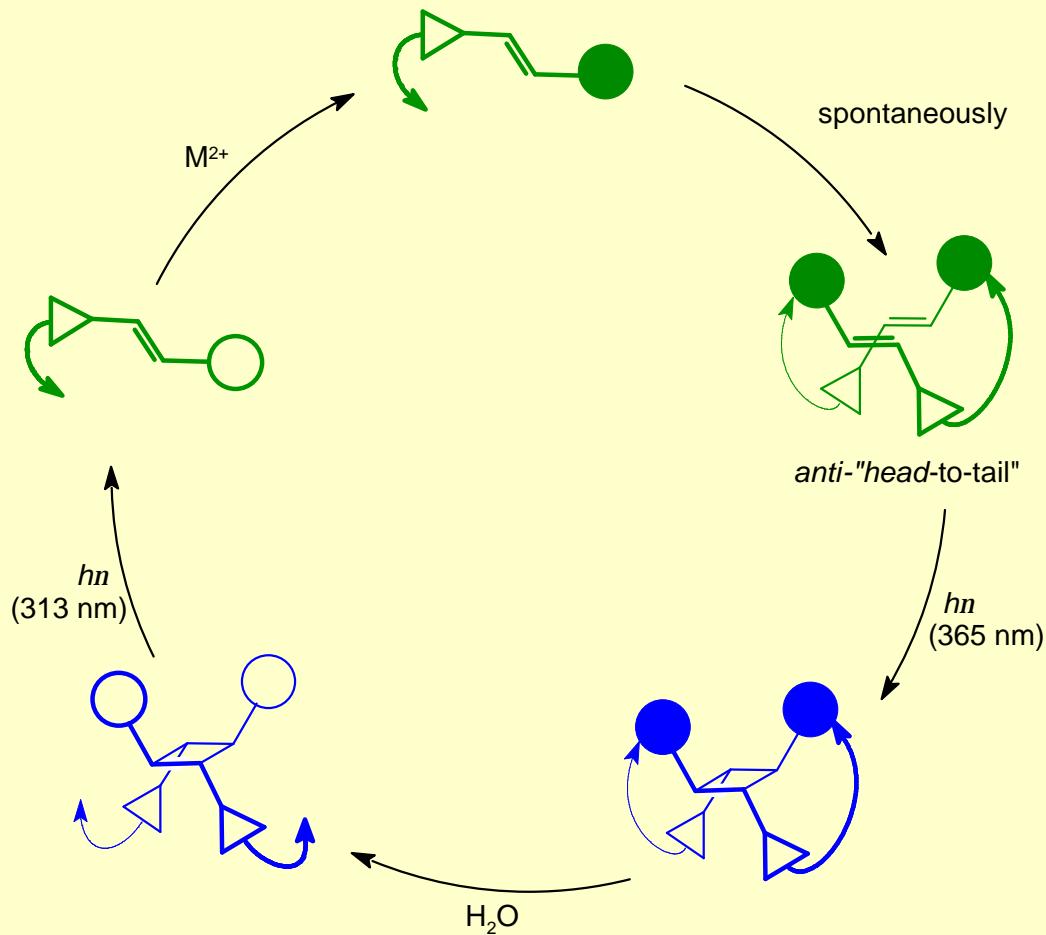
[2 + 2]-Photocycloaddition of CSD



CSD	$n = 3$ $m = 1$	$n = 4$ $m = 1$	$n = 3$ $m = 2$	$n = 4$ $m = 2$
F	0.001	0.01	0.0004	0.06



Photocycle of crown-containing styryl dyes



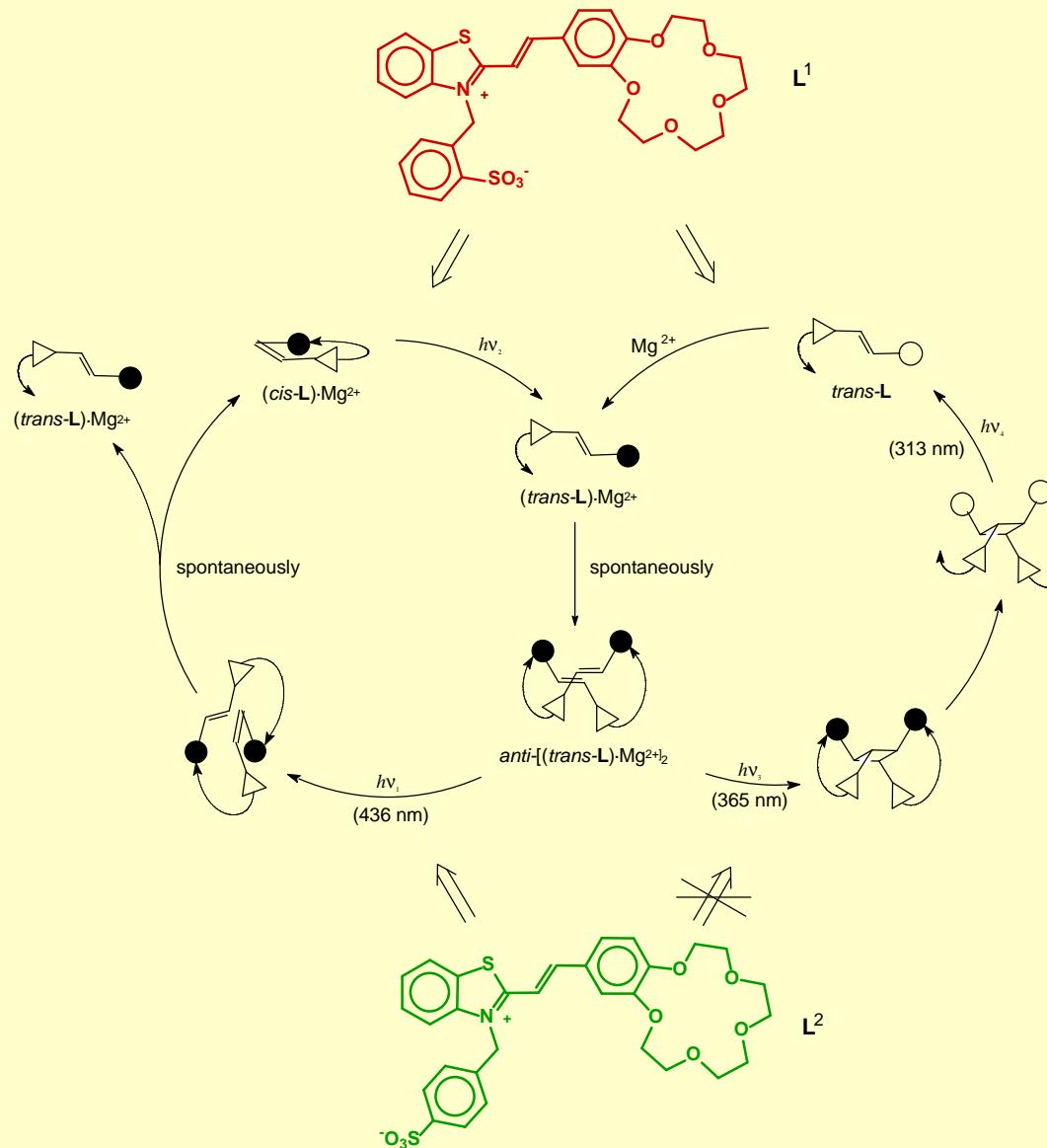
○ is the benzocrown compounds moiety;

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

▷ is the benzothiazolium moiety;

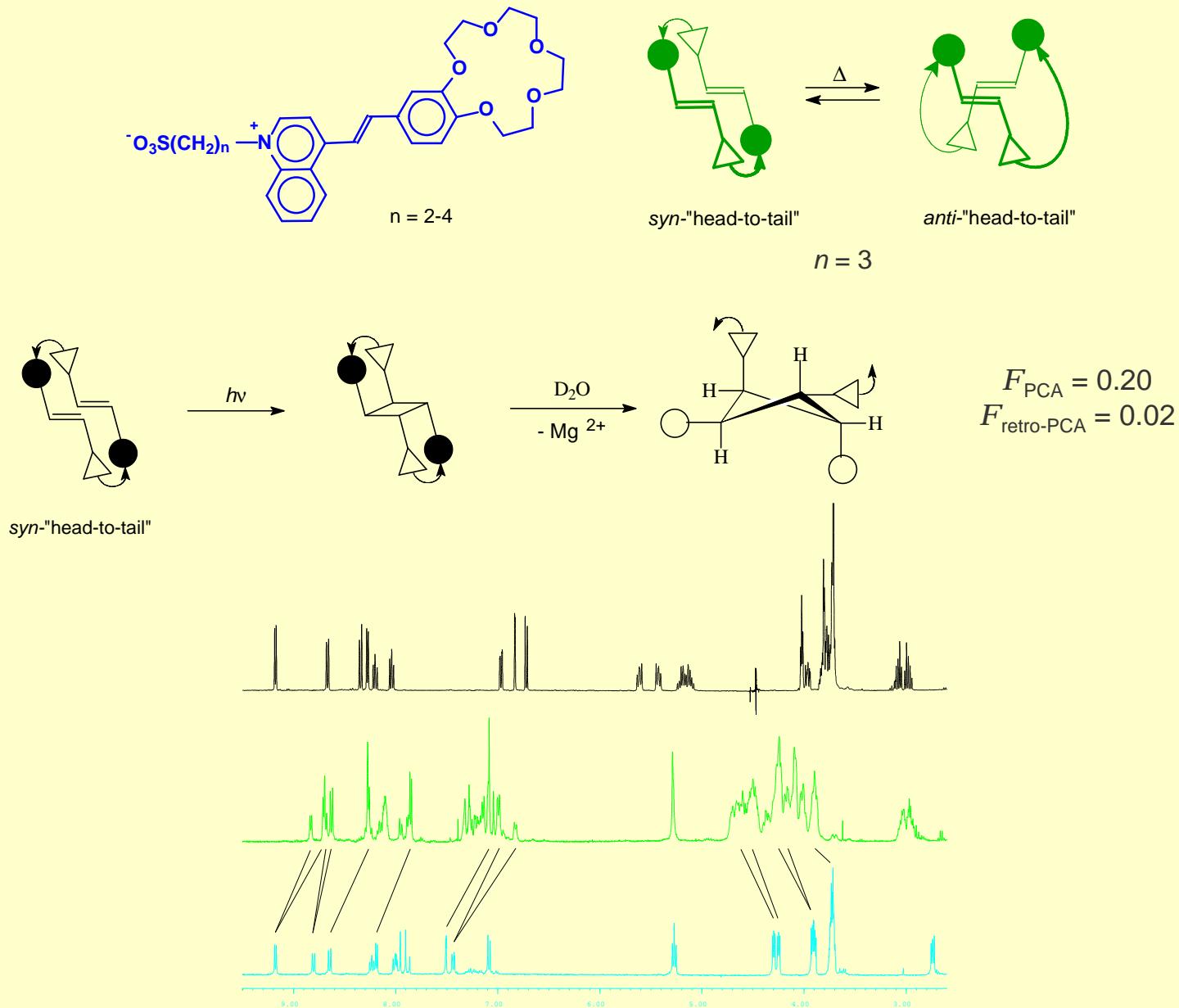
↷ - $(CH_2)_nSO_3^-$

[2 + 2] PHOTOCYCLOADDITION OF MULTIPHOTOCHROMIC CSD

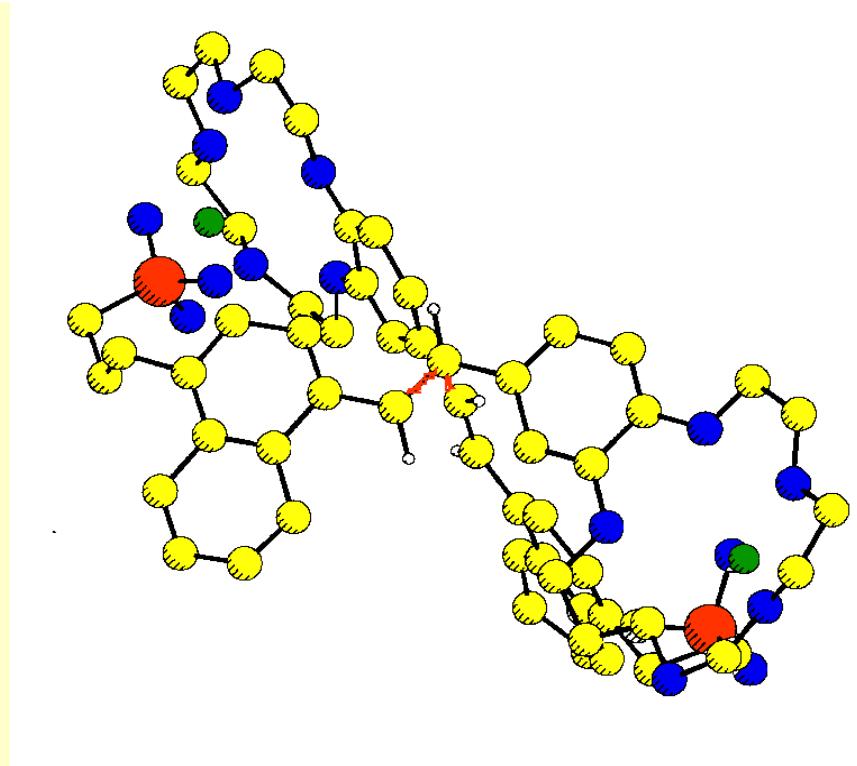
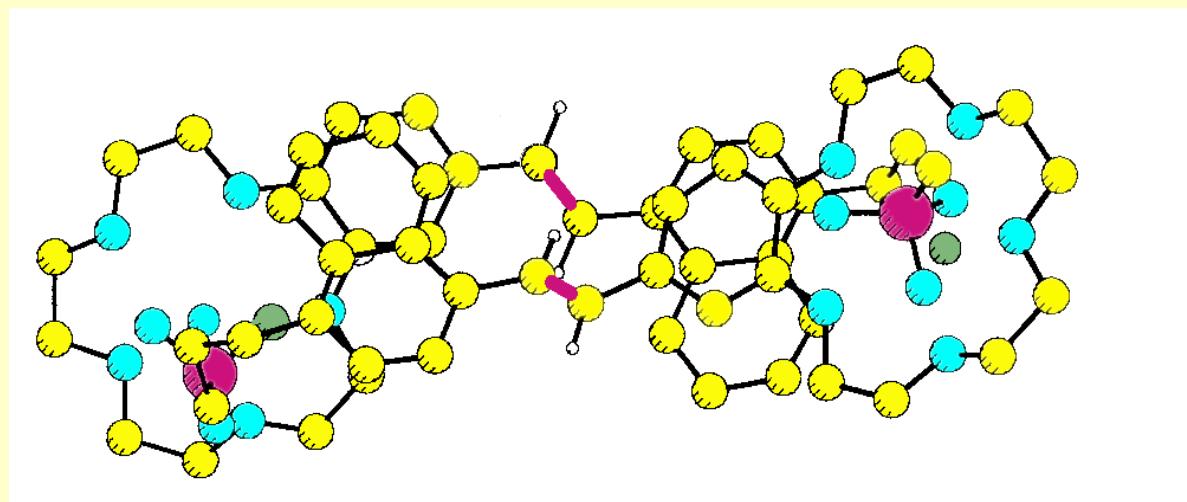


CSD	R, A°	F	$\log K_1$
L^1	6.7	0.018	7.3
L^2	9.9	---	10.0

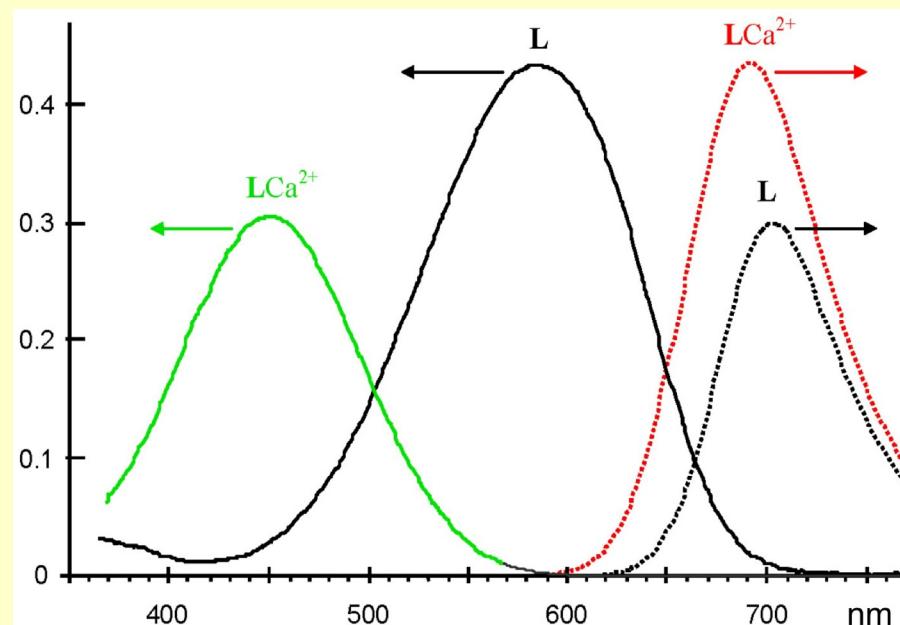
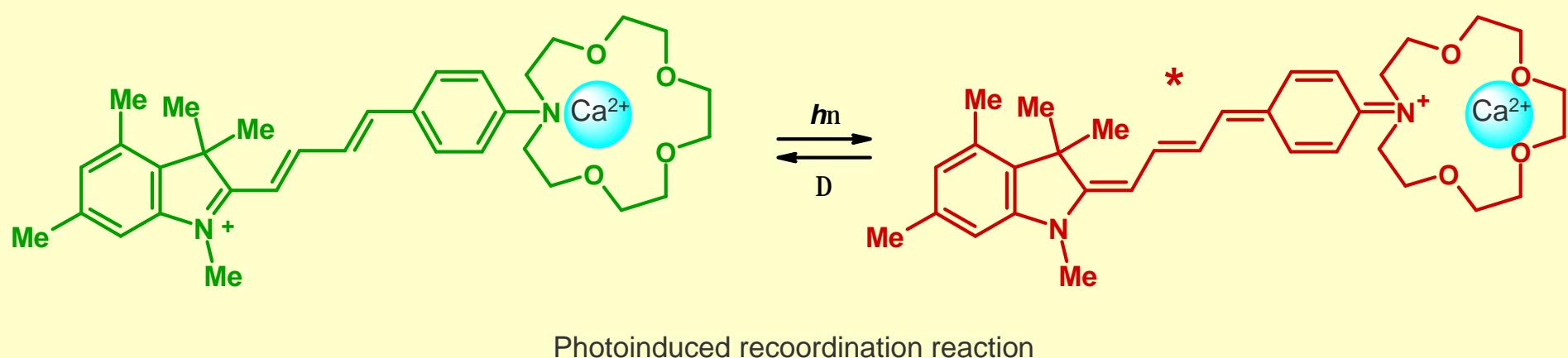
¹H NMR SPECTRA



DIMERIC COMPLEXES



Photoswitchable supramolecular device



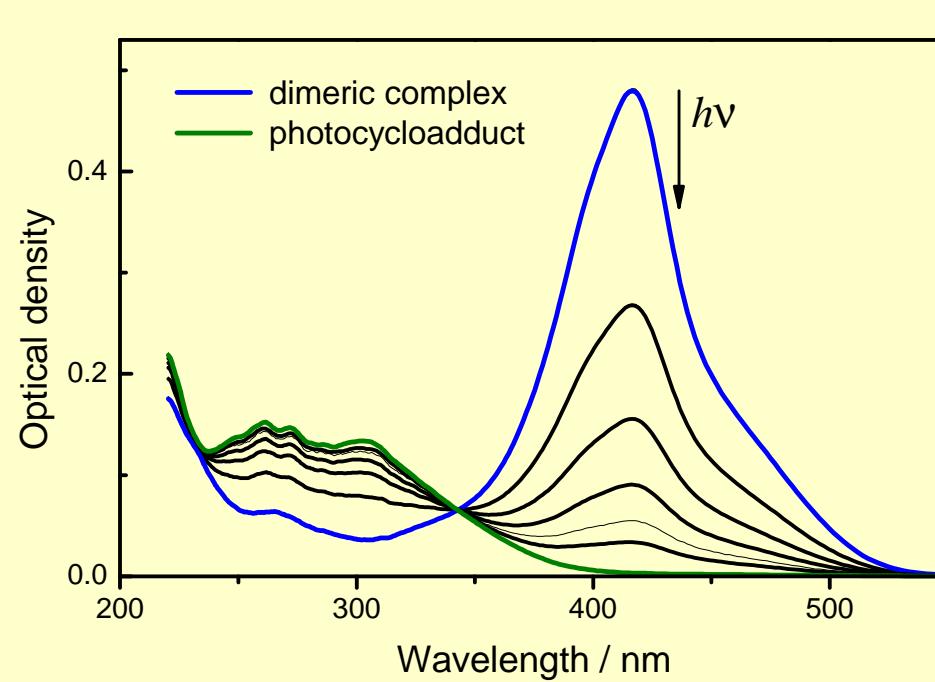
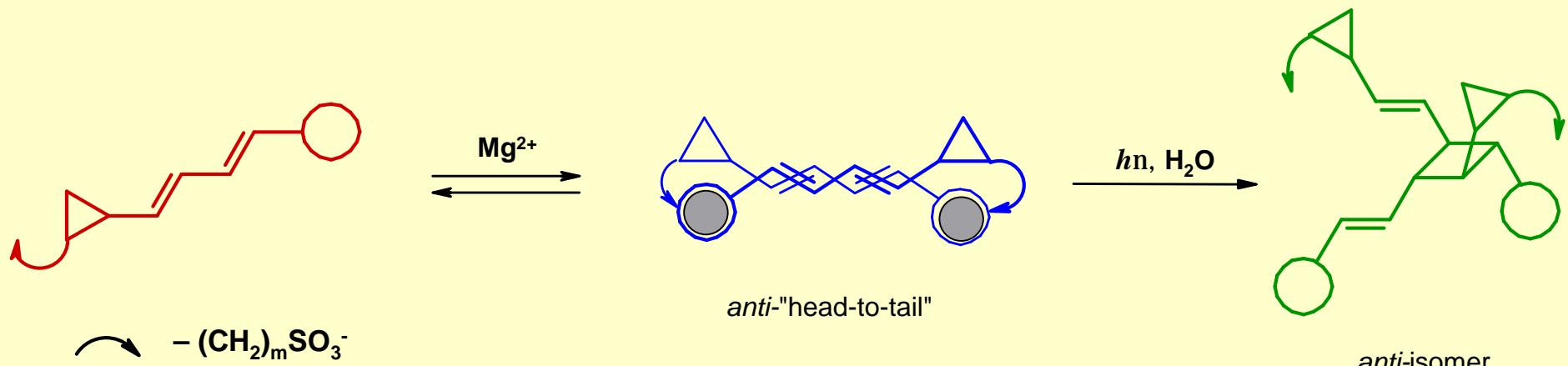
J. Fluor. **1999**, *9*, 33;

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

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

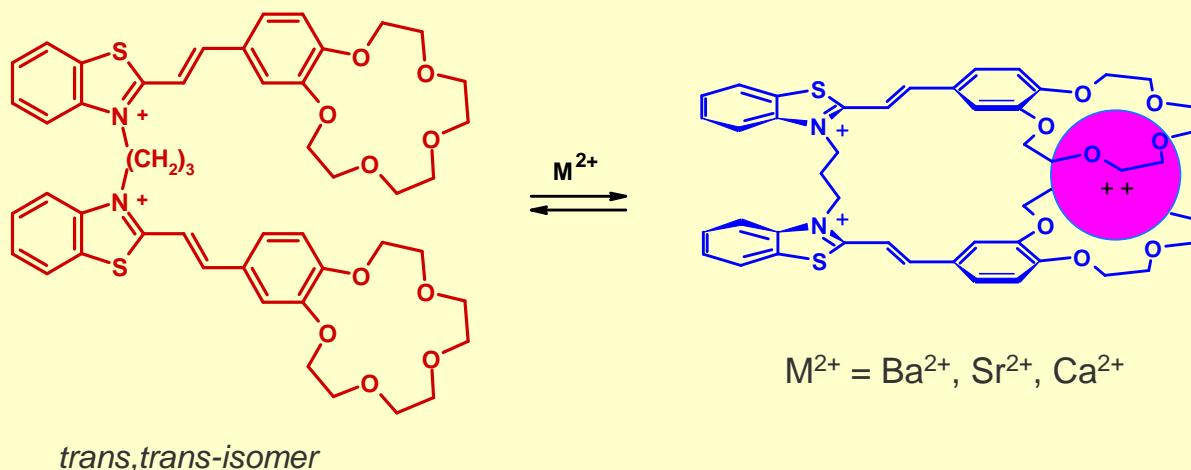
Photochem. Photobio. Sci. **2011**, *10*, 15.

[2 + 2] PHOTOCYCLOADDITION OF CBD

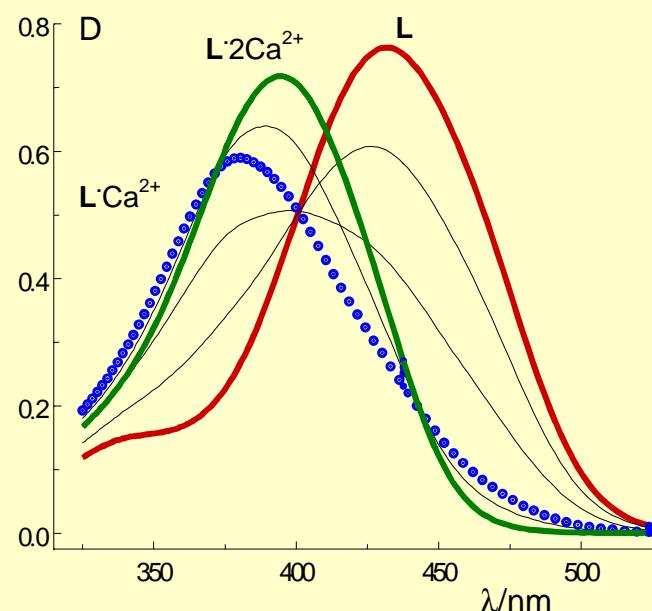


Helv. Chim. Acta 2002, 85, 60;
Photochem. Photobio. Sci., 2011, 10, 15.

Self-assembly of sandwich complexes



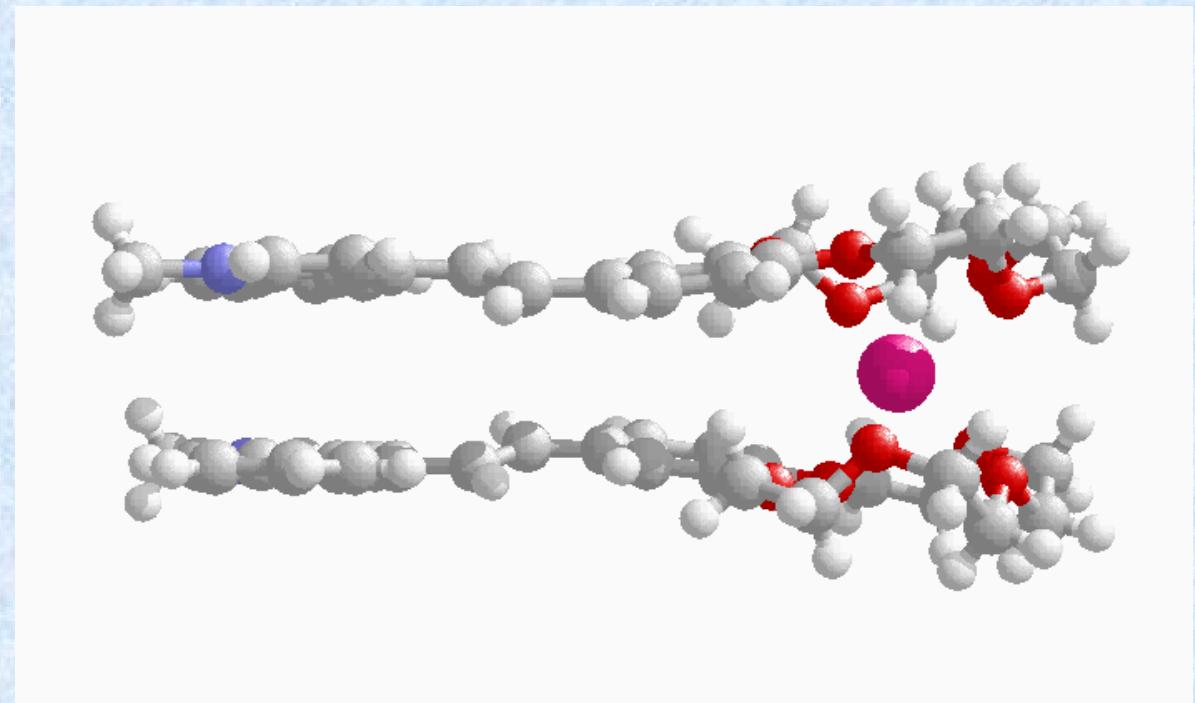
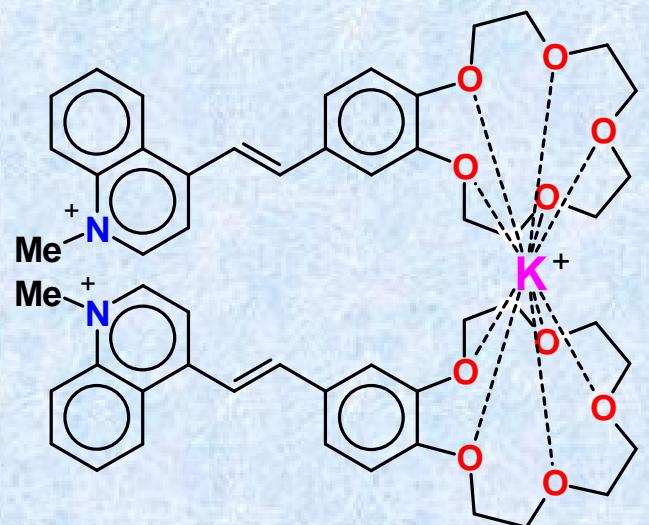
$M^{2+} = Ba^{2+}, Sr^{2+}, Ca^{2+}$



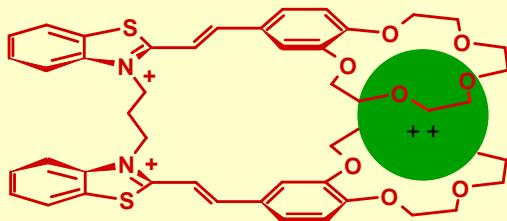
Complex	$\log K_1$	λ_{LM} , nm	$\lambda_L - \lambda_{LM}$, nm
$L \cdot Ba^{2+}$	8.0	390	42
Monomer · Ba ²⁺	4.39	402	28

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

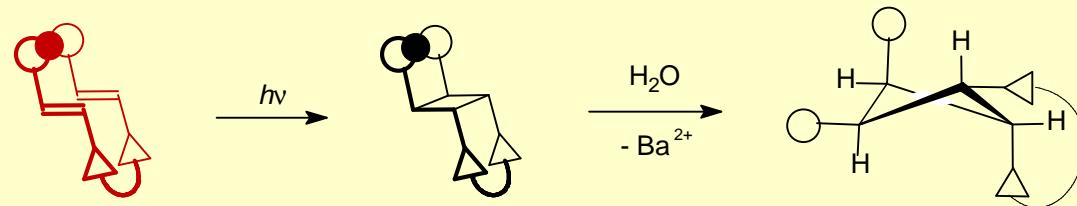
X-ray structure determination of sandwich complex



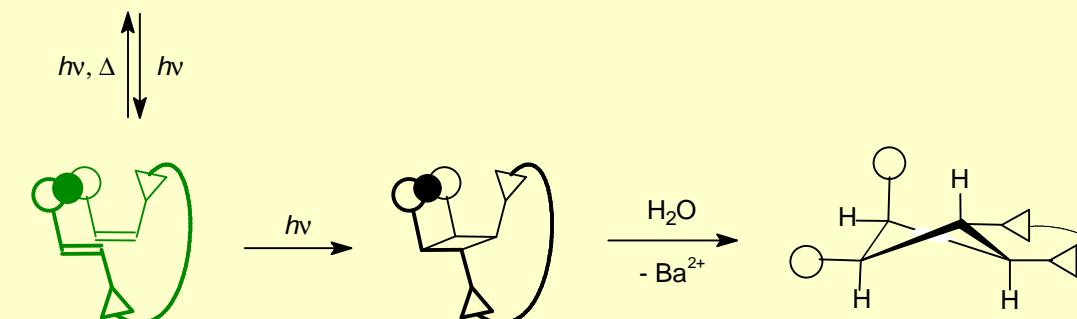
Intramolecular [2 + 2] photocycloaddition of bisCSD



(*trans,trans*-L)·Ba²⁺



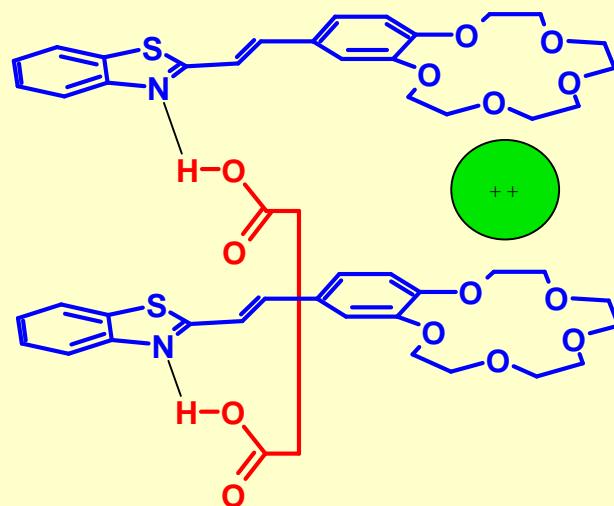
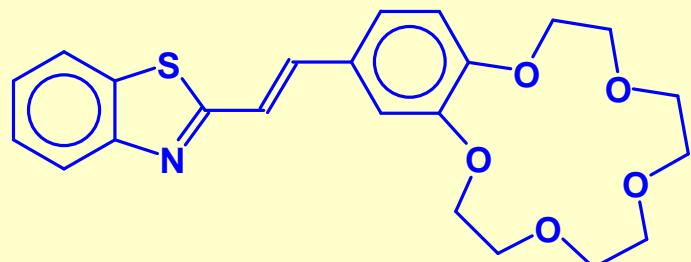
(*trans,trans*-L)·Ba²⁺



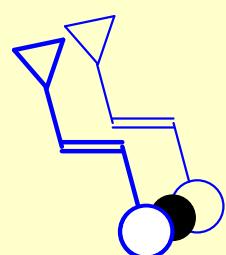
(*trans,cis*-L)·Ba²⁺

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

[2 + 2]-Photocycloaddition of hetarylphenylethenes



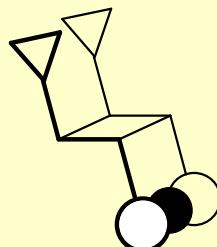
$(\text{CH}_2)_n(\text{COOH})_2; n = 1-4$



$\xrightarrow{h\nu}$
 $F_{\text{PCA}} = 0.13$

syn-"head-to-head"

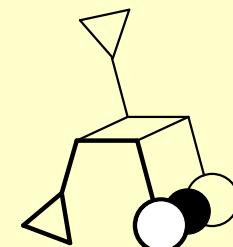
$\log K_{11} = 4.74$



syn-isomer

$\log K_{11} = 7.69$

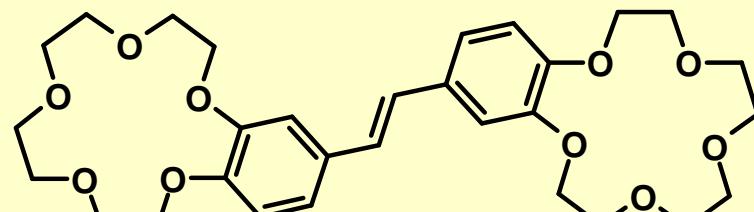
+



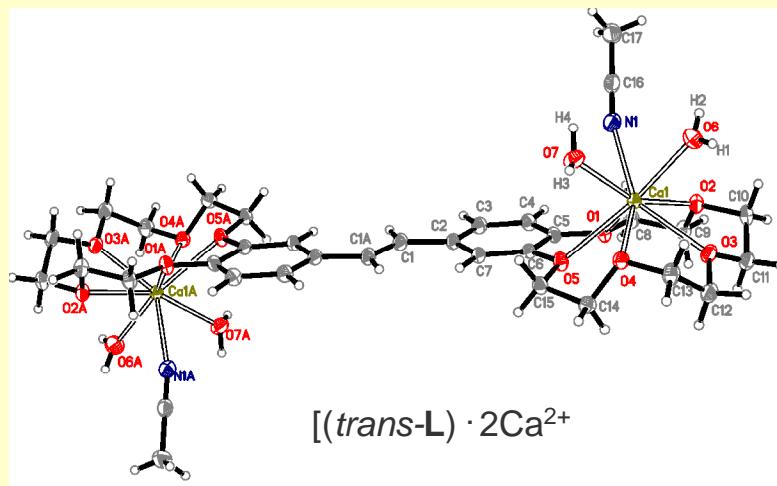
$\log K_{11} = 7.21$

● - $\text{Ba}^{2+}, \text{Sr}^{2+}$

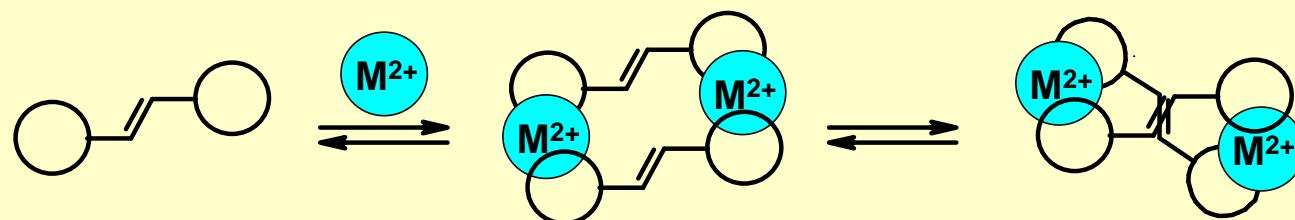
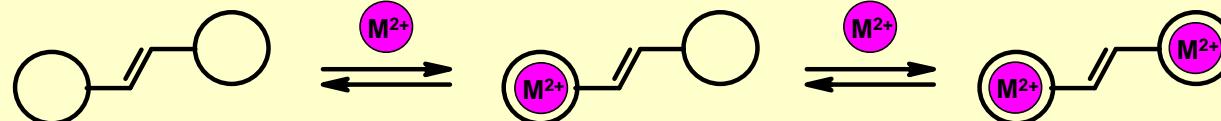
Complex formation of bisCS



trans-L



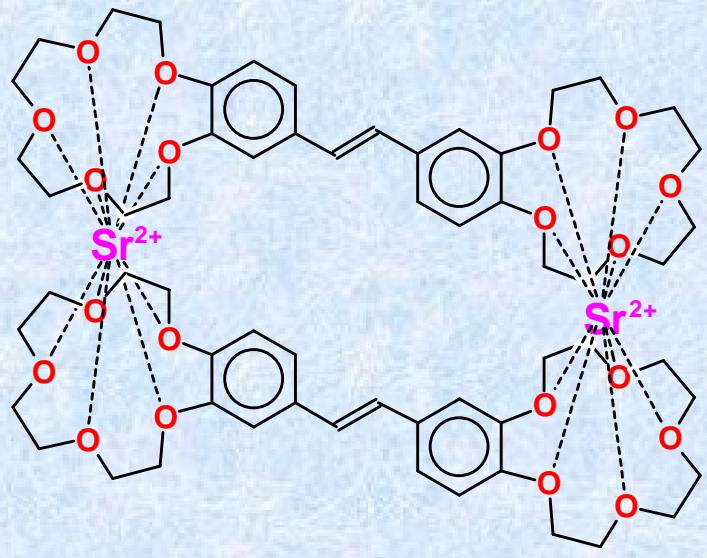
$[(trans\text{-}L) \cdot 2\text{Ca}^{2+}]$



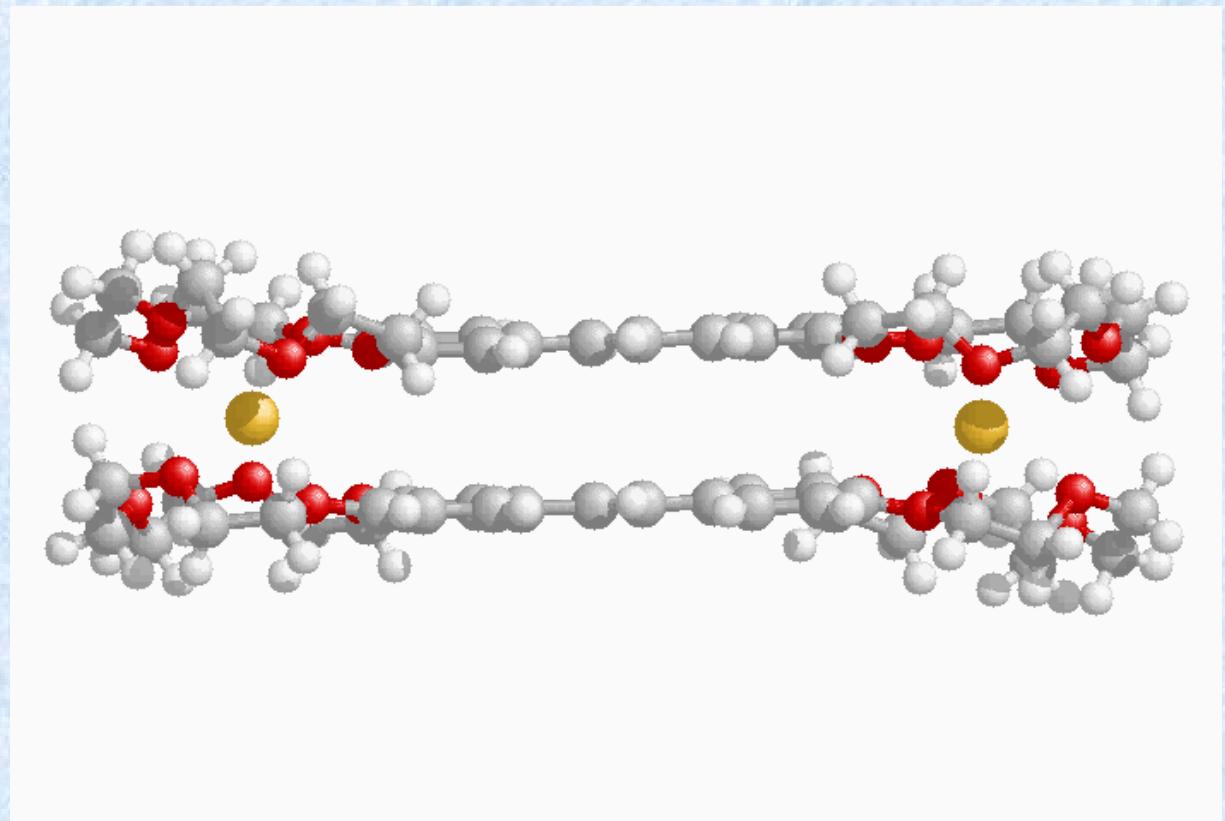
M^{2+} = $\text{Mg}^{2+}, \text{Ca}^{2+}$

M^{2+} = $\text{Sr}^{2+}, \text{Ba}^{2+}$

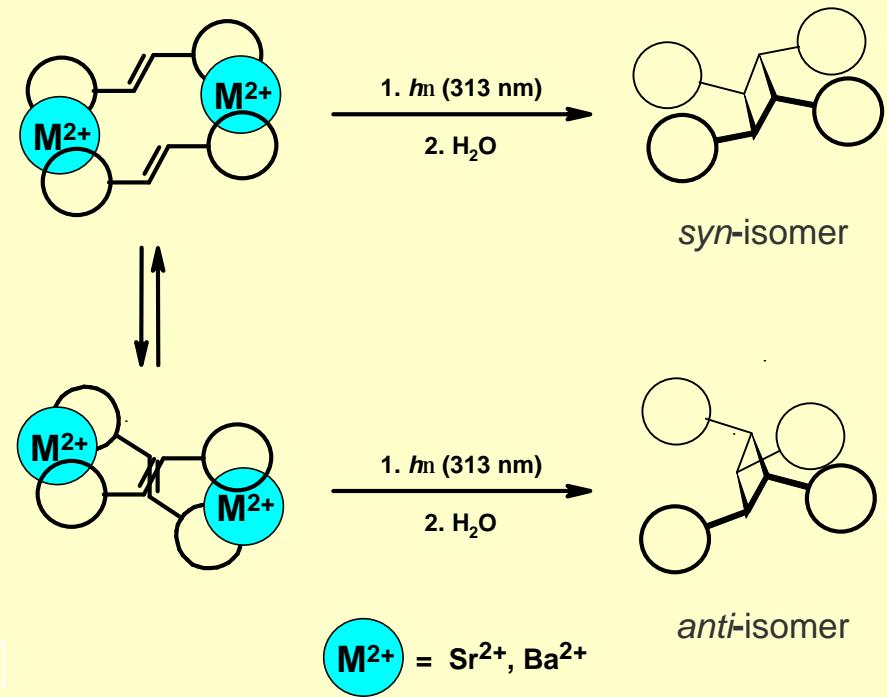
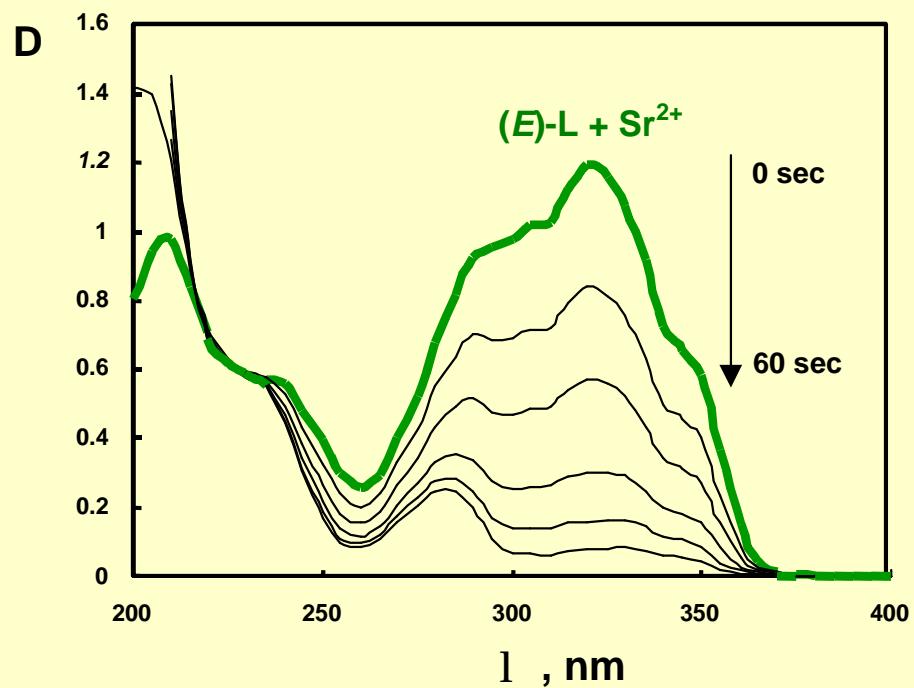
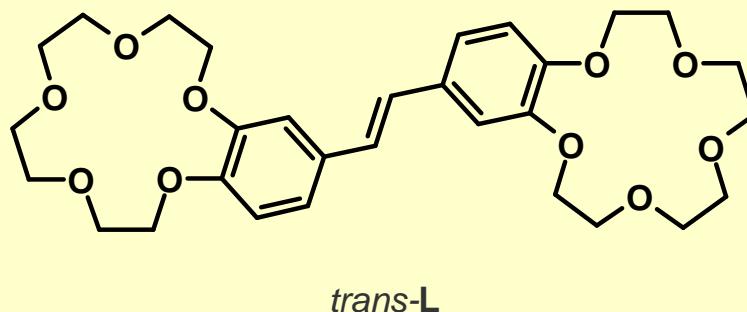
X-ray structure determination of double sandwich complex



2(*trans*-L) · 2Sr²⁺



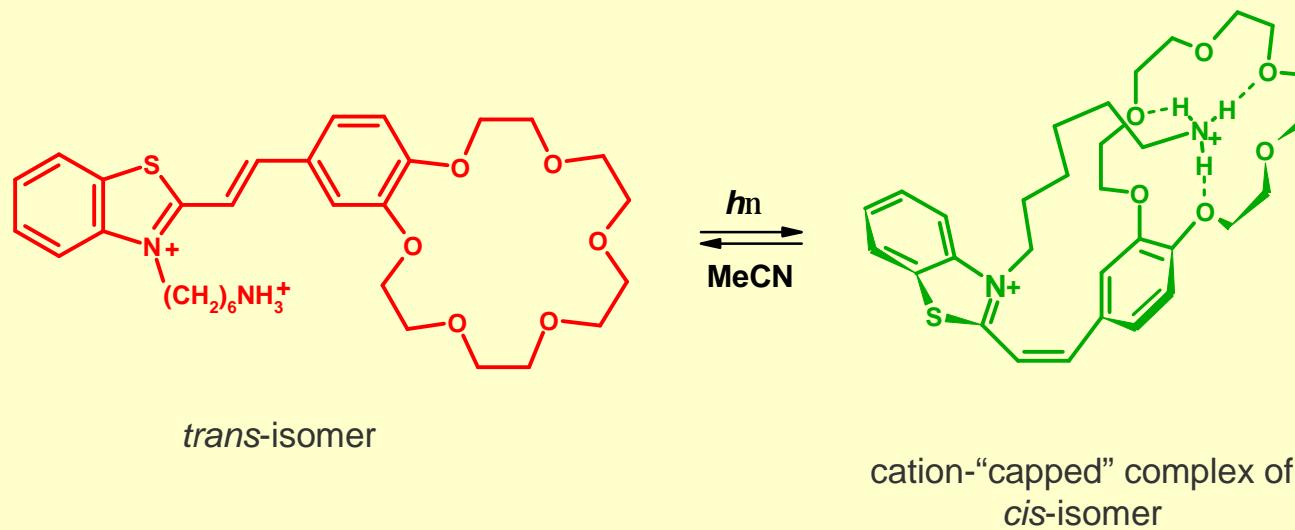
[2 + 2] Photocycloaddition of bisCS



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

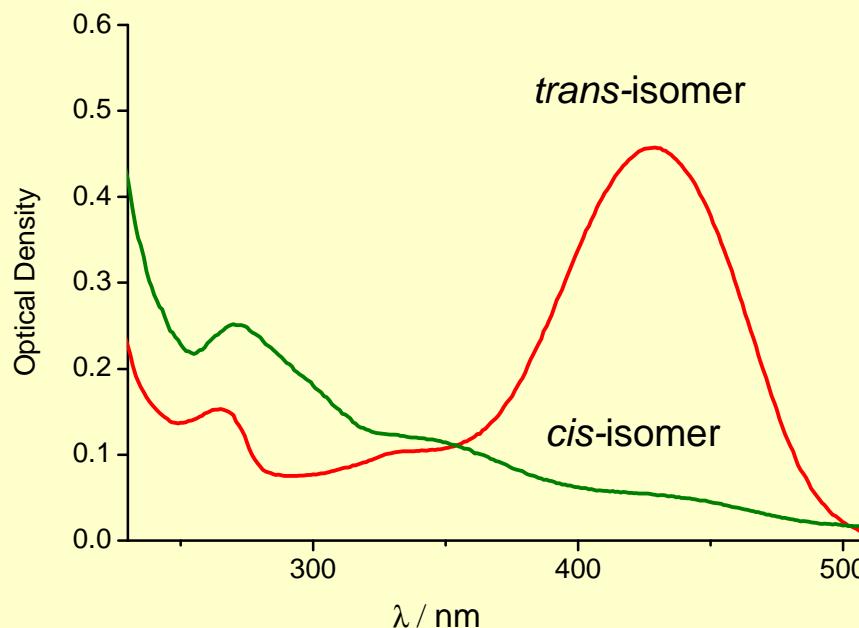
Part II

Intramolecular complexation of *cis*-isomers

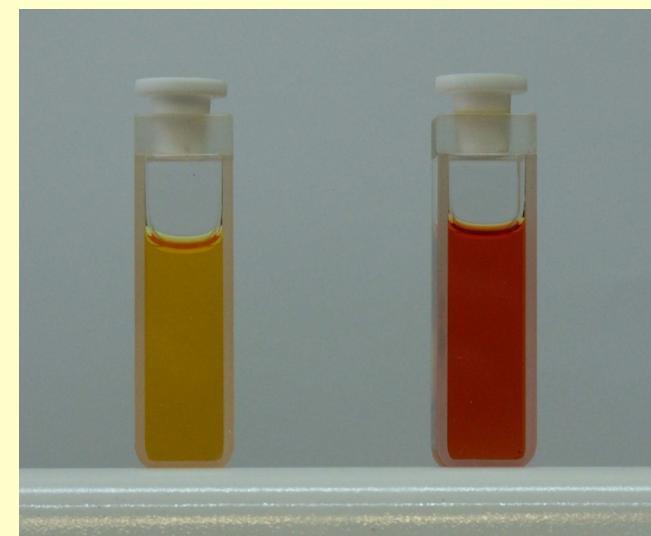
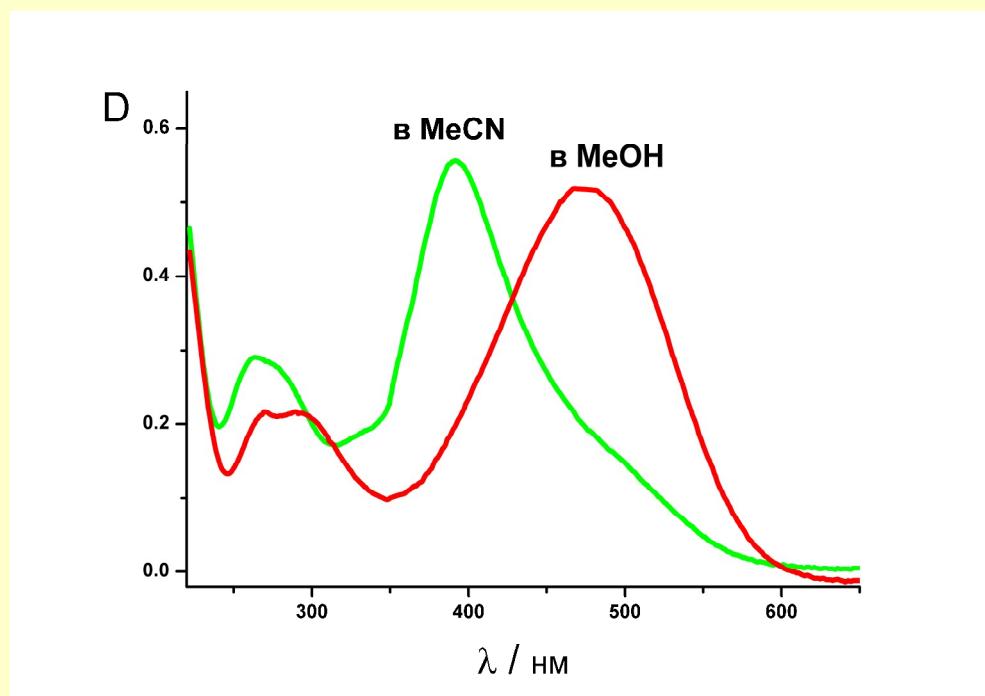
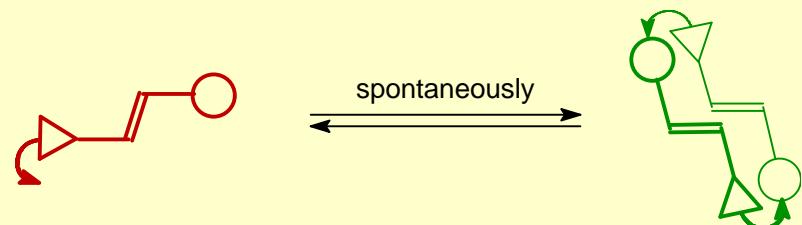
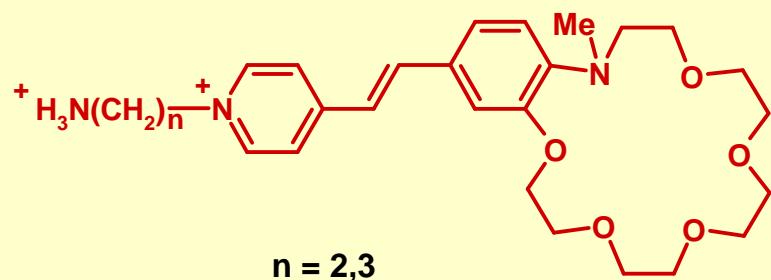


trans-isomer

cation-“capped” complex of
cis-isomer

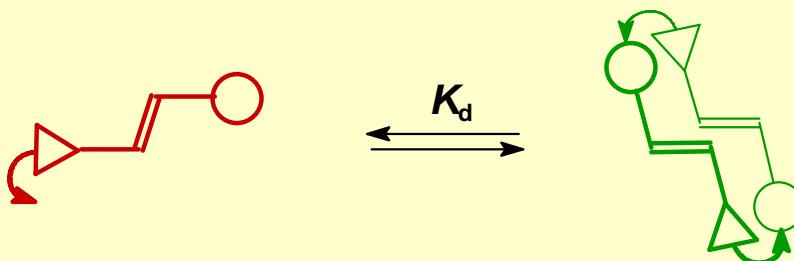


Dimerization of CSD



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

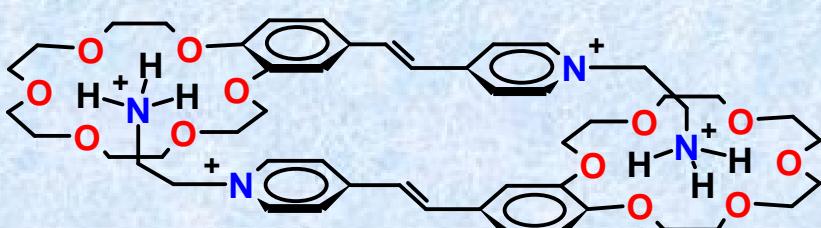
DIMERIZATION



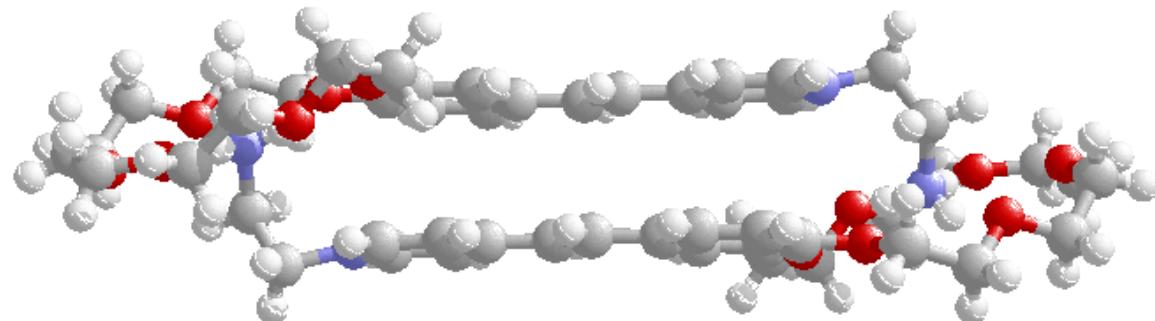
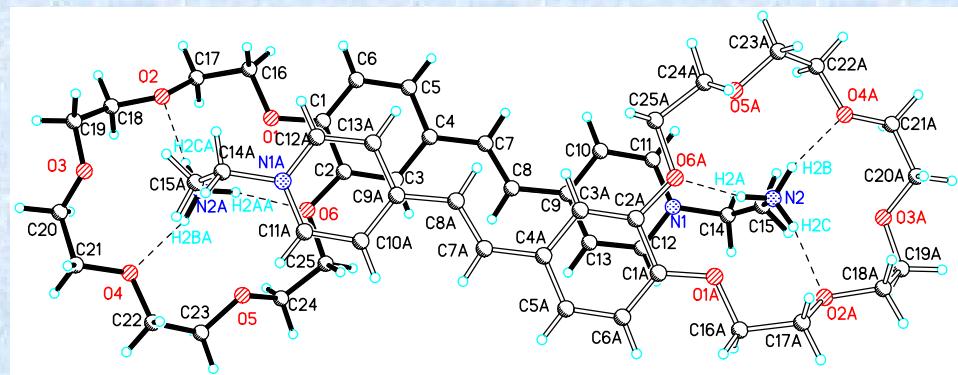
$\log K_d$	$\log K_d$
8.03	5.87
7.90	3.61
7.12	2.44
in CD_3CN	

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

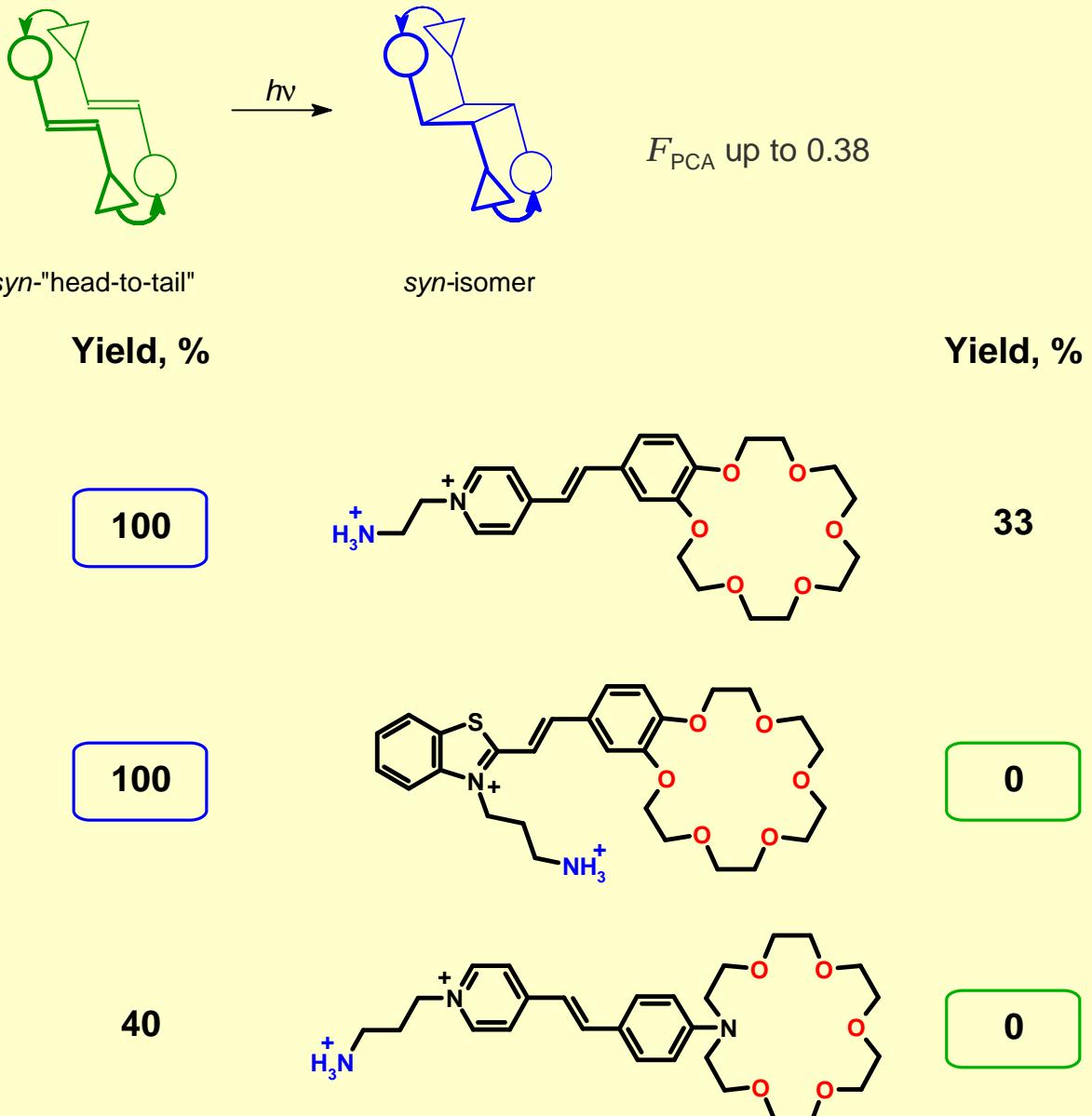
X-ray structure determination of dimeric complex



syn-'head-to-tail' dimeric complex

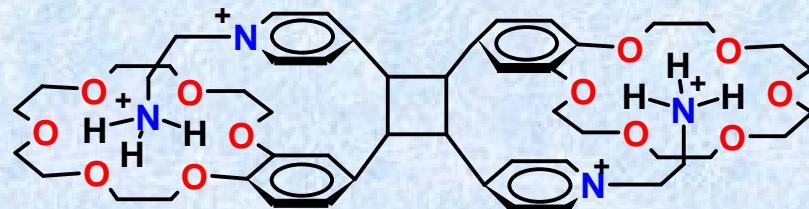


[2 + 2] Photocycloaddition of CSD

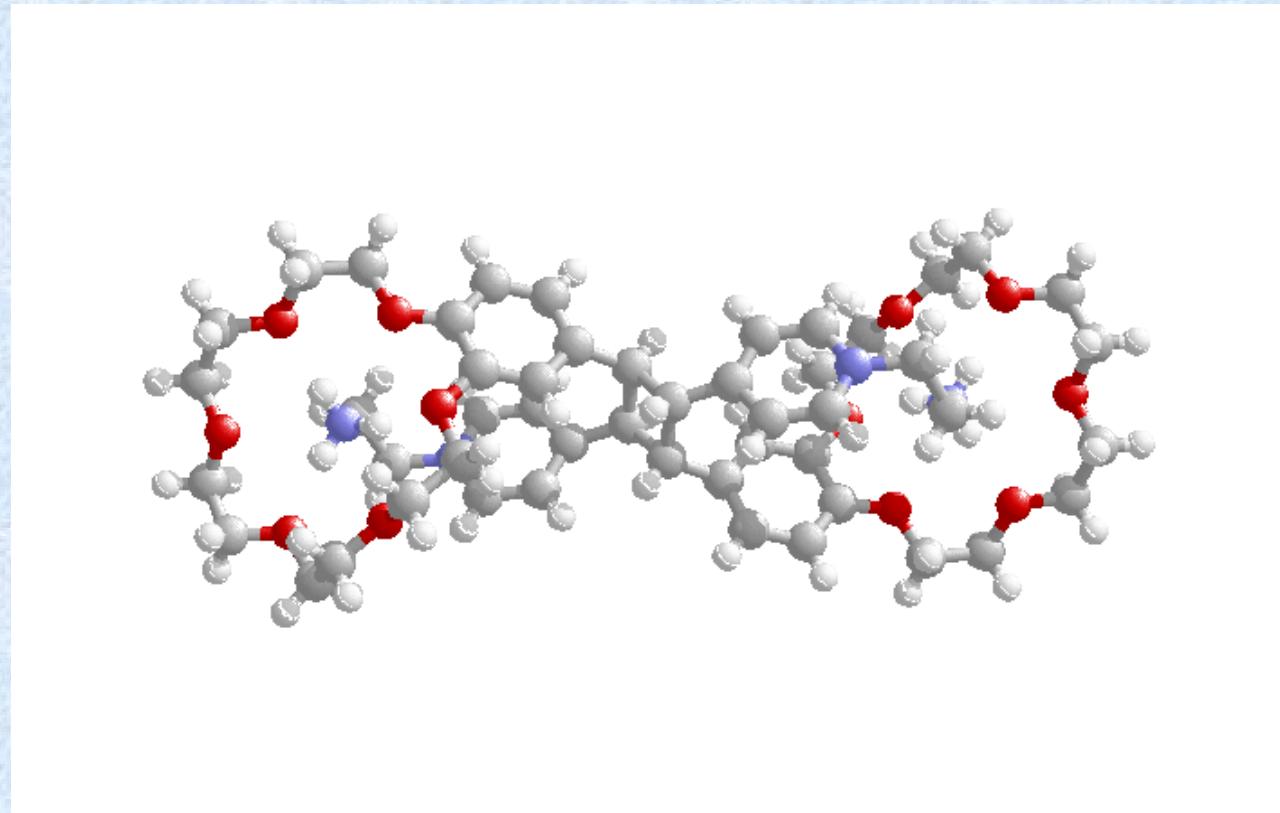
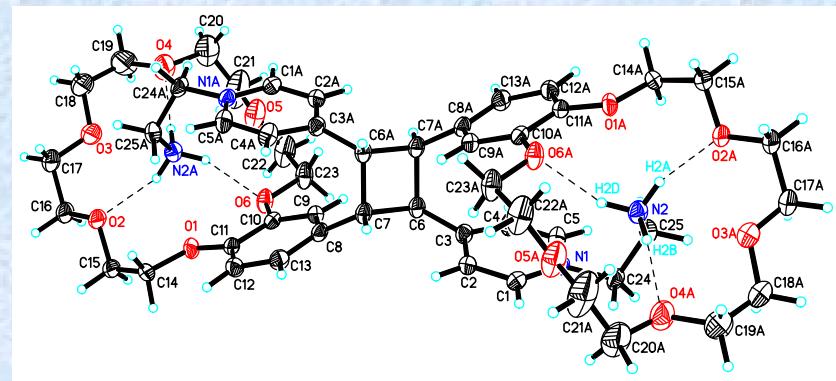


RF patent 2278134 2006;
Russ. Chem. Bull. 2009, 58, 1211;
J. Org. Chem. 2014, 79, 11416;
J. Phys. Chem. A 2015, 119, 13025.

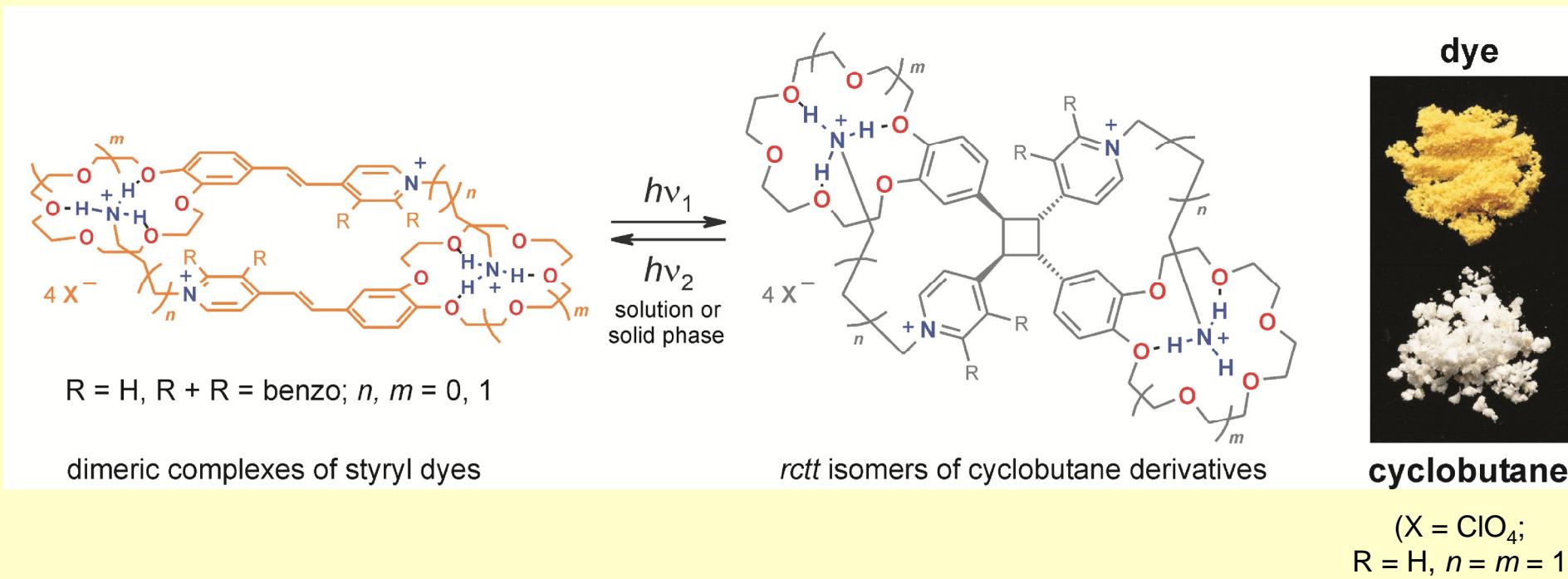
X-ray structure determination of cyclobutane



syn-cyclobutane

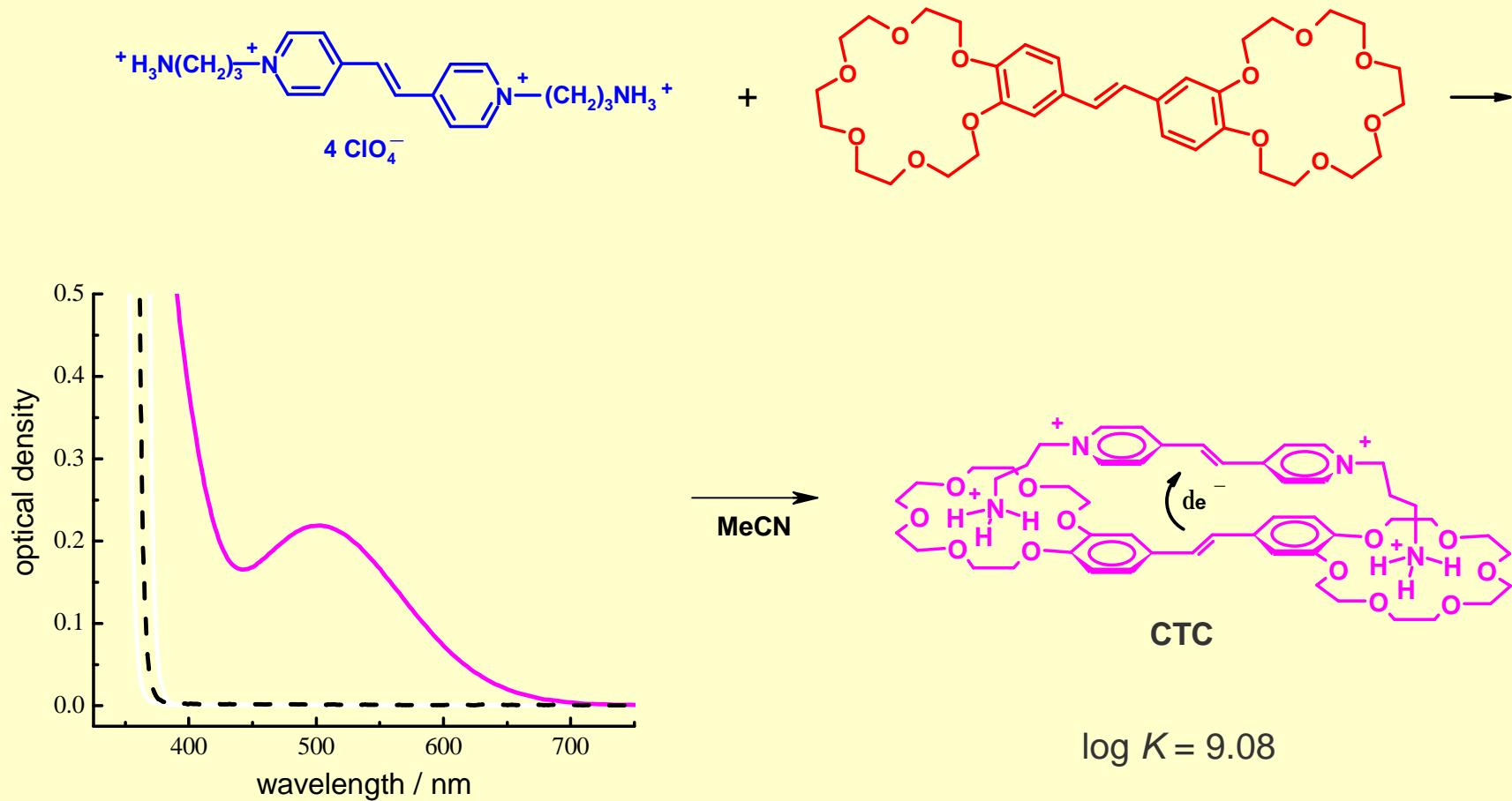


Supramolecular photoswitches based on ammonioalkyl derivatives of crown-ether styryl dyes



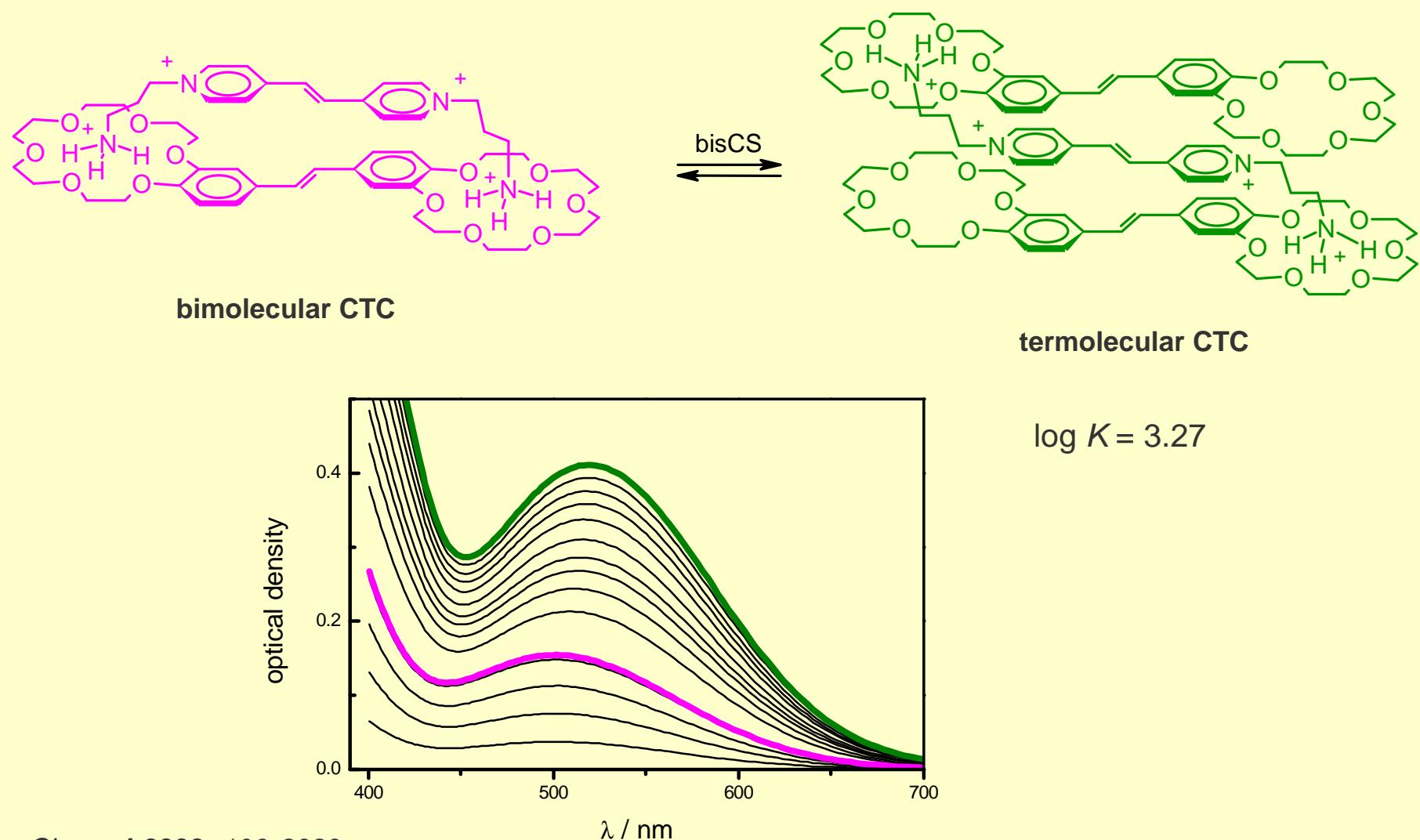
Found property provides grounds for believing that the crystals of these photoactive supramolecular systems could be used for data recording and storage.

Formation of Charge Transfer Complex of bisCS



Org. Lett. 1999, 1, 1697 ;
New. J. Chem. 2005, 29, 881;
J. Org. Chem. 2011, 76, 6768;
Photochem. Photobiol. Sci. 2017, 16, 1801;
ACS Omega 2020, 5, 25993.

Formation of Charge Transfer Complexes



J. Phys. Chem. A **2002**, *106*, 2020;

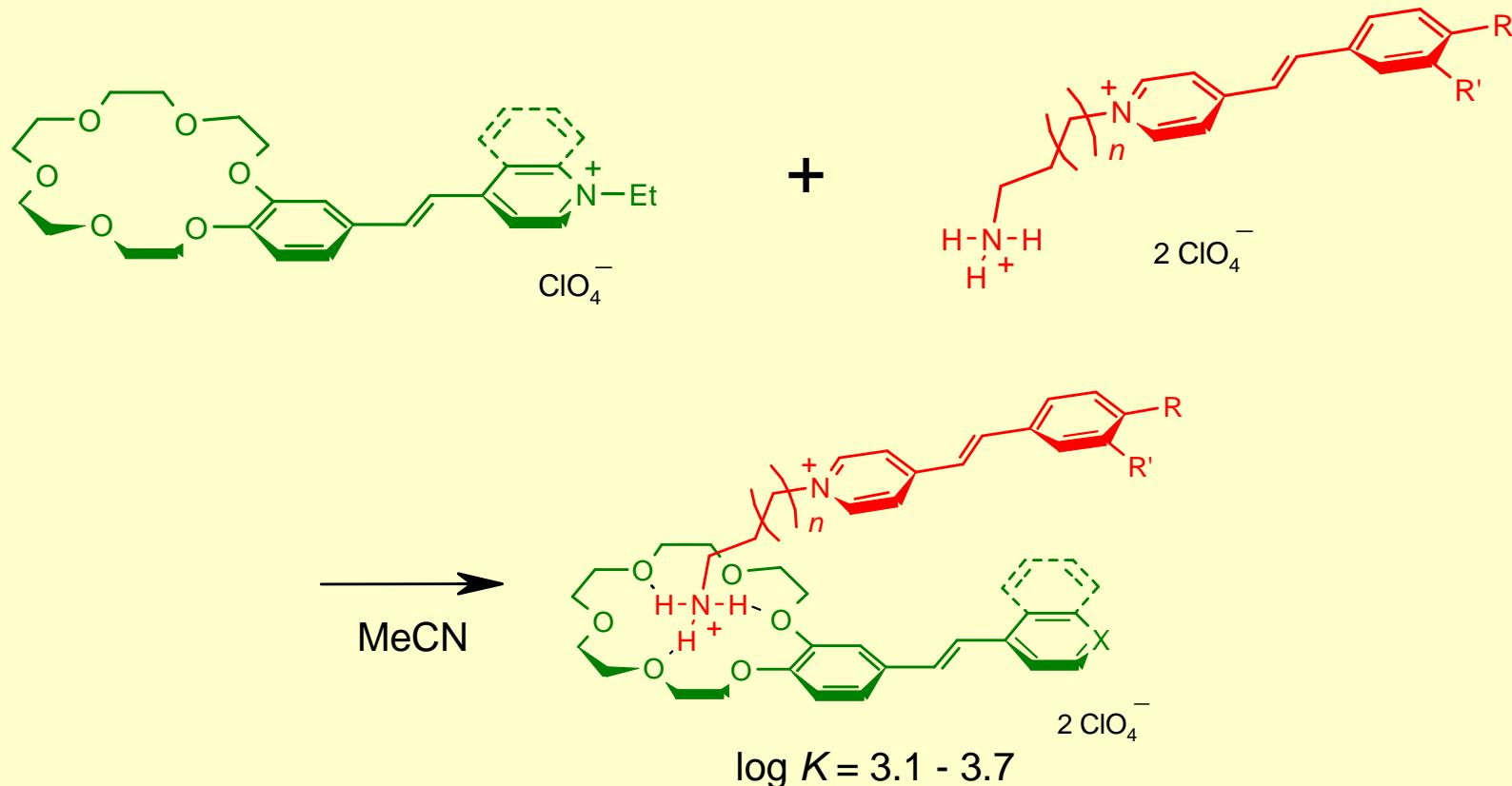
New. J. Chem. **2005**, *29*, 881;

J. Org. Chem. **2011**, *76*, 6768;

J. Photochem. Photobio. A **2019**, *372*, 89.

$$\log K = 3.27$$

Formation of pseudodimeric complexes



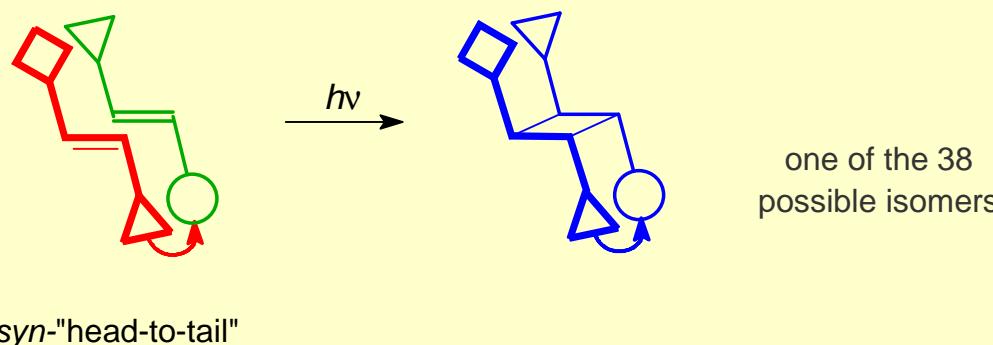
$X = \text{NEt}^+\text{ClO}_4^-$, N, CH

$R, R' = \text{H}, \text{OMe}, \text{SMe}, \text{NMe}_2, \text{NO}_2, \text{Cl}$

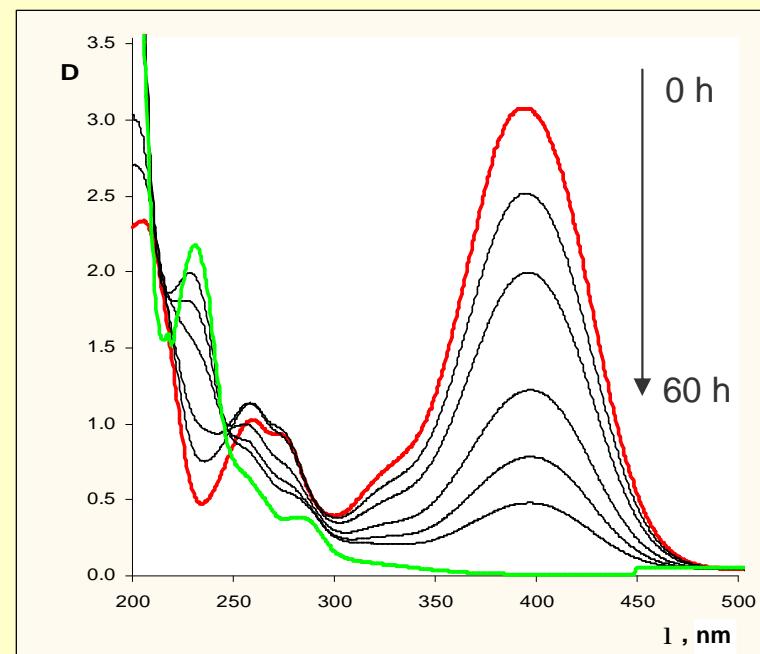
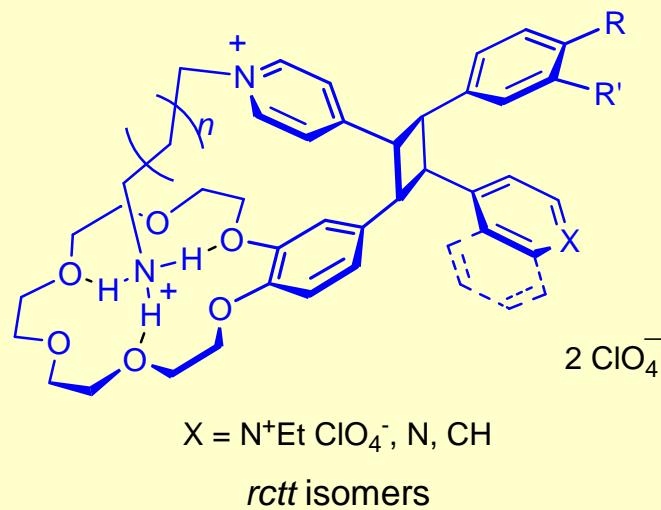
$n = 0, 1, 3$

Mendeleev Commun., 2007, 17, 29;
New. J. Chem. 2016, 40, 7542;
Dyes Pigments 2020, 172, 107825;
J. Org. Chem. 2021, 86, 3164.

[2 + 2] cross-Photocycloaddition



syn-"head-to-tail"



Mendeleev Commun., 2007, 17, 29;

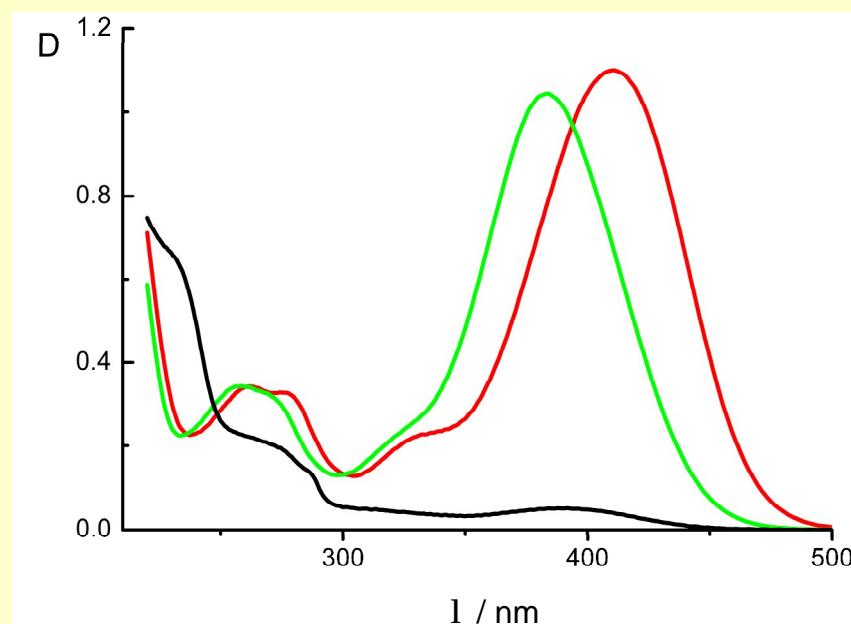
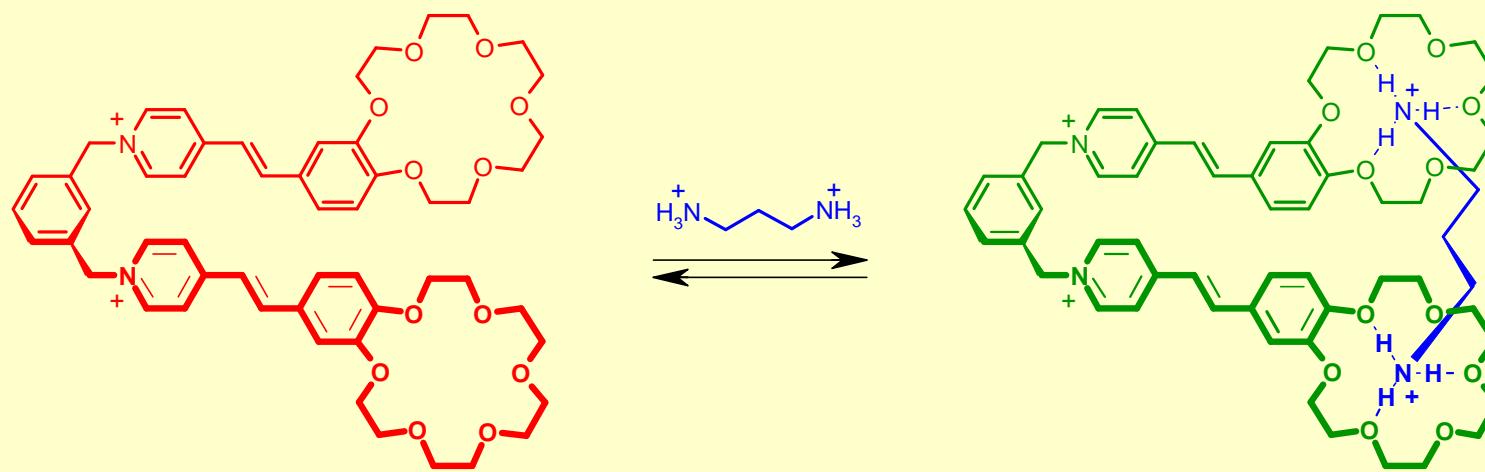
Патент РФ 2383571 2010;

New. J. Chem. 2016, 40, 7542;

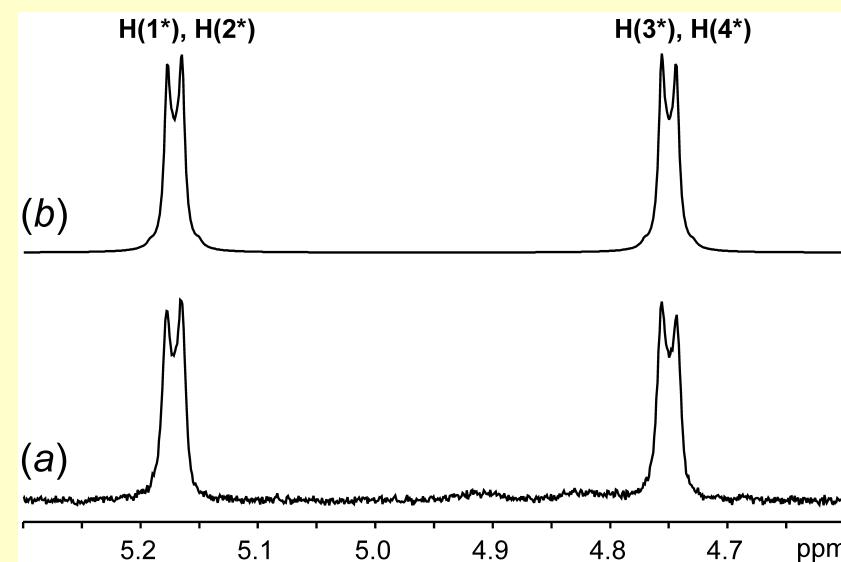
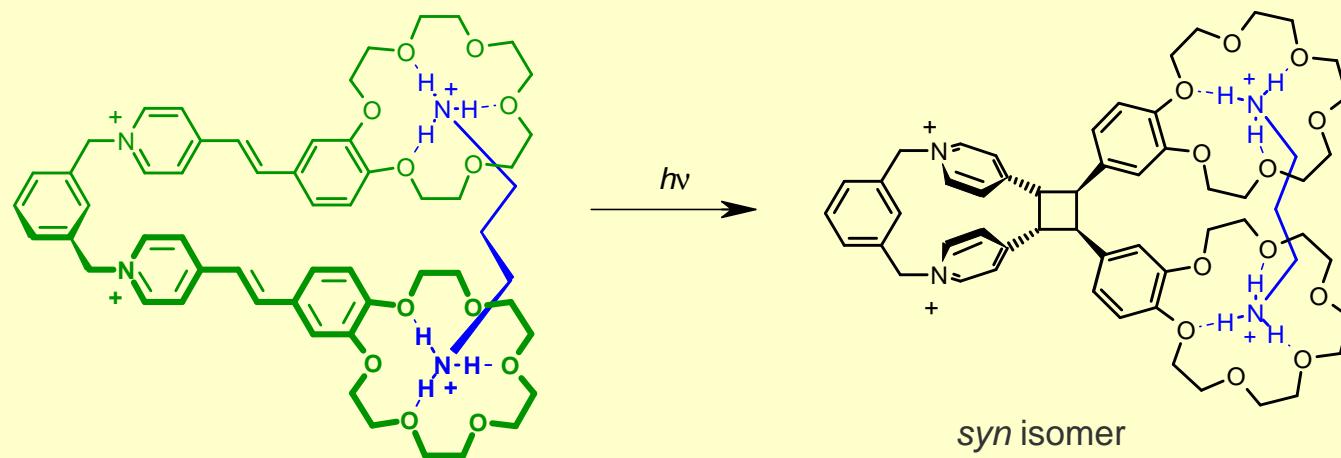
Dyes Pigments 2020, 172, 107825;

J. Org. Chem. 2021, 86, 3164.

FORMATION OF PSEUDOSANDWICH COMPLEXES

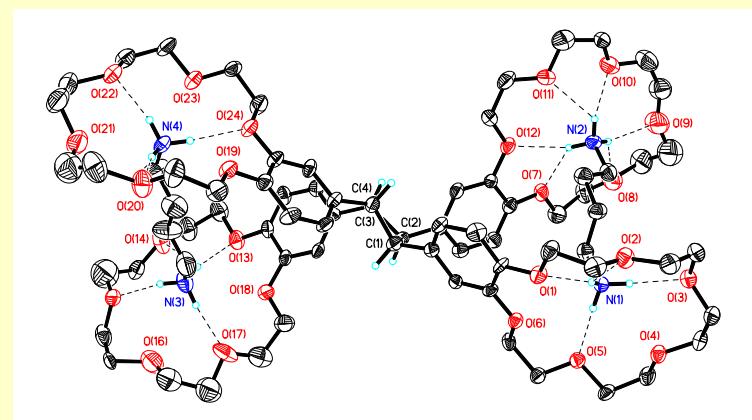
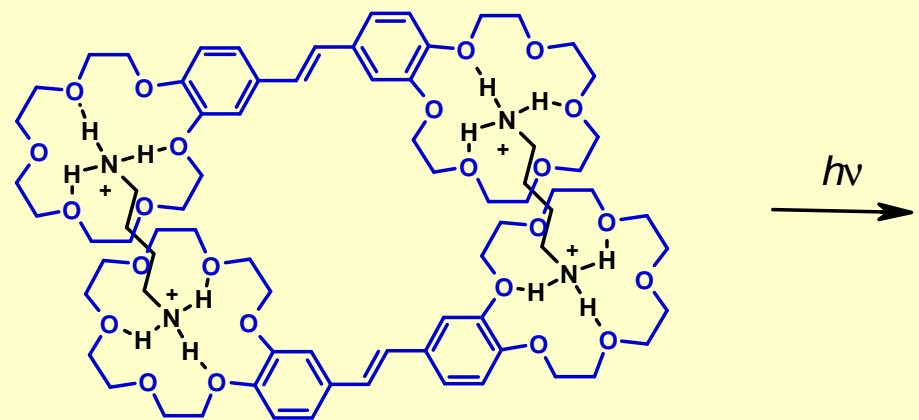
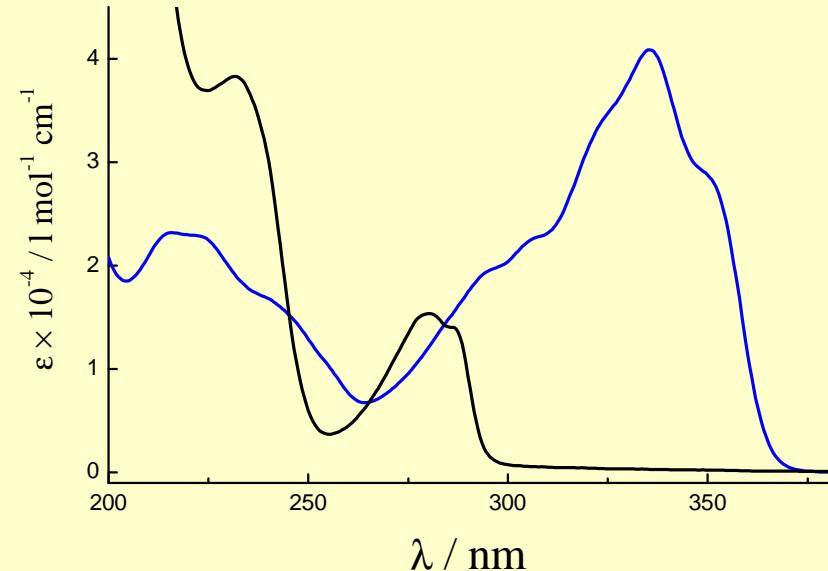
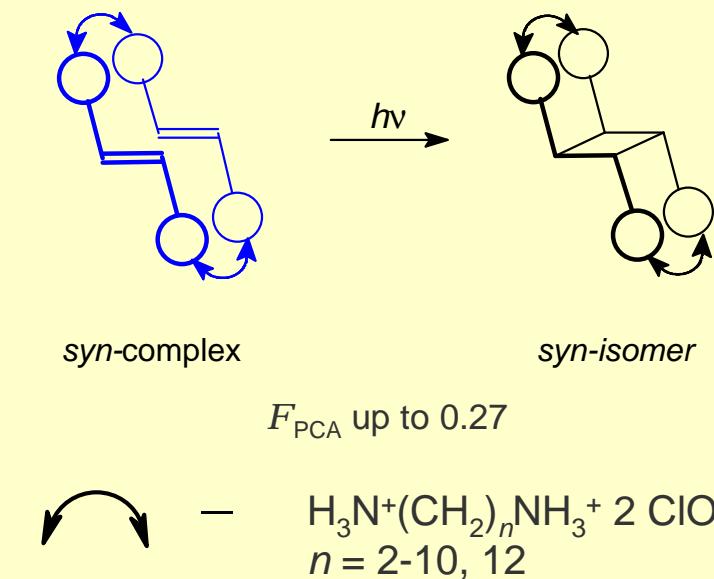


Intramolecular [2+2] photocycloaddition of bisCSD



(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

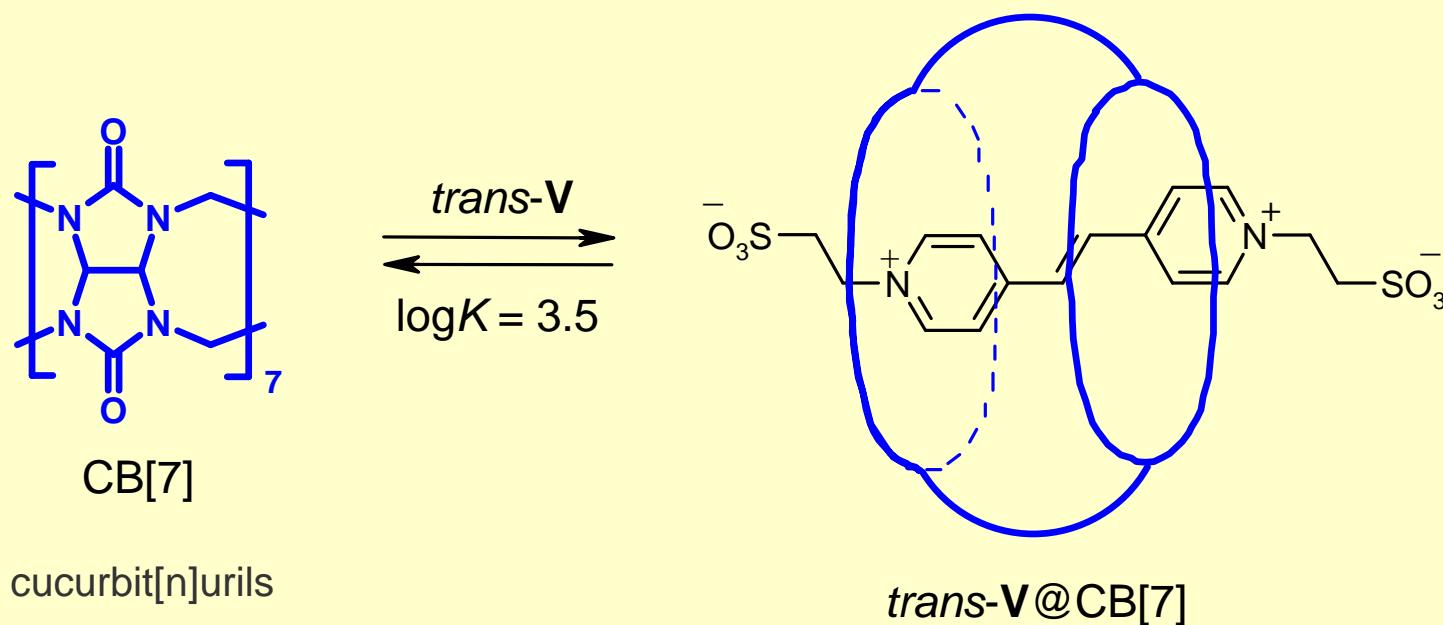


Russ. Chem. Bull. **2009**, *58*, 108;
New. J. Chem. **2011**, *35*, 724;
J. Photochem. Photobiol. A **2017**, *340*, 80;

Self-assembly of photocontrolled supramolecular machines

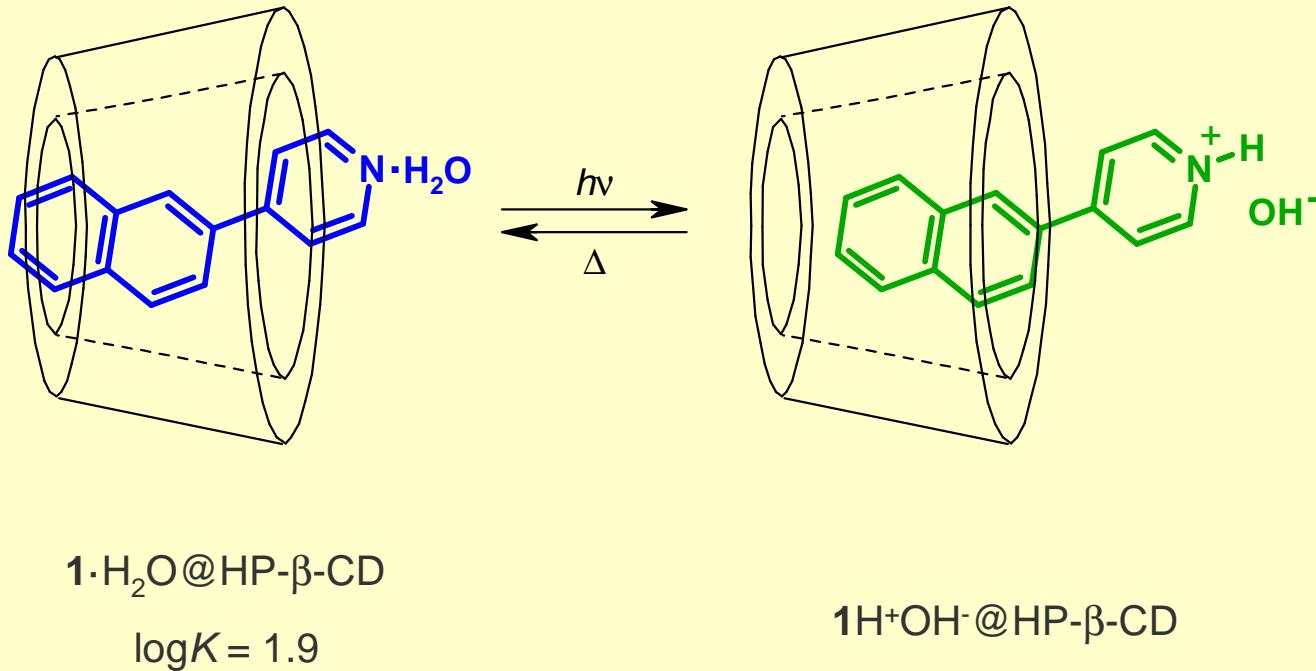
Part III

PSEUDOROTAXANE COMPLEXES OF CUCURBITURILS



Russian Nanotechnologies **2007**, 2, 56;
J. Mol. Struct. **2011**, 989, 114;
Chem. Phys. Lett. **2014**, 610-611, 91;
J. Photochem. Photobio. A. **2018**, 353, 34.

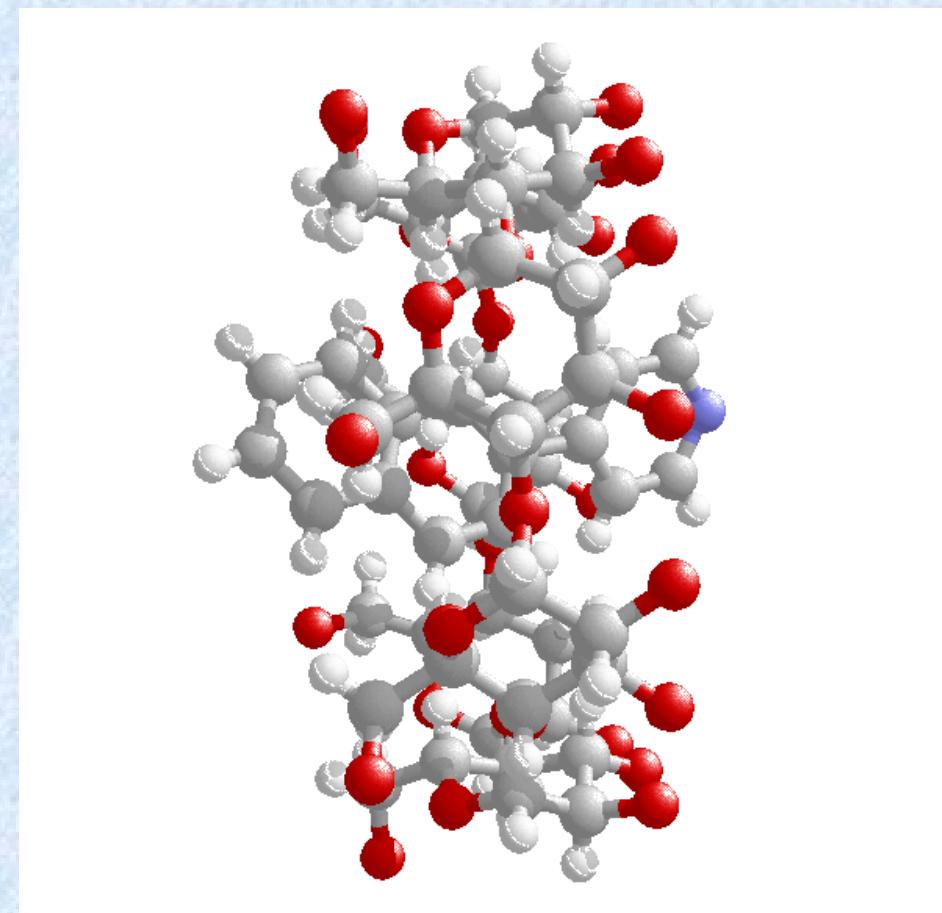
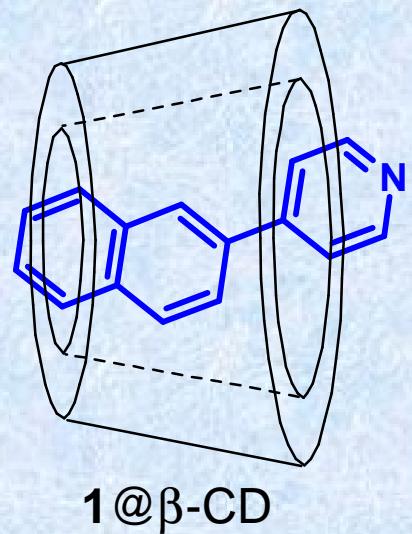
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



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

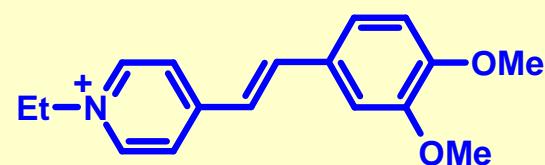
Russ. Chem. Bull. 2004, 53, 2525;
J. Photochem. Photobiol. A 2011, 217, 87;
Russ. Chem. Bull. 2013, 62, 2150.

X-ray structure determination of photocontrolled supramolecular machine

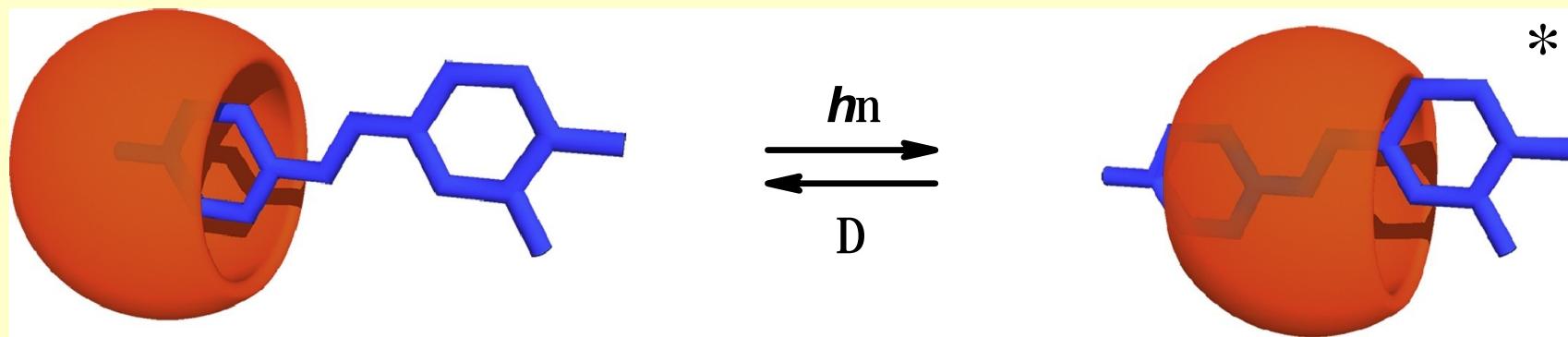


Russ. Chem. Bull. 2004, 53, 2525;
J. Photochem. Photobiol. A 2011, 217, 87;
Russ. Chem. Bull. 2013, 62, 2150.

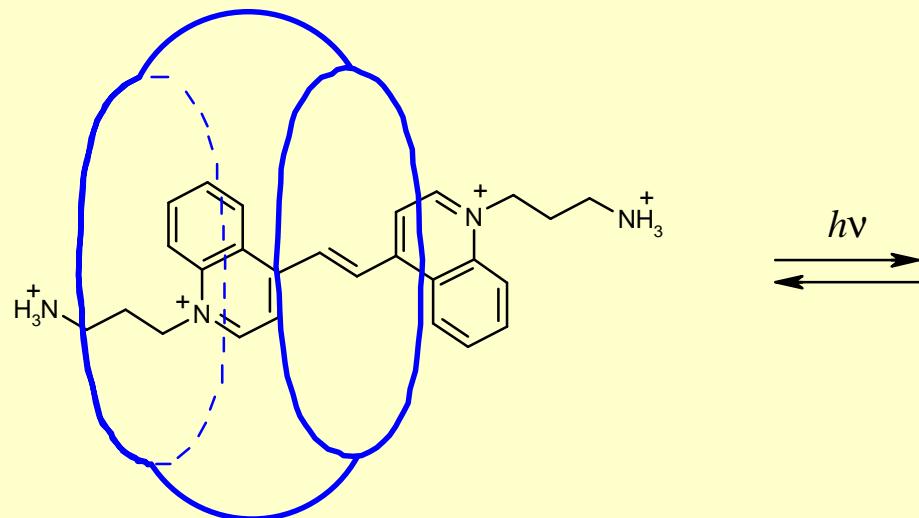
PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



SD

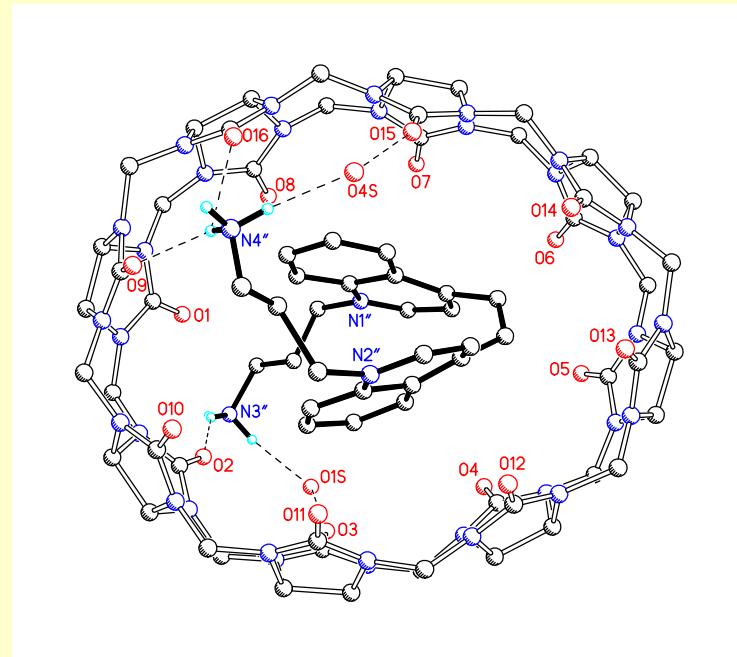


PHOTOCONTROLLED SUPRAMOLECULAR MACHINE



trans-V@CB[8]

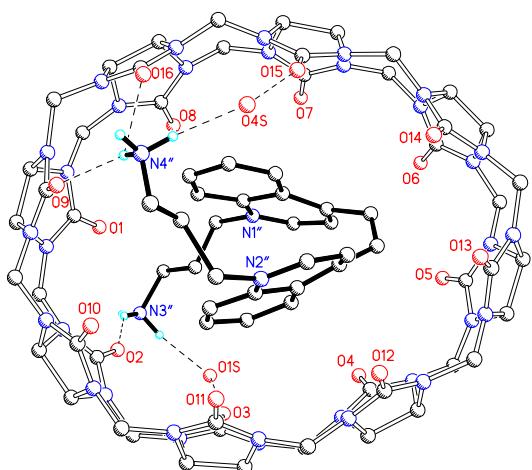
$$\log K = 4.6$$



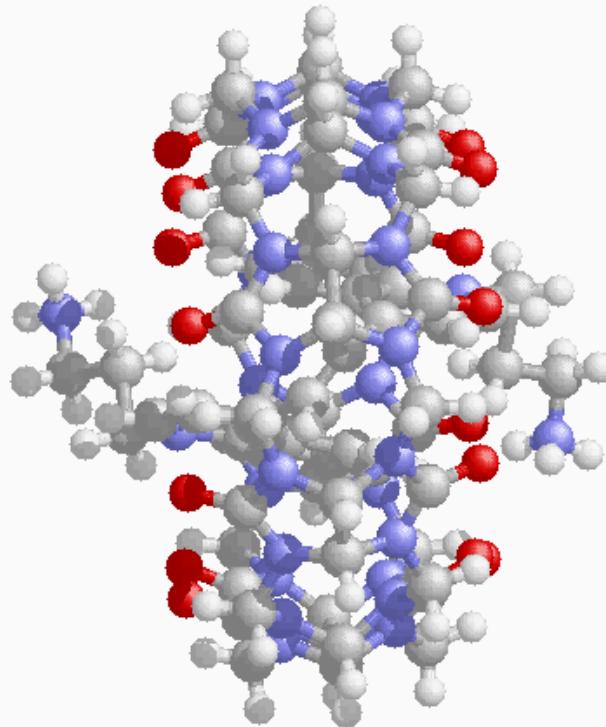
cis-V@CB[8]

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

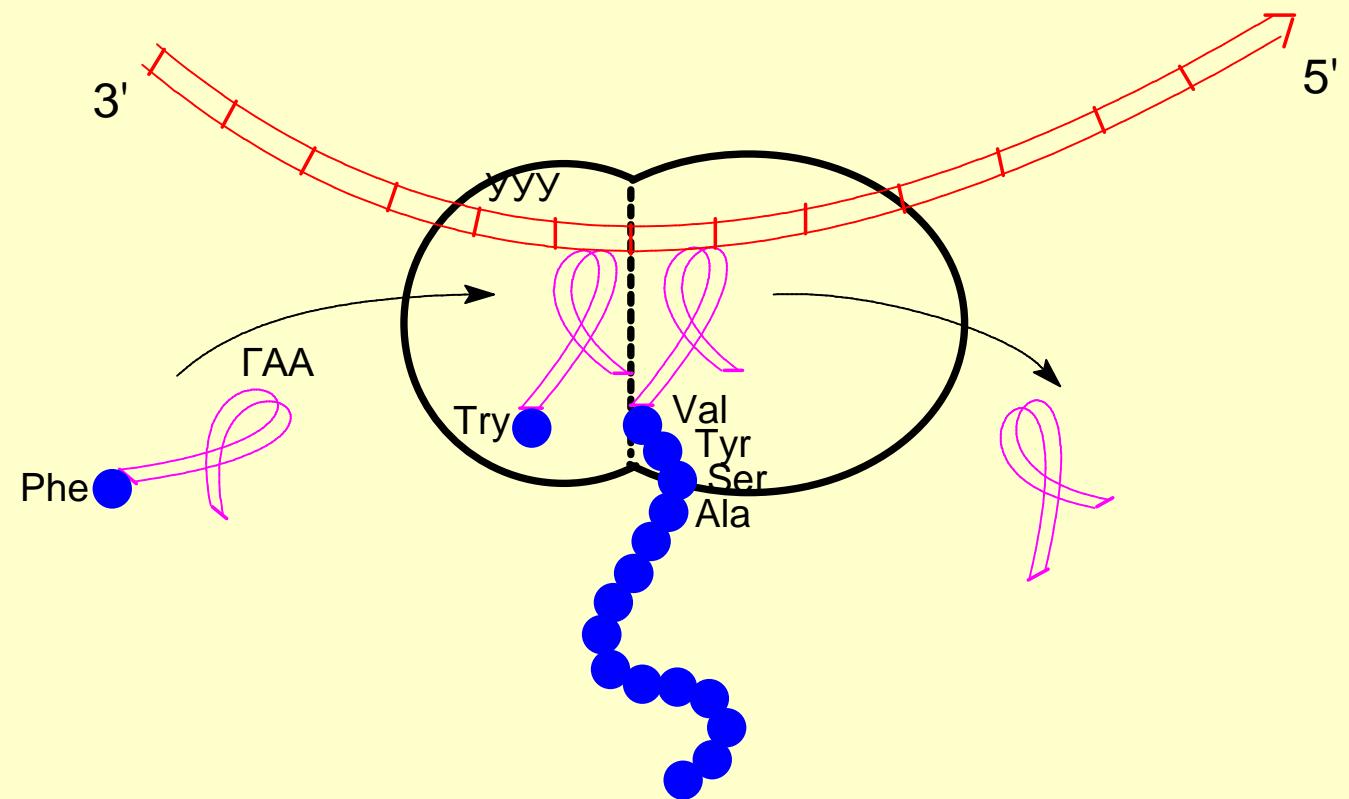
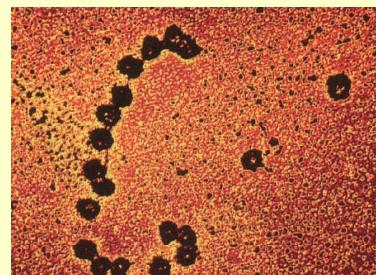
X-ray structure determination of photocontrolled supramolecular machine



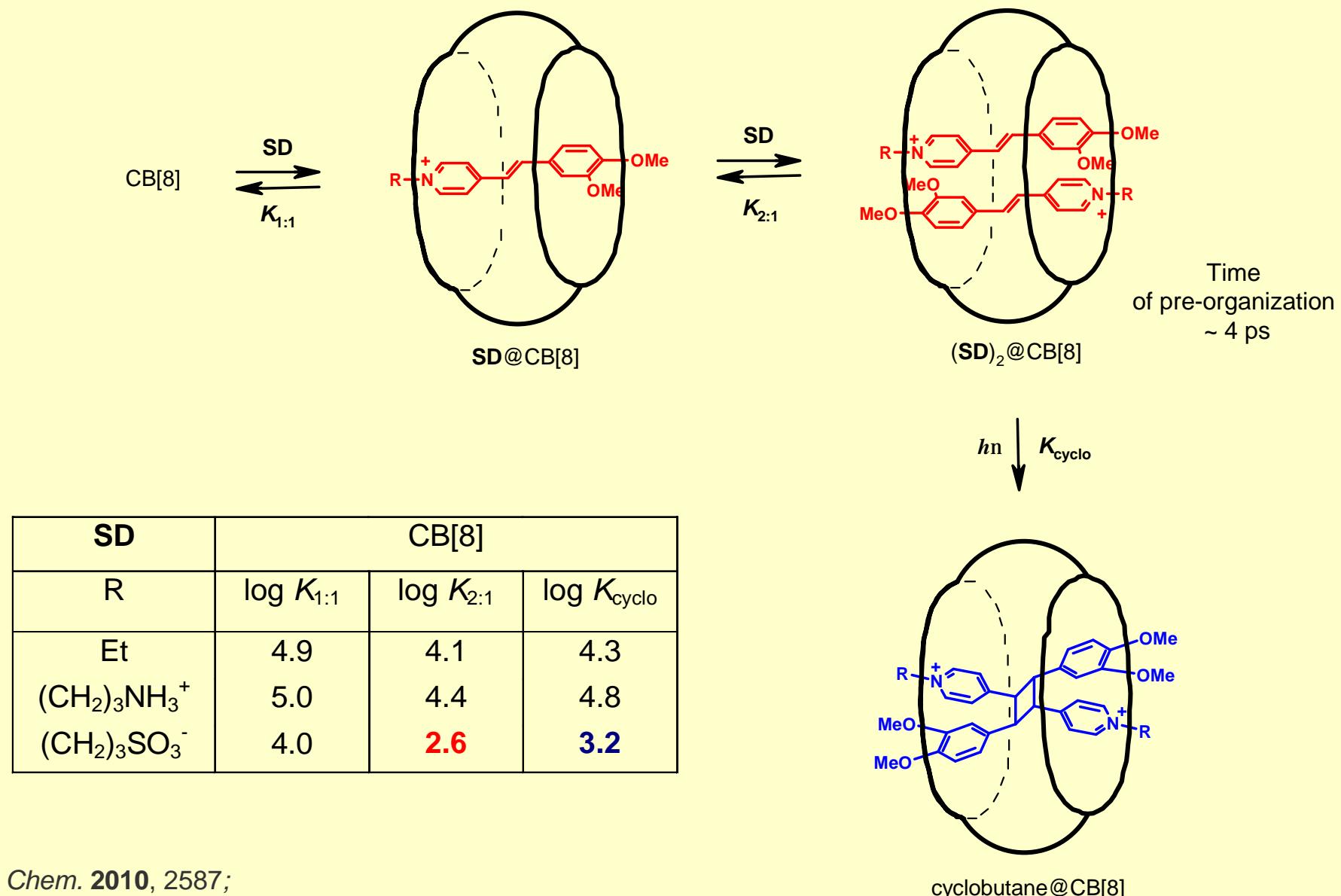
cis-V@CB[8]



Ribosome - natural molecular assembler

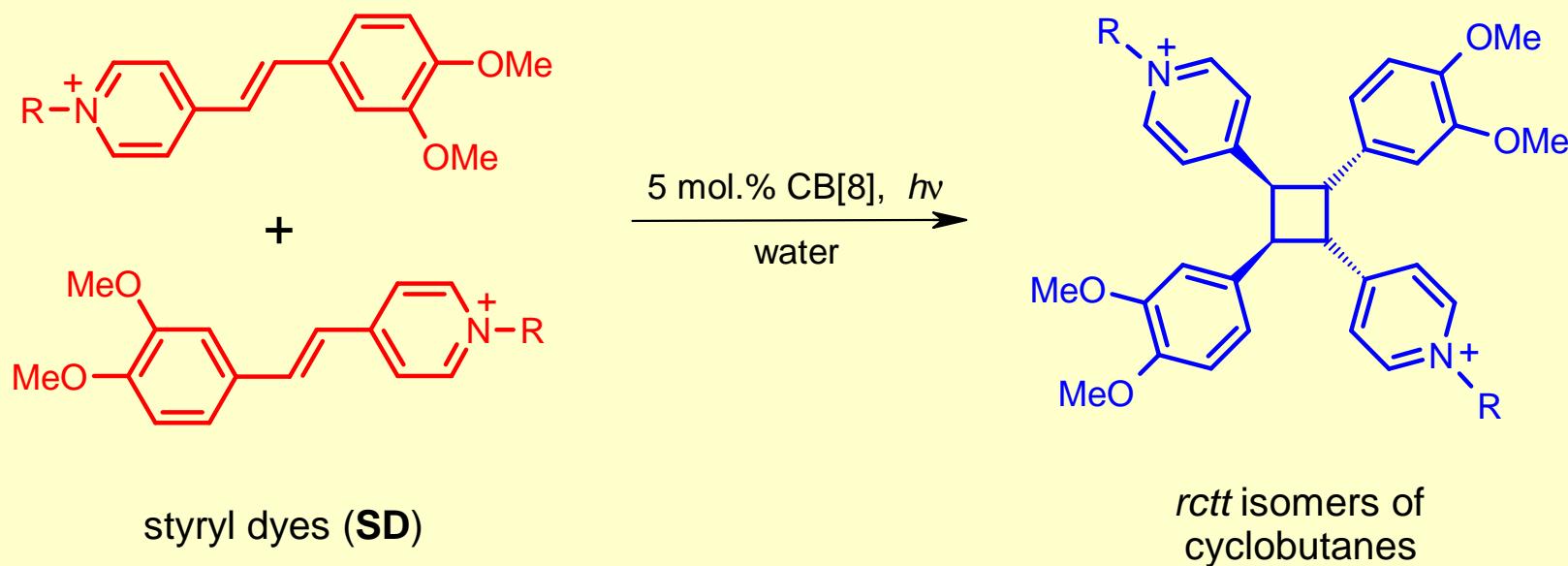


PHOTOCONTROLLED SUPRAMOLECULAR MACHINES

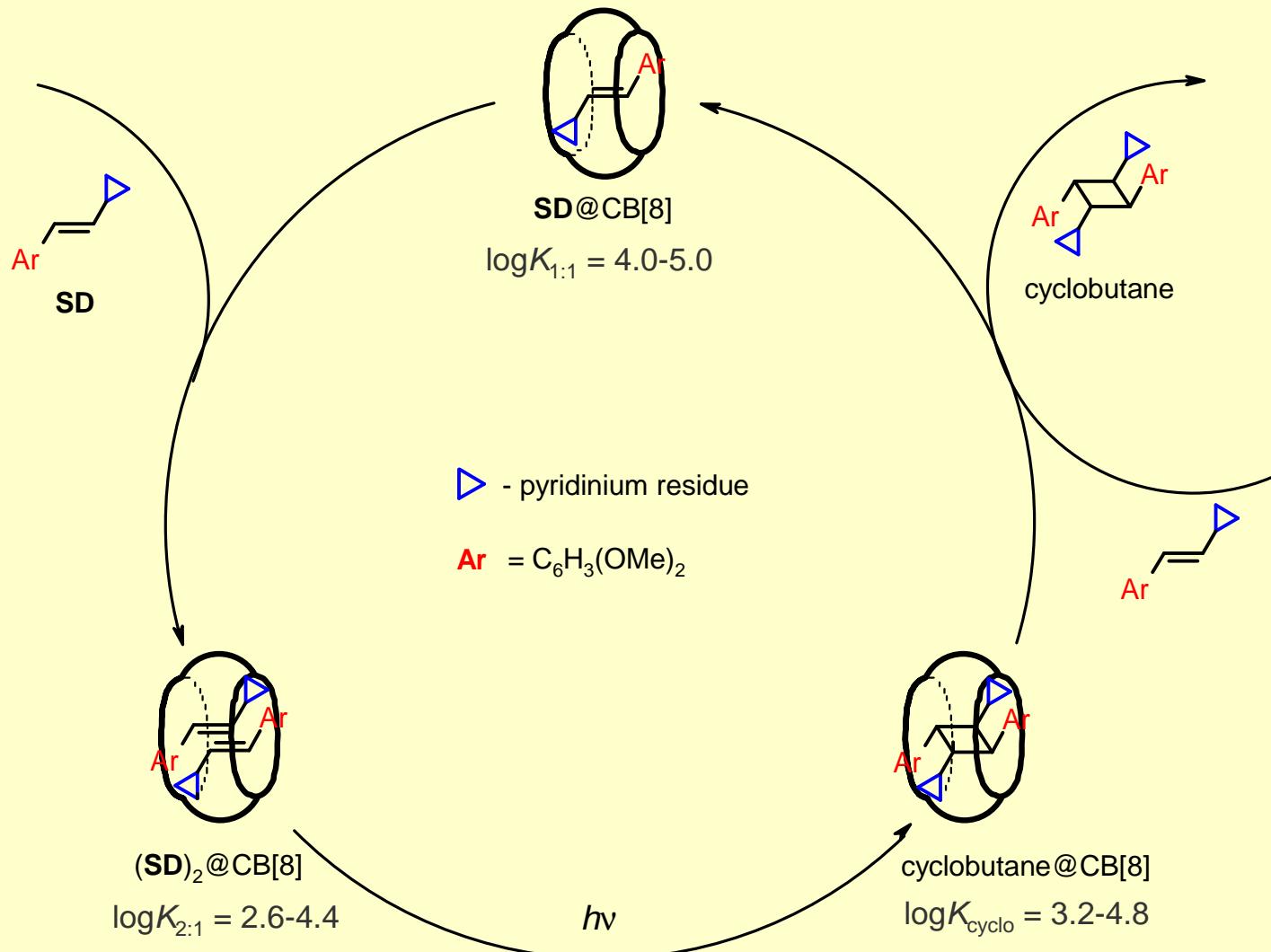


Eur. J. Org. Chem. 2010, 2587;
 J. Phys. Chem. A. 2011, 115, 4505;
 J. Photochem. Photobio. A. 2013, 253, 52;
 Chem. Phys. Lett. 2016, 647, 157.

PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL

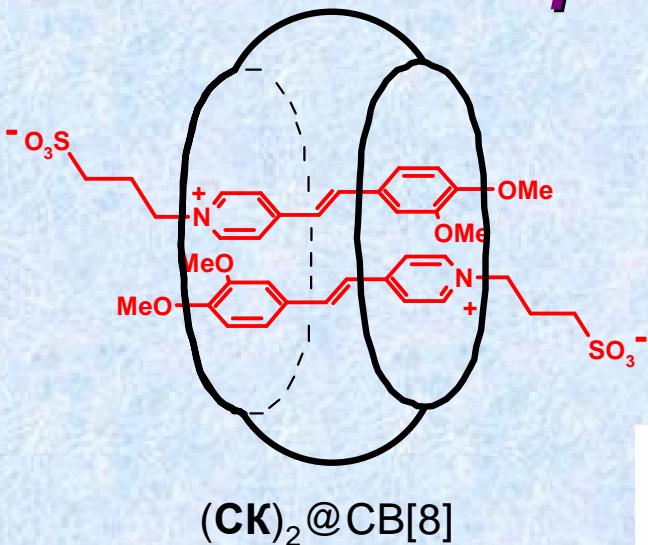


PHOTOCONTROLLED SUPRAMOLECULAR ASSEMBLER BASED ON CUCURBIT[8]URIL

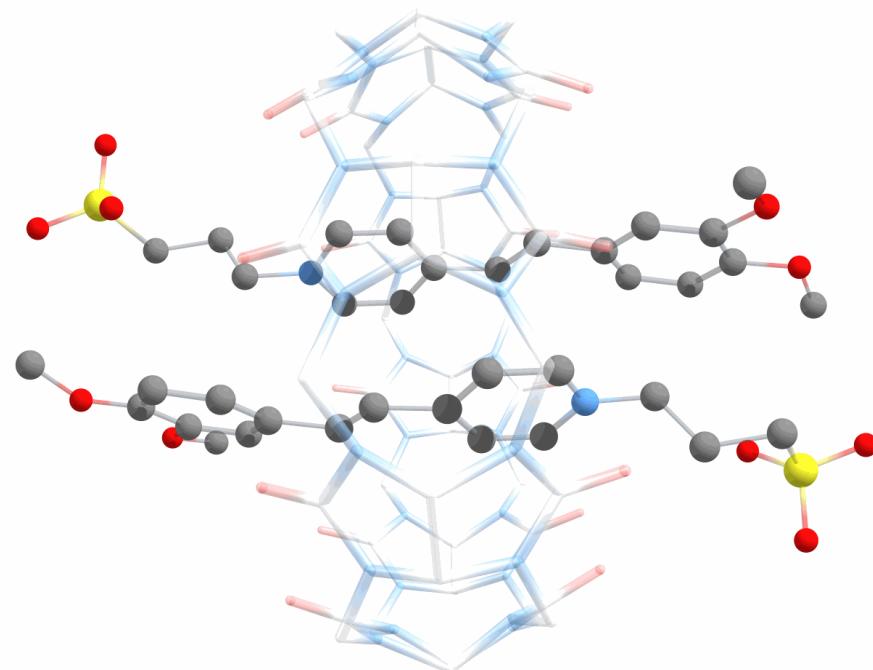


Eur. J. Org. Chem., 2010, 2587;
J. Phys. Chem. A., 2011, 115, 4505;
High Energy Chem., 2014, 48, 253;
Chem. Phys. Lett. 2017, 673, 99.

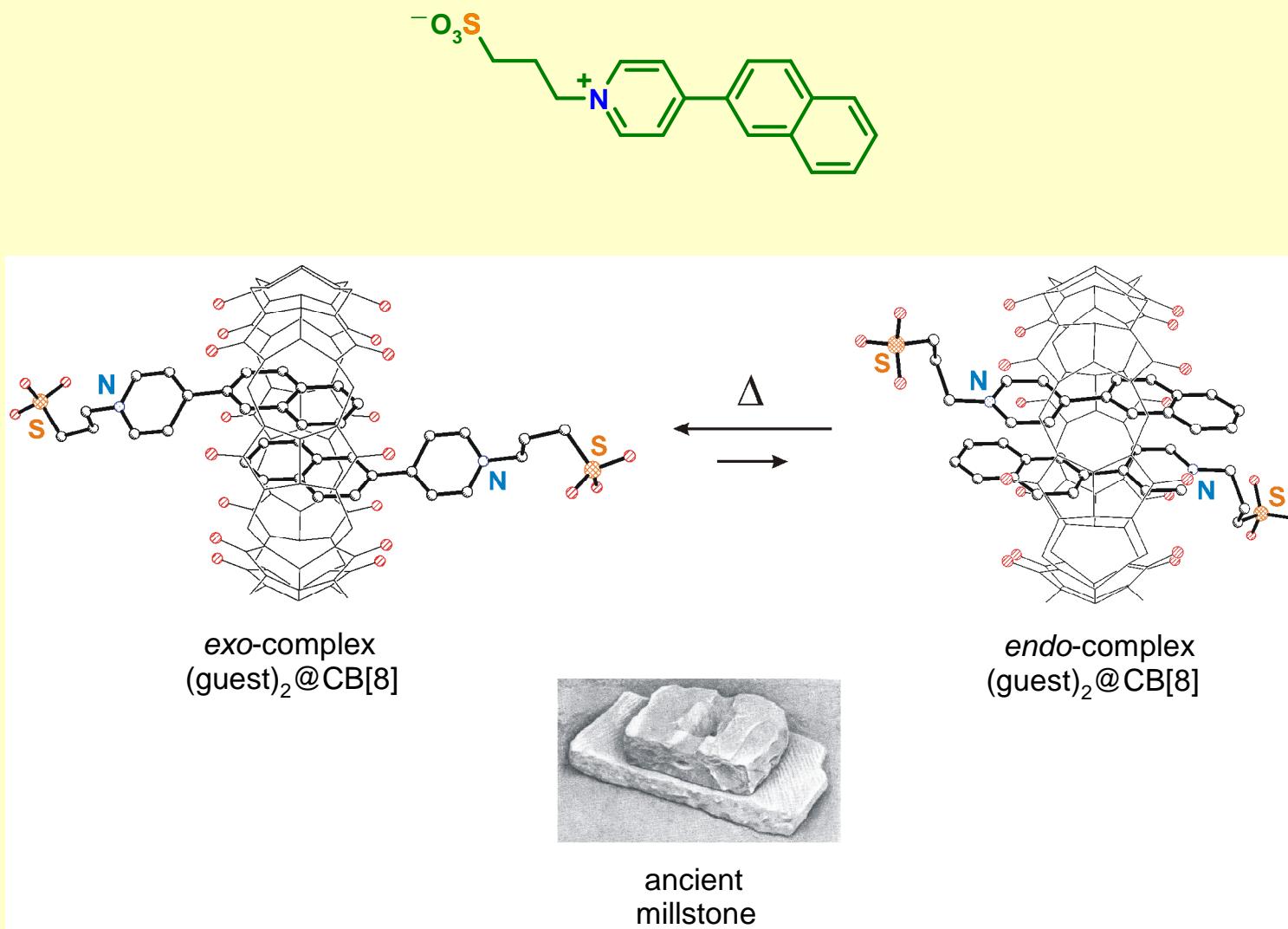
X-ray structure determination of photocontrolled supramolecular assembler



Time of pre-organization ~ 4 ps



SUPRAMOLECULAR MILLSTONES BASED ON CUCURBIT[8]URIL

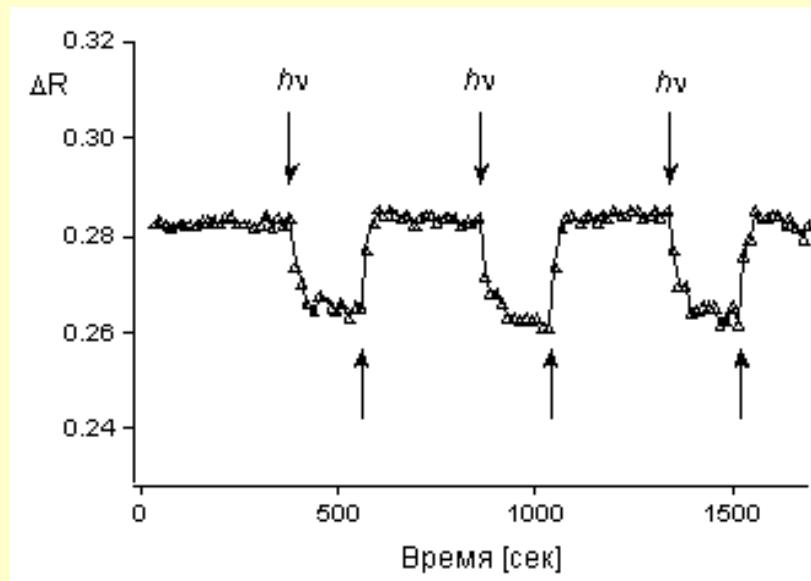
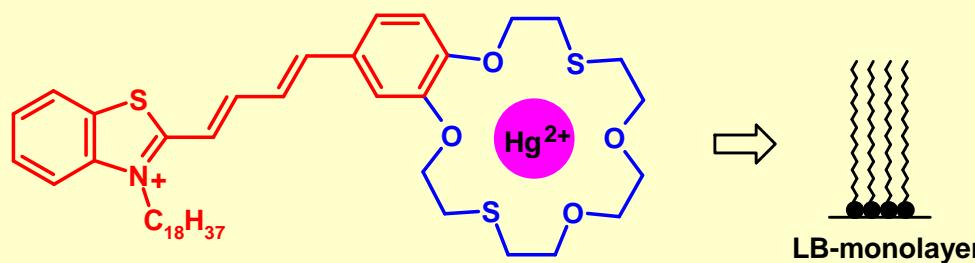


Naphthalene derivatives and cucurbiturils form inclusion complexes of various structures and stoichiometries; guests are capable of translocation in cucurbit[7,8]uril cavities.

**Self-assembly
to light-sensitive LB-monolayers
and crystal engineering**

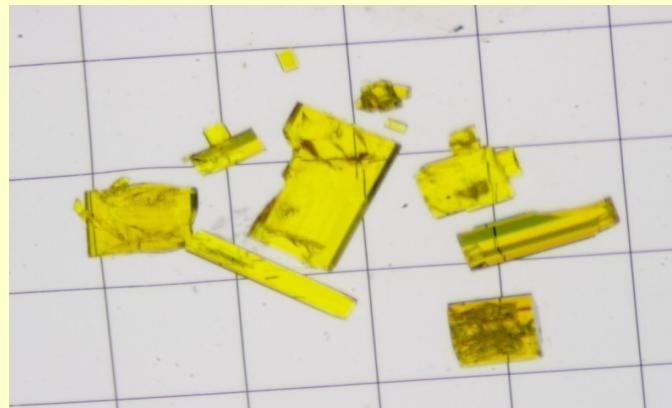
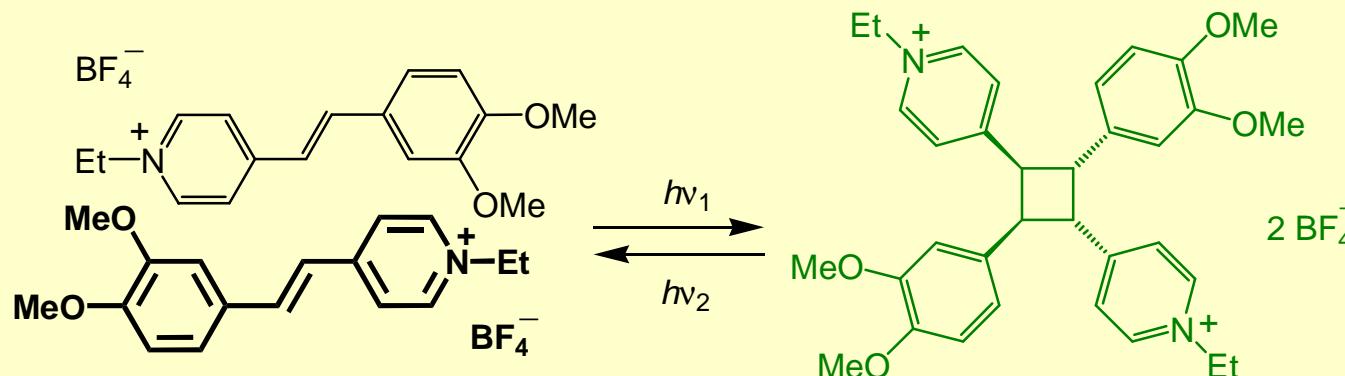
Часть IV

MONOLAYERS OF IONSELECTIVE BUTADIENYL DYE



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

Crystallographic Approach to the [2 + 2] Photocycloaddition (PCA) Topochemical Reactions with Single Crystal Retention



An approach to the analysis of PCA topochemical reactions of unsaturated compounds, occurring in a single crystal with either its retention or decomposition under exposure to visible light, has been developed. The main crystal packings, favorable for photoreaction in crystal, are revealed. Conditions for PCA reaction with single crystal retention are established. The factors increasing the probability of implementing crystal packing motifs that are favorable for this reaction (by chemical modification of structural units) are analyzed.

New. J. Chem. **2007**, *31*, 980;

CrystEngComm. **2016**, *18*, 7506;

Kuz'mina L. G., Gromov S. P., Alfimov M. V. et al. *Crystallography Reports* **2019**, *64*, 691 (review).

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);

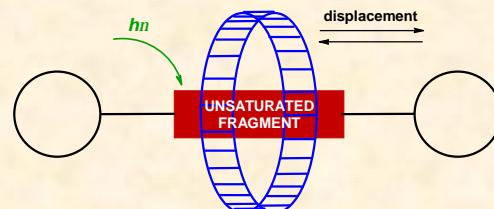
Gromov S. P., Chibisov A. K., Alfimov M. V. *Russ. J. Phys. Chem. B* **2021**, 15, 219 (review).

Supramolecular 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

20 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);

Alfimov M. V., Gromov S. P., Ushakov E. N. in *Russ. Chem. Rev.* **2021**, 90, 1055 (review);

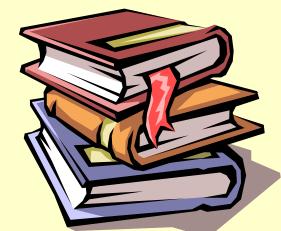
Gromov S. P., Chibisov A. K., Alfimov M. V. *Russ. J. Phys. Chem. B* **2021**, 15, 219 (review).

Publications :

More than 350 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



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- Russian Science Foundation (2014 - 2022)
- The Ministry for Science and Technology of Russia (1999 - 2022)
- RFBR (1994 - 2020)
- Russian Academy of Sciences (2003 - 2019)
- Moscow Government (2003 - 2005)
- The Royal Society (1997 - 2017)
- INTAS (1993 - 2005)
- CRDF (1996 - 2004)
- DFG (1996 - 2004)
- ISF (1993 - 1994)



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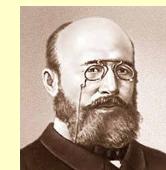
Acknowledgment

Awards and Prizes:

State Prize of the Russian Federation (2018)

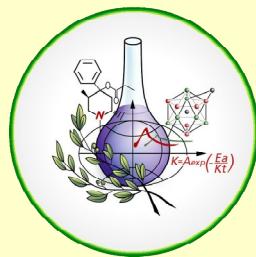


A. Butlerov prize of Russian Academy of Sciences (2006)



Scientific discovery of the USSR (1980)





Thank You

